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Iodine Volatility and pH Control in the AP-600 Reactor

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Prepared for
U.S. Nuclear Regulatory Commission

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Abstract

Two design-basis accidents for the AP-600 reactor are formulated and evaluated, in which significant bypass of the principal pH control system occurs. Some iodine released from the reactor primary system is retained in the Incontainment Refueling Water Storage Tank (IRWST) water, never entering the containment, where trisodium phosphate produces a high pH. Some of this iodine is volatilized and is transported into the reactor containment airspace. In the worst case, a small fraction is released to the environment at design-basis leak rate, yielding a total cumulative iodine release at 30 days of 0.0352 mol (0.023% of core iodine inventory) due to the iodine volatilization bypassing the pH control system. No fission product removal in the containment atmosphere (i.e., natural deposition sprays) is considered.

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Executive Summary

Two design-basis accidents for the AP-600 reactor are formulated and evaluated, in which significant bypass of the principal pH control system occurs. Some iodine released from the reactor primary system is retained in the Incontainment Refueling Water Storage Tank (IRWST) water, never entering the containment, where trisodium phosphate produces a high pH.

This study is a companion to an earlier one, both of which are intended to evaluate pH control and iodine volatilization in the AP-600 reactor under design basis accident conditions. The previous study considered a variation of the 3BE (smallbreak LOCA) sequence (hereafter described as "Accident 1"), and was designed to present a maximum challenge to the capabilities of the containment pH control system.

Accident 2

Accident 2 was originally conceived so as to present the maximum possibility of bypassing the pH control system.

Accident 3

Subsequent to the evaluation of Accidents 1 and 2, Westinghouse personnel suggested that even greater bypass of the pH control system might occur if IRWST drain down began before fission products were deposited. Hence, Accident 3 was conceived as a judicious combination of Accidents 1 and 2. As in Accident 1, the fission product source from the primary system is airborne, and assumed to deposit on wetted containment surfaces. As in Accident 2, drainage gutters route the fission products into the IRWST, rather than into the principal containment.

These accident sequences were formulated so as to bypass the pH control system in the AP-600 containment. Most iodine is eventually transported to the flooded containment, where trisodium phosphate raises the pH high enough to prevent volatilization. However, a substantial fraction (about 20% in Accident 2 and 29% in Accident 3) of the iodine remains in the IRWST, which never fully drains. This water does not access the trisodium phosphate, but instead is the repository for acids produced by radiolysis in containment. The continual lowering of pH in this volume does lead to some production of I_2 , which is vented to the containment airspace, and a small amount vented to the atmosphere.

It should be noted that no credit was taken for deposition processes, which may remove some of the gaseous I_2 . In the IRWST, and to a lesser extent in containment, the condensation of water on walls would both impede permanent deposition and return I_2 to the IRWST pool. Here, it would be re-volatilized and returned to the containment atmosphere, although the time lag would tend to lower the overall environmental source.

It should also be noted that the temperatures assumed for this sequence (111–120°C) are beyond the range for which some of the models have been validated. The hydrolysis reactions have been measured at 25, 50, and 90°C, and extrapolation to slightly higher temperatures is not unreasonable. Data for the radiolysis reactions are sparse at temperatures above 25°C, and indicate that the model slightly overpredicts conversion to I_2 (this is conservative). The chemical equilibrium model is reliable at least to 100°C, and slight extrapolation should be acceptable. The production of HCl is more pronounced at higher temperatures, although this effect is not significant below 150°C. Thus, uncertainties due to temperature extrapolation are not large, and are probably not nearly as great as uncertainties due to sequence formulation.

In the worst case, a small fraction is released to the environment at design-basis leak rate, yielding a total cumulative iodine release at 30 days of 0.0352 mol (0.023% of core iodine inventory) due to the iodine volatilization bypassing the pH control system. No fission product removal in the containment atmosphere (i.e., sprays) is considered.

1 Introduction

This study is a companion to an earlier one,¹ both of which are intended to evaluate pH control and iodine volatilization in the AP-600 reactor under design-basis accident conditions. The previous study considered a variation of the 3BE (small-break LOCA) sequence (hereafter described as "Accident 1") and was designed to present a maximum challenge to the capabilities of the containment pH control system. Two additional accident sequences are described in the present study.

1.1 Accident 2

This accident was originally conceived so as to present the maximum possibility of bypassing the pH control system. Containment flooding leaves a residual amount (about 20%) of water in the In-containment Refueling Water Storage Tank (IRWST), where it is not accessible to pH control chemicals. Typically, under normal operation, containment drainage gutters are set to route all wall condensation (including radiolytically produced acids) into the IRWST, further lowering the pH. Iodine in this water would be subject to volatilization and would be unaffected by the containment pH control system. The actual accident sequence, designated "Spurious ADS," involves the following features:

- (1) Automatic Depressurization System (ADS) Stages 1, 2, and 3 work as intended, but Stage 4 fails.
- (2) Injection works for two Core Make-up Tanks (CMT), two accumulators, the Chemical Volume and Control System (CVS), and the Boric Acid Tank (BAT).
- (3) IRWST injection to core fails, but drainage to containment works fully.
- (4) IRWST gutter works.

Under this sequence, fission products are deposited directly into the IRWST, where no pH control occurs. For simplicity, this source is assumed to be instantaneous, composed of the gap releases and in-vessel releases specified in NUREG-1465.² These amounts, which are identical to those used in the earlier study,¹ are shown in Table 1.1. The sequence begins at this point for purposes of pH and iodine evaluation. Also at initial time, IRWST drainage to the containment begins and subsequently moves most of the iodine (and other fission products) to the containment. Mixing of the water with trisodium phosphate (TSP) raises the pH well above 9, virtually eliminating iodine volatilization. However, the residual water in the IRWST contains about 20% of the iodine released from the primary system; and since no pH control exists, the potential for iodine volatilization is high.

1.2 Accident 3

Subsequent to the evaluation of Accidents 1 and 2, Westinghouse personnel suggested that even greater bypass of the pH control system might occur if IRWST drain-down began before fission products had been deposited. Hence, Accident 3 was conceived by the judicious combination of Accidents 1 and 2. As in Accident 1, the fission product source from the primary system is airborne and is assumed to deposit on wetted containment surfaces. As in Accident 2, drainage gutters route the fission products into the IRWST, rather than into the principal containment.

In practice, this sequence is modeled similar to Accident 2, except for a source term that is time dependent rather than instantaneous. The timing of fission product release from the primary system is exactly that of Accident 1, consisting of gap and in-vessel releases from Reference 2. These are deposited directly into the IRWST, simulating the processes of surface deposition and drainage in condensate. While detailed modeling of the actual processes would involve some lag time, it is expected to be short compared with the accident duration. All other thermal hydraulic conditions in Accident 3 are assumed to be identical to those of Accident 2 and are described in the following section. In addition, all additives and chemicals that would affect pH are also assumed to be identical to those in Accident 2.

Table 1.1 Fission product inventories released into IRWST

AP-600 Fission product group inventories				
Fission product group	Total core inventory (g)	Released to IRWST		
		Fraction	Mass (g)	
1 Xe	41,1900	1.00	411,900	
2 I	18,360	0.40	7,344	
3 Cs	237,600	0.30	71,280	
4 Te	34,250	0.05	1,712	
5 Sr	70,700	0.02	1,414	
6 Mo	243,600	0.0025	609	
7 Ba	107,800	0.02	2,156	
8 La	566,200	0.0002	113	
9 Ce	200,800	0.0005	100	
10 Sb	2,037	0.05	102	
11 U	64,360,000	0.0005	32,180	
12 Ru	612,000	0.0017	1,040	

*See Reference 1.

2 Thermal Hydraulic Conditions

In the early stages, venting of the primary system to the IRWST would raise its level to a maximum and its temperature to saturation. Continued steaming eventually creates a small, but significant, flow from the IRWST gas space to the main containment. However, this gas flow does not actually begin until the water drainage to main containment is complete (since water drainage itself produces a much larger gas inflow). Containment leakage to the environment represents an additional gas flow.

2.1 Pressure and Temperature

According to Westinghouse estimates, the containment pressure will increase to 29 psia within 2 h of ADS operation (Stages 1, 2, and 3) and will decrease to 22 psia after 30 days. Thus, we assume 29 psia for the first 24 h of the sequence, followed by a linear decrease to 22 psia over the remaining 29 days. Assuming the presence of saturation conditions implies temperatures in all gas and water phases of 120°C at the start, decreasing to 111°C after 30 days.

2.2 IRWST Drain

The flow rate of water from the IRWST to the containment was taken from plots of such flow in the AP-600 design document.⁴ The drain flow, as illustrated in Figure 2.1, takes about 5 h to complete.

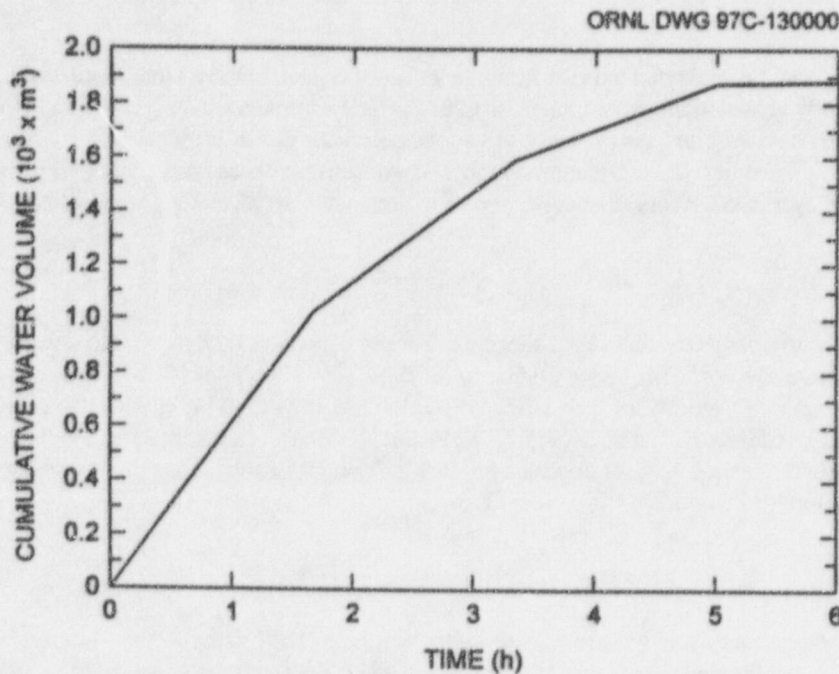


Figure 2.1 Water flow from IRWST to containment

2.3 IRWST Venting

As stated in Section 2, steaming of the IRWST produces a small gas flow to containment after the water drain is complete. The steaming is caused by continued heat generation due to decay heat of the fission products, coupled with condensation of steam on the containment shell. Westinghouse provided estimates³ of 250 cfm at 2 h, 100 cfm at 24 h, and 40 cfm at 6 days. These three values were fit to the empirical form

$$\text{flow rate (m}^3/\text{s)} = A_0 \exp (At + B), \quad (1)$$

resulting in values of $A = 8.54 \times 10^{-6} \text{ (s}^{-1}\text{)}$, $B = 2.53 \times 10^{-3}$. The constant $A_0 = 1 \text{ m}^3/\text{s}$ allows for changing to other units. The flow in Equation (1) was applied after 5 h and lasted throughout the entire 30 days, although it became negligibly small by the end of the accident period.

2.4 Containment Leakage

Westinghouse provided an estimate³ that the containment leakage to the atmosphere was 0.12% per day. Use of this estimate resulted in flow rate of $6.62 \times 10^{-4} \text{ m}^3/\text{s}$ throughout each accident sequence.

3 Containment Chemistry

Most iodine enters containment as CsI aerosol,^{3,6} which is readily dissolved in sumps or surface condensate. Even if released into the containment atmosphere, most iodine will quickly settle onto wetted surfaces and will be washed into sumps or pools. In accident sequences 2 and 3, CsI is released directly into IRWST water. It has been well established⁶⁻⁸ that the volatility of iodine is closely related to the pH of water pools in various containment volumes.

Containment Chemistry

Even highly soluble iodide (I^-) can be converted to other forms (e.g., I_2 and organic iodides) that more easily evaporate from water and could be subsequently vented to the environment. At $25^\circ C$, this conversion is negligible for pH levels greater than 7, but dominant for pH levels less than 3. Thus, the presence of various chemicals that affect water pH is quite important in determining the extent of iodine volatility. In each accident sequence, we consider three such chemicals present in the AP-600 (i.e., borates, phosphates, and hydrochloric acid) that are expected to dominate the calculation of pH in various locations.

3.1 Borates

Most water in these sequences originally contains various forms of borates, which, regardless of initial form, hydrolyzes to form boric acid and various polyborate species.⁹ The concentration in the IRWST is 2700 ppm (0.25 mol/L) as boron. The concentration in the reactor primary system varies, depending on additions from various tanks and accumulators; however, the average is not significantly different from that of the IRWST. While the processes of steaming and condensation produce surfaces wetted with nonborated water, the latter is expected to quickly drain into pools. Thus, all water is assumed to have a boron concentration of 2700 ppm (0.25 mol/L).

3.2 Phosphates

The AP-600 design includes the placement of baskets of trisodium phosphate (TSP) in the lower containment, which will dissolve and increase the pH in the flooded containment. The design specification is for a minimum of 7830 lb of TSP (43% as anhydrous salt, corresponding to the dodecahydrate $Na_3PO_4 \cdot 12H_2O$), which translates to 9309 mol. Invariably, TSP contains small amounts of NaOH (true even of reagent-grade TSP); however, this excess caustic was not considered. (It is conservative to neglect the excess NaOH.) In these accident sequences, the TSP begins dissolving when the water level in containment reaches the floor of the steam generator rooms (83-ft elevation) and is completely dissolved after rising 3 m (9.8 ft) above the floor. It is assumed to be distributed uniformly and instantly throughout all water in the flooded containment (i.e., a well-mixed volume is assumed).

3.3 Acids

Irradiation tends to produce various acids that would decrease pH; therefore, their effects must be considered in assessing overall iodine volatility. Small amounts of nitric acid are produced from the irradiation of air-water mixtures; however, this effect is assumed to be negligible and, therefore, was not included in the present analysis. The irradiation and heating of electrical cable insulation have been shown to produce significant quantities of hydrochloric and sulfuric acids,¹⁰ which are subsequently dissolved in condensate and collected in sumps. In the present sequences, the calculation follows the procedure outlined in Appendix B of Reference 10. Since containment drainage gutters are set to route wall condensation to the IRWST, all acids are deposited there as well.

3.4 Fission Product Sources

In Accident 2, all fission products are assumed to be released through spargers into the IRWST at the start of the accident sequence. Because there is very little gas space in the IRWST at this time, noble gases are assumed to vent instantly into the containment atmosphere. All iodine is assumed to be initially CsI and to be immediately dissolved in IRWST water. In reality, a small quantity of volatile iodine might be present in the source from the primary system; however, our goal is to predict volatilization of that iodine which was initially nonvolatile. The assumption that all iodine occurs initially as iodide allows a clearer assessment of this process. Finally, all other fission products are assumed to be nonvolatile for the entire accident. They are released into water and travel with it either in solution or in suspension. The primary reason for considering noble gases and nonvolatile fission products is to allow calculation of the radiation doses to water pools and gas spaces.

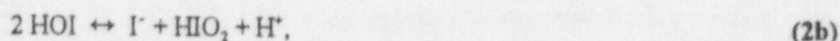
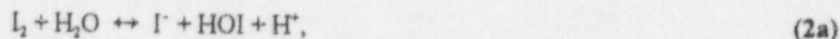
For Accident 3, the release is initially into containment airspace, but all fission products except noble gases become quickly entrained in condensate and deposited in the IRWST. This is true of both CsI and less volatile fission products. Noble gases,

however, are assumed to be instantly released into the containment, as in Accident 2. However, in Accident 3, the releases are timed (see Reference 2), rather than instantaneous.

3.5 Iodine Chemistry

3.5.1 Hydrolysis

In aqueous solution, iodine can undergo hydrolysis, which is described well by the following reaction set:^{8,11}



The end-point oxidation states that I^- and IO_3^- (or HIO_3) are both extremely soluble and, therefore, highly desirable. The HOI and HIO_2 species are reaction intermediates, which may be volatile but 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 levels (i.e., a 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 Reference 11.

3.5.2 Radiolysis

In a radioactive environment, the presence of free radicals induces additional aqueous reactions. The overall result can be described empirically by the equilibrium¹¹

$$\frac{[H^+]^2 [I^-]^2}{[I_2]} = a + b [H^+], \quad (3)$$

where a and b are known coefficients depending only on temperature. The actual rate equations used in this study are based on the catalytic decomposition of hydrogen peroxide, one of the stable by-products 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,¹² and the reverse coefficients are chosen to move steadily toward equilibrium (3).

3.5.3 Gas/Liquid Partitioning

The same equation is used to describe the evaporation of volatile iodine species from water (I_2 or CH_3I) and their dissolution from gas back to the water. 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.¹¹

3.5.4 Organic Iodides

Organic iodides are described empirically by the formation of CH_3I from I_2 in the gas phase. The model used is described fully in Reference 11. Analogous to I_2 , CH_3I is sparingly soluble in water — an effect which is negligible in the accident sequences considered here.

Computation

3.6 Radiation Doses

Several of the models depend on the prediction of decay energy in air or water. Energy outputs for beta and gamma radiation are given in Table 3.1 for each fission product group at various times. These were calculated by using ORIGEN¹³ results for fission product inventories, together with ICRP data¹⁴ for nuclide decay energies.

The doses to water assume that all energy from beta and gamma decay is absorbed in water. They are calculated by combining information from Table 3.1 (interpolated to the correct time) with the water inventories of each fission product group at each time step, as obtained from MAAP reactor analysis code output.

The rate of HCl formation in cable sheathing is based on the energy production rates (both beta and gamma) due to fission products that are airborne or deposited on surfaces. The latter rates are calculated using the procedure described in Reference 10.

Table 3.1 Radiation energy outputs to water pool

Beta-energy output by MAAP fission product group [(MeV/s)/kg × 10⁻¹²]

Time (h)	Xe 1	CsI 2	TeO ₂ 3	SrO 4	MoO ₂ 5	CaOH 6	BaO 7	La ₂ O ₃ 8	CeO ₂ 9	Sb 10	Te ₂ 11	UO ₂ 12
0	12.470	230.89	134.70	38.138	10.040	34.251	69.500	57.823	8.365	650.10	168.00	0.337
1	5.946	185.28	53.26	35.527	4.500	17.302	29.253	34.856	8.292	232.70	66.43	0.169
2	4.729	152.24	29.82	33.271	4.134	9.956	19.828	30.953	8.186	141.80	37.19	0.138
5	3.481	109.61	15.39	28.209	3.987	4.114	11.146	25.192	7.881	87.83	19.20	0.128
10	2.883	88.071	11.891	23.071	3.782	1.564	8.876	19.865	7.405	56.39	14.83	0.120
24	2.068	61.725	8.980	16.831	3.266	0.549	8.418	14.752	6.300	31.67	11.20	0.101
48	1.362	41.878	7.093	13.990	2.537	0.512	7.985	13.030	5.002	24.700	8.846	0.076
96	0.954	24.966	4.869	13.117	1.533	0.505	7.184	11.974	3.698	17.820	6.073	0.043

Gamma-energy output by MAAP fission product group [(MeV/s)/kg × 10⁻¹²]

Time (h)	Xe 1	CsI 2	TeO ₂ 3	SrO 4	MoO ₂ 5	CaOH 6	BaO 7	La ₂ O ₃ 8	CeO ₂ 9	Sb 10	Te ₂ 11	UO ₂ 12
0	19.470	753.32	235.01	60.098	15.169	52.232	56.141	41.486	4.597	2253.0	293.10	0.119
1	8.780	615.56	97.90	49.627	2.386	21.006	10.097	27.007	4.549	793.10	122.10	0.097
2	6.729	500.61	54.26	41.258	1.620	9.718	7.156	22.746	4.481	466.50	67.67	0.092
5	4.005	347.38	25.68	24.911	1.525	4.518	6.473	17.590	4.280	270.70	32.03	0.088
10	2.298	278.13	21.53	12.608	1.447	3.654	6.317	15.348	3.971	161.00	26.85	0.083
24	1.084	199.53	17.62	3.498	1.249	3.317	6.153	14.045	3.255	77.95	21.98	0.070
48	0.529	144.10	12.98	0.592	0.970	3.257	5.900	13.243	2.418	59.510	16.190	0.052
96	0.317	91.37	7.51	0.018	0.586	3.164	5.432	12.067	1.587	44.590	9.368	0.030

4 Computation

The geometry for the sequences in Accidents 2 and 3 involves only the three control volumes listed in Table 4.1. A computational model was constructed to describe each relevant physical and chemical process in the entire system. Rate equations were developed for each process and solved together to give a transient description of convective transport and chemical interactions for the duration of the accident. The sequences are divided into discrete time steps, and at each step the following actions are taken (in the order indicated): (1) sources of fission products or pH-influencing chemicals are introduced; (2) convective flow transfers between different control volumes are computed; (3) the pH within each control volume is

Table 4.1 Control volumes used in accident sequence geometry

Control volume	Total volume (m ³)	Max. water volume (m ³)
Containment	47694	1862
IRWST	2425	2265
Environment		

calculated; and (4) the speciation, chemical interactions, or phase change within each control volume is calculated. Each subcalculation is discussed in more detail in the subsections that follow.

4.1 Sources

In addition to fission products, there are sources of pH-influencing chemicals. Borate is present in all water, as mentioned in Section 3.1. TSP is dissolved during the first few hours, consistent with the water level increase in containment (see Section 3.2). Acid is added as HCl according to the model in Reference 10. The transient additions used for TSP and HCl are shown in Figures 4.1.a-4.1.b. (The production of HCl is due almost entirely to radiation from noble gases, which is the same in each of the sequences considered here.)

4.2 Convective Flow

Transfers of gas or liquid inventories between control volumes are based on the flows discussed in Section 2. The volume fraction of fluid that leaves the control volume during a time step is assumed to carry that same fraction of components. Thus, for a 1-h time step, containment venting to the atmosphere moves .12/24, or .005%, of the containment gas volume (see Section 2.4). Then, in the same time step, .005% of current gaseous iodine and noble gas inventories would also be transferred to the environment.

4.3 Determination of pH

Inventories of all aqueous constituents are updated in the source and flow steps above. The calculation of pH assumes that equilibrium is reached rapidly. The equilibrium calculation model uses the principal subroutine "GASOL" of the code SOLGASMIX.¹⁵ The calculation uses an extended Debye-Hückel form for activity coefficients and includes multiple phosphate and borate species. The model itself and its validation with actual data are described in Reference 11.

4.4 Control Volume Chemistry

The most complicated part of the calculation is the simultaneous solution of all rate equations arising in Section 3.5 relative to iodine hydrolysis, radiolysis, gas/liquid partitioning, and methyl iodide formation. This set of ordinary differential equations is solved by using the routine LSODE and related routines.¹⁶

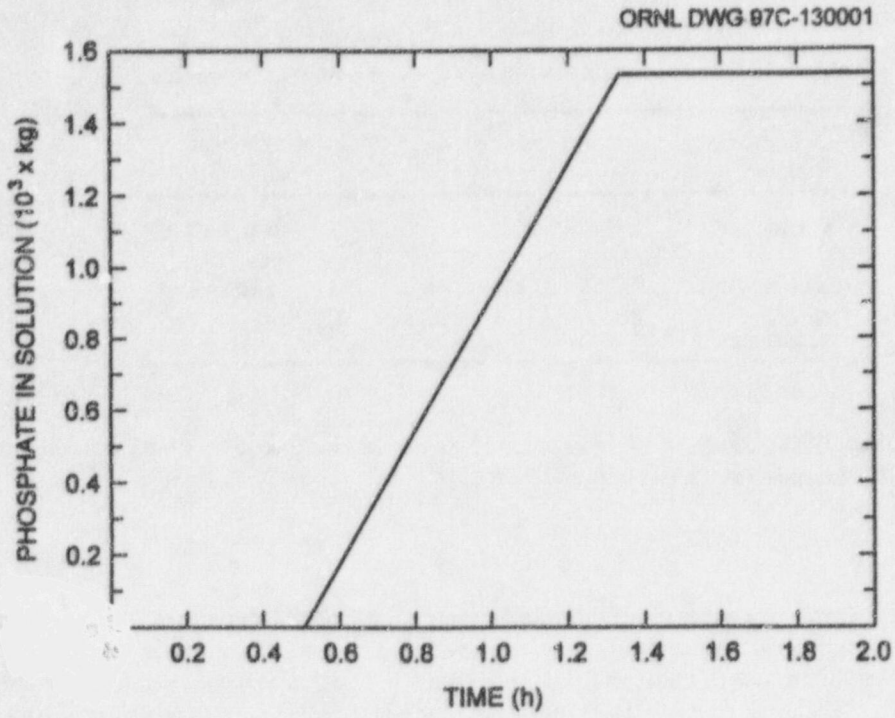


Figure 4.1.a Addition of trisodium phosphate (as anhydrous Na_3PO_4) to containment water

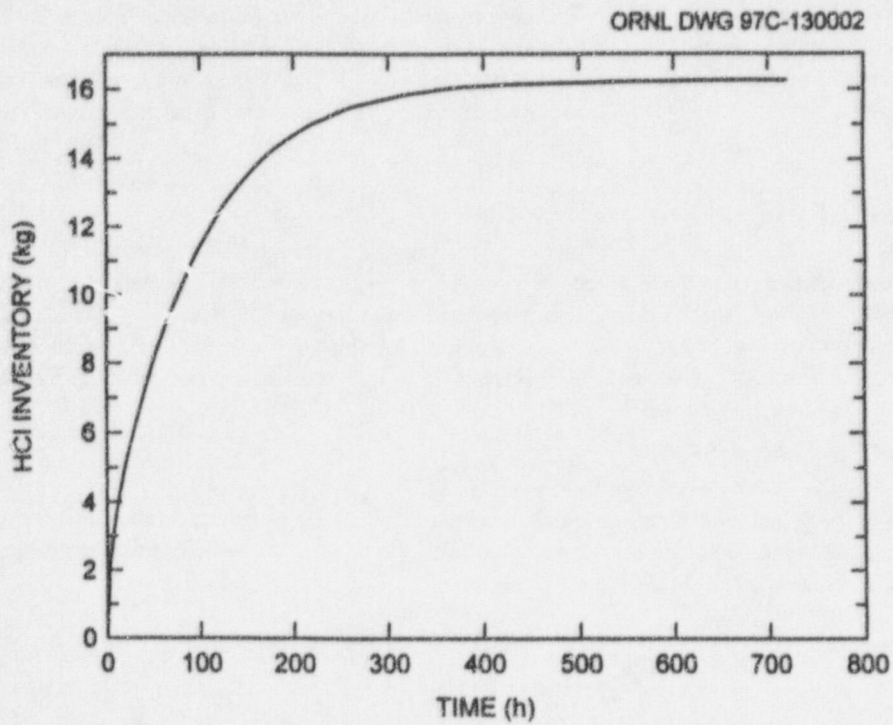


Figure 4.1.b Total acid production from radiolysis

5 Results and Discussion

The model described in Section 4 was run for a 30-day transient in the case of both Accidents 2 and 3. The pH levels in the IRWST and containment water were virtually identical in each sequence (see Figure 5.1). The pH of borated water, which is somewhat below 6, is changed considerably by sources of other chemicals (water is above 100°C). Due to the HCl source, the pH of the IRWST water declined steadily for the first 8 h and, after 30 days, had decreased to almost 3.0. While the pH of the containment water declined briefly, it rose abruptly when phosphate dissolution began and stayed above 9.5 for the remainder of the 30-day transient.

For Accident 2, iodine speciation in the two water pools is depicted in Figures 5.2 and 5.3, which show that a gradual oxidation of I^- to IO_3^- began quickly in each case. Note that the plotted quantity "fraction of containment total" includes all iodine released from the reactor coolant system, which is 40% of the total core inventory. In the IRWST water, the process continued throughout the 30-day accident transient, eventually yielding almost complete conversion to IO_3^- . This is consistent with experimental results at 25°C and is caused by the tandem processes of radiolysis and hydrolysis. In the former, I^- is converted to I_2 ; in the latter, I_2 is converted—primarily to I^- , but also some fraction to IO_3^- . Over time, accumulation of IO_3^- is the inevitable result for moderate pH values. However, in the containment sump, the process was abruptly terminated once the water level rose sufficiently to dissolve TSP (at about 30 min). At this point, the inventories of I_2 and HOI decreased drastically, and the destruction of I^- was effectively ended. In Figure 5.2, inventories of all species increased due to additions from IRWST drainage; however, they stabilized at about 5 h and changed very little after that point. The intermediates HOI and HIO_2 continued to oxidize slowly, and the inventory of IO_3^- eventually exceeded that of HIO_2 (at about 17 days). Note also that the I_2 concentration was much higher in the IRWST water (where the pH was low). While complete oxidation to IO_3^- would occur in a closed volume, the presence of a significant aqueous I_2 inventory in a vented control volume would allow evaporation and escape of gaseous I_2 . This effect can be seen in Figure 5.4, where I_2 has evaporated from the IRWST water into the IRWST airspace and is subsequently vented into the containment airspace. From there, some I_2 is redissolved in the containment water (see Section 3.5.3), while a small amount is actually released to the environment.

The cumulative environmental releases at various times are shown in Table 5.1. The molar amounts are direct output of the calculations. At each time step, the rate of activity released is calculated by

$$\dot{Q}_i = P_i \dot{n}_i,$$

where \dot{Q}_i is the rate of activity release during time step i , \dot{n}_i = total iodine leak rate (mol/s) at step i , and $P_i = P(t)$ [Ci/mol total I] is determined from ORIGEN calculations at various time steps. A good approximation for the AP-600 is

$$\ln(P) = \begin{cases} -3.5089 - 0.09885 t + 0.002420 t^2 & 0 < t < 24 \\ -4.4876 - 0.01424 t + 0.000013 t^2 & 24 < t < 720 \end{cases}$$

where t is in hours. The cumulative activity is, then,

$$Q = \int \dot{Q}(t') dt' = \sum \dot{Q}_i \Delta t_i.$$

The speciation of volatile gaseous iodine, as shown in Figure 5.5, confirms that I_2 is the dominant form, as expected.

The iodine inventories for Accident 3 (see Figures 5.6–5.9) are very similar to the analogous results for Accident 2. Since almost 50% more iodine ends up in the IRWST water, greater volatilization would be expected. This is borne out in Table 5.1, where roughly 50% more iodine is released to the environment at times exceeding 24 h.

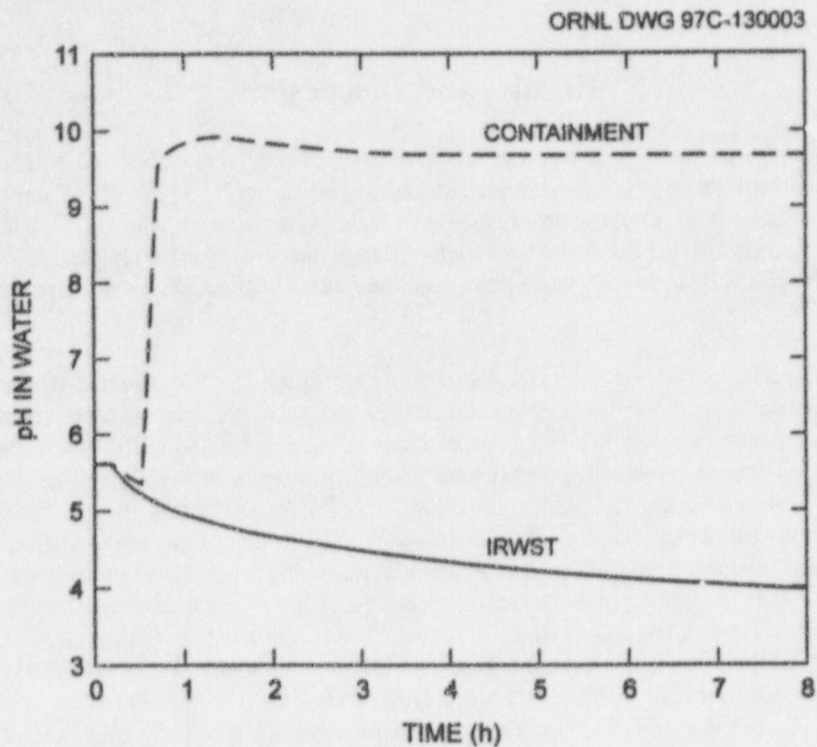


Figure 5.1 Levels of pH in containment volumes

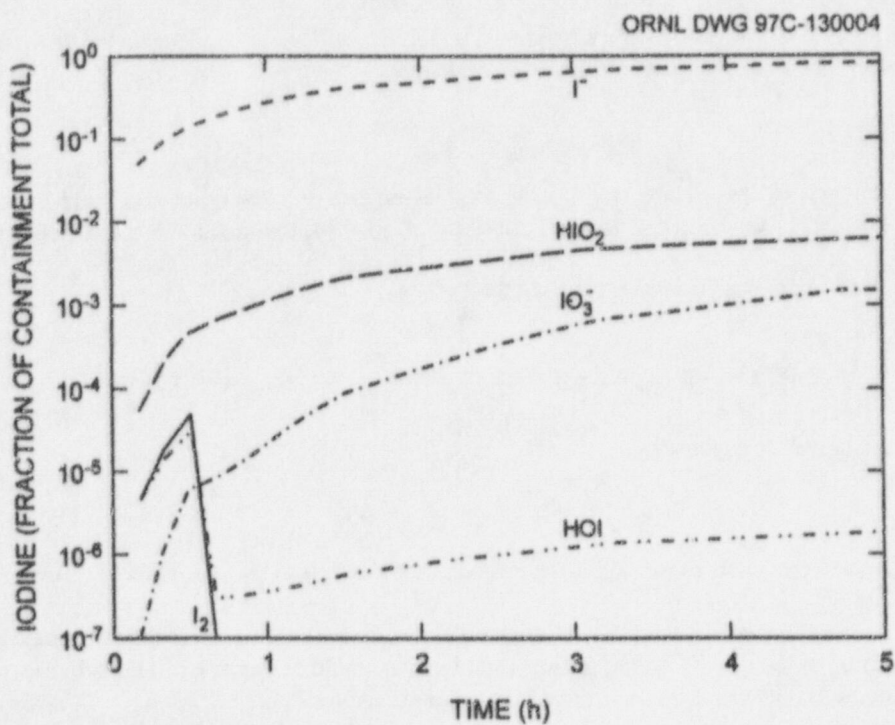


Figure 5.2 Aqueous iodine in containment water (Accident 2)

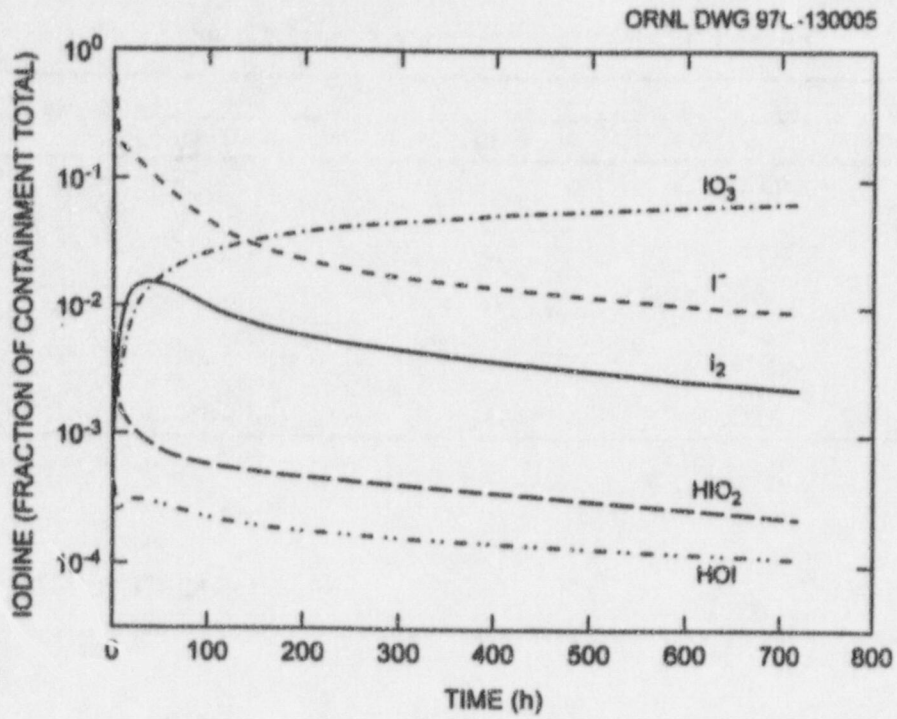


Figure 5.3 Aqueous iodine in the IRWST water (Accident 2)

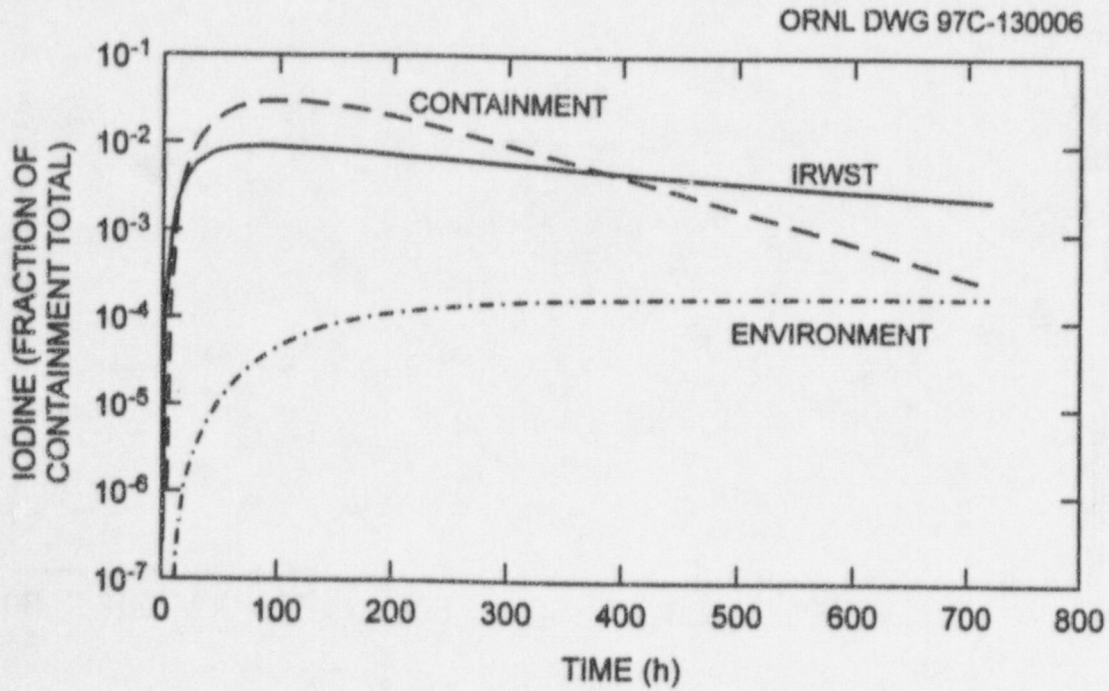


Figure 5.4 Total gas-phase iodine (Accident 2)

Table 5.1 Cumulative environmental releases of iodine

Time	Accident 2		Accident 3	
	mol	Ci	mol	Ci
2 h	10^{-8}	0.013	10^{-12}	10^{-5}
8 h	10^{-6}	1.9	10^{-6}	2
1 d	0.00015	174	0.00022	245
4 d	0.00500	3247	0.00770	4993
30 d	0.02250	5981	0.03519	9326

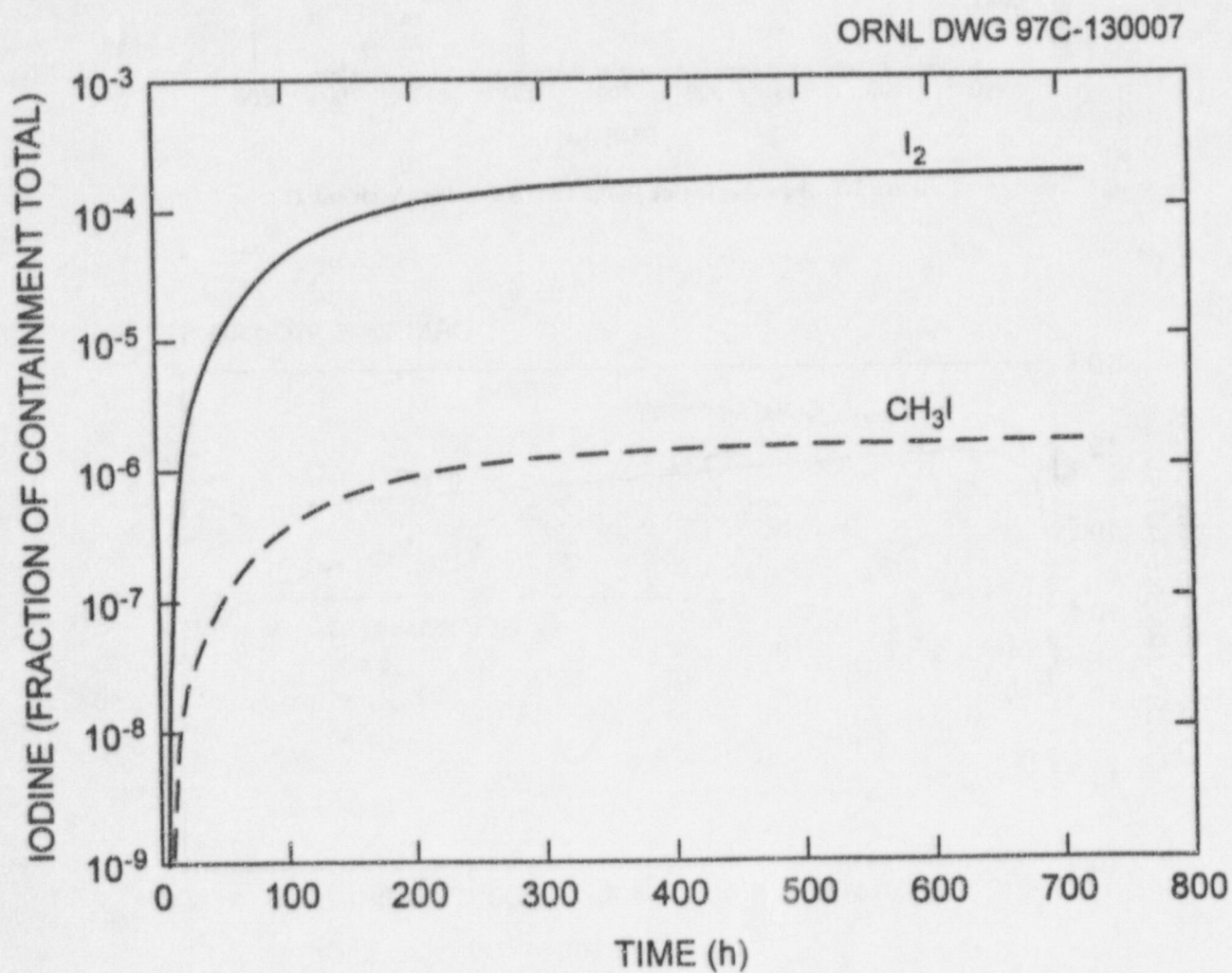


Figure 5.5 Environmental release for Accident 2

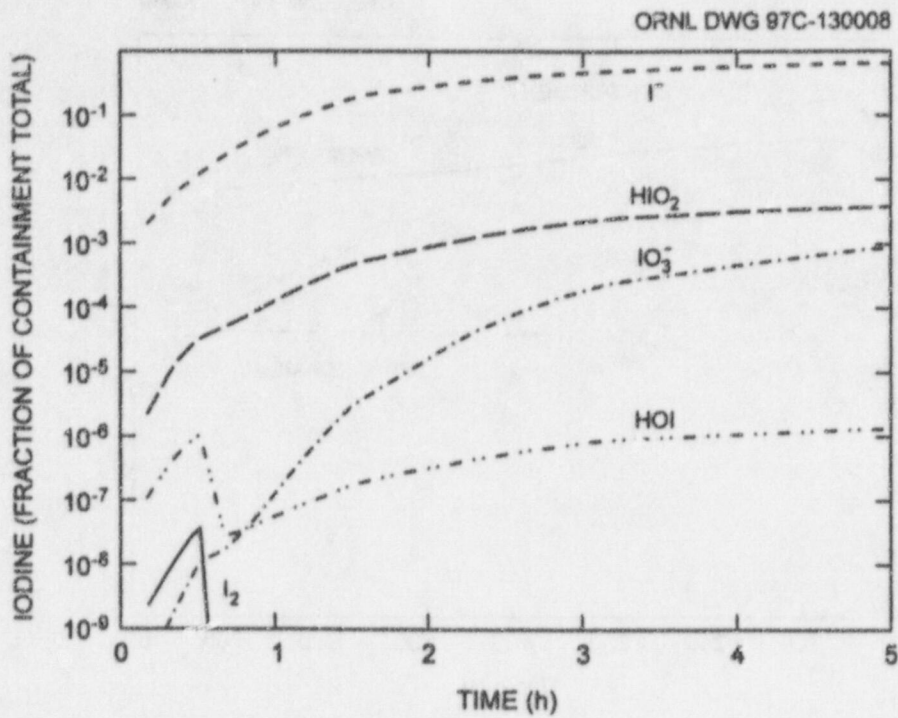


Figure 5.6 Aqueous iodine in principal containment (Accident 3)

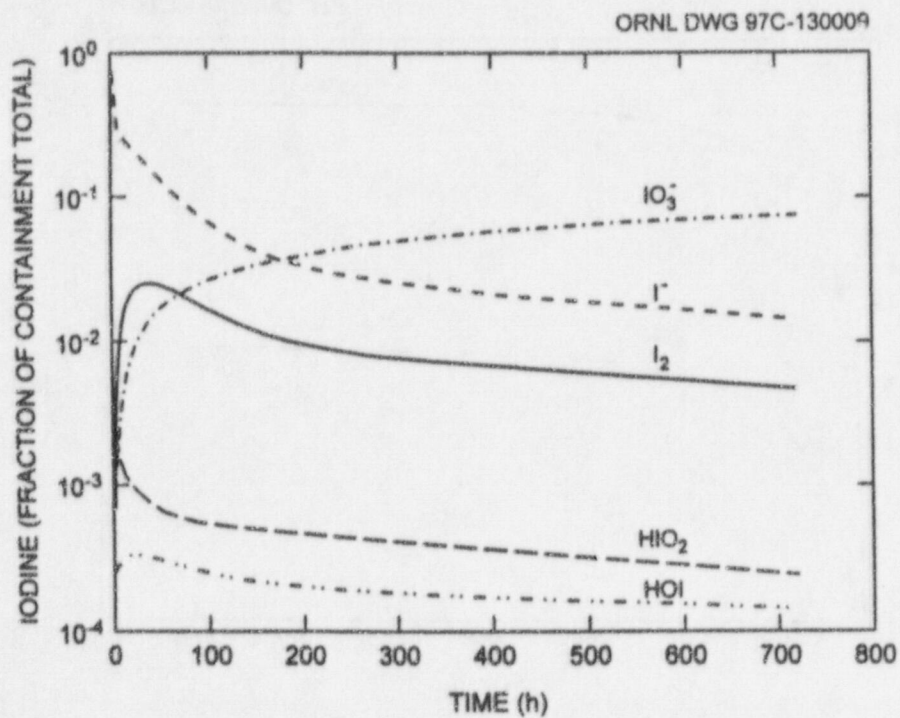


Figure 5.7 Aqueous iodine in the IRWST water (Accident 3)

ORNL DWG 97C-130010

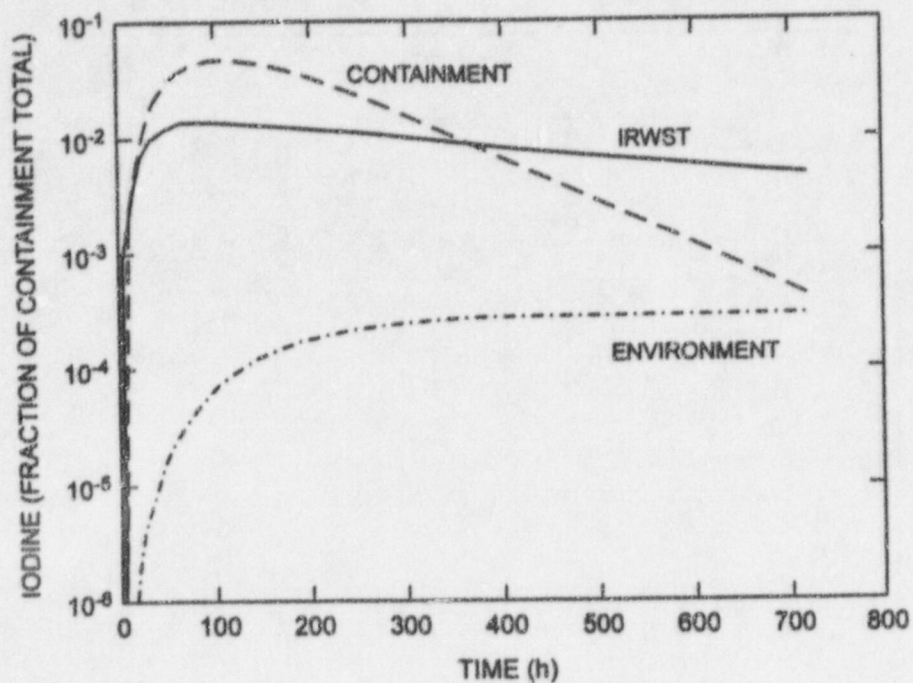


Figure 5.8 Total gas-phase iodine (Accident 3)

ORNL DWG 97C-130011

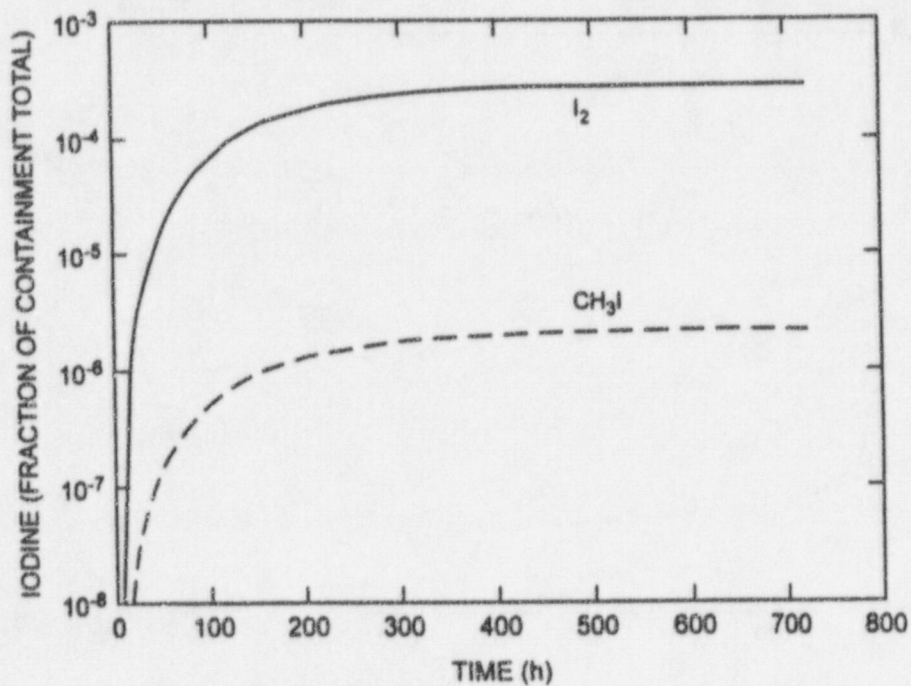


Figure 5.9 Environmental release (Accident 3)

6 Conclusions

These accident sequences were formulated so as to bypass the pH control system in the AP-600 containment following a design-basis accident. Most iodine is eventually transported to the flooded containment, where TSP raises the pH to a level sufficiently high enough to prevent volatilization. However, a substantial fraction (about 20% in Accident 2 and 29% in Accident 3) of the iodine remains in the IRWST, which never fully drains. This water does not access the TSP; instead, it is the repository for acids produced by radiolysis in the containment. The continual lowering of pH in this volume leads to the production of some I_2 , which is vented to the containment airspace; a small amount is released to the environment.

It should be noted that no credit was taken for iodine deposition processes, which may remove some of the gaseous I_2 . In the IRWST, and to a lesser extent in the containment, the condensation of water on walls would (1) impede permanent deposition and (2) return I_2 to the IRWST pool. Here, it would be revolatilized and returned to the containment atmosphere, although the time lag would tend to lower the overall environmental source.

It should also be noted that the temperatures assumed for these accident sequences (111–120°C) are beyond the range for which some of the models have been validated. The hydrolysis reactions have been measured at 25, 50, and 90°C, and extrapolation to slightly higher temperatures is not unreasonable. Data for the radiolysis reactions are sparse at temperatures above 25°C and indicate that the model slightly overpredicts conversion to I_2 (which is conservative).¹¹ The chemical equilibrium model is reliable at least to 100°C, and slight extrapolation should be acceptable. The production of HCl is more pronounced at higher temperatures, although this effect is not significant below 150°C. Thus, uncertainties due to temperature extrapolation are not large — and probably not nearly as great as uncertainties due to sequence formulation.

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10. SUPPLEMENTARY NOTES

J.Y. Lee, NRC Project Manager

11. ABSTRACT *(200 words or less)*

Two design-basis accidents for the AP-600 reactor are formulated and evaluated, in which significant bypass of the principal pH control system occurs. Some iodine released from the reactor primary system is retained in the Incontainment Refueling Water Storage Tank (IRWST) water, never entering the containment, where trisodium phosphate produces a high pH. Some of this iodine is volatilized and is transported into the reactor containment airspace. In the worst case, a small fraction is released to the environment at design-basis leak rate, yielding a total cumulative iodine release at 30 days of 0.0352 mol (0.023% of core iodine inventory) due to the iodine volatilization bypassing the pH control system. No fission product removal in the containment atmosphere (i.e., natural deposition sprays) is considered.

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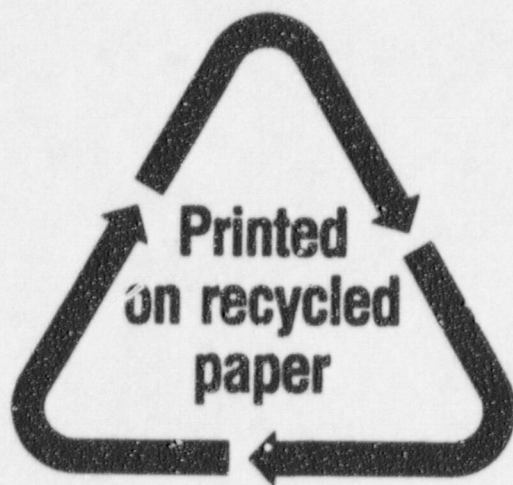
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