ANS Reprint

THE INTERACTION OF IODINE WITH ORGANIC MATERIAL IN CONTAINMENT

RADIOISOTOPES

KEYWORDS: *iodine volatility, organic dissolution, organic iodide formation*

JUNGSOOK CLARA WREN,* JOANNE M. BALL, GLENN A. GLOWA
Atomic Energy of Canada Ltd., Chalk River Laboratories
Fuel Safety Branch, Chalk River, Ontario, Canada K0J 1J0

Received July 17, 1997
Accepted for Publication September 8, 1998

Organic impurities in containment water, originating from various painted structural surfaces and organic containment materials, could have a significant impact on iodine volatility following an accident. To determine the effect of these impurities on iodine volatility under accident conditions, literature, experimental, and modeling studies have been conducted on

1. *the radiolysis of organic compounds in the aqueous phase*
2. *thermal and radiolytic formation and decomposition of organic iodides*
3. *dissolution of organic solvents from various painted surfaces into the aqueous phase*
4. *hydrolysis and aqueous-gas phase partitioning of organic iodides*
5. *iodine deposition on painted surfaces.*

The experimental studies consist of intermediate-scale "integrated effects" tests in the Radioiodine Test Facility and bench-scale "separate effects" tests. Recent findings from these studies and implications of these studies on the safety analysis of an accident in a nuclear power station are discussed.

The studies have shown that organic impurities will be found in containment water as a result of the dissolution of organic compounds from various surface paints. These compounds can have a significant effect on iodine volatility following an accident. The main influence of containment paints on iodine behavior will arise as a result of the aqueous-phase radiolysis of dissolved organic solvents, which are leached from the painted surface by the water. The radiolysis products will decrease the sump pH and dissolved oxygen concentration, consequently increasing the overall rate of conversion of dissolved I^- to volatile I_2. It appears that the rates of these processes may be controlled by the dissolution kinetics of the organic compounds from the surface coatings. Moreover, organic compounds may also react thermally and radiolytically with I_2 to form organic iodides in the aqueous phase. Our studies have shown that the formation of organic iodides in the aqueous phase from soluble organic compounds such as ketones, alcohols, and phenols will have more impact on the total iodine volatility than the formation of CH_3I from CH_4 and I_2 from either the gas or the aqueous phase.

I. INTRODUCTION

It is generally recognized that radioiodine is one of the most hazardous fission products that could be released in the event of nuclear reactor accidents. This is due to the combination of its large inventory in nuclear fuel, a half-life of 8.04 days for the isotope of greatest radiological significance, a complex chemistry that may lead to formation of volatile species, and its hazardous biological effects. Thermodynamic calculations and various experiments have established that under most accident conditions the iodine released from fuel into containment would be primarily in its reduced state as cesium iodide.[1-4] This would initially be dissolved in the water originating from the discharged coolant and any safety spray systems present. However, under the highly oxidizing conditions induced by radiation fields in an accident, nonvolatile I^- initially dissolved in the containment sump will react to form volatile molecular iodine and organic iodides that could become airborne. The time-dependent concentration of airborne iodine in containment, which is subject to release to the outside

*E-mail: wrenc@aecl.ca

atmosphere through containment leakage or controlled venting, is a very important parameter in evaluating potential consequences of an accident. The behavior of iodine under containment accident conditions has thus been a subject of extensive studies for the nuclear industry for many years.[5]

One of the inherent features of containment that must be taken into account when assessing iodine behavior is the structural surfaces. Structural surfaces within a reactor building are normally coated with organic-based paints, which could affect iodine volatility in containment following a reactor accident in two ways: (a) by acting as a source of organic impurities in the sump, which would affect the pH and dissolved oxygen concentration of the sump water and could react with molecular iodine to form organic iodides, and (b) by acting as a site for iodine adsorption, one of the main processes that would limit the airborne iodine concentration.

The effects of organic-painted structural surfaces on iodine behavior under reactor accident conditions have been studied as part of the safety research program on iodine behavior at the Whiteshell Laboratories and Chalk River Laboratories of Atomic Energy of Canada Ltd. (AECL) (Refs. 5 through 21). The program consists of a literature review, chemical kinetic modeling studies, bench-scale "separate-effects" tests, and intermediate-scale "all-effects" experiments, all of which were designed to address these questions:

1. What will be the sources of organic impurities in an accident and how would these organic impurities influence iodine volatility?

2. What will be the major mechanism for the formation of organic iodides in postaccident containment?

3. What will be the key processes governing the rate of organic radiolysis (and subsequent pH and dissolved oxygen changes in the sump) and organic iodide production?

This paper presents recent findings from these studies and discusses the implications of these studies on the safety analysis of an accident in a nuclear power station. The intention of this summary paper is not to present the details of individual experimental data, but to assess the impact of organic impurities on iodine behavior under accident conditions in the light of recent development in our understanding.

II. TECHNICAL BACKGROUND

II.A. The Effect of Organic Impurities on Iodine Volatility

It has been established that under most accident conditions the iodine released from fuel into containment would be primarily in its reduced state as cesium iodide.[1-4] The postulated accidents that are considered in the studies presented here are in-channel accidents such as the loss-of-coolant accident (LOCA), LOCA + loss of emergency core coolant, feeder stagnation break, and feeder off-stagnation break, in which CsI, once released into containment, would quickly be dissolved in the water originating from the discharged coolant and any safety spray systems present. Under these accident conditions, nonvolatile I^- initially dissolved in the containment sump can be oxidized by the following radiolytic processes to form volatile molecular iodine that could become airborne[5,6]:

$$I^- + \bullet OH \rightarrow I\bullet + OH^- \quad (1)$$

$$I\bullet + I\bullet \rightarrow I_2(aq) \quad (2a)$$

$$2I\bullet + 2I^- \rightarrow 2I_2^- \rightarrow\rightarrow I_3^- + I^- \quad (2b)$$

$$I_3^- \leftrightarrow I_2(aq) + I^- \quad (2c)$$

$$I_2(aq) \rightarrow I_2(g) \ , \quad (3)$$

where the hydroxyl radical •OH is formed by water radiolysis and $I_2(aq)$ and $I_2(g)$ are molecular iodine species in the aqueous and gas phases, respectively. Molecular iodine in the aqueous phase can be further oxidized to nonvolatile iodine oxides (IO_x^-) or reduced by thermal or radiolytic processes to return to its original nonvolatile I^- state, the key iodine reduction reactions being[5,6]

$$I_2(aq) + H_2O \rightarrow HOI + I^- + H^+ \quad (4)$$

$$I_2(aq) + O_2^- \rightarrow I_2^- + O_2 \quad (5)$$

$$I_2(aq) + H_2O_2 \rightarrow 2I^- + 2H^+ + O_2 \ , \quad (6)$$

where O_2^- and H_2O_2 are products of water radiolysis, and I_2^- undergoes reactions (2a) and (2b) to form I^- and I_2.

The steady-state concentration of $I_2(aq)$ is determined primarily by the relative rates of the oxidation reactions (1) and (2) and the reduction reactions (4), (5), and (6). Consequently iodine volatility depends strongly on pH and dissolved oxygen concentration because the rates of the iodine reduction reactions are sensitive to these parameters.

Organic impurities in containment water, originating from various painted structural surfaces and organic containment materials,[17] can have a large influence on iodine volatility following an accident.[6,7,9,18-20] Organic impurities in the aqueous phase can influence iodine volatility in two ways:

1. Under the radiation conditions expected during an accident, organic compounds will undergo radiolytic decomposition to form organic acids, which will result in a reduction of the pH and dissolved oxygen concentration in the containment sump. These changes would increase iodine volatility because they decrease the rate of reduction of $I_2(aq)$ to I^- (Refs. 6, 18, 19, and 20).

2. Organic iodides will be formed thermally and radiolytically through reactions of $I_2(aq)$ with organic compounds. The formation and decomposition of organic iodides will affect iodine volatility because these species have different partition coefficients than I_2, and their formation will change the steady-state concentration of $I_2(aq)$. Contrary to the earlier understanding of the impact of organic iodides, our recent studies[7,16,21] indicate that many organic iodides that would be formed in an accident would be less volatile than $I_2(aq)$. They could also hydrolyze to I^- at a rate much faster rate than $I_2(aq)$, particularly at higher temperatures.

There is still controversy[22-28] regarding whether the effect of painted surfaces or organic materials on iodine volatility occurs mainly through heterogeneous reactions on surfaces exposed to the aqueous phase or through homogeneous reactions in the aqueous phase. Various bench-scale tests and intermediate-scale tests in the Radioiodine Test Facility (RTF) (Refs. 6, 7, 9, 18, 19, and 20) suggest that under postulated in-channel accident conditions the key volatile iodine species to consider is I_2, which is generated by homogeneous aqueous phase reactions. Once I_2 becomes airborne, its adsorption on various surfaces has a significant impact on its gas phase concentration. These studies also suggest that the major effect of organic surfaces on iodine volatility is due to the organic solvent they release into the aqueous phase, which affects the aqueous phase chemistry of I_2. Under accident conditions in which the majority of iodine in containment is initially present in water, organic iodides are formed mainly by homogeneous aqueous phase process; heterogeneous reactions on surfaces exposed to gas or aqueous phase do not contribute significantly to the overall organic iodide formation.

Organic impurities in the presence of radiation undergo the following reaction:

$$RH + \bullet OH \rightarrow \bullet R + H_2O \ , \tag{7}$$

where RH is the organic compound (impurity) in the aqueous phase and •OH is the hydroxyl radical formed through radiolysis of water. The organic radical (R•) produced from this reaction continues to react and eventually forms either an organic acid, thereby decreasing pH, or forms an organic iodide:

$$\bullet R + O_2 \rightarrow RO_2\bullet \rightarrow\rightarrow \bullet R' \ , \quad \text{alcohols, aldehydes, acids, and } CO_2 \tag{8}$$

$$\bullet R + I_2 \rightarrow RI + I\bullet \ . \tag{9}$$

The same reaction mechanism is considered to be responsible for organic iodide formation by heterogeneous surface reactions. However, the aqueous phase, with a reasonable concentration of organic impurities, provides the optimum conditions for reaction (7).

The main source of organic impurities in the containment sump is likely to be organic solvents dissolved from painted surfaces, rather than organic compounds resulting from decomposition of paint or other organic polymers such as cable insulation. This is because the rate of dissolution of organic solvents from paint is, in general, faster than the radiolytic decomposition of polymers forming water soluble organic compounds (see Sec. III.C). Thus, the dissolution of organic compounds from the painted surfaces into the containment sump may be one of the key rate-controlling processes for iodine behavior in containment following an accident. Because the impact of organic impurities on iodine volatility is significant, the relative rates for the release, degradation, and formation of organic compounds and organic iodides are very important to any model describing the time-dependent volatility of iodine following an accident.

II.B. Iodine Transport Behavior in Containment

A fraction of the volatile iodine species (I_2 and organic iodides) generated in the aqueous phase in containment will become airborne. Intermediate-scale studies have demonstrated that when CsI solutions are irradiated (see Sec. III), the gas phase iodine concentration initially increases rapidly as a result of the radiolytic production of the volatile iodine species. A maximum or pseudo steady state is soon reached as the rates of oxidation of iodide and reduction of molecular iodine in the aqueous phase equalize. This steady state is reflected in the gas phase concentration. Over the long term, both gas and aqueous phase concentrations slowly decrease as they are depleted by adsorption of the molecular iodine onto gas phase surfaces.

The peak concentration and the following pseudo steady-state concentration of volatile iodine species is determined by the overall rates of volatile iodine production in the aqueous phase, interfacial mass transfer, and surface adsorption. These processes can be represented by

$$NONVI(aq) \rightarrow VOLI(aq) \tag{10a}$$

$$VOLI(aq) \rightarrow NONVI(aq) \tag{10b}$$

$$VOLI(aq) \rightarrow VOLI(g) \tag{11a}$$

$$VOLI(g) \rightarrow VOLI(aq) \tag{11b}$$

$$VOLI(g) \rightarrow I(ad) \tag{12a}$$

$$I(ad) \rightarrow VOLI(g) \ , \tag{12b}$$

where NONVI and VOLI represent nonvolatile iodine species (I^-, IO_3^-, I_3^-, etc.) and volatile iodine species (I_2 and organic iodides), aq and g represent aqueous and gas phases respectively, and $I(ad)$ are the adsorbed iodine species on surfaces in contact with the gas phase.

Each reaction in this simple scheme represents paths containing many different reactions; for example, reactions (10a) and (10b) include reactions (1) through (9) among others. Adsorption on surfaces in contact with the aqueous phase is not included in this simple mechanism

because the adsorbed iodine in the aqueous phase can be treated as one of the NONVI(aq) species. Iodine deposition on the surfaces in contact with the aqueous phase is generally less important. Surfaces in contact with the aqueous phase contribute to the iodine volatility also through reactions (10a) and (10b) by acting either as catalysts for the reduction of $I_2(aq)$ to $I^-(aq)$ or as sources of organic impurities that could result in pH reduction and/or organic iodide formation.

The interfacial mass transfer of volatile iodine between the aqueous and gas phases [reactions (11a) and (11b)] depends on the mass transfer rate coefficient as well as the equilibrium partition coefficient. Unless there is a sudden change in the system, such as deliberate changes in pH or temperature (sometimes deliberately induced in intermediate-scale tests—see Sec. III), changes in volatile iodine concentrations in the three phases are expected to be gradual. Under these conditions, the interfacial mass transfer rate is generally fast when compared to the rate of the changes in species concentrations. The relative ratio of the aqueous to gas phase volatile iodine concentrations is then determined primarily by the equilibrium partition coefficients of the volatile iodine species. These partition coefficients vary considerably from one compound to another; for example, the partition coefficient at 25°C is 4 for CH_3I (Ref. 29), 88 for I_2 (Ref. 30), and 725 for 2-iodophenol (Ref. 21). They also depend strongly on temperature, a factor that plays an important role in the temperature dependence of iodine volatility.

The peak and pseudo steady-state gas phase iodine concentrations are also affected by the surface adsorption rate as follows. Assuming the adsorption is irreversible or the desorption is small, the concentration of VOLI(g) is determined by

$$\frac{d[\mathrm{VOLI}(g)]}{dt} = k_{11a}\cdot[\mathrm{VOLI}(aq)] - k_{11b}\cdot[\mathrm{VOLI}(g)] - k_{12a}\cdot[\mathrm{VOLI}(g)] \ , \tag{13}$$

where

$$k_{11a} = v_{11a}\cdot\frac{A_{aq}}{V_{aq}} \ , \quad k_{11b} = v_{11b}\cdot\frac{A_{aq}}{V_g} \ ,$$

$$k_{12a} = v_{12a}\cdot\frac{A_{gw}}{V_g} \ ,$$

and where

A_{aq} = aqueous-gas interfacial surface area

A_{gw} = gas phase surface area

V_{aq} = aqueous phase volume

V_g = gas phase volume

k_{11} = aqueous phase (a) and gas phase (b) mass transfer rate constant

k_{12} = gas adsorption rate constant

v_{11} = aqueous or gas phase mass transfer velocity

v_{12} = gas adsorption deposition velocity

At the peak, the changes in [VOLI(g)] and [VOLI(aq)] are zero,

$$[\mathrm{VOLI}(g)]_p \approx \frac{k_{11a}}{(k_{11b}+k_{12a})}\cdot[\mathrm{VOLI}(aq)]_p \approx \frac{1}{\left(H+\dfrac{k_{12a}}{k_{11a}}\right)}\cdot[\mathrm{VOLI}(aq)]_p \ , \tag{14}$$

where k represents the rate coefficient and H is the partition coefficient, defined as

$$H = \frac{[\mathrm{VOLI}(aq)]_{eq}}{[\mathrm{VOLI}(g)]_{eq}} = \frac{k_{11b}}{k_{11a}} \ . \tag{15}$$

Equation (14) shows the relationship between the gas and aqueous phase concentrations at the peak. For $k_{12a} < k_{11a}$, i.e., for relatively fast mass transfer rate, Eq. (14) is reduced to

$$[\mathrm{VOLI}(g)]_p \approx \frac{1}{H}\cdot[\mathrm{VOLI}(aq)]_p \ , \tag{16}$$

which means the ratio of the gas to aqueous phase concentrations of the volatile iodine species is determined by their partition coefficient. If the surface area in contact with the gas phase becomes large so that $k_{12a} > k_{11a}$ and the second term in the denominator in Eq. (14) becomes significant, then the aqueous phase mass transfer rate may contribute to the ratio of $[\mathrm{VOLI}(g)]_p$ and $[\mathrm{VOLI}(aq)]_p$. The most conservative case that yields the maximum gas phase concentration would be the case with fast aqueous-gas phase mass transfer.

Following the peak, the concentrations of VOLI(g) and VOLI(aq) change slowly with time due to the combination of aqueous phase reactions and the surface adsorption. However, the change is slow and VOLI(g) and VOLI(aq) can be considered to be near steady state. Under the pseudo steady-state conditions, the relationship between VOLI(g) and VOLI(aq) given in Eq. (14) still hold.

The partition coefficient H, the gas adsorption rate constants k_{12}, and the aqueous phase mass transfer coefficient k_{11} of volatile iodine species, in addition to the rates of the key aqueous phase reactions (1) through (9), are thus required to predict the gas phase iodine concentration in an accident. In this paper, the effects of organic painted surfaces on these parameters under accident conditions are discussed.

III. INTERMEDIATE SCALE STUDIES

Intermediate-scale studies were performed in the RTF at AECL Whiteshell. A diagram of the RTF is shown in Fig. 1. Because the RTF has been described in detail elsewhere,[7,8,11-14] only a brief description of the facility and a typical test procedure are presented here.

The RTF consists of a replaceable, cylindrical main vessel into which a ^{60}Co radiation source can be placed. The radiation source provided an absorbed radiation dose rate in the aqueous phase of ~2.0 kGy·h^{-1} in 1988. (The absorbed dose rate decreases with time as the cobalt source decays with a half-life of 5.3 yr.) The main vessel can be partially filled with water, and selected chemical additives can be added to the aqueous phase to simulate the sump water in containment following an accident. Typically, the aqueous and gas volumes are 25 and 315 dm^3, respectively; the surface areas in contact with the aqueous and gas phases are 52 and 220 dm^2, respectively; and the aqueous and gas phase interfacial area is 37 dm^2. Electrical heaters around the outside of the vessel can control the temperature of the vessel walls in contact with the gas phase up to 110°C and the water temperature up to 90°C. A test generally starts with an injection of ^{131}I labeled CsI into the aqueous phase, to provide an initial aqueous iodide concentration of about 1×10^{-5} mol·dm^{-3}. This is followed by on-line detection of iodine concentrations in the gas and aqueous phases as a function of time. Gas and aqueous speciation samples are also taken periodically. Finally, the iodine surface loadings are determined by washing the vessel at the end of each test, measuring the ^{131}I activity in the washes, and measuring the remaining activity on the surfaces. The final iodine activities on the coupons placed both in the gas and the aqueous phases during the tests are also used to determine and confirm the iodine surface loadings. Analytical procedures used in this experiment have been summarized in detail previously.[8,14]

The effects of radiation, surfaces (including carbon steel with various inorganic and organic coatings, stainless steel, and unpainted concrete), pH, and temperature on iodine volatility have been investigated in the RTF (Refs. 7, 8, and 11 through 14).

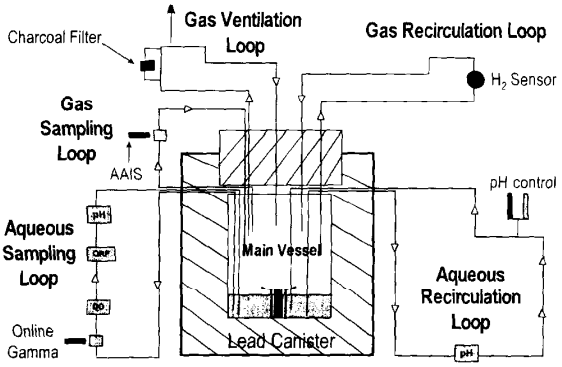

Fig. 1. Schematic diagram of the RTF.

III.A. Iodine Volatility in Organic-Painted Vessels

The RTF tests show that with no pH control, iodine volatility is higher in the presence of organic-painted surfaces than in the presence of inorganic surfaces only.[7,8,11-14] As an example, the gas phase iodine concentration observed in an RTF test performed in a zinc-primed vinyl-painted carbon-steel-lined vessel in the presence of radiation is compared with that of a zinc-primed carbon-steel-lined vessel in Fig. 2. The iodine volatility observed in the vinyl-painted vessel was about three orders of magnitude higher than that observed in the zinc-primed vessel. The RTF tests performed in polyurethane- and epoxy-painted vessels have shown iodine volatility similar to that observed in the vinyl test (Fig. 3). For these tests, the vessel coatings were typically cured in dry air for ~3 months prior to the tests. The constituents of the vinyl, epoxy, polyurethane, and zinc primer paints are shown in Table I.

III.B. Effect of Organic Surface Coatings on pH and Dissolved Oxygen

As discussed in Sec. II, iodine volatility depends on the reduction rate of volatile I_2 to nonvolatile I^- by water radiolysis products, H_2O_2 and O_2^- [reactions (5) and (6)], and also on the hydrolysis rate of I_2 [reaction (4)]. The rates of these iodine reactions strongly depend on pH, causing a pH dependence of iodine volatility that ranges from a $1/[H^+]$ dependence at high-pH values to a $1/[H^+]^2$ dependence at low-pH values.[5,6] The RTF tests in organic-painted vessels have shown that in the absence of pH control, aqueous pH decreased in the presence of radiation, which decreases the iodine reduction rates, thus increasing the iodine concentration in the gas phase. Figure 3 shows both the total gas-phase iodine concentration and the solution pH as a function of time during the tests in organic-painted vessels. The increases in the gas-phase iodine concentration are closely related to decreases in pH.

To confirm the relationship between iodine volatility and pH, an RTF test was performed in a vinyl-painted vessel in which the pH was held at 10 throughout by periodic additions of LiOH. The gas phase iodine concentration observed in this test was initially about two orders of magnitude lower than that observed when the pH was not fixed (Fig. 4). The test in a vinyl-painted vessel with fixed pH still yielded a higher gas phase iodine concentration than the test performed in a zinc-primed vessel with fixed pH. This difference is attributed in part to considerable adsorption of I^- on the zinc coating in contact with the aqueous phase. Posttest examination found ~80% of the initial iodine was adsorbed on the zinc surfaces in contact with the aqueous phase.[11]

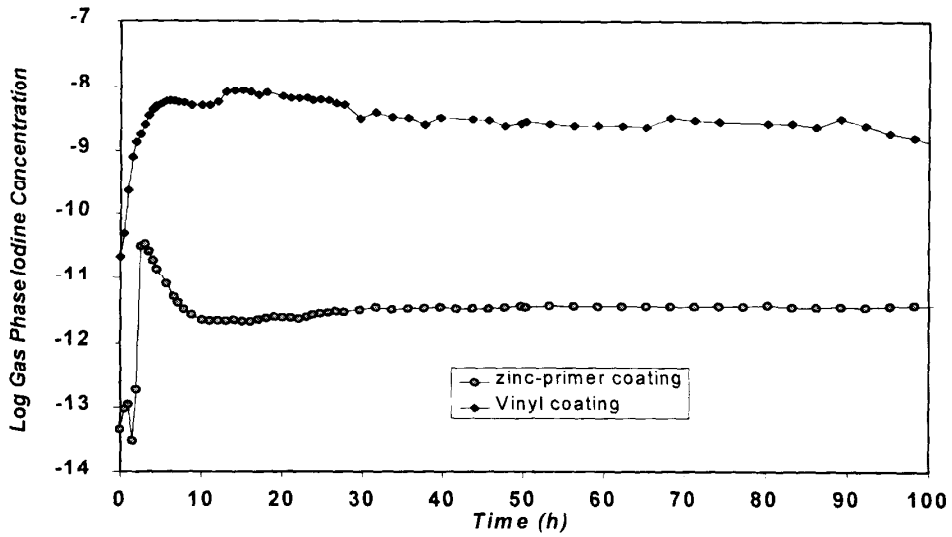

Fig. 2. Effect of surface coating on iodine volatility in the RTF. The tests were performed in the presence of radiation at an absorbed dose rate of ~1.5 kGy·h^{-1}, with an initial pH of 10. The pH of the water was not controlled during the tests.

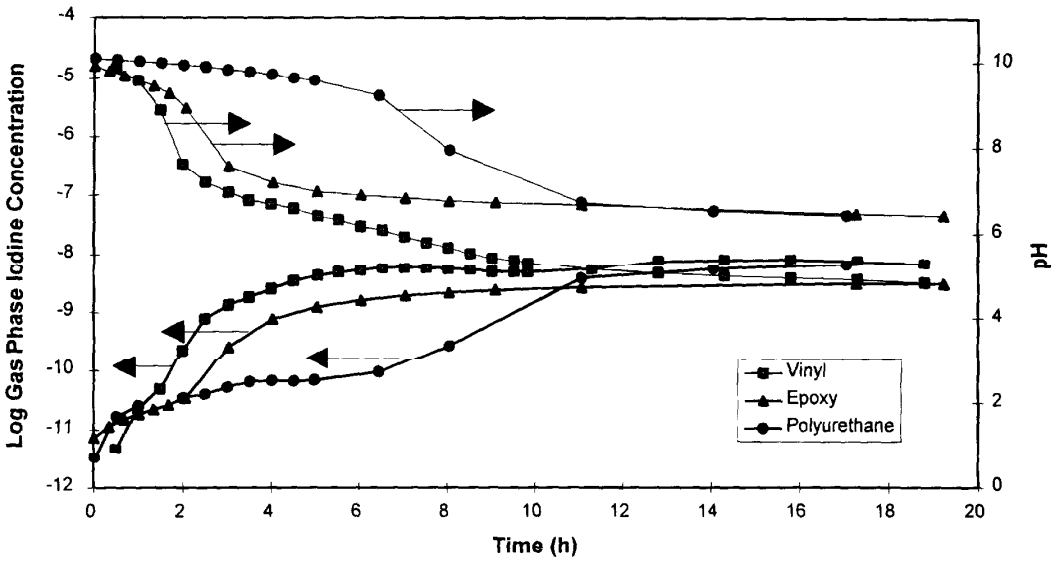

Fig. 3. Effect of organic-painted surfaces on pH and gas phase iodine concentration in the RTF. The tests were performed in the presence of radiation at an absorbed dose rate of ~1.5 kGy·h^{-1}, with an initial pH of 10.

Early modeling studies suggested that the radiolytic formation of nitric acid in air could lead to the low pH observed in some of these experiments.[10] This can be ruled out as the main cause of the pH decrease observed in intermediate-scale studies, however, because the pH decrease was not observed in the absence of an organic coating (e.g., bare stainless steel). Radiolytic formation of HCl can also be excluded as a potential cause for pH reduction with vinyl paint. The rate of HCl production is calculated to be small, based on the known rate of HCl production from the vinyl acetate and vinyl chloride copolymer used as a coating.[10] The most likely cause of the

TABLE I

Constituents of Zinc Primer, Vinyl, Epoxy, and Polyurethane Paints as Applied*

International Intervinux VM HB Vinyl Paint		Carboline Carbozinc 11 Zinc Primer	
Ingredients[a]	wt%	Ingredients	wt%
Methyl ethyl ketone	15 to 40	Part A (base)[b]	
Ethyl 3-ethoxy propionate	10 to 30	Ethanol	30
Tricresyl phosphate	3 to 7	Isopropanol	20
Xylene	1 to 5	Silica	15
Methyl isobutyl ketone	1 to 5	2-butoxy ethanol	10
Silica amorphous	1 to 5	Aluminum silicate	10
Ferric/ferrous oxide	1 to 5	Ethyl silicate	10
		Methanol	10
Thinner		Pigment	5
Methyl isobutyl ketone	30 to 60	Methyl silicate	5
Toluene	30 to 60	Mica	5
		Water	4.4
		Part B (zinc filler)[b]	
		Zinc dust	97
		Zinc oxide dust	3
		Thinner 21	
		Isopropanol	100
		Thinner 26	
		1-methoxy-2-propanol	>1
		2-ethoxy butanol	>1
Ameron Amercoat 66 Epoxy Paint		**Normac NR-5S Polyurethane Paint**	
Ingredients	wt%	Ingredients	wt%
Part A (cure)[c]		Part A[d]	
Polyamide resin	<75	Polyether polyol	42 to 60
Xylene	<30	Methylene bis-(4-Cyclohexylisocyanate)	2.1 to 3.6
Triethylene tetramine	<5	1,1,1-trichloroethane	35 to 55
Part B (resin)[c]			
Epoxy resin	<25	Part B[d]	
Methyl isobutyl ketone	<10	Dihydro-2(3H)-furanone	35 to 60
Xylene	<10	4-4′-methylene dianiline	42 to 50
Methyl n-amy ketone	<10		
2-butoxyethanol	<5	Thinner	
Talc	<40	1,1,1-trichloroethane	96.5
Titanium dioxide	<10	Diethylene ether	2.5
Iron oxide	<10	1,2-butylene oxide	0.5
		Nitromethane	0.3
Amercoat 7 (thinner)	No data provided		

*Paint compositions provided by manufacturers.
[a]Only hazardous materials are listed. Paint is up to 30% solids (vinyl-chloride, vinyl-acetate copolymer) by volume.
[b]One gallon part A (base) mixed with 8 kg (zinc filler). Thinner added as required.
[c]One part A (cure) mixed with 4 parts B (resin). Thinner added as required.
[d]One part A mixed with 0.15 parts B. Thinner added as required.

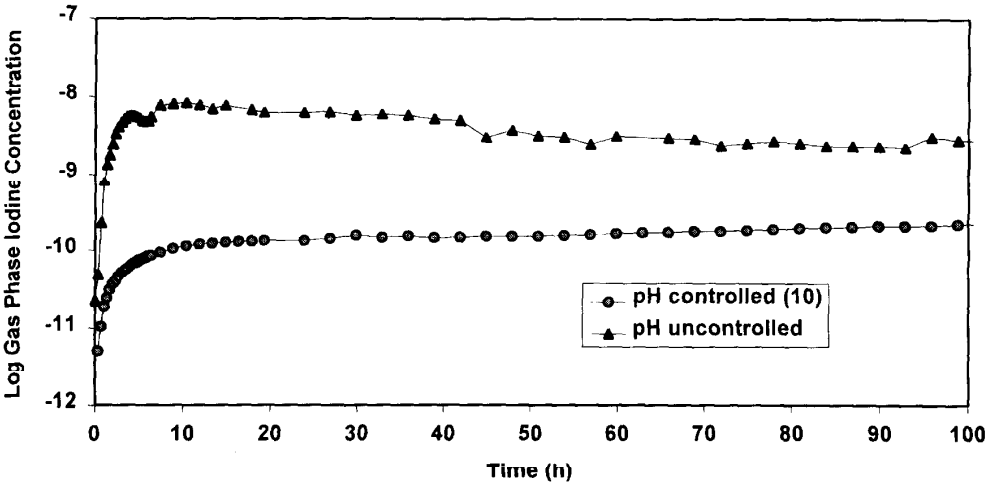

Fig. 4. Effect of pH control on gas phase iodine concentration in the RTF tests performed in vinyl-painted vessels. These tests were performed in the presence of radiation at an absorbed dose rate of ~1.5 kGy·h^{-1}, with an initial pH of 10.

pH decrease in painted vessels is the radiolytic oxidation of organic impurities in the aqueous phase. This assumption has been tested by adding methyl ethyl ketone (MEK) to the aqueous phase during a test performed in a zinc-primed carbon steel vessel (Fig. 5). The addition of MEK resulted in a rapid decrease in pH and dissolved oxygen concentration. Based on our bench-scale studies on the radiolytic decomposition of MEK and methyl isobutyl ketone (MIBK) (see Sec. IV), this can be rationalized by a radiolytic degradation of MEK via reactions (7) and (8).

The idea that surfaces painted with organic coatings in contact with water are a source of organic impurities was further supported by the observed organic

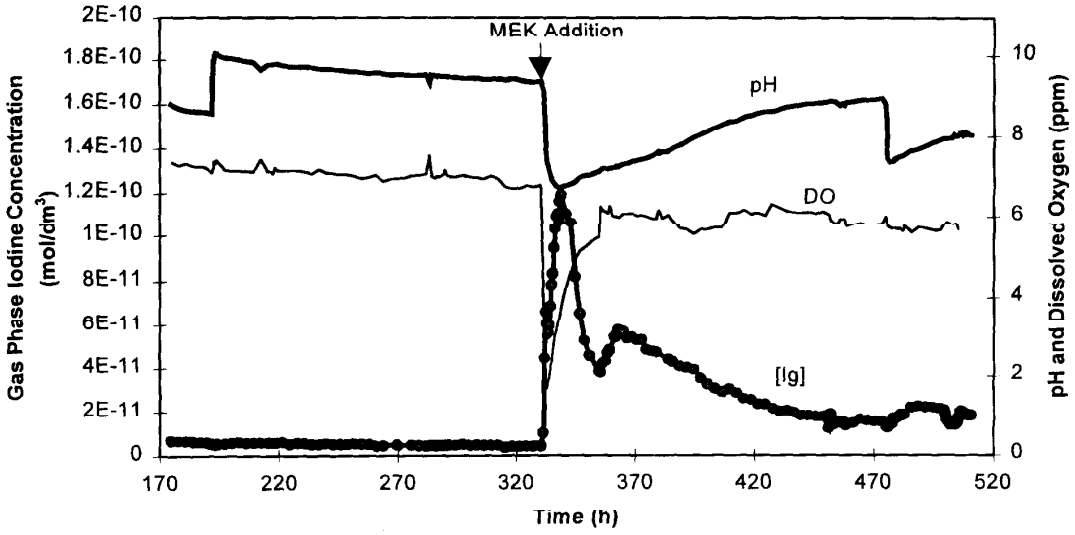

Fig. 5. Effect of MEK addition on pH, dissolved oxygen (DO) concentration, and airborne iodine concentration ([Ig]) in an RTF test performed in a zinc-primed vessel. The test was performed in the presence of radiation at an absorbed dose rate of 1.8 kGy·h^{-1}.

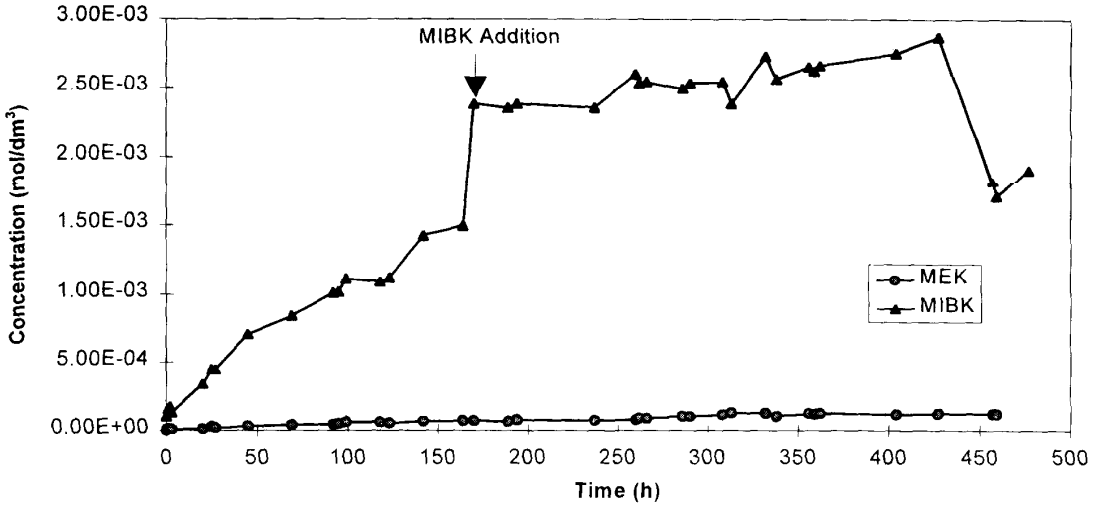

Fig. 6. Aqueous phase concentration of MIBK and MEK in RTF tests performed in a vinyl-painted concrete-lined vessel in the absence of radiation. No measurable amounts of these organic compounds were present in a radiation field. The sudden increase in the MIBK concentration at ~170 h was due to a deliberate injection of 1.0×10^{-3} mol·dm^{-3} MIBK into the aqueous phase.

concentrations in RTF tests that had been performed in organic painted vessels without radiation. Concentrations of $\approx 1 \times 10^{-3}$ mol·dm^{-3} for MIBK, the major constituent of some paint thinners, and $\approx 1 \times 10^{-6}$ mol·dm^{-3} for MEK, toluene, and xylene, other major components of paint solvents and thinners, have been observed in the aqueous phase in these experiments (Figs. 6 and 7). These organic compounds were not found at similar concentration levels in irradiated solutions in contact with the same surfaces because the organic dissolution rates from the painted surfaces into the aqueous phase is slower than their subsequent radiolytic decomposition rates, at least

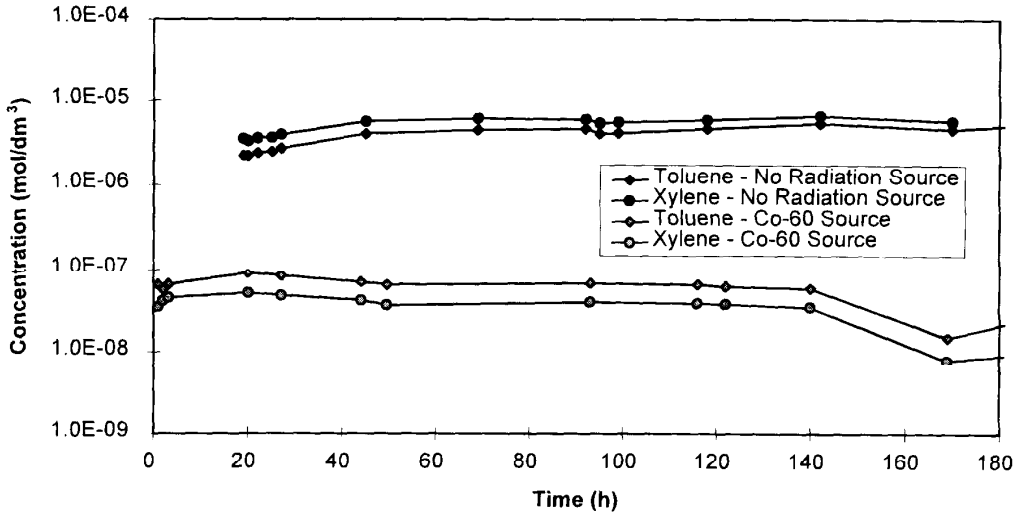

Fig. 7. Gas-phase concentrations of aromatics during RTF tests performed in vinyl-painted concrete-lined vessels with and without radiation.

at 25°C. The relative rates of radiolytic decomposition versus dissolution can be estimated from a comparison of data from two RTF experiments. In the test shown in Fig. 5, an immediate decrease in pH and dissolved oxygen concentration (accompanying the decomposition of MEK) was observed when 1×10^{-3} mol·dm^{-3} MEK was intentionally added to an irradiated solution of CsI. Recovery of the dissolved oxygen concentration, which implies that radiolytic degradation to acids and CO_2 is essentially complete, requires only ~20 h. In contrast, dissolution of MIBK from vinyl paint to reach concentrations of 1×10^{-3} mol·dm^{-3} in the same water volume required almost 100 h (Fig. 6). The relative rates of radiolytic decomposition versus dissolution have been confirmed by bench-scale studies that are discussed in Sec. IV.

The different pH versus time profiles observed in RTF tests performed with different organic coatings (Fig. 3) could potentially result from differences in one of the following:

1. the type of organic species released
2. the aqueous dissolution rates
3. the radiolytic decomposition rates of the organic species.

It has been shown that the major organic solvents released from organic-coated surfaces tested in the bench-scale studies (e.g., MIBK and xylene from vinyl-painted coupons, and heptanone and xylene from epoxy-painted coupons) rapidly decompose to form acidic compounds (e.g., acetic acid and CO_2) in the presence of radiation. These acidic species may be formed in different quantities and by different routes for each type of organic species (e.g., aliphatic versus aromatic compounds). Furthermore, these species influence pH through their buffer capacities, resulting in different pH profiles. Nevertheless, the organic dissolution rate is the first factor that determines the rate of decrease in the aqueous pH.

The pH decreases observed in RTF studies are not generally a linear function of time because the change in pH not only reflects the organic dissolution rate, which determines the acid production rate, but also depends on buffering by dissolved CO_2 produced by radiolysis of organic species. The buffering capacity of the $H_2CO_3/HCO_3^-/CO_3^{2-}$ system decreases considerably at pH values below 9.5, reaches a minimum at pH ~8, and increases again with another maximum at pH 6.37 (Ref. 31). Thus, the decrease in the buffering capacity below pH 9.5 causes the sudden drop in pH observed in the experiment. The final pH values observed with the epoxy- and polyurethane-painted vessels coincide with another buffering zone of the carbonate system (near pH 6.3). The final pH for the vinyl RTF experiment was much lower, 4.8, probably because of the considerably higher release of organics from the vinyl-painted surface than from other organic surfaces, which allowed for significant accumulation of acetic acid ($pK_a = 4.75$).

III.C. Effect of Organic Surface Coatings on Organic Iodide Formation

Although there is still controversy over what the major organic iodide formation mechanisms in postaccident containment will be,[22-28] it is generally accepted that homogeneous gas phase reactions are not likely be a major contributor because concentrations of the requisite radical (R•) and I_2 are relatively low.[25-28] Heterogeneous reactions to form organic iodides would depend on the formation of the precursor organic radicals via the radiolytic decomposition of the polymers that form the bulk of the organic coating. Organic radicals thus formed, however, are likely to remain bound to the surface and are subject to rapid recombination, a phenomenon responsible for cross-linking of polymers.[32] The steady-state concentration of surface radicals available for reaction with I_2 will therefore likely be low. Reactions of I_2 with coating solvent or impurity compounds on surfaces is possible; however, irreversible (i.e., chemically bound) iodine adsorption on organic paints or metal surfaces in the aqueous phase is usually observed to be small[a] (see also Table II).[a] Because of the presence of organic compounds at relatively high concentrations in the aqueous phase and a higher I_2 concentration in the aqueous phase than in the gas phase or on surfaces, our studies on organic iodide formation have mainly focused on the formation and decomposition of organic iodides in the aqueous phase. It has not been resolved unequivocally whether heterogeneous or homogeneous aqueous phase reactions are the main mechanism for organic iodide formation; however, the foregoing argument and our dissolution studies (see Sec. IV.C) and RTF tests strongly suggest the latter.

Intermediate-scale studies (see Figs. 8 and 9) have demonstrated that irradiated CsI solutions in contact with painted surfaces produce organic iodides whose concentration profiles closely followed that of I_2. Figure 9 also shows that when MEK was added into the aqueous phase, the increase in gas phase CH_3I concentration closely followed that of the total gas phase iodine concentration. This data indicates that the organic iodides (including CH_3I) are formed by the reaction of I_2 with organic compounds in the aqueous phase and that these reactions are relatively fast. Various ketone, alcohol, and alkyl radicals formed by the radiolysis of MIBK and MEK would easily react with I_2 [reactions (7) and (8)], methyl iodide being one of the products. Aromatic organic iodides can

[a]An exception is zinc primer, in which adsorption occurs primarily through the interaction of iodide with the zinc surface, and certain types of epoxy paints, in which molecular iodine and organic iodides can react with amines on the epoxy surface.[33]

TABLE II

Effect of Surfaces on Iodine Volatility*

Radiation Field	Vessel Surface	Maximum Gas Phase Iodine Concentration ($mol \cdot dm^{-3}$)	Iodine Lost to Surface (%)	Predominant Loading Surface
Yes	Vinyl	8×10^{-9}	78	Gas
No	Vinyl	4×10^{-11}	12	Aqueous
Yes	Polyurethane	3×10^{-9}	92	Gas
Yes	Epoxy	7×10^{-9}	87	Gas
Yes	Vinyl (at pH 10)	2×10^{-10}	5	Gas
Yes	Stainless steel	6×10^{-10}	86	Gas
No	Zinc primer	1×10^{-10}	82	Aqueous
Yes	Zinc primer	3×10^{-10}	79	Aqueous
Yes	Concrete	1×10^{-12}	45	Gas
No	Concrete	3×10^{-12}	12	Aqueous

*The surface areas in contact with the gas and aqueous phases (220 and 52 dm^2, respectively) and the gas-aqueous interfacial area (37 dm^2) and the gas and aqueous volumes (315 and 25 dm^3, respectively) were the same for all the tests.

be formed by thermal and radiolytic reactions of I_2 with phenol derivatives,[15,16] before they decompose further by radiation. Phenols are formed in significant quantities during the radiolysis of aromatic solvents such as xylene and toluene.

Early studies on organic iodide formation focused mainly on CH_3I because of its high volatility and because methane or other small alkanes were believed to be the major organic impurities in the containment atmosphere following an accident. However, RTF tests performed in organic-painted vessels have found that a large portion of the organic iodides formed from containment paint impurities are less volatile than CH_3I. Figure 8 shows iodine speciation measurements obtained in an RTF test performed with a vinyl-painted vessel. In later stages of the test, the concentration of organic iodides in the gas phase was orders of magnitude lower than that observed in the aqueous phase. If CH_3I were the predominant organic iodide, the gas phase concentration would be expected to be only three times less than the aqueous phase.

Comparison of the gas and the aqueous phase specifications in this and several other RTF tests indicates that the majority of organic iodides formed in the aqueous phase are somewhat less volatile than I_2 and much less volatile than CH_3I. Formation of these species, which are probably highly soluble iodo-ketones, alcohols, phenols, and acids, can thus reduce iodine volatility by reducing the molecular iodine concentration in the aqueous phase. Some of these organic iodides also hydrolyze more rapidly than I_2, essentially acting as catalysts for reducing I_2 to I^-. Bench-scale studies on the hydrolysis and the aqueous gas phase partitioning of these organic compounds as a function of temperature are discussed in detail in Sec. IV.D.

IV. BENCH-SCALE STUDIES

The main objectives of the intermediate-scale RTF studies are to estimate the "all effects" behavior of iodine and to identify unforeseen phenomena. Bench-scale studies were conducted, in parallel with the RTF program, to determine the separate effects of various parameters or processes on iodine volatility and to evaluate the role and importance of phenomena identified in the intermediate-scale studies. These bench-scale studies included measurements of

1. the radiolysis of organic compounds
2. the formation and hydrolysis of organic iodides in the aqueous phase
3. the dissolution of organic solvents from painted surfaces into the aqueous phase
4. hydrolysis rates and partition coefficients of various organic iodides
5. iodine deposition on painted surfaces from the gas phase.

IV.A. Radiolytic Decomposition of Organic Compounds

The radiolytic decomposition of the common paint solvents MEK, MIBK, and toluene in the aqueous phase has been studied as a function of radiation dose, initial organic concentration, and initial pH. Detailed studies were conducted primarily using MEK (Refs. 18 through 21). MEK was chosen as a model organic compound because it is a common solvent. It also has many of the characteristics of common organic species found in containment paints (i.e., a small, volatile, aliphatic ketone,

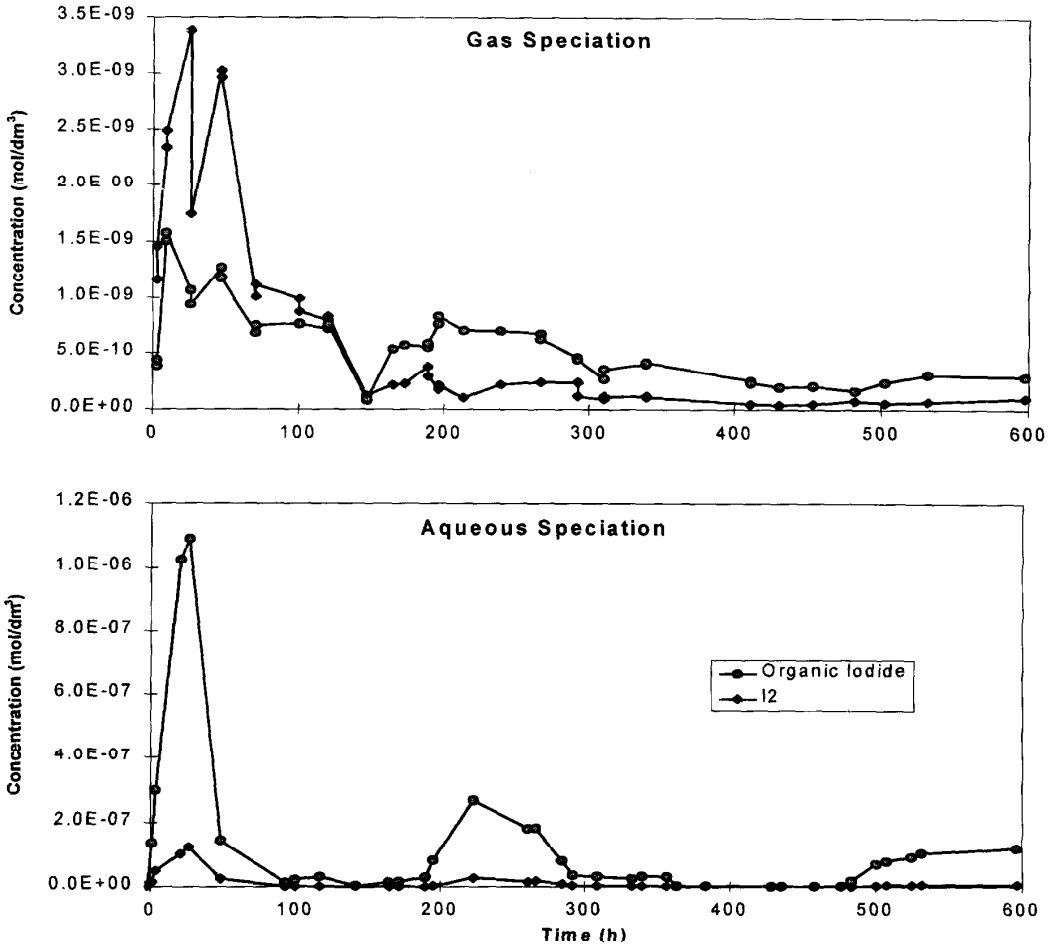

Fig. 8. Aqueous and gas phase iodine speciation in an RTF test performed in a vinyl-painted vessel.

which is comparable to acetone, heptanone, and MIBK). Furthermore, its relatively simple structure allows better quantitative analysis of thermal and radiolytic degradation processes.

In this work, aqueous solutions containing 1×10^{-3} mol·dm^{-3} MEK were gamma-irradiated to a desired absorbed dose up to 13 kGy at a dose rate of ~0.4 kGy·h^{-1} (or 0.12 Gy·s^{-1}), 25°C, and initial pH 10. The concentration used in this study is of the order of the overall organic solvent level expected to be leached into the sump from painted containment surfaces in an accident; this is based on the organic solvent level that has also been observed in both bench-scale studies (Sec. IV.C) and the intermediate-scale studies in the RTF (Sec. III), as a result of organic dissolution from painted surfaces. The decay of MEK and the formation of the MEK decomposition products were followed by various analytical methods to establish decay and formation profiles. This includes high-performance liquid chromatography, gas chromatography, gas chromatography with mass selective detection, and mass spectrometry. Experiments were conducted in air-, argon-, or nitrous oxide-purged aqueous solutions. Nitrous oxide rapidly converts solvated electrons to hydroxyl radicals and is commonly added to isolate the effect of hydroxyl radicals. In some experiments, *tert*-butanol, a hydroxyl radical scavenger, was added to argon-purged solutions to isolate the reactions of solvated electrons. However, the main focus of the work was on aerated solutions. In the tests with aerated solutions, the change in pH (from a starting pH of 10) that resulted from the MEK radiolytic decomposition was also measured. The results of this experimental study, which are summarized in the following discussion, have been reported in detail.[18,19]

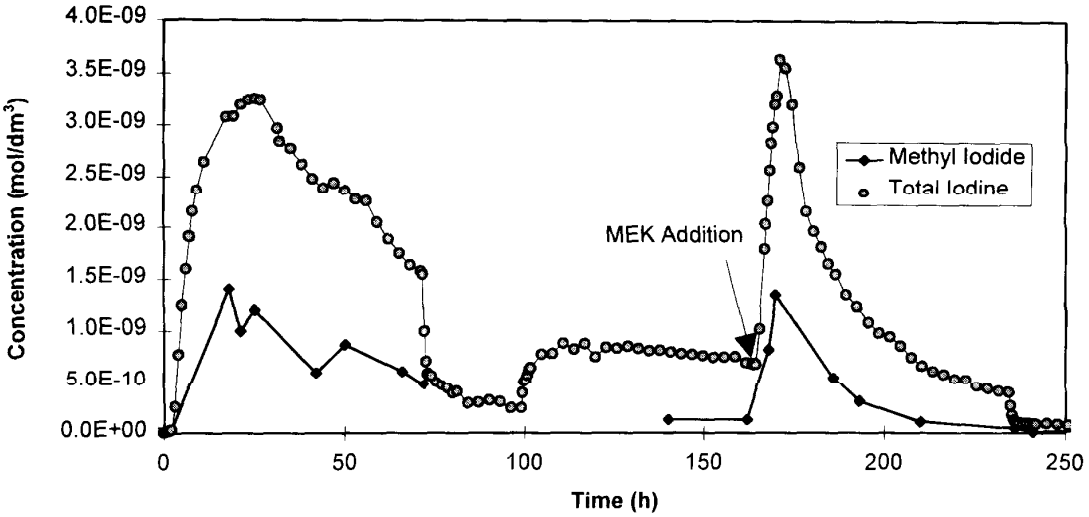

Fig. 9. Effect of organic addition to the aqueous phase on the gas phase iodine concentration and speciation in an RTF test performed in an epoxy primed, polyurethane-painted carbon steel vessel.

The rates observed for the initial loss of MEK were close to the rate of •OH production by gamma radiolysis of water (with and without nitrous oxide present), suggesting that the dominant reaction is •OH with MEK. Furthermore, when •OH was removed from the aqueous solutions, as in the case of *tert*-butanol solutions, MEK was found to decay at a slower rate.

The initial step in MEK degradation is the hydrogen abstraction from MEK by •OH, which forms the MEK radical, MEK•. In the absence of oxygen, the main decay path of the MEK radical is dimerization, to form compounds such as 3,4-dimethyl-2,5-hexanedione.

In the presence of oxygen, MEK• reacts primarily with oxygen to form MEK peroxyl radical, MEK-O_2•. The peroxyl radical then dimerizes to form a tetroxide intermediate, which decomposes to form the observed intermediate products, 3-hydroxy-2-butanone, 2,3-butanedione, acetaldehyde, formaldehyde, acetic acid, and formic acid. The concentrations of these products were followed as a function of time, except for 2,3-butanedione, as solubility problems were encountered during its analysis. The formation of organic acids, and eventually the formation of CO_2, reduces the pH of the solutions.

Based on the experimental results, a detailed reaction kinetic model for the steady-state gamma radiolysis of aerated aqueous solutions containing MEK has been developed. This full model reproduces the experimental data reasonably well. However, MEK is only one of the organic impurities expected to be found in the sump following an accident, and a more generally applicable model would be useful. Furthermore, it consists of more than 150 reactions and, thus, is not practical to be incorporated into LIRIC (Refs. 6, 10, and 13) or into a safety analysis code. Therefore, a simplified model, which is still based on the mechanistic understanding gained from the full model, was developed. The simplified model, consisting of only six reactions and five equilibria (Table III), reproduces the experimental data well. A few examples of the simulation results using the models are shown in Figs. 10 through 13. The predictions of the full and simplified models showed good agreement with the experimental data observed for pH evolution and MEK degradation, as well as product formation and decay. The model has been reported in detail in Ref. 20.

The simplified model has shown that the radiolytic decomposition of MEK in aerated aqueous solutions can be approximated as follows. The four-carbon containing organic species, MEK, initially reacts with the water radiolysis product, •OH and O_2, to form oxidized four-carbon

TABLE III

Reactions in the Simplified MEK Radiolysis Model

MEK $\rightarrow$ 2,3-butanedione
MEK $\rightarrow$ 3-hydroxy-2-butanone
2,3-butanedione $\rightarrow$ acetaldehyde + acetic acid
3-hydroxy-2-butanone $\rightarrow$ acetaldehyde + acetic acid
Acetaldehyde $\rightarrow 2\ CO_2$
Acetic acid $\rightarrow 2\ CO_2$
Acetic acid $\leftrightarrow$ acetate + H^+
$CO_2 + OH^- \leftrightarrow HCO_3^-$
$CO_2 + H_2O \leftrightarrow H_2CO_3$
$H_2CO_3 \leftrightarrow HCO_3^- + H^+$
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$

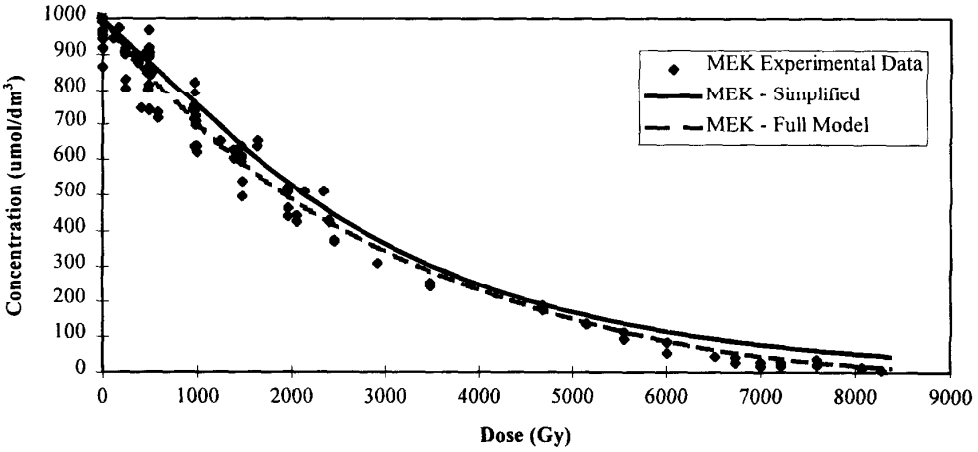

Fig. 10. Dose profile of MEK: experimental data (♦), full-model prediction (- - - - -), and simplified model prediction (——).

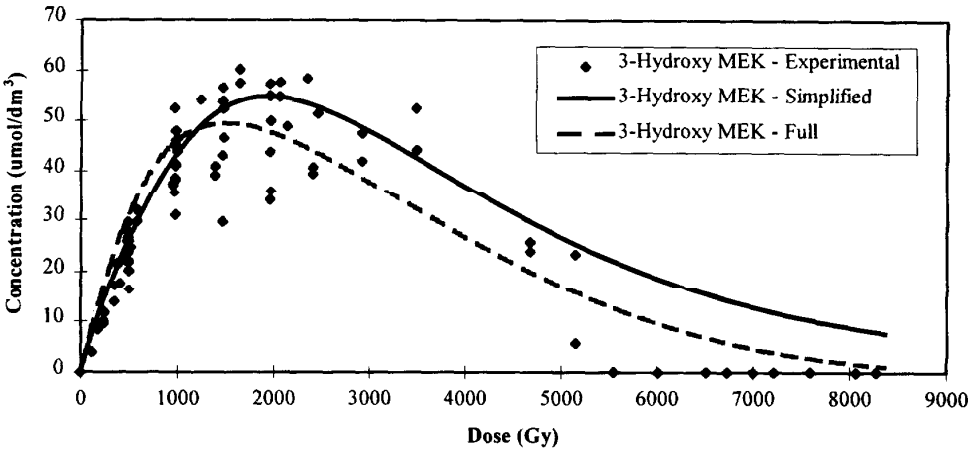

Fig. 11. Dose profile of 3-hydroxy-2-butanone: experimental data (♦), full-model prediction (- - - - -), and simplified model prediction (——).

species, 3-hydroxy-2-butanone and 2,3-butanedione, which continue to decompose to two-carbon-containing organic species, acetaldehyde and acetic acid, and then to one-carbon species, CO_2:

MEK (4-carbon species) to oxidized 4-C (carbon) species by •OH

⇓

Oxidized 4-C species to 2-C species by •OH

⇓

2-C species to CO_2 by •OH .

It may be premature to generalize the simplified reaction scheme to other organic compounds. However, it is reasonable to assume, for example, that five-carbon-containing organic compounds such as MIBK, another common organic solvent, would progress to oxidized five-carbon species, to three-carbon- and two-carbon-containing organic species, to 2-C organic species and 1-C organic species, to eventually all CO_2. Measurements of MIBK concentration and pH as a function of time, without extensive measurements of intermediate products, may be sufficient to extract necessary kinetic information for MIBK. Further generalization may be possible once the relationship between the type of organic species (i.e., number of carbons and functional

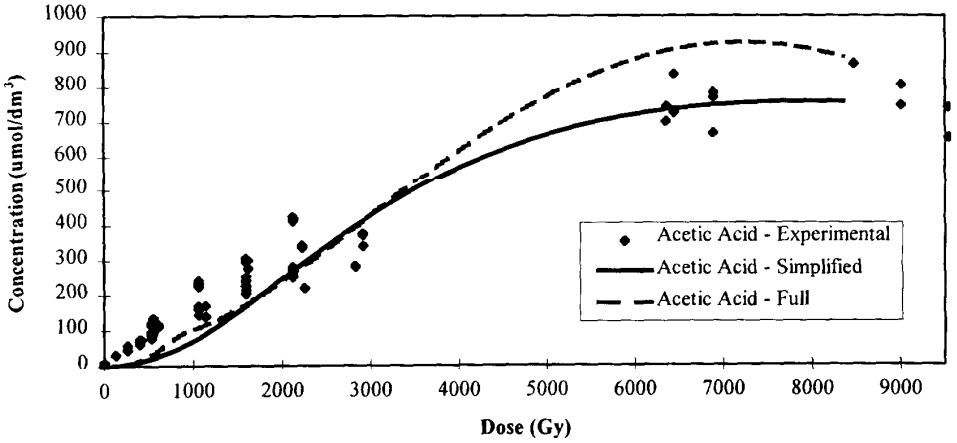

Fig. 12. Dose profile of acetic acid: experimental data (♦), full-model prediction (-----), and simplified model prediction (——).

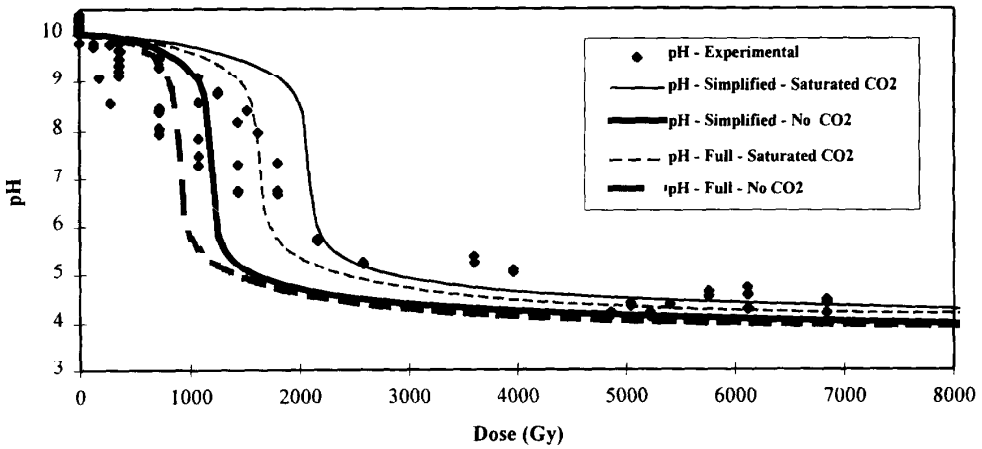

Fig. 13. Dose profile of pH: experimental data (♦), full-model prediction for solution initially saturated with CO_2 (——) and without CO_2 (▬▬), and simplified model prediction for solution initially saturated with CO_2 (-----) and without CO_2 (▬ ▬ ▬).

group) and the rate constant for its reaction with •OH is established. Work on other organic compounds is in progress.

The MEK decay and the pH change as a function of dose (Figs. 10 and 13) suggested that, at gamma-radiation dose rates of 10 and 1 $kGy \cdot h^{-1}$, which are within the range of dose rates expected in containment following an accident, 90% of 1×10^{-3} $mol \cdot dm^{-3}$ MEK would be decomposed within 20 min and 4 h, respectively, by which time the pH would drop to below 5. At low temperatures, the decomposition rate is faster than the rate of the release of organic solvents from painted surfaces (see Sec. III.E and Refs. 17 through 20). This supports our conclusion that the dissolution of organic solvents may be the key rate controlling process for the pH change and organic iodide formation from the reaction of organic radicals with I_2 expected in an accident.[7]

IV.B. Organic Iodide Formation

As stated previously, most of the early research on organic iodide formation in containment focused on the radiolytic production of CH_2I from CH_4 and I_2, because of the high volatility of CH_3I and the lack of information on the type of organic impurities expected in the containment sump. However, more recently, various RTF tests

indicate that although volatile low-molecular-weight organic iodides, such as CH_3I, may comprise a large fraction of the gaseous iodine concentration, overall iodine volatility is mainly affected by processes occurring in the aqueous phase. During the course of the radiolytic decomposition of the organic impurities, various organic radicals are formed, which react readily with I_2 to form various organic iodides. Ketones and phenols also react thermally with I_2 to form soluble organic iodides.

Organic iodide formation from MIBK, MEK, and aromatic compounds in aqueous solutions containing I^- in the presence of radiation is being studied. The yields of organic iodides are measured using radioactive tracer techniques (^{131}I labeled I^-), and production rates are being determined as a function of organic and I^- concentrations, radiation dose, pH, and temperature. Because this study is still in a preliminary stage, this work is not discussed in detail here. However, preliminary results show that at a given pH, iodine volatility initially decreases in the presence of phenols, which are the radiolytic products of aromatic solvents such as xylene and toluene.[16] Preliminary results from MEK studies also show that methyl iodide is formed by a reaction with iodine (I_2) and a methyl radical produced by the radiolysis of organic solvents.

IV.C. Dissolution of Organic Solvents from Painted Surfaces into the Aqueous Phase

The dissolution of organic solvents from painted surfaces into the aqueous phase was studied to determine the time-dependent behavior of pH, dissolved oxygen, and organic iodide concentrations under accident conditions. The rate of release of organic constituents from carbon steel coupons coated with zinc-primed vinyl, zinc-primed polyurethane, and epoxy in the absence of a radiation source over the temperature range 25 to 90°C was studied. This work has been described in detail elsewhere[17]; consequently, only a summary of results is presented here.

Both aliphatic and aromatic organic compounds (paint solvents) were released from the painted surfaces in the absence of radiation. Figure 14 shows the organic compounds detected in the gas phase from immersed vinyl coupons that were previously aged in air for ~2 months at 40°C. The major component of the thinner present in this paint was MIBK, as determined by both gas and aqueous phase analysis. Smaller quantities of toluene, xylene, MEK, and acetone were observed. At the end of a dissolution experiment at 90°C, the whole coupon surface was covered with blisters, 1 to 2 mm in diameter, and the carbon steel was exposed on the edges. Peeling of the vinyl polymer was also observed, revealing yellow discoloration underneath. Ethanol and 2-propanol, the major solvent constituents of the zinc primer base undercoating, were also often observed in solution.

The kinetics of the MIBK dissolution was derived based on the following simple mechanism:

$$\mathrm{MIBK}(ab) \rightarrow \mathrm{MIBK}(aq) \tag{17}$$

$$\mathrm{MIBK}(aq) \leftrightarrow \mathrm{MIBK}(g) \ . \tag{18}$$

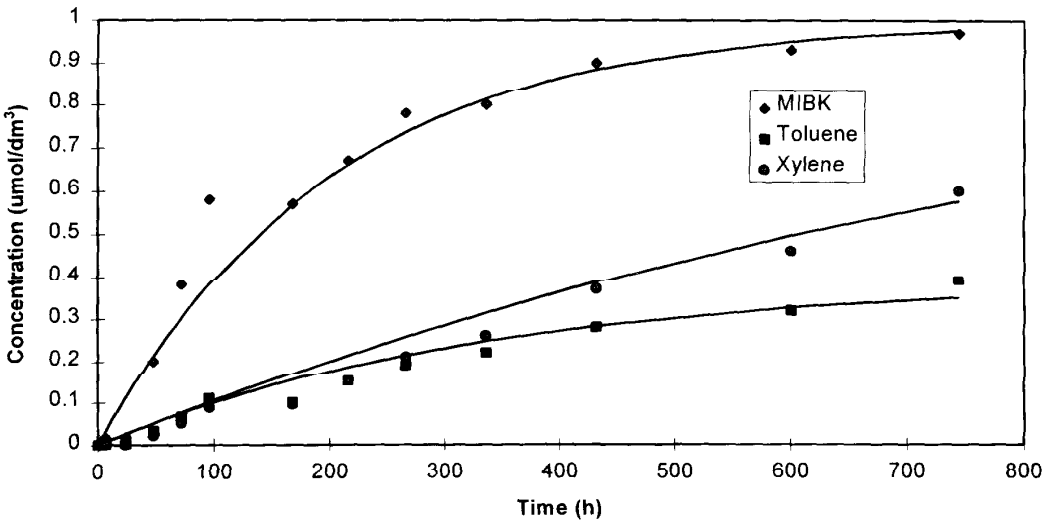

Fig. 14. Organic compounds detected by gas chromatography in the dissolution test with vinyl coupons at 40°C. The curves were fitted to the data using Eq. (19) in the text.

Assuming a fast equilibrium for reaction (18) leads to the following equation for the concentration of MIBK in solution:

$$[\mathrm{MIBK}(aq)]_t = \frac{1}{1 + (V_g/V_{aq})\cdot(1/H)} \cdot \frac{A_{aq}}{V_{aq}} \times [\mathrm{MIBK}(ab)]_o \cdot [1 - \exp(-kt)] \ , \tag{19}$$

where aq, ab, and g in the brackets and subscripts represent aqueous, absorbed, and gas phase, respectively; H is the partition coefficient of MIBK; V is volume; A is surface area; k is the dissolution rate constant (s^{-1}); and $[\mathrm{MIBK}(ab)]_o$ is the MIBK concentration present in the paint polymer phase at the start of dissolution that determines the total amount of MIBK released.

Simulation calculations using Eq. (18) reproduce experimental results very well (as shown in Figs. 15 and 16), indicating that the simple mechanism adequately describes the organic solvent dissolution process. Figures 15 and 16 use the same data except that in Fig. 16 the data at each temperature are normalized to the final MIBK concentration, which is determined by $[\mathrm{MIBK}(ab)]_o$. The dissolution parameters, $[\mathrm{MIBK}(ab)]_o$ and k, were determined from best fits to the experimental data using Eq. (19). The dissolution kinetics of toluene and xylene could be represented in the same way, using the same rate constant k. Furthermore, dissolution of organic species from polyurethane and epoxy paints followed the same mechanism, with approximately the same dissolution rate constant.

The dissolution of organic compounds from vinyl-painted coupons was studied as a function of temperature, aging, pH, and radiation exposure. The dissolution rate constant was observed to depend strongly on temperature, showing an Arrhenius temperature dependence with an activation energy of 82 ± 11 $kJ\cdot mol^{-1}$ (Fig. 17).[b] The pH of the water did not have a significant impact on the dissolution process, and the maximum concentration of MIBK released into the aqueous phase was found to depend only on the age of the vinyl coating (Fig. 18). This implies that the initial MIBK concentration within the coating surface controls the maximum MIBK concentration in solution and that the MIBK content in the coating decreases with aging because of evaporative losses. For a painted surface area-to-aqueous volume of 5.25 cm^{-1}, as much as 2×10^{-3} $mol\cdot dm^{-3}$ MIBK was observed from relatively freshly (~2 months old) painted surfaces.

The effect of radiation on the rate of dissolution of the organic compounds was negligible, although radiation rapidly decomposed the organic compounds once they had been released into the aqueous phase. Release of MIBK from coupons in which dissolution followed a period of irradiation appeared to have the same rate constant, although the final concentrations of MIBK in solution were smaller. Solutions in contact with painted

[b]The activation energy was reported erroneously in the *Proceedings of the 4th Workshop on the Chemistry of Iodine in Reactor Safety*, sponsored by the Committee on the Safety of Nuclear Installations/Organization for Economic Cooperation and Development.

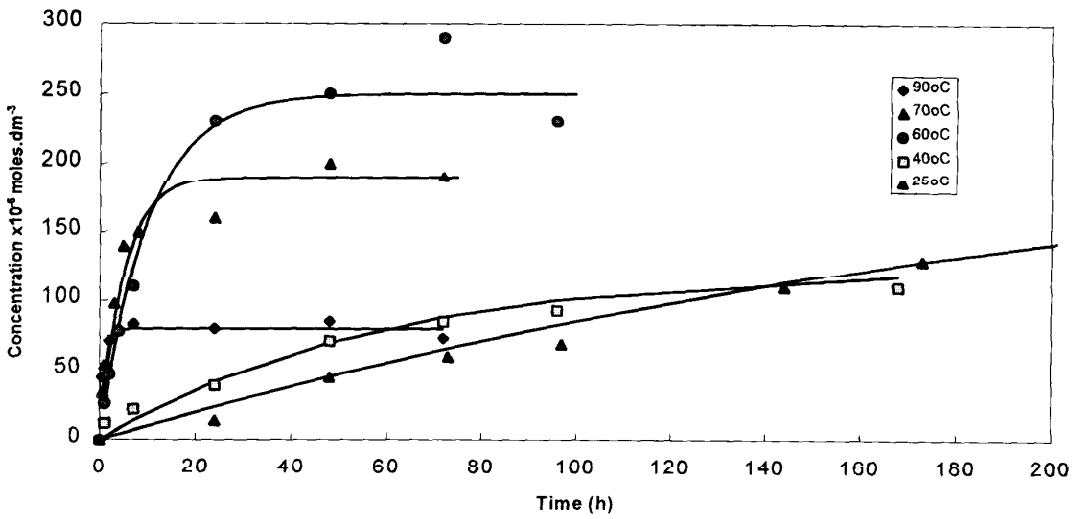

Fig. 15. Dissolution of MIBK from vinyl-painted coupons at pH 10 at various temperatures. The curves are fits to the data using Eq. (19) in the text.

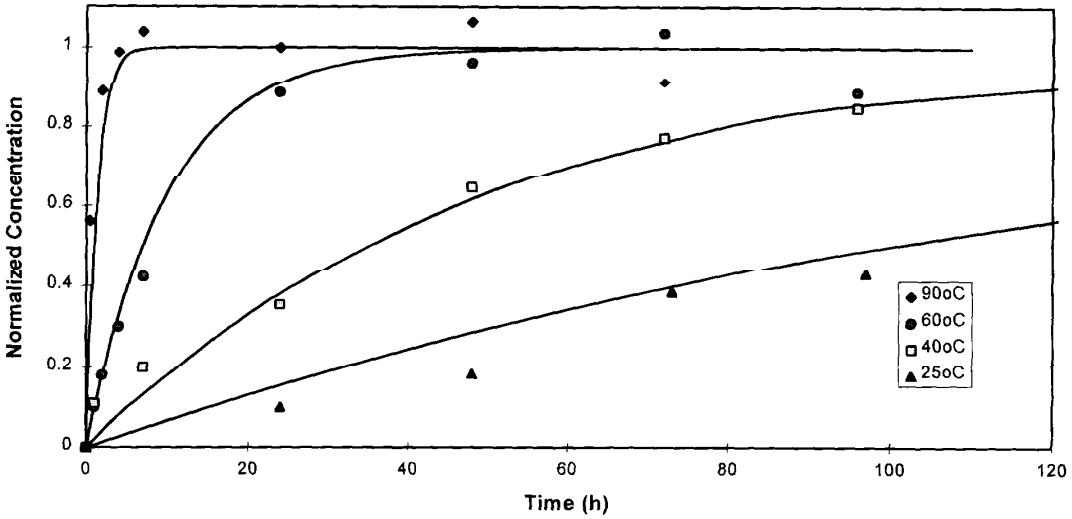

Fig. 16. Dissolution of MIBK from vinyl-painted coupons at pH 10 and at various temperatures. Compared with Fig. 10, the dissolution data at each temperature are normalized to the final MIBK concentration. The curves are fits to the normalized data using Eq. (19) in the text.

coupons that were irradiated subsequent to a dissolution period were found to yield increased gas phase concentrations of acetaldehyde, acetone, and MEK, and reduced concentrations of MIBK; the former three compounds were found to arise as a result of decomposition of dissolved MIBK. Toluene and xylene were not observed because the small amounts present decomposed to phenol derivatives (and to some extent to organic acids), which are nonvolatile and difficult to detect in the gas phase by conventional gas chromatography techniques.

From these observations, we concluded that irradiation (at the doses and dose rates used here) does *not* have a significant impact on the chemistry of the paint coating per se, although it decomposes the organic solvents that have been released to solution, affecting their concentrations observed in the aqueous and gas phases.

Dissolution studies, in combination with the study on the radiolysis of organic compounds and various RTF test results, show that (a) the radiolysis of organic compounds from paint coatings will occur primarily in the aqueous phase and not on the surface, and (b) under reactor accident conditions, the rates of radiolytic decomposition of organic compounds and formation of organic iodides are much faster than the rate of organic dissolution. The latter process appears to be the rate-determining step for the changes in pH, dissolved oxygen concentration, and organic iodide concentration, observed when solutions of CsI are irradiated in the presence of painted surfaces. Consequently, detailed kinetic mechanisms for the radiolytic decomposition of organic compounds and organic iodide formation may not be necessary.

IV.D. Hydrolysis and Aqueous-Gas Phase Partitioning of Organic Iodides

An additional component to the bench-scale studies are measurements of the hydrolysis rates and partition coefficients of organic iodides as a function of temperature. The hydrolysis rates and partition coefficients have been measured for iodomethane, iodoethane, 2-iodobutane, iodoacetic acid, iodoethanol, benzyl iodide, 2-iodophenol, and 2-iodo-2-methylpropane. These compounds were chosen to represent the range of structures of organic iodides that may be found in containment during a LOCA. This study has been published elsewhere.[21]

Organic iodides hydrolyze to give iodide and the corresponding alcohol:

$$RI + OH^-/(H_2O) \rightarrow ROH + I^- + (H^+) \ . \qquad (20)$$

In our studies the hydrolysis rate was determined by monitoring the evolution of I^- using a spectrophotometric method, in which the growth of the absorbance of I^- (ϵ = 12 980 $dm^3 \cdot mol \cdot cm^{-1}$ at 225 nm) was monitored spectrophotometrically. Partition coefficients of organic iodides were determined by withdrawing aqueous and gas samples from solutions of organic iodides in temperature-controlled cells. Analysis of these samples was performed using high-performance liquid chromatography (detection by ultraviolet at 254 nm) and gas chromatography. The data showed that equilibrium was generally reached within an hour, but sampling continued for several hours (every 30 to 60 min).

A summary of the hydrolysis and partition results determined in this study is given in Table IV. In general, the

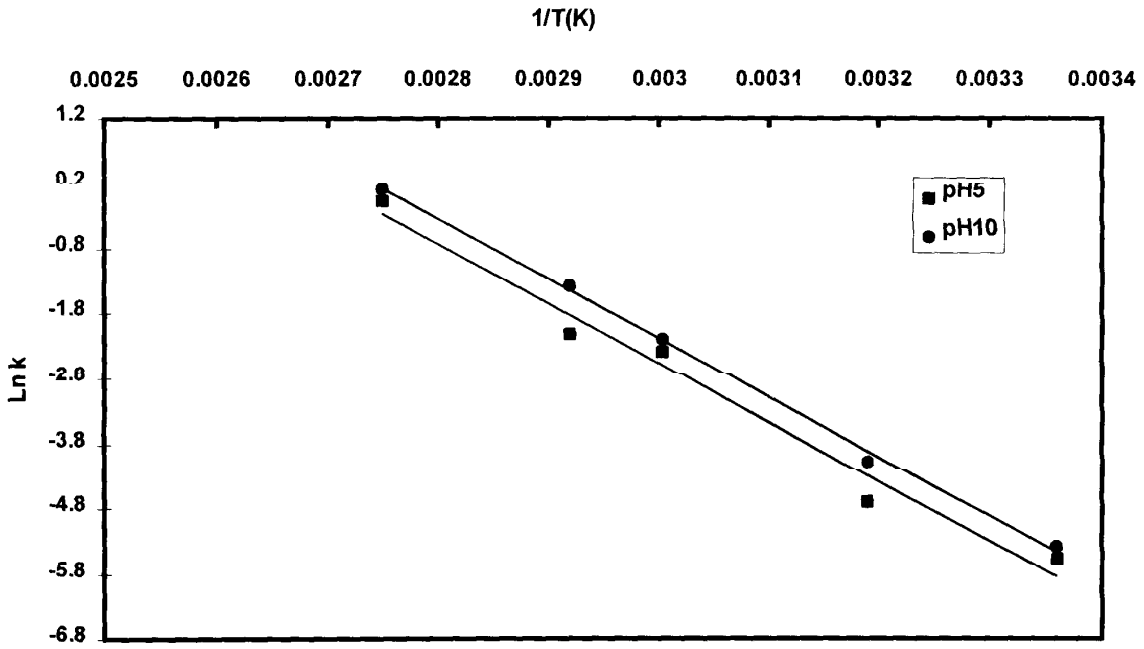

Fig. 17. Arrhenius plot for the dissolution of MIBK in water at pH 10 from vinyl-painted coupons. The line shows the fit for an activation energy of 2.8 kcal·mol^{-1}.

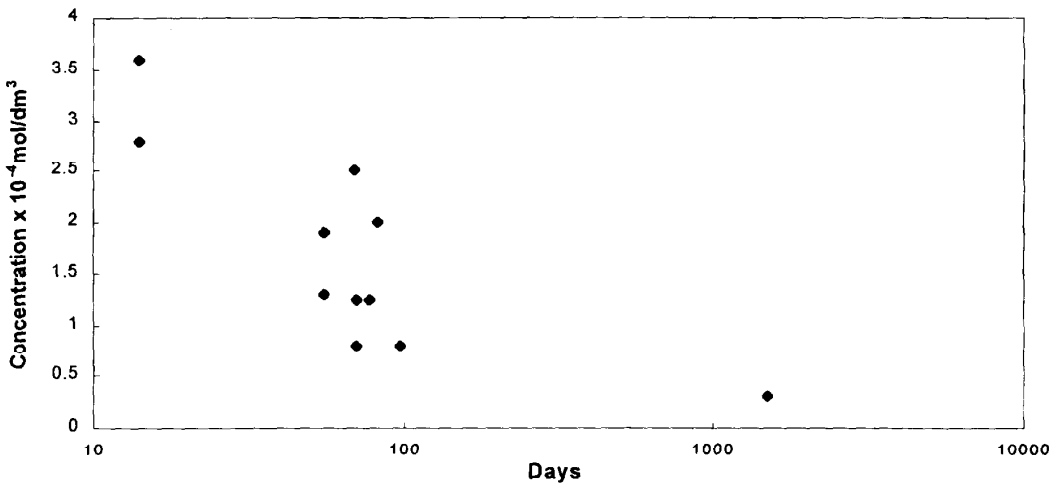

Fig. 18. The maximum MIBK concentration released from vinyl-painted coupons into water as a function of preaging of the painted coupons.

relative hydrolysis rates show a trend that was predicted based on carbon structure alone. The tertiary and the benzyl iodides hydrolyzed the fastest, followed by the secondary iodides, and finally the primary species. If there was an electron withdrawing functional group near the iodide, as was the case for iodoethanol and iodoacetic acid, the rate was reduced. This can be explained by the destabilization of the intermediate carbocation caused by electron density being drawn by electron withdrawing groups. A less stable carbocation intermediate yields a lower hydrolysis rate.

TABLE IV

Hydrolysis Rates and Partition Coefficients of Organic Iodides

Compound	Partition Coefficient at 25°C	Hydrolysis Rate (s^{-1})	Activation Energy (kJ/mol)
Iodomethane	4.8	3.3×10^{-5} at 70°C	104 ± 10
Iodoethane	2.8	7.4×10^{-5} at 70°C	100 ± 6
2-iodobutane	2.2	1.0×10^{-3} at 70°C	97 ± 5
Iodoacetic acid	500000	2.9×10^{-6} at 70°C	132 ± 10
Iodoethanol	71000	1.8×10^{-5} at 90°C[a]	Not determined[a]
Benzyl iodide	Not determined	4.6×10^{-3} at 70°C	93 ± 5
2-iodophenol	725	$<6 \times 10^{-8}$ at 80°C[b]	Not determined[a]
2-iodo-2-methylpropane	Not determined[c]	$>1.2 \times 10^{-2}$ at 25°C[d]	105[e]

[a]Only 1 measurement made due to time required.
[b]Estimated upper limit.
[c]Hydrolysis is too fast to do partition determination.
[d]Lower limit estimated in a 70% methanol, 30% water solution.
[e]Estimate based on data from a 70% methanol, 30% water solution.

Although there was a very wide range of hydrolysis rates, the activation energies for these reactions were all ~100 kJ/mol. The uncertainty quoted in Table IV is the uncertainty in the Arrhenius plot line fitting. The similarity of the activation energies is not surprising given that the mechanism, nucleophile, and the leaving group were the same in all measurable cases. For organic iodides, the range of hydrolysis rates spans several orders of magnitude. Iodine attached to an aromatic ring hydrolyzes so slowly, it is difficult to detect a reaction. Conversely, some compounds hydrolyze so quickly, they hardly have a significant lifetime in an aqueous solution. The most important factor determining hydrolysis rate is carbon structure.

The partition coefficients of the organic iodides studied also ranged over several orders of magnitude. Compounds with carbonyl, alcohol, or carboxylic acid are more water soluble than their unsubstituted counterparts by virtue of the polarity of the carbon oxygen bonds. Because oxygen tends to react very rapidly with organic radicals, to form perhydroxyl radicals, eventually forming alcohols and ketones, these types of organic iodides are expected to be created from organic impurities that may be present in containment. In the presence of radiation and in oxygenated aqueous solutions, aromatic compounds, such as phenol and benzene, are also known to undergo a ring cleavage yielding acids and aldehydes, as well as hydroxylation of the ring.

In the highly oxidizing radiation environment in containment following an accident, large organic iodides and organic impurities will be broken down into smaller, more oxidized compounds and eventually to CO_2. Not only will the initial mix of compounds be difficult to predict, it will also be changing with time. This means that the mix of organic iodides will likely shift from quickly hydrolyzing compounds with low partition coefficients to slowly hydrolyzing compounds that are less volatile. Compounds that are very volatile and hydrolyze slowly, such as methyl and ethyl iodide, are more persistent because they can escape into the gas phase where radiolytic breakdown is less efficient. As a result, to determine iodine volatility after an accident, not all organic iodides should be considered equal. Some organic iodides will increase the overall iodine partition coefficient, whereas others will decrease it. An additional division between these two categories concerns the lifetime of the compound in the aqueous phase. Compounds that quickly hydrolyze have the overall effect of converting I_2 to I^-, whereas compounds that hydrolyze slowly will partition accordingly. Ultimately, all organic compounds will be completely broken down under irradiation, but organic compounds will have significant impact on the overall iodine partition coefficient over their lifetime in the sump.

IV.E. Iodine Sorption on Surfaces in the Gas Phase

The adsorption and desorption parameters of I_2 on painted coupons and tubing in the gas phase are being measured as a function of the I_2 concentration in the gas phase, temperature, and relative humidity. The experimental setup and procedure used for these measurements are very similar to those used for the iodine sorption on stainless steel surfaces.[34,35] The experimental study is still being conducted and thus the work is not discussed in this paper. The results are being used to develop a semimechanistic model to be incorporated into the LIRIC model.[6]

RTF tests have also shown that organic-painted surfaces have large adsorption capacities for iodine in the gas phase (Table II). With the exception of the tests

conducted with zinc primer and vinyl paints in the absence of radiation, gas phase surfaces have shown larger adsorption capacities for iodine than aqueous phase surfaces. It also appears that the fraction of the total iodine deposited on the gas phase surfaces increases with an increase in the iodine concentration in the gas phase. Organic surfaces in the gas phase and bare stainless steel surfaces have similar overall adsorption capacities for iodine.

The following model has been proposed for iodine deposition on painted surfaces:

$$\frac{d[I_2]_g}{dt} = -k_{Ad}\cdot[I_2]_g\cdot\left(1-\frac{[I_2]_s}{[I_2]_s^o}\right) + k_{Des}\cdot\frac{A_{gs}}{V_g}\cdot[I_2]_s \tag{21}$$

and

$$\frac{d[I_2]_s}{dt} = k_{Ad}\cdot\frac{V_g}{A_{gs}}\cdot[I_2]_g\cdot\left(1-\frac{[I_2]_s}{[I_2]_s^o}\right) - k_{Des}\cdot[I_2]_s\ , \tag{22}$$

where

$[I_2]_g, [I_2]_s$ = molecular iodine concentrations in the gas phase ($mol\cdot dm^{-3}$) and on the surface ($mol\cdot dm^{-2}$), respectively

k_{Ad} = adsorption rate constant (s^{-1})

k_{Des} = desorption rate constant (s^{-1})

A_{gs}, V_g = gas phase surface area (dm^2) and volume (dm^3), respectively

$[I_2]_s^o$ = saturation capacity of the surface for I_2 ($mol\cdot dm^{-2}$).

Many RTF and bench-scale studies were used to validate this model and to obtain the adsorption and desorption rate constants and adsorption capacity. A good fit is obtained using this model for a variety of tests with a variety of surfaces. As an example, modeling results and pH input from two experiments performed by irradiating CsI in vinyl-painted vessels, which were aged 3 months and 1 yr, are presented in Figs. 19 and 20. Because LIRIC is not yet able to accurately model organic compound dissolution from the vinyl paint and, thus, the resulting time-dependent pH changes and rates of organic-iodide formation, we did not attempt to simulate the pH or the organic-iodide behavior. As input to the calculations, the pH profile was adjusted to approximately match the experimentally observed pH behavior.

Figures 19 and 20 demonstrate that even without including organic iodide formation in the model, we are able to reproduce RTF data reasonably well as long as the pH input is correct. This demonstrates the relative importance of the effect of organic radiolysis on pH as compared to its effect on organic iodide formation. Organic iodide formation is important, but because its rate is a function of the concentration of molecular iodine (which in turn is a function of pH), it plays only a secondary role in determining iodine volatility. The

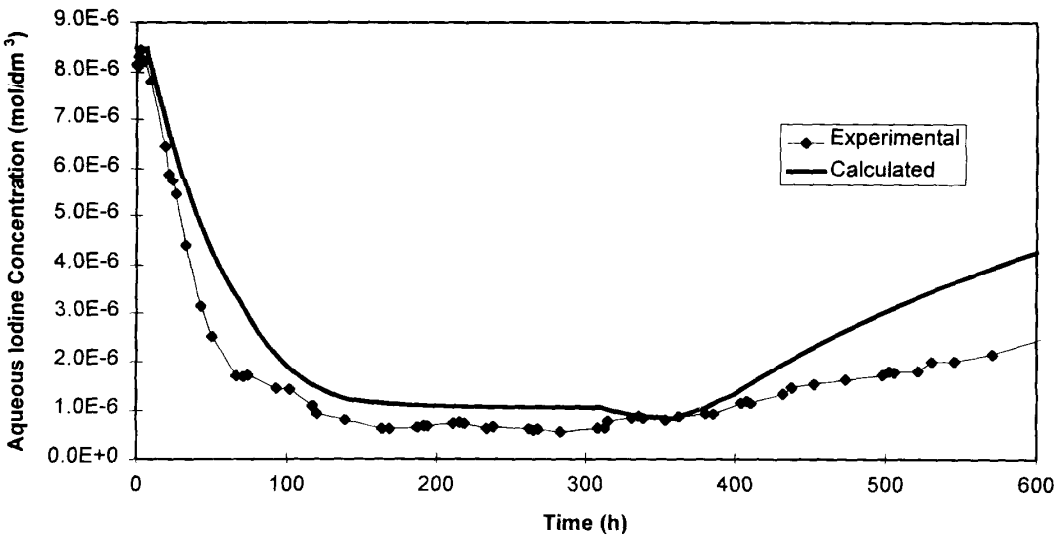

Fig. 19a. Simulation of an RTF test in a vinyl-painted vessel aged 3 months; aqueous phase iodine concentration.

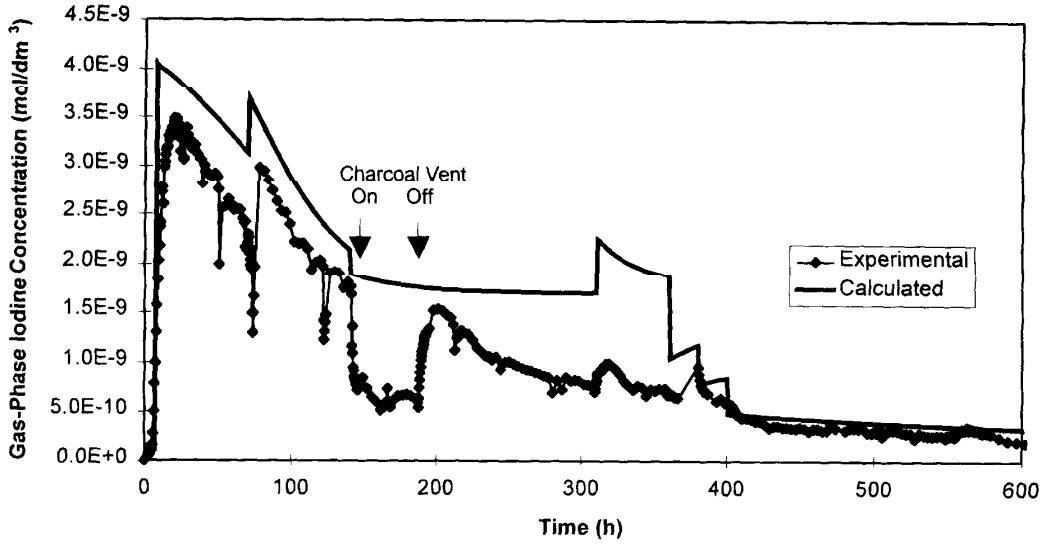

Fig. 19b. Simulation of an RTF test in a vinyl-painted vessel aged 3 months: gas phase iodine concentration.

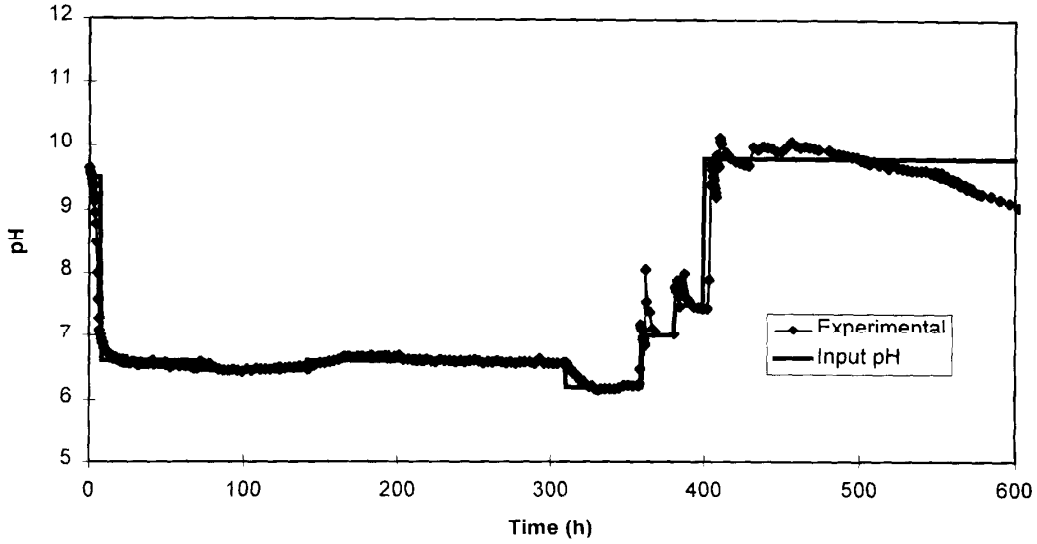

Fig. 19c. Input pH to LIRIC 3.0 for the simulation of RTF test in a vinyl-painted vessel aged 3 months.

formation of organic iodides, which are less volatile than I_2, appears to compensate for the fact that a few very volatile species such as CH_3I are produced. Thus, assuming the iodine in the gas phase is all in the form of I_2 still gives reasonable results.

V. SUMMARY

A comprehensive research program is being conducted at the Whiteshell Laboratories and Chalk River Laboratories of AECL to study the influence of the

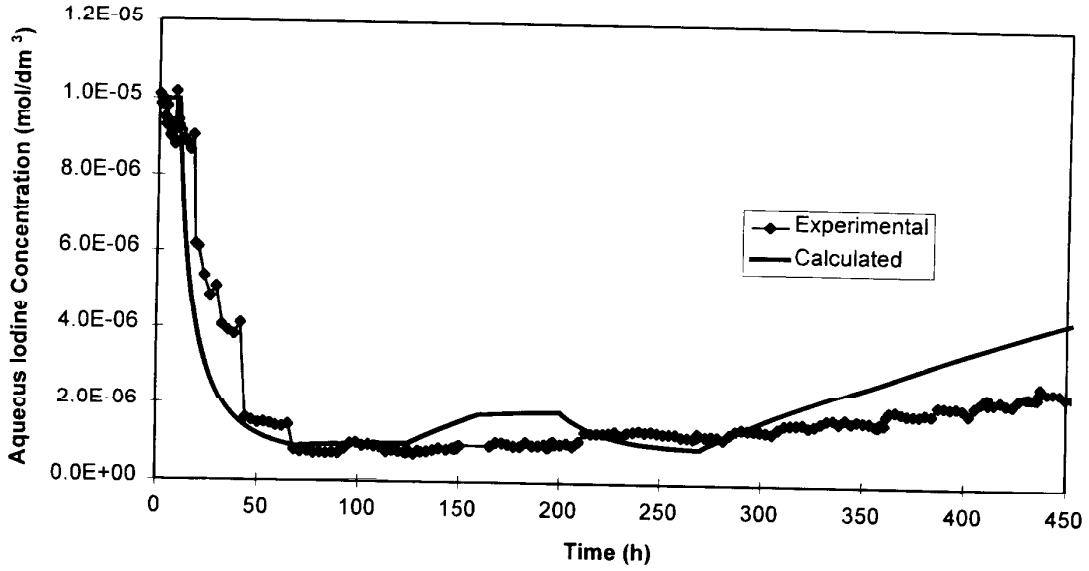

Fig. 20a. Simulation of an RTF test in a vinyl-painted vessel aged 12 months: gas phase iodine concentration simulation of RTF Test 2.4: aqueous phase iodine concentration.

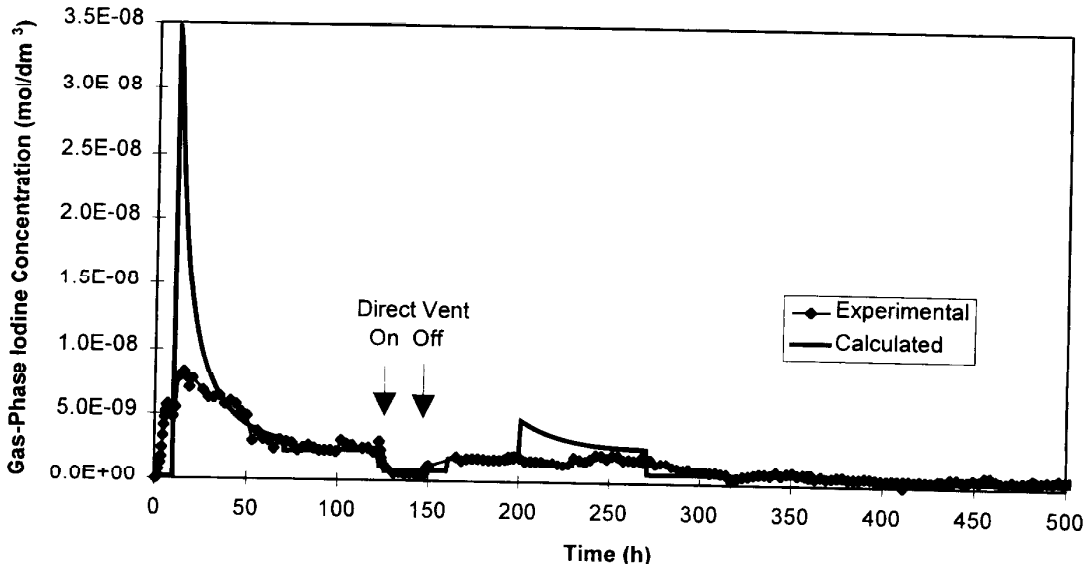

Fig. 20b. Simulation of an RTF test in a vinyl-painted vessel aged 12 months: gas phase iodine concentration.

chemistry of painted surfaces on iodine volatility under postulated reactor accident conditions. The studies involve model development, bench-scale separate effects tests, and intermediate-scale integrated experiments on organic compound dissolution and radiolysis, and iodine surface adsorption and desorption phenomena.

The studies have shown the following:

1. One of the major sources of organic impurities found in containment water will be the organic compounds dissolved from various surface paints.

2. The main impact of surface paints on iodine chemistry will most likely occur through aqueous phase

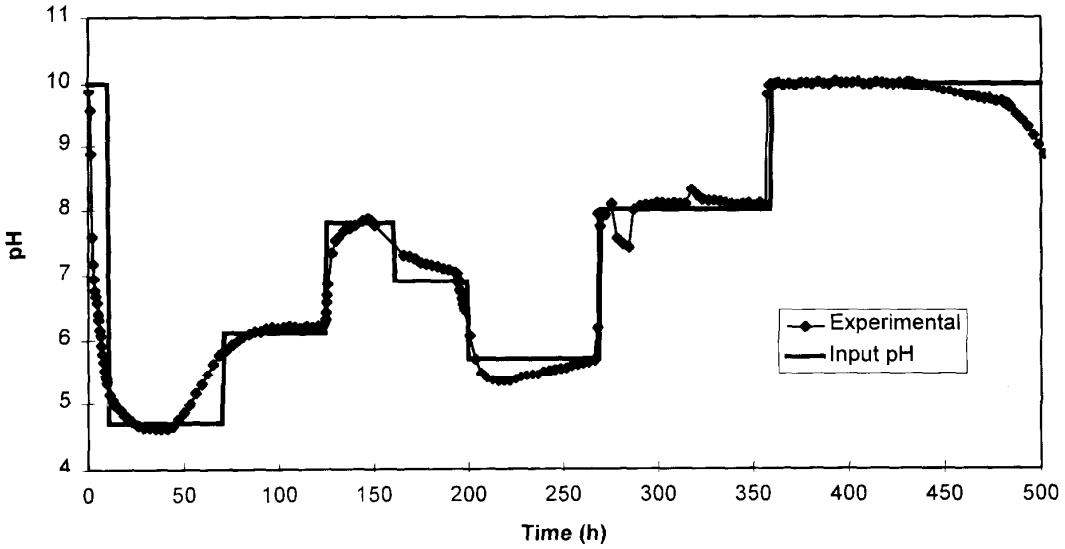

Fig. 20c. Input pH to LIRIC 3.0 for the simulation of RTF test in a vinyl-painted vessel aged 3 months.

reactions of the organic compounds that are released from organic painted surfaces that reduce solution pH and thus promote higher steady-state concentrations of I_2.

3. The rates of the processes described in 2 may be controlled by the dissolution kinetics of the organic compounds from the surface coatings.

4. Organic compounds in the aqueous phase will be primarily responsible for formation of organic iodides. However, organic iodide formation from these species does not necessarily lead to increased iodine volatility.

The identification of aqueous phase reactions as being of primary importance in determining the effect of organic species on iodine volatility and of solvent dissolution as being a key rate-controlling process have several implications for development of a modeling strategy to predict iodine volatility. These findings suggest that iodine volatility will be controlled primarily by the time-dependent pH evolution in the aqueous phase, which will control the peak and pseudo steady-state concentration of aqueous phase I_2 attained. They also suggest that this concentration will be controlled primarily by solvent dissolution kinetics. Finally, the findings of this study demonstrate that because organic iodide formation is tied to both the aqueous I_2 concentration and to the rate of organic release, it can be modeled by a semiempirical approach, using the steady-state concentrations of I_2 and organic compounds at a given pH.

ACKNOWLEDGMENTS

The authors would like to thank J. Elliot and S. Sunder at AECL and K. Weaver at Ontario Hydro Nuclear for helpful discussions and for reviewing this paper. This work was funded by the CANDU Owners Group Research and Development Program, Working Party 06, Containment Behavior, under the joint participation of Ontario Hydro, Hydro Quebec, New Brunswick Power, and AECL.

REFERENCES

1. F. GARISTO, "Thermodynamics of Iodine, Cesium and Tellurium in the Primary Heat Transport System Under Accident Conditions," AECL-7782, Atomic Energy of Canada Ltd. (1982).

2. D. J. WREN, "Kinetics of Iodine and Cesium Reactions in the CANDU Reactor Primary Heat Transport System Under Accident Conditions," AECL-7781, Atomic Energy of Canada Ltd. (1983).

3. D. CUBICCIOTTI and J. E. SANECKI, "Characterization of Deposits on Inside Surfaces of LWR Cladding," *J. Nucl. Mater.*, **78**, 96 (1978).

4. C. V. McISAAC and D. G. KEEFER, "Reactor Building Source Term Measurements," *ACS Symp. Ser.*, **293**, 168 (1986).

5. *Proc. 4th Workshop on the Chemistry of Iodine in Reactor Safety*, Wurenlingen, Switzerland, 1996, Committee on the Safety of Nuclear Installations/Organization for Economic

Cooperation and Development; see also, *Proc. 3rd Committee on the Safety of Nuclear Installations Workshop on Iodine Chemistry in Reactor Safety*, Toki-Mura, Japan, 1991, JAERI-M 92-012, Japan Atomic Energy Research Institute (1992); see also *Proc. 2nd Committee on the Safety of Nuclear Installations Workshop on Iodine Chemistry in Reactor Safety*, AECL-9923, CSNI-149, p. 292, A. C. VIKIS, Ed., Atomic Energy of Canada Ltd. (1989); see also *Proc. 1st Committee on the Safety of Nuclear Installations Workshop on Iodine Chemistry in Reactor Safety*, Harwell, United Kingdom, September 1985, AERE R11974, Atomic Energy Research Establishment (1986).

6. J. C. WREN, G. A. GLOWA, and J. M BALL, "Modelling Iodine Behaviour Using LIRIC 3.0," *Proc. 4th Workshop on the Chemistry of Iodine in Reactor Safety*, Wurenlingen, Switzerland, 1996, Committee on the Safety of Nuclear Installations/Organization for Economic Cooperation and Development.

7. J. C. WREN, J. M. BALL, G. GLOWA, R. PORTMAN, and G. G. SANIPELLI, "The Interaction of Iodine with Organic Material in Containment," *Proc. 4th Workshop on the Chemistry of Iodine in Reactor Safety*, Wurenlingen, Switzerland, 1996, Committee on the Safety of Nuclear Installations/Organization for Economic Cooperation and Development.

8. J. M. BALL, W. C. H. KUPFERSCHMIDT, and J. C. WREN, "Phase 2 Radioiodine Test Facility Experimental Program," *Proc. 4th Workshop on the Chemistry of Iodine in Reactor Safety*, Wurenlingen, Switzerland, 1996, Committee on the Safety of Nuclear Installations/Organization for Economic Cooperation and Development.

9. J. M. BALL, J. B. HNATIW, and H. SIMS, "The Reduction of I_2 by H_2O_2 in Aqueous Solution," *Proc. 4th Workshop on the Chemistry of Iodine in Reactor Safety*, Wurenlingen, Switzerland, 1996, Committee on the Safety of Nuclear Installations/Organization for Economic Cooperation and Development.

10. J. C. WREN, N. H. SAGERT, and H. E. SIMS, "Modelling of Iodine Chemistry; The LIRIC Database," *Proc. 3rd Committee on the Safety of Nuclear Installations Workshop on Iodine Chemistry in Reactor Safety*, Toki-Mura, Japan, 1991, JAERI-M 92-012, p. 381, Japan Atomic Energy Research Institute (1992).

11. W. C. H. KUPFERSCHMIDT, J. B. BUTTAZONI, A. J. MELNYK, R. PORTMAN, and G. G. SANIPELLI, "The Effects of Zinc Primer Surfaces on Iodine Behaviour Within Containment," *Proc. 3rd Committee on the Safety of Nuclear Installations Workshop on Iodine Chemistry in Reactor Safety*, Toki-Mura, Japan, 1991, JAERI-M 92-012, p. 195, Japan Atomic Energy Research Institute (1992).

12. W. C. H. KUPFERSCHMIDT, J. B. BUTTAZONI, G. J. EVANS, B. L FORD, A. S. PALSON, R. PORTMAN, and G. G. SANIPELLI, "Iodine Chemistry in the Presence of Vinyl Surfaces," *Proc. 3rd Committee on the Safety of Nuclear Installations Workshop on Iodine Chemistry in Reactor Safety*, JAERI-M 92-012, Japan Atomic Energy Research Institute (1992).

13. G. J. EVANS, A. MELNYK, J. PAQUETTE, and N. H. SAGERT, "The LIRIC Database/Model," *Proc. 2nd Int. Conf. Containment Design and Operation*, Toronto, Canada, October 1990, S. R. LAWRENCE, Ed., Canadian Nuclear Society (1990).

14. W. C. H. KUPFERSCHMIDT, A. J MELNYK, R. PORTMAN, and G. G. SANIPELLI, "A Description of the Radioiodine Test Facility (RTF) and Results of Initial RTF Full-System Tests," *Proc. 2nd Committee on the Safety of Nuclear Installations Workshop on Iodine Chemistry in Reactor Safety*, AECL-9923, CSNI-149, p. 292, A. C. VIKIS, Ed., Atomic Energy of Canada Limited (1989).

15. J. C. WREN, J. PAQUETTE, D. J WREN, and G. G. SANIPELLI, "The Formation and Volatility of Organic Iodides," *Proc. 1st Committee on the Safety of Nuclear Installations Workshop on Iodine Chemistry in Reactor Safety*, Harwell, United Kingdom, September 1985, AERE R11974, Atomic Energy Research Establishment (1986).

16. G. A. GLOWA, "Phenolic Compounds as Potential Iodine Mitigants in Nuclear Reactor Containment," MSc Thesis, University of Manitoba (1995).

17. J. C. WREN, D. J. JOBE, and G. G. SANIPELLI, "Dissolution of Organic Solvents from Organic-Based Painted Surfaces into Water Under Containment Accident Conditions and Its Potential Impact on Iodine Volatility," *Nucl. Tech.* (submitted for publication).

18. P. DRIVER, "Steady-State γ-Radiolysis of Aqueous 2-Butanone (MEK) and Its Effect on Aqueous Iodine Volatility in Containment," MSc Thesis, University of Manitoba (1997).

19. P. A. DRIVER, G. A. GLOWA, and J. C. WREN, "Steady-State γ-Radiolysis of Aqueous 2-Butanone (MEK) and Its Potential Impact on Iodine Volatility Under Containment Accident Conditions," *Rad. Phys. Chem.* (submitted for publication).

20. P. A. DRIVER, G. A. GLOWA, and J. C. WREN, "Steady-State γ Radiolysis of Aqueous 2-Butanone (MEK) and Its Potential Impact on Iodine Volatility Under Containment Accident Conditions," *Rad. Phys. Chem.* (submitted for publication); see also G. A. GLOWA, P. A. DRIVER, and J. C. WREN, "Irradiation of MEK Part II: A Detailed Kinetic Model for the Degradation of 2-Butanone in Aerated Aqueous Solutions Under Steady-State γ-Radiolysis Conditions," *Rad. Phys. Chem.* (submitted for publication).

21. G. A. GLOWA, J. HNATIW, and G. G. SANIPELLI, "The Hydrolysis Rates and Partition Coefficients of Organic Iodides" (manuscript in preparation).

22. A. K. POSTMA and R. W. ZAVADOSKI, "Review of Organic Iodide Formation Under Reactor Accident Conditions in Water-Cooled Reactors," WASH-1233, U.S. Department of Energy (1972).

23. L. L. BURGER, "Laboratory Study of Interaction of Molecular Iodine with Phenoline 302 Paint," Personal Communication to A. K. POSTMA (1972).

24. R. T. HEMPHILL and C. A. PELLETIER, " Surface Effects in the Transport of Airborne Radioiodine at Light Water Nuclear Power Plants," EPRI-NP-876, Electric Power Research Institute (1978).

25. A. M. DEANE and C. P. DAVIES, "The Formation of Volatile Species at Surfaces from Iodide Ions," AEA-TRS-2000, Atomic Energy Authority (1990); see also, A. M. DEANE and C. P. DAVIES, "Organic Iodine Formation Rates on Surfaces in Pressurised Water Reactor Buildings," AERE-R-13526, Atomic Energy Research Establishment (1989).

26. J. PAQUETTE and B. L. FORD, "The Radiation-Induced Formation of Iodoalkanes and the Radiolysis of Iodomethane," *Proc. 2nd Committee on the Safety of Nuclear Installations Workshop on Iodine in Reactor Safety*, Toronto, Canada, 1988, AECL-9923/CSNI-149, p. 48, Atomic Energy of Canada Ltd. Research (1989).

27. E. C. BEAHM, Y. M. WANG, S. J. WISBEY, and W. E. SHOCKLEY, "Organic Iodide Formation During Severe Accidents in Light Water Nuclear Reactors," *Nucl. Technol.*, **78**, 34 (1987).

28. B. BARTONICEK and A. HABERSBERGEROVA, "Investigation of the Formation Possibilities of Alkyl Iodides in Nuclear Power Plants," *Radiat. Phys. and Chem.*, **28**, 591 (1986).

29. R. J. LEMIRE, J. PAQUETTE, D. F. TORGERSON, D. J. WREN, and D. W. FLETCHER, "Assessment of Iodine Behaviour in Reactor Containment Buildings from a Chemical Perspective," AECL-6812, Atomic Energy of Canada Ltd. (1981).

30. Y. NISHIZAWA, Y. KIGOSHI, S. OHSHIMA, Y. OSAZA, and J. MASKAWA, "Vapor-Water Partition Coefficients of Iodine and Organic Iodides," *J. Atom. Eng. Soc.*, **II**, 205; see also, ORNL-TR-2255, Oak Ridge National Laboratory (1969).

31. R. E. LOEWENTHAL and G. V. R. MARAIS, *Carbonate Chemistry of Aquatic Systems: Theory and Application*, Ann Arbor Science Publishers Inc., Ann Arbor, Michigan (1976).

32. M. DOLE, "Oxidation of Irradiated Polymers," *The Radiation Chemistry of Macromolecules*, p. 263, M. DOLE, Ed., Academic Press, New York (1973).

33. H. S. ROSENBERG, G. E. CREMEANS, J. M. GENCO, D. A. BERRY, and D. L. MORRISON, "Fission-Product Deposition and Its Enhancement Under Reactor Accident Conditions: Development of Reactive Coatings," BMI-1874, Battelle Memorial Institute (1969).

34. J. C. WREN, G. A. GLOWA, and J. MERRITT, "Corrosion of Stainless Steel by Gaseous I_2," COG-97-199, Atomic Energy of Canada Ltd. (1997); *J. Nucl. Mat.* (to be published).

35. J. C. WREN, G. A. GLOWA, and J. MERRITT, "Modelling Gaseous Iodine Adsorption on Stainless Steel," COG-97-240, Atomic Energy of Canada Ltd. (1997); *J. Nucl. Mat.* (submitted for publication).

Jungsook Clara Wren (BS, chemistry, Sogang University, Korea, 1976; PhD, physical chemistry, Kansas State University, 1981) is a senior research scientist in the Fuel Safety Branch at the Chalk River Laboratories of Atomic Energy of Canada Ltd. (AECL). Her background in nuclear safety research includes reaction kinetics of iodine species in gas and aqueous phases, iodine surface chemistry, and abatement of iodine and noble gases. Her research background also includes chemical reactions in high-voltage discharges and radiation fields, and inter- and intra-molecular energy transfer of highly excited molecules.

Joanne M. Ball (BSc, 1983, and PhD, 1988, inorganic chemistry, University of Calgary, Canada) is a scientist in the Fuel Safety Branch at the Chalk River Laboratories of AECL. Her experience in reactor safety research has included serving as principal investigator for the Radioiodine Test Facility (an intermediate-scale facility to study iodine behavior in containment), development of a mechanistic model for iodine behavior, and studies of the reaction kinetics of aqueous iodine species.

Glenn A. Glowa (BSc, University of British Columbia, Canada, 1990; MSc, University of Manitoba, Canada, 1995) is a research scientist in the Fuel Safety Branch at the Chalk River Laboratories of AECL. His current field of study involves several aspects of iodine chemistry that have relevance to reactor safety. This includes the formation and degradation of organic iodides, iodine surface interactions, and computer modeling.