



# THE PRESENT STATUS OF IODINE CHEMISTRY RESEARCH IN CANADA AND ITS APPLICATION TO REACTOR SAFETY ANALYSIS

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## Abstract

The current need to understand iodine chemistry in a reactor safety context has become more sharply focussed as the level of that understanding has advanced. At the same time, the situations of most concern within containment, from an iodine perspective, are also being redefined in the light of that understanding. The present paper summarises these developments.

Over the past five years, considerable advances have occurred in our understanding of iodine chemistry under conditions of interest in reactor accidents. A number of key experiments have yielded important results in the areas of solution chemistry, the role of surfaces, the importance of organics and the effects of impurities. This understanding supplements the already substantial gains made in characterising the key roles of pH and the effects of radiation. All these factors underline the now evident fact that the kinetics of iodine reactions are the controlling factor when radiation is involved, and that a number of reactive species, not present in thermal reactions, effectively control the observed volatility of iodine.

In this paper, recent advances are summarised and the present state of our understanding of iodine chemistry is reviewed. Specifically, an attempt is made to identify those areas where our understanding appears to be relatively complete, and to flag the remaining critical areas where our attention is currently focussed. The state of our modelling capability is reviewed, as is the significance of related areas such as the role of mass transfer. Finally, an overview is presented of the significance of this work for reactor safety, and our expectations for its application over the near term future.

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## 1. INTRODUCTION

Periodic reviews of the state of our understanding of iodine chemistry have shown a continuing trend of increasing understanding, but also of increasing complexity. The most recent round of reviews of this topic, carried out in the early to mid-1980s [1,2], documented work that had been reported on a range of topics relevant to iodine behaviour. Work performed during the ten years since those reviews were published has again revealed an increase in complexity, but this appears to have been offset by a relatively greater advance in our understanding and predictive capabilities. Our view of iodine chemistry under expected post-accident conditions in containment has continued to evolve, but we can venture to say now with some confidence that we have identified the factors that exert primary control over iodine behaviour in containment following an accident.

As specific questions on iodine chemistry are resolved, and as a clearer perspective emerges on broad questions of iodine behaviour, it can be expected that increasing attention will be given to the application of these iodine research results. The complexity of iodine behaviour strongly indicates that its full understanding and application to reactor safety questions will necessarily involve the use of iodine behaviour codes. Due to differences in reactor designs and differences in the conditions expected in containments, a range of situations may present themselves for analysis and resolution, and the impact of iodine behaviour codes as they are applied to these situations may vary from slight to considerable. Therefore, realising the benefits of iodine research may be a somewhat extended process, and the current longer term research campaigns may be succeeded by shorter and more focussed projects aimed at specific applications.

The present paper provides a brief review of the status of iodine chemistry and reflects the view that further work on iodine questions should be increasingly directed toward applications in specific reactor safety and licensing contexts. The paper also considers the state of our modelling and predictive capability, taking the LIRIC code as a representative example. Finally, one perspective on the significance of iodine behaviour for reactor safety is provided.

## 2. RECENT ADVANCES

Since the late 1980s, our understanding of iodine chemistry has improved quite dramatically, and solid advances have been made in four important areas [3,4,5].

1. Kinetics, and not thermodynamics, is recognised as the factor which has the major influence on the ultimate distribution and speciation of iodine, and controls the speed at which those final states are reached.
2. pH has been identified as the key factor affecting iodine volatility above aqueous solutions, and this dependence of iodine volatility on pH is primarily due to the reactions controlling reduction of  $I_2$  in the aqueous phase by  $H_2O_2$  and  $O_2^-$ .
3. It is recognised that organic impurities in the aqueous phase can have an important but complex effect on iodine volatility by (a) their influence on solution pH because of the production of organic acids, (b) the production of volatile, low molecular weight organic

iodides, and (c) their potential, under some conditions, to suppress volatility by interfering with reactions that produce  $I_2$  and by sequestering iodine as aromatic iodides of inherently low volatility.

4. Our predictive capability appears to have improved notably since the last code comparison exercise was carried out [6].

### 3. PRESENT UNDERSTANDING

Our present understanding of iodine chemistry is summarised briefly below under three main headings: iodine behaviour in the aqueous phase, in the gaseous phase and its interactions with surfaces.

#### 3.1 Aqueous Phase

Iodine behaviour overall appears to be dominated by a number of primary influences that exert themselves in the aqueous phase. These influences are the interactions of various water radiolysis products with iodine species, the effects of pH and the role of organic impurities.

##### Effects of Water Radiolysis

The presence of radiation significantly alters iodine behaviour (compared to that in the absence of radiation) due to the reactive species produced by water radiolysis and the interactions of these species with iodine in solution. One consequence of these reactions is the increased volatility of iodine, which can be several orders of magnitude higher than would be indicated by thermodynamic calculations applied to a simpler thermal system. This observation underscores the dominant role of kinetics on iodine chemistry under conditions likely to be of greatest interest in containment, and stresses the need to regard thermodynamic calculations on their own as an unreliable guide to iodine speciation and distribution within containment.

Two products of water radiolysis that strongly influence iodine behaviour are the OH radical and hydrogen peroxide ( $H_2O_2$ ).

The oxidation of  $I^-$  to  $I_2$  is modelled by a multi-step reaction scheme, the important step being the oxidation of  $I^-$  to  $I$  by  $OH^\cdot$ , but also involving  $HOI$ ,  $I_2^-$  and  $I_3^-$  as intermediates. The corresponding thermal reactions resulting in oxidation of  $I^-$  are much slower and this gives rise to the radiolytic route for production of volatile iodine as the dominant route. The radiolytic production of volatile iodine may be influenced by a number of factors, however. One such factor may be the presence of large quantities of organics, which react with  $OH^\cdot$  at rate constants that are generally large. Organics present in the aqueous phase at concentrations in the region of  $10^{-5}$  mol/l or higher could suppress the level of  $OH^\cdot$  and consequently limit the rate at which  $I^-$  is oxidised to  $I_2$ .

$\text{H}_2\text{O}_2$  is a relatively stable water radiolysis product which has great importance for iodine chemistry by virtue of its ability to reduce  $\text{I}_2$ , and because of its relatively high concentrations in solution compared to other radiolytic species. The  $\text{I}_2/\text{H}_2\text{O}_2$  reaction is the primary mechanism by which the strong effect of pH is exerted on iodine volatility.  $\text{H}_2\text{O}_2$  is also subject to influences which may limit or reduce its effect on iodine volatility. Two such influences that are potentially important are significant aqueous concentrations of organics and the presence of transition metal ions. Both these influences tend to reduce the amount of  $\text{H}_2\text{O}_2$  present in solution. This has the effect of increasing the level of  $\text{I}_2$ .

### **Effect of pH**

Solution pH has a profound effect on iodine volatility and is probably the single most important variable influencing iodine volatility. Low pH conditions lead to increased levels of  $\text{I}_2$  in solution, since the reduction of  $\text{I}_2$  by  $\text{H}_2\text{O}_2$  falls off with decreasing pH. Under these conditions, the presence of organics can lead directly to increased production of organic iodides and substantial increases in iodine volatility. This situation has evident safety implications which are discussed below.

### **Effect of Aqueous Organics**

The presence of organics in the aqueous phase can influence iodine chemistry in complex ways. Under the effects of radiation, organic species readily degrade to carboxylic acids, and these may result in significant decreases in the pH. This in turn can result in increased production of  $\text{I}_2$  and subsequently of organic iodides, thereby bringing about an increase in iodine volatility. This action of organics in causing reductions in pH may be their strongest influence on iodine volatility. The drop in pH brought about in this way can be dramatic. In intermediate-scale tests carried out in the Radioiodine Test Facility (RTF), and involving irradiated aqueous solutions containing organics, when the pH was uncontrolled it was observed to fall from an initial value of 9.5 to low values of 6 or less in the space of 5 to 10 hours. It appears that this drop in pH is attributable to the generation of organic acids in the aqueous phase. Organics may also influence iodine chemistry by consuming  $\text{H}_2\text{O}_2$  or  $\text{OH}^-$ . It may also be possible for some organics to reduce iodine volatility. Phenol, for example, undergoes rapid thermal reaction with  $\text{I}_2$  producing a relatively low volatility organic iodide.

## **3.2 Gaseous Phase**

Early large scale studies of iodine reactions with organics in the gas phase attempted to characterise the production of organic iodides by thermal reactions [7]. The results of these tests showed wide variations and involved conditions that are far from representative of those now considered to be important in containment following an accident. (The tests involved no radiation, methane was used as the only organic, and iodine was introduced into the gas phase in molecular form.) If these test results are used to try to estimate the conversion to organic iodides under conditions that are more representative, very small amounts of organic iodides are predicted to be produced. Examination of results from intermediate-scale tests in the RTF show that gas phase organic iodide concentrations can be accounted for by mechanisms that involve

production of these organic iodides in the aqueous phase, and the subsequent partitioning of these species to the gas phase. These results cast doubt on the significance of either thermal or radiolytic production of organic iodides in the gas phase. This view is supported by model calculations which also indicate that formation of organic iodides in the gas phase is probably not significant [8].

### 3.3 Effects of Surfaces

Both early and recent work has demonstrated that surfaces can be very important sinks for iodine. The large body of work published by Genco and Rosenberg [9,10,11], who studied a variety of surface coatings, shows the affinity of  $I_2$  and  $CH_3I$  for various surface materials.

Intermediate-scale studies have also demonstrated that significant fractions, in many cases the majority, of the total iodine can be deposited onto surfaces with organic coatings. These tests have also demonstrated the effect of these surfaces on iodine volatility due to the organic species released to the aqueous phase from the paint on surfaces. Work is underway to develop and validate models that will explain the behaviour observed in these tests.

It has been suggested [12] that surfaces may also be sources of organic iodides. While there is still disagreement as to whether heterogeneous or homogeneous mechanisms dominate in the production of organic iodides, there is some good evidence in favour of the latter mechanism but little in support of the former. The net production of organic radicals on a surface polymer coating by radiolysis is expected to be too low to give rise to the observed organic iodide generation rate. Other mechanisms could be postulated and the question will be resolved only through experiment.

## 4. AREAS CONSIDERED RELATIVELY COMPLETE

Two broad areas of iodine chemistry appear now to be adequately understood. They are

- most areas relying on thermodynamic data, and
- the details of thermal oxidation of iodide to iodine.

Thermodynamic data are seen now to be less important as a means of predicting iodine distribution and speciation. This capability will come only through an understanding of the relevant reaction kinetics. Hence, further or more detailed thermodynamic data are not required, in general. This applies to both the aqueous and gaseous phases since the species present in the latter appear to depend on the speciation and distribution in the former. An exception concerns the thermodynamic data needed for accurate determination of the partition coefficients of some organic iodides.

Thermal oxidation of iodine under condition of interest following an accident is unlikely to be significant. Under these conditions, where radiolysis can be expected to be a factor, the conversion of  $I^-$  to  $I_2$  by the OH radical is very much faster than the corresponding thermal reactions, and can account for the bulk of the  $I_2$  production. Even though uncertainties remain in our understanding of the rate expressions and mechanism for thermal oxidation of  $I^-$ , further work in this area does not appear to be warranted.

## 5. AREAS CONSIDERED INCOMPLETE

Three broad areas have been identified where our understanding of some factors affecting iodine chemistry require further work. Within each of these broad areas, one or more specific items on which our knowledge is still considered inadequate, can be highlighted.

These areas are aqueous chemistry, surface reactions, and mass transfer, and they will be touched on in turn.

### 5.1 Aqueous Chemistry

The kinetic data base for iodine chemistry in the aqueous phase appears to be well established. There are several areas where existing uncertainties should be resolved.

1. The release of organic species to the aqueous phase from surfaces, and the reactions controlling their decomposition in the aqueous phase have an important impact on aqueous iodine chemistry. Our capability for modelling these processes, including the resulting transients in pH and dissolved oxygen, remains incomplete and is the most significant deficiency in the area of aqueous chemistry.
2. Uncertainties remain as to the influence of some metal ions on iodine chemistry, mainly concerning the importance of their catalytic reactions with  $\text{H}_2\text{O}_2$  and  $\text{O}_2^-$ , and the concentrations of these ions that are likely to be present in specific cases.

### 5.2 Surface Reactions

Surfaces in contact with the gas phase have large potential importance as sinks for iodine. The adequacy of existing and proposed models for iodine absorption onto these surfaces needs to be confirmed.

The suggestion that surfaces may also act as sources of organic iodides needs to be pursued. At present, the available evidence indicates that organic iodides are produced in the aqueous phase, but the strength of this iodine sink makes it important to determine the fate of iodine once it is absorbed onto a surface.

### 5.3 Mass Transfer

The modelling of mass transfer at the aqueous-gas phase interface that has been used to simulate the intermediate-scale RTF tests appears to be adequate. For other geometries and larger vessels, providing reasonably realistic predictions of the mass transfer rate may be less straightforward. This is an application question, associated with uncertainties on the effects of different flow or mixing regimes in large volumes, and on differing surface to volume ratios.

## 6. MODELLING CAPABILITY

A number of iodine behaviour codes have been developed over the years. One of these is LIRIC (Library of Iodine Reactions In Containment), which has been evolved by AECL researchers at Whiteshell Laboratories, and is now approaching the point where its qualification for use as an analysis tool is being considered. LIRIC is a mechanistic model and includes about 200 reactions that are of relevance to the prediction of iodine behaviour.

A capability of primary importance for an iodine behaviour code is the ability to predict airborne iodine concentrations with reasonable accuracy. This can only be accomplished if the code incorporates models for all the factors that are important for predicting iodine behaviour, including the various sinks to which iodine might migrate, all factors affecting its volatility, its speciation and the propensities of each of these species to remain airborne or to migrate to one or more of the sinks.

A fuller description of LIRIC and its capabilities is given in Reference 5. Figures shown in that paper and reproduced here as Figures 1 and 2 indicate that for specific tests LIRIC is able to model airborne iodine concentrations well. While some shortcomings of the code have been identified, they do not appear to be major, for the cases against which LIRIC has been tested. Differences between experimental results and code predictions generally represent only small factors, and the code appears to be able to reproduce all the qualitative aspects of iodine behaviour quite well.

Work is presently underway in areas that will lead to code improvements, such as the development of temperature-dependent reaction rate data. Formal code verification and validation work remains to be done.

## 7. SIGNIFICANCE FOR REACTOR SAFETY

Improvements in our understanding of iodine chemistry are significant for reactor safety to the extent that they may affect our assessments of public dose, occupational safety or radiological impact on equipment. The primary factors that are important for any of these assessments are

- (a) the concentration of airborne iodine,
- (b) the various sinks for iodine, including particularly surfaces in contact with the containment atmosphere, and
- (c) our ability to predict any migration of iodine among these sinks for a range of conditions that may occur within containment.

The importance of these three factors has led to them being put forward as basic conditions that could define closure for the iodine issue.

There are a number of aspects of our emerging understanding of iodine that can have direct relevance to reactor safety assessments.

The primary role of pH in determining the volatility of iodine indicates an important sensitivity which we must be able to demonstrate that we understand. This relates not simply to licensing and regulatory questions, but also to the potential costs of having to make overly conservative assumptions, and the need to be able to demonstrate reasonable but adequate margins. A demonstrated understanding of pH and other variables of importance for iodine behaviour will allow more credible and better critical judgements to be made on accident mitigation strategies, on design assist analyses for equipment and on a range of minor plant upsets and significant events. The availability of a reliable iodine behaviour code will also allow more confident interpretation of a wide range of data from operating stations and the necessarily incomplete information that arises from accidents.

To date, Ontario Hydro has been reasonably successful in applying the information coming out of research programmes on iodine chemistry and aerosol physics (particularly water aerosols). Two areas of particular interest are worth noting here. The first is the use of R&D data for improved understanding and modelling of natural processes involving iodine transport in containment. The second relates to better understanding and modelling of engineered systems.

The behaviour of iodine and water aerosols plays an important role in some accident sequences in CANDU reactors, particularly those involving containment bypass. A better understanding of the behaviour of water aerosols and iodine has resulted in conservative and somewhat arbitrary assumptions used in the past being replaced by more realistic assumptions in recent safety report updates. The end result has been a reduction in the significance of iodine as a dose delivery vector.

Carbon filters are used in Ontario Hydro's multi-unit stations as an important engineered safety system. The ability to understand the fate of iodine absorbed by these filters, and the ability to model them realistically based on that understanding can have considerable importance for safety assessments. While the effort that has been expended to provide that ability is outside what would normally be understood as iodine chemistry, it is providing what might well be a textbook example of how a research program should mature and come to fruition.

Work on the behaviour of iodine on these filters has been carried on now over a period of about 15 years, and the research phase is currently coming to an end. Application of these results has begun, and this has already delivered important dose prediction benefits. Further application of research results to provide a firmer basis for the frequency with which the filter carbon should be replaced shows the promise of delivering real economic benefits and improved system availabilities.

In the area of application of results from iodine chemistry research programs, we anticipate in the near to medium term future, a more systematic review of the possible areas where this application could be instituted, evaluated on the basis of perceived need and advantage. Any such application effort has to be tailored to the conditions in a specific plant, at least to some extent. Conditions in reactor containments can vary widely due to differences in geometry and in containment design and functioning, differences in engineered systems (e.g. the presence or absence of sprays, the conditions under which they might be activated, the types and amounts of additives), and differences in accident scenarios and in predicted containment responses. Different containments of nominally the same design can influence iodine behaviour differently because of (for example)

the use of different coatings for containment surfaces, and slight variations in engineered safety systems. The basic purposes of such a review are to extract any operational or dose reduction advantage that might be gained through analysis, to identify any potential for mitigation or intervention and to reduce existing uncertainties and the potential for surprises.

The characteristics that are likely to make such an exercise successful are

- (a) a broad understanding of iodine chemistry under likely accident conditions and the factors most important for it,
- (b) the availability of reliable tools (e.g. computer codes) for the analysis of iodine behaviour,
- (c) maintenance of the appropriate level of expertise and capability, and
- (d) periodic review of the measures in place to deal with iodine issues.

Although we may soon be able to declare the iodine issue closed, this is likely to mean that it has been brought under control, rather than being simply a thing of the past. To maintain control of iodine will require at least some ongoing effort, since neither nuclear stations nor our understanding of them or of the accidents to which they are susceptible, is static.

## **8. CONCLUSION**

Our understanding of iodine chemistry has increased significantly over the past decade. We have now reached the point where we believe that the main factors influencing iodine behaviour have been identified. Iodine behaviour codes have reached a stage of development where they are able to predict at least some intermediate-scale test results with reasonable accuracy. Mechanisms for many effects in iodine chemistry have been evolved and a mechanistic understanding, at least, is in place for others. A number of technical issues that limit our understanding of iodine behaviour have been identified, and a set of general criteria that could be used to define closure of the iodine question have been proposed. It now appears that plans should be developed for bringing the present phase of iodine research to an orderly conclusion, so that the systematic codification and application of our understanding of iodine chemistry could take place.

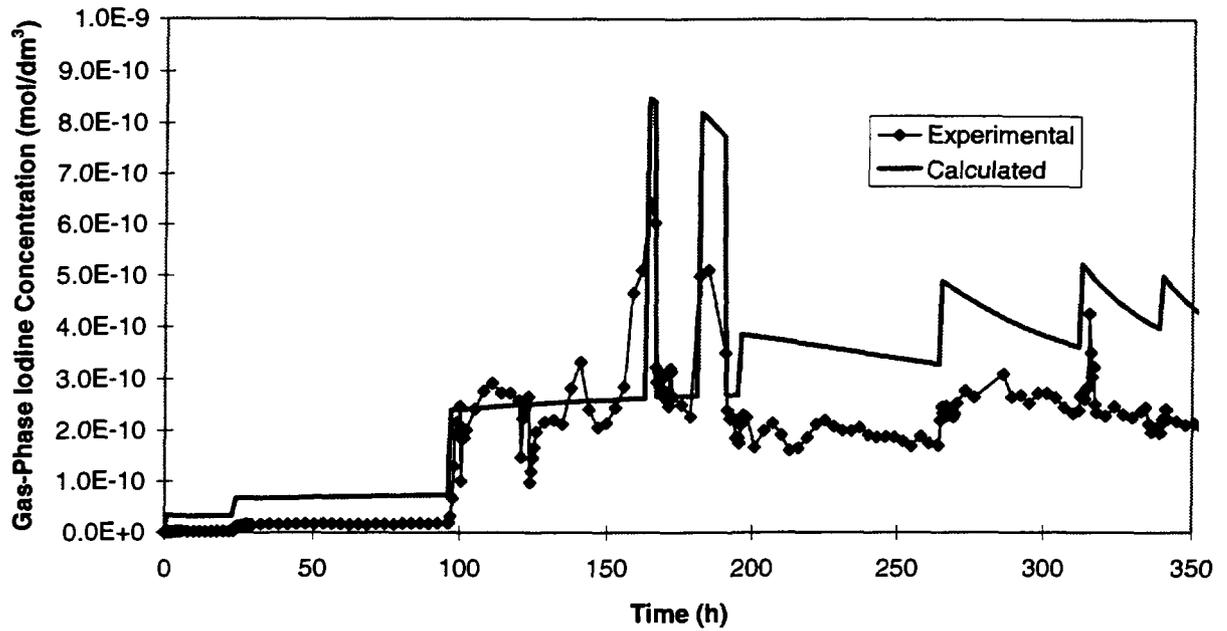
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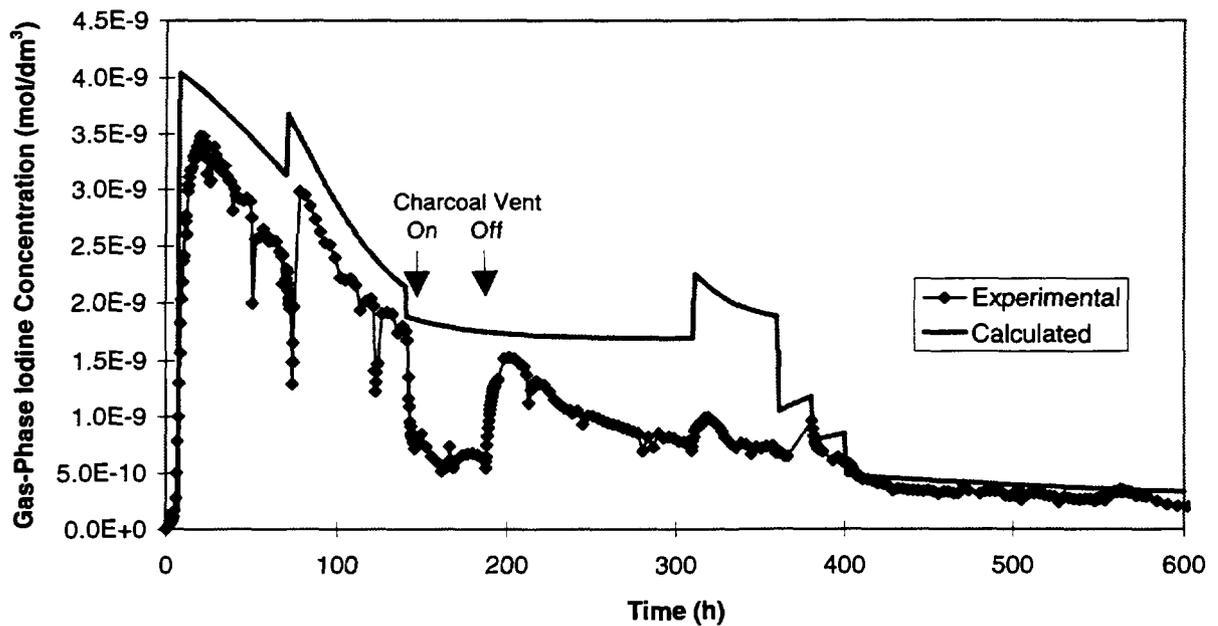
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## 10. ACKNOWLEDGEMENTS

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**Figure 1. Simulation of RTF Test 0.2.1 (Stainless Steel Vessel): Gas Phase Iodine Concentration.**



**Figure 2. Simulation of RTF Test 2.1 (Vinyl Painted Vessel): Gas Phase Iodine Concentration.**