REVIEW OF ORGANIC IODIDE FORMATION UNDER
ACCIDENT CONDITIONS IN WATER-COOLED REACTORS

For

Directorate of Licensing
Accident Analysis Branch
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ABSTRACT

The objective of this study was to determine from available information the degree to which organic iodides could form within the containment system of a light water reactor following a design basis loss of coolant accident. From an analysis of 69 containment experiments, it was concluded that less than 1% of iodine initially airborne (initial conc. of 100 mg/M³) could become converted to organic iodides by non-radiolytic means. Radiolysis experiments showed that gas phase radiolytic formation would add no more than 2.2% to the conversion indicated by containment experiments. Overall, no more than 3.2% of airborne iodine (airborne mass assumed equal to 25% of maximum core inventory) could be converted to organic iodides during the first two hours following fission product release. This percentage conversion to organic iodides is considered a conservative upper bound figure. In reality, much less organic-bound iodine would very likely be formed and the 3.2% conversion figure should be lowered as new information justifies.

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2.0 INTRODUCTION

This report summarizes the results of a comprehensive review of available information of formation of volatile iodides under postulated accident conditions in light water cooled reactors. Organic iodides, sometimes referred to as methyl iodide, present a potential safety problem because they are more difficult to trap than elemental iodine. Because of the method of analysis employed in many of the experiments analyzed in this study, the terms organic iodides and methyl iodide as used herein actually refer to any iodine species trapped on impregnated charcoal and may include hypoiodous acid.

At present, safety analyses performed by the Directorate of Licensing are carried out under the assumption that a maximum of 10% of the iodine initially available for release is present chemically as methyl iodide^(1,2). The mass of iodine which becomes airborne is taken as 25% of the core inventory, so that the current assumption is equivalent to stating that 2.5% of the iodine in the core becomes airborne as methyl iodide. Methyl iodide is removed only slowly by spray systems of current design and for this reason the two hour dose reduction factor which can be achieved by spray cleanup is limited by the methyl iodide fraction assumed present.

During the past 10 years, much information on methyl iodide formation has been obtained from AEC sponsored research programs and from tests performed at British reactor sites. The objective of the present study is to determine, on the basis of all available data, the maximum concentration of organic iodides airborne under light water reactor accident conditions.

3.0 SUMMARY AND CONCLUSIONS

Available information on formation of organic iodides under accident conditions applicable to light water reactors was reviewed to establish the degree to which iodine can become airborne as organic iodides. Organic iodide formation is important in reactor siting because the two hour dose reduction factor which can be achieved under present groundrules is limited by the methyl iodide concentration. The work completed supports the following conclusions.

1. Organic iodides formed in containment vessels consist mainly of alkyl iodides, of which methyl iodide is predominant. Other iodides which may be present would be no more volatile than methyl iodide.
2. Methyl iodide formation in containment vessels has been extensively studied in experiments which employed low radiation levels compared to those expected for design basis loss of coolant accidents. An analysis of 69 containment experiments showed that the fractional conversion of elemental iodine to organic iodide varies with the -0.26 power of the initial concentration. For a release concentration of 100 mg/M^3 (typical concentration for assumptions given in TID-14844)⁽³⁾ a least squares fit of available data indicate that 0.06% of elemental iodine would be converted to organic iodides. A conservative upper limit prediction based on the containment experiments indicates that no more than 1% of released iodine (100 mg/M^3) would be converted to organic iodides.

3. The high radiation field accompanying a postulated loss of coolant accident is expected to play an important role in methyl iodide formation. Gas phase radiolytic formation is expected to dominate compared to radiolytic formation at surfaces or in aqueous solution. At a concentration of 100 mg/M^3 , radiation would cause no more than 2.2% of elemental iodine to be converted to organic iodides.
4. Based on both the containment experiments and the radiation chemistry experiments, no more than 3.2% of elemental iodine (100 mg/M^3) would be converted to methyl iodide during the first two hours following a design basis loss of coolant accident. For less severe accidents, the maximum percentage could be higher because iodine concentrations would be lower.
5. Based on the 69 containment experiments, organic iodide formation appears to be somewhat enhanced in small vessels compared to large ones. On the other hand, radiolytic formation should be independent of vessel size. Thus the maximum percentage conversion is largely independent of vessel surface/volume ratio, hence of vessel size.
6. Available information indicates that the fractional conversion of elemental iodine to methyl iodide would in reality be less than 1% for design basis accident conditions. However, additional information, including experiments carried out under closely simulated accident conditions, appear to be required to provide a basis for lowering the assumed percentage below the 3.2% value projected in this report.

4.0 BACKGROUND

Iodine-131 is the limiting isotope in most radiological evaluations of postulated severe accidents in light water reactors. At present, end-of-the-spectrum type accidents are evaluated using guidelines given in AEC document TID-14844⁽³⁾ and Safety Guides 3 and 4 (References 1 and 2, respectively). According to these guidelines, 25% of the core inventory of iodine is airborne in the containment atmosphere. Of the 25% of the core inventory of iodine which is postulated to remain airborne, 10% (for PWR plants) is assumed to be present chemically as organic iodides. Thus 2.5% of iodine in the core is assumed to become airborne in the containment vessel as organic iodides. In boiling water reactors (BWR), 8% of released iodine (2% of core inventory) is assumed to become airborne as organic iodides. The lower organic fraction for BWR's follows from an assumed relationship between methyl iodide formation and exposed surface area in containment.

The existence of organic iodides in nuclear reactor containment systems has been known since 1960. Mishima⁽⁴⁾ has summarized studies on methyl iodide behavior which were completed prior to 1968.

Megaw and May⁽⁵⁾ carried out experiments in which elemental iodine was vaporized inside the Pluto reactor shell. These early experiments showed that most of the iodine disappeared rapidly by deposition on to surfaces in the reactor shell and that of the remainder which remained airborne for periods of several hours, part became attached to submicron particles in the atmosphere and part appeared to form two iodine compounds. The compounds were subsequently fractionated into two groups by Eggleton and Atkins.⁽⁶⁾ The largest fraction was identified as alkyl iodides, predominately methyl iodide. The smaller fraction was not identified.

Following this early British work, several research groups in the United States as well as in England began to make measurements of organic iodide formation. In the U. S., the organic iodide problem was considered to be a methyl iodide problem, and work on methyl iodide formation and

behavior was undertaken at Oak Ridge, Battelle-Northwest, Battelle-Columbus, Idaho Nuclear, and Brookhaven.

Work at Oak Ridge has focused on the behavior of iodine released into small, model containment vessels, and release of iodine from irradiated fuel in the TREAT facility. The containment vessels used at Oak Ridge include the CMF (0.2 M^3), CRI (3.8 M^3), IPI (0.2 M^3) and NSPP (38 M^3). Most of the Oak Ridge data were obtained in the CRI vessel.

At Battelle-Northwest, experiments have been conducted in the SAT (0.9 M^3), PAT (1.5 M^3), and CSE (750 M^3). One measurement was obtained in the PRTR containment vessel which has a volume of $12,000 \text{ M}^3$.

Work at Battelle-Columbus was designed to point up the mechanisms for methyl iodide formation. Work completed included theoretical studies based on thermodynamic and kinetic calculations, and experimental studies of radiolytic induced reactions between iodine and methane.

Work at Idaho Falls was done in the CDE facility (3.5 M^3). Iodine was released from irradiated fuel and in the form of simulants. Iodine concentrations were typically much lower than for postulated design basis loss of coolant accidents. Some CDE tests which used irradiated fuel involved the highest radiation levels used in any of the containment vessel tests. However, even these relatively high levels were several orders of magnitude lower than those which could be encountered in severe accidents.

Brookhaven work involved measurements of methyl iodide formation from iodine released from trace irradiated fuel, and radiolytic decomposition of methyl iodide. This work was carried out in laboratory glassware, hence represents a very small size scale when compared with full scale containment systems.

The overall formation process for organic iodides may be visualized to involve the following steps.

1. Formation within fuel
2. Surface reactions subsequent to release from fuel
3. Homogenous reactions subsequent to release from fuel.

Step 1, formation in fuel, might be important in experiments but would be negligible in severe accidents. This is so because the high temperatures and radiation levels experienced within fuel tends to preclude the existence of organic iodides. Steps 2 and 3 are expected to dominate under accident conditions. These same processes would be expected to be important in experiments conducted under conditions which simulate the containment environment postulated for accident conditions.

Organic iodides are produced when elemental iodine reacts with organic compounds. Organic sources within a reactor containment system would include lubricants or decomposition products from organic materials used within the containment vessel. Trace level contaminants in the earth's atmosphere could also represent a source of organic material. The reaction with iodine might be a thermally induced gas phase reaction, a radiolytic reaction, or one which occurs on surfaces.

Studies completed by Barnes, et al^(7,8,9) at Battelle-Columbus were directed at thermal and radiolytic formation processes. From chemical equilibrium studies, it was concluded that thermal reactions did not favor formation of methyl iodide. Indeed the equilibrium levels of methyl iodide were insignificant. Thermal reactions could be important only if the kinetics of the several formation steps lead to a non-equilibrium methyl iodide concentration several orders of magnitude higher than the equilibrium concentration.

Radiolytic formation of methyl iodide is more plausible than homogeneous thermal reactions. Studies carried out by Gevantman⁽¹⁰⁾ et al. in the early 1950's showed that radiation caused reaction between iodine and hydrocarbons. Typical results obtained by Gevantman, et al⁽¹⁰⁾ are shown in Figure 1. Methyl iodide was the primary product, with lesser amounts of ethyl iodide, methylene iodide, and hydrogen iodide being formed. The conditions for these experiments were much different than those for reactor accidents, hence the results do not apply directly. The results are indicative, however, that radiation chemistry needs to be considered in assessing methyl iodide formation following postulated severe accidents.

FIGURE 1. Radiolytic Formation of Organic Iodides By Radiation In Methane-Iodine Mixtures. From Gevantman, et al⁽¹⁰⁾

Surface reactions which might lead to methyl iodide formation have been evaluated as part of two studies^(11,12) of organic iodide formation. On the basis of available information it appears that surface reactions contribute little to methyl iodide formation as compared to gas phase reactions.

Parsly⁽¹³⁾ has reviewed recent literature related to methyl iodide formation under accident conditions. His listing of references was used extensively in the present study.

5.0 REVIEW OF MEASUREMENTS OF ORGANIC IODIDE FORMATION IN CONTAINMENT VESSELS

In this section, experimental measurements directly applicable to organic iodide formation in water reactors will be discussed. Only those experiments for which sufficient data were reported to permit estimates of concentration and percent conversion to organic iodides were considered. Experimental results are tabulated in Table I. In addition to the data presented in Table I, the experiments are discussed briefly in the following paragraphs.

Megaw and May⁽⁵⁾ released stable elemental iodine, traced with I-132, into the DIDO and PLUTO reactor containment vessels. The concentrations chosen were very low (0.013 to 14.1 $\mu\text{g}/\text{M}^3$) compared to TID-14844 accidents where initial concentrations are of the order of 100 mg/M^3 . Airborne iodine was sampled by means of a filter pack containing in series a membrane filter, two charcoal impregnated filter papers, and a bed of granulated charcoal. In calculating organic iodide formation, we assumed that all activity retained by the second charcoal impregnated filter paper and by the charcoal bed was associated with organic iodides. This approach may overpredict organic iodides because some elemental iodine would likely penetrate the first charcoal filter paper. The containment vessels had volumes of about 7000 M^3 , and exposed surfaces were typical of those found in power reactors. Conditions used in these tests which were atypical of those for design basis loss of coolant accident (LOCA) conditions include ambient temperature and humidity, the very low iodine concentrations, and the low radiation levels. Less than 1% of released iodine became airborne as organic iodides, and the indicated maximum in organic iodide concentration occurred some 5 hours after release. Our estimates of organic iodide formation in these experiments are in good agreement with those given by Parsly.⁽¹³⁾

Croft and Iles⁽¹⁴⁾ repeated the experiments of Megaw and May⁽⁵⁾ in the pit of the ZENITH reactor. In our analysis of their results, we again added the activity collected by the second charcoal paper to that of the granulated charcoal bed to get organic iodides. Less than 1% of the

released iodine appeared as organic iodides, and the maximum indicated organic iodide concentration occurred shortly after release. Our estimate of organic iodide concentrations are substantially higher than those given by Parsly.⁽¹³⁾

Croft, et al⁽¹⁵⁾ reported experiments on behavior of elemental iodine at much higher iodine concentrations than had been used in earlier British experiments. The experiments were carried out in a tightly sealed, near-cubic, experimental room of 27.4 M^3 volume and 60.2 M^2 wall surface area. The walls of the room were painted with a chlorinated rubber-based paint. This paint is similar to that used in British reactor containment systems. Two elemental iodine releases (stable I_2 + I-131) were made under dry conditions and one was made under moist conditions. The mass of iodine released divided by the volume of the room (termed release concentration in this report) ranged from 113 to 237 mg/M^3 . The fraction of released iodine which became airborne as organic iodides was very small, ranging from 0.016% to 0.024%. In our evaluation the organic iodide fraction was taken as that trapped by the charcoal granule bed. Ideally, we would like to have included activity collected by the second charcoal impregnated filter paper, but available data did not permit this. Typically, the second charcoal paper picks up relatively little activity. Hence, the organic iodide predicted using the charcoal paper activities as well as the granule bed would have been within a factor of two of that given in Table I. The maximum in organic iodide concentration occurred shortly after iodine release. LOCA conditions which were not duplicated in these experiments include temperature and steam content (experiments were done at ambient temperature) and radiation level (radiation levels in the experiments were very low). Our estimates of organic iodide fractions are in good agreement with those presented by Parsly.⁽¹³⁾

Stinchcombe and Goldsmith⁽¹⁶⁾ released elemental iodine tagged with I-131 into the containment shell of the DIDO reactor, which has a volume of approximately 7000 M^3 . The gas phase was sampled using a filter pack similar to that used earlier by Megaw and May.⁽⁵⁾ The filter pack used by Stinchcombe and Goldsmith⁽¹⁶⁾ included two copper gauzes at the

upstream face to collect most of the elemental iodine. We calculated the organic iodide concentration as the sum of that for the second charcoal paper and the charcoal bed. Less than 0.5% of the released iodine was converted to organic forms. The maximum organic iodide concentration occurred shortly after the iodine was released. Compared to a LOCA, these experiments were atypical in terms of low temperature, low steam pressure, low iodine concentration, and low radiation level. Our estimate of the organic iodide fraction is in good agreement with that given by Parsly.⁽¹³⁾ However, Parsly⁽¹³⁾ gives the release concentration as 0.12 g/M^3 whereas the value given by the original authors is $0.12 \text{ } \mu\text{g/M}^3$.

Parker, et al⁽¹⁷⁾ studied the behavior of the iodine in the Confinement Mockup Facility (CMF) at Oak Ridge. Iodine sources included both irradiated UO_2 and stable elemental iodine traced with I-131. The CMF is a small (0.2 M^3) stainless steel pressure vessel located in a hot cell. Five experiments were carried out at room temperature in an air atmosphere. The fraction of iodine in penetrating form was determined from iodine deposition within the Oak Ridge Maypack. The calculational procedures used to determine the penetrating iodine fraction are not described in detail by Parker, et al⁽¹⁷⁾, and we were forced to use the results as presented by the authors. The percent of iodine in penetrating forms varied from 3.7% to 0.3%, for release concentrations of $5 \text{ } \mu\text{g/M}^3$ to 1.75 mg/M^3 . Interestingly, the percentage conversion to "penetrating" iodine forms measured for the simulant tests was comparable to the value obtained for the test which used UO_2 irradiated to a burnup of $7000 \frac{\text{Mwd}}{\text{Mt}}$. These experiments were carried out in air at ambient temperatures and pressures and thus did not duplicate the steam/air atmosphere predicted for a LOCA. Other aspects which were atypical of accident conditions include the very small vessel size, and the low iodine concentrations. The iodine concentrations and percentages converted to organic form could not be independently calculated and, therefore, the original author's numbers were assumed to be correct.

Parker, et al⁽¹⁸⁾ studied the behavior of iodine released from UO_2 and iodine simulants in the Containment Research Installation (CRI) at

Oak Ridge. The CRI vessel has a volume of 3.8 M^3 and used a stainless steel liner for these experiments. Ten experiments were carried out. Heaters installed around the tank wall were used to control temperature, and it is likely that part of the wall was dry. The average relative humidity for a typical test (109 SI) was less than 80% for the first 500 minutes. Organic iodides concentration increased markedly for 200 to 300 minutes and then increased more slowly. The maximum organic iodide concentrations typically occurred at the end of an experiment, which lasted for 1200 minutes. In five of the ten experiments we considered in the present study, iodine was released either as elemental iodine or hydrogen iodide. In the remaining five tests, iodine was released in conjunction with heated UO_2 . In one of these, irradiated UO_2 (6000 Mwd/Mt) was the source of iodine. Iodine release concentrations varied from 0.05 mg/M^3 to 6.7 mg/M^3 , and the percentage conversion to organic iodides ranged from 0.04% to 0.41%. Most of the tests were carried out at temperatures ranging from 100°C to 120°C . The conditions for these experiments were atypical of LOCA conditions in terms of low iodine concentration, small vessel size, and a relative humidity which was less than 100%. Our concentrations and percentages of organic iodides are in good agreement with those given by Parsly.⁽¹³⁾

Parsly⁽¹³⁾ reported a number of experiments on iodine behavior in the Nuclear Safety Pilot Plant (NSPP). The NSPP has a volume of 38.3 M^3 and has stainless steel walls. Parsly⁽¹³⁾ notes that in a number of runs, the Maypack samplers were faulty in that elemental iodine could leak past the silver-plated screens to reach the charcoal beds. This would result in erroneously high methyl iodide percentages and for this reason most NSPP data were ruled out. Only one test was carried out under applicable conditions for which proper Maypack operation was indicated, and for which iodine inventory data were given. In this test, iodine was released from high burnup UO_2 . Parsly⁽¹³⁾ does not state the fuel burnup in Mwd/Mt, but noted that 27.6% of the iodine inventory (28 mg) was released. A maximum of 0.97% of released iodine was found in the organic form. Parsly's⁽¹³⁾ numbers for organic iodide percentage and concentration were

used directly because the experiment was not reported in enough detail to permit independent calculations. The temperature of this run was not specified but since the atmosphere was described as air/steam, we presume that the temperature was similar to that used in the other tests, namely 100 to 108°C. This experiment was atypical of LOCA conditions in terms of the low iodine concentration and the smaller size of the containment vessel.

Parker and Martin⁽¹⁹⁾ have studied iodine behavior in the Containment Research Installation equipped with an Amercoat liner. The Amercoat coating is typical of coatings used in commercial reactors in the U. S. The volume of the CRI is 3.8 M³. In four of five runs, temperature was controlled by wall heaters, resulting in subsaturated conditions and dry wall surfaces. In the last test performed, temperature was controlled by injecting live steam. This procedure eliminated the dry wall surface condition and better duplicates conditions in a LOCA. Temperature in these tests was 115°C with the steam/air ratio being approximately equal to that for a saturated atmosphere of air. Iodine release concentrations varied from 0.1 to 125 µg/M³, and conversion to organic iodides varied from 2.4% to 0.03%. Conditions for these experiments were atypical of those for LOCA in terms of low iodine concentration, small size of vessel, and use of subsaturated conditions in four of the five tests. These tests were reported after Parsly's⁽¹³⁾ review was completed, hence were not reported in it. Parker and Martin⁽¹⁹⁾ noted from these results, a marked dependency of percent conversion to organic iodides on the release concentration. Based on the data obtained in the Amercoat lined CRI, Parker and Martin⁽¹⁹⁾ give an equation for a least squares fit of four data points, assuming an exponential relation. They give

$$\% \text{CH}_3\text{I} = 0.83 e^{-0.0267C}$$

where C = initial iodine concentration, µg/M³.

For LOCA conditions ($C \approx 10^5 \mu\text{g/M}^3$), this equation predicts a methyl iodide percentage of less than 10^{-10} or essentially zero. It is concluded that

these authors noted a valid trend in the decrease of organic iodide percent with higher release concentrations, but that their data fit is not valid for concentration ranges resulting from a TID-14844⁽³⁾ release.

Hilliard, et al⁽²⁰⁾ carried out 21 experiments to study behavior of iodine released as a simulant and from irradiated UO_2 . Concentrations ranged from $0.045 \mu\text{g}/\text{M}^3$ to $106 \text{ mg}/\text{M}^3$. Conversion to organic iodides varied from 3.7% to 0.015%, with the highest percentages occurring at the lowest concentrations. All experiments were carried out at about 80°C , at a total pressure slightly less than one atmosphere. The air/steam ratio was 50%/50% for most tests but some tests were done with less air than the equimolar ratio. About half of the tests were done in a 1.5 M^3 tank painted with Phenoline 300 paint (vessel called the PAT) and about half were done in a stainless steel vessel, having a volume of 0.9 M^3 (vessel called the SAT). In estimating the organic iodide fraction, we assumed that activity collected by the charcoal impregnated filter paper and by the charcoal bed of the Maypack samplers was organic iodides. Highest organic iodide concentrations typically occurred shortly after iodine release. The conditions in these experiments are atypical of those for a LOCA primarily in terms of vessel size and lower temperature and pressure. Concentration data tabulated by Parsly⁽¹³⁾ for these tests are in error by a factor of 1000. Our estimates of organic iodide conversion are appreciably different than those given by Parsly.⁽¹³⁾

Hilliard, et al⁽²¹⁾ reported results of fission product transport tests carried out in the Containment Systems Experiment. In most CSE tests, methyl iodide was intentionally added so that its behavior in containment could be studied. In four tests, however, methyl iodide was not added, permitting organic iodide formation to be measured. Two experiments were done in the drywell vessel (volume 65 M^3) and two in the main vessel (volume 750 M^3). Conversion to organic iodides varied from 0.021% to 0.16% for release concentrations ranging from $0.6 \text{ mg}/\text{M}^3$ to $95 \text{ mg}/\text{M}^3$. The maximum organic iodide concentrations occurred shortly after the iodine release. Concentration data presented by Parsly⁽¹³⁾ for these tests are incorrect by up to 3 orders of magnitude. Our estimates

of organic iodide concentration are appreciably different from the values given by Parsly.⁽¹³⁾ These experiments are atypical of LOCA conditions primarily in terms of radiation levels and the somewhat smaller containment vessel.

Roberts, et al^(22,23) studied iodine behavior in the In-Pile Nuclear Safety Facility at the Oak Ridge Reactor. These studies were designed to determine whether simulant iodine behaved in the same way as iodine released from fuel under accident conditions. Unfortunately, radiation levels were not reported. The fission product aerosol aging chamber was a 0.2 M³ stainless steel drum. The experiments used an atmosphere of 50% steam and 50% air at a temperature of 80°C. Insufficient data were presented to allow an independent calculation of the organic iodide fraction, hence the percentages listed by the original authors were assumed to be correct. Organic iodides amounted to 2.0% and 0.6% for release concentrations of 1.5 mg/M³ and 20 mg/M³, respectively. Parsly's⁽¹³⁾ tabulated data differ by about a factor of 2 from the values we derived from the original papers. The conditions used in these tests are atypical of LOCA accidents in terms of small vessel size, atmosphere composition (relatively low temperature and steam pressure), and low iodine concentrations.

Lorentz, et al^(24,25) performed fuel failure tests in the TREAT facility in which previously irradiated fuel was failed, allowing fission products to escape. Steam and helium flowing past the fuel carried released fission products to Maypack-type adsorbent packs. The transit time of fission products from fuel to collection pack was of the order of seconds. The authors of this work estimated the gas phase concentrations of iodine in the flowing helium/steam mixture to be of the order of 64 µg/M³ and 174 µg/M³ for the two experiments. Of the iodine released, 6.7% and 2.5% appeared as organic iodides, respectively. These tests are atypical in terms of the helium flow, the low iodine concentrations, and the size scale of the equipment. It should be noted that the original authors' numbers for concentration and percent organic iodides were used as given. Parsly⁽¹³⁾ does not give data on these tests because they were not reported at the time his paper was written.

Perkins, et al⁽²⁶⁾ studied the behavior of iodine which became airborne in the containment vessel of the Plutonium Recycle Test Reactor (PRTR) as the result of the combined failure of a pressure tube and defected fuel rod. Of the iodine which eventually reached the containment vessel (12,000 M³ volume) 10% was found airborne in the form of organic iodides. The iodine concentration in the containment vessel was very low. On the basis of release fractions given by Perkins, et al⁽²⁶⁾ and fuel irradiation (1040 Mwd/MT) given by Freshley, et al⁽²⁷⁾, we estimate that 93 micrograms of I₂ reached the containment vessel. The release concentration was thus estimated to be 0.008 µg/M³. It is interesting to note that only 0.1% of fuel inventory of iodine became airborne as organic iodides. This is much less than the 2% and 2.5% currently assumed for BWR's and PWR's, respectively.^(1,2) Conditions which are atypical of LOCA accidents are iodine concentration and containment temperature and pressure. Although the PRTR containment vessel is somewhat smaller than a large power reactor, the difference is a relatively small factor.

Freeby, et al⁽²⁸⁾ studied behavior of fission products released from irradiated fuel (700 Mwd/MT). Two tests with fission products at relatively high radiation level were carried out in the Contamination-Decontamination Experiment (CDE) facilities. The tests were done as part of LOFT support work, hence conditions were selected to be representative of those anticipated for the original LOFT. The CDE containment vessel has a volume of 2.4 M³, hence from a size scale is close to the PAT (1.5 M³) and CRI (3.8 M³). Radiation level was high (250 R/hr) compared to most containment tests, but is low compared to maximum radiation levels of the order of 10⁶ R/hr predicted for design basis loss of coolant accidents (see example calculation given in Appendix A). Maypack samplers were used to sample iodine, and according to the authors, the organic iodide fraction included both organic iodides and hypoiodous acid. It should be noted that the Maypacks used no charcoal impregnated filter papers. This Maypack arrangement represents a deviation from standard design and would surely cause an overestimate in organic iodides because elemental iodine which leaked past the silver membrane

would be counted as organic iodide. The "penetrating" iodide fraction was 6.5% and 7.5% for release concentrations of $1.05 \mu\text{g}/\text{M}^3$ and $1.16 \mu\text{g}/\text{M}^3$. These two tests employed saturated steam/air atmospheres, with initial temperatures near 220°F . Hydrocarbons were present in the containment atmosphere to a level of 4.8 and 19.0 ppm prior to fuel meltdown and 7.0 to 29.0 ppm after meltdown. These tests are atypical of LOCA conditions in terms of the low iodine concentration and small vessel size. Organic iodide concentration attained a maximum shortly after fission product release. Parsly's⁽¹³⁾ data tabulation for these tests is in error.

Nebecker, et al⁽²⁹⁾ carried out a series of tracer tests in the CDE facility in which elemental iodine and xenon were released. The experiments used a saturated steam/air atmosphere at an initial temperature of about 100°C . Iodine was prepared by oxidation of sodium iodide by potassium dichromate. The authors reported that 1% to 15% of the iodine, as released, was in organic form. However, this percentage is higher than the percentage measured in containment so we can conclude only that some of the iodine released may have been released in organic form. Standard Maypack samplers were not used in these tests, hence interpretation of data becomes somewhat subjective. We chose to calculate organic iodide concentration from CSM (Continuous Sampler Monitor) measurements. Organic iodides varied from 1.6% to 13% of released iodine for concentrations ranging from $7.1 \mu\text{g}/\text{M}^3$ to $0.05 \mu\text{g}/\text{M}^3$. Parsly's⁽¹³⁾ summary did not include these measurements. These tests are atypical of LOCA conditions from the standpoint of iodine concentration, relatively low radiation level, and vessel size.

All available applicable data on organic iodide formation in containment vessel tests are summarized in Table 1.

Data given in Table 1 have been shown on a plot in Figure 2, where the percent organic iodide is shown as a function of the release concentration. The line drawn through the data represents the least squares fit, assuming a relationship of the form

$$(\text{Percent Organic}) = a (\text{Release Concentration})^b. \quad (1)$$

TABLE 1. Summary of Available Experimental Data on Organic Iodide Formation Under LOCA Conditions in Water Cooled Reactors

Reference Cited	Type of Release	Release Concentration		Containment Atmosphere	Size of Containment Vessel	Comments	Organic Iodides as % of Release Concentration (This work) (Parsly's Ref)		Data Point Number
Megaw and May (1962) ref. (5)	Elemental I-127+I-132 Crystals	0.013 $\mu\text{g}/\text{M}^3$	0.013 $\mu\text{g}/\text{M}^3$	Ambient temp air in PLUTO & DIDO reactor shells	Volume of 7000 M^3	Vessel was containment structure of operating reactor, therefore, contained typical airborne contaminants and typical material surfaces	0.9	0.9	1
		0.14 $\mu\text{g}/\text{M}^3$	0.14 $\mu\text{g}/\text{M}^3$				0.56	0.56	2
		14.1 $\mu\text{g}/\text{M}^3$	14.1 $\mu\text{g}/\text{M}^3$				0.16	0.30	3
Croft and Iles (1962) ref. (14)	Elemental I-127+I-132 Crystals	0.38 $\mu\text{g}/\text{M}^3$	0.38 $\mu\text{g}/\text{M}^3$	Ambient temp air in ZENITH reactor containment	Pit volume ~ 500 M^3	Vessel was part of containment of operating reactor	0.79	0.053	4
		0.78 $\mu\text{g}/\text{M}^3$	0.78 $\mu\text{g}/\text{M}^3$				0.09	0.028	5
Croft, Iles, Davis (1963) ref. (15)	Elemental I-127+I-131 Crystals	113 mg/M^3	113 mg/M^3	Air, ambient temp, 85% RH	30 M^3 room	Walls and surfaces covered with epoxy resin and chlorinated rubber-based paint to simulate reactor system	0.022	0.021	6
		237 mg/M^3	237 mg/M^3	Air, ambient temp, 65% RH			0.024	0.024	7
		190 mg/M^3	190 mg/M^3	Air, ambient temp, 100% RH			0.016	0.01	8
Stinchcombe & Goldsmith (1966) ref. (16)	Elemental I-127+I-132 Crystals	0.12 $\mu\text{g}/\text{M}^3$	0.12 g/M^3	Ambient air in DIDO containment shell	Volume of 7000 M^3	Vessel was containment building of operating reactor	0.25	0.21	9
		0.12 $\mu\text{g}/\text{M}^3$	0.12 g/M^3				0.41	0.28	10
Parker, et al (1964) ref. (17)	Trace irradi. UO_2	5 $\mu\text{g}/\text{M}^3$	5 $\mu\text{g}/\text{M}^3$	Air, ambient temp, press	Volume of 0.2 M^3	0.2 M^3 , SS test vessel	3.7	3.7	11
	Trace irradi. UO_2	5 $\mu\text{g}/\text{M}^3$	5 $\mu\text{g}/\text{M}^3$	Filtered air, ambient T,P			0.4	0.4	12
	7000 Mw/T UO_2	1.6 mg/M^3	3 mg/M^3	Filtered air, ambient T,P			0.3	0.3	13
	I-127+I-131, elemental	1.0 mg/M^3	1.0 mg/M^3	Filtered air, ambient T,P			0.5	0.5	14
	I-127+I-131, elemental	1.75 mg/M^3	1.75 mg/M^3	Filtered air, 15 psig, amb. T			0.3	0.3	15
Parker, et al (1971) ref. (18)	I-130, elemental	4.8 mg/M^3	not given	Air, ambient temp, press	3.8 M^3 Volume	SS vessel, Run CRI-100 I	0.052	0.034	16
	HI made from H_2 +I-130	2.2 mg/M^3	not given	Air, ambient temp, press			0.046	0.018	17
	I-130, elemental	6.7 mg/M^3	7.9 mg/M^3	Steam/air, 125°C			0.41	0.22	18
	HI made from H_2 +I-130	4.5 mg/M^3	5.3 mg/M^3	Steam/air, 99°C			0.07	0.04	19
	Tracer elemental + Ru, Te, Cs	3.4 mg/M^3	3.9 mg/M^3	Steam/air, 110°C			0.32	0.32	20
	I-129+ UO_2 + Zircaloy	4.5 mg/M^3	5.3 mg/M^3	Steam/air, 110°C			0.28	0.26	21
	I-129+ UO_2 + Zircaloy	2.0 mg/M^3	2.4 mg/M^3	Steam/air, 108°C			0.04	0.04	22
	I-129+ UO_2 + Zircaloy	0.5 mg/M^3	0.63 mg/M^3	Steam/air, 118°C			0.058	0.06	23
	I-129+ UO_2 + Zircaloy	0.05 mg/M^3	0.06 mg/M^3	Steam/air, 115°C			0.17	0.16	24
	UO_2 , 6000 Mw/T	0.27 mg/M^3	0.32 mg/M^3	Steam/air, 111°C			0.12	0.12	25
		(Parsly)	0.2 mg/M^3	Steam/Air			(Parsly)	0.97	26
Parsly (1971) ref. (13)	High Burnup UO_2	(Parsly)	0.2 mg/M^3	Steam/Air	38.8 M^3 Volume Nuclear Safety Pilot Plant (NSPP)	Run 15 in NSPP	(Parsly)	0.97	26

TABLE 1 (Continued)

Reference Cited	Type of Release	Release Concentration		Containment Atmosphere	Size of Containment Vessel	Comments	Organic Iodides as % of Release Concentration		Data Point Number	
		Orig Ref	Parsly s Ref				(This Work)	(Parsly Ref 9)		
Parker, et al (1970)	I-131, carrier-free, elemental	0 1	ug/M ³	Not given	Steam/air, 120°C	3 8 M ³ Volume	Run CRI 115, Amercoat Lining	2 4	not given	27
ref (19)	I-131+I-127, elemental	5	ug/M ³		Steam/air, 115°C	Containment Research	Run CRI 117, Amercoat Lining	0 8		28
	I-131+I-127, elemental	5	ug/M ³		Steam/air, 110°C	Installation (CRI)	Run CRI 118, Amercoat Lining	0 7		29
	I-131+I-127, elemental	35	ug/M ³		Steam/air, 110°C		Run CRI 119, Amercoat Lining	0 3		30
	I-131+I-127, elemental	125	ug/M ³		Steam/air, 110°C		Run CRI-120, Amercoat Lining	0 03		31
Hilliard, et al (1968)	I-131+I-127+UO ₂ aerosol	0 45	mg/M ³	450 mg/M ³	50% air, 50% steam, 80°C	Painted Tank, 1 4 M ³ (PAT)	Run SA 21 (Phenoline 300 Paint)	0 18	0 07	32
ref (20)	I-131+I-127+UO ₂ SS aerosol	0 52	mg/M ³	520 mg/M ³	50% air, 50% steam, 79°C		Run SA 23	0 059	0 03	33
	UO ₂ , trace irradiated	0 045	ug/M ³	0 045mg/M ³	Air, 70°C, 0 2 psig		Run IA 26	1 6	0 25	34
	I-131+UO ₂ SS aerosol	0 33	ug/M ³	0 33 mg/M ³	50% air, 50% steam, 81°C		Run SA 28	2 2	1 0	35
	UO ₂ , trace irradiated	0 18	ug/M ³	0 18 mg/M ³	100% H ₂ O, 82°C		Run IA-32	0 9	0 45	36
	UO ₂ , trace irradiated	0 16	ug/M ³	0 16 mg/M ³	20% air, 80% H ₂ O, 82°C		Run IA-33	1 3	0 5	37
	UO ₂ , trace irradiated	0 29	ug/M ³	0 30 mg/M ³	20% air, 80% H ₂ O, 82°C		Run IA-39	1 2	0 35	38
	UO ₂ , trace irradiated	0 23	ug/M ³	0 23 mg/M ³	20% air, 80% H ₂ O, 84°C		Run IA-40	2 0	0 9	39
	UO ₂ , trace irradiated	0 27	ug/M ³	0 27 mg/M ³	20% air, 80% H ₂ O, 84°C		Run IB 41	3 7	0 7	40
	UO ₂ , trace irradiated	0 27	ug/M ³	0 27 mg/M ³	90% H ₂ O, 1% H ₂ , 9% Ar, 84°C		Run IB-42	0 52	0 1	41
	I-131+I-127+UO ₂ SS aerosol	0 45	mg/M ³	450 mg/M ³	50% H ₂ O, 50% air, 80°C		Run SA 43	0 061	0 025	42
	I-131+I-127+UO ₂ SS aerosol	0 53	mg/M ³	530 mg/M ³		SS Tank, 0 9 M ³ (SAT)	Run SA 44 Stainless Steel Tank	0 11	0 0064	43
	I-131+I-127+UO ₂ SS aerosol	0 54	mg/M ³	540 mg/M ³			Run SB 48	0 35	0 035	44
	I-131+I-127+UO ₂ SS aerosol	0 52	mg/M ³	530 mg/M ³			Run SB 50	0 17	0 035	45
	I-131+I-127+UO ₂ fp aerosol	1 0	mg/M ³	1000 mg/M ³			Run SB-53	0 13	0 02	46
	I-131+I-127+UO ₂ SS aerosol	0 78	mg/M ³	780 mg/M ³			Run SB-60	0 16	0 02	47
	I-131+I-127+UO ₂ SS aerosol	1 50	mg/M ³	1500 mg/M ³			Run SB-61	0 25	0 02	48
	I-131+I-127+UO ₂ SS aerosol	106	mg/M ³	1x10 ⁵ mg/M ³			Run SB-63	0 31	0 02	49
	I-131+I-127+UO ₂ SS aerosol	1 08	mg/M ³	1070 mg/M ³			Run SB-64	0 20	0 018	50
	I-131+I-127	52	mg/M ³	51,000 mg/M ³			Run SB-74	0 015	0 108	51
	I-131+I-127+Cs ₂ O aerosol	0 97	mg/M ³	980 mg/M ³			Run SB-78	0 55	0 05	52
Hilliard, et al (1970)	I-131+I-127+UO ₂ , Cs aerosol	661	ug/M ³	66 mg/M ³	Sat steam/air 250°F	Painted Vessel, 65 M ³	CSE Run D-1	0 076	0 117	53
ref (21)	I-131+I-127+UO ₂ , Cs aerosol	935	ug/M ³	940 mg/M ³	Sat steam/air 250°F		CSE Run D 2	0 021	0 017	54
	I-131+I-127+UO ₂ , Cs aerosol	1166	ug/M ³	129 mg/M ³	Sat steam/air 181°F	Painted Vessel, 750 M ³	CSE Run A-1	0 043	0 37	55
	I-131+I-127+UO ₂ , Cs aerosol	94 3	mg/M ³	1 19x10 ⁵ mg/M ³	Sat steam/air 185°F		CSE Run A-2	0 16	0 10	56
Roberts, et al (1968, 1969)	Irradiated UO ₂ , 16,000 Mw/T	1 5	mg/M ³	3 1 mg/M ³	50% air, 50% steam, 80°C	0 2 M ³ Stainless steel	In Pile experiment 3	2	1 7	57
ref (22) and ref (23)	Trace irrads UO ₂ +I ₂	20	mg/M ³	40 5 mg/M ³	50% air 50% steam, 80°C	Chamber in water pool of ORR	In Pile experiment 4	0 6	1 7	58
Lorentz, et al (1971, 1972)	Irradiated UO ₂ , 650 Mw/T	64	ug/M ³	not given	Steam, helium	Piping of Treat Loop	First Fuel Rod Failure Test in Treat	6 7	not given	59
ref (24) and ref (25)	Irradiated UO ₂ , 2800 Mw/T	174	ug/M ³		Steam, helium	Piping of Treat Loop	Second Fuel Rod Failure Test in Treat	2 5		60

TABLE 1 (Continued)

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Reference Cited	Type of Release	Release Concentration		Containment Atmosphere	Size of Containment Vessel	Comments	Organic Iodides as % of Release Concentration		Data Point Number
		Orig. Ref.	Parsly's Ref.				(This work)	(Parsly's Ref)	
Perkins, et al (1965) ref. (26)	Irradiated UO ₂ -PuO ₂	0.008 µg/M ³	not given	Humid air at ambient cond.	12,000 M ³ Containment vessel of PRTR	Release occurred for intentionally failed fuel rod	10	10	61
Freeby, et al (1969) ref. (28)	Irradiated UO ₂ , 740 Mw/d/T	1.05 µg/M ³	111 mg/M ³	Steam/air, sat'd at 218°F	2.43 M ³ , SS tank	High level CDE Run 3	6.5	3.5	62
	Irradiated UO ₂ , 530 Mw/d/T	1.16 µg/M ³	107 mg/M ³	Steam/air, sat'd at 224°F	"	High level CDE Run 4	7.5	4.5	63
Nebecker, et al (1971) ref (29)	I-131+I-127	2.1 µg/M ³	not given	Steam/air, sat'd at 103°C	2.43 M ³ , SS tank	CDE tracer Run 3 (1% organics)	4.6	not given	64
	I-131+I-127	3.6 µg/M ³	"	Steam/air, sat'd at 110°C	"	CDE tracer Run 4 (1% organics)	4.7	"	65
	I-131+I-127	7.1 µg/M ³	"	Steam/air, sat'd at 102°C	"	CDE tracer Run 6 (4% organics)	5.0	"	66
	I-131+I-127	2.3 µg/M ³	"	Steam/air, sat'd at 102°C	"	CDE tracer Run 9 (7% organics)	4.1	"	67
	I-131+I-127	3.1 µg/M ³	"	Steam/air, sat'd at 99°C	"	CDE tracer Run 10 (15% organics)	1.6	"	68
	I-131+I-127	0.05 µg/M ³	"	Steam/air, sat'd at 98°C	"	CDE tracer Run 11 (7% organics)	13	"	69
	Organic iodides made up 1-15% of iodine injected. Authors of work give numbers shown in parenthesis above.

FIGURE 2. Organic Iodide Formation Following Iodine Release Under Conditions Relating to LOCA for Water Cooled Reactors

For the data shown, $a = 0.188$
 $b = -0.26$

At 100 mg/M^3 , the least squares equation predicts an organic conversion percentage of 0.056%. At low concentrations, such as that which accompanied the PRTR incident ($0.008 \text{ } \mu\text{g/M}^3$), the organic conversion is predicted to be 4%. An upper bound line was fitted to the data by drawing a line parallel to the least squares line through the uppermost point. All data lie below this upper bound, hence it represents a conservative predictor line. At 100 mg/M^3 , this line predicts an organic iodide concentration of 1%. At very low concentrations, e.g. that of the PRTR incident ($0.008 \text{ } \mu\text{g/M}^3$), some 70% of released iodine is predicted to be present as organic iodides.

It is worth noting here that in the upcoming LOFT tests, the iodine release will result in very low concentrations in the containment vessel. Therefore, it would not be surprising if more than 20% of that released would become airborne as organic iodides in the LOFT containment vessel.

The existing data on iodine behavior in containment vessels was analyzed from several viewpoints to gain insight into the formation mechanisms. This was done by segregating the measurements according to certain chosen parameters.

An indication of the effect of containment volume on organic iodide formation is shown in Figure 3, where the data points are identified with specific volume ranges. The lines which appear on the plot represent upper limit lines based on each set of data. The slope of these lines is -0.26 , the value obtained from the least squares analysis of all data points as shown in Figure 2. The highest percentage of organic iodides is associated with the smallest containment volumes. Results are summarized in Table 2, where the upper limit prediction for an initial concentration of 100 mg/M^3 is shown as a function of containment vessel size.

FIGURE 3. Effect of Containment Volume on Organic Iodide Fraction

TABLE 2. Maximum Organic Iodide Concentration Predicted for An Iodine Release of 100 mg/M³ as a Function of Vessel Size

Containment Vessel Volume	Percent Conversion To Organic Iodides
0.2 to 1.0 M ³	1%
1.0 to 10 M ³	0.45%
10 to 1000 M ³	0.20%
1000 to 12,000 M ³	0.14%

It is recognized that factors other than containment vessel size also changed, so that the data do not define an assured, quantitative, relationship. However, the trend is consistent in that the percentage of organic iodides decreases for each step in increased volume. Since these data do not define a reliable size versus percent organic iodide curve which can be extrapolated to full size power reactors, an alternate approach is needed. A conservative approach is to directly use data obtained in smaller vessels for both PWR and BWR containment vessels. According to the percentages shown in Table 2, the application of small scale data results in a factor of conservatism of 7.

Results obtained for various fuel irradiation histories are shown in Figure 4, where the data are segregated into three categories: simulant release, iodine released from trace irradiated UO₂, and iodine, evolved from high burnup UO₂. It appears that there is little difference between simulant iodine and iodine evolved from trace irradiated UO₂. However, the data for high burnup UO₂ tend to fall above the other data. Unfortunately the high burnup data were obtained in the smallest vessels, so one is unable to conclude that fuel irradiation level is an important parameter. For tests done within the same vessel, e.g. the CDE, CRI, CMF, or IPI, results for simulant tests agreed well with results for high level tests, indicating that fuel burnup is not an important factor. Roberts⁽²²⁾ concluded that simulant iodine behaved essentially the same as iodine released from irradiated fuel which is consistent with the above

FIGURE 4. Organic Iodide Formation for Several Iodine Release Sources

conclusion. A conservative approach in applying the test results is to use the high burnup data to predict the LOCA organic iodide percentage conversion.

The data were also segregated according to the group which did the work. The source groups included the British, Battelle-Northwest, Oak Ridge, and Idaho Nuclear. Each of these groups used sampling packs which were not identical in design with those of the other groups. The purpose of this evaluation was to determine if there was an appreciable difference in detection methods. Results from the four sources are shown in Figure 5. Upper bound lines are shown for each of the four groups. Highest organic iodide fractions were found by Oak Ridge workers. Next highest were found by workers at Idaho Nuclear Corp. Third highest conversion was found at Battelle-Northwest and lowest values were found by British workers. It may be noted that the Oak Ridge data are more widely scattered than data from the other three sources. Some Oak Ridge data fall at the top of the grouping, and some fall near the bottom of the data point grouping. The maximum organic iodide conversions predicted for LOCA conditions for each of the data groups is shown in Table 3.

TABLE 3. Maximum Organic Iodide Concentration
Predicted for An Iodine Release of
100 mg/M³ Using Data From Several
Laboratories

<u>Data Source</u>	<u>Percent Organic Iodides</u>
Oak Ridge	1%
Idaho Nuclear	0.4%
Battelle-Northwest	0.3%
British	0.03%

From the data shown in Table 3, it is apparent that Oak Ridge results lead to predicted maximum organic iodide concentrations which are two to three times higher than predicted using data from Battelle-Northwest or Idaho Nuclear. British data indicate a maximum organic iodide conversion only 10% as high as indicated by Battelle-Northwest and Idaho Nuclear data. The lower position of the British data likely results in

FIGURE 5. Organic Iodide Formation As Measured at Several Laboratories

part from the much larger size scale. As noted earlier in this report, the smallest percentage conversions to organic iodides have been observed in the largest test vessels. The higher position of the Oak Ridge data may indicate that their sampling and analytical procedures are biased to indicate higher than true organic iodide levels. However, the experiments were different and the size scale smaller so one cannot be certain that the methyl iodide level is erroneously high. A conservative evaluation may be based on the assumption that the Oak Ridge data are correct. LOCA predictions would thus be based on the highest observed organic iodide percentage.

6.0 THEORETICAL STUDIES OF METHYL IODIDE FORMATION

The magnitude of effort devoted to theoretical studies of methyl iodide formation has been much less than that expended along the experimental front. The most important of the theoretical approaches is that completed at Battelle-Columbus by Barnes, et al.^(7,8,9)

Barnes, et al.^(7,8) began their study by making equilibrium calculations for a system containing 13 chemical species. The species included 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. The concentration levels were obtained from mass balances, based on assumed initial concentrations thought to be typical of LOCA condition. Total pressure was taken as one atmosphere. Typical results of equilibrium calculations are shown in Figure 6 where the gas phase concentration of each species is shown as a function of the assumed equilibrium temperature. The maximum methyl iodide concentration occurred at a temperature of 700°K (427°C) and represented less than 1×10^{-4} percent of the total iodine present. It is interesting to note that essentially all of the iodine is predicted to be present as HI . This is considered beneficial from an accident analysis standpoint because HI is much more soluble in water than elemental iodine.

The equilibrium calculations are summarized in Figure 7 where the fraction of iodine airborne as methyl iodide is shown for steam and air systems as a function of temperature. The highest fraction occurs with

FIGURE 6. Equilibrium Species Concentrations Predicted For Air Saturated With Water at 70°F(8)

FIGURE 7. The Fraction of Iodine Appearing as Methyl Iodide at Equilibrium as Predicted by Barnes, et al.(8)

steam containing only small amounts of oxygen, and even at the maximum represents less than 0.001% of the total iodine airborne. Thus one is forced to conclude that from a thermodynamic point of view, methyl iodide is not a favored chemical specie. If chemical equilibrium is reached, then methyl iodide is unimportant. Since experimental data have shown methyl iodide concentrations much higher than 0.001%, the Battelle-Columbus workers concluded that rate processes, rather than equilibrium, must be the controlling factors.

Initial kinetic calculations presented by Barnes, et al.⁽⁸⁾ were based on a reaction mechanism scheme developed by Golden, et al.⁽³⁰⁾ According to Golden, et al.⁽³⁰⁾, the reaction between methane and iodine can be expressed as

In equation (2), M represents a non-reactive specie. Rate constants for all of these reactions were not available and some had to be estimated. Calculational results for the mechanism described in equations (2), (3), and (4) are shown in Figure 8 for a typical case. An important result of these calculations, as shown in Figure 8, was the predicted occurrence of a maximum in the methyl iodide concentration which was several orders of magnitude higher than the equilibrium concentration. It was postulated that under LOCA conditions, the reaction could be quenched at a point in time (~ 1 minute) where the methyl iodide concentration was high. At the lower temperatures, equilibrium might be attained very slowly, thus resulting in formation of appreciable quantities of methyl iodide. However, this prediction of a transient maximum in methyl iodide concentration was not

FIGURE 8. Species Concentrations As a Function of Time for the Reaction Between CH_4 and I_2 at 1000°K as Predicted by Barnes, et al. (8)

substantiated when a more complete mechanism was considered, and when an inert, non-reacting gas, such as nitrogen or water was added. The added reaction step was

Results of the kinetic calculations with the more complete scheme (Eqs 2, 3, 4, 5) is compared to results based on the initial scheme (Eqs. 2, 3, 4) in Figure 9. Reaction System 2 as identified in Figure 9 is based on Equations 2 through 5 whereas Reaction System 1 uses Equations 2 through 4. The most important aspect portrayed by Figure 9 is that no overshoot in CH_3I above the equilibrium concentration occurs when the more complete mechanism was considered.

The obvious discrepancies in the predictions for the several cases shown in Figure 9 demonstrate the hazard of making such predictions without the benefit of needed experimental data. One concludes from these studies that methyl iodide formation by thermal reactions is not favored by conditions in post accident containment atmospheres, as appreciable quantities of methyl iodide could be predicted only when an incomplete kinetic scheme was considered.

Methyl iodide formation at the Savannah River Reactors was studied extensively, from a theoretical viewpoint, by Durant, et al.⁽³¹⁾ These authors considered formation of methyl iodide in the fuel, in the reactor vessel, and in the reactor building. Based on their postulated formation and decomposition processes, they concluded that only $10^{-6}\%$ of released iodine (the whole core inventory) could become airborne in the containment vessel as methyl iodide. This number is extremely small compared to experimental measurements which have been made, and one must conclude that their calculational model did not include one or more critically important factors.

In summary, we conclude that theoretical studies can serve as a valuable framework for extending the range of applicability of experimental

FIGURE 9. Comparison of CH₃I and HI Concentrations Predicted from Several Calculational Models Used by Barnes, et al.⁽⁹⁾

results, but that in the present case theoretical predictions are not firmly enough based to be a reliable means for predicting methyl iodide formation under accident conditions.

7.0 RADIOLYTIC FORMATION AND DEGRADATION OF ORGANIC IODIDES

Most of the containment type experiments described in Section 5 of this report were carried out under radiation fields which were low level compared to those which could occur in a LOCA. Therefore, radiation chemistry effects need to be superimposed on those obtained in the containment tests. Fortunately, a large body of information regarding radiolysis is available, and can be used to bracket organic iodide formation.

Three kinds of reactions leading to formation of organic iodides can be envisioned. These include radiolysis in water solution, a radiolytic formation process catalyzed by surfaces, and homogenous gas phase radiolytic formation. As will become apparent, radiolytic formation in the gas phase is expected to be by far the most important formation process.

Radiation levels in the containment vessel following a design basis loss of coolant accident may be estimated by calculating the dose from the released fission products. An example calculation of this type is shown in Appendix A of this report. The gas phase dose rate in the containment vessel would be approximately 10^6 R/hr shortly after fission product release. The integrated dose absorbed over the initial two hours following fission product release is estimated as approximately 3×10^6 rads. The total absorbed dose over a thirty day period in the containment atmosphere is calculated to be on the order of 2×10^7 rads.

The contribution of surface reactions to methyl iodide formation has been studied by Denschlag, et al⁽¹²⁾ and by Burger.⁽¹¹⁾ Denschlag, et al⁽¹²⁾ identified three mechanisms by which methyl iodide was produced from interaction of fission product iodine with methane. These were: reaction of methane with iodine atoms produced directly by fission, reaction of methane with iodine atoms produced by beta decay of precursors, and reaction of methane with iodine adsorbed on the wall of the container. The surface reaction was considerably enhanced by gamma radiation, but even under

relatively high radiation fields ($> 10^5$ R/hr) the reaction with surface deposited iodine was slow. The surface reaction could be described as first order, with a reaction half-time of more than 140 days. It was a negligible contributor to methyl iodide formation compared to the homogenous gas phase reactions.

Burger⁽¹¹⁾ studied the radiolytic formation of methyl iodide within chambers containing surfaces coated with a phenolic paint. No evidence of a surface reaction was apparent in these experiments. The primary formation process appeared to be a free radical reaction in the gas phase. The organic contaminants in the gas phase apparently resulted from evaporation of residual solvent from the paint. When the painted surfaces were aged by steaming much less solvent was evolved from the paint, and consequently, less methyl iodide was formed.

From the results of these two studies, we conclude that surface reactions will be unimportant compared to gas phase reactions in the radiolytic formation of methyl iodide.

Radiolysis reactions in aqueous solution have been studied extensively over the past 30 years. While we are not aware of any particular study designed specifically to quantify methyl iodide production under LOCA conditions, available information indicates that liquid phase radiolysis would produce little methyl iodide as compared to gas phase radiolysis.

The very low solubility of volatile alkanes in water is a factor which would limit their radiolysis in the aqueous phase as compared to the gas phase. For example, at 100°C, the equilibrium concentration of methane in water is less than 1% of the concentration in the gas phase. Thus, both the methane/iodine ratio and the absolute methane concentration would be lower in the liquid phase than in the gas phase, favoring gas phase reactions compared to liquid reactions. Long chain organic molecules such as oil or grease have low volatility, and would therefore be contained in the liquid phase. If these molecules were iodinated, they would still be comparatively non-volatile. Thus, we conclude that the low solubility of volatile organics in the aqueous phase tends to limit the importance of liquid phase radiolysis compared to gas phase radiolysis.

Organic impurities in aqueous solution may influence the yield of particular reactions. As an example, the influence of organic contaminants on the oxidation of ferrous ion is described by Spinks and Woods.⁽³²⁾ He lists the following reactions to explain the observed results.

The function of the organic molecules, RH, is to enhance the oxidation of Fe^{2+} . In doing so, it becomes oxidized to an alcohol. If a halogen salt is added, this oxidation mechanism is changed as a result of hydroxyl radicals being replaced by a halogen atom. For example, for chlorine the reactions are⁽³²⁾

This latter set of reactions indicates that organic iodides are not formed when organics and halides are irradiated in water solution. Halide salts are often added to aqueous solution to help identify free radical mechanisms for radiolysis reactions. Examples include studies of Schwarz, et al⁽³³⁾, of Hochanadel⁽³⁴⁾, and of Johnson and Allen⁽³⁵⁾. For iodides and bromides at least, the salts acted catalytically and no chemical changes in the salt occurred. Johnson and Allen⁽³⁵⁾ state "no detectable amount of any oxidized form of bromide or iodide was produced by radiation in the solutions studied".

Finally, methyl iodide in aqueous solution is degraded by radiation. Zittel⁽³⁶⁾ irradiated aqueous solutions of CH_3I in boric acid solutions, and found the apparent $G(-\text{CH}_3\text{I})$ depended on the concentration of CH_3I . Any methyl iodide present in the aqueous phase would be subject to radiolytic decomposition, thus limiting its buildup.

From this brief review of radiolysis in the aqueous phase, we conclude that if methyl iodide is formed in the aqueous phase at all, its rate of formation would be expected to be small compared to formation in the gas phase.

Formation of organic iodides by gas phase radiolysis has been the subject of many studies. These studies have included use of iodine as a free radical scavenger in physical chemical studies, possible use of radiation as a means for synthesizing methyl iodide, and the formation and degradation of methyl iodide under accident conditions in nuclear reactors.

Molecular iodine is one of the favored radical scavengers used to study free radicals formed by gas phase radiolysis. Radicals that are scavenged by iodine can be identified by identifying the radicals that are formed. As pointed out by Spinks and Woods⁽³²⁾, this identification can be accomplished rather elegantly by using radioactive iodine as a scavenger and identifying the radioactive iodides by isotope dilution.

Oxygen readily adds to free radicals, and if present will almost invariably play a part in radiation-induced reactions.⁽³²⁾ Thus one would expect yields of gas phase radiolysis reactions to depend markedly on whether or not air were present.

Early work on radiolytic formation of organic iodides was reported by Gevantman and Williams⁽¹⁰⁾ who irradiated gaseous mixtures of methane and iodine. Typical results of their work were shown earlier in this report in Figure 1. Methyl iodide was the chief organic iodide formed, and represented 80% of the total quantity of organic iodides formed. Hydrogen iodide represented 8%, and ethyl iodide 4% of the iodides, respectively. These studies were designed to shed light on formation mechanisms, and

therefore provide little quantitative information which can be applied to LOCA situations. Results were explainable in terms of free radical reactions. Follow-on work on radiolytic formation of organic iodides was done by Meisels, et. al.⁽³⁷⁾ who studied formation of organic iodides when krypton was added to the gas. Results were similar to those of Gevantman and Williams⁽¹⁰⁾, though HI was not formed to an appreciable extent. These results support a free radical mechanism which leads to formation of organic iodides. The yields for such reactions depend on the nature and concentrations of the surrounding atmospheric molecules. For this reason, yields measured at high methane and iodine concentration would be expected to be much higher than when air and steam were present to the levels applicable to LOCA conditions.

Vilenchich and Hodgins⁽³⁸⁾ irradiated gaseous mixtures of iodine and methane to determine the feasibility of using ionizing radiation as a means for synthesizing methyl iodide. Yields up to 60% were obtained when iodine-methane mixtures (14:1 mole ratio $\text{CH}_4:\text{I}_2$) at a total pressure of 1200 mm were irradiated to a total dose of 10^8 rads. Although these results would not apply to a LOCA, they confirm the radical reaction between iodine and aliphatic hydrocarbons in the gas phase.

Barnes, et al⁽⁹⁾ carried out experiments on radiolytic formation of methyl iodide. These experiments were exploratory and used conditions which do not directly apply to a LOCA. When gas mixtures containing only iodine and methane were irradiated, conversion of I_2 to CH_3I was observed. Typical results are shown on Figure 10. Although the conditions were atypical because of high methane abundance and high iodine concentrations (a minimum of $8,000 \text{ mg/m}^3$) an increased conversion to methyl iodide with increased dosage and methane abundance is shown.

Barnes, et al⁽⁹⁾ also measured methyl iodide formation when water, air and oxygen were present. Their results are reproduced in Figure 11. It is apparent that the addition of both water and air can have an appreciable influence on reducing the methyl iodide conversion. The curve most applicable to LOCA conditions is that for $\text{H}_2\text{O} + 300 \text{ mm O}_2$, and for this case, CH_3I levels off to about 0.3% conversion as dose rate increases.

FIGURE 10. Radiation Conversion of Methane-Iodine to Methyl Iodide As Reported by Barnes, et al. (9)

FIGURE 11. Effect of Water, Air, and Oxygen on Radiation Conversion of Iodine to Methyl Iodide As Measured by Barnes, et al.⁽⁹⁾

It is apparent that CH_3I formation is greatly hindered by the presence of oxygen. Since the oxygen/iodine ratio for LOCA conditions will be much higher than for the experiment which used 300 mm O_2 , less conversion to methyl iodide would be expected for the post-accident case. Charamathieu⁽³⁹⁾ and his associates have reported results of five experiments on the effect of radiation on methyl iodide formation with initial I_2 concentrations of .1 to 10 mg/m^3 . The results are presented in Table 4. Percent conversions varied from 0.2% to 24%, depending on the initial iodine concentration, dose, and gas composition. The presence of a small amount of water vapor greatly reduced the amount of methyl iodide formed. It should be noted that the methane: iodine ratio was equal to or greater than 5.5×10^4 . This high relative abundance would tend to maximize conversion of iodine to methyl iodide. Much lower methane:iodine ratios would exist under the accident situation.

The yield of methyl iodide under postulated accident conditions was predicted from results obtained by Barnes⁽⁹⁾ and Charamathieu⁽³⁹⁾ on the basis of the $G(\text{CH}_3\text{I})$ value. A plot of $G(\text{CH}_3\text{I})$ versus iodine concentration is shown in Figure 12. The dashed curve represents an interpolation line for methane-iodine mixtures which do not contain diluent gases. A solid curve, parallel to the dashed curve, represents an interpolation line for gas mixtures which contain water and/or oxygen. Since both water and air will be present in abundance under accident conditions, the lower curve was used to predict a $G(\text{CH}_3\text{I})$ value for accident conditions. At an iodine concentration of 100 mg/M^3 , the G value is 0.004. For postulated accidents where the absorbed dose is 3.2×10^6 R, one predicts a conversion of 2.2% of elemental iodine to methyl iodide.

The $G(\text{CH}_3\text{I})$ defined by the solid curve in Figure 12 is believed to represent an upper limit to $G(\text{CH}_3\text{I})$ as compared to postulated accident conditions. This expectation is based on the following factors.

- The Battelle work⁽⁹⁾ was done at unrealistically high iodine concentration (20,800 mg/M^3) and therefore the iodine/oxygen ratio was 200 times greater than for postulated accidents. Since oxygen is a competing

TABLE 4. Radiolytic Formation of Methyl Iodide In Gaseous Atmospheres As Measured by Charamathieu⁽³⁹⁾

Mixture	Irradiation Time (hr)	Radiation Dose (rad)	Iodine Concentration ($\frac{g}{cm^3}$) ($\frac{mg}{m^3}$)		CH ₄ Concentration (g/cm ³)	H ₂ O Present (g/cm ³)	CH ₄ :I ₂ Mole Ratio	I ₂ Crystal Temperature (°C)	Mass of CH ₃ I in Ampoule (g)	Percentage of I ₂ Converted to CH ₃ I	Conversion Due to Radiation (%)
I ₂ + CH ₄	0	0	1 x 10 ⁻⁸	10	7 x 10 ⁻⁵		5.5 x 10 ⁴	-35	7.6 x 10 ⁻⁸	1.6	
	64	3 x 10 ⁶	1 x 10 ⁻⁸	10	7 x 10 ⁻⁵			-35	1.89 x 10 ⁻⁷	3.95	2.35
	128	6 x 10 ⁶	1 x 10 ⁻⁸	10	7 x 10 ⁻⁵			-35	2.08 x 10 ⁻⁷	4.33	2.73
I ₂ + CH ₄ + H ₂ O	0	0	5 x 10 ⁻⁹	5	7 x 10 ⁻⁵	7.5 x 10 ⁻⁶	2.7 x 10 ⁵	-35	2.45 x 10 ⁻⁸	1	
	64	3 x 10 ⁶	5 x 10 ⁻⁹	5	7 x 10 ⁻⁵	7.5 x 10 ⁻⁶		-35	2.82 x 10 ⁻⁸	1.22	0.22
	128	6 x 10 ⁶	5 x 10 ⁻⁹	5	7 x 10 ⁻⁵	7.5 x 10 ⁻⁶		-35	3.15 x 10 ⁻⁸	1.31	0.31
I ₂ + CH ₄	0	0	1 x 10 ⁻⁸	10	7 x 10 ⁻⁵		5.5 x 10 ⁴	-35	2.3 x 10 ⁻⁸	0.48	
	64	3 x 10 ⁶	1 x 10 ⁻⁸	10	7 x 10 ⁻⁵			-35	3.7 x 10 ⁻⁸	0.77	0.29
	128	6 x 10 ⁶	1 x 10 ⁻⁸	10	7 x 10 ⁻⁵			-35	6.7 x 10 ⁻⁸	1.4	0.92
I ₂ + CH ₄	0	0	1 x 10 ⁻⁹	1	7 x 10 ⁻⁵		5.5 x 10 ⁵	-54	1.8 x 10 ⁻⁸	3.8	
	64	3 x 10 ⁶	1 x 10 ⁻⁹	1	7 x 10 ⁻⁵			-54	1.13 x 10 ⁻⁷	26.6	21.8
	128	6 x 10 ⁶	1 x 10 ⁻⁹	1	7 x 10 ⁻⁵			-54	7.9 x 10 ⁻⁸	16.4	12.6
I ₂ + CH ₄	0	0	1 x 10 ⁻¹⁰	10	7 x 10 ⁻⁵		5.5 x 10 ⁶	-72	1.8 x 10 ⁻⁸	37	
	64	3 x 10 ⁶	1 x 10 ⁻¹⁰	10	7 x 10 ⁻⁵			-72	2.95 x 10 ⁻⁸	61.4	24.4
	128	6 x 10 ⁶	1 x 10 ⁻¹⁰	10	7 x 10 ⁻⁵			-72	2.85 x 10 ⁻⁸	59	22

FIGURE 12. $G(\text{CH}_3\text{I})$ For Radiolytic Formation In Gaseous Atmospheres

radical scavenger, a decrease in the iodine/oxygen ratio would tend to lower the reaction between organic radicals and iodine.

- The Battelle work⁽⁹⁾ used a methane/iodine ratio of 100, which is much higher than would exist under accident conditions. Even if one were to consider the addition of 3 kg of methane to a containment atmosphere, the methane/iodine ratio would be only 10. A more realistic estimate of 2 ppm methane, results in a methane/iodine ratio of 0.2. A reduction in the methane/iodine ratio would tend to reduce the efficiency of the reaction, and thus the $G(\text{CH}_3\text{I})$ would be expected to be smaller under accident conditions as compared to the Battelle experiments.
- The French work⁽³⁹⁾ was done at more realistic iodine concentrations, but employed very high methane/iodine ratios. These ranged from 5.5×10^4 to 5.5×10^6 . Thus the G value for the experiments would be expected to be higher than for accident conditions where the methane/iodine ratio would be no more than 0.001 times that used in the French experiments.
- The French work used only very low levels of water vapor, and no oxygen. Addition of realistic amounts of air and water would be expected to greatly lower the G value. Thus a lower $G(\text{CH}_3\text{I})$ would be expected for accident conditions than was obtained from their experiments.

By definition, the G value is equal to the number of molecules transformed per 100 ev of energy absorbed. Since 1 rad is equivalent to 6.24×10^{13} ev absorbed per gram, the G value is related to the percentage conversion according to

$$G = \frac{C_o \% N}{6.24 \times 10^{13} \text{ MRp}} \quad (14)$$

where C_0 = initial concentration of converted specie, g cm^{-3}
 $\%$ = percent of specie which is converted, dimensionless
 N = Avagadro's number, $\text{molecules mole}^{-1}$
 M = mole wt. of converted specie in product, g mole^{-1}
 R = absorbed dose, rads
 ρ = density of medium, g cm^{-3}

Equation (14) was used to calculate the percentage conversion to organic iodides for mixtures with various initial concentrations. The interpolation curve shown in Figure 12 (solid line) was used to predict G values. The result is shown in Figure 13. Also shown in Figure 13 is the upper limit conversion indicated by the containment experiments summarized in Figure 2. A total percentage curve is also shown. This total percentage conversion curve, formed by adding results from containment and radiolysis experiments, represents an upper limit estimate for LOCA conditions. At 100 mg/M^3 , the total curve indicates a conversion of 3.2%.

In predicting radiolytic formation, it has been assumed that the initial concentration of iodine persists indefinitely. Under accident conditions, spray washout would typically remove more than 95% of elemental iodine in 10 minutes. In the worst case, assuming sprays did not operate, natural deposition would deplete more than 90% of the elemental iodine within the first two hours. Therefore, the total curve represented in Figure 13 does not account for decreased radiolytic formation of organic iodides expected due to iodine washout. If one accounted only for natural deposition, radiolytic formation of organic iodides would be reduced by a factor of more than two, lowering the total percent converted from 3.2% to 2.1%.

Up to this point, this study has focused on the formation of methyl iodide by radiation processes. To complete the picture, one must also consider radiolytic decomposition. The decomposition of methyl iodide by radiolysis has been studied by Barnes, et al⁽⁹⁾, by Tang and Castleman⁽⁴⁰⁾, and by Zittel.⁽³⁶⁾ The work of Tang and Castleman⁽⁴⁰⁾, is the most complete of the three, and their results will be briefly discussed.

FIGURE 13. Predicted Maximum Conversion of Elemental Iodine To Volatile Organic Iodides

Experimental measurements of methyl iodide decomposition in air at 15°C were conducted by Tang and Castleman⁽⁴⁰⁾ for initial concentrations which ranged from 3×10^{-9} to 2.4×10^{-4} molar. Methyl iodide was introduced into a pyrex or quartz flask (400 ml) along with one atmosphere of dry air. Methyl iodide remaining was measured chromatographically. Results for dry air are summarized in Figure 14. The decomposition rate depends on the initial concentration for concentrations greater than 10^{-6} molar. For accident conditions the methyl iodide concentrations will be less than 10^{-6} molar, and hence the applicable data indicate a first order decomposition rate.

The influence of water vapor is shown in Figure 15, where the percent of CH_3I remaining is shown as a function of absorbed dose for three water vapor concentrations. It is obvious that water vapor can inhibit the decomposition process. The highest water vapor concentration used in the experiments (2.1×10^{-7} mol/cc) is lower than would be present under LOCA conditions. Zittel⁽³⁶⁾ also studied decomposition of methyl iodide in moist air. Zittel's data are in reasonable agreement with those shown as the upper most curve in Figure 15. According to Zittel's data the G value for destruction is near 20, a value considerably larger than the G value for formation as estimated in this work. This should prevent buildup of methyl iodide concentration to an appreciable level.

In summary, it is apparent that methyl iodide is sensitive to radiation, and this would limit its buildup under accident conditions. Ideally, one would predict organic iodide formation under accident conditions accounting for formation and decomposition processes. In order to arrive at a conservative estimates of organic iodide formation, we have purposely neglected decomposition as a separate process, and have based our predictions on observed G values for the formation process. The G values measured for formation are net values, and presumably account for some decomposition which occurs during the formation period. However, decomposition in the formation type experiments would be minor compared to that expected for the accident because the overabundance of iodine and methane used in experiments favor formation compared to decomposition.

FIGURE 14. Summary of Results of Tang and Castleman⁽⁴⁰⁾ on Decomposition of Methyl Iodide by Gamma Radiation in Dry Air at 15°C

FIGURE 15. Effect of Water Vapor on Methyl Iodide Decomposition⁽⁴⁰⁾
By Gamma Radiation as Measured by Tang and Castleman

Our neglecting of decomposition of methyl iodide is a conservative assumption which leads to predicted methyl iodide concentration which are not impractically high for the initial two hour period following a LOCA. However, it is possible that unrealistically high methyl iodide conversions could be predicted for longer time periods if methyl iodide decomposition were neglected. We have not attempted to predict methyl iodide behavior over long time periods.

8.0 ADEQUACY OF EXISTING DATA AS APPLIED TO A LOCA

Existing data, theoretical and experimental, are considered adequate if one can confidently predict an upper bound to the methyl iodide percentage for serious LOCA's of the magnitude described in TID-14844. In this section, potential formation processes will be examined in light of existing data to determine whether the available information allows conservative projections to the LOCA condition.

As noted in the BACKGROUND section of this report, the overall formation process for organic iodides may be considered to involve the following processes.

- A. Formation within fuel
- B. Surface reactions subsequent to release from fuel
- C. Homogenous reactions subsequent to release from fuel

We will briefly discuss each of these processes in light of available information in order to establish whether the contribution of each process can be assessed under accident conditions.

A. Formation Within Fuel

Methyl iodide could conceivably form within the fuel by reaction of iodine with trace level hydrocarbon contaminants. However, the high temperatures and radiation fields existing within operating fuel would prevent buildup of significant quantities of methyl iodide. The theoretical studies of Barnes, et al^(7,8,9) and Durant, et al⁽³¹⁾ would lead one to conclude that the equilibrium methyl iodide percentage in the fuel would be extremely low, less than 0.1%. However, the more convincing evidence comes from experimental measurements where irradiated UO_2 was heated and iodine evolved.

The fractional conversion to organic iodides of iodine released from irradiated fuel was compared to that for iodine released as elemental iodine in Figure 4. It was noted that data on conversion to organic iodides for highly irradiated fuel fell above data obtained with simulants and trace irradiated fuel. However, this enhanced formation is most likely the result of small vessel size, because experiments done in the same vessel do not show an influence of irradiation history. For example, organic iodide formation in CDE was comparable for the two high level runs (points 62 and 63) and the 6 tracer runs (points 64 through 69). This same consistency between tests with highly irradiated and simulants is apparent for all available facilities including CRI, CMF, and IPI. Thus we conclude first that iodine is released from irradiated fuel primarily as elemental iodine. Second, any minor impact of fuel irradiation has been accounted for because the conservative predictor line shown in Figure 2 lies above all data, including that obtained where highly irradiated fuel was the iodine source. In summary, organic iodide formation processes within the fuel have been adequately accounted for in available experiments. The experimental results are in agreement with theoretical predictions which indicate very low equilibrium levels of methyl iodide in fuels.

B. Surface Reactions Subsequent to Release From Fuel

Once iodine is evolved from failed fuel in the core, it will be carried from the primary vessel by flowing steam to the containment vessel. Gas-borne iodine will thus be exposed to fuel rods (Zircaloy), primary system components (stainless steel), and containment vessel surfaces (painted carbon steel, concrete, stainless steel). One can postulate surface catalyzed reactions in which I_2 atoms absorb on a surface, react on the surface with adsorbed hydrocarbon contaminants, and desorb as organic iodides. This kind of surface reaction cannot be adequately handled from a theoretical basis alone so one must rely on applicable experimental measurements. Experiments completed have involved exposure of elemental iodine to all of the surfaces listed above under conditions of temperature and atmospheric composition which include those for LOCA conditions. From experiments involving high radiation fields,

it may be concluded that surface reactions are unimportant compared to gas phase radiolysis. The relatively high surface to volume ratio encountered in experiments tends to amplify whatever surface effects exist. As noted earlier, methyl iodide formation appeared to be highest in the smallest equipment. Since we have placed our upper bound high enough to include all experiments, it seems safe to conclude that surface reactions have been more than adequately accounted for.

C. Homogenous Reactions Subsequent to Release From Fuel

Homogenous reactions could occur in the gas phase or liquid phase to produce organic iodides. In many of the containment experiments, both gas and aqueous phases were present under conditions reasonably duplicating LOCA conditions except for the high radiation fields. Thus any thermal reactions that might occur would have occurred in the containment type experiments and are accounted for. Radiolysis reactions were studied separately, and it appears that radiolysis in the aqueous phase would produce little organic iodide compared to gas phase radiolysis. Several experiments on gas phase radiolysis were used to arrive at a $G(\text{CH}_3\text{I})$. For accident conditions, a smaller $G(\text{CH}_3\text{I})$ would be expected because of lesser amounts of organic materials and iodine, and greater amounts of diluent gases. Also, radiolytic decomposition was not accounted for in a realistic manner, leading to an overprediction in organic iodide formation. In summary, we conclude that homogenous reactions have been accounted for in a conservative manner.

A remaining question centers on possible existence of appreciable quantities of hypoiodous acid in the containment atmosphere. The HOI issue was not raised until after most of the experiments on iodine behavior described in this report had been completed. For this reason, no attempt was made to measure the airborne concentration of HOI. It must be admitted that HOI has not been positively identified as an airborne specie, so discussions related to HOI are conjectural. Based on properties attributed to HOI, it would be expected to deposit on the charcoal components of a Maypack sampler. Little deposition would occur on silver surfaces or on filters. The fractionation of HOI between the charcoal paper and the

charcoal bed components of a Maypack cannot be stated with certainty. In the analysis of organic iodides made in this report, we added the concentrations indicated by the charcoal bed and the charcoal impregnated paper and called the total organic iodides. This was done where detailed Maypack data were available, which included results from Battelle-Northwest and a part of the results from the British and Oak Ridge. In much of the Oak Ridge work, details of this type were not available, and we used the reported values of "organic iodides". For the detailed data then, HOI, if it exists, would be counted as organic iodides. In summary, HOI, if it exists, has been counted as organic iodides in much of the data described in this review.

9.0 POSSIBLE AREA FOR ADDITIONAL WORK

On the basis of the work reviewed in this report, a conservative estimate of organic iodide formation was made. It is quite possible that this estimate is an order of magnitude or more too high. However, it appears that additional experiments carried out under simulated accident conditions would be necessary before significantly lower methyl iodide percentages could be accepted. An experimental program design should allow for the following factors.

1. Temperature range from 25°C to 140°C.
2. Gas phase consisting of 1 atm. of air saturated with water.
3. Aqueous phase containing typical chemical additives.
4. Presence of representative materials including structural materials, coatings, and piping.
5. Organic contaminants typical of aged reactor system.
6. Radiation levels typical of design basis LOCA.
7. Iodine concentrations typical of LOCA release.

It is anticipated that results of a well planned and documented experimental program which included these factors would provide a basis for substantially lowering the assumed methyl iodide level below the value of 3.2% arrived at in this study.

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11.0 APPENDIX A

The calculations which follow develop and document the basis for (1) an initial iodine airborne concentration of 100 mg/m^3 , (2) a two hour average airborne gamma dose of $3.2 \times 10^6 \text{ R}$ for a PWR containment, and (3) the concentrations necessary to give an initial molar ratio of methane to iodine of 1:10.

A. Estimation of Macroscopic Fission Cross Section Averaged Over the Entire Core

$$(1) \quad P = \frac{V \Sigma_f \phi}{3.1 \times 10^{16}}$$

where P = Power (MWt)

V = Active Core Region (cc)

Σ_f = Average Macroscopic Fission Cross Section (cm^{-1})

ϕ = Average Thermal Core Flux ($\text{nts/cm}^2 \text{ sec}$)

For a typical 1972 commercial power reactor

$P = 3600 \text{ MWt}$

$V = 1100 \text{ ft}^3 \quad (3.1 \times 10^7 \text{ cc})$

$\phi = 5 \times 10^3 \text{ nts/cm}^2\text{-sec}$

Solve (1) for Σ_f

$$\Sigma_f = .07 \text{ cm}^{-1}$$

B. Estimation of Core Iodine Inventory

$$(1) \quad A_i(t) = \frac{V_a \Sigma_f \phi}{\lambda_A} (1 - e^{-\lambda_A t}) + A(0) e^{-\lambda_A t}$$

where $A(t)$ = concentration of nuclei i at time t (Atoms/cc)

V_A = fission yield of nuclei i

Σ_f = core averaged thermal macroscopic cross section (cm^{-1})

ϕ = core averaged thermal neutron flux

T = period of reactor operation (sec)

$$\lambda_A = \lambda_A + \sigma_a \phi$$

λ_A = decay constant of nuclei (sec^{-1})

σ_a = absorption cross section (cm^2)

Assuming $A(0) = 0$ at $t = 0$

$$T = 3 \text{ years } (9.52 \times 10^7 \text{ sec})$$

$$\text{and } V = 1100 \text{ ft}^3 (3.1 \times 10^7 \text{ cc})$$

$$(2) \quad B_i(T) = \frac{A_i(T) V M}{N_0}$$

where $B_i(T)$ = grams of nuclei i

M = molecular weight of nuclei (grams g mole^{-1})

N_0 = Avagado's number (atoms g mole^{-1})

Combining (1) and (2) and assumptions:

$$B_i(T) = \frac{V_A \Sigma_f VM}{(\lambda_A + \sigma_a \phi)} (1 - e^{-(\lambda_A + \sigma_a \phi)T})$$

If $\sigma_a \phi \gg \lambda_A$

$$(3) \quad B_i(T) = \frac{V_A \Sigma_f VM}{\sigma_a N_0} (1 - e^{-\sigma_a \phi T})$$

If $\sigma_a \phi \ll \lambda_A$

$$(4) \quad B_i(T) = \frac{V_A \Sigma_f \phi VM}{\lambda_A N_0} (1 - e^{-\lambda_A T})$$

If $\sigma_a \phi \ll \lambda_A$ and $\lambda_A T \gg 1$

$$(5) \quad B_i(T) = \frac{V_A \Sigma_f \phi VM}{\lambda_A N_0}$$

EXAMPLES:

i) For I-127

$$\begin{aligned}\lambda_A &= 0 \\ V_A &= .00137 \\ \sigma_a &= 6.4b = 6.4 \times 10^{-24} \text{ cm}^2 \\ \sigma_a \phi &\gg \lambda_A = \text{use equation (3)} \\ \sigma_a \phi &= 6.4 \times 10^{-24} \times 5 \times 10^{13} \\ &= 3.2 \times 10^{-10} \text{ nts/sec} \\ \sigma_a \phi T &= .030 \\ 1 - e^{-\sigma_a \phi T} &= .0295\end{aligned}$$

$$\begin{aligned}B_i(T) &= \frac{.00137 \times .07 \times 1.1 \times 10^3 \times 2.832 \times 10^4 \times 127 \times .0295}{6023 \times 10^{24} \times 6.4 \times 10^{24}} \\ &= 2880 \text{ grams I-127}\end{aligned}$$

ii) For I-129

$$\begin{aligned}\lambda_A &= 0 \\ V_A &= .01 \\ \sigma_a &= 286 = 28 \times 10^{-24} \text{ cm}^2 \\ \sigma_a \phi &\gg \lambda_A = \text{use equation (3)}\end{aligned}$$

$$B_i(T) = 20,800 \text{ grams}$$

iii) For I-131

$$\begin{aligned}\lambda_A &= 10^{-6} \text{ sec}^{-1} \\ V_A &= .0291 \\ \sigma_a &= .7b = .7 \times 10^{-24} \text{ cm}^2 \\ \sigma_a \phi &= 3.5 \times 10^{-11} \ll \lambda_A \\ \lambda_A T &= 95.2 \gg 1 \text{ use equation (5)}\end{aligned}$$

$$\begin{aligned}B_i &= \frac{.0291 \times .07 \times 5 \times 10^{13} \times 1.1 \times 10^3 \times 2.832 \times 10^4 \times 131}{10^{-6} \times 6.023 \times 10^{23}} \\ &= 684 \text{ grams}\end{aligned}$$

- iv) Calculation for I-132 thru I-135 are similar to I-131. Only the data and results are presented.

Isotope	t 1/2	σ_a	λ_A	B_i (grams)
I-131	8.05d	$\sim .7b$	.0291	684
I-132	2.26h	0	.0426	12
I-133	20.3h	0	.0669	167
I-134	52m	0	.078	8
I-135	6.68h	0	.0617	50
				$\Sigma = 921$ grams

$$\begin{aligned}\text{Total Core iodine inventory} &= 921 + 20,800 + 2880 \\ &= 24,600 \text{ grams}\end{aligned}$$

C. Estimation of Iodine Concentration and Molar Content in a Typical PWR Containment for TID-14844 Release Assumptions

- (1) Volume of a Typical Containment is $2 \times 10^6 \text{ ft}^3$
- (2) 25% of the Iodine inventory is airborne

$$C_T = \frac{24600g}{4} \times \frac{10^3 \text{ mg}}{g} \times \frac{1}{2 \times 10^6 \text{ ft}^3} \times \frac{1}{\frac{2.832 \times 10^{-2} \text{ m}^3}{\text{ft}^3}}$$

$$C_T = 108 \text{ mg/m}^3$$

Gram moles of Iodine Airborne in the containment

$$G_T \sim \frac{6150 \text{ grams}}{258 \text{ grams}} \times \frac{1}{\text{g moles}} = 24 \text{ g moles.}$$

*The molecular weight has been assumed to be 258 since I-129 is the major nuclei present.

D. Estimation of Methane Concentration and Molar Content in a Typical PWR Containment

If methane concentration is 2 ppm⁽¹⁾

$$2 \text{ ppm (by volume)} \times (2 \times 10^6) \text{ ft}^3 = 4 \text{ ft}^3 \text{ methane}$$

$$4 \text{ ft}^3 \text{ methane} \times \frac{28320 \text{ cc}}{\text{ft}^3} \times \frac{\text{g/mole}}{22400 \text{ cc}}$$

5 g moles methane

Molar ratio of Methane to Iodine is 5 g moles : 24 g moles
(approximately 1:5)

A 10:1 methane to iodine molar ratio requires a concentration of 100 ppm methane (approximately 3000 grams of methane in a typical containment).

E. Tabulation of the Airborne Curie Inventory

Assuming an airborne dose of 100% of the Noble Gases and 25% of the Iodines the following table is obtained.

<u>Time Period</u>	<u>Total Inventory Curies</u>	<u>Average Gamma Energy (Mev)</u>
0-2 hours	7.95×10^8	.706
0-8 hours	5.9×10^8	.501
8-24 hours	2.6×10^8	.241
1-4 days	1.8×10^8	.120
4-30 days	4.0×10^7	.102

$$(1) \bar{C} = \sum C_i f_i$$

where $\bar{C}$ = total average curies

C_i = Curies of isotope i released

f_i = average function of isotope i during time interval,
 $t_2 - t_1$

(1) Handbook of Chemistry and Physics, 42nd Ed., page 3391, Chem. Rubber Pub. Co., Ohio.

$$f_i = \frac{\int_{t_1}^{t_2} \sigma e^{-\lambda t} dt}{\int_{t_1}^{t_2} dt}$$

(2) Defined as

$$\bar{E} = \Sigma C_i f_i E_i / \Sigma C_i f_i$$

where E_i = average gamma energy of isotope i

F. Estimation of Gas Phase Containment Dose and Dose Rates During a LOCA

Assume a Cylindrical System shown with a volume ($V =$) $2 \times 10^6 \text{ ft}^3$

Let $H = 100 \text{ ft}$

$$2 \times 10^6 \text{ ft}^3 = 3.14 R^2 200$$

$$R = 56 \text{ ft}$$

Dose Rate at Point P is given by

$$D = \frac{BS_V G (\mu_S H, \mu_S R)}{\mu_S (\text{DCF})} \quad \text{from Rockwell}^{(1)}$$

(1) Rockwell, T., Reactor Shielding Design Manual, TID-7004, March 1956.

where D = Dose Rate (R/hr)

B = Buildup term, assumed to be 1 for air calculations

S_v = volumetric source term (dis/cc-sec)

μ_s = linear absorption coefficient (cm^{-1})

DCF = dose conversion factor ($\text{photons}/\text{cm}^2\text{-sec}/\text{R/hr}$)

Sample calculation:

1) For 0-2 hours (from Section E)

$$\bar{C} = 7.95 \times 10^8 \text{ curies}$$

$$\bar{E} = .706 \text{ MeV}$$

$$S_v = \frac{7.95 \times 10^8 \text{ curies} \times 3.7 \times 10^{10} \text{ dps/curie}}{2 \times 10^6 \text{ ft}^3 \times 2.83 \times 10^4 \text{ cc/ft}^3}$$

$$S_v = 5.2 \times 10^8 \text{ dis/cc-sec}$$

$$\frac{\mu_s}{\rho} (@ E = .7 \text{ MeV}) = .075 \text{ (from Rockwell)}$$

$$\rho_{\text{air}} = 1.3 \times 10^{-3} \text{ gr/cc}$$

$$\mu_s = .075 \times 1.3 \times 10^{-3} = 9.75 \times 10^{-5} \text{ cm}^{-1}$$

$$\mu_s H = 9.75 \times 10^{-5} \times 100 \times 30.48 = .3$$

$$\mu_s R = .17$$

$$G(\mu_s H, \mu_s R) = .21 \text{ (p 366 Rockwell)}$$

$$\text{DCF} = \frac{7 \times 10^5 \text{ photons}/\text{cm}^2\text{-sec @ .7 MeV}}{\text{R/hr}}$$

$$\text{Dose Rate} = \frac{5.2 \times 10^8 \times .21}{9.7 \times 10^{-5}} \times \frac{1}{7 \times 10^5}$$

$$= .016 \times 10^8 \text{ R/hr}$$

$$= 1.6 \times 10^6 \text{ R/hr}$$

$$\text{Average Absorbed Dose for 0-2 hours} = 2 \times 1.6 \times 10^6 \text{ R}$$

$$= 3.2 \times 10^6 \text{ R}$$

ii) For all other time periods the calculation are the same.

Pertinent data and results are tabulated below.

<u>Time Interval</u>	<u>μ_s/ρ</u>	<u>G</u>	<u>DCF</u>	<u>Dose Rate (R/hr)</u>
0-2 hours	.075	.21	7×10^5	1.6×10^6
0-8 hours	.087	.23	9.5×10^5	$.8 \times 10^6$
8-24 hours	.12	.32	2×10^6	$.17 \times 10^6$
1-4 days	.15	.38	5×10^6	$.05 \times 10^6$
4-30 days	.16	.41	6.5×10^6	$.01 \times 10^6$

Average Absorbed Dose

<u>Time Interval</u>	<u>$\Delta T(h)$</u>	<u>Dose Rate (R/hr)</u>	<u>Dose (R)*</u>
0-2 hours	2	1.6×10^6	3.2×10^6
2-8 hours	6	$.8 \times 10^6$	4.8×10^6
8-24 hours	16	$.17 \times 10^6$	2.72×10^6
1-4 days	72	$.05 \times 10^6$	3.6×10^6
4-30 days	624	$.01 \times 10^6$	6.24×10^6

$$\sim \quad 0-30 \text{ day dose} = 18 \times 10^6 \text{ R}$$

*Only gamma radiation has been considered since only gammas have the penetrating power in a containment under DBA conditions. If beta contributions were added to the dose (and the betas treated as gammas) the dose would approximately double.