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THE CHEMISTRY OF FISSION PRODUCT IODINE
UNDER NUCLEAR REACTOR ACCIDENT CONDITIONS*

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ABSTRACT

The radioisotopes of iodine are generally acknowledged to be the species whose release into the biosphere as a result of a nuclear reactor accident is of the greatest concern. In the course of its release, the fission product is subjected to differing chemical environments; these can alter the physicochemical form of the fission product and thus modify the manner and extent to which release occurs. Both the chemical environments which are characteristic of reactor accidents and their effect in determining physical and chemical form of fission product iodine have been studied extensively, and are reviewed in this report.

INTRODUCTION

The radioisotopes of iodine are generally acknowledged to be the radiotoxic species whose release into the environment in the course of a nuclear reactor accident is of the greatest concern.¹⁻³ This is due to the significance of radioiodine in determining early fatalities and latent cancers that may result.⁴ (In contrast, the long-term interdiction of land is determined primarily by the longer-lived radioisotopes of cesium.¹)

Iodine can exist in a number of different chemical valence states; this, and the wide variation of chemical environments to which the fission product can be exposed during a reactor accident, introduces considerable complexity in assessing the behavior of iodine species in such accidents. As a consequence, the "source terms" for iodine for accident assessment purposes remain a subject of intense scrutiny.

In this paper we describe the chemical environments to be expected in severe core damage accidents involving light water-cooled nuclear reactors (LWRs) that are presently in commercial operation, and review the chemistry of fission product iodine as it relates to the accident environments. Lastly, we identify those issues that remain unresolved.

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PERTINENT PHYSICOCHEMICAL FEATURES OF NUCLEAR REACTOR ACCIDENTS

Representative characteristics of both boiling water reactors (BWRs) and pressurized water reactors (PWRs) have been described by Nero.⁵ Both reactor types utilize UO_2 as the fuel in the form of cylindrical pellets which are about 1 cm in diameter and 1-1.5 cm in length. The pellets are stacked within tubes constructed of Zircaloy, a zirconium-based alloy, which are sealed in a helium atmosphere. A number of these fuel rods are then aligned in typically 8x8 (BWR) or 15x15 (PWR) arrays to form fuel assemblies, and the assemblies, in turn, are used to form the core of the reactor. The core of a 1100 MW (electric) PWR contains about 9.8×10^4 kg of UO_2 , whereas a 1220 MW (electric) BWR contains approximately 15.5×10^4 kg of fuel.

The nuclear reaction is controlled through the positioning of a number of stainless-steel rods containing neutron absorbers that are distributed throughout the reactor core. In BWRs, the absorber is B_4C , whereas in PWRs an alloy comprised of silver, indium, and cadmium is customarily employed. PWRs also use boric acid in the coolant to provide additional neutronic control, and LiOH for pH control.

A BWR operates at a nominal pressure of 7.0MPa and a coolant temperature of 290°C. The average temperature of the Zircaloy cladding of the fuel rods is 300°C, whereas the maximum temperature at the center of a fuel pellet is 1830°C. In contrast, a PWR operates at a system pressure of 15.5MPa and with coolant inlet and outlet temperatures of 290°C and 330°C, respectively. The nominal cladding temperature is 350°C, whereas the maximum fuel central temperature is 2280°C.

Walton⁶ theorized that a fragment that is produced by the fission process originates as a fast moving positive ion whose flight is generally terminated through collisions with other atoms within the UO_2 crystal lattice rather than at surfaces or phase boundaries. In the course of its transit, the valence state of the ionic fission fragment can be altered, so that it becomes trapped within the lattice as an impurity atom or ion (of either charge). The UO_2 crystal structure thus serves as the initial barrier to fission product escape.

The fission product impurity atoms or ions can migrate through the crystal lattice as a result of thermal motion and, in those cases in which the fission product is insoluble in UO_2 , such migrations will result in the gradual release of the fission product from the lattice and its accumulation in voids, grain boundaries, or within other crystal imperfections. In these regions it is free to interact chemically with other fission products. Material collected in those regions (including the fuel pellet surfaces) which are interconnected with the void region defined by the fuel external surface and the cladding internal surface is referred to as the "gap inventory." This fraction of the total fission product inventory of a fuel rod is immediately available for release in the event the integrity of the fuel cladding is no longer maintained.

Should failure of the cladding occur (by rupture due to internal pressure in an overheated fuel element, for example), the chemical environment of the fission products that escape from the fuel rods into the

reactor coolant system is suddenly changed from one whose oxygen potential is determined by fuel-cladding-fission product interactions to one in which the oxygen potential is governed by the H_2/H_2O ratio in the primary circuit. (In fuel overheating events, hydrogen is produced as a result of the reaction between steam and the Zircaloy.) In severe core damage accidents, a specification of the chemical conditions within the overheated reactor core is further complicated by the presence of the control rod and core structural components.

Another change in chemical environment occurs when the primary circuit itself is breached. The extent of the change depends upon the particular reactor design, however, as well as upon the nature of the accident. In any event, the oxygen chemical potential of the system is that characteristic of an air environment just prior to the escape of the fission products into the biosphere.

IODINE RELEASE FROM IRRADIATED FUEL

Because of its influence on the thermal performance of the fuel rods, much of the earlier studies of fission product escape from the UO_2 crystal lattice focused on noble gas behavior at relatively low temperatures.⁷ As a consequence, considerable data have been obtained relating to conditions characteristic of normal operation, and both empirical^{8,9} and theoretical¹⁰⁻¹² treatments have been made to describe the manner in which the gap inventories of the noble gases are developed. Interestingly, in general, no distinction is made between the rates of migration of krypton and of xenon through the UO_2 crystal lattice.

Corresponding rates of transport of other fission products are less characterized. Although theoretical treatments of noble gas migration have been extended to include other fission products,¹³ the experimental data base is both sparse and inconsistent. As an example, a number of studies have been conducted of the rates of release of various fission products from lightly irradiated UO_2 .¹⁴⁻¹⁷ These studies employed small, unclad specimens, and generally indicate decidedly different rates of migration for tellurium, iodine, xenon, and cesium, with the rates decreasing in the order presented. On the other hand, direct measurements¹⁸⁻²⁰ of the gap inventories of iodine, xenon, and cesium in commercial irradiated fuel rods indicate that the rates of transport of these fission products are essentially identical. Similarly, measurements²¹⁻²³ of the releases of iodine, krypton, and cesium from commercial irradiated fuel rods likewise indicate identical rates of release beginning at about $1400^\circ C$; at this temperature, transport through the crystal lattice is expected to be the rate-determining process.

There appears to be little doubt that fission product iodine, once released from the UO_2 matrix, becomes combined chemically. Thermodynamics studies²⁴⁻²⁶ indicate that the most likely chemical form is CsI , particularly since the fission process results in about a ten-fold excess of cesium relative to iodine.⁷ However, the possible formation of tellurium iodide,³ uranium iodide,³ and zirconium iodides²⁷ has also been proposed.

Davies et al.^{27,28} reported results of an in-pile experiment in which a test fuel element was at all times maintained well above the sublimation

temperature of elemental iodine. Analysis of the material found deposited on the cladding at the conclusion of the test indicated redistribution of the iodine within the fuel rod toward the cooler region, but almost its total absence in a gas plenum region atop the fuel column. In addition, the redistribution of cesium coincided remarkably with the pattern observed for iodine. These data suggest not only the formation of CsI within the fuel rod, but moreover that the compound is stable in the high radiation (and neutron) fields under which the experiment had been conducted. (Cubicciotti and Davies²⁹ describe experimental results and a possible mechanism for the decomposition of crystalline CsI in a gamma radiation field, but noted no elemental iodine production in the presence of excess cesium. Tests with ZrI_4 , in contrast, yielded no indications of radiation-induced decomposition.)

Measurements^{30,31} of iodine release from commercial, irradiated fuel rods at temperatures up to 1200°C in steam-helium environments indicate the release to be at least an order of magnitude less than the corresponding release of the noble gases. At these temperatures, only the gap inventories are involved and, as stated earlier, the gap inventories (as fractions of total inventory) of krypton and iodine were found to be identical.^{18,19} Moreover, these gap inventory determinations were made by purging the interconnected voids with helium while increasing the fuel rod temperature to 1200°C. The material that was purged from the voids was transported through a gold foil-lined quartz tube along which the temperature was gradually decreased to 200°C, then through particle collection and volatile iodine sorption devices. Virtually all of the iodine that was purged from the gap region deposited in the quartz tube at temperatures well above the sublimation temperature of I_2 . Similarly, the measurements²¹⁻²³ of iodine released from irradiated fuel rods into steam-helium-hydrogen environments at temperatures as high as 2000°C indicated iodine behavior that is consistent with the formation of CsI; only extremely small quantities of the iodine released from the fuel rods in these experiments appeared in a form more volatile than CsI.

In contrast with the observations of iodine releases from clad, highly irradiated, commercial fuel, earlier studies³² which employed unclad and lightly irradiated UO_2 indicated that most of the iodine was released as I_2 , even in a steam-hydrogen environment. In these experiments only microgram quantities of iodine were involved, and cesium releases were not determined; observations of cesium release characteristics might have enabled a determination to be made regarding whether or not the results were due to an inadvertent oxidation of the UO_2 during irradiation or testing, or to oxygen impurities in the apparatus. Studies³³ which were conducted with irradiated U_3O_8 powder apparently yielded no indications of cesium release in an inert atmosphere at temperatures to 1100°C, but did indicate the release of an unspecified iodide species. In an oxygen environment, the iodide was readily converted to I_2 .

Studies of iodine releases from molten UO_2 have also been performed but, as pointed out by Parker and Barton,⁷ these data are inapplicable since, under realistic accident conditions, the inventories of iodine and other moderately volatile species will be essentially exhausted prior to melting of the fuel.

In summary, fission product iodine originates predominantly as a chemically uncombined impurity within the UO_2 crystal lattice. A small fraction escapes from the lattice during reactor operation and apparently combines chemically with cesium which similarly originates as a chemical impurity in the UO_2 crystal structure. The CsI formed constitutes the dominant chemical form of iodine in the gap region, but is only a minor constituent of cesium.

In the event of a loss-of-coolant accident, the internal pressures of the fuel elements cause the claddings to rupture, and the gap inventories of iodine, as CsI, and other volatile fission product species are immediately available for release from the fuel elements. Ever increasing temperatures of the fuel cause additional, independent releases of iodine, cesium, and other fission products from the crystal structure and, unless chemical combination occurs at the crystal surfaces, the fission products escape as atoms from the fuel pellets.

Theoretical calculations³⁴⁻³⁶ of the kinetics processes indicate that gas-phase formation of CsI will nonetheless occur very rapidly at this point, provided the thermodynamics for formation are favorable; this is supported by experimental evidence.^{18,19,21-23,30,31} At this stage, the fission product begins its transport toward the breach in the primary system that probably initiated the loss-of-coolant accident, or resulted from it.

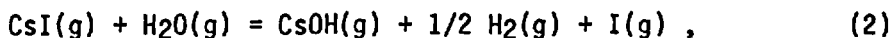
BEHAVIOR OF IODINE IN THE PRIMARY CIRCUIT

As is obvious from the visual examinations that have been made of the core region of the Three Mile Island Unit 2 reactor, the conditions within the core during a severe core damage accident will undergo very large spatial and temporal variations. In addition, the fission products that leave the fuel rods are exposed to new chemical species; these include steam and hydrogen, components of the structural members (iron, chromium, nickel, etc.), and materials employed to control the fission process (silver, indium, cadmium, boron, and carbon).

In a "dry" environment, in which H_2O liquid is not present, the chemical form of fission product iodine is determined by the extent of the decomposition of CsI:



and



and by subsequent reactions of the iodine.

During the reflood phase of the accident, on the other hand, when the severely damaged core is once again submerged in the water coolant, reactions between dissolved iodine species and water radiolysis products can be important. However, whether these reactions lead to significant releases of iodine into the atmosphere depends strongly on the further course of the accident. (If reflood signals the termination of the accident, additional releases of iodine will probably be insignificant.) The reactions that occur in the aqueous system within the primary circuit are similar to those within

aqueous systems in the reactor containment, and are discussed in the next section.

The core and the primary circuit of a LWR are chemically reducing to iodine, hence except for those regions at which the temperatures prohibit compound formation or unless chemical kinetics are determinant, fission product iodine will be transported through the primary circuit, or be deposited on its surfaces, as an iodide. Whether or not it is CsI, however, depends upon the availability of the cesium. For example, the thermodynamics calculations which were performed for the Reactor Safety Study²⁴ indicated CsI to be the predominant iodine species in the gap regions of intact fuel rods. These results were nonetheless discounted because of the neglect of the possible formation of cesium uranate compounds. (The point that cesium release from the gap region was subsequently estimated in the Reactor Safety Study to be about 30 times greater than the corresponding value for iodine apparently was not considered to be contradictory.)

If Cs(g) and CsOH(g) are continuously depleted by the formation of other cesium compounds, reactions (1) and (2) indicate that CsI would eventually decompose. A number of possible cesium compounds which could indirectly result in CsI decomposition have been proposed; these include silicates,³⁷ borates,^{37,38} and chromates.^{38,39} However, the formation of these compounds under actual reactor accident conditions remains an unresolved issue. Tenacious deposits of cesium along primary circuit surfaces, which would be expected to result from interactions with structural components or impurities (Si, Cr), constituted a negligible contribution to the distribution of cesium at Three Mile Island.⁴⁰ Moreover, a number of tests have been conducted to examine the influence of boron, initially as B₄C, on CsI behavior under expected reactor accident core conditions. These tests indicate that the boron oxides which are formed from the reactions of steam with the B₄C at high temperature in turn react quantitatively with the oxides of the structural materials, and thus have no influence on CsI decomposition.^{41,42} (Under very reducing conditions, the production of borane compounds is observed; these compounds are unreactive to CsI.⁴¹)

In summary, kinetics³⁴ and thermodynamics^{35,43} considerations of the Cs-I-O-H system within the primary circuit indicate that the dominant iodine-containing species will be CsI if the Cs/I ratio is unity or larger, and the temperatures are sufficiently low that CsI remains thermally stable. If the Cs/I ratio is significantly reduced from unity because of the formation of other cesium species, then HI or I becomes predominant (although these species should subsequently react with surface or aerosol materials to form other iodides). Several processes have been proposed as mechanisms to curtail the availability of Cs for reaction with iodine, but studies conducted under prototypic accident conditions (including observations at Three Mile Island) suggest that the proposed processes are unimportant in a practical sense.

Radiolysis of steam by gamma radiation has been shown theoretically to alter the kinetics of reactions within the system Cs-I-O-H somewhat, but CsI remains as the dominant iodine-containing species.³⁴ Radiation-induced decomposition of gaseous CsI directly is stated to be of the same order of magnitude as its thermal decomposition at temperatures of about 700°C;³⁴

calculations involving collisions with fission fragments (within intact fuel rods), which are more likely to cause decomposition based upon momentum considerations alone, also indicate the predominance of CsI.⁴⁴ Thus, although many factors exist which could result in CsI decomposition, CsI nonetheless appears to be the most probable chemical form of iodine that is transported through the primary circuit.

BEHAVIOR OF IODINE IN THE REACTOR CONTAINMENT

Most severe core damage accident sequences are expected to result in releases of large quantities of aerosols from the core.⁴⁵⁻⁴⁷ If the release pathway is not intercepted by water, then the iodide which emerges from the primary circuit, if cesium iodide, will be associated with the behavior of the aerosol. Significant decomposition of the CsI in containment enclosures which contain air is not expected unless high temperatures are again encountered as, for example, in the case of a hydrogen burn, and aerosol components capable of depleting the cesium are present. Tests have been conducted which indicate significant formation of I₂ resulting from hydrogen fires in containments containing aerosols comprised of CsI and Al₂O₃.⁴⁸ In inerted containments, such hydrogen burns are not possible without the eventual introduction of air into the containment.

If the iodide emerges from the primary circuit as HI, some fraction will be associated with the aerosols, and the remainder will be available for interaction with surfaces provided by various structures within the containment and with whatever water is present. Thus, the possible release as HI, as opposed to CsI, does not necessarily result in a higher iodine source term value. Similarly, if I₂ were formed as a result of combustion in the containment it too would distribute in part to aqueous phases that may be present, and in part to structure and aerosol surfaces. Hence, in such "dry" accident sequences, aerosol behavior will determine (to varying degrees) the magnitude of the iodine source term.

At the other extreme, total interception of the release pathway by water could occur, as at Three Mile Island and as it is designed to do in BWRs if the pressure suppression pools are not bypassed. In other accident sequences, only partial interception might occur (the actuation of containment spray systems, for example). In either situation, the iodine source terms become dominated by the behavior of iodine in aqueous systems, and by the behavior of the water itself.

Iodine Aqueous Chemistry

In principle, iodine can exist in an aqueous phase in any oxidation state between -1 and +7, but iodide (I⁻), iodine (I₂), and iodate (IO₃⁻) are generally predominant under LWR accident conditions.⁴⁹ A major determinant of the aqueous iodine species is solution pH. Solutions containing iodide, for example, are insensitive to changes in pH over the range 7 to 14, but may yield elemental iodine at lower pH values. In contrast, solutions containing I₂ at low pH readily undergo hydrolysis reactions to yield less volatile iodine species in solution as the pH is increased.⁴⁹

The iodine partition coefficient, which is defined as the ratio of the concentration of all iodine species in solution to the corresponding

concentration in the gas phase, is a measure of the extent to which iodine can be liberated from iodine-containing solutions. Unfortunately, however, the relatively slow approach to equilibrium between vapor and liquid phase components under a wide range of conditions has only recently been recognized,⁵⁰ and this factor confounds a comparison of earlier measurements of the partition coefficient.⁵¹⁻⁵³ Recent studies by Beahm and Shockley⁵⁰ involved determinations of the iodine partition coefficient as a function of time for solutions initially containing molecular iodine, I_2 . Measurements were conducted over a range of concentration, solution pH, and temperature. The experimental data are in excellent agreement with theoretical calculations⁵⁴ for pH 5 solutions at 25°C. At higher pH values, the experimental data appear to have the same functional dependence as that obtained from the kinetics calculations, but displaced in time. Thus, the data indicate that either the rate constants employed in the theoretical calculations are somewhat in error, or that the description of the kinetics mechanisms is deficient. Additional experimental and theoretical work is warranted in order to resolve the issue.

Under reactor accident conditions in which the aqueous system contains sufficiently large amounts of radioactive material that radiolysis of the water becomes significant, the problem is further complicated by reactions between dissolved iodine species and water radiolysis products. Recent studies by both Beahm^{50,55} and Toth^{56,57} and their co-workers on the effects of radiolysis have resulted in the following observations:

1. In closed systems, gamma irradiation of solutions containing 10^{-4} g-at. iodide/L resulted in significant oxidation to I_2 for solutions of pH 4 or less, but conversion of only 0.5% iodide to molecular iodine at pH 6.
2. Volatile iodine was detected when CsI solutions of pH between 5 and 6 were irradiated while being purged with an inert gas. The pH of these solutions was observed to increase with irradiation and oxidation of the iodide, and this resulted in a concomitant decrease in the conversion rate. Most of the conversion occurred in a relatively short period of time (about 10 minutes).
3. The percent of iodide-to-iodine conversion varied inversely with initial iodide concentration. This appears to violate the law of mass action, and thus requires further study.

These studies demonstrate that water radiolysis products can result in the oxidation of iodide ion if the solutions are maintained at low pH. However, both theoretical treatments⁵⁸ and experiment^{50,55-57} indicate no appreciable formation of volatile iodine species in solutions with pH values in excess of 6.

The effect of temperature is primarily controlled by two processes which act in opposition. Increasing temperature generally enhances the escape of molecular iodine from solution, but it also increases the rates and extents of hydrolysis reactions. Thus, the effects of increasing temperature on a solution containing molecular iodine are a decrease in its concentration and an increase in its volatility. The net effect is pH-dependent, but over the

temperature range 20–100°C, the change in the partition coefficient is less than a factor of ten.⁴⁹

Iodide solutions which are not subject to redox stresses are of course unaffected by temperature. Moreover, flashing of iodide solutions will not alter the oxidation state of the iodide, so that the only mechanism which could result in air-borne iodine species is entrainment.

However, evaporation results in changes in concentration and, while not a significant factor if large bodies of water are concerned (e.g., the pressure-suppression pools of BWRs), it can alter iodine behavior in small pools (and specifically in water droplets).⁵⁹ The evaporation of small volumes of iodide solution has been observed to result in the production of small amounts of volatile iodine,⁵⁵ possibly due to oxidation by air. Solutions containing boric acid yielded volatile iodine upon evaporation in amounts proportional to boric acid concentration;⁵⁵ in addition, the amounts of volatile iodine produced were increased in all cases when the solutions were evaporated in the presence of a high gamma-radiation field.⁵⁵ However, the presence of metallic silver has been shown to quantitatively retard iodine volatilization from these solutions,^{55,57} and it is likely that many other metals (e.g., Cu, Fe, Cr) would similarly hinder iodine volatilization.

Organic Iodides

The existence of organic iodides as volatile iodine species has been recognized since 1960, and early studies^{60,61} defined the problem reasonably accurately. Postma and Zavadski⁶² reviewed the issue as it pertains to LWR accidents and concluded that considerably less than 1% of the iodine fission product inventory would appear as organic iodides. Moreover, the analysis assumed only elemental iodine as the remaining (and dominant) iodine form. Much smaller amounts of organic iodides would be expected if the fission product was present as inorganic iodide, rather than iodine. In such a case, however, the organic iodides would be the dominant gas phase species, not because of their presence in large quantity, but rather because other volatile iodine forms are almost nonexistent.²⁶ A more recent estimate of organic iodide formation indicates that only about 0.03% of the total iodine inventory can be expected to appear as volatile organic iodides in an LWR severe core damage accident,⁴⁵ but the application of this result in a generic sense has been challenged.^{63,64}

The precise mechanisms for organic iodide formation remain to be elucidated,⁶⁵ although it has been demonstrated that organic iodides can be formed in the aqueous phase in iodide solutions if the iodide can be oxidized.^{66,67} Previously, only gas-phase formation of organic iodides was believed to be important.⁶²

Hypoiodous Acid (HOI)

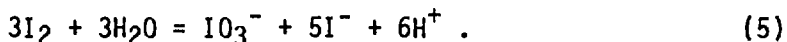
There is general agreement that I₂ hydrolyzes very rapidly in water, and that the reaction can be written in the form²⁶



Furthermore, disproportionation of the hypoiodous acid,



is generally regarded²⁶ as the rate-controlling process for the overall reaction



Thus, the chemical reactivity and volatility of HOI can have an important bearing on iodine behavior in aqueous systems.

For a number of years, however, the very existence of HOI has been questioned. Although the compound had been postulated as a stable species more than 50 years ago,⁶⁸ only recently have electronic spectra of HOI in solution been obtained.^{69,70} Although Kabat⁷¹ claims HOI to be about one-fourth as volatile from solution as I₂, Wren and Sanipelli⁷² were unable to detect HOI in the gas phase unambiguously using mass spectrometry, and Toth et al.⁵⁶ were unsuccessful in establishing its existence in the gas phase using spectrophotometric methods. Thus, although the species HOI is frequently identified as the material that is sorbed by iodophenol,⁷³⁻⁷⁶ its existence in significant concentration in the gas phase is unlikely.

CONCLUDING REMARKS

Significant progress has been made since the issuance of the "Reactor Safety Study,"²⁴ not only in identifying the likely physical and chemical conditions characteristic of severe core damage accidents in LWRs, but also of the probable behavior of fission product iodine nuclides subjected to these conditions. As a consequence, there is adequate justification to re-examine the technical bases for the management of severe core damage accidents.

Nonetheless, a number of issues remain unresolved. The rate of transport of the fission products through the UO₂ lattice continues to be a subject of controversy, although its effect on the determination of the source terms for iodine under severe core damage accident conditions is moot.

Possible decomposition of CsI within the primary system, due indirectly to the formation of chromates, silicates, and/or borates of cesium, is of more significance, since the phenomenon can affect both the mode and timing of iodine escape from the primary circuit. Similarly, the behavior of gas-borne iodides (as an aerosol component or as gaseous HI) in the containment in the event of hydrogen ignition can significantly impact the iodine source terms and requires further elucidation.

The mechanistic descriptions of a number of phenomena involving iodine aqueous chemistry remain incomplete. These include the rates of the hydrolysis reactions and other aqueous phase reactions and the manner in which these reactions affect overall iodine species partition coefficients, the effects of radiolysis on the distribution of iodine chemical species, the role of HOI in iodine aqueous chemistry, and the mechanisms for formation of

organic iodides. In addition, deposition and revaporization of volatile iodine forms on aerosols and other surfaces (paint, metals, concrete) require further elaboration.

Lastly, perhaps the largest area of uncertainty concerns the manner and the extent to which impurities, such as metals and metal ions, influence the iodine source terms. In this case, neither the chemical environment nor the interactions have as yet been adequately described.

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