PROCEEDINGS OF THE SECOND CSNI WORKSHOP ON IODINE CHEMISTRY IN REACTOR SAFETY

Organized under the auspices of the OECD Nuclear Energy Agency, Committee on the Safety of Nuclear Installations

and

Hosted by Atomic Energy of Canada Limited and Ontario Hydro

Toronto, Canada 1988 June 2-3

Edited by A. C. Vikis

1989 March
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EDITORIAL NOTE

In preparing these proceedings, the original manuscripts, as submitted by the authors, were used without further editorial changes.
FOREWORD

The Second CSNI Workshop on Iodine Chemistry in Reactor Safety was held in Toronto, Canada, on 1988 June 2 and 3. The Workshop was hosted by Atomic Energy of Canada Limited (AECL) and Ontario Hydro, and was attended by about forty iodine experts from ten OECD countries. Nineteen research papers were presented on various aspects of iodine chemistry, ranging from the most fundamental to the most applied. These papers and the ensuing discussions indicate that substantial progress was made in understanding the chemistry of iodine in water-cooled power-reactor accidents. The Workshop was a most effective forum for exchanging information on new progress and for delineating problems requiring resolution.

As Chairman of the Workshop, I wish to thank the authors who have made this Workshop possible with their excellent contributions; the Program Committee, namely Dr. E.C. Beahm (USA), Dr. P.N. Clough (UK), Dr. W. Morell (FRG), Dr. P.E. Potter (UK) and Dr. J. Royen (OECD) for preparing the program; and the session Chairmen for running the Workshop. Also, I would like to acknowledge Mr. R.J. Fluke (Ontario Hydro) for his assistance with local arrangements and Dr. W. Kupferschmidt (AECL), Mr. A. Melnyk (AECL) and Mrs. C.J. Rohrig (AECL) for their assistance in organizing the Workshop and preparing these proceedings.

A.C. VIKIS
Chairman, Second CSNI Workshop on Iodine Chemistry in Reactor Safety
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INTRODUCTION

It is my pleasure to welcome you, on behalf of the OECD and its Nuclear Energy Agency, to this Second CSNI Workshop on the Chemistry of Iodine in Reactor Safety, organized in collaboration with Atomic Energy of Canada Limited and Ontario Hydro.

Iodine chemistry continues to enjoy high priority in the CSNI programs of work as part of severe accident source term studies. Following the Three Mile Island accident, considerable interest was generated in the chemical form of iodine in severe accidents. Because of the apparent small release of iodine to the containment, it was suggested that the chemical form of iodine must have hindered its release from the reactor coolant system; it was concluded tentatively that a low-volatility iodide compound, namely cesium iodide, had been formed, and that it had been transported as such within the plant instead of molecular iodine as previously assumed. In fact, there was very little direct evidence from the TMI accident that indicated what the chemical form of the iodine was during reactor coolant system transport or in the containment. Thermodynamic analyses conducted for NUREG-0772 (published in 1981) showed the formation of cesium iodide during transport in the reactor coolant system, but its formation was not favoured in the reactor core. Since the publication of NUREG-0772, additional experimental evidence indicates that other factors may also affect cesium iodide stability in the reactor coolant system. The environment created during a reactor accident contains a large number of chemical species and this results in a complex chemistry. Factors affecting the chemical form of iodine in the reactor coolant system - and therefore its volatility - include the cesium-to-iodine ratio, boron compounds, hydrogen-to-steam ratio, temperature, pH and redox potential of the aqueous medium, and possibly others such as radiation. They will thus depend on the type of accident.

If iodine is transported through the reactor coolant system as cesium iodide, because of its lower volatility, a significant fraction of iodine would be retained by aerosol deposition or condensation. In this case, iodine release to the containment is reduced, which is particularly important in accident analyses involving early containment failures. On the other hand, volatile iodides such as $I_2$ and HI are more readily transported in the reactor coolant system. In this case, the major parameter affecting the release of iodine is the amount of volatile iodide generated in the reactor coolant system.

A detailed understanding of the chemistry of iodine in aqueous solutions is an essential step in the prediction of the magnitude of possible releases of volatile iodine to the environment in water reactor accidents.

The key issues, therefore, are:

1. what are the chemical forms of iodine in the reactor coolant system over the range of severe accident conditions, and
2. how would they affect severe accident iodine source terms.
These issues affect all types of plants and accident sequences. They are important components of the mandate of Principal Working Group No. 4 on the Confinement of Accidental Radioactive Releases of the NEA's Committee on the Safety of Nuclear Installations (CSNI). They have been included in the 1989-1991 programme of work of the Group.

It is my pleasure to thank, on behalf of NEA, Atomic Energy of Canada Limited and Ontario Hydro for the hospitality generously offered to this Workshop. We also would like to thank the members of the Programme Committee, Dr. Beahm, Dr. Clough, Dr. Neeb (represented by Dr. Morell), Dr. Potter and more particularly Dr. Vikis who has taken charge of the Canadian part of the organization of the Workshop. Thanks to their efforts and advice, the meeting will be fruitful and very interesting.

We would also like to thank Ontario Hydro, in particular Mr. Fluke, for organizing yesterday a very informative visit to the Darlington nuclear power plant. Few of us had seen a CANDU reactor before that; the visit and the explanations were most interesting.

J. ROYEN
CSNI SECRETARY
SECOND CSNI WORKSHOP ON IODINE CHEMISTRY
IN REACTOR SAFETY

SUMMARY/RECOMMENDATIONS

The second CSNI Workshop on Iodine Chemistry in Reactor Safety was held in Toronto, on 1988 June 2 & 3, and was attended by about forty iodine experts from ten OECD countries. The Workshop was an effective forum for exchanging information on the behaviour of iodine under power-reactor accident conditions. Overall, it was noted that substantial progress was made in understanding the underlying chemistry of iodine, and that most national programs were now redirecting effort towards the development and validation of models/codes to predict the behaviour of iodine in various design-basis and severe reactor accidents. The Workshop also helped to identify existing weaknesses and current limitations; undoubtedly, information shared at this workshop and the ensuing stimulating discussions will help to guide the course of future research to resolve the remaining uncertainties. The following is a summary of conclusions/recommendations generated by the Workshop.

On the subject of kinetics and mechanisms of iodine reactions, it was agreed that:

1. Oxidation of I⁻ to the I₂ and HOI states is now sufficiently understood, but more experimental studies are required to elucidate the mechanism of formation of the higher iodine oxidation states and to understand formation of organic iodides.

2. Mechanistic studies at iodine concentrations below about 10⁻⁶ to 10⁻⁷ mol·dm⁻³ may not be appropriate because of the potential influence of undefined water impurities.

3. An evaluated kinetic database (rate constants and activation energies) is required for relevant thermal and radiolytic reactions. It is recommended that a specialist group be set up initially to examine the feasibility of formulating such a database. In this respect, it should be noted that an iodine thermodynamic database compilation is in progress under the OECD/NEA program for radioactive waste management.

4. Additional studies are required to examine the effects of organic and inorganic impurities on the thermal and radiolytic reactions of iodine. Also more studies are required to assess the effect of surfaces. Studies of the physical and chemical behaviour of iodine species in the aqueous or gaseous phases, in contact with surfaces, should be undertaken. With respect to the latter, it was noted that detailed mechanistic studies would be too slow in addressing current needs; thus, scoping studies of an empirical nature are recommended initially.
5. There is now conclusive evidence that radiation field strengths of the order expected to be present in reactor accidents would not have an effect on the gas phase decomposition of cesium iodide. Also, modelling studies of radiation-induced reactions in the gas phase, in moist air containing traces of iodine and methane, demonstrate conclusively that no significant amount of organic iodides should form when the hydrocarbon concentrations are less than about $10^{-6}$ mol·dm$^{-3}$; the latter studies also indicate that radiation induced iodine/oxygen reactions may suppress airborne iodine.

With respect to thermodynamic measurements, it was agreed that there is a need for heat capacity data beyond 100°C, for aqueous iodine species. Such data are needed to calculate partition coefficients of iodine in steam-generator tube-rupture accidents and to deal with evaporation to dryness of water pools under severe accidents. In addition, the possibility of volatilization of iodide, through steam dissolution, should be examined. Studies of evaporation to dryness should attempt to a) identify the volatilized products, b) evaluate the phase relations at high borate concentrations, c) measure the borate concentrations in the condensate, and d) study the interaction of evaporating borate films with metal oxide surfaces.

Some progress was noted on the development and validation of models/codes to predict the behaviour of iodine in reactor accidents. Chemical knowledge generated by the underlying research programs is now being used in combination with physics and engineering variables to develop more realistic models/codes. The chemistry-physics-engineering mix varies extensively amongst the various models/codes being developed. The chemical detail required in such models/codes was also discussed. It was concluded that the ultimate test of such models/codes must be their validation. Progress in this direction has been slow due to the unavailability of the required facilities for such validations, but a number of such facilities are becoming available in the future (RTF, ACE, LOFT, PHEBUS) for this purpose.

Considering the quick pace of progress in this area and the number of experimental and analytical programs underway or planned, there was unanimity amongst the experts to consider that a third CSNI Workshop on Iodine Chemistry in Reactor Safety, in about two to three years, would be most beneficial. The Program Committee therefore recommends to CSNI to include such a meeting in the future program of work.
I. KINETICS AND MECHANISMS
KINETICS OF IODINE HYDROLYSIS IN UNBUFFERED SOLUTIONS

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ABSTRACT

The kinetics of hydrolysis or disproportionation of hypoiodite were studied spectrophotometrically in basic solution at an ionic strength of 0.2 M as a function of pH, iodide and total iodine concentration, and temperature. The existence of three independent pathways for this second-order process was confirmed. The pH-stat method was used to monitor the corresponding reaction of hypoiodous acid in weakly alkaline solution. The generalized rate law for the disproportionation is:

\[-d([\text{HOI}] + [\text{OI}^-])/dt = k_a[\text{HOI}]^2 + k_b[\text{HOI}][\text{OI}^-] + k_c[\text{OI}^-]^2 + k_d[I_2\text{OH}^-][\text{OI}^-]\]

The values of \(k_a\) and \(k_b\) are substantially smaller than previously reported. However, an unexplained contribution to the rate law resulting from the pH-stat measurements was also obtained. The rapid recombination of iodide and iodate in HClO₄ solutions was followed by stopped-flow spectrophotometry at three ionic strengths, and over a range of iodide and hydrogen ion concentrations, and at eight temperatures. Fifth-order kinetics were observed with no detectable induction period.

INTRODUCTION

The chemical lability of iodine and its numerous oxidation states have made kinetic and thermodynamic experimental studies of the hydrolysis and/or disproportionation reactions often difficult to interpret unambiguously. This complexity has led to conflicting rate expressions with widely differing rate and equilibrium constants often being reported by various investigators.

Lisbhafsky and Roe [1] were able to clarify the confusing number of rate laws proposed for the REDOX reaction of iodate with iodide to give iodine, known as the Dushman reaction. Nevertheless, these authors recommended that the reaction be reinvestigated by stopped-flow techniques, presumably in order to allow utilization of more acidic conditions thereby eliminating the need for potentially catalytic buffer systems. This approach was taken in the work presented here.

The recent publications by Wren et al. [2] and Paquette and Ford [3] have had a similar effect in consolidating the various mechanisms proposed for the behavior of iodine in basic solutions. They demonstrated that \(I_2\text{OH}^-\) played a direct role in the reaction scheme in addition to the two previously established pathways involving HOI and OI⁻.[4-6] Moreover, they indentified the +III state intermediate, \(I^+\), and measured its relatively rapid rates of recombination with OI⁻ and \(I_2\text{OH}^-\). However, the only attempt to address the hydrolysis, or disproportionation, of iodine in neutral to weakly basic solutions was a brief study in 1980 [1].
Hasty.[7] These investigators conducted four experiments at pH values of 7 - 10 using phosphate, borate and carbonate buffers at concentrations equivalent to an ionic strength of 0.15 M. Consequently, the catalytic effect of these buffers on the rate constants is unknown. In the present study, the pH range of the basic experiments has been extended to lower values than used previously. A pH-stat method was employed at even lower pH where the free OH\textsuperscript{-} no longer effectively poised the pH, in order to remove the influence of buffering agents on the rates of iodine hydrolysis.

Finally it should be noted that disagreement and/or inaccuracies in the published values of the relevant equilibrium constants and their extrapolation to the conditions of interest has an impact on most of the rate constants derived for these reactions. This is particularly apparent at intermediate pH values where either a number of iodine species exist at comparable concentrations, or where minor species may dominate the reaction variable that is being used to monitor the extent of reaction.

EXPERIMENTAL METHODS

The kinetics of hydrolysis in basic solutions were studied spectrophotometrically with 5 cm cells at 370 nm which corresponds to the absorbance maximum of the hypoiodite ion. The concentration of base was at least twenty times the total iodine concentration so that the pH remained virtually constant throughout each experiment and could be calculated from the known stoichiometric molarities. The ionic strength was maintained with NaClO\textsubscript{3}, generally at 0.2 molar.

The pH-stat method involved the quantitative addition of 0.1 molar NaOH to a thermostated (and light-shielded) 100 cm\textsuperscript{3} solution of iodine that had been previously acidified with HNO\textsubscript{3}. The combination glass electrode used to measure the pH was calibrated prior to each experiment with two standard HNO\textsubscript{3} solutions (0.001 and 0.0001 molar), each at an ionic strength matching that of the reaction solution. Thus the measured pH values represent the negative logarithm of the stoichiometric hydrogen molarity and can be compared directly with those calculated from the spectrophotometric experiments. Moreover, liquid junction potential corrections could be ignored because the concentration of the supporting electrolyte, NaNO\textsubscript{3}, was always at least two orders magnitude greater than the total concentration of iodine species.

The kinetics of the Dushman reaction were investigated with a stopped-flow spectrophotometer at 400 nm using NaClO\textsubscript{3} to maintain constant ionic strength. The initial iodate concentration was fixed at 5 \times 10\textsuperscript{-5} M. At 0.1 molar ionic strength the rate dependence on iodide concentration was determined at four hydrogen concentrations (viz. 0.01, 0.005, 0.00255 M using HClO\textsubscript{4} and 0.000697 M using a phosphate-citrate, or McIlvainc, buffer). Six iodide concentrations were investigated, viz. 0.005, 0.01, 0.02, 0.03, 0.04, and 0.05 M. Excellent linear correlations of the observed pseudo-first-order rate constant versus [I\textsuperscript{-}]\textsuperscript{2} at fixed [H\textsuperscript{+}] and [H\textsuperscript{+}]\textsuperscript{2} at fixed [I\textsuperscript{-}] were found. Note that the iodate concentration was sufficiently low as to ensure that the maximum ratio of [I\textsubscript{3}]/[I\textsuperscript{-}] = 0.003 thereby eliminating the term, k'[H\textsuperscript{+}]\textsuperscript{2}[I\textsubscript{3}][I\textsuperscript{-}][I\textsuperscript{-}], from the overall rate law. Furthermore, there was no indication of an induction period, nor any indication that the exponent, or order, with respect to [I\textsuperscript{-}] should be 1.9 rather than 2 within the accuracy
of the data. Finally, the results using the McIlvaine buffer showed no measurable deviation from the second-order rate dependencies obtained with HClO₄ indicating little, if any, catalysis by the buffer.

**RESULTS**

The following equilibria were included in the model to establish the speciation of aqueous iodine by both the spectrophotometric and pH-stat methods:

\[
\begin{align*}
I_2 + H_2O & \rightarrow HOI + I^- + H^+ \\
I_2 + I^- & \rightarrow I_3^- \\
HOI & \rightarrow OI^- + H^+ \\
OI^- + I^- + H_2O & \rightarrow I_2OH^- + OH^- \\
\end{align*}
\]

An additional equilibrium was used in the treatment of these results, mainly in view of the known high extinction coefficient of the I₄⁻ ion.[8]

\[
I^- + I_3^- \rightarrow I_4^- \\
\]

However, the model subsequently showed that this polynuclear iodine species never contributed significantly to the measured absorbance under the basic conditions of these experiments, even in the presence of added iodide. The remaining equations used in the quantitative elucidation of the speciation were a mass-balance equation:

\[
\sum I = 2[I_2] + [I^-] + 3[I^-] + [HOI] + [OI^-] + 2[I_2OH^-] + [IO_3^-] + 4[I_4^-] + 2m_0 + m_1 \quad (6)
\]

and an electron-balance equation:

\[
[I^-] + [I_3^-] + 2[I_4^-] - m_1 = [HOI] + [OI^-] + 5[IO_3^-] \quad (7)
\]

where \(m_0\) and \(m_1\) represent the initial (or added) molarities of iodine and iodide, respectively. Finally, the following two equations related the measured quantities in each type of experiment to the contributing species concentrations:

\[
A_{370} = 5(52.1[I_2] + 19248.[I^-] + 22.9[HOI] + 66.7[OI^-] - 28.7[I_2OH^-] + 21914.[I_4^-]) \quad (8)
\]

where \(A_{370}\) represents the molar absorptivity at 370 nm;

\[
[HOI] + 2[OI^-] + [I_2OH^-] + 6[IO_3^-] = ((V_t([OH^-])_t - V_1[HNO_3])/(100.0 + V_t) - Q_w/[H^+] \quad (9)
\]

where \(V_t\) and \([OH^-])_t\) represent the volume and hydroxide molarities of the
titrant added at time \( t \), respectively; \( Q_w \) is defined as the molar dissociation quotient of water at finite ionic strength (cf. \( K_w \) at infinite dilution) [9]; while \( V_1 \) represents the volume of nitric acid of molarity \([\text{HNO}_3]\) added initially to the 100 cm\(^3\) of reaction solution.

The expressions for the equilibrium quotients corresponding to the equilibria (1) - (3) are: [10,11]

\[
\log Q_1 = \left( \frac{Q_w}{K_w} \right) \left( -6341.9 / T + 66.276 - 23.155 \log T \right) \tag{10}
\]

\[
\log Q_2 = \frac{555.0}{T} + 7.355 - 2.575 \log T \tag{11}
\]

\[
\log Q_3 = \left( \frac{Q_w}{K_w} \right) \left( 2800.48 + 0.7335 T - 80670 / T - 1115.11 \log T \right) \tag{12}
\]

The term \( \left( \frac{Q_w}{K_w} \right) \) in equations (10) and (12) assigns the same ionic strength dependence to these equilibria as for the water dissociation reaction. Equations (2), (4) and (5) are already in their anionic forms, and being isoücolombic, will exhibit minimal ionic strength dependencies. Values for \( Q_4 \) of 0.24 [2] and 0.107 for \( Q_5 \) [8] at 25 °C were adopted, but their temperature dependencies are unknown.

Back extrapolation to zero time of those pH-stat kinetic runs with pH values less than 9.5 allowed for independent computation of \( Q_3 \) given the more established equations (10) and (11). At such low pH, \( \text{I}_2\text{OH}^- \) does not contribute substantially to the iodine speciation. The mean value of \( Q_3 \) obtained by this method is \( 4.5 \times 10^{-11} \) at 25 °C and \( I = 0.2 \), in reasonable agreement with \( 4.141 \times 10^{-11} \) obtained from equation (12). The enthalpy of \( \text{HOI} \) dissociation obtained by differentiation of \( \log Q_3 \) over the range 15 to 45 °C is 18 kJ mol\(^{-1}\) compared less favorably with 28 kJ mol\(^{-1}\) obtained by differentiation of equation (12) with respect to temperature.

THE KINETICS OF HYDROLYSIS IN BASIC SOLUTION

These kinetics were followed spectrophotometrically as outlined above. Similar studies have been carried out in the past with various rate expressions resulting, as discussed and correlated most recently by Wren et al.[2] However, in the present study the pH was varied to lower values than previously at constant ionic strength in order to complement the earlier work and the pH-stat measurements. A strictly second-order rate dependence on hypiodite concentration was observed over the range of hydroxide molarities investigated, viz. 0.2 to 0.004 M, with initial iodine concentrations varying from 1 - 13 x 10\(^{-4}\) M. The change in speciation that occurred in a typical experiment is illustrated in Figure 1 where the dominant forms are \( \text{OI}^- \), \( I^- \) and \( \text{IO}_3^- \). As the decay of the \( \text{OI}^- \) concentration was monitored directly at 370 nm with only small contributions from other absorbing species these results are more precise than those obtained by the pH-stat technique where virtually all the species involved in equations (1), (3) and (4) contribute to the hydrogen ion molarity.

The observed second-order rate constants, \( k_{\text{obs}} \), were fitted as functions of \([\text{H}^+]\) and \([\text{I}^-]\) in accordance with the rate-determining processes summarized by Wren et al.[2] These processes are:
Figure 1. The logarithm of the molarity of species $i$ of iodine (where $\bigcirc$ $I^-$, $\bullet$ $HIO$, $\blacksquare$ $OI^-$, $\nabla$ $I_2OH^-$, $\odot$ $IO_3^-$) given as a function of time. The experimental conditions are: $25 \, ^\circ C$, $pH = 12.323$, $[I_2]_0 = 7.86 \times 10^{-4}$ M and $I = 0.2$ M.

Figure 2. This figure is derived from equation (16) showing the experimental results at $25 \, ^\circ C$ and an ionic strength of 0.2, where the symbols $\square$ represent those experiments in which no iodide was added, while $\bullet$ and $\blacksquare$ correspond to 0.05 and 0.10 molar iodide, respectively.
The resulting rate law is as follows:

$$(1 + [H^+]/Q_3)k_{obs} = k_1 + k_2[H^+]/Q_3 + k_4Q_4[I^-][H^+]/Q_w$$  \hspace{1cm} (16)$$

Equation (16) yielded the following rate constants at 25 °C and 0.2 molar ionic strength: $k_1 = 0.049 \pm 0.019 \text{ M}^{-1} \text{ sec}^{-1}$, $k_2 = 11.09 \pm 0.54 \text{ M}^{-1} \text{ sec}^{-1}$, and $k_4 = 6.65 \pm 0.18 \text{ M}^{-1} \text{ sec}^{-1}$. A plot of $(1 + [H^+]/Q_3)k_{obs}$ versus the sum of the terms on the right-hand side of equation (16) is shown in Figure 2. The value of $k_1$ is remarkably close to the value of 0.048 M$^{-1}$ sec$^{-1}$ published by Li and White.[5] An increase in rate would be anticipated with increasing ionic strength for a reaction between like charges and this is confirmed by the results of Haimovich and Treinin [6] who reported $k_1$ values of $0.040 \pm 0.004 \text{ M}^{-1} \text{ sec}^{-1}$ in 4 M NaOH and $0.027 \pm 0.002 \text{ M}^{-1} \text{ sec}^{-1}$ in 6 M NaOH. However, in the present study no significant effect of ionic strength was observed up to one molar ionic strength. The value of $k_2$ is considerably smaller than $40 \pm 7 \text{ M}^{-1} \text{ sec}^{-1}$ reported earlier [2] and may reflect an inherent improvement in accuracy by studying the reaction to lower [OH$^-$] when this pathway dominates in the absence of added iodide ion. The temperature dependencies of $k_1$ and $k_2$ were determined from additional spectrophotometric measurements at 15.0, 34.4, and 44.8 °C. These experiments were carried out at relatively high pH, corresponding to initial hydroxide molarities in the range 0.2 to 0.05 where the hydrolysis path represented by equation (16) is too slow to contribute significantly. This restriction being necessary because $Q_4$ is known only at 25 °C. Application of the Arrhenius equation in the linear form,

$$\ln k = \ln A - \frac{E_a}{RT}$$  \hspace{1cm} (17)$$

led to the following parameters for paths (13) and (14): $\ln A = 7.13 \pm 0.88$ and $E_a$ (activation energy) = 20.7 ± 2.2 kJ mol$^{-1}$; and $\ln A = 123.2 \pm 0.2$ and $E_a = 28.0 \pm 0.5$ kJ mol$^{-1}$, respectively.

Equations (13) - (15) are the minimum necessary to describe the spectrophotometric results presented in this study. Thus the term $b[OI^-]/[OH^-]$ observed by earlier workers [2,4] was not invoked directly in the current treatment. Although the previous data were obtained at higher hydroxide molarities, $[OI^-]/[OH^-]$ may be rewritten as $[H^+]^2/[OI^-]/Q_w$ and is therefore kinetically indistinguishable from the term $k_4[H^+]/Q_3$ in equation (16), i.e. reaction (14).

In order to evaluate the validity of the rate constants obtained from the spectrophotometric measurements, their sensitivity to uncertainties in the relevant equilibrium quotients needs to be determined. The three values reported for $Q_4$ differ considerably: 0.24 [2], 0.13 [12] and 0.03 [13]. The most recent value was accepted in the above analysis. Reanalysis with $Q_4 = 0.12$ gave virtually identical fitting statistics and the following rate constants: $k_1 = 0.049 \pm 0.020$, $k_2 = 11.06 \pm 0.58$, and $k_4 = 13.08 \pm 0.37$.
M\(^{-1}\) sec\(^{-1}\) at 25 °C and 0.2 M ionic strength. The equilibria (1) and (2) lie too far to the right and left, respectively, to have any affect on the speciation under these basic conditions. However, by changing Q\(_3\) at 25 °C and 0.2 M ionic strength from 4.141 \times 10^{-11}, calculated from equation (12), to 2.411 \times 10^{-11}, the accepted infinite dilution value, a significantly poorer fit resulted with \(k_1 = 0.002 \pm 0.037, k_2 = 7.18 \pm 0.63,\) and \(k_4 = 10.36 \pm 0.35\) M\(^{-1}\) sec\(^{-1}\).

THE KINETICS OF HYDROLYSIS IN WEAKLY BASIC SOLUTION

The speciation at these intermediate pH values is more complex in terms of the number of species with comparable concentrations. This point is illustrated in Figure 3. By analogy to the system at higher pH, reactions (14) and (15) would be expected to be important, with additional competing reaction routes defined by equations (18) and (19).

\[
\begin{align*}
  k_3: & \quad 2\text{HOI} \rightarrow \text{I}_2^+ + \text{I}^- + 2\text{H}^+ \\
  k_5: & \quad \text{HOI} + \text{I}^- + \text{H}^+ \rightarrow \text{I}_2^+ + 2\text{I}^- + 2\text{H}^+
\end{align*}
\]

A rate law was formulated to correct the observed rate constant for contributions from reactions (14) and (15) so that the residual rate could, in principle, be assigned to pathways such as presented in equations (18) and (19). If only equations (14) and (15) were considered this version of the rate law would be as follows:

\[
(1 + Q_3/[H^+])k_{\text{obs}} = k_2Q_3/[H^+] + k_4Q_4Q_3^2[I^-]/Q_w[H^+]
\]

Note that in these experiments no excess iodide was added initially and therefore [I\(^-\)] was taken as the mean value generated during the reaction with uncertainties as great as ± 15%. A linear correlation involving the left hand side minus the right hand side of equation (20) versus [I\(^-\)]/[H\(^+\)] (see Figure 4) was found to best represent these results yielding an intercept (i.e. \(k_3\)) of 1.4 ± 0.9 M\(^{-1}\) sec\(^{-1}\) at 25 °C and a slope of (1.42 ± 0.08) \times 10^{-7} M\(^{-1}\) sec\(^{-1}\). Attempts to include a third term in this regression with merely a first-order dependence on [I\(^-\)], as would arise if reaction (19) made a significant contribution, proved this term to be statistically unimportant. At this time no alternative reaction pathway can be envisaged that would account for this reciprocal dependence on hydrogen ion concentration. More importantly, \(k_3\) is approximately two orders of magnitude smaller the previously reported viz. 250 ± 160 M\(^{-1}\) sec\(^{-1}\).[7]

Assuming Q\(_4\) = 0.12 and repeating the above analysis leads to \(k_3 = 1.9 \pm 0.8\) M\(^{-1}\) sec\(^{-1}\) with a slope of (8.0 ± 0.6) \times 10^{-7} with a significant improvement in fit. Variations in the other equilibrium constants, which are known to much better precision the Q\(_4\), have a relatively minor influence.

The kinetics were also investigated at higher iodide concentrations (0.05 - 0.2 M), however, under these conditions I\(^2\) dominates the speciation to the extent that the concentrations of HOI and OI\(^-\) are small and their values are too uncertain to give reliable rate constants (e.g. in an experiment at 25 °C, pH = 9.51, [I\(_2\)] = 1.21 \times 10^{-3} M, and [I\(^-\)] = 0.200 M, the resulting speciation after three minutes reaction time was: [I\(_2\)] =
Figure 3. The logarithm of the molarity of species $i$ of iodine (where $\Box I_2$, $\bigcirc I^-$, $\triangle I_3^-$, $\bullet HOI$, $\square OH^-$, $\diamond IO_3^-$) is given as a function of time. The experimental conditions are: 25 °C, pH = 10.00, $[I_2]_0 = 9.61 \times 10^{-4}$ M, and $I = 0.2$ M.

Figure 4. The ordinate is derived from equation (20) and shows a linear correlation with $[I^-]/[H^+]$ for the pH-stat experiments at 25 °C and an ionic strength of 0.2.
5.85 x 10^{-6}, [I^-] = 0.196, [I_2^-] = 7.85 x 10^{-4}, [I_2O^-] = 1.65 x 10^{-5}, [HOI] = 8.95 x 10^{-8}, [OI^-] = 1.21 x 10^{-3}, and [I_2OH^-] = 3.1 x 10^{-9} M). Additional experiments are needed at lower iodide concentrations near 0.01 M to rationalize this "apparent [I^-]/[H^+]" term.

KINETICS OF THE DUSMAN REACTION

\[ IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \]  \hspace{1cm} (21)

As mentioned earlier, only a single fifth-order process was observed for this multistep process at 0.1 M ionic strength and 25 °C. It was assumed that the reaction order did not vary over the range of temperature (i.e. 15 to 67 °C) and sodium perchlorate concentration (0.015 to 1.0 M) investigated. These results, including the Arrhenius parameters, are summarized in Table 1. The rate constant interpolated to 0.2 M ionic strength is 3.97 x 10^8 M^{-4} sec^{-1}, in excellent agreement with the results of Schildcrout and Fortunato [14], viz. (4.23 ± 0.16) x 10^8 M^{-4} sec^{-1}, which were acknowledged by Liebhafsky and Roe[1] as being the most precise data available. Their activation energy of 33 ± 8 kJ mol^{-1} at this condition is in reasonable agreement considering the narrow temperature range investigated of 15 °.

Table 1: Rate Parameters for The Dushman Reaction.

<table>
<thead>
<tr>
<th>t °C</th>
<th>I M</th>
<th>k_{obs} M^{-4} sec^{-1}</th>
<th>ln A</th>
<th>E_a kJ mol^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>0.015</td>
<td>6.72 x 10^8</td>
<td>29.5 ± 0.3</td>
<td>22.6 ± 2.3</td>
</tr>
<tr>
<td>25.0</td>
<td>0.10</td>
<td>4.27 x 10^8</td>
<td>28.4 ± 0.2</td>
<td>21.1 ± 0.5</td>
</tr>
<tr>
<td>25.0</td>
<td>1.00</td>
<td>2.62 x 10^8</td>
<td>30.0 ± 0.3</td>
<td>26.2 ± 0.8</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The results of this study, in conjunction with recently published work, have established the rate constants k_1 and k_3 in unbuffered media. The temperature dependence of k_1 is also defined. However, the exact values of k_2 and k_4 are dependent on determining a precise value for Q_4. Perhaps multiscan stopped-flow spectrophotometry would be most suited for this purpose in view of the transient nature of I_2OH^- . The kinetics of the Dushman reaction in buffered and unbuffered solutions are now well understood.

ACKNOWLEDGMENTS

Much of this work was accomplished during a summer research program by Leslie J. Lyons who at that time was an undergraduate at Colgate University, New York. Dr. Lyons' current address is the Department of Chemistry, Northwestern University, Illinois. The research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract DE-ACOR-8AOR21400 with Martin Marietta
REFERENCES


DISCUSSION

P.E. POTTER  Can you estimate the enthalpy of reaction from information on analogous systems, for example Br?

D.A. PALMER  I am not sure whether the bromine analog of I$_2$OH~ exists. Moreover, the formation quotient of I$_2$OH~ needs to be established before we try to estimate its temperature dependence.

K. ISHIGURE  You mentioned that it is not possible to estimate the activation energy for $k_4$ because you do not know the temperature dependence of $Q_4$. Is it not possible to estimate the temperature dependence of $Q_4$ theoretically, based on the fact that reaction (4) has the same number of negative ions on both sides of the equation?

D.A. PALMER  The isocoulombic approach minimizes the effect of temperature on the enthalpy of reaction (i.e. it is very useful when the heat capacity change is not known), but it does not allow us to predict the magnitude or even the sign (at moderate temperatures) of $\Delta H_R$.

P.E. POTTER  Do we need to measure $Q_4$ using spectrophotometric techniques?

D.A. PALMER  The main concern, or need for further study, involves the stability of the species I$_2$OH~ which has been well characterized and shown to exist in both kinetic and equilibrium experiments. The kinetic results of my work would favour a formation quotient ($Q_4$) perhaps an order of magnitude less than 0.24. Stopped-flow spectrophotometry may offer the best means of studying this equilibrium.

W.G. BURNS  (a) Have you considered the results reported by Buxton and Sellers in J. Chem. Soc. Faraday Trans. I. on the uncatalyzed reaction HOI + HOI?

(b) In our work on disproportionation reported at the 1985 CSNI Iodine Workshop we found, in getting good correlation between observation and disproportionation rate constants and equilibrium constants, that it was not necessary to include the species I$_2$OH~ for such reactions in a first order approximation?

D.A. PALMER  (a) I believe Buxton and Sellers reported a rate constant of approximately 5 M$^{-1}$s$^{-1}$ for the uncatalyzed bimolecular reaction of HOI. This is in reasonable agreement with our value of ca.2 M$^{-1}$s$^{-1}$.
(b) Based on our spectrophotometric results I would suggest that at very high pH and in the absence of added iodide, the species $\text{I}_2\text{OH}^-$ could be excluded from your analysis. Indeed, our pH-stat and spectrophotometric data (in the absence of added $\text{I}^-$) correlate better when this species is ignored.
RADIolytic and Surface Reactions of Dilute Iodine Solutions


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Abstract

The radiation chemistry of caesium iodide and iodate in dilute aerated aqueous solution (e.g. 3.4 x 10^-6M of I^-) containing boric acid (0.2M) has been studied using ¹³¹I as a tracer. For CsI, yields of I₂ showed considerable scatter but those of IO₃⁻ were reproducible; these were measured as a function of dose-rate and temperature. Yields of iodine had a maximum value of ca. 0.3μM at 30°C to ca. 0.05μM at 90°C. Iodate yields at 30°C showed no marked effect of dose rate in the range 0.04 to 3 Mrad/hr, and decreased to <.1μM at 90°C. The mechanism of this effect which may be a temperature dependent radiolytic reduction of IO₃⁻ is being studied for incorporation into a detailed radiolytic model described in a separate paper in this workshop.

Reactions of I₂ with surfaces have also been studied in solution and in the vapour phase. Three types of steel in both vapour and solution were found to cause a reduction of I₂ to I⁻ at 100°C, with a rate dependent on the nature of the steel surface, a freshly machined surface being more reactive than an aged surface. Surfaces coated with an epoxy phenolic paint were found to be very reactive towards iodine in solution and in the vapour especially at elevated temperatures (100°C) causing reduction of I₂ to I⁻, but the surface also could react to remove ca.50% of the initial inventory of I₂. Results for reaction with concrete surfaces were consistent with alkaline hydrolysis and disproportionation.

The paper concludes that more work is needed on the individual reactions involved in the radiolysis of dilute aqueous iodide solutions especially at elevated temperatures. In a reactor fault the effect of surfaces is likely to be important especially those of concrete and paint.
1. **INTRODUCTION**

In fault conditions in light water reactors iodine is one of the two most important fission products, the other is caesium; both have the potential to present a significant radiological hazard because of their biological activity. It is important to be able to predict the behaviour of iodine in such circumstances in order to make an acceptable safety case, and to provide the basis for any strategy for chemical intervention. Although large scale integral experiments will provide much useful information for the prediction of iodine behaviour in fault conditions, computer models present the only practical means of correlating a wide range of possible scenarios.

In order to use computer codes to predict satisfactorily the chemistry of iodine in fault conditions, the effect of thermal oxidation, thermal hydrolysis reactions, radiolysis reactions including those of hydrogen peroxide, as well as reactions with surfaces of interest have to be considered, and experimental studies of solutions at relevant iodine concentrations are required. The aim of the Harwell programme has been to develop a comprehensive mechanistic computer model [1] based on the FACSIMILE code [2]. Such models rely on experimental data both to provide input such as rate constants and equilibrium constants, but also these experiments serve to test the predictions of the programme. We are carrying out an experimental programme addressing the points listed above and we describe some of our results in this paper. [Computer modelling is being described separately in this workshop.]

2. **EXPERIMENTAL**

Irradiations were normally carried out using $^{60}$Co sources except for the high dose rate experiments which were carried out in the spent fuel storage pond. Solutions were made up using AnalAr reagents either with triply distilled water or MilliQ water (Millipore Waters). $^{131}$I was purchased from Amersham International plc in reducing agent free form. Measurement of iodine speciation in inactive solutions was carried out using a variety of methods. Iodide, iodine and iodate were analysed by a colorimetric method using leuco crystalviolet [3]. In addition iodide was analysed by specific iodide ion electrode or by HPLC using electrochemical or UV detection. $I_2$ and $I_3^-$ were analysed directly by spectrophotometry using a multi-wavelength method. Hydrogen peroxide was estimated by the method of Hochanadel [4] and also by HPLC.

Radioactive solutions were initially analysed by the method described by Lin[5]. In order to validate this method we 'spiked' a solution of $I_2$ in boric acid (0.2M) with $^{131}$I and extracted the $I_2$ into benzene from successively diluted solutions. The percentage recovery is shown in fig. 1. It was found that the recovery fell with increasing dilution. In an alternative method an aliquot of 50 ml. of the molecular iodine solution reacted with phenol (1ml, 5x10^-4M for 5 mins) and the resulting iodophenol extracted into benzene, with results also shown in fig. 1. Clearly more is extracted by the phenol method. The fall in extraction efficiency with dilution is attributed to addition of impurities and stable iodide in the boric acid diluent, the difference
between the methods is probably due to the increased formation of HOI at low concentration where HOI reacts with phenol, but is not extracted directly by benzene. Organic iodine was estimated by extraction of the initial solution with benzene followed by back extraction of I\textsubscript{3} by exchange with excess sodium iodide (10\textsuperscript{-3} M). This method was chosen since we found that organic compounds which could ionize were back extracted using the sodium hydroxide method described by Lin. A summary of our method is shown in fig 2. Radioactive samples were counted using a sodium iodide crystal and an Ortec 7450 multi-channel analyser.

The reaction with paint was studied by exposing painted mild steel and stainless steel samples of known geometrical surface area, ca 90 cm\textsuperscript{2}, to iodine solution at constant temperature. At lower temperatures, up to 50°C, the painted samples were immersed in the iodine solution which was periodically analysed for iodine and iodide. At 100°C the painted samples were suspended above the iodine solution and analysis for iodine and iodide only carried out at the end of the experiment. In a limited number of experiments the iodine solution was spiked with radiiodine and at the end of the experiment the activity in solution, in the gas phase, and on the painted surface was measured.

Measurements of iodine hydrolysis were made using a purpose built spectrophotometer system consisting of a xenon arc lamp, beam splitter, photomultiplier and lock-in amplifier, this is shown schematically in fig. 3. This allowed measurements to be made at elevated temperatures not possible in commercial spectrophotometer systems.

3. RESULTS AND DISCUSSION

**Thermal oxidation**

Experimental studies on the thermal oxidation of iodide to iodine by oxygen have been discussed previously [6,7]. These results showed that at temperatures of interest in a fault the rate of oxidation is relatively slow over timescales of importance. The authors found ca. 2% oxidation from solutions containing 10\textsuperscript{-1} to 10\textsuperscript{-3} M CsI over a period of 50 hours. These studies were at very high concentrations compared to those in a fault and further work at lower concentrations (ca. 1 \mu M) are required.

**Thermal hydrolysis of iodine**

I\textsubscript{2} is known to hydrolyse in dilute solution according to reaction

\[ I_2 + H_2O = HOI + I^- + H^+ \]  \hspace{1cm} (1)

This equilibrium is strongly temperature dependent and there is some discrepancy in the reported values for the equilibrium constant at elevated temperature. HOI formation is important for two reasons, firstly because increased HOI formation reduces the amount of I\textsubscript{2}, and HOI is thought to be less volatile, secondly HOI is thought to be a precursor of radiolytically formed iodate which is non-volatile. The hydrolysis may be followed by disproportionation in reactions (2) and (3), where reaction
(2) is thought to be rate determining.

\[
\text{HOI} + \text{HOI} = \text{IO}_2^- + \text{I}^- + 2\text{H}^+ \quad (2)
\]

\[
\text{HOI} + \text{IO}_2^- = \text{IO}_3^- + \text{I}^- + \text{H}^+ \quad (3)
\]

We have measured the equilibrium constant of reaction (1) up to 100°C with results shown in fig. 4. The data are superimposed on fig. 1 taken from ref. [3]. It can be seen that they deviate from the Oak Ridge extrapolated evaluation [9] at temperatures above 75°C and fall between the predictions of Turner and the upper values suggested by Lemire et al [17].

**Radiolysis reactions**

The radiolysis of solutions of CsI at concentrations >10⁻⁵ M is well understood and the mechanisms adequately modelled. At lower concentrations (e.g. 3.4 μM) pertinent to a loss of coolant accident (LOCA) the correlation is less accurate. This is partly due to the low concentrations of radicals, intermediates and products which are of similar magnitude. It is difficult to study absorptions of intermediates derived from low reactant concentrations directly and it seems that mechanisms applicable at higher concentrations require modification.

Irradiation of CsI gives rise to I₂ and IO₃⁻ as shown in figs 5 and 6, although, in contrast to the results of Lin [5], we do not find complete oxidation to iodate, but only ca. 10% conversion of iodide to iodate, and ca. 20% to iodine. Iodine yields normally show considerable scatter at these low concentrations. Fig 7. shows the effect of temperature on the yield of iodate for 1 Mrad dose. The trend is for the iodate yield to fall at higher temperature.

The general effect of irradiation on CsI solutions of increasing dilution is shown in fig. 8. This shows the fall in yield of I₂ and increase in iodate as initial iodide concentration falls. In order to confirm the lack of complete oxidation we irradiated solutions of iodate (3.4 μM) in order to measure any reduction. We measured total iodide formation (after addition of phenol to convert any iodine to iodophenol) at the end of irradiation, and the results for aerated solutions are shown in fig. 9. These results show virtually complete reduction to I⁻ similar to the equilibrium concentrations found from irradiation of I⁻ shown in fig. 9, and iodine (as iodophenol) was not detected.

The present radiolytic model does not model the net production of iodate particularly accurately because the mechanism for iodate formation and destruction in dilute solution is not yet fully worked out.

A qualitative explanation for the trend for the production of iodate at low concentrations is straightforward. In more concentrated solutions the following reactions (simplified) dominate
\begin{align*}
I^- + \text{OH} & = I + \text{OH}^- \quad (4) \\
I + I^- & = I_2^- \quad (5) \\
I_2^- + I_2^- & = I_3^- + I^- \quad (6)
\end{align*}

Hydrolysis of \( I_2 \) is reduced at high \([I^-]\) and efficient scavenging of \( \text{OH} \) by \( I^- \) (4) precludes reactions with \( \text{OH} \) and \( I_2 \) or \( \text{HOI} \). There is also an important reduction reaction (7).

\[ I_2 + \text{O}_2^- = 2I^- + \text{O}_2 \quad (7) \]

which results in the formation of a steady state of \( I_2 \) with virtually no iodate formed. In addition, reactions of hydrogen peroxide can continue after the end of the irradiation. At low concentration reaction (4) occurs initially but \( \text{HOI} \) is also formed by reaction (1) and \( I^- \) can be substantially depleted; subsequent reactions of \( \text{HOI} \) described by Buxton [10] may then occur.

\begin{align*}
\text{HOI} + \text{OH} & = \text{IO} + \text{H}_2\text{O} \quad (8) \\
\text{IO} + \text{IO} & = \text{I}_2\text{O}_2 \quad (9)
\end{align*}

Buxton then postulated a mechanism for the production of \( \text{IO}_3^- \)

\begin{align*}
\text{I}_2\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{IO}_2^- + \text{HOI} + \text{H}^+ \quad (10) \\
\text{IO} + \text{IO}_2^- & \rightarrow \text{IO}^- + \text{IO}_2 \quad (11) \\
\text{IO}_2 + \text{H}_2\text{O} & \rightarrow \text{HIO}_3^- + \text{H}^+ \quad (12)
\end{align*}

Buxton [11] has also measured the rate of reaction of \( \text{O}_2^- \) with \( \text{IO} \) (12) to be \( 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) presumably by the reaction:

\[ \text{IO} + \text{O}_2^- = \text{IO}^- + \text{O}_2 \quad (13) \]

When this reaction is incorporated into our model the yield of \( \text{IO}_3^- \) is greatly reduced. The model also predicts more iodate at elevated temperature because of an increase of reaction (1) followed by (8), whereas in practice we find less. Another possibility for iodate production is by the reactions:

\begin{align*}
\text{I} + \text{O}_2 & = \text{IO}_2 \quad (14) \\
\text{IO}_2 + \text{H}_2\text{O} & = \text{HIO}_3^- + \text{H}^+ \quad (15)
\end{align*}

followed by reaction (12) leading to iodate, where the equilibrium of reaction (14) may lie to the left at high temperature. Reactions of \( \text{O}_2^- \) with iodate are uncertain and no measured rate constant is available. An additional possibility for lower iodate yields at higher temperatures is that the equilibrium of (2) may lie more to the left at higher temperature. We have also studied the effect of dose rate using 0.04 0.4 and 3 MRad hr\(^{-1}\)
and found essentially no measureable effect on iodate but a possible effect on iodine yield as shown on fig. 5 and 6.

Reactions of hydrogen peroxide

Hydrogen peroxide is a radiolysis product and can both

\[ I^- + H_2O_2 = HOI + OH^- \] (16)

and reduce HOI and IO-

\[ H_2O_2 + HOI = H_2O + O_2 + I^- + H^+ \] (17)

\[ H_2O_2 + IO^- = H_2O + O_2 + I^- \] (18)

Reaction (17) is slow but reaction (18) is fast. The rate constant for reaction (16) is well known, with values of \(1 \times 10^{-2} \) M\(^{-1}\) s\(^{-1}\) measured by Liebhafsky\[12\] and \(1.4 \times 10^{-2} \) M\(^{-1}\) s\(^{-1}\) measured by Burns et al \[6\]. Reaction (18) has also been measured by Burns who obtained a value of ca. \(1 \times 10^9 \) M\(^{-1}\) s\(^{-1}\). However Ishigure \[13\] measured the reaction and found a value of \(1 \times 10^{-7} \) M\(^{-1}\) s\(^{-1}\). These effects may be due to the presence of boric acid and part of our programme is to remeasure the rate constant and its temperature dependence at different boric acid concentrations.

A comparison of results and data from a FACSIMILE program used to give a best fit by varying \(k_{16}\) and \(k_{18}\) is shown in fig 10. This shows a very good fit for \(k_{16} = 0.015\) and \(k_{18} = 1.869 \times 10^9\) M\(^{-1}\) S\(^{-1}\). Also included in the figure are results of increasing and decreasing \(k_{18}\), the program predicts a significant change in final \(I_2\) concentration and neither value models our results accurately.

Surface reactions

Both surfaces and impurities will be of considerable importance in the chemistry of iodine in fault conditions. Solutions will be far from the purity used in laboratory experiments. Initially the surfaces which we have considered are steel, concrete and paint (epoxy phenolic), the latter being the predominant surface when concrete has been treated with an anti dust coating.

We have studied the effect of steel surfaces on iodine solutions at temperatures up to 100°C with results shown in fig. 11. It may be seen that steel causes the slow reduction of iodine with the most reactive surface being that of a freshly machined steel surface, but one unlikely to be present during a fault. It was found that such surfaces tended to react in discrete areas to give rust like markings suggesting an auto catalytic reaction as proposed in ref.[14].

Concrete was found to react according to expectation because of its alkaline nature, causing disproportionation, the rate of which would be dependent on the nature of the surface and the surface film.
The most important surface in terms of its reactivity appears to be paint. The paint tested was an epoxy phenolic compound coated onto either mild or stainless steel. Initial studies show a fast reaction with iodine especially at elevated temperature to give $I^-$ but ca. 50% of the inventory of iodine (table 1) was not recovered. More detailed studies of the change of iodine concentration with time gave results shown in fig. 12. This shows a very fast reaction at 50°C corresponding to an initial deposition velocity of $1.8 \times 10^{-3}$ cm s$^{-1}$. The reaction would probably be too fast to measure at 100°C under our experimental conditions.

In order to locate the residual iodine we also carried out some tracer experiments with results shown in table 2. These results showed that, in agreement with the inactive work, up to 50% of the iodine was found as iodide, the remainder was found on the surface, or in the form of organic iodine, or analysed as iodate. The organic fraction could be back-extracted from the organic solvent by alkali; the iodate fraction could include an ionic organic fraction. The observations are in accord with a reaction similar to the phenol/iodine reaction which proceeds via HOI formation as described in the previous workshop [15].

$$PhOH + I_2 = Ph(OH)I + I^- + H^+$$

This could lead to the formation of iodide and an iodophenol partially dissolved from the surface. The nature of the compound is uncertain but could be a phenolic derivative. We are attempting to analyse the organic phase by GC-mass spectrometry, but so far have only identified small amounts of tri-iodo phenol. Formation of iodate is unlikely, so the compound that is analysed as iodate may be an ionic organic molecule such as a tertiary amine.

4. CONCLUSIONS

Thermal oxidation would seem to be of little importance on short timescales but experiments at low concentrations are required to confirm the mechanisms found at high concentrations.

The hydrolysis of iodine is important and there is a wide range of data available including our own measurements. An independent evaluation of the data is now required.

Radiolysis reactions of dilute solutions are now well enough known but more work is required to elucidate mechanisms for iodate formation and destruction at low concentrations.

Rate constants for peroxide reactions are well known at room temperature and our knowledge of temperature dependencies up to 100°C is being improved. Measurements of final product yields at higher temperatures are being made to test extrapolations.

Reactions of surfaces are important particularly those of paint. These surfaces have a twofold importance, firstly the reaction with $I_2$ serves as a sink for $I_2$ and could reduce the fraction of the released
iodine which is volatile. Secondly the desorption of organic iodine could lead to the production of volatile compounds after subsequent radiolysis reactions, but these may well be slow.

In general our knowledge of iodine chemistry is improving although there are still shortcomings at low concentrations and elevated temperatures.

The use of computer models serves both to help in the understanding of the processes but most importantly for the purposes of this paper to help highlight those areas which are important and where data are poor.

In the conclusions of the last workshop it was felt that an agreed data base would be desirable and we feel that this is even more so now. The number of the different reactions makes it onerous for any one group fully to understand the whole range. There is now a wealth of data some of which is discrepant which could be evaluated by subdivision of the different areas and allocated different groups if there is sufficient interest and if such a programme could be co-ordinated.

Acknowledgements

This work was funded by the CEGB. We acknowledge the help of S. Saunders in iodine analyses and studies on the $\text{H}_2\text{O}_2$ reaction. We also acknowledge the work of Dr M Matsuda (Hitachi) for work on $\text{I}_2$ hydrolysis.
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### TABLE 1

**THERMAL REACTION OF IODINE SOLUTIONS WITH PAINTED SURFACES IN SOLUTION AND IN THE GAS SPACE ABOVE THE SOLUTION**

<table>
<thead>
<tr>
<th>CONDITION</th>
<th>TIME/hr</th>
<th>Aqueous pH</th>
<th>$I_2/\mu M$</th>
<th>$I^-/\mu M$</th>
<th>PERCENTAGE RECOVERY BY AQUEOUS EXTRACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Temp</td>
<td>0</td>
<td>5.4</td>
<td>52.2</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Surface in Vapour</td>
<td>0</td>
<td>4.6</td>
<td>23.2</td>
<td>25.4</td>
<td>68%</td>
</tr>
<tr>
<td>Ambient</td>
<td>0</td>
<td>5.4</td>
<td>52.2</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Surface in Solution</td>
<td>22.5</td>
<td>NM*</td>
<td>2.5</td>
<td>56</td>
<td>58%</td>
</tr>
<tr>
<td>100°C</td>
<td>0</td>
<td>5.4</td>
<td>45.8</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Surface in Vapour</td>
<td>0.5</td>
<td>5.0</td>
<td>0.7</td>
<td>46.8</td>
<td>51%</td>
</tr>
<tr>
<td>100°C</td>
<td>0</td>
<td>5.4</td>
<td>45.8</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Surface in Water</td>
<td>1.3</td>
<td>4.9</td>
<td>1.7</td>
<td>43.4</td>
<td>46%</td>
</tr>
</tbody>
</table>

*Not Measured

### TABLE 2

**THERMAL REACTION WITH PAINT ABOVE A 50\mu M I_2 SOLUTION AT 100°C**

Final Location of iodine as a percentage

<table>
<thead>
<tr>
<th>TIME AT TEMP/mins</th>
<th>% ON PAINT</th>
<th>$ZI^-$ Aqueous</th>
<th>$ZI_2$ Aqueous</th>
<th>% ORGANIC IODINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>22</td>
<td>59</td>
<td>0.5</td>
<td>18</td>
</tr>
<tr>
<td>100</td>
<td>17</td>
<td>50</td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>90</td>
<td>17</td>
<td>59</td>
<td>0.7</td>
<td>24</td>
</tr>
</tbody>
</table>
Extracted directly by Benzene

Reacted with Phenol, extracted into Benzene as iodophenol

FIG. 1. % EXTRACTION AGAINST CONCENTRATION FOR A SUCCESSIVELY DILUTED I₂ SOLUTION
**Fig 2 - SCHEMATIC REPRESENTATION OF MEASUREMENT OF SPECIATION OF IODINE IN DILUTE ACTIVE SOLUTIONS**

50cm$^3$ OF SOLUTION with $\sim$1µCl $^{131}$I

**ANALYSIS OF I$_2$/IO$_3^-$ species**

- ADD 1cm$^3$ OF 5x10$^{-4}$M PHENOL  
  $(I_2 + PhOH \rightarrow Ph(OH)I + I^-)$
  THEN SHAKE WITH 50cm$^3$ OF CCl$_4$

  aq | organic

- CONTAINS I$^-$ AND IO$_3^-$/IO$_4^-$ SPECIES
  SHAKE WITH 25cm$^3$ OF I$_2$/CCl$_4$ SOLN (3g/l)
  THEN WASH WITH 25cm$^3$ OF CCl$_4$

  aq | organic

- CONTAINS THE I$_2$ AS IODOPHENOL

  CONTAINS ANY I$^-$, IO$_3^-$/IO$_4^-$ SPECIES

**ANALYSIS OF OrgI SPECIES**

- SHAKE WITH 50cm$^3$ OF CCl$_4$ TO REMOVE ORGANIC IODINE AND I$_2$

  organic | aq

- CONTAINS ORGANIC IODINE AND I$_2$
  SHAKE WITH 50cm$^3$ OF 10$^{-2}$M I$^-$
  TO EXCHANGE $^{131}$I IN I$_2$

  aq | organic

- CONTAINS ANY I$^-$, IO$_3^-$/IO$_4^-$ SPECIES

  organic

- CONTAINS 1$^{31}$I IN ANY ORGANIC IODINE ONLY

CONTAINS 1$^{31}$I IN THE IO$_3^-$/IO$_4^-$ SPECIES ONLY

CONTAINS THE 1$^{31}$I FROM THE I$^-$ THROUGH THE EXCHANGE REACTION

$I^- + I_2 \rightarrow ^*$I$_2^*$ + I$^-$
FIG. 3. SCHEMATIC REPRESENTATION OF SPECTROMETER FOR HIGH TEMPERATURE SAMPLES
FIG. 4. TEMPERATURE DEPENDENCE OF K₁
FIG. 5. $I_2$ YIELDS FROM IRRADIATION OF $3.4 \times 10^{-6}$ M I$^-$, 0.2 M $H_3BO_3$ AT AMBIENT TEMPERATURE

FIG. 6. $IO_3^-$ YIELDS FROM IRRADIATION OF $3.4 \times 10^{-6}$ M I$^-$, 0.2 M $H_3BO_3$ AT AMBIENT TEMPERATURE
FIG. 7. IO$_3^-$ YIELD FROM 3.4 x 10$^{-6}$M CsI, 0.2M BORIC ACID AFTER 1 Mrad AGAINST TEMPERATURE

FIG. 8. % OXIDATION OF I$^-$ AT 1 Mrad AGAINST INITIAL I$^-$ CONCENTRATION
FIG. 9. I\(^{-}\) YIELDS FROM IRRADIATION OF 3.4 \(\mu\)M IO\(_3^—\), 0.2 M BORIC ACID

Experimental Facsimile prediction (\(K_{16} = 0.015\))

\[K_{18} = 3.66 \times 10^8\]

\[K_{18} = 1.869 \times 10^9\]

\[K_{18} = 8.165 \times 10^9\]

Experimental Facsimile prediction (\(K_{16} = 0.015\))

\([H_2O_2] = 1.8 \times 10^{-4}\) M

\([I^-] = 10^{-3}\) M

FIG. 10. \([I_2] + [I_3^-]\) PRODUCTION FROM H\(_2O_2\)/I\(^-\) SOLUTION (0.2 M H\(_3BO_3\)) AT 25°C
[I₂] = 50μM, Volume of Soln = 50 cm³

- Freshly machined surface (not-immersed)
- Stainless steel balls (immersed)
- Stainless steel gauze (not-immersed)

FIG. 11. REDUCTION OF I₂ SOLUTIONS IN THE PRESENCE OF STAINLESS STEEL SURFACES AT 100°C FOR 4 HOURS

FIG. 12. LOSS OF I₂ FROM REACTION WITH PAINTED STEEL AT 50°C AND 25°C
DISCUSSION

**P.N. CLOUGH** Your results seem to show some dramatic effects of impurities on iodine behaviour. Do you have a feeling yet for whether the "dirt" is going to downrate behaviour in a real accident situation?

**W.G. BURNS** In answer to the question as to whether iodine volatility will, in a reactor accident, be dominated by the effects of surfaces and impurities, I would say that this needs to be assessed by modelling calculations which scale up effects observed in relevant smaller scale tests. Our laboratory scale tests with painted steel surfaces suggest that these would possibly have important effects but we need to go through the calculation which simulates phenomena in the presence and absence of the painted surfaces in order to make reliable predictions. Dissolved impurities such as the Fe(II) ion were found to cause no effect in increasing the amount of $I_2$/HOI formed from I$^-$.

**A.C. VIKIS** You referred to the progressive oxidation of I0 to higher oxidation studies. I know that reaction has been documented in the gas phase, but has it been documented in solution?

**W.G. BURNS** No, at the moment it is a reasonable suggestion that we need to firm up experimentally in the future.

**E.C. BEAHM** Your Figure 8 (Iodate formation as a function of concentration) did not give a pH. Don’t you think following Lin, that this will depend on pH?

**W.G. BURNS** Our experiments on iodate were not done over a wide range of pH. We are ready to believe that the extent of radiolytic iodate formation is dependent on pH.

**D.A. PALMER** In your spectrophotometric work on the iodine disproportionation reaction to HOI and I$^-$ what material was used to make the cell and did you reverse the temperature cycle to ensure iodine stoichiometry was preserved?

**W.G. BURNS** We were very thorough in our methods, and in all cases of estimating the effect of temperature on the extraction coefficient and of measuring the hydrolysis of $I_2$ before appreciable iodate has been formed. We reversed the temperature increase and found that to within 1% the $I_2$ absorbance was the same as at the beginning. The apparatus was made of silica.
H. SHIRAISHI  Is oxygen contained in your solution? Our experiments suggest that little \( IO_3^- \) is formed when oxygen is present in the solution. I think the yield of \( I_2 \) or HOI must be very small in your solutions. Do you think that there is some process which accelerates oxidation of HOI to \( IO_3^- \) in aerated solutions?

W.G. BURNS  Yes, we are almost always concerned with aerated solutions. As shown in Figure 8 of our paper, although in aerated solutions containing 0.2 M boric acid the percentage of oxidation to iodate increases by a factor approximately 20 as the initial \([I^-]\) decreases from \( 10^{-4} \) to \( 3 \times 10^{-6} \) M, the value at \( 3 \times 10^{-6} \) M is only 10%, so I would agree that little \( IO_3^- \) is formed when oxygen is present.

I believe that the process which converts \( I_2/\text{HOI} \) to \( IO_3^- \) is radiolytic oxidation, possibly

\[
\text{HOI} + \text{OH} \rightarrow IO^- + H_2O \\
IO^- + \text{OH} \rightarrow H^+ + IO_3^-
\]

where \( IO_3^- \) reacts with HOI to give \( IO_3^- \). IO also might react with \( \text{H}_2\text{O}_2 \) in two pathways,

\[
\text{H}_2\text{O} + \text{IO} + \text{HO}_2 \rightarrow IO^- + \text{H}_2\text{O} + \text{O}_2 \\
\text{IO} + \text{HO}_2 \rightarrow IO^- + \text{H}_2\text{O} + \text{O}_2
\]

and if the second is more prominent at higher temperature this would explain the lower yield of iodate we observed at 100°C compared with 25°C.
Factors Affecting Radiolysis of Dilute Iodine Solutions

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University of Tokyo
Tokyo, Japan

ABSTRACT

The effect of radiation on the chemical forms of iodine species in dilute aqueous solutions has been investigated using a semi-batch type flow-system and a pulse radiolysis, and the recent results are summarised. It was found that the several factors have a large influence on the chemical form of iodine species in the radiolysis of their dilute solutions, and they are the concentration of the iodine species, pH of the systems, the concentrations of oxygen dissolved, temperature and initial oxidation state of iodine species. Among them, pH is the most important. To explain these effects some kinetic data of aqueous iodine systems were obtained by the pulse radiolysis.

1. INTRODUCTION

It has been recognised that the radiolytic effect may be one of the most important factors which control the chemical forms of iodine species after cesium iodide (CsI) released from failed fuels is dissolved into aqueous phase in containment in a sever nuclear reactor accident. Extensive efforts have been devoted to the studies of the radiolytic effect in the past several years by a few workers(1)~(3).

The effect of radiation on the chemical forms of iodine species has been continuously investigated by the authors by means of product analysis using a semi-batch type flow-system(4)~(6). A merit of employing this flow system is that the analysis of the radiolytic products can be carried out in less than one minute without the disturbance of the post-irradiation reactions mainly due to hydrogen peroxide.

The radiolytic reactions in dilute iodine solutions are very complicated and found to be affected by several factors. The factors examined in this study were the concentration of iodine species, pH of the systems, oxygen, temperature and initial oxidation state of iodine species.

Pulse radiolysis has been employed to obtain kinetic data on elemental reactions of the aqueous iodine systems, and these data are useful to explain the effects of the above factors.

A part of these results was reported in the first Workshop(4), and this paper summarises the recent results.
2. PULSE RADIOLYSIS

The pulse radiolysis apparatus employed was already described briefly in the previous paper\(^4\). The results obtained are summarized in Table I. The reaction of \(\text{O}_2\) with \(\text{I}_2\) is very important, in the neutral or alkaline solutions containing oxygen, as already described\(^4\). It is to be noted that \(\text{HO}_2\) radical, which is an important species in acidic solution containing oxygen, reduces \(\text{I}_2\) to \(\text{I}^-\) at significant rate, while it more rapidly oxidized \(\text{I}_2^-\) to yield \(\text{I}_2\).

3. PRODUCT ANALYSIS USING A SEMI-BATCH FLOW SYSTEM

3.1 CONCENTRATION OF CsI

Gamma irradiations were carried out with initially deaerated CsI solutions at neutral pH in concentration of \(10^{-4}\), \(10^{-5}\) and \(10^{-6}\) mol dm\(^{-3}\). The irradiation brought almost always an approximate steady state in the distribution of iodine species, and this indicates that a subtle balance is readily attained between rapid oxidation and reduction in the systems.

In the \(10^{-4}\) mol dm\(^{-3}\) CsI solutions, \(\text{I}_2\) is the major product in the steady state, while \(\text{I}^-\) is the most predominant component in the \(10^{-6}\) mol dm\(^{-3}\) solutions.

It was confirmed that the radiolytic products other than iodine species accumulate in the systems with increasing dose. The accumulation of these products gives a large influence on the oxidation-reduction balance. For instance, \(\text{H}_2\text{O}_2\)

\[
\text{H}_2\text{O}_2 + e^-_{\text{aq}} \rightarrow \text{OH} + \text{OH}^- \quad (1)
\]

\[
\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{O}_2 + \text{I}^- + \text{H}_2\text{O} \quad (2)
\]

converts the most reductive species, \(e^-_{\text{aq}}\) to the oxidising one, \(\text{OH}\), in one hand, but reduces \(\text{O}_2^-\) to yield \(\text{I}^-\), on the other hand, counterbalancing the increase in the oxidising power by eq.(1). The accumulation of \(\text{O}_2\) suppresses the formation of \(\text{OH}\) radical

\[
\text{O}_2 + e^-_{\text{aq}} \rightarrow \text{O}_2^- \quad (3)
\]

though reactions (1) and (3), resulting in increasing the reduction power, because \(\text{O}_2^-\) reduces \(\text{I}_2\) and \(\text{I}^-\) very rapidly.

3.2 EFFECT OF pH

The pH of the system is the most important factor controlling the oxidation-reduction balance in the irradiated iodine systems. For instance, when the deaerated \(10^{-4}\) mol dm\(^{-3}\) CsI solution was irradiated at pH 5, the level of \([\text{I}_2]\) increased by a factor of 5\(\sim\)6, as shown in Fig.1 in comparison with that at pH 7, whereas almost no net oxidation took place at pH 9. This extraordinary effect of pH will be mainly due to the change in the reaction
rate of $H_2O_2$ with HOI. The rate constants

$$H_2O_2 + HOI \rightarrow H_2O + I^- + O_2 + H^+ \quad (4)$$

$$HOI \rightleftharpoons H^+ + OI^- \quad (5)$$

of reaction (2) and (4) were measured to be $1.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $200 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The dissociation equilibrium of HOI shifts to the right side at high pH, and this results in the significant increase in the reducing power in the redox balance.

There may be another possibility that the dissociation equilibrium of HO$_2$, eq.(6), makes

$$HO_2 \rightleftharpoons H^+ + O_2^- \quad (6)$$

variable contribution to the redox balance, especially in the systems containing oxygen, depending on pH of the solutions.

$$I_2 + O_2^- \rightarrow I^-_2 + O_2 \quad 5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (7)$$

$$I_2 + HO_2 \rightarrow I^-_2 + O_2 + H^+ \quad 5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (8)$$

$$I^-_2 + HO_2 \rightarrow I_2 + HO_2^- \quad 4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (9)$$

In the neutral and acidic solutions, $O_2^-$ reduces $I_2$ to $I^-_2$ very rapidly, while HO$_2$ radical, which makes a large contribution in the acidic solutions, reduces $I_2$ less rapidly but simultaneously oxidizes $I^-_2$ very fast.

3.3 EFFECT OF OXYGEN

Oxygen has a significant influence on the redox balance in the radiolytic reactions. It is to be noted that oxygen is one of the major products in the radiolysis of the systems and accumulated with increasing dose even in the initially deaerated solutions.

A radiolysis result of the neutral $10^{-4}$ mol dm$^{-3}$ CsI solutions saturated with simulated air (Ar gas containing 20% $O_2$) is shown in Fig.2. The level of $I_2$, the oxidized product, is lower by a factor of three than that of the corresponding deaerated system. On the other hand, no oxidation of iodide was observed with the $10^{-5}$ and $10^{-6}$ mol dm$^{-3}$ CsI solutions saturated with the simulated air.

This suppression of oxidation by oxygen may be explained by a large contribution of reaction (3) in the presence of $O_2$ to lead to the suppression of $OH$ radical formation through reaction (1).

When natural air was used instead of simulated air in this experiment, the degree of oxidation was larger. This is due to the effect of carbon dioxide contained in air which makes the system a little more acidic. The detail is described elsewhere.
3.4 **EFFECT OF TEMPERATURE**

It is essential to investigate the effect of temperature on the radiolysis of the iodine solutions, since the temperature in containment is considered to rise considerably in a severe accident.

In Fig.3 the distribution of the iodine species is shown for the deaerated $10^{-4}$ mol dm$^{-3}$ CsI solutions irradiated at 80°C. Molecular iodine is a sole major product at 80°C as is the case with the result at 25°C, but its level declines very rapidly at 80°C with a maximum peak at an early stage which is comparable to that at 25°C. A similar situation was also observed with the $10^{-5}$ and $10^{-6}$ mol dm$^{-3}$ CsI solutions.

This faster decrease of the $I_2$ level at 80°C may be ascribed to an assumed larger activated energy of non-radical reaction (2). Most of the reactions involved in these systems are of radical type and reasonably presumed to have rather low activation energies, $\sim$5 KJ mol$^{-1}$, corresponding to diffusion-controlled reactions in the aqueous systems.

3.5 **INITIAL OXIDATION STATE OF IODINE**

As a comparative experiment, the radiolysis was carried out with deaerated $I_2$ solutions. In Fig.4 the distribution of the iodine species is shown for the neutral $5 \times 10^{-7}$ mol dm$^{-3}$ $I_2$ solutions irradiated at 25°C. The system attained a steady state after some time of irradiation as is the case with the system starting from $I^-$ state, and the final distribution of the iodine species is almost the same as that observed with the corresponding $1 \times 10^{-6}$ mol dm$^{-3}$ $I^-$ solutions.

On the other hand, oxidation proceeded a little more extensively at the final stage with the $5 \times 10^{-6}$ and $5 \times 10^{-5}$ mol dm$^{-3}$ $I_2$ solutions than with the corresponding $I^-$ solutions. This difference may arise from the variation of pH in the systems. When $I_2$ is converted to $I^-$ and/or $IO_3^-$, the negative charges of the products must be compensated by the increase in [H$^+$]. This results in a small shift to the oxidation side in the redox balance of the system. The pH changes in the $5 \times 10^{-7}$ mol dm$^{-3}$ $I_2$ solutions are smaller than those in the $5 \times 10^{-6}$ and $5 \times 10^{-5}$ mol dm$^{-3}$ $I_2$ solutions. Thus, it may be concluded that if the concentration of total iodine element and the final pH are the same between two systems, the product distributions of the iodine species are identical in the steady state irrespective of the initial oxidation state of the iodine species.

4. **CONCLUSION**

Radiolytic reactions of dilute iodine solutions are very complicated and largely affected by several factors such as concentration of iodine species, pH, oxygen concentration, temperature and initial oxidation state of iodine. Among them, pH is one of the most important factors.

The presence of oxygen and increase in temperature may not give deleterious effect to the distribution of iodine species under a reactor
accident condition from a practical point of view.

Pulse radiolysis is a very powerful tool to analyse the complicated phenomena and gives data helpful to the understanding of the mechanism.

REFERENCES


Table I  Rate constants measured at 22 ± 2°C

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate coefficients / M⁻¹S⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Oxidation reaction</td>
<td></td>
</tr>
<tr>
<td>I⁻ + OH → I + OH⁻</td>
<td>( k₁ = (1.5±0.5) \times 10^{19} )</td>
</tr>
<tr>
<td>B. Recombination reactions</td>
<td></td>
</tr>
<tr>
<td>I + I⁻ → I₂⁻</td>
<td>( k₂ = (1.9±0.5) \times 10^{19} )</td>
</tr>
<tr>
<td>I + I₂⁻ → I₃⁻</td>
<td>( k₄ = (8.4±0.5) \times 10^{9} )</td>
</tr>
<tr>
<td>I⁻ + I₂⁻ → I₃⁻ + I⁻</td>
<td>( k₅ = (4.9±0.3) \times 10^{9} )</td>
</tr>
<tr>
<td>C. O₂⁻ reactions</td>
<td></td>
</tr>
<tr>
<td>I₂⁻ + O₂⁻ → I₂⁻ + O₂</td>
<td>( k₁₈ = (5.0±1.0) \times 10^{9} )</td>
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<tr>
<td>I₂⁻ + O₂⁻ → 2I⁻ + O₂</td>
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<tr>
<td>I⁻ + O₂⁻</td>
<td>&lt;5 \times 10^{8}</td>
</tr>
<tr>
<td>NOI + O₂⁻</td>
<td>&lt;2 \times 10^{8}</td>
</tr>
<tr>
<td>D. HO₂⁻ reactions</td>
<td></td>
</tr>
<tr>
<td>I₂⁻ + HO₂⁻ → I₂⁻ + HO₂⁻</td>
<td>( k₁₄ = (4.0±0.5) \times 10^{9} )</td>
</tr>
<tr>
<td>I₁⁻ + HO₂⁻ → I⁻ + O₂ + H⁺</td>
<td>( k₁₈ = (5.0±2.0) \times 10^{7} )</td>
</tr>
<tr>
<td>E. Reactions related to equilibria</td>
<td></td>
</tr>
<tr>
<td>I + I⁻ → I₁⁻</td>
<td>( k₅₁ = (1.1±0.5) \times 10^{19} )</td>
</tr>
<tr>
<td>I₂⁻ + OH⁻ → I⁻ + HOI</td>
<td>( (6.0±4.0) \times 10^{9} )</td>
</tr>
</tbody>
</table>

**Fig. 1** The distribution of iodine species in the deaerated \( 10^{-4} \) mol dm⁻³ CsI solution irradiated at 25°C and at pH 5.

Dose rate 0.38 Mrad/hr
Fig. 2 The distribution of iodine species in the neutral
$10^{-4}$ mol dm$^{-3}$ CsI solution saturated with
simulated air.
irradiated at 25°C, dose rate 0.38 Mrad/hr

Fig. 3 The distribution of iodine species in the deaerated
$10^{-4}$ mol dm$^{-3}$ CsI solution irradiated at 80°C at pH 7.
Dose rate 0.38 Mrad/hr
The distribution of iodine species in the deaerated $5 \times 10^{-7}$ mol dm$^{-3}$ I$_2$ solutions irradiated at 25°C and at pH 7.

Dose rate 0.38 Mrad/hr
DISCUSSION

A.C. VIKIS I have a problem with the $\text{H} + \text{I}^- \rightarrow (\text{HI}^-) \rightarrow \text{I} + \text{H}$ reaction suggested in your presentation. The way I look at it is that HI already has the rare gas configuration. To stabilize an electron on a rare gas would be difficult.

K. ISHIGURE We have no pulse radiolysis experimental evidence of the oxidation of I$^-$ by H but just literature data. This reaction does not make significant contribution to the whole mechanism under the present condition and has no effect on the discussion mentioned here.

W.G. BURNS How did you obtain the rate constant values for reactions (2) and (4)?

K. ISHIGURE We observed that some buffer reagents have catalytic effects on the reactions of $\text{H}_2\text{O}_2$ with HOI and OI$^-$. The values we presented here were measured by the extrapolation of the data to remove the catalytic effects of the buffer used.
THE RADIATION-INDUCED FORMATION OF IODOALKANES 
AND THE RADIOLYSIS OF Iodomethane

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ABSTRACT
The γ-radiolysis of iodide, iodine, iodate and periodate solutions 
containing methane has been investigated. Iodoalkanes are produced in these 
solutions upon irradiation. In the case of unbuffered iodide, iodate and 
periodate solutions at an initial concentration of 10^{-4} \text{ mol.dm}^{-3}, nearly all of 
the initial iodine is transformed into iodoalkanes after the absorption of a 
4-kGy radiation dose. A mechanism is proposed that accounts for these 
observations. The γ-radiolysis of iodomethane has also been investigated. 
Iodomethane is removed by reactions with the hydroxyl radical, the solvated 
electron, the hydrogen atom and the perhydroxyl radical. The radiolysis 
product is iodide, iodine, or both, depending on the chemical conditions.

1. INTRODUCTION
The formation of organic iodides can affect the volatility of 
radiiodine following a severe nuclear reactor accident. Organic iodides with 
a low molecular weight are volatile. Also, their low reactivity makes them 
more difficult to contain than inorganic forms of iodine. As an example, 
iodomethane has a liquid/gas partition coefficient of 3.4 at 25°C [1] compared 
to 80 for I_2 at the same temperature [2]. Thus, even a small amount of organic 
iodides can have a large impact on the partitioning of iodine between an 
aqueous and a gaseous phase. Measurements performed at Three Mile Island-2 
after the 1979 March accident indicated that organic iodides were the 
predominant iodine species in the containment building atmosphere [3]. The 
presence of organic iodides has also been observed in large-scale tests 
simulating reactor accidents [4].

A good understanding of the mechanisms of formation and removal of 
organic iodides under these chemical conditions is necessary in order to model 
the behavior of iodine in containment buildings and to design effective 
abatement systems. Volatile organic iodides can be formed by thermal and 
radiolytic reactions in the gaseous phase, at surfaces and in the aqueous 
phase. Recently, Beahm et al [5], Lutz and Kelly [6], Bartoníček and 
Habersbergerová [7], and Ono et al [8] have observed that iodoalkanes are 
formed when solutions containing iodide or iodine are irradiated in the 
presence of organic materials. Although most of these experiments were 
qualitative in nature, they indicate that radiolytic reactions could play an 
important role in the formation of organic iodides following a nuclear reactor 
accident.

This paper describes an experimental study of the formation of 
ioodoalkanes in irradiated solutions containing various iodine species and
methane. Aqueous solutions containing iodide, iodine, iodate or periodate were irradiated in a gamma-cell in the presence of methane. The effects of concentration, pH and radical scavengers, including nitrous oxide, sodium formate, hydrazine and oxygen, were examined. The γ-radiolysis of iodomethane was also studied, since radiolysis could be effective in removing iodoalkanes from solution.

2. EXPERIMENTAL

2.1 Materials

Distilled water was redistilled from an alkaline permanganate solution and distilled again in an all-glass still. Sodium iodide, resublimed iodine, sodium iodate, sodium meta-periodate, hydrazine sulfate, sulfuric acid and monohydrogen sodium phosphate were ACS- or reagent-grade chemicals from the Fisher Scientific Company. All were used as received. Nitrous oxide and methane gases (Ultra High Purity) were from Matheson. Compressed air (Ultra Zero) was from Canadian Liquid Air. Argon (99.9995%) was from Linde. Iodomethane (99%) was from Aldrich Chemical and was used as received.

2.2 Procedures

Solutions made by volume were saturated with the appropriate gas mixtures by bubbling the mixture through the solution at atmospheric pressure for about twenty minutes. Irradiations were performed in Pyrex flasks (25 cm³) fitted with a ground-glass stopcock. To prevent leaks, the glass joints were lubricated with a minimum amount of Fluorolube™ (Fisher Scientific Company) or silicone (Dow Corning) grease. Tests have shown that this procedure did not affect the radiolysis results. The flasks were cleaned thoroughly before use and baked at 550°C for twelve hours to destroy organic contaminants. Some solutions were irradiated in flame-sealed glass ampoules (10 cm³), keeping the gas volume above the solutions to a minimum (about 1 cm³). The radiolysis experiments were carried out using two ⁶⁰Co γ-ray sources with dose rates of about 0.5 Gy.s⁻¹ and 5.5 Gy.s⁻¹ (2 Mrad.h⁻¹). Dose rates were measured with the Fricke dosimeter and were corrected for the decay of the ⁶⁰Co sources. Solutions were analyzed within a few hours after irradiation. Solutions identical to the ones used in the radiolysis experiments, but which were not irradiated, were also analyzed as blanks. All the experiments were done in triplicate.

2.3 Analytical Methods

The triiodide ion concentration was determined by measuring the absorbance of the solutions at 350 nm, using a Hewlett-Packard model 8450A spectrophotometer. The extinction coefficient for triiodide, ε, has a value of 25 700 dm³·mol⁻¹·cm⁻¹ at that wavelength. Iodine was determined by measuring the absorbance of the solutions at 460 nm (ε = 740 dm³·mol⁻¹·cm⁻¹) and correcting for the absorbance due to I₃⁻ (ε = 1 000 dm³·mol⁻¹·cm⁻¹). Iodide was determined from the I₃⁻ and I₂ concentrations using the equation

\[ [I^-] = \frac{[I_3^-]}{[I_2]}K_1, \tag{1} \]

where K₁ is the equilibrium constant for the triiodide ion formation and has a
value of 746 dm$^3$.mol$^{-1}$ at 25°C [9]. Alternatively, the absorbance of the solutions at 225 nm ($\varepsilon = 13 \, 200$ dm$^3$.mol$^{-1}$.cm$^{-1}$) was used. The iodoalkane concentrations were determined using either gas chromatography (GC) or high-performance liquid chromatography (HPLC); most analyses were performed using the latter technique.

The GC analysis were performed using a Varian model 3700 instrument equipped with a $^{63}\text{Ni}$ electron-capture detector. A glass column (3.78 m x 1 mm I.D.) packed with 10% Fluorad FC-431™ on 80/100 mesh Chromosorb W-HP (Chromatographic Specialties Incorporated) was used. The column was maintained at 60°C and the detector operated at 210°C. The carrier gas was an argon/methane mixture flowing at a rate of 0.5 cm$^3$.s$^{-1}$. The iodoalkanes were extracted from the liquid phase using a head-sampler device. The instrument was calibrated before each series of measurements. The detection limit for iodomethane was about $10^{-9}$ mol.dm$^{-3}$ in the aqueous phase, and the reproducibility was ± 5%.

The HPLC analyses were performed in isocratic mode using a Waters Associates instrument. A reverse-phase column (octadecyldimethylsilyl, LC-18-DB, Supelco Incorporated) was used with a 67/33 (vol.%) methanol/water mixture as the mobile phase. Detection was done using a Waters Associates model 441 absorbance detector set at 254 nm. The system was equipped with an automatic sampling device and operated under the control of a microcomputer. The detection limit for iodomethane was about $1 \times 10^{-6}$ mol.dm$^{-3}$ and the reproducibility was ± 5%. No interference from iodide, iodate or periodate was noted. However, the reproducibility of the analysis for periodate solutions was not as good as for the experiments with iodide and iodate (± 10%, as opposed to ± 5%) because of partial degradation of the column by the strongly oxidizing periodate ion. If iodine was the major species, it interfered with the determination of iodoalkanes. The interference was eliminated by adding hydrazine sulfate to a concentration of $10^{-3}$ mol.dm$^{-3}$ to the irradiated solutions. Tests with mixtures of iodine and iodomethane demonstrated that hydrazine rapidly reduces iodine to iodide under these conditions, without affecting the concentration of iodomethane. The excess hydrazine sulfate did not interfere with the iodoalkane determination. The system was calibrated before and during each series of measurements with solutions containing iodomethane, iodoethane and iodide, iodate or periodate, as appropriate.

Formaldehyde was determined by spectrophotometry, using the pentane-2,4-dione/ammonium acetate method [10]; the detection limit was $1 \times 10^{-6}$ mol.dm$^{-3}$. Methanol was determined by oxidation to formaldehyde using permanganate and subsequent reaction with pentane-2,4-dione/ammonium acetate [11]; the detection limit was about $3 \times 10^{-6}$ mol.dm$^{-3}$. Formic acid was determined by spectrophotometry, following reduction to formaldehyde with nascent hydrogen and reaction with naphthalene-4,5-dihydroxy-2,7-disulfonic acid (chromotropic acid) [12]; the detection limit was about $3 \times 10^{-6}$ mol.dm$^{-3}$. 
3. RESULTS

3.1 Iodide solutions

Irradiation of iodide solutions buffered to a pH of 7 (monohydrogen sodium phosphate, $2.0 \times 10^{-3}$ mol dm$^{-3}$) and saturated with a 50/50 (vol.%) $\text{N}_2\text{O}/\text{CH}_4$ gas mixture resulted in the formation of iodine and iodomethane. Figure 1 shows the data obtained for a solution containing sodium iodide at an initial concentration of $1.0 \times 10^{-4}$ mol dm$^{-3}$. From the known solubility of methane and nitrous oxide in water at 20°C [13], their initial concentrations would have been $7.20 \times 10^{-4}$ mol dm$^{-3}$ and $1.25 \times 10^{-2}$ mol dm$^{-3}$, respectively. Iodomethane ($G = 0.17 \pm 0.02$, where $G$ stands for the number of molecules produced for each 100 eV, or $1.602 \times 10^{-12}$ J, absorbed) and iodine ($G = 0.93 \pm 0.02$) are formed initially. The concentration of iodomethane reaches a maximum of $3.7 \times 10^{-5}$ mol dm$^{-3}$ at an absorbed dose of 2.0 kGy and decreases with the dose for higher absorbed doses. The concentration of iodine ($I_2 + I_3$) reaches a maximum of $2.9 \times 10^{-5}$ mol dm$^{-3}$ at an absorbed dose of 0.5 kGy and decreases with the dose for higher absorbed doses. The concentration of iodide decreases rapidly with an increase in the absorbed dose, goes through a minimum of about $1.5 \times 10^{-5}$ mol dm$^{-3}$ at 1.2 kGy and then increases with increasing doses. The remaining iodine species is likely iodate. Formaldehyde was present at a concentration of $3.4 \times 10^{-5}$ mol dm$^{-3}$ in solutions that had absorbed 3 kGy; methanol and formic acid were not detected. Increasing the dose rate from about $0.55$ Gy s$^{-1}$ (0.2 Mrad h$^{-1}$) to about 5.5 Gy s$^{-1}$ did not markedly affect the results.

Irradiation of unbuffered iodide solutions saturated with a 50/50 (vol.%$) \text{N}_2\text{O}/\text{CH}_4$ gas mixture resulted in the formation of iodate and iodomethane. Figure 2 shows the data obtained for a solution containing sodium iodide at an initial concentration of $1.0 \times 10^{-4}$ mol dm$^{-3}$. The concentration of iodomethane increases slowly with the absorbed dose for doses below 2 kGy and then increases abruptly with the dose for doses above 2 kGy (slope $= 0.40 \pm 0.05$ molecule$\cdot$(100 eV)$^{-1}$, 100 eV = $1.602 \times 10^{-17}$ J). Almost all of the initial iodide (and 13% of the initial methane) is converted to iodomethane after 5 kGy of energy has been absorbed by the solution. The concentration of iodomethane then decreases with an increase in absorbed dose for doses in excess of 5 kGy. The concentration of iodide decreases rapidly with an increase in the absorbed dose and levels off at a value of about $8 \times 10^{-6}$ mol dm$^{-3}$ for doses between 2.5 and 6.5 kGy. It then goes through a maximum ($2.5 \times 10^{-5}$ mol dm$^{-3}$) at an absorbed dose of 8 kGy. No iodine or triiodide could be detected in any of the solutions; the detection limit is $2 \times 10^{-6}$ mol dm$^{-3}$ for $I_2$ and $1 \times 10^{-7}$ mol dm$^{-3}$ for $I_3$. The concentration of the remaining iodine species was calculated from an iodine mass balance equation and is also illustrated in Figure 2. These species were assumed to be hypiodious acid and iodate. Their concentration goes through a maximum at an absorbed dose of 2 kGy, then through a minimum at a dose of 5 kGy and increases with the dose for doses in excess of 5 kGy. The pH of the solutions increased with the dose from a value of about 7 for unirradiated solutions to a value of about 10.5 for solutions that had absorbed 2 kGy.

Solutions containing sodium iodide at a concentration of $1.0 \times 10^{-4}$ mol dm$^{-3}$ and sodium formate at a concentration of $1.0 \times 10^{-2}$ mol dm$^{-3}$ were saturated with methane and irradiated to an absorbed dose of 1 kGy. No iodoalkanes could be detected using HPLC. The concentration
of iodide was not affected by the irradiation. Solutions containing sodium iodide at a concentration of $1.0 \times 10^{-4}$ mol dm$^{-3}$ were saturated with a 50/50 (vol.%) air/CH$_4$ mixture and irradiated to absorbed doses of up to 4 kGy. No iodoalkane could be detected using HPLC. The concentration of iodide was not affected by the irradiation.

### 3.2 Iodine solutions

Solutions containing iodine at a concentration of $4.0 \times 10^{-4}$ mol dm$^{-3}$ and at a pH of 3 (sulfuric acid) were saturated with a CH$_4$/N$_2$O (50/50 vol.%) mixture and irradiated to absorbed doses of up to 3.5 kGy. Iodine was removed with a G-value of $0.20 \pm 0.02$. Iodomethane was present at a concentration of about $1 \times 10^{-6}$ mol dm$^{-3}$ after the absorption of a 3.5-kGy dose. However, the concentration of iodomethane was higher when a significant volume of gas phase (40 vol.%) was present, indicating that iodomethane can be formed by radiation-induced reactions in the gas phase under these conditions.

### 3.3 Iodate solutions

Irradiation of unbuffered iodate solutions saturated with a 50/50 (vol.%) N$_2$O/CH$_4$ gas mixture resulted in the formation of iodoalkanes in the aqueous phase. These were identified as follows. The HPLC chromatograms for the irradiated solutions displayed two peaks that had retention times identical to those obtained with standard solutions containing iodomethane and iodoethane. The GC chromatograms displayed three peaks that had retention times identical to those obtained with standard mixtures of iodomethane, iodoethane, and 1-iodopropane. A gas chromatograph/mass spectrometer instrument was used to analyze the gas phase above a solution irradiated to a dose of 3 kGy; iodomethane and iodoethane were positively identified.

Figure 3 shows the data obtained following irradiation of solutions containing sodium iodate at an initial concentration of $1.0 \times 10^{-4}$ mol dm$^{-3}$. The initial concentrations of methane and nitrous oxide were $7.2 \times 10^{-4}$ mol dm$^{-3}$ and $1.25 \times 10^{-2}$ mol dm$^{-3}$, respectively. The concentration of iodomethane increases linearly with the absorbed dose (G-value = $0.25 \pm 0.02$), goes through a maximum at an absorbed dose of about 5 kGy and then decreases with an increase in the absorbed dose for doses above 5 kGy. The concentration of iodoethane followed a similar pattern (Figure 4), but was lower by a factor of about twenty. Essentially all the initial iodate is converted to iodomethane after 5 kGy of energy has been absorbed by the solution. No iodine or triiodide could be detected in any of the solutions. A small amount of iodide was present in solutions that had absorbed in excess of 4 kGy. This is also shown in Figure 3. Formaldehyde was present at a concentration of $2.6 \times 10^{-5}$ mol dm$^{-3}$ in solutions that had absorbed a dose of 4 kGy; methanol and formic acid were not detected. The pH of the solutions decreased slightly with increasing doses, from a value of 6.5 for unirradiated solutions to a value of 5.5 for solutions that had absorbed 10 kGy.

Figure 5 shows the results obtained with solutions containing iodate at an initial concentration of $1.0 \times 10^{-3}$ mol dm$^{-3}$, saturated with a 50/50 (vol.%) N$_2$O/CH$_4$ mixture and irradiated to absorbed doses of up to 4 kGy. The concentration of iodomethane increases slowly with the absorbed doses for doses of up to 0.75 kGy, increases more rapidly with the dose for doses between 0.75 and 4 kGy [slope = $0.40 \pm 0.05$ molecules $(100 \text{ eV})^{-1}$] and levels
off for doses near 4 kGy. The concentration of iodoethane followed a similar pattern but was lower by a factor of about 20.

Solutions containing sodium iodate at a concentration of 1.0 x 10^{-4} mol dm^{-3} and sodium formate at a concentration of 1.0 x 10^{-2} mol dm^{-3} were saturated with methane and irradiated to an absorbed dose of 1 kGy. Iodomethane was present at concentrations close to the GC detection limit (about 10^{-9} mol dm^{-3}). Identical results were obtained when the initial iodate concentration was 1.0 x 10^{-3} mol dm^{-3}. Solutions containing sodium iodate at a concentration of 1.0 x 10^{-4} mol dm^{-3} and hydrazine at a concentration of 1.0 x 10^{-3} mol dm^{-3} were saturated with methane and irradiated to an absorbed dose of 1 kGy. Iodomethane, iodoethane and 1-iodopropane were identified using GC, all at concentrations close to the detection limit. Identical results were obtained when the initial iodate concentration was 1.0 x 10^{-3} mol dm^{-3}. Solutions containing sodium iodate at a concentration of 1.0 x 10^{-4} mol dm^{-3} and saturated with a 50/50 (vol.%) air/CH_{4} mixture were irradiated to absorbed doses of up to 4 kGy. Iodide and iodomethane were present in the irradiated solutions at a concentration of 6.8 x 10^{-6} mol dm^{-3} and 2.8 x 10^{-6} mol dm^{-3}, respectively, for an absorbed dose of 1 kGy and at a concentration of 3.3 x 10^{-5} mol dm^{-3} and 6.9 x 10^{-5} mol dm^{-3}, respectively, for an absorbed dose of 4 kGy. Thus, the presence of air strongly inhibits the formation of iodoalkanes at low absorbed doses, but less so at higher doses.

3.4 Periodate solutions

Figure 6 shows the results obtained with solutions containing periodate at an initial concentration of 1.0 x 10^{-4} mol dm^{-3}, saturated with a 50/50 (vol.%) N_{2}O/CH_{4} mixture and irradiated to absorbed doses of up to 4 kGy. The concentration of iodomethane increases slowly with the absorbed dose for doses up to 0.50 kGy, increases more rapidly with the dose for doses between 0.50 and 3.0 kGy [slope = 0.40 ± 0.05 molecules-(100 eV)^{-1}] and levels off for doses near 3.5 kGy. Formaldehyde was present at a concentration of 2.6 x 10^{-5} mol dm^{-3} in solutions that had absorbed a dose of 4 kGy; methanol and formic acid were not detected. Solutions containing periodate at an initial concentration of 1.0 x 10^{-4} mol dm^{-3}, saturated with a 50/50 (vol.%) Ar/CH_{4} mixture were irradiated to absorbed doses of up to 4 kGy. The concentration of iodomethane increased linearly with the absorbed dose (G-value = 0.30 ± 0.05) for doses of up to 3.5 kGy and then leveled off. There was no detectable induction period. Iodoethane was also present, but the concentrations were lower than that of iodomethane by a factor of about 20.

Solutions containing sodium periodate at a concentration of 1.0 x 10^{-4} mol dm^{-3} and sodium formate at a concentration of 1.0 x 10^{-3} mol dm^{-3} were saturated with methane and irradiated to absorbed doses of up to 4 kGy. No iodoalkane could be detected in any of the solutions using HPLC. No iodine or triiodide could be detected either. About 70% of the initial periodate was reduced to iodide after a dose of 1 kGy had been absorbed by the solution. Solutions containing sodium periodate at a concentration of 1.0 x 10^{-4} mol dm^{-3} and saturated with a 50/50 (vol.%) air/CH_{4} mixture were irradiated to absorbed doses of up to 4 kGy. Iodide and iodomethane were present in the irradiated solutions at a concentration of 1.2 x 10^{-5} mol dm^{-3} and 5.7 x 10^{-6} mol dm^{-3}, respectively, for an absorbed dose of 1 kGy and at a concentration of 3.2 x 10^{-5} mol dm^{-3} and 7.9 x 10^{-5} mol dm^{-3}, respectively, for an absorbed dose of 4 kGy. Thus, the presence of air
strongly inhibits the formation of iodoalkanes at low absorbed doses, but less so at higher doses.

3.5 Iodomethane solutions

Iodomethane solutions at an initial concentration of 3.0 x 10^{-3} \text{ mol.dm}^{-3}, a pH of 3 (sulfuric acid) and saturated with either N_{2}O (2.5 x 10^{-2} \text{ mol.dm}^{-3}) or argon were irradiated. The only radiolysis product was iodine for solutions saturated with N_{2}O. Iodine and iodide in roughly equal yields were the radiolysis products for solutions saturated with argon. The G-value for iodomethane was -0.50 \pm 0.02 for solutions saturated with N_{2}O and -1.00 \pm 0.02 for solutions saturated with argon.

Irradiation of iodomethane solutions at a pH of 3 and in the presence of 10^{-2} \text{ mol.dm}^{-3} 2-methyl-2-propanol (t-butyl alcohol) yielded iodide with a G-value of 0.48 \pm 0.02. Trace amounts of iodine and triiodide were also present. For iodomethane solutions saturated with air at a pH of 3, the radiolysis products were iodine for absorbed doses of up to 2 kGy and iodine and iodide for higher doses. The G-value was -1.74 \pm 0.02. Iodomethane solutions saturated with argon at a pH of 6 yielded a mixture of iodine and iodide in roughly equal proportion upon irradiation. The G-value was -1.36 \pm 0.02. These data are summarized in Table 1.

4. DISCUSSION

The \(\gamma\)-irradiation of water produces a mixture of radical and molecular species according to the reaction

\[
4.15H_{2}O \rightarrow 2.7e_{aq} + 2.70H + 2.7H^{+} + 0.6H + 0.45H_{2} + 0.7H_{2}O_{2}
\]

where the coefficients are the G-values. Nitrous oxide scavenges solvated electrons, yielding more OH radicals

\[
e_{aq} + N_{2}O \rightarrow OH + OH^{-} + N_{2}
\]

The rate constant for Reaction (3) is 8.7 \times 10^{9} \text{ dm}^{3}.\text{mol}.\text{s}^{-1} [14]. Nitrous oxide reacts slowly with the hydrogen atom (k = 2.3 \times 10^{6} \text{ dm}^{3}.\text{mol}.\text{s}^{-1}) [15], so that 90\% of the radicals available in solutions containing sufficient N_{2}O are OH radicals and 10\% are hydrogen atoms.

4.1 Iodide solutions

From Figure 1, irradiation of buffered iodide solutions (pH 7) saturated with a N_{2}O/CH_{4} mixture (50/50 vol.\%) produces iodine and iodomethane. The formation of iodine under these conditions is consistent with the results obtained by Buxton and Sellers [16]. Iodide in these solutions is oxidized by OH radicals, according to the following reaction sequence:
OH + I⁻ → I₂ + OH⁻  \quad (4)

2I₂ → I₃ + I⁻  \quad (5)

I₃ ↔ I⁻ + I₂  \quad (6)

I₂ + OH⁻ ↔ HOI + I⁻  \quad (7)

Equilibrium (7) is to the left at these OH⁻ and I⁻ concentrations. No iodate is expected to be formed initially since HOI is a necessary precursor to iodate. Buxton and Sellers [16] found a value of 3.3 x 10⁻⁵ mol.dm⁻³ for the concentration of (I₂ + I₃) in a 1.0 x 10⁻⁴ mol.dm⁻³ iodide solution that had been saturated with nitrous oxide and had absorbed a 0.464-kGy radiation dose; we have found a similar value of 2.9 x 10⁻⁵ mol.dm⁻³.

Methyl radicals are formed by the reaction of OH radicals with methane in aqueous solution:

CH₄ + OH → CH₃ + H₂O  \quad (8)

The rate constant is 1.2 x 10⁸ dm³.mol⁻¹.s⁻¹ [17]. Thus, methane will compete with iodide for OH radicals in our solutions. The initial yield of methyl radicals is given by

\[ G_{CH₃} = \frac{G_{OH} k₈[CH₄]}{(k₈[CH₄] + k₄[I⁻])} \],  \quad (9)

were \( G_{OH} \) is the yield of OH radical, \( k₈ \) is the rate constant for the reaction of OH with methane and \( k₄ \) is the rate constant for the reaction of OH with iodide (2.8 x 10¹⁰ dm³.mol⁻¹.s⁻¹) [18]. Substituting the appropriate numerical values in Equation (9) gives \( G_{CH₃} = 0.16 \). Methyl radicals could also be formed by reaction with iodine atoms:

CH₄ + I → CH₃ + HI  \quad (10)

Methyl radicals react rapidly with I₂ in both the gas phase [19] and the aqueous phase (\( k = 6.0 \times 10⁹ \) dm³.mol⁻¹.s⁻¹) [20], yielding iodomethane and iodine atoms

\[ CH₃ + I₂ → CH₃I + I \].  \quad (11)

Thus, in our solutions iodomethane is likely formed by Reaction (11). The observed G-value for the formation of iodomethane (0.17 ± 0.02) indicates that all the methyl radicals are efficiently scavenged by I₂. The resulting iodomethane is removed by radiolytic processes at high absorbed doses.

It is apparent from Figure 2 that irradiation of unbuffered iodide solutions saturated with an N₂O/CH₄ mixture (50/50 vol.%) produces first iodate and then iodomethane. The formation of iodate is consistent with the results obtained by Buxton and Sellers [16]. The pH of the solutions should increase with the progress of the radiolytic oxidation because of Reaction (4); this is observed in our experiments. The low iodide ion concentration and the rising
pH should shift equilibrium (7) to the right. The resulting HOI would be oxidized to iodate through a series of reactions involving the OH radical and the oxiodine species I0, HIO2, IO2, and HIO3. Buxton and Sellers [16] report that the concentration of (I2 + I3) is less than 10^-6 mol.dm^-3 after a dose of 0.464 kGy has been absorbed by a 1.0 x 10^-4 mol.dm^-3 iodide solution saturated with N2O. Our results are in agreement with these observations since no iodine or triiodide could be detected in our experiments, which were performed under similar conditions. Buxton and Sellers found a value of 3 x 10^-5 mol.dm^-3 for the concentration of (HOI + IO3) after the absorption of a 0.464-kGy radiation dose; similarly, we have found a value of 2.2 x 10^-5 mol.dm^-3.

Reaction (11) could produce iodomethane in the aqueous phase, with a maximum yield of 0.16 under our experimental conditions. This is consistent with the low yield of iodomethane (about 0.1) observed for doses below 1 kGy.

The yield of iodomethane increases abruptly as the absorbed dose reaches a value of 2 kGy. This coincides with the maximum in the concentration of iodate. The solution is at that point equivalent to an iodate solution containing methane and N2O. Possible mechanisms for the formation of iodoalkanes under these conditions are discussed later. The resulting iodomethane is removed by radiolysis at absorbed doses in excess of 5 kGy, yielding iodide and iodate. This is expected since the reaction of iodomethane with OH radicals produces I2, which disproportionates to iodide and iodate in basic solution.

Formate is an efficient scavenger of both H and OH radicals, yielding the carboxyl radical anion, CO2, a strong reducing agent:

\[ \text{H/OH} + \text{HCO}_2 \rightarrow \text{H}_2/\text{H}_2\text{O} + \text{CO}_2 \].

Addition of 10^-2 mol.dm^-3 sodium formate to a 10^-4 mol.dm^-3 iodide solution saturated with methane should suppress the radiolytic oxidation of iodide and the formation of methyl radicals. No iodoalkane nor oxidized iodine species were detected under these conditions, which confirms that the formation of iodoalkanes results from oxidative processes.

Oxygen is an efficient scavenger of solvated electrons and hydrogen atoms, yielding O2 at pH values above 4.8, which rapidly reduces I2 (k = 6.0 x 10^9 dm^3.mol.s^-1) [21]. Oxygen also scavenges methyl radicals, yielding methylperoxyl radicals (k = 4.7 x 10^9 dm^3.mol.s^-1) [20]:

\[ \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \].

The absence of iodomethane and oxidized iodine species following the irradiation of 1.0 x 10^-4 mol.dm^-3 iodide solutions saturated with an air/CH4 (50/50 vol.%.) mixture is likely due to the reduction of any I2 by O2 and to the scavenging of methyl radicals by dissolved oxygen.
4.2 Iodine solutions

Iodine is an efficient scavenger of OH radicals in the aqueous phase; the reaction

$$I_2 + OH \rightarrow HOI + I$$  \hspace{1cm} (14)$$

has a rate constant of $1.1 \times 10^{10}$ dm$^3$.mol$^{-1}$.s$^{-1}$ [21]. We observed, however, a low yield ($G_{I_2} = -0.20 \pm 0.02$) for the removal of $I_2$ from acidic solutions saturated with a CH$_4$/N$_2$O (50/50 vol.% mixture). This implies that iodine is efficiently regenerated. Hypolodous acid disproportionates to iodate and iodine at low pH. The overall reaction can be written as [22]

$$5HOI \rightarrow 2I_2 + IO_3^- + 2H_2O + H^+.$$  \hspace{1cm} (15)$$

The equilibrium is to the right at a pH of 3. Recombination of iodine atoms will also regenerate iodine. Thus, the overall reaction sequence is

$$5I_2 + 5OH \rightarrow 5HOI + 5I \rightarrow 4.5I_2 + IO_3^- + 2H_2O + H^+,$$  \hspace{1cm} (16)$$

which gives $G_{I_2} = -0.54$, somewhat higher than the observed value. Hydrogen peroxide ($G_{H_2O_2} = 0.7$) reduces iodate to iodine in acid solutions, although the reaction is relatively slow [23]. This would lower the iodine removal yield further.

The maximum yield of methyl radicals in solutions containing $4.0 \times 10^{-4}$ mol.dm$^{-3}$ I$_2$ is $G_{CH_3} = 0.1 \{G_{CH_3} = G_{OH}k_8[CH_4]/(k_8[CH_4] + k_{14}[I_2])\}$, which is consistent with the low yield of iodomethane in these solutions.

4.3 Iodate solutions

Iodomethane, iodoethane and 1-iodopropane are formed when iodate solutions saturated with N$_2$O/CH$_4$ (50/50 vol.% are irradiated. Iodate reacts slowly with OH radicals ($k = 1.7 \times 10^7$ dm$^3$.mol$^{-1}$.s$^{-1}$) [24]. In solutions containing methane and nitrous oxide, the maximum yield of iodine species in an oxidation state above that of iodate is given by

$$G = G_{OH}k_1[IO_3^-]/(k_1[IO_3^-] + k_8[CH_4])$$  \hspace{1cm} (17)$$

where $k_1$ is the rate of reaction between OH radicals and IO$_3^-$ and $k_8$ is the rate of reaction between OH radicals and CH$_4$. Substituting the appropriate numerical values in Equation (17) gives 0.1. The observed yield of iodomethane of $0.25 \pm 0.02$ indicates that the formation of iodoalkanes does not occur primarily through the radiolytic oxidation of iodate.

The only other primary radical present in these solutions is the hydrogen atom, which reduces iodate ($k = 9.5 \times 10^7$ dm$^3$.mol$^{-1}$.s$^{-1}$) [15]. This would lead to the formation of oxygenated iodine species such as HIO$_3$, IO$_2$, IO$_3^-$, IO, HOI, and eventually to I$_2$. The maximum yield of I$_2$ under these conditions is $G_{H}/10 = 0.06$ and Reaction (11) alone cannot account for the observed yield of iodomethane. Hydrogen peroxide also reduces iodate, but the reaction is slow at neutral pH [23] and its contribution should not be important.
Oxyiodine radicals are powerful oxidizing agents. To account for the relatively high yield of iodomethane in these solutions, we suggest that methyl radicals act as a reducing agent toward oxyiodine radicals. The following reaction sequence could occur:

\[
\begin{align*}
\ IO_3^- + H & \rightarrow \ HIO_3 \quad (18) \\
\ HIO_3 + CH_3 & \rightarrow \ CH_2O + HOI + OH^- \quad (19) \\
\ HOI + CH_3 & \rightarrow \ CH_3OH + I \quad (20) \\
\ CH_3 + I & \rightarrow \ CH_3I. \quad (21)
\end{align*}
\]

Since the yield of methyl radicals is much higher than the yield of hydrogen atoms under the conditions of our experiments, the yield of iodomethane would be limited by the hydrogen atom yield. The hydrogen atom reacts with nitrous oxide as well as with iodate. From the reaction rates and concentrations involved, the fraction of the hydrogen atom yield available for reaction with iodate is 0.25, giving a product yield of 0.15, which is compatible with the observed yield of iodomethane of 0.25 ± 0.02. Methyl radicals could also react with iodate to produce oxyiodine species. The above mechanism is consistent with the presence of formaldehyde in the irradiated solutions. The Gibbs energy of formation of CH₃(aq) can be estimated at 164 kJ.mol⁻¹ from the known Gibbs energy of formation of CH₃(g) and the Gibbs energy of solvation of CH₄ [25]. The Gibbs energy of formation of HIO₃ can be estimated at 50 kJ.mol⁻¹ from the values given by Sharma and Noyes [26] and Kläng et al [27]. The Gibbs energies of formation of HOI, formaldehyde, methanol and the aqueous iodine atom are known [21,25]. These Gibbs energy values indicate that Reactions (19) and (20) are exoergic by 650 and 400 kJ.mol⁻¹, respectively, and are highly favored thermodynamically. Because of the complex rearrangement, Reaction (19) would be relatively slow and could well be a multistep process. Other mechanisms are of course possible.

Thus, the formation of iodomethane in iodate solutions containing methane and N₂O likely could occur through the reduction of iodate by the hydrogen atom and the methyl radical, followed by successive reduction of oxyiodine species by methyl radicals. Iodoethane and other iodoalkanes are probably formed in a similar manner, the initial hydrocarbons originating from methyl radical recombination. The yield of iodomethane in unbuffered solutions that initially contained iodide (Figure 2) subsequently converted to iodate is higher than in solutions that initially contained only iodate (0.40 ± 0.05 versus 0.25 ± 0.02). This is because a substantial concentration of HOI and oxyiodine species is already present in the former case.

Increasing the initial iodate concentration to 1.0 x 10⁻³ mol·dm⁻³ results in an induction period before iodomethane is formed and in a higher yield of iodomethane once it is formed in constant yield. At the higher iodate concentration, iodate competes with methane for OH radicals thus reducing the yield of methyl radical and the rate of Reactions (19-21). Sodium formate scavenges OH radicals and should thus prevent the formation of methyl radicals. This is consistent with the formation of only trace amounts (about 10⁻⁹ mol·dm⁻³) of iodomethane in irradiated iodate solutions containing iodate and formate. Hydrazine also appears effective in suppressing the formation of iodoalkanes in these solutions. Hydrazine reduces I₂ and HOI at a diffusion-
controlled rate [28,29]. This would prevent Reactions (11) and (20) from occurring, thus inhibiting the formation of iodoalkanes. The presence of air inhibits the formation of iodoalkanes at low doses, but less so at higher doses. The inhibition is likely due to scavenging of methyl radicals [Reaction (13)]. The effect is attenuated at high absorbed doses as oxygen initially present at a concentration of about $1.2 \times 10^{-4}$ mol dm$^{-3}$ is being depleted by radiolytic reactions.

### 4.4 Periodate solutions

Iodoalkanes are formed when periodate solutions containing methane are irradiated. Periodate reacts with the OH radical at a diffusion-controlled rate (about $5 \times 10^9$ dm$^3$.mol$^{-1}$.s$^{-1}$) [16]. The maximum yield of methyl radical in a solution containing $10^{-4}$ mol dm$^{-3}$ periodate and saturated with a 50/50 (vol.%) N$_2$/CH$_4$ mixture would be 0.8. This figure could vary by a factor of two in one direction or the other, given that the precise value for the rate of reaction between periodate and the OH radical is not known.

Buxton and Sellers [16] have proposed, based on pulse radiolysis experiments, that OH oxidizes periodate to IO$_4^-$, which reacts further with IO$_4^-$ and water to produce a mixture of hydrated iodine (VII) and iodine (VIII) species. It is unlikely that these species would react directly with either methane or methyl radicals to produce iodoalkanes. The only other primary radical species beside OH in solutions containing N$_2$O is the hydrogen atom H, which is produced with a yield of 0.6. The hydrogen atom should reduce periodate, although the rate of the reaction has not been measured.

Under these conditions, the maximum yield of I$_2$ that could be available for production of iodomethane by Reaction (11) is $G_{H}/14 = 0.04$. This does not account for the observed yield of $0.40 \pm 0.05$. Hydrogen peroxide reacts rapidly and quantitatively with periodate in acidic, neutral and basic solutions, yielding iodate and oxygen. The reaction is autocatalyzed by iodate [30] and proceeds by two reaction channels [31]: one is a two-electron reduction of periodate to iodate, and the other involves IO$_3$,

$$IO_4^- + H_2O_2 \rightarrow IO_3^- + O_2 + H_2O.$$ \hspace{1cm} (22)

Thus iodate and iodine(VI) radical species could be produced with a yield of up to $G_{H_2O_2} = 0.7$.

We suggest that iodoalkanes are formed in these solutions by a mechanism similar to that proposed for iodate solutions, i.e., successive reduction of oxyiodine radicals by methyl radicals. In addition to Reaction (22), the following reaction sequence could occur:

$$IO_4^- + OH \rightarrow IO_4^- + OH^-$$ \hspace{1cm} (23)

$$IO_4^- + CH_3 \rightarrow CH_2O + IO_3^- + H^+$$ \hspace{1cm} (24)

$$IO_3^- + OH \rightarrow IO_3^- + OH^-$$ \hspace{1cm} (25)

$$IO_4^- + H \rightarrow IO_3^- + OH^-$$ \hspace{1cm} (26)

$$IO_3^- + CH_3 \rightarrow CH_2O + HI0_2$$ \hspace{1cm} (27)
HI₀₂ + HI₀₂ → IO³⁻ + HOI + H⁺, \hspace{1cm} (28)
followed by Reactions (20) and (21). Reaction (28) is known to occur rapidly at near neutral pH [32]. Reactions (24) and (27) are exoergic by 700 and 460 kJ·mol⁻¹, respectively, using the Gibbs energy of formation estimated by Klöning et al [27], and are thermodynamically favored. Simulations using the computer program MAKSIM [33] indicated that the above mechanism could result in the production of iodomethane with a yield of 0.3, in agreement with the experimental observations. The mechanism is also consistent with the presence of formaldehyde in the irradiated solutions. The short induction period is probably required for the various intermediates to reach a steady-state concentration.

The yield of reducing radicals in periodate solutions saturated with Ar/CH₄ (50/50 vol.%) is Gₑ⁺ + Gₑ⁻ = 3.3. The yield of I₂ available for production of iodomethane by radiolytic reduction of periodate followed by Reaction (11) would be 0.24. The yield of methyl radicals would be about 0.4 as opposed to 0.8 in 1.0 × 10⁻⁴ mol·dm⁻³ IO₄⁻ solutions saturated with CH₄/N₂O. This is consistent with the observed yield of 0.30 ± 0.05 for iodomethane. Thus, iodomethane is formed mostly by Reaction (11) in periodate solutions saturated with an Ar/CH₄ mixture.

The presence of air inhibits the formation of iodoalkanes at low doses in periodate solutions, but less so at higher doses. The inhibition is likely due to scavenging of methyl radicals [Reaction (13)]. The effect is attenuated at high absorbed doses, as oxygen initially present at a concentration of about 1.2 × 10⁻⁴ mol·dm⁻³ is being depleted by radiolytic reactions.

4.5 Iodomethane solutions

The results in Table 1 indicate that iodomethane is removed by reaction with the OH radical, the solvated electron, the hydrogen atom and the HO₂ radical. Since the yields are all relatively low, iodomethane is regenerated efficiently under these conditions.

The only product in the radiolysis of acid iodomethane solution saturated with N₂O is iodine, which is consistent with the occurrence of the overall reaction

\[ \text{CH}_3\text{I} + \text{OH} \rightarrow \text{CH}_3\text{OH} + \text{I}. \hspace{1cm} (29) \]

The OH radicals are scavenged in the presence of 2-methyl-2-propanol (t-butyl alcohol), leaving the solvated electron and the hydrogen atom as the only radical species. The solvated electron reacts rapidly with H⁺, and in acid iodomethane solutions competition will occur between the two reactions:

\[ \text{CH}_3\text{I} + e_{aq}^- \rightarrow \text{CH}_3 + \text{I}^- \hspace{1cm} (30) \]

and

\[ \text{H}^+ + e_{aq}^- \rightarrow \text{H}. \hspace{1cm} (31) \]
The rate of Reaction (30) is not known accurately, although it is probably lower than that of Reaction (31), which is \(2.4 \times 10^{10} \text{dm}^3\text{mol}^{-1}\text{s}^{-1}\) [14]. Thus, the hydrogen atom is likely the dominant radical species under the conditions of our experiments and appears to remove iodomethane more effectively than the OH radical. The reaction is likely

\[
\text{CH}_3\text{I} + \text{H} \rightarrow \text{CH}_3 + \text{I}^- + \text{H}^+ .
\]  

(32)

The yield for removal of iodomethane at a pH of 3 in the presence of argon is 1.00 ± 0.02, of which 0.48 ± 0.02 is from the combined reactions of the solvated electron and the hydrogen atom. This leaves a yield of 0.52 resulting from reactions with the OH radical. This is consistent with iodine and iodide being produced in roughly equivalent proportions under these conditions. Since \(G_{\text{CH}_3\text{I}}\) is -0.50 ± 0.02 in solutions saturated with \(N_2O\), where \(G_{\text{OH}}\) is twice as large as in solutions saturated with argon, it appears that the OH radical is more effective in removing \(\text{CH}_3\text{I}\) in the later solutions. This indicates that some of the reactions regenerating iodomethane are brought about by the OH radical.

A comparison of \(G_{\text{CH}_3\text{I}}\) in solutions saturated with argon at pH values of 3 and 6 should highlight the effect of the solvated electron since Reaction (31) will not occur at the higher pH values. From the results in Table 1, it appears that the solvated electron is more effective than the hydrogen atom in removing iodomethane.

In the presence of air at a pH of 3, the radical \(\text{HO}_2\) will be formed by the following reactions:

\[\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \]  

(33)

\[\text{e}_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^- \]  

(34)

\[\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^- . \]  

(35)

Since \(G_{\text{CH}_3\text{I}}\) is -1.74 ± 0.02 under these conditions, it appears that \(\text{HO}_2\) is quite effective in removing iodomethane, probably through the reaction

\[
\text{CH}_3\text{I} + \text{HO}_2^- \rightarrow \text{CH}_3\text{O}_2\text{H} + \text{I}^- .
\]  

(36)

This is consistent with the presence of only \(I_2\) in these solutions.

5. CONCLUSION

Iodoalkanes are formed when solutions containing iodide, iodine, reactions leading to the formation of iodoalkanes are

\[
\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}^- \]  

(11)

and

\[
\text{CH}_3 + \text{I} \rightarrow \text{CH}_3\text{I} .
\]  

(21)
In the case of iodate and periodate, these reactions are preceded by reactions involving the methyl radical and oxyiodine species:

\[
\text{CH}_3 + \text{IO}_x \rightarrow \text{CH}_2\text{O} + \text{HIO}_{x-1} .
\] (37)

The formation of iodoalkanes is inhibited by the presence of air and hydrazine because of scavenging of methyl radicals by oxygen in the case of air and of scavenging of I\(_2\) and HOI in the case of hydrazine.

Iodomethane is removed from solution by reaction with the OH radical, the solvated electron, the hydrogen atom and the perhydroxyl radical. The perhydroxyl radical, which occurs in air-saturated solutions, seems to be the most effective, which is favorable from a reactor safety viewpoint.

It can be assumed that similar reactions would also occur with other hydrocarbons; however, organic molecules having a functional group might behave differently.

6. ACKNOWLEDGEMENT

We thank W.C.H. Kupferschmidt and G.G. Sanipelli for their help with the HPLC analysis technique, W.E. Lawrence for performing the formaldehyde analysis and N.H. Sagert for numerous discussions. This work was funded jointly by Atomic Energy of Canada Limited and Ontario Hydro, Hydro Québec and the New Brunswick Electric Power Commission under the CANDU Owner's Group (COG) program, Working Party 06, Work Package 425.

Table 1. Summary of data obtained for the radiolysis of iodomethane (3 x 10\(^{-3}\) mol·dm\(^{-3}\)) solutions.

<table>
<thead>
<tr>
<th>CONDITIONS</th>
<th>MAJOR PRODUCTS</th>
<th>(-G(\text{CH}_3\text{I})) ± 0.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}_2\text{O}, \text{pH} = 3)</td>
<td>(\text{I}_2)</td>
<td>0.50</td>
</tr>
<tr>
<td>(\text{Ar}, \text{pH} = 3)</td>
<td>(\text{I}_2, \text{I}^-)</td>
<td>1.00</td>
</tr>
<tr>
<td>(\text{t-BuOH}, \text{pH} = 3)</td>
<td>(\text{I}^-)</td>
<td>0.48</td>
</tr>
<tr>
<td>(\text{air}, \text{pH} = 3)</td>
<td>(\text{I}_2)</td>
<td>1.74</td>
</tr>
<tr>
<td>(\text{Ar}, \text{pH} = 6)</td>
<td>(\text{I}_2, \text{I}^-)</td>
<td>1.36</td>
</tr>
</tbody>
</table>
REFERENCES


Figure 1. Concentration of iodomethane (circles), iodide (triangles) and iodine (I$_2$ + I$_3^-$) (squares) as a function of the absorbed dose for solutions containing initially 1.0 x 10$^{-4}$ mol.dm$^{-3}$ sodium iodide, buffered at a pH of 7 (phosphate, 2.0 x 10$^{-3}$ mol.dm$^{-3}$) and saturated with a CH$_4$/N$_2$O (50/50 vol.%) gas mixture.
Figure 2. Concentration of iodomethane (circles), iodide (triangles) and (HOI + IO₃⁻) (squares) as a function of the absorbed dose for solutions containing initially 1.0 x 10⁻⁴ mol.dm⁻³ sodium iodide saturated with a CH₄/N₂O (50/50 vol.%) gas mixture.
Figure 3. Concentration of iodomethane (circles) and iodide (triangles) as a function of the absorbed dose for solutions containing initially $1.0 \times 10^{-4}$ mol.dm$^{-3}$ sodium iodate saturated with a CH$_4$/N$_2$O (50/50 vol.%) gas mixture.
Figure 4. Concentration of iodoethane as a function of the absorbed dose for solutions containing initially $1.0 \times 10^{-4}$ mol dm$^{-3}$ sodium iodate saturated with a CH$_4$/N$_2$O (50/50 vol.%) gas mixture.
Figure 5. Concentration of iodomethane as a function of the absorbed dose for solutions containing initially $1.0 \times 10^{-3}$ mol dm$^{-3}$ sodium iodate saturated with a CH$_4$/N$_2$O (50/50 vol.%) gas mixture.
Figure 6. Concentration of iodomethane as a function of the absorbed dose for solutions containing initially $1.0 \times 10^{-4}$ mol dm$^{-3}$ sodium meta-periodate saturated with a CH$_4$/N$_2$O (50/50 vol.% gas mixture.}
DISCUSSION

W.G. BURNS I would agree with your qualitative mechanisms for the reaction of dissolved I\(^-\), I\(_2\) and iodate to produce methyl iodide in the presence of methane. However, I believe that the quantitative calculations when you use 50% nitrous oxide may be in error because such a large concentration (ca 10\(^{-2}\) mol dm\(^{-3}\)) affects not only the bulk but spur reactions insofar as these can be distinguished from each other. Note that Appleby and Schwarz (J. Phys. Chem. 73, 1937 (1969)) used 7 x 10\(^{-4}\) M N\(_2\)O, ca 4.5% saturated to scavenge e\(_{aq}\) to obtain the extra spur G(e\(_{aq}\)) as G(N\(_2\)). Calculations and experiments (R. H. Bisby, R.B. Cundall, H.E. Sims and W.G. Burns, Disc. Faraday Soc. 63, 237 (1977), H.A. Schwarz, J. Phys. Chem 73, 1937 (1969) and R.H. Schuler, A.L. Hartzell and B. Behar, J. Phys. Chem. 85, 192 (1981)) suggest that the value of G(OH) in the presence of concentrated (0.01 to 0.02 mol dm\(^{-3}\)) N\(_2\)O is given by the sum of your interpretation; points which you do not seem to have incorporated are that G(H\(_2\)) is reduced from 0.6 to 0.39 and G(H\(_2\)O\(_2\)) is increased by about 50% in strong N\(_2\)O solutions. The effect may be smaller in your case, but I think your text should suggest that you are aware of these effects.

J. PAQUETTE This topic has been addressed by Schuler, Hartzell and Behar in J. Phys. Chem. 85, 192 (1981). Their general equation for the scavenging of OH radicals from N\(_2\)O-saturated solutions is:

\[
G = 5.2 + 3.0 \frac{(k_2[S]/\lambda)^{1/2}}{1 + (k_2[S]/\lambda^{3/2})}
\]

Schuler et al admitted that 5.2 is surprisingly low given that one expects an OH yield of 3.2 to be produced by reaction of electrons with N\(_2\)O (from H.A. Schwarz, J. Phys. Chem. 73, 1928 (1969) in addition to the yield of 2.7 from the direct radiolysis of water. Their explanation is that all of the OH radicals produced as a result of reaction of e\(_{aq}\) with OH within the tracks are themselves lost in intratrack processes. Accordingly, I had used a value of 5.4 for the initial yield of OH radical in my calculations, which is close enough to 5.2.

B.J. HANDY The results of CH\(_3\)I formation are interesting in that IO\(_3\) may be important in the later stages of a reactor fault. Do you think that the mechanism proposed involving CH\(_4\) in solution is important in a reactor fault bearing in mind that the concentration of dissolved CH\(_4\) could be several orders of magnitude smaller that in your experiments?
J. PAQUETTE  The effect would be much attenuated at low methane concentrations. Also, in air-saturated solutions oxygen would scavenge methyl radicals reducing further the yield of organic iodides.

E.C. BEAHM  The question about relevance to reactor accidents should also include the fact that there will be many other organic materials, for example ethylene, producing a much larger fraction as organic iodide than methane in our tests.

J. PAQUETTE  The behaviour of hydrocarbons other than methane would be similar to that of methane. Molecules with double bounds or other functional groups could behave quite differently.

A.C. VIKIS  One would expect a significant activation energy associated with the reaction: \( \text{CH}_3 + \text{IO}_3 \rightarrow \text{CH}_2\text{O} + \text{HOI} \). Thus, the use of \( 10^8 \text{ M}^{-1}\text{s}^{-1} \) rate constant may be too high.
AQUEOUS IODINE AT LOW CONCENTRATIONS AND HIGH TEMPERATURES*

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ABSTRACT

Measurements of iodine speciation in aqueous solution at 285°C and 1000 psig show a higher percentage as I₂ in solutions at tracer concentrations than at higher concentrations. A $1 \times 10^{-9}$ M I⁻ solution resulted in 2% I₂, whereas a $1 \times 10^{-4}$ M I⁻ solution had only 0.1% I₂. These tests indicate that iodine at tracer concentrations can have a species distribution in solution that is not expected or observed at higher concentrations.


†British attache from AERE, Harwell, England.
1. INTRODUCTION

1.1 BACKGROUND

Pressurized water reactors (PWRs) are designed to withstand certain postulated accidents, called design basis accidents. The release of radioactive fission products to the environment through a path opened following a rupture of one tube in the steam generator falls into this category of accidents. The release doses depend directly on the concentration levels of fission products in the primary coolant, and, therefore, these levels are kept below those that could result in exceeding allowable release doses in the regulatory document 10 CFR 100.¹

As described by Hopenfeld,² the partition coefficient (PC) that expresses the volatility of iodine is a very important factor in dose calculations. A high partition coefficient would tend to increase the retention of iodine within the secondary circuit, resulting in relatively small off-site radioactivity release. Conversely, low partition coefficients would tend to yield high dose releases.

Thermochemical data are not available at temperatures of interest to calculate iodine partitioning. The reducing conditions expected in primary coolant systems would suggest that I₂ will not be stable. However, tests of primary coolant show large variations in I₂ content.³ It may be
that the results reflect the very low concentrations \(10^{-9} \text{ to } 10^{-12}\) where anomalous behavior may exist.

Styrikovitch,\(^4\) obtained data on iodine volatility attributed to HOI solutions, showing strong pH dependence. Based on studies of iodine species in reactor coolant, however, a study by Martucci indicates that iodine volatility does not depend on pH.\(^3\)

Because of these uncertainties and the lack of data, a program was undertaken to study iodine behavior under prototypic conditions representing a steam generator tube rupture accident.

This was carried out in a two-part experimental program consisting of tests on primary coolant from reactor plants and also laboratory tests under simulated conditions. These were compared and interrelated to permit evaluation of iodine volatility in steam generator tube rupture accidents.

1.2 IODINE AT LOW AQUEOUS CONCENTRATIONS

It is well known that very low concentrations of many materials exhibit behavior that is unlike the interactions of the same materials at high concentrations.\(^5\) Tracers have been called a special state of matter because of the often unusual properties they display. Unusual or tracer behavior is often observed at concentrations \(<~10^{-5} \text{ to } 10^{-6}\) M.\(^5\) Many of the unusual interactions can be explained by fundamental chemistry. For example, at very low concentrations, chemical reactions that have rates dependent on the trace element to greater than first order are
not as likely to occur because of the law of mass action. Because reac-
tion paths that are available at high concentrations are sometimes not 
operable at low concentrations, other interactions that were overwhelmed 
at high concentrations may become important.

In addition, at very low concentrations, there can be impurities in 
the system, often undetectable, which may actually have a greater concen-
tration than the tracer element. The concept of "omnipresence concentra-
tion" has been introduced by Noddack\(^6\) to illustrate that every element has a 
borderline concentration at which it can be found virtually everywhere. 
For example, the "omnipresence concentration" of such common elements as 
Si, Mg, Ca, and Fe is of the order of \(10^{-3}\%\). The importance of the 
omnipresence of impurities is that they can interact with the tracer 
element and cause it to show unusual behavior.

Anomalous behavior of low concentrations of radiiodine has been 
reported since the very earliest studies.\(^7\) Generally, the anomalies con-
sist of unexpected distributions of iodine species and unidentified 
iodine species.\(^7\)\(^-\)\(^9\) The hydrolysis of iodine, given in Eq. (1), provides 
a clue to this behavior:

\[
3\text{I}_2 + 3\text{H}_2\text{O} \rightleftharpoons 5\text{I}^- + \text{IO}_3^- + 6\text{H}^+. 
\] (1)

In this reaction, iodine appears in 3 oxidation numbers, and there is 
little doubt that other oxidation numbers must be involved since the 
reactant \(\text{I}_2\) has a value of 0 and the products have values of -1 and +5. 
At tracer concentrations, bimolecular reactions of iodine species would 
not readily occur, and intermediate oxidation states could persist or 
react by alternate mechanisms.
In the simulated steam generator tests that are reported in this work, the aqueous iodine concentration was $10^{-9}$ M; the primary coolant in operating PWRs would have iodine concentrations less than or approximately equal to this value. Thus, tracer effects along with more common processes, such as oxidation, hydrolysis, and adsorption, will determine which iodine species will be in the solution.

2. EXPERIMENTAL

2.1 SIMULATED STEAM GENERATOR TESTS

The experimental system, used to study the vapor-liquid partitioning of iodine in a simulated PWR steam generator, consists of a large (152-cm-long, 8.9-cm-diam) stainless steel autoclave, which is heated electrically in 3 zones along its length and is connected to a separate condenser vessel via an orifice and air-operated valve. A schematic diagram of the system is shown in Fig. 1.

The experimental procedure was as follows. Feed solutions were prepared the day before the experiment. Sufficient orthoboric acid (JMC puratronic grade) to give a concentration of 0.05 to 0.5 M, usually 0.2 M, was dissolved in demineralized-distilled water. If necessary, the pH was adjusted by addition of 1.0 M NaOH, and the volume was adjusted to 1.2 L (some tests were carried out with 1.75 L or 4.0 L feed solution). Just before the experiment, the $^{131}$I tracer was added. The tracer was received in the form of "carrier free" Na $^{131}$I in 0.1 M NaOH solution (DuPont); this was diluted and added to the feed solution to give
\[ 1 \times 10^{-6} \text{ Ci/mL} \]. This gave a total iodine concentration in each of the experiments of 1 to 5 \( 10^{-9} \text{ M} \).

If the experiment was to be carried out in an argon atmosphere, the feed solution would be sparged with argon for 16 h. A 20 mL sample was taken for iodine analysis, and the solution was loaded into the pressure vessel using a stainless steel funnel at the top. Further argon sparging could take place at this stage; oxygen-free argon was supplied to the bottom of the vessel, and the oxygen content of the exhaust gas was monitored with an oxygen analyzer. The oxygen content was always <2.5 \( 10^{-7} \text{ atm O}_2 \) before the test was started when oxygen-free conditions were required. In order to reduce the amount of inert gas, the chamber was vacuum pumped to 0.2 atm before the start of the test. After closing all valves to the vessel, the simulated steam generator was heated to 286°C and 1000 psi pressure.

The use of radioactive tracers at low concentrations in a large vessel at high temperature and pressure makes it necessary to ensure that appropriate handling and operating procedures are followed. This involves, among other good practice techniques, thoroughly cleaning the system between runs and also maintaining a temperature profile that eliminates steam condensation at the top of the pressure vessel. Steam reflux in the pressure vessel removes iodine from the vapor phase and results in an erroneously low apparent iodine volatility.

After a period of equilibration at steady temperature and pressure, usually 4 to 6 h after startup, a sample of the vapor phase was taken by opening the air-operated valve for 10 to 20 s and allowing steam to pass
through the orifice into the condenser. After waiting a few minutes to allow cooling, the condensate was drawn off from the bottom of the condenser. At this time, a sample of liquid was also taken from the main vessel. Samples were taken in this way periodically throughout the test. Adsorption of iodine from solution onto vessel walls was determined by comparing the $^{131}\text{I}$ in the liquid samples with that in the feed solution and correcting for the amount in the gas phase.

The amount of $^{131}\text{I}$ in the liquid and condensate fractions was determined by counting 1 mL aliquots using a Nuclear Data System 680 with a NaI well detector. The data were corrected for decay, background, and counter efficiency. Samples were counted for between 1 and 16 h according to their activity; this gave statistical counting errors of between 0.03 and 2.0%.

Iodine speciation in the liquid samples was determined by extracting (with minimum delay time) 10 mL of sample solution into 10 mL CCl$_4$ to remove I$_2$ and organic iodides; the phases were separated, and 1 mL of the aqueous phase containing the I$^-$ and IO$_3^-$ fraction was counted as above. The organic phase was then back extracted with 10 mL of 0.10 M NaOH, 0.01 M NH$_2$OH·HCl solution to convert the I$_2$ to I$^-$ and extract it back into the aqueous phase, with any organic iodides remaining in the organic portion. The phases were again separated and counted as before.

At the end of the experiment, the heaters were switched off and the system allowed to cool overnight. The solution was then drained from the bottom of the vessel and was refilled with distilled water to wash any residues from the inside of the vessel; this, too, was drained off and the
process repeated two to three times to ensure that all chemicals were removed before a new test was begun.

3. EXPERIMENTAL RESULTS

3.1 LABORATORY TESTS

3.1.1 Partition Coefficients

PCs are a convenient way of expressing volatility. They can be given in terms of concentrations per unit volume or in terms of mass. In this work, the iodine PC is defined as:

\[
PC = \frac{\text{concentration of iodine species in aqueous solution}}{\text{concentration of iodine species in gas}}.
\]  

(2)

Because the concentration of iodine species in the gas appears in the denominator of the PC equation, small values of the PC correlate with high volatility, and large values correlate with low volatility. PCs, given on a concentration basis as in Eq. (2), may be converted to PC on a mass basis by multiplying by the gas-to-aqueous-density ratio:

\[
\text{iodine PC (mass basis)} = PC \cdot \frac{\text{density of gas}}{\text{density of aqueous}}.
\]  

(3)

The PCs given by Eqs. (2) and (3) refer to the concentration or mass of all of the iodine species. For example, the concentration in the aqueous phase may be made up of \(I^-\), \(IO_3^-\), \(I_2\), and possibly other chemical species. It is sometimes useful to define a PC in terms of one species only. Since we expect \(I_2\) and organic iodide to be the dominant volatile iodine species in these tests, we define two additional PCs as follows:
PC of $I_2 = \frac{\text{concentration of } I_2 \text{ in aqueous solution}}{\text{concentration of } I_2 \text{ in gas}}, \quad (4)$

and

PC of $CH_3I = \frac{\text{concentration of } CH_3I \text{ in aqueous solution}}{\text{concentration of } CH_3I \text{ in gas}}. \quad (5)$

Several tests were run, at pH 5, to evaluate the effect of the temperature profile in the pressure vessel on the measured PCs. In a test where the aqueous temperature was $\geq 2^\circ$C hotter than the top of the steam space, a PC of $3.7 \times 10^9$ was measured. When the situation was reversed and the top of the steam space was $\geq 10^\circ$C greater than the aqueous solution, a PC of $3.50 \times 10^2$ was measured. All of the PCs reported in this section were run with a temperature profile such that the top of the pressure vessel near the opening for the steam sample was $\geq 10^\circ$C hotter than the aqueous surface, and there was a smoothly decreasing temperature gradient from the top of the vessel to the aqueous surface. This was done to prevent reflux in the pressure vessel and ensure that the true equilibrium PC was measured.

The experimental matrix for the simulated steam generator tests consisted of tests run at pH 5, 7, and 9 (measured at 25°C) with an atmosphere of air/steam or argon/steam. All of the tests in this matrix were run in a 0.2 M borate solution. Table I gives the results of these tests in terms of PC and the percentage of iodine in aqueous solution as $I_2$ and organic iodide. Hydrolysis of $I_2$ and oxidation of $I^-$ are the two
processes that may be cited as important in determining the iodine speciation and, thereby, the PCs in these tests. In iodine solutions with concentrations above tracer levels, hydrolysis of I$_2$ depends on pH.$^{11}$ This is also probably true of iodine in tracer concentrations. Results given in Table 1 show that in either argon/steam or air/steam tests run at pH 9 gave a lower I$_2$ percentage than those run at pH 5. The PCs at the higher pHs were higher than those at low pH, and this is the behavior that would be expected in solutions with a lower percentage of I$_2$.

After all of the simulated steam generator tests at low iodine concentrations (ca. $10^{-9}$ M) were completed, several tests were run at concentrations near $10^{-4}$ M to compare with tests at tracer concentrations and to obtain data on the aqueous/gas partitioning of I$_2$ at 285°C. A test run in argon/steam at pH 5 with $1 \times 10^{-4}$ M I$^-$ gave 0.1% I$_2$ in aqueous solution and a PC of $8 \times 10^3$. The low percentage of I$_2$ and the relatively high PC in this test, compared with results under similar conditions shown in Table 1, indicates that the aqueous iodine behavior is different at tracer levels than at concentrations above tracer levels. The low percentage of I$_2$ in the test run with $1 \times 10^{-4}$ M I$^-$ is more consistent with what might be expected for an iodide solution at very low oxygen content.

3.1.2 Adsorption of Iodine from Solution

Adsorption of tracer elements from aqueous solution onto surfaces often depends on pH. Generally, the adsorption of anions is enhanced at
low pH, and the adsorption of cations is enhanced at high pH. A somewhat simplified rationale for this is that at high pH, tracer anions must compete with OH\textsuperscript{−} for the available adsorption sites, and at low pH, cations must compete with H\textsuperscript{+} ions. For adsorption of I\textsuperscript{−}, this can be expressed as:

\[(\text{OH}^-)_{\text{surface}} + \text{I}^- \rightleftharpoons (\text{I}^-)_{\text{surface}} + \text{OH}^- . \]  

(6)

Following the treatment given by Benes and Majer,\textsuperscript{5} a distribution coefficient q is defined by:

\[q_{\text{I}^-} = \frac{m_s}{m_L}, \]  

(7)

where \(m_s\) and \(m_L\) represent the amounts of I\textsuperscript{−} adsorbed on the surface and in solution, respectively. Assuming the equilibrium given by Eq. (6) and a constant number of adsorption sites, it can be shown\textsuperscript{5} for anions, such as I\textsuperscript{−}, that:

\[\log_{10} q = k - \text{pH} , \]  

(8)

where the constant k includes terms for the initial concentration of the tracer, the equilibrium constant for Eq. (6), the number of adsorption sites, and the dissociation constant of water. In any real system, it would be very difficult to evaluate k by any technique other than empirical measurement.

The present study is consistent with the general expectation of adsorption of I\textsuperscript{−}. Tests that were run at a pH of 7 or greater (measured at 25°C) gave little indication of adsorption onto the walls of the container. However, tests run at lower pH always had an initial aqueous \(^{131}\text{I}\) count rate greater than that obtained when the sample was in the system at operating conditions.
Table 2 gives values of the distribution coefficient $q_1$ that shows less adsorption at the higher pHs. One test run at pH 5 had $1 \times 10^{-3} \text{M}$ NO$_3^-$ in solution and resulted in a distribution coefficient 0.53, only slightly greater than values obtained at pH 7 or 9. This is consistent with the argument that the extent of adsorption depends on the number of ions competing for adsorption sites.

4. DISCUSSION

4.1 FORMATION OF I$_2$ AT TRACER CONCENTRATIONS

In the simulated steam generator iodine tests, there is clearly some mechanism capable of maintaining a fraction of the aqueous iodine in the form of I$_2$. The mechanism is most effective at low pH and with oxygen in the system. Since iodine hydrolysis [Eq. (1)] is faster at high pH and oxidation of I$^-$ becomes easier with increasing oxygen in the system, the results of these tests are in line with expectations.

Some additional observations provide insight into the mechanism. First, it must be capable of maintaining a concentration of I$_2$ even though hydrolysis is destroying it. We ran a test in argon/steam at pH 5 with conditions as shown in Table 1 but with iodine initially as I$_2$ with a concentration of $5 \times 10^{-5} \text{M}$ ($1.0 \times 10^{-4} \text{ g-at. I as I}_2/\text{L}$). The liquid samples taken from the pressure vessel system had only 0.3% I$_2$, with the remainder as I$^-$ and IO$_3^-$· Thus, hydrolysis was very effective at removing I$_2$ at pH 5 (measured at 25°C) when the system temperature was 285°C.

The second observation was that under a given set of conditions, a higher percentage of I$_2$ can be formed at tracer concentrations than at
higher concentrations. This indicates a mechanism that is either not effective, i.e., cannot compete with other processes, at higher concentrations or one that is limited in the total amount of iodine that it can maintain as I₂.

A third observation was that the fraction as I₂ decreased when nitrate ions were in the system. A test at tracer iodine concentration with 10⁻³ M NO₃⁻ gave 0.4% I₂ rather than 2% without the nitrate. This could indicate that the reaction forming I₂ occurs on the surface since the nitrate also resulted in lower adsorption of iodine on the vessel surface (Table 2). Alternatively, it could indicate that a reaction in solution was inhibited by the excess anion. Fudge and Sykes have studied the effect of nitrate, and other anions, on the reaction:¹²,¹³

\[
\begin{align*}
\text{Fe}^{3+} + \text{I}^- & \leftrightarrow \text{FeI}^{2+}, \\
\text{FeI}^{2+} + \text{I}^- & \leftrightarrow \text{Fe}^{2+} + \text{I}_2^-, \\
\text{Fe}^{3+} + \text{I}_2^- & \leftrightarrow \text{Fe}^{2+} + \text{I}_2, \\
2\text{Fe}^{3+} + 2\text{I}^- & \leftrightarrow 2\text{Fe}^{2+} + \text{I}_2. 
\end{align*}
\]

Their studies were carried out at 20°C. There was some retardation of the reaction rate due to nitrate, but it only amounted to a few percent at 1 × 10⁻² M NO₃⁻, the lowest concentration used. However, in their tests the Fe⁺³ and I⁻ concentrations were well above tracer levels, 1.67 × 10⁻³ M and 5.0 × 10⁻³ M, respectively. The retardation was attributed to the formation of FeNO₃⁺², which lowers the concentration of ferric ions.
We may also propose a surface reaction that directly involves oxygen:

\[
2\text{I}^- + \frac{1}{2}\text{O}_2 \not\rightarrow \text{O}^- + \text{I}_2 ,
\]

\[
\text{Fe}^{+2} + \text{O}^- \not\rightarrow \text{FeO} ,
\]

\[
\text{Fe}^{+2} + 2\text{I}^- + \frac{1}{2}\text{O}_2 \not\rightarrow \text{FeO} + \text{I}_2 .
\] (10)

In the tests run in argon/steam, the gaseous oxygen content was \(<2.5 \times 10^{-7}\) atm. If we assume the equilibrium at 285°C,

\[
\text{O}_2 \not\rightarrow \text{O}_2 ,
\]

(11)

this corresponds to an aqueous \(\text{O}_2\) concentration of \(<10^{-9}\) M. This is of the same magnitude, \(10^{-9}\) M, as the aqueous iodine concentration in the simulated steam generator tests.

It does not appear to be possible to choose between the mechanism given by Eqs. (9) and (10) or perhaps others, based on the present studies.

4.2 HI AS A SOURCE OF IODINE VOLATILITY

This work has centered on \(\text{I}_2\), with some measurements of organic iodides, as the potential sources of volatile iodine in steam generator accidents. The chemical species HI may also be mentioned as an additional possibility. At the relatively high aqueous temperatures in the primary coolant, the dielectric constant of water is not as great as it is at lower temperatures, and there may be some association of \(\text{H}^+\) and \(\text{I}^-\) even in such a strong acid as HI.
If we assume the following equilibria,

\[ \text{HI}_{\text{aq}} \rightleftharpoons \text{H}^+ + \text{I}^- , \]  
(12)

\[ \text{H}^+ + \text{I}^- \rightleftharpoons \text{HI}_{\text{gas}} , \]  
(13)

we can calculate a PC due to HI, based on Eq. (13). To do this, we recognize that in aqueous solution the concentration of I\textsuperscript- \gg concentration of HI, so we define the PC due to HI gas as:

\[ \text{PC (due to HI) = } \frac{\text{concentration of I}^- \text{ aqueous}}{\text{concentration of HI gas}} \cdot \]  
(14)

Using the ideal gas law and thermochemical data from Barner and Scheuerman\textsuperscript{14} we find at 285°C (558 K):

\[ \text{PC (due to HI) = } \frac{9.6 \times 10^2}{\text{H}^+ \text{ concentration}} \cdot \]  
(15)

From this it seems that very high hydrogen ion concentrations would be required to make PC (due to HI) low enough to create a volatility problem. For example, a PC (due to HI) of 2000 would require the extremely high H\textsuperscript+ concentration of 0.48 M.

This analysis is supported by a test run at pH 5 (measured at 25°C) with an iodine concentration of 1 × 10\textsuperscript{-4} M. Under the normal operating conditions of argon/steam at 285°C, the measured PC was 8 × 10\textsuperscript{3}, and this was, at least, partially due to the 0.1% I\textsubscript{2} in the aqueous solution.

4.3 INTERRELATION OF PRIMARY COOLANT TESTS AND SIMULATED TESTS

In the simulated tests, it was possible to measure both iodine speciation in solution and the iodine PC, whereas only iodine speciation could be measured in the primary coolant tests of Voilleque. The
conversion of aqueous iodine speciation data into PCs requires values for the PC of \( I_2 \) and possibly the PC of \( \text{CH}_3\text{I} \) as defined in Eqs. (4) and (5). Attempts to directly measure the PC of \( I_2 \) in the simulated steam generator pressure vessel were unsuccessful. Samples containing \( I_2 \) above tracer concentrations require a low pH to prevent hydrolysis. As described in Sect. 4, a test at pH 5 containing \( 5 \times 10^{-5} \text{ M} \) \( I_2 \) resulted in almost complete hydrolysis of the \( I_2 \). A similar test at pH 2 produced a large amount of corrosion products from the vessel walls, which obscured attempts at analysis of iodine species.

Values of PC of \( I_2 \) have been evaluated by Parsly at temperatures up to \( \sim 185^\circ\text{C} \), the boiling point of iodine.\textsuperscript{15} Palmer et al.\textsuperscript{16} fit Parsly's data as:

\[
\log_{10} \text{PC of } I_2 = \frac{5615.4}{T} - 25.179 + 0.02990T. \tag{16}
\]

At \( 185^\circ\text{C} \), Eq. (16) gives a PC of \( I_2 \) of 6.0. Extrapolation to temperatures above \( 185^\circ\text{C} \) gives increasing values for PC of \( I_2 \). At \( 285^\circ\text{C} \), a value of 37 is calculated from Eq. (16).

If it is assumed that the PC values from the simulant tests given in Table 1 were due only to volatility of \( I_2 \), we calculate an average PC of \( I_2 \) for those tests of 23.7 ± 17.8. From this and the extrapolation using Eq. (16), we estimate the PC of \( I_2 \) at \( 285^\circ\text{C} \) as 25 ± 15. From this estimated range, we calculate that \( 1.25 \pm 0.75\% \) \( I_2 \) in the primary coolant would result in a PC of 2000. This may be compared to data on primary coolant during shutdown and during power operation as given by Voilleque.
elsewhere in these proceedings. In general, the percent $I_2$ during shutdown is well above $1.25 \pm 0.75\%$, and during power operation, it is at or below this value.

5. CONCLUSIONS

The simulant steam generator tests indicate that iodine at tracer concentrations can have a species distribution in solution that is not expected or observed at higher concentrations. This is in line with previous work on radioiodine at tracer concentrations but at lower temperature.$^7-^9$

This work has concentrated on iodine at primary coolant conditions. During a steam generator tube rupture accident, there may be some mixing of primary and secondary coolant. The extent of this mixing would have to be evaluated in model calculations of these accidents. Secondary coolant generally contains ammonia or morpholine for pH control and hydrazine as a reducing agent. It is clear from the tests in this work that high pH and reducing conditions favor low percent $I_2$. Thus, large-scale mixing of primary and secondary coolant should decrease the percent $I_2$. Additional studies on this effect and on the possibility of volatile iodine species formed in the reaction of iodine with morpholine degradation products would be useful.
6. REFERENCES


Table 1. Summary of steam generator iodine experiments
286°C, 1000 psi, 0.2 M borate, 1.0E-9 M I⁻

<table>
<thead>
<tr>
<th>atm</th>
<th>pH at 25°C</th>
<th>% I₂ in liquid</th>
<th>% organic I in liquid</th>
<th>Partition coefficient PC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>5</td>
<td>2.04</td>
<td>0.11</td>
<td>6.87E+02</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.44</td>
<td>0.07</td>
<td>5.18E+03</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.02</td>
<td>0.00</td>
<td>4.75E+04</td>
</tr>
<tr>
<td>Air</td>
<td>5</td>
<td>22.00</td>
<td>3.95</td>
<td>3.50E+02</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1.20</td>
<td>0.15</td>
<td>8.88E+02</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.12</td>
<td>0.01</td>
<td>7.16E+03</td>
</tr>
</tbody>
</table>

Table 2. Distribution coefficients for the adsorption of iodine on stainless steel pressure vessel walls

<table>
<thead>
<tr>
<th>pH</th>
<th>Solution volume (mL)</th>
<th>Distribution coefficient q = mₛ/m₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7-5.2</td>
<td>1200</td>
<td>~.23</td>
</tr>
<tr>
<td>5.0</td>
<td>1200</td>
<td>0.53 (NO₃⁻ added)</td>
</tr>
<tr>
<td>5.0</td>
<td>1200</td>
<td>1.95 (air)</td>
</tr>
<tr>
<td>3.8</td>
<td>1200</td>
<td>1.45 (0.5 M H₃BO₃)</td>
</tr>
<tr>
<td>7.0</td>
<td>1200</td>
<td>0.26</td>
</tr>
<tr>
<td>7.0</td>
<td>1200</td>
<td>0.33</td>
</tr>
<tr>
<td>7.0</td>
<td>4000</td>
<td>0.00</td>
</tr>
<tr>
<td>9.0</td>
<td>1200</td>
<td>0.10 (0.5 M H₃BO₃ air)</td>
</tr>
</tbody>
</table>
FIGURE 1: Experimental System for Investigating Iodine Transport from a Simulated Steam Generator
DISCUSSION

W.G. BURNS You spoke of cases in which the surfaces were in contact with oxygen, also that oxidation of I⁻ to I₂ by the surface may have occurred. Does this relate to surfaces present in a working reactor heavily dosed with hydrogen?

S.R. DAISH The strongly reducing conditions found in the primary coolant would tend to reduce the possibility of the surface oxidation mechanism and in this way our system is behaving differently from a working reactor. However, in the case of a tube rupture accident some oxygen may enter the system from the atmosphere.

B.J. HANDY How confident are you in the solvent extraction method used in determining iodine speciation in the light of the very low concentrations of iodine employed?

S.R. DAISH Total mass balance for the various species determined from solvent extraction was usually greater than 90% which gave us fairly good confidence in the technique.

G.J. EVANS I have found using an extraction procedure with chloroform that extensive water rinsing of the chloroform prior to determining the molecular iodine and organic iodide fractions was required as often up to 99 percent of the total iodine was in the form of iodide (I⁻). I have found that the procedure provides reliable and useful results.

J.P. LONGWORTH Is the water/gas partition in equilibrium and can you get rate of approach to equilibrium data out of your experimental procedure?

S.R. DAISH Vapour and liquid samples were taken after the system had been at a steady temperature and pressure for 2-3 hours. So we were fairly confident that it was at equilibrium. Rate of approach to equilibrium could be obtained from the system although we have not done this.

P.E. POTTER What do you use for the dissociation constant of HI(aq).

E.C. BEAHM We used an equilibrium calculation and the assumption that I⁻ was the dominant aqueous species.
AN EXPERIMENTAL STUDY OF DILUTE AQUEOUS RADIOIODINE VOLATILITY

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ABSTRACT

The partitioning of iodine between moist air and CsI solutions in the concentration range of $10^{-4}$ to $10^{-8}$ M, has been investigated experimentally using radiochemical methods. In this paper the observed dependencies of the partition coefficient on time, solution pH, iodide concentration, water quality, and gamma irradiation are discussed emphasizing their relevance to trace iodide oxidation. The partition coefficient decreased over time at a rate that appeared to be governed by the rate of iodide oxidation. After about one week a near constant value was reached that depended upon the pH and iodide concentration of the solution. For a $10^{-6}$ M CsI solution of pH ca. 5, prepared using high purity water, the partition coefficient was ca. $10^5$; lower values were observed using solutions prepared using lower quality water. The rate of thermal iodide oxidation was found to be proportional to the square root of the hydrogen ion and iodide concentrations for solutions prepared in higher quality water. The thermal production of gaseous organic iodides was significant even at room temperature and organic iodides were eventually the predominant form of gaseous iodine. The gamma-photon irradiation of acidic $10^{-5}$ M iodide solutions caused the radiolytic oxidation of iodide resulting in the production of large amounts of volatile species of iodine and partition coefficients below $10^3$. The final value of the partition coefficient following the irradiation of these solutions did not depend on the irradiation dose rate for dose rates ranging from 100 to 20,000 Gy/hr.

1. INTRODUCTION

The extent of radioactive releases from containment to the environment following many postulated reactor accidents is governed by the fraction of the radioactive material in containment that is airborne. This is particularly true in situations in which post accident venting of the containment atmosphere is inevitable. For example, although the vacuum building associated with Ontario’s electrical generating reactors would delay the release of radioactive material to the environment following more probable accidents, venting of air from containment through filtered air discharge systems would have to
be initiated within several days of the accident in order to avoid uncontrolled releases through overpressurization. Such venting could occur at earlier stages in severe accidents involving a breach of containment in order to control releases of activity to the environment. The radiological hazard posed by post-accident releases of radioactive material greatly depends upon the amount of radioiodine released, due, in part, to its rapid transport through the food chain. Consequently, an understanding of iodine volatility in containment, based upon which the extent of post accident releases of radioiodine to the environment could be predicted, is important in assessing the potential consequences of reactor accident scenarios.

The volatility of radioiodine in containment is commonly described in terms of the water-air volumetric partition coefficient, defined as the ratio of the total concentration of iodine in aqueous solution divided by that in the gas phase. The partition coefficient depends upon the chemical speciation of the iodine and could theoretically range over orders of magnitude, due to the diverse volatilities of the many possible iodine species. Fortunately, it has been determined that radioiodine released from reactor fuel into an aqueous environment would be predominantly released in the form of iodide which is essentially involatile. However, iodide may be oxidized leading to the formation of volatile iodine species such as molecular iodine and some organic iodides, all of which may undergo elimination reactions. One pathway for the elimination of molecular iodine is through the formation of iodate and theoretical analysis [1] has indicated that, in air saturated solutions, iodate is the predominant form of iodine once equilibrium is achieved. However, the rate of iodate formation would likely be very slow following most reactor accidents and it is unlikely that equilibrium would be achieved within the time frame relevant to post accident releases of radioiodine to the environment. Thus, the partitioning of radioiodine in containment would not be dictated by the equilibrium speciation but rather, would vary over time depending on the relative rates of reactions causing the formation and elimination of volatile species.

The speciation of the iodine at any given time following an accident is greatly affected by the chemical environment within containment. Parameters such as the pH and total iodine concentration of the solution and the concentrations of oxidizing and reducing agents present, some due to the radiolysis of water, would dictate the speciation of radioiodine and hence its overall volatility. The results presented in this paper are part of an experimental study of the partitioning and speciation of radioiodine being conducted at the University of Toronto. In this study, the partition coefficient and speciation is being measured using Iodine-131 labelled CsI solutions; the parameters being varied include the total iodine concentration, the solution pH, and the exposure to gamma-photon irradiation. The gaseous and aqueous radioiodine speciation is
being determined using radiochemical methods as these provide
the sensitivity required to measure the very low concentrations
of iodine species involved. The system is being studied on the
small scale as it was anticipated that using a simpler system,
would better allow the resolution of the effects of the many
potential variables thereby providing a bridge between the
fundamental studies of individual reactions, and the large scale
experimental simulations of reactor accidents. In this paper,
results relating to temporal variations in the partition coeffi-
cient are emphasised along with the relevance of these results
to iodide oxidation.

2. EXPERIMENTAL METHOD

2.1) Reagents

High grade reagents were used throughout the research. The
water was purified by reverse osmosis followed by filtration and
deionization using a Barnstead "nanopure" system involving two
beds of mixed ion exchange resins for the removal of inorganic
substances, a 0.2 micron filter for the removal of bacteria and
a charcoal bed for the removal of organic substances, reputedly
able to reduce the concentration of organic substances to less
than 10 parts-per-billion.

Stock $10^{-2}$ M CsI solutions were prepared by dissolving
Aldrich gold label CsI; more dilute $10^{-4}$ M and $10^{-6}$ M stock-
solutions were prepared by sequential dilution. The I-131
tracer was purchased from Amersham in 10 to 20 mCi allotments
and was reported to contain less than 1 microgram of stable I-
127 per 20 mCi of I-131.

2.2) Equipment

The experiments were performed using Pyrex Erlenmeyer
flasks fitted with specially designed tops; a ground glass joint
provided the seal between the flask and the top. The tops were
equipped with three pyrex inlet/outlet lines each of which could
be sealed using a ground glass stop-cock; one inlet line
discharged at the bottom of the flask, into any solution in the
flask, the second discharged a few centimeters from the bottom,
just above the surface of the solution while the third
discharged at the top of the flask. The total volume of the
flasks ranged from 60 to 300 ml; the smaller flasks were built
in order to allow a greater number of solutions to be irradiated
simultaneously within the limited space of the irradiation cell.

Gaseous iodine within the flasks was sampled by pulling air
from the flasks through species-selective gaseous-iodine adsor-
bents. A gas sampler consisting of a series of Teflon
cartridges, each containing a different adsorbent was built for
this purpose. The small dimensions of the cartridges allowed
them to be placed directly into the well of the NaI gamma detector used to measure the I-131 activity. Pieces of Teflon tubing approximately 10 cm in length were used to connect the sampler to flasks; the short length of the tubing allowed the measurement of any retained I-131 using the well detector. Teflon tape helped in obtaining a good seal between the teflon tubing and the cartridges in the sampler.

2.3) Procedures

The behaviour of iodine within the liquid and gas phases was studied through the use of sealed flasks containing air and a test-solution of known CsI concentration and pH. The test-solutions were prepared by filling one third of the volume of the flasks with water and adding an appropriate volume of an I-131 labelled stock solution having a CsI concentration 100 times that of the test-solution produced. The labelled stock-solution had been tagged with I-131 several days earlier by adding approximately 1 mCi of I-131 tracer solution to ten mL of a stock CsI solution; the labelling occurred through atom-exchange resulting in the I-131 tracer having the same speciation as the stable I-127. The test-solutions produced had specific activities on the order of 35,000 Bq/ml. The pH of the test-solutions was adjusted by adding appropriate volumes of lithium hydroxide and sulphuric acid solutions. The flasks containing the test-solutions were shaken at room temperature for periods of up to a month using a wrist-action shaker to insure good contact between the liquid and gas phases. No attempt was made to keep the solutions in the dark.

The partitioning of the iodine and the gaseous speciation was determined every few days by pulling a known volume of the air within a flask, usually about 75 percent, through the gas sampler thereby obtaining a measure of the concentration of gaseous iodine. In experiments in which temporal variation of the partition coefficient was being studied, only 25 percent of the air within a flask was sampled in any measurement in order to minimize the effect of sampling on the system. The flow rate was measured using a rotameter with an aspirator as the vacuum source; a flow-rate of 90 mL/min was used. A second valve was opened in order to allow make-up air to enter the flask preventing the development of vacuum within the flask during sampling. The gas sampling was performed in a fumehood in order to prevent human exposure to gaseous radioiodine. On occasion the top of a flask was removed after sampling and several milliliters of the solution were collected for measurement of the aqueous I-131 activity and for assaying the aqueous speciation. The pH and oxidation potential of the solution were also determined using a Ag/AgCl/Pt combination electrode for the oxidation potential measurement.

The gaseous speciation was determined through the use of species-selective adsorbents developed by Keller et al.[2]. The adsorbents used, in order of contact with the airborne
iodine were: cadmium iodide for the retention of molecular iodine, p-iodophenol for the retention of hypoiodous acid and triethylenediamine (TEDA) impregnated charcoal for retention of any remaining species such as organic iodides. In addition, two pieces of teflon fibre, having pore diameters of 2 to 5 microns, were placed at the entrance to the sampler as monitors for any liquid aerosols entering the sampler. This precautionary measure was continued even though experiments involving involatile tracers revealed that it was unnecessary. Numerous tests, performed in order to verify the reliability of the methodology used to determine the gaseous iodine speciation, are summarized elsewhere [3,4] and are described in detail in a soon to be completed thesis [5]. This testing demonstrated that cadmium iodide is highly efficient in the retention of both molecular iodine (>90%) and iodoform (>85%). Iodophenol was found to be efficient not only in the retention of a gaseous iodine species present above hypoiodous acid solutions (>90%) but also in the retention of higher-molecular-weight organic iodides such as butyl iodide (>65%) while only lower-molecular-weight organic iodides such as methyl and ethyl iodide were capable of effectively penetrating both cadmium iodide and iodophenol to be trapped on the charcoal.

The I-131 activity of the species selective adsorbents were all assayed using a well shielded 3 x 3 well type NaI detector with an efficiency of approximately 70 percent for the 364 keV gamma produced by the decay of I-131. A window was set so as to eliminate interference from the 164 keV gamma produced by the decay of Xe-131. The empty gas sampling cartridges were monitored for activity prior to every use in order to account for the presence of any residual activity from previous uses.

In order to investigate the effects of gamma-photon irradiation, flasks were placed in a Co-60 gamma irradiation cell which provided a well known dose rate that could be varied from 100 to 400 Gy/hr. Later in the study some measurements were made using a newer irradiation cell able to provide dose rates of 20 kGy/hr. Measurements of the partition coefficient and gaseous speciation were typically initiated within 20 minutes of removing a flask from the cell. Irradiation times varied from 1 to 6 days providing radiation doses ranging from 12 to 72 kGy.

3. RESULTS AND DISCUSSION

3.1) Temporal Variations in the Partition Coefficient

The solutions examined in this research initially contained iodine predominantly in the form of involatile iodide thus little gaseous iodine was expected to be present. It was observed that the partition coefficient decreased over time indicating that reactions were occurring leading to the formation of volatile forms of iodine. The rate of reduction of
the partition coefficient provided a measure of the rate of formation of these volatile species of iodine and, since the formation of these volatile species required the oxidation of iodide, the temporal variation in the partition coefficient allowed insight into the rate of iodide oxidation under the conditions investigated.

In FIGURE 1, temporal variation in the partition coefficients of three $10^{-8}$ M CsI solutions of pH ca. 5.5 and two $10^{-6}$ M CsI solutions of pH ca. 4.7 can be seen. The spread between the results obtained under similar conditions, gives a measure of the experimental precision; it can be seen that on average the reproducibility was well within 20 percent.

The partition coefficient dropped by an order of magnitude over the first six to eight days then reaching a more constant value. These kinetic trends were reasonably consistent with those reported by Marshall [6] under similar conditions. For example, for a ca. $10^{-7}$ M NaI solution of pH 5, Marshall found that the partition coefficient dropped by a factor of ca. 20 over the first four days reaching a constant value of $5 \times 10^4$ while for a $2 \times 10^{-13}$ M solution of the same pH, he found that the partition coefficient dropped by a factor of ten over ca. six days reaching a constant value of $1.5 \times 10^3$. However, Marshall's results did not suggest any reduction in the partition coefficient over time for solutions of higher pH and total iodine concentration. Reductions in the partition coefficient over time under such conditions were observed in this research although the magnitude was not as large as that for the solutions presented in FIGURE 1.

If the formation of volatile species of iodine had proceeded without any destruction of the volatile species formed, the observed partition coefficients would have continued to decrease over time, although the rate of reduction would have decreased due to the inversely proportional relationship between the partition coefficient and the concentration of volatile iodine species. However, following the initial drops already discussed, very little change of the partition coefficient over time was observed indicating that a steady state was attained. The term steady state is used as there is no basis for believing that equilibrium between the iodine species in these air saturated solutions was achieved within the duration of these experiments. At equilibrium, iodate would have been the predominant species of iodine, yet a radiochemical solvent extraction procedure [5] revealed that less than one percent of the aqueous iodine was in the form of iodate. The occurrence of a steady state required that a pathway for the elimination of the volatile species of iodine existed. Three potential pathways existed: 1) the reaction of volatile inorganic species such as molecular iodine with organic impurities to form organic iodides followed by the hydrolysis of these organic iodides; 2) the disproportionation of molecular iodine leading to the formation of iodate; or 3) the walls of the flask acting as a sink for
volatile species of iodine. Based on the present understanding of the very slow rate of iodate formation [7], under the conditions of these experiments, this pathway could not have made a significant contribution to the elimination of volatile species of iodine. Simulation of the experimental findings using a theoretically based computer code revealed that the elimination pathway involving the formation and subsequent hydrolysis of organic iodides, was reasonably consistent with the known rate constant for the hydrolysis of methyl iodide. It is anticipated that this code will be described in a future publication in addition to the description provided in a soon to be completed thesis [5].

3.2) Steady State Values of the Partition Coefficient

A knowledge of how the steady state values of the partition coefficient depended on the pH and iodide concentration of solutions was considered to be greatly important to reactor safety analysis. Determining and understanding the dependence of the partition coefficient on these parameters were the main purposes of the research. Kinetic experiments such as those described through FIGURE 1, revealed that the partition coefficient reached close to constant values six days after solutions were prepared. Consequently, averaging values of the partition coefficient that were measured six days or more after preparing an iodide solution of given pH and concentration, provided reasonably time-independent evaluations of the partition coefficient. By studying solutions ranging in pH from 2 to 12 and in iodide concentration from $10^{-4}$ to $10^{-8}$ M, the dependence of the partition coefficient on these parameters was experimentally determined.

The effect of varying pH or the total iodine concentration on the partition coefficient can be seen in FIGURE 2 in which the logarithm of the partition coefficient is shown for solutions of differing pH and iodide concentrations. Each point shown was derived from a different solution and represents a mean value, averaged over of up to 8 measurements made using the given solution. Over 150 measurements of the partition coefficient are included in FIGURE 2. The precision associated with the mean values, as expressed by the standard deviation was less than 50 percent of the mean; a sample error bar is included in the upper left hand corner of FIGURE 2. Variations due to kinetic effects greatly contributed to the imprecision of the mean values presented in this figure. In the experiments shown in FIGURE 1, in which kinetic effects did not contribute to the irreproducibility, the precision was better than 20 percent.

For an increase in the pH of a solution from 2 to 12 while holding the iodide concentration constant, the volumetric partition coefficient increased by about two orders of magnitude which indicates that the total amount of airborne iodine
decreased by the same amount. Specifically, for an iodide concentration of $10^{-8}$ M, the partition coefficient increased from a value of approximately 2500 at a pH of 2 to a value of approximately 300,000 at a pH of 11. For an increase in the iodide concentration by four orders of magnitude, while holding the pH constant, the partition coefficient increased by one to two orders of magnitude; at a pH of ten, for example, $H$ was found to be 300,000 and 7,000,000 at, respectively, iodide concentrations of $10^{-8}$ M and $10^{-4}$ M.

It is apparent from the results presented in FIGURE 1, that under acidic conditions the partition coefficient increased with increasing pH and with increasing iodide concentration. Iodide is not volatile and is not known to react with non-halogenated organics. The formation of volatile species of iodine required the oxidation of iodide and thus, the dependence of the partition coefficient on pH and the iodide concentration allowed insight into the dependence of the rate of iodide oxidation on these parameters. Sigalla and Herbo [8] measured the rate of iodide oxidation in very acidic $10^{-1}$ M to $10^{-2}$ M iodide solutions and proposed the rate law shown in equation 3.1, offering a consistent mechanism. They rejected a second mechanism, giving a rate law with iodide to the half power, even though it also gave reasonable agreement with their data.

$$d[I^-]/dt = k_1[O_2][I^-][H^+] \quad (3.1)$$

The trends shown in FIGURE 2, strongly suggest that, in acidic solutions the predominant mechanism for iodide oxidation involves iodide and the hydrogen ion to the half power giving the rate law shown in equation 3.2. The difference between this rate law and that proposed by Sigalla is attributed to the much higher iodide and hydrogen ion concentrations used in Sigalla's research. It should be noted that the oxygen concentration has not been included in the rate law given by equation 3.2, as the iodide oxidation may not have been limited to reaction with dissolved oxygen. Although the experimental methodology used did not lend itself to precise evaluation of rate constants, modeling of the experimental results indicates that the value of $k_2$ is on the order of $10^{-9} \text{ s}^{-1}$.

$$d[I^-]/dt = k_2[H^+][I^-]^{0.5} \quad (3.2)$$

As shown in FIGURE 2, under basic conditions, although $H$ is still dependant on the iodide concentration, the dependance on pH is much less significant suggesting that under basic conditions, the mechanism for iodide oxidation in very dilute iodide solutions does not involve the hydrogen ion.

3.3) The Effect of Water Quality on Iodine Partitioning

The water used in the majority of the research, referred to here as the "nanopure water", was purified by reverse osmosis
followed by deionization/ filtration using a Barnstead "nanopure" system. A few experiments were also performed using commercially distributed water for high performance liquid chromatography (HPLC) purchased from Fisher Scientific. This water was reportedly purified by distillation followed by deionization/filtration. The partition coefficient of iodine between air and $10^{-4}$ M CsI solutions of pH ca. 4, prepared with the HPLC water, were much lower than those for similar solutions prepared using the nanopure water.

The lower partition coefficient observed with the HPLC water instigated experiments using tap water. It was found that the amount of gaseous iodine initially present above CsI solutions prepared using tap water was far greater than that observed for the solutions prepared using the nanopure water or even the HPLC water. As can be seen in FIGURE 3, for the solutions prepared with HPLC or tap water, the partition coefficient decreased very rapidly over time, reaching a minimum value within one day. This was attributed to rapid oxidation of iodide due to oxidizing agents, likely molecular chlorine in the case of the tap water, in addition to oxygen being present in the water. In the case of the solutions prepared with tap water, the increase in the partition coefficient, after an initial drop to below 1000 during the first day, was originally attributed to the disproportionation of molecular iodine to iodate. However, the observed rate of molecular iodine disappearance, as indicated by the rate of increase of the partition coefficient, was far faster than the expected rate of iodate formation [7] and following the experiment, less than two percent of the total iodine in the tap water solution was found to be in the form of iodate. Thus, some other pathway for the elimination of molecular iodine must have existed. It should be noted that the measured redox potential of the tap water was almost twice that of the nanopure water while there was no significant difference between the redox potential of the HPLC water and that of the nanopure water.

The lower values of the partition coefficient observed for the acidic $10^{-4}$ M solutions prepared with HPLC water were also attributed to oxidizing agents, other than oxygen, being present in the water. This was confirmed in an experiment in which nitrogen saturated HPLC water was used; the observed values of the partition coefficient were no different from those determined for air saturated HPLC water ($2 \times 10^4$). Experiments were also conducted with $10^{-5}$ and $10^{-7}$ M CsI solutions prepared using HPLC water. For these more dilute solutions, the difference in the partition coefficients, between similar solutions prepared with the HPLC and nanopure water, was much smaller than in the case of the $10^{-4}$ M CsI solutions. In addition, when the HPLC water was used, the partition coefficient observed for the $10^{-5}$ M solution ($2 \times 10^5$) was an order of magnitude higher than that for the $10^{-4}$ M solution ($2 \times 10^4$) suggesting that the presence of the oxidizing agent in the HPLC water resulted in a rate law for iodide oxidation different than that described in equation 3.2,
obtained using the nanopure water.

The experiments involving different types of water demonstrated that oxidizing agents can greatly increase the extent of thermal iodide oxidation. The partition coefficient determined using the purified HPLC water demonstrated that such oxidizing agents can be present in significant amounts even in purified water and confirmed that the nanopure water used in the study was of higher quality. The extent of iodide oxidation following a reactor accident would be greatly dependent on the redox conditions of the solution produced. Under such conditions redox agents would be present, due not only to both materials in the core and reagents deliberately added, but also due to species produced through the radiolysis of water; the resulting quality of the water would likely be closer to that of tap water than to that of the nanopure water used in this research. Now that information on iodine partitioning between air and good quality water is available, experiments should be conducted using water more representative of that expected following postulated reactor accidents. Experiments involving gamma irradiation, such as those considered later in this paper, partially meet this objective.

3.4) Temporal changes in the Gaseous Iodine Speciation

Presented in FIGURE 4 are the temporal changes in the percentage of the gaseous iodine activity retained on the charcoal as measured above the acidic solutions considered in FIGURE 1. Based on testing of the species-selective gaseous-iodine adsorbents, this activity was attributed to organic iodido similar to methyl iodide referred to here as lower-molecular-weight organic iodides. As can be seen in FIGURE 4, a buildup of lower-molecular-weight organic iodides occurred in the gas phase over the same period of time as the reduction in the partition coefficients shown in FIGURE 1.

Between 70 to 90 percent of the gaseous iodine was eventually in the form of lower-molecular-weight organic iodides. This was found to be the case for the majority of the solutions studied ranging in pH from 4 to 7. Under more acidic conditions, molecular iodine was the predominant form of gaseous iodine.

Experiments were conducted in order to determine the source of these organic iodides. When water from a different laboratory, cleaned by distillation in addition to filtration/deionization and reverse osmosis, was used the abundance of gaseous organic iodides was no different. However, when HPLC water was used to prepare the $10^{-4}$ M solutions discussed in the previous section, the gaseous iodine was almost entirely in the form of molecular iodine. For $10^{-5}$ and $10^{-7}$ M solutions prepared with HPLC water, up to 60 percent of the gaseous iodine was eventually in the form of these organic iodides suggesting that insufficient organic material may have
been present to react with all the molecular iodine produced in the case of the $10^{-4}$ M solution. In order to investigate whether the formation of the organic iodides could have been due to the direct iodination of methane a few percent methane was added to the air above two $10^{-4}$ M iodide solutions prepared with HPLC water. No buildup of gaseous organic iodides was observed confirming, as expected theoretically, that the thermal iodination of methane by molecular iodine is not significant.

The nanopure water used in the majority of this research was reported to contain less than 10 ppb of organic material. However, this low concentration of organic material still represented ten times the total concentration of iodine and at least a hundred times the concentration of volatile iodine species in the case of the $10^{-8}$ M iodide solutions. Following a reactor accident, the concentration of organic material would also likely be far greater than the total concentration of iodine, thus, gaseous organic iodides would likely be significant. Although the organic reagents responsible for the formation of the organic iodides observed in this research could not be identified, the results demonstrated that significant amounts of gaseous organic iodides can be formed in the absence of irradiation. Also, the measurements of temporal variations in the gaseous iodine speciation indicated that the build up of gaseous organic iodides is a slower process requiring one to two weeks to reach a maximum.

3.5) The Effect of Irradiation of Iodine Partitioning

In order to study the effects of gamma irradiation on iodine volatility, cesium iodide solutions were irradiated in a Co-60 gamma cell using dose rates ranging from 100 to 20,000 Gy/hr. Following the irradiation, the concentration and speciation of the gaseous iodine above these solutions was determined; in some cases the aqueous iodine speciation was also determined using radiochemical solvent extraction. The production of volatile forms of iodine, as measured by the partition coefficient, provided insight into the radiolytic oxidation of iodide.

The effect of irradiation on the partitioning of iodine between air and $10^{-5}$ M CsI solutions of pH 5 is shown in FIGURE 5. Two such solutions were irradiated, one at a dose rate of 100 Gy/hr and the other at a dose rate of 400 Gy/hr, however, since no difference between these irradiated solutions was observed, the results from both were included in FIGURE 5. The irradiation caused a rapid drop in the partition coefficient which reached a relatively constant value of 500 within ca. 20 hours. This value of the partition coefficient was far lower than the value of 500,000 observed for similar unirradiated solutions. Thus the irradiation caused a large increase in the concentration of volatile species within the solutions. In experiments with more basic and more dilute iodide solutions,
the effect of irradiation was not as great. For example, when $10^{-8}$ M CsI solutions of pH ranging from 3 to 9 were irradiated, no significant reduction in the partition coefficient was observed as compared to that for similar unirradiated solutions.

The radiation-induced production of volatile iodine species was attributed to the radiolytic oxidation of iodide. This oxidation would likely have been due to reaction with the hydroxyl radical produced by the radiolysis of water. In these acidic aerated solutions, reducing radicals such as the solvated electron and atomic hydrogen would have been eliminated through the formation of HO₂, and thus would no longer have been available to reduce the oxidized iodide back to iodide.

It is believed that the volatile species formed was primarily molecular iodine, however, the gaseous speciation analysis provided unusual results. Following irradiation, the majority of the gaseous iodine collected during sampling was retained by the teflon tubing used to connect the flasks to the gas sampler. This trend was particularly apparent after shorter periods of irradiation. In numerous experiments, conducted with both irradiated and unirradiated molecular iodine solutions, it was demonstrated that this short length of teflon tubing retained less than 10 percent of the molecular iodine collected from a flask. Thus the possibility arose that some unknown species of iodine, more easily retained than molecular iodine, may have been produced by the radiolysis. It is hoped that further research will help to resolve this hypothesis.

The effect of dose rate on iodine partitioning was also studied. Presented in FIGURE 6 are the partition coefficients determined for $10^{-5}$ M CsI solutions of pH 5 following irradiation at a variety of dose rates. It is apparent that the final value of the partition coefficient did not depend on the dose rate. In addition the partition coefficient reached a relatively constant value below 1,000 after the solutions absorbed 2,500 Gy of radiation. Thus the duration of time prior to reaching a constant partition coefficient did depend on dose rate. For example, at a dose rate of 20,000 Gy/hr the partition coefficient dropped below 1,000 after ca. 8 minutes of irradiation while at a dose rate of 100 Gy/hr, 18 hours of irradiation were required before the partition coefficient dropped below 1,000. Following a severe reactor accident dose rates on the order of 20,000 Gy/hr could occur. If the solution pH were to reach as low as 5, a significant portion of the iodide released into containment could be oxidized within the first hour following fuel failure. It should be noted that for $10^{-5}$ M iodide solutions of pH 9, the final value of the partition coefficient was inversely dependent on the dose rate.

The development of a more complete understanding of the effects of irradiation on iodine partitioning and speciation is considered to be very important to predicting the behaviour of
radioiodine following reactor accidents. It is hoped that further research, including the development of a computer code to model the plethora of possible radiolytic interactions, will help to provide the required understanding. Experimental research will continue to emphasise the radiolysis of dilute iodide solutions as the existing data base indicates that results obtained for more concentrated iodide solutions have very limited relevance to reactor accident scenarios.

4. CONCLUSIONS

The partition coefficient of iodine between air and solutions initially containing iodide decreases over time at a rate that appears to be governed by the rate of iodide oxidation. After about one week a near constant value is reached that is dependent upon the pH, total iodine concentration and the concentration of oxidizing agents in the solution. In higher purity water, the rate of thermal iodide oxidation is proportional to the square root of the hydrogen ion and iodide concentrations. The thermal production of gaseous organic iodides is significant even at room temperature. The organic species involved in the formation of these organic iodides have not been identified however, results from this study indicate that the thermal iodination of methane is not significant. The radiolytic oxidation of iodide under acidic conditions causes the production of large amounts of volatile species of iodine when $10^{-5}$ M iodide solutions are irradiated. The final value of the partition coefficient following the irradiation of these solutions does not depend on the irradiation dose rate.

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6. REFERENCES


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Figure 1) Temporal Variations in the Partition Coefficient For Unirradiated CsI solutions of pH 5.

Figure 2) Steady State Values of the Partition Coefficient as a Function of pH and Iodide Concentration.
Figure 3) The Effect of Water Quality on Temporal Variations in the Partition Coefficient. [iodide] = 10⁻⁴ M, pH=4.

Figure 4) Temporal Variations in the Abundance of Gaseous Organic Iodides. pH=5.
Figure 5) The Effect of Irradiation on Temporal Variations in the Partition Coefficient. [iodide]$=10^{-5}$ M, pH=5.

Figure 6) The Dependence of the Partition Coefficient on Irradiation Dose. [iodide]$=10^{-5}$ M, pH=5.
DISCUSSION

P.N. CLOUGH Sigalla and Herbo observed strong photo-catalysis in their experiments. Did you find a similar effect?

G.J. EVANS I did not perform any experiments in the dark thus I do not know whether photo-catalysis was significant.

W.G. BURNS Do you think there may have been chlorine in the water?

G.J. EVANS Chlorine may have been present in the water and caused some iodide oxidation. In the case of the tap water, for example, I believe that the observed reduction in the partition coefficient was due to the presence of $10^{-5} \text{ M Cl}_2$ in the water. For a $10^{-4} \text{ M iodide solution}$, this would have resulted in a partition coefficient of 800 in agreement with the observed value. In the case of the higher purity "nanopure" water, it would be difficult to dismiss the possibility that chlorine contributed to the observed oxidation although, the slow rate of iodide oxidation suggests it was not the principle oxidizing agent.

A.C. VIKIS Was exposure to air a static one? What was the chemical purity of air used?

G.J. EVANS The air used in the flasks was laboratory air and thus may have contained some organics. The exposure was static.

E.W. THORTON Could the author please clarify the sampling procedure. Was there a continuous purge of air through the flask or was the gas phase sampled periodically?

G.J. EVANS The air within the flasks was static, every few days the flask would be sampled which involved pulling about 25% of the air in the flask through the adsorbents. Thus the sampling may have disturbed the system somewhat but not to a significant extent. There was no continuous purge of air.

P.E. POTTER Could you tell me what was found on the iodophenol?

G.J. EVANS The iodophenol was found to retain both a species believed to be hypoiiodous acid and higher-molecular-weight organic iodides such as butyl iodide. This did not cause an unresolvable conflict, as in other experiments, hypoiiodous was found to be quite involatile. In general, only a small percent of the total gaseous activity was retained on the iodophenol.
THE INFLUENCE OF RADIATION ON THE STABILITY OF 
CsI IN FLOWING STEAM

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ABSTRACT

In the recent past, concern was raised regarding the potential of ionizing radiation to affect the stability of CsI in a reactor coolant system following the release of fission products during a severe accident. We have conducted a series of experiments to specifically address the issue of CsI stability and its potential for reaction, in steam, with Type 304 stainless steel while exposed to a radiation field.

The experiments were conducted in a 2.5-cm stainless steel flow pipe at temperatures between 900 and 950°C, and at 100 kPa. Molecular CsI, at concentrations ranging from 60 to 240 ppm, was passed through the flow pipe in steam and collected in the water condensed at the end of the pipe. The condensate was analyzed for Cs⁺ and I⁻ concentrations. The ratio of these ions is an indicator of the fraction of CsI that dissociated during the transit of the pipe. A specially constructed flask containing 12 kCi (444 TBq) of cobalt-60 provided a radiation field of 0.3 to 9 krad/min (3 to 90 Gy/min).

The results of the tests showed no correlation between CsI stability and the applied radiation field. The fraction of CsI dissociated, as measured by a deficiency of Cs⁺ in the condensate, varied between 0 and 35% with a weak correlation for increasing dissociation with decreasing CsI concentration. It is assumed that the cesium not found in the condensate formed CsOH in the pipe during transit, and then reacted with the stainless steel.

The results of these tests are in good agreement with a prediction of the impact of the radiation field and also the expected thermal decomposition of the CsI under the thermodynamic conditions of the experiments.

1. INTRODUCTION

Historically, the potential release of radioactive iodine isotopes has been one of the more important hazards associated with reactor accidents. Following the accident at TMI-2, where only very small quantities of radiiodine were airborne, the hazard due to iodine release has been reevaluated. Over the course of the past several years, the chemistry of iodine relevant to accident conditions has been extensively
reviewed. It is now generally agreed that the release of radioactive iodine will be greatly mitigated during accidents in water-cooled nuclear reactors by a variety of mechanisms.

The primary mechanisms for mitigation are related to the release of most of the iodine from the reactor core as CsI and the high solubility of CsI to form I⁻ in aqueous solution. Studies of fission product release from irradiated fuel [1] supported by thermodynamic calculations [2] show that most of the iodine will initially be released as CsI during a severe reactor accident. This salt molecule is hygroscopic, highly soluble in water, and will condense at a relatively high temperature (m.p. 621°C) to form aerosol particles. During an accident, aerosol particles will be subject to rapid growth in size and removal from the atmosphere by a variety of mechanisms. Both the formation of aerosol-borne CsI and the water solubility of iodine will lead to a very low airborne concentration of radioactive iodine during the course of a reactor accident.

Our knowledge of the chemistry of iodine is sufficiently great to determine that the potential for large releases of airborne iodine throughout the course of an accident in a water-cooled accident is quite low for most conditions. The focus of the more recent studies has been on those physical and chemical conditions where our knowledge base was previously limited (e.g., in the mechanisms for forming volatile organic iodides) or where the formation of CsI and dissolution of iodine might not be favoured.

Results obtained by Elrick and Powers [3] suggested that ionizing radiation in the reactor coolant system could destabilize CsI sufficiently to significantly affect the chemistry of the iodine entering the containment building. Our work further investigates the impact of ionizing radiation and the results show that radiation can be neglected in comparison to the more important thermodynamic and kinetic influences on the stability of CsI.

EXPERIMENTAL

The experiments were carried out to determine the behaviour of CsI flowing in steam through Type 304 stainless steel piping. Two tests were carried out with no radiation field present while the remainder of the tests were carried out in a specially constructed irradiation flask. Figure 1 shows a schematic of the flow system for the radiation experiments.

Steam was generated in a superheater at 900°C, from distilled water flowing at a rate of 43 mL/h. This steam was passed through approximately 1.5 m of 2.5-cm O.D. stainless steel piping until it reached a condenser. The stainless steel piping was located inside a 2.5-cm I.D. Inconel pipe. The stainless steel liner-pipe was changed after each experiment. Molecular CsI was generated by evaporating CsI from an alumina crucible into an argon flow. This flow merged with the steam flow just after the superheater as shown in Figure 1. The entire flow system was trace heated and instrumented with thermocouples. The condensate leaving the condenser was collected at intervals for analysis and the
noncondensible gases were vented through a water trap. Samples of the noncondensible gases were also analyzed by mass spectrometry to monitor for air leaks and to measure the hydrogen concentration. The pressure in the piping was 100 kPa.

A strip of 304 stainless steel sample coupons was located inside the pipe. After the tests, selected sample coupons were examined using a scanning electron microscope. The condensate samples were analyzed for pH and for Cs⁺ and I⁻ content using atomic absorption spectrometry and inductively coupled plasma spectrometry, respectively.

For the tests with a radiation field, a Fission Transport Test Flask was constructed to contain 12 kCi (444 TBq) of cobalt-60. Figure 2 shows a cutaway drawing of the flask with the test assembly in place. The flask was designed to contain four 45-cm-long pencils of cobalt-60 in four rotatable cylinders as shown in Figure 3. Rotation of these lead filled cylinders permits continuous adjustment of the radiation field along the central axis of the flask from 0.3 to 9 krad/min. The experiments were conducted using these two extreme values of the radiation field. Figure 4 shows the radiation field profile along the central axis of the flask with all four source pencils located in the maximum field positions.

RESULTS

Two tests were conducted with no radiation field present. For the tests, the 304 stainless steel liner pipe and coupons were prepared using two different methods. One method consisted of a simple degreasing using acetone and distilled water rinses. The second method consisted of a degreasing rinse and a series of acid and base rinses similar to those used by Elrick and Powers [3]. There was essentially no difference observed in the results from these two tests. Table 1 shows the analyses of the condensate samples, obtained at hourly intervals, from the test with the simply degreased pipe. The table lists the pH of condensate samples collected at hourly intervals, the Cs⁺ and I⁻ concentrations, the Cs/I atomic ratio. The data show that the Cs/I atomic ratio in the condensate was 0.95 ± 0.05. For the test with the acid and base rinses, the condensate Cs/I atomic ratio was 0.90 +/- 0.05. Within experimental error, these values agree. All of the tests with the radiation field were conducted with the 304 stainless steel prepared using only the degreasing rinses.

Nine tests were conducted with both the high (9 krad/min) and low (0.3 krad/min) fields for a range of CsI concentrations in the steam flow. The results of a typical test are shown in Table 2. This table includes the H₂/Ar ratio measured in samples of the noncondensible gases. The distilled feedwater starts at a pH near neutral, but the pHs of the condensate samples are all low, in contrast to the pHs of the samples from the tests with no radiation field. The last line refers to the water collected after rinsing deposited material from the sample coupons.

The Cs/I atomic ratios for the condensate samples in Tables 1 and 2 are always less than one. This is consistent with thermal decomposition of CsI,
CsI + H₂O → CsOH + HI,

followed by reaction of the CsOH with the stainless steel surfaces. The
reaction of CsOH with 304 stainless steel has been well established by
Elrick et al. [4].

In all tests, the sample coupons and liner pipe were coated with a
powdery white deposit at the end near the condenser. This deposit was
readily removed by a water rinse. Analysis of this rinse, e.g., the last
line of Table 2, showed that this deposit was essentially pure CsI. The
CsI would have condensed because of the temperature gradient of the
surfaces near the condenser. Since the pH of the rinse water is very close
to neutral and was never found to be basic, it appears that the powder
deposit did not contain any CsOH.

The mass balance in many of these tests was poor (40 to 107% CsI
recovery) owing to the temperature gradients in the apparatus and the
condensation of CsI in locations that prevented easy recovery. This is
reflected in the fact that, for all tests, the bulk of the CsI collected
was found in the post-test rinses and not in the condensate samples.
However, since the aim of the experiments was to observe the dissociation
of CsI and there is no evidence of condensed CsOH, an accurate mass balance
is unnecessary.

Table 3 lists the average Cs/I ratios in the condensates for a
number of tests conducted with both high and low radiation fields and a
range of CsI concentrations in the steam. The results clearly indicate
that the strength of the radiation field has no apparent influence on the
condensate chemistry and hence the stability of CsI in the flow system. In
fact, the average Cs/I ratio for the high-field tests is actually
marginally higher than that for the low field tests (0.88 vs 0.85) but both
agree within experimental error (± 0.05).

Figure 5 shows a plot of the Cs/I ratio in the condensate as a
function of the CsI concentration in the steam. The data are very
scattered and do not show a strong correlation. If we eliminate the one
rogue point at 75 ppm, there is a weak correlation between the fractional
decomposition of the CsI and the concentration of CsI in the steam. As
will be discussed, this finding is in accord with our expectations from
thermodynamic equilibrium calculations.

The low pH of the condensate samples was a matter of concern
throughout these tests and much effort was expended to identify its cause.
Table 4 shows the results of some anion analyses of the feedwater,
solutions made up from the CsI used in the generator and condensate
samples. The table indicates that the only anion of consequence present in
the water was I⁻. There were no significant impurities in the CsI stock
chemical. We also condensed CsI immediately after evaporation from the
oven, during calibration tests, and solutions of this powder did not have a
low pH.

The presence of I⁻ is consistent with decomposition of CsI in
steam to form HI. For most of our experiments, it is possible to justify
the observed pHs solely on the basis of the presence of I⁻. An excess of
I\(^-\) over Cs\(^+\) of 10 to 100 mg/L would lead to a solution pH of 3 to 4. This explanation, however, is not sufficient for those experimental results where the CsI ratio in the condensate was greater than one and the pH was below 5. We have not been able to resolve the cause of the low pHs completely. It is worth noting that Sallach et al. [5] also observed low condensate pHs in similar experiments that they could not explain. In their tests, they observed F\(^-\) ions from an unidentified source. We have not observed any significant concentration of F\(^-\) in our condensate samples. We suspect that there is a corrosion process active leading to the low pHs, which, at present, we do not understand.

The assumption arising from our results is that a small fraction of the CsI dissociates in steam at 900°C leading to formation of CsOH, which in turn reacts with the stainless steel surfaces. The reaction of CsOH with 304 stainless steel has been observed by Elrick et al. [4] in tests similar to ours. They found the reacted cesium associated with silicon in the oxide layer formed on the stainless steel. Elrick and Powers made similar observations in their work [3]. We have looked for cesium on selected sample coupons in our experiments using X-ray fluorescence and scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX).

The X-ray fluorescence analysis failed to detect any cesium above the background threshold level. Figure 6 shows an SEM micrograph of a sample coupon. The oxide layer shows a characteristic duplex structure with an outer iron-rich magnetite phase and an inner chromium-rich spinel phase. In other work, the cesium has been observed concentrated at the interface between the two layers associated with silicon. We made several attempts to find cesium there in our sample coupons but failed to do so. Figure 7 shows a typical EDAX spectrum of the interface region. We must attribute our failure to the large surface area of stainless steel in our experiments and the small amount of cesium that reacted. The available surface area for deposition is 1600 cm\(^2\). If 15% of 100 ppm of CsI decomposes in steam to give CsOH, which reacts uniformly, then there would be 1.2 x 10\(^{-7}\) mol/cm\(^2\) of Cs on the surface. If all the Cs were in a 0.01-\(\mu\)m band at the interface, the concentration would be approximately 1 molar %. Unfortunately, this is below the detection limit for our SEM/EDAX system. Thus, our inability to find the cesium is likely due to limitations of detection sensitivity. It should be noted that Sallach et al. [5], in their study of the reaction of CsI with stainless steel, also failed to observe cesium in the oxide layer at concentrations above background.

DISCUSSION

The results of this study clearly indicate that a moderate radiation field will not substantially affect the stability of CsI in high-temperature steam. Although this result contradicts the earlier observations of Elrick and Powers [3], it is in agreement with an analysis of the expected impact of gamma radiation on the system.
Since CsI is present in the steam in dilute concentration, the primary deposition of absorbed energy will occur in the water molecules. Irradiation of the water molecules can lead to the formation of ions and radicals. These, in turn, can potentially react with the CsI molecules. The following is an abbreviated mechanism of the possible reactions.

\[
\begin{align*}
H_2O + \text{gamma} & \rightarrow H_2O^+, \text{OH} \\
H_2O^+ + H_2O & \rightarrow H_3O^+ + OH \\
H_2O^+ + \text{CsI} & \rightarrow \text{CsI}^+ + H_2O \\
\text{CsI}^+ & \rightarrow \text{Cs}^+ + I \\
\text{Cs}^+ + \text{wall} & \rightarrow \text{trapped Cs} \\
\text{OH} + \text{CsI} & \rightarrow \text{CsOH} + I \\
\text{CsOH} + \text{wall} & \rightarrow \text{trapped Cs}
\end{align*}
\]

The efficiency for these mechanisms depends on the yield for ion and radical production from the gamma radiolysis. The G value for OH radical production from gamma radiolysis of steam is approximately 7 [6]. The G value for \(H_2O^+\) production is approximately 2 [7]. Based on these, in 100 kPa of steam at 900°C, the rate of radical production with a 10 krad/min field is \(1.4 \times 10^{11}\) molecules/cm\(^3\)s. At 100 ppm, the concentration of CsI is \(6.3 \times 10^{14}\) molecules/cm\(^3\). Hence the maximum destruction rate of CsI by reaction with radiolytically produced radicals is \(2.2 \times 10^{-2}\)%/s. For the flow rate used in the experiment, the residence time in the radiation zone of a given gas volume is only 1.3 s. Hence a negligible fraction of the CsI can be destroyed by these mechanisms.

There are other reactions occurring in the gas phase that will compete for the radicals and ions produced by radiolysis and these will reduce the impact on the stability of CsI. A theoretical maximum to the impact of radiation may be estimated by assuming that all of the absorbed energy from the radiation field goes into breaking the CsI bond \(D_o = 3.56\) eV [8]. In this case, the maximum destruction rate, assuming no back reactions, would still be only \(8.7 \times 10^{-2}\)%/s.

The most important factor affecting CsI in these experiments is its thermodynamic stability. At elevated temperatures, CsI, like all molecules, will be subject to thermally induced decomposition. As a result, CsI will be in thermal equilibrium with other species, including CsOH. This equilibrium will be determined by the temperature, pressure and gas composition of the system.

We have calculated the equilibrium speciation for systems relevant to our experimental conditions using the database and computer code of Garisto [2]. Figures 8 shows the equilibrium speciation for 100 ppm of CsI in steam. At a temperature of 900°C (1173 K), Figure 8 shows that approximately 10% of the cesium will be present in the system as CsOH. Thus, in our experiments, if equilibrium is achieved during the transit
time of the apparatus, approximately 10% of the CsI may actually be transported as CsOH. Chemical kinetics calculations suggest that this is a reasonable assumption [8]. Since CsOH is well known to react with stainless steel, it is not surprising that we observe Cs/I ratios less than one in the condensate water.

At a concentration of 100 ppm, CsI is the dominant species in the system. However, lower CsI concentrations will shift the equilibrium to favour the stability of CsOH. Figure 9 shows the speciation for 1 ppm of CsI in steam. At 900°C for this system the dominant species is actually CsOH. This shift in equilibrium is important to remember in assessing the implications of experiments performed with very low concentrations of iodine and cesium and extrapolating to accident conditions where high fission product concentrations prevail.

Finally, it is important to note that other chemical species in the system can also affect the stability of CsI. Figure 10 shows the speciation for a system with 100 ppm in 90% steam/10% H₂. The presence of additional hydrogen in this system results in a significant increase in the relative stability of CsI. In our tests, hydrogen is continuously produced along the steel pipe and this will tend to alter the CsOH concentration along the flow system. This complicates the chemistry of the system considerably and makes analysis of the reaction rates difficult.

CONCLUSION

Based on the results of this study several conclusions can be drawn:

1. The chemical behaviour of CsI in the reactor coolant system will not be strongly influenced by the presence of a moderate radiation field.

2. Dissociation of CsI in steam to form CsOH will be controlled by the equilibrium chemistry in the reactor coolant system with the important variables being the Cs/I ratio, the CsI concentration and the temperature.

3. At 900°C, CsI does not react readily with 304 stainless steel.

4. A fraction of the cesium transported as CsI may react with stainless steel (as CsOH) depending on the thermodynamic conditions in the reactor coolant system.

In applying these conclusions to accident analyses, it is important to remember that the conditions that prevail during an accident do not remain constant. The equilibrium description of the fission product chemistry will change during an accident and there will certainly be times, at the beginning and end of the fission product release phase, when CsI is not thermodynamically stable. Also, although equilibrium will likely be achieved at very high temperatures, reaction kinetics, particularly for very low fission product concentrations, may distort the chemistry of the
system considerably. Nonetheless, the results of this work indicate that, in addition to the complexities of the reactor coolant chemistry which we already face, we do not have to add the influence of a radiation field.

ACKNOWLEDGEMENTS

The authors thank R.L. Ritzman for helpful discussions during the progress of this work. The thermodynamic calculations were performed by F. Garisto. This work was funded by the Electric Power Research Institute.

REFERENCES


TABLE 1
TEST #1

Test Conditions

\[ \text{H}_2\text{O} \quad - \quad 43 \text{ mL/h (0.04 mol/min)} \]
\[ T \quad - \quad 900 \pm 10^\circ\text{C} \]
\[ \gamma \text{ Field} \quad - \quad 0 \]
\[ \text{CsI} \quad - \quad 100 \text{ ppm} \]
\[ \text{Degreased 304 stainless steel (SS)} \]

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>pH</th>
<th>Cs (mg/L)</th>
<th>I (mg/L)</th>
<th>Cs/I atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.7</td>
<td>280 ± 10</td>
<td>318 ± 10</td>
<td>0.84 ± 0.05</td>
</tr>
<tr>
<td>2</td>
<td>5.4</td>
<td>340</td>
<td>347</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>5.8</td>
<td>360</td>
<td>363</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>5.7</td>
<td>370</td>
<td>368</td>
<td>0.96</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>360</td>
<td>365</td>
<td>0.94</td>
</tr>
<tr>
<td>6</td>
<td>6.1</td>
<td>370</td>
<td>364</td>
<td>0.97</td>
</tr>
<tr>
<td>7</td>
<td>5.6</td>
<td>360</td>
<td>364</td>
<td>0.94</td>
</tr>
<tr>
<td>8</td>
<td>6.1</td>
<td>350</td>
<td>359</td>
<td>0.93</td>
</tr>
</tbody>
</table>

TABLE 2
TEST #6

Test Conditions

\[ \text{H}_2\text{O} \quad - \quad 43 \text{ mL/h} \]
\[ T \quad - \quad 934 \pm 2^\circ\text{C} \]
\[ \gamma \text{ Field} \quad - \quad 9 \text{ krad/min} \]
\[ \text{CsI} \quad - \quad 140 \text{ ppm} \]

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>pH</th>
<th>Cs (mg/L)</th>
<th>I (mg/L)</th>
<th>Cs/I atomic ratio</th>
<th>Cs/I Atom Ratio</th>
<th>H\textsubscript{2}/Ar Volume Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedwater</td>
<td>7.2</td>
<td>&lt; 0.2</td>
<td>&lt; 0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>2.8</td>
<td>450 ± 10</td>
<td>628 ± 10</td>
<td>0.68 ± 0.05</td>
<td>0.68</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>3.2</td>
<td>380</td>
<td>453</td>
<td>0.80</td>
<td>0.78</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>300</td>
<td>370</td>
<td>0.78</td>
<td>0.83</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>3.3</td>
<td>300</td>
<td>344</td>
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<td>0.88</td>
<td>0.7</td>
</tr>
<tr>
<td>5</td>
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<td>382</td>
<td>0.88</td>
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<td>0.6</td>
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<tr>
<td>6</td>
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<td>387</td>
<td>0.91</td>
<td>0.84</td>
<td>0.6</td>
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<tr>
<td>7</td>
<td>3.6</td>
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<td>375</td>
<td>0.84</td>
<td>0.86</td>
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<tr>
<td>8</td>
<td>3.8</td>
<td>270</td>
<td>299</td>
<td>0.86</td>
<td>1.04</td>
<td>-</td>
</tr>
</tbody>
</table>

Rinse
### TABLE 3
**Cs/I Ratios as a Function of Radiation Field**

<table>
<thead>
<tr>
<th>Test</th>
<th>[CsI] ppm</th>
<th>γ Field</th>
<th>Average Cs/I</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>60</td>
<td>Low</td>
<td>0.79</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>High</td>
<td>0.97</td>
</tr>
<tr>
<td>5</td>
<td>130</td>
<td>Low</td>
<td>0.84</td>
</tr>
<tr>
<td>6</td>
<td>140</td>
<td>High</td>
<td>0.84</td>
</tr>
<tr>
<td>7</td>
<td>175</td>
<td>High</td>
<td>0.97</td>
</tr>
<tr>
<td>8</td>
<td>210</td>
<td>Low</td>
<td>0.94</td>
</tr>
<tr>
<td>9</td>
<td>240</td>
<td>High</td>
<td>0.95</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>Low</td>
<td>0.81</td>
</tr>
<tr>
<td>12</td>
<td>150</td>
<td>High</td>
<td>0.81</td>
</tr>
</tbody>
</table>

* Low Field — 0.3 krad/min
  High Field — 9 krad/min

### TABLE 4
**Feedwater and Condensate Analysis**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Feedwater a (mg/L)</th>
<th>Feedwater a (mg/L)</th>
<th>CsI Solution b (mg/L)</th>
<th>Condensate c (mg/L)</th>
<th>Condensate c (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I⁻</td>
<td>&lt; 0.40</td>
<td>&lt; 0.40</td>
<td>500</td>
<td>358</td>
<td>550</td>
</tr>
<tr>
<td>F⁻</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
<td>&lt; 0.03</td>
<td>0.29</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.25</td>
<td>0.17</td>
<td>0.20</td>
<td>0.20</td>
<td>1.82</td>
</tr>
<tr>
<td>Br⁻</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
</tr>
</tbody>
</table>

a Separate samples of distilled water used to generate steam.
b 500 mg/L solution from CsI stock.
c Condensate samples from two tests.
FIGURE 1: Schematic of the Apparatus for the Experiments in the Irradiation Flask

FIGURE 2: Cutaway Drawing of the Fission Transport Test Flask (FTTF)
FIGURE 3: Cross-section of the FTTF Showing the Locations of the Cobalt-60 Pencils in the Rotatable Source Drums

FIGURE 4: Central Gamma-Field Intensity as a Function of Distance Along the Irradiation Zone with Four 111 TBq Cobalt-60 Pencils Located in the Maximum Field Position (1 Rad/s = 0.01 Gy/s)
FIGURE 5: Averaged Cs/I Ratio in the Condensate as a Function of the CsI Concentration in the Steam Flow

FIGURE 6: SEM Micrographs of the Oxide Layer on a Sample Coupon After a Test. The right image is an enlargement of the left micrograph.
FIGURE 7: EDAX Spectra of the Interface Between the Two Oxide Layers Showing Chromium Rich (E2 and E3) and Iron Rich (F) Phases

FIGURE 8: Thermodynamic Equilibrium Calculation of Species Concentrations for 100 ppm of CsI in Steam. Below 900 K the dominant species is CsI(c), not shown.
FIGURE 9: Thermodynamic Equilibrium Calculation of Species Concentrations for 1 ppm of CsI in Steam. Below 900 K the dominant species is CsI(c), not shown.

FIGURE 10: Thermodynamic Equilibrium Calculation of Species Concentrations for 100 ppm of CsI in 90% Steam/10% H₂. Below 900 K the dominant species is CsI(c), not shown.
DISCUSSION

J.P. LONGWORTH What were the mass transfer rates to the surface and would you expect significant removal of any CsOH produced by thermal decomposition of CsI?

D.J. WREN The steam flow in our tests was laminar and transport of CsOH to a surface was diffusion controlled. The diffusion time for transport from the centre of the pipe to the wall was on the order of the transport time through the pipe, i.e. a few seconds.

J.P. LONGWORTH In longer residence time reactor accident sequences would you expect higher production of CsOH (for example, you observed 5% in your short residence time experiments and 25% in the longer residence time experiment)?

D.J. WREN Clearly the residence time will be very important in determining the fraction of Cs from CsI, as CsOH, which can react with a surface. The equilibrium CsI + H₂O ⇌ CsOH + HI is very rapidly established at > 900°C. The actual amount of CsOH reacting with a surface will depend on mass transport of water through the gas phase and the surface oxide layer in addition to the residence time. It must also be remembered that there will be an excess of CsOH present due to the Cs/I > 1 ratio in the fuel. Thus there should not be any apparent decomposition of CsI until the excess CsOH has reacted with the surfaces available.

P. KLAZEK Did you try to duplicate Sandia experiments? If so, were you able to reproduce their results? i.e., did you observe a different result or are you arguing the interpretation of the Sandia observations?

D.J. WREN Our experiments duplicated the original conditions of flow rate, material and concentrations, and we bracketed their radiation field. We could not reproduce their results. We saw less decomposition and no influence of radiation on the fraction of CsI decomposed.

P. KLAZEK Since Sandia now agrees with your interpretation, how do they explain their original observations?

D.J. WREN Elrick & Powers now agree that radiation is not important. They have not explained their earlier results. More recently, they have performed other experiments with no radiation field, and they can explain the decomposition observed there in terms of CsI thermal decomposition to CsOH and subsequent reaction of the CsOH with the surfaces.
A.C. VIKIS Often we are concerned that products formed at high temperatures are frozen as the system enters the low temperature regime, because of kinetics. Do these experiments tell us anything about this concern?

D.J. VREN It is difficult to draw conclusions on kinetics from our experiments since they were not designed for this purpose. It is also a little difficult to calculate the thermodynamic equilibrium at every point in our system due to a dynamic increase in the $H_2$ concentration along the length of the pipe as the surface is oxidized by the steam. However, we did not observe any evidence for CsOH deposited as a solid at the end of our apparatus (either on coupons or the pipe) along with the solid CsI which was collected. Rinses of these deposits never had a pH greater than 7. One would have expected at least a few % CsOH in the solid condenser if the gas phase composition at 900°C was "frozen" during the cooling and condensation, but essentially no CsOH if the equilibrium shifts to that relevant at lower temperatures during the short time (fractions of a second) that it takes for the gas to transit the temperature gradient from 900°C to the condensation temperature. This suggests that in this temperature range the reaction kinetics are at least fast enough to prevent products formed at high temperatures from being frozen in a highly non-equilibrium state.

P.E. POTTER We should say that one can observe considerable decomposition of CsI with formation of CsOH with surface oxides, it is essential to define conditions accurately.

S. DICKINSON We did some studies of the reaction of cesium hydroxide vapour with 304 stainless steel, using similar conditions and cesium hydroxide concentrations as you have used. We also found that we could not detect any Cs in the oxide surface using EDAX (Energy Dispersive X-ray Analysis) - we had to go to a more sensitive analytical technique such as SIMS (Secondary Ion Mass Spectrometry) before we found the cesium. This would support your assumption about the fate of the "missing" cesium.

R. TZMAN The paper shows that radiation in the RCS circuit of a reactor will probably have no impact on CsI stability but there is a thermal hydrolysis equilibrium that will exist. At high enough temperatures, low enough CsI concentrations, and long enough residence times, high levels of decomposition can occur. These can be permanently fixed by reaction of the CsOH hydrolysis product with oxidized stainless steel surfaces but the degree depends on all the associated conditions including the presence of hydrogen and other species that could be present in the RCS, such as basic acid and materials vaporized from the overheated fuel. The real situation is obviously complex and not easily predicted.
DISCUSSION ON SESSION I

K. ISHIGURE We are getting a better understanding of the radiolytic reactions of iodine systems. The next job is to investigate the effect of impurities on these reactions. We want to know which impurities should be examined and at what levels. Is there anyone who can comment on this?

P.N. CLOUGH There has been concern that attempts to extrapolate kinetics and mechanisms from high concentrations typical of severe accidents may be misleading for application at lower concentration in design basis accidents. Do the experts think that with the greatly increased information now available, unified approaches spanning the full concentration range are valid, or appropriate? Also, when considering very low trace concentrations of iodine \( < 10^{-8} \) M, has any serious consideration been given to the ambient background concentrations of iodine which might be present, for example at nuclear power stations on coastal sites?

J. PAQUETTE Comment on low concentrations. At low concentrations the effects of impurities can be quite important since the concentration of impurities would be higher than that of iodine. This is not the case for higher concentrations of iodine.

B.J. HANDY I refer to Steve Daish's paper on results from ORNL. It was suggested that I\(^-\) would be oxidized to I\(_2\) by Fe(III) in the magnetite oxide layers. I suggest that any oxidized iodine species would be reduced rapidly by the Fe(II) in the magnetite and that the only iodine species would be I\(^-\). Have you any comments on this?

E.C. BEAHM On the Fe(III) reaction, clearly this would not be expected at equilibrium.

K. ISHIGURE I already mentioned that we have been getting a better understanding, but we still do not know much about the mechanism of formation of the iodine species with high oxidation states, such as IO\(_5\). For instance, when we do computer simulations on the radiolysis of iodide solutions, the calculated results agree rather well with experiments in systems where I\(_2\) is the only major product, but the agreement is not good with dilute iodide solutions. Another area is the formation of organic iodides. We need to do more in these areas.
J. PAQUETTE  Organic iodide formation. Organic iodides can be formed in all three phases: aqueous, gaseous, and on surfaces; in the aqueous phase: thermal and radiolytic reactions and on surfaces via thermal and radiolytic reactions with paints. In the gas phase radiolytic reactions are less likely than in other phases due to scavenging of organic radicals by atmospheric oxygen.

B.J. HANDY  I agree with Jean Paquette’s comments on the possible mechanisms, on organic iodide formation, but feel that surface processes are probably not important. Has anyone any views on this?

E.C. BEAUM  In our studies most of the organic iodide was formed in aqueous solution rather than in the gas or solid phases.

E.C. BEAUM  Don Palmer’s statement about moderately high pH is applicable to the chemistry study, but is extremely high compared to reactor water pool conditions.

J. PAQUETTE  A comment relating to Palmer’s paper: J.C. Wren et al. (Can. J. Chem. 64, 1986) could detect I$_2$OH$^-$ using Raman Spectroscopy in 1N NaOH. However, when the pH was lowered to 10, I$_2$OH$^-$ could not be detected, which is as expected since I$_2$OH$^-$ should be less stable at low pH.
II. THERMODYNAMIC MEASUREMENTS
ON THE EXISTENCE OF IODIDE BORIC ACID COMPLEXES IN SATURATED STEAM

D.J. Turner

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ABSTRACT

Current knowledge concerning the behaviour of ions in high temperature water and in steam suggests that heavily solvated, but otherwise relatively free ions, could exist in saturated steam at much lower temperatures than would conventionally be considered possible. At realistic pH levels, the thermodynamic stability of ions in steam at 285°C does not have to be very great for dissociated species to predominate over molecular HI. It is also suggested that, largely as a consequence of entropy effects, an iodide, solvated in part by H₃BO₃ molecules, could be even stabler at sufficiently high levels of H₃BO₃. Thus the volatility could be expected to increase with H₃BO₃ concentration but not with [H⁺]. Such trends have recently been observed in laboratory studies at ORNL.

In attempting to model the vapour phase behaviour of iodine in SGTR faults, it is important to realize that these ionized species will not behave like normal gaseous molecules. Their behaviour is likely to be largely determined by the transformations they undergo in temperature and pressure gradients.

1. INTRODUCTION

In order to ensure that environmentally significant quantities of fission products could not escape from an operating PWR it is necessary to give detailed consideration to a number of hypothetical accident sequences and their consequences. One such involves the simultaneous occurrence of a leak from a ruptured steam generator tube and either a stuck-open relief valve or a main steam line break. In this type of accident, primary coolant will escape into the steam generator and be evaporated to an extent which depends on the details of the accident.

In assessing how much iodine could escape, it is important to know the fraction which becomes volatilized. This is likely to depend on the extent to which evaporation of the coolant has occurred, on the temperature of the solution and on its pH. Since the water in both the primary and secondary circuits will normally be chemically reducing, the iodine will only be present as iodide until oxygen can reach the steam generator. Significant cooling will normally have occurred first.

Before this, the complex equilibria involving the very volatile I₂ and its oxidation products would not be involved. Thus, one might expect it to be a relatively straightforward matter to estimate the fraction of iodine
that would be in the vapour phase during the earlier stages of any specific fault sequence.

In practice it has not proved straightforward, partly because there are still serious differences between the various measured extents of iodide partitioning and partly because none show the dependence on composition which was expected. The paper discusses some of these discrepancies and offers a qualitative explanation.

2. PREDICTION OF IODIDE PARTITIONING

Except at very high temperatures, it is not normally expected that ions would be significantly volatile. Thus, since HI is a strong acid at room temperature, one would expect its dilute solutions to be largely dissociated and the iodide levels above them very low. At higher temperatures, the acid becomes weaker, so that the dissociation equilibrium

\[ HI = H^+ + I^- \]  (1)

will lie increasingly to the left as temperatures increase and one might expect to be able to detect some HI in the vapour even over quite dilute solutions.

In a mixture where other species (e.g. borate and lithium) greatly predominate over iodide, the pH will be determined by the other (higher concentration) species, so that the fraction of iodide present as HI and hence the volatility, should be proportional to the hydrogen ion concentration, \([H^+]\).

In other words, the water/steam partition coefficient, P should be given by

\[ P = \frac{[HI] + [I^-]}{[HI]_v} \approx \frac{[I^-]}{[HI]_v} = \frac{D.K}{[H^+]_v} \]

where D is the water/steam distribution coefficient for molecular (fully associated) HI and K is its dissociation constant. Concentrations (all in molal units) are suffixed by v for the vapour phase. No suffix implies the aqueous phase.

When we first considered this system [1], the main object was to make the best possible estimates of D and K but to ensure that, where there were uncertainties, the estimated iodide volatilities would err on the conservative (high) side. D is determined by the difference in free energy of hydration of the molecule in the liquid and vapour phases. In another context, the various terms which determine these free energies have been considered [2]. From this work it seems clear that, in the absence of significant hydrogen-bonding to either solute, D would be very similar for HI and for the similarly sized, isoelectronic rare gas Xe.

The hydrogen atom in molecular HI must lie well within the electron cloud of the halogen atoms as it does even when combined with much
smaller atoms like O and F [3]. Since H-bonding is generally only a major influence in the chemistries of the elements of the first period and decreases in importance quickly for later periods, its influence should be negligible in the solvation of HI. Thus it would be surprising if D for molecular HI differed markedly from its value for Xe. HI does have a small dipole moment so that even if there were no H-bonding it would presumably favour the aqueous phase slightly more than would Xe. The effect is probably not large, however, and any errors introduced would tend to overestimate the steam solubility and therefore be pessimistic with respect to estimates of iodine volatility.

The dissociation constant of HI has not been measured. However, that for HCl as well as for NaCl and KCl has been measured along the SVP curve to 306°C [4]. Those for HBr [5], NaCl [6], NaBr [7] and NaI [8] have been extensively studied between 400°C and 800°C over a wide density range. Simple relationships between ionic dissociation constants, solvent densities and temperature have been found [9], [10]. They allow the supercritical data to be roughly extrapolated to 300°C.

These studies imply dissociation constants of a rather similar magnitude for all the halides with the acids being significantly weaker electrolytes than their salts. Detailed consideration is given in the Appendix to the differences between the various halides and reasons advanced why the dissociation constant of HI is taken here to have a value close to twice that of HCl. Accordingly (using the more conservative of the two available sets of data) it was initially assumed that at 300°C, K for HI is roughly 0.07.

From these values of D and K and from the appropriate pH (calculated from knowledge of the relevant chemistry), P values were calculated at 285°C and compared with what data were then available [11], [12], [13]. It was necessary to apply a degree of selectivity among the various experimental findings [1] as there were fairly wide discrepancies. However, there appeared to be valid reasons for rejecting the most extreme values and it was concluded [1] that P would always exceed a value of $10^3$ for any real fault involving a steam generator tube break. This value means that iodide volatility would be insignificant compared with 0.1% mechanical entrainment of droplets.

The exercise also supported our expectation that the assumptions involved in the estimation of D and K were pessimistic. They predicted HI volatilities roughly ten times higher than the better experimental information. For reasons discussed at greater length in the Appendix it seems likely that K is more in error than D. The reason, basically, is that the conventional dissociation constant counts both molecular HI and $H_3O^+I^-$ ion pairs as associated. Clearly, only molecular HI is likely to be as volatile as Xe. Also the selected K value was conservative.

On this basis, we concluded [1] that the dissociation constant of molecular HI at 300°C is 0.7 mol kg$^{-1}$. The values recommended for assessing steam volatilities at lower temperatures [14] were obtained by interpolating between this value and the 25°C value of McCoubrey [15] using the method outlined in the Appendix.
At this stage it was possible to feel reasonably happy that we had a consistent, reliably conservative, picture of how much iodide could enter the vapour phase at any temperature relevant to design basis faults. Better experimental data were clearly needed, but it was appreciated that these were difficult to obtain. When available, the assessment could obviously be updated.

3. MEASUREMENTS OF IODIDE PARTITIONING

The most obvious feature of the measurements just referred to [11], [12], [13], apart from the discrepancies manifested, was their failure to show the expected dependence of $P$ on $\text{pH}$. In view of the discrepancies, this is perhaps not surprising. However, the results of Martucci [11], exhibited neither significant scatter nor a $\text{pH}$ dependence, despite the fact that the solutions must have spanned a range of nearly 1 $\text{pH}$ unit. They suggested a $P$ value of $3.3 \pm 0.5 \times 10^4$ independent of composition.

Recently, a new, quite extensive, set of measurements has been reported from the Oak Ridge National Laboratory (ORNL) by Clinton and Simmons [16]. The experiments covered a wide range of $\text{pH}$, borate and lithium concentrations appropriate to PWR primary circuit chemistry. Again the results were rather unreproducible but they still clearly showed a lack of $\text{pH}$ dependence at fixed boric acid concentration. They did show, however, a marked increase in iodine volatility with increasing borate concentration, $P$ values decreasing from nearly $2 \times 10^4$ in pure water to $200$ in 0.2 molal borate for argon sparged (presumably oxygen free) solutions.

It can be notoriously difficult to make measurements of this kind which are both reproducible and unbiassed, even in systems which are not subject to oxidation problems. Some of the unreproducibility in this case is undoubtedly a consequence of oxygen in the system. This would be expected to lead to high volatility since $I_2$ is very volatile and HIO is believed to be significantly volatile near 300°C [17]. Even in the argon sparged solutions, it is possible that, in between runs, partial oxidation of any magnetite on the vessel's internal surface takes place. This might lead to some oxidation subsequently and an overall decrease in the measured values of $P$. However, it does not explain the effect of added borate or the absence of an effect of $\text{pH}$. (All known iodine hydrolysis reactions predict higher volatility at low $\text{pH}$.)

In this paper we shall consider the possibility that iodide does represent the predominant iodine species in the argon sparged solutions. If one is prepared to consider the possibility that (under the $\text{pH}$ conditions of interest) iodide enters the steam predominantly in the ionized form, the lack of an influence of $\text{pH}$ on $P$ becomes understandable. Recent work in our laboratory appears to be relevant in this context.

4. IONS IN A COMPRESSIBLE SOLVENT

Our work in this area stems from the fact that there is virtually a complete absence of reliable equilibrium constants of certain kinds for aqueous electrolyte systems above 300°C along the saturation line. Data in steam are also lacking except in the highly compressed supercritical fluid. Fig. 1 illustrates the areas of pressure and density where reliable ionic
dissociation constants have been measured. Clearly, most power plant
(boiling at 350°C) operate in the region where there are no experimental
data. Clearly, also, there are no data at all for saturated steam.

Serious experimental difficulties are encountered when working in
this area. However, in the author’s opinion [18], [19] the main problem is
that the standard theories for electrolyte solutions (Debye-Hückel theory,
Onsager conductance law, the Bjerrum theory of ion association and their
various improvements) apply only to incompressible solvents. Steam and
water, in the region of current interest, definitely are not incompressible.
The small programme at CERL, which includes both experimental and
theoretical work, was started to address this problem. The associated
complication of gravitationally induced sedimentation is also receiving some
attention [18], [20].

In addition to our work, studies of some of the main
(non-gravitationally disturbed) aspects of the problem are being actively
pursued elsewhere [21]—[29]. Of particular relevance in the present context
is a point made by Quint and Wood [29] that, in theory, an isolated ion in
saturated steam could electrostrict around itself an infinite amount of
water. In practice, although one expects very large hydration numbers for
those ions which do enter the vapour phase, the size of the clusters is
extremely sensitive to the vapour pressure and an isolated ion in perfectly
isothermal saturated steam bears little relation to the real world. Such
factors as competition for water by other ions, temperature gradients and
gravitational and surface influences would mean that, in practice, an ion
really just attracts as many water molecules to itself as other factors,
such as these, allow.

It is the electric field of the ion which is responsible for the
phenomenon and, since the field extends much less far for a dipolar
ion-pair, we would expect much smaller hydration numbers for such species
than for isolated ions. The conductance results of Marshall and his
collaborators [30], which were obtained on a variety of supercritical
systems, do suggest the liberation of significant numbers of water molecules
(close to 10) on the formation of ion pairs. However, there are doubts
about exactly how valid is the method of data treatment used [31] and, on
the basis of more straightforwardly interpreted data, the number of water
molecules suggested as being released (10 from Marshall’s work) seems too
small. From available density measurements on supercritical NaCl solutions
[32], [33] it is clear that many thousands of water molecules can be
electrostricted per pair of ions in dilute solution [18]. One would expect
most to be lost on ion pairing.

In steam of much lower density, it would seem reasonable to assume
that, since the dielectric constant of the solvent is much lower, any ions
present would be strongly paired and hence would be hydrated to a
comparatively small extent. Recent theoretical work [34], however, shows
that this assumption is far too naive. To date, only the slightly
compressible case has been considered [35]—[37] but two approaches have been
treated: one based on analytical approximations and the other employing
Monte-Carlo simulations.
Both show clearly that a major influence of allowing the solvent to be compressible is to decrease the charge density of the ion atmosphere near to the central ion. This implies that the solvent is more favoured there than would have been expected for an incompressible solvent. Under the conditions of much greater compressibility of present concern it is reasonable to expect a much larger effect. Thus one might well expect paired ions to be predominantly solvent separated and even isolated ions to be at least plausible components of steam of sub-critical density. These would be as heavily hydrated as competition with other ions, surface effects and gravitational sedimentation allow.

One consequence of such large hydration numbers and the correspondingly large enthalpy and entropy changes on de-solvation is that, in a slightly non-isothermal situation, one might anticipate considerable differences in the sizes of the solvated ions, the hydration numbers being smaller in the hotter regions. Thus large equilibrium Soret effects could be anticipated. The writer has, for some time, considered that the poor reproducibility of measured steam-water partition coefficients in water (usually at higher temperatures than 285°C) was in part a consequence of such phenomena. However, until the recent theoretical conclusions were established [34]-[37], he had not realized how extensively any ion pairs could be solvated. Accordingly, his first thoughts concerning the ORNL results were that they would be easier to understand if one could believe that there was a significant concentration of strongly hydrated ions in the vapour.

So far, we have only considered the form of any ions or ion pairs there may be in the steam. There remains the question of their likely concentrations at equilibrium in 285°C saturated steam.

5. STEAM AS A SOLVENT FOR IONS

It is well known that, at a density, \( \rho \), of 1.0 kg/dm\(^3\) (over a wide temperature range) water is a good solvent for ions whereas, as mentioned earlier, in air, one needs to supply a great deal of thermal energy to force many ions into the vapour. At 400°C and \( \rho = 0.3 \) kg/dm\(^3\), NaCl (among other salts) is sufficiently soluble for its dissociation constant to have been measured [6]. But for steam at 285°C, \( \rho \), the density, is 0.036 kg/dm\(^3\) which is nearly ten times lower. In general it is found, both for salts [38], [39] and non-electrolytes [40] that solubility in the vapour parallels the density. Also, the steam-water partition coefficients for simple 1:1 salts are generally of a similar order of magnitude (at fairly high densities) with NaCl amongst the least steam volatile salts.

The best studied system is NaCl-water and, if one assumes that the strong electrolytes LiI and H\(_3\)IO\(^+\) behave like NaCl, then, based on Martynova’s [41] results, we would expect water-steam partition coefficients, \( P \), to lie between \( 10^8 \) and \( 10^5 \) at 285°C. The higher figure was attributed to fully ionized species and the lower one to ion pairs. This

* This formula is used to indicate that the predominant associated form of the acid will consist of ion pairs between H\(_3\)O\(^+\) and I\(^-\) — See Appendix and Ref. [1].
division can be considered as a very valuable, though purely operational one but, in view of the recent theoretical work [34] discussed earlier, the author is now inclined to take them more literally than he and others have in the past. At a sodium chloride concentration corresponding to the electrolyte concentrations used in most of the ORNL work, a partition coefficient, \( P \), of the order of \( 5 \times 10^6 \) is probably a reasonable estimate. Lithium chloride would be over ten times more steam volatile than NaCl at 285°C [38] so that a realistic value of \( P \) could be about \( 5 \times 10^5 \) assuming that these extrapolations are valid.

On the basis of these arguments, it seems that it may not have been correct [1], [14] to discount the partitioning into steam of ions compared with neutral HI - at least not at 285°C and above. A \( P \) value of \( 5 \times 10^5 \) is only 25 times higher than most of the better ORNL values [16] applicable to zero boric acid concentrations. Such a factor may well be attributable to extrapolation errors. It thus seems worth considering whether an additional factor, plausibly attributable to boric acid, could reduce \( P \) further.

In what follows, the iodine species will be referred to as \( I^- \) although it is realized that \( \text{Li}^+ \) or \( \text{H}_3\text{O}^+ \) ions may be close by. Even if they are, all three species will be heavily hydrated, so that it is justifiable to think only of \( I^- \) hydrates. Boric acid is a Lewis acid and probably exists in the vapour phase, with a water adduct, as a roughly tetrahedral species \( \text{B(OH)}_3\text{H}_2\text{O} \). In the liquid phase, undissociated acid is the predominant form, its concentration varying by less than 1% over the pH range of current concern. Thus the borate level in the vapour will depend only on the liquid phase concentration, and not on pH.

The concentration of molecular boric acid in the vapour phase will be quite significant, so the \( I^- \) has a choice of neighbouring ligand between \( \text{H}_2\text{O} \) or \( \text{H}_3\text{B}0_3\text{H}_2\text{O} \) molecules. Anions invariably are solvated by the H atom end of a water molecule because of the small positive charge which results from the polarity of the OH bond. Similar electrostatic forces (weak H-bonds) would attract the boric acid molecule to \( I^- \) but, in this case, the ligand could attach itself by 3 (if OH groups only were used) or possibly 4 (if two OH and one \( \text{H}_2\text{O} \) groups were used). One could therefore anticipate an entropy induced advantage to complexing with boric acid which is closely analogous to that which is responsible [42] for the stability of the chelates of metal ions.

Some support for this argument is claimable from the results of mass spectral analyses of "cluster ions" in the stratosphere [43]. Predominantly the anions are species such as \( \text{HSO}_4^- (\text{H}_2\text{SO}_4)_n \). It has been found that, despite the relatively large vapour pressure of \( \text{H}_2\text{O} \) and the fact that the predominant cationic species are \( \text{H}_3\text{O}^+ (\text{H}_2\text{O})_m \) clusters, water molecules are significantly absent from the smaller cluster anions and only start to be taken up when \( n > 2 \). There will, of course, be heat as well as entropy effects, but the behaviour of \( \text{HNO}_3 \) and its replacement by \( \text{H}_2\text{SO}_4 \) is more easily rationalized as an entropy effect. Basically, solvation of ions in the gas phase is strongly favoured in terms of the enthalpy, but opposed by the entropy - because of the large loss of translational freedom of \( \text{H}_2\text{O} \) molecules. A process which can make the entropy change less unfavourable will obviously stabilize the gaseous cluster ion.
Irrespective of the relative importance of the two effects, however, it seems clear that the postulated species $\text{I}^-{(\text{H}_3\text{BO}_3)}_x\text{H}_2\text{O}_z$ is far more likely to exist than not. If the concentration of $\text{H}_3\text{BO}_3$ in the vapour at $285^\circ\text{C}$ is sufficiently high, this species will predominate over $\text{I}^-{(\text{H}_3\text{O})}_x$ (the species whose $P$ was earlier estimated at $5 \times 10^8$) and the dependence of $P$ on $\text{H}_3\text{BO}_3$ concentration but not on pH is readily explained.

We conclude that the ORNL results [16] probably represent the partition into the vapour of the species $\text{I}^-{(\text{H}_3\text{O})}_x$ and $\text{I}^-{(\text{H}_3\text{BO}_3)}_y{(\text{H}_2\text{O})}_z$. Heavily hydrated cations will be associated (at a currently unspecified distance) with all such species. We also conclude that, under PWR primary circuit conditions, these species predominate over HI molecules in the vapour phase so that the presently used methods of estimating iodine volatilities in steam generator tube rupture (SGTR) faults may be inappropriate.

6. RELEVANCE TO MODELLING OF SGTR FAULTS

If we accept that, for realistic pH values at $285^\circ\text{C}$, $\text{I}^-{(\text{H}_3\text{O})}_x$ and $\text{I}^-{(\text{H}_3\text{BO}_3)}_y{(\text{H}_2\text{O})}_z$ predominate over HI in the vapour, it is important to know whether this also applies at lower temperatures. If the partition coefficients of the simple iodide and of HI both had the same dependence on steam density and if the pH were temperature independent, then the relative concentrations of these two species would be independent of temperature. However, salts and non-electrolytes behave rather differently. It is reasonable to assume that $\text{H}_3\text{O}^-\text{I}^-$ behaves like a fully associated salt. For salts it is generally found that the log of the partition coefficient varies approximately linearly with the log of the density ratio of the two phases [38], [39]. The analogous plots for non-electrolytes (generally curved) show the opposite temperature dependence. If one assumes, as we have previously [1] that HI behaves like Xe, then, at constant pH, the ratio of HI to $\text{I}^-$ would be expected to increase with decreasing temperature but by how much it is impossible to say.

The question naturally arises as to whether these species could be responsible for the higher than expected carryover of iodide in Handy’s [44] experiments at $100^\circ\text{C}$. The author would still feel happier with some other explanation but, so far, has been unable to find a convincing reason for rejecting this possibility.

If we wish to attempt to model SGTR faults and ionized species do have to be considered as major contributors to the level of iodine in the vapour, it is important to realize that they will not behave like normal gaseous molecules. Thus, they are most unlikely to obey the gas laws and their behaviour in temperature and pressure gradients will largely determine their fate.

7. CONCLUSIONS

An assessment of what is currently known about the behaviour of ions in steam suggests that they may play a much more important rôle in steam generator tube rupture (SGTR) faults than has been believed in the past. Under the conditions of temperature and pH which apply early in these faults, it seems likely that reasonably free iodide ions predominate over
molecular HI. This may also be true at temperatures as low as 100°C, although it seems unlikely.

The ions in saturated steam will be heavily solvated and are likely to be stabilized by the presence of boric acid vapour. This stabilization probably involves the formation of hydrogen-bonded chelate rings - i.e. it is primarily an entropy effect. The recent ORNL measurements of Clinton and Simmons [16] probably represent the partitioning of hydrated (and loosely ion paired) iodide together with iodide-boric acid complexes which are also highly solvated.

In attempting to model the vapour phase behaviour of iodine in SGTR faults, it is important to realize that these ionized species will not behave like normal gaseous molecules. For example, they will not obey the gas laws. Their behaviour is likely to be largely determined by the transformations they undergo in temperature and pressure gradients.

8. ACKNOWLEDGEMENTS

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9. REFERENCES


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**Fig. 1.** Water conditions under which studies of electrolyte dissociation have been made.
APPENDIX

ION ASSOCIATION IN STRONG ACIDS

There are a number of complications in connection with the associated forms of relatively strong electrolytes which need to be considered in assessing the range of values which K for HI might be expected to take. Weak association is notoriously difficult to define quantitatively both for non-electrolytes and electrolytes (see Ref. [45]). With electrolytes, the concept is usually only invoked when the concentration dependence of some property (for example activity coefficient or conductivity) fails to follow the theoretical expectations of a strong electrolyte. Inevitably, since usable theories involve approximations and there is no universal agreement on which are best, there is uncertainty in the magnitude of the association constant which is used to fit the experimental data. This problem arises to some extent with both the hydrogen halides and their salts.

The problem is closely linked with the fact that, for salts at least, the associated form is ill-defined. No covalent bond exists between a pair of such ions even when they are in contact and, in most interpretations of, for example, conductance data, the associated form is believed to comprise contact ion pairs plus a number of other pairs where the ions are separated to various extents by solvent molecules.

With the hydrogen halides, one expects there to be analogous ion pairs derived from the species H\textsubscript{3}O\textsuperscript{+} and X\textsuperscript{-} but, in addition, there will be real covalently bound HX molecules and it is only these molecules which would be expected to have volatilities comparable with Xe.

Qualitatively, we might expect K values for halide salts whose variation with ion size should be explicable electrostatically, and whose parent acid had a somewhat lower dissociation constant due to the additional presence of molecular HX. We might also expect to find that, though absolute values of K might differ as a result of different methods of data treatment, the expected trends in behaviour for data treated by the same method would show up in any reasonably good method of treatment. This is exactly what is found in practice with the studies of Wright, Lindsay and Druga [4] based on Noyes' conductance data at 306°C [46] and in the various studies of Quist, Marshall et al. at higher temperatures and pressures [5]-[10].

The former (306°C) dissociation constants are as follows (all in moles kg\textsuperscript{-1}). K(NaCl) = 0.093; K(KCl) = 0.12; K(HCl) = 0.035, Marshall's (extrapolated to 300°C) results are K(NaCl) = 0.46; K(NaBr) = 0.50; K(NaI) = 0.98; K(H\textsuperscript{+}) = 0.15. The latter result for NaCl is roughly 5 times the SVP data and all the results are consistently higher. However, within each set of data, the differences with ion size and between acids and salts look very similar. Clearly it is prudent in the first instance to use the lower set of dissociation constants (corresponding with higher predicted volatilities). Accordingly, Marshall's results were only used to help estimate K for HI from the SVP data on HCl.
The SVP data [4] unfortunately only cover the chlorides, but the difference in $K$ for the appreciably different sized cations $\text{Na}^+$ and $\text{K}^+$ is small. One would not anticipate an appreciably larger difference between the dissociation constants of $\text{NaCl}$ and $\text{NaBr}$ or $\text{NaBr}$ and $\text{NaI}$ and the results of Quist and Marshall suggest that this is the case [6], [7], [8]. The differences are in the direction expected on simple electrostatic grounds, the dissociation constants increasing slightly from $\text{NaCl}$ to $\text{NaBr}$ to $\text{NaI}$. Based on these trends and the differences measured between the acids and their salts [4], [5], [7] a reasonable, rather conservative, assumption would seem to be that the dissociation constant of $\text{HI}$ under SVP conditions has a value roughly twice that of $\text{HCl}$ (0.035) so that we take its value as 0.07.

Significantly, in both sets of work, $K$ for the sodium salt is roughly 3 times the value for the acid and, on the basis of the SVP work [4] this ratio is comparable (3.4) for the potassium salt. Since $\text{H}_3\text{O}^+$ is close in size to $\text{K}^+$, it could be argued that the greater concentration of associated species in the acid represented the contribution of molecular $\text{HX}$ in which case 2/3 or so of what conductance studies see as an associated $\text{HX}$ species are in fact covalent molecules. It could equally mean that the potentially H-bonding ion $\text{H}_3\text{O}^+$ forms stronger ion pairs than the bare cations and there is some evidence that this is so for ion pairs between $\text{H}_3\text{O}^+$ and $\text{SO}_4^{2-}$ [47]. In deciding to use the conventional values of $K$ as determined by conductance we are again making the conservative choice since we are implicitly assigning the high volatility of molecular $\text{HI}$ to the low volatility ion pairs as well as to the molecular species. If the second explanation for the relatively low dissociation constants of the acids is correct, then use of the conventional $K$ could considerably overestimate the volatility of $\text{HI}$-containing solutions. In view of the rather small differences in $K$ for acids and their salts, this would seem to be quite likely.

As was shown in the main part of this paper, the iodine volatility predicted for PWR plant on zero solids treatment appears to be significantly overestimated and this should be the case if our understanding of the chemistry is correct since, at all stages of choice, we have made the more conservative assumption. For the reasons given above, the author believes that the discrepancy between prediction and plant findings is much more likely to lie in the choice of $K$ than in the choice of $D$. In Section 2 it was suggested that our initial choice of $K$ was roughly ten times lower than necessary and should be corrected by this factor for future analyses. (Recent attempts to estimate $P$ for $\text{HI}$ by extrapolation from low temperature volatility data [50] imply that our estimates are very conservative.)

It remains to describe how the above assumption was combined with 25°C data to give the set of $K$ values between the two temperatures which was recommended for assessing $\text{HI}$ volatility at intermediate temperatures [14].

Water is a much poorer solvent for ions at 300°C than at 25°C so that if conductance measurements cannot assign unambiguous equilibrium constants to 'strong electrolytes' at 300°C, as most authorities agree [45], they certainly cannot do so at 25°C. The approach of McCoubrey [15] nicely circumvents this problem by using a thermochemical cycle which involves an absolute minimum of assumptions (none of which could be seriously
challenged. Furthermore, his approach defines $K$ in terms of molecular HI only, which is what is required for our purposes.

The dissociation reaction itself, $HI = H^+ + I^-$, because it forms two ions from a neutral molecule is of a type which inevitably has a large (negative) heat capacity at high temperatures [48]. Thus we cannot reasonably interpolate between the data at $25^\circ C$ and $300^\circ C$ on the assumption of a temperature independent $\Delta H$ and $\Delta S$. If, however, the reaction is written in the isoelectronic form $HI + OH^- = H_2O + I^-$ (having an equilibrium constant $K_I$), then this reaction is likely to have reasonably temperature independent $\Delta H$ and $\Delta S$ values. In a great majority of cases studied to date, reactions of this type are found to have rather low (even essentially zero) heat capacities. $K$ is readily related to $K_I$ since $K = K_I K_W$ and good data on $K_W$ are available [49]. After using the $25^\circ C$ and $300^\circ C$ data to obtain $K_I$, the intermediate temperature data were interpolated and converted back to the $K$ values which may be found in ref. [14] and which are reproduced in the following Table. Interpolated values of $D$ for Xe and (by assumption) HI are also listed.

<table>
<thead>
<tr>
<th>Temp ($^\circ C$)</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$ (mol kg$^{-1}$)</td>
<td>$1.1.10^6$</td>
<td>$1.8.10^6$</td>
<td>$4.7.10^2$</td>
<td>17</td>
<td>0.7</td>
</tr>
<tr>
<td>$D$</td>
<td>$4.0.10^{-5}$</td>
<td>$1.9.10^{-6}$</td>
<td>$7.1.10^{-4}$</td>
<td>$2.3.10^{-3}$</td>
<td>$7.7.10^{-3}$</td>
</tr>
</tbody>
</table>

$D$ is for molal units in both phases.

**DISCUSSION**

P.P.S. SALUJA If the room-temperature dissociation constant were known accurately, one could determine it to higher temperatures ($300^\circ C$) using heat capacity data.

D.A. PALMER The HCl dissociation constant at $300^\circ C$ may be estimated to within a factor of 2 or 3 based on calorimetric data. This error will be reflected in estimating the dissociation constant of HI by analogy to HCl or NaCl.
IODINE DISPROPORTIONATION EQUILIBRIA UP TO 300°C

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ABSTRACT

The high-temperature behaviour of aqueous iodine is important to the nuclear industry because of the radiological significance of radioactive iodine in nuclear reactor safety and nuclear waste management. We have used calorimetric data to determine the equilibrium constant of the iodine disproportionation reaction

\[ 3I_2(aq) + 3H_2O(1) \rightleftharpoons 5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \]

up to a temperature of 300°C. Thermodynamic data derived from our heat capacity measurements for I^-(aq), IO_3^-(aq) and H^+(aq) were used in these calculations. Similar data for I_2(aq) and H_2O(l) were obtained from the literature. The equilibrium constant values determined by the calorimetric method are in good agreement with recent values obtained by the potentiometric method and with reassessed literature values.
1. **INTRODUCTION**

Interest in aqueous iodine chemistry was revived following the nuclear reactor accident at TMI-II in 1979. The high-temperature behaviour of the iodine-water system (or iodine hydrolysis) is important in understanding the volatility of iodine and, consequently, in determining the radioactive iodine release in the reactor containment building and to the environment [1-2]. The iodine hydrolytic sequence is quite complex because of the number of oxidation states available to iodine (e.g., -1(I^-), +1(HOI), +5(IO_3^-), +7(IO_4^-)). The key reaction in iodine hydrolysis, known as the iodine disproportionation reaction (IDR), involves disproportionation of molecular iodine, I_2(aq), to nonvolatile iodide, I^-(aq), and iodate, IO_3^-(aq):

\[
3\text{I}_2(\text{aq}) + 3\text{H}_2\text{O(1)} \rightleftharpoons 5\text{I}^- (\text{aq}) + \text{IO}_3^- (\text{aq}) + 6\text{H}^+(\text{aq})
\] (1)

This forward reaction is also referred to as the reverse Dushman reaction [3-4], or the iodate formation reaction [5]. Although other reactions in the iodine-water chemistry have been extensively studied and reviewed [1-2], the IDR has been neglected until recent experimental investigations of Mesmer and co-workers at ORNL [2], Turner and co-workers at CEGB [5] and Vikis and co-workers at AECL [6]. Also, the empirical attempts in the past to estimate the temperature dependence of the equilibrium constant, \(K_{IDR}\), of this reaction led to a wide range of values [1-2]; e.g., at 150°C, the predicted values differ by 16 orders of magnitude, depending on the assumptions used, such as Criss-Cobble correspondence principle [7] or Helgeson's extrapolation equation [8], and the uncertainties in the room temperature data.

Our objective in this paper is to demonstrate the temperature dependence of \(K_{IDR}(T)\) can be reliably calculated using a very few thermodynamic (in particular, heat capacity) measurements, conducted over a modest temperature range (25 to 100°C) for only four aqueous systems (i.e., CsI, CsIO_3, HCl and CsCl). More importantly, this technique forms the basis of a more reliable extrapolation of \(K_{IDR}\) from 100°C to higher temperatures (100-300°C). We compare calorimetrically determined \(K_{IDR}\) values with the recently obtained results using potentiometric methods [2,5]. We conclude that the large uncertainties in the earlier literature values of \(K_{IDR}\) at high temperatures have been significantly reduced as a consequence of recent work in three laboratories – AECL, ORNL and CEGB.

2. **THEORETICAL BASIS FOR \(K_{IDR}\) DETERMINATION**

In this section, we outline and discuss the general approach and thermodynamic relations for calculating the equilibrium constant of the IDR, \(K_{IDR}\), over the temperature range of 25 to 300°C.
2.1 GENERAL APPROACH

The equilibrium distribution of iodine among different aqueous species [I_2(aq), I^-(aq), IO_3^-(aq), IO_4^-(aq), I^+(aq)] is governed by the various equilibrium constants. In particular, the temperature dependence of the equilibrium constant of the IDR, K_{IDR}(T), is given by the thermodynamic relation:

$$\Delta_{IDR}G^°(T) = -RT \ln K_{IDR}(T)$$  \hspace{1cm} (2)

or

$$\log_{10} K_{IDR}(T) = \frac{-\Delta_{IDR}G^°(T)}{2.3026 RT}$$  \hspace{1cm} (3)

where $\Delta_{IDR}G^°(T)$ is the temperature-dependent Gibbs energy change of the IDR and is given by

$$\Delta_{IDR}G^°(T) = \Sigma \Delta_f G^°_P(T) - \Sigma \Delta_f G^°_R(T)$$  \hspace{1cm} (4)

where $\Delta_f G^°_P(T)$ and $\Delta_f G^°_R(T)$ are, respectively, the temperature-dependent standard Gibbs energies of formation of product species and reactant species over the temperature range of interest (25-300°C), and $T$ is the absolute temperature.

An excellent approach [9-10] for obtaining temperature-dependent Gibbs energies for aqueous species, $\Delta_f G^°(T)$, from a minimum amount of experimental data, is to measure heat capacities of representative solutions (in this case, iodide and iodate) over a "reasonable" range of temperature (25-100°C). The temperature-dependent heat capacity data can then be integrated to provide the required Gibbs energies and other thermodynamic properties of aqueous reactant or product ions. In addition, the data up to 100°C lead to more reliable extrapolations of $K_{IDR}$ to 300°C than the earlier extrapolations based only on the 25°C data. This extrapolation procedure eliminates the need for heat capacity measurements in the 100 to 300°C range, which are not only difficult but also require two types of calorimetric designs, one for the 25-150°C temperature range and the other for the 100-300°C range [9].
2.2 THERMODYNAMIC RELATIONS FOR THE IODINE DISPROPORTIONATION REACTION

The Gibbs energies of formation for aqueous species, \( \Delta_f G_{as}^0(T) \), at elevated temperatures can be accurately calculated using experimentally derived heat capacities and the following exact thermodynamic relation:

\[
\Delta_f G_{as}^0(T) = \Delta_f G_{as}^0(298.15) - S^0(298.15) (T-298.15) - T \int_{298.15}^{T} \frac{C_{P,as}^0(T)dT}{T}
\]

\[\leq \]

\[
+ \int_{298.15}^{T} C_{P,as}^0(T)dT
\]

(5)

where \( \Delta_f G^0(298.15) \) and \( S^0(298.15) \) are standard Gibbs energy of formation and entropy at room temperature (for convenience, the room temperature 298.15 K has been abbreviated to 298 K in the rest of this paper). \( C_{P,as}^0(T) \) is the temperature-dependent partial molar heat capacities for the aqueous species of interest. Similarly, the Gibbs energy of reaction, \( \Delta_{IDR} G^0(T) \), and the equilibrium constant, \( K_{IDR}(T) \), for the overall disproportionation reaction, Eq. (1), can be calculated at higher temperatures using the following expressions:

\[
\Delta_{IDR} G^0(T) = \Delta_{IDR} G^0(298) - \Delta_{IDR} S^0(298)(T-298) - T \int_{298}^{T} \frac{\Delta_{IDR} C_P^0(T)dT}{T}
\]

\[\leq \]

\[
+ \int_{298}^{T} \Delta_{IDR} C_P^0(T) dT
\]

(6)

and

\[\log_{10} K_{IDR}(T) = -\Delta_{IDR} G^0/(2.3026 RT)
\]

(3)

where \( \Delta_{IDR} G^0(298) \) and \( \Delta_{IDR} S^0(298) \) are, respectively, the change in the Gibbs energy and entropy of the IDR at room temperature. \( \Delta_{IDR} C_P^0(T) \) is the difference in the partial molar heat capacities of the product species, \( C_{P,p}^0(T) \), and the reactant species, \( C_{P,r}^0(T) \), over the temperature range of interest (25-300°C) and is given by:

\[
\Delta_{IDR} C_P^0(T) = \Sigma C_{P,p}^0(T) - \Sigma C_{P,r}^0(T)
\]
For Reaction (1),

$$
\Delta_{\text{IDR}} C_p^o(T) = 5C_p^{\text{I}_2(aq)}(T) + C_p^{\text{IO}_3(aq)}(T) + 6C_p^{\text{H}_2O(1)}(T) - 3C_p^{\text{I}_2(aq)}(T) - 3C_p^{\text{H}_2O(1)}(T)
$$

(7)

3. THERMODYNAMIC DATA REQUIREMENTS FOR $K_{\text{IDR}}$ CALCULATIONS TO 300°C

A close examination of the IDR [Eqs. (1), (6) and (7)] indicates that room-temperature thermodynamic data for the overall IDR and temperature-dependent partial molar heat capacities for each of the five reaction species are needed for calculating disproportionation equilibrium constants, $K_{\text{IDR}}(T)$, in the 25 to 300°C range. The sources of the thermodynamic data at ambient temperature and the high-temperature data are discussed below.

3.1 ROOM-TEMPERATURE DATA FOR IDR

Values of $\Delta_{\text{IDR}} G^o(298)$ and $\Delta_{\text{IDR}} S^o(298)$ are available in the literature [2,5] and are quite reliable. For this work, the 298 K values for $\Delta_{\text{IDR}} G^o$ and $\Delta_{\text{IDR}} S^o$ taken from the recent work at ORNL [2] are 267.87 kJ·mol$^{-1}$ (or $10^{10} K_{\text{IDR}}(298) K = -46.93 \pm 0.22$, and 16 $\pm$ 9 J·K$^{-1}$·mol$^{-1}$, respectively.

3.2 THERMODYNAMIC DATA FOR REACTANTS $I_2(aq)$ AND $H_2O(1)$

For $I_2(aq)$, the $C_p^o(T)$ values were taken from a recent assessment [11] of Lindenberg’s data [12] on the temperature dependence of the solubility of iodine in water from 0 to 112.3°C. The temperature-dependent heat capacity function for $I_2(aq)$ is given by

$$
C_p^o[I_2(aq)] = 2.0504 \times 10^2 + 0.24691 T + \frac{2.7974 \times 10^6}{T^2}
$$

(8)

The $C_p^o$ values for $I_2(aq)$ at 25, 50, 75 and 100°C were calculated using Equation (8) and are given in Table 1. For $H_2O(1)$, $C_p^o(T)$ values, obtained from Kell [13], are also given in Table 1.
3.3 THERMODYNAMIC DATA FOR I^-(aq), IO_3^-(aq) AND H^+(aq)

An optimum approach, which we adopted, involved heat capacity, \( C_p \), measurements in the 25-100\(^\circ\)C temperature range for aqueous electrolyte solutions containing each of the three product ionic species [9-10]. In particular, heat capacity, \( C_p(T,m) \), measurements for CsI, CsIO_3, HCl and CsCl were completed at four temperatures (25, 50, 75 and 100\(^\circ\)C at a constant pressure of 0.6 MPa) over a wide concentration (molality, \( m \)) range [9]. A state-of-the-art heat capacity flow microcalorimeter system used for these measurements is shown schematically in Figure 1. Details of the apparatus used for this work and the procedure are described in detail elsewhere [9, 14]. Subsequently, Pitzer's ion-interaction model [10] was applied to our measured data to develop equations and parameters permitting interpolation of thermodynamic data (heat capacity, Gibbs energy, enthalpy, etc.) within the experimental temperature range (25-100\(^\circ\)C) and reliable extrapolation to the 100-200\(^\circ\)C range [9-10, 14-16]. The temperature and pressure dependence of heat capacities, \( C^°(T,P) \), and derived thermodynamic properties (e.g., Gibbs energies, \( G^°(T,P) \)) were represented by equations that use theoretical principles to combine the short-range (virial-type) and the long-range (coulombic or Debye-Hückel type) interactions for modelling aqueous ionic solutions [10].

The temperature-dependent \( C^° \) values for aqueous CsI, CsIO_3, HCl and CsCl at 25, 50, 75 and 100\(^\circ\)C were obtained from recently published data from our laboratory [9-10]. The conventional \( C^° \) values for aqueous ions as a function of temperature can be calculated using the standard convention, \( C^°_p[H^+(aq)] = 0 \) J·K\(^{-1}\)·mol\(^{-1}\), at all temperatures. Thus, the \( C^°_p \) values for the three product species at each temperature were calculated using the following equations:

\[
C^°_p[C\text{I}^-(aq)] = C^°_p[H\text{Cl}(aq)]
\]

\[
C^°_p[\text{Cs}^+(aq)] = C^°_p[\text{CsCl}(aq)] - C^°_p[H\text{Cl}(aq)]
\]

\[
C^°_p[I^-(aq)] = C^°_p[\text{CsI}(aq)] - C^°_p[\text{Cs}^+(aq)]
\]

or

\[
C^°_p[I^-(aq)] = C^°_p[\text{CsI}(aq)] - C^°_p[\text{CsCl}(aq)] + C^°_p[H\text{Cl}(aq)]
\]

Similarly,

\[
C^°_p[\text{IO}_3^-] = C^°_p[\text{CsIO}_3(aq)] - C^°_p[\text{CsCl}(aq)] + C^°_p[H\text{Cl}(aq)]
\]

Thus, \( C^°_p \) values for the product ionic species (the right-hand side of Eq. (1)), at each temperature, are given by

\[
\sum C^°_p = 5 \ C^°_p[\text{CsI}(aq)] + C^°_p[\text{CsIO}_3(aq)] - 6 \ C^°_p[\text{CsCl}(aq)]
\]

\[
+ 6 \ C^°_p[H\text{Cl}(aq)]
\]
The conventional ionic $\Delta_C^0$ values for $I^-(aq)$ and $IO_3^-(aq)$ calculated from Equations 9-11 are given in Table 1 at 25, 50, 75 and 100°C along with $\Delta_C^0(T)$ values for the IDR.

The partial molar heat capacity data, $C_P(T)$, for reactant and product species from Table 1 were used in Eq. (7) to calculate the change in the partial molar heat capacities, $\Delta_{IDR}C_P(T)$, for Reaction (1). The calculated $\Delta_{IDR}C_P$ values at each of the four temperatures are also listed in Table 1. Until recently such high-temperature data for aqueous species and for reactions in solutions have generally been unavailable [2,5,9] to allow comparisons with the literature. In particular, a single value of $-1802 \pm 41 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $\Delta_{IDR}C_P$ has recently been reported by Palmer et al. [2] at ORNL. This value is based on the temperature dependence (second derivative) of the equilibrium constant, $K_{IDR}$, determined by the potentiometric measurements of iodine solutions and it represents a temperature-averaged effective value, $\Delta_{IDR}C^°(T)$, constant over the experimental temperature range (277-482 K). The temperature-averaged value for $\Delta_{IDR}C^°(T)$, derived from our calorimetric data at four temperatures is, $-1754 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Good agreement between the $\Delta_{IDR}C^°$ values determined by these two methods offers further confirmation to our premise (see Section 4.2 for a detailed discussion) that even a poor estimate of heat capacities can yield reliable equilibrium constant data for reactions in solutions at higher temperatures, provided room-temperature data for the reaction are available.

4. RESULTS AND DISCUSSION

4.1 EQUILIBRIUM CONSTANT, $K_{IDR}$ AT 50, 75 AND 100°C

Calculation of the high-temperature equilibrium constants for Reaction (1) requires the temperature dependence of the reaction heat capacity, $\Delta_{IDR}C^°(T)$. Over the experimental temperature range of 25-100°C, $\Delta_{IDR}C^°$ changes only by about 7% (120 J K^{-1} mol^{-1}) with an average value of $-1754 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Since the calculated value of $K_{IDR}$ is not very sensitive to the small changes (7%) in $\Delta_{IDR}C^°$, the reaction heat capacity, $\Delta_{IDR}C^°(T)$, is assumed to remain constant at an effective value of $-1754 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ over the experimental range of temperature (298-373 K). Thus, Eq. (6) for $K_{IDR}$ calculations can be reduced in practice to the following simplified form, similar to the expression used frequently in the literature [8,11]:

$$\Delta_{IDR}G^°(T) = \Delta_{IDR}G^°(298) + [\Delta_{IDP}C^°]_{298} - \Delta_{IDR}S^°(298)](T - 298) - T \Delta_{IDP}C^°(298) \ln(T/298)$$

(13)
The assumption that \( \Delta_{IDR} C^\circ_{P,298} \) remains constant between 25°C and 100°C introduces an error that is generally much less than the precision of the room-temperature data for aqueous species and reactions.

The Gibbs energy of reaction, \( \Delta_{IDR} G^\circ \), and the equilibrium constant, \( K_{IDR} \), were calculated from Eqs. (13) and (3), respectively, at 50, 75 and 100°C. Our \( K_{IDR}(T) \) values at these temperatures are compared with the \( K_{IDR}(T) \) results of Palmer et al. [2] and the \( K_{IDR}(T) \) results of Ashton et al. [5] (Table 2). These literature values of \( K_{IDP} \) have been determined recently by direct potentiometric measurements for Reaction (1) in the temperature range 3.8-209°C by Palmer et al. [2] at ORNL and in the range of 25-200°C by Ashton et al. [5] at CEGB, U.K. It should be noted that Ashton et al. [5] consider their \( K_{IDR} \) results below 100°C less reliable because of the poor (sluggish) response of the \( \text{I}_2/\text{I}_3^- \) electrode. The agreement among the calorimetrically determined equilibrium constants, \( K_{IDR} \), and the potentiometric set of \( K_{IDP} \) data [2] at three modest temperatures of 50, 75 and 100°C is excellent (Table 2).

Next, we discuss our calculation procedure for predicting the values of \( K_{IDP} \) at "higher" temperatures (100-300°C), beyond those verified by the direct heat capacity measurements in the 25-100°C range. These calculations will permit a comparison of the calorimetric predictions with the recent experimental \( K_{IDR} \) determinations of Palmer et al. [2] and Ashton et al. [5] in the 100 to 200°C temperature range, and with the reassessed literature values of Turner [1] in the 200-300°C range. In addition, we compare our \( K_{IDR} \) values, interpolated at 35.1 and 73.5°C, and extrapolated to two lower temperatures of 3.8 and 14.7°C with the \( K_{IDR} \) values of Palmer et al. [2] directly determined at these temperatures.

### 4.2 Predictions of Equilibrium Constants, \( K_{IDR} \), to 300°C

The prediction of \( K_{IDR} \) to 300°C uses the well-known advantage of the heat capacity approach [9,11,17]. Simply stated, the premise is that even a poor extrapolation of experimental reaction heat capacities, \( \Delta_{IDR} C^\circ_{P} \), in the 25 to 100°C temperature range to higher temperatures (~300°C) should yield quite accurate values of \( K_{IDR} \). The underlying principle is that the \( \Delta_{IDR} C^\circ_{P}(T) \) is related to the second temperature derivative of the equilibrium constant, \( \log_{10} K_{IDR}(T) \), according to the well-known thermodynamic relations:

\[
\frac{\partial \ln K_{IDR}(T)}{\partial T} \bigg|_P = \frac{\Delta_{IDR} H^\circ(T)}{RT^2}
\]  

(14)
Thus, even the most accurate, directly determined data for the equilibrium constants, K(T), as a function of temperature do not provide a reliable determination of the heat capacity change, \( \Delta C^\circ_p \), for a given reaction [17]. In particular, even small errors of \( \pm 0.00025 \) pK units (corresponding to an error of \( \pm 0.00025 \) in the equilibrium constant, K) for an acid-base equilibria, \( \text{AH}^+ + B \rightleftharpoons A^- + BH^+ \), can lead to large uncertainties in reaction heat capacities, \( \Delta C^\circ_p \), exceeding in some cases \( \pm 80 \text{ J K}^{-1} \cdot \text{mol}^{-1} \) for a 50 K range. Conversely, even a poor estimate of the temperature dependence of \( \Delta C^\circ_p \) can provide quite accurate equilibrium constants, K, up to rather high temperatures, provided that the reaction Gibbs energy, \( \Delta G^\circ \), and entropy, \( \Delta S^\circ \), are known accurately at room temperature.

The 298 K data for Reaction (1) is available from the assessment of earlier literature [1,2] and has also been confirmed recently [2] by a direct determination of K at 298 K, where potentiometric measurements are relatively easy and, thus, more reliable. Reaction heat capacities, \( \Delta C^\circ(T) \), as a function of temperature, which are required for K(T) calculations in the higher temperature range of interest (100-300°C), can be approximately determined from the experimentally determined \( \Delta C^\circ \) values at 25, 50, 75 and 100°C either by a graphical extrapolation of the experimental values, or using a heat capacity function, \( \Delta C^\circ(T) \), based on the reaction heat capacities at 25, 50, 75 and 100°C (See Table 1). However, an explicit function for the temperature-dependence of the reaction heat capacity, \( \Delta C^\circ(T) \), beyond the experimental temperature range of 25 to 100°C is not used in the present calculations in view of a very limited data set for \( \Delta C^\circ \). In this paper, the high-temperature (100-300°C) values for K have been calculated using the \( \Delta C^\circ \) value of \(-1723 \text{ J K}^{-1} \cdot \text{mol}^{-1} \) and the simplified expression, Eq. (13), for \( \Delta G^\circ(T) \) rather than the exact thermodynamic relation, Eq. (6).

A more quantitative and detailed treatment, using a rigorous function for the temperature-dependence of the reaction heat capacity, \( \Delta C^\circ(T) \), which is derived from a larger data set of iodide and iodate containing solutions, is currently being examined to further refine K predictions, particularly in the 200-300°C temperature range. This work [18] will be published in the near future along with our high-temperature studies for (a) the triiodide equilibria, \( \text{I}_2(aq) + \text{I}^-(aq) \rightleftharpoons \text{I}_3(aq) \), (b) \( \text{I}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOI}(aq) + \text{H}^+(aq) + \text{I}^-(aq) \), and (c) \( \text{HI}(aq) \rightleftharpoons \text{H}^+(aq) + \text{I}^-(aq) \).
4.3 COMPARISON OF K_{IDR} PREDICTIONS TO 300° WITH THE LITERATURE

Earlier, we demonstrated an excellent agreement (see Section 4.1 and Table 2) between our K_{IDR} values up to 100°C with the literature K_{IDR} data derived from the potentiometric measurements [2,5]. Figure 2 shows a comparison of K_{IDR} values to 300°C, predicted from our calorimetric data in the 25 to 100°C range, with the literature K_{IDR} values up to about 300°C [2,5]. These recent K_{IDR} values have been independently determined by Palmer et al. [2] and Ashton et al. [5] using potentiometric measurements. In addition, the literature K_{IDR} values, based on Turner's reassessment [1] of the old (1964) iodine volatility data, are included in Figure 2 for comparison. The agreement between the various sets of K_{IDR} values in the 100-175°C temperature range is very good. However, our K_{IDR} values in the 175-209°C temperature range differ somewhat from the K_{IDR} values of Ashton et al. [5]. In addition, experimental K_{IDR} values in the 25-200°C, reported by Ashton et al. [5], differ from those reported by Palmer et al. [2]. Several factors contributing to these discrepancies have been discussed by Ashton et al. [5].

The small differences in the calorimetrically determined K_{IDR} values and three sets of K_{IDR} values in the literature [1,2,5] arise from several factors: (a) experimental uncertainties in the potentiometric measurements from various corrections, such as activity coefficients, to the raw data; (b) poor response of the I_2/I_0^- electrode; (c) interference by the species of the chosen acid used as a supporting electrolyte, HClO_4, in the measurements of Palmer et al. [2] or HCl in the measurements of Ashton et al. [5], such as formation of ICl_3^-; and (d) existence of uncharged species of other oxidation states (+2 or +3, e.g., HIO_2) in the solutions used for potentiometric measurements. Also, the assumptions made to extrapolate K_{IDR} values, beyond the temperature range verified by experiments (in particular, 100-300°C for the calorimetric method and 200-300°C for the potentiometric method) are not completely valid. Thus, the agreement in the K_{IDR} values over the entire temperature range of 25-300°C is quite acceptable.

4.4. TEMPERATURE-DEPENDENT EQUATION FOR K_{IDR} VALID IN THE 25-300°C RANGE

The values of log_{10}K_{IDR}, calculated from our calorimetric data, are shown in Figure 2 and also listed in Table 3. A least squares fit of the K_{IDR} values derived from the data in the 25-100°C temperature range and the extrapolated K_{IDR} data in the 100-300°C temperature range yield the following simplified equation:

$$\log_{10} K_{IDR} = \frac{A}{T} + B + C \log_{10} T$$  \hspace{1cm} (18)

where A, B and C are constants having values of -41.997, 621.94 and -213.39, respectively; and T is the absolute temperature. This equation reproduces
equilibrium constants, $K_{IDR}$, within 0.1 below 200°C, and within 0.3 between 200° and 300°C.

5. CONCLUSIONS

Our limited calorimetric heat capacity data for only a few electrolytes (in this case, CsI, CsI$_2$, HCl and CsCl in the moderate temperature range of 25 to 100°C) help reduce the large uncertainties in the thermodynamic parameters of the key hydrolysis equilibrium (IDR) in the temperature range 25 to 300°C. Our conclusions are also supported by the recent, independent experimental studies at two other laboratories, ORNL, U.S.A. [2] and CEGB, U.K. [5]. Similar studies for reactions involving other important iodine species (e.g., HOI, HI and I$_3^-$) are in progress [18].

6. ACKNOWLEDGEMENTS

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**TABLE 2**

EQUILIBRIUM CONSTANTS FOR IODINE DISPROPORTIONATION REACTION, $K_{IDR}$, AT 50, 75 AND 100°C
CALCULATED USING CALORIMETRIC DATA FOR REACTION HEAT CAPACITIES, $\Delta_{IDR}C^o_p \gamma$: A COMPARISON WITH LITERATURE

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<td>41.0, 41.3</td>
<td>39.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Av. 41.2 (also 39.0)</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 3

**HIGH-TEMPERATURE EQUILIBRIUM CONSTANTS, $K_{I^{2+}}$, OF IODINE DISPROPORTIONATION REACTION IN WATER: PREDICTIONS TO 300°C AND A COMPARISON WITH THE RECENT LITERATURE**

<table>
<thead>
<tr>
<th>TEMPERATURE (°C)</th>
<th>-log$<em>{10} K</em>{I^{2+}}$ (Calorimetric: This Work)</th>
<th>-log$<em>{10} K</em>{I^{2+}}$ (Potentiometric: Ref. [2])</th>
<th>-log$<em>{10} K</em>{I^{2+}}$ (Potentiometric: Ref. [5])</th>
<th>Reassessed Literature Ref. [1]</th>
</tr>
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<tbody>
<tr>
<td>3.8</td>
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<td>14.7</td>
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<td>46.9</td>
<td>45.5, 44.7</td>
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<td>25.1</td>
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<td>46.9</td>
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<td>46.9</td>
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<td>45.3</td>
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<td>50.0</td>
<td>43.5</td>
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<td>100.0</td>
<td>39.5</td>
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<td>41.2, 39.0</td>
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</tr>
<tr>
<td>100.1</td>
<td>39.5</td>
<td>39.6</td>
<td>--</td>
<td>39.6</td>
</tr>
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<td>100.3</td>
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</tr>
<tr>
<td>120.0</td>
<td>--</td>
<td>--</td>
<td>38.3</td>
<td>--</td>
</tr>
<tr>
<td>125.0</td>
<td>(38.4)</td>
<td>--</td>
<td>38.2</td>
<td>--</td>
</tr>
<tr>
<td>126.3</td>
<td>--</td>
<td>38.5</td>
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<td>38.9</td>
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<td>140.0</td>
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<tr>
<td>150.0</td>
<td>(37.8)</td>
<td>--</td>
<td>37.6</td>
<td>--</td>
</tr>
<tr>
<td>152.6</td>
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<td>38.1</td>
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<td>38.9</td>
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<td>155.0</td>
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<td>170.0</td>
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<td>--</td>
<td>37.2</td>
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<tr>
<td>175.0</td>
<td>(37.5)</td>
<td>--</td>
<td>36.8</td>
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</tr>
</tbody>
</table>

continued...
<table>
<thead>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>178.6</td>
<td>(37.5)</td>
<td>37.6</td>
<td>--</td>
<td>--</td>
<td>39.4</td>
</tr>
<tr>
<td>200.0</td>
<td>(37.6)</td>
<td>38.1</td>
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<tr>
<td>208.8</td>
<td>(37.6)</td>
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<td>--</td>
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<tr>
<td>209.0</td>
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<td>--</td>
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<td>40.7</td>
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</tr>
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<td>225.0</td>
<td>(37.8)</td>
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</tr>
<tr>
<td>250.0</td>
<td>(38.3)</td>
<td>--</td>
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<td>--</td>
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</tr>
<tr>
<td>275.0</td>
<td>(38.9)</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<tr>
<td>287.0</td>
<td>(39.3)</td>
<td>(39.9)</td>
<td>--</td>
<td>--</td>
<td>46.0</td>
</tr>
<tr>
<td>300.0</td>
<td>(39.7)</td>
<td>(40.4)</td>
<td>--</td>
<td>--</td>
<td>47.0</td>
</tr>
<tr>
<td>326.85</td>
<td>(40.6)</td>
<td>(41.4)</td>
<td>--</td>
<td>--</td>
<td>49.7</td>
</tr>
</tbody>
</table>

* Values in parenthesis are extrapolated K_{IDR}
Figure 1: High-temperature heat capacity flow microcalorimeter system
EQUILIBRIUM CONSTANTS FOR IODINE DISPROPORTIONATION REACTION UP TO 300°C

Figure 2: Temperature dependence of the equilibrium constant, $K_{\text{IDR}}$, of iodine disproportionation reaction in water; A comparison with the literature data [1, 2, 5].
DISCUSSION

E.C. BEAHM
About the heat capacity of aqueous I$_2$, how high in temperature do you have data? You may be able to use Palmer's paper and the equilibrium I$_2$(aq) $\leftrightarrow$ I$_2$(gas) to back out a heat capacity for I$_2$ up to $\sim$185°C.

P.P.S. SALUJA

E.W. THORNTON
I would like to ask the author why he has chosen not to write the iodine disproportionation reaction in the isocoulombic form? One would expect this to assist with extrapolating the ΔC$_p$ values to high temperatures.

P.P.S. SALUJA
The isocoulombic hypothesis needs to be re-examined for reactions involving species which have widely different solvation characteristics as a function of temperature (solvational structural changes).
III. REVOLATILIZATION STUDIES
IODINE VOLATILITY FROM EVAPORATING PRIMARY COOLANT FILM IN STEAM ATMSPHERES

B. J. Handy and D. G. Jones

National Nuclear Corporation Limited
Warrington Road, Risley, Warrington
Cheshire, WA3 6BZ, United Kingdom

ABSTRACT

The work is relevant to iodine behaviour during SGTR faults in a PWR and is a sequel to previous work (1) in which high iodine volatility was observed under certain conditions from evaporating primary coolant in nitrogen atmospheres. The experiments described involve the measurement of iodine carry-over from boric acid/lithium hydroxide solutions containing iodide. The carry-over was confirmed to be due to HI volatility and increased with increasing temperature of the evaporation surface. The carry-over decreased with high pH solutions and exhibited only a small dependence on steam flowrate. Experiments were carried out with both glass and metal surfaces and the time dependancy of the iodine release was studied. The results obtained from glass surfaces are directly compared with the results from the previous work reported in inert atmospheres and conclusions are presented with respect to iodine behaviour in evaporating solutions in steam atmospheres.

1. INTRODUCTION

The work described addresses the retention of iodine from evaporating films of boric acid, lithium hydroxide/iodide solutions in steam atmospheres. These experiments in steam atmospheres follow those reported earlier (1) in which solutions of similar composition were evaporated in nitrogen atmospheres. The work is appropriate to iodine behaviour in PWR Steam Generator Tube Rupture (SGTR) faults and the results could be used as an input to assess the degree of retention of iodine in cases where "dry-out" conditions prevail.

The earlier results in nitrogen atmospheres indicated that up to 60% of the iodine was volatilised when simulated primary coolant solutions were evaporated to a dry film at 95°C and up to 90% of the iodine was released when the heating of the dry film was continued. The volatile species was believed to be hydrogen iodide (HI) which was released during the last stages of evaporation. As the carrier gas was nitrogen in these experiments, the partial pressure of the water vapour changed during the evaporation process, the largest change occurring close to and during dry-out. The release rate of HI was greatest during dry-out and may therefore be dependent on the vapour pressure of water. This would result in a dependence on the degree of superheat on the evaporating surface.

The experiments described in this paper were carried out in steam atmospheres at ambient pressure (steam at about 100°C) and at various surface temperatures. The degree of superheat was therefore constant within a given experiment and hence its effect could be studied.
Carry-over measurements using surface temperatures of up to 180°C were made as these temperatures are typical of those expected on SG tubes during the part of some SGTR fault sequences where steam temperatures are relatively low. Other aspects studied include pH effects, flowrate effects, the time dependence of iodine release, and mechanical carry-over.

2. EXPERIMENTAL

2.1 Principle of Experiments

The experimental method consisted of evaporating in a steam atmosphere a boric acid/lithium hydroxide solution containing iodine as the anion I\textsuperscript{-} and to determine the fraction of iodine carried over in the vapour relative to that retained in the residue. Typical concentrations of the components of PWR primary coolant during a SGTR fault are:

(a) boric acid; 850ppm as B (0.079M)
(b) lithium hydroxide; 0.5ppm as Li, (7 x 10\textsuperscript{-5}M).

The experiments were carried out at concentrations of 10\textsuperscript{-3}M iodide and a UV spectrophotometric method was used for iodine determination.

2.2 Apparatus

A diagram of the apparatus is shown in Fig. 1. Before commencement of a run, steam was generated in an autoclave at ambient pressure and directed through flasks A and B. The steam flowrate was controlled by the power input to the autoclave (i.e. boiling rate) and the whole system was allowed to achieve a steady state condition before evaporation. The steam temperature was monitored by a thermocouple T\textsubscript{1}, and flask A was immersed in an oil bath maintained at a constant temperature. The temperature of the solution inside flask A was monitored by thermocouple T\textsubscript{2} which was in contact with the inside surface of the flask. Flask A and associated steam lines were insulated and trace heated to prevent condensation.

When steady state conditions were established, a one millilitre sample of solution was taken with a syringe and injected slowly into flask A via a septum needle to the bottom of the flask using the guide tube C. Flask A was a 25ml pyrex conical evaporation flask, and flask B was a similar flask used as the condensate flask maintained at 0°C in an ice bath. The steam flowrate was determined by measuring the time to reach dry-out, and the total volume of condensate in flask B.

2.3 Iodine Detection

A Lambda 3 Perkin Elmer UV/visible spectrophotometer was used to determine iodide concentrations. The solutions were placed in quartz cells and the absorbance of I\textsuperscript{-} at 225nm was measured. The residue in flask A was dissolved in known volumes of water in order to compare directly with the absorbances of solutions in flask B.
2.4 Chemicals

The following is a list of chemicals and gases with the grades used in these experiments:

- Boric acid "Spec. pure" ex Fisons
- Lithium hydroxide ex BDH
- Potassium iodide 'Analar' ex BDH
- Nitrogen - BOC white spot

3. RESULTS AND DISCUSSION

3.1 General Observations

In these steam atmosphere experiments a substantial fraction of iodine was carried over into the condensate if the solutions were evaporated to a dry film, and enhanced volatility was observed if these dry films were heated further. This trend is in agreement with the results in inert atmospheres reported earlier (1).

In all of the experiments the only iodine species detected in both residue and condensate was the anion I⁻. This is also in agreement with the results reported earlier and confirms that the volatile species is HI.

3.2 Effect of Surface Temperature

In these experiments the initial iodide concentration was 10⁻³M, and the boric acid and lithium hydroxide concentrations were 850ppm B and 0.5ppm Li. The steam flowrate was maintained at about 0.7dm³ min⁻¹. The surface temperature range covered was 130°C to 190°C and the steam temperature was maintained at 110-115°C. Table 1 summarises the results and carry-over values for both the dry film stage and after further heating of this residue are reported. The carry-over at the dry film stages ranged from 13% at a surface temperature of 130°C to 48% at a surface temperature of 190°C. The carry-over in nitrogen at 95°C was about 60% at the dry film stage for a similar solution composition (1). Further heating in nitrogen resulted in 90% carry-over. The result for the lowest recorded temperature in steam (130°C) indicates that the iodine carry-over at a given temperature is significantly less (by a factor of 6) in steam atmospheres than for nitrogen atmospheres. Even at the higher temperature of 170°C the carry-over results are smaller than those in nitrogen by a factor of 2, and only at surface temperatures of 180-190°C are carry-overs of up to 90% observed.

3.3 Effect of pH

In these experiments the iodine carry-over was measured at four pH values using different concentrations of boric acid and lithium hydroxide to adjust the pH. The solution composition in each case was (a) 3500ppm B, (b) 1700ppm B, (c) 850ppm B, 0.5ppm Li and (d) 5ppm Li. A surface temperature of 180°C was used in all of these experiments and the steam flowrate was 0.7 dm³ min⁻¹. The initial iodide concentration
was $10^{-3}$M. The results are summarised in Table 2. The data show that the iodine carry-over is lower at high pH. This trend is to be expected for volatility arising from HI and agrees with the general trend observed in the earlier work (1).

3.4 Evaporation on Inconel Surfaces

Evaporation of solutions on Inconel 600 surfaces were performed in steam atmospheres to be more representative of conditions in a steam generator during an SGTR. The Inconel 600 was in the form of a foil of thickness 200μm. The foil was carefully inserted into the evaporation flask before a run and spread over the bottom surface of the flask forming a "tray" which assumed the same shape as the flask. The evaporation of the solutions on Inconel therefore occurred on the identical geometry to evaporation on glass. The solution composition in these experiments was $10^{-3}$M iodide, 850ppmB and 0.5ppm Li. The range of surface temperatures studied was 140°C - 180°C and the steam flowrate was 0.7dm$^3$min$^{-1}$. The results are summarised in Table 3 and indicate that the carry-over from Inconel is a factor of two lower than that from glass. This is presumably a result of the adsorption of iodide ion into the oxide layer. It can be seen that for complete volatilisation at 180°C from Inconel surfaces over 60% of the iodine was retained, and that at 160°C and 140°C over 75% of the iodine was retained.

Comparison of the results with those reported earlier for nitrogen atmospheres showed a similar trend; that is the carry-over was a factor of two greater from glass surfaces than from Inconel 600. The numerical values of the carry-over, however, were different owing to the different geometry of the evaporating surface in the two sets of experiments.

3.5 Time Dependence of Carry-over

In these experiments the carry-over was measured at various time intervals after dry-out had occurred to establish whether iodine could be carried over on a longer time scale than the time to reach dry-out. The composition of the solution was 850ppmB, 0.5ppm Li and $10^{-3}$M iodide. The surface temperature was 180°C and the steam flowrate was 0.7dm$^3$ min$^{-1}$. The results are summarised in Table 4 for both glass surfaces and Inconel surfaces. It is seen that after complete volatilisation of iodine, no further significant iodine release was observed from glass surfaces. From Inconel surfaces however, some iodine was released up to 15 min after dry-out.

In further experiments the carry-over was measured at various time intervals prior to and including the early stages of dry-out. The experimental parameters were identical to those described above, and the results are shown in Table 5. It can be seen that the majority of the iodine was carried over during the last stages of evaporation and this agrees with the results of the earlier work in nitrogen atmospheres.
3.6 **Effect of Flowrate**

In order to assess the importance of mass transfer effects, the carry-over was studied as a function of steam flowrate. The solution composition was 850ppm B, 0.5ppm Li and $10^{-3}$M iodide. The surface temperature was 180°C and solutions were evaporated to the dry film stage only. The results are shown in Table 6 and it is seen that the carry-over increased with increasing steam flowrate. The dependence on flowrate, however, was small in that the carry-over increased only by a factor of 1.5 for an order of magnitude change in steam flowrate. The results imply that the mass transfer rate of iodine into the vapour phase increases more than the water evaporation rate when the flowrate increases. This is in contrast to the earlier results in nitrogen atmospheres where the carry-over decreased with increasing nitrogen flowrate (1).

3.7 **Mechanical Carryover Studies**

In a number of tests, the possibility of mechanical carryover was investigated at various surface temperatures by measuring the potassium concentration using atomic absorption spectroscopy for both the residue and condensate after evaporation of $10^{-3}$M iodide solutions. For all cases studied, potassium carryover was less than 4% (cf iodine carry-over of up to 89%) for complete volatilisation at 180°C and 1% (cf iodine carry-over of 13%) for dry film evaporation at 130°C. This confirms that the volatile species is hydrogen iodide and not mechanical carryover of potassium iodide.

3.8 **Condensation Tests**

In order to measure iodine carry-over in a condensing situation, 1 ml solutions of $10^{-3}$M iodide, 850ppm B, 0.5ppm Li were evaporated for 15 minutes at a surface temperature of 95°C. Carryover of iodine under these conditions was typically of the order of 1-2%, confirming the limited extent of iodine carry-over in a condensing medium.

4. **Conclusions**

4.1 The following conclusions arise from the results of experiments described in this paper.

1. In all of the experiments the anion iodide, $I^-$, was the only iodine species detected in both the condensate and residue. This confirms the conclusions of the work reported earlier that the volatile species was HI.

2. The carry-over due to entrainment was small.

3. Most of the iodine was carried over during the last stages of evaporation.

4. For a given surface temperature the carry-over was lower in steam atmospheres than in nitrogen atmospheres.
5. The percentage carry-over increased with increasing evaporating surface temperature, i.e. increased with the degree of superheat.

6. The carry-over decreased with increasing pH.

7. The carry-over from Inconel 600 surfaces in steam was a factor of two less than that from glass surfaces of similar geometry.

8. After the initial release of iodine at the "dry-out" point of evaporation, prolonged heating of the dry film did not result in further iodine release.

9. A small dependency on flowrate was observed. A factor of ten increase in flowrate increased the carry-over by a factor of 1.5.

4.2 Work is continuing in the following areas:

1. Further studies on Inconel surfaces at different surface temperatures.

2. The effect of iodine concentrations down to $10^{-9}$M.

REFERENCES


ACKNOWLEDGMENTS

This work was carried out for the Central Electricity Generating Board and is published with their permission and the permission of the Directors of NNC.
TABLE 1

EFFECT OF SURFACE TEMPERATURES ON IODINE CARRY-OVER

\[ [I^-] = 10^{-3} \text{M} \quad B = 850 \text{ppm} \quad \text{Li} = 0.5 \text{ppm} \quad \text{Steam flowrate} = 0.7 \text{ dm}^3/\text{min} \]

<table>
<thead>
<tr>
<th>Surface Temperature °C</th>
<th>Dry film stage</th>
<th>Carry-over % Complete volatilisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>48 (22-63)</td>
<td>-</td>
</tr>
<tr>
<td>180</td>
<td>39 (21-56)</td>
<td>77 (54-89)</td>
</tr>
<tr>
<td>170</td>
<td>27 (19-37)</td>
<td>47 (42-53)</td>
</tr>
<tr>
<td>160</td>
<td>23 (13-35)</td>
<td>44 (34-46)</td>
</tr>
<tr>
<td>150</td>
<td>19 (12-29)</td>
<td>32</td>
</tr>
<tr>
<td>140</td>
<td>17 (13-24)</td>
<td>25 (19-32)</td>
</tr>
<tr>
<td>130</td>
<td>13 (12-14)</td>
<td>24 (21-27)</td>
</tr>
</tbody>
</table>

Figures in brackets indicate range of values.
TABLE 2

PERCENTAGE CARRY-OVER AT VARIOUS $\text{H}_3\text{BO}_3$/LiOH CONCENTRATIONS AND INITIAL pH

$[\text{I}^-]=10^{-3}\text{M}$. Surface temperature = 180°C. Steam flowrate = 0.7 dm$^3$/min

<table>
<thead>
<tr>
<th>Solution composition</th>
<th>pH $180^\circ\text{C}$</th>
<th>pH $100^\circ\text{C}$</th>
<th>Carry over% (Dry film stage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500ppmB 0 Li</td>
<td>4.6</td>
<td>4.4</td>
<td>45 (25-73)</td>
</tr>
<tr>
<td>1700ppmB 0 Li</td>
<td>4.8</td>
<td>4.7</td>
<td>41 (27-55)</td>
</tr>
<tr>
<td>850 ppmB 0.5 ppm Li</td>
<td>5.9</td>
<td>5.8</td>
<td>39 (30-46)</td>
</tr>
<tr>
<td>0 B 5ppm Li</td>
<td>8.3</td>
<td>9.1</td>
<td>5 (3-8)</td>
</tr>
</tbody>
</table>

Figures in brackets indicate range of values

pH$_{180}$ for pure water = 5.7

pH$_{100}$ for pure water = 6.1
TABLE 3
COMPARISON OF CARRY-OVER ON GLASS AND INCONEL SURFACES

\[ [I^-] = 10^{-3} \text{M}, B = 850 \text{ ppm}, \text{Li} = 0.5 \text{ppm}. \text{ Steam flowrate} = 0.7 \text{dm}^3 \text{ min}^{-1}. \]

<table>
<thead>
<tr>
<th>Surface Temperature °C</th>
<th>Inconel 600</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry Film</td>
<td>Complete Volatilisation</td>
</tr>
<tr>
<td>180</td>
<td>25 (11-45)</td>
<td>33 (25-44)</td>
</tr>
<tr>
<td>160</td>
<td>14 (11-18)</td>
<td>23 (13-35)</td>
</tr>
<tr>
<td>140</td>
<td>12 (19-32)</td>
<td>23 (19-32)</td>
</tr>
</tbody>
</table>

Figures in brackets indicate range of values.

TABLE 4
TIME DEPENDENCE OF CARRY-OVER (%)

\[ [I^-] = 10^{-3} \text{M}, B = 1700 \text{ ppm}, \text{Li} = 0.5 \text{ppm}. \text{Surface temperature} = 180° \text{C}. \text{ Steam flowrate} = 0.7 \text{dm}^3/\text{min}

<table>
<thead>
<tr>
<th>Dry film</th>
<th>Glass surface</th>
<th>Inconel surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>39 (31-56)</td>
<td>25 (11-45)</td>
</tr>
<tr>
<td>Complete volatilisation</td>
<td>77 (54-89)</td>
<td>32 (25-44)</td>
</tr>
<tr>
<td>+ 15 min</td>
<td>71 (59-78)</td>
<td>42 (32-59)</td>
</tr>
<tr>
<td>+ 30 min</td>
<td>75 (63-88)</td>
<td>41 (34-48)</td>
</tr>
</tbody>
</table>
### TABLE 5

**TIME DEPENDENCE OF CARRY-OVER PRIOR TO DRY-OUT (%)**

\[ [I^-] = 10^{-3} \text{M} \text{ B = 850ppm, Li = 0.5ppm. Surface temperature = 180°C, Steam flowrate = 0.7dm}^3 \text{min}^{-1} \]

<table>
<thead>
<tr>
<th>Evaporation Stage</th>
<th>Carryover %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 ml of solution remaining (50% evap)</td>
<td>7 (5-9)</td>
</tr>
<tr>
<td>0.2 ml of solution remaining (80% evap)</td>
<td>11 (6-14)</td>
</tr>
<tr>
<td>Initial stages of dry film formation</td>
<td>18 (18-19)</td>
</tr>
<tr>
<td>Dry film</td>
<td>39 (21-56)</td>
</tr>
</tbody>
</table>

### TABLE 6

**EFFECT OF STEAM FLOWRATE ON CARRY-OVER**

Surface temperature = 180°C, B = 850ppm, Li = 0.5ppm, \([I^-] = 10^{-3} \text{M. Evaporation to dry film} \]

<table>
<thead>
<tr>
<th>Steam flow dm(^3) min(^{-1})</th>
<th>Carry-over %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 - 1.0</td>
<td>39</td>
</tr>
<tr>
<td>1.5 - 2.0</td>
<td>36</td>
</tr>
<tr>
<td>2.0 - 2.5</td>
<td>52</td>
</tr>
<tr>
<td>3.0 - 3.5</td>
<td>70</td>
</tr>
<tr>
<td>5.0</td>
<td>55</td>
</tr>
</tbody>
</table>
FIG. 1. EXPERIMENTAL ARRANGEMENT.
DISCUSSION

D.J. WREN Have you considered the potential reactions of the lithium and boron with the surfaces and their influence on HI formation, particularly to explain the differences in glass and Inconel results? Also, have you considered experiments with stainless steel? It may be that reactions of lithium with a steel oxide could affect the volatilization of HI, similar to the observations at higher temperatures with Csl.

B.J. HANDY We have measured carry-over from low alloy steel surfaces in our earlier work in N₂ atmospheres and found that retention of iodine on low alloy steel was greater than on glass surfaces. We assume that this was caused by adsorption of iodine into the oxide layer on the surface.

S. DICKINSON You mentioned that the only species carried over was hydrogen iodide. Did you analyse the condensate for boron? You would expect some boric acid carryover at these temperatures.

B.J. HANDY No, we did not analyse for boron in experiments but boric acid carry-over was observed in previous experiments.

E.W. THORTON I think that over the range of the experimental conditions shown, the pH variation in the presence of boric acid (table 2) was quite small and the % carry-over of iodine correspondingly relatively constant. The results might be due to detailed crystallization effects in the drying film and not only to the effect of pH.

B.J. HANDY Under acidic conditions the concentrated solutions that have evaporated will be dominated by their iodic acid content. The pH of this solution will not vary significantly with iodic acid concentration and this is maintained in the small variation in iodine carry-over under acidic conditions. Under alkaline conditions, however, where LiOH concentrations determine the pH the carry-over is markedly reduced as shown by the data.

E.C. BEAHM This looks like a good candidate for David Turner’s model especially if borate in the condensate is measured.
REVOLATILISATION OF FISSION PRODUCTS, ESPECIALLY IODINE, FROM WATER PHASES EVAPORATING TO DRYNESS

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Hot Laboratory
CH-5303 Würenlingen, Switzerland

Abstract

Aqueous phases in a hypothetical core melt accident can, in an extreme case, evaporate to dryness as a result of ventings or a leaking containment. Resulting chemical reactions can lead to the formation of new volatile iodine species. These can significantly increase the iodine source term. The formation of volatile hydroiodic acid, HI, by action of boric acid on cesium iodide has already been shown in ORNL work.

This paper describes a stainless steel autoclave system with γ shielding. Its most important new feature is a "movable" heated bottom. By continuously lifting the bottom during evaporation of about one litre of water the interface between the phases will always be held at the same position. Wall effects are thereby minimalised or at least held constant.

The composition of the aqueous phase (sump simulation) can to a large extent be chosen freely. Radiotracers (MBq 131I, 123Te and others as Lanthanides) are used and their distribution between the aqueous phase, aerosol filter and condenser during the evaporation process is investigated.

In a preliminary series of experiments, ORNL data at various pH values were reproduced. Furthermore, it is shown that the addition of simulated "structure" and core material (powdered concrete, silicon dioxide, calcium carbonate, iron oxide ( magnetite ), silver, cadmium and others) partially have a significant effect on the degree of iodine revolatilisation.
1 Introduction

During a controlled venting of a containment to release pressure or leakages caused by accidents, sumps can, in an extreme case, evaporate to dryness. Fission products can by two phenomena enter the air/vapour phase, filter systems and eventually escape into the environment:

- Resuspension of solid particles
- Formation of new volatile chemical reaction products

The second phenomenon appears immediately before the water phase has completely dried out. In both areas of interest very little experimental work has been performed, but their great importance has been recognised [1].

During revolatilisations and especially when radiolytically and thermally induced reactions interact, it has already been shown that the iodine can vapourise completely [2].

The experimental work exhibits two technically difficult to control aspects:

- Exact controllable and reproducible thermal conditions during the last part of the evaporation stage.
- Controllable secondary effects.
  Wall effects can completely ruin results when the wall surface presented to the gas phase changes significantly during evaporation.

The autoclave system shown represents an attempt to consider both these aspects.
Figure 1: Diagram of the autoclave system
2 Description of the equipment

The autoclave system is made completely out of stainless steel. It has a volume of 1.3 litre and an internal diameter of 200 mm. The temperature of the complete top, bottom and wall surfaces is thermostatically regulated within ± 2 K by a circulating heat fluid (1).

An electrical heating element (2) is mounted in the centre of the bottom. It has a diameter of 86 mm and a rating of 500 W maximum. The bottom or piston can be moved vertically by a step motor (3) and spindle system (4). The bottom is raised during the experiment so that the water meniscus is always in contact with the conductivity control electrodes (5). The piston is sealed with a rubber O-ring. To exclude all possible chance that radioactive tracers could escape into the laboratory atmosphere, a stainless steel bellows (6) is welded between the wall or cylinder and the piston.

The equipment has been optimally designed to study revolatilisations, but it has hardly an acceptable geometry for aerosol resuspension studies. The first component in the off-gas system downstream from the autoclave is an aerosol filter (7). This serves to separate definite gaseous reaction products from droplets carried over as well as resuspended solid aerosols.

After filtering the gaseous reaction products, they are collected in a condenser (8). A condenser trap (9), provided with, for example, strongly alkaline water, ensures an efficient and quantitative collection of volatile iodine species possibly present in the off-gas.

Temperature is measured and controlled by 7 K-type thermocouples (10). They are placed in the electrically heated zone and at various positions in the autoclave mantle. They are connected to a data acquisition system (Keithley Inc.) complete with an on-line IBM-AT compatible personal computer. It also performs temperature control of the autoclave. The amounts of radioactive tracers employed allow operation and servicing of the equipment without remote control manipulators. To further reduce the operational dose rate, the autoclave is placed behind 50 mm of lead shielding.

The photos (figures 2 and 3) show the equipment. Figure 2 shows a general view of the autoclave with cover. The connections for the heating fluid can be seen on the cover and the thermocouples are visible in the background. Figure 3 displays the autoclave with cover removed. The step motor is shown bottom left with the vent directly above.
Figure 2: General view of the autoclave

Figure 3: Autoclave with cover removed
3 Aquisition of Results

Normally the total revolatilisation is of primary interest. It can be won directly from the condensate γ spectra using radiotracers of MBq activity in the initial solution.

Alternately classical wet analytical methods are available using ion selective electrodes for high volatilities (whole % ranges) as well as adapted filter systems for special applications. Filters allow, especially in the case of iodine, a determination of the volatile species: I₂, HI and CH₃I.

4 Results

Runs are shown for iodine volatilisation of cesium iodide solutions containing boric acid evaporated to dryness. The global volatilisation reaction can be described as follows:

\[ 3 \text{CsI} + \text{H}_3\text{BO}_3 \rightarrow 3 \text{HI} + \text{Cs}_3\text{BO}_3 \]

The volatilisation is examined as a function of the initial pH value. The effects of suspended solid additives such as metallic silver, iron oxides, zirconium oxide, concrete dust and components are also investigated.

It cannot be overstated that all the results shown are of a provisional nature. In particular, considering the improvised experimental setup, no definite information about the time and temperature development during the last phase of the evaporation stage can be given. The stated initial pH is only of limited value. The additives and the temperature increase have a considerable although poorly definable effect on the pH value during the evaporation stage.
Table 1: Revolatilisation during evaporation of cesium iodide solutions 1. $10^{-4}$ mol. l$^{-1}$

<table>
<thead>
<tr>
<th>Run Nr.</th>
<th>Boric acid [ppm]</th>
<th>Other additives</th>
<th>pH (start)</th>
<th>Iodine volatilized [%]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2000</td>
<td>-</td>
<td>4.5</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2000</td>
<td>Ag ($1.10^{-2}$ mol.l$^{-1}$)</td>
<td>5.0</td>
<td>14.2</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>3</td>
<td>2000</td>
<td>-</td>
<td>7.5</td>
<td>2.1</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>4</td>
<td>2000</td>
<td>Ag ($1.10^{-2}$ mol.l$^{-1}$)</td>
<td>7.5</td>
<td>2.1</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>6</td>
<td>2000</td>
<td>Fe(OH)$_3$ 2000 ppm</td>
<td>5.0</td>
<td>34.8</td>
<td>freshly precip. Fe(OH)$_3$</td>
</tr>
<tr>
<td>7</td>
<td>2000</td>
<td>Fe(OH)$_3$ 2000 ppm</td>
<td>8.0</td>
<td>7.1</td>
<td>freshly precip. Fe(OH)$_3$</td>
</tr>
<tr>
<td>10</td>
<td>2000</td>
<td>CaCO$_3$ 2000 ppm</td>
<td>7.9</td>
<td>4.1</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>11</td>
<td>2000</td>
<td>concrete &quot;dust&quot;</td>
<td>8.1</td>
<td>4.7</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>12</td>
<td>2000</td>
<td>SiO$_2$ &quot;dust&quot;</td>
<td>4.8</td>
<td>15.4</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>13</td>
<td>2000</td>
<td>Magnetite 2000 ppm</td>
<td>7.8</td>
<td>10.9</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
<td>-</td>
<td>6.7</td>
<td>2.6</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>16</td>
<td>2000</td>
<td>-</td>
<td>7.6</td>
<td>1.8</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>19</td>
<td>2000</td>
<td>ZrO$_2$ 2000 ppm</td>
<td>6.2</td>
<td>15.0</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>20</td>
<td>2000</td>
<td>Magnetite 2000 ppm</td>
<td>5.0</td>
<td>11.6</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>21</td>
<td>2000</td>
<td>ZrO$_2$ 2000 ppm</td>
<td>6.2</td>
<td>16.1</td>
<td>phosphate buffered</td>
</tr>
<tr>
<td>22</td>
<td>-</td>
<td>ZrO$_2$ 2000 ppm</td>
<td>6.8</td>
<td>2.8</td>
<td>phosphate buffered</td>
</tr>
</tbody>
</table>
5 Discussion

The present poor control over the time and temperature development immediately before dry up aggravates a comparison between the data presented and ORNL values [2]. The latter show for the two pH values of 4.4 and 7.0 the identical volatilisations of 7.2 and 6.8 % respectively. The basic experimental conditions (CsI initial concentration 1.10^{-4} mol \cdot 1^{-1} ; Boric acid 2000 ppm) were identical.

In neutral pH conditions no effect of the boric acid or of the buffer concentration can be shown (e.g. Runs 3, 15 and 16 with a volatilisation of 1.8 - 2.6 %). The fact that generally, including boric acid free solutions, a volatilisation can be seen, still obligates further investigations.

In contrast to the measurements from [2], a significant volatilisation increase resulted with decreasing pH values (Runs 1, 2 and 12).

An addition of metallic silver had no effect whatsoever (Runs 2 and 4). This is a clear indication that the volatile iodine species is III and not I_2, because silver is inactive with iodide. This does not contradict the marked scavenger effect that silver shows in combined experiments (evaporation and γ field) [2]. Radiolytically produced elemental iodine (but not III) quickly reacts to form the completely non-volatile and radiolytically stable silver iodide.

The effect of core structure material (aerosols) and concrete decomposition products as catalysts and/or scavengers for volatile iodine species was investigated. The concrete components CaCO_3 (Run 10), SiO_2 (Run 12) and concrete dust (Run 11) effect, at the 2000 ppm level, no significant change of revolatilisation but merely showed the mentioned pH dependence.

Different conditions prevail after the addition of conceivable aerosols originating from core structure materials. Magnetite shows at neutral pH a significant increase of volatilisation but exhibits hardly a pH dependence. The conditions are markedly different when freshly precipitated Fe(III) hydroxide additive is used. While the data in middle pH range (Run 7) resemble those of the magnetite values, the volatilisation at pH 5 is about a third of the total iodine inventory.

The data obtained with a zirconium oxide additive are not yet conclusive. The values increase from pH 7 (Run 22) to pH 6 (Run 19 and 21) by a factor of 5.

Concluding, it is shown that conceivable "impurities" from core structure and concrete can potentially increase the revolatilisation of iodine during evaporation of "core melt sumps", especially when a reduction of pH by an increase of acid concentration takes place simultaneously.
6 Continuing work

In continuing this work, which is still in the initial stage, the following crucial points will be considered:

- Exact reproducible clean-condition experiments which will confirm the provisional data presented in this paper.
- Examination and modelling of the causes for the basic volatilisation of about 2 % of the iodine inventory, including systems without additives.
- Use of further relevant additives and study of their effects as catalysts or scavengers.
- Runs with other potentially (during evaporation) volatile fission products. The system tellurium oxide / tellurate is of current interest.

References

[1] P.N. Clough (Chairman)
OECD/NEA/CSNI Group of Experts on the Source Term (GREST)
Selected Source Term Topics

Chemistry and Transport of Iodine in Containment

DISCUSSION

W. MORELL
Have you performed revolatilization experiments using each additive plus silver-metal? This way you can exclude revolatilization (silver works as a I₂-catcher).

M. FURRER
Not yet.

W.G. BURNS
In what form do you think the iodine was being volatilized?

M. FURRER
Only iodide could be shown in the condensate and silver aerosols had no effect on volatility. My conclusion is that the volatile species was HI.
DISCUSSIONS ON SESSIONS II AND III

P.P.S. SALUJA  I$_2$(aq) heat capacity as a function of temperature to be reconsidered.

B.J. HANDY  What was the iodide concentration in your present work?

E.W. THORTON  Most of these experiments were performed at [I$^-$] = 10$^{-3}$ M. However, in the previous work in N$_2$ atmospheres this carry-over of iodine was studied in the range 10$^{-9}$ M to 10$^{-3}$ M and no difference in carry-over measurements was observed. We will be measuring carry-over in steam atmosphere at 10$^{-9}$ M iodine in the near future, but do not expect to see any significant change.

M. FURRER  The statement that the volatile species in our work was HI is based on the fact that only I$^-$ could be shown in the condensate. I$_2$ and IO$_3$ could not be shown by wet chemistry/extraction techniques. But contributions of these two species in the 1% range were possibly overlooked.

D.J. WREN  With regards to the volatilization from drying films, I am concerned that reactions of the cation species (Li, Cs) with the surface (particularly glass) could be influencing the volatilization. It would explain the formation of HI as opposed to I$_2$.

B.J. HANDY  I agree solid phase reactions are an important aspect. Abnormally high reaction rates in solid phases have been known for many years, and there is no reason why the I$^-$/$\text{H}_3\text{BO}_3$ reaction should be an exception provided that there is a large enough surface area for reactant contact.
IV. MODEL/CODE DEVELOPMENT
THE USE OF THE FACSIMILE PROGRAM IN THE SPECIATION OF IODINE IN A PWR REACTOR CONTAINMENT FOLLOWING A LOSS OF COOLANT ACCIDENT.

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ABSTRACT

Iodine is released in a loss of coolant PWR accident from defected fuel as caesium iodide which ionises to produce the I\textsuperscript{-} ion on contact with water whether this water be the original coolant water before blowdown, or the water from the reactor water storage tank during the refill phase. Iodine exists in a variety of oxidation states of which I\textsuperscript{-} is the lowest, and the more oxidised form of I\textsubscript{2}, or its hydrolysis product HOI, are volatile and have the potential to constitute a radiological hazard. Recent work has suggested that thermal oxidation of I\textsuperscript{-} to I\textsubscript{2} by oxygen is not important but that radiolytic oxidation can produce I\textsubscript{2} from I\textsuperscript{-} usually up to a limiting concentration. Computer simulation of the chemistry of laboratory observations has proved to be reasonably successful. This paper explores the extension of such modelling to the detailed situation of a reactor accident where the aqueous medium exists in the forms of aerosol, spray, sump and reactor water, being mixed and contacted with the large volume of containment air in a way dictated by the thermal hydraulics of the accident.

The chemical modelling is flexible and produces credible results which suggest, for example, a large degree of volatilization when the iodine is released before blowdown, but a very small proportion of vaporised iodine when iodide is released below the water surface during refill.

1. INTRODUCTION

A knowledge of the concentration of volatile radioactive iodine in the containment following a LOCA in a PWR is important in assessing the radiological hazard because the iodine in such form is instantly available for release through any breach. The same is true of any iodine contained in the blowdown aerosol, whose properties, however, are not the same as those of iodine as a volatile species.

In a design base LOCA we can assume that the iodine will be released to the surrounding aqueous medium, whether it be the original coolant water, or the refill water from the emergency core cooling systems, as caesium iodide, which produces the iodide ion on solution. Iodine exists in a variety of oxidation states, from -1 to +7, of which I\textsuperscript{-} is the lowest and some of which are volatile, see Table 1. Some species like I\textsuperscript{-}, IO\textsuperscript{-}, IO\textsuperscript{-2}, IO\textsuperscript{-3}, and IO\textsuperscript{-4}, are expected to be involatile, while species such as I\textsubscript{2},...
and 10, and also stable oxides are expected to have insignificant concentrations, so the species on which attention is focussed are molecular iodine, I\(_2\) and hydpoiodous acid, HOI, which has been difficult to prove to be a genuine volatile species.

Studies of the thermal oxidation by oxygen of iodide ion to aqueous molecular iodine, which is known to be in equilibrium with aqueous hypoiiodous acid, in reaction [1]

\[
I_2 + H_2O = H^+ + I^- + HOI
\]  

suggest that the effects of such thermal oxidation are insufficient to present a significant radiological hazard. However, the same is not true of radiolytic oxidation, where at appropriate concentrations appreciable conversion of I\(^-\) to I\(_2\)/HOI can readily occur at dose rates prevailing in the water in a shut down PWR. The chemical mechanism of this oxidation, involving the species from aqueous radiolysis, namely e\(_{aq}\), H, OH, O\(_2\), NO\(_2\), H\(_2\)O\(_2\), H\(_2\)\(\), has, over the past few years, become sufficiently well understood, thanks partly to work on the individual reaction steps by pulse radiolysis, that computer modelling of laboratory experiments can give reasonable agreement between calculation and observation [3].

It is the purpose of this paper to explore the possibility of extending such modelling from the laboratory situation, usually of small samples in glass vessels, to the large scale accident condition where large masses of the relevant solution are present, either minutely divided as aerosol and spray droplets, or massively as a sump pool, or filling the reactor vessel. Each form has its characteristic ability to volatilise iodine, (e.g. rapidly for the aerosol, slowly for the pool), so that the final outcome of the radiolytic chemistry in producing vapour phase iodine will be strongly dependent on thermal hydraulic and mass transfer effects which are implicit in the description of the physical parameters of the accident sequence.

The modelling proceeds in stages, starting with the more easily modelled effects from a well mixed pool in contact with a well mixed gaseous space. In the next stage we consider the radiolysis of the blowdown aerosol containing iodide in a large gaseous space being sprayed with pure boric acid solution which falls into the sump. The final stage treats a fully compartmentalised model comprising 1) the blowdown aerosol, 2) the spray, 3) the sump, 4) the top of the reactor, 5) the bottom of the reactor and of course the vapour phase. We use an example of a detailed accident description which provides the time-dependent masses of water and drop size distribution, and temperature, combined with realistic mass transfer coefficients of species to the gas phase.

These form the input to the FACSIMILE [4] computer package which predicts the iodine speciation in the vapour and in each of the five liquid compartments, using chemistry combined with transport and flow, where the first three compartments have direct access to the vapour phase. The FACSIMILE program is well suited to such a simulation because it deals efficiently with the arrayed variables and physical parameters of the six
compartments, and the flow between compartments can be coded succinctly and efficiently using the "TRANSPORT" mode.

2. MODELLING
2.1 Chemical Mechanism

We used the set of equations already described, and reduced the number of equations involving the radiolytic reactions of iodine species, while retaining all the inter-reactions of the aqueous radiolytic species, and all the thermal reactions of iodine species [3]. The number of radiolytic iodine reactions, originally 68 was reduced to 29, by listing in ascending order the reaction rates for a series of relevant simulations for I− radiolytic oxidation at initial concentrations up to 3x10−5M, dose rate up to 20 kGy h−1. The slowest reactions were successively removed and the system retested. Many reaction products were found to be formed by parallel routes, one of which was greatly predominant, and we found that the 29 reactions in Table 2 gave results to within 0.2% of those for the original 68 reactions. The complete set of reactions also incorporates the hydrolysis of I2 to HOI, the disproportionation of HOI to iodate and the thermal oxidation of I− to I2/HOI by hydrogen peroxide and the reduction by hydrogen peroxide. For all of these thermal reactions at a variety of temperatures we have obtained very good correlation between model predictions and observations [2]. The radiolytic oxidation to I2/HOI proceeds by reaction of I− with OH, the radical ion O2− acting as a reductant which limits the extent of oxidation. The general mechanism was found to give reasonable agreement in radiolysis experiments [3]. Iodate is formed here by successive radiolytic oxidation of HOI first to IO, as suggested by Buxton and Sellers [5], and then by HO2 to IO3, via HIO2, an adduct of OH− and IO.

2.2 Mass Transfer to the Gas Phase

For this part of the modelling we have been helped by a study of this topic specifically for fission product species, by R C Hewison [6]. We consider the liquid and gas phases both to be well mixed, and make the usual assumption that the interface itself offers no resistance to mass transfer. The overall mass transfer coefficient K is then given by the equation

\[ \frac{1}{K} = \frac{1}{K_g} + \frac{1}{(RK_w)} \]

(2)

where \( K_g \) is the gas side and \( K_w \) the waterside mass transfer coefficient, and
R is the partition coefficient (equilibrium aqueous concentration/equilibrium gaseous concentration). Following Hewison we have in the containment conditions for the aerosol, the spray and the sump used values for $K_g$ of 0.10, 0.11 and $2.2 \times 10^{-4}$ ms$^{-1}$; the values used for $K_w$ were $0.0018$, $5 \times 10^{-5}$, and $3 \times 10^{-6}$ ms$^{-1}$ respectively for all species. For all species and temperatures used here we found that the waterside mass transfer was limiting. The rate constant for vaporization of a molecule $M$ in the reaction

$$ M(aq) = M(g) $$

is given by the equation

$$ -dc/dt = k_f c - k_r C $$ (4)

which defines $k_f$ and $k_r$, where $c$ is the aqueous and $C$ the gaseous concentration. The value of $k_f$ is given by $KA/(vR)$ where $v$ is the aqueous volume and $A$ the interfacial area. Large differences, dependent on $A/v$, for the surface to volume quotient are possible since for spherical micron diameter droplets, its value, given by $3/radius$ is ca $10^{-6}$ m$^{-1}$, whereas for a pool 1 metre deep the value is 1 m$^{-1}$. In equation (4) $k_f$ is given by $k_f R$, and this equation must be complemented by one for the gas phase, derived from the principle of mass conservation, in equation (5), where $V$ is the gas volume

$$ -d(cv)/dt = d(CV)dt $$ (5)

Since $V$ is essentially invariant, but $v$ varies considerably with time (5) can be expanded into (6)

$$ -Vdc/dt = cdv/dt + vdc/dt $$ (6)

and for more than one liquid volume we have

$$ -Vdc/dt = \sum(c_i dv_i/dt + v_i dc_i/dt) $$ (7)

Such equations are implemented in the program for each water compartment in contact with the gas for the species $I_2$, HNOI, $O_2$ and $H_2$.

For the spray its capacity to remove volatiles in reaction (4) is limited by the lifetime of the aqueous species with respect to removal into the sump, so that concentrations are far removed from the equilibria of reactions of the type (4). For the aerosol, the spray and the sump, typical values of $k_f$ for $I_2$ were $1.3 \times 10^3$, 0.56, and $5 \times 10^{-6}$ s$^{-1}$ respectively, and these values reflect the form and conditions of the water mass in question.
2.3 Mass Transfer between aqueous compartments

In FACSIMILE the "TRANSPORT" code requires coefficients $n_i$ and $s_i$ to be specified for the equation

$$f_i = n_i c_i - s_i c_{i+1}$$

where $f_i$ is the net rate of transfer of mass e.g. in mole $s^{-1}$ between zone $i$ and zone $i+1$ where the concentrations of the species in question are $c_i$ and $c_{i+1}$ respectively. This method was used here with $n_i$ obtained from the flow rate or rate of volume change derivable from the accident sequence specification. The program automatically increments the values of $dc_i/dt$ and $dc_{i+1}/dt$ appropriately to cause the required effect. This was done for all iodine species, boric acid, and the stable radiolytic products $H_2$, $O_2$, and $H_2O_2$. Account was also taken of the effect of dilution and density change on the water volumes and solute concentrations.

2.4 Physical description of an example of a PWR LOCA

This description, which is one example of a number under test, is incorporated in Figures 1 and 2, where Fig. 1 shows schematically the water flow paths and the parts of the water inventory modelled with the FACSIMILE array mode in the compartmentalised model being developed at Harwell.

The compartments at present used are 1) the blowdown aerosol, 2) the spray, 3) the sump, 4) the top of the reactor (top fifth) and 5) the bottom of the reactor. The gas phase is treated separately as a space containing non-arrayed variable concentrations of molecules which partition between the vapour and the aqueous phases 1), 2) and 3), but this could be extended. Reaction, for example among gaseous species or with surfaces present could be incorporated at a later stage. The dotted lines indicate that in a typical LOCA for 2800s after the initial blowdown the spray system is fed, and the reactor is refilled by the pure aerated and borated water in the accumulator and storage tanks. After the reactor is filled mixing occurs between the top and bottom water at a rate a quarter of the spray rate. After 2800s pumps recirculate the contaminated sump water through the spray system and the top fifth of the reactor, where again the water flow interchanges partially with the water in the lower four fifths of the reactor.

Figure 2 gives an example of the way the temperature and the water masses in the different "compartments", aerosol, spray, sump, top of reactor, bottom of reactor, could change with time after a LOCA. Note that the bottom of the reactor is full at 590s and that the reactor is completely full at 770s. The mass present as spray stays constant after the first half minute at 2.85 metric tons, and the spray for the first 2800s accumulates in the sump at a rate of ca 0.26 metric tons/s. The reactor make-up water fills the reactor, then overflows into the sump at a similar rate. Comparable rates of suction and discharge are maintained by the pumps during the recirculation phase.
The data represented in Figure 2 are held in a dataset which contains a list of times up to $10^6$ s, and values at these times of the mass present in the different forms, the temperature, and the aerosol median radius. The increase with time of the latter and the decrease of the aerosol mass represent its slow agglomeration and incorporation into the sump.

3. RESULTS FROM CHEMICAL MODELLING

3.1 Model a) EYEBATH Sump alone

Some results of this model have been presented [3] and Figures 3 and 4 show the pH, the rate constant for disproportionation, $k_4$, the absolute temperature, the inorganic vapour phase radioactivity due to $^{131}$I INGAC and the log of the Vapour Distribution Factor $V_{F_{AV}}$, (time dependent partition coefficient). This is expressed as the mass of iodine atoms per unit volume in the aqueous phase divided by that in the vapour phase. In this case the iodine, released as $3.4\times 10^{-6}$ M I$^-$ in 230 m$^3$ of 0.1M aqueous boric acid is introduced into a well mixed pool ca 1 m deep, in contact with vapour phase, volume $8.83\times 10^4$ m$^3$, and the solution is diluted eightfold with boric acid over two hours. The temperature falls from 150° to 100°C linearly in the first two hours. From the first to the third hour the pH is caused to rise linearly to pH 8 to represent the effect of added phosphate buffer. The values of $k_f$, the partitioning rate constants from the aqueous to the gas phase, are low because of the low surface to volume quotient. The graph indicates the extent of oxidation and volatilization of the iodine. Since the inventory of iodine released has an activity $4.7\times 10^4$ TBeq, only a small fraction, ca $2\times 10^{-5}$ becomes volatilised. Fig 3 uses the temperature dependent equilibrium constant of reaction (1) from reference 1, whereas Fig 4 uses higher values of this hydrolysis constant from reference 7. The iodine volatility is very dependent on this constant, so we have carried out experiments on its value at temperatures up to 115° C. Fig 5 shows some results for the proportion of I$_2$, measured by absorption spectrophotometry, as a function of time after introducing ca $2\times 10^{-5}$ molar I$_2$ into a cell in a purpose built spectrophotometer using phase locked amplifiers for estimating the measuring and reference beams. The results obtained in 0.01 M boric acid solution allow the disproportionation rate constant, and $K_1$ to be estimated using the FACSIMILE 'VARY' facility which provides the value requested with confidence limits, and definitely show that the $K_1$ values from ref 1 are much closer to those observed, so we use these values, which give considerably lower iodine volatility, in further simulation.

3.2 Model b) EYEDROP Aerosol, Spray and Sump

In this model we follow the parameters of Fig 2 and assume that the iodine has been released to the coolant before blowdown, so the
starting point is the aerosol of mass 240 metric tons containing $3.4 \times 10^{-6}$ M I\(^-\). This is irradiated with a dose-rate 5 kGy h\(^{-1}\) and the gas is sprayed with 0.2M boric acid solution at a rate 0.26 M s\(^{-1}\) inside a volume 8.83x10\(^4\)m\(^3\) of air. We model the partitioning of the radiolytic iodine which is replenished on volatilization until about one tenth of the original iodide is volatilised, at an early time, after which the speciation changes to iodate. At the same time partitioning to the spray occurs from the vapour, and the HOI and I\(_2\) scrubbed out are carried into the sump. Figure 6 shows the varying proportions of the original iodine in the aerosol (FRISOL) in the vapour as I\(_2\) (FRI2VAP), in the vapour as HOI (FRHOIVAP), and in the sump (FRISUMP). The ready volatilization is a consequence of the finely divided aqueous medium. Increasing the efficiency of removal of I\(_2\) and HOI by the spray by a factor 10 caused FRI2VAP and FRISUMP to decrease by only a few percent. This is because the spray volume is only ca 2.85m\(^3\) compared with 8.8x10\(^4\)m\(^3\) for the vapour.

Figure 7 shows another example which has the same conditions as figure 6 but with the initial [I\(^-\)] increased to $3.4 \times 10^{-5}$ M. The peak in the I\(_2\) vapour fraction is larger and later than in figure 6, and the proportion of HOI is lower as a result of the generally higher concentrations. Later tests have shown that the high proportion of the original I\(^-\) which appears as vapour phase I\(_2\) is caused by the unrealistically large value of the dose rate chosen for these cases.

3.3 Model c) EYEBOX Compartmentalised model. All 5 liquid compartments and vapour phase before and after recirculation.

In this case the concentrations of the chemical species in the water in the five compartments are represented by arrayed variables and their reactions are modelled separately but with the same chemical reaction mechanism. We were able to model the effect of iodide present at the start, in the aerosol, also the effect when iodide was introduced at the bottom of the reactor when the reactor was say half full. This provided a comparison with earlier tests (EYEBATH model) where iodide was released into a large body of water. The model provides the iodine concentration in each of the species contained in Table 2 for each compartment, and figure 7 shows an example when for the parameters of Fig 2, $3.4 \times 10^{-6}$ M I\(^-\) was considered to be present in the aerosol at the start. The dose rates in the five compartments were respectively 5, 0.01, 0.01, 1.0 and 50 kGy h\(^{-1}\) as shown in Table 3 which gives the dose rate and I\(^-\) release conditions used for Figs 8 to 11. The results show, as in Fig 6, an early burst of volatile iodine which gradually subsides as iodine changes to iodate. In this case however, we model the fractions of the current inventory of released iodine in the spray, and the reactor parts, as well as in the vapour species, the aerosol and the sump. The fraction in the spray increases suddenly when recirculation begins at 2800s, and this brings about a continuation of the broad peak in the volatile iodine fraction. Eventually as oxidation and disproportionation to iodate occur, the volatile iodine fraction subsides to very low values.
In figure 8 the dose rate to the aerosol was set at 5 kGy h\(^{-1}\), and in figure 9 we show the effect of reducing this to 0.01 kGy h\(^{-1}\), a value which is more realistic for a LOCA. The general features of the time variation of the fractions are similar to those in figure 8, but the five-hundredfold reduction in dose rate has brought about only a twentyfold reduction in vapour phase I\(_2\) with the peak at about 800s compared with 100s for figure 8. The general insensitivity of iodine formation to dose rate and to dose is in keeping with previous work on a laboratory scale [8].

In Figure 10 we depict a condition in which at the start of the fault, still following the parameters of Figure 2, the blowdown occurs before the fuel cans release iodine. The programme had been set initially to have very small concentrations, of I\(_2\) \(10^{-20}\) mole l\(^{-1}\) and of I\(^-\) \(10^{-9}\) mole l\(^{-1}\) in all compartments. The dose rates set in the compartments were respectively 0.01, 0.01, 0.01, 1.0 and 50 kGy h\(^{-1}\), i.e. with negligible values outside the reactor. Up to 350s the large calculated fractions for the vapour phase represent a negligible hazard because the inventory of released iodine is negligible. At 350s when the reactor is half full we release \(6.8 \times 10^{-6}\) M I\(^-\) into the water in the bottom of the reactor, representing the amount needed to give \(3.4 \times 10^{-6}\) M in the full reactor circuit. The fractions of iodine in other compartments fall nearly to zero at 350s, and the conditions for release of volatile iodine from the large water masses are even less favourable than those of the pool situation of type a). At 770s when the reactor is full the mixing at a quarter of the spray rate between the top and bottom reactor water which occurs, causes the top reactor fraction to increase, and this falls again when recirculation, starting at 2800s begins to mix all the water except the aerosol. The fraction in the spray rises at this time but the fraction of iodine in the aerosol stays at ca 10\(^{-3}\) or below this as iodate is formed and that of volatile iodine stays negligible.

Figure 11 shows the effect when half the iodine is released before blowdown and half during refill when the reactor is half full. The dose rates, given in Table 3 are the same as for figure 10.

Before the time of release in the reactor, 350s, the fractions resemble those in figure 7, with an even earlier peak in FRI2VAP, but with a greater fraction of HOI volatility because of the lower concentration in the aerosol. At 350s when the iodine release occurs the fraction in the reactor bottom rises quickly to just above 0.5 and that in the aerosol falls to about 0.43, the remainder being in the vapour and sump. Mixing then occurs after the reactor is full as in Fig 8, and again when recirculation occurs. There is a discernable extension at the broad peak in FRI2VAP caused by recirculation of the spray at ca 3000s and the general behaviour is a mixture of the effects seen in figures 8 and 20.

**DISCUSSION**

This type of modelling appears to confirm, and quantify commonsense concepts about the way in which iodine will be distributed and volatilised in the situations considered. Iodine is first radiolytically
oxidised to iodine, and its voltilization then strongly depends on the state of division of the aqueous medium, so we find very appreciable volatilization for the aerosol, very little for release into a large quantity of water, and intermediate effects when some iodine is released before blowdown and some during refill. Since iodine exists in all the oxidation forms given in Table 1, a chemistry model is essential to obtain details which allow prediction of overall effects, and since the gas space is so large compared with the liquid, volatilization can have a large effect on dissolved concentrations in a situation where lower concentrations of I\(^{-}\) are more readily oxidised to the involatile iodate ion.

Further development of the model could allow vapour phase reactions with surfaces either in a well-mixed or a diffusional method of calculation, and allow other parts of the water, e.g. the top of the reactor, to contact the gas space. The methods used could also, in principle, be extended to estimate the effects of iodine release in locations other than the containment, for example the auxiliary building. Sensitivity studies are beginning, and as well as tests on sensitivity to the values of chemical equilibrium and rate constants, important input parameters are rates and equilibrium constants for the partitioning of iodine and of HOI, the latter of which needs more study.

Partial validation of the model on a small scale has already taken place, and could be improved by laboratory irradiation experiments at ca 100°C with a variety of ratios of gas to liquid volume, but for reliable overall validation the model would need to be applied to a reasonably large scale equipment where ideally experiments with water in the form of aerosol formed part of the program.

The model is well placed to take advantage of developments in the field of aerosol settling and impaction by spray and should be of help in refining estimates of radiological hazard caused by iodine release in design base reactor faults. In its present form it runs in under 250s CPU time, to 3x10^5 s simulated time on the Harwell IBM 4020 computer giving complete speciation in all five aqueous compartments and in the vapour phase.

CONCLUSIONS

The compartmentalised chemistry model appears to give credible results which show very large differences in iodine volatilization dependent on the circumstances of the fault sequence used. In particular if iodide is released before blowdown a large fraction of the iodine inventory may appear as vaporised I\(_2\) and HOI whereas if iodide is released during refill below the water level very small amounts become volatilised.

ACKNOWLEDGEMENTS

This work was funded by the CEGB. We acknowledge the work of Dr M Matsuda (Hitachi) for work on I\(_2\) hydrolysis.
REFERENCES


TABLE 1 Oxidation states of some iodine species in water.

<table>
<thead>
<tr>
<th>State</th>
<th>Species</th>
<th>State</th>
<th>Species</th>
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<tr>
<td>-1</td>
<td>I⁻</td>
<td>0</td>
<td>I₂</td>
</tr>
<tr>
<td>+4</td>
<td>IO⁺</td>
<td>+5</td>
<td>IO₅⁺</td>
</tr>
<tr>
<td>+2</td>
<td>HOI</td>
<td>+6</td>
<td>IO₆⁺</td>
</tr>
<tr>
<td>+3</td>
<td>IO₃⁺</td>
<td>+7</td>
<td>IO₇⁺</td>
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Table 3. Dose-rates, and iodide release concentrations and times for Figures 8 to 11

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<tr>
<th>Fig</th>
<th>Dose-rate in kGy h⁻¹</th>
<th>Released [I⁻]/M</th>
<th>Time of release/s</th>
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<td>( I + \text{OH} = \text{HOI} )</td>
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<tr>
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<td>( I_2^- + I^- = I_3^- + I^- )</td>
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FIG. 1 SCHEME OF REACTOR CONTAINMENT WITH COMPARTMENTS
\[ [I^-] = 3.4 \times 10^{-6} \text{M} \quad k_f = 3 \times 10^{-6} \text{s}^{-1} \text{ for } I_2, \quad 2.7 \times 10^{-6} \text{s}^{-1} \text{ for } HOI, \quad \text{Dose rate} = 5.0 \text{ kGy/h} \]

**FIG. 3. EYEBATH MODEL, SUMP ALONE, IODINE PARTITIONING.**

\[ [I^-] = 3.4 \times 10^{-6} \text{M} \quad k_f = 3 \times 10^{-6} \text{s}^{-1} \text{ for } I_2, \quad 2.7 \times 10^{-6} \text{s}^{-1} \text{ for } HOI \quad \text{Dose Rate} = 5.0 \text{ kGy/h} \quad K_I \text{ from ref. 7} \]

**FIG. 4. EYEBATH MODEL, SUMP ALONE, IODINE PARTITIONING.**
$I_2 + H_2O = HOI + I^- + H^+$ (equilibrium const. $K_e$)
$2HOI = IO_2^- + I^- + 2H^+$ (rate const. $K_r$)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Calculated by FACSIMILE</th>
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$(K_e = 2.6 \times 10^{-11} M^2, K_r = 40 M^{-1} s^{-1})$

Run 3 ($71^\circ C$)
$(5.1 \times 10^{-11}, 45)$
Run 4 ($86^\circ C$)
$(7.0 \times 10^{-11}, 65)$
Run 1 ($95^\circ C$)
$(8.7 \times 10^{-11}, 80)$
Run 2 ($99^\circ C$)

$\Sigma [I]$ as $I_2 = 2.7 \times 10^{-5} M$
$H_3BO_3 = 1 \times 10^{-2} M$

FIG.5 ESTIMATE OF EQUILIBRIUM CONST. AND RATE CONST.
Fig 8  Fractions of Iodine in Containment Compartments  EYEBOX

Fig 9  Fractions of Iodine in Containment Compartments  EYEBOX
Fig 10 Fractions of Iodine in Containment Compartments

Fig 11 Fractions of Iodine in Containment Compartments
DISCUSSION

P.N. CLOUGH How do you handle the washout of the aerosol by the sprays?

W.G. BURNS The effects of agglomeration and settling of the aerosol and of impaction by the spray are included implicitly in the model by way of the input information. This includes the time dependent mass of the spray and the mean drop radius also the time dependent aerosol mass, its median drop radius and standard deviation. At present, we consider the aerosol drops all to have the same radius but more groups with differing radii could be considered. The data used in these early runs of the model do not take into account the recent developments in the modelling of aqueous aerosol behaviour. A sensitivity analysis is currently proceeding which includes the use of data from such recent modelling.

K. ISHIGURE Did you consider the partitioning of gaseous products such as $\text{H}_2$ and $\text{O}_2$ which will have a large effect on the radiolysis in the aqueous phase?

W.G. BURNS The modelling at present takes account of the gas partitioning of four volatile species $\text{I}_2$, $\text{HOI}$, $\text{H}_2$ and $\text{O}_2$ with three compartments, the aqueous aerosol, the spray, and the sump. We plan also to include the stream of water issuing from the reactor top after the reactor core is covered with water. The partitioning rate constants of course are very different for the three water masses because of their very different states of division.

G.J. EVANS I would like to know how the pH in containment varies following the postulated accidents.

W.G. BURNS The pH is controlled by boric acid (0.2 M in the original water, 0.1 M in the emergency core cooling water) and after 1 h we simulated the effect of addition of potassium dihydrogen phosphate by forcing the pH to go linearly with time from its value at 1 h to pH 8 at 3 h and to stay at pH 8.

C.F. WEBER Have you tested the chemical and mass transfer models with experimental data?

W.G. BURNS We have not done work on validation of this model at any scale, but it would not be difficult to mount a small scale experiment where the gas/liquid ratio was nearer 100:1 rather than the usual ca 1:1 which would test the effect of this important feature of the model. Note that in some of his experiments Ed Beahm has done radiolysis experiments with a gas flow through or over the irradiated solution and this gives high conversions to iodine, as occurs in some cases of the use of this model.
MODELLING THE CHEMISTRY OF IODINE

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ABSTRACT

We have assembled a kinetic model, based on elementary chemical reactions, that describes the chemical behavior of iodine in aqueous solution as a function of time and various parameters such as pH, concentration and radiation field. The model is conceptually divided into six sections: aqueous iodine chemistry, aqueous organic iodide chemistry, water radiolysis, radiolysis of iodine solutions, radiolysis of organic iodide solutions and mass transfer.

The model indicates that, in the absence of a radiation field, the rate of production of volatile iodine species is controlled by the rate of oxidation of the iodide ion. The volatile iodine species are dominated by organic iodides if organic impurities are present. The single most important parameter controlling iodine volatility is the pH of the solution; high pH values tend to minimize iodine volatility. In the presence of a radiation field, the volatility of iodine is controlled by the radiation-induced oxidation of the iodide ion. Again, iodine volatility is dominated by organic iodides if organic impurities are present. High pH values minimize iodine volatility.

A sensitivity analysis has been performed on some sections of the model to identify reactions to which the volatility of iodine is most sensitive. In the absence of a radiation field, the volatility is most sensitive, first, to the rate of oxidation of the iodide ion, and, second, to the rate of mass transfer of volatile species between the aqueous and the gaseous phases. This approach should be useful in identifying reactions for which accurate rate constants are required and in decreasing the complexity of the model.

1. INTRODUCTION

A model that describes the chemistry of iodine in aqueous solution is required to predict the behavior of radioiodine following a severe nuclear reactor accident or a design basis accident. An iodine chemistry model can also be used to plan experiments and interpret the results of large-scale tests simulating accidents.
In the last Workshop on Iodine Chemistry in Reactor Safety [1], we presented a detailed kinetic model describing the behavior of iodine in solution as a function of various chemical factors such as pH, and concentration, both in the presence and absence of a radiation field. Over the last few years progress has been made in various areas of iodine chemistry. Sellers [2] has published an extensive iodine kinetic database. Burns and Marsh [3-4] have studied the thermal oxidation of iodide near neutral pH and at low iodide concentration. Furrow [5] has determined the rates of reactions of iodine(I) and iodine(III) species. Buxton and Sellers [6] have published a study of the rate of disproportionation of iodine(I) and the radiation-induced interconversion of iodide and iodate. Ishigure et al [7-8] have performed radiolysis experiments with solutions containing low concentrations of various iodine species and oxygen; their results complement older data by Lin [9]. Schwarz and Bielski [10] have published a pulse radiolysis study of the reactions of iodine species with the radicals HO$_2$/O$_2$, which are important in air-saturated solutions. A variety of workers have examined the radiation-induced formation of organic iodides in solution [11-14]. Mohan and Asmus [15] have obtained the rate constants for various oxidation reactions by radical species originating from iodomethane. Paquette and Ford [16] have studied the radiolysis of iodomethane.

We have revised our model to take these new results into account. We have paid particular attention to the radiation-induced reactions involving iodine and oxygenated radical species since these would be important in air-saturated solutions. We have also performed a sensitivity analysis on some sections of the model to identify the reactions to which the volatility of iodine is most sensitive and to evaluate the potential of these techniques for reducing the complexity of the model.

2. COMPUTATIONAL METHOD

The kinetic calculations were performed using the computer program MAKSIM [17]. The program uses a modified Gear algorithm to solve the set of ordinary differential equations representing the chemical system. It uses sparse matrix techniques to minimize memory requirement and computing time. The calculations were performed in double precision on a Digital Equipment Corporation VAX 8650 computer.

The sensitivity analysis calculations were performed using a modified version of the computer program described by Valko and Vadja [18]. The program uses a generalized Runge-Kutta method of order four to perform the numerical integration and an embedded third-order method to control step size. The method is stable enough to handle stiff differential equations [19-20]. In that program, the sensitivity analysis is performed by the decomposed direct method, as originally proposed by Dickinson and Gelinas [21]. The algorithm described by Valko and Vadja was modified to implement relative error control in order to improve performance. The user interface was the same as in the program MAKSIM. The accuracy of the numerical integration was checked by running test cases and comparing the results with those obtained with the program MAKSIM. The test cases described by Carver et al [22] were used for that purpose. The sensitivity analysis part of the program was checked using
the test cases given by Valko and Vadja. The accuracy of the calculated sensitivities was also verified using mass balance considerations. The calculations were done on a Floating Point Systems model M64/140 computer. Most of the computer code was written in Fortran but a few subroutines were written in assembly language to improve computation speed.

3. **KINETIC DATABASE**

As previously described, the model is conceptually divided into six sections: aqueous iodine chemistry, aqueous organic iodide chemistry, water radiolysis, radiolysis of iodine solutions, radiolysis of organic iodide solutions and mass transfer. The most complex part of the model is the section dealing with the radiolysis of iodine solutions. The origin of some of the rate constants used in the model is discussed briefly below.

3.1 **Aqueous Iodine chemistry**

The rate constants for thermal reactions are essentially the same as previously reported [1], with only some exceptions. We have used the mechanism and the rates proposed by Burns and Marsh [3] for the oxidation of iodide to iodine by dissolved oxygen. The latter have performed experiments near neutral pH at iodide concentrations as low as $10^{-3}$ mol dm$^{-3}$. These conditions are closer to the conditions expected for reactor accidents than in the older experiments, which were performed at low pH and high iodide concentrations. Nevertheless, experiments at still lower concentrations would be desirable. The oxidation of iodide is catalyzed by a variety of inorganic ions. The mechanisms are complex and not yet fully understood. To take possible catalytic effects into account, we have multiplied the rate constants given by Burns and Marsh [3] by a factor of three.

The disproportionation of iodine(I) to iodide and iodate has been examined by a variety of authors [3,5-6,23-30]. We have used the mechanism and rates proposed by Buxton and Sellers [6]. The reaction is catalyzed by hydroxyl, borate, phosphate, and, presumably, other ions. To take catalytic effects into account, we have used the rates corresponding to a borate concentration of $10^{-2}$ mol dm$^{-3}$. The base catalysis effect was taken into account by assuming that three parallel reactions are occurring: HOI with HOI, HOI with $O_1^-$ and $O_1^-$ with $O_1^-$. 

Hydrogen peroxide is produced with a low yield during the radiolysis of water and it reacts with iodine species in various oxidation states. It oxidizes iodide to iodine at moderate rates at neutral pH (Harcourt-Essen reaction) and reduces $I_2$ to iodide at a rate which increases with the pH. It also rapidly oxidizes iodine to iodate in acidic solutions and slowly reduces iodate to iodide and iodide at neutral pH. It reduces rapidly $O_1^-$ to iodide. The mechanisms are generally complex and, under some conditions, can result in oscillating reactions. As before, we have used the simplified chemical model proposed by Eldelson and Noyes [31] for the Bray-Liebhafsky oscillating reaction. We have replaced some of their estimated rate constants with values measured recently by Furrow [5] for the reactions of iodine(I) and iodine(III) species. It should be pointed out that this mechanism has been established for
acidic solutions (pH of about 2) and might not be entirely applicable at higher pH values. We have also used the values reported by Ishigure et al. [8] for the rates of reaction of hydrogen peroxide with HOI and $O_1^-$. 

3.2 Aqueous organic iodide chemistry

Organic iodides can be formed in solution by reaction between $I_2$ and $HOI$ and organic impurities, which are ubiquitous in containment buildings. Aromatic molecules, such as phenols and anilines, are iodinated at rates that are close to the diffusion-controlled limit. Aliphatic molecules are usually iodinated at a slower rate. We have used two different rate constants for the formation of organic iodides by thermal reactions: a second-order rate constant of $10^8$ dm$^3$.mol$^{-1}$.s$^{-1}$, which represents iodination of aromatic compounds, and a second-order rate constant of $10^2$ dm$^3$.mol$^{-1}$.s$^{-1}$, which represents iodination of aliphatic molecules. It was assumed that $I_2$ and $HOI$ were equally reactive.

Organic iodides hydrolyze slowly in water. Aliphatic, allylic and benzyl iodides yield the corresponding alcohol and iodide. The rate of hydrolysis increases on going from primary to secondary to tertiary compounds. The presence of an allyl group enhances the rate of hydrolysis by a factor of 5 to 100, while the presence of a benzyl group enhances the rate by a factor of about 50 [32]. We have used the rates for iodomethane given in reference [32] since these should be the lowest hydrolysis rates for organic iodides and thus are conservative.

3.3 Radiolysis of water

As before, we have modelled the radiolysis of water using the reaction set given by Boyd et al. [33]. These authors have compared their model predictions with experimental results from the radiolysis of pure water and water containing initially added oxygen, hydrogen and hydrogen peroxide, as a function of dose rate and pH. They obtained good agreement except at pH values above about twelve, where some of the rate constants are poorly known.

3.4 Radiolysis of iodine solutions

This is by far the most complicated part of the model because of the large number of stable and radical iodine species spanning a range of six oxidation states. We have adopted the reaction set proposed by Buxton and Sellers [6] for the radiation-induced interconversion of iodide and iodate. Most of the rate constants are from the extensive compilation of Sellers [2]. The rate constants for the reduction of HOI by the solvated electron and the oxidation of HOI by the OH radical are from a recent paper by Buxton et al. [34]. The rate constants for the reactions of various iodine species with the $HO_2/O_2$ radicals are from Ishigure [7] and Schwarz [10].

3.5 Radiolysis of organic iodide solutions

Iodomethane and iodoethane are formed by the reaction of methyl and ethyl radicals with elemental iodine in solution [11-14]. The reaction is probably quite general and should occur with most organic radicals. The main
mechanism for the formation of organic radicals is hydrogen abstraction by the OH radical. We have used the known rate constants for the formation of methyl radicals from methane [35] and for the reaction of I₂ with methyl radicals [36]. The reaction scheme proposed by Paquette and Ford [16] for the formation of organic iodides from iodate solutions was also used. These authors have proposed that methyl radicals can reduce oxyiodine radicals according to the general reaction

$$\text{CH}_3 + \text{IO}_x \rightarrow \text{CH}_2\text{O} + \text{HI}_x.\text{I}$$

In the presence of oxygen, the reaction

$$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$$

is important ($k = 4.7 \times 10^9 \text{dm}^3\text{.mol}^{-1}\text{.s}^{-1}$ [36]) since it results in scavenging of organic radicals and could prevent the radiation-induced formation of organic iodides.

Iodomethane reacts with the solvated electron, the OH radical, the hydrogen atom and the H₂O₂ radicals. Not all of the rates are known accurately. Mohan and Asmus [15] have recently demonstrated that the radical species resulting from the reaction of hydroxyl radicals with iodomethane is a strong oxidizing agent and can oxidize iodide to iodine. These mechanisms were included in our model and were assumed to be general for organic iodides.

3.6 Mass transfer

Mass transfer between an aqueous and a gaseous phase is a complicated function of geometry and turbulence in both phases. As before, we have used the simplest form of mass transfer, which assumes that both phases are well mixed. It was assumed that there is a resistance at the water/air interface for the transfer of material to the gas phase and that the rate of the reverse process can be determined from the known equilibrium volatilities.

4. RESULTS AND DISCUSSION

The simulations were performed for the following standard conditions. The concentration of iodine was 10⁻⁵ mol.dm⁻³, as iodide. The concentration of organic impurities was 10⁻⁶ mol.dm⁻³ and was assumed to remain constant during the course of the simulations. The concentration of oxygen, which was assumed to remain constant during the course of the simulations, was 2.5 x 10⁻⁴ mol.dm⁻³, corresponding to air-saturated water at 25°C. The pH was either 5 or 9. The second-order rate constant for the reaction between organic material and I₂ or HOI was either 10² or 10⁸ dm³.mol⁻¹.s⁻¹. The radiation dose rate was 2.8 Gy.s⁻¹ (1 Mrad.h⁻¹). The simulations were performed for up to 10⁵ s, at which time radioactive decay of iodine-131 becomes important.

4.1 Thermal reactions

Figure 1 shows the simulation results for solutions containing initially iodide and dissolved oxygen at pH values of 5 and 9. The partition
coefficient, defined here as the total iodine concentration in the aqueous phase over the total iodine concentration in the gaseous phase, decreases slowly with time as iodide is oxidized to iodine by dissolved oxygen. The partition coefficient is lower at lower pH values, since the equilibrium between HOI and I$_2$ favors I$_2$ at low pH and the rate of oxidation of iodide is proportional to the hydrogen ion concentration. The predominant species in the gas phase is elemental iodine.

Figure 2 shows the results for solutions containing initially iodide, dissolved oxygen and organic material. The partition coefficient is lower than in the absence of organic material and is dominated by organic iodides. It decreases with time initially as volatile organic iodides are formed from iodine and hypoiodous acid. The partition coefficient tends to level off at longer time, where hydrolysis of organic iodides becomes important. As can be seen from Figure 2, the value of the partition coefficient is strongly affected by the pH and the rate of the reaction between I$_2$/HOI and organic material. High pH values and a low rate of reaction favor a high partition coefficient.

4.2 Radiation-induced reactions

Figure 3 shows the simulation results for solutions containing initially iodide and dissolved oxygen at pH values of 5 and 9, subjected to a radiation dose rate of 2.8 Gy·s$^{-1}$ (1 Mrad·h$^{-1}$). The partition coefficients are generally lower than in the absence of radiation because of radiolytic oxidation of iodide to iodine. The predominant species in the gas phase is elemental iodine. Here again, high pH values tend to favor high partition coefficients, since the radiation-induced steady state leans more toward iodide or iodate at the higher pH values and the equilibrium between HOI and I$_2$ favors HOI at high pH.

Figure 4 shows the results for solutions containing initially iodide, dissolved oxygen and organic material, subjected to a radiation dose rate of 2.8 Gy·s$^{-1}$ (1 Mrad·h$^{-1}$). The partition coefficient is lower than in the absence of organic material and lower than in the absence of radiation. At longer times, radiolytic removal of organic iodides becomes important. Organic iodides are the predominant iodine species in the gas phase. Again, high pH values favor high partition coefficients. It should be pointed out that organic iodides originate almost exclusively from thermal reactions, since organic radicals are efficiently scavenged by dissolved oxygen (Reaction (2)). Thus, the formation of organic iodides is not directly induced by radiation, but is rather a secondary effect resulting from the radiolytic oxidation of iodide to I$_2$/HOI, followed by thermal reactions with organic impurities.

4.3 Sensitivity analysis

A sensitivity analysis of a chemical reaction set gives the dependance of the species concentration on the rate constants as a function of time. Thus, it can be useful in identifying the rate constants that should be determined accurately and in identifying unimportant reactions. It can be used as an objective guide for simplification of complicated chemical models. A sensitivity analysis amounts to calculating $(dC_i/dk_j)_t$, where C is the
concentration and k the rate constant for all the species and rate constants of the chemical system as a function of time. As such, it is computation-intensive. High-speed computers and efficient algorithms have made it possible to perform sensitivity analysis on large chemical reaction sets [37]. We have performed a sensitivity analysis of some sections of our model to illustrate the potential of this technique in identifying the important factors controlling the volatility of iodine.

A sensitivity analysis was performed on the combined aqueous iodine chemistry and aqueous organic iodide chemistry sections of the model. The reaction set is given in Table 1. The elementary sensitivity coefficients, ((dC_i/dk_j)_t, the partial derivative of the concentration of species i at time t with respect to the rate constant j) were normalized according to

\[ \frac{d(ln C_i)}{d(ln k_j)} = \left( \frac{k_j}{C_i} \right) \left( \frac{dC_i}{dk_j} \right) \]  

Selected results are given in Table 2, which shows the six largest (in absolute value) normalized sensitivity coefficients, d(ln C)/d(ln k), at time 10^4 s and at a pH of 9, for the gaseous species RI(g), representing volatile organic iodides.

As expected, the concentration of gaseous organic iodide is most sensitive to the rate of oxidation of iodide by dissolved oxygen, which implies that oxidation is the rate-determining step. The next largest sensitivity coefficient is for the transfer of organic iodide between the aqueous and the gaseous phases. Thus, an accurate value of mass transfer rates is important in modelling the behavior of iodine in such a system. The next three largest sensitivity coefficients are related to the rates of reactions producing organic iodides in solution. At a pH of 9, HOI predominates over OI^- (pK_a = 11) and, accordingly, the concentration of organic iodides is more sensitive the rate of reaction of organic material with HOI than that with OI^- . The concentration of organic iodides is less sensitive to the rate of the reaction of organic material with I_2, since at pH 9 the equilibrium between HOI and I_2 is rapidly established and favors HOI. The formation of iodate is not important because the rate of formation of organic iodides from HOI is faster than the rate of disproportionation of HOI to iodate.

The time-dependent behavior of the partition coefficient can be reproduced accurately for these conditions using only the first three reactions given in Table 2. Since the full reaction set consists of 34 reactions (Table 1), this is a considerable simplification of the model.

Table 3 shows the six largest (in absolute value) normalized sensitivity coefficients, d(ln C)/d(ln k), at time 10^3 s and at a pH of 5 for the gaseous species RI(g), which represents volatile organic iodides. Again, the concentration of organic iodide in the gas phase is most sensitive to the rate of oxidation of iodide by dissolved oxygen. The second largest sensitivity coefficient is for the formation of organic iodides from the reaction of organic material with elemental iodine. At this low pH, I_2 predominates over HOI, and, as a result, the concentration of organic iodides is far less sensitive to the rate of the reaction of organic material with HOI than that with I_2. Here again, the concentration of organic iodides is quite sensitive to the rates of transfer of organic iodides between the aqueous and the gaseous phases.
Table 4 shows the five largest (in absolute value) normalized sensitivity coefficients, \( \frac{d(\ln C)}{d(\ln k)} \), at time \( 10^3 \) seconds and at a pH of 5 for the gaseous species \( I_2(g) \). Gaseous elemental iodine can be the dominant iodine species in the gas phase if no organic impurities are present or if the rate of reaction between iodine and organic materials is low. Here again the largest sensitivity coefficient is for the oxidation of the iodide ion by dissolved oxygen. The second largest coefficient is for the transfer of iodine between the aqueous and the gaseous phases.

Based on the above results, the reduced reaction set in Table 5 was established. This reaction set consists of the oxidation of iodide by dissolved oxygen, the iodine hydrolysis equilibrium, the reaction of \( HOI \) and \( I_2 \) with organic impurities and the rates of mass transfer of volatile species between the aqueous and the gaseous phases. The reduced set (6 reactions) gives results identical to those of the full reaction set (34 reactions) for the whole time and pH range studied. This illustrates the potential of the sensitivity analysis technique for model reduction.

5. CONCLUSIONS

Computer modelling of the behavior of iodine under chemical conditions typical of reactor accident situations have shown that the single most important factor controlling the volatility of iodine is the pH of the aqueous phase; high pH values favor low volatility. A sensitivity analysis of the chemical model shows that, in the absence of a radiation field, the concentration of volatile iodine species is most sensitive to the rate of oxidation of iodide by dissolved oxygen and to mass transfer effects. Unfortunately, both of these factors are difficult to quantify accurately. More experimental work is needed on the rate of oxidation of iodide at low iodine concentrations and near-neutral pH conditions typical of reactor accident situations. The rate of thermal oxidation will be less important in the presence of a strong radiation field, were radiolytic oxidation is expected to be predominant. Mass transfer between an aqueous and a gaseous phase is a complicated function of geometry and turbulence in both phases, and is best studied using large-scale facilities. This study has also demonstrated the potential of sensitivity analysis techniques for simplification of complex chemical models. It would be interesting to extend the study to the full iodine model, which includes radiation effects.

6. ACKNOWLEDGEMENT

We thank G. Strobel of the Computing and Information Systems Branch for his assistance with the Floating Point Systems computer. This work was funded jointly by Atomic Energy of Canada Limited and Ontario Hydro, Hydro Quebec and the New Brunswick Electric Power Commission under the CANDU Owner’s Group (COG) program, Working Party 06, Work Package 425.
TABLE 1

IODINE THERMAL REACTIONS. RH REPRESENTS ORGANIC IMPURITIES AND RI REPRESENTS VOLATILE ORGANIC IODIDES.

1. \( H^+ + OH^- \rightarrow H_2O \)  & \( K(1) = 1.438E+11 \)
2. \( H_2O \rightarrow H^+ + OH^- \)  & \( K(2) = 2.596E-05 \)
3. \( I^- + O_2 \rightarrow H_2O_2 + HOI - H_2O \)  & \( K(3) = 3.470E-03 \times H^+ \)
4. \( I_2 + I^- \rightarrow I_3^- \)  & \( K(4) = 1.000E+10 \)
5. \( I_3^- \rightarrow I_2 + I^- \)  & \( K(5) = 1.316E+07 \)
6. \( I_2OH^- + H^+ \rightarrow I_2OH^+ \)  & \( K(6) = 2.000E+00 \)
7. \( I_2OH^- + H^+ \rightarrow I_2 + H_2O \)  & \( K(7) = 1.000E+10 \)
8. \( I_2 + OH^- \rightarrow I_2OH^- \)  & \( K(8) = 1.000E+10 \)
9. \( I_2OH^- \rightarrow I_2 + OH^- \)  & \( K(9) = 3.000E+05 \)
10. \( I_2OH^- \rightarrow HOI + I^- \)  & \( K(10) = 0.940E+02 \)
11. \( HOI + I^- \rightarrow I_2OH^- \)  & \( K(11) = 3.200E+05 \)
12. \( HOI + HOI \rightarrow HIO_2 + I^- + H^+ \)  & \( K(12) = 2.200E+01 \)
13. \( HOI + OI^- \rightarrow HIO_2 + I^- \)  & \( K(13) = 4.000E+01 \)
14. \( OI^- + OI^- \rightarrow IO_2 + I^- \)  & \( K(14) = 7.000E-02 \)
15. \( HOI + HIO_2 \rightarrow IO_3^- + I^- + H^+ + H^+ \)  & \( K(15) = 2.400E+02 \)
16. \( IO_3^- + I^- \rightarrow H_2I_2O - H^+ - H^+ \)  & \( K(16) = 6.700E+02 \times H^+ \)
17. \( H_2I_2O \rightarrow I^- + IO_3^- + H^+ + H^+ \)  & \( K(17) = 1.670E-05 \)
18. \( H_2I_2O + I^- \rightarrow HOI + HOI + OI^- \)  & \( K(18) = 1.267E+04 \)
19. \( HIO_2 + HIO_2 \rightarrow IO_3^- + HOI + H^+ \)  & \( K(19) = 3.000E+13 \times OI^- \)
20. \( HIO_2 + I^- \rightarrow HOI + OI^- \)  & \( K(20) = 5.000E+09 \)
21. \( HIO_2 + IO_3^- \rightarrow HIO_3^- + HIO_3 \)  & \( K(21) = 4.200E+04 \times OI^- \)
22. \( H^+ + OI^- \rightarrow HOI \)  & \( K(22) = 1.000E+10 \)
23. \( HOI \rightarrow H^+ + OI^- \)  & \( K(23) = 1.000E-01 \)
24. \( RH + HOI \rightarrow RI + H_2O \)  & \( K(24) = 1.000E+02 \)
25. \( RH + I_2 \rightarrow RI + I^- + H^+ \)  & \( K(25) = 1.000E+02 \)
26. \( RH + OI^- \rightarrow RI + I^- + OH^- \)  & \( K(26) = 1.000E+02 \)
27. \( RI + H_2O \rightarrow ROH + I^- + H^+ \)  & \( K(27) = 1.000E-09 \)
28. \( RI + OH^- \rightarrow ROH + I^- \)  & \( K(28) = 6.510E-05 \)
29. \( I_2 \rightarrow I_2(g) \)  & \( K(29) = 4.000E-01 \)
30. \( I_2(g) \rightarrow I_2 \)  & \( K(30) = 3.220E+01 \)
31. \( HOI \rightarrow HOI(g) \)  & \( K(31) = 4.000E-01 \)
32. \( HOI(g) \rightarrow HOI \)  & \( K(32) = 9.800E+03 \)
33. \( RI \rightarrow RI(g) \)  & \( K(33) = 4.000E-01 \)
34. \( RI(g) \rightarrow RI \)  & \( K(34) = 2.150E+00 \)
TABLE 2
NORMALIZED SENSITIVITY COEFFICIENTS (S) AT $10^4$ s AND pH 9 FOR RI(g)

<table>
<thead>
<tr>
<th>S</th>
<th>REACTION</th>
<th>$k$ or $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>$\text{I}^- + \text{O}_2 + \text{H}^+ \rightarrow \text{HOI} + \text{H}_2\text{O}_2$</td>
<td>$3.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.84</td>
<td>RI $\leftrightarrow$ RI(g)</td>
<td>$1.9 \times 10^{-1}$</td>
</tr>
<tr>
<td>0.70</td>
<td>RH + HOI $\leftrightarrow$ RI + H$_2$O</td>
<td>$1.0 \times 10^2$</td>
</tr>
<tr>
<td>$7.0 \times 10^{-3}$</td>
<td>RH + OI$^-$ $\rightarrow$ RI + OH$^-$</td>
<td>$1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>$6.8 \times 10^{-3}$</td>
<td>RH + I$_2$ $\leftrightarrow$ RI + HI</td>
<td>$1.0 \times 10^2$</td>
</tr>
<tr>
<td>$2.4 \times 10^{-3}$</td>
<td>HOI + I$^-$ $\leftrightarrow$ I$_2$OH$^-$</td>
<td>$3.2 \times 10^2$</td>
</tr>
</tbody>
</table>

TABLE 3
NORMALIZED SENSITIVITY COEFFICIENTS AT $10^3$ SECONDS AND pH 5 FOR RI(g). S REPRESENTS THE NORMALIZED SENSITIVITY COEFFICIENT, $k$ IS THE RATE CONSTANT IN UNITS OF SECONDS, MOLES AND dm$^3$, AND $K$ IS THE EQUILIBRIUM CONSTANT.

<table>
<thead>
<tr>
<th>S</th>
<th>REACTION</th>
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<tbody>
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<td>$\text{I}^- + \text{O}_2 + \text{H}^+ \rightarrow \text{HOI} + \text{H}_2\text{O}_2$</td>
<td>$3.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>0.88</td>
<td>RH + I$_2$ $\rightarrow$ RI + HI</td>
<td>$1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.84</td>
<td>RI $\leftrightarrow$ RI(g)</td>
<td>$1.9 \times 10^{-1}$</td>
</tr>
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<td>$1.0 \times 10^2$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-2}$</td>
<td>I$_2$ $\leftrightarrow$ I$_2$(g)</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>$1.5 \times 10^{-3}$</td>
<td>HOI + I$^-$ $\leftrightarrow$ I$_2$OH$^-$</td>
<td>$3.2 \times 10^2$</td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$</td>
<td>I$_2$OH$^-$ + H$^+$ $\leftrightarrow$ I$_2$ + H$_2$O</td>
<td>$5.0 \times 10^9$</td>
</tr>
</tbody>
</table>
### TABLE 4

NORMALIZED SENSITIVITY COEFFICIENTS (S) (S) AT 10³ SECONDS AND pH 5 FOR I₂⁻

<table>
<thead>
<tr>
<th>S</th>
<th>REACTION</th>
<th>k or K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>I⁻ + O₂ + H⁺ → HOI + H₂O₂</td>
<td>3.7 × 10⁻³</td>
</tr>
<tr>
<td>0.99</td>
<td>I₂⁻ ↔ I₂(g)</td>
<td>1.2 × 10⁻²</td>
</tr>
<tr>
<td>8.0 × 10⁻²</td>
<td>HOI + I⁻ ↔ I₂ + OH⁻</td>
<td>1.4 × 10⁴</td>
</tr>
<tr>
<td>7.7 × 10⁻²</td>
<td>I₂OH⁻ + H⁺ ↔ I₂ + H₂O</td>
<td>5.0 × 10⁹</td>
</tr>
<tr>
<td>4.0 × 10⁻²</td>
<td>RH + I₂ ↔ RI + HI</td>
<td>1.0 × 10²</td>
</tr>
</tbody>
</table>

### TABLE 5

REDUCED REACTION SET

1. I⁻ + O₂ + H⁺ → HOI + H₂O₂
2. HOI + I⁻ + H⁺ ↔ I₂ + H₂O
3. RH + I₂ ↔ RI + HI
4. RH + HOI → RI + H₂O
5. RI ↔ RI(g)
6. I₂ ↔ I₂(g)
REFERENCES


FIGURE 1. Partition coefficient as a function of time for a solution containing initially iodide and dissolved oxygen at pH 5 and 9.
FIGURE 2. Partition coefficient as a function of time for a solution containing initially iodide, dissolved oxygen and organic material at pH 5 and 9. The rate of the reactions between $I_2$/HOI and organic material was set at either $10^2$ or $10^8$ dm$^3$.mol$^{-1}$.s$^{-1}$. 
FIGURE 3. Partition coefficient as a function of time for a solution containing initially iodide and dissolved oxygen at a pH of 5 or 9, subjected to a radiation dose rate of 2.8 Gy⁻¹ (1 Mrad·h⁻¹).
FIGURE 4. Partition coefficient as a function of time for a solution containing initially iodide, dissolved oxygen and organic material at a pH of 5 or 9, subjected to a radiation dose rate of 2.8 Gy⁻¹ (1 Mrad·h⁻¹). The rate of the reactions between I₂/HO₂ and organic material was set at either 10² or 10⁸ dm³·mol⁻¹·s⁻¹.
DISCUSSION

J.P. LONGWORTH The previous paper suggested that back reactions, i.e., mass transfer back from the vapour into the solution, may dominate behaviour particularly at late times.

J. PAQUETTE Our sensitivity analysis shows that the concentration of volatile iodine species is very sensitive to mass transfer effects. We have used in our model one of the simplest forms of mass transfer. It was assumed that both the gas and aqueous phases are well mixed and that there is a resistance at the water/air interface for the transfer of material from the aqueous phase to the gas phase. The rate of the reverse process was determined from the known equilibrium volatilities. This is obviously a gross oversimplification since mass transfer between an aqueous phase and a gaseous phase can be a complicated function of geometry and turbulence in both phases.

W.G. BURNS How did you obtain the rate of the reaction making I₂ from I⁻?

J. PAQUETTE We have used the rate law given by Burns and Marsh in W.G. Burns and W.R. Marsh, "The Thermal and Radiolytic Oxidation of Aqueous I⁻ and the Hydrolysis and Disproportionation of Aqueous I₂", United Kingdom Atomic Energy Authority, Harwell Laboratory, report AERE R 10767 (1986). Their rate constant was multiplied by a factor of three to take into account potential catalytic effects from trace amounts of metallic impurities.
RADIOLYSIS OF IODINE IN MOIST AIR: A COMPUTER STUDY

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ABSTRACT

The gas phase radiolysis of moist air, with small additions of methane and molecular iodine, has been modelled in an attempt to judge the effects of radiation fields on the chemistry of the gas phase in the containment space after a nuclear accident. The model does not allow for any interchange of species between the gas phase and liquid water, as would be the case in a real accident.

Use of the currently accepted rate constants makes it clear that methyl iodide cannot be formed by abstraction of iodine atoms from I₂ by methyl radicals, as sometimes assumed. The oxygen present in the air competes far too efficiently for the methyl radicals. Thus, the observed methyl iodide yields must arise in other ways.

Iodine molecules were converted into oxygenated species such as IO₂ and I₂O₃ during the first two minutes after an accident, assuming a dose rate of 2.2 x 10¹⁵ eV∙dm⁻³·s⁻¹. The main route for oxidation is the reaction of hydroxyl radicals with iodine molecules. This reaction has been shown to be fast, at least in the gas phase. The oxygenated iodine species are presumably converted into soluble species such as I₄O₉, but not enough rate constants are available to model this conversion successfully.
1. INTRODUCTION

One aspect of the work on iodine chemistry in reactor safety being carried out at the Whiteshell Nuclear Research Establishment is the development of computer models to predict the concentration of various iodine-containing species following a nuclear accident [1]. As a preliminary step in the development of such models, it was considered desirable to model, in isolation, the effects of the gas phase radiolysis of moist air containing traces of hydrocarbon and molecular iodine, and to compare the results obtained with the experimental data available.

It is well known that the radiolysis of air creates an environment that is, on the whole, oxidizing in nature, and large concentrations of ozone and nitric acid are produced [2]. Thus, it was suggested at the previous conference in this series that the effect of the radiation field might be sufficient to oxidize a considerable percentage of the iodine to soluble oxides in a relatively short time [3]. This work is intended to explore this possibility a little more thoroughly, using a computer model. The model would then be coupled to other models being developed for liquid phase and heterogeneous reactions of iodine species to give a complete description of the chemistry anticipated during a nuclear accident.

2. CALCULATIONS AND RESULTS

The gas phase radiolysis of moist air, with additions of methane and iodine, was modelled using the computer program MAKSIMA-CHEMIST [4-6]. This program uses stiff, sparse integration methods to obtain a solution for sets of many simultaneous mass action kinetics equations.

2.1 Radiolysis of Moist Air

The first step in this work was to model the radiolysis of moist air, using equations and yields from Busi et al. [7,8] and from Willis and Boyd [9]. This database was developed by Busi et al. to model the electron-beam induced oxidation of SO\(_2\) and NO\(_x\) in flue gas and was a very useful starting point for this work. The nitrogen atom yield used by Busi et al. [7] of 3 molecules per 100 eV (1.6 x 10\(^{-17}\) J) is lower than that often assumed [9,10], which is closer to 6 molecules per 100 eV. This lower yield was used by Busi et al. [7] to give better agreement with experiments on the radiation-induced removal of NO\(_x\) and SO\(_x\) from flue gases [11]. A similar approach was used by Slater [12], who justified his lower yields for nitrogen atoms on efficient quenching of nitrogen atom precursors by CO\(_2\) and H\(_2\)O as well as by nitrogen molecules. Ionization cross sections were taken from Willis and Boyd [9]. The total pressure was taken as atmospheric and the moist air was taken as 74.2% N\(_2\), 18.6% O\(_2\), and 7.2% H\(_2\)O. This corresponds to air saturated with water vapour at 40°C. When these percentages were corrected for the stopping powers, as determined from
Willis and Boyd [9], we calculated that 85.2% of the energy was originally deposited in the N$_2$, and 7.4% in the O, and the H$_2$O alike. Direct energy absorption by the smaller components of air was not considered.

Using these relative stopping powers, the yields in G units (molecules for each 100 eV) were calculated and are shown in Table I. A negative yield, of course, indicates consumption. The yields of excited molecular species were combined, following Busi et al. [7]. The reactions used in this model for moist air radiolysis and the rate constants assigned by Busi et al. [7] are shown in Table II, Reactions (1) to (45). The units are mol·dm$^{-3}$, s units, as appropriate, and a reactant in brackets (c.f. reaction (45)) means that the reactant is included in the stoichiometry, but is not included in the mass-action rate law. The rate constants are for room temperature, but most of the reactions of the primary species have activation energies in the range of 16 + 8 kJ·mol$^{-1}$, so temperature changes should only have moderate effects on the radical yields. Experimentally, the removal of NO from flue gas by electron beam irradiation is not affected by temperature changes in the range of 100 to 150°C [13]. The dose rate was taken as 10 kGy per hour, which, with this mixture, means a dose rate of $2.20 \times 10^{15}$ eV·dm$^{-3}$·s$^{-1}$.

In agreement with experiment [2,14], this model predicts nitric acid formation with a G value of about 3.19 molecules per 100 eV, and also a significant ozone yield of 1.65 molecules per 100 eV. Other significant yields are H$_2$O$_2$ (0.09) and H$_2$O (0.25). The predicted yield of N$_2$O is quite low, however, while the experimental results indicate a measurable yield of 0.38 [14]. The model predicts that the ions H$_3$O$^+$ and CO$_2^-$ should dominate in recombination processes, even though CO$_2$ is present only in small amounts.

2.2 Radiolysis of Moist Air with Methane and Iodine

Once reasonably satisfactory predictions were obtained for the model of the radiolysis of moist air, small additions of methane and iodine were considered. The reactions involving methane and iodine as used by Castleman [15] were added, as proposed by Paquette and Wren [16]. The entire reaction set, along with the associated rate constants is shown in Table II. Methane and molecular iodine were then added to the initial reactants. In most of our calculation the initial methane and iodine concentrations were $2.14 \times 10^{-8}$ and $7.85 \times 10^{-9}$ mol·dm$^{-3}$, respectively. These were the concentrations used by Habersbergerova and Bartonicek [17] who have carried out experiments under conditions closest to those we wanted to model. A few runs were made for what were considered more realistic accident conditions. These involved nitrogen and oxygen concentrations corresponding to a total pressure of 1.5 atmospheres, and a water concentration corresponding to the vapour pressure at 70°C ($1.09 \times 10^{-2}$ mol·dm$^{-3}$). The iodine concentration was increased to 39 mmol·dm$^{-3}$ and the methane to 82 mmol·dm$^{-3}$. Qualitatively, the results

* $1 \text{ atm} = 101.325 \text{ kPa}$
were very similar to those obtained using our standard conditions. It took about four times as long to oxidize the iodine, which is reasonable since about five times as much was considered present.

In this set of equations CH\textsubscript{3}I is produced when methyl radicals abstract iodine atoms from I\textsubscript{2}. However, as has been recognized, the modern values of the rate constants for the iodine abstraction by methyl radicals, Reaction (46), and oxygen molecule addition to methyl radical, Reaction (50), are such that the iodine abstraction cannot compete with the oxygen addition in an air atmosphere [18-21]. Thus the predicted methyl iodide yield is very low. It is very much lower than the experimental results of Habersbergerova and Bartonicek [17]. The methyl iodide produced in the experiments may arise from surface reactions, from reactions in an aerosol or possibly by reactions involving the CH\textsubscript{3}O\textsubscript{2} radical or its products. Such reactions, and certainly the rate constants assigned them, would be highly speculative at present. Thus the matter of CH\textsubscript{3}I yields will not be considered further.

The Reaction scheme used has a number of possible pathways for the oxidation of iodine. One pathway is by energy transfer from excited states of nitrogen and oxygen to iodine molecules, leading to dissociation of the iodine molecules to atoms (Reactions (64) and (65)). These reactions compete, of course, with normal quenching as represented by reactions (66) and (67). The rate constants for quenching are not well known and have been estimated using current knowledge [22]. Other pathways considered are the reaction of oxygen atoms with iodine, Reaction (70), and the reaction of ozone with iodine, Reactions (73) and (74). In the first case, the reaction is slow because of the low steady-state concentration of oxygen atoms, and the second is slow because the rate constant is relatively low. If only the above pathways are considered, the oxidation rate for iodine is low.

The major pathway for the oxidation of iodine in the model, as presented, is the reaction of hydroxyl radicals with iodine to give HOI and iodine atoms, Reaction (68). The rate constant data for Jenkin et al [23] were used, and they imply a fast reaction. The conclusion that the reaction is fast is supported by comparison with data for the reactions of other halogens with hydroxyl radicals [24], and by comparison with other similar reactions, such as OH reaction with CF\textsubscript{3}I [25]. On the other hand, for many years the reaction was assumed not to occur at all in liquid water [26,27]. Recently however, a rate constant has been obtained by pulse radiolysis [28] and this rate constant is very close to that previously measured in the gas phase. Thus, the current picture seems to be that this reaction does occur and is fast. The stability of the HOI formed is not well known. Assumptions have to be made about the rates of reactions of radicals with HOI. The unimolecular decomposition rate was estimated from the thermodynamic calculations of Garisto [29]. These calculations predict that the HOI molecule will have appreciable stability towards unimolecular decomposition. Rate constants for reaction involving IO were taken from Baluch et al. [20].

Typical results from the model are shown in Figure 1, 2 and 3. For the data presented in these figures the methane and iodine concentrations were those used by Habersbergerova and Bartonick [17], as noted above. The model shows that the iodine concentration is reduced by several orders of
magnitude in the first two minutes, and that the iodine is converted into oxygenated species, represented here by I$_2$O$_3$. Eventually, the oxygenated iodine species are presumably converted into I$_4$O$_9$ and other solid I$_x$O$_y$ polymer [30-32], but rate constants are not available for further steps along the transformation, and thus, it was not considered useful to include such steps. If only those iodine oxidation pathways that do not involve HOI are considered, it takes about 20 minutes to oxidize the I$_2$ to I$_2$O$_3$, compared to the two minutes taken if the HOI pathways are included. These times are all relatively short when considered on the timescale of events in any nuclear accident.

The model, with rate constants as presented, shows that HOI concentrations rise to the appreciable levels of $3 \times 10^{-9}$ mol·dm$^{-3}$ and then drop sharply as the iodine is consumed (Figure 1). The I$_2$ also rises to a flatter maximum, but then drops sharply as the iodine is consumed. Using these rate constants, IO$_2$ rises to a steady value of $2 \times 10^{-10}$ mol·dm$^{-3}$, whereas I$_2$O$_3$, considered the final oxygenated product, becomes the major iodine-containing species. No rate constant was included for unimolecular decay of IO$_2$.

Figure 2 shows the consumption of methane and the formation of the major methylated products. There is some indication of a small early perturbation in the decay of methane, but generally this decay takes place with a half life of about 1200 s, and seems to be independent of the iodine oxidation. This is a bit of an artifact because of the scales. When the data are examined more closely, it is seen that methane consumption does not really get underway until the iodine is consumed. As well as the two products indicated, minor amounts of methane and formaldehyde are predicted. Finally, Figure 3 shows yields of hydrogen, hydrogen peroxide, ozone and nitric acid. The hydrogen and nitric acid yields rise smoothly with time and do not seem to be affected by the iodine oxidation. Both the ozone and, to a much lesser extent, the hydrogen peroxide have rather lower yields initially, but then, when the iodine is exhausted, begin to rise quickly. Thus, with this scheme, the oxidizing agents created by radiolysis of water vapour, principally the hydroxyl radicals initially, only begin to form ozone after the iodine is consumed.

3. DISCUSSION AND CONCLUSION

This work has presented a picture of the gas phase radiolysis of moist air in the presence of small amounts of iodine and methane, as predicted by reactions and rate constants available. There are a large number of problems with the model. In the first place the rate constants for later reactions are not well known, so that the final products are not well predicted. It seems likely, however, that the iodine is converted into water-soluble iodine oxide, and the methane is converted into various methylated nitrogen oxides.

Reaction involving key species such as HOI and I$_2$O$_2$ are not well known. In some cases I$_2$O$_3$ is considered an unstable intermediate, but its lifetime is not well known. Similarly, HOI has been postulated for many reactions, but its stability and properties are not well established. Some good spectroscopic data on these species would be invaluable at present.
Also, more information is needed on the basic yields of atom products in the presence of water molecules and other potential quenchers.

In any case, the model, as presently available, predicts that, in moist air with methane and iodine, iodine oxidation takes place initially, and, with the concentrations and dose rates used, consumes the iodine in about two minutes. After that, the methane is oxidized to various methylated nitrogen oxides and ozone is formed.

4. ACKNOWLEDGEMENTS

A.C. Vikis suggested this problem and J. Paquette, F. Garisto and R.J. Lemire have provided extremely valuable assistance. This work was funded jointly by Atomic Energy of Canada Limited and Ontario Hydro, Hydro Québec and the New Brunswick Electric Power Commission under the CANDU Owner's Group (COG) program, Working Party 06, Work Package 425.
REFERENCES


19. D.M. Golden, R. Walsh and S.W. Benson, "The Thermochemistry of the Gas Phase Equilibrium I\textsubscript{2} + CH\textsubscript{4} \rightleftharpoons CH\textsubscript{3}I + I\textsubscript{2} and the Heat of Formation of the Methyl Radical", J. Amer. Chem. Soc. 87, 4053 (1965).


TABLE I

INITIAL YIELDS AND CONCENTRATIONS USED FOR RADIOLYSIS OF MOIST AIR

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>YIELD (molecules·(100 eV)^{-1})</th>
<th>INITIAL CONCENTRATION (mol·dm^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>-3.885</td>
<td>2.00 x 10^{-2}</td>
</tr>
<tr>
<td>O\textsubscript{2}°</td>
<td>-0.256</td>
<td>5.00 x 10^{-3}</td>
</tr>
<tr>
<td>N\textsubscript{2}°</td>
<td>0.254</td>
<td>0.00</td>
</tr>
<tr>
<td>O\textsubscript{2}°</td>
<td>0.144</td>
<td>0.00</td>
</tr>
<tr>
<td>N\textsuperscript{2}°</td>
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<td>0.00</td>
</tr>
<tr>
<td>N\textsuperscript{2}</td>
<td>0.160</td>
<td>0.00</td>
</tr>
<tr>
<td>O\textsuperscript{2}</td>
<td>1.991</td>
<td>0.00</td>
</tr>
<tr>
<td>N\textsuperscript{2}</td>
<td>0.605</td>
<td>0.00</td>
</tr>
<tr>
<td>N\textsuperscript{2}°</td>
<td>0.096</td>
<td>0.00</td>
</tr>
<tr>
<td>O\textsuperscript{2}°</td>
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</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>-0.340</td>
<td>1.20 x 10^{-3}</td>
</tr>
<tr>
<td>H\textsubscript{2}O°</td>
<td>0.093</td>
<td>0.00</td>
</tr>
<tr>
<td>OH\textsuperscript{+}</td>
<td>0.027</td>
<td>0.00</td>
</tr>
<tr>
<td>H\textsuperscript{2}°</td>
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<td>H\textsuperscript{-}</td>
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<td>0.00</td>
</tr>
<tr>
<td>OH\textsuperscript{+}</td>
<td>0.165</td>
<td>0.00</td>
</tr>
<tr>
<td>e\textsuperscript{-}</td>
<td>3.000</td>
<td>0.00</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>0.00</td>
<td>7.28 x 10^{-6}</td>
</tr>
</tbody>
</table>
### TABLE II

**REACTIONS USED IN THE MODEL**

<table>
<thead>
<tr>
<th>EQUATION NUMBER</th>
<th>REACTION</th>
<th>RATE CONSTANT (mol·dm⁻³·s units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N₂⁺ + H₂O ⏸→ H₂O⁺ + N₂</td>
<td>1.40 x 10⁻¹²</td>
</tr>
<tr>
<td>2</td>
<td>N₂⁺ + H₂O ⏸→ H₂O⁺ + N</td>
<td>1.40 x 10⁻¹²</td>
</tr>
<tr>
<td>3</td>
<td>O₂⁺ + H₂O ⏸→ H₂O⁺ + O²</td>
<td>1.00 x 10⁻¹⁰</td>
</tr>
<tr>
<td>4</td>
<td>O⁺  + H₂O ⏸→ H₂O⁺ + O</td>
<td>1.40 x 10⁻¹¹</td>
</tr>
<tr>
<td>5</td>
<td>H₂O⁺ + H₂O ⏸→ H₃O⁺ + OH</td>
<td>7.20 x 10⁻¹¹</td>
</tr>
<tr>
<td>6</td>
<td>N₂⁺ + O₂ ⏸→ N₂ + O₂⁺</td>
<td>2.50 x 10⁻¹⁰</td>
</tr>
<tr>
<td>7</td>
<td>e⁻  + O₂ ⏸→ O₂⁻</td>
<td>3.20 x 10⁻¹⁰</td>
</tr>
<tr>
<td>8</td>
<td>H₃O⁺ + O²⁻ ⏸→ H + O₂ + H₂O</td>
<td>2.50 x 10⁻¹¹</td>
</tr>
<tr>
<td>9</td>
<td>H₃O⁺ + e⁻ ⏸→ H + H₂O</td>
<td>2.50 x 10⁻¹¹</td>
</tr>
<tr>
<td>10</td>
<td>N + N ⏸→ N₂</td>
<td>1.00 x 10⁸</td>
</tr>
<tr>
<td>11</td>
<td>H + O₂ ⏸→ HO₂</td>
<td>6.50 x 10⁹</td>
</tr>
<tr>
<td>12</td>
<td>OH + HO₂ ⏸→ H₂O + O₂</td>
<td>5.60 x 10⁻¹⁰</td>
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<tr>
<td>13</td>
<td>NO + OH ⏸→ HNO₂</td>
<td>4.90 x 10⁹</td>
</tr>
<tr>
<td>14</td>
<td>NO₂ + OH ⏸→ HNO₃</td>
<td>4.80 x 10⁹</td>
</tr>
<tr>
<td>15</td>
<td>NO⁺ + O ⏸→ NO₂</td>
<td>1.60 x 10⁹</td>
</tr>
<tr>
<td>16</td>
<td>NO₂ + O ⏸→ NO₃</td>
<td>1.30 x 10⁹</td>
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<td>17</td>
<td>NO₂ + O ⏸→ NO + O₂</td>
<td>5.60 x 10⁹</td>
</tr>
<tr>
<td>18</td>
<td>NO⁺ + O₂ ⏸→ NO₂⁺ + O₂</td>
<td>1.20 x 10⁷</td>
</tr>
<tr>
<td>19</td>
<td>NO₂ + O₃ ⏸→ NO₃ + O₂</td>
<td>4.80 x 10⁴</td>
</tr>
<tr>
<td>20</td>
<td>NO²⁺ + O₂⁻ ⏸→ NO₂ + OH</td>
<td>6.00 x 10⁹</td>
</tr>
<tr>
<td>21</td>
<td>NO₂ + HO₂ ⏸→ HNO₂ + O₂</td>
<td>1.80 x 10⁸</td>
</tr>
<tr>
<td>22</td>
<td>NO + N ⏸→ N₂ + O</td>
<td>1.30 x 10¹⁰</td>
</tr>
<tr>
<td>23</td>
<td>NO₂ + N ⏸→ 2NO</td>
<td>3.50 x 10⁹</td>
</tr>
<tr>
<td>24</td>
<td>NO₂ + N ⏸→ N₂O + O</td>
<td>4.60 x 10⁹</td>
</tr>
<tr>
<td>25</td>
<td>HNO₂ + OH ⏸→ N₂O₂ + H₂O</td>
<td>4.10 x 10⁹</td>
</tr>
<tr>
<td>26</td>
<td>HNO₂ + HNO₂ ⏸→ NO + NO₂ + H₂O</td>
<td>1.80 x 10⁶</td>
</tr>
<tr>
<td>27</td>
<td>HNO₂ + HNO₃ ⏸→ 2NO₂ + H₂O</td>
<td>8.20 x 10⁴</td>
</tr>
<tr>
<td>28</td>
<td>NO₂ + NO₃ ⏸→ N₂O₅</td>
<td>1.80 x 10⁹</td>
</tr>
<tr>
<td>29</td>
<td>N₂O₅ ⏸→ NO₂ + NO₃</td>
<td>2.90 x 10⁻¹</td>
</tr>
<tr>
<td>30</td>
<td>N₂O₅ + H₂O ⏸→ 2HNO₃</td>
<td>2.50 x 10³</td>
</tr>
<tr>
<td>31</td>
<td>NO + NO₃ ⏸→ 2NO₂</td>
<td>6.00 x 10⁹</td>
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<tr>
<td>32</td>
<td>e⁻  + NO₂ ⏸→ NO₂⁻</td>
<td>2.50 x 10¹⁰</td>
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<tr>
<td>33</td>
<td>e⁻  + NO₃ ⏸→ NO₃⁻</td>
<td>2.50 x 10¹⁰</td>
</tr>
<tr>
<td>34</td>
<td>H₃O⁺ + NO₂⁻ ⏸→ H + NO₂ + H₂O</td>
<td>2.00 x 10¹²</td>
</tr>
<tr>
<td>35</td>
<td>H₃O⁺ + NO₃⁻ ⏸→ H + NO₃ + H₂O</td>
<td>2.00 x 10¹²</td>
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</tbody>
</table>

continued...
<table>
<thead>
<tr>
<th>EQUATION NUMBER</th>
<th>REACTION</th>
<th>RATE CONSTANT (mol·dm⁻³·s⁻¹ units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>e⁻ + CO₂ ----&gt; CO₂⁻</td>
<td>8.50 x 10⁴</td>
</tr>
<tr>
<td>42</td>
<td>O₂⁻ + CO₂ ----&gt; CO₂⁻ + O₂</td>
<td>2.50 x 10¹¹</td>
</tr>
<tr>
<td>43</td>
<td>CO₂⁻ + H₃O⁺ ----&gt; H + H₂O + CO₂</td>
<td>1.00 x 10¹²</td>
</tr>
<tr>
<td>44</td>
<td>O₂⁺ + CO₂⁻ ----&gt; CO + O₂ + O</td>
<td>2.50 x 10¹¹</td>
</tr>
<tr>
<td>45</td>
<td>CO + OH (+O₂) ----&gt; CO₂ + HO₂</td>
<td>8.20 x 10⁷</td>
</tr>
<tr>
<td>46</td>
<td>CH₃ + I₂ ----&gt; CH₃I + I</td>
<td>1.00 x 10¹⁰</td>
</tr>
<tr>
<td>47</td>
<td>I + I ----&gt; I₂</td>
<td>2.00 x 10⁹</td>
</tr>
<tr>
<td>48</td>
<td>CH₃ + I ----&gt; CH₃I</td>
<td>2.00 x 10⁹</td>
</tr>
<tr>
<td>49</td>
<td>H + I₂ ----&gt; HI + I</td>
<td>1.00 x 10⁷</td>
</tr>
<tr>
<td>50</td>
<td>CH₃ + O₂ ----&gt; CH₃O₂</td>
<td>1.00 x 10⁹</td>
</tr>
<tr>
<td>51</td>
<td>CH₃ + O₂ ----&gt; HCOH + OH</td>
<td>3.00 x 10⁴</td>
</tr>
<tr>
<td>52</td>
<td>CH₃O₂ + CH₃O₂ ----&gt; CH₃OH + HCOH + O₂</td>
<td>1.30 x 10⁸</td>
</tr>
<tr>
<td>53</td>
<td>CH₃O + NO₂ ----&gt; CH₃NO₃</td>
<td>7.20 x 10⁹</td>
</tr>
<tr>
<td>54</td>
<td>CH₃O + NO ----&gt; CH₃NO₂</td>
<td>1.20 x 10¹⁰</td>
</tr>
<tr>
<td>55</td>
<td>OH + CH₄ ----&gt; CH₃ + H₂O</td>
<td>1.00 x 10⁸</td>
</tr>
<tr>
<td>56</td>
<td>O₂⁻ + OH⁺ ----&gt; O₂ + OH</td>
<td>2.00 x 10¹¹</td>
</tr>
<tr>
<td>57</td>
<td>CO₂⁻ + OH⁺ ----&gt; CO₂ + OH</td>
<td>2.00 x 10¹¹</td>
</tr>
<tr>
<td>58</td>
<td>O₂⁻ + H⁺ ----&gt; O₂ + H</td>
<td>1.00 x 10¹²</td>
</tr>
<tr>
<td>59</td>
<td>CO₂⁻ + H₂⁺ ----&gt; CO₂ + H₂</td>
<td>1.00 x 10¹²</td>
</tr>
<tr>
<td>60</td>
<td>2CH₃O₂ ----&gt; (CH₃)₂O₂ + O₂</td>
<td>1.80 x 10⁷</td>
</tr>
<tr>
<td>61</td>
<td>2CH₃O₂ ----&gt; CH₃O₂ + O₂</td>
<td>7.80 x 10⁷</td>
</tr>
<tr>
<td>62</td>
<td>CH₃O₂ + NO ----&gt; CH₃O + NO₂</td>
<td>4.00 x 10⁹</td>
</tr>
<tr>
<td>63</td>
<td>CH₃O₂ + NO₂ ----&gt; CH₃O₂NO₂</td>
<td>6.00 x 10⁸</td>
</tr>
<tr>
<td>64</td>
<td>N₂ + I₂ ----&gt; N₂ + 2I</td>
<td>1.00 x 10⁸</td>
</tr>
<tr>
<td>65</td>
<td>O₂⁺ + I₂ ----&gt; O₂ + 2I</td>
<td>1.00 x 10⁸</td>
</tr>
<tr>
<td>66</td>
<td>N₂⁺ + N₂ ----&gt; 2N₂</td>
<td>1.00 x 10⁶</td>
</tr>
<tr>
<td>67</td>
<td>O₂ + N₂ ----&gt; N₂ + O₂</td>
<td>1.00 x 10⁶</td>
</tr>
<tr>
<td>68</td>
<td>OH + I₂ ----&gt; HOI + I</td>
<td>1.32 x 10¹¹</td>
</tr>
<tr>
<td>69</td>
<td>HOI ----&gt; OH + I</td>
<td>7.00 x 10⁻¹⁸</td>
</tr>
<tr>
<td>70</td>
<td>0 + I₂ ----&gt; IO + I</td>
<td>2.40 x 10¹⁰</td>
</tr>
<tr>
<td>71</td>
<td>0 + IO ----&gt; O₂ + I</td>
<td>3.00 x 10¹⁰</td>
</tr>
<tr>
<td>72</td>
<td>I + O₃ ----&gt; IO + O₂</td>
<td>6.00 x 10⁸</td>
</tr>
<tr>
<td>73</td>
<td>I₂ + O₃ ----&gt; IO + I + O₂</td>
<td>9.00 x 10³</td>
</tr>
<tr>
<td>74</td>
<td>I₂ + O₃ ----&gt; IO + IO₂</td>
<td>9.00 x 10³</td>
</tr>
<tr>
<td>75</td>
<td>IO + O₃ ----&gt; IO₂ + O₂</td>
<td>2.00 x 10⁸</td>
</tr>
<tr>
<td>76</td>
<td>IO + IO₂ ----&gt; I₂O₃</td>
<td>1.00 x 10⁹</td>
</tr>
<tr>
<td>77</td>
<td>OH + HOI ----&gt; H₂O + IO</td>
<td>1.50 x 10¹¹</td>
</tr>
<tr>
<td>78</td>
<td>H + HOI ----&gt; H₂ + IO</td>
<td>5.00 x 10¹⁰</td>
</tr>
<tr>
<td>79</td>
<td>HOI + HNO₂ ----&gt; INO₂ + H₂O</td>
<td>5.00 x 10⁵</td>
</tr>
<tr>
<td>80</td>
<td>2INO₂ ----&gt; I₂ + 2NO₂</td>
<td>1.50 x 10⁷</td>
</tr>
<tr>
<td>81</td>
<td>I + ÍNO₂ ----&gt; I₂ + NO₂</td>
<td>5.00 x 10¹⁰</td>
</tr>
</tbody>
</table>
FIGURE 1: Gas Phase Radiolysis of Moist Air containing CH\textsubscript{4} and I\textsubscript{2}.
Concentrations are shown for I\textsubscript{2} (---), IO ( - - -), HOI (-----) and I\textsubscript{2}O\textsubscript{3} (-----).
FIGURE 2: Gas Phase Radiolysis of Moist Air containing CH₄ and I₂. Concentrations are shown for CH₃NO₂ (— • —), CH₃ONO₂ (---) and CH₄ (—→).
FIGURE 3: Gas Phase Radiolysis of Moist Air containing CH₄ and I₂. Concentrations are shown for H₂O₂ (\(\cdots\cdot\)), H₂ (\(\cdot\cdot\)), O₃ (\(---\)) and HNO₃ (\(\cdots\cdots\)).
DISCUSSION

D.J. WREN Have you considered adding 2-3% H$_2$ to the atmosphere and what would be the implications of added H$_2$?

N.H. SAGERT We have not yet considered this case, although it could be run easily. Probably a small amount of hydrogen would combine with oxygen, eventually. The iodine would be oxidized while there was an overwhelming amount of hydrogen present, but OH + I$_2$ is much faster than OH + H$_2$, so a small amount of H$_2$ would have little effect.

J.P. LONGWORTH The dose used are presumably due to 100% of noble gases, and I think your implication is that, if there is any I$_2$ airborne it will rapidly be transferred into more soluble forms. Are these implications for the aqueous modellers in that the initial forms varied now be different from I$^-$?

N.H. SAGERT This oxidation could well increase the amount of oxidized iodine species in solution. However the total burden of iodine in the gas phase is probably very small compared to that in the liquid.

M. FURRER Would the highest iodine-oxides eventually have to be added to the iodate-inventory of the water phase?

N.H. SAGERT Yes, it is likely that the iodine oxides would add to the iodate in the water eventually (see refs [30], [32] and S. Sunder and A. Vikis, Can. J. Spect. 32, 45 (1987).

A.C. VIKIS What Dr. Sagert says in this paper is that, contrary to what was believed in the past, gas phase radiation chemistry should suppress airborne iodine. Radiation-induced oxidation of airborne iodine was postulated by A.C. Vikis and D.F. Torgerson at the previous CSNI Iodine Workshop. The present paper by Dr. Sagert is a more sophisticated verification of this postulate. We also plan to verify these findings experimentally.

H. SHINAISHI Isn't there any possibility that methyl peroxy radical reacts with iodine species?

N.H. SAGERT The methyl peroxy radicals are generally considered unreactive towards abstraction. Combination reactions are possible but were not considered.
CHEMISTRY AND MASS TRANSPORT OF IODINE IN CONTAINMENT


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ABSTRACT

TRENDS is a computer code for modeling behavior of iodine in containment. It tracks both chemical and physical changes and features such as calculation of radiation dose rates in water pools, radiolysis effects, hydrolysis, and deposition/revaporization on aerosols and structural surfaces. Every attempt has been made to account for all significant processes. Reaction rate constants for iodine hydrolysis and radiolysis were obtained by a variable algorithm that gives values closely modeling experimental data.

TRENDS output provides the distribution of iodine in containment and release from containment as a function of time during a severe accident sequence. Initial calculations with TRENDS have shown that the amount of volatile iodine released from containment is sensitive to the value of the liquid-gas (evaporation) mass transport coefficient for I₂.

1. INTRODUCTION

The TRENDS code for calculation of iodine behavior and release in containment is a system of FORTRAN routines in which the objective is the quantitative determination of fission product transport and retention characteristics during severe reactor accidents. It represents a best estimate of nuclide behavior under the hypothetical conditions of various severe accident sequences. Every attempt has been made to account for all significant physical processes, even though the mechanisms may not be well known and only sparse data are available. In doing so, mechanistic models are usually, but not always, used. Since many physical processes are modeled in greater detail than previous studies, the results should yield considerably more insight into the mechanisms and consequences of fission product redistribution.

The particular models used to describe the behavior of iodine are given in the following sections.

2. DESCRIPTION OF TRENDS

2.1 MODELS AND EQUATIONS

2.1.1 Chemical Forms

Five iodine species are explicitly considered, as shown in the first column of Table 1. The phases in which each form can exist are also listed. The release of iodine from either the reactor coolant system (RCS) or fuel rubble can occur in any of the forms listed. Subsequent interconversions between different species are modeled as follows:
\[
\begin{align*}
I_2(g) & \rightarrow CH_3I(g), \quad (1a) \\
I^-(aq) & \rightarrow CH_3I(aq), \quad (1b) \\
I^-(aq) & \rightarrow I_2(aq), \quad (1c) \\
I_2(aq) & \rightarrow AgI(s), \quad (1d) \\
I^-(aq) + AgI(s), \text{ and} \\
CH_3I(aq) + AgI(s). \quad (1f)
\end{align*}
\]

Table 1. Iodine chemical forms in containment following an accident

<table>
<thead>
<tr>
<th>Species</th>
<th>Phases considered</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(_2)</td>
<td>Gas, aerosol, liquid, surfaces (paint, steel, concrete), deposited aerosol</td>
</tr>
<tr>
<td>CH(_3)I</td>
<td>Gas, liquid, surface (paint)</td>
</tr>
<tr>
<td>CsI or I(^-)</td>
<td>Gas, aerosol, liquid, surfaces, deposited aerosol</td>
</tr>
<tr>
<td>HI</td>
<td>Gas, aerosol, surface (steel), deposited aerosol</td>
</tr>
<tr>
<td>AgI</td>
<td>Precipitate</td>
</tr>
</tbody>
</table>

The iodine model follows 20 inventory locations within each containment volume.

2.1.2 Gas-Liquid Partitioning

Iodine entering water as iodide (i.e., CsI or HI) should remain dissolved as long as it is in ionic form. However, the species I\(_2\) and CH\(_3\)I can evaporate from water into the containment gas space and from there be convected to other control volumes or even to the outside environment.

Within the TRENDS code, solubilities are measured in terms of partition coefficients (Henry's Law constants), defined as the equilibrium ratio

\[
P = \frac{C_g}{C_a^*}.
\]

For I\(_2\) and CH\(_3\)I, partition coefficients have been measured and are used as functions of temperature only (Hasty, 1968)*:

*Data Calculated from FACT, a copyrighted product of Thermfact Ltd/Ltee., 447 Berwick Ave., Mount-Royal, Quebec, Canada, H3R 1Z8.*
\[
\log_{10} P_{I_2} = 6.29 - 0.0149 T, \\
\log_{10} P_{CH_3I} = -4.82 + \frac{1597}{T},
\]

(3) (4)

\(T\) in K.

Since Eq. (2) models only equilibrium and volatile gases may take time to diffuse to the surface before evaporation, it is necessary to consider the transient delaying behavior. Liss and Slater (1974) studied the evaporation of various gases from ocean water and have applied the following model:

\[
\frac{1}{A} \frac{dN_g}{dt} = h_e (P_{C_g} - C_t),
\]

(5)

where

- \(A\) = interfacial surface area (cm\(^2\)),
- \(h_e\) = gas-liquid (evaporation) mass transfer coefficient (cm/s),
- \(N_g\) = mass in gas phase (g).

From these data, values of \(h_e\) for \(I_2\) and \(CH_3I\) can be determined as

\[h_e(I_2) = 1.84 \times 10^{-3}, \ h_e(CH_3I) = 3.0 \times 10^{-3} .\]

(6)

TRENDS uses Eq. (5) to describe evaporation processes and currently uses the values from Eq. (6) for coefficients.

2.1.3 Convection Between Volumes or Leakage

The change in airborne concentration of any species \(C_i\), due to convective flow into or out of a control volume, is modeled by

\[
\frac{dC_i}{dt} = S_i - \frac{C_i}{V} \sum_j Q_j,
\]

(7)

where \(Q_j\) is the volumetric flow out pathway \(j\), \(V\) is the volume of the cell (containment or subcompartment), and \(S_i\) is the source of species \(i\) into the control volume (from other volumes).

2.1.4 Removal via Condensing Steam (Diffusiophoresis)

It is assumed that input is available to TRENDS for the rates of steam condensation onto containment surfaces and onto aerosols and for other thermal hydraulic conditions in containment. Diffusiophoretic removal of all vapor species, then, is modeled by the equation

\[
\frac{dC_i}{dt} = - \frac{X_s}{X_s + X_a \sqrt{M_a/M_s}} \frac{Q_s C_i}{V},
\]

(8)

where
\( X_g \) = mole fraction of steam in the containment atmosphere,
\( X_n \) = mole fraction of noncondensables in the containment atmosphere,
\( M_s \) = molecular weight of steam,
\( M_a \) = average molecular weight of the noncondensables,
\( V \) = containment cell volume,
\( Q_g \) = volumetric steam condensation rate onto the particular surfaces.

2.1.5 Convective Transport to/from Surfaces

Surface reactions of \( I_2 \), CH\( _3 \)I, or HI with the fixed surfaces listed in Table 1 are modeled by equations of the form

\[
\frac{dC_s}{dt} = vC_g - wC_s ,
\]

where \( C_s \) and \( C_g \) are the surface- and gas-phase concentrations (g/cm\(^2\) and g/cm\(^3\), respectively), \( v \) is the deposition velocity (cm/s), and \( w \) is the revaporization rate constant (s\(^{-1}\)). Where data exist, the parameters \( v \) and \( w \) are estimated from experimental values obtained under similar conditions; otherwise, they are assumed to be zero.

Mass transport models in TRENDS calculate transport of vapor species to containment walls and to aerosols. A detailed description of these models will be given in a separate report.

2.1.6 Organic Iodide Formation

The equation for organic iodide formation by gas or gas/surface reactions can be expressed as:

\[
\frac{dc}{dt} = \alpha (C^* - C) ,
\]

where

\( C \) = concentration of organic iodide at time \( t \),
\( C^* \) = equilibrium concentration of organic iodide,
\( \alpha \) = organic iodide formation constant (s\(^{-1}\)).

The value of \( \alpha \) was taken (Beahm et al., 1985) as \( 5.1 \times 10^{-3} \), and \( C^* \) was related to the gaseous \( I_2 \) concentration, \( C_{H_2} \), by the relation:

\[
C^* = 1.89 \times 10^{-2} C_{H_2}^{0.8} \text{ mg/m}^3 ,
\]

based on tests involving irradiated fuel.

TRENDS also includes a model for the radiation-induced conversion of iodide ion, I\(^-\) (aqueous), into methyl iodide, CH\( _3 \)I. This model is described in Sect. 2.1.7.

2.1.7 Radiolysis of Aqueous Iodide

The conversion of I\(^-\) to \( I_2 \) or to CH\( _3 \)I is a process that is strongly dependent on pH as well as on absorbed dose to the water (Wisbey et al., 1986).
Initial calculations with TRENDS used the following model for radiolysis: for a given pH, the mass fraction of I₂ formed (denoted by x) will generally be a monotonically increasing function of the total dose D. Typically, the experimental data asymptotically approach some limiting fraction. A simple form that can easily be fit to these data is

\[ x(D) = x_\infty (1 - e^{-bD}), \]  

(12)

where both \( x_\infty \) and the constant \( b \) may depend on pH. More terms could be added if greater accuracy is required; however, the form of Eq. (12) has proven quite satisfactory and is currently in TRENDS for both I₂ and CH₃I.

Differentiating Eq. (12) yields the rate

\[ \frac{dx}{dt} = x_\infty b e^{-bD}. \]  

(13)

If the current I₂ fraction \( x \) had resulted from the radiolysis of a single batch of I⁻, then the absorbed dose necessary to have achieved this is

\[ D = \frac{1}{b} \ln \left(1 - \frac{x}{x_\infty}\right). \]  

(14)

Recent experiments have shown that iodine added to previously irradiated water behaves as if it had been present during the entire radiation period. Thus, if convective mixing of several batches at different times has occurred, then Eq. (14) is still a good estimate of past dose history. In practice, Eq. (14) is substituted into Eq. (13) to get:

\[ \frac{dx}{dt} = bD (x_\infty - x), \]  

(15)

which represents a rate equation for the formation of I₂ based on only the current mass fraction \( x \), the dose rate \( D \), and the empirical parameters \( x_\infty \) and \( b \).

It should be noted that although \( b \) and \( x_\infty \) are determined from data for \( x < x_\infty \), Eq. (20) is also used for \( x > x_\infty \).

2.1.8 Silver Iodide Formation

If sufficient quantities of silver are available, then I₂, I⁻, or CH₃I could react with it to form AgI. The reactions are essentially irreversible, and the resulting AgI forms a solid precipitate that immobilizes the iodine completely. As in the initial description of radiolysis of I⁻ to form more volatile species, the TRENDS code uses empirical rather than detailed reaction models.

The conversion of I⁻ and CH₃I is catalyzed by water radiolysis products (no reaction occurs without radiation). From recent reviews of data, it appears that the fraction \( F \) of combined I⁻ and CH₃I inventories converted to AgI can be described by a function of the form

\[ F = \frac{[\text{AgI}]}{[\text{I}]} = 1 - e^{-x}, \]  

(16)
where \( x \) increases with both dose and initial mass ratio \( [\text{Ag}]_0/[I]_0 \). Although the following form has no particular theoretical basis, it can easily be fit to the data:

\[
F = 1 - \exp(-\alpha D^\beta R_0),
\]

where

\[
R_0 = \frac{[\text{Ag}]_0/[I]_0} = \text{initial mass ratio},
D = \text{cumulative absorbed dose (M}_{\text{rad}}).
\]

The constants \( \alpha \) and \( \beta \) are determined from fits to data as

\[
\alpha = 6.22 \times 10^{-3},
\beta = 0.42.
\]

Multiplying Eq. (17) by the constant \( [I]_0 \), differentiating, and rearranging yields the rate equation

\[
\frac{d[\text{AgI}]}{dt} = -\frac{d[I]}{dt} = \alpha \beta D^{\beta-1} D [I] R_0. \tag{18}
\]

Thus, the changing behavior depends on the cumulative dose \( D \), dose rate \( \dot{D} \), initial ratio \( R_0 \), and current concentration \( [I] \) of \( I^- \) and \( \text{CH}_3\text{I} \) combined. In practice, the TRENDS calculation uses Eq. (18) if \( [\text{Ag}] > [I] \), but only after the total dose has exceeded the threshold value \( D > 0.8 \text{M}_{\text{rad}} \).

The reaction of silver and \( I_2 \) to form \( \text{AgI} \) is not affected by radiation and is modeled by the first-order irreversible reaction

\[
\frac{d[I_2]}{dt} = k [I_2]. \tag{19}
\]

The rate constant taken from the IMPAIR code is \( k = 8.36 \times 10^{-6} \text{ s}^{-1} \). This is applied in TRENDS whenever the silver molarity exceeds ten times the iodine molarity.

2.2 KEY INPUT PARAMETERS

The results of the BMI-2104 calculations for the selected sequences were used as input initial and boundary conditions for the TRENDS calculations. These inputs basically consisted of containment temperatures and pressures; quantities and locations of water pools; steam condensation rates onto aerosols and containment surfaces; sources of fission products and aerosols from the RCS and from core-concrete interactions; containment failure time and leakage rates; convective flows between cells; and the aerosol transient (location, size, and quantity) within containment. These "inputs" were obtained from the BMI-2104 MARCH, SPARC, and NAUA computer results, redigitized, and input into TRENDS as functions of time.

The iodine release from the RCS was parameterized in two ways. An initial calculation was made in which the conversion of \( \text{CsI} \) to \( \text{HI} \) was assumed to be zero, and the BMI-2104 sources were then preserved intact. For the case of
100% conversion to HI, all of the iodine released from the fuel was assumed to enter the containment as HI with no CsI or CsOH. In the former case, the TRENJDS results for release of iodine gaseous species are added to the CsI aerosol release calculated by BMI-2104. In the latter case, the TRENJDS calculation represents the full iodine source term. To exercise the liquid/gas partitioning features of TRENJDS, it is also necessary to quantify the following key influencing parameters: the pH of water pools, the irradiation level for water pools, and the quantity of silver deposited into water pools.

2.3 PRELIMINARY SEQUENCE CALCULATIONS

Operation of TRENJDS was tested by running calculations of TMLB' (station blackout) sequences (Surry) and TC (transient without scram) sequences (Peach Bottom). In these calculations, it was assumed that iodine entered containment as either CsI or HI to enable evaluation of all models. Figure 1 gives an example of the type of output that was obtained. This shows iodine inventories that were obtained throughout a TMLB' sequence when it was assumed that the entire core inventory of iodine entered containment as HI. In this sequence, there was time for rate-controlled processes to become effective before containment failure; this is illustrated in Fig. 1, and it shows that (I$_2$ + CH$_3$I) aqueous, I$_2$ deposited on surfaces and AgI have increased to their maximum values by the time of containment failure at ~75 min into the sequence. The overall effect of the rate processes is to decrease the airborne iodine by aerosol settling, deposition onto surfaces, and conversion into AgI or (I$_2$ + CH$_3$I) aqueous, which results in lowering the overall release of iodine. Clearly, the extent of iodine release and the distribution of iodine in containment will depend on the specific sequence and the knowledge or assumption of the amount and chemical form(s) of iodine that enters containment.

3. CONTINUING DEVELOPMENT OF TRENJDS

The accident sequences, mentioned in Sect. 2.3, that were calculated with TRENJDS were run with iodine volatility data that were experimentally measured for the specific sequences and modeled as described in Sect. 2.1.7. This approach is valid and permitted testing of the models in TRENJDS, but it severely limits the application of TRENJDS for use by other investigators. To overcome this, we are in the process of making TRENJDS portable so that it may be used by others. The three additions necessary for portability are: (1) internal calculation of pH, (2) calculation of radiation dose rates, and (3) internal calculation of volatility effects—hydrolysis and radiolysis.

3.1 CALCULATION OF pH

Experimental tests have shown that solution pH is a major factor in determining the extent of I$_2$ and organic iodide formation in solution. The GASOL routine from the well-known SOLGASMIX computer program is being used to calculate the aqueous solution equilibria necessary to determine the hydrogen ion concentration and, thereby, the pH. Table 2 gives the chemical species that are considered in these calculations. Thermochemical data were fit from 298 to 373 K to the free energy expression:

$$\Delta G^0 \text{ formation} = a + bT \text{ (Kelvin)}.$$  (20)
Fig. 1. Surry TMLBε pH (HI) case containment.
Table I • Chemical species in pH calculations

Aqueous species: \( H^+ \), \( OH^- \), \( B(OH)_4^- \), \( H_3BO_3 \), \( B_2(OH)_7^- \), \( B_3(OH)_10^- \), \( Ba(OH)_2 \), \( Ca_3(PO_4)_2 \), \( CaH_2PO_4 \), \( Ca(H_2PO_4)_2 \), \( H_2O \), \( HPO_2^- \), \( Kf^- \), \( NO_3^- \), \( CO_3^- \), \( HCO_3^- \), \( H_2CO_3 \), \( H_2O \).

Solids: \( Ca_3(PO_4)_2 \), \( CaHPO_4 \), \( Ca(H_2PO_4)_2 \), \( H_2O \), \( CaO \), \( (CaO)(B_2O_3) \), \( CaO \), \( CaCO_3 \).

Gases: \( Ar \), \( CO_2 \), \( H_2O \).

Free energy data for the borates and phosphates were derived from Mesmer et al. (1972) and Mesmer and Baes (1974), respectively, and the remaining data were taken from Barner and Scheuerman (1979). The Debye-Hückel equation was used to calculate activity coefficients for the aqueous ions.

3.2 CALCULATION OF RADIATION DOSE RATES

The reaction of iodine species with radiolysis products of water makes it necessary to calculate water pool radiation dose rates to evaluate the formation of volatile \( I_2 \) and organic iodides.

The problem is calculating the radiation dose to a water pool resulting from suspended or dissolved fission products. In any such pool, some fraction of the radiation energy will be absorbed by the pool. Figure 2 shows plots of the fraction of energy absorbed in water vs the surface-area-to-volume ratio of the pool. For a given source energy, there was a linear relationship between the fraction absorbed and the surface-area-to-volume ratio. Thus, the energy fraction absorbed can be expressed as:

\[
\text{energy fraction absorbed} = a + b \left( \frac{S}{V} \right),
\]

where

\[
S/V \quad \text{surface to volume ratio (m}^{-1}),
\]
\[
E \quad \text{source energy (MeV)}.
\]

Values for the constants have been calculated as:

\[
a = 1.062 - 0.051 \sqrt{E},
\]
\[
b = 0.0355 - 0.0216 \sqrt{E}.
\]

Calculation of the dose rate then is a matter of summing the contributions from each radionuclide.

3.3 CALCULATION OF HYDROLYSIS/RADIOLYSIS

The quantitative description of aqueous iodine behavior has been described in numerous articles, yet it remains a somewhat elusive subject.
Fig. 2. Energy absorbed in water from volumetric gamma sources.
Researchers use different assumptions and their data reflect different experimental conditions. Quite often, the attempt is made to model overall reaction progression in only one direction (i.e., either the forward hydrolysis or the reverse "Dushman," but not both). One of the goals of this work is to present a comprehensive and unified view of iodine hydrolysis, which will encompass the wide range of conditions encountered in reactor containments during accident sequences.

In pure water, $I_2$ hydrolyzes to form $I^-$ and $I_3^-$ and can be described by the overall reaction

$$3I_2 + 3H_2O \rightarrow 5I^- + I_3^- + 6H^+.$$  

(22)

However, this form is inadequate to fit all data or to describe the detailed processes that occur in reactor accidents where radiation and chemical impurities will be present.

Several researchers have developed complicated models of iodine radiolysis, which include the following three reversible reactions to describe hydrolysis processes:

$$I_2 + H_2O \leftrightarrow I^- + HOI + H^+$$  \hspace{1cm} (23a)

$$2HOI \leftrightarrow I^- + HIU_2 + H^+$$  \hspace{1cm} (23b)

$$HI0 + HIU_2 \leftrightarrow I^- + HIU_3 + H^+.$$  \hspace{1cm} (23c)

This model has been useful and popular even though not all the species or reaction steps have been confirmed. For this reason, several of the rate constants are not known from direct experiment, although rough heuristic estimates are available. The system includes species at all oxidation states except +2 and +4 and involves two-electron transfers in the last two steps.

In attempting to formulate a system of reactions in which all oxidation states between -1 and +5 are represented, the following premises have been followed:

1. Only oxidation state changes of ±1 can occur.
2. No specie can be oxidized by another with a lower oxidation state.
3. $I^-$ is the dominant reducing agent.

The last assumption is quite reasonable, since $I^-$ will be the strongest reducing species and will generally be present in greater abundance than most others. The resulting formation includes five forward reaction steps and five reverse steps (the Dushman reaction):

$$I_2 + H_2O + I^- + HI0 + H^+$$  \hspace{1cm} (24a)

$$2HI0 + \frac{1}{2}I_2 + IO + H_2O$$  \hspace{1cm} (24b)

$$2IO + H_2O + HOI + HI0_2$$  \hspace{1cm} (24c)

$$2HI0_2 + IO + IO_2 + H_2O$$  \hspace{1cm} (24d)

$$2IO^2 + HI0^2 + HI0^3.$$  \hspace{1cm} (24e)
\[ H^+ + I^- + HI_3 + \frac{1}{2} I_2 + I_2 + H_2 O \]  
\[ H^+ + I^- + IO_3^- + \frac{1}{2} I_2 + H_2 O \]  
\[ 3H^+ + I^- + HI_3 + \frac{1}{2} I_2 + I_2 + H_2 O \]  
\[ H^+ + I^- + I^- + \frac{1}{2} I_2 + H_2 O \]  
\[ H^+ + I^- + HI_3 + I^- + \frac{1}{2} I_2 + H_2 O \]  
\[ H^+ + I^- + HI_3 + I^- + \frac{1}{2} I_2 + H_2 O \]

Even though the reactions in system (24) were selected by reasonable criteria, it is important to note that none except Eqs. (24a) and (24j) have been studied very extensively or can be verified rigorously. As mentioned previously, only \( I^- \), \( I_2 \), and \( HI_3 \) (or the ionized form \( IO_3^- \)) have been documented as legitimate species, the others being somewhat speculative. As a result, these systems are not so much mechanistic (corresponding to known chemical mechanisms) as empirical, with parameters (i.e., the rate constants) that are determined by fitting the models to data of overall system behavior.

Either system (23) or (24) will result in rate expressions that are used to form a set of ordinary differential equations describing the transient behavior of each species concentration in the system. This system also involves rate constants \( k_j \) and has the form

\[
\frac{dC_i}{dt} = f_i(C_1, C_2, \ldots, C_I; k_1, k_2, \ldots, k_j) \quad i = 1, \ldots, I, \quad (25)
\]

where

- \( C_i \) = concentration of species \( i \),
- \( k_j \) = rate constant for the \( j \)th reaction,
- \( C_{i0} \) = initial concentration of species \( i \).

The functions \( f_i \) are generally nonlinear in the concentrations \( C_i \), although often linear in the rate constants \( k_j \).

If all rate constants were well known, it would remain simple to solve system (25) in order to simulate iodine hydrolysis. However, as mentioned previously, this is not the case with either reaction set (23) or (24). If sufficient data were available, then Eq. (25) could be solved repeatedly until an appropriate choice of constants was found, which would result in calculated concentration values close to those of the experiments. Although this process is feasible, it could become quite expensive or unwieldy, since it involves nonlinear optimization over many variables and repeated solution of the ordinary differential equation (ODE) system (25).

Recent experiments have yielded over 130 data points at temperatures 25°C, 50°C, and 90°C and pH values 2.8 to 9.0. A least squares residual is a good measure of the deviation between the calculated concentrations [see Eq. (25)] and the data points:

\[
R = \sum_{i,n} [C_i(t_n) - \hat{C}_{i,n}]^2, \quad (26)
\]
where $\hat{C}_{1n}$ is the experimentally measured concentration of species $i$ at time $t_n$. A quantitative optimization problem, which seeks to minimize the least squares error, can now be formulated while simultaneously satisfying Eq. (25). The resulting problem is that of constrained optimization with a set of differential equations as constraints; similar problems arise in economics and optimal control theory, and although they are quite complicated, solutions are possible.

In this work, a combination of heuristic search, steepest descent, and variable metric methods were used to obtain optimal parameter estimates. Shown in Table 3 are calculated rate constants using only data at 25°C. These constants represent system (24) with the first reaction replaced by the equivalent form

$$I_2 + OH^- + I^- + HOI.$$  

Using these values, system (25) is solved at several different pH values, with results shown in Figs. 3 and 4 for pH 7 and 2.8. As seen in the figures, the calculated curves match the experimental data fairly well, indicating applicability under fairly diverse conditions. Furthermore, these represent both forward hydrolysis and the reverse Dushman reaction with a single set of reactions and rate constants.

Table 3. Calculated rate constants

<table>
<thead>
<tr>
<th>K</th>
<th>Rate constants at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.06 \times 10^8$</td>
</tr>
<tr>
<td>2</td>
<td>$3.47 \times 10^6$</td>
</tr>
<tr>
<td>3</td>
<td>$8.93 \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>$1.04 \times 10^5$</td>
</tr>
<tr>
<td>5</td>
<td>$1.10 \times 10^5$</td>
</tr>
<tr>
<td>6</td>
<td>$3.27 \times 10^5$</td>
</tr>
<tr>
<td>7</td>
<td>$1.06 \times 10^6$</td>
</tr>
<tr>
<td>8</td>
<td>$7.39 \times 10^5$</td>
</tr>
<tr>
<td>9</td>
<td>$5.36 \times 10^5$</td>
</tr>
<tr>
<td>10</td>
<td>$3.97 \times 10^{11}$</td>
</tr>
</tbody>
</table>

$\min^{-1} \ (\text{gmol/L})^{-1}$

Hydrolysis

$\min^{-1} \ (\text{gmol/L})^{-2}$

"Dushman reaction"
Fig. 3. Iodine hydrolysis at pH 7.
Fig. 4. Reverse hydrolysis at pH 2.8.
4. ONGOING MODEL DEVELOPMENT

Additional work needed to make TRENDS portable:

(1) further validation of pH calculations in systems that include combinations of borate, phosphate, and carbonate buffers;

(2) fitting of hydrolysis data at temperatures above 298 K;

(3) fitting of radiolysis data to rate constants; and

(4) improvements in mass transport models of vapors to aerosols and to walls in the reactor containment. This includes accounting for microscale turbulence of aerosols and treatment of vapors interacting with both dry and wet walls.

5. REFERENCES


DISCUSSION

G.J. EVANS Could you give an indication of the values of pH and dose rate that you have calculated using your code. Did the dose rate exceed 2 Mrad/h in any of the sequences you studied?

E.C. BEAHM The severe accident sequences that we evaluated with this code did not have pH adjustment by sprays or additives in containment. The lowest pH was 3.4 for so-called dry containment station blackout sequence with the assumption that the entire core inventory of iodine entered containment as HI. The highest pH was ~ 9. We did not have a water pool dose rate exceeding 2 Mrad/h. The maximum was ~ 1.2 Mrad/h. The dose rate varies throughout a sequence; in the case of the station blackout, calculation introduction of core-concrete debris into the sump resulted in an increase from ~ 0.15 Mrad/h at ~ 450 min into the sequence to ~ 1.2 Mrad/h at 1100 min.

J.P. LONGWORTH 1) Have you or will you compare results of your model with data from other labs and 2) do you intend to include liquid aerosols and soluble species behaviour?

E.C. BEAHM We will compare results of our model with data that were kindly provided by Bob Burn's group.

We do intend to include aqueous aerosols and soluble species. This work has just begun with an evaluation of activity relations of HI, H⁺, I⁻, at very high concentrations.

J. PAQUETTE It seems that in trying to avoid complexity you eventually end up with something that is as complex as what the chemists are using, if not more. A similar situation could occur with radiolytic reactions.

R. RITZMAN Does the dose rate calculation in TRENDS include the contribution from β-radiation as well as from gamma radiation absorption?

E.C. BEAHM Yes.

D.A. PALMER In regards to your ten equation sequence, would the fit to your experimental results be improved by including an 11th equation, for example a two electron transfer. If so, when does such a sequence reach the limiting number of steps or reactions?
Furthermore, could you vary the experimental reaction conditions (e.g., pH) to highlight just a few of your steps and see if the rate constants obtained fit those obtained from your overall fit of the iodine/iodate reaction? In other words, do you plan to test your kinetic model to establish that your rate expression for each reaction are real and not just fitting equations?

E.C. BEAHM

We do not believe that the mechanism for iodine hydrolysis and reverse hydrolysis is known.

In response to this, we have formulated a set of premises which allows modeling of these reactions:

1. Only oxidation changes of ± 1 can occur.
2. No species can be oxidized by another with a lower oxidation state.
3. I⁻ is the dominant reducing agent.

The 10 reaction set results from these premises. They have the additional feature that any one electron change reaction, in this system, can be represented by some linear combination, and that the observed iodine hydrolysis behaviour of I₂, I⁻, and IO³⁻ can be reproduced by a simple logic algorithm based on the original premises.

W.G. BURNS

Have you ever obtained evidence that the reaction which makes I₂ from H⁺, I⁻ and O₂ can be reversed, so that I₂ reacts with water to form O₂. Some of our experiments suggests that this can happen.

E.C. BEAHM

We have not looked at that possibility.

P. KLAEZK

Given that TRENDS is to be applicable for all BWR/PWR containments, have you included, or are you planning to include considerations of large transient perturbations such as hydrogen combustions? (i.e., for BWR MARK I, MARK II and PWR containments).

E.C. BEAHM

Yes, we use input from other codes in the NRC Source Term Code Package. To this time, the sequences have not included hydrogen burns.
S. DICKINSON  You mentioned that you break the deposition of iodine into aerosols. Do you take any account of the chemical reactions that might occur between the deposited iodine and the aerosol material, for example, if you deposit iodine or cesium iodide onto cadmium aerosol, you produce cadmium iodide, which is then another iodine species which needs to be considered.

E.C. BEAHM  We do not have aerosol chemical reactions in TRENDS at this time. As part of support work for the EPRI-ACE program, we will be doing experimental studies of iodine aerosol interactions.
DISCUSSIONS ON SESSION IV

D.J. WREN
It is clear from the sensitivity analysis of Paquette that mass transfer rates are very important. I believe that it is necessary for models to develop good descriptions for mass transfer within the liquid phase since this mass transfer rate is likely to be the limiting rate in the transfer to the gas phase.

G.J. EVANS
I understand that the main chemical pathway for the elimination of volatile species is disproportionation in the British and American model. I have found suggestions in my experimental research that the formation and subsequent hydrolysis of organic iodides play an important role in the elimination of volatile inorganic iodine species.

P.N. CLOUGH
In considering mass transfer of iodine from water pools, we need to make a clear distinction between severe accidents where the pools will be boiling due to decay heat, and design based accidents where they will not. Mass transport will be much enhanced from the liquid phase in boiling pools.

P.E. POTTER
In the modelling of iodine behaviour presented by W.G. Burns some iodine is in fact in the form of HOI(g). Does this molecule really contribute to the gas phase; what should be used for the value of partition coefficient at temperatures above 25°C?

D.J. WREN
While there is some uncertainty in the volatility of HOI, it is really only important at very low iodine concentrations. There the problem is actually likely to be dominated by the formation and volatility of organic iodide. Also, as the concentration of iodine becomes very low, the total activity in the system becomes so low that uncertainties become unimportant.

J.P. LONGWORTH
On the HOI question; maybe the formation of HOI vapour is not the only issue, but maybe loss of HOI from solution affects the chemistry and the rate at which species are redissolved from the -phere.

B.J. HANDY
Referring back to the need to know the partition coefficient for HOI at high temperatures, this information is necessary to calculate overall mass transfer coefficients for HOI in Dr. Burns model. How sensitive is the mass transfer coefficient to the partition coefficient?
W.G. BURNS Very sensitive in certain conditions.

B.J. HANDY In other words the $1/k_q$ term in

$$\frac{1}{K_{eq}} = \frac{1}{k_q} + \frac{1}{k_u R}$$

is incumbent compared with $1/k_u R$?

W.G. BURNS Yes.
V. LARGE-SCALE TESTS/OTHER
MEASUREMENTS OF RADIOIODINE SPECIES IN SAMPLES OF PRESSURIZED WATER REACTOR COOLANT

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ABSTRACT

Samples of primary coolant at two pressurized water reactors (PWRs) in the United States have been collected and analyzed to determine the fraction of the radioiodine present in volatile forms. The volatile species, I₂ and organic iodides, would be available for prompt release following a steam generator tube rupture (SGTR) accident which overpressurizes the secondary coolant system and causes a venting to the atmosphere. Coolant samples were collected at full power, during power reduction at the start of an outage, and up to 40 hours after shutdown at two PWRs. Radioiodine concentrations spiked as power was decreased and an increase in the volatile species fraction to about 20% was seen within two hours of shutdown. A second peak of 30 to 40% volatile species occurred at ~1.5 days after shutdown. Because the consequences of a SGTR accident depend upon the potential for coolant release as well as the volatile iodine concentrations, only the first spike is significant for dose assessment.

1. INTRODUCTION

One of the design basis accidents for a PWR is the rupture of a steam generator tube. This failure releases primary coolant at high temperature and pressure and the associated radioactivity into the secondary coolant system. Release of radioactivity to the environment will occur if the secondary system is overpressurized and the relief valves open. The magnitude of the resulting thyroid dose to persons offsite depends in part upon the amount of volatile radiiodine in the primary coolant. Iodine present as I₂ or organic iodides is more available for prompt release following initiation of a tube rupture accident. The purpose of this work was to measure the volatile fraction of radiiodine isotopes present in primary coolant of PWRs.

Previous measurement results exhibited variability but indicated that the volatile species fraction (FV, the sum of the concentrations of I₂ and organic iodides divided by total iodine concentration) could be large. Measurements at five nuclear power stations reported by Martucci[1] showed values of FV ranging from <0.9% at two plants to about 20% at the other three. At two plants, the volatile iodine species was mainly (about 70%) I₂; at the other, only 10% was in elemental form. The boron, hydrogen,
and lithium concentrations in the coolant were documented at the five plants. The measured concentrations of $H_2$ ranged from 19 to 45 cc/kg; the values of FV were not correlated with the measured values of $[H_2]$. The coolant boron and lithium levels ranged from about 200 to 1000 ppm and 0.09 to 1.8 ppm, respectively; neither variable was correlated with FV.

Results of a time sequence of measurements of volatile radioiodine fraction in coolant samples collected prior to and during the course of a shutdown were reported by Mandler et al.[2]. Fourteen samples were collected during a period beginning about 30 hours prior to reactor trip and extending to about 50 hours after the trip. At about 7 hours after shutdown, the volatile iodine fraction was 37% of the total $^{131}I$ in primary coolant. The increase in FV (from <1% prior to shutdown) appeared to be correlated with additions to the coolant from the borated water storage tank (BWST). The boration process also lowered the pH from 9.1 to 5.8. A second increase in FV from about 2% to nearly 10% followed the addition of hydrogen peroxide to the coolant. Separation of the volatile fraction into $I_2$ and organic iodides was performed on only one sample; iodide and iodate fractions were determined for each sample.

Both of the studies cited above support the need for additional measurements. In the first case, there is a need to understand the reason(s) for the order of magnitude differences among the measured values of FV at different plants. The second study identified potential changes in FV apparently due to changes in operating conditions that could be important in the event of an accident. Oxygenated fluid, like that from the BWST, could be added to the primary system to replace coolant lost due to leakage during a SGTR accident.

The measurements reported here were performed to obtain additional data on the forms of radioiodine in coolant at operating PWRs. In addition, collection of primary coolant parameters measured by the plant operator at the times of sampling was given priority. Those data provide a basis for assessing the effects of operational changes on the iodine species distributions. The methods used for coolant sample collection and analysis are described in Section 2. The results of the coolant species measurements are presented in Section 3. Also included in that section are the data on other plant variables obtained from the participating utilities. Data interpretation and discussion are presented in Section 4. Section 5 contains the conclusions drawn from the measurements and analyses.

The fractional amounts of the radioiodine forms in coolant samples are described using the following conventions. The radioiodine fractions are symbolized as follows: $F_1$ refers to the iodide form, $F_2$ refers to iodates and periodates, $F_3$ refers to elemental iodine, and $F_4$ refers to the organic iodides. In each case, the fraction is that part of the total $^{131}I$ (or other iodine isotope) activity present in the specified form at the time of sampling. The procedure used to achieve separation of these four components is described below.
2. ANALYTICAL METHODS

Primary coolant samples, obtained by utility personnel using the normal reactor coolant sampling line, were delivered to the radiochemistry laboratory area for processing. Coolant samples are withdrawn from the letdown line upstream of the coolant filtration and ion exchange beds. Prior to sample collection, the sampling line was flushed to assure that fresh coolant was obtained. The time between collection and the first separation averaged 26 minutes. Most (72%) of the samples were delivered in 25 minutes or less. A delay of more than 40 minutes was experienced for three coolant samples.

After receipt, the samples were subjected to a series of chemical separation steps. First, the carrier free 50-mL sample was contacted with an equal volume of CCl₄, in which the volatile species are soluble. Then, the elemental iodine fraction was back extracted from the CCl₄ phase into thiosulfate solution containing iodide carrier. The CCl₄ phase and the thiosulfate solution were counted to determine the organic iodide (F4) and elemental iodine (F3) activities, respectively. The aqueous phase from the first separation was contacted with 50 mL of CCl₄ containing 3 mg/mL of dissolved I₂. The iodide fraction (F1) exchanges with the elemental iodine in the CCl₄; the iodate and periodate activity (F2) remains in the aqueous phase. These fractions were counted to determine the radioiodine activities present in those forms. This chemical separation technique was basically the same as that employed in References 1 and 2 and is based upon procedures developed by Castleman et al.[3] and subsequently by Lin[4].

Each of the four separated fractions was counted using a calibrated gamma spectrometry system with a high-resolution solid state detector. The counting system was transported to each plant and set up near the radiochemical separation work area to provide rapid counting capability for the samples and assure the detection of short-lived radioiodines (¹³²I, ¹³⁴I, and ¹³⁵I).

The detector calibration technique for extended samples was developed by Cline[5]; it employs sources traceable to the National Bureau of Standards. Counting times were necessarily limited to about 1000 s because of the large number of analyses required in a relatively short time. Under these conditions, a typical minimum detection limit was about 0.2 nCi/g (corrected to the time of sampling), although both lower and higher values were achieved for some individual samples. Corrections were made for radioactive decay between sampling and analysis for all counting results, but were important for only the very short-lived radioiodines.

3. RESULTS

Measurements of radioiodine concentrations and chemical forms in coolant were performed at two PWRs in the United States. To understand the results, the radioiodine data must be examined in the context of other plant parameters. The plant operating conditions affect radioiodine levels in the
coolant and the potential for subsequent release to the environment. For this reason, the plant operating parameters are presented in the first subsection and the radioiodine data follow in Section 3.2.

3.1 PLANT OPERATING CONDITIONS

Both sets of measurements were organized around a scheduled plant shutdown (defined to occur at $t = 0$ h). Coolant samples were collected and analyzed according to the protocol described above from about -35 h to +50 h at Plant 1 and from about -19 h to +38 h at Plant 2. During these intervals, the plant staff were also collecting routine samples for their own purposes. Data on the pH of the coolant and the $H_2$ and boron concentrations in coolant were obtained from the staff. Also provided to us were records containing data on thermal power level and primary coolant temperature and pressure at various times during the period of interest.

Reduction in reactor power level began several hours before shutdown at both plants; the rate of decrease was about 15% per hour. Power reduction was preceded by degassing of the primary system which reduced the $H_2$ concentration from the normal operating level of about 35 cc/kg to less than 10 cc/kg. After shutdown, the coolant temperature was reduced from the normal range of 525--550°F to about 200°F by +2u h. Figure 1 shows the coolant temperature and pressure data for Plant 2. Pressure reduction began soon after shutdown and was accomplished in two steps. Normal operating pressure was about 2250 psi. At +15 h the pressure was about 1700 psi and the second reduction to about 150 psi occurred between +20 h and +22 h. The rate of temperature reduction at Plant 1 was similar, but the decrease did not begin until about +10 h. Pressure reduction at Plant 1 was also delayed.

Boration of the primary coolant was accomplished by addition of boric acid at both plants, but the times of boration differed. Figure 2 shows the boron concentration and pH measurement results for Plant 1. At Plant 2, the boric acid addition occurred promptly after shutdown and the boron concentration was increased from about 70 ppm prior to shutdown to 750 ppm by 2 h. The pH decreased from 7.5 during operation to about 6.2 at +22 h.

At Plant 1, hydrogen peroxide was added to the coolant at +41 h. This practice is followed at some PWRs to increase the solubility of radioactive corrosion products in coolant and then to remove them before the clean-up system is shut down[6]. No peroxide was added to the coolant at Plant 2.

3.2 DATA FOR RADIOIODINES

The measured concentrations of $^{131}I$ in reactor coolant at the two plants are shown in Figure 3. The maximum concentration at Plant 1, about 7 times the average pre-shutdown value, was observed at +21 h. It is likely
that an initial peak (before +10 h) was missed. At Plant 2, the concentra-
tion peaked at +6 h; the maximum value was about 15 times the concentration
measured at -6 h. Because the concentrations of $^{131}$I in coolant in Plant 1
were rather low, more of the counting results for separated fractions were
less than the detection limit. Typical counting uncertainties for $^{131}$I at
Plant 1 were 15 to 25% before shutdown and 5 to 10% afterwards. At Plant 2,
counting uncertainties for $^{131}$I were 5 to 10% before shutdown and only 2 to
4% for later samples.

The elemental iodine fractions (F3) for $^{131}$I measured at the two
plants are shown in Figure 4. Circled values are minimum detectable
fractions for the analysis. Sharp increases in F3 were observed at shutdown
and the maximum value was seen at times between 35 and +40 h. Fractional
uncertainties for the plotted values of F3 were about 30% at Plant 1 and
about 5% at Plant 2. At both plants, the values of F3 for $^{132}$I, $^{134}$I, and
$^{135}$I also increased at shutdown to between 15% and 20%. The behavior of
$^{133}$I at Plant 2 was similar. However, at Plant 1 no spike in the $^{133}$I
centration was observed and the activity in this fraction was generally
below the detection limit.

Organic iodide fractions were generally small. Only one positive
value was observed for $^{131}$I at Plant 1; F4 was 6.3% at +29 h. The result
for $^{132}$I at the same time was 4.5%. At Plant 2, F4 was between 2.3% and
3.9% at +0.3 h for all five radioiodines. The highest values for F4 were
seen at +21 h when results for the four longer lived isotopes ranged from
4.7% to 6.5%. This occurred soon after the second stage of depressurization
and the startup of the shutdown cooling system.

The fractional concentrations of iodates in the coolant at Plant 1
are shown in Figure 5. The values of F2 were less than 7%, and many were
below the detection limit, until +42 h. At that time, F2 increased dra-
merically and remained very high until +47 h. Similarly large values of F2
were observed for $^{132}$I at the same times. Concentrations of F2 were below
the detection limits for $^{133}$I, $^{134}$I, and $^{135}$I at the time. At Plant 2,
there was a gradual increase in F2 after 20 h and the maximum value for $^{131}$I
was only 8.2%. There were similar increases in F2 for $^{132}$I, $^{133}$I, and $^{135}$I
at Plant 2. The maximum value of F2 was 15% for $^{132}$I at +36 h.

4. DISCUSSION

The amounts of the various radioiodine isotopes in the coolant
depend upon processes governing transport from fuel to coolant as well as
the coolant clean-up rate. Iodine moves from the fuel pellets to the plenum
within the fuel rod and subsequently into the coolant via penetrations in
the fuel cladding. If it is assumed, as a first approximation, that the
input from plenum to coolant is a constant during the time periods between
samples, then the coolant concentration data can be used to determine the
magnitude of the radioiodine inputs during those periods. The average
radioiodine input to the coolant between times $t_1$ and $t_2$ ($I_{C12}, \mu Ci/s$) is:

$$I_{C12} = \lambda_e [Q_2 - Q_1 \exp (-\lambda_e (t_2 - t_1))] / [1 - \exp (-\lambda_e (t_2 - t_1))]$$
In this equation, $\lambda_e$ is the effective removal rate constant (s$^{-1}$) for radioiodine from the coolant and $Q_1$ and $Q_2$ are the radioiodine activities ($\mu$Ci) in coolant at the two times. The effective removal rate constant $\lambda_e$ is $\lambda + \lambda_{cu}$, where $\lambda$ is the radioactive decay rate constant (s$^{-1}$) and $\lambda_{cu}$ is the rate constant (s$^{-1}$) describing removal by the cleanup system, namely $(F_{cu}/M_C)\varepsilon$. In this ratio, $F_{cu}$ is the cleanup flow rate (g s$^{-1}$) and $M_C$ is the mass (g) of the reactor coolant. The efficiency of the cleanup demineralizer for radioiodine ($\varepsilon$) is near unity. Values of $\lambda_{cu}$ can be computed from data on the removal of the activation product $^{24}\text{Na}$ from the coolant following shut-down[7]. Values of $\lambda_{cu}$ estimated using $^{24}\text{Na}$ are $2.8\times10^{-5}$ s$^{-1}$ at Plant 1 and $1.6\times10^{-5}$ s$^{-1}$ at Plant 2. The principal reason for the difference is a smaller primary coolant mass at Plant 1.

Results of the calculations for four radioiodines at Plant 2 are shown in Figure 6 for the time period during which the cleanup system was in operation. The primary injection of activity occurred at shutdown, but there was a second pulse in the injection rate at about +20 h when the second depressurization occurred. The input of $^{132}\text{I}$ to coolant is the sum of contributions from the decay of $^{132}\text{Te}$ and plenum-to-coolant transfer and does not exhibit the same sharp rise after shutdown. The ratio of the peak injection rate to the quasi-equilibrium value prior to shutdown was 66 for $^{131}\text{I}$, 1.4 for $^{132}\text{I}$, 12 for $^{133}\text{I}$, and 1.7 for $^{135}\text{I}$.

At Plant 1, the picture is incomplete because it is likely that the initial peak in coolant activity was not observed. The coolant was kept at operating temperature and pressure for ten hours after shutdown, so the conditions were not typical of a rapid shutdown. Radioiodine injection rates were not calculated from the measurements.

Examination of the data on the measured elemental iodine fractions at Plant 1 shows that the peak in F3 for $^{131}\text{I}$ (Figure 4) occurred during the last phase of power reduction. The highest values of F3 for $^{132}\text{I}$, $^{134}\text{I}$, and $^{135}\text{I}$ were also found in the sample collected at -1.8 h. Boration did not begin until about +10 h and could not be the reason for the elevated values of F3 at shutdown. The addition of boric acid did not appear to have a marked effect on F3, which remained at 1 to 2% in 'e samples collected between +9 and +23 h. The foregoing observations suggest that the rise in F3 at the time Plant 2 was shut down was due to the power, temperature, and pressure changes that were occurring, rather than to the addition of boric acid (which also occurred immediately after shutdown).

Increases in F3 at both plants appear to be the result of the injection of elemental iodine from the fuel rod plenums into the coolant. Figure 4 shows that $I_2$ in the coolant does not remain for long; estimated removal half-times of 2.2 to 2.5 h were estimated from ti. data collected at shutdown.

At Plant 1, the maximum value of F3 occurred at +39 h, before hydrogen peroxide was added to the coolant. It is believed that this peak is also due to the final cooling and depressurization of the coolant. At Plant 2 also, the highest F3 occurred late in the shutdown (+34 h).
is no clear correlation of this value with plant operations. Cooldown and depressurization had been completed and the shutdown cooling system had been operating for some time.

The principal effect of peroxide addition at +41 h was the conversion of radioiodine to the iodate forms. The results in Figure 5 show this change in F2 clearly. At Plant 2, where the coolant was oxygenated slowly during operation of the shutdown cooling system, a gradual increase in the iodate fraction was observed. This oxygenation may also have contributed to the late peak in F3 observed at Plant 2.

The largest organic iodide fractions were also observed well after shutdown. At Plant 2, F4 was about 3% for all radioiodines at shutdown, but the values for all detectable isotopes were between 5 and 6% at about +21 h. At Plant 1, F4 was generally below the detection limit for 131I, but was about 6.3% at +29 h. For 132I, F4 was 3.8% in the same sample. The isotopes 132I, 134I, and 135I present as organic iodides were detectable in several samples before and near t = 0, but F4 did not exceed 2.5%.

The potential offsite dose from volatile radioiodines depends primarily upon two time dependent factors. They are the volatile activity concentrations of the five isotopes and the effective coolant release to the environment. Also affecting the calculation of potential dose are the assumed atmospheric dispersion parameter, the exposed individual's breathing rate, and the dose conversion factors for the radioiodines. The driving forces for the release are the pressure and temperature of the primary system. When this is considered, it is clear that the most important volatile iodine measurements are those near the time of shutdown. Increases in the volatile iodine fraction which occur when the pressure and temperature have been lowered are not important to an assessment of the consequences of SGTR accidents. The effective coolant release to the environment may consist of several pulses. The actual amounts of volatile radioiodine released depend upon the time history of their availability, as well as the primary system temperature and pressure, the magnitude of the primary to secondary leakage, mixing and removal processes on the secondary side, and the set points of the secondary side relief valves[8].

The volatile activity concentrations measured at Plant 2 are considered more representative of the potential accident situation than those at Plant 1 which was kept at operating temperature and pressure for ten hours after shutdown. The data show that most of the volatile iodine that was present in PWR coolant near shutdown was elemental iodine, rather than organic iodides. This fact may be considered in detailed evaluations of the iodine transport through the steam generator. Radioiodine in elemental form will deposit on surfaces in the steam generator and the steam dryer, but organic forms will not be removed by this process. Scavenging by secondary side liquid will also be more effective for elemental iodine. The relative importance of the two forms will depend upon the assumptions made about the effectiveness of these processes for removal of elemental iodine.
5. **CONCLUSIONS**

During temperature reduction and depressurization, the release rates of radioiodines from the plenums of the fuel rods to the coolant are elevated and a spike in the concentration of radioiodine in the coolant is observed. A significant fraction of the radioiodine injected into the coolant from the fuel rod plenums appears to be in the form of elemental iodine. About 20% of the total radioiodine was found to be I$_2$ in samples of coolant collected near the time of shutdown. Boration (and acidification) of the coolant using boric acid did not cause an increase in elemental iodine fraction. Volatile iodine fractions of about 30 to 40% were found at later times (about +35 h) at both plants. One of the peaks could have resulted from the final depressurization of the coolant, but the operational cause of the other is not clear. Contrary to a previous report, measurements showed that addition of hydrogen peroxide to the coolant at one plant did not increase the elemental iodine fraction but the iodate/periodate fraction rose dramatically.

A STGR accident would cause a shutdown and provide a path for discharge of radionuclides to the environment. The potential offsite dose depends upon the volatile iodine species concentrations and several other factors. The initial increase in the volatile iodine fraction and the spike in radioiodine concentration are important to the assessment of offsite dose. However, the later increase in the elemental iodine fraction is of little consequence.

**ACKNOWLEDGEMENT**

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6. **REFERENCES**


Figure 1. Reactor Coolant Temperature and Pressure, Plant 2
Figure 2. Reactor Coolant Boron Concentrations and pH, Plant 1
Figure 3. Measured Concentrations of $^{131}\text{I}$ in Reactor Coolant
Figure 4. Measured Fractions of $^{131}$I Present as Elemental Iodine
Figure 5. Measured Fractions of $^{131}\text{I}$ Present in Iodate or Periodate Form
Figure 6. Average Inputs to Coolant of Radioiodine Isotopes, Plant 2
DISCUSSION

J.P. LONGWORTH Since it is the volatility of the species which is of concern, is it possible to measure this directly - even if only at 25°C it will tell you something additional about the species?

P.G. VOILLEQUÉ This might be done at 25°C, but there is no way to do a major experiment at a plant. We are reluctant to ask too much of potential participating utilities; as I indicated, we made significant impositions upon them as it is.

B.J. HANDY Would you expect any oxidation of your sample to occur, after taking them from the reactor but before bringing them to the laboratory?

P.G. VOILLEQUÉ The average time between sample collection and the first extraction was about 25 minutes, and a small amount of air was present in the sample bottles. However, our laboratory measurements (at higher I concentrations) showed no oxidation effects. The field samples were all treated in the same way and we observed activity in F3 only at certain times; there was not correlation between F3 and the time between collection and extraction on CCl₄.

B.J. HANDY Typical total iodine concentrations in primary circuit on PWR under normal operation are in the range $10^{-10}$ M - $10^{-12}$ M. At this concentration, the I₂ present will be almost 100% hydrolysed. When the results are reported for I₂, do you really mean I₂, or do you mean its hydrolysis products e.g., HOI?

P.G. VOILLEQUÉ No, we do not expect to extract the HOI into CCl₄.

G.J. EVANS I have attempted to extract solutions believed to contain HOI with chloroform and found that the amount of HOI extracted was insignificant. The solutions were prepared by adding "carrier-free" I-131 to a hypochlorite solution of pH 8.

E.C. BEAHM What was the extent of the iodine spike in these plants?

In the U.S. the present regulations on iodine partition coefficients in a steam generator tube rupture accident is 2000 (on a concentration basis). With ~ 20% as I₂, the partition coefficient would likely be much less than this.
The most representative data were collected at Plant 2. The $^{131}$I concentration increased by a factor of 12. The iodine spiking magnifies the potential dose from the accident. A steam generator tube rupture would cause a prompt shutdown which would produce an iodine spike (Fig. 3) and also a peak in the volatile iodine fraction (Fig. 4). The potential dose from the SGTR accident is proportional to both quantities.
A DESCRIPTION OF THE RADIOIODINE TEST FACILITY (RTF)

AND RESULTS OF INITIAL RTF FULL-SYSTEM TESTS


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ABSTRACT

A new research installation, the Radioiodine Test Facility (RTF), has recently been constructed at the Whiteshell Nuclear Research Establishment. This facility incorporates many of the features of a reactor containment building, thereby allowing the study of iodine behaviour within containment under simulated reactor accident conditions. This paper describes the design and operation of this facility. In addition, results of the full-system commissioning test program are presented. These tests were conducted using I\(^-\), I\(_2\) and CH\(_3\)I in a stainless steel vessel in the RTF. This work demonstrated that the RTF could be safely operated over an extended period. Results from the test with I\(_2\) suggest that surface effects may be important in determining iodine containment chemistry.

1. INTRODUCTION

In the event of a loss-of-coolant-accident (LOCA), the behaviour of radiiodine and other fission products in a reactor containment building would be a complex function of many variables [1]. These variables include the factors affecting the chemical nature of the system as well as those influencing the physical transport of the fission products. Large-scale integrated tests have primarily focused on physical transport phenomena and have addressed only the most elementary aspects of fission product chemistry [2-6]. On the other hand, most of the recent work investigating chemical reactions of iodine has been limited to separate-effects bench-scale experiments [7-10]. Although this has resulted in a good understanding of iodine chemistry, the complex nature of conditions within containment make such tests inadequate for predicting iodine behaviour in a LOCA.

A new research installation, the Radioiodine Test Facility (RTF) was built at the Whiteshell Nuclear Research Establishment (WNRE). To study the complex chemical behaviour of radiiodine under realistic accident conditions. This facility was designed to conduct fully integrated tests on iodine behaviour that would explore a wide variety of chemical phenomena, including radiation, surface effects and water chemistry, as well as engineering-based parameters such as surface-to-volume ratio, gas and liquid recirculation rates.
and venting [11]. Information derived from these tests will be used to verify models [12,13] developed from separate-effects bench-scale experiments. It is also envisaged that these tests will assist in the identification of important chemical phenomena meriting further bench-scale investigation.

This paper describes the RTF in detail and presents some of the results obtained during the full-system commissioning of this facility.

2. DESCRIPTION OF RADIOIODINE TEST FACILITY

The Radioiodine Test Facility is an intermediate-scale installation designed to simulate as closely as possible conditions within reactor containment under various accident conditions. A schematic of this facility is shown in Figure 1. The principal component of this facility is the Main Vessel, a 340-dm$^3$ cylindrical vessel (0.918 m x 0.688 m ID) simulating the containment building. This vessel is housed in a large 19.5-t lead-shielded canister (1.765 m height x 1.289 m diameter) whose purpose is to provide adequate shielding for the incorporation of cobalt-60 irradiation sources into the Main Vessel. The maximum quantity of cobalt-60 to be introduced into this facility is [444 TBq (12 kCi)], which corresponds to an average dose-rate of approximately 10 kGy/h within the vessel. As a result, radiation fields similar to those expected within containment shortly after a LOCA can be simulated in this facility. A cross-sectional view of the lead canister and Main Vessel is shown in Figure 2.

Through the use of band and trace heaters, the Main Vessel can be maintained at temperatures up to 80°C. This is the initial temperature expected within CANDU containment in a severe LOCA. The effect of different surfaces on iodine behaviour can also be tested in this facility. This is achieved through the replacement of the Main Vessel: vessels of different composition, including carbon steel, stainless steel and concrete, can be readily placed within the facility and tested. In addition, each of these vessels can be coated with different paints, such as zinc primer and various epoxy- and vinyl-based paints, to determine the effect of different exposed surfaces on iodine volatility.

Test solutions for the RTF can be prepared in the Mixing Vessel, a 110-dm$^3$ tank. In normal use, appropriate quantities of water and other reagents needed to achieve the desired test conditions are added to the Mixing Vessel and heated to the desired temperature (<80°C). The solution is then transferred to the Main Vessel and iodine (as iodine-131-labelled I$_2$, CH$_3$I or CsI) added separately via an in-line sampling station. This signifies initiation of the test.

A third tank, the Chemical Spray Solution Vessel, has a 1115-dm$^3$ capacity and contains the wash solution used to clean the facility between tests. Cleaning is affected by pumping the wash solution (e.g., hydrazine, dilute NaOH) into the Main Vessel via the spray header. This is repeated until the washings reveal negligible amounts of iodine.

Associated with the Main Vessel are a series of gas and aqueous phase loops. These loops, fabricated of 316 stainless steel, are connected through the top of the Main Vessel via the canister manifold and serve a variety of
purposes. The Aqueous Recirculation Loop provides variable mixing of the aqueous phase with flow rates in the range 0 to 10 dm$^3$·min$^{-1}$. In addition, a provision to recirculate either through a submerged perforated pipe or spray nozzle is included. The latter can also be used to test the effectiveness of various spray solutions on airborne iodine abatement; these solutions can be delivered from either the Mixing or Chemical Spray Solution Vessels.

The Aqueous Sampling Loop enables on-line monitoring of the test solution in the Main Vessel. This loop is usually operated at a flow rate of 0.5 dm$^3$·min$^{-1}$. Included on this loop for detection of changes in water chemistry are a dissolved oxygen probe, pH and Eh sensors and a rapid scanning fibre optic spectrophotometer. This loop also possesses a sampling station that enables aqueous samples to be withdrawn for off-line analysis in the laboratory. This sample station may also be used to introduce other chemical reagents to study the effects of impurities on iodine behaviour.

The Gas Recirculation Loop serves a variety of purposes. With flow rates variable over the range 0 to 20 dm$^3$·min$^{-1}$, variable mixing of the gas phase in the Main Vessel is possible. In addition, a hydrogen detector has been included because of the potential buildup in the Main Vessel of H$_2$ arising from water radiolysis in tests where the cobalt-60 sources are used. At elevated hydrogen levels, the gas phase in the Main Vessel is diverted through a platinum-based hydrogen recombination catalyst until safe hydrogen levels within the RTF are obtained. This loop also possesses a gas cooler to remove excess heat produced when the hydrogen recombiner is activated.

Iodine revolatilization rates can be ascertained using the Gas Ventilation Loop. This loop contains a charcoal filter for the removal of airborne iodine. Since the gas flow rate can be varied over a wide range (0 to 10 dm$^3$·min$^{-1}$), the effect of iodine removal from the gas phase can be studied at rates greater than, as well as less than, those corresponding to iodine revolatilization from the aqueous pool and/or walls. This loop can also be utilized to increase the gas phase recirculation provided by the Gas Recirculation Loop by by-passing the charcoal filter. A sample station is also included in this loop.

The Gas Sampling Line on the RTF is similar to the Aqueous Sampling Loop. Samples can be readily removed from the facility through a sampling station and analyzed in the laboratory using gas chromatographic techniques. In addition, a specially designed device for airborne iodine analysis, the Automated Airborne Iodine Sampler (AAIS), has been incorporated into this loop. Gas samples are automatically withdrawn from the Main Vessel for predetermined periods by this device at flow rates up to 2 dm$^3$·min$^{-1}$ and passed through charcoal-containing cartridges where the airborne iodine is trapped. These cartridges are then automatically inserted into a 3 in. x 3 in. (76 mm x 76 mm) well-type NaI(Tl) scintillation detector where the trapped iodine-131 is counted using an on-line $\gamma$-counting system (EG&G Ortec, Mississauga). This provides an extremely sensitive measurement of the total airborne concentration of iodine in the Main Vessel. Cartridges containing species-selective adsorbents can also be periodically introduced to obtain information on the nature of the volatile radioliodines. For example, CdI$_2$-coated sorbents can be utilized for determining airborne molecular iodine.
All loops are insulated to prevent appreciable heat loss. In addition, the gas phase loops are heat-traced. This is required to circumvent the development of "cold spots" where condensation of the moist gas phase could occur. In normal operation, the gas phase loops are operated at temperatures several degrees above the temperature within the Main Vessel. There is also a provision to activate a cooling system on the Aqueous Recirculation Loop in the event that aqueous temperatures exceed those desired.

To reduce the likelihood of significant iodine-131 releases from the RTF in the event of a gas leak, this facility is completely enclosed within a polycarbonate enclosure. This enclosure in turn is exhausted at a flow rate of 1440 dm³ min⁻¹ to the building exhaust via HEPA and charcoal filters. Also, to contain potential liquid releases, the entire RTF resides on a large drip tray drained to the building's active waste system. Leak and radiation detection sensors are installed within the facility.

Operator exposures and contamination are minimized by having the entire facility controlled and monitored remotely. A Programmable Logic Controller (PLC) is used to operate the pumps and solenoid valves associated with each of the loops. Only those operator-selected operations that are compatible with the PLC's programming can be engaged. In addition, the PLC monitors the status of numerous safety-related sensors (i.e., radiation monitor, H₂ detector) and sounds an alarm if an unsafe condition arises.

The facility is instrumented with a variety of sensors in addition to those already noted above. For example, each of the loops is equipped with resistance temperature detectors (RTDs) for accurate temperature measurement. The Mixing and Main Vessels are also equipped with RTDs, the latter having four for measurement at the gas phase vertical wall, at the water/air interface, and of the bulk aqueous and gaseous phases. These same vessels are also equipped with pressure sensors and, along with the Chemical Spray Solution Vessel, possess level sensors.

All the sensors and instrumentation associated with the RTF are interfaced to an IBM PC/XT-based data acquisition system. Data from all the sensors are stored on the microcomputer's 20 megabyte hard disk at acquisition rates of up to one scan per minute, except for the γ-counting and spectrophotometric systems, which have a minimum cycle time of 15 min. Once daily, acquired data are transferred from the microcomputer to the on-site VAX computer cluster on which computations are undertaken.

Special facilities are required to change the Main Vessel or to remove from or place into the lead canister the cobalt-60 sources. These operations require the use of a specially designed Hot Cell, which accommodates the lead canister, and an overhead crane, which effects transfer of the canister to and from this Hot Cell. Canister transfer is initiated when the lead canister is disconnected from the process loops at the manifold and the enclosure partially disassembled. The canister is then lifted by the overhead crane, to the entrance of the Hot Cell complex, where it is placed on a trolley used to transport the canister into the Hot Cell. Once in position in the shielded cell, the canister lid can be removed and the vessel changed or the cobalt-60 irradiation sources removed, as required. Similar procedures are followed when returning the lead canister to the RTF.
3. COMMISSIONING TEST PROGRAM

After the completion of construction and testing of sub-system components in 1988 January, a series of three fully integrated commissioning tests were performed. The primary objective of these tests was to examine for extended time periods the operational performance of all system components under a variety of anticipated experimental conditions. A second objective was to develop and validate operating procedures, analytical techniques and the RTF computer software. Finally, these commissioning tests provided an early opportunity to obtain experimental data on the behaviour of iodine in a series of integrated tests. Only preliminary experimental results addressing this third objective are considered in this paper.

The commissioning tests were performed in a stainless steel vessel in the absence of a radiation source. Iodine species were labelled with iodine-131 tracer to facilitate analysis of both the gas and aqueous phases. Initial conditions for the commissioning tests are summarized in Table 1. These test conditions were chosen to acquire operating experience on the behaviour of different chemical forms of iodine in the facility at different temperatures (up to 80°C) and at different pH values in buffered and unbuffered solutions. The aqueous-to-gas-phase ratio chosen (25 dm$^3$ to 315 dm$^3$) corresponds to that anticipated under severe accident conditions within CANDU containment. The recirculation rates chosen were the maximum possible so that well-mixed conditions could be assumed within the Main Vessel.

A description of each commissioning test and the results obtained are given below.

3.1 Commissioning Test #1

In the first commissioning test, methyl iodide was added directly to the aqueous phase in the Main Vessel of the RTF, via one of the sampling stations, to give a $10^{-5}$ mol.dm$^{-3}$ solution. As expected, because of its high volatility, methyl iodide transferred rapidly into the gas phase, as demonstrated by the rapid increase in the airborne iodine concentration shown in Figure 3. Within three hours of the initiation of the test, the concentration of methyl iodide in the gas phase was found to reach a maximum value. Partition coefficients, defined as the ratio of total iodine in the aqueous phase to the total iodine concentration in the gas phase, were found to reach values in the range of 2.4 to 3.5 in the same time period. These results are in reasonable agreement with those of bench-scale studies [14,15].

After the initial peak, the airborne iodine concentration was observed to decline slowly with time, with the exception of a few sudden drops, as illustrated in Figure 3. The sudden drops in the airborne iodine concentration observed at 22 h and 117 h were caused when the sub-loop containing the hydrogen recombiner was activated in order to determine the effect of this device on the airborne methyl iodide concentration. The recombiner has a significant affinity for methyl iodide, although only 12% of the airborne methyl iodide was removed per pass through the catalyst bed. This retained iodine was very strongly adsorbed on the platinum-based catalyst since numerous attempts to remove it at the conclusion of the test proved
unsuccessful. It is interesting to note that upon isolation of the recombiner sub-loop, the airborne methyl iodide concentration quickly increases as a result of mass transfer of methyl iodide from the aqueous solution. The third sharp decrease in the airborne iodine activity was observed at 141 h, when the Gas Ventilation Loop was activated to test the performance of the charcoal filter in removing methyl iodide. As shown in Figure 3, negligible levels of airborne methyl iodide remain after deactivation of the charcoal filter. A methyl iodide removal efficiency of approximately 50% was calculated for this on-line filter system.

In the periods between these events, the gradual decline in the airborne iodine concentration was found to be reasonably well represented by a first order rate equation with a rate constant of about \(1.5 \times 10^{-6} \text{ s}^{-1}\). Mechanisms that may account for this behaviour include a slow conversion of methyl iodide to a less volatile species and/or the adsorption of methyl iodide onto solid surfaces within the Main Vessel. The pseudo-first order rate for hydrolysis of methyl iodide under the conditions of this test is calculated to be \(5.3 \times 10^{-7} \text{ s}^{-1}\) based on previous work \([16,17]\). As such, it is likely that methyl iodide hydrolysis accounted for a significant fraction of the decrease with time in volatile iodine concentration. This hypothesis is supported by the gradual increase in the partition coefficient from approximately 3 to about 8 as the test proceeded. Furthermore, the absence of any measurable iodine-131 on any of the Aqueous or Gas Recirculation Loops or on the Main Vessel itself at the end of the Full-System Commissioning Test Program suggests surface adsorption of iodine may not have been a major factor. Indeed, methyl iodide is known to have little affinity for metal surfaces, including stainless steel surfaces \([18]\).

3.2 Commissioning Test #2

In the second commissioning test, the behaviour of elemental iodine at 80°C was investigated in a two-stage experiment. The first stage (Test 2A) was initiated by adding elemental iodine to give a \(10^{-5} \text{ mol.dm}^{-3}\) aqueous iodine solution in the Main Vessel. As in the previous test, the initial transfer of iodine to the gas phase was rapid, with a maximum airborne iodine concentration being achieved within the first three hours. This is shown in Figure 4. After reaching a maximum value, the airborne iodine concentration was observed to decrease rapidly over the next 15 - 20 h, followed by a slower decline to a steady-state level. This behaviour differs from that observed in the previous test and suggests that different mechanisms were responsible in determining the iodine volatility during the early and latter stages of this test.

Analysis of the aqueous phase revealed that the total iodine concentration remained constant throughout the test. This suggests that the reaction of elemental iodine to form a less volatile species, and not surface adsorption, was the predominant mechanism for the decline in the airborne iodine concentration. This is also consistent with the observation that there was no significant adsorption of iodine-131 on any of the surfaces. Nevertheless, this does not preclude the possibility that surface reactions may have been responsible for the formation of the involatile iodine species. This may, at least partially, account for the increase in the partition coefficient from approximately 3000 to 26 300 at the end of this test stage at
Under the conditions of this test, a partition coefficient of approximately 14 would be expected if all the iodine in the RTF were in the form of $I_2$.

Similar results were also observed in stage 2B of the second commissioning test, where an additional $10^{-5}$ mol dm$^{-3}$ of elemental iodine was injected into the aqueous phase. The resulting transient response of the airborne iodine concentration is shown in Figure 5. As in stage 2A of this test, the airborne iodine concentration rises rapidly at first, reaching a maximum level within the first three hours. This is followed by a sharp decrease in the airborne iodine concentration over the next 10 h. After this period, the airborne iodine concentration declines gradually with time. Exceptions to this gradual decline are observed at 42 h and 91 h after the second injection of $I_2$, when the airborne iodine concentration is observed to decline sharply because of the activation of the hydrogen recombiner and Gas Ventilation Loop, respectively. After terminating the operation of the Gas Ventilation Loop, an increase in the airborne iodine concentration is observed, presumably because of mass transfer to the gas phase, followed by the general decrease in airborne iodine concentrations already noted. As in stage 2A, the total iodine concentration in the aqueous phase remained constant throughout the experiment. This, coupled with the decrease in gas phase iodine concentrations with time, results in a dramatic increase in the partition coefficient during the course of this test: from 3000 in the early stages of the test to approximately 110 000 after 120 h.

In both stages of this test, the decline in the total airborne iodine concentration was not well represented by a single first order rate equation. The decline in the airborne iodine concentration in the first half of each stage can be represented by a first order rate equation with a rate constant of $3.0 \times 10^{-5}$ s$^{-1}$. Similarly, in the latter half of both stages, the decline in the total airborne iodine concentration follows a first order rate expression with a rate constant of $5.9 \times 10^{-6}$ s$^{-1}$. The nature of these reactions is unknown, although it is likely that reactions on the stainless steel surfaces of the Main Vessel play a significant role. The most likely reaction would be reduction of iodine to iodide on the surface, a suggestion consistent with the findings of Burns et al reported elsewhere in this Conference Proceedings [19].

### 3.3 Commissioning Test #3

The third commissioning test was intended to investigate the behaviour of a $10^{-5}$ mol dm$^{-3}$ CsI solution at 25ºC in the RTF. The resulting transient response of airborne iodine for the first 400 h of the test is presented in Figure 6. The sudden rise in the airborne iodine concentration in the first 5 h was unexpected. Under these experimental conditions, CsI has no appreciable vapour pressure and oxidation by dissolved $O_2$ to more volatile iodine forms is slow [20]. It is known, however, that the reaction

$$2I^- + 1/2O_2 + 2H^+ \longrightarrow I_2 + H_2O$$
can be catalyzed by metal ions such as Cu$^{2+}$ and Fe$^{3+}$ [21,22]. Analysis of an aqueous sample taken prior to the addition of the CsI was found to have an Fe concentration of $2 \times 10^{-5}$ mol dm$^{-3}$. Based on the results of Fudge et al [22], it is very unlikely on kinetic grounds that such a process could result in the airborne iodine concentrations observed in the early stages of this test.

Another more likely explanation for the observed airborne iodine concentration is contamination by volatile organic iodides of the iodine reagent solution used in this experiment. This hypothesis is supported by the similarity in the transient behaviour of airborne iodine in this test with that observed for Test 1, where methyl iodide was used. In this test, the gradual decrease in the airborne iodine concentration followed first-order kinetic behaviour with a rate constant of $2.0 \times 10^{-6}$ s$^{-1}$. This value is similar to the value of $1.5 \times 10^{-6}$ s$^{-1}$ measured in Test 1 and suggests that trace amounts of methyl iodide were inadvertently introduced into the RTF. It should be noted that with as little as 0.0025% of the iodine added to the RTF in the form of methyl iodide, airborne iodine concentrations similar to those observed in Test 3 would be expected.

The total iodine concentration in the aqueous phase was constant over the first 400 h of the third commissioning test. As in the other tests, this revealed that loss of iodine to surfaces was insignificant. During this period, the partition coefficient increased from a minimum value of 7 800 to 165 000.

The third commissioning test was continued for an additional 12 days to demonstrate the ability of this facility to operate for an extended period, to rigorously test safety systems installed on this facility and to examine the effects of other variables not adequately addressed in the earlier tests. The results of this testing are illustrated in Figure 7. At 406 h into Test 3, the pH of the aqueous solution was reduced from 7.4 to approximately 2.7 by addition of nitric acid. As expected, this resulted in a significant increase in airborne iodine concentrations. At 420 h, all recirculation pumps were deactivated and then reactivated at 460 h. The observed decrease in the rate of airborne iodine evolution during this period is presumably due to a decrease in the mass transfer coefficient arising from the negligible flow in the Main Vessel. When the pumps were reactivated, a significant increase in the rate of revolatilization of iodine was observed.

At 482 h, the Main Vessel was vented to atmosphere to relieve a 20 kPa overpressurization arising from a pressure test of the facility. This resulted in a 13% drop in the airborne iodine level. The concentration of airborne iodine then continued to increase because of the earlier addition of nitric acid and resumption of gas and aqueous phase recirculation.

Since subsequent tests in the RTF will utilize a 444-TBq (12-kCi) cobalt-60 irradiation source and will result in the production of hydrogen from water radiolysis, H$_2$ was repeatedly added to the Main Vessel and the response of the automated hydrogen recombination system tested. Shown in Figure 7 is the effect on airborne iodine concentrations when the hydrogen recombiner was automatically activated on 17 separate occasions. As demonstrated in the earlier commissioning tests, use of the hydrogen recombiner resulted in a lowering of airborne iodine levels but upon isolation of the recombiner, airborne levels, increased. The average decrease in the
airborne iodine concentration after operating the recombiner for 10 min. at a flow rate of 20 dm³ min⁻¹ was approximately 27%. No deterioration in hydrogen removal efficiency (100%) was observed over this series of tests.

Also during this test, iron(III) in the form of ferric nitrate was added to ascertain its effect on airborne iodine levels. A significant increase was observed at 553 h when 1 x 10⁻⁶ mol dm⁻³ Fe(NO₃)₃ was added to the test solution, although it must be noted that a fraction of this increase was due to the revolatilization of iodine after isolation of the hydrogen recombiner at 553.5 h. Ferric nitrate (1 x 10⁻⁵ mol dm⁻³) was also added at 579 h. A considerably smaller effect on iodine volatility was observed with the second addition of ferric nitrate.

4. COMMISSIONING PROGRAM SUMMARY

The three commissioning tests undertaken in the RTF were very successful in demonstrating the capabilities of this facility. These tests illustrated that this facility could be safely operated over extended periods (up to 28 days) and at elevated temperatures. Both these capabilities are important for the experimental program planned for this facility. Furthermore, this series of tests revealed that nearly all of the on-line instrumentation performed as intended. The successful use of the Automated Airborne Iodine Sampler for obtaining data on the total gas phase iodine concentration as a function of time was particularly noteworthy.

Important information on the behaviour of various forms of iodine within a stainless steel vessel was also obtained. For all three tests, irreversible plateout onto stainless steel surfaces was shown not to be a dominant process, although for the I₂ test, surface effects may have played a role in determining the aqueous iodine chemistry. For the methyl iodide test, the decrease in gas phase concentration can be attributed largely to hydrolysis. The interpretation of the CsI test is complicated because of the likely contamination of the test solution with methyl iodide.

It was also important that any inadequacies associated with the facility be determined prior to initiation of the experimental program. Several alarm system program errors were detected and subsequently corrected. The affinity of the hydrogen recombiner for airborne iodine was also unanticipated. Although not a serious problem since it was demonstrated that the recombiner needs to be activated for only 10 min. to reduce H₂ levels to acceptable levels, knowing the efficiency of this system for removing H₂ will be useful information for future tests. Other hydrogen removal systems are also under consideration.

Although the intent of the commissioning program was principally to demonstrate the operation of the RTF, not iodine behaviour under accident conditions, these tests also illustrated the importance of utilizing appropriate analytical techniques to determine gas and aqueous phase speciation of iodine. Clearly, to determine the relevant chemistry within this facility, the chemical form of iodine must be determined. To this end, radiochemical solvent extraction procedures are being assessed for use in aqueous phase speciation. This will be supplemented by spectrophotometry and High-Performance Liquid Chromatography will be also employed. Speciation of
gas samples will be achieved using species-selective adsorbents in conjunction with the Airborne Iodine Sampler installed in the RTF. Samples will also be analyzed off-line using a Gas Chromatograph equipped with electron capture and photoionization detectors.

5. FUTURE STUDIES

The planned program to be conducted in the RTF consists of a number of distinct multi-test phases. As currently formulated, Phase 1 will consist of five distinct tests conducted in a Main Vessel constructed of carbon steel and coated with zinc primer paint. Zinc primer is one of several paints used in CANDU containment buildings. Furthermore, to provide early data on iodine behaviour under containment accident conditions, the 444-TBq (12-kCi) cobalt-60 irradiation source will also be utilized, with CsI as the chemical form of iodine. The pH range of 7 to 10 will be studied and the effects of impurities such as methane and methyl ethyl ketone (MEK) will be tested. Other variables to be specifically tested include varying recirculation rates, hydrazine addition for iodine mitigation and venting.

Phase 2 will be similar to that of Phase 1 except lower radiation fields (0 and 0.1 kGy/h) will be tested.

Subsequent test phases in the RTF, although not yet fully defined, will focus on the effects of other surfaces; in particular, epoxy and vinyl painted surfaces and concrete. In each phase, radiation effects, various impurities, pH and mitigation strategies will be studied, so that important integral data on the behaviour of iodine can be obtained for use in validating computer codes that model containment iodine chemistry.

ACKNOWLEDGEMENTS

This work was funded jointly by Atomic Energy of Canada Limited and Ontario Hydro, Hydro Quebec and the New Brunswick Electric Power Commission under the CANDU Owner’s Group (COG) program, Working Party 06, Work Package 425.
TABLE 1: SUMMARY OF EXPERIMENTAL CONDITIONS FOR THE RTF FULL-SYSTEM COMMISSIONING TESTS

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<th>Test #1</th>
<th>Test #2</th>
<th>Test #3</th>
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<td><strong>Initial Iodine Species</strong></td>
<td>CH$_3$I</td>
<td>I$_2$</td>
<td>CsI</td>
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<tr>
<td><strong>Initial Iodine Concentration</strong></td>
<td>$10^{-5}$ mol.dm$^{-3}$</td>
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<td>80°C</td>
<td>25°C</td>
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<tr>
<td><strong>pH</strong></td>
<td>7 (buffered)</td>
<td>5.5</td>
<td>7 (buffered)</td>
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Gas Recirculation Rate: 20 dm$^3$.min$^{-1}$
Gas Ventilation Rate: 10 dm$^3$.min$^{-1}$
Aqueous Recirculation Rate: 10 dm$^3$.min$^{-1}$
Aqueous Phase Volume: 25 dm$^3$
Gas Phase Volume: 315 dm$^3$
REFERENCES


FIGURE 1. Schematic of Radioiodine Test Facility.
FIGURE 2. Cross-Sectional View of Lead Canister and Main Vessel.
FIGURE 3. Total Airborne Iodine Concentration as a function of time for Commissioning Test 1.
COMMISSIONING TEST 2A: ELEMENTAL IODINE
AIRBORNE IODINE -131 vs TIME

FIGURE 4. Total Airborne Iodine Concentration as a function of time for Stage 2A of Commissioning Test 2.
FIGURE 5. Total Airborne Iodine Concentration as a function of time for Stage 2B of Commissioning Test 2.
FIGURE 6. Total Airborne Iodine Concentration as a function of time for Stage 3A of Commissioning Test 3.
COMMISSIONING TEST 3B: CESIUM IODIDE

Total Airborne Iodine Concentration vs Time

FIGURE 7. Total Airborne Iodine Concentration as a function of time for Stage 3B of Commissioning Test 3. The asterisks (*) on the x ordinate indicate the times at which the hydrogen recombiner was activated.
DISCUSSION

P.N. CLOUGH
Do you have plans to measure the uptake of iodine on the walls of the system - which appears to have been important in the second commissioning test with I₂?

W.C.H. KUPFERSCHMIDT
It is our intention to obtain an estimate of iodine losses to surfaces within the RTF after each run by washing and decontaminating exposed surfaces using the installed spray dousing system. The wash solutions will then be analyzed for total iodine. To obtain a better measure of the uptake of iodine on surfaces within the RTF would require the opening of the facility after each test and analyzing either the surface itself or coupons which would be placed in the RTF prior to each test. This is not feasible for each test. We may decide however, if results of future tests warrant it, to do this for a selected number of tests.

J. PAQUETTE
What is the recombiner made of?

W.C.H. KUPFERSCHMIDT
The H₂ recombiner is comprised of the wet-proofed catalyst developed at CRNL. This catalyst is a teflon-coated platinum-based system.

S. DICKINSON
I'm not familiar with how recombiners work. Was the reduction in vapour-phase iodine species, when the recombiners were activated, an effect of the removal of hydrogen from the system or were the iodine species being removed by the recombiner?

W.C.H. KUPFERSCHMIDT
The recombiner shows an affinity for airborne iodine whether H₂ is present or not.

W.G. BURNS
Can you tell us how you measured the partition coefficient, and did you measure [I⁻] in the water phase, especially in the I₂ experiment?

W.C.H. KUPFERSCHMIDT
The Automated Airborne Iodine Sampler (AAIS) installed on the Gas Sampling Loop is used to ascertain the concentration of ¹³¹I in the gas phase. As described in my presentation, a known volume of gas from the RTF's Main Vessel is passed through a cartridge containing TEDA-impregnated charcoal. The cartridge is then automatically inserted into a well-type NaI(Tl) scintillation detector and the total ¹³¹I concentration ([¹³¹I]₀) can then be calculated. At the same time, aqueous samples are collected from the Aqueous Sampling Loop and gamma counted, thereby providing a measure of the aqueous phase ¹³¹I.
concentration ([\(^{131}\)I],i_g). The reported partition coefficient is given by the expression 
\([^{131}\text{I}];_\text{aq}/[^{131}\text{I}];_g\).

In answer to your second question, these full-system commissioning tests were designed to test the operation of the RTF, not to necessarily obtain data on the behaviour of iodine. As such, analytical support of these tests was minimal and aqueous [I\(^{-}\)] was not determined. I should note, however, that there will be full analytical support provided when the experimental program is initiated later this year.

G.J. EVANS

Did you get to see any evidence of the molecular iodine dissociation using HPLC and gas chromatography?

W.C.H. KUPFERSCHMIDT

As noted above, analytical support for these tests was minimal. As such, molecular iodine dissociation was not observed. It should be noted that this phenomenon would be difficult to measure using these techniques.
PHEBUS F.P. is a global experiment intended to give the best possible representation of the behaviour of fission products during PWR severe accident.

The main objectives of the programme are:

- validation of code systems
- improvement of severe accident knowledge (i.e. help the management of such accidents).

I. DESCRIPTION AND REPRESENTATIVITY STUDY

The figure 1 gives a diagram of the PHEBUS Experimental System for the F.P. project. The general conception of the circuits takes into account the representation of all the reactor components concerned for different scenarios (following the leakpath of the radioactivity).

The fuel representativity is insured by:

- a twenty rods PWR type assembly with spacing grids and one absorb rod (Silver, Indium, Cadmium)

- high burn up irradiated fuel reirradiated in the facility from one to 3 weeks to restore a representative level of residual power and radioactivity

- experimental sequence: reproduction of the "core" conditions during the release of volatile species (evolution of temperatures, pressure, flow rate, fluid composition).

The scale reduction involves for the experiment compared to the reactor larger surface to volume ratio. This is the major representativity problem to face for the circuits.
The representativity studies of the experimental circuits are based on:

a) A qualitative analyse of the important phenomena for the reactor followed by a synthesis of reactor calculations made in 1987 by the european partners of the project. This work has led to a quantification of the experimental parameters (thermalhydraulics residence time, concentrations, etc...)

b) Two complementary studies

. At the end of 1987, the general tendancies have been determined with a scaling study; during 1988 "loop" calculations are in progress (by France, C.C.E. and members countries) using code systems.

. The second study (by C.E.A.) uses chemical engineering technics and particularly the concepts of residence time and contact time (calculations and experiments).

The objective of these two approaches is the dimensionning of the circuits in 1988.

2. INSTRUMENTATION ASPECTS

The instrumentation is located in the test train (fuel), in the experimental circuits (simulation of the primary circuit) and in the F.P. Tank (simulation of the containment).

The different measurements concern:

- the thermalhydraulic parameters: temperatures (fuel, fluid, structures), pressures, flow rates, levels, moisture

- the characterisation of aerosols (suspended mass, size distribution).

- the identification of the chemical species (i.e location and characterisation of deposits).

The instrumentation involves on line measurements and post test examination of the fuel and structure coupons. Different techniques will be used: 

- spectrometry,
- pH metry, chemical analysis, surface analysis....

The planning project sets the first test for the end of 1990.
What measurements of iodine are planned?

The species of iodine will be determined by γ-spectrometry and chemical analysis for the two phases (aqueous and gaseous).
PLANNED WORK AT JAERI FOR IODINE CHEMISTRY DURING REACTOR ACCIDENT

M. Saeki

Radiochemistry Laboratory,
Department of Chemistry,
Japan Atomic Energy Research Institute,
Tokai, Ibaraki, 319-11, Japan

The Radiochemistry Laboratory and the Fuel Reliability Laboratory II in Japan Atomic Energy Research Institute have been planned a study for radioiodine chemistry during a nuclear reactor accident. The objective of this work is to confirm the mechanism for the formation of organic iodides and to obtain the time-dependent conversion rate of iodide ion (I⁻) in a water pool to volatile iodine forms (organic iodides and/or I₂).

Figure 1 shows the behavior of iodine in a reactor containment during an accident of a nuclear reactor. High radiation fields can be present in the water pool. Thus, the radiation induced reaction leading to the formation of organic iodides can occur between iodine and organic compounds involved in the water pool or at surfaces. In the planned work, the possible mechanisms for the formation of volatile iodine will be examined.

Figure 2 shows simplified schematic view of the experimental set-up which will be made. A Gammacell 220 will be used as the gamma ray source. We are planned to control the conditions of the atmosphere and solution, independently. The planned experimental conditions are as follows:

- pH range : 2 - 12
- pH additives : H₃BO₃, LiOH
- Dose rate : ca. 10⁶ R·h⁻¹ (ca. 10⁴ Gy·h⁻¹)
- Iodine concentration : 10⁻⁴ - 10⁻⁸ mol·dm⁻³
- Organic additives : Paint, Ion-exchange resin etc.
- Temperature range : Room temperature - 80°C

It has been confirmed experimentally by several groups that the pH of the solution affects strongly the rate of oxidation reaction of I⁻ and the final product distribution of iodine [1-3]. This means that the pH of the solution also controls the equilibrium concentration of I₂ in the solution. Since the primary reaction to form organic iodides is presumed to be reaction (1), the concentration of I₂ is very important factor for the development of an iodine behavior-model.

\[ I₂ + \text{organic radical} \rightarrow \text{organic iodide} + I \]  (1)
According to the report from American Physical Society study group on severe accident at nuclear power plants, the oxidation reaction of nitrogen has been known for a long time, and the resultant nitric acid would reduce the pH of water pools in the containment [4]. However, there are a few careful studies concerning this problem [5-6]. Thus, additional experiments for it might be necessary.

The concentration of organic sources (or organic radicals) may be another important factor in order to construct a complete code for iodine behavior involved the roles of organic iodides in the containment, because the concentration can be higher than that of $I_2$ in a water pool in some cases. Thus, efforts will be made to approach this problem.

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6. E. C. Beahm, Private communication at this workshop.
Figure 1  EFFECT OF RADIATION ON VOLATILITY OF IODINE
Figure 2  SCHEMATIC VIEW OF EXPERIMENTAL SET-UP
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IODINE CHEMISTRY IN REACTOR SAFETY

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