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STUDIES ON THE EFFECTS OF ORGANIC-PAINTED SURFACES ON pH AND ORGANIC IODIDE FORMATION

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ABSTRACT

The effects of organic-painted structural surfaces on iodine behaviour under reactor accident conditions have been studied. Organic impurities in containment water derived from these painted surfaces could have a significant impact on iodine volatility following an accident. This impact has been evaluated by experimental and modelling studies on (1) the radiolysis of organic compounds in the aqueous phase, (2) thermal and radiolytic formation and decomposition of organic iodides, (3) dissolution of organic solvents from various painted surfaces into the aqueous phase, and (4) hydrolysis and aqueous-gas phase partitioning of organic iodides. The experimental studies consist of intermediate-scale "integrated effects" tests in the Radioiodine Test Facility (RTF) and bench-scale "separate effects" tests. This paper summarizes recent findings from these studies and discusses their significance for managing iodine behaviour in a reactor containment following a severe accident.

1. INTRODUCTION

Organic impurities in the containment sump water could have a significant impact on iodine volatility following an accident. Organic compounds dissolved in the sump water will undergo radiolytic decomposition to form organic acids and eventually CO₂, lowering the pH of the sump water. Since iodine volatility in containment following an accident will depend strongly on the pH of the sump water, the control of the sump water pH at a high value is, considered to be one of the most practical and promising methods of controlling iodine behaviour. Organic impurities in the aqueous phase will also form organic radicals which can react with iodine species to form organic iodides. In contrast to molecular iodine (I₂), organic iodides in the gas phase are more difficult to remove by engineered systems, such as spray or filters, and are considered to be more of a safety issue. From the perspective of severe accident management therefore, the effect of organic impurities on aqueous pH and organic iodide formation are of great interest.

To identify the sources of organic impurities in the sump water and to quantify their effects on iodine volatility, pH and organic iodide formation, we have performed extensive experimental and modelling studies. A comprehensive review of these studies has been published elsewhere (Wren, 1999-1). This paper summarizes recent findings from these studies and discusses their significance for managing post-accident iodine behaviour in a reactor containment.

2. IODINE CHEMICAL AND TRANSPORT BEHAVIOUR WITHIN CONTAINMENT

2.1 Homogeneous Aqueous Phase Reactions of Iodine

Thermodynamic calculations and various experiments have established that under most accident conditions, the iodine released from fuel into containment would be primarily in its reduced state as cesium iodide. Cesium iodide is highly soluble in water and would readily dissolve in the water originating from the discharged coolant and safety spray systems. Subsequently, in the presence of dissolved oxygen in the water (from the containment atmosphere) and high radiation fields from released fission products, non-volatile Γ dissolved in the containment sump water would react to form volatile iodine species (mainly I_2 and some organic iodides). A fraction of the volatile iodine species formed in the aqueous phase would be transferred to the gas phase to form airborne iodine. Regardless of the accident sequence, or the initial speciation of iodine released from fuel, the net conversion of non-volatile iodine to volatile iodine in the sump water is the major source of airborne iodine.

Iodine chemistry in containment is a dynamic equilibrium involving reactions that lead to the oxidation of non-volatile Γ to volatile I_2 and organic iodides, and reactions which convert these volatile species back to Γ :

| Non-Volatile Iodine \rightarrow Volatile Iodine | (1) |
|---------------------------------------------------|-----|
| Volatile Iodine \rightarrow Non-Volatile Iodine | (2) |

The net production of volatile iodine is determined by the overall rates of Processes (1) and (2). Except for unusual circumstances, not likely to be encountered in containment, iodine will quickly make its way to the aqueous phase during the earliest stages of an accident. Therefore, processes that generate volatile iodine in the aqueous phase will be the major source of iodine in the gas phase and control of iodine concentrations in the gas phase will be dependent upon controlling the production of volatile iodine in the aqueous phase. Athough there are some areas of iodine behaviour where large uncertainties still exist, a relatively clear picture of aqueous phase iodine chemistry has emerged. The current understanding of the chemistry of iodine in the aqueous phase under accident conditions is summarized below.

Aqueous Phase Conversion of Non-Volatile Iodine to Volatile Iodine

In the presence of high radiation field following an accident, non-volatile I^- initially dissolved in the containment sump water will be oxidized by the following reaction sequence to form volatile molecular iodine (I_2) (Wren, 1999-2):

$$I^- + \bullet OH \rightarrow I \bullet + OH^-$$
 (3)

$$\mathbf{I}_{\bullet} + \mathbf{I}_{\bullet} \rightarrow \mathbf{I}_2(\mathbf{aq})^1 \tag{4}$$

¹ Note that the designation (aq) is assigned only to volatile species (e.g., molecular iodine, organic iodide, and organic compounds, see below) to differentiate them from the same species in the gas phase, e.g., $I_2(g)$.

where hydroxyl radical (•OH) is formed by water radiolysis² (Buxton, 1988). Under accident conditions the rate of thermal oxidation of I^- to I_2 , known to be catalyzed by light and impurities in water, is negligible compared to the radiolytic oxidation described above.

Organic iodides may also be formed through the reaction of $I_2(aq)$ and organic impurities present in the sump water. Organic impurities in the presence of radiation undergo the following reaction (Wren 1999-1, Driver, 1999).

$$RH(aq) + \bullet OH \rightarrow R \bullet + H_2O$$
(5)

where RH is the organic compound (impurity) in the aqueous phase. The organic radical (R•) produced from this reaction eventually forms either an organic acid, thereby decreasing the pH of the sump water, or an organic iodide.

•R + O₂(aq)
$$\rightarrow$$
 RO₂• $\rightarrow \rightarrow$ •R', alcohols, aldehydes, acids and CO₂ (6)
•R + I₂(aq) \rightarrow RI(aq) + I• (7)

Reactions (3) to (7) result in the conversion of non-volatile iodine to volatile iodine in the aqueous phase. They are fast free radical reactions with relatively low activation energies (i.e. they are not strongly dependent on temperature). The production rate of the key reactant •OH (and therefore that of volatile iodine species) increases with an increase in the radiation dose rate. Reaction (6) produces acids that can lower the sump water pH (its importance is discussed below) and promote the formation of volatile iodine species.

Aqueous Phase Conversion of Volatile Iodine to Non-Volatile Iodine

Volatile iodine in the aqueous phase, $I_2(aq)$, can follow two chemical paths. It can be oxidized further to non-volatile iodine oxides (IO_x) , or it can be reduced back to non-volatile I⁻. The second of these two is the major path (Wren 1999-1,2) with the key reactions being:

| $I_2(aq) +$ | $H_2O \rightarrow$ | HOI | $+ I^{-} +$ | H^{+} | (8) |
|-------------|----------------------|----------|--------------|------------------|------|
| $I_2(aq) +$ | $O_2^- \rightarrow$ | I_2^- | $+ O_2(aq)$ | | (9) |
| $I_2(aq) +$ | $H_2O_2 \rightarrow$ | $2I^{-}$ | $+ 2H^{+} +$ | $O_2(aq)$ | (10) |

where O_2^- and H_2O_2 are products of water radiolysis (O_2^- from the reaction of e_{aq}^- and dissolved oxygen), and HOI and I_2^- are in equilibrium with I_2 .

Volatile organic iodides, RI(aq), can also be decomposed radiolytically to release iodide and organic radicals, or hydrolyze to form non-volatile I^- and a corresponding alcohol (Wren, 1999-1):

$$RI(aq) + H_2O \rightarrow I^- + H^+ + ROH(aq)$$
(11)

$$RI(aq) + OH^- \rightarrow I^- + ROH(aq)$$
(12)

$$(aq) + OH^{-} \rightarrow I^{-} + ROH(aq)$$
 (12)

 $^{^{2}}$ 4.1 H₂O = 2.6 e_{aq}⁻ + 0.6 •H + 2.7 •OH + 0.7 H₂O₂ + 2.6 H⁺ + 0.45 H₂. Coefficients in this equation are the G-values for primary radiolysis products from γ -radiolysis of water (units of molecules produced per 100 eV absorbed dose).

Reactions (8) to (12) are the key reactions that are involved in the conversion of volatile iodine species to non-volatile iodine in the aqueous phase. Their rates, except for the electron transfer reaction (9), are a strong function of temperature (Burns, 1990) increasing with an increase in temperature. Although increasing temperature also increases the partitioning of volatile iodine species into the gas phase, the strong temperature dependence of the iodine reduction reactions result in iodine volatility decreasing with increasing temperature.

The rates of all of the iodine reduction reactions increase with increasing pH (Burns, 1990, Schwarz, 1986, Ball, 1997-2). The overall pH dependence of iodine reduction is complex, however over a pH range of 5 to 10, it results in the aqueous concentration of volatile³ iodine species increasing by approximately by an order of magnitude with a decrease in pH by one unit. Therefore, maintaining the pH of the reactor sump at a high value following an accident may be one of the practical mitigation methods that can be considered.

2.2. Heterogeneous Surface Reactions of Aqueous Iodine Species

In addition to the homogeneous reactions shown in Reactions (3) - (12), aqueous iodine species can undergo heterogeneous surface reactions. Irreversible chemical adsorption of iodine species on surfaces has the potential to reduce the overall iodine inventory in the aqueous phase, thereby resulting in the reduction of the net volatile iodine production. Although many painted surfaces or clean steel surfaces in contact with water are not very good iodine adsorbers (Wren, 1999-3, Ball 1997-1), inorganic zinc primer coated surfaces in contact with water at high pH (9 - 10) have been shown to retain iodine effectively (Kupferschmidt, 1992). Another metal surface which has a great affinity for iodine is silver. Discussion on iodine behaviour on these surfaces can be found elsewhere and is not presented here.

Direct chemical reaction of aqueous iodine species on surfaces has been invoked as a route for formation of organic iodides (Deane, 1990). There are numerous ways in which substituents on painted surfaces could react with iodine species to form organic iodides. It is difficult however, to formulate any radiolytic or thermal reaction that would cleave organic iodides from a polymer backbone at a rate sufficient to release large quantities of organic iodides. By analogy to polyvinyl chloride, which contains organic chloride substituents, painted surfaces containing organic iodide substituents would be far more likely to release iodine atoms than organic iodides upon exposure to radiation (Dole, 1973). The experiments described by Deane do not present unequivocal evidence that organic iodides observed in the gas phase originated directly from iodine reactions on surfaces in contact with the aqueous phase. Deane's observations could also be attributed to homogeneous reactions between iodine species and organic compounds dissolved in residual water on the surfaces or in pores and channels within the coating.

 $^{^{3}}$ Note that iodine species other than I₂(aq) and RI(aq) are soluble in water, i.e., non-volatile. There is speculation that HOI and I• may contribute to iodine volatility, but their presence in the gas phase over water containing these species has not been observed unambiguously.

2.3 Iodine Transfer between the Gas and Aqueous Phases

Volatile iodine species are continually transported between the aqueous and gas phases, (and to and from surfaces), eventually achieving a state of dynamic equilibrium. The relative concentrations of a species in the aqueous and gas phases at equilibrium, referred to as the partition coefficient, depends on temperature, whereas the speed at which the system reaches equilibrium depends on the gas-aqueous interfacial mass transfer rate and mixing rates within both the aqueous and gas phases. These rates depend on fluid flow conditions and also on temperature.

It is essentially impossible to establish unambiguously the gas-aqueous interfacial mass transfer rate under accident conditions. Nevertheless, under accident conditions in which there is an ample supply of hot water, evaporation and condensation on surfaces will occur, and the gas-aqueous interfacial mass transfer rate can be assumed to be very fast. Under these conditions the equilibrium partition coefficients of the volatile iodine species will be the factors controlling the relative amounts of iodine in the gas phase. These partition coefficients vary considerably from one compound to another (e.g. the partition coefficient at 25° C is 4 for CH₃I, 88 for I₂, 725 for 2-iodophenol (Wren,1999-1)). They also depend strongly on temperature. For significant volatile iodine species the partition coefficient decreases with an increase in temperature (i.e., they become more volatile).

2.4 Iodine Behaviour in Gas Phase

Gaseous iodine species, whether released initially from fuel or formed in the aqueous phase and subsequently transferred into the gas phase, will undergo homogeneous and heterogeneous (surface) reactions during the course of an accident. Among the homogeneous gas phase reactions, the most important are those of I_2 with volatile organic compounds to form organic iodides, and of organic radicals with oxygen to form organic acids. These have the same mechanisms as do the aqueous phase processes, (Reactions (5)-(7)). The reaction of I_2 with ozone and •OH to form nonvolatile solid iodine oxides (Sagert, 1989) also occurs in the gas phase. Finally, organic iodides formed in the gas phase or transferred there from the aqueous phase are subject to radiolytic decomposition. In general, homogeneous reactions of iodine species in the gas phase are not as important as aqueous and surface reactions of I_2 . The gas phase reactions are much slower than their counterpart aqueous phase reactions because the less dense containment atmosphere does not adsorb as much ionizing radiation to produce reactive radicals (including •OH and •R). In addition, the concentrations of iodine species in the aqueous phase are higher than those in the gas phase.

2.5 Heterogeneous Surface Reactions of Gas Phase Iodine Species

The interaction of iodine with painted surfaces in the gas phase have been studied by numerous groups, and the results of these studies are crucial to interpreting and modelling iodine behaviour. One of the most important features regarding iodine deposition is that molecular iodine is readily adsorbed on many surfaces, whereas organic iodides are much less likely to be retained. In RTF experiments (Ball 1997-1, Kupferschmidt, 1992), this adsorption results in the attenuation of observed gaseous I₂ fractions relative to the fractions of organic iodides. It also results in a large portion of the iodine inventory in many experiments being retained on gas phase surfaces.

Deposition studies performed on relatively dry surfaces are of limited applicability to the problem of predicting iodine behaviour during a severe accident. High temperatures and the large amount of hot water present in containment can be expected to result in extensive production of water vapour and condensation on all containment surfaces. The resulting water films, are not in hydraulic contact with the large water inventory in the containment building sump and will be continually removed and replenished (by draining and condensation). Although the iodine content, the organic and inorganic impurity content and the pH of these films will different from that of the sump water, they will still act as an aqueous phase from the perspective of dissolution of organic materials from paints, and as a medium for homogeneous aqueous phase reactions of iodine.

The rate constant for adsorption of molecular iodine in condensing water films, as observed in the PHEBUS RTF⁴ tests is smaller than that observed for iodine adsorption on dry surfaces (Wren, 1999-4). Desorption of iodine from the wet surfaces can be ignored because iodine, once absorbed in a condensing water film, will be quickly hydrolyzed to form non-volatile I^- or transferred from the wall by drainage into the sump water. At this point, there is insufficient information to determine whether the deposition process involves iodine absorption into water aerosol droplets that are carried with the steam to walls by processes such as thermophoresis, or whether gas-phase molecular iodine adsorption occurs directly onto the wet wall surfaces.

Heterogeneous processes on gas phase surfaces have been used to explain organic iodide formation in the gas phase from painted surfaces previously exposed to molecular iodine (I_2) (Deane, 1989, Bennett, 1970). However, as is the case for heterogeneous aqueous phase reactions, the evidence that organic iodide formation occurs on the surface is ambiguous. In the experiments reported by Bennett, the small amounts of organic iodide formed could also be explained by invoking homogeneous gas phase reactions between molecular iodine which was reversibly adsorbed on the surface, and released to react with organic species in the gas phase.

3. EFFECTS OF ORGANIC COMPOUNDS

Organic compounds can influence iodine volatility by changing the pH of aqueous solutions, and by promoting the formation of organic iodides. From previous discussion on iodine behaviour, it can be summarised that the pH change is the most important of these effects, and that it controls the amount of organic iodide formation. Radiolysis of organic materials in water decreases the aqueous pH, thereby increasing the amount of I_2 in the aqueous phase. Organic iodide production is most likely to occur by homogeneous aqueous phase reactions of organic radicals with I_2 because the largest portion of the iodine inventory in an accident is initially in the aqueous phase, and homogeneous aqueous phase reactions are the most efficient way of producing free organic radicals. Therefore, the net rate of production of organic iodides will always be only a fraction of the net rate of production of I_2 , and therefore dependent upon pH. Various intermediate- and bench-scale experimental studies are presented below to support and/or confirm the importance of these effects.

Figure 1 shows pH changes and gas phase iodine concentrations as a function of time observed in intermediate-scale tests performed in organic painted vessels in the Radioiodine Test

 $^{^4}$ vessel wall temperature of 75-80°C and water temperature of 90°C

Facility (RTF).⁵ All three organic painted vessels showed similar results: the pH decreased with time, and an increase in the gas phase iodine concentration closely followed the decrease in the pH.



Figure 1 Log of concentration of iodine in the gas phase, and aqueous pH as a function of time observed from irradiated (1.5 kGy·h⁻¹) solutions of CsI in organic painted vessels.

Both nitric acid production by the radiolysis of air, and hydrochloric acid (HCl) production from chloride substituents in the paint have been ruled out as the cause for these pH changes, the former because large pH changes were not observed in RTF tests performed in the absence of painted surfaces, and the latter because painted surfaces without chlorine substituents have the same effect on aqueous pH. The most likely cause of the pH decrease in painted vessels is the radiolytic oxidation of organic impurities in the aqueous phase to form organic acids and CO_2 , which reduces the pH of the solutions (Reaction 7). This assumption was tested by adding MEK (methyl ethyl ketone), one of the common organic solvents used for paints, into the water phase during an RTF test performed in a zinc-primed vessel. The addition of MEK resulted in significant decreases in pH (from ~ 10 to ~6) and dissolved oxygen concentration, and an increase in the gas phase iodine concentration (Figure 2).



⁵ Tests were performed at 25°C, initial I concentration of ~ 1 x 10⁻⁵ mol·dm⁻³, initial pH of 10, dose rate of ~ 1.5 kGy·h⁻¹. The volume of the gas phase was 315 dm³ and that of the aqueous phase, 25 dm³.

Figure 2 Concentration of iodine in the gas phase, aqueous pH and dissolved oxygen from an irradiated solution of CsI in a zinc-primer coated vessel. The increase in iodine concentration coincides with the addition of MEK to produce a 1×10^{-3} mol·dm⁻³ solution.

3.1 Organic Radiolysis

The decomposition of aqueous organic compounds under radiolytic conditions has been examined extensively by experimental and modelling studies. Studies performed on the radiolytic decomposition of MEK have established that, in aerated aqueous solutions, MEK decomposes into 3-hydroxy-2-butanone and 2,3-butandione which further decompose to acetaldehyde and acetic acid, formaldehyde and formic acids, and eventually to CO_2 (Driver, 1999, Glowa, 1999). The formation of carboxylic acids and CO_2 lowers the pH of the solutions. The decomposition of MEK, formation of the radiolysis products, and the associated pH changes have been successfully modelled using recently developed kinetic models for MEK (Glowa, 1999, Wren, 1999-1). Work on a generic organic decomposition model, which incorporates experimental studies on other common paint solvents such MIBK (methyl isobutyl ketone), xylene and toluene, is on-going, and is therefore not discussed in detail here. Nevertheless it has been established that there is a predictable relationship between the type and quantity of organic compound in aqueous solution, the dose-rate at which it is decomposed, and the final pH of the solution.

The key conclusions from organic radiolysis studies that are relevant to iodine chemistry are that organic impurities will be decomposed to organic acids and CO_2 , lowering the pH of the sump water (Reaction (6)), and that radiolytic decomposition of organic compounds is a very fast process: Approximately 90% of 1×10^{-3} mol·dm⁻³ MEK would decompose in 4 h at a dose rate of 1 kGy·h⁻¹, with a minimum pH being attained within about 1 h. Therefore, the effects of organic impurities must be considered not only because of the potential for them to form organic iodides, but because of their direct impact on net molecular iodine production (see Reactions (3) to (12)).

3.2 Organic Dissolution Studies

There are many potential sources of organic impurities in containment. These include surface coatings (organic paints), cable sheathing (polymers), lubricants (grease and oils), etc. Beahm (1986) has estimated that the radiolysis of many of these sources could produce organic compounds in the gas phase at a rate of $1 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}$. Many of these, being small alkanes would not be water soluble. The most important organic impurities in terms of iodine behaviour are those that have the highest solubility in water because the homogeneous aqueous phase reaction (Reaction (6)) to form organic acids involves the solvated water radiolysis product •OH. Long chain organic molecules (components of oil), and non-polar alkyl-organic compounds (such as methane, ethane, etc.) that may be formed from the pyrolysis of organic polymers, are not very soluble in water, and will not be as likely to produce organic acids as will the more soluble organic compounds like ketones and alcohols.

Studies on the dissolution kinetics of organic solvents from various containment paint surfaces, including vinyl-, polyurethane-, and epoxy-coatings, have established that solvents from these paints will be a large source of organic impurities in the aqueous phase in containment under accident conditions (Wren 1999-1). These studies show that the concentration of an organic solvent in aqueous solution [ORG(aq)] at time t follows first order kinetics, i.e.

$$[ORG(aq)]_t \propto [ORG(ab)]_0 \cdot (1 - exp(-kt))$$
(13)

where aq, and ab represent aqueous, and absorbed phase, respectively, k (s⁻¹) is the dissolution rate constant and $[ORG(ab)]_o$ (mol·dm⁻³) is the maximum concentration of solvent in the paint polymer phase at the start of dissolution available to be released into water.

The dissolution kinetics of many common solvents found in paint applications (e.g. toluene, xylene, MIBK and MEK), from polyurethane, vinyl and epoxy paints followed the same mechanism, with approximately the same dissolution rate constant k. This rate constant was found to be independent of the age of the paint (although $[ORG(ab)]_0$ was a function of paint age), pH and radiation exposure, but dependent upon temperature, with an activation energy ranging between 80 and 100 kJ·mol⁻¹ for the three paint types studied. (Wren,1999-1). These studies also showed that the effect of radiation on the <u>rate</u> of dissolution of the organic compounds from painted surfaces was negligible, although radiation rapidly decomposed the organic compounds once they had been released into the aqueous phase.

The concentration of organics available to be released into the aqueous phase in dissolution studies $[ORG(ab)]_0$, was found to decrease with the age of the coating, implying the organic content in the coating decreases because of evaporative losses. Even after several years, however, there are significant quantities of organic solvents which are available to be released by dissolution. For example, studies on Ripolin epoxy paint have shown that for an aqueous surface area to volume ratio of 0.13 cm⁻¹, as much as 5 x 10⁻⁵ mol·dm⁻³ MIBK was released from paint aged for four years. Numerous other organic solvents, such as xylene, toluene and acetone were also detected.

3.3 Rates of Decomposition vs. Dissolution of Organic Compounds

Decomposition studies of MEK have established that 90% of a 1 x 10⁻³ mol·dm⁻³ solution of MEK would decompose in 4 hours when irradiated at 1 kGy·h⁻¹, with the minimum pH value being reached within the first hour (Driver, 1999). Consequently, the pH changes observed in Figure 1 are slower than expected if the radiolytic decomposition of organic impurities is rate determining (e.g. for the fastest pH decrease, a minimum is reached only after 4 h), implying that another process is controlling the rate of the pH change. Dissolution studies described in the previous discussion have established that the rate of dissolution of these organic solvents from containment paints at room temperature is slow relative to the rate at which these solvents undergo radiolytic decomposition.

| organic solvent in the paint matrix | \rightarrow organic impurities in water: | slow | (14) |
|-------------------------------------|--------------------------------------------|------|------|
| organic impurities in water | \rightarrow acids and CO ₂ : | fast | (15) |

A number of examples are available to illustrate Equations (14) and (15). In Figure 2 for example, an immediate decrease in pH and dissolved oxygen concentration (accompanying the decomposition of MEK) was observed when MEK was intentionally added to an irradiated

solution of CsI to give a concentration of 1×10^{-3} mol·dm⁻³. Recovery of the dissolved oxygen concentration, which implies that radiolytic degradation to acids and CO₂ is essentially complete, requires only about 20 h. In contrast, dissolution of MIBK from vinyl paint to reach concentrations of 1×10^{-3} mol·dm⁻³ in the same water volume required almost 100 h (Figure 3). The relative rates of dissolution vs. decomposition of organic solvents has also been demonstrated in numerous intermediate-scale studies where, for a given paint surface, observed concentrations of paint solvents such as toluene and xylene were orders of magnitude higher in tests performed in the absence of radiation than in the presence of radiation. The much higher concentrations observed in the absence of radiation imply that radiation rapidly decomposes these solvents in the aqueous phase (Wren, 1999-1).



Figure 3 Dissolution of MIBK observed in an RTF test performed in a vinyl painted vessel in the absence of radiation. The sharp increase in MIBK concentration coincides with an intentional addition of the ketone.

The relative rates of radiolysis and dissolution dictate that the dissolution rate will control the rate at which organic compounds decompose, and acid is formed in the aqueous phase. The rate constant for dissolution of solvents from organic paints appears to be independent of solvent or paint type, and the final pH of solution is controlled by the amount of solvent in the paint. These findings greatly simplify development of models to predict the effects of organic compounds on iodine volatility. Because iodine volatility is mainly due to I_2 , it will be controlled primarily by the time-dependent aqueous phase pH evolution, which will in turn be controlled by solvent dissolution kinetics, it is not necessary to construct detailed models for the decomposition of organic compounds in order to predict iodine behaviour. An assessment of the effects of organic compounds on aqueous pH and iodine volatility, requires only an estimate of the amount and type of solvent in the paint.

3.4 Organic Iodide Formation

Discussions in Section 2 have suggested that aqueous phase homogeneous processes will be of primary significance in determining the rate of organic iodide formation under accident conditions. As a result, the findings of the dissolution and radiolysis studies discussed in Sections 3.1 to 3.3 also have implications for organic iodine behaviour. The fact that dissolution from paints results in concentrations of organic compounds which are sufficient to alter the pH of the aqueous phase via Reaction (6), implies that there will be a variety organic radicals in solution, all of which will also be available to react with molecular iodine (I_2) (Reaction (7)). Furthermore, if organic iodides are formed primarily from homogeneous aqueous reaction of I_2 with organic radicals, their rate of formation will be very dependent upon the concentration of I_2 in the aqueous phase, and therefore also sensitive to pH changes induced by organic radiolysis.

Confirmation that, in the presence of painted surfaces, organic iodide formation is primarily by aqueous phase homogeneous processes (Reaction (7)) has been obtained from several RTF experiments. In experiments with epoxy, polyurethane and vinyl painted vessels, it was observed that the temporal behaviour of organic iodides in the gas phase and aqueous phases were closely related to the behaviour of the aqueous pH, implying the participation of I_2 in the primary formation process (I_2 concentrations would be pH dependent (Reaction (9)-(12)). The quantities of organic iodides formed were much too large to be accounted for by homogeneous gas phase processes involving I₂, therefore the experiments demonstrate that organic iodide formation is occurring primarily in the aqueous phase. Furthermore, in all of these experiments, a large portion of the organic iodides formed from the paint impurities in the aqueous phase are much less volatile than CH₃I. Based on a partition coefficient of 3 for CH₃I at room temperature, if CH₃I were the predominant organic iodide in the aqueous phase, the gas phase concentration, would be expected to be only three times less than the aqueous phase. In most experiments, the concentration of organic iodides in the gas phase was an order of magnitude lower than that observed in the aqueous phase indicating that in the presence of organic compounds derived from containment paints, formation of many organic iodides which are less volatile than I₂ (e.g. highly soluble iodoketones, alcohols, phenols, and acids) compensate for the effects of forming a few organic iodides which are more volatile than I₂.

Because it would be extremely difficult to identify all of the organic iodides which could form, and to assign partition coefficients to each of them, developing an organic iodide model for predictions of iodine volatility will probably have to rely on obtaining an estimate for an overall partition coefficient for organic iodides. Detailed studies on organic iodide formation from several solvents found in paints will provide data on the distribution of organic iodides likely to be found. From this data, a weighted average for the partition coefficient for organic iodides can be obtained.

3.5 An Integrated Test on Dissolution vs. Radiolysis

From analysis of the dissolution, radiolysis and intermediate-scale studies described in the previous sections, a number of hypotheses have been formulated. These are:

- 1) Organic impurities which will have the greatest effect on iodine volatility are those which can change the aqueous pH, and promote organic iodide formation, i.e. water soluble organic compounds. A significant source of these impurities will be containment paints from which organic compounds can be leached.
- Radiolysis of organic materials to form organic radicals is a faster process than dissolution of organic compounds from containment paints. Consequently the latter process will be the rate determining step in formation of organic acids and organic iodides.

3) Many organic iodides that are more soluble, and less volatile than I_2 will be formed as a result of radiolysis of iodide solutions in contact with containment paints.

These hypothesis have been tested in an RTF experiment designed to examine the effect of rate of dissolution of containment paint solvents on an irradiated solution of CsI. The test was performed in a stainless steel vessel at a dose-rate of about 0.7 kGy-h⁻¹. Dissolution of the solvent from a painted surface was simulated by adding the solvent slowly (via syringe pump) to the aqueous phase in the RTF main vessel. In the first 24 hours of the experiment, the pH was controlled at 10, and there was no introduction of organics. Then, pH control was removed and MIBK was added at a rate similar to its rate of dissolution from vinyl paint at 25°C. After several days, the organic addition was stopped and the pH was controlled at pH 8 for 24 hours. Finally, pH control was removed, and a second addition of MIBK was initiated at a rate 5 times faster than the first. Selected results from the experiment are shown in Figures 4 to 6.



Figure 4 Iodine speciation measurements and pH in an irradiated solution (0.7 kGyh⁻¹) of CsI in a stainless steel vessel. Iodine volatility and pH changes are associated with the addition of solutions of MIBK.

Figure 4 clearly shows that the concentration vs. time profiles of organic iodides in the aqueous phase and in the gas phase are closely related to each other, and to the aqueous pH, indicating that homogeneous aqueous phase processes are responsible for the production of both. Furthermore, the aqueous phase concentrations are two orders of magnitude greater than the gas phase concentrations confirming that the overall partition coefficient for organic iodides is much greater than that of CH_3I .

Figure 5 shows the measured dissolved oxygen concentration in the aqueous phase, as compared with the concentration expected for air saturated water. The lower oxygen concentration during MIBK addition arises as a result of oxygen consumption by organic radicals, and as one would expect, when MIBK addition is faster, there are more organic radicals formed, and more oxygen consumed. The fact that the oxygen concentration reaches a steady-state has important implications regarding the reactions of organic compounds in the aqueous phase:





Figure 5 Dissolved oxygen concentration resulting from addition of MIBK into an irradiated solution (0.7 kGyh⁻¹) of CsI in a stainless steel

A steady-state concentration of oxygen in the aqueous phase implies that the concentration of organic radicals (\cdot R) in the aqueous phase is relatively constant, or at steady-state. The fact that [\cdot R] is at steady-state is supported by the organic iodide concentration in Figure 4, which remains constant during addition of MIBK. A steady-state concentration of \cdot R requires in turn that the concentration of the precursor (RH) is also at steady-state. In short, the steady-state concentration achieved by the dissolved oxygen confirms that introduction of organic compounds (RH) is the rate-determining step for the formation of organic radicals, and therefore for subsequent reactions of the radical with O₂ to produce organic acid, and with I₂ to produce organic iodides.

Figure 6 presents the most convincing data regarding the influence of "dissolution rate" on pH changes. The addition of MIBK, beginning at 50 h in the experiment resulted in formation of acid at a rate of about 6 x 10^{-10} mol·dm⁻³·h⁻¹. Increasing the rate of addition of MIBK by a factor of five resulted in a five-fold increase in the rate of acid production.



Figure 6 Aqueous [H⁺] concentrations resulting from addition of MIBK into to an irradiated solution of CsI

The observation that the organic compounds (RH) and organic radicals (\cdot R) attain steady state concentrations in irradiated solutions in contact with containment paints greatly simplifies modelling both pH changes and organic iodide formation. As mentioned previously, since dissolution is the rate determining step for acid and organic iodide it is not necessary to model radiolytic decomposition of organic compounds in detail in order to accurately predict the rates of these processes. Both of these phenomena will be solely dependent upon the quantities, and types of organic material present in the paint, the temperature, and the dose-rate (because I₂ and \cdot OH concentration will be dependent upon dose-rate). A semi-empirical model, to predict the phenomena of pH change and organic iodide formation can be easily constructed utilizing steadystate approximations for [RH] and [\cdot R]. A model developed using this approach is near completion.

3.6 Mitigation Strategies

Based on experimental observations⁶, we have concluded that the main driver for changing the pH of the sump water during the course of a severe accident (after the effects of chemical additives contained in all water sources have been considered) will be the radiolytic degradation of organic impurities in the sump water. Aqueous pH dictates the net rate of formation of molecular iodine (I_2) and organic iodides in the aqueous phase, therefore pH control is the most effective way to minimize the production of volatile iodine species.

Experiments have also shown that, under radiolytic conditions, the pH of the sump will be directly related to the amount of the dissolved organic impurities. Consequently, reliable information on the inventory of soluble organic material in containment paints is expected to be important in determining the amount of buffering agent needed to control the pH of the sump water following an accident.

4. CONCLUSIONS

Studies on the influence of the chemistry of painted surfaces on iodine volatility under postulated reactor accident conditions have shown that:

- 1) One of the major sources of organic impurities found in containment water will be the organic compounds dissolved from various surface paints.
- 2) The main impact of organic compounds on iodine behaviour will be through aqueousphase reactions of these organic compounds to reduce solution pH, and promote higher steady-state concentrations of I₂.

⁶ Under RTF conditions (gas/aqueous volume ratios of ≈ 10 , dose-rate of 2 kGy•h⁻¹, and aqueous surface/volume ratios of 20 m⁻¹), the theoretical rate of production of nitric acid, (a G-value of 3.19 was reported by Sagert), could induce pH changes at a rate comparable to the changes produced by dissolution and radiolysis of organic solvents from containment paints. Nevertheless, in several intermediate-scale studies performed at similar dose-rates in the absence of organic materials, the pH changes expected due to formation of nitric acid in the gas phase were not observed.

- 3) The rates of the processes described in 2 are likely to be controlled by the dissolution kinetics of the organic compounds from the surface coatings.
- 4) aqueous phase reactions will be primarily responsible for formation of organic iodides, but organic iodide formation does not necessarily lead to increased iodine volatility.

The identification of aqueous phase reactions as being of primary importance in determining iodine volatility, and of solvent dissolution as being a rate-controlling process for the pH evolution, have implications for both modelling and mitigating iodine volatility. Iodine volatility will be controlled primarily by pH changes in the aqueous phase, which in turn will be dependent upon solvent dissolution kinetics. Control of the pH in the aqueous phase will therefore be essential for mitigation, and predicting pH changes will be required for modelling iodine behaviour. Ensuring pH control will rely upon knowledge of the quantities and types of soluble organic material in containment paints. This information will also be required for predicting iodine volatility, since the net rate of production of I_2 and organic iodides will depend upon the rate of dissolution of these materials into the aqueous phase.

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REFERENCES

- Ball, J.M., Kupferschmidt, W.C.H., and Wren, J.C., 1997-1. Phase 2 Radioiodine Test Facility experimental program, Proc. of the Fourth CSNI/OECD Workshop on the Chemistry of Iodine in Reactor Safety, Wurenlingen, Switzerland. 63.
- Ball, J.M., Hnatiw, J.B., and Sims, H., 1997-2. The reduction of I₂ by H₂O₂ in aqueous solution, Proc. of the Fourth CSNI/OECD Workshop on the Chemistry of Iodine in Reactor Safety, Wurenlingen, Switzerland. 507
- Beahm, E. C., Wang, Y., Wisebey, S. J., 1987. Organic iodide formation during severe accidents in light water nuclear reactors. *Nuclear Technology*, **78**, 34.
- Bennett, R.L., Slusher, R. and Adams, R.E., Reactions of iodine vapor with organic paint coatings. Oak Ridge National Laboratory Report, ORNL-TM-2760, 1970.
- Burns, W.G., Matsuda, M, and Sims, H.E., 1990. Temperature dependence of the equilibrium constant for iodine hydrolysis at temperatures between 25 and 120°C. *Journal of the Chemical Society, Faraday Transactions*, **86**, 1443.
- Buxton, G.V., Greenstock, C.L., Helman, W.P. and Ross, A.B., 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/·O-) in aqueous solution. *Journal of Physical and Chemical Reference Data*, **17**, 513.
- Deane, A.M., and Davies, C.P., The formation of volatile species at surfaces from iodide ions, AEA-TRS-2000, 1990.
- Deane, A.M., and Davies, C.P., Organic iodine formation rates on surfaces in pressurised water reactor buildings, AERE-R-13526, 1989.
- Dole, M., 1973. Oxidation of irradiated polymers. In: *The Radiation Chemistry of Macromolecules*, Academic Press, 263.Driver, P.A., Glowa, G.A., and Wren, J.C., 1999.

Steady-state γ -radiolysis of aqueous 2-butanone (MEK) and its potential impact on iodine volatility under containment accident conditions. *Radiation Physics and Chemistry*, to appear.

- Glowa, G.A., Driver, P.A. and Wren, J.C., 1999. Irradiation of MEK part II: A detailed kinetic model for the degradation of 2-butanone in aerated aqueous solutions under steady-state γ-radiolysis conditions. *Radiation Physics and Chemistry*, to appear.
- Kupferschmidt, W.C.H., Buttazoni, J.B., Melnyk, A.J., Portman, R. and Sanipelli, G.G., 1992. The effects of zinc primer surfaces on iodine behaviour within containment, Proc. of the Fourth CSNI/OECD Workshop on the Chemistry of Iodine in Reactor Safety, September, Tokaimura, Japan, 195.
- Sagert, N.H., Radiolysis of iodine in moist air: a computer study. 1989. Proc. of the Second CSNI Workshop on Iodine Chemistry in Reactor Safety. Toronto, ON., Atomic Energy of Canada Limited Report, AECL-9923/CSNI-149, 235, 1989.
- Schwarz, H.A. and Bielski, B.H.J., 1986. Reactions of HO₂ and O_2^- with iodine and bromine and the I_2^- and I atom reduction potentials. *Journal of Physical Chemistry*, **90**, 1145.
- Wren, J.C., Ball J.M., and Glowa, G.A., 1999-1. The interaction of iodine with organic material in containment. *Nuclear Technology*, **125**, 337-362.
- Wren, J.C., Ball, J.M., and Glowa, G.A., 1999-2. The chemistry of iodine in containment. submitted to *Nuclear Technology*.
- Wren, J.C., Glowa, G. A., Merrit, J., 1999-3. Corrosion of stainless steel by gaseous I₂. Journal of Nuclear Materials, 265, 161-177.
- Wren, J.C., Glowa, G.A., and Ball, J. M., 1999-4. A simplified model for containment iodine chemistry and transport model description and validation using stainless steel RTF test results, Proc., OECD Workshop on Iodine Aspects of Severe Accident Management Vantaa, Finland, May 18-20, 1999.