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**IODINE REVOLATIZATION
IN A GRAND GULF LOCA**

**C. F. Weber
E. C. Beahm**

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Computational Physics and Engineering Division

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1. INTRODUCTION

Evaluation of reactor severe accident sequences has generally assumed that the dominant form of iodine is CsI.¹ Emitted from the reactor coolant system as an aerosol, the iodide easily deposits on surfaces or enters water. Deposited particles may be washed into sumps or pools if water films from sprays or condensation are present on the containment surfaces. Otherwise, the deposited species are fairly stable, and unlikely to move.

In water, CsI readily dissolves into the constituent ions Cs^+ and I^- , both of which are quite stable. However, under certain conditions I^- could react with various other aqueous species and form non-trivial amounts of I_2 . While some I_2 will stay dissolved, it evaporates from water much more readily than other species. Once in the gas space, it may be carried with leakage or venting flow into the environment. Thus, the aqueous conversion of I^- to I_2 presents a significant additional threat of environmental release.

It has been shown^{2,3} that the conversion of iodide to molecular iodine takes place only in acidic solutions. At 25°C, the reaction is quite slow for pH above 5, and quite rapid for pH under 3. At 90°C, the reaction proceeds rapidly for pH < 5. Thus, the revolatilization of iodine is dependent primarily on pH and, to a lesser extent, temperature.

This study is an attempt to quantify iodine revolatilization from water pools using mechanistic models. A Loss of Coolant Accident (LOCA) at the Grand Gulf Nuclear Station has been chosen for the sample calculation. This sequence has been recently modeled using the MELCOR code,⁴ forming a basis for this analysis. As is the case in all Boiling Water Reactor (BWR) plants, the pressure suppression pool at Grand Gulf has no pH control; hence, there exists the real possibility of lowered pH and iodine revolatilization.

Under Nuclear Regulatory Commission (NRC) guidance, models of iodine behavior under various severe accident conditions have been developed at Oak Ridge National Laboratory (ORNL). These models have come to be known collectively as the 'TRENDS' code. NRC support of model development ended in 1992, before any formal documentation or code development was undertaken. However, at the same time a need arose to actually apply most of the iodine chemistry and interaction models to postulated severe accident sequences at the High Flux Isotope Reactor (HFIR) in Oak Ridge. As a part of this work, substantial documentation was accomplished.⁵ In addition, the code HFIR-TRENDS was developed to actually perform the calculations. This code is not easily exportable or transportable to other plants or sequences, inasmuch as many statements are tailored to the particular plant (HFIR) for which they were written. Later, certain parts of HFIR-TRENDS were appropriated and modified so as to simulate three Westinghouse AP-600 design basis accidents.^{6,7} Again, the code was specifically tailored to the plant and accident sequence.

The TRENDS models do not include primary system, aerosol, or thermal hydraulic analyses. In the past, basic plant analyses were done using the MELCOR code for the HFIR analysis and MAAP code for the AP-600 reactor. Transient variables such as temperatures, pressure and fission product inventories were then input into the TRENDS analysis. Likewise, the TRENDS analysis for Grand Gulf is based on the recent MELCOR results, which will be described in more detail in the next section.

2. DATA AND ASSUMPTIONS

As mentioned, the TRENDS calculation does not perform the basic accident analysis, but rather imports such information as flow rates and temperatures. In the present study, all such information was obtained from Ref. 4. The nodalization for the TRENDS analysis is exactly the same as for the underlying accident analysis. The control volumes are listed in Table 1, together with their total volumes, and gas-liquid interfacial areas. [Interfacial flow areas were obtained from the volume look-up tables by assuming a completely open top surface; if the volume V is a linear function of elevation h , the interfacial area is $A=(V_2 - V_1)/(h_2 - h_1)$.] Almost all flow paths used in the TRENDS analysis also correspond to analogous flows in the MELCOR calculation, listed in Table 2.

The TRENDS analysis requires a calculation only every two to three minutes during the transient. If MELCOR time steps occur at roughly this interval or greater, they are followed exactly. If MELCOR times are more frequent, then data from multiple times are combined so as to produce a single average value for a TRENDS time step. At each time step, the following transient information from MELCOR results are imported into TRENDS:

- 1) Temperatures (liquid and gas) for each control volume
- 2) Flow rates (liquid and/or gas) for flow paths between control volumes
- 3) Liquid volumes (where not zero)
- 4) Deposition rate of CsI into water pools
- 5) Pressure in various regions of the reactor containment
- 6) Dose rates to water pools and airspaces.

The dose rates themselves are calculated as follows. MELCOR results provide inventories (kg) of each fission product group in each control volume at each time step. Molar dose rates for each group (MeV/s-mol) were obtained during the previous study⁶ using ORIGEN results for individual nuclide inventories in the AP-600 reactor, combined with ICRP decay data. These are shown in Table 3 for both β and γ radiation. (While ORIGEN calculations reflect assumptions of burnup and fuel composition for the AP-600 sequence, it is expected that the results do not differ substantially from what would be expected in Grand Gulf. In any event, such distribution data are not available for Grand Gulf, and would require additional time and expense to obtain them.) Multiplication of the molar dose rate by group molecular weight and group mass produces the dose rate contribution for the fission product group.

The dose rate for each control volume is then obtained by summing the dose rates for each fission product group within the volume. The resulting dose rate in water pools is shown in Fig. 1. Similar results are also available for the drywell airspace and containment airspace.

The refueling pool was not considered in the present analysis for several reasons. All distinct flows are outward, however water enters through the "rain" of containment sprays. The pool eventually fills up and overflows into the pressure suppression pool. Within a few hours almost all fission products are in the latter, even those that migrated through the refueling pool first.

Finally, the source terms for this calculation [which determine the CsI deposition in 4) above] are based on NUREG-1465,⁸ as described in ref. 4. Total amounts added are stated in Table 3, along with the energy deposition rates for each group.

Table 1. Control volume data

Index	Description	Volumes (m ³)		Interface area (m ²)
		Total	Liquid	
1	dry-head-seal	133.1	0.	0.
2	pedestal-cavity	259.5	.15	32.7
3	weir-wall-ann.	462.9	353.8	62.5
4	drywell-ann-4	1777.	0.	0.
5	shield-wall-ann.	380.1	0.	0.
6	drywell-ann-3	1319.	0.	0.
7	drywell-ann-2	2867.	0.	0.
8	drywell-ann-1	1165.	0.	230.4
9	drywell-head	161.5	0.	38.1
10	suppression-pool	7989.	3509.	619.1
11	wetwell-ann-1	3712.	0.	0.
12	upper-pool-ann-1	1625.	0.	0.
13	refuelpool	2154.	2067.	285.3
14	upper-ctmt-reg1	3535.	0.	0.
15	upper-ctmt-reg2	3535.	0.	0.
16	dome-hemisphere	10560.	0.	0.
17	ww-ann-lower	2392.	0.	0.
18	ww-ann-upper	2392.	0.	0.
19	upper-pool-ann-2	1707.	0.	0.
20	pump-sampling	354.7	0.	0.
21	main-steam-room	475.7	0.	0.
22	rwcu-hx-room	297.3	0.	0.
23	valve-nest-room	90.8	0.	0.
24	rwcu-filter-dem	129.5	0.	0.
25	rwcu-pump-room	21.8	0.	0.
26	rwcu-tank-room	97.6	0.	0.
27	equip-hatch	1582.	0.	0.
28	enclosure	16990.	0.	0.
29	SGTS			
30	environment			
31	reactor vessel			

Table 2. Inter-compartmental flows

Index	Source	Sink	MELCOR-ID
1	31	2	19+20+21
2	31	8	22+23
3	31	10	100+102
4	8	7	201
5	7	6	202
6	6	4	203
7	4	1	204
8	5	1	205
9	9	1	206
10	2	5	207
11	8	2	208+209
12	4	19	210
13	3	10	211+212+213
14	7	3	214
15	7	10	215
16	9	1	216
17	10	11	301
18	11	12	302
19	19	17	303
20	17	18	304
21	17	14	305
22	18	15	306
23	18	16	307
24	15	16	308
25	14	15	309
26	13	14	310
27	12	19	311
28	28	30	312
29	19	20	313
30	22	21	314
31	19	22	315
32	13	10	316
33	12	23	317
34	19	24	318
35	12	25	319
36	25	26	320
37	10	27	321
38	27	11	322
39	27	12	323
40	27	19	324
41	27	17	325
42	18	28	399
43	16	28	400
44	28	30	401
45	28	29	402

Table 3. Nuclide group inventories and dose rates

Nuclide Group	Total Release (kg)	Specific dose (MeV/s) / mol * 10 ⁻¹⁴				Molecular Weight
		gamma		beta		
		2 hr	10 hr	2 hr	10 hr	
1 Xe	463.7	8.678	2.964	6.098	3.718	131.3
2 Cs	61.55	13.99	5.261	14.33	2.25	149.913
3 Ba	4.15	27.31	11.5	32.76	18.99	137.34
4 I (as I ₂)	.30	1234	687.8	365	217.2	253.8
5 Te	2.04	98.01	37.34	46.86	18.65	143.6
6 Ru	0.77	10.19	9.167	9.167	7.324	101.07
7 Mo	0.88	2.1	1.876	5.36	4.904	95.94
8 Ce	0.30	18.53	16.69	27.9	25.16	140.12
9 La	0.11	35.01	26.23	35.01	23.17	138.91
10 U	--	0.1113	0.008796	0.0284	0.01208	270.03
16 CsI Aerosol	12.85	1248	693.1	379.33	219.45	259.8
17 I organic vapor	.01	1234	687.8	365	217.2	253.8

3. CHEMISTRY MODELS

The TRENDS analysis models certain chemical reactions not considered in major accident analysis codes such as MELCOR and MAAP. This additional analysis centers on two areas of importance: determination of pH in water pools, and speciation of iodine.

3.1 DETERMINATION OF pH

The calculation of pH is performed in each control volume at each step, immediately prior to the iodine speciation calculation. It assumes that the system is constantly in chemical equilibrium with respect to species that significantly affect pH. Internal coding ensures that time steps are small, so that changes in chemical inventories of each control volume are also small. The actual equilibrium computation is performed using the principal subroutines of the SOLGASMIX code, as described in refs. 5 and 6. With no borates or phosphates, the only significant additives are fission products and acids generated radiolytically in containment airspace and deposited into water.

The rate of HCl production is based on energy deposition rates (both β and γ) due to fission products that are airborne or deposited on surfaces. Acid production rates are calculated from the procedure described in ref. 3, Appendix B. This empirical model is based on dose rates (described in Sect. 2) and amount of cable insulation present (estimated as 9835 lb in the drywell and 1.764×10^5 lb in the containment). Since most flow in containment tends to be downward toward the wetwell water, all acids produced in containment were assumed to deposit in the wetwell water immediately. Acids produced in the drywell were routed to the sump during the first 20 minutes and afterward to the wetwell (consistent with water and gas flows).

The irradiation of air-water systems also is known to produce nitric acid. However, the quantity expected is dwarfed by the HCl production and hence, was not considered in the present study.

3.2 IODINE CHEMISTRY

While all iodine enters water pools as iodide (I^-), it may change to more volatile forms during the course of the accident. The iodine species distribution is determined by solving rate equations described below.

3.2.1 Hydrolysis

In aqueous solution, iodine can undergo hydrolysis which is described well by the reaction set^{5,9}

The endpoint oxidation states I^- and IO_3^- (or HIO_3) are both highly soluble, and therefore highly desirable. The species HOI and HIO_2 are reaction intermediates which may be volatile, but which are regarded as having short lifetimes. However, molecular iodine I_2 is stable and sparingly soluble. It can be seen in the above reactions that low pH (i.e., large H^+ concentration) will result in more I_2 , and less I^- and IO_3^- . Each forward and reverse reaction gives rise to a single rate equation, as described in ref. 5.

3.2.2 Radiolysis

Under radiation, the presence of free radicals induces additional aqueous reactions. While not as well understood, the overall result can be described empirically by the equilibrium⁵

$$\frac{(\text{H}^+)^2 (\text{I}^-)^2}{(\text{I}_2)} = a + b (\text{H}^+) \quad (3)$$

where a and b are known coefficients depending only on temperature. The actual rate equations used are based on the catalytic decomposition of hydrogen peroxide, one of the stable byproducts of irradiating water. The peroxide inventory is estimated empirically based on cumulative dose, pH, dissolved oxygen content, and temperature. The forward rate coefficients are then based on the data of Liebhafsky,¹⁰ and the reverse coefficients chosen to move steadily toward equilibrium (3).

3.2.3 Gas/Liquid Partitioning

The same equation is used to describe evaporation of volatile iodine species from water (I_2 or CH_3I) or their dissolution from gas. The model is based on the equilibrium partition coefficients (inverse of Henry's Law constant) for each species, and rate equations obtained from natural convection correlations.⁵

3.2.4 Organic Iodides

Organic iodides are described empirically as the formation of CH_3I from I_2 in the gas phase. The model used is described fully in ref. 5. As is I_2 , CH_3I is sparingly soluble in water, an effect which is negligible in the present sequence.

4. RESULTS AND CONCLUSIONS

The TRENDS models are applied at each time step to each control volume. Significant amounts of water occur only in the wetwell and drywell sump (the refueling pool is not a factor, as discussed earlier). In Fig. 2, we show the radiolytic acid production feeding into each of these pools. Since the water is initially neutral and no chemical additives are present, the acid additions are the major factors affecting pH. In Fig. 3, we see the downward trend of pH resulting from these acid additions.

The conversion of iodide (I^-) to molecular iodine (I_2) is most noticeable in the wetwell, since this is the repository of most iodide and HCl. Gradually, during the transient small amounts of more volatile iodine are formed. While iodide remains the dominant form, noticeable amounts of I_2 and intermediate species are created.

Once produced in water, some I_2 is free to evaporate into airspace. Fig. 4 indicates the increase in all airborne iodine throughout the transient. This is compared to the MELCOR result for CsI aerosol, which decreases dramatically due to containment sprays. The I_2 in the airspace can be vented to the enclosure building or the environment. In the present accident sequence, the only path to the environment was through the SGTS, which was assumed to operate as in MELCOR. However, both are dwarfed by the MELCOR gaseous release during the first 12 h because MELCOR does not model spray washout of gaseous iodine. Steadily increasing throughout the transient, the revolatilization release is eventually more than an order-of-magnitude higher than the MELCOR aerosol release. Also, 99% of iodine flowing directly through the SGTS was retained in filters. The remaining 1% was released to the environment. In addition, a small flow bypassing the SGTS filters vented directly into the environment. The total released from these two paths is shown in Fig. 5.

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Figure 1. Radiation Doses to Water Pools

Figure 2. Radiolytic Acid Generation

Figure 3. Water Pool pH

Figure 4. Iodine in Containment Gas Space

Figure 5. Iodine Released to the Environment

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