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Organic Iodide Formation Following Nuclear Reactor Accidents

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Prepared for the
U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Under Interagency Agreement DOE 40-551-75

OPER 860310003B 851130
MAR PDR NUREG
CR-4327 R PDR

FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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NUREG/CR-4327
ORNL/TM-9627
Dist. Category R3

Chemical Technology Division

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E. C. Beahm
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Manuscript Completed — April 1985
Date of Issue — December 1985

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final report.

Prepared for the
U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Washington, DC 20555
under Interagency Agreement DOE 40-551-75

NRC FIN No. B0453

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract No. DE-AC05-84OR21400

ABSTRACT

A wide variety of organic materials will be present in containment following a light-water reactor accident. Organic iodides can be produced by the reaction of fission product iodine with these organic materials. This report emphasizes the importance of free radicals and radiation in leading to the formation of organic iodide. The ultimate aim is a description of the rate of formation and removal of organic iodide, within the time span of a core heatup event, that can be used in a model of iodine behavior in containment.

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1. EXECUTIVE SUMMARY

Inorganic iodide species can react with a wide variety of organic compounds to produce organic iodides. In addition to straightforward reaction of organic compounds and iodine species, radiation in containment could bring about free radical reactions not otherwise possible. Despite several reviews of this subject within the last 15 years, the sources and rates of organic iodide production are not well characterized. The state of knowledge is especially poor with respect to the formation rate within the time span of a core heatup event.

The reactions to form or decompose organic iodides are best viewed as a dynamic system in which iodine species enter containment and interact with a complex gas mixture with transport to and from surfaces and aqueous solution. Three approaches for evaluating the chemistry of this dynamic system can be suggested: (1) calculational studies of gas phase and gas phase/aqueous solution reactions, (2) laboratory-scale experiments, and (3) large-scale containment tests.

The formation of organic iodides may be limited by the amount or the chemical form of the organic compounds. The lower limit of organic compounds is set by the normal background of hydrocarbons in air, 5×10^{-8} to 1×10^{-7} mol/L. The maximum concentration will be set by the interaction of radiation with organic materials in containment. An organic gas concentration of ~2 orders of magnitude above normal background can be attained 1 h after a light-water reactor accident.

A review of a number of large-scale containment tests shows that the total concentration of organic iodide formed tended to be relatively insensitive to the concentration of iodine released. The tests run with irradiated fuel gave higher percentage conversion to organic iodide than simulant tests.

The rate of formation and removal of organic iodide can be expressed by the equation:

$$\frac{dC}{dt} = \alpha (C^* - C) - QC,$$

where

C = concentration of organic iodide at time t,
C* = equilibrium concentration of organic iodide,
Q = a constant for removal of organic iodide,
 α = organic iodide formation constant (s^{-1}).

Evaluation of α and C^* , based on data in the literature, indicates that both constants could be in a range where the upper limit is a factor of ~60 times the lower limit. This wide range is due in part to the simplification that relates organic iodide only to the iodine (I_2) release concentration.

The organic iodide program at Oak Ridge National Laboratory includes both calculation of equilibria accompanied by the absorption of radiation and an experimental program to examine both formation and removal of organic iodides.

2. REVIEW

2.1 INTRODUCTION

Inorganic iodine species can react with a wide variety of organic compounds to produce organic iodides. The types of organic compounds susceptible to reaction with iodine species include (reacting iodine species shown in brackets): alkenes [I_2 , HI]; alkynes [I_2 , HI]; alcohols [HI]; ethers [HI]; methyl ketones [OI^-]; amines [HI]; diazonium compounds [KI]; and aniline [I_2].

In addition to direct reactions of organic compounds and iodine species, radiation in the containment building could bring about reactions not otherwise possible. Free radicals, atoms or groups of atoms that are quite reactive due to an unpaired electron, can form when radiation interacts with many types of molecules. Iodine is a very effective scavenger of free radicals to the degree that it is used to measure the extent of free radical formation in studies of the irradiation of organic compounds. The products of iodine reacting with organic free radicals are organic iodides.

Such an array of possible reactions leading to the formation of organic iodides should make one cautious in assigning a simple reaction mechanism. Clearly, there is more involved than the reaction of methane with elemental iodine (I_2).

Reactions to form organic iodides can be both beneficial and detrimental. The resulting iodine compound could be immobilized or it could form a penetrating volatile organic compound. In fact, both processes may occur simultaneously with a given source of organic material. Thus, for example, Rosenberg et al.¹ reported that an epoxy-based coating Amercoat 66 (used on drywell walls) sorbed 3.3 mg/cm² of I_2 at 90°C. Under similar conditions, at 100°C with the same coating, Bennett et al.² clearly show that methyl iodide and ethyl iodide are produced when I_2 is introduced into the system.

Both gas phase reactions and surface reactions may contribute to the formation of organic iodides. A review report by Postma and Zavadoski³ cites gas phase reactions under the influence of radiation as the principal source of organic iodides. Alternatively, Durant et al.⁴ considered

a two-step reaction process where the first stage of the reaction is the addition of I_2 to reactive groups on the coating surface, which is then followed by the formation of low-molecular weight organic iodine compounds. Thus, it may not be prudent at this time to assign a single source when there exists such a large number of possible reaction types, sites, and conditions. It may be more important to stress the dynamic nature of reactions involving organic iodine. Thus, we may expect a dynamic interaction between sorption and desorption of iodine species, desorption of organic species prior to reaction with iodine, radiation-induced formation and decomposition of organic compounds, and organic compounds containing iodine, as well as interaction with water pools. We may cite the interaction with water pools. For each I_2 converted to an organic iodide, an equal amount of I_2 would be delivered to the containment atmosphere from the sump as long as the aqueous I_2 concentration is high enough to maintain the equilibria. On the other hand, organic iodides may hydrolyze in water to form alcohols and I^- . For example, Lemire et al.⁵ report that for pH = 10 and T = 80°C, 43% of the initial methyl iodide in water remains after 1 h for an initial concentration of 10^{-6} mol/L.

Despite several reviews of this subject within the last 15 years, the sources and rates of organic iodide production in containment are not well characterized. The state of knowledge is especially poor with respect to estimation of formation rate within the time span of a core heatup event. According to Postma and Zavadoski,³ the steady state level of organic iodide produced in ~70 containment tests may be predicted from:

$$\text{percent organic iodide formation} = 0.188 \times C_M^{-0.26}, \quad (1)$$

where C_M is the iodine concentration as I_2 in the vapor in terms of mg/m³. Equation (1) represents a mean with data scatter about a factor of 15 above and below the mean. When radiation effects are included, the uncertainties can be even greater.

In the present examination of the chemistry of organic iodide formation in containment, we describe reactions of organic compounds with iodine in the next section (Sect. 3). In Sect. 4, the types of organic material in containment are discussed, followed by a short critique of large-scale tests of organic iodide formation, and a concluding discussion.

3. REACTION OF ORGANIC COMPOUNDS WITH IODINE

3.1 GAS PHASE REACTIONS

The chemical system of interest for the formation of organic iodides in containment includes the fission product material released from the primary system, steam, liquid water, air, organic material, and metal and concrete surfaces. These materials will be reacting in a radiation field of variable intensity. Postma and Zavadoski³ calculated a dose rate of

1.6×10^6 rad/h immediately following a light-water reactor (LWR) accident, assuming 100% release of noble gases and a 25% release of iodine in a volume of 2×10^6 m³. After 1 d, the calculated dose rate decreased to 1.7×10^5 rad/h. In another series of dose rate calculations, Bonzan and Lurie⁶ calculated a gamma dose rate of 4.99×10^6 rad/h after 1 h and 1.699×10^6 rad/h after 1 d at midradius of a 6.28×10^4 -m³ containment vessel.

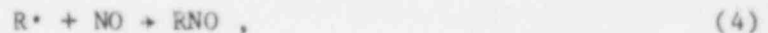
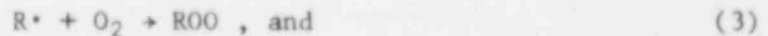
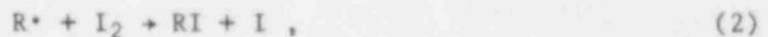
Table 1 presents a list of gaseous chemical species that may be part of the chemical reactions leading to the formation of organic iodides. Only gaseous species and carbon species that contain one or two carbon atoms and have thermodynamic properties readily available are included. In an accident situation, many of these species will be present in very small amounts, but it may be possible to conceive of additional species that should be included. The organic iodide species, along with I₂ and HI, are likely to be the principal gaseous iodine chemical forms. It is somewhat uncertain what amounts of the remaining iodine species (I, HOI, NOI, IO, CNI, COI₂) may be present, but it would be surprising if they attained concentrations comparable to the first five iodine species given in the table.

Table 1. Gaseous species list

CH ₃ I	CH ₂ O	NO ₃
C ₂ H ₅ I	HCO	NO ₂
CH ₂ I ₂	C ₂ H ₄ O	N ₂ O
I ₂	CH ₂ CO	NO
HI	HCOOH	CN
I	CH ₃ COOH	HCN
HOI	CH ₃ CH ₂ OH	CN ₂
NOI	CO ₂	C ₂ N ₂
IO	CO	CNO
CNI	H ₂ O ₂	CHNO
COI ₂	HO ₂	CH ₃ NO ₂
CH ₄	H ₂ O	CH ₃ NO ₃
CH ₃	OH	N ₂ H ₄
CH ₂	O ₃	N ₂ H ₂
CH	O ₂	NH ₃
C ₂ H	O	NH ₂
C ₂ H ₂	HNO	NH
C ₂ H ₄	HNO ₂	N ₃
C ₂ H ₅	HNO ₃	N ₂
C ₂ H ₆	N ₂ O ₅	N
CH ₃ OH	N ₂ O ₄	H ₂
CH ₃ OO	N ₂ O ₃	H
CH ₃ OOH		

The nitrogen compounds in the table would arise from the interaction of radiation with N_2 gas in air. Harteck and Dondes⁷ report the formation of nitrogen oxides and ozone when mixtures of oxygen and nitrogen are irradiated. In the presence of steam and/or liquid water, nitrogen compounds containing hydrogen can form. For example, nitric acid, HNO_3 , can be produced by the irradiation of moist air in sufficient quantity to lower the pH of droplets produced by condensing steam or of sump water. Linacre and Marsh⁸ report a G value [defined as the number of molecules produced (or decomposed) per 100 eV absorbed], $G(NO_3^-)$, of 2.2 for the irradiation of water vapor + air.

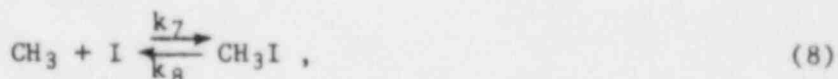
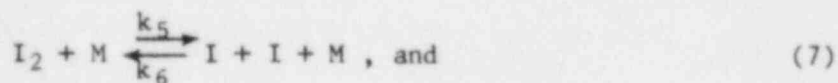
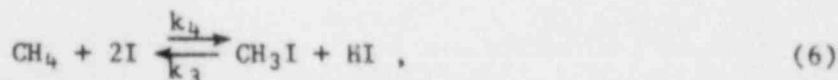
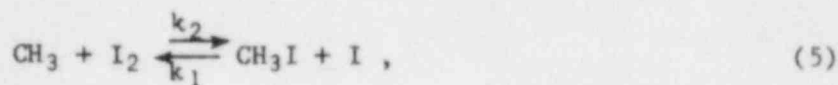
There are a number of free radicals in the species list given in Table 1: CH_3 , CH_2 , C_2H_5 , I, H, O, N, OH, HO_2 , and CH_3OO . Free radicals react readily with each other or with a number of other species called free radical scavengers. In this system, prominent radical scavengers include I_2 , O_2 , and NO. Thus, there will be a competition among the radical scavengers for the free radicals. These free radical reactions could be quite important in determining the amount of organic iodine in containment atmosphere. The scavenging reactions can be written as:



where R = an organic group.

The result of reaction (2) is the formation of an organic iodide. The extent that reaction (2) can occur depends on the amount of organic radicals present, the amount of I_2 present, and the removal of organic free radicals by other reactions such as those shown by reactions (3) and (4). The competition between radical scavengers does not bear a simple relationship to the relative amounts of the scavengers. Földiák⁹ reports that the competition of two radical scavengers, I_2 and galvinoxyl, cannot be accounted for in terms of data from systems containing each scavenger separately.

Barnes et al.¹⁰ have performed equilibrium calculations of the reaction of methane with I_2 . The calculations were based on a system composed of H_2O , CO_2 , HI, N_2 , CH_3OH , I_2 , CH_3I , H_2 , O_2 , CO, CH_4 , CH_2O , and solid carbon over a temperature range from 300 to 1000 K. The total iodine concentration was varied from 4×10^{-12} to 4×10^{-6} g-at./L in a mixture of steam and air. The highest fraction of methyl iodide (CH_3I) was calculated when only steam was present. However, in all cases, the calculated amounts of CH_3I were >2 orders of magnitude below those determined experimentally (see Sect. 5). From the comparison of equilibrium calculations and experimental measurements, Barnes et al.¹⁰ concluded that experimental values represented nonequilibrium conditions produced at higher temperatures and "frozen" in at lower temperatures. However, chemical kinetics calculations of the system of reactions (5) to (8),

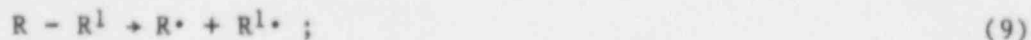


(M = an inert molecule) did not show a significant amount above the equilibrium values.

The discrepancy between calculated amounts of CH_3I and experimental data indicates that important factors were not included in the calculational parameters. The list of species in the calculations of Barnes et al.¹⁰ included only 13 items, compared to over 60 species cited in Table 1. Also, radiation effects were not included in these calculations. A program is now underway at Oak Ridge National Laboratory (ORNL) to use the SOLGASMIX equilibrium computer routine with the species listed in Table 1 and absorption of radiation.

The importance of free radical reactions leading to the formation of organic iodides cannot be overstated. Organic molecules readily form free radicals as a result of normal aging, from thermal degradation, or by irradiation. Free radicals are produced by dissociation, ion-molecular reactions, or neutralization, as shown:

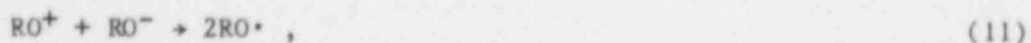
dissociation,



ion-molecule reaction,



neutralization,



where R, R^1 are organic groups, and Q represents a metal.

Nakashima and Tachikawa¹¹ have cited the importance of free radical-iodine reactions in an experimental study of the reaction of iodine with

propane (C_3H_8). These tests were conducted in a quartz tube with a carrier gas of either oxygen or helium at temperatures between 523 and 773 K. Note that these temperatures exceed those expected in containment after a nuclear reactor accident. At 558 K, with O_2 carrier gas, the yield of organic iodides (CH_3I , C_2H_5I , $i-C_3H_7I$, $n-C_3H_7I$) was 8% of the total iodine, and at 756 K, the organic iodide yield was 90%. The increase in organic iodide yield at higher temperatures was attributed to the competition of oxygen and iodine for the organic free radicals. At the higher temperature, thermal decomposition of the oxygenated radicals could regenerate the organic free radicals.

Gevantman and Williams¹² used iodine as a free radical scavenger in a study of the radiolysis of methane. The principal radical products detected were $CH_3\cdot$ (70% relative yield), $CH_2\cdot$ (8.5% relative yield), $H\cdot$ (8.5% relative yield), and $C_2H_5\cdot$ (4.5% relative yield). These products were detected as CH_3I , CH_2I_2 , HI , and C_2H_5I , respectively.

Although they bear no simple relationship with system parameters, such as concentration of reacting species, dose rate, or temperature, G values are convenient measures of the effect of radiation. Postma and Zavadoski³ used literature data to obtain a plot of $G(CH_3I)$ versus gas phase iodine concentration. They noted that $G(CH_3I)$ was higher for a methane-iodine mixture that did not contain water vapor and/or oxygen. The $G(CH_3I)$ straight line curve that they obtained from mixtures of methane-iodine-water vapor and/or oxygen was taken to be the upper limit to $G(CH_3I)$. From this they calculated a conversion of 2.2% of I_2 to CH_3I at an iodine concentration of 100 mg/m^3 and a total absorbed dose of $3.2 \times 10^6\text{ R}$.

The assumed straight-line relationship between $G(CH_3I)$ and iodine concentrations may be an oversimplification of a complex set of interactions. Data published after the Postma and Zavadoski report indicate that the complexity of the relationship between the gaseous components air-water vapor-methane-iodine and $G(CH_3I)$ values can be substantially greater.

Habersbergerova and Bartonicek^{13,14} studied radiation effects in the methane-iodine-water vapor-air system. The methane and iodine concentrations used in these studies were: methane, $2.1 \times 10^{-8}\text{ mol/dm}^3$ to $9.1 \times 10^{-7}\text{ mol/dm}^3$; iodine, $2.6 \times 10^{-11}\text{ mol/dm}^3$ to $7.4 \times 10^{-8}\text{ mol/dm}^3$. The concentration of CH_3I initially rose to a maximum, then decreased to a constant value with continuing irradiation. The constant value ranged from 1.6% conversion up to 100%. In general, lower concentrations of I_2 and CH_4 in the mixture gave a higher degree of conversion of I_2 to CH_3I . However, as shown in Table 2, the conversion also depends on the relative amount of methane in the system. Table 2 also gives a comparison of $G(CH_3I)$ measured by Bartonicek and Habersbergerova¹³ with values calculated using data from Postma and Zavadoski.³ Their first four tests give results close to the calculated values, but the other three measurements yield G values that are significantly greater than the calculations.

Table 2. Comparison of G(CH₃I) from measurements^a and calculated values^b

Concentration (mol/dm ³)		G(CH ₃ I) measured ^a × 10 ³	G(CH ₃ I) calculated ^b × 10 ³	% of I ₂ converted to CH ₃ I measured values ^a
I ₂	CH ₄			
7.4 × 10 ⁻⁸	5.4 × 10 ⁻⁷	1.3	1.0	4.7
7.8 × 10 ⁻⁹	3.4 × 10 ⁻⁷	~0.2	0.3	1.6
1.0 × 10 ⁻⁹	3.0 × 10 ⁻⁷	~0.2	0.3	8.5
2.6 × 10 ⁻¹¹	3.5 × 10 ⁻⁷	~0.2	0.25	100.0
7.8 × 10 ⁻⁹	2.1 × 10 ⁻⁸	1.2	0.3	23.8
7.8 × 10 ⁻⁹	3.7 × 10 ⁻⁸	2.1	0.3	27.6
5.7 × 10 ⁻⁹	9.1 × 10 ⁻⁸	6.6	0.3	21.8

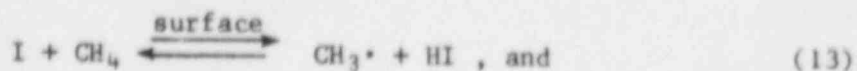
^aTaken from B. Bartonicák and A. Habersbergerova, "Radiation Chemistry of Methyl Iodide with Respect to Nuclear Power Plant Safety," Jad. Energ. 26, 181 (1980).

^bTaken from A. K. Postma and R. W. Zavodoski, Review of Organic Iodide Formation Under Accident Conditions in Water-Cooled Reactors, WASH-1233, Atomic Energy Comm., 1972.

Irradiation can lead to the formation of CH₃I and also to its removal by decomposition and conversion to other products. This behavior will lead to a net amount of CH₃I being formed that depends on system conditions. Values of percent CH₃I in Table 2 reflect the net amount.

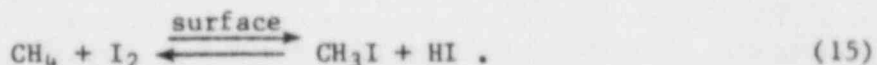
3.2 HETEROGENEOUS (GAS-SURFACE-AQUEOUS) REACTIONS

Dynamic processes involved in the formation and removal of CH₃I include interaction of gases with surfaces and liquid water. Durant et al.⁴ have considered the formation of CH₃I on surfaces from a theoretical viewpoint, discounting radiation effects. The reaction mechanism that was assumed is expressed by the equations:





The overall equation for this mechanism can be written:



Because of limited data for the rates of Eqs. (12) to (14), the average rate of formation of CH_3I was reduced to an equation with an overall rate constant, k_s , and written as:

$$\frac{\Delta[\text{CH}_3\text{I}]_{\text{surface}}}{\Delta t} = k_s [\text{I}_2]_{\text{surface}}^{1/2} \quad (16)$$

where

$\Delta[\text{CH}_3\text{I}]_{\text{surface}}$ = change in CH_3I concentration on a surface,

$[\text{I}_2]_{\text{surface}}$ = I_2 concentration on surface,

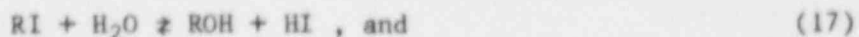
t = time.

They obtained estimated values of k_s by examining large-scale tests of organic iodide formation as given in the literature (see Sect. 5).

This approach is laudable in that it recognizes the importance of evaluating the rate of formation of CH_3I . However, it assigns the entire rate to a simple surface mechanism, which is then reduced to an equation with a single constant. The omission of other chemical effects, for example, reaction of gas species and radiation, limits the usefulness of this analysis.

Surface reactions may play a role in the dynamics of organic iodide formation and removal, but they are not likely to occur without interaction with species in the gas phase. Steel surfaces reportedly¹⁵ have a catalytic effect, under irradiation, on the amount of methane produced in the reaction of carbon dioxide with hydrogen (see Sect. 4).

Liquid water, either as a surface film or in a pool or sump, could play a key role in movement and removal of organic iodides. Formation of organic iodides in water pools is discussed in Sect. 6.2. Organic iodides and I_2 hydrolyze in water solution, as expressed by the overall reactions:



The rate of hydrolysis will be dependent on pH, temperature, and concentration. Methyl iodide is more volatile than I_2 , the partition coefficient (defined as concentration of iodine specie in aqueous solution

divided by concentration of iodine specie in gas) being ~3 for CH_3I and 86 for I_2 at 298 K.

The relatively low partition coefficient for CH_3I can lead to its transport from the aqueous phase. The transport of organic iodide to and from aqueous pools can be examined using standard mass transport equations. Following Liss and Slater,¹⁶ the organic gas exchange between water and air is described as a two-layer film system. The main body of water and gas is assumed to be mixed, and the main resistance to gas transport comes from the gas and liquid interfacial layers. The rate of mass transfer can be expressed in terms of the mass transfer coefficient for the gas film, k_g , and the mass transfer coefficient for the liquid film, k_l . The overall coefficient, on a liquid phase basis, is given by:

$$\frac{1}{K_1} = \frac{1}{k_l} + \frac{PC^0}{k_g}, \quad (19)$$

where

K_1 = the overall liquid coefficient, m/s,

k_l = mass transfer coefficient for the aqueous film, m/s,

k_g = mass transfer coefficient for the gas film, m/s,

PC^0 = the partition coefficient for the vaporizing species, CH_3I or I_2 (concentration in aqueous phase/concentration in gas phase).

The mass flux across the gas-liquid phase boundary can be expressed as:

$$J_1 = K_1(i) [Cl_1 - Cg_1 \cdot PC_1^0], \quad (20)$$

where

J_1 = the mass flux of species i , mol/m² s,

Cl_1 = aqueous concentration of species i , mol/m³,

Cg_1 = gas concentration of species.

The mass flux equation can be integrated, if it is assumed that there is no other method of loss, to give:

$$\frac{dCl_1}{dt} = -Kl_1 (Cl_1 - Cg_1 \cdot PC_1^0)/L, \quad (21)$$

where L is the depth of the pool, m, and

$$Cl_1 = Cg_1 \cdot PC_1^0 + (Cl_1^0 - Cg_1 \cdot PC_1^0) \exp(-Kl_1/L). \quad (22)$$

If the concentration in the gas is negligibly low, then:

$$Cl_1 = Cl_1^0 \exp[-Kl_1/L]. \quad (23)$$

The half-life, $t_{1/2}$, for organic iodide vaporization may be defined as the time necessary for the aqueous concentration to drop to one-half its original value by vaporization. Thus,

$$t_{1/2} = \frac{0.693 \cdot L}{Kl_1} \quad (24)$$

Using the method of Liss and Slater,¹⁶ we calculate for CH_3I :

$$Kl(\text{CH}_3\text{I}) = 3.00 \times 10^{-5} \text{ m/s} \quad (25)$$

This gives

$$t_{1/2}(\text{CH}_3\text{I}) = 2.3 \times 10^4 \cdot L \quad (26)$$

From Eq. (24), a pool 1 m in depth would require 2.3×10^4 s (6.4 h) to vaporize one-half of its CH_3I .

Radiation produces water radiolysis products, such as OH , H_2O_2 , H , and e_{aq}^- , which can react with dissolved iodine species. These interactions are pH dependent. At a pH < 7.0,¹⁷ iodide ions, I^- , can be converted into I_2 . A pH effect is also likely when organic iodide solutions are irradiated. Habersbergerova and Sistek¹⁸ report that the irradiation of solutions containing $0.1\text{--}1.8 \times 10^{-4}$ m CH_3I borated (0.28 m H_3BO_3 + 0.153 m NaOH) at pH 9.5 produced a decrease in the concentration of CH_3I and the formation of I^- . At a dose of 10^4 rad, the CH_3I was quantitatively transformed into I^- . Shankar et al.¹⁹ detected I_2 [$G(\text{I}_2) = 2.05$] instead of I^- when 0.1 m CH_3I solutions at pH 6 were irradiated. This result is consistent with the observation that I^- can be converted to I_2 under irradiation at pH < 7.

3.3 ORGANIC TELLURIUM COMPOUNDS

Inorganic tellurium, in the form of Te, alkali metal tellurides, or tellurium halides, can react with a variety of organic compounds. In general, these reactions are not as well studied as those leading to the formation of organic iodides. Elemental tellurium reacts with organic halide compounds to produce tellurides and can also replace hydrogen or SO_2 groups in organic compounds.²⁰ In addition,²⁰ deposits of elemental tellurium were reportedly removed by reactions with organic free radicals generated by the decomposition of a host of organic species, including methane, butane, acetone and several other ketones, diethyl ether, and benzophenone. As noted in Sect. 3.1, free radicals in a radiation field can form from neutral molecules. The volatility of organic tellurium compounds varies with molecular size and structure. Dimethyl telluride $(\text{CH}_3)_2\text{Te}$, has a boiling point of 94°C at a pressure of 0.103 MPa (770 torr), and diethyl telluride $(\text{CH}_3\text{CH}_2)_2\text{Te}$, has a normal boiling point of $137\text{--}138^\circ\text{C}$.²⁰

The process of beta decay of atoms contained in various types of organic molecular systems can lead to the formation of organic species containing the daughter element. The recoil energy of beta release may lead to the formation of fragment molecules, or it may be absorbed by the parent molecule and its surroundings. Organic tellurium compounds have been formed by decay of organic ^{125}Sb molecules.²¹

An interesting corollary to the radiogenesis of organic tellurium compounds is the beta decay of organic tellurium compounds to form organic iodides. Thus, Llabador and Adloff²² report that diphenyl ^{132}Te , $(\text{C}_6\text{H}_5)_2^{132}\text{Te}$, and dibutyl ^{132}Te , $(\text{C}_4\text{H}_9)_2^{132}\text{Te}$, produced significant quantities (>30% yield) of $\text{C}_6\text{H}_5^{132}\text{I}$ and $\text{C}_4\text{H}_9^{132}\text{I}$.

3.4 SUMMARY OF REACTION OF ORGANIC COMPOUNDS WITH IODINE

The reactions that were emphasized in this section involved free radicals and radiation effects. The importance of free radicals in the formation of organic iodides is not a new idea. More than 20 years ago, Atkins and Eggleton²³ suggested that organic free radicals reacting with iodine were the source of organic iodides in the DIDO and PLUTO reactor shells.

The reactions to form or decompose organic iodides are best viewed as a dynamic system in which iodine species enter containment and interact with a complex gas mixture (Table 1), with transport to and from surfaces and aqueous solution where further reactions may occur. Three approaches for evaluating the chemistry of this dynamic system can be suggested. The first approach involves calculational studies of gas phase reactions and reactions involving the gas phase and aqueous solution. These calculations would need to include the species listed in Table 1 plus absorption of radiation. This type of calculation is underway at ORNL and is discussed in Sect. 6.

The second type of study includes laboratory-scale experiments to evaluate the rate of formation and decomposition of organic iodides under reactor accident conditions. The work of Habersbergerova and Bartonicek,^{13,14} cited above, is an example of this type of study. Work of this type is also underway at ORNL (see Sect. 6).

The third type of study involves the release of iodine into large vessels. These experiments are considered in Sect. 5.

4. ORGANIC MATERIAL IN CONTAINMENT

A wide variety of organic materials will be present in reactor containment. In this section, we consider materials such as coatings, oils, seals, and plastics. Emphasis will be placed on the degradation of these materials by radiation and the resultant formation of vapors and free radicals.

It should be borne in mind, however, that the organic species produced by materials in containment or in the reactor vessel will be an addition to the ambient concentration of hydrocarbons. The worldwide background methane concentration is $870 \mu\text{g}/\text{m}^3$ ($5.4 \times 10^{-8} \text{ mol}/\text{L}$), and the background of larger hydrocarbons is $160 \mu\text{g}/\text{m}^3$.²⁴ In addition, urban air contains several hundred micrograms per cubic meter of "natural gas" methane that must be included in the worldwide background. Thus, we must expect a background in containment of methane and higher hydrocarbons of $\sim 5 \times 10^{-8}$ to $1 \times 10^{-7} \text{ mol}/\text{L}$.

We may note that the background amount for hydrocarbons is within the range of methane concentrations used in the study of Habersbergerova and Bartonicek,^{13,14} as cited in the previous section. It is well to observe that these investigators detected a significant I_2 to CH_3I conversion with these methane concentrations.

4.1 PAINTS AND COATINGS IN CONTAINMENT

4.1.1 Types of Organic Compounds

The types of organic compounds in paint coatings vary with the type and manufacturer of the paint. Table 3 lists the types of organic compounds evaporated from two types of paint,²⁵ showing that a wide variety of organic compounds may be present. These compounds could include saturated hydrocarbons, unsaturated hydrocarbons, carbonyls, esters, aromatics, or amines.

Table 3. Organic compounds evaporated from paints

Enamel surface coating		Modified acrylic, polyester enamel	
Chemical name	Wt %	Chemical name	Wt %
Mineral sprits (alkanes)	67.7	Naptha	12.4
Isomers of xylene	4.0	Toluene	4.8
Toluene	3.2	Methyl ethyl ketone	41.24
Acetone	6.3	Butyl cellulose	31.00
Methyl ethyl ketone	6.8	Isobutyl acetate	12.92
Methyl isobutyl ketone	2.7		
Methyl alcohol	0.7		
Ethyl alcohol	0.5		
Isopropyl alcohol	1.9		
N-butyl alcohol	2.8		
Ethyl acetate	0.3		

4.1.2 Reaction of Paints with Iodine

Bennett et al.² have studied the formation of organic iodides that result from the reaction of iodine (I_2) vapor with organic paint coatings in the absence of radiation. They used Amercoat 66 (epoxy-based) and Phenoline 302 (phenolic-based) paints. Methyl iodide and larger alkane iodides were detected with a gas chromatograph. The yield of organic iodides increased as the temperature of the reaction system increased. The organic iodide concentration was ~ 10 times higher at 150°C than at 100°C and ~ 100 times higher at 250°C than at 100°C . The maximum conversion was $\sim 10^{-3}\%$, and the yield of organic iodide was not significantly changed by the presence of water vapor or hydrogen.

The initial I_2 concentrations in these experiments were varied from 1 to 23 g/m^3 . In accident situations, the air concentrations of I_2 are expected to be several orders of magnitude smaller. However, Bennett et al. expect relatively more organic material to be present in reactor containment than in their experimental tests.

In addition to organic iodides, hydrocarbon compounds were detected in this study. A test simulating an aged coating was conducted with a coating that was heated to 100°C in flowing nitrogen for 1 week. The CH_3I was not significantly reduced, but the amount of ethyl iodide, $\text{C}_2\text{H}_5\text{I}$, decreased to their limit of detection. Bennett et al. suggest that this result indicates that most of the $\text{C}_2\text{H}_5\text{I}$ comes from reaction with organic vapor, while CH_3I results from reaction with coating surfaces.

One other interesting aspect of the Bennett studies should be noted. In the tests with paint surfaces that were not aged, the amount of $\text{C}_2\text{H}_5\text{I}$ was greater than or approximately equal to the amount of CH_3I .

4.1.3 Organic Iodide Sorption or Desorption on Paint

Rosenberg et al.¹ studied the sorption-desorption characteristics of CH_3I on commercial coatings: acrylic latex-base (Amercoat 1756), vinyl-base (Amercoat 33HB), epoxy-base (Amercoat 66), and phenolic-base (phenoline 302) paints. Only the sorption and desorption of CH_3I were considered, not its formation rate or mechanism. It was concluded that none of the commercial coatings had any significant effect in reducing airborne CH_3I concentrations during a loss-of-coolant accident. Conversely, some commercial coatings approach "perfect sink" characteristics for I_2 .

4.1.4 Effect of Radiation on Paint

Schönbacher et al.²⁶ studied the effects of radiation on a number of commercial paint coatings. The basic effect of radiolysis in paint coatings is to break up the highly polymeric binders, resulting in changes in the structure, oxidation, embrittlement, blistering, and evolution of gases. These studies found that the extent of radiation damage depended only on the absorbed dose, not on the dose rate.

Also, the extent of radiation damage is quite variable, depending on pigments, additives, and the type of paint.²⁶ Highly pigmented coatings are generally more resistant to radiation than those containing lesser amounts of pigments. Carbon black inhibits radiation damage, and titanium dioxide appears to accelerate damage.

The surface on which the coating is applied can influence the radiation stability of the coating. Degradation begins at lower doses for coatings on steel than coatings applied to asphalt.

Radiation effects are usually reported in terms of darkening or blistering of the coatings. The effects that are important to the formation of organic iodides are likely to include the release of organic vapors, the creation of chemically reactive surface sites, and the formation of organic free radicals.

4.2 INSULATION AND SEALS

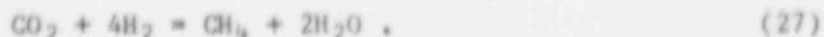
The largest amount of organic material in containment occurs in cable insulation and jacketing.²⁷ Other organic materials occur in seals, gaskets, connectors, circuit boards, and lubricants.

Many of these materials are in the form of polymers, such as polyethylene, polyvinyl chloride, neoprene, and hypalon. The natural aging of these polymers will be accelerated by radiation. The combination of aging and radiation damage will produce changes in polymer structure, gaseous products, and oxidation. Typical results for the irradiation of polyethylene indicate the formation of peroxy radicals ($\text{ROO}\cdot$) and the evolution of H_2 , CO , and CO_2 gases.²⁸ Peroxy radicals result from the reaction of oxygen (O_2) with organic free radicals. Since iodine is also a good free radical scavenger, irradiation of organic polymers in the presence of both air and iodine (I_2) vapor may yield organic iodides as well as organic peroxides.

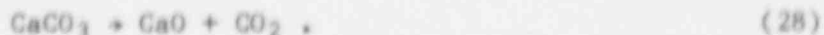
The stability of a polymer to aging and radiation degradation depends on its chemical structure. Aromatic polymers, such as polystyrene, tend to be more stable in a radiation field, while Teflon and KEL-F have very poor resistance to radiation damage. Sisman et al.²⁹ have described the relative radiation resistance of a large number of common polymers.

4.3 GAS PHASE PRODUCTION OF METHANE

Small amounts of methane may be produced in containment by the radiation-induced reaction of CO_2 with H_2 . The overall reaction can be written:



In a severe accident, decomposition of concrete could produce additional CO_2 , at temperatures $>1167 \text{ K}$,³⁰ by the reaction:



Air contains ~0.05 wt % CO₂. Studies of the coolant composition of advanced gas-cooled reactors (AGRs) have shown that a steady-state methane concentration is attained by the introduction of hydrogen or methane into the CO₂ coolant.¹⁵ The presence of mild steel in the system gave a significant increase in the steady-state level of methane. The steady-state concentrations of methane in these tests ranged up to 400 volumes per million.

It is difficult to convert results from AGR coolant to conditions that might exist in containment. The coolant tests were run with CO₂ gas that contained additional H₂, CH₄, or CO in the ranges of <1000 ppm. In containment, the level of hydrogen could be approximately the same or even greater than the level of carbon dioxide.

4.4 ORGANIC MATERIAL IN PRIMARY SYSTEM

4.4.1 Carbon Impurities in Fuel

Uranium oxide (UO₂) or uranium alloy used as fuel in nuclear reactors contains trace amounts of uranium carbide and uranium hydride impurities.⁴ These impurities could produce small amounts of organic compounds inside the fuel. In uranium oxide analyzed at Savannah River,⁴ the hydrogen content averaged ~0.5 ppm by weight and the carbon, 500 ppm. If all the hydrogen reacted, 2 ppm methane would form as:



Methane, measured in fission gases at the Savannah River plant, averaged 0.02 cm³ per kg UO₂ (0.014 ppm by weight). This work demonstrated that far less than the maximum 2 ppm methane was formed.

The small amount of methane that formed could react with fission product iodine to form CH₃I inside the fuel.

The Savannah River study also evaluated the maximum amount of iodine that could theoretically be converted to CH₃I. Based on total conversion of hydrogen to methane (2 ppm), they calculated the maximum % I₂ inventory converted to CH₃I to be 0.035. When the actual measured values of methane were used in the calculation, the maximum % I₂ inventory converted to CH₃I decreased to 0.00067.

4.4.2 Ion-Exchange Resin

Ion-exchange resins may be degraded by radiation following a nuclear reactor accident. A compilation of experimental data by Wyant³¹ indicates that quaternary amine-type exchangers are more susceptible to radiation damage than the sulfonic acid types, and the sulfonic acid types are more susceptible than the phenolics.

Bartonicek et al.³² studied the radiolysis of the amine-based resin AV-17 × 8 cs. The resin was irradiated wet to doses up to 2.3 × 10⁶ Gy.

In the solution above the resin, trimethylamine [up to 0.19 mol/L $(\text{CH}_3)_3\text{N}$], dimethylamine [up to 0.04 mol/L $(\text{CH}_3)_2\text{NH}$], methylamine (up to 0.0 mol/L CH_3NH_2), and ammonia (<0.01 mol/L NH_3) were measured. Gaseous radiolytic products included hydrogen, methane, ethane, and unidentified C_3 and C_4 hydrocarbons. The concentration of methane above the aqueous solution was 4 orders of magnitude higher than the average worldwide background of 5.4×10^{-8} mol/L.

4.4.3 Boron Carbide-Steam Reaction

Boiling-water reactor control rods contain ~1000 kg of boron carbide (B_4C). Some pressurized-water reactors (PWRs) also contain B_4C control material. The B_4C can be exposed to steam at temperatures $>1400^\circ\text{C}$, the melting point of its stainless steel containers. The reaction of B_4C with steam can be described by the three reactions:



The relative importance of these reactions depends upon the steam pressure, the initial hydrogen pressure, the temperature, and reaction rates. High hydrogen-to-steam ($\text{H}_2/\text{H}_2\text{O}$) ratios and low temperatures favor the formation of methane (CH_4), and low hydrogen-to-water ratios favor carbon dioxide (CO_2) formation. Figure 1 shows calculated values of mol CH_4 produced as a function of temperature for three hydrogen-to-steam ratios ($\text{H}_2/\text{H}_2\text{O}$). The mol CH_4 given are based on the B_4C -steam reaction of the entire boiling-water reactor (BWR) core inventory of boron carbide. Reaction of lesser amounts of control rod material would be proportionally lower.

The mol amounts of methane shown in Fig. 1 are the results of equilibrium thermodynamic calculations without radiation. Radiation in the reactor vessel would convert some of the methane to organic free radicals, such as CH_3 and CH_2 . The reaction of iodine with organic free radicals was discussed in Sect. 3.

4.5 SUMMARY OF ORGANIC MATERIALS

The formation of organic iodides may be limited by the amount or the chemical form of the organic compounds. The short review presented here illustrated the wide variety of organic materials that are present in reactor containment. The lower limit of organic compounds is set by the normal background of hydrocarbons in air (i.e., 5×10^{-8} to 1×10^{-7} g-mol/L). This background of organic species is composed largely of the saturated hydrocarbons methane and ethane. Materials such as paints, seals, insulation, and ion-exchange resin could be sources of many different types of organic compounds. Radiolysis of these materials can produce organic compounds and free radicals as degradation products.

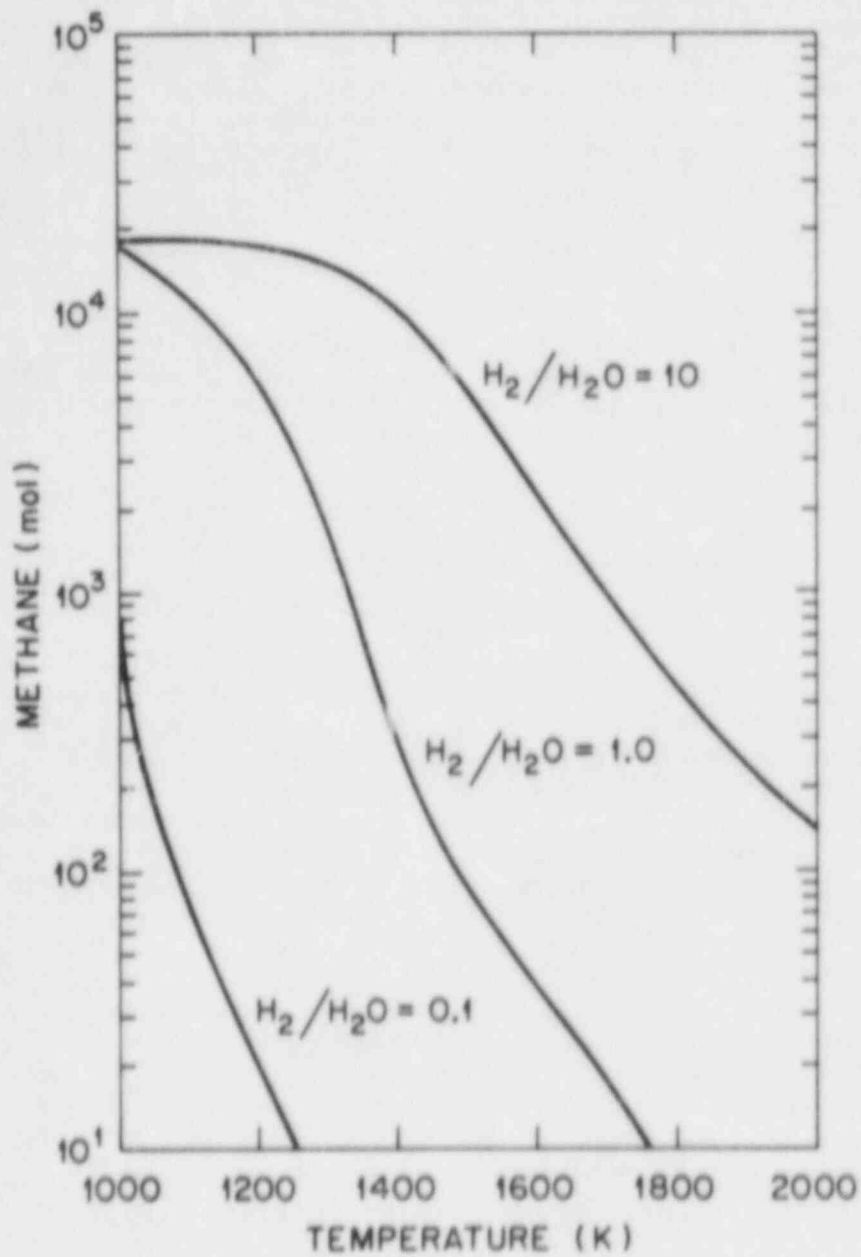


Fig. 1. Methane (mol) calculated from the B_4C -steam reaction.

Wing³³ has performed a calculational study of the amount of organic gases generated from the postaccident radiolysis of organic materials in containment. In these calculations it was assumed that the fission products remain airborne and are uniformly distributed in containment. The fission product inventory and radiation levels were taken from recent reports on the best-estimate LOCA radiation signature.⁶ In one series of calculations based on the plant parameters of a BWR plant (containment volume $4.64 \times 10^4 \text{ m}^3$), Wing gave a maximum rate of organic gas generation of $4.8 \times 10^{-1} \text{ mol/s}$ at 2000 s after an accident. Figure 2 gives a plot of the cumulative buildup of organic gas concentration, due to radiolysis, as a function of time after the accident. This figure was prepared by using data given by Wing³³ and assuming a total retention of gas in a volume of $4.64 \times 10^4 \text{ m}^3$. An organic gas concentration of ~ 2 orders of magnitude above ambient is indicated 1 h after the accident. For comparison, assume a hypothetical core in which the entire core inventory of iodine was distributed in a volume of $4.64 \times 10^4 \text{ m}^3$, giving an iodine concentration of $3 \times 10^{-6} \text{ g-mol/L}$. This simple analysis indicates that radiolysis of organic materials in containment could produce gas phase organic gas concentration that greatly exceeds the gas phase iodine concentration.

The atmosphere of the Three Mile Island Unit-2 (TMI-2) reactor building contained 0.069 mol % hydrocarbons 13 months after the accident of March 28, 1979.³⁴ This corresponds to a hydrocarbon concentration of $\sim 3 \times 10^{-5} \text{ mol/L}$. At this time, the organic iodide concentration was measured as 3 to $4 \times 10^{-11} \text{ } \mu\text{Ci } ^{129}\text{I/cm}^3$ or $\sim 2.5 \times 10^{-10} \text{ g } ^{129}\text{I/L}$ as organic iodide.

5. CONTAINMENT VESSEL EXPERIMENTS

5.1 BACKGROUND OF TESTS

During the 1960s many large-scale experiments were carried out to evaluate the formation and removal of organic iodides. In 1972 a major review of containment vessel experiments³ cataloged 69 separate tests. The studies were carried out in vessels that ranged in size from 0.2 m^3 to $12,000 \text{ m}^3$.

In general, the tests were run by releasing iodine (I_2) or HI into the vessel and then evaluating the amount of I_2 and organic iodide in the gas. The designation of iodine as inorganic or organic was based on the part of the filter pack that trapped the iodine. The vessel atmosphere varied from ambient temperature air to a number of steam/air or steam/helium combinations.

5.2 OVERVIEW OF TEST RESULTS

Postma and Zavadoski³ derived an equation relating the percent organic iodide formed to the initial concentration of I_2 . The least squares fit of 69 experiments gave the equation:

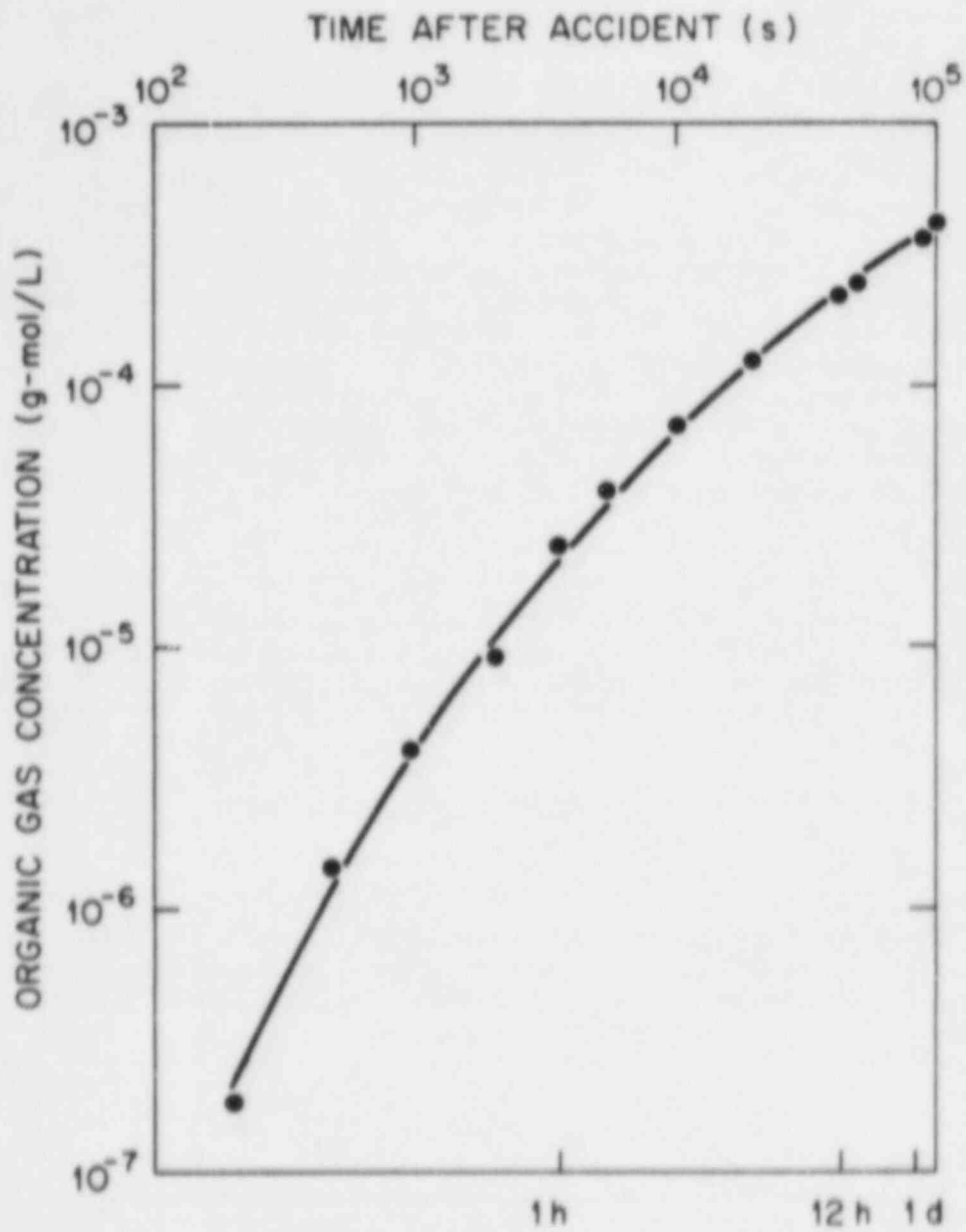


Fig. 2. Cumulative organic gas concentration due to organic material radiolysis.

$$\text{percent organic iodide formed} = 0.188 \times C_m^{-0.26}, \quad (1)$$

where C_m is the concentration (mg/m^3) of I_2 in the vapor. The initial I_2 concentrations that were fit to this equation varied from $0.008 \mu\text{g}/\text{m}^3$ to $237 \text{ mg}/\text{m}^3$. The data scatter for Eq. (1) was a factor of ~ 15 .

Postma and Zavadoski further note that a high percent conversion to organic iodides was obtained at lower concentrations and smaller vessel sizes.

5.3 DISCUSSION OF CONTAINMENT TESTS

Examination of the data obtained in containment experiments reveals a broad scatter in the percent of iodine release that was converted to organic iodide. This may be due, in part, to the difficulty in identifying and measuring extremely low iodine concentrations. For example, in tests run by Megaw and May,³⁵ the percent conversion to organic iodide corresponded to vapor phase iodine concentrations of 9×10^{-16} g-at. l/l. to 2×10^{-13} g-at. l/l. This gives iodine species concentration as low as 5×10^8 molecules/l.

In most tests, organic iodides were identified by their position in the filter system. Thus, it was assumed that inorganic iodine was removed by certain filters or carbon impregnated material. However, Collins et al.³⁶ have shown that the interpretation of the distribution of iodine forms in terms of iodine activity on filter materials can lead to misclassification. Factors that can give errors in the interpretation include gas residence time in the individual components of the filter pack, the total time the gas is passed, the humidity of the gas, the amount of iodine presented to the carbon, and the surface of the carbon impregnated filter. These investigators have shown significant differences in the distribution of CH_3I on May Pack components by simply changing the relative humidity of the gas.

An additional factor in most containment tests is the absence of radiation levels that are expected in a severe accident. The observation that high elemental iodine concentrations correlated with low percent conversion to organic iodide may be due, in part, to chemical reactions that are restricted by the amount of reactive organic compounds. As noted in Sect. 4, radiation can degrade organic material and produce free radicals. Thus, radiation could change the chemical interactions enough to give relationships of concentration of I_2 versus percent conversion to organic iodide that are different from the unirradiated containment tests.

Tests involving irradiated fuel tend to show a higher percentage of the iodine released converted to organic iodide. Equation (33) gives a fit of seven experiments performed with irradiated fuel:³⁷⁻⁴⁰

$$\text{percent organic iodide} = 1.89 \times C_m^{-0.18}, \quad (33)$$

This equation has the same form as Eq. (1), which was a fit by Postma and Zavadoski, of both simulated iodine release and release from irradiated

fuel. The percent organic iodide given by Eq. (33) is ~1 order of magnitude greater than the values given by Eq. (1).

In the first TREAT fuel rod failure experiment,³⁷ 6.7% of the iodine that left the primary vessel was organic iodide. In this test the TREAT reactor reached a power of 30 MW at 8 s and was shut down at 28 s when the cladding temperature was 965°C. Thus, fission product release occurred under intense irradiation. The carrier gas was a mixture of steam and helium.

In the second TREAT fuel rod failure experiment, a cladding temperature of 1316°C was reached, and 2.5% of the iodine carried out of the primary vessel was organic iodide. Most of the organic iodide was believed to have formed between 1.5 min and 17.5 min after the start of the test. It is interesting to observe that although the second test gave a 2.5% conversion to organic iodide compared with 6.7% in the first test, the total amount of organic iodide formed was almost identical in the two experiments.

Examination of experiment D-1 of the Containment Systems Experiment⁴¹ indicates that organic iodides build up rapidly after iodine release. In this experiment, 43.17 mg of iodine, including 31 µg of organic iodide, was released into a 65-m³ vessel filled with air and steam, maintained at 122°C and 0.334 MPa (48.5 psia) by injection of steam. In addition to elemental iodine and organic iodine, particulate iodine and unknown iodine forms were also present in the vessel. The documentation of this experiment by Hilliard and Coleman⁴¹ includes data on the amounts of elemental iodine, organic iodide, particulate iodine, and unknown iodine forms at 15, 30, 40, and 50 min after the start of the experiment. Analysis of these data, using an iodine mass balance (see Fig. 3), shows that a maximum amount of organic iodide occurs at ~2 min after the start of the experiment. Also, the amount of elemental iodine decreases in uniform manner after 2 min. The data used in Fig. 3 at times >15 min, as well as the initial organic iodide concentration, were taken directly from the reported experimental results. The derived value for the initial amount of elemental iodine was obtained from the amount of iodine released less the amount of iodine as organic iodide, particulate iodine, and unidentified iodine forms.

It could be argued that the maximum in organic iodine early in the experiment is due to production of organic iodide in the iodine release apparatus used in the Containment Systems Experiment. However, the small amount of organic iodine at time zero and tests of the iodine release apparatus reported in BNWL-1001⁴² do not indicate that this is the source of organic iodide. Experiments of Megaw and May³⁵ and of Croft and Iles⁴³ also show organic iodine levels that peak early in the tests.

In a series of tests in the Containment Research Installation, Parker et al.⁴⁴ reported that a significant portion of the organic iodide formed promptly at the start of the tests. However, plots of percent of inventory as organic iodide vs time (Fig. 1.16, Parker et al.) gave an

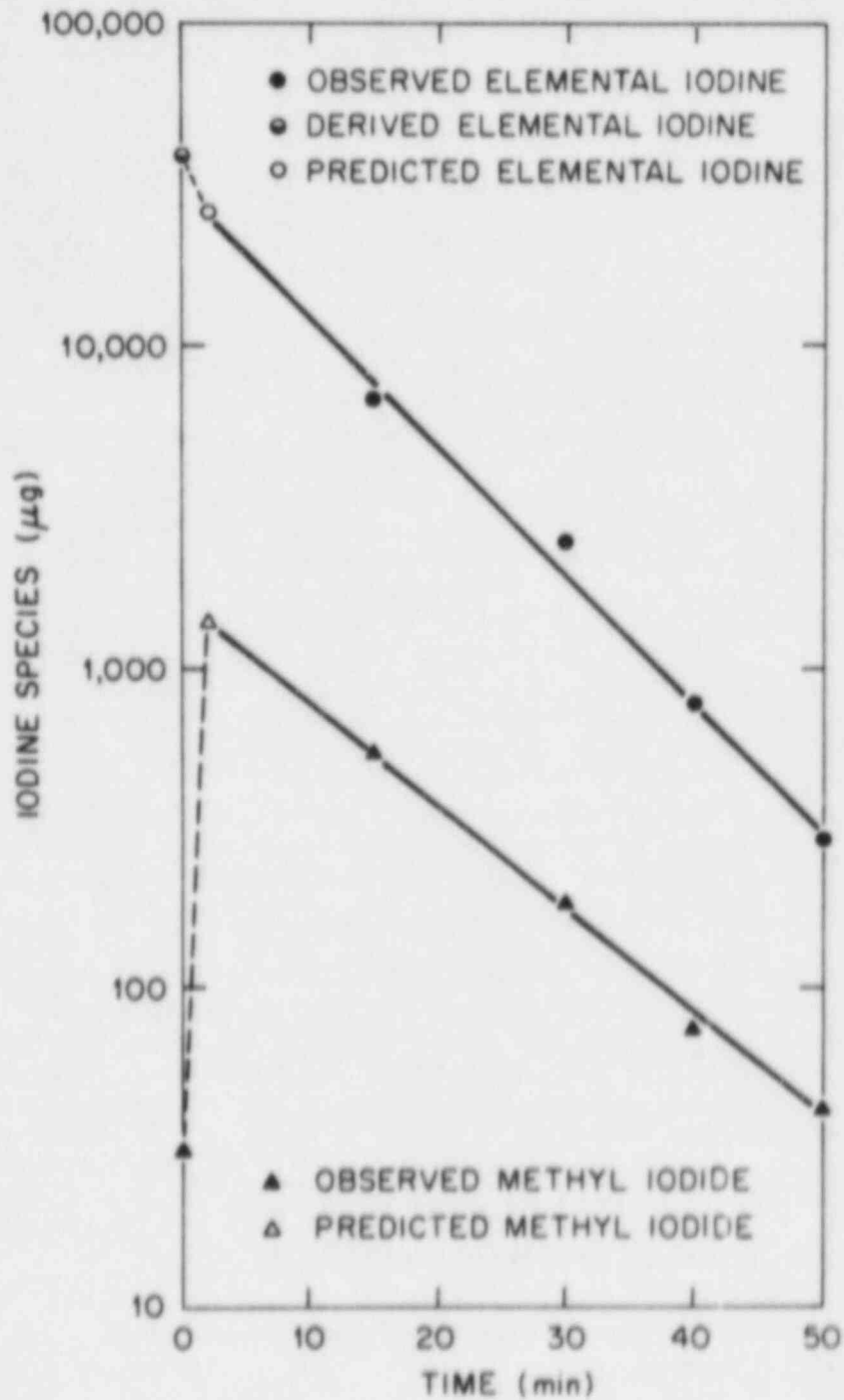


Fig. 3. Mass of iodine species from containment system experiment D-1.

increase with time (positive slope) at times as great as 2000 min. In these tests only the portion of iodine that desorbed from charcoal in a moist-air elution was identified as organic iodine. This method tends to give lower values than those obtained by assigning all iodine on charcoal as organic.

5.4 SUMMARY OF CONTAINMENT TESTS

The review of Postma and Zavadoski³ showed that low iodine releases resulted in relatively high percent conversion to organic iodide and high iodine releases correlated with low percent conversion to organic iodide. This is the basis for the correlation given by Eq. (1). Stating this observation in another way, we may say that the total concentration of organic iodide formed tended to be relatively insensitive to the concentration of iodine released. This tendency is especially noticeable when a given test series at a single facility is examined. For example, the two TREAT experiments had release concentrations of $64 \mu\text{g}/\text{m}^3$ and $174 \mu\text{g}/\text{m}^3$, with a conversion to organic iodide of 6.7% and 2.5%, respectively.^{37,38} This resulted in $4.3 \mu\text{g}/\text{m}^3$ converted to organic iodide in both tests. In another example, four tests by Parker and Martin in the Containment Research Installation had ^{131}I plus ^{127}I release concentrations of $5 \mu\text{g}/\text{m}^3$, $1 \mu\text{g}/\text{m}^3$, $35 \mu\text{g}/\text{m}^3$, and $125 \mu\text{g}/\text{m}^3$, with percent conversion to organic iodide of 0.8, 0.7, 0.3, and 0.03, respectively.⁴⁵ The resultant conversion to organic iodide was then $4.0 \times 10^{-2} \mu\text{g}/\text{m}^3$, $3.5 \times 10^{-2} \mu\text{g}/\text{m}^3$, $1.0 \times 10^{-1} \mu\text{g}/\text{m}^3$, and $3.8 \times 10^{-2} \mu\text{g}/\text{m}^3$, respectively.

The tests run with irradiated fuel and its accompanying radiation gave higher percentage conversion to organic iodide than simulant tests. This comparison is important because any conceivable accident would occur in the presence of radiation.

Examination of many of the containment tests shows that a substantial proportion of the organic iodide formed within minutes of release.

The first sample of reactor building atmosphere following the accident at TMI-2 was taken 75 h after shutdown. The measured level of iodine (inorganic plus organic) at that time was 0.005% of the core inventory.⁴⁶ All measurements of TMI-2 reactor building iodine indicate that the principal species were organic. However, the long time interval before the first sample prevents a definitive analysis of the mechanism of formation or levels at shorter times.

6. CONCLUDING DISCUSSION

6.1 ASSESSMENT OF ORGANIC IODIDE FORMATION RATE

The ultimate aim of studies of organic iodide formation in containment is a description of the amounts of organic iodide that can be expected after an LWR accident. What is really needed for this description are rates of formation and removal that can be used to express the change of organic iodide concentration with time. A suitable form for this is given by the equation:

$$\frac{dC}{dt} = \alpha(C^* - C) - QC, \quad (34)$$

where

- C = concentration of organic iodide at time t ,
 C^* = equilibrium concentration of organic iodide,
 Q = a constant for removal of organic iodide; this may include gas flow to the off-gas treatment system or leakage,
 α = organic iodide formation constant (s^{-1}).

Additional terms may be used to account for organic iodide dissolved in water, and the whole expression should be included in a series of differential equations that accounts for inorganic as well as organic iodine forms. The iodine transport and chemistry model "Impair," as developed at KFK and modified at ORNL, has the proper structure for evaluating organic and inorganic iodine concentrations.

Two constants in Eq. (34) need further evaluation before calculations of organic iodide concentrations in containment can be performed. As noted in Sect. 5, the containment tests indicated that a large proportion of the organic iodide formed in a matter of minutes. The formation of organic iodide, expressed as the first term on the right of Eq. (34), can be integrated to give:

$$C(t) = C^*(1 - e^{-\alpha t}) + C(0) e^{-\alpha t}, \quad (35)$$

If we assume that 99% of the value of C^* is reached in a given time, t , then:

$$0.99 = \frac{C(t)}{C^*} = 1 - e^{-\alpha t}, \quad (36)$$

when

$$t = 60 \text{ s (1 min)},$$

$$\alpha = 7.7 \times 10^{-2} \text{ s}^{-1},$$

and when

$$t = 3600 \text{ s (1 h)},$$

$$\alpha = 1.3 \times 10^{-3} \text{ s}^{-1}.$$

As a preliminary estimate, α can be approximated as $1.3 \times 10^{-3} < \alpha < 7.7 \times 10^{-2}$.

Evaluation of C^* is more difficult. Containment experiments can be used as a guide, but there is a range of values for expressing C^* values. Equations (1) and (33) have the form:

$$\begin{aligned} \% \text{ organic iodide} &= a \cdot (\text{release concentration})^b \\ &= a \cdot C_m^b \end{aligned} \quad (37)$$

From this, C^* can be expressed as:

$$C^* = \frac{a}{100} \cdot C_m^{b+1} \quad (38)$$

Postma and Zavadoski³ gave values of $a = 0.188$, $b = -0.26$ for 69 containment experiments. Equation (33), based on seven experiments that used irradiated fuel, gave $a = 1.89$, $b = -0.18$. In the review by Postma and Zavadoski, they show a curve (Fig. 13 in ref. 3) that represents the maximum percent conversion to organic iodides from containment experiments plus radiolysis experiments. From this curve, we calculated $a = 11.5$, $b = -0.28$. Use of these data gives C^* that is a factor of 60 greater than the average value from the 69 containment tests. It may seem prudent to use these constants as they give the greatest conversion to organic iodides. However, these constants also indicate a 100% conversion to organic iodide when the release concentration, C_m , is $< 4.4 \times 10^{-4} \text{ mg/m}^3$. Figure 4 shows values of C^* plotted according to Eq. (38), with three different values for a and b .

This evaluation of a and C^* indicates that, based on present data, both constants could be in a range where the high value is a factor of ~60 times the low value. The wide range of organic iodide concentration for a given release concentration, illustrated in Fig. 4, is due in part to the simplification that relates organic iodide only to the iodine release concentration. Other factors are likely to be important as well. In Sect. 5, examples were given that showed in some test series there was little or no difference in the concentration of organic iodide when the amount of iodine released was varied. This indicates that other factors, most likely the amount of organic compounds amenable to reaction or the chemical form of iodine, are important in determining the extent of reaction.

In addition, accident conditions will involve circumstances and materials that cannot be duplicated in large containment tests. For example, the iodine transport and release model IMPAIR allows for the formation of silver iodide as part of its iodine balance. In laboratory-scale experiments at ORNL, we observed that the combination of silver and radiation is very effective in converting either organic iodine or inorganic iodine into silver iodide. For example, a sample of 1×10^{-4} molar CH_3I in water containing a suspension of aerosol material from fission product release test HS-4⁴⁷ ($\sim 5 \times 10^{-3} \text{ M}$ in silver metal) was irradiated to 1 Mrad in a 0.8 Mrad/h ^{60}Co gamma source. As a result of the irradiation, 98% of the iodine in the CH_3I was converted to silver iodide.

6.2 ORGANIC IODIDE RESEARCH AT ORNL

An experimental and calculational program has started recently at ORNL, aimed at obtaining data for improving the understanding and

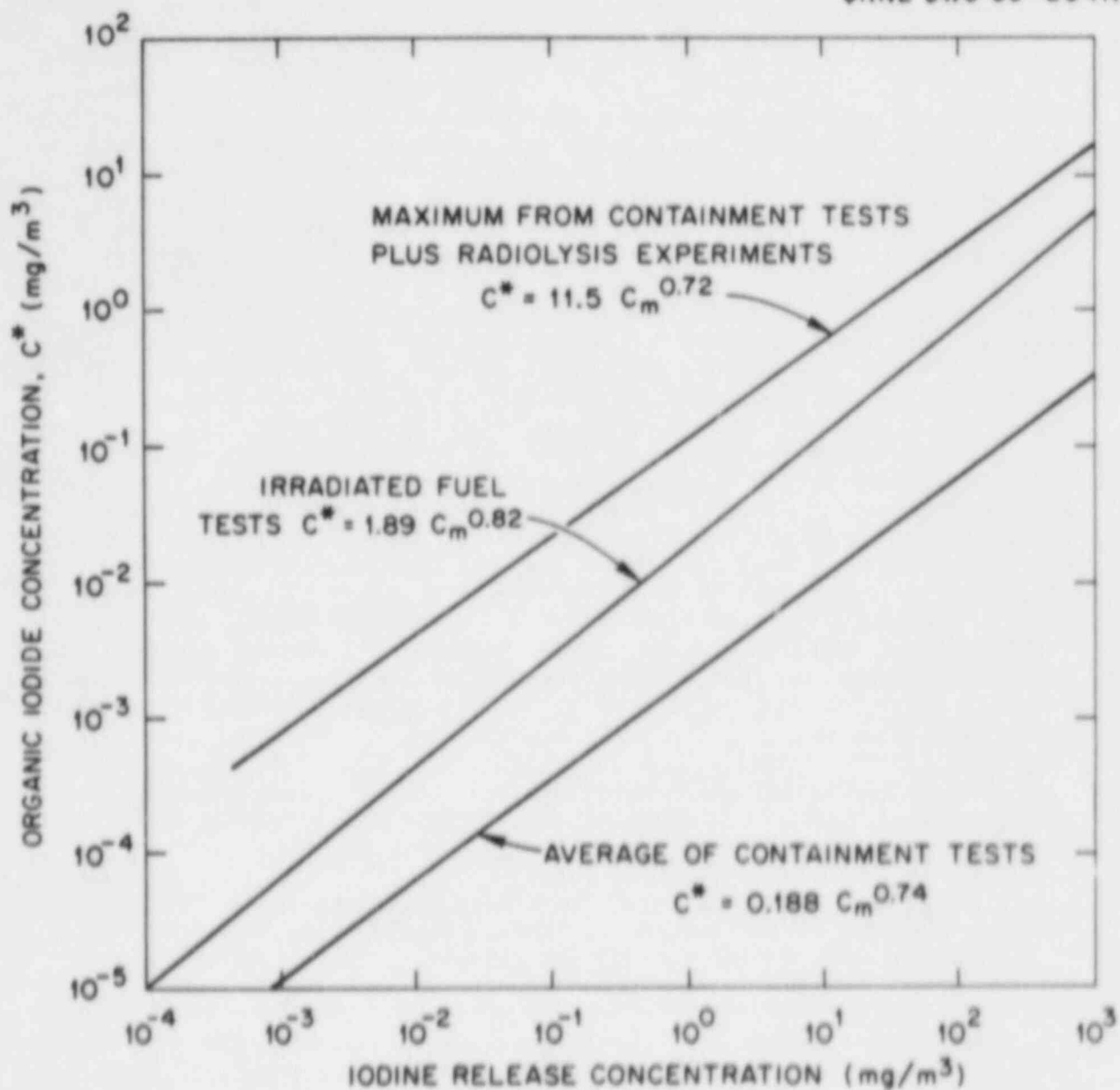


Fig. 4. Organic iodide concentration related to iodine release concentration.

predictability of organic iodides in containment. Three types of experimental tests have been planned in this work to reflect three configurations in containment that may lead to the formation of organic iodides. In the first series of tests, a selected gas mixture is bubbled through a water solution of iodine species at a given pH with or without gamma irradiation. Results of these tests are subsequently described. The second series of tests employs a quiescent water pool-air combination, and the third series will examine formation of organic iodide in a dry system. It may be noted that the containment vessel tests described in Sect. 5 reflect largely the latter case of the formation of organic iodide in the absence of water pools. In an actual LWR accident situation, organic iodides could form in water pools as well. The tests employing gas bubbling through a water pool represent the discharge of fission products and organic gas (i.e., methane) into a suppression pool accompanied by radiation.

Organic iodide formation processes are being studied in a glass apparatus, as shown in Fig. 5. This system permits studies with dry gas or an aqueous solution on the bench top or in a 0.8 Mrad/h ^{60}Co gamma source. Gas mixtures are prepared with mass flowmeters and enter the vessel through a glass frit. Hooks are provided inside for hanging coupons of painted surfaces or other organic material. Collector traps (TENAX, Carboxack B coated with SP1000 and Ambersorb XE340) are placed at the top of the vessel to retain organic iodides. After an experiment the traps are removed and placed in a Perkin-Elmer Sigma 1 gas chromatographic system. The traps are then heated to 150°C in flowing inert gas to desorb the organic iodides.

The gas chromatographic system has been calibrated to quantitatively determine CH_3I , $\text{C}_2\text{H}_5\text{I}$, and diodomethane, CH_2I_2 . The detection limit for CH_3I and $\text{C}_2\text{H}_5\text{I}$ is $\sim 0.02 \mu\text{g}$.

Tables 4 and 5 give test results from experiments designed to examine the release of a gas containing organic material, methane, in a water pool. The gas was carried into 150 mL of solution, at a flow rate of 1 L/h, through a glass frit that was located beneath the surface.

Several conclusions are readily apparent from these initial tests. First, the formation of organic iodide was greatly enhanced by radiation. In a test run using a solution of $2 \times 10^{-4} \text{ M}$ I_2 in pure water and $1 \times 10^{-2} \text{ mol}$ CH_4 , without radiation, the conversion to organic iodide was $< 1 \times 10^{-3}\%$. An identical test run with 1 Mrad irradiation resulted in a $> 20.7\%$ conversion to organic iodide.

The results also show that I_2 forms organic iodide much more readily than does I^- . The percent conversion to organic iodide, as listed in Table 4, for samples that initially contained I^- is consistently less than those given in Table 5 for samples of I_2 . The conversion to organic iodide as a function of pH, as shown by the bottom three rows of Table 4, also indicates that I_2 is the species that is reacting to form organic iodide. Iodide ions in solutions at pH ~ 7 can be converted to I_2 in the

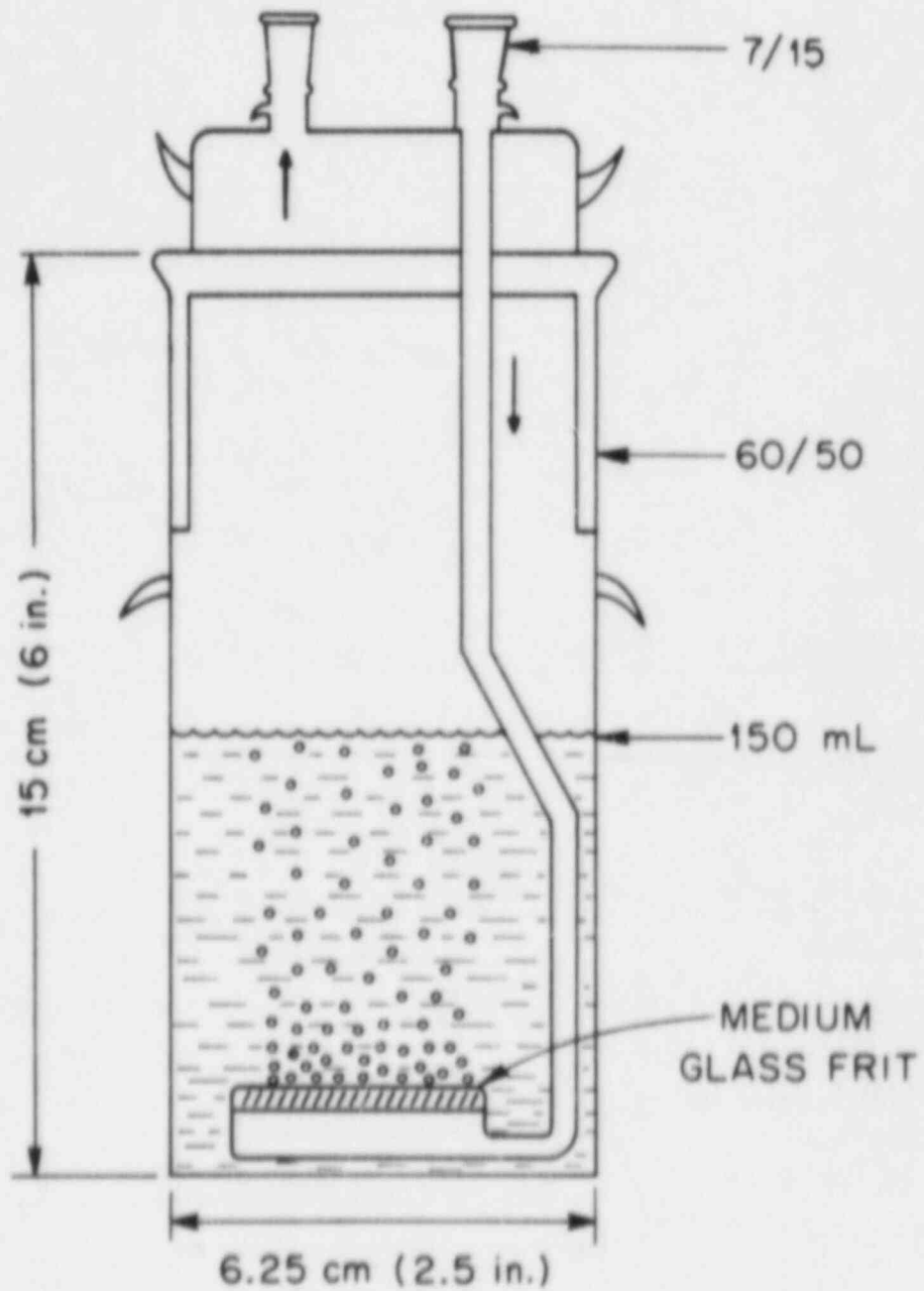


Fig. 5. Apparatus for measuring formation rate of organic iodide.

Table 4. Organic iodide formation in an iodide system with irradiation in a ^{60}Co gamma source (0.7 Mrad/h)

Test conditions 2×10^{-4} M CsI and 1×10^{-2} mol CH_4	% conversion of iodide ion to organic iodide			% of methane used to form CH_3I
	Gas phase	Aqueous phase	Total	
Pure water, 1 Mrad irradiation	6.2×10^{-3}	1.69×10^{-1}	1.75×10^{-1}	5.3×10^{-4}
Pure water, 4 Mrad irradiation	2.99×10^{-2}	2.82×10^{-1}	3.12×10^{-1}	2.4×10^{-4}
2000 ppm borate pH 4.4 1 Mrad irradiation	2.29×10^0	5.64×10^0	7.93×10^0	2.4×10^{-2}
2000 ppm borate pH 6.0 1 Mrad irradiation	5.57×10^{-2}	2.47×10^{-1}	3.03×10^{-1}	9.1×10^{-4}
2000 ppm borate pH 9.0 1 Mrad irradiation	6.2×10^{-3}	$<3.52 \times 10^{-2}$	$<4.14 \times 10^{-2}$	$<1.2 \times 10^{-4}$

Table 5. Organic iodide formation in an iodine (I_2) solution with methane-argon in a ^{60}Co gamma source (0.7 Mrad/h)

Test conditions	% conversion of iodine to organic iodide			% of methane used to form CH_3I
	Gas phase	Aqueous phase	Total	
1×10^{-4} M I_2 in pure water, 1×10^{-2} mol CH_4 , 1 Mrad irradiation	$>2.22 \times 10^0$	1.85×10^1	$>2.07 \times 10^1$	$>6.1 \times 10^{-2}$
1×10^{-5} M I_2 in pure water, 1×10^{-2} mol CH_4 , 1 Mrad irradiation	1.75×10^0	8.24×10^0	9.99×10^0	3.3×10^{-3}
1×10^{-5} M I_2 in pure water, 2×10^{-3} mol CH_4 , 1 Mrad irradiation	5.5×10^{-1}	1.09×10^1	1.15×10^1	1.7×10^{-2}

presence of radiation (see Sect. 3.2). Thus, the effect of different pHs on the yield of organic iodides, as shown in Table 4, was likely due to the conversion of some I^- to I_2 at the lower pHs and the subsequent radiation induced reaction of I_2 with organic material.

Another interesting result of these studies is that the organic iodide must have formed predominantly in the aqueous phase rather than in the gas phase. The organic iodide partition coefficients observed in these tests show that more organic iodide was present in the aqueous phase than would be expected in an equilibrium gas-aqueous partitioning. Thus, the organic iodide must have formed predominantly in the aqueous phase and was then stripped to the gas phase. It should be noted that this observation of organic iodide formation occurring largely in the aqueous solution rather than the gas applies to this system, in which an organic gas is bubbled beneath the surface. The interaction of organic material with a quiescent pool may give entirely different results, as will be investigated in additional tests.

It is clear, however, that the potential for forming organic iodide in LWR containment is not exhausted by containment tests such as those described in Sect. 5. The description of organic iodide formation, as presented in Eqs. (34) to (38), will need to be expanded with additional data to include water pool effects. The research program at ORNL has been set up to provide information on organic iodides involving water pools and also to alleviate the considerable uncertainty in the description of organic iodides [Eqs. (34)-(38)] that is based on the large-scale containment tests.

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Organic Iodide Formation Following Nuclear Reactor Accidents					
5. AUTHOR(S)				4. DATE REPORT COMPLETED	
E. C. Beahm, W. E. Shockley, and O. L. Culberson				MONTH: April YEAR: 1985	
7. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)				6. DATE REPORT ISSUED	
Oak Ridge National Laboratory P. O. Box X Oak Ridge, TN 37831				MONTH: November YEAR: 1985	
10. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)				8. PROJECT/TASK/WORK UNIT NUMBER	
U.S. Nuclear Regulatory Commission Fuel Systems Research Branch Washington, DC 20555				9. FIN OR GRANT NUMBER	
				B0453	
12. SUPPLEMENTARY NOTES				11. TYPE OF REPORT	
				NUREG/CR-4327 ORNL/TM-9627	
13. ABSTRACT (200 words or less)				6. PERIOD COVERED (Inclusive dates)	
<p>A wide variety of organic materials will be present in containment following a light-water reactor accident. Organic iodides can be produced by the reaction of fission product iodine with these organic materials. This report emphasizes the importance of free radicals and radiation in leading to the formation of organic iodide. The ultimate aim is a description of the rate of formation and removal of organic iodide, within the time span of a core heatup event, that can be used in a model of iodine behavior in containment.</p>					
14. DOCUMENT ANALYSIS -- KEYWORDS/DESCR PTORS				15. AVAILABILITY STATEMENT	
Light-water nuclear reactor Organic material Organic iodides Source terms					
16. IDENTIFIERS OPEN ENDED TERMS				16. SECURITY CLASSIFICATION	
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