NUREG/CR-5950
ORNL/TM-12242

Iodine Evolution and pH Control

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Prepared for
U.S. Nuclear Regulatory Commission

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NUREG/CR-5950
ORNL/TM-12242
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Manuscript Completed: October 1992
Date Published: December 1992

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Prepared for
Division of Safety Issue Resolution
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555
NRC FIN L2039

Abstract

In accident sequences where pH falls below ~7, I_2 will form in irradiated water pools. In containments where no pH-control chemicals are present, the acidity or basicity will be determined by materials that are introduced into water as a result of the accident itself. The most important acids in containment will be nitric acid, produced by irradiation of water and air, and hydrochloric acid, produced by irradiation or heating of electrical cable insulation. The maximum duration of a basic pH, in the absence of pH-control chemicals, was calculated to be ~60 to 100 h.

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Symbols

$A_{\beta H}$	Asborption of beta radiation energy by Hypalon
$A_{\gamma H}$	Absorption of gamma radiation energy by Hypalon
b	Strong base, -b strong acid
B	Buffer capacity
BWR	Boiling-water reactor
C	Concentration
D	Diffusion coefficient (cm^2/s)
E_β	Total beta radiation energy release rate (MeV/s)
E_γ	Total gamma radiation energy release rate (MeV/s)
G	Radiation G value (molecules/100 eV)
G_r	Grashof number (Hewison, 1987)
k	Rate constant
K	Equilibrium constant, combination of rate constants
l	Length
L	Liter
LWR	Light-water reactor
M	Molar (mol/L)
mol	Gram mole
N	Total mass of EPR/Hypalon cable insulation
PC	Partition coefficient

P_r	Prandtl number (Hewison, 1987)
PWR	Pressurized-water reactor
R_e	Reynolds number (Hewison, 1987)
$R_{\beta H}$	HCl generation rate from beta radiolysis of Hypalon (g-mol/s)
$R_{\gamma H}$	HCl generation rate from gamma radiolysis of Hypalon
S	Total surface area of electrical cables (cm^2)
S_c	Schmidt number (Hewison, 1987)
S_h	Sherwood number (Hewison, 1987)
T	Temperature
$\phi_{\beta C}$	Beta radiation flux on electrical cables (MeV/cm^2-s)
$\phi_{\gamma C}$	Gamma radiation flux on electrical cables (MeV/cm^2-s)

pH is the major factor in determining the extent of I_2 in solution. In containment where no pH-control chemicals are present, the acidity or basicity of the water pool will be determined by materials that are introduced into containment as a result of the accident itself. These materials may be fission products (i.e., cesium compounds), thermally produced products (i.e., core-concrete aerosols), or compounds produced by radiation (i.e., nitric acid).

In situations where pH levels fall below ~7, the formation of I_2 will occur in irradiated iodide solutions. A correlation between pH and iodine formation is needed so that the amounts of I_2 in water pools can be assessed. This, in turn, determines the amount of I_2 in the atmosphere available for escape by containment leakage. A number of calculational routines based on more than 100 differential equations representing individual reactions can be found in the literature. In this work, it is shown that a simpler approach based on the steady-state decomposition of hydrogen peroxide should correctly describe iodine formation in severe accidents. Comparisons with test data show this approach to be valid.

The most important acids in containment will be nitric acid (HNO_3), produced by irradiation of water and air, and hydrochloric acid (HCl), produced by irradiation or heating of electrical cable insulation. The most important bases in containment will be cesium hydroxide, cesium borate (or cesium carbonate), and in some plants pH additives, such as sodium hydroxide or sodium phosphate.

Some aspects of the timing of pH changes can be obtained from what is known about fission product release into containment. Initially, the pH should be basic because of cesium entering water pools as hydroxide, borate, or carbonate. However, once fission products enter a water pool, a radiation dose rate is established, and nitric acid begins to form and neutralize the basic solutes. This leads to an interesting trade-off — a high concentration of fission products that contain basic solutes brings about a high initial pH but also a high radiation dose rate, which results in a relatively high production of nitric acid. From these offsetting effects, we may calculate the time necessary to reduce the initial basic pH down to 7.0. This time can be considered to be the maximum duration that a basic pH will occur in the absence of pH control additives. It is a maximum because it considers only the basic contribution to pH and the formation of nitric acid.

The maximum duration of a basic pH was calculated for the seven accident sequences that were evaluated in NUREG/CR-5732 (Beahm, 1991). The time to reach pH 7 is remarkably similar for the calculations where the assumed initial form of cesium was hydroxide. This similarity appears in spite of water volumes that ranged from 3.00×10^4 gal (1.15×10^5 L) to 1.37×10^6 gal (5.17×10^6 L) in the different sequences. This maximum duration for a basic pH is ~100 h. The times for pH >7 were ~60 h when it was assumed that cesium entered a water pool as cesium borate ($CsBO_2$). Thus, ~60 to 100 h is the maximum duration that a basic pH may be maintained in the absence of pH control additives. A pH <7 may be attained in <24 h if boric acid or HCl becomes a component of the water pool.

Amounts of hydrochloric acid on the order of 10^3 to 10^4 mols may be anticipated in some accident sequences. This would introduce chlorine containing species that are 10 to 100 times the amount of iodine containing species.

There are two major uncertainties that result from the production of HCl in containment. The first is the uncertainty in the formation of I_2 during irradiation of water pools that contain both chloride and iodide ions. The model for steady-state fraction of iodine as I_2 does not specify a mechanism for the initial production of I_2. There are no experimental data on irradiation of solutions containing chloride and iodide at pH <7. In the absence of experimental data, the range of applicability of the steady-state model remains speculative. As was the case in solutions containing iodide alone, it is only pH <7 that would be of any importance in I_2 formation.

The second uncertainty is in the behavior of I_2 and organic iodide in charcoal filter systems when any combination of HCl, HOCl, Cl_2, or organic chlorides are present. Again, there are no experimental data on this. The evaluation in Appendix D.4 was based

on chemical reactions that may be expected to occur, and these indicate that both the capacity and retention of iodine species in charcoal filters will be degraded when chlorine species are present.

1 Introduction

There is evidence that pH* is the major factor in determining the extent of I_2 in solution (Deane, 1986; Vikis, 1989). Iodine in solution as I_2 will partition to the atmosphere and be available for release through containment leakage. In containments where no pH-control chemicals are present, the acidity or basicity of the water pool will be determined by materials that are introduced into containment as a result of the accident itself. These materials may be fission products (i.e., cesium compounds), thermally produced products (i.e., core-concrete aerosols), or compounds produced by radiation (i.e., nitric acid). A list of materials that will determine pH in a severe accident is provided in Table 1.1.

Table 1.1 Materials that will determine pH in containment water pools

- Boron oxides (acidic)
- Basic fission product compounds such as cesium hydroxide or cesium borates (basic)
- Iodine as HI (acidic)
- pH additives (basic)
- Atmospheric species such as carbon dioxide or nitric acid (acidic)
- Core-concrete aerosols (basic)
- Hydrochloric acid from cable insulation (acidic)

Because pH values lower than ~7 are associated with the formation of I_2 in irradiated water pools, it is necessary to assess the materials listed in Table 1.1 to obtain some sense of the pH values that may be attained in severe accidents. Further, because it is desirable to maintain pH values of 7 or above, the ability to maintain or buffer pH in the presence of a number of acids and bases must also be evaluated. In this work, the assessments are based on the amounts of materials that may be present in containment, along with calculations of pH values. At Oak Ridge National Laboratory (ORNL), a computer program based on the main subroutine of the SOLGASMIX code was written to calculate pH in containment water pools for use in TRENDS (Transport and REtention of Nuclides in Dominant Sequences). This routine was used in evaluating pH values in the present study. A description of this routine is given in Appendix A.

In situations where pH levels fall below ~7, the formation of I_2 will occur in irradiated iodide solutions. A correlation between pH and iodine formation is needed so that the amounts of I_2 in water pools and the containment atmosphere can be assessed. A number of calculational routines based on more than 100 differential equations representing individual reactions can be found in the literature. In this work,

*pH values given in this study refer to 298 K (77°F).

it is shown that a simpler approach based on the steady-state decomposition of hydrogen peroxide should be adequate for describing iodine formation in severe accidents.

The work of Liljenzin (1990) and (Fridemo, 1988) on the pyrolysis of electrical cable insulation alerted us to the possibility that the formation of hydrochloric acid (HCl) in containment would need to be considered in evaluations of pH. As this possibility was examined, it became clear that (1) radiation, as well as heat, could produce HCl, and (2) HCl may react with metals and with the products of water radiolysis in containment.

2 Acids and Bases in Containment

2.1 Background

The materials listed in Table 1.1 are shown alternately as acids and bases. If a water pool in containment could be described as a single large sink for all of these chemicals, it would be possible to determine an overall pH based on assumed amounts of each material. Because of the different types of acids and bases, the calculation of an overall pH would require a suitable computer routine, such as the one developed for TRENDS. However, during a severe accident, these materials may influence pH levels at different times or may react prior to having any influence on pH at all. For example, fission product cesium compounds may increase pH and later be neutralized by an acid (see Table 1.1). Alternatively, boric acid sprays with a pH <7 may contact surfaces and then enter a water pool where the pH is subsequently increased. Thus, pH can vary with time during a sequence and from one sequence to another; it will certainly vary for each reactor plant.

2.2 Acidic Materials in Containment

2.2.1 Boric Acid

Boric acid will enter containment from accumulators, refueling water storage tanks, sprays, and the reactor coolant system (RCS). Boron concentrations of more than 4000 ppm boron (as boric acid) may be attained in the water pool. Boric acid sprays would have a pH of ~5 and would come into contact with most surfaces in containment.

In systems that employ pH-control chemicals (Section 2.3.3), a large portion of the basic material is used to increase the pH of boric acid solutions. The use of a borate, such as $Na_2B_8O_{13} \cdot 4H_2O$ (disodium octaborate; trade name, Polybor), would enable boron to be introduced in a preneutralized form (Hodge, 1992). Boron constitutes 21 wt % $Na_2B_8O_{13} \cdot 4H_2O$ but only 17.5 wt % boric acid. Borates are also easier to dissolve and more soluble than boric acid. If a borate, such as disodium octaborate, was stored in aqueous solution prior to use, it would be necessary to have an inert cover gas over the solution to prevent reaction with atmospheric CO_2, which occurs with all basic materials that are stored in air.

2.2.2 Iodine as HI

Hydriodic acid (HI) is a strong acid, but relatively small amounts are likely to be in containments. An evaluation of iodine chemical forms in light-water reactor (LWR) accidents suggested that iodine entering containment from the RCS may be described as 5% in the form of elemental iodine and HI, with not less than 1% as either elemental iodine or HI; the remaining 95% would be CsI (Beahm, 1991). The total amount of iodine in containment would be on the order of 100 mol, so less than ~5 mol as HI is anticipated.

2.2.3 Carbon Dioxide

Pure water will attain a pH that approaches 5.65 due to the absorption of CO_2 from air and the subsequent formation of carbonic acid. Other sources of CO_2 include limestone concrete, which is ~30 wt % CO_2, and pyrolysis or radiolysis of electrical cable insulation.

Carbonic acid is a weak acid, but CO_2 is readily absorbed by water and basic materials. Hydroxides may be converted to carbonate by absorbing CO_2 and, in the case of total conversion, some bicarbonate may also form. The carbonate or bicarbonate would give a pH that is lower than that of the original hydroxide.

2.2.4 Nitric Acid

Nitric acid (HNO_3) is produced by the irradiation of water and air. The mechanism for nitric acid is not known. Two types of test were run at ORNL to evaluate the formation of HNO_3. In the first test, water and flowing air were irradiated. After passing through the irradiator, the air was bubbled through pure water to strip any acidic gases. These tests showed that acid appeared only in the sample water and not in the flowing gas. Details of these tests are given in Table 2.1. In the other series of tests, water and air were irradiated in a closed vessel. Acidity was measured with a pH electrode and the correlating

Table 2.1 Acid formation from irradiation of water and air*

Irradiation time	Sample volume, cc	Trap volume, cc	Sample pH	Trap pH
6 h, 14 min	96	65	3.7	7.2
6 h	100	65	4.4	7.7

*Acid formation from irradiation of water and air: ^{60}Co γ dose rate 5.3×10^5 rad/h; 350 cc vessel with 23 cc outlet tube to trap; breathing air flow rate 16.7 cc/min; air introduced ~3 cm above water surface; air exit at top of vessel; initial pH 6.6 to 6.7; gas trap pure water cooled in an ice bath.

nitrate ions were measured with a specific ion electrode. The radiation G value (molecules/100 eV) for nitric acid formation based on radiation absorption by water was:

$$G(HNO_3) = 0.007 \text{ molecules/100 eV} . \quad (1)$$

This radiation G value corresponds to 7.3×10^{-6} mol HNO_3/L Mrad (Megarad). Thus, for a pool dose rate of 1 Mrad/h, starting from neutral solution, pH levels of 5.1 and 4.1 would be reached in 1 and 10 h, respectively. Radiation dose rates as calculated for a previous study ranged from ~0.4 Mrad/h in a boiling-water reactor (BWR) suppression pool to >5 Mrad/h in a pressurized-water reactor (PWR) sump (Beahm, 1991).

2.2.5 Acids from Electrical Cable Insulation

2.2.5.1 Description of Electrical Cable Insulation

Electrical cables have been modeled as a copper core with an ethylene-propylene rubber elastomer as insulator and a jacket of Hypalon (Bonzon, 1980; Wing, 1984). Hypalon is a registered trademark of DuPont for chlorosulfonated polyethylene rubbers. The prevalence of the combination of ethylene-propylene rubber and Hypalon can be confirmed by an examination of final safety analysis reports for reactor plants. In these reports, the organic materials present in containment are given in Section 6.

Hypalon is a chlorosulfonated polyethylene, $C_{85}H_{157}Cl_{13}SO_2$. This material as described by the formula contains 27 wt % chlorine. The chlorine content of different types of Hypalon varies from 24 wt % to 43 wt % (Ostrowski, 1985). The actual wt % chlorine of as-fabricated material is approximately one-half these values because of the addition of fillers and other materials. Assuming a nominal 17.5 wt % chlorine as-fabricated, ethylene propylene rubber/Hypalon would contain ~1 mol of chlorine for each pound of cable insulation. From the description of electrical cables (Bonzon, 1980), cable insulation in containment would be 46.4 wt % Hypalon, with the remainder as ethylene propylene rubber. Wing reports that a survey of the total estimated weight of cable insulation materials ranges from 16,600 to 190,000 lb. A survey made for the present study found approximately the same range, as shown in Table 2.2. Smaller amounts of chlorine in the form of polyvinyl chloride (PVC) gaskets or insulation material may also be found in containments.

The formulation of Hypalon typically used in cable materials includes clay as a filler, lead monoxide for viscosity stabilization, carbon black for weathering, and a number of organic additives (Fabris, 1973; Verbanc, 1981).

The chlorine content of electrical cable insulation is emphasized here because studies of the radiolysis or pyrolysis of Hypalon and other polymers which contain chlorine have found that the vapor produced is mostly HCl (Arakawa, 1986; Liljenzin, 1990). This is known as dehydrochlorination. Hypalon performed well in IEEE standard tests for electrical cables in nuclear power generating stations (Boston Insulated Wire, 1975). However, such tests measure flammability and electrical properties of the cable insulation, not gaseous products. Flame resistance and radiation resistance of chlorine containing polymers is brought about by dehydrochlorination. The emitted HCl reacts with free radicals, such as OH, produced by flames or

Table 2.2 Amounts of EPR/Hypalon cable insulation for selected plants*

Plant	Cable insulation (lb)	Comments
Catawba	16,662	PWR
River Bend Station	37,419	BWR
Palo Verde	39,500	PWR
Seabrook	50,000	PWR
Fermi 2**		BWR
	137,000	Excluding drywell
	5,340	Drywell
Grand Gulf		BWR
	176,400	Excluding drywell
	9,835	Drywell

*Source of data: updated final safety analysis reports.
**An additional 15% of cable is in conduit.

radiation to stop reaction chains that would damage the backbone of the polymer:

$$HCl + OH \rightarrow Cl + H_2O. \qquad (2)$$

2.2.5.2 Acids Produced by Radiation

Arakawa et al. (1986) have investigated gas evolution from irradiated chlorine-containing polymers. Most of their irradiations were carried out at room temperature; however, some specimens were heated to 266°F (130°C) after irradiation. Three types of chlorosulfonated polymers were irradiated: (1) pure polymer of Hypalon-40; (2) Hypalon-40 with added vulcanizers, MgO, Nocceler TRA (dipentamethylenethiuram tetrasulfide), TiO_2, and fillers such as calcium carbonate; and (3) a special formulation of Hypalon of unknown composition. Irradiation of pure Hypalon-40 gave radiation G values (molecules HCl/100 eV) of 2.1 for HCl and 1.8 for SO_2. However, the evolution of SO_2 reached a maximum at a radiation dose of ~5×10^7 rad, whereas HCl evolution continued to increase at doses up to the maximum used in these tests (1.16×10^8 rad). Heating specimens to 266°F (130°C) after irradiation yielded additional HCl. This additional HCl would increase the radiation G value to 3.4. These radiation G values were obtained from experiments performed in vacuum. The tests in oxygen at room temperature resulted in a G value of 4.8 for HCl.

Tests that were run with Hypalon-40 plus the vulcanizers and fillers did not produce detectable amounts of HCl or SO_2. This formulation contained magnesium oxide and calcium carbonate, which are able to neutralize HCl in situ. The formulation of Hypalon typically used in cable materials does not include magnesium oxide or calcium carbonate (Clough, 1982). Basic fillers, such as calcium carbonate, reduce the flame resistance of chlorinated polymers so they are not used in applications where flammability characteristics are important. A typical flame resistant Hypalon formulation contains PbO, clay, iron oxide, and a chlorinated saturated

hydrocarbon (Fabris, 1973). In addition, tests conducted on in situ absorption of HCl during pyrolysis of chlorine-containing polymers showed that the efficiency of acid neutralization depended on the amount and type of fillers, and the total percentage of absorbed HCl varied from 21.8 to 84.4% (O'Mara, 1971). Thus, acid evolution at room temperature in the presence of added basic materials may not reflect acid evolution at elevated temperatures in the presence of the same basic materials.

In the absence of other data, we will adopt a radiation G value of 2.1 for the formation of HCl by irradiation of Hypalon. This is the value that was reported for irradiation of pure Hypalon-40 at room temperature in vacuum (Arakawa, 1986). It is less than the value for irradiation in oxygen. The use of fillers and vulcanizers in the Hypalon in reactor containments may vary, and it is not likely that irradiation would occur at normal room temperature during a severe accident. Thus, the presence of oxygen and elevated temperatures produce G values in excess of 2.1, but fillers and vulcanizers favor G values of <2.1. For comparison, we note that the radiation G value for HCl produced by irradiation of PVC at room temperature was reported as 7.7 in vacuum and 18.3 in oxygen. Even at room temperature, the fillers and vulcanizers were not able to neutralize all the acid produced by irradiation of PVC (Arakawa, 1986).

The amount of HCl produced by the irradiation of electrical cable is estimated as 4.6×10^{-4} mol of HCl per lb of insulation per Megarad. This estimate is based on the model description of electrical cable and a radiation G value of 2.1. The total amount of HCl produced per Mrad, based on the plants cited in Table 2.1, would range from 7.7 mol/Mrad for Catawba to 86 mol/Mrad for Grand Gulf. The overall extent of HCl production would depend on the total dose.

The amount of HCl produced in the six plants listed in Table 2.1 has been calculated using a procedure given by Wing (1984). In this procedure, energy deposition on the cable insulation was obtained from the "Updated Best-Estimate LOCA Radiation Signature" of Thayer et al. (1981). The total amount of cable insulation in containment was assumed to be located in trays midway between the center and walls of containment. The calculation for evolution of HCl was the same as Wing's calculation for the evolution of organic gases and hydrogen except for the amounts of cable insulation, the volume of containments, and the radiation G value. These calculations employed G(HCl) of 2.1, whereas Wing used a value of 0.15 for organic gases and hydrogen. Wing had to use an estimated G value because no experimental data on Hypalon irradiation were available at the time of his report. Recently, Arakawa et al. (1986) gave data that correspond to a G value for H_2 evolution from Hypalon of 0.29 to 0.58.

The overall amount of HCl calculated to be produced by irradiation of the containment inventories of cable insulation and the "Updated Best-Estimate LOCA Radiation Signature (Thayer, 1981) are given in Table 2.3. Using 17.5 wt % chlorine for as-fabricated Hypalon, the fractional release of chlorine as HCl was calculated to be 5 to 15% at 12 h and 9 to 25% at 1 d. Thus, because of the large amounts of cable insulation in containments, significant quantities of HCl may be produced and the cable material will still retain most of its original chlorine.

The method for calculation of dehydrochlorination of Hypalon by radiation is given in Appendix B.

2.2.5.3 Acids Produced by Pyrolysis

The pyrolysis of Hypalon has been described as a three-stage process with each successive stage occurring at a higher temperature (Smith, 1966): Stage 1, loss of SO_2 groups; Stage 2, loss of HCl (dehydrochlorination); and Stage 3, breakdown of the hydrocarbon chain. Thermal analysis of the pyrolysis of Hypalon 20 and Hypalon 40 by Smith showed that these materials behaved similarly: the loss of $-SO_2$ groups occurred at temperatures near 392°F (200°C), loss of HCl occurred at temperatures near 572°F (300°C), and breakdown of the hydrocarbon chain occurred at temperatures near 752°F (400°C). From data given by Smith, the half life for release of HCl was 1 h at 486°F (252°C) and 1 min at 666°F (352°C).

Liljenzin conducted a series of tests in a nitrogen/steam atmosphere to study gas evolution during the pyrolysis of electrical cable insulation (Liljenzin, 1990; Fridemo, 1988). These tests showed that both condensible and noncondensible gases and acidic substances were given off at temperatures as low as 752°F (400°C). The acidic substances were mainly

Table 2.3 HCl generation for radiolysis of Hypalon using Updated Best Estimate LOCA Radiation Signature

Plant	g-mol HCl			
	1 h	12 h	1 d	4 d
Catawba	2.7×10^2	2.6×10^3	4.3×10^3	1.1×10^4
River Bend Station	3.9×10^2	3.8×10^3	6.3×10^3	1.6×10^4
Palo Verde	3.0×10^2	2.9×10^3	4.8×10^3	1.3×10^4
Seabrook	3.3×10^2	3.2×10^3	5.3×10^3	1.4×10^4
Fermi 2	8.2×10^2	2.2×10^3	1.3×10^4	3.4×10^4
Grand Gulf	2.2×10^3	2.2×10^4	3.6×10^4	9.2×10^4

HCl, SO_2, and CO_2, which are similar to the gases that evolved from the irradiation of electrical cable insulation. Materials that were tested included PVC and Lipalon. Lipalon reportedly contains 17.5% chlorine and 1.1% sulfur (Fridemo, 1988).

Liljenzin reported that acidic gases were released from electrical cable insulation that was heated at temperatures of 752°F (≥400°C). The amounts of acid produced by pyrolysis, in a nitrogen/steam atmosphere, from insulation in typical Swedish BWR containments were 1.6×10^3 mol at 752°F (400°C), 1.3×10^4 mol at 1112°F (600°C), and 1.2×10^4 mol at 1472°F (800°C).

In the Swedish work (Liljenzin, 1990), two accident sequences were used to evaluate the pH of water volumes as a function of time. In these calculations, it was assumed that the organic material below the BWR vessel was pyrolyzed at 1472°F (800°C). It was also assumed that the amount of pyrolyzed material increased from zero to half of the maximum amount possible as a linear function of the amount of core-melt leaving the vessel. In both a TB and AB sequence, the wetwell pH was initially basic because of cesium hydroxide and subsequently reached a pH of ~3 in 3 to 4 h. It should be noted that radiation-induced nitric acid formation was not included in these calculations.

2.3 Basic Materials in Containment

2.3.1 Basic Fission Product Compounds

Cesium may enter containment in the form of cesium hydroxide, cesium borate, or cesium iodide. Cesium in other forms, such as zirconate and molybdate, are also possible. Cesium hydroxide and cesium borates are basic materials. In containment, cesium hydroxide may react with CO_2 to produce cesium carbonate. If all the cesium hydroxide in a region within containment is converted to cesium carbonate, further reaction with CO_2 would produce cesium bicarbonate.

The amount of cesium entering containment would be ~500 to 1000 mol. When this material enters water pools, the concentration would be on the order of 10^{-3} to 10^{-4} mol/L, depending on the volume of water in containment. The reaction of cesium hydroxide with boron oxides or CO_2 results in a partial neutralization of the hydroxide. Thus, a 10^{-4} *M* solution of cesium hydroxide would have a pH of ~10, but the same concentration of a borate or a carbonate would give a lower pH. In TRENDS models, a variety of chemical forms may be selected for cesium, and it should be noted that retention of cesium in the hydroxide form, even in controlled laboratory atmospheres, is extremely difficult.

2.3.2 Core-Concrete Aerosols

Aerosols from limestone concrete will contain the basic oxides CaO, Na_2O, and K_2O. The amounts of basic materials will vary from sequence to sequence and for different reactor systems. These basic materials will be constituents of aerosol material that contains other products such as silicon dioxide (SiO_2), iron oxide (FeO), fission product oxides such as La_2O_3, and metals such as silver or manganese. The influence of core-concrete aerosols on pH will depend on the extent to which the basic oxides can enter solution.

A series of pH tests was run at ORNL on aerosol material from the SURC3 (Copus, 1990) experiment that was kindly supplied by Sandia National Laboratory (SNL). Results of these tests are given in Table 2.4. Material from Impactor D gave a basic pH; however, since there was no buffer capacity (see Section 2.3.3.1), the pH decreased by more than one unit on standing in air.

2.3.3 Chemical Additives to Control pH

2.3.3.1 pH Buffers

The measure of pH buffer capacity, B, is defined as

$$B = \frac{db}{d\,pH}, \qquad (3)$$

where

db = an increment of strong base
(-db = an increment of strong acid), and
d pH = the change in pH that results from the addition of an increment of acid or base.

Bates has shown that buffer value may be expressed in terms of the equilibrium constant for dissociation of the weak acid (Bates, 1973):

$$B = \frac{db}{d\,pH} = 2.303\left[\frac{KC\,(H^+)}{(K + (H^+))^2} + (H^+) + (OH^-)\right], \qquad (4)$$

where

K = equilibrium constant for dissociation of the weak acid or weak base,

C = initial concentration, for example, of boron in a borate buffer or of phosphorus in a phosphate buffer (mol/L),

(H^+) = hydrogen ion concentration (mol/L), and

(OH^-) = hydroxide ion concentration (mol/L).

A borate buffer that controls pH at values near 9.2 has a dissociation constant of 5.8×10^{-10}, and a phosphate buffer that controls pH at values near 7 has a dissociation constant of 6.3×10^{-8} (Dean, 1985).

Table 2.4 Results of pH tests on material obtained in core-concrete interaction experiment SURC3*

Sample	Concentration (g/L)	pH	Comments
Impactor D	1.0	9.52	No buffer capacity
Impactor D	0.1	8.50	
Preseparator D	1.0	7.25	
Impactor D after sitting in air for 1 d	1.0	8.33	Decrease in pH most likely due to dissolution of CO_2 from air

*Tests were run at ORNL on material supplied by SNL.

In a buffer solution, the maximum buffer value is attained when the hydrogen ion concentration equals the dissociation constant or $K = (H^+)$. When this occurs,

$$B_{maximum} = \frac{2.303\ C}{4} = 0.576\ C\ . \qquad (5)$$

The importance of this result is that a given concentration of a phosphate buffer would have the same buffer value at a pH near 7 as a similar concentration of a borate buffer would have at a pH near 9.

The use of these equations for buffer value may be illustrated by assuming that an increment of acid, -db, will be added to a water pool in which we wish to maintain pH. The amount of strong acid will be x mols, which will be present in a total volume of V_L (liters):

$$-db = \frac{x}{V_L}\ . \qquad (6)$$

The pH change would be obtained as follows:

$$d\ pH = \frac{x}{V_L} / \frac{2.303\ KC\ (H^+)}{(K + (H^+))^2}\ . \qquad (7)$$

At the maximum buffer value,

$$d\ pH = \frac{x}{V_L} / 0.576\ C\ . \qquad (8)$$

As an example, we may calculate the concentration of a borate buffer that will maintain the pH level within 0.1 unit when 10^3 mol of acid is added to containment water pools. The value of V_L will range from ~10^5 to 5×10^6 L. At the maximum buffer value at a pH of 9.2 for a borate buffer, the pH would decrease by only 0.1 unit when the borate buffer concentration was 0.17 mol/L and $V_L = 10^5$ or when the concentration was 3.5×10^{-3} mol/L and $V_L = 5 \times 10^6$. Similar concentrations of a phosphate buffer would maintain the pH level to within 0.1 unit at a pH near 7.

2.3.3.2 Materials for pH Control

The pH buffer materials for use in containment must be borate or phosphate. No other chemical additives would have the desirable pH range and chemical stability. Typically, the phosphate is in the form of trisodium phosphate that is held dry in baskets that are located in containment. The amounts of trisodium phosphate may be quite large; 26,500 lb (3.2×10^4 mol) of $Na_3PO_4 \cdot 12H_2O$ is in place at Palo Verde according to the updated final safety analysis report. Borate buffers are made up of sodium hydroxide and boric acid that are stored separately and combined in spray systems. Boric acid would also be used in sprays in passive pH control of trisodium phosphate.

The combination of trisodium phosphate and boric acid would result in a phosphate-borate buffer with a total buffer value that is the sum of the values for the two components. This may be illustrated by an example based on data from Palo Verde. After the initiation of boric acid spray, the sump would contain 4400 ppm boron as boric acid and 2000 ppm phosphate, according to the updated final safety analysis report. Table 2.5 gives some calculated pH values based on information for the sump at Palo Verde. A pH of 7.7 was calculated for the conditions expected in the sump. However, most of the trisodium phosphate in the sump would be used to neutralize the boric acid. This is shown by the value of the pH that is given on the far right of Table 2.5, for the case where no boric acid was assumed. This result will generally be observed whether pH control is attained by sodium hydroxide or by trisodium phosphate. Most of the base will be used to neutralize the boric acid. An alternative to boric acid may be suggested. Disodium octaborate contains 21% boron by weight, whereas boric acid is only 17.5% boron. In addition, disodium octaborate solutions would have a pH of 8.0 to 8.5, and this material is more soluble than boric acid (see Section 2.2.1).

Two potential difficulties may be cited with regard to passive trisodium phosphate:

(1) Calcium oxide or calcium hydroxide from core-concrete aerosols may react with phosphate in

Table 2.5 Calculated pH levels for various assumptions based on information for sump at Palo Verde

pH value		
7.7	8.6	10.4
4400 ppm boron as boric acid plus 2000 ppm PO_4^{3-} (condition expected)	4400 ppm boron as "Polybor" plus 2000 ppm PO_4^{3-}	2000 ppm PO_4^{3-}

water to form calcium phosphates which would precipitate as solids from solution according to the following equation:

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \text{ (solid)} . \quad (8)$$

This would decrease the ability to control pH by removing phosphate from solution.

(2) During storage, trisodium phosphate may react with CO_2 in air to form a carbonate.

3 Model of Iodine Radiolysis

3.1 Background

The task of obtaining rate constants to be used in describing iodine behavior in containment involves the complete mechanistic evaluation of iodine in water, including hydrolysis, reverse hydrolysis, oscillatory mechanisms, and redox reactions. Studies of iodine behavior in water began more than 100 years ago. The primary advantage that we have now over earlier investigators is the availability of computers and routines for solving large systems of differential equations associated with reaction kinetics. However, the earlier investigators did not try to contend with the interaction of iodine species and the products of water radiolysis. In recent years, this problem was approached by performing experiments on the irradiation of aqueous iodine and setting up methods for solving a large set of differential equations, more than 100 in some cases, in an attempt to reproduce the experimental results by calculation.

The practical problem to be considered is the extent of release of iodine from containments during reactor accident events. To some extent, this puts limits on the range of conditions that must be evaluated. For example, the events of interest in a water pool will probably be restricted to a pH range between ~3 and 8. At pH values above 8, conversion of I^- to I_2 by radiolysis is very small and hydrolysis is quite rapid. It is not likely that pH values below ~3 will be attained in reactor accidents (with the possible exception of evaporation to dryness, which is not considered here). If this did occur, it is not difficult to predict what would happen by using experimental data on radiolysis effects and reverse hydrolysis. Other important parameters, such as temperature, iodine concentrations, and radiation dose rates, may also be delimited if we consider only the conditions of importance in reactor accidents.

A useful model must not require information that is not available in normal accident sequence calculations. It must also be efficient, easy to understand and use, and accurately reflect available data. It is desirable to use mechanistic formulations as much as possible; however, empirical elements will no doubt be required as well.

Based on the results of experimental studies, we may summarize the formation of I_2 during the radiolysis of I^- as follows:

(1) At pH <3, virtually all iodine is converted to I_2; for pH >7, only a tiny fraction is converted. For 3 < pH < 7, conversion is highly variable (see Figure 3.1).

(2) For a given pH and temperature, there is a threshold radiation dose to the water, which, if exceeded, ensures that conversion will reach the steady-state value. If iodine is not added until this dose is reached, then steady-state conversion occurs very rapidly (within a few minutes). If dose is lower than the threshold value, then conversion will occur gradually until the steady state is reached.

(3) At very low aqueous iodine concentrations, $< \sim 10^{-6}$ g-atom I/L, there is a tendency for iodate formation in the presence of irradiation and a tendency for iodine to show anomalous behavior in the absence of irradiation. Data in this region are less reliable, and, therefore, modeling results will exhibit greater uncertainty. Fortunately, the total quantity of iodine is low in this case as is the fraction as I_2.

Our approach to the use of kinetic rate expressions is based on a narrowing of the problem to a range of parameters that are of practical interest and involves identifying the process(es) that bring about the plateau in fraction of I^- converted to I_2 at a given pH. This approach was selected rather than using more than 100 individual reactions because many if not most of the rate constants in the large set of reactions must be estimated, and, as a result, have large individual uncertainties that would be perpetuated into the overall calculation.

3.2 Description of the Model

The plateau in fraction of I^- converted to I_2 implies that a steady-state process is reached during irradiation. During the irradiation of water, free radical products such as OH· or H· are present at very low concentrations on the order of 10^{-10} *M* or less.

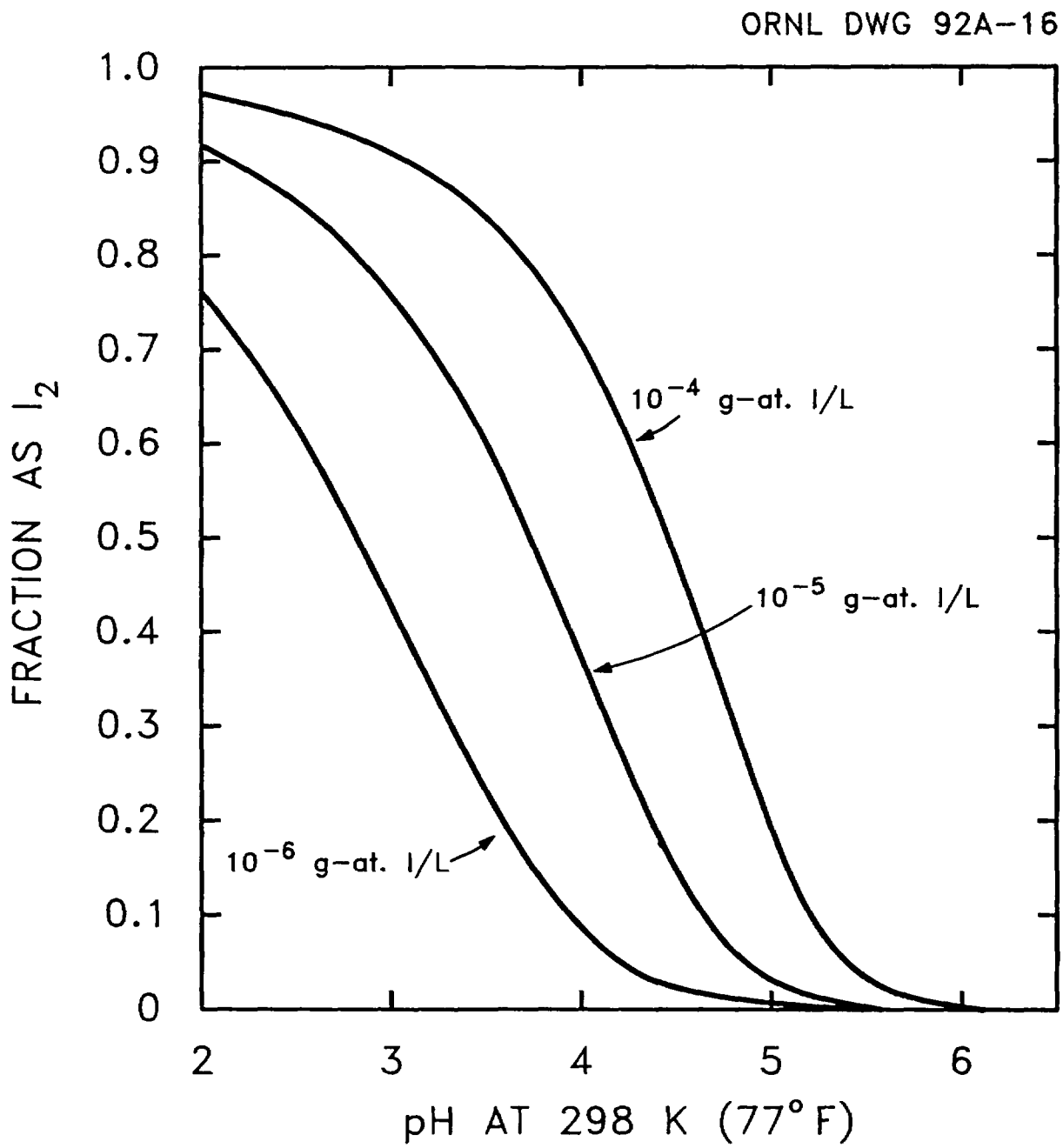

Figure 3.1. Model calculations of fraction as I_2 vs pH

However, hydrogen peroxide (H_2O_2) will be present at concentrations that are comparable to iodide concentrations in containment water pools: 10^{-4} to 10^{-6} *M*. The concentration of H_2O_2 will depend on the radiation dose and on the extent of reaction with other species in solution, such as I^- or Cl^-.

Hydrogen peroxide reacts with both I^- and I_2 as follows:

$$2I^- + 2H^+ + H_2O_2 \rightarrow I_2 + 2H_2O \ , \quad (10)$$

$$I_2 + H_2O_2 \rightarrow 2I^- + 2H^+ + O_2 \ . \quad (11)$$

These reactions generated much interest in the 1920s and 1930s. Abel (1928) proposed a mechanism that gives the following relationship between I^-, I_2, and H^+:

$$\frac{(H^+)^2 (I^-)^2}{(I_2)} = d + e\,(H^+) \ , \quad (12)$$

where (H^+), (I^-), and (I_2) are concentrations in mol/L (*M*) and d and e are constants. The constants are derived from a combination of three reaction rate constants and two equilibrium constants, as described in Appendix C. This equation can be solved for (I_2) if (H^+) and (I^-) are known. The value of (H^+) can be obtained if the pH is known: $pH = -\log_{10}(H^+)$. For iodine concentrations $> \sim 10^{-6}$ *M*, iodate concentrations are small in irradiated solutions; thus, we may say that:

$$\text{Total iodine concentration } \frac{(\text{g-atom I})}{\text{L}} = (I^-) + 2(I_2) \ . \quad (13)$$

(Note: Because I_2 contains 2 g-atom I per mol and I^- contains only 1 g-atom, it is convenient to use g-atom rather than mol in aqueous iodine concentrations.) Figure 3.1 gives plots of fraction of I^- converted to I_2 as a function of pH that were calculated from Equation 12 and $d = 6.05 \times 10^{-14}$, $e = 1.47 \times 10^{-9}$ (see Appendix C). The curves have the expected sigmoid shape that has been observed in studies of iodine radiolysis (Lin, 1980), and the calculated values are in reasonable agreement with experimental measurements as shown in Appendix C. The shape of these curves reveals a difficulty in both the experimental and calculational approaches to iodine radiolysis. There is a steep transitional region where a small change in pH results in a large change in the fraction as I_2. The pH region from ~3 to ~6, which is of interest in containment water pools, is precisely the one that is most sensitive to small changes in pH.

At a given pH, the curves show that the fraction as I_2 will be decreased as the total iodine concentration decreases. Thus, a large water volume would have a smaller fraction as I_2 than a small volume containing the same amount of iodine.

This model does not specify a mechanism for the initial production of I_2 or H_2O_2. The production of H_2O_2 in irradiated water is well documented (Buxton, 1988). The model represents the catalytic decomposition of H_2O_2 by iodine species, and H_2O_2 does not appear in the overall equation (Eq. 12) that represents this process. With this model, the only effect of different radiation dose rates would be the time required to reach steady state. Experimentally, it has been observed that at dose rates > ~0.3 Mrad/h, steady state would be reached within a few hours.

3.3 Iodine Distribution

3.3.1 Iodine Partition Coefficient

The equilibrium distribution of I_2 is represented by the partition coefficient, $PC(I_2)$:

$$PC(I_2) = \frac{(I_2)aq}{(I_2)gas} \ , \quad (14)$$

where $(I_2)aq$ is the aqueous I_2 concentration, *M*, and $(I_2)gas$ is the gaseous I_2 concentration, *M*. The partition coefficient for I_2 can be obtained from

$$\log_{10} PC(I_2) = 6.29 - 0.0149\,T \quad (15)$$
$$T\ (K) \ .$$

The distribution of I_2 may be calculated using the iodine model (Section 3.2) to obtain $(I_2)aq$ and using $PC(I_2)$ to obtain $(I_2)gas$. This would give the equilibrium distribution that is likely in a bubbling

suppression pool. In a quiescent pool, it might take some time to approach such an equilibrium.

3.3.2 The Behavior of I_2 and CH_3I in Steam Suppression Pools

The results of suppression pool experiments performed at five different laboratories were analyzed for efficiency of absorption of I_2 and CH_3I by Rastler (1981). In most cases, the apparatus was designed to be a scale model of a nuclear reactor emergency steam suppression pool.

The important finding of this analysis is that the mass transfer between iodine in the gas input steam (bubbles) and iodine in the pool water was very fast. In all cases, equilibrium or near-equilibrium was reached. This was demonstrated in the following ways.

(1) Iodine trapping was independent of the depth of immersion of the bubbler. Immersion depths were typically 30 to 120 cm. A miniature apparatus tested by Diffey (1965) was effective because of the small bubbles formed (3-cm immersion with 0.3-cm-diam outlet).

(2) Air bubbled through the pool after iodine addition was stopped contained the same concentration of iodine as during the addition phase. This demonstrates that equilibrium was reached during desorption as well as adsorption.

(3) Mass transfer of iodine from a noncondensing gas was as complete as when part or all of the gas was steam that condensed in the pool.

(4) The amount of untrapped iodine was essentially directly proportional to the volume of uncondensed gas.

(5) The I_2 or CH_3I partition coefficients (iodine concentration in the pool/average concentration in the gas leaving the pool) were very close to those from the literature for the given concentration, pH, and temperature.

(6) Mass transfer from the surface of the pool to the gas space above it was significant. This was the principal iodine loss mechanism when the iodine was input with pure steam. Stanford (1972) modeled this mechanism.

The Steam Generator Heavy Water Reactor mockup provides a variety of test conditions (Rastler, 1981; Section 7.1.2). The steam content ranged from 0 to 100%. Three elution tests were performed. The resulting decontamination factors scattered more than desirable even after correcting for the air flow rate. Part of this might result from air flow time differences that were not mentioned in Rastler's review. A copy of the original work could not be located. The initial pool temperature was 10°C which should have resulted in essentially 100% steam condensation for the 100% steam tests. The DFs for the 100% steam runs were not any higher than those runs which included moderate volume air flow. This suggests that there was significant iodine transfer from the pool to the gas space above by way of the pool surface.

A study conducted in the United Kingdom (Diffey, 1965; Rastler, 1981; Section 7.1.3) used two different sizes of apparatus and included HI as well as I_2 and CH_3I. It was concluded that "with a favorable geometry, the penetration of methyl iodide, hydrogen iodide, and elemental iodine at high concentrations is limited to approximately that by which Henry's law can be theoretically predicted to be in equilibrium with the solution formed." Tests with low concentration I_2 showed much better retention of iodine in the water.

The PIREE experiment (Rastler, 1981; Section 7.1.4) was not designed to study nuclear reactor steam suppression pools, but it provided similar results. The experiment consisted of testing I_2 in high pressure, high temperature CO_2 bubbled into a pressurized 148 ft^3 (42 m^3) tank. The depth of bubbling was varied by changing the amount of water in the tank. There was no effect of bubbling depth when the results were corrected for the volumes of water and CO_2. One difference from other studies is the DFs were not higher for the low iodine concentration studies. This might possibly be the result of organic iodide contamination of the source I_2 or organic iodide formation in the high-temperature, high-pressure CO_2 carrier gas.

A test conducted at ORNL (Stanford, 1972; Rastler, 1981; Section 7.1.6) used I_2 with conditions selected

"to conform as closely as possible to the design basis accident." Tests were performed with I_2 in pure steam and in steam with 2% air. Decontamination factors for the pure steam tests averaged about a factor of 3 higher than for the 2% air tests. The volume of air in the air-steam mixture appeared to be more than three times the air space above the water. Iodine transfer from the pool surface to the air space above the pool was shown to be significant in the tests that used only steam and iodine as the input mixture. For all cases of a steam-air-iodine input, calculations showed that an equilibrium was reached between iodine in rising air bubbles and the surrounding water.

Another test series (Siegworth, 1971) used a 1/10,000 scale model of a Mark I BWR pressure suppression system. Only CH_3I was tested. A downcomer immersion depth of 1 ft resulted in CH_3I absorption only 20% less than for a 4-ft immersion depth. Critical information, such as time of CH_3I injection and air flow volume, were not given.

In summary, it appears that the mass transfer of vapor forms of iodine (I_2, HI, and CH_3I) is rapid enough in steam suppression pools that equilibrium between gas bubbles and pool water can be assumed. For sub-cooled pools, the steam will be condensed and only the noncondensible gases (usually air, inerting N_2, and H_2) will carry iodine through the pool. For steam-saturated pools, the volume of uncondensed steam will also transport iodine through, but equilibrated with, the pool water.

The transport of particles from the bubbles is slower than for iodine in vapor form but has been found to be significant. Most of the iodine sorbed or condensed on the particles will dissolve in the pool and contribute to the gas/water equilibrium. The amount of iodine transported from particles in the bubbles to pool water in soluble form is probably close to 100%.

When the volume flow rate of gas (air, N_2, H_2, and steam) bubbling from the surface of the pool is small, the transfer of iodine between the pool is small, the transfer of iodine between the pool surface and the gas space above it can become significant. Induced and natural convection in the pool will probably keep it well mixed. For a closed system, such as a Mark I torus, gas to liquid iodine equilibrium will probably be maintained.

The above observations and suggestions provide a simple method for assisting in the calculation of iodine behavior in suppression pools. Note that the transport of particulate iodine with gas flowing out is not quantified here. If this simplified method is used, it may be desirable to show that mass transfer for the particular geometry and accident conditions approaches the assumed equilibrium conditions on a plant-by-plant basis.

3.3.3 Evaporation of Volatile Iodine Species from Water

Consider the problem of I_2 evaporation from a containment pool or sump to a gas space. This is generally modeled by assuming a two-film model:

$$\text{Flux across interface} = K(C_\ell - PC \cdot C_g), \quad \frac{1}{K} = \frac{1}{k_\ell} + \frac{PC}{k_g}, \qquad (16a,b)$$

where

k_ℓ and k_g denote liquid and gas-phase film transfer coefficients (cm/s), C_ℓ and C_g are bulk concentrations (mol/cm^3), and PC is the equilibrium partition coefficient (inverse of Henry's Law Constant).

Hewison (1987) gives a thorough discussion of the assumptions implicit in interphase transport modeling in general, and the two-film model applied to reactor accident situations.

For transfer in the gas film, Yuill et al. (1970) suggest the following coefficients, derived for forced convection parallel flow over an immovable flat surface:

$$\frac{k_g \ell}{D} = \begin{Bmatrix} 0.664\ Re^{0.5}\ Sc^{0.33} & Re \le 2 \times 10^4 \\ 0.036\ Re^{0.8}\ Sc^{0.33} & Re > 2 \times 10^4 \end{Bmatrix} \qquad (17)$$

and assume no transfer resistance in the liquid. One problem with this approach is that use of a forced convection correlation presupposes one-dimensional semi-infinite plane flow of know velocity. Obviously, a containment is a closed compartment, with two-dimensional surface and unknown flow velocities.

Hewison also uses Equation 17 in the gas film and suggest a liquid phase coefficient derived from a

natural convection correlation, which assumes a temperature gradient in the liquid:

$$Sh = \frac{kl}{D} = \left\{ \begin{array}{c} 0.54\ (GrPr)^{0.25} \\ 10^5 < GrPr < 1 \times 10^7\ (laminar) \\ 0.14\ (GrPr)^{0.5} \\ 2 \times 10^7 < GrPr < 3 \times 10^{10}\ (turbulent) \end{array} \right\} . \quad (18)$$

Equation 18 is derived using the mass-transfer analogy to heat transfer for an infinite heated horizonal surface, and is consistent with the natural convection heat transfer correlations used in the CONTAIN code (Washington, 1991) (applying to both fluids) for water warmer than air.

When air is warmer than water, natural convection should not occur, although other forces (e.g., venting) may still induce circulating flows. Without such flows, molecular diffusion would be the mechanism of equilibration. The CONTAIN code (Washington, 1991) uses a correlation for heat transfer in this situation and the mass-transfer analogy is employed here as well:

$$Sh = 0.27(Gr\ Pr)^{0.25} . \quad (19)$$

Natural convection correlations (such as Equation 18) are usually derived for semi-infinite surfaces. While there has been considerable study of natural convection in closed compartments, we have not seen any geometry that matches the general situation expected in a containment, which should include (1) rectangular or cylindrical and (2) heated floor or cooled ceiling. Furthermore, the fluid-fluid interface presents a different situation, since Equation 18 was derived from experiments using a fluid-solid interface. And finally, all correlations (including those that assume a heat-mass transfer analogy) and almost all experiments concerning mass transfer assume that the driving force is a concentration gradient. In our situation, concentrations of fission-product species are expected to be so small (10^{-4} - 10^{-6} M) that negligible contributions to fluid circulation should result. Thus, we actually have mass transfer in natural convection driven by a temperature gradient. Very few studies discuss this phenomenon, although Khair (1985) showed smaller mass transfer by an order of magnitude in a computer calculation of flow near a semi-infinite heated vertical surface.

4 Analysis and Conculsions

Some aspects of the timing of pH changes can be obtained from what is known about fission product release into containment. Initially, the pH should be basic because of cesium entering water pools as some combination of hydroxide, borate, or carbonate. However, once fission products enter a water pool, a radiation dose rate is established and nitric acid begins to form and to neutralize the basic solutes. This leads to an interesting trade-off — a high concentration of fission products that contain basic solutes brings about a high initial pH but also a high radiation dose rate, which results in a relatively high production of nitric acid. From these offsetting effects, we may calculate the time necessary to reduce the initial basic pH to 7.0. This time can be considered to be the maximum duration that a basic pH will occur in the absence of boric acid, cable decomposition products, and core-concrete aerosols. It is a maximum because it considers only the basic contribution to pH and the necessary result of the introduction of fission products into a water pool (i.e., formation of nitric acid).

This maximum duration of a basic pH was calculated as follows: (1) The radiation energy deposited in water pools and the amounts of cesium (in mols) were obtained from Tables E1 through E4 of NUREG/CR-5732 (Beahm, 1991) (*Iodine Chemical Forms in LWR Severe Accidents*); the water pool volumes were obtained from the same report. (2) It was assumed that all of the cesium in containment entered the water pools as cesium hydroxide (CsOH) or cesium borate ($CsBO_2$). (3) The formation of nitric acid was calculated from the radiation G value (Section 2.2.4).

The results of these calculations are listed in Table 4.1 for the seven accident sequences that were evaluated in NUREG/CR-5732. The times to reach pH 7 are remarkably similar for the cases where the assumed initial chemical form of cesium was hydroxide, despite the range in water volumes from 3.00×10^4 gal (1.15×10^5 L) to 1.37×10^6 gal (5.17×10^6 L). The calculated times are similar because of the trade-off in amount of fission products that enter the pool and the formation of nitric acid, which have already been described.

The time durations for pH level above 7 are shorter when it is assumed that cesium enters a water pool as $CsBO_2$. This is because this assumption implies a partial neutralization before reaction with nitric acid:

$$CsOH + H_3BO_3 \rightarrow CsBO_2 + 2H_2O \ . \quad (20)$$

The range of values in this case is somewhat greater than that with cesium hydroxide because a borate buffer forms (Section 2.3.3.1).

From this evaluation, ~60 to 100 h is the maximum duration that a basic pH may be maintained in the absence of pH-control additives. A pH of 7 or less may be attained in times shorter than this if boric acid or a strong acid, such as HCl, is present in the water pool. For example, boric acid at concentrations of $>$~0.12 *M* would attain a pH of 7 in 24 h in the Grand Gulf suppression pool during the TC sequence. Strong acids, in amounts ≥500 to 1000 mol, would also produce a pH of 7 in 24 h or less in any of the accident sequences.

A survey of accident sequence calculations that employed the Source Term Code Package (Gieseke, 1984; Denning, 1986) revealed that temperatures in excess of 572°F (300°C) in containments is often predicted. In these sequences as well as those where radiation dose rates in containment approach those of the "Updated Best-Estimate LOCA Radiation Signature" (Thayer, 1981), amounts of HCl on the order of 10^3 to 10^4 mols may be anticipated. This would introduce into containment amounts of chlorine containing species that are 10 to 100 times the amounts of iodine containing species.

Some plants that employ pH control chemicals will be able to maintain pH ≥ 7 even with this influx of HCl. In containments where pH control chemicals are not used, Table 2.3 may be used as a guide to the timing of the decrease in pH due to HCl. At times between 1 and 12 h, the amount (mols) of HCl would exceed the amount (mols) of cesium in containments. This timing, based on radiation degradation of chlorosulfonated polyethylene, is supported by the evaluation

Table 4.1 Nitric acid neutralization of cesium compound—maximum time to reach pH 7.0

Plant and sequence	Time (h) Cesium hydroxide (CsOH)	Cesium borate ($CsBO_2$)
Grand Gulf		
TC	98	60
TQUV	110	67
Peach Bottom		
TC2	99	58
AE	110	75
Sequoyah		
TBA	118	99
Surry		
TMLB'	104	101
AB	124	121

of Liljenzin (1990) that was based on thermal degradation as cited in Section 2.2.5.3 of this report.

The evaluation of HCl emission from electrical cable materials was based on a model description of ethylene propylene rubber insulation and Hypalon jacketing that was used in previous studies (Bonzon, 1980; Wing, 1984). Other chlorinated polymers, neoprene and chlorinated polyethylene, are also used in some containments. Dehydrochlorination of these materials by radiation or by heat is similar to Hypalon (Arakawa, 1986; Smith, 1966).

Hydrochloric acid in containment may do more than decrease pH. The following interactions of chlorine species in containment are evaluated in Appendix D:

(1) the competitive reaction of Cl^- and I^- with OH radicals,

(2) the aqueous to gaseous partition coefficient of Cl_2 and HOCl,

(3) the effect of organic chlorides on the formation of organic iodides, and

(4) the influence of gaseous chlorine species on the capacity and retention of iodine species in charcoal filters.

Here are some of the important interactions of chlorine species. In irradiated water pools, chloride ions will react in acid solutions with water radiolysis products to form Cl_2 and other oxidized chlorine species:

$$2Cl^- + 2OH \rightarrow Cl_2 + 2OH^- . \qquad (21)$$

Iodide ions (I^-) readily react with chlorine to form I_2:

$$2I^- + Cl_2 \rightarrow I_2 + 2Cl^- . \qquad (22)$$

The reaction shown in Equation 22 is the basis of a standard method of analysis for chlorine in water. The model of iodine radiolysis (Section 3), based on reaction with H_2O_2, did not specify a mechanism for initial I_2 formation, and it is likely that this model would still be valid even if Equations 21 and 22 occur. However, the total iodine concentrations where iodate ions (IO_3^-) appear in irradiated solutions may be different when Cl^- is present. In solutions without Cl^-, iodate forms only at concentrations of $< \sim 10^{-6}$ g-atom total iodine/L. It is not clear whether this will occur at the same total iodine concentration in a solution that contains Cl^-. Thus, Cl^- may influence the range of total iodine concentrations in situations where the model is applicable.

Hydrochloric acid or chlorine may affect retention in charcoal filter systems. In impregnated filters, HCl may interact with the deposited chemicals; alternatively, it may occupy surface sites instead of iodide. If chlorine enters a filter system, a reaction expressed in Equation 22 may occur and I_2 could form from deposited iodide (I^-).

Also, because it is a strong acid, HCl will react with metals to form hydrogen.

Two major uncertainties result from the production of HCl in containment. The first is the uncertainty in the formation of I_2 during irradiation of water pools that contain both chloride and iodide ions. As noted previously in Section 3.2, the model of steady-state fraction of iodine as I_2 does not specify a mechanism for the initial production of I_2. There are no experimental data on irradiation of solutions containing chloride and iodide at pH < 7. In the absence of experimental data, the range of applicability of the steady-state model remains speculative. As was the case in solutions containing iodide alone, it is only pH < 7 that would be of any importance in I_2 formation.

The second uncertainty is in the behavior of I_2 and organic iodide in filter systems when some combination of HCl, HOCl, Cl_2, or organic chlorides are present. Again, there are no experimental data on this. The evaluation in Appendix D.4 is based on chemical reactions that may be expected to occur, and these indicate that both the capacity and retention of iodine species in charcoal filters will be degraded when chlorine species are present.

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Appendix A. Model for Calculation of pH

The pH model, SOLGASPH.FOR, is based on the main subroutine of the SOLGASMIX program. This subroutine obtains the equilibrium distribution of species by finding the minimum free energy. The pH model is used to calculate hydrogen ion concentrations for use in the modeling of radiolytic conversion of aqueous I^- to I_2 and iodine hydrolysis. In these applications, it may be said that it is only acidic pH values that are consistent with iodine as I_2. Radiolytic conversion of I^- to I_2 does not occur in basic solutions, and I_2 in basic solutions is hydrolyzed to I^- and IO_3^-. Thus, a pH of 10.0 compared to 9.5 or even 9.0 is of little significance. At both pH 10.0 and 9.5, no radiolytic conversion of I^- to I_2 will occur, and the hydrolysis of I_2 is very rapid. On the other hand, a pH of 4.0 compared to 4.5 or 5.0 would be quite important with respect to the chemical forms of iodine. The pH range of ~3.5 to 5.5, depending on total iodine concentration, is the range where the transition of I^- to I_2 occurs during irradiation.

The species included in the calculation of pH are listed in Table A.1. The order given in Table A.1 is the order that they are indexed in the calculational routine. In PWR containments where pH control chemicals are used, borate buffers, phosphate buffers, or a combination of the two are formed. The direct calculation of pH in these complex solutions is difficult because of the low hydrogen ion concentrations (~10^{-9} to 10^{-3} *M*) that are expected in water pools during severe accidents. In the process of computer calculation of equilibrium, the contribution of the hydrogen ion to the total free energy is very small. For this reason, hydrogen ion concentrations in borate or phosphate buffer systems are calculated after the free energy minimization from equilibrium expressions for the borate of phosphate species. A comparison of calculated and measured pH values in these systems, given in Table A.2, shows that this technique is quite effective in yielding good calculated values of pH.

Data for the free energies of formation of the borate and phosphate species were obtained from Mesmer (1972) and Mesmer (1974), respectively. All other free energy data were obtained from the FACT system (FACT, 1985). The free energy data were cast into the form:

$$\frac{\Delta G^\circ}{R} = GVAL1 + GVAL2 \cdot T \,, \quad (A.1)$$

where

ΔG° = the standard free energy of formation,

R = the universal gas constant in energy units consistent with ΔG°,

GVAL2 and GVAL2 = constants fit from tabulated data, and

T = temperature in K.

Activity coefficients for the aqueous ions were calculated from the Debye-Hückel expression as described by Barner (1978).

Table A.1 Species in pH calculation

Gas	Aqueous solution	Solid precipitate
Ar	H_2O	$Ca_3(PO_4)_2$
H_2O	H_3BO_3	$CaHPO_4$
CO_2	K^+	$Ca(H_2PO_4)_2H_2O$
	$B(OH)_4^-$	$CaO \cdot B_2O_3$
	NO_3^-	$CaCO_3$
	H^+	CaO
	OH^-	
	$B_2(OH)_7^-$	
	$B_3(OH)_{10}^-$	
	$B_4(OH)_{14}^{-2}$	
	HCO_3^-	
	CO_3^{-2}	
	H_2CO_3	
	PO_4^{-3}	
	HPO_4^{-2}	
	$H_2PO_4^-$	
	Ca^{+2}	

Table A.2 Comparison of some measured and calculated pH values

Materials (mol/m^3)	Calculated pH	Measured pH	Reference for measured value
98.4 NaOH, 40.2 H_3BO_3, 40.2 H_3PO_4	8.9	9.0	ORNL
83.7 NaOH, 41.6 H_3BO_3, 41.6 H_3PO_4	7.9	8.0	ORNL
50.76 NaOH, 44.9 H_3BO_3, 44.9 H_3PO_4	6.0	6.0	ORNL
45.5 NaOH, 45.5 H_3BO_3, 45.5 H_3PO_4	5.0	5.0	ORNL
69.7 NaOH, 43.0 H_3BO_3, 43.0 H_3PO_4	7.0	7.0	ORNL
50 $NaHCO_3$	8.1	8.15	ORNL
20.87 $Ca(OH)_2$	12.3	12.26	ORNL
16.7 $Ca(OH)_2$, 10.0 H_3PO_4	11.6	11.4	ORNL
10.0 $Na_2B_4O_7$	9.0	9.2	*Handbook of Chemistry and Physics*,* and ORNL
10.0 $Na_2B_4O_7$ at 368 K	8.4	8.8	*Handbook of Chemistry and Physics**
55.7 NaOH, 50.0 H_3PO_4	6.0	6.0	ORNL
79.63 NaOH, 50.0 H_3PO_4	6.9	7.0	ORNL
96.8 NaOH, 50.0 H_3PO_4	7.9	8.0	ORNL
2.61 NaOH, 50.0 H_3BO_3	7.8	7.8	Lange's Handbook**
16.3 NaOH, 50.0 H_3BO_3	8.7	8.8	Lange's Handbook**
40.8 NaOH, 50.0 H_3BO_3	9.5	9.8	Lange's Handbook**

**Handbook of Chemistry and Physics*, 66th Edition, R. C. Wheat, Editor, CRC Press, Boca Raton, Florida, 1985.
***Lange's Handbook of Chemistry*, N. A. Lange, Editor, Handbook Publishers, Sandusky, Ohio, 1949.

Appendix B. General Method for Calculation of Dehydrochlorination of Hypalon by Radiation

The rate of HCl generation can be written as:

$$R = R_{\gamma H} + R_{\beta H} , \qquad (B.1)$$

where R is the total HCl generation rate from γ and β radiolysis of Hypalon, and $R_{\gamma H}$ and $R_{\beta H}$ are the HCl generation rates due to gamma and beta radiolysis, respectively. The units for the rates are g-mols/s.

From Wing (1984)

$$R_{\gamma H} = G_H \cdot \phi_{\gamma C} \cdot S \cdot A_{\gamma,H} , \qquad (B.2)$$

where

G_H = radiation G value (molecules HCl/100 eV) for radiolysis of Hypalon,

$\phi_{\gamma C}$ = gamma radiation energy flux (MeV/cm^2 s) on the Hypalon surface,

S = total surface area, cm^2, of the cables, and

$A_{\gamma H}$ = absorption of gamma radiation energy by Hypalon.

The G value will be 2.115 molecules HCl/100 eV

$$G_H = 2.115 \frac{\text{molecules}}{100 \text{ eV}} \cdot \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} \cdot \frac{10^6 \text{ eV}}{\text{MeV}} \qquad (B.3)$$
$$G_H = 3.512 \times 10^{-30} \frac{\text{g mol}}{\text{MeV}} .$$

The gamma radiation energy flux will be given by (after Wing, 1984)

$$\phi_{\gamma C} = \frac{E_\gamma}{V} \cdot \frac{(1 - e^{-3.74 \times 10^{-5} r})}{3.74 \times 10^{-5}} \left(\frac{\text{MeV}}{\text{cm}^2 \text{ s}}\right), \qquad (B.4)$$

where E_γ is the total gamma energy release rate (MeV/s), and r is the radiation length in containment air; given by Wing as r = 2.23 × 10^3 cm.

The magnitude of S will vary for each containment cable inventory. It is given by

$$S = \ell \cdot 2.261 \, \pi ,$$

where ℓ is the total length of cable, and 2.261 is the cable diameter (Bonzon, 1980).

The total mass of EPR/Hypalon cable insulation is N lbs, then

$$N \text{ lbs} \cdot 453.59 \frac{\text{g}}{\text{lb}} = 4.5359 \times 10^2 \text{ N grams} .$$

The weighted density of EPR/Hypalon cable is 1.40 g/cm^3 (Wing, 1984).

$$\text{Volume EPR/Hypalon} = \frac{4.5359 \times 10^2 \text{ N (g)}}{1.40 \text{ (g/cm}^3)} \qquad (B.5)$$
$$= 3.24 \times 10^2 \cdot \text{N (cm}^3) .$$

This volume of EPR/Hypalon can be equated with the dimensions of the cable as:

$$\ell \cdot \left[\pi\left(\frac{2.261}{2}\right)^2 - \pi\left(\frac{1.458}{2}\right)^2\right] = 3.24 \times 10^2 \cdot \text{N}, \qquad (B.6)$$
$$\ell \cdot 2.3455 = 3.24 \times 10^2 \cdot \text{N, or}$$
$$\ell \text{ (cm)} = 1.38 \times 10^2 \cdot \text{N} .$$

From this,

$$S = 1.38 \times 10^2 \cdot \text{N} \cdot 2.261 \, \pi, \quad \text{or} \qquad (B.7)$$
$$S = 9.81 \times 10^2 \cdot \text{N (cm}^2) .$$

From Wing,

$$A_{\gamma H} = 1.79 \times 10^{-2} . \qquad (B.8)$$

Then,

$$R_{\gamma H} = 3.512 \times 10^{-20} \cdot \left(\frac{g\ mol}{MeV}\right) \cdot \frac{E_\gamma}{V} \cdot 2.1395 \times 10^{3} \left(\frac{MeV}{cm^2\ s}\right) \cdot 9.81 \times 10^{2} \cdot N\ (cm^2)\ 1.79 \times 10^{-2} \quad \text{(B.9)}$$

$$R_{\gamma H} = 1.32 \times 10^{-15} \cdot \frac{E_\gamma \cdot N}{V}$$

where V is the net free volume of the containment building (cm^3).

The expression for $R_{\beta H}$ is obtained in a similar manner. From Wing (1984),

$$R_{\beta H} = G_H \phi_{\beta,C} S\ A_{\beta,H} \cdot \quad \text{(B.10)}$$

The definitions of G_H and S are as above, and $\phi_{\beta,C}$ and $A_{\beta,H}$ are the beta analogs of $\phi_{\gamma,C}$ and $A_{\gamma,H}$.

The magnitude of $\phi_{\beta,C}$ is (Wing, 1984)

$$\phi_{\beta,C} = \frac{E_\beta}{3.96 \times 10^{-2}\ V} \left(\frac{MeV}{cm^2\ s}\right), \quad \text{(B.11)}$$

and $A_{\beta,H}$ is given by:

$$A_{\beta,H} = 1.0.$$

Then $R_{\beta,H}$ can be written as:

$$R_{\beta,H} \left(\frac{g\text{-}mol}{s}\right) = 3.512 \times 10^{-20} \left(\frac{g\text{-}mol}{MeV}\right) \cdot \frac{E_\beta}{3.96 \times 10^{-2}}\ V \cdot 9.81 \times 10^{2} \cdot N\ (cm^2) \quad \text{(B.12)}$$

$$R_{\beta,H} \left(\frac{g\text{-}mol}{s}\right) = 8.70 \times 10^{-16} \cdot \frac{E_\beta \cdot N}{V}.$$

The magnitudes of N and V can be obtained from updated final safety analysis reports.

Appendix C. Steady-State Model of Iodine Radiolysis

The model is based on the decomposition of H_2O_2 by I^- and I_2 as developed by Abel. This treatment proceeds as follows: Experimental studies of Abel (1928) indicate that the reaction of I^- with H_2O_2 is first order in (I^-) and in (H_2O_2). Thus, this process can be described as rate 1 = $k_1 (I^-) (H_2O_2)$. At steady state, it has been proposed that rate 1 is balanced by the rate of reaction of H_2O_2 with both HIO and IO^-. This rate is expressed as rate 2 = $k_2 (H_2O_2) (HIO) + k_3 (H_2O_2) (IO^-)$. By definition at the steady state, rate 1 = rate 2:

$$k_1 (I^-) (H_2O_2) = k_2 (H_2O_2) (HIO) + k_3 (H_2O_2) ((IO^-) \quad (C.1)$$

or

$$k_1 (I^-) = k_2 (HIO) + k_3 (IO^-) . \quad (C.2)$$

The equilibria

$$I_2 + H_2O \rightleftharpoons H^+ + I^- + HIO \quad (C.3)$$

and

$$HIO \rightleftharpoons H^+ + IO^- \quad (C.4)$$

are quite rapid, so we may substitute for HIO and IO^- as follows:

$$(HIO) = K_1 \frac{I_2}{(H^+)(I^-)} , \quad (C.5)$$

$$(IO^-) = \frac{K_2 (HIO)}{(H^+)} = \frac{K_2K_1 (I_2)}{(H^+)^2 (I^-)} , \quad (C.6)$$

where K_1 and K_2 are the equilibrium constants for Equations C.3 and C.4, respectively. Equations C.5 and C.6 may be substituted into Equation C.2 to give

$$k_1 (I^-) = k_2 \cdot \frac{K_1 (I_2)}{(H^+) (I^-)} + k_3K_2 \frac{K_1 (I_2)}{(H^+)^2 (I^-)} \quad (C.7)$$

$$= K_1 \frac{(I_2)}{(H^+)^2 (I^-)} \{k_3K_2 + k_2 (H^+)\} . \quad (C.8)$$

Rearranging Equation C.8 gives

$$\frac{(H^+)^2 (I^-)^2}{(I_2)} = \frac{K_1}{k_1} \{k_3K_2 + k_2 (H^+)\} . \quad (C.9)$$

The constants d and e are defined as:

$$d = \frac{K_1K_2 \cdot k_3}{k_1} , e = \frac{K_1k_2}{k_1} ; \quad (C.10)$$

then

$$\frac{(H^+)^2 (I^-)^2}{(I_2)} = d + e (H^+) .$$

At 25°C, the constants are as follows:

$k_1 = 1.2 \times 10^{-2}$ L/mols·s (Liebhafsky, 1932A),

$k_2 = 3.7 \times 10^{1}$ L/mols·s (Liebhafsky, 1932B),

$k_3 = (6.6 \pm 2.0) \times 10^{7}$ L/mols·s (Shiraishi, 1991),

$K_1 = 4.77 \times 10^{-13}$ (Palmer, 1985), and

$K_2 = 2.31 \times 10^{-11}$ (Eigen, 1962).

Thus,

$d = 6.05 \times 10^{-14} \pm 1.83 \times 10^{-14}$,

$e = 1.47 \times 10^{-9}$.

These data were obtained at 77°F (25°C). The experimental values were obtained at ambient

conditions, which would be near 77°F (25°C). There is some additional experimental evidence that the conversion of I^- to I_2 decreases with increasing temperature. Tests of Burns (1990), on irradiation of 1×10^{-4} g-atom I^-/L solutions, gave ~45% conversion to I_2 at 86°F (30°C) but ~10% conversion at 158°F (70°C).

A series of tests were run at ORNL at 198°F (92°C). In these tests, samples were taken by pressurizing the sample container during irradiation and thereby forcing a portion of the iodine solution up a narrow tube and into isooctane. With this technique, the sample was stripped of I_2 only a few seconds after it left the irradiation zone. With initial iodide concentrations of $\sim 1 \times 10^{-4}$ g-atom I^-/L, at pH 4.0, the measured fraction as I_2 was 38.9% and the model calculation gave 72.6%.

At pH 5.0, the measured value was 3.1%, and the calculated value was 17.9%. Thus, the model tends to overestimate the extent of conversion to I_2 at temperatures >86°F (30°C). The two equilibrium constants, K_1 and K_2, can be given for temperatures in excess of 86°F (30°C), but at this time, there is no good representation of the rate constants k_1, k_2, and k_3 at these temperatures; so it is recommended that the data for 25°C (77°F) be used until such data are produced.

Table C.1 gives measured values of the fraction of initial iodide that was converted to I_2 on irradiation, as well as the corresponding calculated values. Of the four sets of experimental data, the correspondence between calculated and experimental values is best for the data of Burns (1990). The worst model fit of experimental data was at pH 4.4 to 4.5 and an initial concentration of 1×10^{-5} g-atom I^-/L. In one case, Naritomi (1991) give 2.5% conversion at pH 4.4, and the calculated value was 18%. In the other case, the ORNL data give 42% conversion at pH 4.5, and the calculated value was 13.9%. It appears that the value of 2.5% at pH 4.4 and the 42% at pH 4.5 are not compatible with each other and both may be somewhat in error. At a concentration of 5×10^{-5} g-atom I^-/L and pH 4.6, Burns (1990) give a value of ~30% conversion to I_2, and the calculated value is almost identical to this at 29.2%. Burns (1990) noted that concentrations $<10^{-4}$ g-atom I^-/L gave scattered results.

Table C.1 Comparison of model of iodine radiolysis with measured values

pH	Concentration initial I^- g-atom/L	Measured % as I_2	Calculated % as I_2	Comments
4.6	1×10^{-4}	43.4 and 46.0	42.6	Burns (1990)
4.6	$\sim 5 \times 10^{-5}$	~30	29.2	(Data taken from curve in report)
5.6	1×10^{-4}	5.4 and 7.8	1.9	
6.6	1×10^{-4}	<0.01 and 0.017	0.021	0.2 *M* boric acid
3.0	1×10^{-4}	93.8	91.6	Lin (1980)—pH not buffered and may
5.0	1×10^{-4}	8.0	17.9	have varied during irradiation.
6.6	1×10^{-4}	1.7	0.021	Initial value given—4.5 Mrad/h
4.4	1×10^{-5}	2.5	18.0	Naritomi (1991)
5.2	1×10^{-4}	12.3	9.4	
5.3	1×10^{-5}	0.33 and 0.63	0.73	
5.8	1×10^{-5}	0.16	0.08	
5.8	1×10^{-4}	1.2	0.79	
6.2	1×10^{-5}	0.038 and 0.15	0.013	
6.2	1×10^{-4}	0.49	0.13	
5.7	1×10^{-5}	0.16	0.13	
5.7	1×10^{-4}	3.7	1.2	
4.5	1×10^{-5}	42.0	13.9	ORNL data—0.37 Mrad/h in 0.2 *M*
4.7	6.67×10^{-5}	35.0	29.4	boric acid
4.7	7.0×10^{-5}	34.0	30.2	
5.0	2×10^{-4}	18.8	27.8	

Appendix D. Chlorine Interactions in Containment

D.1 Competitive Reactions of Cl^- and I^- with OH Radicals

The initial step in the oxidation of I^- or Cl^- in irradiated water will be the reaction of these ions with the OH radical. When both I^- and Cl^- are in solution, there will be a competition between these ions to react with OH.

The probability for the reaction of Cl^- with OH is:

$$\frac{k_{Cl}\,(Cl^-)}{k_{Cl}\,(Cl^-) + k_I\,(I^-)} = \frac{1}{1 + \dfrac{k_I\,(I^-)}{k_I\,(Cl^-)}}\,. \qquad \text{(C.1)}$$

The probability for the reaction of I^- with OH is:

$$\frac{k_I\,(I^-)}{k_{Cl}\,(Cl^-) + k_I\,(I^-)} = \frac{1}{1 + \dfrac{k_{Cl}\,(Cl^-)}{k_I\,(I^-)}}, \qquad \text{(D.2)}$$

where

k_{Cl} = rate constant for $Cl^- + OH \rightarrow$,

k_I = rate constant for $I^- + OH \rightarrow$, and

( ) = denotes concentration in mol/L.

The number of OH radicals that are produced per unit radiation energy input of 100 eV will be represented by G_{OH}. Then the number of Cl^- reacted per unit radiation energy input, G_{Cl^-} will be:

$$G_{Cl^-} = \frac{G_{OH}}{1 + \dfrac{k_I\,(I^-)}{k_{Cl}\,(Cl^-)}}\,, \qquad \text{(D.3)}$$

and the corresponding number of I^- reacted per unit radiation energy will be:

$$G_{I^-} = \frac{G_{OH}}{1 + \dfrac{k_{Cl}\,(Cl^-)}{k_I\,(I^-)}}. \qquad \text{(D.4)}$$

The ratio of G_{Cl^-} to G_{I^-} will be:

$$\frac{G_{Cl^-}}{G_{I^-}} = \frac{\dfrac{G_{OH}}{1 + \dfrac{k_I\,(I^-)}{k_{Cl}\,(Cl^-)}}}{\dfrac{G_{OH}}{1 + \dfrac{k_{Cl}\,(Cl^-)}{k_I\,(I^-)}}} \qquad \text{(D.5a)}$$

$$\frac{G_{OH}}{\dfrac{1 + k_I\,(I^-)}{k_{Cl}\,(Cl^-)}} \cdot \frac{1 + \dfrac{k_{Cl}\,(Cl^-)}{k_I\,(I^-)}}{G_{OH}} \qquad \text{(D.5b)}$$

$$\frac{G_{Cl^-}}{G_{I^-}} = \frac{k_{Cl}\,(Cl^-)}{k_I\,(I^-)}\,. \qquad \text{(D.5c)}$$

At 77°F (25°C), $k_{Cl} = 4.3 \times 10^9$, $k_I = 1.1 \times 10^{10}$ (Buxton, 1988). From this:

$$\frac{G_{Cl^-}}{G_{I^-}} = 3.9 \times 10^{-1} \cdot \frac{(Cl^-)}{(I^-)}\,. \qquad \text{(D.6)}$$

When the chloride ion concentration is > ~2.5 times the iodine concentration, oxidation of Cl^- will predominate over oxidation of I^-.

D.2 The Gaseous/Aqueous Partition Coefficient of Cl_2 and HOCl

Elemental chlorine, Cl_2 formed by reaction of Cl^- with water radiolysis products in acid solutions, will hydrolyze to form HOCl, and it will partition, be distributed, between the gas phase and the aqueous phase. Thermochemical data obtained from the FACT

(1985) system have been used to evaluate partitioning and hydrolysis of Cl_2. It should be noted that iodide as I^- in aqueous solution or as deposited on a surface or in a metal iodide would react with Cl_2 or HOCl either aqueous or gaseous to form I_2:

$$2I^- + Cl_2 \rightarrow I_2 + 2Cl^- . \qquad (D.7)$$

The partition coefficient for Cl_2, $PC(Cl_2)$ is defined as:

$$PC(Cl_2) = \frac{\text{concentration of } Cl_2 \text{ in aqueous phase}}{\text{concentration of } Cl_2 \text{ in gas phase}} .$$

If it is assumed that Cl_2 behaves ideally (activity coefficient equals one) in both the aqueous and gas phase, the constant for the equilibrium between Cl_2 in the gas and in solution may be written as:

$$\frac{C_{Cl_2}\text{ (aqueous)}}{P_{Cl_2}} = \frac{C_{Cl_2}\text{ (aqueous)}}{8.205 \times 10^{-2} \cdot 2.98 \cdot C_{Cl_2}\text{ (gas)}} = 6.26 \times 10^{-2} , \qquad (D.8)$$

where C_{Cl_2} (aqueous), C_{Cl_2} (gas) are the Cl_2 concentrations (mol/L) in the aqueous and gas phases, respectively, and P_{Cl_2} is the partial pressure of Cl_2. Rearranging Equation D.8 gives:

$$PC\ (Cl_2) \text{ at } 25°C = \frac{C_{Cl_2}\text{ (aqueous)}}{C_{Cl_2}\text{ (gas)}} = 1.5 . \qquad (D.9)$$

This partition coefficient may be compared to the partition coefficient for I_2 at 77°F (25°C), 70.8, as calculated from Equation 15. Thus, Cl_2 is much more volatile from solution than I_2.

The hydrolysis of Cl_2 may be written as:

$$Cl\text{ (aqueous)} + H_2O \rightleftharpoons HOCl + H^+ + Cl^- . \qquad (D.10)$$

The equilibrium constant at 77°F (25°C) may be rearranged to give:

$$\frac{C_{Cl_2}\text{ (aqueous)}}{C_{HOCL}\text{ (aqueous)}} \approx 2.2 \times 10^3 \cdot C_{H^+}\text{ (aqueous)} \cdot C_{Cl^-}\text{ (aqueous)} , \qquad (D.11)$$

where as before C_{Cl_2}, etc., refer to the concentration in mol/L. This is written as an approximation because all activity coefficients, even those of the ions, are taken as unity. The relation given by Equation D.11 is shown only to indicate that under most circumstances the concentration of HOCl in solution would be greater than the concentration of Cl_2 because C_{H^+} (aqueous) and C_{Cl^-} (aqueous) would both be $<10^{-2}$ mol/L.

The partition coefficient for HOCl at 77°F (25°C), calculated in the same manner as the partition coefficient for Cl_2, is 33. The volatility of HOCl from solution is thus intermediate between Cl_2 and I_2.

D.3 The Effect of Organic Chlorides on the Formation and Retention of Organic Iodides

The pyrolysis or radiolysis of cable insulation may produce hydrocarbon gases as well as HCl (Wing, 1984; Liljenzin, 1990) (also, Section 2.2.5). The co-occurrence of hydrocarbon gases and chlorine species could result in the formation of organic chlorides. For this evaluation, methyl chloride, CH_3Cl, will represent all organic chlorides, and methyl iodide, CH_3I, will represent organic iodides.

The reaction of I_2 with CH_3Cl to form CH_3I should not occur because of unfavorable thermodynamics:

$$CH_2Cl + 1/2I_2 \rightleftharpoons CH_3I + 1/2Cl_2 . \qquad (D.12)$$

However, a similar reaction of HI with CH_3Cl could occur if the ratio,

$$\frac{P_{CH_3I} \cdot P_{HCl}}{P_{CH_3Cl} \cdot P_{HI}} \sim < 7 \times 10^3 ,$$

where P_{CH_3I}, etc. are the partial pressures of the iodine or chlorine species. Occurrence of this reaction is based on the postulated gaseous equilibrium:

$$CH_3Cl + HI + CH_3I + HCl \; . \qquad (D.13)$$

As noted in Section 2.2.2, it is not likely that large amounts of HI will be in containment.

If the chloride ion concentration in aqueous solutions is great enough to scavenge OH radicals (see above Appendix D.1), then reaction of dissolved organic gases may be suppressed:

$$CH_4 + OH \rightarrow CH_3 + H_2O \; . \qquad (D.14)$$

This reaction is the initial step in the formation of CH_3I in solution (Paquette, 1990). If scavenging of OH by Cl^- occurs, then CH_3 will not be available to form CH_3I by the reaction:

$$CH_3 + I_2 \rightarrow CH_3I + I \; . \qquad (D.15)$$

Thus, a high chloride concentration in solution could indirectly result in a decrease in the extent of CH_3I formation.

The behavior of CH_3Cl in charcoal filter systems should be similar to the behavior of CH_3I. Thus, CH_3Cl would occupy the same type of sites (see Appendix D.4) and may decrease the capacity for CH_3I absorption.

D.4 The Influence of Gaseous Chlorine Species on the Capacity and Retention of Iodine Species in Filters

Hydrochloric acid or chlorine may affect the capacity and retention of iodine species in filters. Containment filters have activated charcoal that may be impregnated with triethylenediamine (TEDA) and/or an iodide, such as KI. There are no experimental data on how radioiodine removal by charcoal filters is effected by HCl or Cl_2, but it is possible to predict their interactions with activated charcoal and the impregnants.

The retention of I_2 by activated charcoal has been described by Evans (1975) in the reaction:

$$I_2 + 2K^+ + 2OH^- \rightarrow 2K^+ + 2I^- + H_2O + 1/2O_2 \; . \qquad (D.16)$$

In this reaction, the potassium ions (K^+) and hydroxide ions (OH^-) arise from the natural content of the material or from impregnants. Coconut charcoal is valued because of its relatively large inventory of K^+ and OH^-. Studies of the adsorption of I_2 on basic oxides that were conducted at ORNL found that the products were iodide (I^-) and iodate (IO_3^-) (Beahm, 1990). Evans (1975) admits that iodate may also form along with iodide on activated charcoal. In the presence of HCl or Cl_2, we would expect that reaction D.16 will be superceded by:

$$HCl + K^+ + OH^- \rightarrow 2K^+ + 2Cl^- + H_2O \qquad (D.17)$$

or

$$Cl_2 + 2K^+ + 2HO^- \rightarrow 2K^+ + 2Cl^- + H_2O + 1/2O_2 \; . \qquad (D.18)$$

Reaction D.18 may also have an oxychloride anion such as ClO_3^- as a product. The result of the interactions of HCl or Cl_2 would be to reduce the capacity of activated charcoal to absorb iodine. Radioiodine that is adsorbed may react with Cl_2 as expressed in Equation D.6 to form I_2.

Potassium iodide as an impregnant on charcoal removes radioiodine by isotopic exchange. If Cl_2 is introduced, the following reaction would occur:

$$2KI + Cl_2 \rightarrow 2KCl + I_2 \; . \qquad (D.19)$$

In this case, the I_2 released would most likely be natural iodine with a small fraction as radioiodine.

However, the ability of this impregnant to remove radioiodine as I_2 would be degraded.

Triethylenediamine (TEDA) impregnant binds methyl odide (CH_3I) in a quaternary ammonium salt:

$$N(CH_2CH_2)_3N + 2CH_3I \rightarrow [H_3CN^+(CH_2CH_2)_3N^+CH_3]2I^- . \quad (D.20)$$

Hydrochloric acid would react with TEDA to form triethylenediamine hydrochloride:

$$N(CH_2CH_2)_3N + 2HCl \rightarrow [HN^+(CH_2CH_2)_3N^+H]2Cl^- . \quad (D.21)$$

This would prevent the reaction of TEDA with CH_3I. The basic TEDA would prefer to react with the strong acid HCl. Wren (1991A, 1991B) studied the weathering of TEDA impregnated charcoal by SO_2. In a wet charcoal bed, the SO_2 most likely deposited on the charcoal as sulfuric acid H_2SO_4. The fraction of CH_3I released was much higher for the wet charcoal bed compared to a dry bed under the same SO_2 loading. This result was most likely due to the reaction of sulfuric acid with the basic TEDA. In the case of HCl, moisture should not be necessary for the destruction of TEDA because it is already a strong acid.

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NRC FORM 335 (2-89) NRCM 1102, 3201, 3202

U.S. NUCLEAR REGULATORY COMMISSION

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(See instructions on the reverse)

1. REPORT NUMBER (Assigned by NRC. Add Vol., Supp., Rev., and Addendum Numbers, if any.)

NUREG/CR-5950
ORNL/TM-12242

2. TITLE AND SUBTITLE

Iodine Evolution and pH Control

3. DATE REPORT PUBLISHED

MONTH	YEAR
December	1992

4. FIN OR GRANT NUMBER

L2039

5. AUTHOR(S)

E.C. Beahm, R.A. Lorenz, C.F. Weber

6. TYPE OF REPORT

Technical

7. PERIOD COVERED *(Inclusive Dates)*

8. PERFORMING ORGANIZATION – NAME AND ADDRESS *(If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address; if contractor, provide name and mailing address.)*

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Division of Safety Issue Resolution
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555

10. SUPPLEMENTARY NOTES

11. ABSTRACT *(200 words or less)*

In accident sequences where pH falls below ~7, I_2 will form in irradiated water pools. In containments where no pH-control chemicals are present, the acidity or basicity will be determined by materials that are introduced into water as a result of the accident itself. The most important acids in containment will be nitric acid, produced by irradiation of water and air, and hydrochloric acid, produced by irradiation or heating of electrical cable insulation. The maximum duration of a basic pH, in the absence of pH control chemicals, was calculated to be ~60 to 100 h.

12. KEY WORDS/DESCRIPTORS *(List words or phrases that will assist researchers in locating the report.)*

Iodine
Source Terms
Containment Chemistry
pH Control
Dehydrochlorination
Charcoal Filters
Hydrochloric Acid
Borate Buffer
Phosphate Buffer

13. AVAILABILITY STATEMENT

unlimited

14. SECURITY CLASSIFICATION

(This Page)

unclassified

(This Report)

unclassified

15. NUMBER OF PAGES

16. PRICE

NRC FORM 335 (2-89)

Printed on recycled paper

Federal Recycling Program

NUREG/CR-5950

IODINE EVOLUTION AND pH CONTROL

DECEMBER 1992

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

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