Iodine Behavior in Containment

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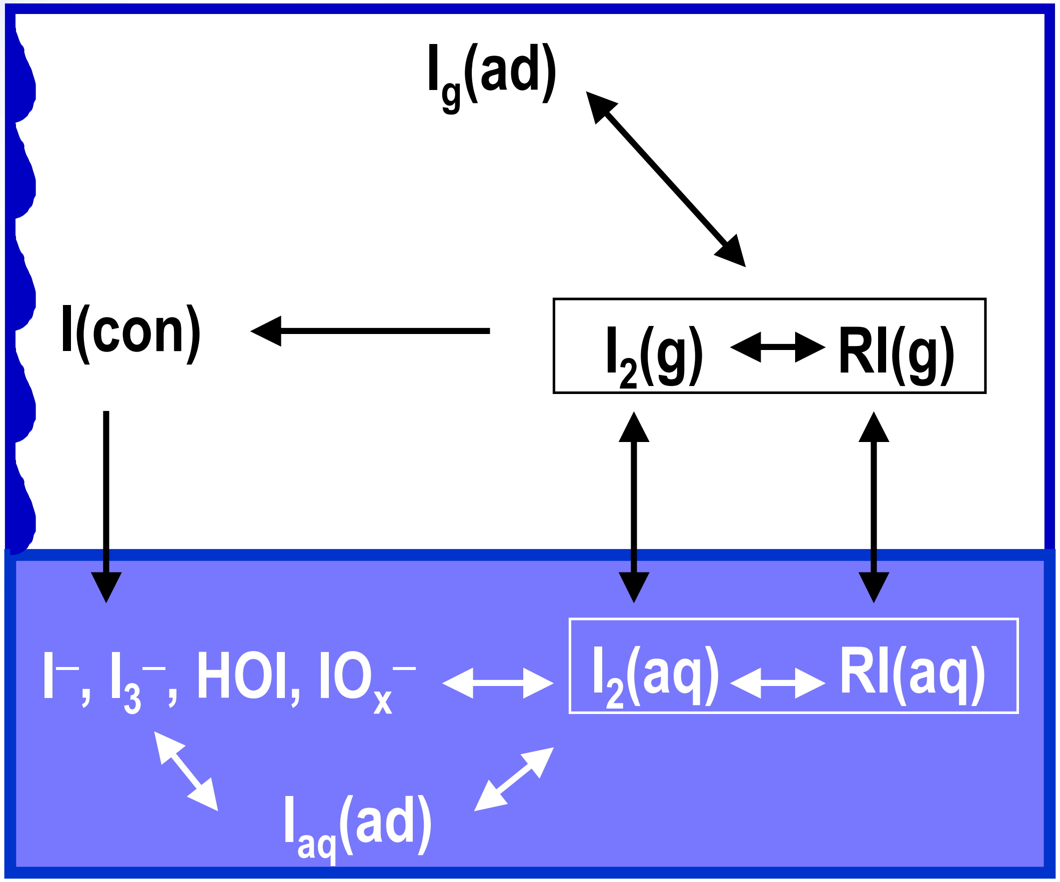
Background

- Iodine is the single most important nuclide with potential for public dose in the event of a severe core damage accident
- AECL recognized the importance very early
  - Mechanistic approach to fully understanding release fraction
    - Not bounding
    - Based on fundamental understanding coupled with validation tests
  - AECL established a program over 20 years ago
- Results
  - Best models in the world
  - Well validated
  - High confidence, Low uncertainty

Iodine Volatility in Containment

- Iodine would be released from fuel into containment mainly as CsI (& HI), which would dissolve as non-volatile iodide upon contact with water.
- However, under the oxidizing and high radiation environment following an accident, non-volatile iodide would react and become volatile and partition into the gas phase.
- The primary concern is the time dependent concentration of gaseous iodine as a result of the radiolytic production in containment following an accident.

Iodine Interconversion and Mass Transport



Accident Conditions

- $D_R < 10$ kGy/h
- $T < 130^oC$
- pH: 11 – 5
- Initial concentration
  $< 10^{-4}$ [I^-] M
- Condensing
- Variety of surfaces

Information Required

- Fraction of iodine in the gas phase as a function of time
  - Rate of interconversion of non-volatile iodine (I^-, I_3^-, etc) to volatile species (I_2 & RI) in water
  - Rate of transport of volatile iodine species between the aqueous and gas phases and surfaces

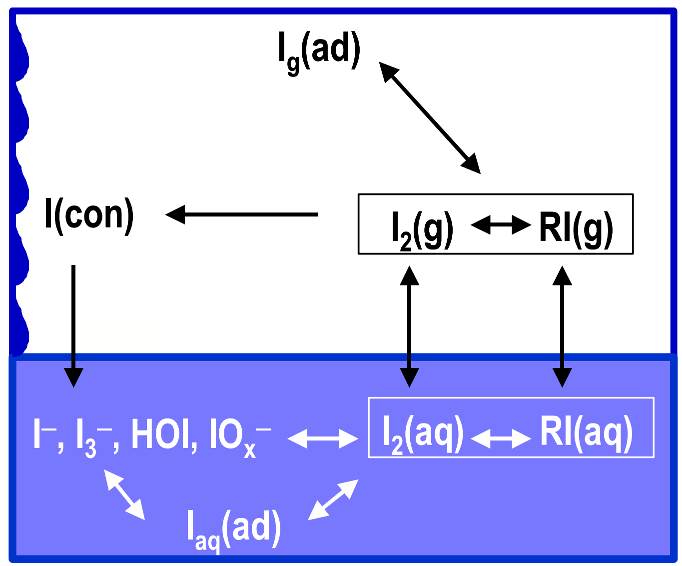
Complexity of the Iodine System

Inter-dependent rxns, having different dependences on conditional parameters

Difficult to separate the effects of individual factors

Difficult to extract a scaling factor

Inter-dependent homogeneous, heterogeneous processes



Continuous radiation

The kinetics of each rxn path needed to model

Iodine in various oxidation states

Large no. of rxns to model

Effects of organic impurities & trace metal ions

Iodine conversion via rxns with water radiolysis products, •OH, •O_2^-, H_2O_2

AECL's Iodine Program Components

- Engineering-scale integrated-effects tests in the Radioiodine Test Facility (RTF)
- Supporting bench-scale tests to separate and quantify individual effects
- Development and validation of containment iodine behavior models, LIRIC & IMOD, for safety analysis
- International collaboration
  - EPRI ACE and ACEX contracts
  - Leading the International Standard Problem (ISP) on iodine code comparison exercises
  - COG-IPSN information exchange

RTF Program

- RTF
  - Miniature containment, which could simulate a wide range of post- accident conditions
  - The most important integrated facility in the world designed to examine the iodine chemistry and transport processes together
- Objectives
  - Evaluate the relative importance of various processes
  - Effects of individual components in an integrated test facility
  - Unforeseen phenomena
- Significant contributions to understanding
  - Revealed the importance of many unexpected phenomena that were not previously observed in large-scale or bench-scale studies

Supporting Bench-Scale R&D Areas

- **Objectives:**
  - To aid in the interpretation of the RTF test results
  - To develop models that would have solid technical basis for their predictable capability

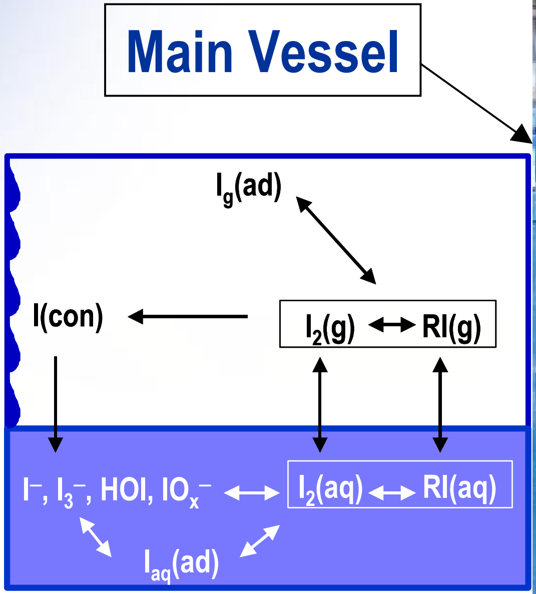
- **Study Components:**
  1. Aqueous Phase Chemistry
     a. Inorganic Iodine Reactions
     b. Steady-State Water Radiolysis
     c. Reactions of Organic Impurities and Organic Iodides
  2. Aq-Gas Phase Partitioning
  3. Iodine – Surface Interaction

Model Development & Validation

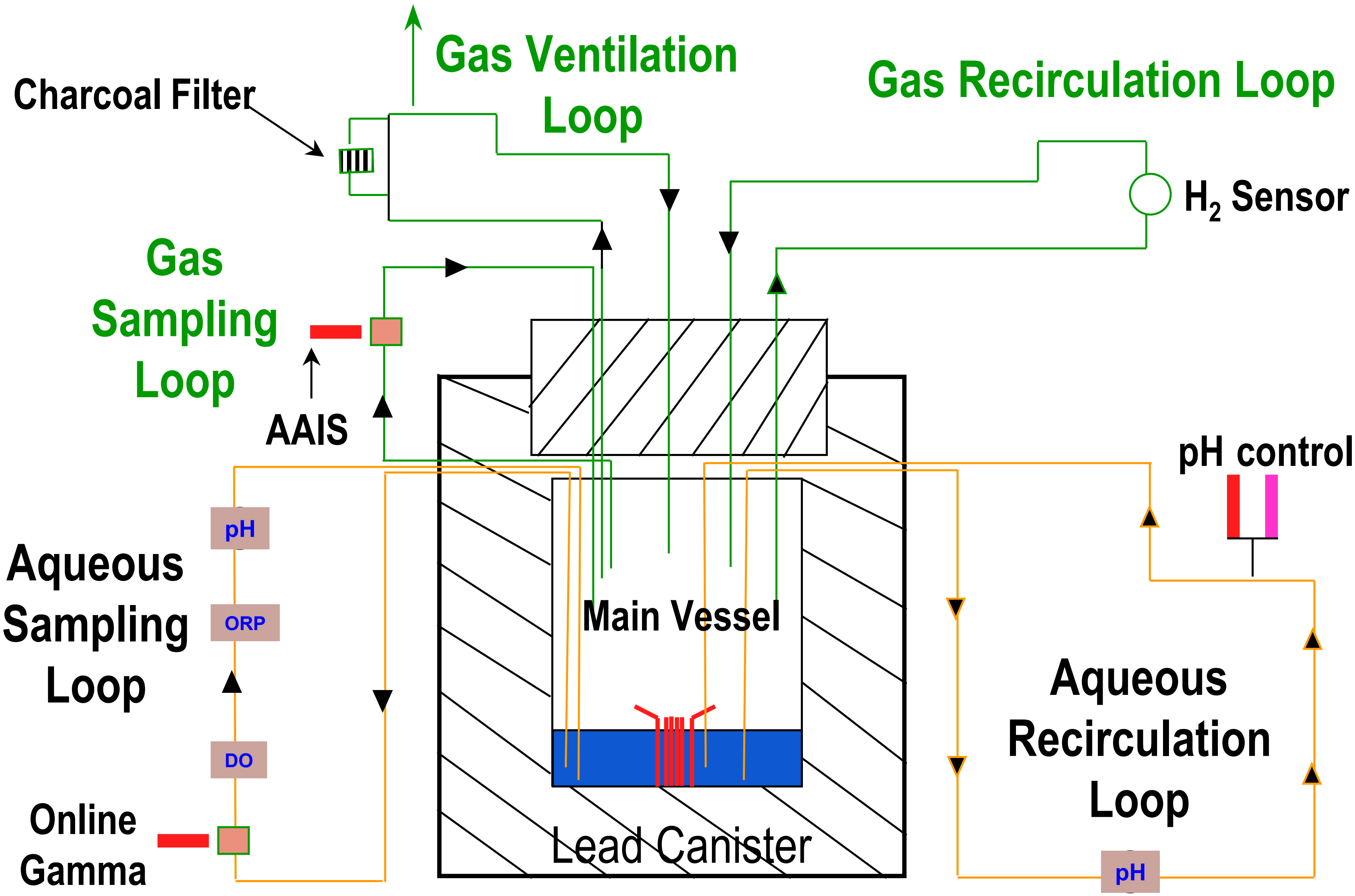
- LIRIC
  - A comprehensive mechanistic model, consisting of about 200 chemical reactions and transport equations
  - Epitome of our current understanding
  - Performs well when tested against bench-scale and RTF tests carried out over a wide range of conditions
- IMOD
  - Constructed based on extensive LIRIC analysis and simulations of various RTF tests
  - A smaller, simpler model, but maintains many of the capabilities of LIRIC
  - Integrated into a larger safety analysis code

RTF Program

Radioiodine Test Facility



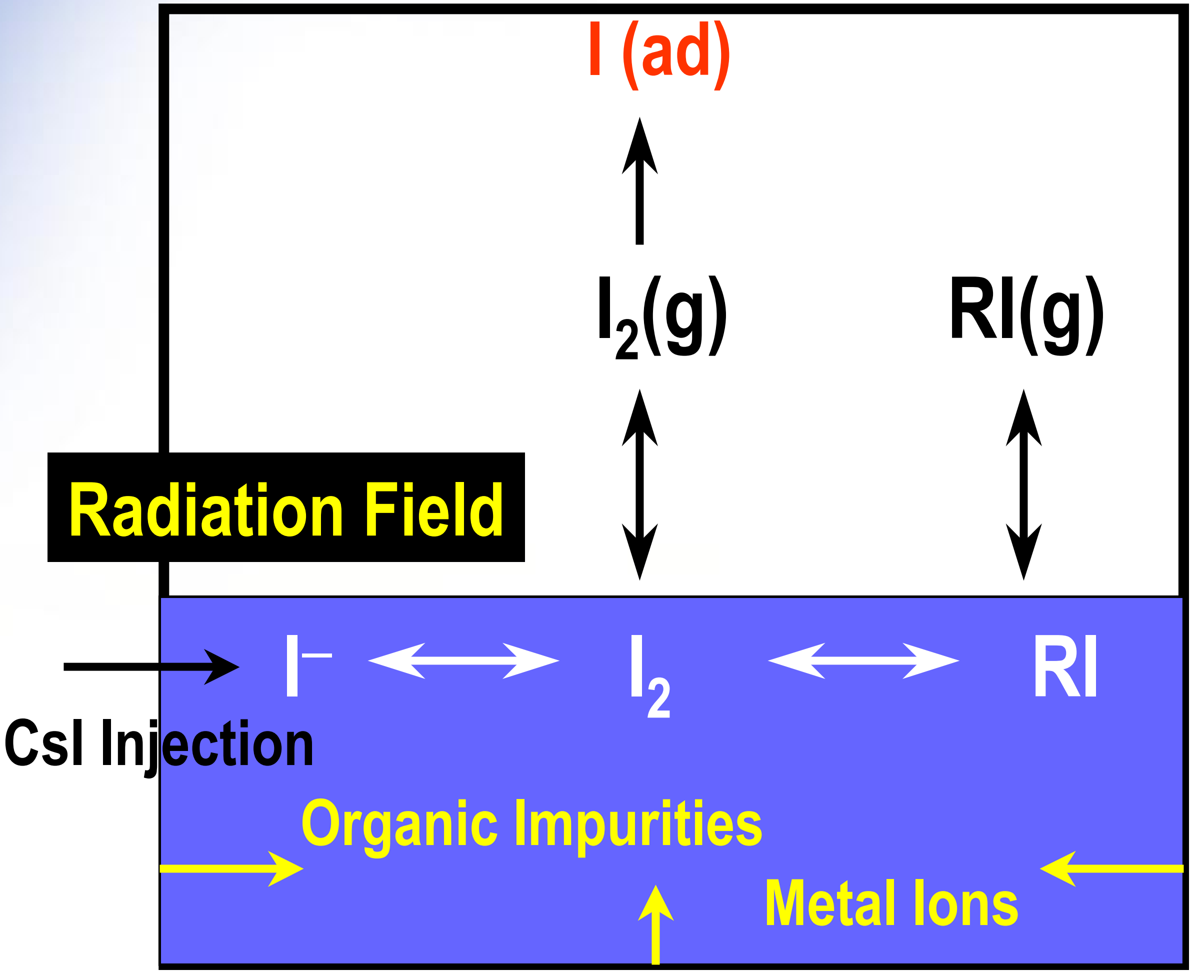
RTF Schematic

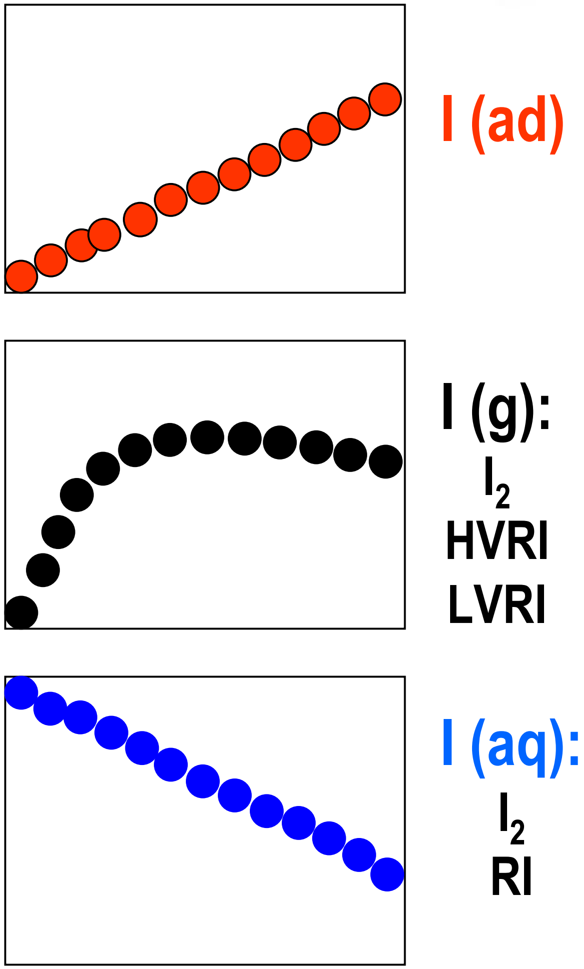


Radioiodine Test Facility

- Main features
  - Well instrumented and controlled
  - A replaceable 340 L vessel
  - Provides many combinations of
    - Reaction media (gas, water, surfaces)
    - Conditions (pH, T, radiation dose, chemical additives)
  - Equipped with on-line sensors and off-line measurements
    - On-line: [I(g)], [I(aq)], pH, DO
    - Off-line: iodine speciation, organic and anions, trace metals

Typical RTF Test





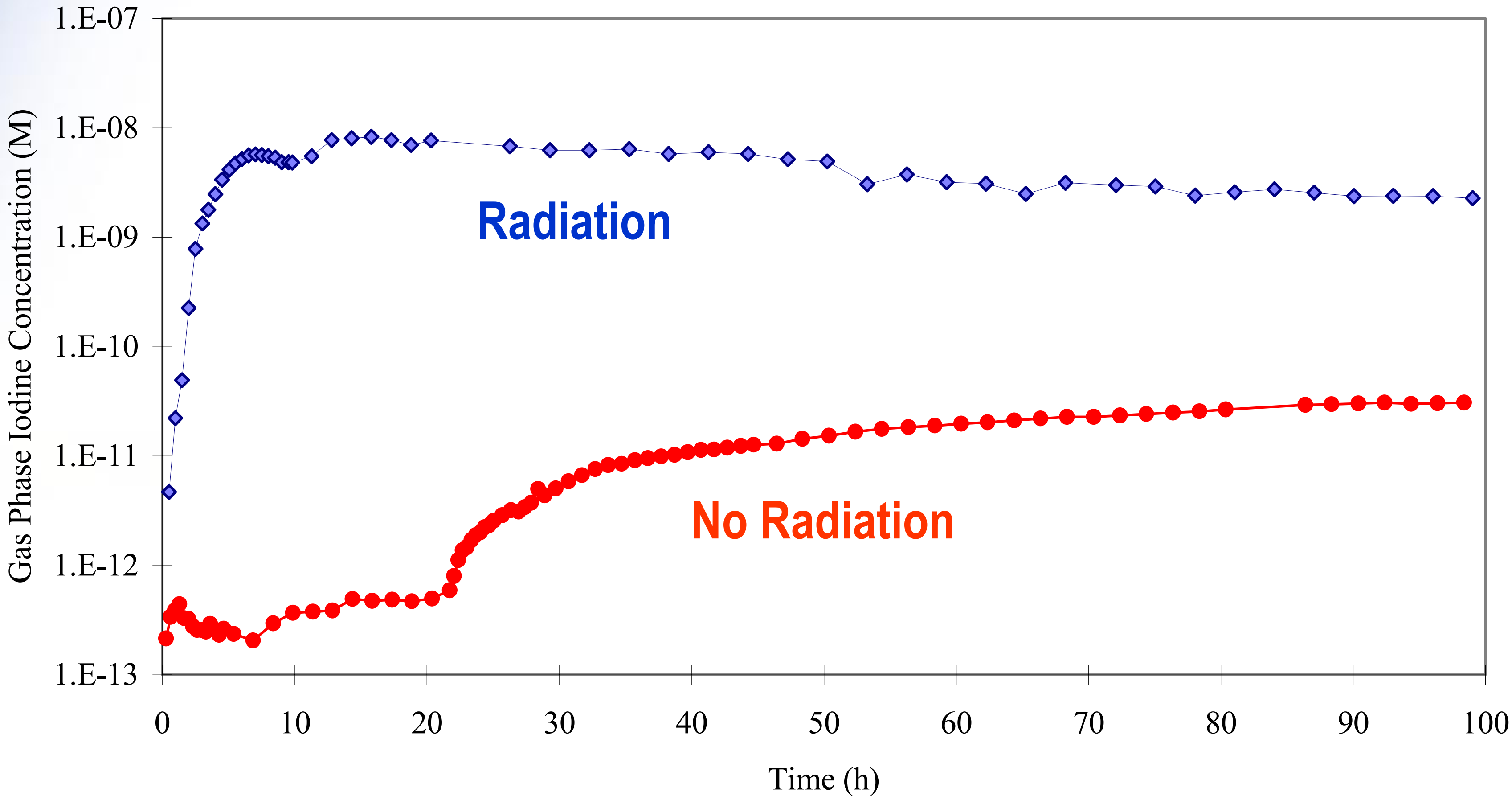
50 RTF Tests

- Type of Vessel Surface
  - Stainless Steel (electropolished, untreated)
  - Organic Coatings on carbon steel or concrete (Vinyl, Epoxy, Polyurethane)
  - Inorganic Coatings (zinc primer)
- Radiation on, Radiation off
- pH controlled, pH uncontrolled
  - pH range: 4.5 – 10.5
- Temperature
  - constant throughout exp; 25, 60, 90°C
  - steps from 25 to 80°C
- Condensing, Non-condensing
- Organic and Inorganic Additives

Technical Contributions of the RTF Program
1. The Effect of Radiation

- The RTF test program provided concrete data, showing that iodine behavior in the presence of a steady-state radiation source dramatically differs from that of non-radiolytic conditions
- The gas phase iodine concentrations and iodine speciation observed in the RTF tests were very different from those predicted from the equilibrium thermodynamic calculations.

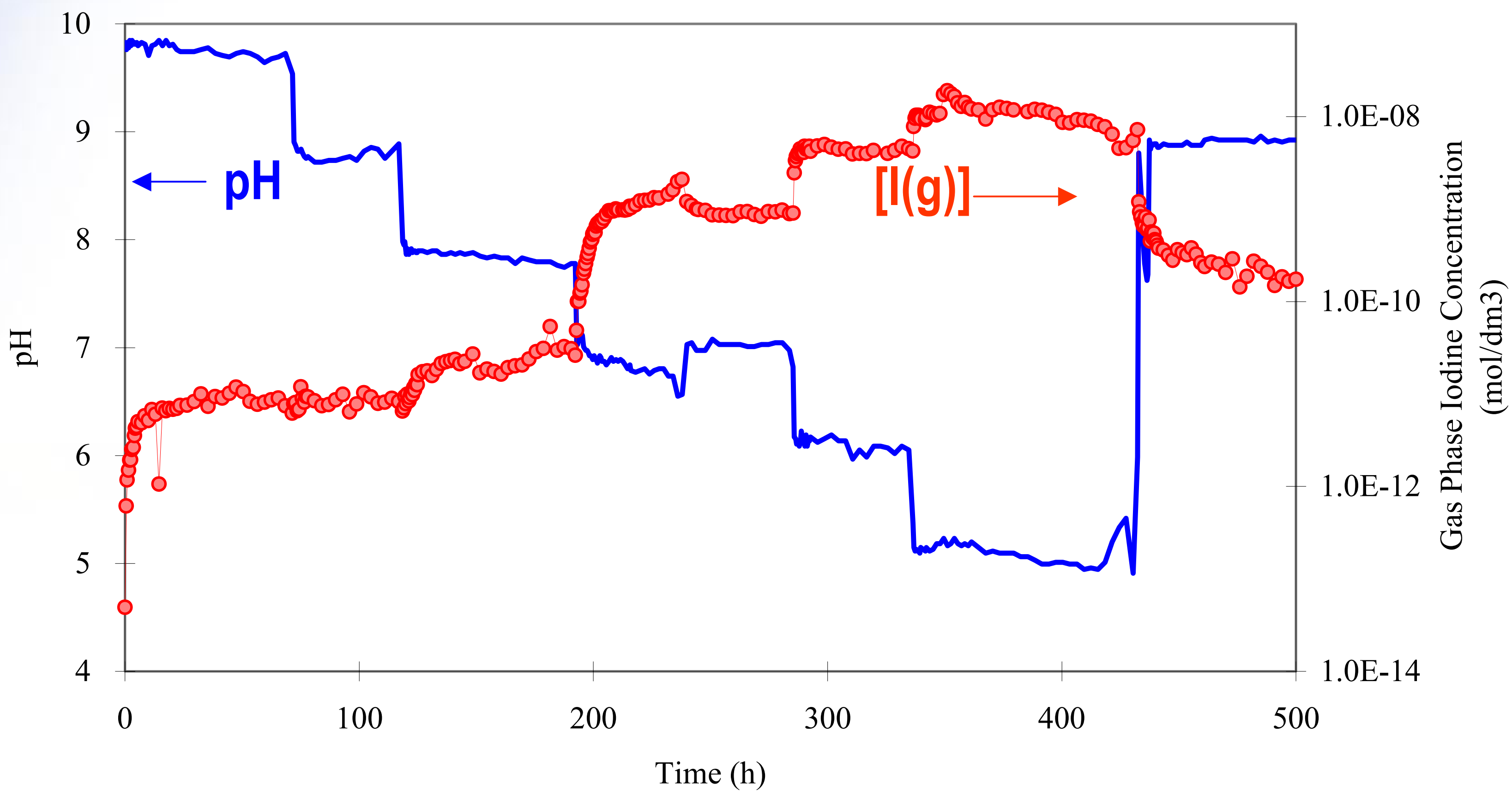
Effect of Radiation
(Vinyl Vessel, 25°C, D_R = 0 or 1.4 kGy/h)



Technical Contributions of the RTF Program
2. The Effect of pH

- The RTF studies firmly established the effect of pH on iodine volatility in a containment-like vessel.
- [I(g)] increases by a factor of 5 – 10 with a decrease in pH by one unit. A higher dependence at a lower temperature.
- The early assessments emerged following the TMI accident postulated that a sufficiently high pH in containment water would keep iodine trapped in the containment sump water as I^-.
- However, the observed pH dependence of iodine volatility was different from those predicted from the equilibrium thermodynamic calculations.

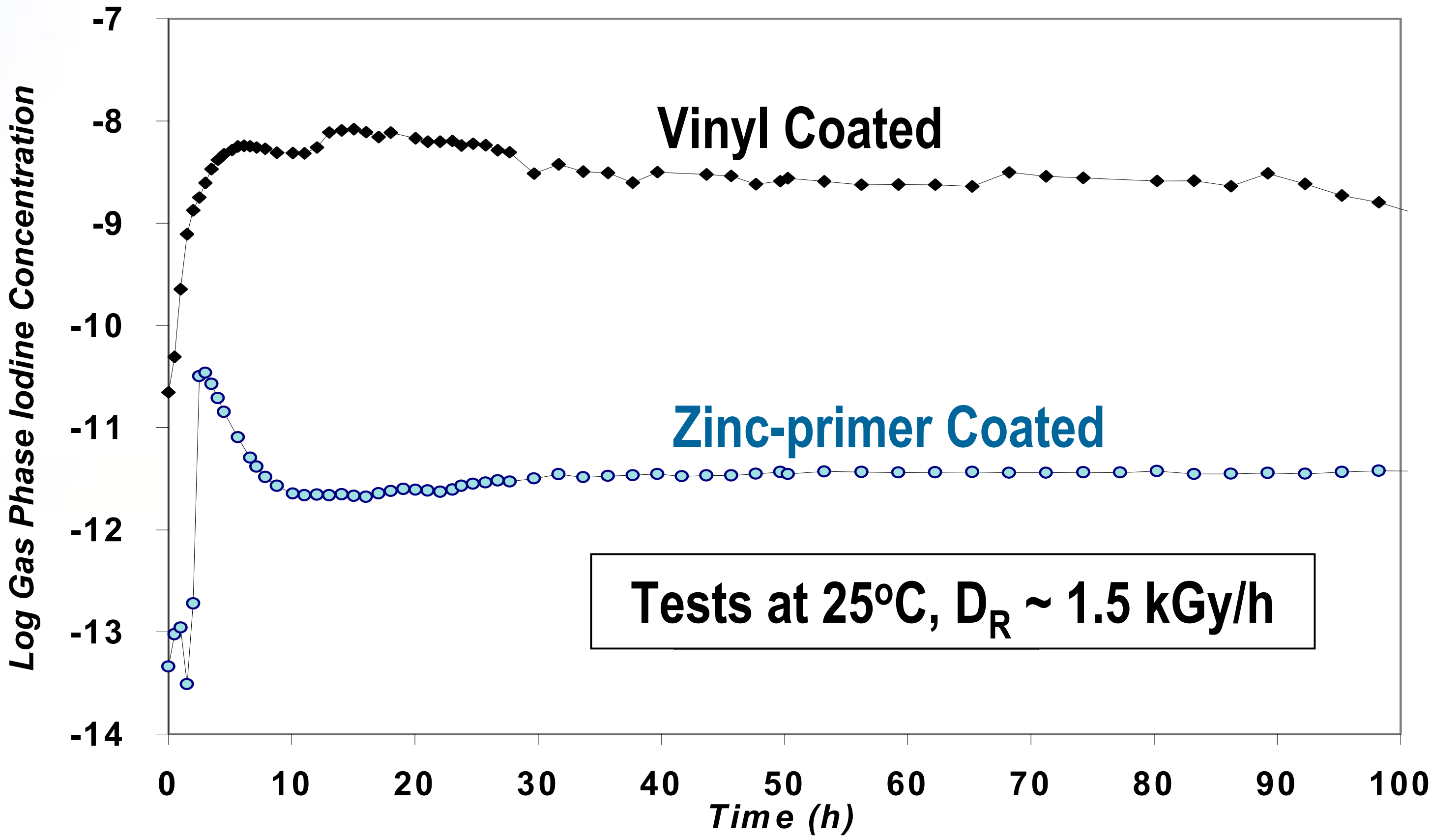
Effect of pH
(Stainless Steel Vessel, 60^{o}C, D_R = 0.78 kGy/h)



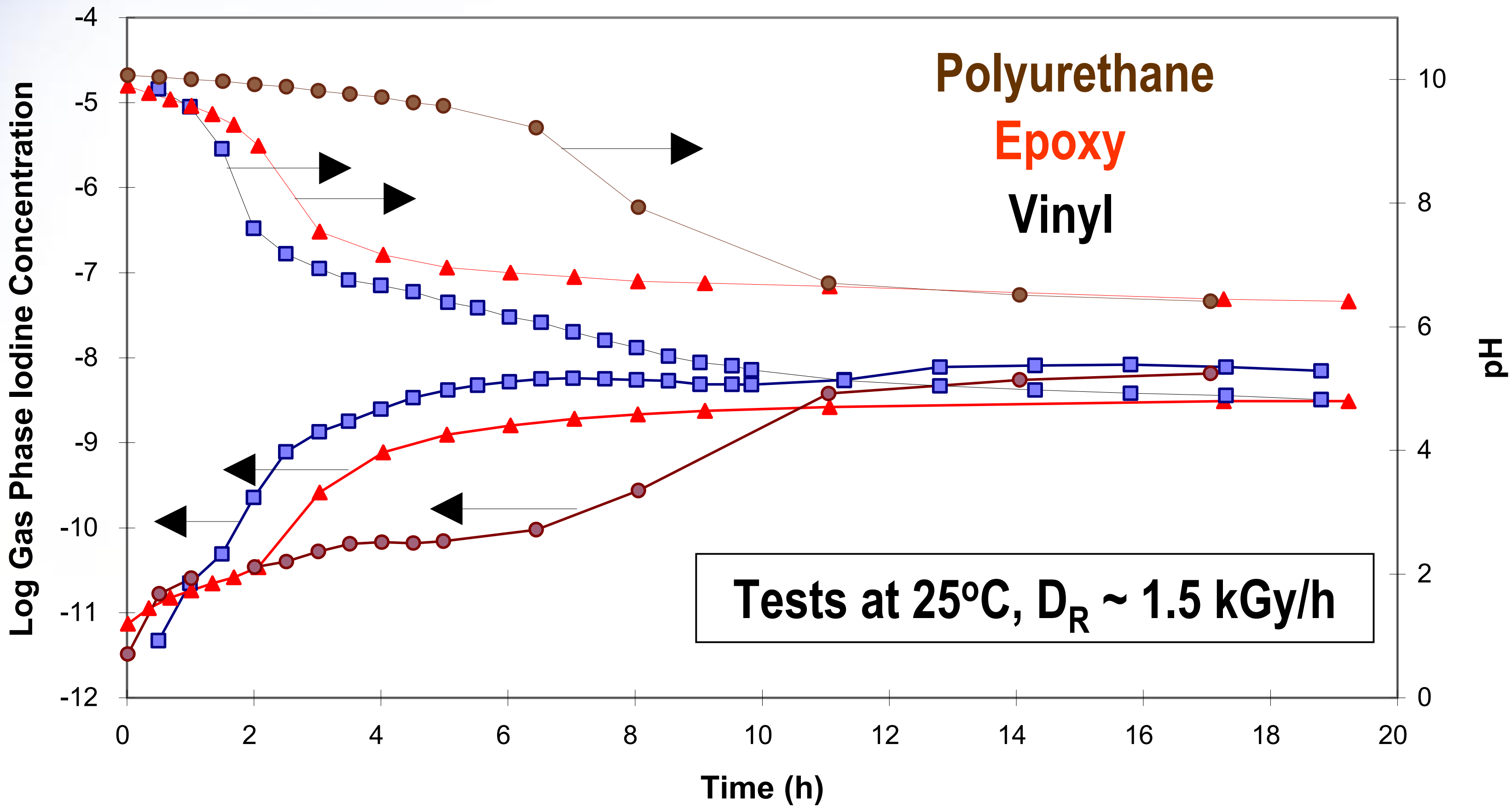
Technical Contributions of the RTF Program
3. The Effect of Surface

- The RTF program demonstrated that containment surfaces have a major influence on iodine behavior, especially under radiation conditions.
- Surfaces influence iodine volatility through more ways than simply iodine deposition and reactions on surfaces.
- In a radiation field, the surfaces may govern
  - The pH of the sump water
  - Iodine speciation in water, hence, the partitioning of iodine between the gas phase, the aqueous phase and surfaces

Effect of Surface
Organic- vs. Inorganic-Based Paint

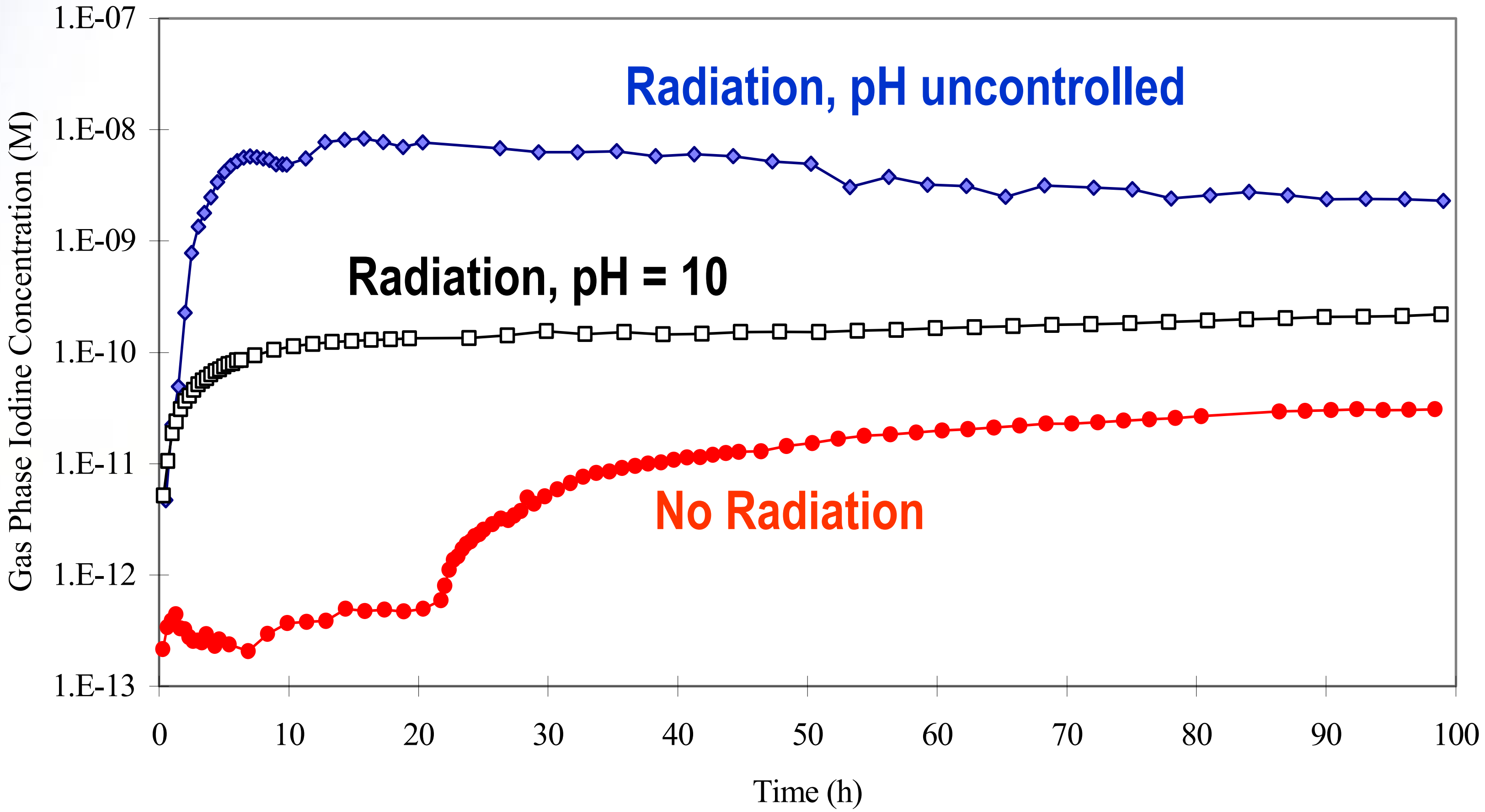


Organic Surfaces on pH & [I(g)]



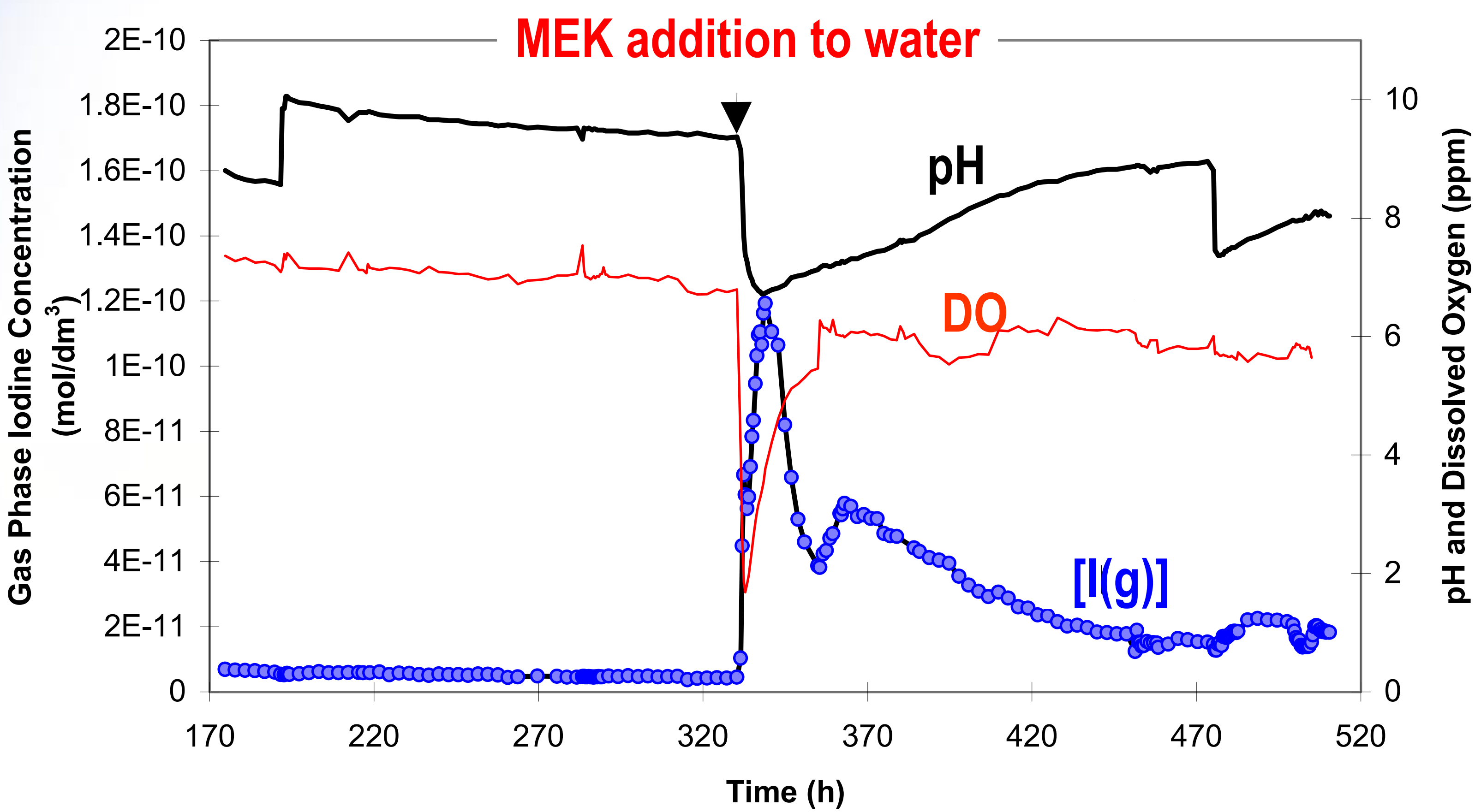
Surface affects iodine volatility, mainly via its impact on pH

Effect of pH under Radiation
(Vinyl Vessel, 25°C, D_R = 0 or 1.4 kGy/h)

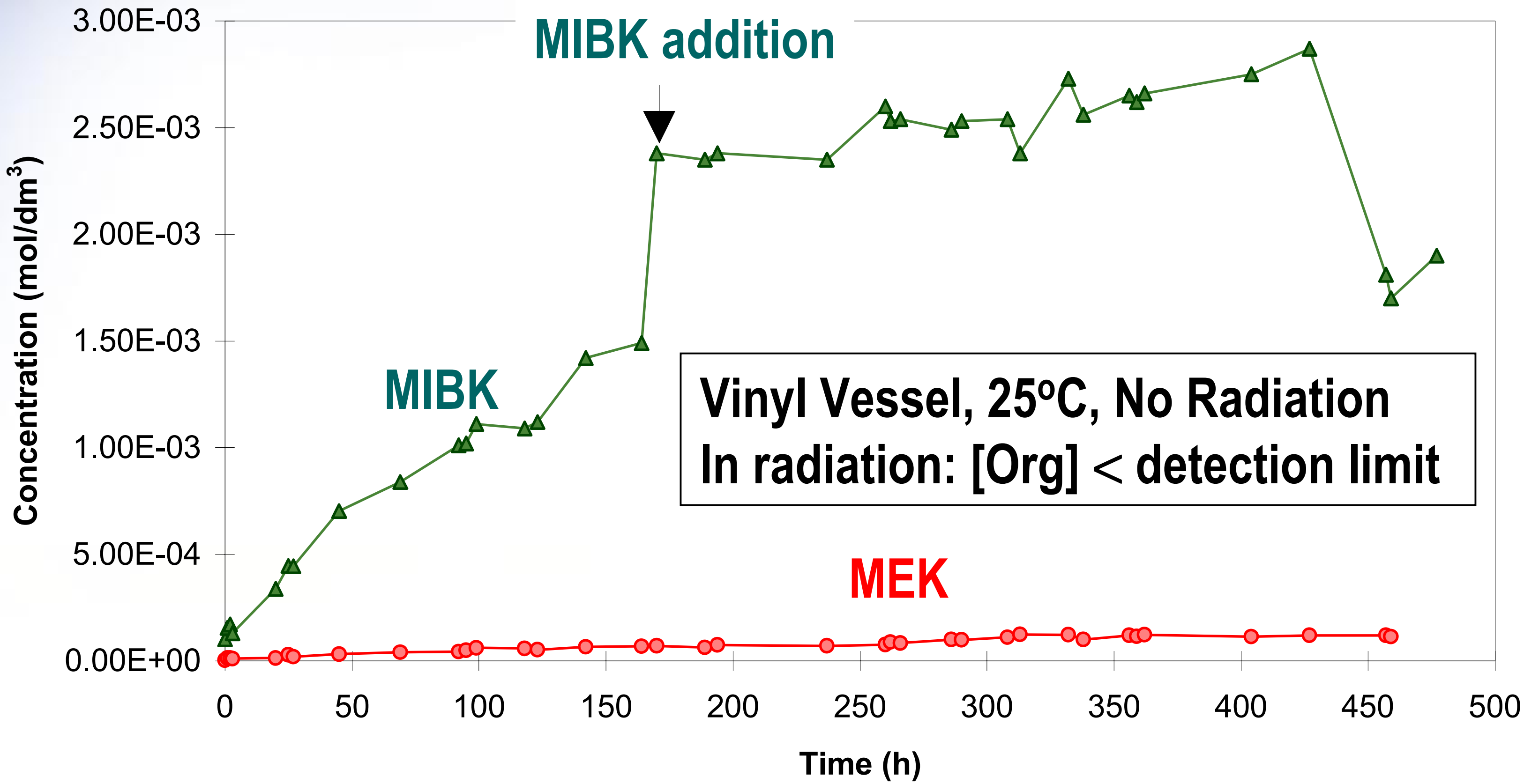


Cause for the pH Change in Organic Vessels

MEK addition in an RTF test (zinc-primed, 25°C, ~1.8 kGy·h^{-1})



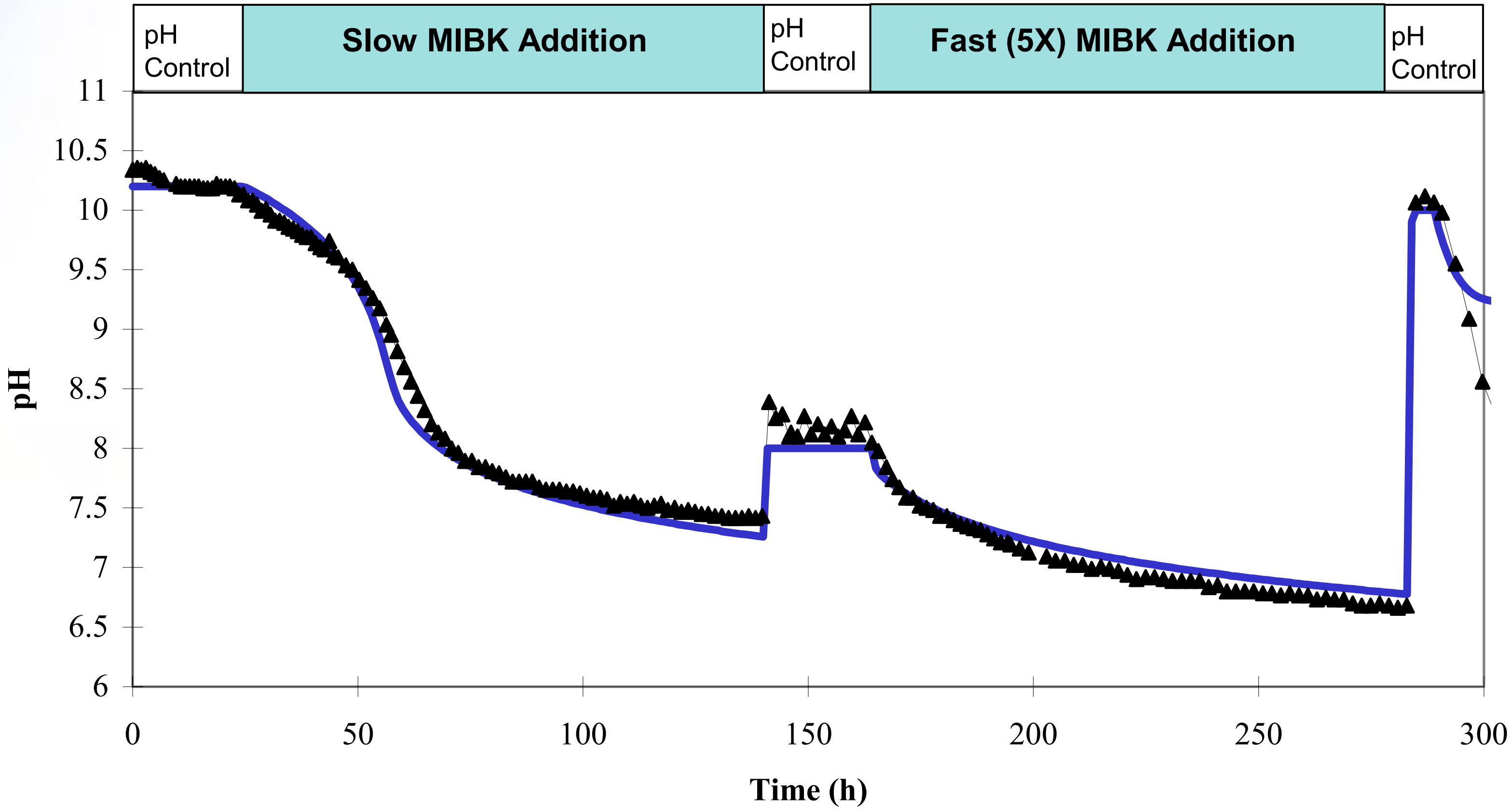
Organic Concentrations in Water



pH change due to organic impurities dissolved from surface into water

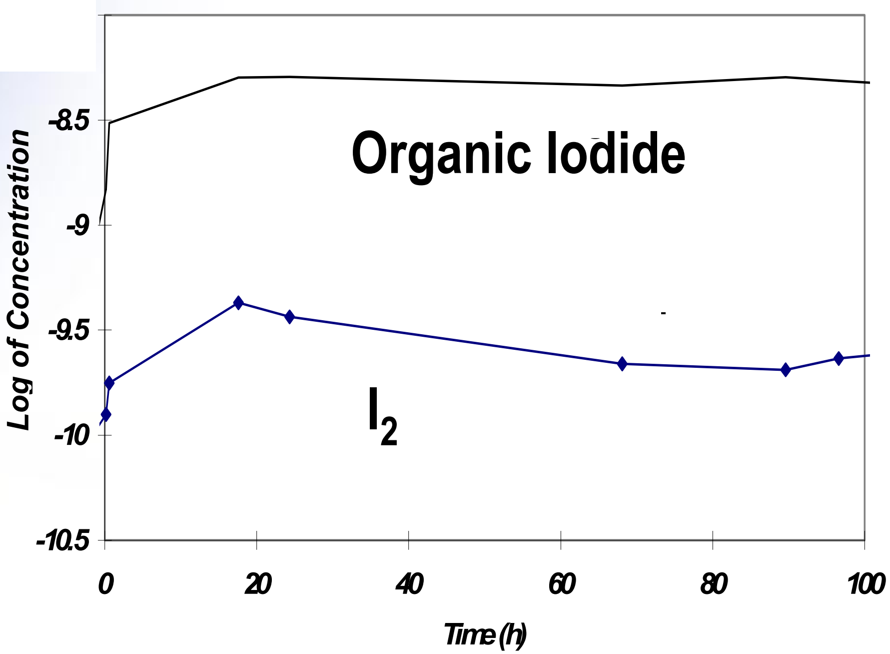
pH Change due to Slow, Continuous MIBK Addition

(Electropolished SS vessel, 25°C, ~0.6 $kGy \cdot h^{-1}$)

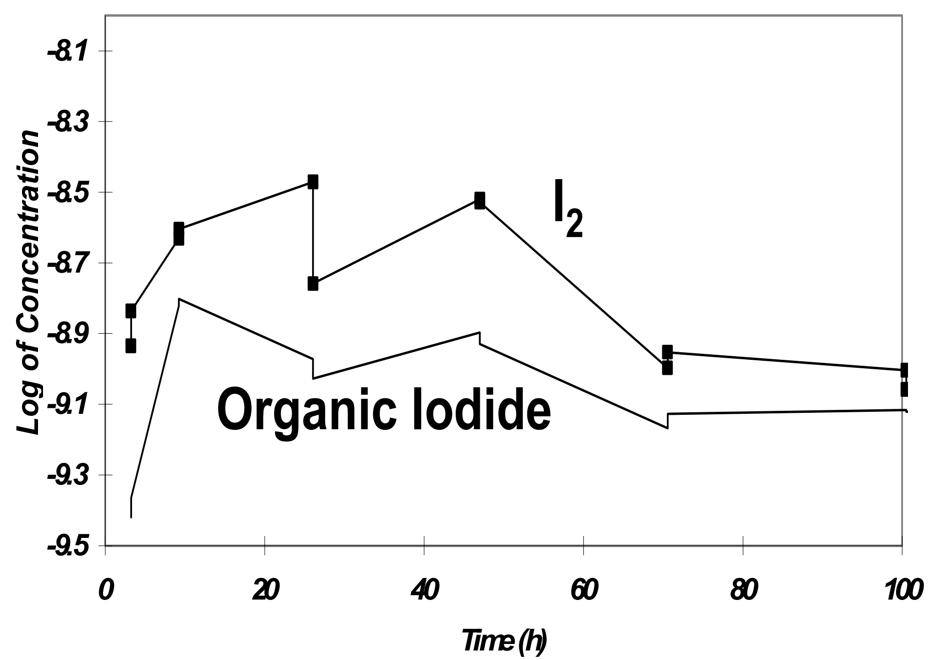


Organic Iodide Production (Vinyl Vessel, 25°C, D_R ~ 1.4 kGy/h)

Aqueous Concentrations



Gaseous Concentrations



- A variety of organic iodides could be formed
- Ave. volatility of organic iodide < volatility of CH_3I, $\approx I_2$

Surface Loading Observed in the RTF (1)

Radiation Field	Vessel Surface	Maximum Gas Phase Iodine Concentration ($mol \cdot dm^{-3}$)	% Iodine Lost to Surface
Yes	Vinyl	8×10^{-9}	78
No	Vinyl	4×10^{-11}	12
Yes	Polyurethane	3×10^{-9}	92
Yes	Epoxy	7×10^{-9}	87
Yes	Vinyl at pH 10	2×10^{-10}	5
Yes	Stainless Steel	6×10^{-10}	86
No	Zinc	1×10^{-10}	82
Yes	Zinc	3×10^{-10}	79

Surface Loading Observed in the RTF (2)

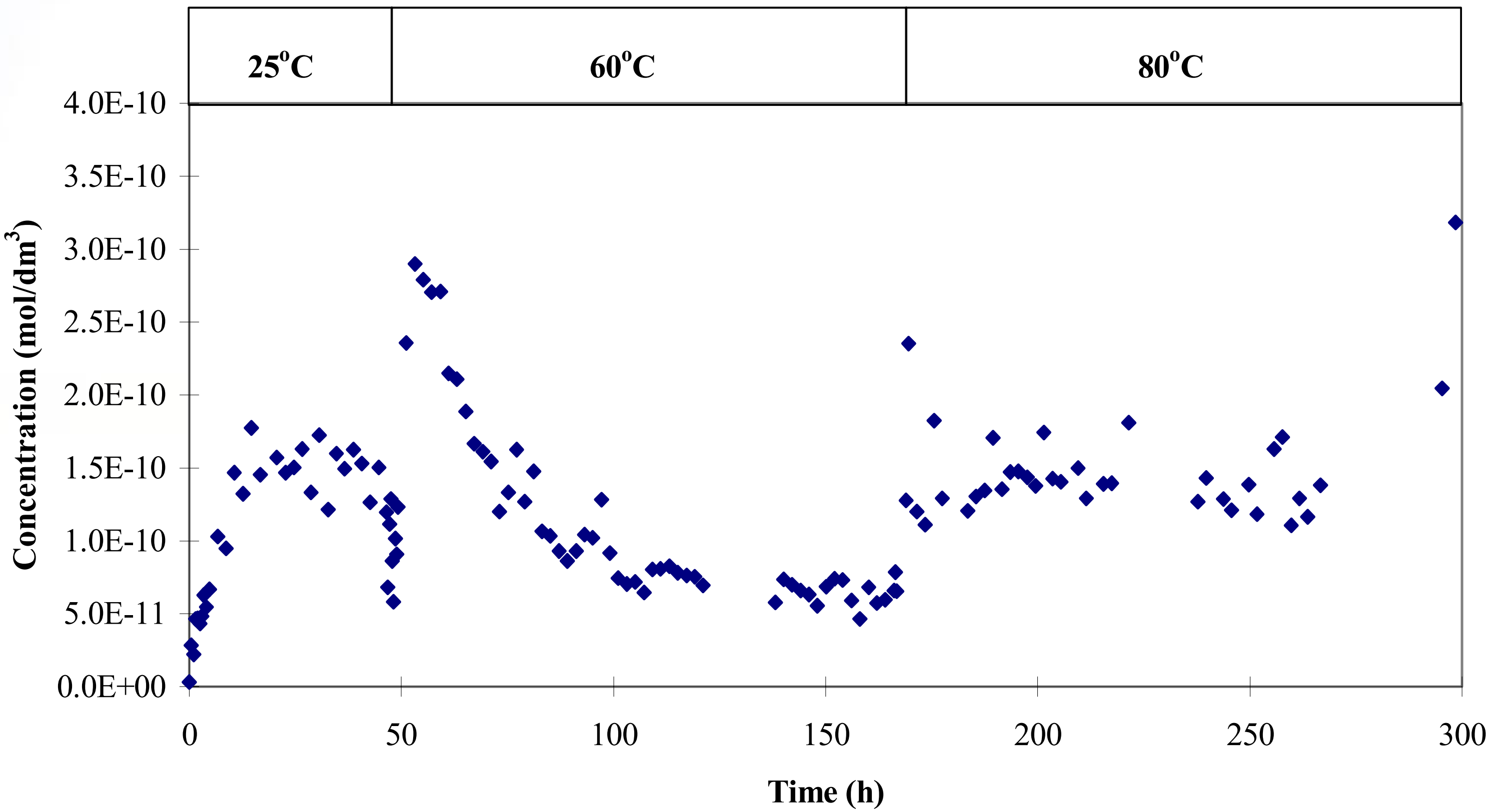
- **Surface adsorption is greater in the presence of radiation, except for the test with the zinc primer surface.**
  - **In the absence of radiation, adsorption occurred mainly in the aqueous phase.**
  - **In the presence of radiation, the iodine adsorption occurred mainly in the gas phase and was more significant.**
- **The observed surface loading was related to the gas phase iodine concentration.**
  - **The concentration was higher in the presence of radiation**
  - **Equally significant on bare stainless steel and painted surfaces**
  - **When the pH was kept high, the surface loading was significantly reduced.**

Technical Contributions of the RTF Program
4. The Effect of Temperature

- **The prevalent presumption was that iodine volatility would increase considerably with an increase in temperature**
  - **Mainly based on the fact that the partition coefficients of volatile iodine species (I_2 and organic iodides) would decrease exponentially with increasing temperature.**
- **The RTF tests show that iodine volatility is relatively insensitive to temperature**
  - **The hydrolysis rates of I_2 and organic iodides to non-volatile iodide in solution increases exponentially with T, effectively counterbalancing the partitioning behavior.**
  - **Temperature also affects the net surface adsorption rates of iodine species**

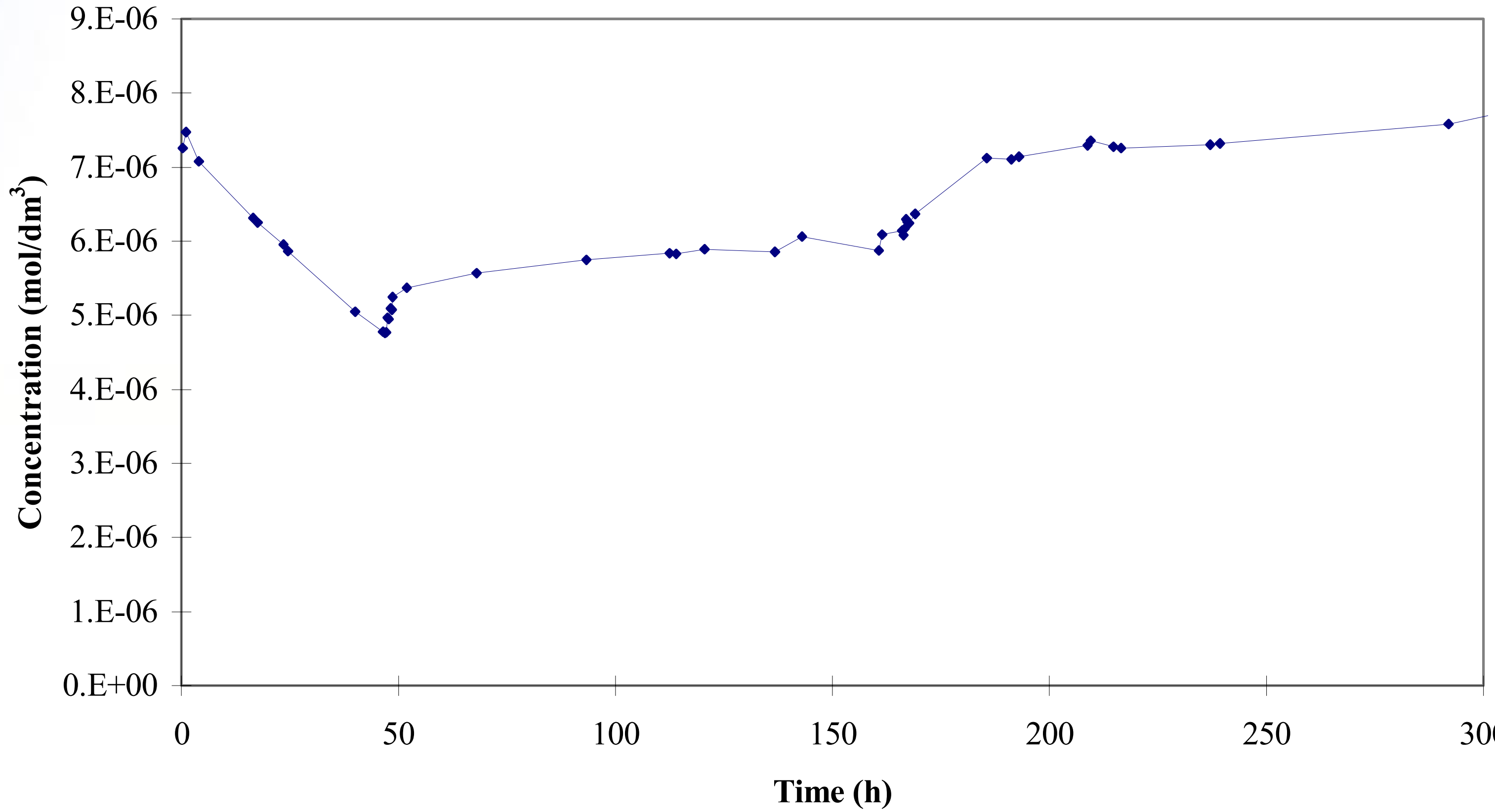
Effect of Temperature
(Stainless Steel Vessel, D_R = 0.67 kGy/h)

Total Gas Phase Iodine Concentration



Effect of Temperature
(Stainless Steel Vessel, D_R = 0.67 kGy/h)

Total Aqueous Phase Iodine Concentration



Other RTF Studies

- The effect of silver, boric acid, organic polymers and hydrazine additives on iodine chemistry
- The role of condensation and aqueous-gas phase mass transfer on iodine mass transport

Summary of the RTF Program (1)

- The RTF studies have identified the key processes that must be considered in determining iodine volatility under post-accident containment conditions, and the parameters to which these processes are sensitive.
- Iodine volatility increases dramatically in the presence of radiation
- Iodine volatility increases with a decrease in pH
  - Thermodynamic considerations do not explain the quantitative effect of pH on iodine volatility observed in the RTF
- Iodine volatility does not vary appreciably with temperature.
  - This observation was contrary to the early assumption that temperature would increase iodine volatility substantially.

Summary of the RTF Program (2)

- Surfaces (particularly organic) play a significant role in determining iodine volatility, through their indirect impacts on pH and iodine speciation and by adsorbing significant amount of iodine
  - The surface impact on pH is the result of organic impurities dissolved from the surface into the aqueous phase.
  - Under radiolysis conditions, a variety of organic iodides could be formed in the presence of organic-based painted surface. Most of these organic iodides are, however, far less volatile than CH_3I.
- Containment surfaces can absorb considerable amount of iodine, providing “iodine sinks”

Supporting Bench-Scale Program

Supporting Bench-Scale R&D Areas

- Aqueous Phase Chemistry
  1. Inorganic Iodine Reactions
  2. Water Radiolysis
  3. Reactions of Organic Impurities and Organic Iodides
     - Source of organic compounds dissolved in water
     - Radiolytic decomposition of organic impurities
     - Organic iodide formation and decomposition
- Aq-Gas Phase Partitioning
- Iodine – Surface Interaction

Aqueous Chemistry
1. Inorganic Iodine Reactions (1)

- **The most fundamental process determining iodine volatility**
  - **Non-volatile iodine species are continually converted to I_2, which then undergoes various reactions, including**
    - **conversion back to non-volatile species,**
    - **aqueous-gas phase interfacial mass transfer,**
    - **organic iodide formation, etc.**
- **As many as 80 reactions have been used to describe this process under the post-accident containment conditions**
  - **Thermal iodine reactions and equilibria**
  - **Reactions of iodine species and water radiolysis products**

Aqueous Chemistry
1. Inorganic Iodine Reactions (2)

- **Key oxidation reactions**

  $I^- + \bullet OH \longrightarrow \bullet I + OH^-$: rate determining

  $\bullet I + \bullet I \longrightarrow I_2$

- **Key reduction reactions**

  $I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$

  $I_2 + \bullet O_2^- \longrightarrow \bullet I_2^- + O_2$

  $I_2 + H_2O_2 \longrightarrow 2I^- + 2\,H^+ + O_2$

- **Modeling iodine behavior requires quantitative description of the I_2 production in the aqueous phase.**
  - **Reaction kinetics as a function of T, pH, $[I^-]_o$, dose rate, etc.**

Aqueous Chemistry
1. Inorganic Iodine Reactions (3)

- **Key AECL Contributions**
  - **Critical review of all the potential inorganic iodine reactions and their rates & equilibrium constants, K_{eq}**
    - **The reaction mechanisms, individual rate constants and their dependence on pH and temperature are well established.**
  - **Established the reaction mechanism and kinetics, e.g.,**
    - **HOI disproportionation (to I^- and IO_3^-) and iodine equilibria**
    - **Reduction of I_2 by H_2O_2**
    - **T dependence of K_{eq} of the iodine hydrolysis**

Aqueous Chemistry
2. Water Radiolysis Reactions

- **Containment water subjected to continuous irradiation:**

$$H_2O \longrightarrow \bullet OH,\ e_{aq}^{-},\ \bullet H,\ H_2,\ H_2O_2,\ HO_2\bullet$$

- **The water radiolysis products react with each other, dissolved O_2 (DO), iodine, metal ions and organic impurities**
- **Modeling iodine behavior requires quantitative description of the behavior of water radiolysis products**
- **AECL's work**
  - **A water radiolysis model for continuous irradiation constructed.**
  - **The sub-model in LIRIC has been validated for its ability to model H_2 production, radiolysis of organics, iodine behavior**

Aqueous Chemistry
3. Organic Reactions (1)

- **Organic impurities dissolved in water significantly affect iodine volatility**
  - **Organic impurities decompose by radiolytic reactions to organic acids and CO_2, affecting**
    - **the behavior of water radiolysis products**
    - **pH**
  - **Organic radicals react with I_2 to form organic iodides**
    - **Some organic iodides are more volatile and more difficult to remove than I_2**

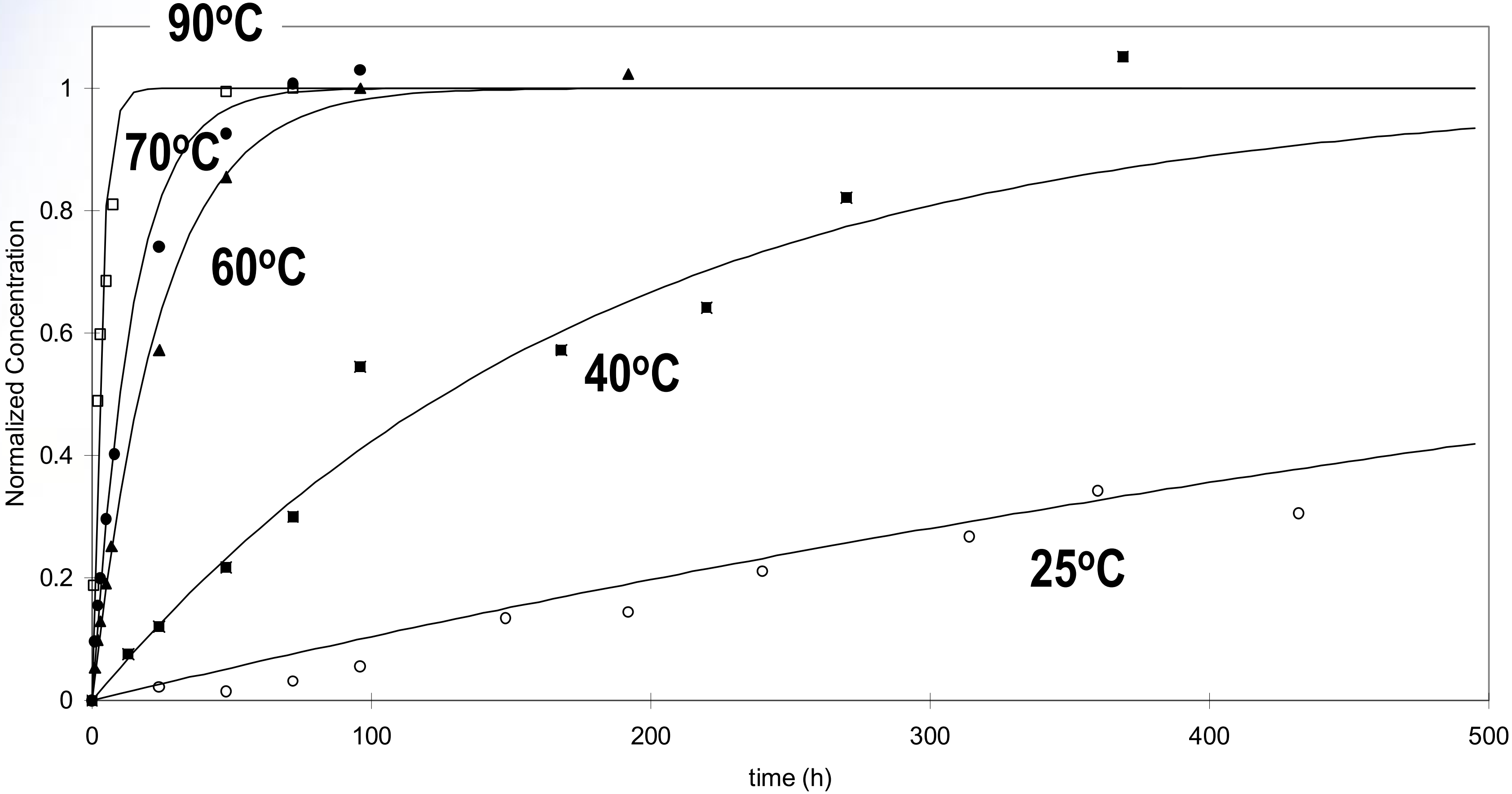
Aqueous Chemistry
3. Organic Reactions (2)

- Key organic processes to consider for iodine modeling
  a. Sources of organic compounds dissolved in water
  b. Radiolytic decomposition of organic impurities
  c. Organic iodide formation, decomposition and aqueous-gas phase partitioning
- These processes are complex
- The additional challenge is how to handle a wide range of organic impurities and organic iodides

a. Sources of Dissolved Organic Compounds

- Organic compounds that would have a significant effect on iodine behavior are dissolved organic compounds
- A major source of dissolved organic impurities is organic solvents trapped in paint matrix
  - Paint- or other organic-polymers do not dissolve easily in water
- AECL's work on organic solvent release from a painted surface into the aqueous phase
  - The release kinetics follows a first-order kinetics
  - The k depends on water diffusion thru the pores in the paint matrix, and is a function of T and paint thickness
  - Various paints and solvents show same kinetic behavior
  - The absolute amount released depends on paint aging

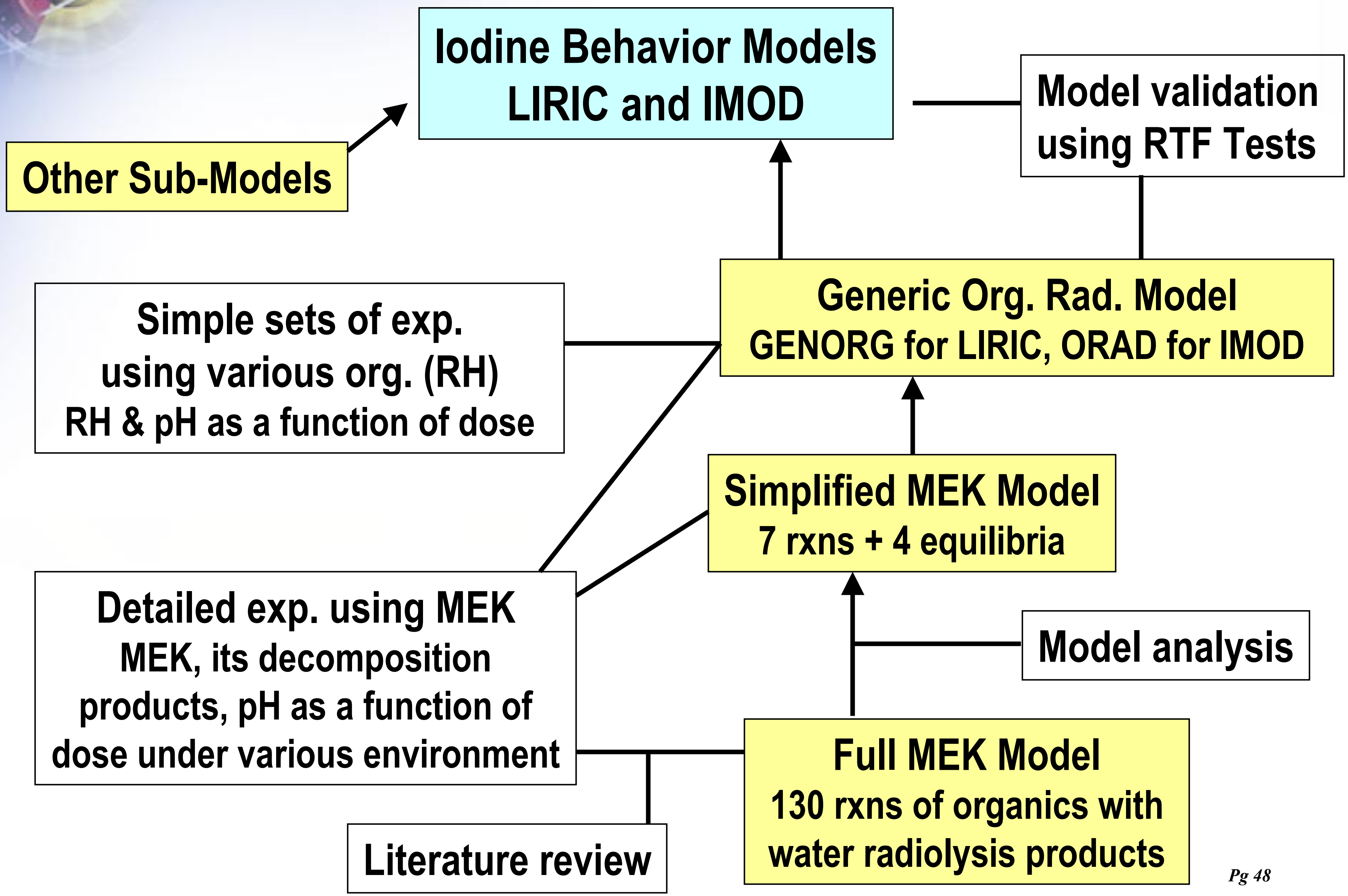
MIBK Release from Epoxy Surface into Water
Observed vs. Calculated Using the Dissolution Sub-Model



b. Radiolytic Decomposition of Organic Impurities

- Dissolved organic impurities decompose by radiolytic reactions to organic acids and CO_2, affecting
  - the behavior of water radiolysis products
  - pH
- Iodine models need a simple, generalized organic radiolysis sub-model to handle a large number of organic types
- The objectives of the sub-model is to predict
  - pH of the containment sump water
  - Concentrations of organic radicals
  - Concentrations of water radiolysis products, such as •OH, $\bullet O_2^-$, etc

Organic Radiolysis Model Development Steps



Objectives of Organic Radiolysis Sub-Models

ORAD for IMOD

[Wat. Rad. Prod.] as a function of [Org], D_R

GENORG for LIRIC

Full Water Radiolysis Model

Simplified MEK Model

Full Water Radiolysis Model

Full MEK Model

Full Water Radiolysis Model

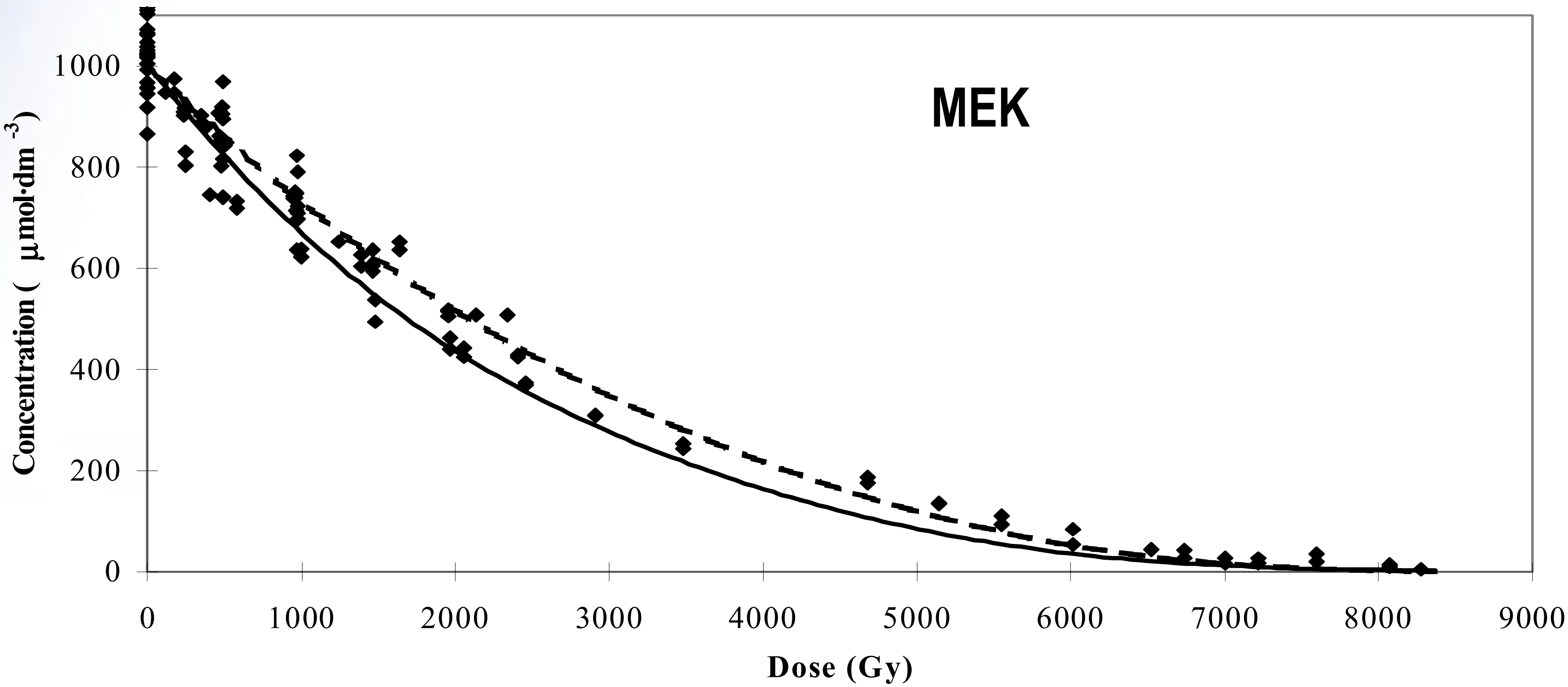
Validation

- pH & [Org] vs D_R
- pH, [MEK], [Int. Prod.] vs D_R

Common Objectives

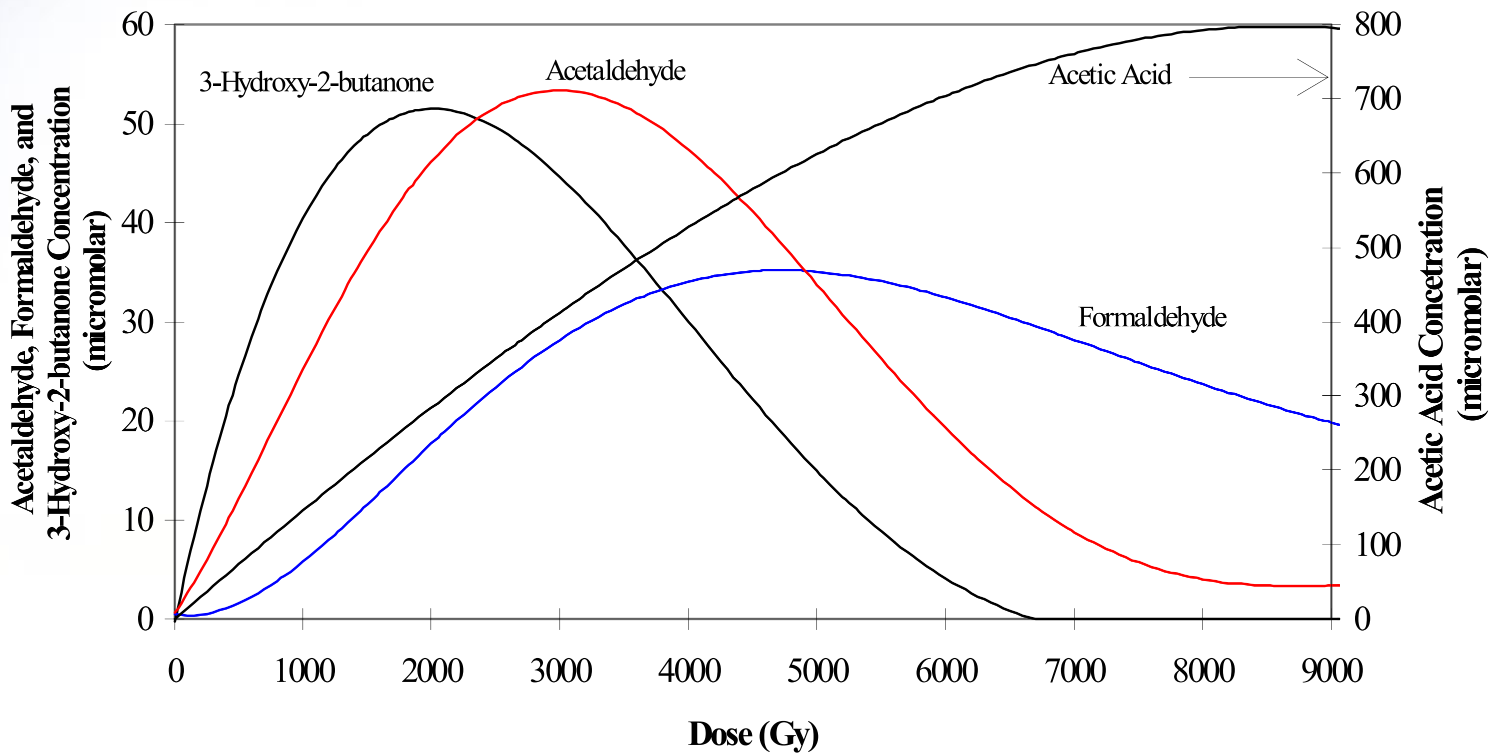
- pH
- [Wat. Rad. Prod.]
- [Org Radical]

Radiolytic Decomposition of MEK
MEK Behavior



Full MEK Model — — — · Simple MEK Model

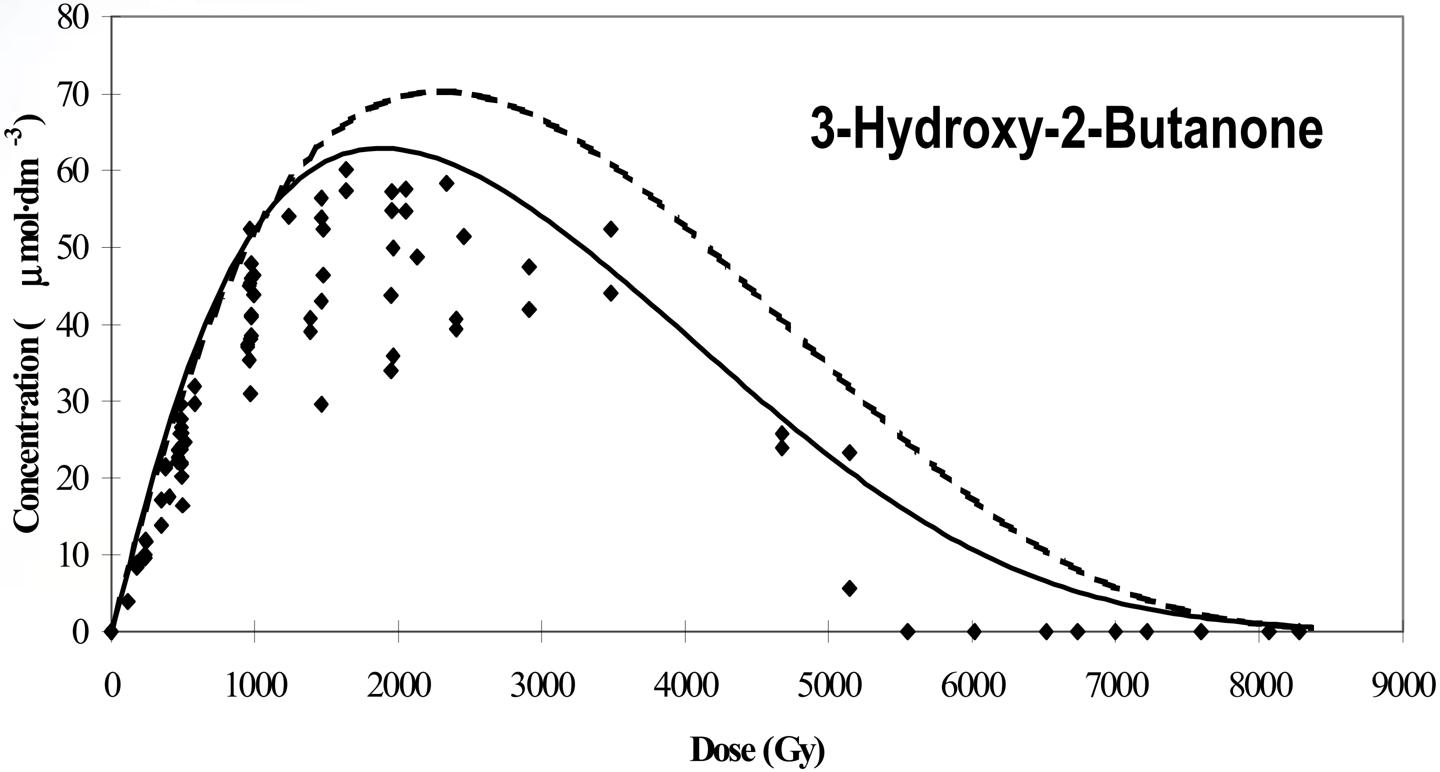
Radiolytic Decomposition of MEK
Observed Intermediate Decomposition Products



MEK → **3-OH-2-butanone, 2,3-butanedione** → **Acetaldehyde, Acetic Acid** → **Formaldehyde, Formic Acid** → **CO_2**

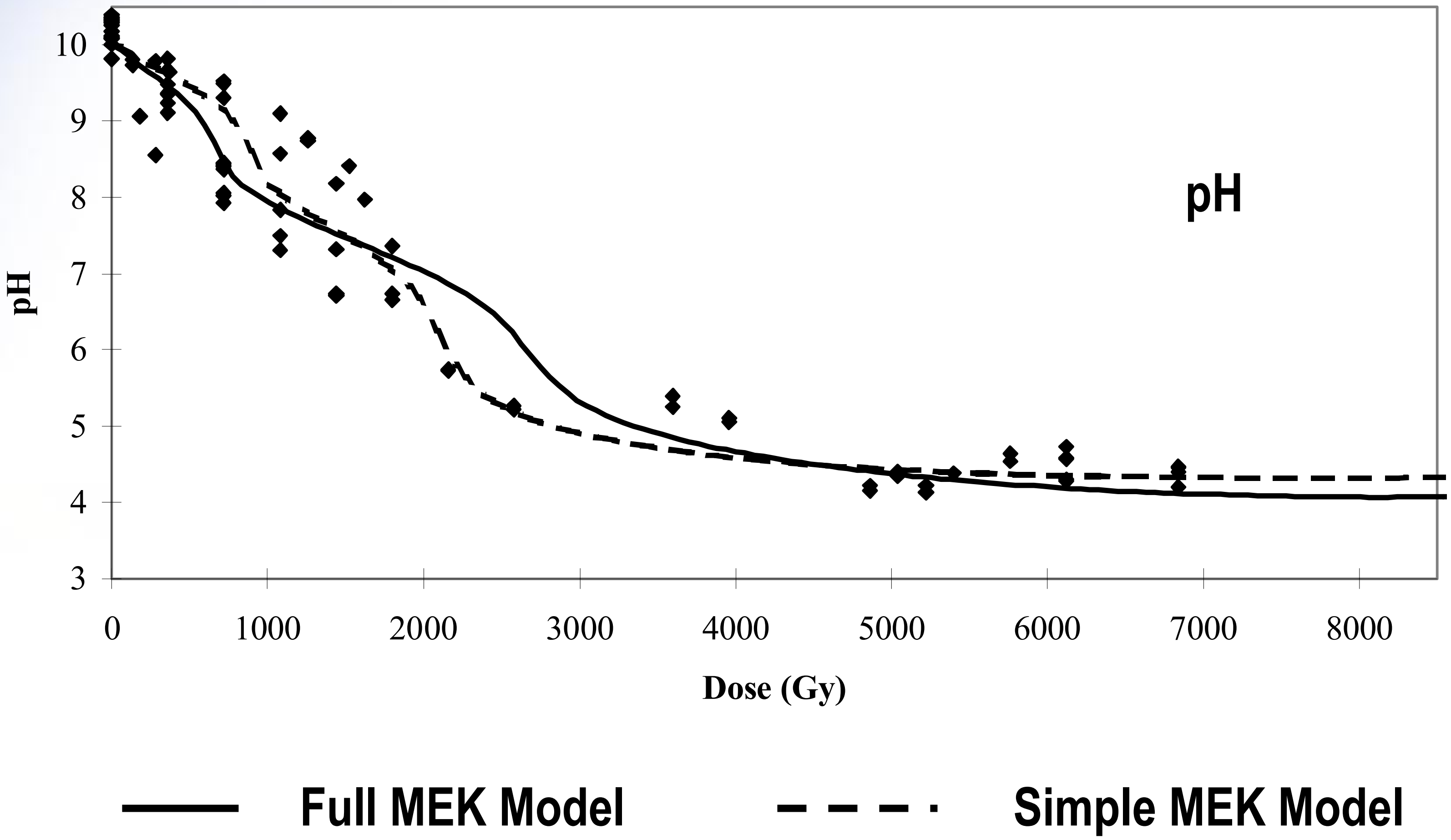
(4-C RH) **(4-C RH with O)** **(2-C RH with O)** **(1-C RH with O)**

MEK Model Simulations

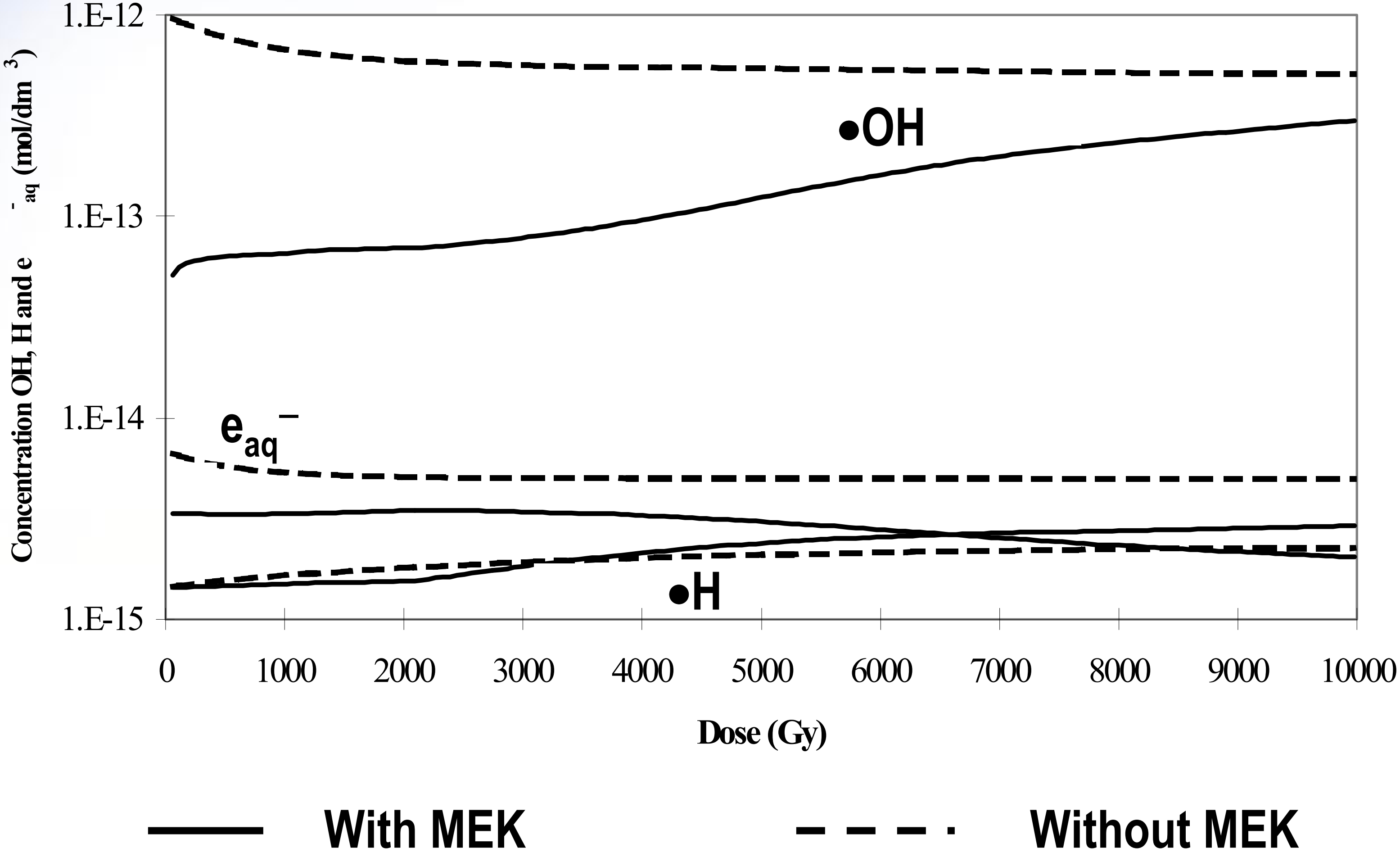


Full MEK Model — Simple MEK Model

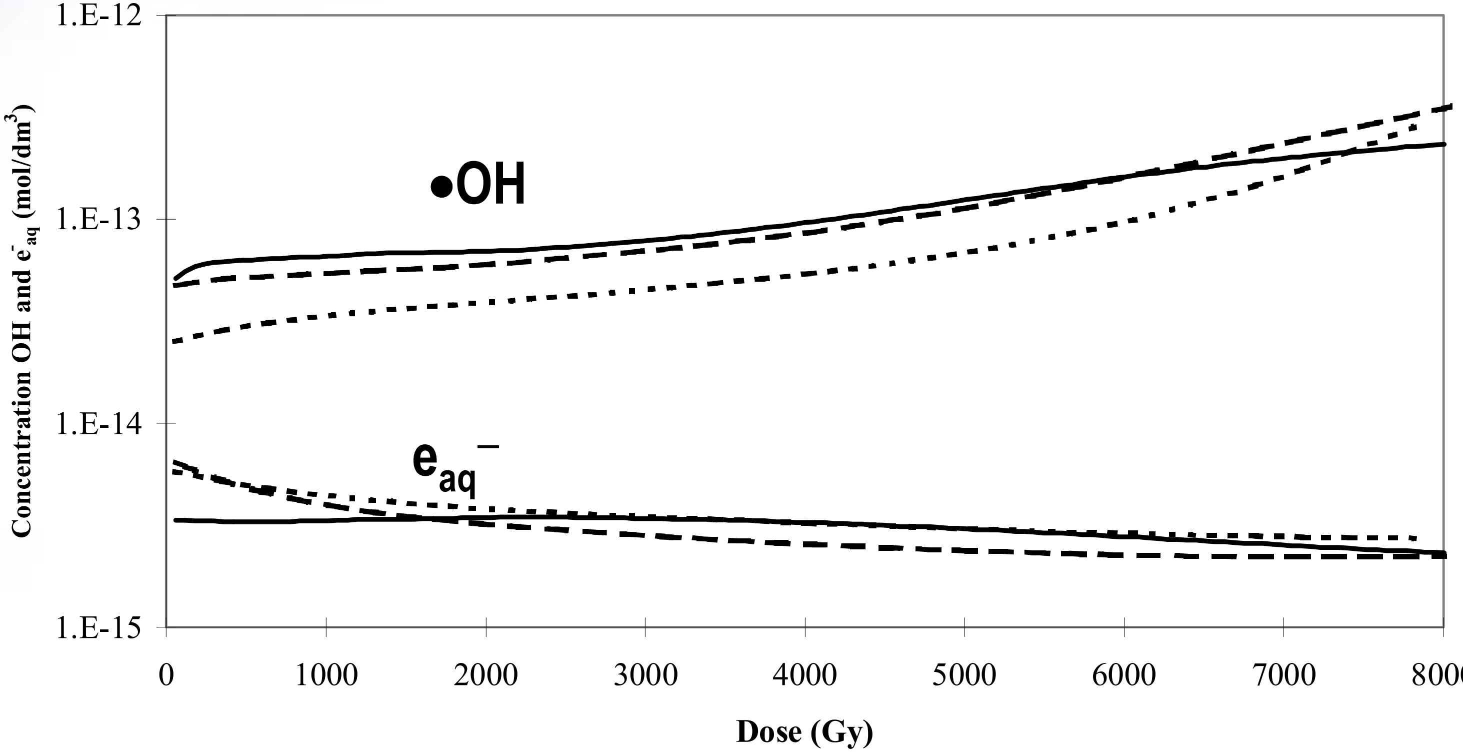
MEK Model Simulations



Full MEK Model Prediction

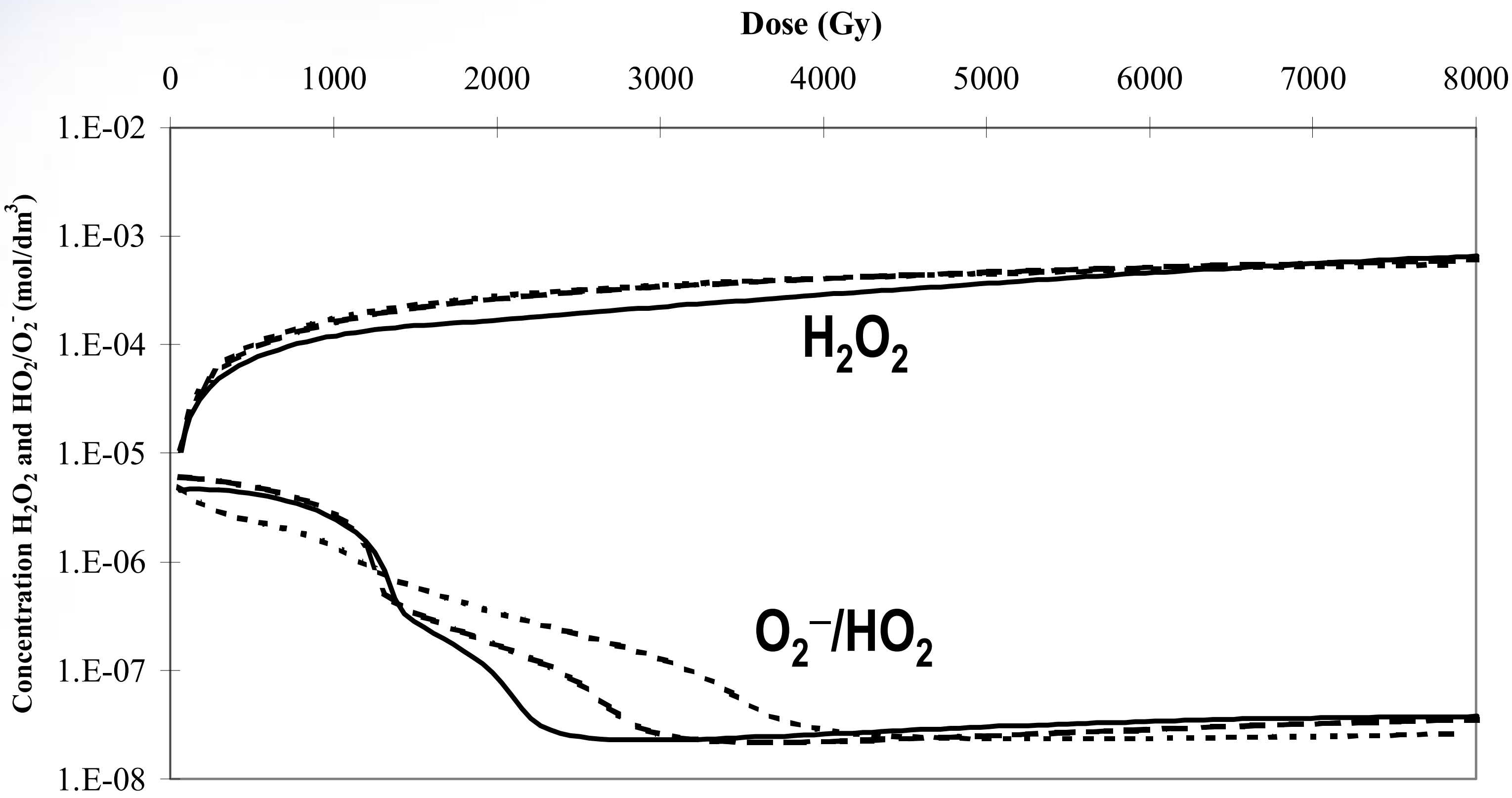


MEK Model Simulations



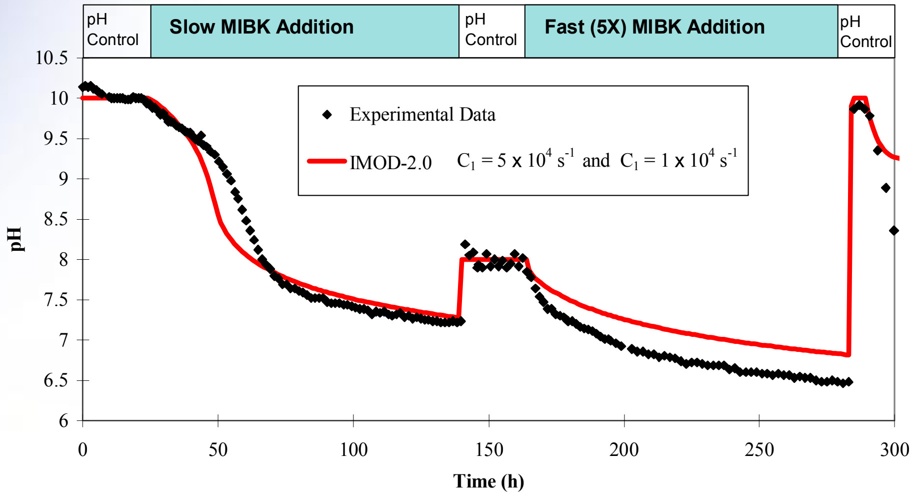
—— Full MEK Model   – – Simple MEK Model   •••• Gen Org Model

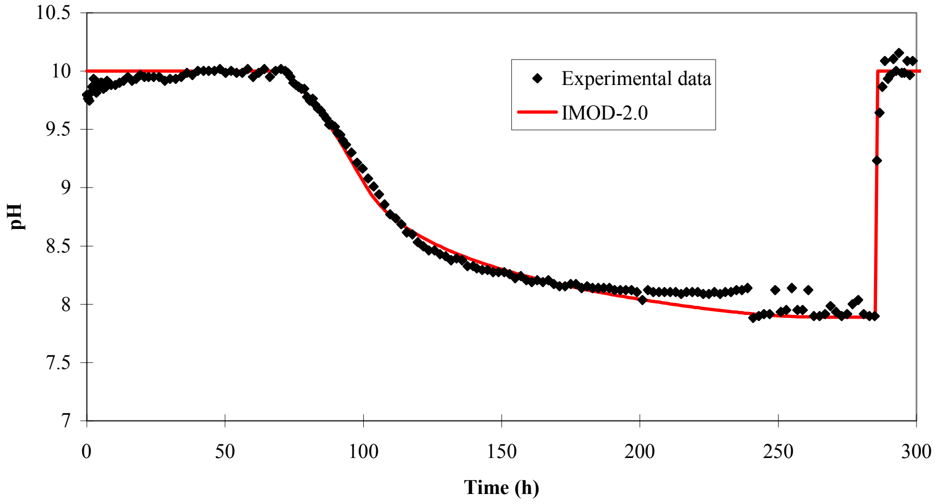
MEK Model Simulations



— Full MEK Model – – Simple MEK Model •••• Gen Org Model

Generic Organic Radiolytic Decomposition Model
pH Simulations of RTF Tests





Organic Iodide Behavior

- Processes to be modeled
  - Organic iodide formation
  - Decomposition by hydrolysis
  - Decomposition by radiolysis
  - Aqueous-gas phase partitioning
- A wide range of organic iodides
- The rates of these processes were measured on a wide range of organic iodides as a function of T
- A review of the rates shows that RI can be grouped into High & Low Volatility organic iodides, HVRI & LVRI

Aqueous-Gas Phase Partitioning

- I_2 and RI partition with the gas phase according to
  - Mass transfer across the aqueous-gas phase interface
  - Henry's Law constants
- A first order mass transfer rate based on a two-resistance model is adequate
- AECL's studies concentrate on
  - Building database on the partitioning coefficients of organic compounds and organic iodides
  - Developing a sound strategy for grouping of the organic species

Surface Interactions

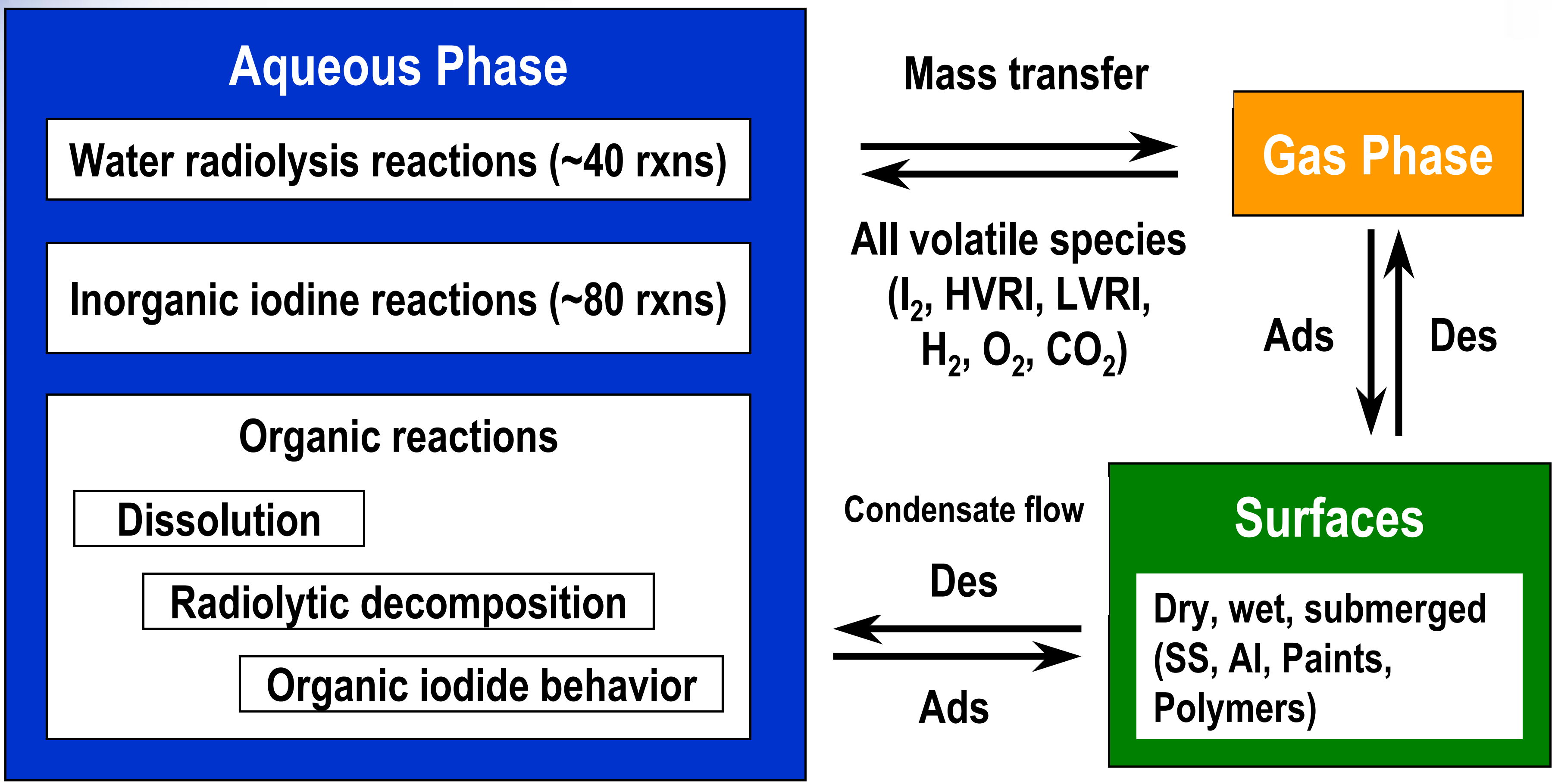
- Containment surfaces include stainless steel, aluminum, painted steel, painted concrete, plastics
- Dry, submerged, condensing films
- Some of the surfaces change their characteristics during iodine adsorption (e.g., Stainless Steel)
- Most surface interaction can be adequately described using a simple first order rate equation
- AECL's studies concentrate on building database on the adsorption rate constants

Iodine Behavior Models
LIRIC and IMOD

LIRIC
(Library of Iodine Reactions in Containment)

- **Comprehensive mechanistic model, consisting of about 300 chemical reactions and physical processes**
- **Epitome of our current understanding**
- **Has successfully simulated RTF tests performed over a wide range of conditions**
- **Has been available for the support of safety analysis**
- **Due to its complexity and size, integration of LIRIC into a safety analysis code is undesirable.**

LIRIC-3.x

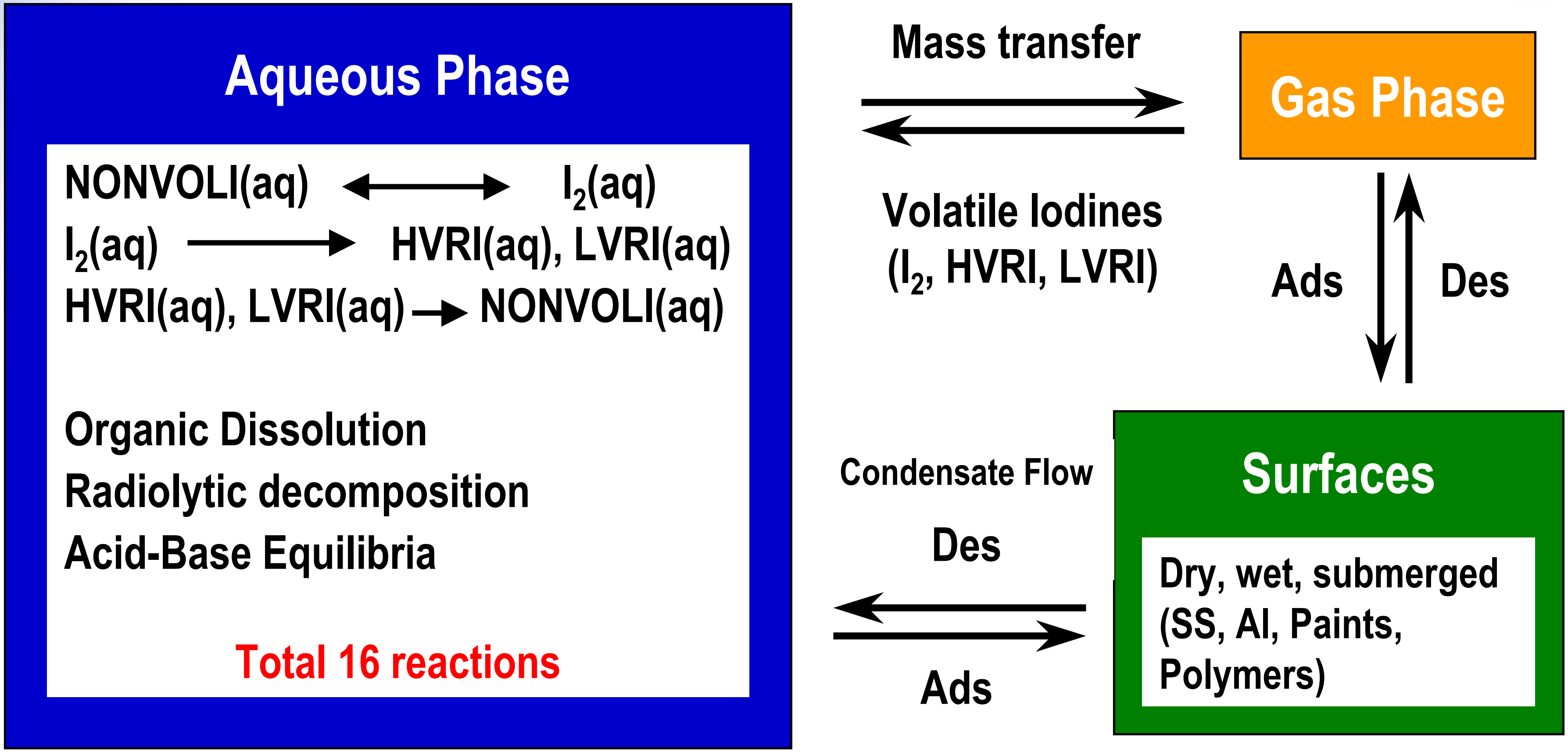


Aqueous Phase
Water radiolysis reactions (~40 rxns)
Inorganic iodine reactions (~80 rxns)
Organic reactions
Dissolution
Radiolytic decomposition
Organic iodide behavior
Mass transfer
All volatile species (I_2, HVRI, LVRI, H_2, O_2, CO_2)
Gas Phase
Ads
Des
Condensate flow
Des
Ads
Surfaces
Dry, wet, submerged (SS, Al, Paints, Polymers)

Mechanistic LIRIC Model → Simple Iodine Model

- **LIRIC has reproduced various bench-scale and RTF test results performed over a wide range of conditions, indicating the key processes determining iodine volatility are adequately modelled in LIRIC**
- **Sensitivity analysis and simulations of various RTF tests using LIRIC have enabled us to construct IMOD, which is smaller and very simple, but maintains many of the capabilities of LIRIC.**

IMOD-2.x



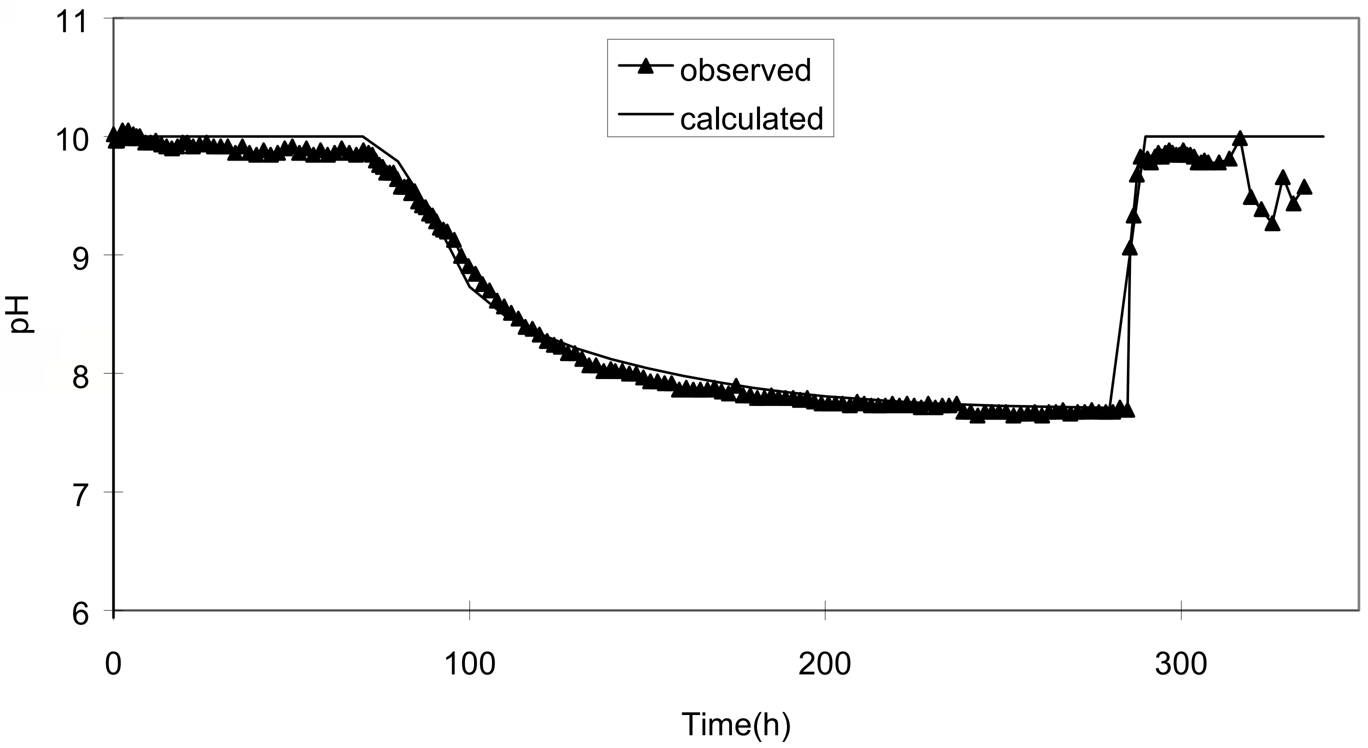
Aqueous Phase
NONVOLI(aq) ⟷ I_2(aq)
I_2(aq) → HVRI(aq), LVRI(aq)
HVRI(aq), LVRI(aq) → NONVOLI(aq)
Organic Dissolution
Radiolytic decomposition
Acid-Base Equilibria
Total 16 reactions
Mass transfer
Volatile Iodines
(I_2, HVRI, LVRI)
Gas Phase
Ads
Des
Condensate Flow
Des
Ads
Surfaces
Dry, wet, submerged
(SS, Al, Paints,
Polymers)

Performance of LIRIC-3.3 & IMOD-2.1

- Have reproduced the results of RTF tests performed over a wide range of conditions to within ~ experimental uncertainties
- Comparisons over a set of results, not just one parameter
  - Gas phase total iodine concentration
  - Aqueous phase total iodine concentration
  - Iodine speciation; I_2 and Organic Iodides in the presence of painted surfaces
  - pH evolution, when pH was not controlled
- Outside the RTF conditions, IMOD-2.1 results are comparable with LIRIC-3.3 results
- Testing the models against two CAIMAN tests are underway through ISP-41F Phase 2

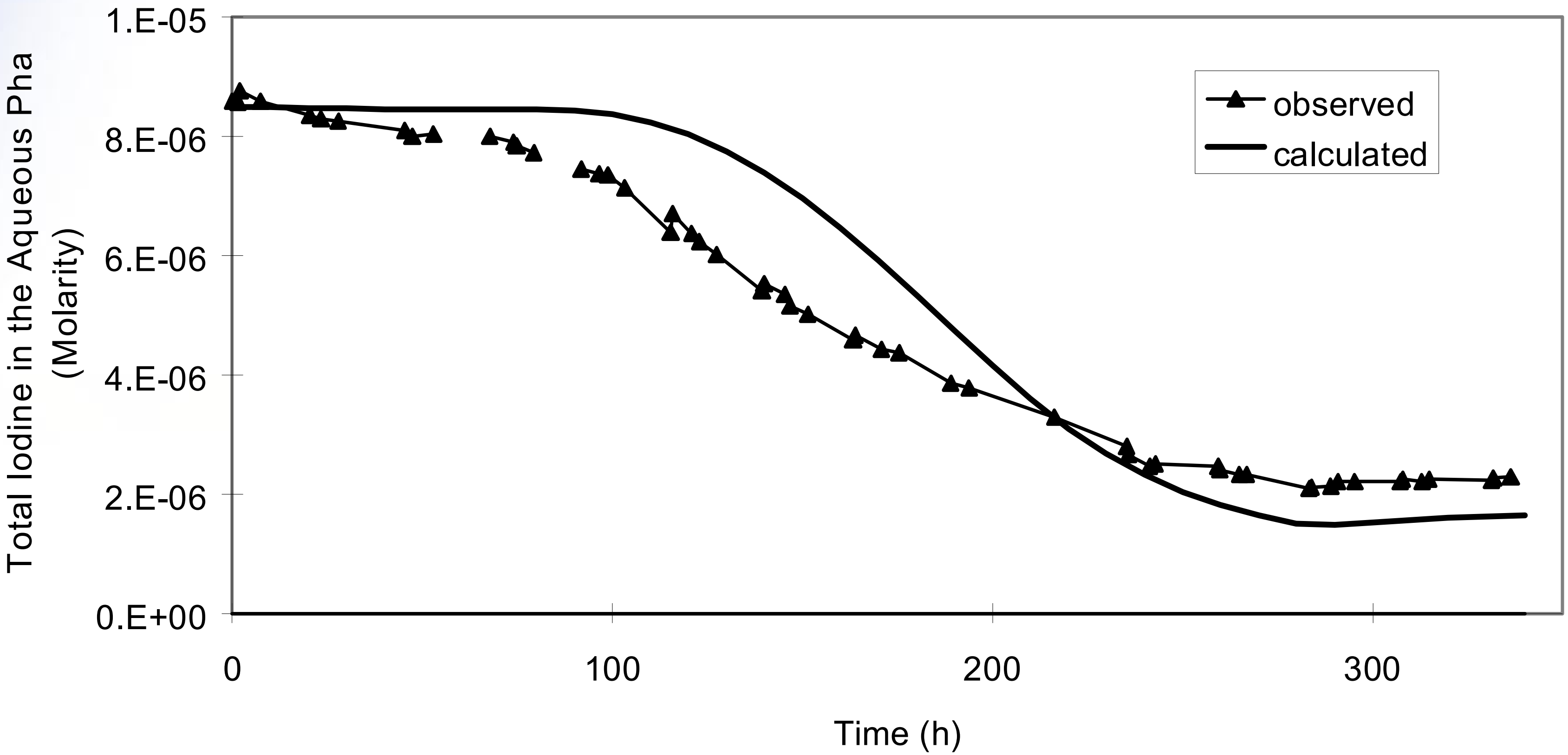
IMOD Simulations of an RTF Test
(10^{-5} M CsI, 60°C, 0.6 kGy/h, Epoxy painted vessel)

pH



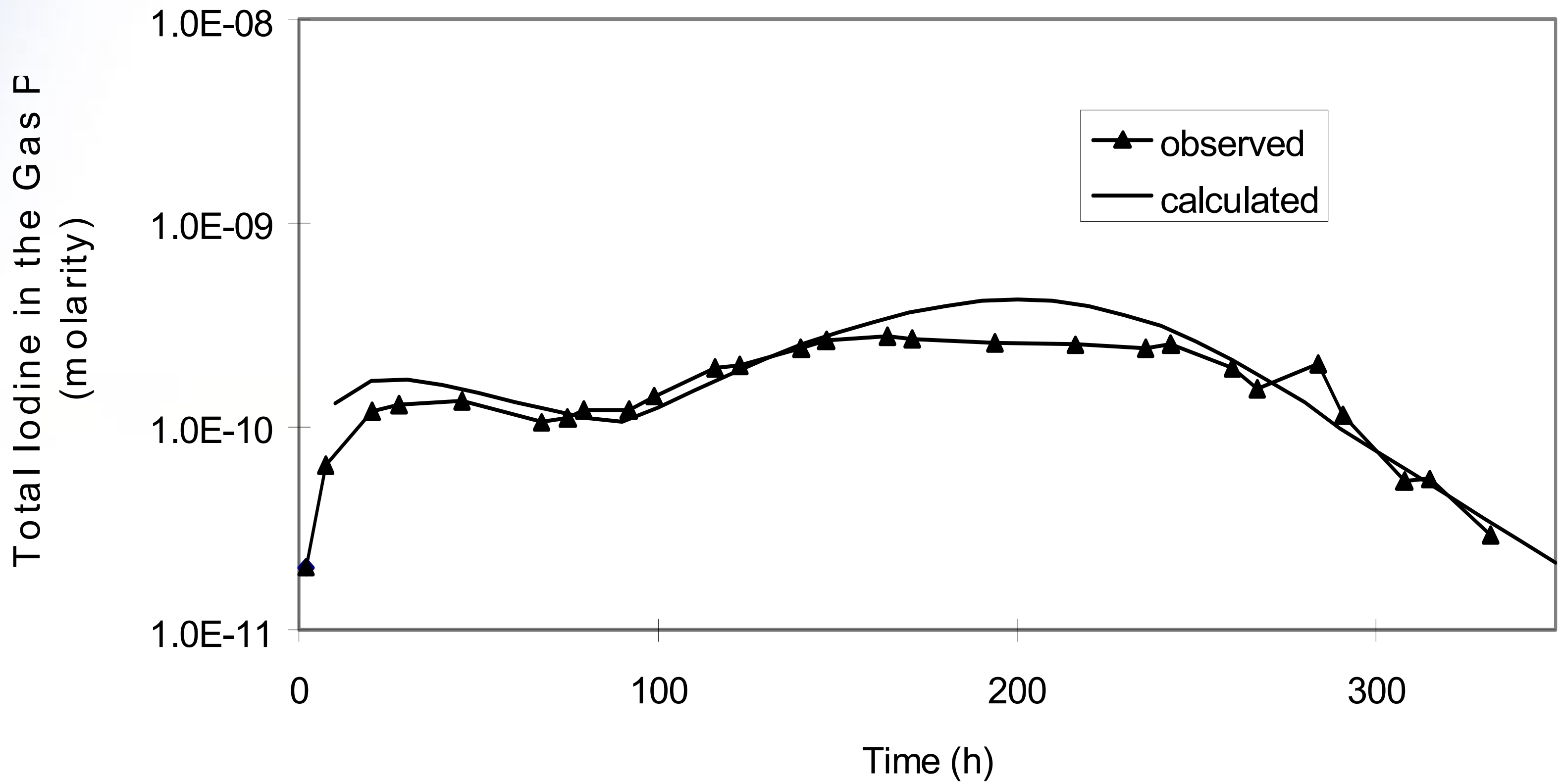
IMOD Simulations of an RTF Test
(10^{-5} M CsI, 60°C, 0.6 kGy/h, Epoxy painted vessel)

[I(aq)]



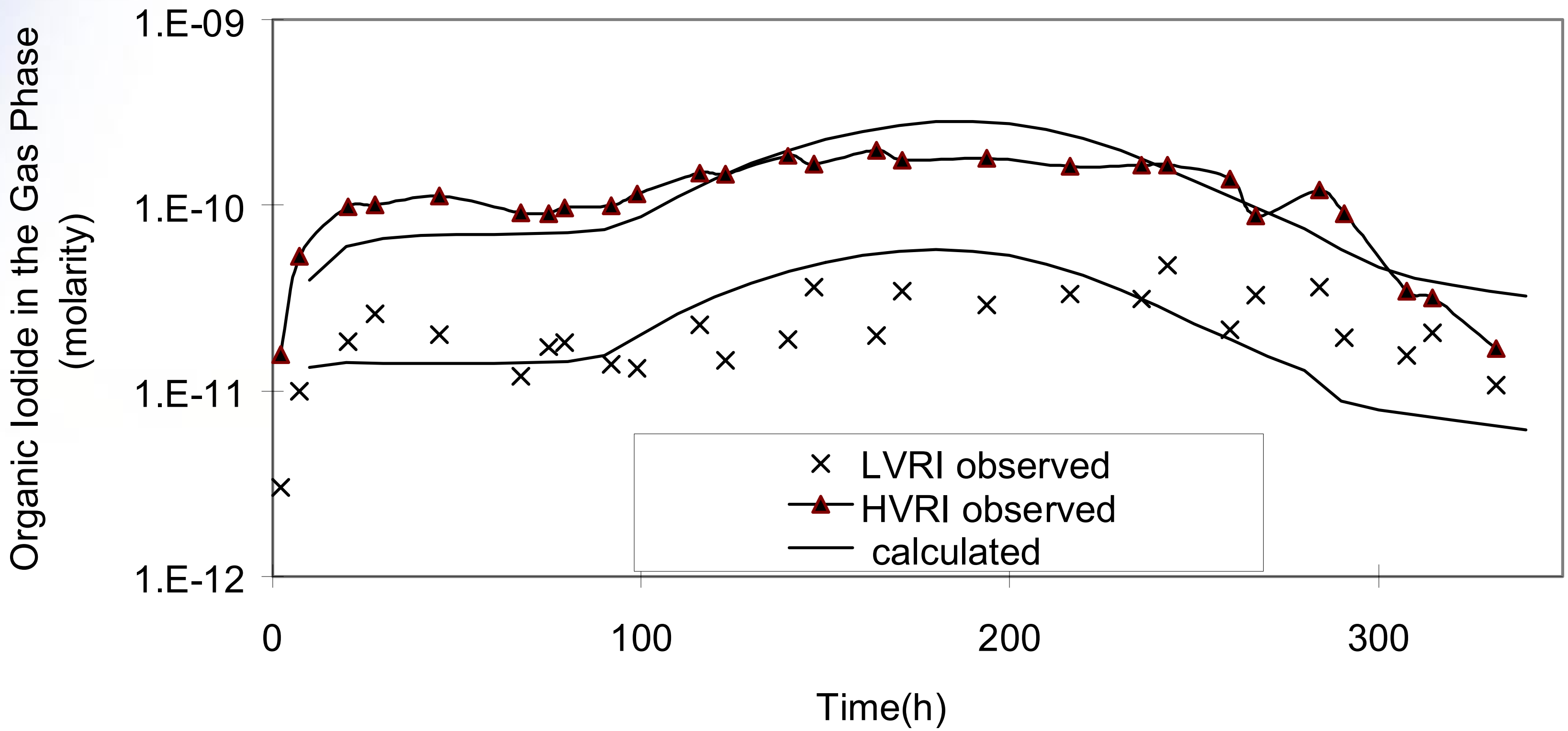
IMOD Simulations of an RTF Test
(10^{-5} M CsI, 60°C, 0.6 kGy/h, Epoxy painted vessel)

[I(g)]



IMOD Simulations of an RTF Test
(10^{-5} M CsI, 60°C, 0.6 kGy/h, Epoxy painted vessel)

[HVRI(g)] and [LVRI(g)]



Summary

- AECL's integral approach has contributed significantly to understanding of iodine behavior in containment
  - Mechanistic approach based on fundamental understanding coupled with validation tests
- AECL has robust models (IMOD-2 & LIRIC 3)
  - Models & their components (sub-models) have solid bases
  - Well validated
  - High confidence, Low uncertainty
- The results are highly relevant to Severe Core Damage Accidents
  - Safety analysis
  - Accident management

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