

Iodine Behavior Within Confinement

Advanced Containment Experiments Extension (ACEX) Project

Technical Report

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REPORT SUMMARY

Release of radioactive iodine during a severe reactor accident could have serious public health implications. This report summarizes research conducted by the Advanced Containment Experiments (ACE) Project on the behavior of iodine within reactor containment and integrates the results into computer codes that model this behavior.

Background

The ACE Project sponsored several experiments to measure the behavior of iodine within reactor containment, but the results of these studies were not fully factored into the models and computer codes used to simulate such behavior. With the support of 15 international participants, EPRI organized the ACE Extension (ACEX) Project to assess the available data, to use it to validate existing computer codes, to formulate additional models and codes, and to support limited new measurements, thereby achieving an international consensus on the behavior of iodine within containment.

Objective

To summarize the ACEX Phase B work on the behavior of iodine within containment.

Approach

The project team reviewed the available ACEX reports and summarized the work and results.

Results

The ACEX Project enlarged the ACE experimental database and generated many useful improvements to the models for iodine behavior within containment. The project had five objectives: quantifying the effects of organic reactions, quantifying the effects of structural surface interactions, standardizing the aqueous iodine data base, specifying useful mass transfer models, and defining a methodology for pH prediction. The Project achieved closure on almost all issues. Important phenomena are now understood sufficiently to recommend either semi-mechanistic models or experiments that would lead to empirical models. The principal iodine sinks have been identified and, in most cases, the models or data needed to evaluate their stability have been specified. However, resources were insufficient to fully resolve issues relating to the prediction of organic iodine speciation.

EPRI Perspective

During a postulated severe reactor accident, the release of radioactive iodine would be a major contributor to public health consequences. An adequate understanding of iodine behavior within containment allows not only an accurate prediction of such consequences but, more importantly, provides the basis for accident management to minimize the release magnitude. The ACEX Project has largely achieved an international consensus on the understanding of iodine behavior within containment. Existing iodine behavior models are successful in predicting inorganic iodine speciation and volatility for specified aqueous pH conditions. However, the complication arising from the presence of organic materials has not been fully resolved, and a lack of resources prevented development of a pH calculation model for BWR systems.

Keywords

Radioiodine Nuclear containment Nuclear aerosols Iodine chemistry

ABSTRACT

The Advanced Containment Experiments Extension (ACEX) consortium, representing 15 organizations from 12 countries, assessed available data on iodine behavior within containment, including data generated by the previous ACE consortium. ACEX used this information to validate existing models and computer codes and to develop new ones. The consortium also supported limited new measurements. As a result of this work, the ACEX consortium has achieved an international consensus on the understanding of iodine behavior. This report summarizes 10 reports, which provide the detailed results and presents the main conclusions of the project.

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CONTENTS

1 INTRODUCTION	. 1-1
2 BACKGROUND	. 2-1
3 QUANTIFYING THE EFFECTS OF ORGANIC REACTIONS	. 3-1
4 QUANTIFYING THE EFFECTS OF STRUCTURAL SURFACE INTERACTIONS	. 4-1
5 AQUEOUS IODINE KINETICS DATA BASE	. 5-1
6 SPECIFYING INTERFACIAL TRANSFER MODELS	. 6-1
7 METHODOLOGY FOR pH PREDICTION IN PWR SUMP WATER DURING SEVERE ACCIDENTS	. 7-1
8 DISCUSSION AND CONCLUSIONS	. 8-1
9 REFERENCES	. 9-1
A LIST OF ACEX-B REPORTS	.A-1

1 INTRODUCTION

The Advanced Containment Experiments (ACE) Project was organized by EPRI and was sponsored by an international consortium consisting of twenty-one sponsors. It consisted of four phases important to the understanding and management of postulated severe accidents in Light Water Reactors as follows:

- Phase A Measurement of the efficacy of eight filtration devices proposed for containment venting to remove fission product aerosols.
- Phase B Measurement of the behavior of iodine during several interactions within containment.
- Phase C Measurement of the release of low volatility fission products and the ablation of concrete during molten corium concrete interactions (MCCI).
- Phase D Measurement of the heat transfer rates from molten corium to an overlying layer of water during molten corium concrete interactions (MCCI) and hence, a determination of the coolability of molten corium in the event of a postulated severe accident.

The ACE Project generated a large body of data on the above subjects. The information was intended to provide testing and validation of models in computer codes that are used for the analysis of severe accidents. However, since ACE was conceived to be primarily an experimental project, there was a minimum amount of model development and assessment, and reliance was placed on analysis by participants. The Advanced Containment Experiments Extension (ACEX) Project was intended to increase the value of the ACE data to the reactor safety community through a well-coordinated, systematic effort aimed at its interpretation, analysis, and use.

Many of the ACE sponsors plus some new ones sponsored the ACEX Project. The sponsors were: Tractebel, Belgium; Ontario Power Group, Canada; Valtion Teknillinen Tutkimuskeskus (VTT), Finland; Institute de Protection et de Surete Nucleaire (IPSN), France; Gesellschaft für Reaktorsicherheit (GRS), Germany; Agenzia Nazionale per la Protezione della'Ambiente (ANPA) and ENEL S.p.a. (ENEL), Italy; Japan Atomic Energy Research Institute (JAERI), Japan; Unidad Electrica, S. A. (UNESA), Spain; Vattenfall, Sweden; Paul Scherrer Institute (PSI), Switzerland; Nuclear Electric, United Kingdom; and Depatrtment of Energy, EPRI, and U.S. Nuclear Regulatory Commission, United States of America.

Introduction

A Project Board, consisting of representatives from each co-sponsor, guided the project. A Technical Advisory Committee (TAC), consisting of specialists from each country, provided technical oversight. The TAC provided valuable technical input to the EPRI staff, which managed the work.

The total funding over a four-year period was approximately \$2.4 million. The Project Board directed its expenditure to be distributed: 10% for Pool Scrubbing, 30% each for Iodine, molten corium concrete interactions (MCCI), and Coolability. This report is a summary of the iodine work and results. The work was done concurrently at several different laboratories over a period of approximately four years.

2 BACKGROUND

The ACE Phase B experiments [1] on iodine behavior observed that:

- 1. Iodine volatility is essentially independent of which iodine species, viz. elemental iodine, cesium iodide, methyl iodide, was initially present. This finding showed that the chemical system is reasonably well behaved with strong driving forces for reaching equilibrium. Thus, initial speciation does not have to be an experimental parameter nor a particular concern in iodine model development.
- 2. In the presence of a strong radiation field, total iodine partition coefficients are very sensitive to the aqueous phase pH. Under alkaline (pH = 8-9) conditions, overall iodine volatility is low, levels of organic iodine species are low even when epoxy paint is present, and iodine concentrations on vessel surfaces are low. Under acidic (pH = 4-6) conditions, the converse is true. Accident management should strive to establish and maintain alkaline conditions within containment.
- 3. During hydrogen combustion, contrary to dry conditions, modest steam partial pressure prevented decomposition of the iodide during and after energetic deflagrations.
- 4. The presence of reactive aerosols within containment vessels at gram/cubic meter concentrations is a very effective sink for both HI and I_2 such that these iodine species, which may exist as vapors initially, soon behave as particulates. Since the transport properties of particles are different from those of vapors, this finding has important implications for models or computer codes, which seek to predict the time-dependent behavior of iodine within containment during severe accidents.

ACE Phase B concluded that iodine models and computer codes needed more development and testing against measurements in order to treat additional phenomena and to produce more uniform and accurate predictions of key experiments. In particular, the iodine specialists agreed that considerable uncertainty exists about how to model organic compound interactions and how the various surface (wet and dry) interactions should be treated.

Following ACE-Phase B, there was general agreement among iodine specialists that enough data had been accumulated to support reasonably good quantification of the important phenomena in a number of areas, e.g. the effect of aqueous pH, ambient radiation, inorganic reactions, initial iodine speciation, reactive bulk aerosols, temperature. Most of these phenomena are incorporated to varying degrees in the existing computer codes that are used to calculate iodine behavior in containment vessels.

Background

A consistent observation about gaseous iodine species within the TMI-2 containment and the ACE large-scale CSTF experiments [2] was that organic iodides were the predominant long-term species. The ACE-RTF experiments [3] further showed that there was significant decomposition of organics by radiolytic processes. There are many sources of organic materials in a reactor containment building. Sump water samples from Canadian reactors have been analyzed and found to contain a wide variety of organic chemicals, and a study [4] of German reactors showed a wide range of organic contaminants in the ventilation exhaust stream. Likely sources of these materials are constituents in paints, coatings, insulation, seals, gaskets, connectors, ion-exchange resins, lubricants, etc. One large source may be from electrical cable insulation and jacket materials, made mostly of ethylene propylene rubber, hypalon, and neoprene. Most organic materials are degraded by aging and by the effects of radiation, which causes organics to be released to both the aqueous and gaseous phases.

The effects of radiolysis in the aqueous environment and subsequent organic iodine behavior are still not well understood. Organic iodides are seen to dominate the gaseous iodine species within a reactor containment building in the long term, but no models exist that provide an adequate quantification nor reasonable mechanistic explanation for their occurrence. Whether surface, solution, or gas phase reactions dominate remains contentious.

Within the context of the above observations, the ACEX-B iodine chemistry project established the objective of achieving an international consensus on current understanding in five areas of uncertainty: (a) quantifying the effects of organic reactions, (b) quantifying the effects of structural surface interactions, (c) standardizing the aqueous iodine data base, (d) specifying useful mass transfer models, and (e) defining a methodology for pH prediction.

3 QUANTIFYING THE EFFECTS OF ORGANIC REACTIONS

As a consequence of the perceived importance of volatile organic iodide formation to reactor siting, extensive experimental programs were performed during the 1960s and 1970s to develop quantitative guidelines for predicting organic iodide formation in loss-of-coolant accidents. Most of this work focused on elemental iodine as being the dominant form released to the containment in such accidents. Models and correlations were derived and some were used in siting evaluations.

Since the TMI-2 accident, experimental work on iodine behavior in containment has focused on cesium iodide (CsI) as being the dominant released form. This highly soluble salt would be expected to readily contact and dissolve in available containment water volumes. Separate effects and integral tests performed in the 1980s and early 1990s have produced a sizeable body of data concerning the stability of these aqueous solutions (and iodine volatility) in accident environments including the effects of radiation, temperature, chemical additives, structures, and the presence of organic coatings/components.

The ACEX Project did a critical assessment (TR-B-04) of the above information to identify important reaction processes, to evaluate the possible impact that organic substances present in containments will have on iodine behavior, and to support recommendations for modeling improvements and associated testing. The assessment suggests that radiolytic processes in the aqueous phase will play the most important role in determining iodine behavior in an accident because: (a) the concentration and total inventory of iodine will be significantly higher in the aqueous phase than in the gas phase, (b) the concentration of ionizing radicals resulting from radiation absorption will be greater in the aqueous phase than in the gas phase, and (c) the concentration of organic impurities in the aqueous phase could be orders of magnitude higher than in the gas phase.

The assessment identified a number of potential sources of organic compounds within containments and concluded that the water soluble components of paints will probably have the greatest impact on iodine behavior because they can:

- 1. undergo radiolytic oxidation to organic acids, thereby decreasing solution pH and O₂ concentrations; conditions which favor higher concentrations of I, via oxidation of I
- 2. react with OH radical, thereby competing with the oxidation of I to I,, or
- 3. form organic iodides by radiolytic or thermal reactions whose impact on iodine volatility will be dependent on whether the species are more or less volatile than I_2 .

The primary route for organic iodide formation is by reaction of organic radicals with I_2 . Thus, the rates and amounts of organic iodide formed are almost entirely dependent on the rate and amount of aqueous I_2 formed. Accordingly, organic iodides should represent only a fraction of the volatile iodine species formed in the aqueous phase. With respect to organic iodide formation, this assessment concluded that: (a) there are no available mechanistic models except for the simple hydrocarbon CH_4 , and (b) existing empirical models are inadequate due to the past lack of understanding about the relationship between their formation and organic radiolysis, pH, and I_2 reaction kinetics. It also concluded that the complexity involved in organic iodide formation precludes the development of a fully mechanistic model for the process, but that it should be possible to use existing information to formulate a pilot approach. Such a trial model must address the following issues:

- 1. Organic iodide formation by aqueous phase processes, which may include wetted surfaces.
- 2. Dependence of organic iodide formation on organic concentration, dose-rate, I_2 concentration, dissolved oxygen concentration, and pH.
- 3. Formation of organic iodides more complex and less volatile than methyl iodide.
- 4. Changes in the aqueous phase and in the subsequent redox behavior of iodine, which will be induced by organic radiolysis.

Two separate but similar semi-mechanistic approaches, extrapolated from an existing model for CH_4 and I_2 reaction kinetics and satisfying the above criteria, were recommended for consideration. One approach consisted of a generalized set of reactions, which model the rates of organic iodide formation and destruction by both radiolytic and thermal processes in an aqueous medium. The second approach consisted of a larger set of more specific reactions for modeling the same phenomena. In each approach, steady-state assumptions can be applied to simplify the resulting expressions so that controlling variables can be identified and tested. The testing process requires data from separate effects and integral experiments, some of which is available and some of which must come from new work. The necessary new experiments to support this effort were specified and are incorporated in the recommendations of a panel of international experts that was convened at an ACEX Iodine Experts Review meeting. They recommended further work on four subjects as follows:

- OR1 Evaluate and establish the dissolution kinetics of organic solvents from vinyl, epoxy, and polyurethane painted surfaces as a function of temperature to determine the types and amounts of organic compounds released from containment paints.
- OR2 Evaluate the radiolytic decomposition of organic compounds as a function of radiation dose, iodine and dissolved oxygen concentrations, and concentration of organic compounds to determine the H^{\dagger} and organic iodide production yields.
- OR3 Evaluate hydrolysis rates and partition coefficients of organic iodides as a function of temperature to provide data that can be used as a technical basis for organic iodide grouping and can be used for organic iodide model development.
- OR4 Evaluate semi-empirical models for the impact of organic reactions on volatility, pH change, and organic iodide production with an objective of selecting a generalized model that can predict pH, volatility, and organic iodide production yields as a function of a manageable number of parameters. Assembling and evaluating a data set for model validation, based on existing data and that generated from the previous sub-tasks.

ACEX-B only had resources to complete sub-tasks OR1 and OR3. The dissolution of solvents from paints was measured by immersing painted coupons in water within a sealed vessel. The coupons received under- and top-coats of paints typically used in PWR and CANDU containments. In addition to paint type, the experimental design examined the effects of pre-irradiation of the coupons, pH, coating thickness and surface/volume ratio, aging, and temperature. To enlarge the database, the ACEX-B experiments were aggregated with some earlier experiments sponsored by the CANDU Owners' Group. [5, 6] The measurements showed that:

- 1. for a given paint containing various solvents, the release rate was independent of the nature of the solvent, pre-irradiation, and pH of the water,
- 2. the release rate did depend somewhat on the paint type, but rate constants for release of a given solvent from different paints were within a factor of 2 to 3,
- 3. the release rate for solvents from all of the paints could be described by using a first-order kinetic model,
- 4. the pseudo first-order rate constant for release was dependent on paint thickness and temperature, whereas the total amount of solvent released depended primarily upon paint thickness and age, and
- 5. the solvent release process is governed by the rate of absorption of water by the coupons, a process that is controlled by Fickian diffusion.

Based upon the measurements, a model for solvent release was formulated and is reported in ACEX-TR-C38.

Models to predict the production and state of volatile iodine species during a potential reactor accident need information about the partition of organic iodides between the aqueous and gaseous phases, and about their hydrolytic conversion to non-volatile iodide ions. Available measurements of these phenomena were analyzed to estimate partition coefficients and hydrolvsis rate constants. Given the large number of organic iodides expected to be present within containment, it is unfeasible to account for and to model the unique characteristics of each one. Measured partition coefficients and hydrolysis rates were reviewed in order to provide guidelines on how to contend with the expected diverse mixture of organic iodides. Most organic iodides will be much less volatile than I₂. These less volatile organic iodides, as well as highly volatile organic iodides, must be considered during the calculation of total gas phase iodine. Based upon their partition coefficients relative to elemental iodine, organic iodides were divided into two groups; high and low volatility. Hydrolysis of organic iodides has an extremely wide range of rates but, based upon their rates, they can be effectively divided into two groups; primary and secondary organic iodides. These groupings can be combined into a 2×2 matrix creating four classes of organic iodides. If further simplification is desired, these four groups can be further reduced into two groups based upon volatility only. Partition coefficients and hydrolysis rate constants for both four and two groups are stated in ACEX-B-C39. The report also presents a generic rate equation, which describes the rate of radiolytic decomposition of organic iodides.

4 QUANTIFYING THE EFFECTS OF STRUCTURAL SURFACE INTERACTIONS

It has been known for many years that surface reactions are potentially important in the behavior of iodine in a reactor containment following a Loss of Coolant Accident (LOCA), and there has been much experimental work on surface reactions by many groups. More recently, in the ACE RTF experiments, [3] solutions of CsI were irradiated in epoxy painted vessels and steel vessels. The results from this consistent set of integral tests in a reasonably large-scale facility have emphasized the importance of surfaces. In tests where a significant amount of I_2 was formed, a substantial fraction of the total iodine inventory was deposited on surfaces in contact with the gas phase in stainless steel vessels and ones with epoxy painted surfaces. When modeling studies were performed to simulate these tests, there was agreement on the importance of surfaces but modeling of specific processes was one of a number of aspects of these tests, which required further work. This task of the ACEX program had three objectives:

- 1. Review the literature on iodine reactions with painted surfaces and with steel.
- 2. Suggest candidate models to simulate the reactions.
- 3. Review the need for further work.

Before summarizing the work, it is worth restating the likely conditions within containment and some possible surface reaction pathways. Following a LOCA, there will be hot water pools and substantial quantities of steam. If the safety features work properly, the sprays will have activated. Thus, at least initially, almost all surfaces will have water films caused by condensation and sprays. If adsorption at a surface occurs followed by chemical reaction with steel to produce FeI₂ and there is a water film present, the product could dissolve in the water and be returned to the sump, so that the surface has acted as a reductant towards I₂. The effect of this process on the gas phase iodine concentration will depend on the relative rates of volatilization from the sump, and transfer and reduction at the walls. Similar arguments would apply to a painted surface where the reaction will almost certainly form organic iodine, possibly with the co-formation of Γ , which could redissolve. At elevated temperatures, the organic iodine may readily hydrolyze to iodide.

With respect to iodine reactions with painted surfaces, there are comprehensive measurements of deposition velocities for Γ and I_2 from solution and for I_2 from the gas phase for a range of paint types. There is a large amount of data for dry surfaces but virtually no information on chemical reactions. The presence of an aqueous film or bulk water can have a significant influence on the behavior; some groups observed that reaction occurs at a painted surface followed by release into solution of some of the iodine as iodide; the amount transformed is probably temperature dependent. There is little information in the literature on the effects of radiation on iodine

reactions. Four models were posited in TR-B-06 representing increasing degree of complexity. Of these, the one including deposition and desorption with chemi- and physi-sorption steps was recommended for further development and validation against experiments. These experiments should include measurements of iodine absorption by wet paints, with and without a radiation field.

With respect to iodine reactions with steel surfaces, there is extensive literature, cited in TR-B-06, for high temperatures expected in the primary coolant system, but very little information for conditions expected within containment, viz. <150 C and high humidity. Many measurements show deposition velocity decreases with temperature, which suggests that any deposition/desorption model must be able to simulate the effects of temperature. From a range of possible models, one involving five reaction steps was recommended in TR-B-06. Validation of this model would require further measurements of gaseous I₂ reactions with steel at temperatures <150 C as a function of relative humidity, I₂ loading concentration, and oxygen concentration. Experiments are also needed to establish the temperature dependence and reaction kinetics of aqueous I₂ with steel for temperatures <150 C.

Following the above recommendations, the ACEX program sponsored additional measurements, described in TR-C41, of iodine deposition on painted surfaces and steel under containment conditions, viz. <150 C and humidity. Deposition velocities of I_2 with paint were found to be dependent on I_2 concentration, temperature, and humidity, with deposition at 100 C and high humidity being close to mass transfer controlled in containment conditions. Paint shows a relatively high capacity for iodine under these conditions. I_2 also appears to react in solution with a solute derived from paint but the reaction was too fast to measure. The measurements of iodine deposition on steel were not particularly reproducible. It was found that the deposition velocity is dependent on iodine concentration but only weakly dependent on temperature and humidity. The surface capacity of steel for I_2 showed significant temperature dependence.

A prime objective of this work was to validate the previously proposed model. Such validation was not feasible for steel given the scatter of data, although the slight negative temperature dependence of the deposition velocity can be rationalized. It was possible to fit the data with 'limited sites' model but this is of little use. Similar comments apply for painted surfaces. However, in this case, since the capacity of paint for I_2 is relatively large, a simple deposition velocity assuming a mass transfer limit is probably the best approach. A general-purpose model to represent all paints of all ages is unlikely to be justified.

It was concluded that further work on iodine reactions with surfaces is unlikely to be justified apart from academic study of underlying mechanisms, particularly for steel reactions.

5 AQUEOUS IODINE KINETICS DATA BASE

In the event of a severe accident, fission product iodine would be released from the reactor fuel into the coolant water primarily as non-volatile iodide, which can be oxidized to volatile forms by reactions with radiolysis products of water. Computer models are used in reactor safety applications both for predictive purposes and to understand the factors controlling iodine behavior under accident conditions. Despite their complexity, mechanistic models are preferred since, by representing the important kinetic processes with chemical equations and their rate constants, they can be used with some confidence outside the range of conditions against which they were tested. During the past 15 years, two mechanistic models with generally the same iodine reaction sets have been developed: INSPECT (IodiNe SPECiation and Transport) [7] by AEA Technology, and LIRIC (Library of Iodine Reactions in Containment) [8] by AECL. They both use a comprehensive data set of respectively about 200 and 300 chemical reactions compiled from literature values. Of these, 80 or more apply specifically to reactions of inorganic iodine species within the aqueous phase. As part of this task, the models and their recommended iodine reaction sets will be compared later in this section.

One disadvantage of using complex models incorporating large numbers of reactions is that it is difficult to appreciate which reactions are the most important for the conditions of interest and, thus, to make judgments about which uncertainties in the kinetic data have a significant impact on the models' predictions. This ACEX-B task, by doing sensitivity analyses, showed that the sizes of the INSPECT and LIRIC reaction sets could be substantially reduced without loss of accuracy.

For the INSPECT model, an examination of the full inorganic iodine reaction set showed that most reactions were not important for the accident conditions of interest and that 25 reactions should be adequate. Predictions of the full and reduced reaction sets were compared to data from sparging experiments. [9, 10] In all cases, it was found that the reduced reaction set produces results, which are close to, or indistinguishable from, the full inorganic iodine reaction set. This agreement provides confidence that the reduced set contains all of the important reactions for modeling the test conditions.

For the LIRIC 3.1 model, an examination of the full inorganic iodine reaction set showed that most reactions were not important for the accident conditions of interest and that 21 reactions should be adequate. The reduced reaction set model was named LIRIC-RED 1.0. Predictions of the full and reduced reaction sets were compared to data from RTF experiments [11] It was found that predictions by LIRIC 3.1 and LIRIC-RED 1.0 were graphically indistinguishable. This agreement provides confidence that the reduced set contains all of the important reactions for modeling the test conditions.

Aqueous Iodine Kinetics Data Base

Finally, the reduced reaction sets for INSPECT and LIRIC were compared to RTF experimental data and agreement was sufficiently close for reactor safety applications. The main difference between the reduced LIRIC and reduced INSPECT models is that the former includes the extra reaction of H_2O with Fe⁺⁺. When this reaction is incorporated into INSPECT, there is very good agreement between the two models; further modification is not warranted.

The inorganic iodine reaction sets in INSPECT and LIRIC have been reduced to a number of key reactions which simulate most of the key processes but which are no longer a comprehensive description of iodine chemistry. The reduced reaction sets should be appropriate for the description of inorganic iodine in reactor containment, but care should be taken with its application, for example:

- 1. Reactions between iodine and organic material are not part of the reduced set. They require additional reactions, which are the subject of Section 3.
- 2. Appropriate mass transfer rates should be chosen for specific conditions such as sump or blow-down aerosol, and reactions with surfaces,
- 3. Care should be taken in application of the LIRIC reaction set to continuously de-aerated solutions, but the set may be used for inert atmosphere applications, as long as oxygen is not continuously removed from solution, and
- 4. The reaction sets should not be used without suitable modification to simulate experiments where, for example, N_2O has been used.

6 SPECIFYING INTERFACIAL TRANSFER MODELS

The airborne iodine concentration within containment is determined by a combination of (a) chemical kinetics, and (b) interfacial transfer rates. Thus, an ability to predict interfacial transfer rates within containment is important. Following an accident, interfacial transfers may occur between structural surfaces, the gaseous, and the aqueous phases, e.g. pool, water droplets, falling films. A knowledge of interfacial transfer rates is also important to interpreting results from medium- and large-scale experiments. In such experiments, airborne iodine concentrations are usually the most reliable measure of iodine volatility, yet the theoretical understanding of the underlying chemistry relates to the aqueous phase. A proper knowledge of the rate of interfacial transfer provides the critical link between these measurements and the underlying theory. The objective of this task was to evaluate and, if possible, improve the ability to estimate interfacial transfer rates within containment. There were two sub-tasks: a review and compilation of the relevant correlations and understanding of mass transfer across air-water interfaces, and an interpretation of this understanding in relation to the effects of structural surface interactions, whose quantification was described in Section 4.

Based upon the information compiled and reviewed by this work, including comparisons to ACE-B measurements in the RTF facility,³ it was concluded that the liquid and gas phase mass transfer coefficients were reasonably well defined for droplets, falling films, and shallow weakly mixed pools, but less so for deep quiescent pools. It was also concluded that most of the parameters required in order to calculate mass transfer rates, such as diffusion coefficients, partition coefficients, fluid viscosities, and densities, are readily available or can be accurately estimated for the 25 to 150 C range of interest. The partition coefficients of the volatile iodine species are reasonably well established although some uncertainty remains with respect to iodine atoms at temperatures other than 25 C.

Accordingly, it was recommended that further detailed work, described in TR-B-05, was not justified on most issues. The only issue meriting further work concerned the potential for rapid thermal or radiolytic reactions to enhance the liquid mass transfer coefficients for volatile iodine species. However, the potential impact of this phenomenon is constrained by the limitations in the gas phase mass transfer rate. Therefore, further work by the ACEX-B program was not recommended.

7 METHODOLOGY FOR pH PREDICTION IN PWR SUMP WATER DURING SEVERE ACCIDENTS

During a postulated severe accident, iodine released from the fuel is initially a vapor and then in an aerosol such as CsI. In a PWR, it is transported through the reactor coolant system (RCS) and the containment atmosphere to the containment sump. CsI dissolves in the water to produce I and Cs⁺ ions. It has been shown that Γ is transformed by radiolysis to produce elemental iodine, which can interact with organic matter to produce organic iodine. These are volatile species that can be released from the sump into the containment atmosphere from where they are available for release to the environment. The transformation of Γ is a function of the acidity of the sump water, which means that, in order to estimate the gaseous iodine source term, the pH of the sump water must be ascertained.

During such an accident, in addition to the RCS, the containment sump would collect water from engineered safety systems, e.g. accumulator tanks, containment sprays, that contain chemical additives, e.g. boric acid, lithium hydroxide, sodium hydroxide. These chemicals are important in determining the pH of the sump water. This ACEX-B task (a) reviewed PWR design features to ascertain the likely concentrations of chemicals in the sump water, (b) reviewed the literature on estimating pH, and (c) recommended a methodology for estimating pH. In addition, some bench-scale experiments were performed to measure partition coefficients as a function of pH under radiation and in the presence of painted surfaces. Resources were insufficient to support a parallel task for BWRs.

The study focused on the French 900 and 1300 MWe PWRs. It concluded that the Swedish Ringhals plant, a Westinghouse design, was very similar. During normal operation, reactor power is controlled by adjusting the concentration of boron in the water of the reactor coolant system, whose pH is controlled by adding lithium hydroxide (LiOH). As the boron concentration changes, the concentration of LiOH is adjusted to maintain a constant pH of 6.9. The water in the engineered safety features also contains boron. When the containment sprays are activated, sodium hydroxide is added to the water to prevent the formation of crystals in the system, by making it alkaline. Finally, in the event that molten fuel interacts with the concrete basemat, many other chemicals would be released and transported to the containment sump.

As stated earlier, many experiments ¹ have shown that the pH of the sump water has a strong influence on the formation of volatile iodine species. By using information on the design of these systems and the chemical compositions of the materials, the study developed a methodology for estimating the pH of sump water. The model is described in TR-B-03. It accounts for the sources of sump water and the chemical additives that are used as discussed earlier. It also accounts for two potential acid sources: generation of nitric acid from radiolysis of containment air, and carbon dioxide produced from extended interaction of molten corium with carbonate-rich

Methodology for pH Prediction in PWR Sump Water During Severe Accidents

concrete basemat material. During the initial stages of an accident, the sump water would be alkaline. Without containment sprays, the pH can soon become quite acidic with values in the range of 3 to 4 depending upon the amount of nitric acid formation. With activation of containment sprays, the pH would become strongly alkaline (pH of 8.6) and nitric acid formation is insufficient to produce any significant change. Carbon dioxide generation from extended corium-concrete interaction can reduce the sump water pH but the process is gradual and appreciable CO_2 partial pressures are needed to cause an unit decrease in pH. It should be noted that there are other potential sources of acid that are not considered in this model; probably the most important is the formation of organic acids from radiolysis of dissolved organic solvents. However, the model provides a good starting point, and this feature can be added when an adequate sub-model is available.

Seventy-eight bench-scale experiments were performed at Cadarache, France, to measure the production of elemental iodine by radiolysis as a function of pH. CsI was dissolved in water containing boric acid and lithium hydroxide to simulate PWR sump water and subjected to a total radiation dose of 22 Mrad. As stated in the following table, the percentage of initial iodine inventory converted into elemental iodine decreased significantly as the pH increased:

pH of water	5.0	6.4	8.2
% converted to I_2	60	12	2

Coupons coated with epoxy paint typical of French PWRs were placed in the gas and aqueous phases. It was found that the fraction of the initial Γ inventory deposited on the paint was inversely proportional to the pH of the solution, viz. as the pH increases, the deposition fraction decreases. This effect is obviously directly related to the effect of pH on the formation of I₂. A major finding of these experiments was that, in all cases, the epoxy paint was very effective in trapping the elemental iodine.

When the painted coupons were present, the volatile iodine, I_2 plus organic iodides, remaining in the aqueous and gaseous phases as the percentage of initial iodide inventory decreased significantly as the pH increased as stated in the following table:

pH of water	5.0	6.4	8.2
% I_2 plus organic iodides	<4	<2	<0.1

From the viewpoint of safety, these results are extremely important and should be confirmed for higher temperatures (than 43 C), which are more representative of accident conditions. If pH control is effective in maintaining the pH value above neutral, very little of dissolved iodine will be converted into elemental iodine.

8 DISCUSSION AND CONCLUSIONS

The ACEX-B project enlarged the ACE-B experimental database and generated many useful improvements to the models for iodine behavior within containment. The accomplishments may be summarized by section as follows:

- Sect. 3. Formulation of a model for release rates of organics from paint. Classification of and recommended correlations for partition coefficients and hydrolysis rate constants for organic iodides.
- Sect. 4. Compilation of existing data and generation of additional measurements for iodine reactions with painted surfaces and steel. Models for the reactions were formulated but the available data was either too scattered or irreproducible to validate them. It was concluded that further work on such reactions would be unjustified.
- Sect. 5. Demonstration that the inorganic iodine reaction sets in INSPECT and LIRIC could be reduced from ~80 to ~25 and still make adequate predictions of available measurements.
- Sect. 6. Compilation of data and correlations for mass transfer between air-water-structural interfaces. It was concluded that measurements of mass transfer coefficients are reasonably well defined and that data are available to estimate most of them. It was recommended that no further work be sponsored on this subject by ACEX.
- Sect. 7. Development of a model to estimate pH of sump water for PWRs. Additional benchscale radiolysis measurements of elemental iodine as a function of pH confirmed earlier experimental findings that maintaining high pH was important to minimizing airborne iodine within containment and potential accident consequences.

The ACEX Phase B project established the following criteria for closure of the issue of iodine behavior within containment: (a) models should predict the gaseous fraction of iodine and the dominant species to within an order of magnitude, (b) the main sinks for iodine and their stability should be known, and (c) important phenomena should be understood by providing reasonable mechanistic explanations.

These criteria have been fulfilled to varying degrees. For example, the important phenomena are now understood sufficiently to recommend either semi-mechanistic models or experiments that would lead to empirical models. The principal iodine sinks have been identified and, in most cases, the models or data needed to evaluate their stability have been specified. However, such evaluations have not been fully completed due to lack of resources or inadequate data. Existing iodine behavior models are successful in predicting inorganic iodine speciation and volatility for

Discussion and Conclusions

specified aqueous pH conditions. However, the complication arising from the presence of organic materials has not been fully resolved. Important new data on this issue were generated in response to the OR1 and OR3 recommendations of the ACEX Iodine Experts, but there were insufficient resources to act on their OR2 and OR4 recommendations. Lack of resources also prevented development of a pH calculation model for BWR systems. Barring unforeseen complications, performance of these remaining tasks should result in satisfying the first of the three iodine closure criteria.

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A LIST OF ACEX-B REPORTS

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TR-B-02	"Quantifying the Effects of Structural Surface Interactions," S. Dickinson, AEA Technology, J. C. Wren, AECL—Draft issued November 1995, final report subsumed into TR-B-06.
TR-B-03	"Methodology for the pH Prediction in PWR Sump Water under Severe Accident Conditions," V. Crutel, D. Maro, IPSN—Final issued December 1997
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