



RESULTS FROM PHASE 2 OF THE RADIOIODINE TEST FACILITY EXPERIMENTAL PROGRAM

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Abstract

A series of intermediate-scale experiments were conducted in the Radioiodine Test Facility (RTF) in a vinyl-painted, zinc-primer coated, carbon steel vessel in order to assess the effects of vinyl surfaces on iodine volatility in both the presence and absence of radiation. This test series, Phase 2 of a larger, comprehensive program assessing a variety of containment surfaces, also examined the effects of organic (i.e., methyl ethyl ketone) and inorganic (i.e., hydrazine) additives, pH, and venting on the aqueous chemistry and volatility of solutions initially containing cesium iodide. These tests have clearly demonstrated that organics are released to the aqueous phase from the vinyl coating and that, under radiation conditions, these organics can have a significant effect on the formation of volatile iodine species. In particular, the RTF results suggest that radiolytic decomposition of the released organics results in dramatic reductions in pH and dissolved oxygen concentration, which in turn are responsible for increased formation of molecular iodine and organic iodides. When the pH was maintained at 10 (Test 3), much lower iodine volatility was observed; low iodine volatility was also observed in the absence of radiation. This test series also demonstrated that vinyl surfaces, particularly those in contact with the gas phase, were a sink for iodine.

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1. INTRODUCTION

The Radioiodine Test Facility (RTF) at Whiteshell Laboratories was designed for the purpose of conducting integrated tests to provide information on both the chemical and physical behaviour of iodine in containment under accident conditions. The objectives of the program are to confirm that safety and licensing assumptions regarding iodine releases are conservative, to identify unforeseen phenomena that may not be evident from separate-effects tests, to provide data for model development, and to test proposed accident management strategies.

The Phase 1 RTF experimental program [1], which examined iodine volatility in a zinc-primed, carbon steel vessel, demonstrated that kinetic processes play the most important role in determining iodine volatility in accident conditions. Results from this test series identified several factors that significantly influence the speciation and distribution of iodine. These were pH, radiation, the presence of organic and inorganic impurities in the aqueous phase, and the adsorption of iodine on containment surfaces.

The Phase 2 experimental program continued the examination of the effects of containment surfaces on iodine volatility. In this test series, the interior of the RTF's main vessel (see Figure 1) was painted with a vinyl-chloride, vinyl-acetate co-polymer. Test 1 was an "all effects" test, in which iodine volatility was examined at various pH values. The effects of venting the gas phase through TEDA (triethylene-diamine)-impregnated charcoal, and the influence of methyl ethyl ketone (MEK), and hydrazine additives on iodine volatility in the presence of radiation were also studied. Test 2, which was performed in the absence of radiation, examined the relative contribution of thermal processes to iodine volatility under the same conditions. In Test 3, the effect of maintaining a high aqueous pH was demonstrated by performing the entire test at a pH of 10. Finally, because Tests 1 to 3 indicated that substantial amounts of organic material were released to the aqueous phase from vinyl paint, a fourth test was performed in which the vinyl paint was aged 12 months prior to the test; for the earlier tests, the coating was aged for approximately 3 months. This fourth test was to ascertain the role that solvent residues from the paint application played in contributing to the observed organic concentration.

This document provides experimental results of each of the Phase 2 tests, with identification of the major trends observed, and a rationalization of some of the key findings. Conclusions regarding the influence of organic-based coatings on iodine volatility are also discussed.

2. EXPERIMENTAL PROCEDURES

A detailed description of the Radioiodine Test Facility, and of the analytical procedures used in each experiment, is given in References 1 and 2. For these experiments, data such as pH, oxidation-reduction potential and hydrogen concentration were collected automatically by on-line sensors. The concentration of iodine in the gas phase was also measured on-line, using the automated airborne iodine sampler (AAIS) [3], whereas aqueous iodine concentrations were measured on-line by a gamma counter installed in the aqueous sampling loop. During each test, off-line samples were also taken for the analysis of anions, hydrogen peroxide, organic compounds and iodine speciation. Iodine speciation measurements in the gas phase

were performed by passing a gas sample from the gas ventilation loop through a syringe and into a length of teflon tubing containing species-selective adsorbents [4]. Aqueous iodine speciation measurements were performed using a series of solvent extractions, followed by radiochemical analysis of the various separated fractions.

Before each test, the carbon steel vessel (350 dm³) was dry sandblasted. Application of a zinc-primer base (Carboline Zinc 2 Nuclear Grade Grey) followed. Intervinix HB paint was then applied in two stages: first as a wet, thin overcoat, and then after 24 h, as a thicker (125 µm) overcoat. The typical curing period for the paint was approximately 3 months, with the exception of Test 4, in which the coating was aged for 12 months. Coupons painted with the same paint were placed in the main vessel during the test to estimate deposition of iodine on surfaces. These were cylindrical in geometry (5.7 cm² each). Typically, three coupons were suspended in the gas phase, and three were placed on the floor of the vessel.

One day prior to the addition of ¹³¹I-labelled CsI solution, and several days after the installation of the ⁶⁰Co source, the main vessel was rinsed with distilled water several times using the spray header. A 25 dm³ water charge was then added and recirculated through the on-line loops for approximately 18 h. This solution was then discarded and a fresh 25 dm³ water charge was subsequently added. The gas phase was then purged for 2 h with ultra-pure air at 10 dm³·min⁻³ before the addition of the ¹³¹I-labelled CsI solution. Gas and aqueous phase samples were also taken for analysis by gas chromatography and high performance liquid chromatography (HPLC) prior to addition of the tracer solution.

The ¹³¹I-labelled tracer was purchased as NaI in 0.05 mol·dm⁻³ NaOH. A CsI solution of the appropriate concentration was prepared and adjusted to pH 10, and the iodine tracer subsequently added. The solution was then purged with argon (0.003 dm³·min⁻¹) for 18 h, and analyzed for I⁻, I₂, IO₃⁻ and organic iodides. Transfer of the tracer-labelled solution to the main vessel was accomplished by the use of an appropriately sized stainless steel container equipped with swagelok "quick-connectors", which facilitated easy and rapid introduction of the solution to the RTF's main vessel via the aqueous sampling loop.

Additives (i.e., methyl ethyl ketone (MEK) and hydrazine (N₂H₄)) were introduced into the aqueous phase of the main vessel, also via the aqueous sampling loop, using syringes with swagelok connections. The loop was then flushed with distilled water. In Tests 1 and 2, pH was adjusted by manual additions of 0.1 mol·dm⁻³ H₂SO₄ or LiOH. In Tests 3 and 4, pH was controlled using a computer-operated pH control system, which controlled syringe pumps containing H₂SO₄ and LiOH.

The gas ventilation loop of the RTF contains a TEDA (triethylene-diamine)-impregnated charcoal trap, holding approximately 400 g of the charcoal, which can be valved in and out of the loop. Two venting procedures were used during this test series. The first, designated as a charcoal filter test, involved recirculating the gas phase through the gas ventilation loop, thereby maintaining a closed system. The second procedure, designated as a direct vent, was performed by exhausting the gas phase through the charcoal filter while maintaining the pressure within the RTF's main vessel by adding ultra-pure air.

Table 1 gives a brief description of the Phase 2 test matrix and Table 2 outlines the general operating conditions.

Table 1: Phase 2 Experimental Test Matrix

Test	Radiation Source*	pH	additives	venting	desorption stages (latter stage of test)
1	252 TBq ⁶⁰ Co 1.7 kGy·h ⁻¹	initially 10, uncontrolled	MEK, hydrazine	yes	pH controlled first at 8, then at 10
2	none	initially 10, uncontrolled	MEK, hydrazine	yes	pH controlled at 10
3	210 TBq ⁶⁰ Co 1.3 kGy·h ⁻¹	controlled at 10	MEK, hydrazine	yes	pH controlled at 10
4	187 TBq ⁶⁰ Co 1.2 kGy·h ⁻¹	initially 10, uncontrolled	MEK, hydrazine	yes	pH controlled at 10

* The average dose rate in the gas and aqueous phase, designated in Table 1, was determined based on Fricke dosimetry performed in 1989, with adjustments made for source decay over the three-year time span of the Phase 2 experimental program.

Table 2: General Experimental Conditions

PARAMETER	CONDITION
Main Vessel	Vinyl-painted, zinc-primer coated Carbon Steel
Operating Temperature	25°C
Initial Iodine Species	1 x 10 ⁻⁵ mol·dm ⁻³ CsI
Initial pH	10 (controlled or uncontrolled)
Aqueous Recirculation Loop	10 dm ³ ·min ⁻¹
Aqueous Sample Loop	1.0 dm ³ ·min ⁻¹
Gas Recirculation Loop	20 dm ³ ·min ⁻¹
Gas Ventilation Loop	0/10 dm ³ ·min ⁻¹
Aqueous Volume	25 dm ³
Gaseous Volume	315 dm ³
Aqueous Surface Area	5165 cm ²
Gaseous Surface Area	22089 cm ²
Aqueous/Gas Boundary Area	3696 cm ²

3. RESULTS

3.1 The Effect of Organic Impurities

3.1.1 Initial Test Stages

Table 3 summarizes the results from the initial stage of each test. This stage is defined as the period of time before venting, or intentional addition of impurities. Figure 2 shows the major differences observed in the gas phase iodine concentration in each of the four tests.

Table 3: Summary of Results from Initial Test Stages

Test	Maximum $[I_g]$ (mol·dm ⁻³)	Initial pH change (0-50 h)	Initial DO change (ppm) (0-50 h)	Gas Phase Speciation ^a		
				I ₂ (%)	LMWRI (%)	HMWRI (%)
Test 1	3.0 x 10 ⁻⁹	10 - 6.5	8.2 - 4.1	40-50	20-25	6-9
Test 2	3.5 x 10 ⁻¹¹	9.7 - 7.9	8.0 - 8.5	6-25	60-80	10-15
Test 3	2.0 x 10 ⁻¹⁰	10; pH controlled	3.6 - 1.3	6-25	60-90	4-15
Test 4	8.0 x 10 ⁻⁹	10 - 4.6	6.1 - 1.2	60-80	20-40	5-8

^a LMWRI: low molecular weight organic iodides - up to C₃H₇I.

HMWRI: high molecular weight organic iodides - larger than C₃H₇I.

Three important observations can be made regarding the behaviour of iodine during this stage of each test:

1. In the tests performed with radiation, there was a decrease in dissolved oxygen concentration during the first 20 h of the test. The pH also decreased if not controlled. Under these conditions, the gas phase iodine concentrations were 2 orders of magnitude higher than in the absence of radiation.
2. In the tests performed with radiation, iodine volatility was an order of magnitude lower when pH was controlled at 10 than when pH was not controlled [see Figure 2].
3. In the absence of intentionally added organic impurities, a minimum of 25% and a maximum of 95% of the iodine in the gas phase was in the form of organic iodides. Aqueous phase organic iodide concentrations were often orders of magnitude higher than gas phase organic iodide concentrations observed at comparable times (see Figure 3).

3.1.2 Addition of Methyl Ethyl Ketone

Methyl ethyl ketone (MEK), a thinner used in many paint applications, is one of many organic impurities that could be released to the aqueous phase from containment paints and was, therefore, chosen as an additive to assess the effect of organic impurities on iodine volatility. The pH and dissolved oxygen behaviour exhibited in Tests 1 and 4 when MEK was added (to give an initial aqueous phase concentration of $1 \times 10^{-3} \text{ mol-dm}^{-3}$) (Table 4) was similar to that observed in the initial stages of each test. However the increase in gas phase iodine concentration as a result of these changes was more modest than that observed in the initial test stages, because the iodine inventory in the aqueous phase was significantly depleted by this time. The slight increases in the total gas phase iodine concentration were primarily due to an increase in the amount of organic iodides in the gas phase - that is, the fraction of organic iodides in the gas phase increased as a result of MEK addition.

In Test 3, where pH was maintained at 10, addition of MEK also resulted in a decrease in the dissolved oxygen concentration, and the amount of LiOH required to maintain the pH at 10 increased. A small increase in the gas phase iodine concentration was observed, which resulted primarily from an increase in the concentrations of organic iodides. In Test 2, which was performed without radiation, the concentration of organic iodide in the gas phase also increased subsequent to MEK addition. However, organic iodide concentrations increased steadily throughout the test in the absence of perturbations, such as venting, and it is difficult to assess whether MEK addition had any impact on this trend.

Table 4: Effects of Addition of MEK

Test	Change in Gas Phase Iodine Concentration	pH Change	Dissolved Oxygen Change	Change in Gas Phase Organic Iodide Concentration
1	increase	decrease	decrease	increase
2	increase	no change	no change	small increase
3	increase	controlled	decrease	small increase
4	increase	decrease	decrease	increase

3.2 BEHAVIOUR OF IODINE WITH VENTING

Venting of the gas phase was performed for each test to estimate the efficiency of TEDA-impregnated charcoal for removing iodine. In-test and post-test analysis of the adsorption of iodine on the charcoal revealed that 95% and 98% of the volatile iodine that passed through the recirculation loop was adsorbed on the charcoal filters in Tests 1 and 3, respectively. The remainder of the iodine was retained on the recirculation loop. In Test 4, the gas phase was vented by exhausting it through an external charcoal filter and replacing it with ultra-high purity air.

In general, iodine speciation measurements performed on the gas phase indicated that venting decreased the concentration of all of the iodine fractions in the gas phase (I_2 , LMWRI, HMWRI). However the fraction of the gas phase in the form of organic iodides decreased more than the fraction in the form of molecular iodine. This is consistent with I_2 being replenished more rapidly during venting than were organic iodides.

3.3 Behaviour of Iodine with Hydrazine Addition

In the presence of radiation, the addition of hydrazine resulted in a rapid decrease in the dissolved oxygen concentration and a transient increase in the gas phase iodine concentration. The time required for the dissolved oxygen concentration to recover to its steady-state value varied between 10 and 20 h. Addition of hydrazine in the presence of MEK produced similar dissolved oxygen and gas phase iodine concentration transients in Tests 1, 3 and 4. Although hydrazine addition resulted in a slight decrease in the dissolved oxygen concentration in the non-radiation test, no significant change in the gas phase iodine concentration was observed.

3.4 Adsorption of Iodine by Surfaces

Table 5 summarizes the adsorption behaviour exhibited in each of the tests.

Table 5: Summary of Adsorption Behaviour

Test	Maximum $[I_g]$ ($\text{mol}\cdot\text{dm}^{-3}$)	% $[I_g]^a$ lost to surfaces	% on vinyl paint ^a	% on other surfaces	Loading on Aqueous Coupons ($\text{nmol}\cdot\text{cm}^{-2}$)	Loading on Gas Coupons ($\text{nmol}\cdot\text{cm}^{-2}$)
Test 1	3.0×10^{-9}	78	47	31	>10	>100
Test 2	3.5×10^{-11}	15	15	-	32	5
Test 3	2.0×10^{-10}	5	4	1	14	4
Test 4	8.0×10^{-9}	74	42	32	27	344

^a estimated by assuming that wall deposition was the same as that observed on coupons placed in the gas and aqueous phases.

In Tests 1 and 4, over 70% of the iodine initially added to the aqueous phase was adsorbed by surfaces. Analysis of the coupons, which were suspended in the main vessel during both these tests, indicated that less than half of the iodine losses were the result of adsorption of iodine on the vinyl paint; however it is likely that coupon loading underestimated the extent of vinyl surface deposition. For example, γ -counting of the main vessel after Phase 2 - Test 4 indicated that deposition on the gas phase surfaces near the liquid-gas interface was approximately 10 times higher than that on the upper surface of the vessel (where the gas coupons were placed). Although analysis of sections of the gas recirculation and gas sampling loops revealed that there was considerable deposition on these surfaces during both

tests as well, it is difficult to estimate the total amount of iodine adsorbed on these surfaces.

In Test 2, which had no radiation source, surface adsorption of iodine was much less than in the radiation tests. Surface loading in Test 3, a radiation test performed using pH control, was comparably low, despite the fact that total gas phase iodine concentrations were higher than in Test 2. Gas phase loadings observed in Test 3 compare well with those observed in bench-scale static deposition studies performed under radiation conditions at pH 9.4 [2].

Table 6 summarizes the iodine desorption behaviour observed in Tests 1, 2 and 4 when aqueous pH was increased during the latter stages of each test.

Table 6: Summary of Desorption Behaviour

Test	pH	Gas Phase Iodine Concentration (nmol·dm ⁻³)	Aqueous Iodine Concentration (μmol·dm ⁻³)	Log Partition Coefficient [I _{aq}]/[I _g]	Desorbed Iodine (%)
	6.0 → 7.5 7.5 → 10	0.7 → 0.6 0.6 → 0.4	0.7 → 0.9 0.9 → 2.0	3.0 → 3.2 3.2 → 3.7	~ 13
2	7.3 → 10	0.7 → 0.3	no significant change	5.3 → 5.7	-
3	10	0.2	9.0	4.6	-
4	6 → 8 8 → 10	2.0 → 1.0 1.0 → 0.4	1.2 → 1.4 1.4 → 2.6	2.7 → 3.1 3.1 → 3.8	~ 14

In general, increasing the aqueous phase pH resulted in a decrease in gas phase iodine concentration and an increase in aqueous phase iodine concentrations. However in both Tests 1 and 4, increasing the aqueous pH to 10 did not reduce the gas phase iodine concentration to the same level as that observed in Test 3, where the pH was maintained at 10.

4. RATIONALIZATION OF KEY FINDINGS

The key findings of this test series can be rationalized as follows. In the presence of radiation and the absence of pH control, the radiolysis of water and of dissolved organic compounds released from the vinyl paint resulted in four conditions that led to the formation of volatile iodine species. These are

1. The rapid oxidation of I⁻ to I₂ by ·OH;
2. Reduction in pH, which favoured formation of volatile I₂;
3. Reduction in the concentration of dissolved oxygen, which depleted the steady-state concentration of O₂⁻, an effective reductant for I₂; and

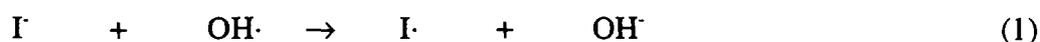
4. Formation of organic radical intermediates in solution, which reacted with I_2 to form volatile organic iodides.

Conditions 1 to 3 contributed most significantly to the increase in iodine volatility under radiation conditions. This was demonstrated by the low iodine volatility exhibited in Test 2, which was performed in the absence of radiation, as well as in Test 3, where maintaining a high pH resulted in low iodine volatility, even when the concentration of organic compounds in the aqueous phase was significant.

4.1 Effect of Radiation

Radiolytic Formation of I_2

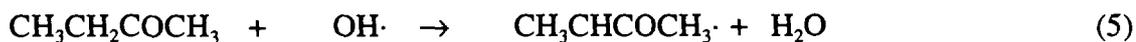
The oxidation of iodide by $OH\cdot$ is the predominant mechanism for formation of I_2 in aqueous solution under radiation conditions.



The reaction is fast, with the rate-determining step (1) having a rate constant of $9.6 \times 10^9 \text{ mol dm}^{-3}\cdot\text{s}^{-1}$ [5]. This is several orders of magnitude higher than the rate constants for thermal oxidation of iodine by peroxide or oxygen [6]. I_2 is volatile, as are many organic iodides that are formed in the aqueous phase primarily by reaction of I_2 , or its hydrolysis products, with organic compounds and radicals [10]. Therefore, the overall effect of radiation is that it increases the rate of formation of volatile iodine species. This is demonstrated in the RTF tests by the much higher gas phase iodine concentrations that were attained in the radiation tests, as compared to the non-radiation test (Test 2).

Radiolysis of Organic Impurities

Studies performed on the radiolysis of MEK have established that in the presence of oxygen, decomposition occurs by reaction of an organic radical with oxygen [6].



Reactions (5) to (7) account for the decrease in aqueous pH and in dissolved oxygen concentrations observed in each radiation test after MEK addition. Because the steady-state concentration of I_2 is expected to be higher at low pH and dissolved oxygen concentration

(Section 4.2) and because an increased concentration of I_2 , organics and organic radicals favour formation of organic iodides, these changes ultimately lead to higher gas phase iodine concentrations.

There are several possible sources of water-soluble organic impurities in the vinyl paint formulation which was used to coat the interior of the main vessel. These include methyl isobutyl ketone (MIBK), xylene, ethyl 3-ethoxy propionate, and tricresyl phosphate, which are used as thinners and radical inhibitors, and methyl ethyl ketone and toluene, which comprise the solvent system for paint application [7]. High-performance liquid chromatography and gas chromatography analyses for Tests 1 to 4 confirmed that a variety of organic impurities were present in the aqueous phase in each test. It can be inferred that these organic impurities originated from dissolution of solvents from within the paint, and that they did not result solely from solvent residues on the paint surface. This inference can be made because the vessel surface was washed repeatedly prior to the initiation of each test, and because organic concentrations and acid production were significantly higher in Test 4 as compared to Test 1, despite the fact that the vessel surface was aged for 12 months prior to test initiation.

The radiolytic decomposition of some of these impurities would likewise explain the pH changes and low dissolved oxygen concentrations observed in Tests 1 and 4 prior to the intentional addition of organic impurities into the aqueous phase. For example, an intermediate-scale study performed in a vinyl-painted, concrete-lined vessel has shown that MIBK, MEK, xylene and toluene are released from paint surfaces in the absence of radiation (Figure 4). Bench-scale and intermediate-scale experiments have also ascertained that, under radiation conditions, MIBK decomposes rapidly to acetone, which undergoes further decomposition to acetaldehyde and formaldehyde, acetic acid, and finally CO_2 [8,9].

Organic Iodide Formation

Formation of substantial quantities of organic iodides were observed in each test. The rate of formation of these species was dependent primarily on the rate of reaction of I_2/HOI in the aqueous phase with organic compounds and radicals, and was therefore enhanced by radiation and by low pH values. However, long-term steady-state gas phase organic iodide concentrations observed in Test 2 exceeded those observed in radiation conditions at high pH. This was largely because there was no radiolytic pathway for decomposition of organic iodides under these conditions, and thermal decomposition of organics is comparatively slow at room temperature. Thus, formation of organic iodides by thermal processes alone can have an impact on long-term gas phase iodine concentrations.

Organic iodide concentrations measured in the aqueous phase were often an order of magnitude higher than those measured in the gas phase [Figure 3]. This, along with speciation analysis, confirms that organic iodides, which are more complex and have a higher partition coefficient than CH_3I (partition coefficient at room temperature is 3), are formed in substantial quantities. A variety of possible mechanisms, including iodination of ketones and phenols, which are formed by radiolysis of toluene and xylene, may account for the presence of these less volatile species.

4.2 Effect of pH

The effect of pH on iodine volatility is demonstrated by the significant difference in gas phase iodine concentrations observed when pH was controlled at 10 (Test 3) and when pH was uncontrolled (Tests 1 and 4). This effect has been demonstrated in other intermediate-scale studies [1,11] and may be rationalized by considering the pH dependence of a number of processes.

The equilibrium concentration of I_2 in irradiated solutions is extremely sensitive to pH. This dependency results from the oxidation-reduction reactions which I_2 and I^- undergo with water and its radiolysis products. I_2 may be reduced to I^- by reaction with O_2^- [12], with HO_2^- [13], or with OH^- .



O_2^- has a pK_a of 4.75; therefore, Reaction 8 is pH dependent. Moreover, the general overall rate law [13] for the reduction represented by Reactions 9 and 10 is

$$-d[I_2]/dt = k[H_2O_2][I^-]/(k'[H^+]^2 + k''[H^+]) \quad (12)$$

The $1/[H^+]^2$ dependence at low pH values makes the overall reduction of iodine by this process very dependent upon pH, and is the most important factor in determining the pH dependence of iodine volatility.

The formation and hydrolysis of organic iodides are also pH-dependent processes. Since organic iodides are generally produced by reaction of organic compounds with I_2 or its hydrolysis products, their formation rate is dependent upon the steady-state concentration of I_2 , and, hence, pH. Organic iodide hydrolysis, to form alcohols, and halide elimination, to form alkenes, are also pH-dependent reactions [12].



The dramatic difference between iodine volatility observed in Test 3 (pH = 10) and Tests 1 and 4 results from a combination of all of these processes.

4.3 Effect of Hydrazine Addition

Hydrazine is strongly reducing in nature and, as such, might be expected to decrease iodine volatility by reducing I_2 to I^- , or by decreasing the rate of thermal oxidation of I^- to I_2 by

depleting dissolved oxygen. In the presence of radiation, however, the addition of hydrazine was generally observed to increase iodine volatility modestly. This behaviour may be attributed in part to a decrease in the steady-state concentration of O_2^- (formed by reaction of e^- with O_2), caused by the consumption of dissolved oxygen by hydrazine. Since O_2^- is an effective reductant for I_2 , the depletion of this species results in higher steady-state concentrations of I_2 . Hydrazine is decomposed rapidly by radiation; therefore, the increase in iodine volatility associated with its addition is a transient phenomenon.

4.4 Adsorption of Iodine by Surfaces

A comparison of the maximum surface loading achieved in each of the four tests shows that gas phase adsorption was higher in Test 4 than in Test 1 and that adsorption in Tests 1 and 4 was significantly greater than that for Tests 2 and 3. This trend is easily rationalized by comparing the observed gas phase iodine concentrations and speciation. Although the chemical nature of iodine species irreversibly retained on painted surfaces has not been established, it is reasonable to assume that, in analogy to solution chemistry, the interaction of iodine species with organic compounds on gas phase surfaces is primarily by reaction with I_2 . Consequently, the amount of iodine irreversibly retained on gas phase surfaces should be a function of the gas phase molecular iodine concentration, which was highest in Tests 1 and 4. The higher aqueous phase surface loading observed in Test 2 is somewhat surprising. However, it may imply that in the presence of radiation, there is appreciable radiolytic destruction of organic iodides on aqueous phase surfaces.

There is considerable evidence that a portion of the iodine on surfaces in contact with the gas phase was reversibly adsorbed. In Tests 1 and 4, increasing the aqueous pH during the latter stages of the test resulted in an increase in the aqueous phase iodine concentration that was considerably greater than could be accounted for by the apparent loss of iodine from the gas phase. Although significant reductions in the gas phase iodine concentrations accompanied pH increases, the gas phase iodine concentrations observed after pH adjustments were still higher than those observed in Test 3 where pH was maintained. This behaviour implies that, as volatile iodine species were repartitioned from the gas phase as a result of their hydrolysis and reduction in the aqueous phase, iodine reversibly adsorbed on the gas phase surfaces (presumably as I_2) was desorbed to maintain the equilibrium between the gas phase surfaces and the gas phase. The net effect of increasing aqueous pH was, therefore, to transfer iodine from gas phase surfaces to the aqueous phase, with the total gas phase iodine concentrations remaining relatively unaffected. This interpretation is substantiated by the changes in iodine speciation observed while venting, which increased the fraction of molecular iodine in the gas phase with respect to the organic iodide fraction. In Test 2, where there was minimal gas phase surface adsorption, repartitioning of iodine from the gas to aqueous phase was only partially offset by desorption of iodine from gas phase surfaces. As a result, increasing the aqueous phase pH had a significant impact on the gas phase iodine concentration.

4.5 Evaluation of Mass Transfer

Mass transfer coefficients for Tests 1 to 3 have been previously evaluated by use of a simple analytical model to fit data obtained from post-vent recovery of the gas phase iodine

concentration [16]. A reasonable fit of the experimental results obtained from the venting in Test 1 was obtained by using a gas phase mass transfer coefficient (k_g) of $5 \times 10^{-3} \text{ dm}\cdot\text{s}^{-1}$. This is similar to the value obtained from analysis of experimental results from other RTF tests, and is, therefore, viewed as the best available estimate.

An estimate of the lower limit for the gas phase mass transfer coefficient and the deposition velocity for adsorption of iodine in the gas phase may also be obtained from the rate of loss of iodine from the gas and aqueous phase for Tests 1 and Test 4. An examination of data from these tests show that iodine behaviour during the period prior to initiation of venting was very similar. In both cases, the gas phase iodine concentration increased rapidly to a maximum, and then decreased slowly until the direct vent was initiated. The aqueous iodine concentration showed an initial rapid decrease, followed by a slower decrease after the maximum gas phase concentration was attained. The calculated first-order rate constant for loss of iodine from the aqueous phase during this period was similar in both tests ($1 \times 10^{-5} \text{ s}^{-1}$ in Test 1 and $8.6 \times 10^{-6} \text{ s}^{-1}$ in Test 4).

From the mass transfer relationships (16,17) and the calculated first-order rate of total loss of iodine from the aqueous phase and of I_2 from the gas phase, a value for k_{ads} , the rate constant for adsorption of iodine on the gas phase surfaces, can be obtained. This derivation assumes that the overall mass transfer rate (k_t) was fast compared with adsorption in the gas phase and that the loss of iodine in the aqueous phase is represented only by loss of I_2 in the gas phase. The assumption is reasonable because iodine behaviour in the gas and aqueous phases was apparently "coupled" during this time, and because losses of iodine to the aqueous phase surfaces were minimal when compared to those in contact with the gas phase.

From the following relationships

$$\frac{dC_1}{dt} = k_t \frac{A_1}{V_1} (HC_g - C_1) = k_{obs} [C_1] \quad (14)$$

$$\frac{dC_g}{dt} = k_t \frac{A_1}{V_g} (C_1 - HC_g) - k_{ads} [C_g] = k_{obs} [C_g] \quad (15)$$

where

- C_g = concentration of molecular iodine in the gas phase
- C_1 = concentration of molecular iodine in the liquid phase
- k_t = overall mass transfer coefficient
- H = partition coefficient of I_2 (= 80 at 25°C)
- A_1 = area of the liquid gas interface = 37 dm^2
- V_1 = volume of liquid phase = 25 dm^3

$$\begin{aligned}
 V_g &= \text{volume of gas phase} = 315 \text{ dm}^3 \\
 k_{\text{obs}} &= 1 \times 10^{-5} \text{ s}^{-1} \text{ rate constant for loss of [I] in the aqueous phase} \\
 k'_{\text{obs}} &= 7 \times 10^{-6} \text{ s}^{-1} \text{ rate constant for loss of [I] in the gas phase}
 \end{aligned}$$

k_{ads} is calculated to be

$$k_{\text{ads}} = 6 \times 10^{-5} \text{ s}^{-1}.$$

This can be converted to a deposition velocity by the relationship

$$k_{\text{ads}} = k_{\text{dep}} \frac{A_{\text{gw}}}{V_g} \quad (16)$$

where A_{gw} is the area of the gas phase surfaces (220 dm²)

which gives

$$k_{\text{dep}} = 9.3 \times 10^{-5} \text{ dm}\cdot\text{s}^{-1}.$$

This is within the range of initial deposition velocities reported by Rosenberg for vinyl painted surfaces [15].

An estimate of the minimum value for the overall mass transfer coefficient, k_t , may also be obtained, and by using the value of $1.5 \times 10^{-4} \text{ dm}\cdot\text{s}^{-1}$ for the liquid phase mass transfer coefficient k_l , which was previously determined [16] from analysis of O₂ mass transfer, a value of k_g , the gas phase mass transfer coefficient, may be determined. Using these values and the equations

$$k_{\text{obs}} = k_t \frac{A_l}{V_l} \quad (17)$$

$$\frac{1}{k_t} = \frac{H}{k_g} + \frac{1}{k_l} \quad (18)$$

k_t and k_g are calculated to be $8 \times 10^{-6} \text{ dm}\cdot\text{s}^{-1}$ and $7 \times 10^{-4} \text{ dm}\cdot\text{s}^{-1}$, respectively.

The limiting value for k_t , calculated from the loss of iodine from the aqueous phase as a result of deposition on gas phase surfaces, is considerably less than the overall mass transfer

rate calculated from other RTF data ($\approx 1.5 \times 10^{-4} \text{ dm}\cdot\text{s}^{-1}$) [17]. This indicates that the rate of adsorption onto surfaces in contact with the gas phase is not limited by the overall mass transfer rate. It should also be noted that the value for gas phase mass transfer derived here is greater than the calculated deposition velocity for Tests 1 and 4. This implies that deposition is not limited by the rate of gas phase mass transfer, and is, therefore, presumably limited by the rate of chemical reaction on the surface.

5. SUMMARY

The results of this test series confirmed a number of observations made in the Phase 1 experimental program regarding the effects of radiation, organic impurities and pH on iodine volatility. It has also provided additional chemical information regarding organic-based containment paints, and physical information regarding surface deposition, and gas phase mass transfer. The key findings of this program may be summarized as follows:

1. Iodine volatility in the presence of radiation is strongly dependent upon aqueous pH.
2. Vinyl surfaces exposed to iodine in the gas phase act as effective "sinks" for iodine.
3. In the presence of radiation, organics originating from the vinyl surfaces undergo oxidative degradation to form organic acids. This radiolytic process has an adverse effect on iodine volatility.
4. Iodine is strongly retained on vinyl surfaces, and the deposition rate appears to be slower than the rate of mass transfer in the gas phase.

Although most of these findings are easily rationalized, the effect of pH on iodine volatility is the only phenomenon that is mechanistically understood. Adsorption of iodine on painted surfaces has been studied to some extent, but the rate of adsorption as a function of gas phase iodine concentrations has not been examined and desorption behaviour for most paints is not well established. The mechanism and rate of release of solvents from polymers is also not known. The radiolytic degradation products of methyl isobutyl ketone, ethanol and other common paint solvents would be expected to be similar to those observed for MEK. Therefore, detailed mechanistic studies of the radiolysis of MEK may provide enough information to model their radiolytic behaviour. The rate of their release into the aqueous phase, however, can only be obtained by examining the containment paints themselves. As such, studies of the release of solvents from containment surfaces are needed to quantify their influence on iodine volatility.

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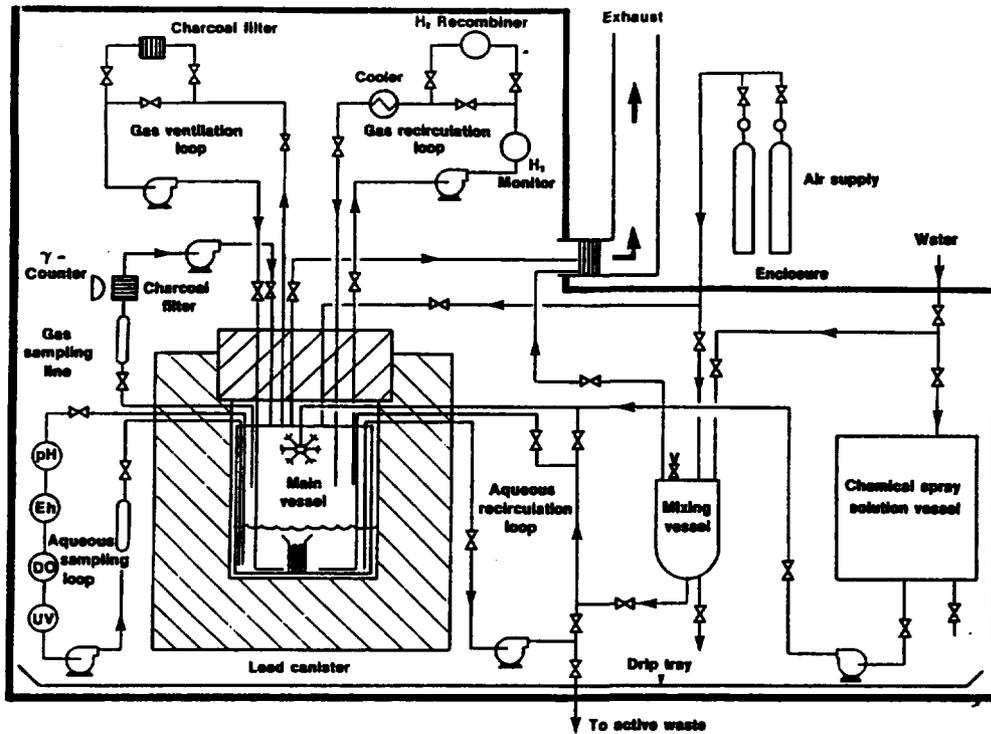


Figure 1. Schematic of Radioiodine Test Facility

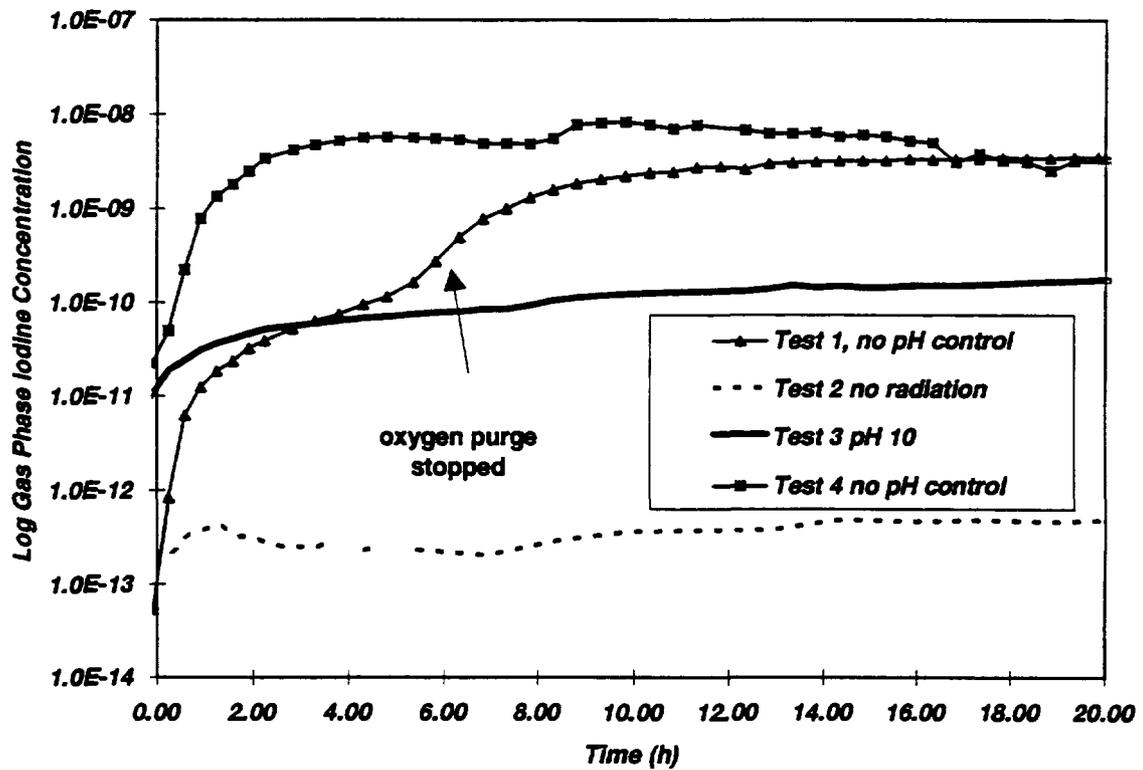


Figure 2. Total gas phase iodine concentrations for Tests 1-4 (initial 20 hours)

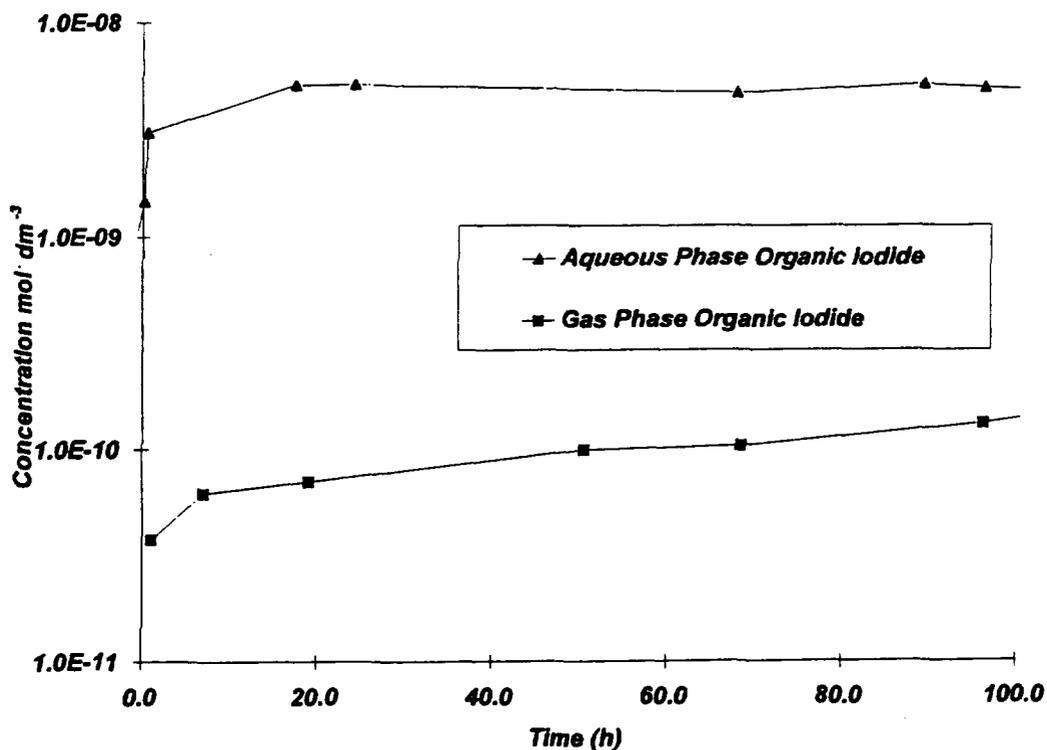


Figure 3. Comparison of gas phase with aqueous phase organic iodide concentrations for Phase 2-Test 3.

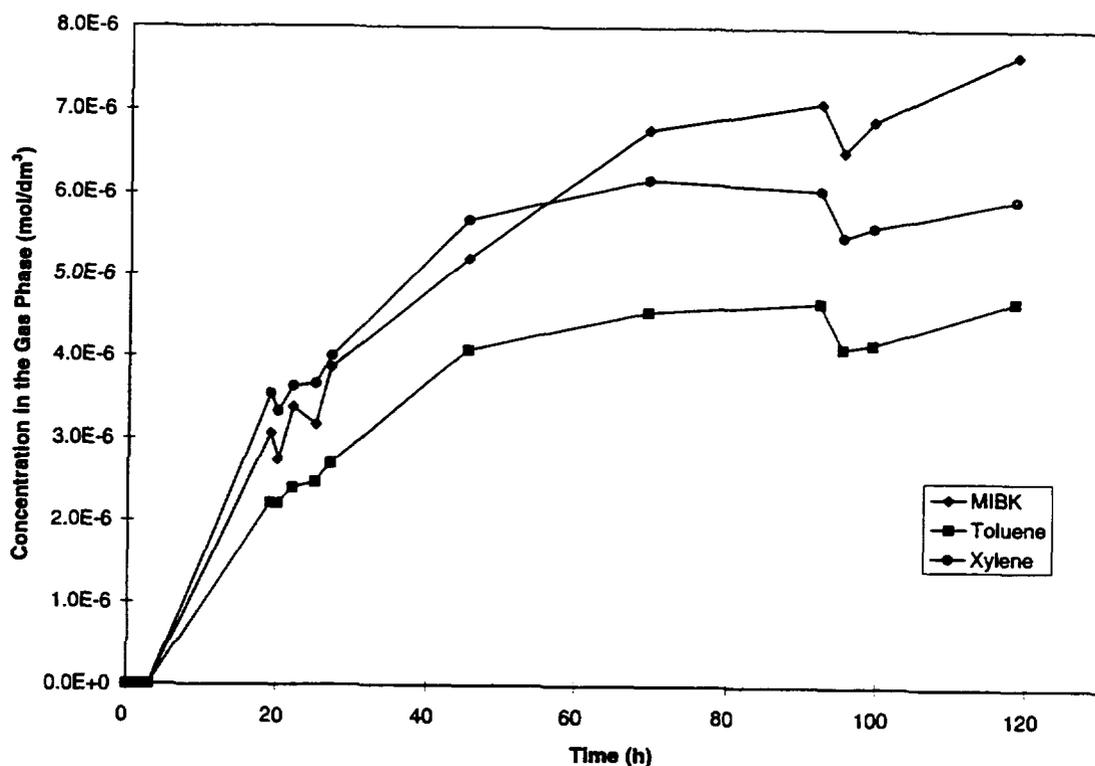


Figure 4. Concentration of organic compounds in the gas phase as a function of time in an intermediate-scale study performed in a vinyl-painted vessel in the absence of radiation