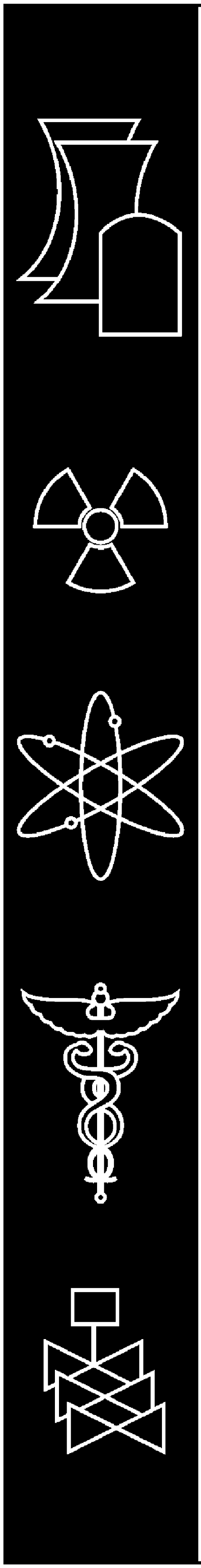
NUREG-1861



# Peer Review of GSI-191 Chemical Effects Research Program

U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Washington, DC 20555-0001

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**NUREG-1861**

# Peer Review of GSI-191 Chemical Effects Research Program

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**Prepared for**
**Division of Fuel, Engineering and Radiological Research**
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**Washington, DC 20555-0001**

# ABSTRACT

The U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Regulatory Research (RES), has a policy of initiating formal peer reviews for research programs that are on the cutting-edge of technology and will influence important regulatory decisions. Such is the case for the series of research projects that RES has sponsored to (1) resolve Generic Safety Issue 191, "Assessment of Debris Accumulation on PWR Sump Performance," and (2) inform the NRC's regulatory decisions regarding the potential for chemical byproducts to clog sump screens in the post-loss-of-coolant accident environment in pressurized-water reactors (PWRs).

This NUREG-series report describes the chemical effects peer review assessment process and summarizes its significant findings. It is important to mention that this peer review is not a consensus review. Each reviewer was asked to provide an individual evaluation based on his or her particular area of expertise. The research projects addressed by the peer review included integrated chemical effects testing (ICET) and ICET followup testing and analysis conducted at Los Alamos National Laboratory, chemical speciation prediction conducted through the Center for Nuclear Waste Regulatory Analyses at Southwest Research Institute, and accelerated chemical effects head loss testing conducted at Argonne National Laboratory. The chemical effects peer review evaluated the technical adequacy and uncertainty associated with the RES-sponsored research results, and identified outstanding chemical effects issues. The results of this peer review will support NRC staff audits and evaluations of industry responses to Generic Letter 2004-02, "Potential Impact of Blockage on Emergency Recirculation During Design-Basis Accidents at Pressurized-Water Reactors." The final assessment reports from the peer reviewers are included as appendices to this NUREG-series report.

# FOREWORD

The U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Regulatory Research (RES), has a policy of initiating formal peer reviews for research programs that are on the cutting-edge of technology and will influence important regulatory decisions. Such is the case for the series of research projects that RES has sponsored to (1) resolve Generic Safety Issue 191 (GSI-191), "Assessment of Debris Accumulation on PWR Sump Performance," and (2) inform the NRC's regulatory decisions regarding the potential for chemical byproducts to clog sump screens in the post-loss-of-coolant accident (LOCA) environment in pressurized-water reactors (PWRs). Chemical effects in the sump pool of a PWR represent a relatively new research area that has proven to be quite complex. Recognizing this complexity, RES decided that an independent peer review was necessary to assess the technical adequacy of the chemical effects research program and to help the staff identify outstanding chemical effects issues.

The chemical effects peer review group consisted of five members selected from industry and academia for their diversity in their affiliations and technical expertise. The technical areas reviewed were (1) the integrated chemical effects testing (ICET) and ICET followup analysis and testing conducted at Los Alamos National Laboratory, (2) chemical speciation prediction conducted at the Center for Nuclear Waste Regulatory Analyses, and (3) accelerated chemical effects head loss testing conducted at Argonne National Laboratory. The review group participated in kickoff and final meetings, which promoted discussion and enabled the members to exchange information and address questions. The members then developed individual preliminary reports addressing various questions that arose during the kickoff meeting, as well as individual final reports (provided as appendices to this NUREG-series report) that provided formal assessments of both prior and ongoing research activities.

Significant general findings from the peer review included (1) the ICET was representative and identified some important contributing materials and interactions; (2) the chemical speciation prediction study identified required capabilities and limitations of commercially available codes, and revealed that more rigorous code development is needed to develop an adequate assessment tool; and (3) the chemical effects head loss testing project revealed that smaller-scale testing should be conducted to allow more rapid evaluation, in parallel, so that more parameters can be identified and evaluated in several smaller loops, rather than one loop.

The peer review panel did an excellent job of engaging the NRC staff and contractors in discussing the research projects and sharing their insights. Their feedback has been especially valuable in improving our understanding of the mechanisms underlying development of chemical byproducts. This NUREG-series report captures those insights, and is expected to be helpful to the nuclear power industry as it considers changes to plant designs and operation toward the resolution of GSI-191. The information developed by the peer review group will also assist the staff of the NRC's Office of Nuclear Reactor Regulation (NRR) in evaluating licensees' responses to Generic Letter (GL) 2004-02.

Brian W. Sheron

Brian W. Sheron, Director
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission

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# ACKNOWLEDGMENTS

The author wishes to thank Argonne National Laboratory for providing the contractual support, hosting the chemical effects peer review kickoff meeting, and presenting and making available the technical information that the peer reviewers needed to complete their mission. The author also wishes to thank the Southwest Research Institute (SWRI) and the Center for Nuclear Waste Regulatory Analyses (CNWRA) for hosting the second chemical effects peer review meeting. In addition, the author wishes to thank SWRI, CNWRA, and Los Alamos National Laboratory for presenting and making available the technical information that the peer reviewers needed to complete their mission.

The author would also like to acknowledge Robert Tregoning for his technical guidance and leadership in discussions during the peer review meetings. Finally, the author would like to thank Ann Ramey-Smith, Robert Tregoning, and Bhagwat Jain for their advice and review of this report.

# ABBREVIATIONS

| | |
|---|---|
| ACRS | Advisory Committee on Reactor Safeguards |
| ANL | Argonne National Laboratory |
| Cal-Sil | Calcium Silicate |
| CNWRA | Center for Nuclear Waste Regulatory Analyses |
| ECCS | Emergency Core Cooling System |
| ECP | Electrochemical Corrosion Potential<br>[also known as Reduction-Oxidation (Redox) Potential] |
| EDO | Executive Director for Operations (NRC) |
| EDS | Energy Dispersive Spectroscopy |
| EPRI | Electric Power Research Institute |
| ESEM | Environmental Scanning Electron Microscopy |
| FTIR | Fourier Transform Infrared Spectroscopy |
| GL | Generic Letter |
| GSI | Generic Safety Issue |
| HPSI | High-Pressure Safety Injection |
| ICET | Integrated Chemical Effects Testing |
| ICP | Inductively Coupled Plasma |
| LANL | Los Alamos National Laboratory |
| LOCA | Loss-of-Coolant Accident |
| NPSH | Net Positive Suction Head |
| NRC | U.S. Nuclear Regulatory Commission |
| PZC | Point of Zero Charge |
| PSD | Particle Size Distribution |
| PWR | Pressurized Water Reactor |
| QLR | Quick Look Report |
| RCS | Reactor Coolant System |
| RES | Office of Nuclear Regulatory Research (NRC) |
| RHR | Residual Heat Removal |

| | |
|---|---|
| SEM | Scanning Electron Microscopy |
| STB | Sodium Tetraborate |
| SWRI | Southwest Research Institute |
| TEM | Transmission Electron Microscopy |
| TSP | Trisodium Phosphate |
| TSS | Total Suspended Solids |
| UNM | University of New Mexico |
| XRD | X-Ray Diffraction |

# SYMBOLS

| | |
|---|---|
| Al | Aluminum |
| $Al(OH)_3$ | Aluminum Hydroxide |
| $Al(NO_3)_3$ | Aluminum Nitrate |
| $Al(NO_3)_3 \times 9H_2O$ | Aluminum Nitrate Nonahydrate |
| $Al_2O_3$ | Aluminum Oxide |
| | |
| Ca | Calcium |
| $CaCl_2$ | Calcium Chloride |
| $Ca_3(PO_4)_2$ | Calcium Phosphate |
| Cu | Copper |
| | |
| $Fe_3O_4$ | Magnetite (Black Iron Oxide) |
| | |
| $H_2O_2$ | Hydrogen Peroxide |
| HCl | Hydrochloric Acid |
| $HNO_3$ | Nitric Acid |
| | |
| LiOH | Lithium Hydroxide |
| | |
| NaOH | Sodium Hydroxide |
| $NaAl(OH)_4$ | Sodium Aluminate |
| $Na_2B_4O_7$ | Sodium Tetraborate |
| $Na_3PO_4$ | Trisodium Phosphate |
| | |
| Zn | Zinc |

# 1. INTRODUCTION

## 1.1 Objectives

The principal objective of the chemical effects peer review group was to assess the technical adequacy of research activities, sponsored by the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Regulatory Research (RES), related to chemical effects in pressurized-water reactor (PWR) sump pool environments. Toward that end, the peer review members focused only on those programs in which RES is specifically evaluating chemical effects. A second principal objective was to have the peer reviewers recommend improvements to RES programs in the area of chemical effects, and to identify additional important technical issues that RES is not currently addressing. A third objective was to attempt to gain a theoretical understanding of the relevancy of these chemical effects in the post-loss-of-coolant accident (LOCA) environment. The final objective was to address specific questions from NRC staff, as described in Section 3 of this report. In so doing, RES hoped that the peer reviewers' comments and suggestions, together with their expertise in the various technical areas, would help the NRC staff to better understand these questions. In addition, it is important to mention that this peer review was not a consensus review. Rather, each reviewer was asked to provide an individual evaluation based on his or her particular area of expertise.

## 1.2 Description of Generic Safety Issue 191 and Chemical Effects Background

Generic Safety Issue (GSI) 191, "Assessment of Debris Accumulation on PWR Sump Performance," was established to assess the potential for transportation and accumulation of debris that is generated during a LOCA to impede or degrade emergency core cooling system (ECCS) performance in operating commercial PWRs. The ECCS is required to meet the criteria of Title 10, Section 50.46, of the *Code of Federal Regulations* (10 CFR 50.46), "Acceptance Criteria for Emergency Core Cooling Systems for Light-Water Nuclear Power Reactors." In particular, 10 CFR 50.46(b)(5) requires licensees to design their ECCS systems with capability for long-term cooling. That is, after successful initiation, the ECCS must be able to provide cooling to maintain the core at an acceptably low temperature for a sufficient duration.

In this report, "chemical effects" include corrosion products, gelatinous material, or other chemical reaction products that form as a result of the interaction between the PWR containment environment and containment materials following a LOCA. Reaction products or precipitates may be generated as a result of chemical reactions between ECCS recirculation sump fluid or containment spray fluid and exposed materials in containment, such as zinc in coating materials or galvanized steel, aluminum in scaffolding, thermal insulation and electrical or electronic materials, exposed carbon steel, concrete, fiberglass debris, and so forth.

In a meeting in February 2003, the NRC's Advisory Committee on Reactor Safeguards (ACRS) raised a concern based on its review of staff activities related to the resolution of GSI-191 (Reference 1). Specifically, the ACRS was concerned that chemical effects could significantly increase the pressure drop (or "head loss") across ECCS recirculation sump screen debris beds at a PWR. The ACRS stated that previous work related to GSI-191 did not consider the potential for chemical interactions between the cooling water and exposed materials within containment to generate new forms of debris with unique screen blockage characteristics, or to affect the head loss behavior of previously investigated debris types. To support this concern, the ACRS cited evidence including the gelatinous material discovered in the post-LOCA sump pool of the containment following the 1979 accident at Three Mile Island, Unit 2 (References 2 and 3).

In response to the ACRS concern that gelatinous substances or agglomerates could form and have the potential to affect head loss, especially in concert with other debris transported to the sump screen, a small-scale study of head-loss flow and quiescent immersion corrosion was performed at the University of New Mexico (UNM), under the direction of Los Alamos National Laboratory (LANL). The purpose of this study was to determine whether debris generation and sump screen head loss can be affected by chemical interactions between the ECCS recirculation water and exposed metal surfaces, inorganic zinc-based paint chips, and fiberglass insulation debris. This study is described in NUREG/CR-6868, "Small-Scale Experiment: Effects of Chemical Reactions on Debris-Bed Head Loss" (Reference 3), which assesses the potential for chemically induced corrosion products and chemical degradation effects to impede the performance of ECCS recirculation following a LOCA. In addition, NUREG/CR-6868 presents observations gleaned from scoping tests that were conducted to experimentally assess the degree of influence and the mechanisms by which water chemistry and temperature may influence the head loss characteristics of an ECCS sump screen following a LOCA in a PWR nuclear power plant. An independent expert review panel reviewed the NUREG/CR-6868 study, and recommended conducting a follow-on study involving integrated chemical effects testing of representative amounts of multiple containment materials in a simulated post-LOCA environment.

As part of the resolution of GSI-191, the NRC and the nuclear industry jointly developed an integrated chemical effects testing (ICET) program to determine whether chemical reaction products can form in representative PWR post-LOCA containment sump environments. The ICET series, conducted at UNM under the direction of LANL, involved five tests, each of which represented a different subset of expected post-LOCA environments within existing PWR plants (References 4–9). Results showed that chemical byproducts were present in the test solutions, fibrous insulation samples, and sediment of all five ICET environments, and some of these products were amorphous in nature. Inductively coupled plasma (ICP) results, for example, indicated that for Test #1, aluminum and sodium were present in the greatest concentrations in the test solution, while for Test #5, the highest concentrations were sodium, aluminum, calcium, and silica.

A follow-on study was conducted at LANL to provide a better understanding of the aluminum chemistry in post-LOCA PWR containment environments (Reference 10). More specifically, that study addressed the conditions for generating aluminum-based precipitates, characterizing properties and particle size distributions of those precipitates, developing surrogate precipitates and solutions, and determinating the adequacy of the surrogates by comparison to ICET-generated precipitates and solutions.

A second area of investigation involved chemical effects head loss testing conducted by Argonne National Laboratory (ANL). The objective of this research was to measure the head loss associated with simulated ICET environments, to improve our understanding of the effects of key environmental variables on chemical product formation and head loss (Reference 11). A third area of investigation involved a chemical speciation analysis performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) at the Southwest Research Institute (SWRI). This research involved analytical, thermodynamic simulation of the ICET series to predict the chemical species formed in those environments (Reference 12).

Given the significance of this issue, the NRC **has requested** all PWR licensees perform an evaluation of the potential for excessive head loss attributable to the accumulation of debris on the containment sump screen. Toward that end, Generic Letter (GL) 2004-02, "Potential Impact of Blockage on Emergency Recirculation During Design-Basis Accidents at Pressurized-Water Reactors," requests that licensees evaluate the maximum head loss postulated from debris accumulation (including chemical effects) on the submerged sump screen (Reference 13).

Chemical effects in the sump pool of a PWR plant represent a relatively new research area that has proven to be quite complex. Recognizing this complexity, RES decided that an independent peer review was necessary to review the technical adequacy of RES-sponsored research activities related to chemical effects in PWR sump pool environments. In addition to reviewing and commenting on the research that was underway, this external peer review group helped the staff identify and prioritize issues in the chemical effects arena.

The NRC has an aggressive resolution schedule associated with GSI-191. Toward that end, the staff will use information developed through the peer review effort in evaluating licensees' responses to GL 2004-02 and conducting audits to ensure appropriate resolution.

## 1.3 Peer Review Motivation

Following RES Office Instruction PRM-010 (Reference 14), "Peer Review of RES Projects," all RES programs and products are candidates for peer review. This includes programs conducted under contract, as well as research performed within NRC by RES staff members. A peer review is defined as a form of deliberation involving an exchange of judgments about the appropriateness of methods and the strength of the author's conclusion. Peer review occurs when a draft product is reviewed for quality by specialists who were not involved in producing the draft. Acceptable peer review can involve either NRC staff or specialists who are external to, and do not work for, the NRC. Peer review involves either one independent reviewer or a team of reviewers in which each member provides a final independent assessment, and the results of peer reviews are made publicly available.

The RES policy with regard to peer review groups is to encourage a formal and independent peer review of research products consistent with the nature, importance, and timeliness of the information to be disseminated. Peer review fosters confidence in the research products and helps maintain high standards of competence in research programs. It is expected that peer reviews will provide critical assessments regarding those research products, will help in judging the technical adequacy of the results for the proposed solutions, and can aid in bringing the widest and best available knowledge to bear on the quality of the research products. However, RES does not rely on peers to achieve resolution of technical issues. To the contrary, the NRC staff's technical expertise, leadership, and effective communications are vital aspects of the process of achieving resolution of technical issues.

External peer review is a recommended strategy for promoting broader understanding and context for issues that are technically complex, have potentially significant implications, span many technical disciplines, and are emerging within the agency. On the basis of those criteria, the RES staff identified the research on sump pool chemical effects as a logical peer review topic. There is little information on chemical product formation in representative plant sump environments. This is a new technical area of investigation, and it is sufficiently complex to warrant independent assessment and consultation. Moreover, the research conducted in the chemical effects arena could significantly affect the resolution of GSI-191. In addition, there is no clear idea of the appropriate approach and how applicable the results are in comparison with the three areas of investigation. Thus, RES believed that the peer review group members would help to improve our understanding of this issue by providing review comments, suggestions, and possible contributions for issue resolution. RES decided that an independent peer review was necessary to assess the technical adequacy of the chemical effects research program and to help the staff identify outstanding chemical effects issues.

## 1.4 Structure of this Report

The body of this NUREG-series report is divided into five sections:

- Section 1 defines the objectives of the chemical effects peer review group assessment, and provides related background information concerning GSI-191 and chemical effects, as well as the peer review and motivation.
- Section 2 describes the structure and approach of the peer review group (e.g., how the members of the group were selected).
- Section 3 describes each of three research areas, and summarizes the key findings of the peer review in each area.
- Section 4 presents a concluding statement, which summarizes the insights that emerged from the peer review, and discusses how those insights will be used.
- Section 5 lists the references cited in this report.

Finally, the five appendices that accompany this report present the final independent assessment reports from each of the five chemical effects peer review group members, as well as a more in-depth description of the motivation for this peer review.

# 2. PEER REVIEW STRUCTURE AND APPROACH

## 2.1 Peer Review General Approach and Information

The NRC established the chemical effects peer review group to evaluate the technical adequacy of RES-sponsored activities related to chemical effects in PWR sump pool environments. Toward that end, the review encompassed the integrated chemical effects testing conducted at LANL, chemical speciation prediction activities conducted at CNWRA, and chemical effects-accelerated head loss testing conducted at ANL. Because of the complexity of these programs, RES aimed to ensure diversity in both the members' affiliations and their technical expertise. Approximately 3–4 months were spent gathering recommendations for peer review candidates and assembling a group that spanned a broad range of affiliations and also had diverse technical expertise and experience.

To decide upon the final peer review group, RES considered recommendations from multiple sources, such as the NRC staff, the ACRS, the nuclear power industry, and NRC contractors who were conducting research in the chemical effects area. The selected chemical effects peer review group consisted of five members drawn from national laboratories, academia, and industry. These peer review group members possessed diverse backgrounds and expertise in areas such as gel formation, filtration, analytical and experimental chemistry, corrosion and metallic corrosion, experimental testing, nuclear waste, and electrochemistry. The intent was that the individual members would interact as a group and look at the chemical effects issues using a holistic approach. Each peer reviewer was asked to address a set of defined questions in the three program areas. The questions and responses are defined and anwered in Section 3 of this report. The NRC also provided the peer review group members with initial documentation relevant to the ongoing technical program areas. The formality of that documentation varied as a function of the program. This initial documentation included the following references:

- ICET Data Reports 1, 2, and 3 and the accompanying appendices (References 15–17)
- ICET Test Plan (Reference 18)
- ANL Quick Look Report: Tests 1 and 2 (Reference 19)
- CNWRA 2004-07 Report (Reference 20)
- NUREG/CR-6873 (Reference 21)

After providing the peer review members with the initial documentation, the NRC conducted a chemical effects peer review group kickoff meeting at ANL in October 2005. The purpose of that meeting was to summarize the initial technical documentation and identify the important technical issues and questions that the NRC wanted the peer review group to assess in its review. In addition, representatives of the various program areas from the national laboratories and nuclear power industry gave a number of oral presentations, which provided the latest technical information and research findings since the initial documentation was prepared. The meeting participants also discussed the plans and philosophy behind the ongoing NRC-sponsored research, identified additional information that the peer reviewers needed to complete their preliminary assessment, and planned the peer review group activities for the next several months.

The peer reviewers submitted their preliminary individual assessment reports in December 2005. The purpose of those reports was to provide an informal assessment of both prior and future research activities. The NRC intended that these preliminary assessment reports would identify any major deficiencies or course changes that the research programs should make at that time. The peer reviewers' preliminary assessment reports also included lists of follow-on questions to be discussed in the second chemical effects peer review group meeting. The NRC staff especially wanted the peer reviewers to raise technical questions regarding the need for additional information, so that the NRC staff could provide the needed information during the second peer review group meeting so the peer reviewers would have the information available to them as they prepared their final assessment reports.

The NRC staff subsequently summarized the results and recommendations of the reviewers' preliminary assessment reports, and organized the key points of each program area. The staff disseminated this summary of results and recommendations to LANL, CNWRA, and ANL for consideration, review, and action. Each research organization took the lead in addressing the issues and questions identified by the preliminary assessment reports corresponding to their technical area. This helped the NRC staff and the national laboratories to properly address the issues and questions from the peer reviewers.

After a thorough review of the preliminary assessments reports, the staff then distributed the preliminary assessment reports to the peer review group members. In so doing, the staff expected the peer reviewers to continue their detailed review of NRC activities to raise issues or concerns that arose subsequent to the preliminary assessments. Toward that end, the staff also provided the peer reviewers with new information regarding ongoing research activities. That information included the following followup technical documents:

- ICET Data Reports 4–5 and the accompanying appendices (References 11 and 12)
- ANL Quick Look Report: ICET-3 Tests 4–11 (Reference 22)
- CNWRA speciation draft NUREG/CR, "GSI-191 PWR Sump Screen Blockage Chemical Effects Tests: Thermodynamic Simulations" (Reference 1)

In March 2006, the NRC staff held a second chemical effects peer review group meeting at SWRI. The purpose of this second meeting was to provide the group members with new information regarding research activities conducted between October 2005 and March 2006. Toward that end, representatives from LANL, ANL, and CNWRA presented information relevant to their respective research areas and, along with NRC staff, addressed the peer reviewers' questions and clarified remaining issues that they raised in their preliminary assessment reports. Most importantly, this second meeting fostered interaction among the reviewers to support their final assessments. In addition, the NRC asked the reviewers to submit any additional requests for information before providing their final individual assessment reports.

In May 2006, the peer reviewers submitted their final individual reports, which provided formal assessments of both prior and ongoing research activities. All five of these final assessments are included as appendices to this NUREG-series report.

## 2.2 Peer Reviewer Selection and Qualifications

The NRC staff selected the peer review group members on the basis of their technical expertise, experience, skills, and affiliations. Characteristics such as discipline, point of view, diversity of experience, and type of institution played an important role in the selection process. As a result, the selected group of peer reviewers is sufficiently diverse to fairly represent the relevant scientific and technical perspectives and fields of knowledge needed to address the program areas of interest. Specifically, the staff initially identified the following technical specialties for the selection of the peer review group:

- gel/amorphous product formation and characterization
- analytical chemistry
- metallic corrosion processes
- experimental testing and analysis
- theoretical chemistry/speciation prediction
- industrial filtration processes
- fluid (e.g., water and wastewater) treatment processes
- manufacturing gels, chemicals, and insulation materials

In addition, to be selected, each reviewer had to be recognized as an expert in one or more of these technical specialties. Each reviewer also had to demonstrate active participation in numerous reviews in his or her respective area(s) of expertise, and had to have made numerous presentations at technical conferences, and written numerous papers for publication in conference proceedings and journals. Finally, the staff selected the peer review group members to cover a broad range of technical expertise. Table 2-1 identifies the five selected peer reviewers, along with their respective affiliations and areas of technical expertise.

### Table 2-1. External Peer Reviewers

| Name | Position/Affiliation | Areas of Technical Expertise |
|---|---|---|
| John Apps | Senior scientist<br>Earth Sciences Division<br>Lawrence Berkeley National Laboratory<br>Earth Sciences Division<br>Berkeley, CA 94720 | Geochemical modeling and gel formation (gel/amorphous product formation and characterization)<br>Chemical speciation modeling (theoretical chemistry/speciation prediction)<br>Nuclear waste isolation |
| Wu Chen | Senior specialist<br>The Dow Chemical Co.<br>B-1402, 2301 N. Brazosport Blvd.<br>Freeport, TX 77541 | Fluid/particle separation<br>Industrial filtration processes |
| Calvin Delegard | Staff scientist<br>Pacific Northwest National Laboratory<br>PO Box 999, MS P7-25<br>Richland, WA 99352 | Experimental testing and analysis<br>Analytical chemistry (applied/process chemistry)<br>Nuclear materials safeguards |
| Robert Litman | Independent consultant<br>Radiochemistry Laboratory Basics<br>28 Hutchinson Drive<br>Hampton, NH 03842 | Analytical chemistry<br>Metallic/corrosion processes<br>Nuclear plant systems and chemistry |
| Digby Macdonald | Professor of Materials Science and Engineering, and Director of the Center for Electrochemical Science and Technology<br>Pennsylvania State University<br>0201 Steidle Bldg.<br>University Park, PA 16802 | Electrochemistry and thermodynamics science<br>Metallic/corrosion processes<br>Experimental testing and analysis |

# 3. PRINCIPAL REVIEW AREAS

## 3.1 Integrated Chemical Effects Testing

### 3.1.1 Program Description

The primary objectives of the ICET research program were to (1) determine, characterize, and quantify chemical reaction products that may develop in a PWR containment pool in a representative post-LOCA environment, and (2) determine and quantify any gelatinous material(s) that could be produced during the post-LOCA recirculation phase. Toward that end, the ICET series simulated the chemical environment present in a containment water pool following a LOCA, and monitored the chemical system for an extended period of time to identify the presence, composition, and physical characteristics of chemical products that formed during the test. By contrast, the ICET series was not designed to evaluate debris or sediment transport, bound the chemical environment present in a containment water pool, or measure head loss associated with any chemical byproducts. Within those constraints, the ICET series was conducted at UNM under the direction of LANL, in accordance with the test plan shown in Table 3-1.

**Table 3-1. ICET Test Plan**

| Test | Buffering Agent | Initial Target pH | Boron (ppm) | Insulation Mixture |
|---|---|---|---|---|
| 1 | Sodium Hydroxide (NaOH) | 10 | 2800 | 100% fiberglass |
| 2 | Trisodium Phosphate (TSP) ($Na_3PO_4$) | 7 | 2800 | 100% fiberglass |
| 3 | TSP ($Na_3PO_4$) | 7 | 2800 | 80% cal-sil<br>20% fiberglass |
| 4 | Sodium Hydroxide (NaOH) | 10 | 2800 | 80% cal-sil<br>20% fiberglass |
| 5 | Sodium Tetraborate (STB) ($Na_2B_4O_7$) | 8 – 8.5 | 2400 | 100% fiberglass |

The ICET research program consisted of five distinct 30-day tests, each of which was intended to simulate a subset of current operating PWR plants. The ICET apparatus consisted of a large stainless steel tank with heating elements, spray nozzles, and associated recirculation pump and piping to simulate the post-LOCA chemical environment. Submerged samples of structural metals, concrete, and insulation debris were scaled in proportion to their relative surface areas found in containment, and in proportion to a maximum test dilution volume of 250 gallons (946 liters) of circulating fluid.

The primary differences among the ICET tests were the buffering agent and insulation material. The three types of buffering agents were sodium hydroxide (NaOH), trisodium phosphate (TSP), and sodium tetraborate (STB, used in ice condenser plants). The materials tested in this environment included representative amounts of submerged and unsubmerged aluminum (Al), copper (Cu), zinc (Zn), concrete, carbon steel, and insulation samples. Representative amounts of concrete dust and latent debris were also added to the test solution.

All of the ICET tests were conducted in an environment that simulated expected containment pool conditions during recirculation. The initial chemical environment contained 2,800 mg/L of boron (2,400 ppm for STB plants), 100 mg/L of hydrochloric acid (HCl), and 0.7 mg/L of lithium hydroxide (LiOH). Each test was conducted for 30 days at a constant temperature of 60 °C (140 °F) and consisted of an initial 4-hour spray phase to simulate containment spray interaction with the unsubmerged samples. Water was circulated through the bottom portion of the test chamber throughout each test to achieve representative flow rates over the submerged specimens. The system was then monitored while corrosion and mixing occured for 30 days (a time frame comparable to the ECCS recirculation mission time).

The test solution pH also differed in each test, varying from approximately 7.3 in ICET Test #2 to approximately 9.8 in Test #4. Precipitates at test temperature were visible for only Test #3. However, test sample solutions for Tests #1 and #5 produced precipitates upon cooling to room temperature, although Tests #2, #3, and #4 did not. In each test, turbidity measurements were taken at 60 °C (140 °F) and 23 °C (73 °F), and measurements at both temperatures yielded similar results in Tests #2, #3, and #4. However, in Tests #1 and #5, the turbidity at 23 °C (73 °F) deviated from those at 60 °C (140 °F). Total suspended solids (TSS) were also measured in each test and, with the exception of Test #5, all tests reached a maximum TSS value by the first day and decreased to a value relatively close to the baseline measurement for the duration of the test.

Throughout the ICET series, daily water samples were taken to determine the composition of the solution by inductively coupled plasma (ICP) analysis with a standard list of elements. Boron was present in high concentrations in all tests. In Test #1, aluminum and sodium were present in the greatest concentrations of all tested elements. In Test #2, silica and sodium were the dominant elements in solution. Silica, sodium, and calcium elements were present in the greatest concentrations in Test #3. In Test #4, silica, sodium, calcium, and potassium were present in the greatest concentrations. Sodium, aluminum, calcium, and silica were the dominant elements in the Test #5 solution.

The amounts and types of deposits seen on the fiberglass insulation varied from test to test because of differences in solution chemistry. Comparison revealed that the greatest degree of deposition occurred in Test #3, followed in order by Tests #1, #4, and #2, while Test #5 samples had the fewest deposits. Analyses of the cal-sil samples revealed large amounts of phosphorous on the exterior of samples obtained from Test #3, but not those obtained from Test #4. Moreover, the interior of the cal-sil samples from Tests #3 and #4 showed that the phosphorus did not penetrate the solid.

The system effect on the coupons also differed for each test, as did the sediment produced. Tests #1 and #5 showed the largest amount of coupon corrosion (e.g. 25% and 5% loss of pre-test mass in submerged aluminum coupons respectively), while the conditions in Tests #2 through #4 did not appear to cause significant coupon corrosion. By contrast, Tests #3 and #4 produced the most sediment, which consisted of a large amount of chemical precipitate and sediment attributable to the large amount of cal-sil added to the tank. Tests #1, #2, and #5 produced the smallest amount of sediment, which was largely composed of materials from the insulation (fiberglass) and debris added to the tank. Overall, the ICET results demonstrated that changes to one important environmental variable (e.g., pH adjusting agent, insulation material) can significantly affect the chemical products that form.

### 3.1.2 Summary of Peer Review Key Findings

The review focused on a predetermined set of ICET-related technical questions. Those questions and the related responses from the peer reviewers are summarized as follows:

**Question 1:** Have the principal sump pool variables, which affect chemical byproduct formation environment, been adequately simulated?

**Response:** The majority of the reviewers agree that the types of materials that are present in PWR containments have been appropriately selected. They also stated that the concentrations of chemicals used during the operation of a PWR are approximately in the range of anticipated chemical concentrations. The reviewers also noted that other chemical constituents have not been simulated, the analysis lacks consideration of redox effects and radiolysis, and the tests did not adequately model the steep cyclic temperature transients of recirculating coolant or the hot fuel cladding and pressure vessel surfaces.

**Question 2:** Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?

**Response:** In general, the reviewers suggest comprehensive evaluation of the physical, chemical, and mineralogical properties of the observed precipitates during the experiments, along with detailed evaluation of all of the data to better understand the effects of chemical product formation. Some of the reviewers suggest that temperature has a significant effect on solubility and the types of compounds that will form. They recognize temperature as a difficult aspect to model and recommend further work.

**Question 3:** What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects), and how should their effect be characterized by testing or analysis?

**Response:** In general, the reviewers think that field visits to operating PWR facilities could unearth limitations or omissions not otherwise anticipated. Considerations from the reviewers are diverse and are summarized as follows:

(a) failure to control or monitor $CO_2$ uptake, which could deviate significantly from the actual post-LOCA environment of a PWR

(b) presence of suspended solids from the reactor coolant system (RCS) and how they could change their chemical form

(c) effects of organic coatings to estimate the quantities of coatings involved, their properties, and the secondary effects of radiation and hydrothermal reactions (reactions with hot water) on the organic materials

(d) effects of high- and low-temperature heat transfer surfaces on collection and dissolution of solid phases to determine the importance of surface deposition

(e) effect of liquid coming into contact with fuel in the reactor vessel to understand heat and radiolytic effects

(f) effects of silica in the water storage systems and RCS on the total mass of material precipitating

(g) simulation of the production of hydrogen peroxide ($H_2O_2$, to determine redox potential) and nitric acid ($HNO_3$, lowers the pH of the solution)

**Question 4:** Were the methods used within the ICET program to characterize and analyze chemical byproducts sufficient?

**Response:** The reviewers agree that the methods used within the ICET program were not sufficient to characterize and analyze chemical byproducts. Much more serious work needs to be done to characterize the physical, chemical, and mineralogical properties of the precipitates and coatings as a basis for subsequent conceptual and computer modeling. Some X-ray diffraction (XRD) and transmission electron microscopy (TEM) work was performed during the course of ICET or during follow-up work, but in general, the tests should have incorporated the following analytical techniques as part of their standard analysis:

(a) Particle size distribution (PSD)
(b) Fourier transform infrared spectroscopy (FTIR)
(c) X-ray diffraction (XRD)
(d) Transmission electron microscopy (TEM)

## 3.2 Chemical Speciation Prediction Program

### 3.2.1 Program Description

The objective of the chemical speciation prediction program (performed at CNWRA) was to evaluate the accuracy of thermodynamic predictions on the quantities and species of chemical products formed. Toward that end, four chemical modeling software programs — EQ3/6, PHREEQC, Geochemist’s Workbench REACT, and OLI Systems StreamAnalyzer — were evaluated to assess their ability to perform aqueous speciation and mass transfer calculations relevant to post-LOCA conditions. The code comparison exercise considered several example simulations, each of which was representative of post-LOCA conditions in alkaline, borated containment water at temperatures between 60 °C (140 °F) and 110 °C (230 °F).

The reactor system components included galvanized steel (a source of dissolved zinc), carbon steel (a source of dissolved iron), aluminum scaffolding, copper fans and instrument lines, glass fiber insulation material, and concrete. The modeling software was used to identify the over-saturated secondary solids that would precipitate, and calculate the final solution composition. The most important differences in results were traceable to different sets of solid phases in the thermodynamic database files accompanying each modeling code, rather than to different capabilities of the codes themselves.

The benchmarked simulations considered a set of blind predictions using the EQ3/6 code, and the predicted results were compared to data from the corresponding ICET experiment. In some cases, observed final concentrations in the sampled water were higher than the initial source-term estimates, indicating that the input value source-term contribution for that element had been underestimated. In other cases, the identity and quantity of precipitate did not conform to observations from the ICET experiment, indicating kinetic restrictions on precipitation under the modeled conditions.

Another set of simulations, called “informed predictions,” used the OLI StreamAnalyzer code and its accompanying thermodynamic database. The general modeling approach was similar to the approach used for the blind predictions with EQ3/6. In this case, each ICET experiment was represented by a set of source-term water compositions at different times of exposure, estimated from the initial composition of the containment water and experimentally determined corrosion rates of sample materials. The results of the informed predictions corresponded to the ICET experiment results more closely than the blind predictions, largely because of the revised element release rates for aluminum and insulation materials, for exposure times of up to 148 hours. Beyond that timeframe, final concentrations of calcium, silica, and aluminum were typically over-predicted, indicating a possible inert stage of the metal surface or formation of an inhibitive surface coating on the insulation material during the experiment. These changes in release rate were not included in the source-term water concentrations for informed predictions.

The differences in results for the blind and informed predictions were attributed to differences in the lists of potential precipitates provided in the thermodynamic database files that accompany the modeling software. For the informed simulations in which precipitation affected the solution chemistry, good agreement was obtained between predicted and observed results for calcium concentration under the conditions in ICET Test #1 (alkaline water buffered to pH values near 10 by NaOH) because of the precipitation of monohydrocalcite, for silica concentration under the conditions in ICET Tests #2 and #3 (solution buffered to near-neutral pH by TSP) because of the precipitation of amorphous silicon dioxide, and for phosphorous concentration under the conditions in ICET Test #3 because of the precipitation of calcium phosphate.

This study concluded that chemical modeling software is a broadly useful tool for assessing the potential effects of post-LOCA interaction on sump screen blockage. However, its predictive capability was hindered by insufficient thermodynamic data for relevant phases and aqueous species in the code database, and by limitations in the kinetic data for the dissolution of reactive materials in the presence of co-dissolving materials.

### 3.2.2 Summary of Peer Review Key Findings

The review focused on a predetermined set of technical questions related to prediction of chemical speciation. Those questions and the related responses from the peer reviewers are summarized as follows:

**Question 1:** Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?

**Response:** The reviewers agree that even though this chemical speciation analysis represents a significant improvement over earlier work, it does not exploit existing capabilities of the selected codes to their fullest advantage. Specifically, two physical effects not modeled were the radiation field from the fuel, and the layer of corrosion products on the interior surface of the RCS. The reviewers note that concessions had to be made for the seeming lack of $CO_2$ to form low-solubility carbonates. Reaction rates (kinetics) also are not handled well by the modeling software; therefore, the models may not reflect the evolving concentration profiles. As the models are refined, they should provide closer matching of the observed ICET concentrations, the concentrations observed in the supplemental CNWRA testing, and the concentrations in systems not replicated in the ICET experiments. In addition, non-equilibrium concentration of radiolysis products (and even species in the absence of radiolysis) cannot be addressed by the selected codes.

**Question 2:** Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?

**Response:** The reviewers agree that the plan for benchmarking codes is satisfactory, provided that the actual processes are accurately simulated. Some reviewers think that the capabilities of the codes currently being used are not being used to full advantage and, as a result, the value of the associated experimental studies is diminished. In addition, the reviewers note that small-scale testing is a valid approach to gain more information, especially on the kinetic and equilibrium behaviors of the key solutes and solid phases.

**Question 3:** What is the most appropriate way to measure the uncertainty associated with these codes?

**Response:** The reviewers suggest various ways to measure the uncertainty associated with the codes, noting that it is difficult to measure the overall uncertainty of the output of any multi-component chemical simulation, because a large number of parameters are involved with widely varying levels of accuracy. First, a sensitivity analysis of empirical or deterministic models is suggested. Second, comparison of the code predictions against the results of targeted small-scale tests is a feasible way to strengthen the codes and identify and measure their uncertainties. Third, the most realistic values should be utilized, and runs should be replicated using Monte Carlo methods to determine variations in parameters deemed to have the greatest uncertainties and considered to be most critical to model output. The cumulative variation in outputs can then be adopted as a measure of uncertainty.

## 3.3 Chemical Effects Head Loss Testing Program

### 3.3.1 Program Description

The objective of the chemical effects head loss testing program (performed at ANL) was to evaluate the head loss associated with chemical byproducts observed during the integrated chemical effects testing by LANL/UNM, and to understand how relevant changes within the environment affect chemical byproduct formation, physical characteristics, and any associated head loss. The head loss testing was done in a piping loop containing a simulated sump pool environment intended to be representative of post-LOCA buffering environments. The test screen had an effective diameter of ≈16.5 cm (≈6.5 inches), and the fluid volume in the loop was 0.12 $m^3$ (4.2 $ft^3$). At 3.05 cm/s (0.1 ft/s), the transit time around the loop was ≈4 minutes.

Two types of perforated plates were used in the testing. One had a 51-percent flow area and staggered holes with a diameter of 0.48 cm ($^3/_{16}$ inch), while the other had a 40-percent flow area and staggered holes with a diameter of 0.32 cm (⅛ inch). In scaling results from the ANL test facility, the mass of chemical product per unit area of screen must be considered. Thus, the amount of chemical product produced scales with fluid volume, while the screen area per fluid volume determines the product mass per unit screen area. The ANL initial tests results are described in detail in ANL's 1st and 2nd Chemical Effects/Head Loss Testing QLRs (References 19 and 22), dated September 16, 2005, and January 20, 2006, respectively.

The initial head loss testing focused on the environment corresponding to ICET Test #3, which contained cal-sil insulation and used TSP buffering. In that test, calcium phosphate [nominally $Ca_3(PO_4)_2$] became apparent within 30 minutes after initiating TSP injection into the recirculation loop. The first ANL head loss test (ICET #3-1) was intended to simulate the $Ca_3(PO_4)_2$ precipitate concentration created by the initial burst of dissolved calcium (Ca) that formed within the first 30 minutes of ICET Test #3, prior to metering TSP into the chamber. Dissolution testing of the ICET Test #3 cal-sil loading [19 g/L (0.190 lb/gal) submerged cal-sil] showed that during the 30 minutes between the introduction of the cal-sil and the initiation of TSP injection, head loss would increase significantly as a result of $Ca_3(PO_4)_2$ precipitate corresponding to 200 ppm of dissolved Ca.

The second ANL head loss test (ICET #3-2) was parametric and tested several dissolved Ca concentrations to determine the effect of a range of cal-sil loadings on head loss. In both tests, a physical debris bed was formed, approximately 1.59 cm (⅝ inch) thick, consisting of equal amounts [15 g (0.53 oz.)] of NUKON® fiber and cal-sil insulation. Dissolved Ca was then added to the test loop, which contained TSP-buffered borated water, to form $Ca_3(PO_4)_2$ precipitates. In this configuration, ICET #3-2 resulted in head loss increases for precipitate loadings that were one-twentieth of those used in ICET #3-1 (10 ppm of dissolved Ca), and loadings corresponding to 25 ppm of dissolved Ca increased the head loss to more than 4.2 m (13.8 ft).

ANL also performed additional head loss tests, tests of settling rates of $Ca_3(PO_4)_2$ precipitates, and cal-sil dissolution tests in TSP solutions. The objective of the head loss tests was to assess the pressure drop across debris beds created by various mixtures of cal-sil, fibrous insulation, and $Ca_3(PO_4)_2$ precipitates. In addition, ANL evaluated the effects of the degree of cal-sil dissolution that will occur before the debris bed forms, as well as the relative arrival time of the precipitates and insulation debris at the screen. Toward that end, ANL selected debris loadings and test temperatures that were reasonably representative of those expected in limiting design-basis analyses for plants with updated sump screen configurations. The test conditions used in this series of tests are summarized in Reference 22.

The results of the ANL head loss tests in environments similar to those in ICET Test #3 demonstrate that chemical products [$Ca_3(PO_4)_2$ precipitates] associated with TSP-buffered containment environments can significantly contribute to head loss. Moreover, the head losses associated with fiberglass insulation and cal-sil debris beds can be much smaller than those that occur across debris beds in which some of the cal-sil has been dissolved and the resulting Ca reacts with phosphate to form $Ca_3(PO_4)_2$ precipitates. Notably, the rate of cal-sil dissolution depends somewhat on the initial pH in the sump pool, as well as the rate of TSP dissolution. However, even with instantaneous TSP dissolution and cal-sil concentrations as low as 0.5 g/L ($5.01E^{-3}$ lb/gal), the equivalent dissolved Ca could be high enough within a few hours to produce significant increases in head loss compared to that attributable to the equivalent particulate loading. The $Ca_3(PO_4)_2$ precipitate settling rate is also important in determining the transportability of the precipitate. The rate varies with concentration. For example, at a concentration of 75 ppm Ca with no bulk directional flow, the estimated settling rate is 8 mm/min (0.31 inch/min).

In an environment similar to that used for ICET Test #3, the chemical products in the ANL head loss tests formed either by actual dissolution of cal-sil (an integral test) or by the addition of dissolved Ca as calcium chloride ($CaCl_2$). Moreover, the chemical products formed by either manner are calcium phosphates, and the surrogate product is very similar to that formed in the integral test. By contrast, in the environment used for ICET Test #1, the main chemical product is aluminum hydroxide [$Al(OH)_3$]. However, aluminum hydroxide may exist in either amorphous or crystalline forms, and these forms can have very different properties. For example, the solubility of amorphous $Al(OH)_3$ can be 500 times as great as the solubility of some crystalline forms of aluminum hydroxide. Thus, it is important to note that in ICET Test #1, dissolved Al formed slowly by corrosion of the Al plates.

The precipitation process is complex, and the Al can be present as dissolved Al, colloidal product, and solid precipitates. The existing amounts of the various forms, even for the same total Al content can be highly time-dependent, and may depend on the timing of the addition of material to the coolant, the change in temperature or pH over time, and the degree and order of mixing. The solid products in ICET Test #1 have been shown to be primarily amorphous $Al(OH)_3$. There is a very high degree of hydration, and product exists as agglomerations of nano-sized particles, but the degree and strength of agglomeration and the actual effective hydrodynamic size of the product is difficult to characterize.

The ANL head loss tests for the ICET Test #1 environment were based on the use of surrogate chemical products. The test fluid had boric acid and lithium hydroxide levels consistent with the ICET test, but aluminum nitrate nonahydrate [$Al(NO_3)_3 \times 9H_2O$] was added to generate $Al(OH)_3$ products (rather than actual dissolution of Al metal). Nonetheless, bench scale tests showed that the products were amorphous, and their physical appearance and behavior were qualitatively similar to the products observed in the ICET #1 integral test. Particle size measurements showed that products were agglomerated, and the measured particle size could vary depending on whether the solution was quiescent or deflocculated by ultrasound.

The initial ANL head loss tests in the ICET Test #1 environment attempted to simulate the ICET test where the dissolved Al level was ≈ 375 ppm. For these tests, ANL prepared a solution containing boric acid, LiOH, and NaOH. A NUKON® debris bed was formed, and the system was heated to 60 °C (140 °F). $Al(NO_3)_3 \times 9H_2O$ was then added to obtain a dissolved Al level of 375 ppm, and the pH was adjusted to match the conditions in ICET Test #1.

In the first ANL test in this environment, the flow velocity in the loop was kept at 30 mm/s (0.1 ft/s), and a heavy “snowfall” was observed as the Al solution was added. [The addition of $Al(NO_3)_3$ appeared to result in a local decrease in pH and concomitant increase in Al concentration that exceeded the solubility limit; however, the “snow” dissolved in a few minutes.] High head losses were observed almost immediately upon introduction of the Al solution, even though the temperature remained at 60 °C (140 °F) and there was no visible buildup of precipitate on the debris bed or anywhere else in the loop. As the temperature decreased, the pressure drop across the bed continued to increase, although no precipitate was observed on the bed. At 32 °C (90 °F) the pressure drop was so high [4.2 m and 6 psi] that flow velocity could not be maintained. In a repeat test with 375 ppm dissolved Al, a new distribution header was used for the Al solution, and much less snow formed when the solution was added to the loop. In addition, in the repeat test at 375 ppm, no increase in pressure drop was observed at temperature or as the loop cooled to 38 °C (100 °F) until about 120 minutes after addition of Al. Once the pressure drop began to increase, it rapidly climbed from 0.015 m and 0.3 psi to 2.6 m and 5 psi in approximately 30 minutes. Again, the pressure drop occurred with no visible precipitate.

ANL also performed additional tests with lower levels of dissolved Al. In initial tests with 100 ppm and 200 ppm of Al, no pressure drop increases were observed over a 6-hour test period as the temperatures decreased from 60 °C (140 °F) to 27 °C (80 °F). A second test was run with 100 ppm dissolved Al at 27 °C (80 °F) for 8 days, also with no significant increase in pressure drop. Nitric acid was then added to decrease the pH by 0.2 units, and the pressure drop immediately began to increase, although there was again no visible precipitate. The process was at least somewhat reversible in terms of temperature. That is, when the temperature increased, the pressure drop decreased, and when the temperature decreased, the pressure drop increased. However, the temperature holds were not long enough to fully assess the degree of reversibility.

In a third test with 100 ppm dissolved Al, 15 nm aluminum oxide ($Al_2O_3$) particles were added after ≈1 day in an attempt to accelerate the precipitation process. The pressure drop began to increase ≈4 days after the particle addition, so any connection seems remote. In this case, the pressure drop increased to ≈2.6 m (5 psi), and loop velocity could no longer be maintained. Again, no product was visible during the test, but a colloidal suspension did become visible in samples of fluid removed from the loop at the end of the test and aged for 3–4 days.

ICET Test #5 involved an STB buffer, and the dissolved Al level (≈ 50 ppm) was lower than in ICET Test #1, but the pH was also lower (≈8.5). Only a limited amount of precipitates were observed during the test, but somewhat more became visible during longer-term storage of fluid from the test. The corresponding ANL head loss tests again used $Al(NO_3)_3 \times 9H_2O$ as a surrogate for Al from actual dissolution. For these tests, ANL prepared a solution containing boric acid, LiOH, and STB. A NUKON® debris bed was formed, and the system was heated to 60 °C (140 °F). $Al(NO_3)_3 \times 9H_2O$ was then added to obtain a dissolved Al level of 50 ppm. Because the aluminum nitrate addition lowered the pH, ANL also added NaOH to match the pH in ICET Test #5. The test was run for 6 days with no indication of increased pressure drop. The pH was then decreased 0.2 units, nanoparticles were added, and the test was continued for another ≈5 days with no indication of increased pressure drop. The dissolved Al level was then increased to 100 ppm, which corresponds to a very conservative estimate of submerged area of Al for most plants. With this amount of dissolved Al, the pressure drop rapidly increased until the pump could no longer maintain the fluid velocity.

ANL also performed a second test with the STB buffer, in which the physical debris bed contained 15 g (0.53 ounce) each of NUKON® and cal-sil. The initial head loss when this debris was added to the loop was somewhat greater than that observed in tests with similar NUKON/cal-sil loadings, but this may be attributable to test-to-test variability. The pressure drop decreased over time during the test to levels typical of pure NUKON® loading, suggesting that the cal-sil was dissolving, the particulate loading on the bed was decreasing, and no chemical products were forming that could lead to high pressure drops.

### 3.3.2 Summary of Peer Review Key Findings

The review focused on a predetermined set of technical questions related to chemical effects head loss testing. Those questions and the related responses from the peer reviewers are summarized as follows:

**Question 1:** Is the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?

**Response:** The majority of the reviewers agree that the current head loss testing facility is insufficiently flexible for evaluation of multiple chemical environments or replication of tests to establish reproducibility, and the test loop does not provide the same type of stagnant environment that would be encountered in the submerged portion of the containment building. Some recommendations are as follows:

(a) Use multiple small bench-scale facilities that could be run simultaneously, with stepped variations in critical parameters, so that the sensitivity and magnitude of potentially adverse conditions could be rapidly mapped as a function of these parameters.

(b) A smaller test loop might be designed to model the operation of a vertical screen, rather than the tested perpendicular dead-end screen.

(c) A smaller test loop would also allow easier testing at temperatures that vary with time, and might allow exposed high and low temperature surfaces.

**Question 2:** What is the best method for incorporating time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?

**Response:** The reviewers suggest various methods to incorporate time-dependent effects in simulation testing:

(a) With the variability in individual PWR designs and differing operating histories, there is a need to concentrate on the most critical parameters and efficiently study their effects through small-scale bench tests. Once the degree of variability and its importance has been established, small-scale loop and head-loss tests could be conducted on a suitable range of variably aged samples.

(b) Study the effect of temperature through small bench-scale tests, followed by limited small-scale loop and head-loss tests. Confirmatory tests using the present facilities should be conducted only after assessing the impact of all relevant parameters.

(c) Kinetic models, coupled with thermodynamic codes, should be considered, making sure that the codes accurately simulate radiolysis and redox effects.

**Question 3:** What metrics are most appropriate for evaluating the results of simulated chemical products with those that formed during the ICET program?

**Response:** The reviewers identified various metrics for evaluating the results of simulated chemical products:

(a) In the filtration/head-loss testing, the aluminum corrosion product was introduced by neutralizing aluminum nitrate [$Al(NO_3)_3$] with sodium hydroxide (NaOH). This method is not representative of the way aluminum solids arise in the post-LOCA cooling water system. It is proposed that the aluminum be introduced in another manner, either by corroding a coupon of aluminum in NaOH or by adding sodium aluminate solution [$NaAl(OH)_4$].

(b) The testing performed for the ICET program showed the importance of pH, Cal-Sil dissolution, borate, aluminum corrosion, phosphate, NUKON® fiberglass, and concrete on solids formation. The head loss testing could focus on varying these components, plus study the effects of temperature differentials and hot and cold surfaces, to create the solids present in the post-LOCA environment.

**Question 4:** Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical byproduct are known?

**Response:** The reviewers think that methods to predict head loss or filtration behavior based on physical properties may or may not exist, noting that a reason for this is the secondary effect of coprecipitated or agglomerated materials. Another reviewer opined that models that predict head loss cannot account for the effects of gelatinous or amorphous materials. However, even if such parameters could be identified and measured, the coolant solutes and suspended solids continue to react as shown by ICET and other testing. Another reviewer suggested treating this problem with a kinetic model for hydrolysis, polymerization, coagulation, and precipitation in a highly non-equilibrium environment, recognizing that none of the present codes has this capability.

# 4. CONCLUDING STATEMENT

The principal objectives of the chemical effects peer review were met. Overall, the peer reviewers assessed and independently confirmed the technical adequacy of the three research programs related to chemical effects in PWR sump pool environments, including the integrated chemical effects testing at LANL, chemical speciation prediction activities at CNWRA, and chemical effects accelerated head loss tests at ANL.

The peer review members provided their final assessments of these three RES-sponsored research programs areas, and independently offered recommendations for improvement. Even though the peer reviewers sometimes expressed different opinions in addressing the specific questions provided by the NRC staff regarding the various research programs, their input based on their technical expertise is very valuable and will help the NRC to identify important technical issues for further consideration. As a result, this peer review yielded the following benefits for the NRC:

- The reviewers' comments and suggestions provided significant feedback on how one might possibly refine the testing programs to ensure that they are more representative of the actual PWR environment.
- The reviewers' comments and suggestions will provide the NRC's Office of Nuclear Reactor Regulation (NRR) with a measure for use in assessing the reliability and strength of industry-sponsored testing in the chemical effects arena. NRR will consider outstanding technical issues identified by the chemical effects peer review panel.

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For more information on the ICET program, see http://www.nrc.gov/reactors/operating/ops-experience/pwr-sump-performance/tech-references.html.

# Appendix A

CONTRIBUTION TO THE REPORT

OF THE

# CHEMICAL EFFECTS PEER REVIEW GROUP

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FINAL REPORT

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# ABSTRACT

A joint U.S. Nuclear Regulatory Commission (NRC) and industry sponsored program was conducted to evaluate the chemical processes following a Loss of Coolant Accident (LOCA) in a pressurized water reactor (PWR), to address problems associated with the clogging of pump recirculation screens by secondary precipitates and gels. The program consists of three tasks: (1) Chemical modeling at the Center for Nuclear Waste Regulatory Analysis (CNWRA) at the Southwest Research Institute, (2) Performance of an Integrated Chemical Effects Test (ICET) series at the University of New Mexico under the direction of Los Alamos National Laboratory (LANL), and (3) Accelerated head loss testing at Argonne National Laboratory (ANL). The Chemical Effects Peer Review Group was asked to review the technical adequacy of the tree tasks. In response, the reviewer studied three reports by CNWRA, five ICET reports by LANL, and three reports by ANL. A number of documents supporting oral presentations at two meetings held at ANL on October 18-19, 2005, and at Southwest Research Institute on March 27-29, 2006, respectively, were also reviewed together with material supplied by NRC. Additional documents, scientific papers and reports were also consulted to aid in the subsequent evaluation and provide corroborating arguments in support of the reviewer's findings. This report constitutes the response by one of the members of the Peer Review Group, who was chosen for his expertise in chemical modeling.

The reviewer concludes that the ICET program has made substantial progress towards understanding and quantifying the chemical processes that could lead to sump screen blockage during the emergency cooling phase following a LOCA at an operating PWR. However, the chemical modeling conducted as part of this program falls far short of what is needed, either to interpret the completed or ongoing experimental studies supporting the program, or ultimately, to construct a simulator for evaluating PWR plant response following a LOCA; this, despite the significant improvement in technical understanding and competence reflected in the third report of the series generated by CNWRA. The reviewer recommends substantive refinements and improvements to any future modeling, by taking better advantage of the kinetic data acquired in the course of the program, developing a dedicated thermodynamic database, which incorporates those aqueous species and product phases of relevance to the test conditions, and more fully utilizing the reaction progress features available in state-of-the-art codes. Only after these recommendations are implemented will it be possible to fully interpret the experimental results of the ICET and head loss test series, refine the thermodynamic and kinetic parameters in the chemical simulators, and provide ongoing support and guidance to future experimental research.

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# TABLES

# EXECUTIVE SUMMARY

A joint U.S. Nuclear Regulatory Commission (NRC) and industry sponsored program was conducted to evaluate the chemical processes following a Loss of Coolant Accident (LOCA) in a pressurized water reactor (PWR), to address problems associated with the clogging of pump recirculation screens by secondary precipitates and gels. The program consists of three tasks: (1) Chemical modeling at the Center for Nuclear Waste Regulatory Analysis (CNWRA) at the Southwest Research Institute, (2) Performance of an Integrated Chemical Effects Test (ICET) series at the University of New Mexico under the direction of Los Alamos National Laboratory (LANL), and (3) Accelerated head loss testing at Argonne National Laboratory (ANL).

NRC convened the Chemical Effects Peer Review Group, which was asked to review the technical adequacy of the tree tasks. to focus on responding to the following technical questions:

## Analytical Simulation

- Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?
- Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?
- What is the most appropriate way to measure the uncertainty associated with these codes?

## ICET Series

- Have the principal sump pool variables, which affect chemical by-product formation in the post-LOCA environment, been adequately simulated?
- Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?
- What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects) and how should their effect be characterized by testing or analysis?
- Were the methods used within the ICET program to characterize and analyze chemical by-products sufficient?

## Head Loss Simulation Testing and Analysis

- Is the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?
- What is the best method for incorporating time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?
- What metrics are most appropriate for evaluating the results of simulated chemical products with those that formed during the ICET program?
- Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical by-product are known?

In order to respond to the technical questions posed, the reviewer studied three reports by CNWRA, five ICET reports by LANL, and three reports by ANL. A number of documents supporting oral presentations at two meetings held at ANL on October 18-19, 2005, and at Southwest Research Institute on March 27-29, 2006, respectively, were also reviewed together with material supplied by NRC. Additional documents, scientific papers and reports were also consulted to aid in the subsequent evaluation and provide corroborating arguments in support of the reviewer's findings.

The following report constitutes the response by one of the members of the Peer Review Group, who was chosen for his expertise in chemical modeling. The report is sub-divided into five parts. The first is an introduction defining the background, scope and objectives of the review, the second addresses the analytical computer simulations to evaluate the requirements for the ICETs, the third contains a review of the adequacy of the ICET series, and the fourth part is a review of the head loss tests and supporting research. The report concludes with a list of cited references. Findings, conclusions and recommendations are not allocated separate parts, as these topic are adequately covered within parts 2, 3 and 4 of the report that address the modeling and experimental parts of the program, and are briefly summarized below.

Part 2 contains an in-depth review of three reports produced by the CNWRA. The simulations in all three reports are summarized in tabular form, and the reviewer gives the conclusions reached by the authors together with his comments and observations. The adequacy of the modeling work in relation to support for the experimental studies is then reviewed. The limitations of the work described in the three reports are then discussed, with both general comments, and detailed comments relating to specific sections of each text. Recommendations for future modeling are then made, based on the limitations of the reported work, and required improvements. The section concludes with responses to the questions posed by NRC for the Analytical Simulations, as listed above.

Part 3 lists the specifications for the ICET series. Both general and detailed comments by the reviewer follow for each of the five reports describing the procedures and results of each test. After reviewing all five reports, the reviewer concluded that a *post mortem* evaluation of the ICET runs should be conducted in order to resolve issues of data interpretation and increase confidence in subsequent modeling analyses. A section is therefore included with specific recommendations. The section concludes with responses to the questions posed by NRC for the ICET Series, as listed above.

Part 4 addresses the head loss testing and supplementary bench-scale testing and analysis to aid in the interpretation of both head loss and the ICET series. Three preliminary reports specifically addressing the head loss tests done to date and supplementary oral presentations given at the December 18-19, 2005 meeting at ANL were reviewed. Specific head loss tests completed to date are listed. Both general and detailed comments by the reviewer follow for the reports and oral presentations. The section concludes with responses to the questions posed by NRC for the head loss simulation testing and analysis, as listed above.

The reviewer concludes that the ICET program has made substantial progress towards understanding and quantifying the chemical processes that could lead to sump screen blockage during the emergency cooling phase following a LOCA at an operating PWR. However, the chemical modeling conducted as part of this program falls far short of what is needed, either to interpret the completed or ongoing experimental studies supporting the program, or ultimately, to construct a simulator for evaluating PWR plant response following a LOCA; this, despite the significant improvement in technical understanding and competence reflected in the third report of the series generated by CNWRA. The reviewer recommends substantive refinements and improvements to any future modeling, by taking better advantage of the kinetic data acquired in the course of the program, developing a dedicated thermodynamic database, which incorporates those aqueous species and product phases of relevance to the test conditions, and more fully utilizing the reaction progress features available in state-of-the-art codes. Only after these recommendations are implemented will it be possible to fully interpret the experimental results of the ICET and head loss test series, refine the thermodynamic and kinetic parameters in the chemical simulators, and provide ongoing support and guidance to future experimental research.

# 1 INTRODUCTION

A joint U.S. NRC/industry sponsored program was undertaken through a memorandum of understanding between NRC and the Electric Power Research Institute (EPRI) in order to evaluate chemical processes following a Loss of Coolant Accident (LOCA) in a pressurized water reactor (PWR), particularly with respect to problems associated with the clogging of pump recirculation screens by secondary precipitates and gels. The program consists of three tasks:

1. Chemical speciation prediction being conducted at the center for Nuclear Waste Regulatory Analysis (CNWRA) (**Analytical Simulation**)

2. Integrated Chemical Effects Test (ICET) series being conducted at the University of New Mexico under the direction of Los Alamos National Laboratory (LANL) (**ICET Series**)

3. Chemical effects accelerated head loss testing being conducted at Argonne National Laboratory (ANL) (**Head Loss Simulation Testing and Analysis)**

The Chemical Effects Peer Review Group was asked to review the technical adequacy of the tree tasks. In particular, the group was asked to focus on responding to the following technical questions:

## 1.1 Analytical Simulation

- Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?
- Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?
- What is the most appropriate way to measure the uncertainty associated with these codes?

## 1.2 ICET Series

- Have the principal sump pool variables, which affect chemical by-product formation in the post-LOCA environment, been adequately simulated?
- Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?
- What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects) and how should their effect be characterized by testing or analysis?
- Were the methods used within the ICET program to characterize and analyze chemical by-products sufficient?

## 1.3 Head Loss Simulation Testing and Analysis

- Is the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?
- What is the best method for incorporating time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?
- What metrics are most appropriate for evaluating the results of simulated chemical products

with those that formed during the ICET program?
- Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical by-product are known?

## 1.4 Response

The program is here reviewed in three parts. The first addresses the analytical computer simulations to evaluate the requirements for the ICETs, the second contains a review of the adequacy of the ICET series, and the third part is a review of the head loss tests and supporting research.

# 2 ANALYTICAL SIMULATIONS

The Center for Nuclear Waste Regulatory Analysis (CNWRA) was asked to perform computer-based modeling with the following objectives:

1. To determine the need for a pressurized test loop for the ICETs
2. To assess whether gelatinous products could form following a LOCA
3. To gain insights into important parameters
4. To attempt to predict ICET results.

The reason for conducting such computer based modeling was that it would "…allow rapid and relatively inexpensive identification of the critical chemistry, time, temperature, pressure and pH variables that affect chemical product formation" (Jain et al., 2005).

To meet the above-cited objectives, a literature survey was conducted to determine the corrosion rates of materials exposed to cooling water following a LOCA. These materials included aluminum, copper, carbon steel, and galvanized steel (zinc), fiberglass insulation and concrete. Estimated conservative values for corrosion rates of these materials were made on the basis that corrosion rates at 90°C would be representative, and that the concentrations of the corrosion products would be dependent on time (up to 15 days), and the estimated total surface areas of the exposed materials. Two alternative aqueous solutions were assumed, one consisting of a solution of 0.259 mol/L $B(OH)_3$ plus 0.15 mol/L NaOH, buffered at a pH = 10, and the other consisting of 0.259 mol/L $B(OH)_3$ plus $Na_3PO_4$, buffered at a pH = 7.

Preliminary modeling was conducted using OLI system Inc.'s Stream Analyzer Version 1.2 and Environmental Simulation Program (ESP) Version 6.6 (OLI Systems inc., 2002a,b) by assuming the equilibrium partitioning of the total concentration of corrosion products between the aqueous phase, and solid phases at given times following a LOCA, and at temperatures ranging downwards from 150°C to 60°C. Sensitivity studies were also conducted by varying the concentrations of the individual corrosion products by +/- 1-2 orders of magnitude at an unspecified time at 60 and 130 ºC.

The results and findings of the preliminary modeling are described in a report by Jain et al. (2004), which was subsequently attached as Appendix C to a later report by Jain et al. (2005). A listing of the simulations conducted by Jain et al. (2004) is given in Table 1

Jain et al. (2005) conducted electrochemical corrosion rate studies on aluminum, carbon steel, copper and zinc in 0.259 mol/L $B(OH)_3$ plus 0.15 mol/L NaOH, solutions buffered at a pH = 10. Studies were also conducted to measure the chemical corrosion of glass used to fabricate NUKON fiberglass insulation, and the chemical corrosion of concrete in the same solution. These measurements allowed for refinement of the postulated corrosion rates and thermodynamic simulations were repeated using revised conservative estimates of the corrosion rates of the tested materials. The follow-on simulations used the same software as in the preceding report. A listing of the simulations conducted by Jain et al. (2005) is summarized in Table 2.

## Table 1: Simulations conducted by Jain et al. (2004)

***B(OH)3/NaOH Solution Buffered at pH = 10***

| No. | T, °C | P, kPa | Time, hr | SpecifiedConditions | Output Reported |
|---|---|---|---|---|---|
| 1 | 60 | 101 | - | 0.26 mol/L B(OH)$_3$<br>0.23 mol/L NaOH<br>pH = 10 | pH, Eh ($V_{SHE}$) |
|  | 90 | 101 |  |  |  |
|  | 130 | 304 |  |  |  |
|  | 150 | 507 |  |  |  |
| 2 | 60 | 101 | 0.5 | As above, plus predicted concentrations of dissolved components at 0.5 hr from Zn, Al, carbon steel, Cu, Nukon™, concrete particles and concrete. Amounts estimated based on corrosion rate at 90 C for 0.5 hr. | Solid phases precipitated in mol/L or percent as f(T). Elemental distribution in solid phases as f(T, P). |
|  | 90 | 101 |  |  |  |
|  | 130 | 304 |  |  |  |
|  | 150 | 507 |  |  |  |
| 3 | 60 | 101 | 360 | As above, but for an additional 0.24 mol/L B(OH)3 to maintain pH at 10. | Solid phases precipitated in mol/L |
| 4 | 60 | 101 | 0.5? | As for 3, above, but pH varied between 7 and 11 | Solid phases precipitated in mol/L, plotted as a function of pH |
|  | 130 | 304 |  |  |  |
| 5 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but Zn aqueous concentration varied | Variation in quantity of precipitated Zn-containing phases as a function of concentration at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| 6 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but Al aqueous concentration varied | Variation in quantity of precipitated Al-containing phases as a function of concentration at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| 7 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but Fe concentration varied | Variation in quantity of precipitated Fe-containing phases as a function of concentration at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| 8 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but aqueous concentration of concrete components varied | Variation in quantity of precipitated phases as a function of dissolved $Ca_2SiO_4$ concentration at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| 9 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but aqueous concentration of Nukon™ components varied | Variation in quantity of precipitated phases as a function of dissolved Nukon™ components at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| ***B(OH)3/Na3PO4 Solution Buffered at pH = 7*** |  |  |  |  |  |
| 1 | 60 | 101 | - | 0.26 mol/L B(OH)$_3$<br>0.0084 mol/L $Na_3PO_4$<br>pH = 7 | pH, Eh ($V_{SHE}$) |
|  | 90 | 101 |  |  |  |
|  | 130 | 304 |  |  |  |
|  | 150 | 507 |  |  |  |
| 2 | 60 | 101 | 0.5 | As above, plus predicted concentrations of dissolved components at 0.5 hr from Zn, Al, carbon steel, Cu, Nukon™, concrete particles and concrete. Amounts estimated based on corrosion rate at 90 °C for 0.5 hr. | Solid phases precipitated in mol/L or percent as f(T). ). Elemental distribution in solid phases as f(T, P). |
|  | 90 | 101 |  |  |  |
|  | 130 | 304 |  |  |  |
|  | 150 | 507 |  |  |  |
| 3 | 60 | 101 | 360 | As above, but for an additional 1.5 mol/L B(OH)$_3$ to maintain pH at 7. | Solid phases precipitated in mol/L compared with results above at 130 °C. |
| 5 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but Zn aqueous concentration varied | Variation in quantity of precipitated Zn-containing phases as a function of concentration at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| 6 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but Al aqueous concentration varied | Variation in quantity of precipitated Al-containing phases as a function of concentration at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| 7 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but Fe concentration varied | Variation in quantity of precipitated Fe-containing phases as a function of concentration at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| 8 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but aqueous concentration of concrete components varied | Variation in quantity of precipitated phases as a function of dissolved $Ca_2SiO_4$ concentration at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |
| 9 | 60 | 101 | 0.5? | Sensitivity Study: As for 3, above, but aqueous concentration of Nukon™ components varied | Variation in quantity of precipitated phases as a function of dissolved Nukon™ components at 60 and 130 °C. |
|  | 130 | 304 |  |  |  |

Table 2: Simulations conducted by Jain et al. (2005)

| No. | T, °C | P, kPa | Time, hr | SpecifiedConditions | Output Reported |
|---|---|---|---|---|---|
| 1 | 60 | 101 | - | 0.26 mol/L $B(OH)_3$<br>0.23 mol/L NaOH<br>pH = 10 | pH, Eh ($V_{SHE}$) |
| | 90 | 101 | | | |
| | 110 | ≈140 | | | |
| 2 | 60 | 101 | 0.5 | As above, plus predicted concentrations of dissolved components at 0.5 hr from Zn, Al, carbon steel, Cu, Nukon™, concrete particles and concrete | Solid phases precipitated in mol/L or percent as f(T) |
| | 90 | 101 | | | |
| | 110 | ≈140 | | | |
| 3 | 60 | 101 | 0.5 | As above, except that dissolved Cu and carbon steel components were omitted for times > 32 hr. For times ≥ 180 hr dissolved components from Nukon™ were fixed. | PH, Eh ($V_{SHE}$)<br>Solid phases precipitated in mol/L or percent as f(time). Elemental distribution in solid phases as f(time). Concentrations of dissolved components in aqueous phase as f(time). |
| | | | 4 | | |
| | | | 32 | | |
| | | | 148 | | |
| | | | 240 | | |
| | | | 360 | | |

It should be noted that in neither report was any consideration given to the corrosion of Cal-Sil insulation, which is commonly used instead of fiberglass in many PWRs. Furthermore, Jain et al. (2005) did not consider $Na_3PO_4$ buffering at pH = 7. Therefore, the modeling did not fully account for all operating conditions in the subsequent ICETs

The conclusions reached by both Jain et al. (2004) and the covering report by Jain et al. (2005) can be summarized as follows:

1. The chemical processes occurring during the period following a LOCA, when temperatures are greater than 100°C, are similar in character and magnitude to those occurring at temperatures below 100°C, and therefore, the costs associated with the design and operation of a pressurized high temperature (150°C), elevated pressure (5 atm) ICET circuit would not be justified by the additional information obtained.

2. The contributions to the formation of screen clogging precipitates arising from the corrosion of copper, steel and zinc, are insignificant compared with those arising from the corrosion of fiberglass insulation and aluminum.

3. The impact of concrete corrosion on screen clogging is expected to be minor, and is associated primarily with cement dust and scaling debris, rather than corrosion of concrete surfaces of the containment vessel and interior structural members

4. There would be a potential for gel formation, based on their finding that one of the principal precipitants from the alkaline solution, $NaAlSi_3O_8$ would likely form a gel. Such gel formation could enhance screen clogging following a LOCA.

The reviewer concurs with the first three conclusions. Conclusion (4 might also be valid in that some siliceous precipitate might accumulate as a gelatinous solid. However, the extent to which such a solid would form depends on the rapidity with which silica accumulates in solution, the extent of neutralization due to the corrosion of aluminum, and falling temperature. The latter two processes would destabilize colloidal silica and lead to gel formation. However, neither Jain et al. (2004), nor Jain et al. (2005) provide adequate justification or arguments to support this position. When reference is made to the original objectives of their work, it is clear that only

Objective (1 was fully met. Objective (3 regarding acquisition of insights into important parameters governing the operation of ICETs, were met in part as a result of the literature survey regarding corrosion rates in Jain et al. (2004) and additional experimental work reported in Jain et al. (2005). In this regard, the computer modeling provided only a limited contribution towards meeting this objective.

The authors placed significant faith in the output generated by the computer simulations, much of which is misleading or erroneous, Other important conclusions are embedded in the text, or could have been reached without recourse to the extensive simulations conducted in both reports, The limitations, deficiencies and further conclusions are discussed below in Section 2.2: Limitations of Current Modeling Work.

A third report was subsequently released in draft form by the CNWRA (McMurry et al. (2006) The main purpose of the underlying study was to further evaluate the use of thermodynamic simulation software as a tool to investigate chemical interactions that could affect sump pump performance after a LOCA. The report covers four tasks:

1. An evaluation of aqueous chemical modeling software
2. EQ3/6 thermodynamic simulations of the ICET series.
3. StreamAnalyzer simulations of the ICET series
4. An assessment of modeling chemical effects under plant-specific conditions.

The software comparison involved the testing of four generally available chemical modeling codes: EQ3/6 (Wolery, 1992; Wolery and Daveler, 1992; LBNL, 2003), the REACT module of Geochemist's Workbench (xxx), StreamAnalyzer (OLI Systems, Inc., 200a) and PHREEQC (U.S. Geological Survey, 200x). Model input for all four codes was based on the hypothetical post-LOCA containment water composition derived from Jain et al. (2005), and representing the species dissolved in 0.26 mol/L B(OH)3 adjusted to pH = 10 with NaOH. Separate runs were conducted at 0.5 hr at 90 and 110 C, and at 0.5, 4, 72, 148 and 360 hr at 60 C, assuming cumulative concentrations of debris or structural material corrosion products in solution at the specified time and temperature. The codes were used to determine the final equilibrium solution composition and the identity and quantity of co-existing phases that would precipitate from an initially supersaturated solution of specified composition. The authors found that the EQ3/6 code was most convenient to use for the problem at hand, as it never failed to converge, and automatically identified the thermodynamically most stable phase assemblage. However, the EQ3/6 thermodynamic database for aqueous species contained only a limited number of borate species, and therefore the code's ability to simulate the properties of borate solutions was questioned. In contrast, StreamAnalyzer contained a much more substantial borate species database. McMurry et al. therefore decided to conduct replicate simulations of the ICET series using both EQ3/6 and StreamAnalyzer.

The initial conditions for the ICET simulations using both EQ3/6 and StreamAnalyzer were as specified in Table 3. For EQ3/6, separate runs were conducted at 0.5, 32, 148 and 360 hr at 60 C, assuming cumulative concentrations of debris or structural material corrosion products in solution at the specified time and temperature. The corrosion rates were based on those determined in Jain et al. (2005). Dissolved O2 and CO2 , equilibrated with respect to the atmosphere were accounted for in the input. The runs were repeated in under two separate conditions: (1) By including all relevant phases in the thermodynamic database, and (2) By suppressing some 40 odd phases that were deemed unlikely to form in the system under study, or which had precipitated under Case (1), but which were known not to form under actual ICET conditions. The StreamAnalyzer runs were conducted at 0.5, 32, 148, 360 and 720 hr at 60°C. The corrosion rates of Nukon and cal-sil were based on more recent experimental data. Because Al in solution was found to inhibit Nukon dissolution, the dissolution rate in the ICET #1 and ICET #5 was fixed at that after 90 hours for all runs representing times greater than 90 hr. The corrosion products of Cu and Fe were omitted in order to avoid convergence problems. Dissolved O2 and CO2 were not included in the input. The selective suppression of those phases not observed to form in favor of those observed during the ICET series was also practiced. For example, all silicates were suppressed. Therefore the outputs from the EQ3/6 and StreamAnalyzer runs could not be compared rigorously.

The comparison between the ICET series and model results provided a basis for a critical assessment of limitations of the simulations due to (1) lack of thermodynamic data for relevant phases and aqueous species in the code databases, (2) limitations in the kinetic data relating to the dissolution of reactive materials in contact with buffered borate cooling waters, especially in relation to a failure to take into account coupled effects on dissolution kinetics due to the co-dissolution of other materials (3) an inadequate characterization of Al corrosion under ICET conditions including the effects of passivation by Ca silicates, (4) inhibition of Nukon dissolution by dissolved aluminum, (5) saturation of cal-sil containing phases in solution, (6) an incomplete characterization of secondary precipitates and (7) limitations in accounting for the role of $CO_2$ and the precipitation of carbonates. Overall, the modeling in McMurry et al. (2006) reflected a better understanding of the issues involved.

McMurry et al. (2006) reached essentially the following conclusions:

1. Despite the noted limitations, the StreamAnalyzer generally provide good agreement with experimental results, particularly at modeled times of ≤140 hr.

2. Improved results with StreamAnalyzer compared with those using EQ3/6 depended less on the software than on revised and more accurate estimates of the aqueous phase starting compositions, and on the preferential selection of secondary precipitates.

3. More generally, widely supported programs such as EQ3/6 or PHREEQC provide modeling advantages in terms their flexibility in suppressing the precipitation of specified phases, and the ease with which thermodynamic databases can be modified to better represent the system being modeled.

## 2.1 The Adequacy of Analytical Simulations conducted in Support of ICETs and Head Loss simulation Testing and Analysis

The objectives of the NRC sponsored work at the CNWRA and whether these objectives were met is spelled out below.

*To determine the need for a pressurized test loop for the ICET'.s*

The evaluation showed that there was no compelling need for a pressurized test loop for ICETs. However, actual chemical processes likely to take place at any temperature and pressure following a LOCA, were not quantitatively demonstrated.

*To assess whether gelatinous products could form following a LOCA.*

No information was provided that would demonstrate that gelatinous products would form following a LOCA.

*To gain insights into important parameters.*

The experimental studies to quantify metal and other debris corrosion rates by Jain et al. (2005) ands subsequent refinement of Nukon and cal-sil leaching kinetics by McMurry et al. (2006) are a valuable contribution towards model development, and helped show which debris components were important, and which were less so. However, the data developed were not used to their fullest advantage in subsequent modeling.

*To attempt to predict ICET results.*

ICET results were predicted only in a rudimentary sense.

In the following discussion, the reviewer is responsive to pertinent technical questions posed by NRC for the Chemical Effects Peer Review Group. However, because the current modeling work falls short of what is needed, the reviewer also provides and expanded critique of the limitations of the work done so far, and recommends an amended approach that would be both scientifically defensible, and provide a more meaningful basis for model calibration and verification using the results of the ICETs and the Head Loss Simulation Testing. Such an approach might permit the resulting model to be customized for predictive simulations of the consequences of hypothetical LOCAs with respect to specific PWR designs. The work done so far has only begun to address the requirements for model calibration or validation with the ICETs and the Head Loss Simulation Testing.

## 2.2 Limitations of Current Modeling Work

### 2.2.1 General Comments

The modeling work described by Jain et al. (2004), Jain et al. (2005) and McMurry et al. (2006) suffers from several limitations and deficiencies. The limitations and deficiencies apply primarily to the first two reports, as some have been partially addressed, or at least identified, in the last report. Full advantage has not been taken of available software capabilities to provide an adequate framework for follow-on experiments and analysis. Specific issues are as follows:

1. The thermodynamic database for OLI Systems Inc. codes lists phases solely by their chemical composition, e.g., $NaAlSi_3O_8$. Specific polymorphs are not identified by their mineral names, properties, or Greek alphabet prefix, as is customary in the geochemical or materials science literature, respectively. Thus there are 5 polymorphs of albite ($NaAlSi_3O_8$) listed in the output provided in Appendix B to Jain et al. (2004), i.e., Appendix C of Jain et al. (2005). The source of the data contained within the database is not given, so there is no way of finding out whether the data is correct or when it was last updated or revised. Inspection of the listing of participating phases suggests that they might be rock-forming minerals that would form under hydrothermal, metamorphic or magmatic conditions. Such a database is largely unsuitable or useless for the simulations being conducted, and would yield meaningless results.

2. The OLI Systems codes are designed to explore the operation of systems in which reaction rates are sufficiently fast that equilibrium is assumed, and that complex flow

streams between multiple reactors can be modeled. A particular feature of the OLI Systems codes is that they are capable of modeling very high ionic strength solutions (up to 30 *M*) using Pitzer (1991) or Bromley (1972) electrolyte models. The capabilities of these codes are either insufficient, or not critical for the system being modeled. The absence of provisions that would allow for the evolution of a system under specified kinetic controls is particularly critical.

3. For reasons that are discussed further below, phases that would nucleate and precipitate following a LOCA, would probably be amorphous or poorly crystalline, and colloidal or microcrystalline in size. Such phases would be far more soluble than the thermodynamically most stable phases for the specified conditions. A more suitable thermodynamic database than that used with the OLI Systems codes for phases that would form under such conditions is that used with the MINTEQ code (Felmy et al., 1984), which is designed for relatively low temperature (0 – 100°C) aqueous chemical processes. However, it is up to the modeler to ensure that the thermodynamic database contains those phases most likely to nucleate and precipitate under the conditions to be modeled. It is not sufficient to take an off-the-shelf code and associated database without first establishing its suitability, or revising the database through addition of more appropriate phases and their properties. Jain et al. (2005) may have been aware of the limitations of the OLI Systems database, as they refer to the phases as “potentially amorphous”, but took no action to correct for the problem. McMurry et al, in contrast, were fully aware of the limitations, and attempted to correct the problem, at least in part, by suppressing certain phases from participating in the equilibrium calculation while using both EQ3/6 and the OLI Systems StreamAnalyzer.

3. All of the calculations performed using OLI Systems Inc. codes assume a given initial concentration of components in solution, which are then distributed between the aqueous phase, and thermodynamically most stable solid phases. However, in Jain et al. (2004) and Jain et al. (2005), the initial conditions are incompletely specified, i.e., whether a vapor phase is assumed to be present, and if so, how much? How was the oxidation state specified? Was the pH fixed, as suggested in the text, or was it a dependent variable? The “Typical OLI Simulation Output”, given in Appendix B of Jain et al. (2004) indicates that Zn, Al, Cu and Fe were specified as being in their metallic state in the “Stream Inflows”, and as cited in Table 3-3 of Jain et al. (2005). Furthermore, the output indicates that hydrogen was generated, but remained entirely in the aqueous phase, instead of partitioning into a vapor phase. No mention is made of the input pH, so it must be presumed to be a dependent variable, i.e. pH = 6.9771 as cited for the output. The code option “Redox selected” was also invoked, which allowed calculation of the Eh = -0.339 V.

4. The purpose of the studies by Jain et al. (2004) and Jain et al. (2005) was to provide guidance in the design and operation of the ICET and head loss experiments. Because the ICETs and Head Loss Simulation tests are both conducted with limited headspace, the absence of a coexisting vapor or vapor phase should be of limited concern if the computer calculations are used for the purpose of predicting, or simulating these tests. However, this presumes that the limited headspaces have not been exposed to atmospheric exchange for a significant period of time. Such exchange, particularly with respect to CO2, could have a significant impact on the chemical evolution of the system over time, and should require that such uptake be taken into account, if necessary. Jain et al. (2004) and Jain et al. (2005) did not consider the effect of scavenging $CO_2$ from the air as possibly impacting the evolving

chemistry and nature of the precipitates. Calculations by the reviewer suggest that the potential quantity of calcium precipitated, as calcite through uptake of atmospheric $CO_2$ in a containment building would be less than 1 % of the total calcium brought into solution by the dissolution of fiberglass. However, calcite might nucleate and precipitate early in the post-LOCA cooling cycle, and facilitate subsequent heterogeneous nucleation and precipitation of calcium phosphates and silicates. Furthermore, the amount of CO2 taken up during operation of any of the ICETs may have proportionately exceeded that which could have been scavenged from the atmosphere in the containment building. Thus, although the omission might be justified, because atmospheric $CO_2$ would be a minor component, its effect on precipitation kinetics could be significant. McMurry et al. have drawn attention to the limitations in accounting for the role of $CO_2$ and the precipitation of carbonates. The ultimate goal of all simulations undertaken in the program should be to predict adverse conditions following a LOCA in an operating PWR. Due consideration should therefore be given to eventually simulating actual post-LOCA cooling operations by including a coexisting gas phase equivalent in volume to that of the containment building.

5. The calculated Eh values presented in Tables 3-2 and 4-1 of Jain et al. (2004) and in Tables xx of McMurry et al (2006) are probably meaningless under the conditions of the ICETs, as it is highly unlikely that the circulating aqueous phase would achieve internal equilibrium with respect to participating redox pairs. Therefore, Eh should not be emphasized. This same caveat applies with even greater force to actual conditions following a LOCA. Hydrogen from the corrosion of aluminum would degas into the air of the containment building, and oxygen would continue to saturate the circulating coolant water. However, as other members of the Chemical Effects Peer Review Group have pointed out, e.g. McDonald (2006), significant radiolysis of the circulating coolant could occur with formation of H2O2, depletion of oxygen, and production of additional hydrogen. Attainment of a meaningful calculated solution Eh would be unlikely, as the circulating coolant would not be able to achieve homogeneous equilibrium during the frame it would be recirculated. Furthermore, radiolytic effects could be adequately simulated only through modification of the existing a geochemical modeling code to account for an imposed radiation flux.

6. As noted above, the thermodynamic calculations presented by Jai et al. (2004) and Jain et. (2005) assume a certain quantity of Zn, Al, Cu or Fe is available for corrosion after a given time, and is supplied as input to the model in the metallic state. Thermodynamic equilibrium is then assumed through reaction of the constituent metals with the aqueous phase, and precipitation of corrosion products. This causes the calculated Eh to fall sharply to approximately –0.4 V at pH = 7, (e.g., see Appendix B of Jain et al., 2004), and even lower at higher pH. Under such conditions, Cu is stable in its native state, rather than as an oxide, as is confirmed by the reported results of the simulations in both Jain et al. (2004) and Jain et al. (2005). Dissolved copper in the recirculating coolant would plate out on exposed aluminum and steel surfaces, and be quantitatively removed from solution, in conformity with the modeling results. The presence of native copper in contact with exposed steel or aluminum could enhance the corrosion rate of either through galvanic coupling. In contrast, the dissolution of metallic Fe, i.e., steel, would lead to immediate oxidation with precipitation of Fe oxides under oxidizing alkaline conditions, as oxidation of $Fe^{2+}$ is catalyzed by $OH^-$ (Singer and Stumm, 1968, 1970). Passivation of the Fe could result if $Fe_3O_4$ precipitates on exposed steel surfaces, as is suggested by Jain et al.

(2005, p. 2-2). At lower pH, i.e., at a pH ≈ 7, $Fe^{2+}$ is likely to accumulate in the aqueous phase, but the presence of oxygen will ensure that precipitation in the III state will occur during circulation of the coolant. It is quite unlikely that iron would at any time precipitate in the Fe(II) state as reported in the simulations, i.e., see p. 3-4 of Jain et al. (2004). It would have been more appropriate, therefore, to assume an excess of oxygen to have been present during the computation of the species distribution between the aqueous and solid phases, rather than ignoring it as was done by the authors.

7. The chemical composition of the concrete and concrete dust is presumed to consist of $Ca_2SiO_4$ (belite), a phase known to occur in five polymorphic forms (Taylor, 1997). However, $Ca_2SiO_4$ is one of the principal ingredients of cement before it is mixed with water to produce a cement paste, and does not persist in concrete or concrete dust. Ordinary Portland cement (OPC) reacts with water to form principally C-S-H (CaO-$SiO_2$-$H_2O$) "gel' and portlandite ($Ca(OH)_2$). It is these phases that should be considered if *fresh* concrete were to be leached by the recirculating coolant. However, neither the exposed concrete faces nor concrete dust in the containment building are likely to be fresh. After 30 years exposure to the atmosphere, a substantial fraction of both the exposed C-S-H gel and the portlandite would have been carbonated (Parrot and Killoh, 1989), i.e. they would have converted to a mixture of amorphous silica and either vaterite or calcite (Slegers and Rouxhet, 1976). Therefore, exposed cementitious materials would most likely be carbonated, and the modeling should reflect this state of affairs.

8. There are inherent limitations to all modeling work done to date, because the dissolution rates of debris and construction materials are represented by computing a fictive accumulated concentration of dissolved species in solution after fixed time periods, and then distributing the dissolved species among precipitated phases. While it is understandable that the initial stage of modeling should involve such scoping calculations, this approach seriously limits realistic simulations of the ICETs or head loss tests. Several codes are available in either the academic or commercial sector that allow simulations in which dissolution and precipitation rates are kinetically controlled, e.g. EQ6 (Wolery and Daveler, 1992), TOUGHREACT (Xu et al., 2004), the Geochemist's Workbench (Bethke, 2005) and PHREEQ-C (Parkhurst and Appelo, 2005). While some effort would be required to incorporate appropriate kinetics for heterogeneous reactions in these codes, this is not insuperable, and would greatly enhance the value of the modeling. The major difficulty with the study of the evolution of a chemical system with time is largely overcome in this program, because Jain et al. (2004) and Jain et al. (2005) have already undertaken an extensive literature search and conducted experimental studies to measure the corrosion rates of affected materials, and this work is supplemented by further studies of the dissolution rates of Nukon and cal-sil reported by McMurry et al. (2006). Furthermore, the TOUGHREACT code also permits non-isothermal simulations to be conducted. Therefore, a simulation of both variable dissolution and precipitation rates during cooling could be accomplished. Such modeling would also possess the added advantage that the kinetic parameters could be refined using output data from the ICET and head loss tests.

9. McMurry et al. (2006) correctly identify additional limitations hindering an improved predictive capability for current modeling activities. They include (1) a lack of thermodynamic data for relevant phases and aqueous species in the code databases,

(2) limitations in the kinetic data relating to the dissolution of reactive materials in contact with buffered borate cooling waters, and (3) an incomplete characterization of secondary precipitates. However, these problems are not insuperable, and much progress can be made by a further review of the literature, particularly in relation to work conducted with respect to metastable calcium phosphate precipitates (Van Kemenade and de Bruyn, 1987) and metastable aluminum oxy-hydroxides (Van Straten and De Bruyn, 1984). The extensive data on borate species in solution undoubtedly has a source (ref), and suitable analysis could permit its consolidation in the databases f the code of choice. The limitation in current kinetic data, e.g., inhibition of Nukon dissolution by dissolved aluminum, and the potential passivation of aluminum by dissolved silica (+ calcium?), clearly mandate additional experimental studies to characterize the interactive kinetic behavior of concurrently corroding materials. Finally, the inadequate characterization of precipitates during the ICETs may necessitate dedicated experiments to collect sufficient material for more detailed characterization.

10. In Jain et al. (2005), sensitivity studies were conducted by arbitrarily varying the corrosion rates of the various materials, one at time, over very large, and possibly unrealistic ranges. Apart from the fact that the kinetic rate parameters are only a few of the total number of parameters in the models that contribute to uncertainty, the selection of the magnitudes of these parameters tended to be made on the basis of conservatism rather than accuracy. Ideally, the uncertainties in all parameters should be embedded in the chemical modeling simulator, and the uncertainties in all calculated results carried through to the output. Attempts to do this have so far been exceedingly limited, e.g. see Najm et al. (2003) and Reagan et al. (2004). Add-on modules to address this problem have been developed for the PHREEQC code (Ekberg and Emren, 1996; Ekberg et al., 2000). Given the current limitations of code development, it would seem that the most pragmatic approach would be to conduct multiple realizations, each time varying the critical input parameters using a Monte Carlo approach, and evaluating the overall uncertainty in output parameters.

11. It has been noted that all simulations conducted to date ignore the presence of a radiation flux, which would induce radiolysis in the water and some of the dissolved species, e.g. bicarbonate. Preliminary simulations show that a variety of radiolysis products are formed, including H2O2, H2, with corresponding reduction in dissolved oxygen. Radiolysis could cause the oxidation state of the aqueous phase to rise, as H2 would partition into the atmosphere of the containment building. It is not certain what the overall effect would be on precipitate formation and sump-screen clogging. However, the issue should be reviewed in the event that it may have a significant impact on real world behavior.

### 2.2.2 Detailed Comments

#### 2.2.2.1 Jain et al. (2005)

2-2. Reference is made to the variability in Fe corrosion with temperature due to lower dissolved oxygen at elevated temperatures. However, rates of reaction are likely to increase and $O_2$ diffusion rates also. A more likely reason is the more rapid and coherent build-up of a passivating oxide layer on the steel surface.

2-4. Reference is made to “stones” in concrete. The correct terminology is “coarse aggregate”.

Dicalcium silicate is referred to as the reactant in concrete. This is incorrect. It should be C-S-H gel or $Ca(OH)_2$.

4-1 The simulation is limited to pH = 10 with a $B(OH)_3$/NaOH mixture. However, that is not what is meant. The pH would vary with time depending on the amount of debris dissolved and the initial contribution of $CO_2$ that would be stripped from the air in the containment building. The latter process would not be relevant to ICET or head loss tests, where the air headspace is small.

It is stated that corrosion rates at pH = 7 are expected to be similar to those at pH = 10, but the corrosion of Nukon is reported as being three times slower at the lower pH.

It is not clear whether the cited pH values are measured or calculated at the operating temperature, or are referenced to 25°C. As noted elsewhere, pH should be considered a dependent parameter, as treated in the modeling.

4-2 The text is confusing. No reference is made to whether corrosion products of metal are incorporated or the metals themselves. Only reference to the incorporation of a metals is the reference that “…most of the copper added as copper metal in the simulation remained as copper metal”, and in Table 3-3.

Repeated reference is made to “…potentially amorphous solid phases…” Either they are or they are not amorphous in the simulation. Did the authors check to find out whether the product phases in the simulation were specified as amorphous or crystalline?

Repeated reference is made to ”…soluble phases of silica [such as] $H_3SiO_4^{-1}$ and $NaHSiO_3$…” or “…the calcium-bearing soluble phase was $CaH_2SiO_3$”. This is incorrect. What the authors are referring to as aqueous species in a homogeneous aqueous phase.

Reference is made to the “…speciation of solid phases..” Presumably, the authors mean distribution of solid phases?

A statement is made that “Copper was thermodynamically stable and showed no corrosion.” Yet published Eh-pH diagrams show that under the Eh-pH conditions reported in Table 3-2 of Appendix C, CuO, i.e. a Cu(II) containing phase would be more stable than copper. Only by reference to Appendix B of Jain et al. (2004) can it be discerned that the redox potential is determined by the corrosion principally of aluminum, and that the Eh and pH are in the region of –0.4 V and 7.0 respectively.

4-5 Reference is made to the formation of $CaSiO_3$ and $SiO_2$. These formulas correspond to the minerals wollastonite and quartz, which are unlikely to coexist at the temperatures and pressures of post LOCA coolant circulation. A more likely assemblage would be tobermorite + gyrolite or the Z-phase, or gyrolite or the Z phase + amorphous silica. $CaSiO_3$ and $SiO_2$ is a fictive model assemblage generated by the simulator, and highlights the problem associated with the use of off-the-shelf databases and uncritical acceptance of the model results.

4-10 It is inappropriate to discuss the stability field of albite ($NaAlSi_3O_8$) in relation to gibbsite $Al(OH)_3$ using an Eh-pH diagram. No redox reactions are involved. If the stability relations of these two phases require graphical examination, then an activity diagram using chemical potentials $Na_2O$, $Al_2O_3$ and $SiO_2$ should be generated. The authors would then discover that other phases should also be taken into consideration such as beidellite, kaolinite, halloysite or allophane.

4-11 The solubility boundaries in this Eh-pH diagram should be defined by a Total Aluminum concentration. Without such data, the figure is inadequately defined.

Appendix B

B-2 The authors note that the rates of Nukon dissolution clearly vary as a function of time, as. Yet, for reasons of conservatism, they adopted a maximum initial rate of corrosion as being representative. The cause of the non-linearity in rates over time was not evaluated, although it was assumed that it was due to the formation of secondary layers [leached layers?] on the surface (Appendix C, p. 2-10). However, it could also be due to the dissolution of a more highly reactive disturbed layer, the precipitation of secondary phases, or an approach to metastable equilibrium of the glass with the aqueous solution. For meaningful modeling, the mechanisms should be identified, and a suitable algorithm describing the temperature dependent process incorporated in a simulator. See notes elsewhere concerning the use of “conservative” versus realistic values in modeling.

### 2.2.2.2 Jain et al. (2004) [Appendix C of Jain et al. (2005)]

xii Throughout Appendix C, reference is made to the precipitation of $Ca_5(OH)(PO_4)_3$, or apatite as the phase that would precipitate through the reaction of dissolved $Ca^{2+}$ with $Na_3PO_4$. In actual fact, this phase is slow to crystallize, and it is far more likely that metastable poorly crystallized phosphates will form, especially at high degrees of supersaturation (Van Kemenade and De Bruyn,1987; Van Cappellen, 1991). Therefore, permitting this phase to control the solubility of $Ca^{2+}$ and $PO_4^{3-}$ in solution is unrealistic.

1-3 Table 1-2. The analysis of the “gel” in this table is essentially meaningless, as the reported constituents add up to only 0.0131% of the total mass. What accounted for the remaining 99.99%?

2-8 Concrete is not a mixture of tricalcium silicate, dicalcium silicate, etc. The first two are the principal phases present in cement before it is mixed with water and aggregate to produce concrete. Corrosion rates cited in Jantzen (1984) are with respect to fresh concrete. The assumption is that none of the cementitious materials exposed in the interior of a containment building would have undergone carbonation, which is highly unlikely given the duration of exposure of exposed concrete faces to the atmosphere. Concrete dust would be especially subject to very rapid carbonation, converting the cement reaction products into $CaCO_3$ (calcite, vaterite) + $SiO_2$ (amorphous silica).

3-1 It is stated that “Simulations were conducted at pH 10…” and that a pH of 10 was obtained by adding 0.23 [mol/L]…NaOH.” and that “Additional 0.24 [mol/L] $H_3BO_3$ was needed to maintain pH at 10.” The statements are confusing. As far as the reviewer can ascertain, the input to the OLI Systems codes did not permit the specification of pH, and furthermore, pH could not be maintained in the simulation through the addition of $B(OH)_3$. Throughout Section 3, figures contain captions referring to “simulated containment water at pH 10" or similar phraseology. It is not stated whether "pH 10" refers to the initial pH before reaction or after, and whether the pH is referenced to 25 °C or the temperature of the simulation. Inspection of Table 3-2 and reference to Appendix B suggests that "pH 10" refers to the pH of the simulated containment water alone at 60°C, and therefore does not reflect the final pH of the aqueous phase in equilibrium with secondary precipitates.

The authors refer to the "hourly corrosion amount of each component", when in fact, they are referring to the half-hourly corrosion amount.

3-2 It is not clear what reaction determines the redox state for borated water in Table 3-2. Note that reference is made elsewhere that oxygen and $CO_2$ was not included in the initial chemical composition of the aqueous phase.

3-5 Note the argument that "…similar solid phases are formed in the first half hour of the LOCA event at 150°C as those from a 15-day or longer simulation test at 60°C." Presumably, this is one of the reasons justifying the exclusion of elevated pressure ICETs. However, these results are primarily an artifact of the database, and might not be valid if more realistic secondary precipitates were incorporated in the model.

3-7 It is noted that the formation of iron phases depends on pH. Thus, with increasing pH, iron is found in $Fe_3Si_2O_5(OH)_4$, then $Fe_3O_4$, then $Ca_3Fe_2Si_3O_{12}$ and finally $CaFe_2O_4$. This sequence shows that the oxidation state for iron goes from II to II/III to III to III, indicating higher oxidation states with increasing pH. This finding is the result of allowing native metals to dissolve in a system where the only oxidant is the water itself. This is inconsistent with the role of oxygen in oxidizing Fe to the II state in neutral to alkaline solutions. See the reviewer's comment regarding $OH^-$ catalysis under item 6 on p. 9. Therefore, $O_2$ should have been specified as an input species.

3-16 The final statement: "This fiber insulation…" is ambiguously worded. The reviewer presumes that the authors are referring to the lack of variation in the makeup of the precipitated phases with varying fiberglass concentrations, rather than the mass of secondary precipitates, which does vary. Also, it should be noted that in the simulations the concentration of fiberglass reaction products is roughly equivalent to that of concrete, e.g., see Table 3-1. Therefore, it would not be expected that variation of fiberglass reactant composition would have much impact on the results.

4-1 It is stated that "An additional amount of 1.5 [mol/L] $H_3BO_3$ was needed to maintain a pH 7." Yet subsequent tables refer only to simulated containment water containing 0.26 mol/L Boron. What does the quoted statement mean? Was this additional quantity of $B(OH)_3$ added to the input composition in order to maintain an output pH of 7?

It is not clear what reaction determines the redox state for borated water in Table 4-1. What causes the Eh to be lower than that of the alkaline borated water given in Table 3-2?

4-12 It is stated that "The fiber insulation sensitivity analysis at pH 7 indicated no significant impact on the formation of solid phases…" See comment for pp. 3-16. The real reason for the lack of variation is primarily because its reaction products are roughly equivalent to those that form from concrete.

5-2 Item (v). There is a real danger in placing too much faith in the finding that the retrograde solubility of secondary calcium silicate phases could assist in the unclogging of pump strainers. In reality, secondary colloidal/gelatinous hydrated calcium aluminum silicates, once formed, would be unlikely to redissolve within the time frame of interest. The ICET and Head Loss tests would help answer this question.

6-1 This section on gel formation is devoid of meaningful content. Better descriptions of gelation phenomena, and their causes, especially with respect to the formation of silica gel, can be found in the literature (Scherer, 1999; Lasaga, 1998; Lyklema, 1991; Weres et al., 1980).

7-1 It is claimed that the report validates OLI Systems, Inc software for speciation in borated waters. However, the relevant validation study is reported only in Appendix A, Section 2. If the findings of the validation study are of sufficient importance to be included in the Conclusions, then this work should have been incorporated in the main body of the text.

7-2 7.1 Conclusions For convenience, the eight bulleted conclusions relating to the circulated alkaline borate water are numbered in order to facilitate comment.

*$NaAlSi_3O_8$, $Ca_3Fe_2Si_3O_{12}$ and $Fe_3Si_4O_{10}(OH)_2$ were dominant solid phases that contributed to over 90 percent of the solid phases formed between 150°C [302°F]. 507 kPa [5 atm] and 60°C [140°F].*

Phases cited are unlikely to form under LOCA conditions

*The $Ca_3Fe_2Si_3O_{12}$ solid phase was formed at 150°C [302°F]. 507 kPa [5 atm]. while $Fe_3Si_2O_5(OH)_4$ was formed at 60°C [140°F]. This transformation was attributed to the retrograde solubility of calcium in iron bearing minerals. Despite these phase changes, all the iron was present in the solid phase.*

Cited phases are unlikely to form under LOCA conditions. Stabilization of $Ca_3Fe(III)_2Si_3O_{12}$ and $Fe(II)_3Si_2O_5(OH)_4$ with iron in different oxidation states is an artifact of the specified initial conditions for the distribution of species. As noted above, the distribution of Fe is a function of $(OH)^-$ dependent oxidation kinetics

*Copper had no influence on the precipitation of solid phases, and no corrosion of copper is expected.*

This conclusion is correct.

*The contribution from zinc was insignificant compared to other solid phases and was limited to 5 percent to the total quantity of solid phases.*

This conclusion is justified by the presented literature data on zinc corrosion, and the magnitude of exposed galvanized steel.

*Sensitivity analyses for aluminum indicated formation of $Al(OH)_3$ for aluminum concentrations exceeding 2 x 10-4 mol/L at 60°C [140°F]. The formation of $Al(OH)_3$ was not observed at 130°C [266°F]. 304 kPa [3 atm].*

The precipitation of $Al(OH)_3$, or AlO(OH) at temperatures higher than 60°C, depends on their being an insufficiency of silica to form phases such as beidellite, kaolinite, halloysite, allophane, etc. Their failure to precipitate as stable phases in the simulations suggests either an insufficiently comprehensive thermodynamic database, or erroneous data.

*Sensitivity analyses for concrete indicated, irrespective of the temperature and pressure, for* $Ca_2SiO_4$ *exceeding* $1 \times 10^{-3}$ *mol/L, the concentration of* $CaSiO_3$ *increased with an increase of concrete concentration.*

Wollastonite ($CaSiO_3$), is a high temperature phase, and is unlikely to precipitate under post LOCA conditions. The fact that fresh concrete contains C-S-H gel and portlandite, rather than $Ca_2SiO_4$, and that aged concrete most likely to be exposed to the atmosphere would be carbonated to a significant depth, essentially invalidates this conclusion.

*In a 15-day simulation at 60°C [140°F], all solid phases (except copper) present in the simulated containment water were solid silicates.*

This conclusion is generally valid except for the precipitation of minor calcite and magnetite or hydroxy-magnetite on exposed steel surfaces. Both phases would probably be present if more accurate simulations had been performed.

*As silicon concentration was reduced, the concentration of silicate phases reduced also. In an alkaline environment, the solubility of silica increased with an increase in pH and temperature. Since silicates were major corrosion products, a strong influence of pH and temperature was observed on the formation of the dominant solid phases in the simulated containment water. However, at pH 10, irrespective of the temperature, pressure, and concentration, silicates of aluminum and iron contribute 90 percent of the solid phases.*

The conclusions of this item are generally correct.

7-3 For convenience, the eight bulleted conclusions relating to circulated $Na_3PO_4$ buffered borate water are numbered in order to facilitate comment.

*There were significant differences in the solid phase formation in Na3PO4 containing simulated containment water at pH 7 from that in alkaline simulated containment water at pH 10.*

This conclusion is valid

*At pH 7,* $Ca_5(OH)(PO_4)_3$ *was the dominant solid phase containing almost 100 percent of calcium, while at pH 10, calcium was approximately 1 percent insoluble at 60°C*

*[140°F].*

Precipitation of apatite ($Ca_5(PO_4)_3(OH)$) as a dominant phase is unlikely. Amorphous to poorly crystalline precursors such as $Ca_4(PO_4)_3H$ (Van Kemenade and De Bruyn, 1987; Van Cappellen, 1991) are more likely .

*A significantly larger quantity of solid phases was formed in a solution containing* $Na_3PO_4$ *compared to alkaline containment water.* $Ca_5(OH)(PO_4)_3$ *and* $NaAlSi_3O_8$ *contributed to over 90 percent of the solid phases.*

This conclusion is likely valid.

*Sensitivity analyses for concrete indicated increase in the $Ca_5(OH)(PO_4)_3$ concentration with a increase in the concrete concentration. For concentrations of concrete exceeding 3 x 10-4 mol/L, $Ca_5(OH)(PO_4)_3$ coexisted with solid SiO2 phase. The concentrations of these two phases far exceeded contributions from other solid phases.*

This conclusion is generally valid. However the precipitating phases are unlikely to be apatite and quartz.

*Copper had no influence on the precipitation of solid phases.*
This conclusion is correct.

*The sensitivity analyses for aluminum indicated an increase in the concentrations of $NaAlSi_3O_8$ with an increase in aluminum concentration. Formation of $Al(OH)_3$ and AlO(OH) was observed for aluminum concentrations exceeding 3 x 10-4 mol/L at 60°C [140°F] and 130°C [266°F], 304 kPa [3 atm], respectively. In a 15-day simulation, aluminum was present exclusively as $NaAlSi_3O_8$.*

The precipitation of $Al(OH)_3$, or AlO(OH) at temperatures higher than 60°C, depends on their being an insufficiency of silica to form phases such as beidellite, kaolinite, halloysite, allophane, etc. Their failure to precipitate as stable phases in the simulations suggests either an incomplete thermodynamic database, or erroneous data.

*Both iron and zinc showed a decrease in solid phase concentration with decrease intemperature and pressure. The contribution of zinc was below 2 percent and that of iron is below 9 percent compared to the total solid phases. Other than a reorganization of iron phases, no significant changes were observed.*

This conclusion is likely valid.

*The dominant solid phases formed after 15 days were $Ca_5(OH)(PO_4)_3$ and $NaAlSi_3O_8$ with minor quantities of $Ca_2Mg_5Si_8O_{22}(OH\}_2$, $Fe_3Si_4O_{10}(OH)_2$, $SiO_2$, and $Zn_2SiO_4$ in the simulated containment water.*

For reasons stated elsewhere, the phases identified are unlikely to form under post LOCA cooling operation.

Appendix A

A-16 The test results for the dissociation constant of boric acid in 3 mol/L NaCl are only fair. Although the discrepancies between experimental and modeled values are significant, it is difficult to ascertain whether such would adversely affect the findings of the report.

A-18 The differences between the calculated concentrations of $Zn^{2+}$ and $Ca^{2+}$ and the respective measured concentrations, illustrated in Tables A-8 - A-11 are substantial, and suggest defects in the either the thermodynamic data or the electrolyte model being used in the code.

#### 2.2.2.3 McMurry et al. (2006)

1-1 It would be helpful if specific references could be given regarding the previous at the Barsback plant in Sweden, and strainer clogging events in U.S. boiling water reactors. Otherwise the assertions appear to be merely anecdotal.

2-5 It is not clear why StreamAnalyzer generated an output Eh of –0.600 V at pH = 10, as specification of dissolved iron as $Fe^{3+}$ (Table 2-2) should have poised the Eh at a much higher value. The actual conditions that result in such a low initial Eh should be explained. In any event, it is not clear why Eh had to be specified as input in any of the runs, unless the objective was to ensure final equilibrium with respect to some reduced phase, such as copper or magnetite. The outputs of subsequent runs to model the ICET series did not report Eh.

2-6 With reference to Table 2-4, note that $B(OH)_4^-$ and $BO_2^-$ are essentially equivalent. Also, the extensive list of borate species listed in the StreamAnalyzer database may be because this code is capable of modeling high ionic strength solutions, i.e. up to 30 molal where such species may be present in significant concentrations. It is quite possible that under the conditions of the present simulations, most, if not all of those additional species would be present at concentrations too low to significantly affect the results. Because the dissociation constants for these species are not listed in the report, it is not possible to check this postulate. However, the authors should check how significant these species are in affecting the results.

2-7 Charge balancing is a necessary requirement if total mass is to be redistributed among several phases, and should not be considered an artificial constraint. Much depends how it is accomplished. It appears that charge balancing was performed through adjustment of pH, which is satisfactory in strongly buffered systems, but may not always be an appropriate strategy.

2-8 Perhaps it should be emphasized that the inter-code comparison presented in section 2 is really an evaluation of the consequences of using different databases. The databases of all four codes are unsuitable for the problem at hand. Therefore the main purpose of the study is defeated, unless the databases are modified through incorporation of the thermodynamic properties of phases known to be relevant to the ICETs.

Tbl 3.2 The corrosion rates of metals, Nukon, and concrete and cal-sil insulation are given in different units (g/m2/hr, mg/h, mol/L). An explanation is called for in the accompanying text.

3-2 It is stated that cal-sil insulation was assumed to dissolve such that Ca and $SiO_2$ ions were contributed to the containment water in “equal molecular proportions”. Yet the analysis in Table 3-3 indicates that the molar ratio is 2.4:1. Some explanation for the ratio chosen is called for. In view of the fact that a significant quantity of $Na^+$ seems to be released from cal-sil during leaching experiments, e.g. see ref, this should have been included in those simulations where cal-sil was involved.

3-2 Mention is made that the water supplied t0 the tank was in equilibrium with dissolved carbon dioxide. Is this in reference to solution buffered with NaOH to pH = 10? If so, far too much $CO_2$ would have been taken up to realistically represent the amount of CO2 likely absorbed during the ICET series.

Tbl 3.3 The sources of the analyses for both Nukon and cal-sil are not given.

3-3 The most serious discrepancy between the EQ3/6 modeled results and the ICET #1 is the almost quantitative removal of Al from solution in the modeled results. The suppression of diaspore is appropriate, but the resulting induced precipitation of dawsonite and near quantitative removal of Al raises questions regarding the validity of the thermodynamic data for the participating phases and aqueous species. The cause of the discrepancy should be identified.

3-4 Note that the chemical analysis of the precipitate from ICET #1, which contained carbonate as well as aluminum, boron and sodium, could have taken up carbon dioxide from the atmosphere after sampling.

3-5 Inspection of the EQ3/6 simulation 2nd trial results for ICET #2 suggest that the depressed silica concentration is due to the precipitation of kaolinite rather than a less stable form such as allophane. The depressed Ca concentration is probably due to precipitation of apatite rather than a metastable form of $Ca_3PO_4$, e.g. see van Kemenade and De Bruyn (1987).

3-6 Inspection of the EQ3/6 simulation 2nd trial results for ICET #3 suggest that the depressed pH is due at least in part to the precipitation of apatite rather than a metastable form of $Ca_3PO_4$. The elevated Ca concentration is a consequence of the lowered pH. The elevated phosphorus concentration may also be due to the equilibrium of the system with respect to apatite at lowered pH, as raising $[OH]^-$ by $10^{2.4}$ would depress phosphate accordingly. This assertion appears to be supported by the ICET #3 results of the StreamAnalyzer simulation, (see note to pp. 4-7).

3-7 Although EQ3/6 simulation 2nd trial results for ICET #4 corresponds well with the experimental results for Ca, Si and Al, these results may be fortuitous. It is unlikely that kaolinite would be a precipitant at the prevailing pH of the system, and within the short time frame of the test. In nature, smectitic phases would be replaced by zeolites at pH ≈ 10. Bench-scale testing to determine the nature of any precipitates that would form under the specified conditions might help identify the composition and nature of precipitants that control the aqueous phase composition.

3-8 The EQ3/6 simulation 2nd trial results for ICET #5 predict the precipitation of gibbsite, which is less stable than boehmite at 60°C. In actual fact, it is more likely that pseudoboehmite would precipitate under the conditions of the test (Van Straten and De Bruyn, 1984), as is suggested by a prediction of a lower Al concentration in solution than actually observed.

3-10 Note that the rationale for using StreamAnalyzer in subsequent simulations was because of the expanded database of borate species in the database for this code. However, the significance of these species under the conditions of the ICET series was not evaluated in the report. Appendix C to this report is a summary of a StreamAnalyzer run for ICET #1 after 148 hr at 60°C. The output of this run allows an example calculation of the distribution of borate species for the specified conditions, where B = 0.259 mol/L and pH = 10. It shows that $B(OH)_4^-$ = 69.2%, $B(OH)_3$ = 8.0%and $B_4O_5(OH)_4^{2-}$ = 6.7%. All other species contribute less than 6% each to the total boron concentration. Thermodynamically, the only other borate species of potential importance is $CaH_2BO_3^+$, which, although of insignificant concentration (0.00017 mol/L), is actually responsible for complexing 76% of the dissolved $Ca^{2+}$, and could therefore have a profound impact in lowering the chemical potential of CaO in solution.

4-2 If X-ray diffraction analysis indicated that aluminum oxyhydroxide formed during ICET #1, it would be interesting to know whether the pattern reflected truly crystalline boehmite, or pseudoboehmite, which is a poorly crystalline precursor, and commonly confused with the former. See note to pp. 3-8, above. As noted elsewhere, merely specifying the formula of the precipitate INS not sufficient, and a serious disadvantage to using the OLI Inc. codes.

Tbl 4-3 Note that borate species but not their concentrations are listed in this table and others in the StreamAnalyzer simulations. Therefore their significance in affecting the results cannot be compared to model results using EQ3/6.

4-4ff The simulation results for ICET #2 using StreamAnalyzer indicate several problems. The Ca concentration is still too low; suggesting that the $Ca_3(PO_4)_2$ phase in the StreamAnalyzer databases is not appropriate for the case under study. Furthermore, it is unlikely that berlinite would precipitate, as very acid conditions are required to prevent Al hydrolysis. The literature should be searched for more suitable Al-hydroxy-phosphate phases to substitute for berlinite.

4-5 The assumption that cal-sil can be represented by CaSiO3 is inconsistent with the chemical analysis for this material in Table 3-3.

4-6 The dissolution tests for cal-sil suggest that saturation with respect to some Ca bearing phase was attained within 200 hr of the start of leaching. Failure to take this into account may explain the excessive Ca concentrations in solution in the ICET #3 simulations. The authors allude to this possibility on pp. 4-7. If this phenomenon was observed during the cal-sil dissolution experiments, why was this not taken into account in the simulations?

4-7 The precipitation of $Ca_3(PO_4)_2$ in the StreamAnalyzer simulation of ICET #3 avoids the pH shift due to apatite precipitation in the EQ3/6 ICET #2 simulation. This indirectly confirms that apatite could not be the phosphate phase precipitating in this experiment.

4-8ff The very large difference in Al concentration between ICET #1 and ICET #4 may suggest that reaction is taking place between the dissolved Al and the cal-sil to produce some hydrated Ca-Al silicate. However, other explanations include the inhibition of Al corrosion by hydrated Ca silicate coating, or secondary precipitation of a hydrated Ca-Al silicate, as suggested by the authors. Resolution of this issue should be particularly amenable to bench-scale testing.

5-3 The authors point out that precipitation and subsequent dissolution of Ca-phosphate precipitate after 9 days in ICET #3 is not explained by the modeling. The Na and PO4 analyses of the aqueous phase reveal sharp discontinuities at about 15 days, the former falling in concentration by 500 mg/L and the latter rising by 0.2 mg/L. If these discontinuities are real and not artifacts of sampling and/or analysis, then some clue might be provided regarding the chemical reactions that could have taken place. Both CNWRA and LANL should coordinate their efforts in attempting to resolve this question regarding the purported disappearance of the initial calcium phosphate precipitate. stable.

5-5 Note that the occurrence of borax and tincalconite may have been due to the effects of sample drying in the presence of the coexisting aqueous phase from which the precipitate was taken, resulting in concentration of borate and precipitation of the observed phases. Note, however, that neither the EQ3/6 nor the StreamAnalyzer databases appear to contain data pertaining to a range of naturally occurring Ca- and Na- borosilicates, amorphous or poorly crystalline forms of which might precipitate in the systems under investigation.

## 2.3 Recommendations for Future Modeling

Before serious modeling is undertaken, a conceptual understanding of the chemical processes involved is essential. The nature of the problem then determines what algorithms would most satisfactorily represent the processes involved, and whether computer codes exist that would do justice in realistically simulating those processes. Chemical reactions between water containing $B(OH)_3$ and suitable pH adjusters, such as NaOH or $Na_3PO_4$, and insulating and structural materials results in supersaturation with respect to various silicates, aluminosilicates, phosphates and minor oxides and borates. Because of the presence of pre-existing particulate material, much of it in active suspension, heterogeneous nucleation of solid phases would be induced upon reaching a critical nucleation threshold (Lasaga, 1998; Stumm, 1992). Empirical calculations indicate that this would probably be at a concentration about 10 times that required to achieve saturation, but could be significantly less.

The nucleating phase is commonly that which possesses the minimum interfacial free energy of all candidate phases. Usually such a phase is also the least stable phase when present as a macroscopic particle. Once nucleation has occurred, the degree of supersaturation falls rapidly, and the crystal growth rate slows, the interfacial free energy contribution also falls, and the crystallites become increasingly stable. At some point, the nucleating phase becomes supersaturated with respect to a more stable phase with higher interfacial energy, and that phase can initiate growth on a suitable substrate, as illustrated by Parks et al. (1990) for the system $SiO_2$.

Solutions containing silica commonly nucleate and grow as small colloidal particles of uniform size that can be stabilized in solution by the enveloping electrical double layer (e.g., see Iler, 1979). Because saturation has been reached, the colloidal particles can persist indefinitely in a metastable state. Destabilizing factors such as a change in ionic strength or pH can, however, overcome the repulsive effects of the electrical double layer (EDL) and lead to the aggregation of the colloidal particles to form a viscoelastic gel, a form of polymerization. Such gels can contract and fracture through syneresis (Scherer, 1999), and will eventually redissolve and recrystallize to thermodynamically more stable phases, but over time frames far longer than that required for coolant circulation following a LOCA.

During a LOCA, supersaturation, heterogeneous nucleation, colloid stabilization, and gel formation are likely to be the important processes. Recrystallization to form more stable phases would generally take place over timescales longer than the period of coolant recirculation. Therefore, the most suitable model for simulating a post LOCA system is one that takes such mechanisms into account. Unfortunately, although the theory for such chemical processes is quite well understood (Lyklema, 1991), only rarely have attempts been made to model such systems (Steefel and Van Cappellen, 1990; Ozkan and Ortoleva, 2000), and no off-the-shelf simulator is presently available to simulate these processes. Given the nature of the problem and time and financial constraints, it would probably be difficult to justify formulation of the needed algorithms and generation of appropriate code for this project. Therefore, an alternative simpler, but less rigorous approach should be taken, which ignores nucleation phenomena and coagulation, and gelatinous products are allowed to precipitate directly from solution. Several codes, noted above can be readily adapted for such a purpose, provided that the thermodynamic properties of the least stable phases are incorporated in the thermodynamic database and the more stable phases are suppressed. It should be borne in mind that very fast kinetic reactions that would achieve essential equilibrium in a matter of minutes should be ignored and equilibrium assumed, whereas reactions taking a year or more to achieve 90% equilibration can also be ignored as being too slow to be relevant.

In summary, the following steps should be taken for meaningful simulation of ICET and loop tests in addition to the debris and metal dissolution studies already accomplished:

1. Review the literature to identify candidate metastable colloidal and micro particulate phases that form or nucleate from solutions with similar chemical compositions to those postulated.
2. Analyze data to determine phase solubilities as a function of composition and pH, and temperature, if possible.
3. Calculate the solubility products of the phases as a function of temperature, using suitable approximation techniques, where appropriate thermodynamic data is unavailable.
4. Derive kinetic data for dissolution and precipitation reactions, where available, and calculate their temperature dependence, i.e., the apparent activation energies. If temperature dependent data is unavailable, estimates should be taken from closely analogous reactions. Although such estimates could be very inaccurate, this is not critical, as the rates of reaction and specific characteristics of the precipitates can be refined from the experimental results of the ICET and loop tests, and supplementary laboratory experiments as needed.
5. Insert the resulting data in the thermodynamic and kinetic databases of an appropriate code, e.g., EQ3/6 or TOUGHREACT, and run simple simulations to duplicate nucleation and precipitation data from which the thermodynamic and kinetic data were derived.
6. Depending on the selection of code and its features, conduct non-isothermal simulations of the kinetics of dissolution of debris and precipitation of reaction products, assuming oxygen saturation and $CO_2$ uptake. Depending on the features available in the simulator, hydrogen might be beneficially treated as an “inert’ product species, i.e., one that cannot react chemically with an oxidant to produce water, whereas oxygen can be made reactive. Such conditions would lead to more realistic simulations of the system being modeled.
7. As Jain et al. (2005) have determined, the omission of zinc and copper components from the simulations is unlikely to have a significant impact on results. If the simulations are conducted with an initial elevated pH, i.e., pH = 10, then the impact of Fe corrosion products might be omitted. However, if $Na_3PO_4$ buffers the pH at $\approx 7$, then the effect of iron corrosion might be included to accommodate the early nucleation of amorphous ferric hydroxides in suspension. This matter should be evaluated further before a final determination is made.
8. If possible, simulations should be set up to duplicate precisely, the actual sequence of steps undertaken during the course of ICET and lop tests.
9. Results of the ICET and loop tests can be used to refine the kinetics of reactions under operating conditions, which, in turn could be used for simulations of postulated LOCA events at actual PWR plants.

Even with perfect algorithms simulating the chemical processes that could take place, there will undoubtedly be aspects of the chemistry that are not fully understood or may be omitted from the model. Some possible limitations and how they might be addressed are given below.

1. The Nukon fiberglass insulation is coated with a phenyl formaldehyde resin based insoluble polymer (Jain et al. (2004, p 2-8). Yet experiments to measure corrosion of the fiberglass were conducted on uncoated glass coupons. The extent to which this coating would impede corrosion of the underlying glass appears to be minor. However, if the resin dissolves into an alkaline aqueous phase, the dissolved species could inhibit nucleation and growth of solid phases. Small-scale testing should be conducted to ascertain the importance or otherwise of dissolved organics on nucleation and precipitation kinetics of solid phases.
2. As noted by Jain et al. (2005) and McMurry et al. (2006), all kinetic parameters were determined either from experimental studies in the literature, or on additional experimental studies, where the complex interaction between dissolution processes of separate materials was not addressed. Examples already noted include inhibition of Nukon fiber dissolution by dissolved Al, and possible inhibition of Al corrosion by dissolved Ca and SiO2. Another example is the suppression of copper dissolution in the presence of less noble metals, thus: Cu>Fe (steel) ,>Zn> Al. Such second order interactions are difficult to identify, but could adversely affect the value of any simulator as a predictive tool for potential real events. Should circumstantial evidence from the ICET or head loss tests suggest second order interactions, experimental factorial design studies might be necessary to identify the second-order effects even though they may not be adequately defined.
3. Corrosion data for various participating metals, was extracted from the published literature and tabulated in Jain et al. (2004). The data showed wide variability depending on the specific corrosion conditions, and the nature of the alloy being subject to corrosion. Numerous different aluminum alloys are commercially available, but the variability in alloy dependent corrosion rates was not addressed. Given the corrosive environment of alkali borate solutions, the nature of the alloy in setting corrosion rates may not be important, but this issue does not appear to have been addressed.

## 2.4 Analytical Simulations: Questions and Answers

NRC posed the following questions relating to analytical simulations for consideration by the Peer Review Group. Answers are provided in response.

Q *Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?*

R (The speciation analysis conducted by McMurry et al. (2006) represents a significant improvement over earlier work, but does not exploit existing capabilities of the selected codes to fullest advantage. Nor is the present analysis adequate, because of over-reliance on existing and irrelevant thermochemical data for solid phases that were provided with the selected codes.

Q *Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?*

R Yes. The plan is generally satisfactory, but, as noted above, the capabilities of the codes currently being used are not being used to full advantage, and therefore, the value of the associated experimental studies are diminished. Furthermore, modeling studies supporting ongoing small-scale testing are currently not being done. With full exploitation of codes currently being used, and ongoing modeling support for small-scale testing, the program could be much more effective.

Q *What is the most appropriate way to measure the uncertainty associated with these codes?*

R Measurement of overall uncertainty of the output of any multi-component chemical simulation is difficult, because a large number of parameters are involved with widely varying levels of accuracy. In general, methods to address uncertainty in such simulations are in their infancy and have not been developed to a satisfactory level. The best approach in the present circumstances is to avoid the temptation to adopt unrealistically conservative values for the base case, but to utilize those values deemed to be most realistic. Then replicate runs can be made using Monte Carlo methods to determine variations in those parameters deemed to have the greatest uncertainties and most critical to model output. The cumulative variation in outputs can then be adopted as a measure of uncertainty. Further discussion of this issue is given in section 2.2 Limitations of Current Modeling Work.

# 3 INTEGRATED CHEMICAL EFFECTS TESTS

The NRC Office of Nuclear Regulatory Research (RES) sponsored the Integrated Chemical Effects Test (ICET) program at the University of New Mexico under the direction of the Los Alamos National laboratory (LANL). The primary objectives for the ICET series were to:

1. Determine, characterize, and quantify chemical reaction products that may develop in the containment sump under a representative post-LOCA environment
2. Determine and quantify any gelatinous material that could be produced during the post-LOCA recirculation phase.

There were five tests in the series. The test matrix is given in Table 3.

Table 3. ICET Matrix

| Test No. | PH Control System | Insulation Material |
|---|---|---|
| **1** | Sodium Hydroxide: pH ≈ 10 | 100% Fibrous (NUKON) |
| **2** | Tri-sodium phosphate: pH ≈ 7 | 100% Fibrous (NUKON) |
| **3** | Tri-sodium phosphate: pH ≈ 7 | 80% Particulate (Cal-Sil)<br>20% Fibrous (NUKON) |
| **4** | Sodium Hydroxide: pH ≈ 10 | 80% Particulate (Cal-Sil)<br>20% Fibrous (NUKON) |
| **5** | Sodium Tetraborate: pH ≈ 8 | 100% Fibrous (NUKON) |

Extended reports have been written for all five tests, (Dallman et al., 2005a,; Dallman et al., 2005b; Dallman et al., 2005c,d Dallman et al., 2006) and brief summary reports have been written for the first two and last two (Anonymous, 2005c, Anonymous, 2005a,b). In addition, an oral presentation regarding all tests was given at Argonne National Laboratory on October 18-19, 2005 (Letellier, 2005).

Reviews follow of the work summarized in the above-cited references.

## 3.1 ICET #1

The ICET #1 used a circulating fluid consisting of 2,800 mg/L boron, 100 mg/L HCl (about 12 N, as cited in a subsequent ICET report) and 0.7 mg/L LiOH. According to Letellier (2005) the solution was made up using 15.14 kg $B(OH)_3$, 5.87 kg NaOH, 0.66 g LiOH and 214 mL HCl in 250 gallons. Within 30 minutes of the start of the test, an additional 2.27 kg NaOH was introduced during an initial 4-hr spray stage., the quantity of NaOH added being that necessary to attain an initial pH = 10. The primary insulation debris consisted of NUKON fibers.

### 3.1.1 Specific Comments

p. 1 Section 2.0. In view of what follows from the tests, what are the concerns that the decay heat removal (DHR) heat exchangers might be fouled with precipitates of the type observed to form during ICET test #1? Letellier (2005, Slide 21) believes there is justification for concern that calcium silicate will coat heat exchanger pipe internals, but other precipitates do not appear to be considered..

p. 2 It is noted that "…the test tank is capable of maintaining both a liquid and vapor environment…". However, a realistic air/liquid volume ratio that would replicate that typical of a post-LOCA environment was not attempted. The post-LOCA air volume in a containment building would be effectively isolated from the atmosphere outside. Therefore, the mass of $CO_2$ available that would be stripped from the air inside the containment building is limited, However, during initiation of the ICET #1, the system was exposed to atmospheric $CO_2$ for some period of time, and an unknown quantity of $CO_2$ was absorbed, possibly proportionately in excess of that which would be absorbed in a real LOCA. Chemical analyses for dissolved $CO_2$ during the test have not been reported, so it is not possible to say whether the observed decline in pH could be attributed to $CO_2$ uptake.

p. 19 The discussion of the XRD technique does not indicate what the composition was of the target anode. Presumably, it is copper. This information, is needed to interpret the XRD patterns of Figs 55 and 56.

With respect to wet chemical analyses, no mention is made of sample handling, other than the sample size, and whether or not the sample was filtered. In the handling of all alkaline solutions, it is essential to avoid atmospheric exposure to prevent $CO_2$ uptake. There is no mention that stabilizing agents were added to the solutions to prevent precipitation. Nor is any information given as to how the samples were conditioned prior to ICP analysis. If precipitates formed, as is noted subsequently, are the ICP analyses of the supernatant or the total supernatant plus precipitate? See also comments to p. 28 of the ICET #3 report.

p. 20 Apparently the pH meter was calibrated with certified buffers at pH = 4, 7 and 10. and automatic temperature compensation was used. But at what temperature was the pH measured? At 25 or 60°C? Was provision taken to ensure that $CO_2$ uptake did not occur during measurement? Elsewhere, it is noted that the pH electrode for continuous monitoring of pH was calibrated initially, but not at the end of the experiment. After 30 days of continuous operation, the pH could have drifted substantially, and it would have been essential to recalibrate to quantify the extent of drift during the course of the experiment.

p. 24 Under hydrogen generation, it is stated that nearly constant levels of hydrogen were observed for the first 17 or 18 days … but that they subsequently declined and hydrogen "…was undetectable for the last 5 days of the test…". This raises the question, why? One would have expected that the aluminum coupons would have corroded relatively uniformly throughout the test. pH did not fall sufficiently for passivation to have occurred. What about the role of dissolved Cu(II) as a catalyst? Was there a build-up of silica or other passivating material on the aluminum coupons? A suitable explanation found or this matter should be investigated further. It would be helpful in the post mortem analysis of ICET experiments to have some redundancy built into the analytical procedures, so that appropriate mass balance calculations could have been conducted with confidence. Thus, it would have been useful to have made quantitative determinations of hydrogen concentration in the vapor and the aqueous phase, as well as monitoring dissolved oxygen concentration.

p. 28 Mg(II) in the NUKON glass fiber could, if it were to go into solution, adversely affect the kinetics of calcium carbonate precipitation, and possibly other calcium containing phases. This consideration might have to be addressed, or at least recognized, in subsequent computer modeling and calibration studies.

p. 28 Reference is made to the NUKON glass fiber containing 3% of a phenolic resin binder. Elsewhere (p. 33) it is noted that the resin was responsible for causing a yellow coloration of the water. Furthermore, it is noted that precipitation did not seem to affect the intensity of this color. This raises the question as to what the solubilized constituents are, and whether they affect the kinetics of nucleation and precipitation. Letellier (2005) noted that the circulating ICET solutions were analyzed for Total Organic Carbon (TOC), and that a search was made for organic compounds causing the yellow, amber or tea colored solution. However, these analyses have not been incorporated in any reports so far. Such analyses might help identify potential sorbents. A small bench-scale test could be conducted to determine whether nucleation and precipitation kinetics are affected.

pp. 28*f* Regarding the SEM images of the fiberglass after exposure to the circulating water for 30 days,, i.e., see Fig. 22 and 23, the reviewer is concerned about the mechanism of formation of the membrane-like material stretching between the exposed glass fibers. So far, the identity of this material remains unclear although Letellier (2005) and Klasky (2005) believe it to consist primarily of Na, B and O. Elsewhere, Letellier noted that the membrane like material is “an artifact of draining”, and Klasky (2005) noted that rinsing of the film with DI water resulted in its disappearance. This suggests that it is most likely a solution residue.

p. 35 4.5.2 Turbidity. The turbidity analyses at 25 °C, reproduced graphically in Fig. 29 (p. 37) raise some interesting questions. It appears that the turbidity at 23 °C remained low until after Day 7, when a sharp rise is observed, gradually flattening off and stabilizing after Day 20. the break in continuity is also observed in other data sets for Total Suspended Solids (Fig. 30), kinematic viscosity (Fig. 36, p. 42), Ca concentration (Fig. 44, p. 47), Cu concentration (Fig. 45, p. 48), Zn concentration (fig. 47, p. 49, Na concentration (Fig. 48, p. 49). Although the discontinuities may in some cases be the product of a vivid imagination, the data do suggest that critical (heterogeneous) nucleation threshold may have been reached in the aqueous solution after 7 days at operating temperature (60°C). Thereafter, the system might have achieved saturation with respect to one or more phases at 60°C, as is evidenced by the fact that samples held at 60°C did not form precipitates (p. 36). Furthermore, only a small depression in temperature of 5 °C is sufficient to induce precipitation (Fig. 31). The linear relationship between TSS and temperature in Fig.31 also intersects at T = 60°C at approximately 0 mg/L TSS, again suggesting that the solution is just saturated with respect to some phase. It appears that any precipitates, even if formed in suspension, became entrained or grew within the debris accumulations in the test loop. Tiny particles also appear to have grown on the NUKON fibers, perhaps having nucleated and grown *in situ*, rather than having been entrained from suspension. Unfortunately, current information on the nature and identity of the precipitates provides only a limited basis for developing a working hypothesis. Further characterization work, already underway, i.e., Klasky (2005) and modeling is needed to help resolve the unanswered questions.

p. 35 4.5.3 Total Suspended Solids. The study conducted to measure the quantity of suspended solids as a function of temperature (Fig. 31), and the follow-on test in which cooled samples were reheated to 60°C provides tantalizing evidence that the saturating phase at 60°C in the circulating loop was metastable with respect to a less soluble phase, at least above 40°C. Whether this was due to Ostwald ripening, or the nucleation and growth of another phase, or to precipitation of a carbonate due to $CO_2$ absorption from the atmosphere, can only be guessed at without more detailed analysis.

p. 40 4.5.4 pH. The decline in DAS pH over the course of the experiment could be due to instrument drift. Discrepancies between the DAS and grab sample pHs could be due to the former being measured at a different temperature than 60°C, and that temperature compensation was insufficient. Fluctuations in the grab sample readings appear to be random, when compared with the DAS measurements.

p. 42 4.5.6 Shear-dependent Viscosity This technique can provide valuable supplementary information concerning colloid formation and subsequent gelation in the aqueous phase. The results, indicating non-Newtonian behavior in quenched 25 °C samples during the later stages of the test, are suggestive. But does the technique allow one to discriminate between colloid formation, flocculation, or gelation? The filter clogging behavior of the observed precipitates could differ substantially, depending on their aggregation characteristics.

p. 47 4.5.7 Metal Ion Concentrations Note the reviewer's caveats concerning sample handling under the comments to p. 19. The Al concentration stabilizes after 15 – 20 days, but Ca, Cu and Si stabilize after about 7 days, and decline slowly thereafter. Zn declines to 8 days, then shows a "hop". Na shows a discontinuity at about 7 days, and a maximum after 15 days, followed by a decline to 20 days after which the concentration stabilizes. This suggests that the precipitate in the circulating loop may have been a Ca (+ Na) silicate, with minor Al substitution for tetrahedral Si. and possibly minor calcium carbonate (either calcite, or a les stable polymorph such as aragonite or vaterite). However, the system is somewhat undersaturated with respect to C-S-H "gel" (Chen et al., 2004), and is the precipitate is therefore unlikely to be a disordered tobermorite (Merlino et al., 2000). Because B and Na are major components in the aqueous phase, it is not surprising that the mineralogical analysis of the precipitates that form in the sample containers following cooling to room temperature, and after separation and drying, may contain proto-tincalconite and borax. However, the precipitate observed upon cooling might well also be present at saturation in the loop at 60°C. A distribution of species analysis and calculation of the saturation indices of potential precipitates may shed further light on this matter.

p. 50 Precipitated Solids The 15-day filtered test sample at 50,000-x magnification suggests that primary particulates, approximately 5 nm in diameter, formed initially. The 30-day unfiltered sample (Fig. 52) indicates a somewhat coarser primary particle about 10 nm in size. Both Fig 49 and 52 show that the initial particles tend to coagulate into larger particles containing between 5 and 20 of the initial particles, and that these, in turn, tended to agglomerate in still larger particles. However, apart from the initial aggregation into 6-20 membered nanoparticles, subsequent aggregations cannot be described as gelation, but rather as flocculation. Neither the degree of adhesion, nor the concentration of aggregated particles is sufficient to induce the formation of a true gel. The authors of the report note this. The initial particles, by virtue of their small size, would have a very large surface area, and, even if well crystallized, would contain only a few unit cells. Therefore, the solubility of such material is probably one to two orders of magnitude greater than the equivalent macroscopic solid. The observations substantiate the contention that the precipitating phases are metastable with respect to more stable phases in the same multi-component chemical system, and that computer modeling studies must take this condition into account.

## 3.2 ICET #2

The solution was made up using 15.14 kg $B(OH)_3$ and 0.66 g LiOH in 250 gallons. A mix of 1.893 kg trisodium phosphate (TSP) and 0.300 kg B(OH)3 was metered into the system during the first two hours of the test, an a similar mix of TSP plus $B(OH)_3$ plus 214 mL concentrated HCl was added during the next two hours. The primary insulation debris consisted of NUKON fibers.

### 3.2.1 Specific Comments

p. 27 The presence of secondary $Cu_2(CO_3)(OH)_2$ on the copper coupons, and the signal for C appearing in many of the EDS scans raises the question as to whether the collected samples were exposed to atmospheric contamination following sampling, or whether carbonates precipitated because the circulating fluid had been exposed to atmospheric $CO_2$. The carbon observed in the EDS traces might also be due to the adsorption of dissolved organic components of the phenolic resin. Also, it is noted in section 3.3 (p. 12) that confusion may have occurred identifying carbon for boron. The absence of analytical data for dissolved carbonate species (or alkalinity) in the circulating water, makes it difficult to establish whether carbonates are contributing to the precipitate load in addition to phosphate, and indeed, whether mixed carbonate-phosphates might be precipitating. Letellier (2005) noted that carbonate analyses were performed. However, it is not clear whether these analyses were of the circulating solution.

p. 42 In this report, no results are presented of high magnification TEM of secondary precipitates or coatings. Therefore, it is not possible in this case to determine whether the precipitates represent an aggregation of nanoparticles, or are fine crystals with distinct morphology. We do not know whether the particles have a narrow or broad size distribution, or whether the distribution might be bi-modal. Also, TEM studies would help determine whether more than one phase had precipitated during the run. It is not clear whether XRD analyses revealed a crystalline or substantially amorphous solid. This kind of information is critical in formulating conceptual models for computer simulations of both laboratory tests and real scenarios.

p. 42 Some effort should have been made to characterize the chemistry and mineralogy of the adhering coating on the metal coupons. In particular, the deposits on the submerged Al coupons appeared to be discrete “rosettes” (Figs 4-3 and 4-5 on p. 22). It would be interesting to know why this aggregation of material occurred, and whether it is really aluminum hydroxide as claimed.

p. 46 The adhering material on the fiberglass, imaged by ESEM, and illustrated in Figs 4-50 and 4-52 display shrinkage cracks. If they were caused by dehydration during sample preparation, then the material could be a flocculent. However, if they are due to syneresis, then the adhering material could legitimately be considered a gel.

p. 50 Examination of the 30-day fiberglass sample from within the birdcage, revealed the presence of lath-like crystals, which were analyzed by EDS. It would have been desirable to have characterized this crystalline material further using TEM.

p. 58 The inadvertent generation of enhanced turbidity in the sample taken on Day 3, due to excessive cooling before measurement, indicated that the solution may have been saturated or near saturation with respect to some phase at operating temperature, and that prolonged cooling might have induced precipitation. It is unfortunate that the studies conducted in ICET #1, were not repeated to determine the degree of under-cooling needed to generate a precipitate, and the stability of the precipitate upon reheating. Note that such a study provides helpful information regarding the thermodynamic and kinetic properties of precipitates, especially in relation to the fouling of heat exchangers in the system.

p. 65 As with ICET #1, a yellow coloration of the circulated water occurred, which is probably due to the leaching of the phenolic resin. As noted in the comments to ICET #1, the presence of organics may affect the rate of precipitation of phases from a supersaturated solution.

## 3.3 ICET #3

The solution was made up using 15.14 kg $B(OH)_3$ and 0.66 g LiOH in 250 gallons. A mix of 1.893 kg TSP and 0.300 kg $B(OH)_3$ was metered into the system during the first two hours of the test, an a similar mix of TSP plus $B(OH)_3$ plus 214 mL concentrated HCl was added during the next two hours. The primary insulation debris consisted of 80% particulate cal-sil and 20% NUKON fibers.

### 3.3.1 Specific Comments

p. i The abstract notes that "…the bottom of the tank was filled with a sediment that had a pinkish white deposit on top." Elsewhere, on p. 78 it was noted that the sediments were both yellowish and pink, but the order was not stated. On p. 68 it is also noted that the cal-sil that was heated, had a pinkish hue, and that the untreated cal-sil was yellowish, the color change being potentially due to the transformation of ferric hydroxide to hematite. This suggests that the last layer to sediment out was the heat-treated material, suggesting a smaller particle size. The report does not discuss the likely particle distribution of cal-sil debris. A size distribution analysis of heat-treated and untreated samples would be useful in quantifying the behavior of this material following a LOCA.

p. I It is not clear whether 3.786 kg of STP was added as the hydrate ($Na_3PO_4.12H_2O$) or in the anhydrous form. This ambiguity extends to citations elsewhere in the text.

p. 20 It is noted that an apparent "…dissolution of white particulate was observed occurring from Day 7 through Day 9." This phenomenon appears to be correlated with a measurable perturbation in the Al concentration, which persisted from Day 8 through Day 15, a slight fluctuation in $SiO_2(aq)$ commencing on Day 7, and a progressive rise in Na concentration, starting about Day 9 and returning to a normal trend after Day 15. The authors are silent on these matters, so it is not clear whether the observed analytical fluctuations in solution chemistry are artifacts or are real. See also comments to p. 58 of ICET #2. Although this issue may not be important in the overall scheme of things, computer modeling that does not account for such fluctuations would be considered suspect in predictive modeling. Therefore it is important that these observations be explained. Kieser and Park (2005?) noted that if the dissolved concentration of TSP exceeds 1000 ppm, the initially precipitated Ca phosphate begins to dissolve, while the solution pH rises to 8-8.75. These conditions were not evident in the current test, but a possible relationship between these disparate observations should be investigated.

p. 20 The fact that the flow meter fouled with precipitate after Day 8 is an indication that such precipitates are also likely to coat the interior of the heat exchangers that cool the circulating coolant. Whether they would also coat the reactor core is uncertain, because it depends on the degree of supersaturation of the precipitating solid, and whether the temperature dependence on solubility is pro- or retrograde. (Indications are that it is prograde. See comments to p. 20). Kieser and Park also note that a rise in pH permits the bonding of calcium phosphate particulates to steel piping. This issue would further complicate cooling following a LOCA. Letellier (2005) has already noted that there is concern regarding the precipitation of calcium silicate on the internal surfaces of pipes.

p. 20 The differential variation in pH between the bench-top measurements and the in line measurements over the course of the test is –0.18 units. This again raises the question of post test calibration of the in-line pH probe, and whether bench-top measurements were taken at room temperature or at 60°C, The automatic temperature compensation may not have been adequate.

p. 28 The Al concentration in Fig. 3-8 shows an inexplicable jump in concentration between Day 8 and Day 16. No explanation is given. However, Letellier (2005) notes that it is not significant. Strange and inexplicable variations in chemistry are noted elsewhere. One cannot help speculate that these fluctuations may have been the result of sample aging. It looks suspiciously like aqueous samples were collected and submitted for analysis in batches, and that the fluctuations observed are the consequence of faulty sample preservation. See also comments to p. 19 of ICET #1.

p. 30 In Fig. 3-13, the $SiO_2$(aq) concentration reaches a maximum on Day 2, suggesting that nucleation occurred around that time.

p. 32 Fig. 3-16 shows an inexplicable jump in $PO_4$ concentration between Day 13 and Day 16. No explanation is given. See p. 20 comments regarding dissolution/precipitation.

p. 33 It is stated that deposits formed in the interior of the fiberglass insulation are likely to have been “chemically originated”. However, elsewhere it is also noted that “deposits are pervasive throughout the fiber”, and further, “…[t]he drying process caused the formation of flocculence through chemical precipitation” (whatever that means). The reviewer is concerned that the sample preparation procedures for SEM examination may be introducing artifacts that could be confounded with chemical processes that occurred during the test run. Note that the EDS spectra of the flocculent precipitates displayed in Figs 3-24,3-30, 3-33, 3-36, 3-41, 3-43 and 3-47 are all somewhat similar and consist primarily of O, Na, Si and Ca, those principal components in aqueous solution, which are measurable by EDS. The presence of C may be due to carbonate species in solution, analyses of which, unfortunately, have not been reported. Thus it is important that either the sample preparation procedure needs to be changed, or some way of discriminating between the artifact and the real thing needs to be devised.

p. 34 Note that the adhering flocculent material appears to be physically entrained, rather than having nucleated on the fibers, and that the fibers do not appear to have been corroded. This suggests that the fibers may have been protected from corrosion by saturation with respect to $SiO_2$(aq) by the cal-sil and with respect to Al and B by the corroding Al coupons and by the presence of $B(OH)_3$ component in solution. Thus, the measured corrosion rates of NUKON, reported in Appendix B of Jain et al. (2005), might not be applicable to systems in which cal-sil debris are present.

p. 55 With reference to the particles shown in Fig. 3-55, and the EDS spectrum of the same in Fig. 3-56, it should be noted that fine particles of cal-sil could be chemically altered in the presence of TSP solution to form mixed Ca–phosphate/silicate phase. The authors allude to this possibility on p. 68. They note further that phosphate diffusion into the interiors of the particles is limited, but unfortunately provide no quantitative evidence to support this contention. The phosphate uptake should be examined through separate bench-scale tests and instrumental analysis. Note also, on pp. 58-60, white and dark particles are separately analyzed, one showing elevated P (dark particles), in comparison with the other light particles. This again suggests more than one generation of particulate formation, which is not readily explained by the simple precipitation of a calcium phosphate compound. (The reviewer recognizes that EDS analyses of small particles may result in overlap with adjacent particles with differing chemical composition.

p. 63 Care should be taken not to assume that an EDS spectrum of a particle is representative of the bulk composition. The particle illustrated in Fig. 3-70 looks like some coarse particulate material that has been coated with a secondary amorphous or microcrystalline material. Thus the EDS spectrum is that of the coating, and it cannot be assumed that the interior is of the same composition, i.e., some calcium phosphate.

p. 68 The source and provenance of the cal-sil is not disclosed. Therefore the reader cannot ascertain whether the cal-sil is of recent manufacture, is old stock, or was removed from an operating PWR after having been in service for a protracted period of time. The fact that some of the material was heat treated, suggests that the cal-sil was not previously exposed to operating conditions. Like concrete, the cal-sil could have undergone carbonation during storage, and the chemical composition of the sample included secondary calcite and amorphous silica, decomposition products of C-S-H gel or tobermorite. The fact that the XRD spectra on p. 82 includes that due to calcite, a large diffuse peak at 12° $2\Theta$ in addition to tobermorite spectra (9A-tobermorite and 14A(?)-tobermorite) is suggestive of an old-stock sample that has significantly carbonated, and that subsequent thermal treatment led to the formation of 9A-tobermorite. The chemical analysis of the 30-Day sediment on p. 82 (which is presumably dominantly cal-sil) suggests there is a slight excess of $SiO_2$ over that required to form tobermorite alone. However, a significant portion of the tobermorite may have been carbonated. It is essential the analyses for contained $CO_2$ be conducted.

Note that the cal-sil insulation in an operating PWR, and exposed to temperatures as high as 260°C, might not have undergone carbonation to the same extent, as calcium silicate tends to be more stable than calcite in the presence of reactive silica at atmospheric pressure at 260°C. Furthermore, containment with SS or aluminum cladding could limit access by atmospheric $CO_2$. Thus the cal-sil used in ICET #3 and in ICET #4 may not be representative of a real world condition.

p. 69 Very little information is given anywhere in the report on the chemistry and structure of the adhering coatings on the metal coupons. Clearly, the corrosion of Al is non-uniform as evidenced by the illustrations on p. 69. It would be useful to know why. Also, the coatings should be fully characterized with supporting TEM and XRD studies. Finally, we do not know whether the Al coupons are pure aluminum sheet or some Al alloy, which might corrode differently from the pure substance.

p. 84 XRD analyses confirm that the initial gel like Ca phosphate contains $Ca_4H(PO_4)_3.H_2O$ as anticipated in the reviewer's comments regarding the CNWRA report on computer modeling. However, it is interesting to note that a double salt incorporating $NaHCO_3$.H2O actually formed. The XRD pattern in Fig. 3-122 also contains a diffuse ring at about 12° 2 $\Theta$, which is not explained. Does it relate to the sample or to sample preparation? The gel-like calcium phosphate should be more fully characterized, with additional high magnification TEM, surface area measurements, and chemical analyses. This again indicates the importance of monitoring the alkalinity or $CO_2$ content of the circulating water in order to permit calculation of the solubility characteristics of this material.

## 3.4 ICET #4

Before the start of the test, 15.14 kg of $B(OH)_3$, 8.47 kg of NaOH, 212 mL of 12.24 N HCl and 0.663 g LiOH were dissolved in the circulating fluid. Within 30 minutes of the start of the test, additional NaOH solution of unspecified strength was introduced during an initial 4-hr spray phase, the quantity of NaOH added being that necessary to attain an initial pH = 10. The solution formulation appears to be essentially similar, if not identical to that for ICET #1. However, instead of exposure to insulation composed entirely (100%) of NUKON fiberglass, the insulation consisted of 80% cal-sil and 20% NUKON. This is assumed, based on the test series parameters given in Table 2 of the test report for ICET #1. However, the ICET #4 deviated from the initial plan in using NaOH to buffer the pH at 10 rather than TSP to buffer the pH at 7.

Results can be compared with those of ICET #1, which utilized circulating water of the same composition. The major difference between the two tests is the presence of cal-sil, which significantly impacted the solution chemistry.

Noteworthy differences are:

- The turbidity measurements at 60°C and 25°C were essentially identical. Therefore, unlike ICET #1, there was no tendency for precipitation to occur during sample cooling.
- Instead of a progressive buildup of Al in solution to about 350 mg/L apparently reflecting the solubility of $Al(OH)_3$, Al quickly fell to undetectable concentrations in solution after two days
- $Ca^{2+}$ concentration was about 3 times higher.
- $SiO_2(aq)$ rose progressively to about 180 mg/L compared with 13 – 18 mg/L in ICET #1. Na showed an upward trend in concentration from 6,000 mg/L to about 11,000 mg/L after 30 days. This is in contrast to the trend in ICET #1, which remained essentially constant at about 5,000 mg/L between 3 and 30 days.

The upward trend in Na concentration over the course of the test needs to be explained. It could be due to the leaching of Na from the cal-sil, as suggested by the bench-scale dissolution tests of Park et al. (2005) (See comments under Park et al., 2005). However, the associated Nukon fiberglass contains about 17% $Na_2O$, and the relatively slow release rate might be attributed to Na leaching from the fibers.

There appears to be no evidence for the formation of secondary precipitates, which suggest that precipitation, if it occurred, was minor in quantity. Only minor corrosion products were observed on the submerged metal coupons. Corrosion products on submerged Al coupons appear to be limited to minor oxidation products, and perhaps minor adsorbed $SiO_2$.

The most striking feature of this test is the lack of corrosion of the submerged Al coupons. A SEM/EDS study of the uncontaminated surface indicates that only an al hydroxide layer is present on the surface, with minor adsorbed(?) silica. It is tempting to speculate that the adsorbed silica passivates the aluminum and inhibits corrosion at pH = 10. Letellier (2005), however, attributes the lack of corrosion to the formation of a "calcium-carbonate passivation layer". Further electrochemical studies to investigate the potential role of silica in passivating Al are merited.

One other interesting set of results pertains to the XRD and XRF analyses of the Day 30 sediment, which is believed to consist primarily of fine cal-sil debris. It appears that cal-sil is composed primarily of three phases: tobermorite, 9-A tobermorite and calcite (Fig. 3-129). From Table 3-6, the Si:Ca molar ratio is calculated to be 1:0.89, which is consistent with a material originally containing tobermorite-like phases with excess portlandite, the latter converting to calcite upon exposure to air. However, the Si:Ca molal ratio is inconsistent with that reported by McMurry et al. (2006) in their Table 3-3, which shows a molar ratio of 1:2.4. An explanation for this discrepancy is called for.

## 3.5 ICET #5

Before the start of the test, 6.48 kg of $B(OH)_3$, 10.0 kg of borax, and 0.284 g LiOH were dissolved in the circulating fluid. Apparently, HCl was also added, leading to a bench top pH of 8.34 at 60°C. The primary insulation debris consisted of 10% NUKON fibers.

The ICET #5 results can be compared with those of ICET #1, which utilized circulating water of somewhat similar composition, and insulation debris was similarly restricted to 100% Nukon. A major difference between ICET #1 and #5 is the lower pH of the latter, which varied between 8.1 and 8.5, compared with about 9.4 for the former. This directly affected the Al concentration in solution, i.e., a concentration between 30 and 50 mg/L in ICET #5 compared with about 350 mg/L in ICET #1. Ca concentrations are somewhat higher (about 20-30 mg/L versus 12 mg/L), whereas the $SiO_2(aq)$ concentration is about 10 mg/L versus 13 – 18 mg/L. Another similarity between ICET #5 and ICET #1 is the tendency for precipitates to form from solution samples after cooling to room temperature as determined by turbidity analysis., see Fig. 4. Precipitates were also observed to have formed in the test loop, although the quantities were minor, and were not explicitly characterized.

It is difficult to speculate what went on during this test without more information. Some of the fluctuations in turbidity, and in Al, Ca, Si and Na concentrations, suggest erratic behavior under conditions that should have been relatively stable once saturation and precipitation had occurred. It is not clear whether these effects are real or are artifacts. If they are real, then an interpretation is called for. Such an interpretation could be aided by supplementary thermodynamic and kinetic modeling of the test.

Most, if not all of the corrosion product SEM/EDS analyses show significant concentrations of carbon. When compared with the associated oxygen concentrations, there is too much carbon present to represent the carbon as being exclusively due to the presence of carbonate. It seems more likely that the carbon may be due to adsorption or co-precipitation of the phenolic resins originally coating the Nukon insulation. It is, of course, recognized that the sensitivity of EDS to carbon is poor, and therefore, the computed atomic percentages of carbon are subject to large uncertainties.

The presence of quartz in the particulate deposits at the bottom of the tank, as reported in section 3.5, is unlikely to have originated with a crystalline form of fiberglass debris, but rather was associated with the concrete particulate material deliberately added at the beginning of the test.

### 3.6 Recommended *Post Mortem* Evaluation of ICET Runs

If aqueous solution samples are still available, analyze for alkalinity or $CO_2$ content. Re-measure pH at ambient, i.e., room temperature.

Perform a distribution of species analysis using a standard distribution of species code, e.g. EQ3/6 or PHREEQ-C using the initially measured pH at 60°C to determine the degree of imbalance between cations and anions. Explore the option that calcite, vaterite or aragonite might be saturated, through charge balancing on $HCO_3^-$. If carbonate saturation cannot be demonstrated, proceed with an evaluation of saturation solubilities of the precipitates.

Conduct in-depth evaluations of the morphology, crystallinity, specific surface area, and chemistry of precipitates and coatings using available instrumentation.

Review the literature on microcrystalline and amorphous phases that form in the multi-component system under study.

Derive solubility data of the participating solid phase precipitates, taking into account possible contributions by the interfacial free energy.

Attempt to establish rates of precipitation at 60°C., based on an interpretation of available data, supplemented with any available literature data.

Formulate and conduct additional lab tests to quantify poorly known parameters of critical importance.

The thermodynamic and kinetic parameters can be used as input to a non-isothermal chemical reaction simulator, e.g. TOUGHREACT.

Implementation of the above guidance is seriously complicated by the omission of alkalinity or carbonate analyses. It is not certain *a priori* how much useful information can be obtained from such an analysis, but the resulting information is absolutely necessary if a satisfactory computer simulator is to be developed.

### 3.7 ICET Questions and Answers

Answers are provided below to the questions posed to the Peer Review Group by NRC.

**Q.** *Have the principal sump pool variables, which affect chemical by-product formation in the post-LOCA environment, been adequately simulated?*

**A.** Given the complexity of the problem, and the need to get started on some kind of simulation, the reviewer believes that the approach to simulating a post-LOCA environment (Andreychek, 2005) was satisfactory, and the ICET series yielded useful information.

**Q.** Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?

**A.** This question can only be answered through a comprehensive evaluation of the physical, chemical and mineralogical properties of the observed precipitates, a detailed evaluation of all of the data, especially that which relates the aqueous phase composition, with the thermodynamic properties (i.e. solubilities) and kinetic properties (i.e. nucleation and growth) of the precipitates. Quantitative information concerning the kinetics of corrosion of the debris and metal coupons under the full range of operating conditions is also required. Additional bench-scale testing to evaluate the temperature dependence of key kinetic processes, such as that currently under way at ANL (See comments regarding Park et al., 2005). Electrochemical corrosion studies also should be made of aluminum alloys in solutions with varying chemical compositions, including those resulting from cal-sil dissolution. Further work needs to be accomplished before a satisfactory computer simulator could be calibrated using the experimental data obtained from the ICET series, this simulator being necessary for more realistic non-isothermal runs replicating realistic post-LOCA conditions.

**Q.** *What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects) and how should their effect be characterized by testing or analysis?*

**A.** The most glaring omission is the testing was failure either to control or to monitor $CO_2$ uptake. This has resulted in conditions that could deviate significantly from the actual post-LOCA environment in the containment building of a PWR. The second is an adequate *a priori* characterization of the cal-sil used in some of the tests. The history of the material may differ from that in an operating PWR, especially with respect to the degree of carbonation. This same problem also applies to the cementitious materials used in the test. Under real conditions, these materials could be substantially carbonated at the time of a hypothetical LOCA. As noted in the preceding question, the temperature dependent variation of a number of key parameters have not been studied in the presence of cal-sil disintegration and dissolution products. This applies especially with respect to aluminum corrosion. Regarding other materials omitted from consideration, such as coatings, free insulation, etc., the reviewer can only express his opinion that no significant adverse consequences would be expected from these materials, as already noted by Andreychek (2005). Some protective paint coatings could peel off *en masse*, and accumulate as flakes on the screens.

Some variables and materials were included in the ICET runs, but could well have been omitted, based on the earlier computer simulations conducted at CNWRA (Jain et al., 2005) and in hindsight. For example, copper, galvanized steel, IOZ coated steel, and uncoated steel coupons were incorporated, but appeared to have had little impact on precipitate formation or ultimately on screen clogging. These materials could be omitted from further consideration, unless the impact of post-LOCA cooling on corrosion and the integrity of structural materials is of interest, i.e. see Andreychek, 2005, p. 13).

The reviewer is similarly of the opinion that the release of small quantities of HCl from PVC insulation may have only a minor effect on precipitate production.

The reviewer believes that field visits to operating PWR facilities could unearth other limitations or omissions not otherwise anticipated. Out-of-scope issues relating to the fouling of heat exchangers and possibly the reactor core with precipitating phosphates or other compounds have not been addressed, and could also adversely affect reactor cooling.

**Q.** *Were the methods used within the ICET program to characterize and analyze chemical by-products sufficient?*

**A.** In terms of the diversity of instrumental methods used, the ICET program was satisfactory. For the purposes of detailed modeling, it would have been useful to have measured the specific surface areas of the precipitates, using either the BET method or possibly a dye adsorption technique. However, the real criticism that might be leveled at the test reports is not so much the diversity of facilities used, but rather the lopsided emphasis on the ESEM, SEM and EDS characterization of precipitates and coatings. Much more serious work needs to be done characterizing the physical, chemical and mineralogical properties of the precipitates and coatings as a basis for subsequent conceptual and computer modeling. As noted in answers to preceding questions, this characterization work needs to be done in conjunction with additional laboratory testing and computer modeling. Fortunately, this deficiency is being rectified through supplementary bench-scale studies at ANL and LANL.

# 4 HEAD LOSS SIMULATION TESTING AND ANALYSIS

Supplementary Chemical Effects Head Loss Tests are being conducted at the Argonne National Laboratory. The objective of the tests is to assess the pressure drop across a surrogate sump screen due to debris with or without secondary calcium sulfate precipitates. The tests are therefore conducted to augment the findings of ICET #3 by establishing a basis for predicting sump screen performance degradation following a LOCA in PWR s using STP as a pH buffer in the circulated coolant. The findings of completed tests are presented in two informal reports (Oras et al., 2005, 2006). Head-loss testing is also described in a preliminary 8-page report (Anonymous, 2005c), which briefly describes Tests ICET-3-1 and ICET-3-2. Shack et al. (2005) also made an oral presentation on October 19, 2005, in which the preliminary results of Test #3 were described. A listing of the completed tests is summarized in Table 4.

Table 4. Chemical Effects Head Loss Tests

| **Test No.** | **Insulation Material** | | **Conditions** | |
|---|---|---|---|---|
| | **NUKON g** | **Cal-Sil g** | **Presoak** | **TSP and or Ca additions** |
| **ICET-3-1** | 15 | 15 | No | TSP: initially in loop. 200 ppm Ca as $CaCl_2$ added to simulate Ca dissolving from Cal-Sil. |
| **ICET-3-2** | 15 | 15 | No | TSP: initially in loop. 10, 25, 50 ppm Ca as $CaCl_2$ added stepwise, in loop. |
| **ICET-3-4** | 7 | 25 | Yes | TSP: 1/8 initially in loop, 7/8 metered |
| **ICET-3-5** | 7 | 25 | Yes | TSP: none |
| **ICET-3-6** | 15 | 15 | Yes | TSP: 1/8 initially in loop, 7/8 metered |
| **ICET-3-7** | 15 | 15 | Yes | TSP: none |
| **ICET-3-8** | 15 | 0 | No | TSP: initially in loop. 43.5 ppm Ca as $CaCl_2$ added (= dissolution of cal-sil.) |
| **ICET-3-9** | 15 | 0 | No | TSP: initially in loop. |
| **ICET-3-10** | 15 | 15 | Yes | TSP: 1/2 metered during pre-soak; 1/2 metered. 9, 18, 27 ppm Ca as $CaCl_2$ added stepwise, in loop. |
| **ICET3-3-11** | 15 | 15 | Yes | TSP: none |
| **-** | 0 | 0 | No | $Al(NO_3)_3.9H_2O$ addition to simulate corrosion of Al structures. |

Associated research is also being conducted at Argonne National Laboratory. The work is ongoing and only oral presentations and a summary in Oras et al. (2006) are available for review. The primary purpose of the associated work is to identify important environmental variable governing the screen clogging associated with the formation of chemical precipitates.

In particular, the investigators are concerned with the dissolution of cal-sil and formation of calcium phosphates over a range of simulated sump pool conditions. :

- To examine a broader range of conditions than examined in ICET
- To simulate chemical precipitate formation rather than conduct integrated tests
- Answer critical questions relating to the appropriateness of the produced precipitates and the right amounts. Especially critical is the mass of chemical precipitate that can accumulate per unit area of sump screen.

## 4.1 General Comments

The overall scope of the research under way at ANL is appropriate and reasonable. Of particular interest were slides # 6 and 8 supporting the oral presentation (Shack et al., 2005), in which were tabulated the parameters of relevance to post-LOCA cooling (See also, Andreychek, 2005, Table 7). It is clear that the large variability in parameters between different plants presents a challenge in designing a test program that adequately addresses this variability. Noteworthy is the observation that the ICET #1 achieved a circulating aluminum concentration of 375 mg/L, which is for the most part well over an order of magnitude greater than expected in all plants but one containing a large quantity of structural aluminum. Addressing such variability could tax the resources of the research team at ANL unless a suitable strategy is adopted for an efficient set of experiments. This strategy might be best implemented through a series of bench-scale tests to evaluate critical processes and their controlling parameters, with suitable data developed for incorporation in a computer simulator. Factorial design studies might also be conducted using appropriate test designs, particularly where parameter interactions are not understood.

Of the test work done so far, most has concentrated on the use of a TSP to buffer pH following a LOCA in a PWR containing cal-sil insulation. The head loss test series ICET-3-1 – ICET-3-11 have effectively demonstrated the potentially serious consequences associated with the use of STP as a pH buffer. The various conditions studied in this series represents the very worst-case scenario with the predictable formation of abundant flocculent calcium phosphate precipitates. The series appears to be conducted with a definite plan in mind. However, the large potential range and variability in parameters under study, and the limited number of tests possible prevents formal study of the sensitivity of the various parameters to screen blockage under actual field conditions. This is especially relevant to the reported non-linear behavior of head loss in response to stepwise additions of CaCl2, and to the fact that head losses became excessive before the full range of TSP additions could be metered in to the test loop. Furthermore, the discrepant results between tests that were essential duplicates, e.g., ICET-3-7 and ICET-3-11, raises the question of reproducibility. Clearly, it would be both time consuming and costly to run the tests a sufficient number of times to obtain a quantitative measure of reproducibility. It is not clear how the investigators plan to overcome these limitations. Although work is progressing well, the reported results give the impression of an *ad hoc* rather than systematic approach at tacking the problems involved.

An independent test used added $Al(NO_3)_3.9H_2O$ to simulate the corrosion of Al structures at post-LOCA elevated pH conditions (pH = 10) where precipitates are relatively minor and are most likely to form during progressive cooling. The test was conducted at a series of declining temperature steps, and therefore approximated the non-isothermal conditions prevailing during post-LOCA cooling. Unfortunately, the test was compromised by the “instantaneous” addition of Al, which would not reflect the progressive corrosion of aluminum components following an actual LOCA. It is not certain that precipitates, as observed in the course of ICET #1 and #5, would in combination with NUKON cause screen blockage. However, the test is suggestive that an adverse condition could arise. Emphasis should therefore be placed on the defining the range of conditions where screen blockage is probable under ICET #1 and ICET #5 conditions.

Many of the tests could be simulated using chemical modeling software. Coordination of work by CNWRA and ANL would greatly assist in the interpretation of results, and facilitate model refinement.

## 4.2 Specific Comments

### 4.2.1 Head Loss Tests

#### 4.2.1.1 Anonymous, 2005c

p. 1 Reference is made to the precipitate being $Ca_3(PO_4)_2$, which "…was confirmed by later analysis." Since there are a variety of known Ca-phosphates, the identity should have been better characterized.

#### 4.2.1.2 Oras et al. (2005)

p. 2 Reference is made to the hydrolysis of potassium and sodium released from the cal-sil. Potassium is a minor component of cal-sil, and sodium constitutes a smaller molar concentration than Ca. It is not clear what the state of the sodium is in the cal-sil, i.e., whether present as NaOH or $NaHCO_3$, or combined with Ca as a silicate. However, leaching tests by Park et al. (oral presentation, October 18-19, 2005) suggest that a significant quantity of Na is released upon leaching of cal-sil. This appears to be corroborated by the ICET #4 test results, which show a progressive increase in Na concentration with time during exposure to cal-sil. In any case, the Ca probably contributes as much to raising the pH as the Na.

It is also stated that cal-sil is "…mostly $CaSiO_3$…" In fact, it appears to consist primarily of tobermorite and minor calcite. See comments to p. 82 of the ICET #3 report.

#### 4.2.1.3 Oras et al. (2006).

Figures Some of the figures are difficult to follow. Labels describing the test conditions can be confused with the legend, e.g., see Figure 4, or appear to be labels describing some aspect of a graph, e.g., Figure 2. In one case, a label has no explanation in the associated text, e.g., the label "Add 1/2 NUKON/CalSil slurry" in Figure 2. The onset of physical screen clogging by debris is claimed on p. 8 to occur "within the first 6 minutes (or after approximately one test loop recirculation)", but elsewhere, it is claimed that one pass round the loop is ≈ 4 minutes (p. 13). However, clogging is shown to occur within 2 minutes in Figure 18. It would help if test conditions were boxed on the graphs to avoid confusion with labels. Also, it would help if additional information were added to the graphs where appropriate, such as the timing of STP additions.

p. 3 Reference is made to cal-sil dissolution being limited by the solubility of calcium silicate ($CaSiO_3$). See comment regarding p. 2 of Oras et al. (2005). Any sodium silicate that might have been used in the manufacture of cal-sil has probably been converted to calcium carbonate and amorphous silica by the time it was used for the head loss loop tests.

p. 5 in Table 1 it is stated that any remaining fraction of TSP was metered in during a 30-60 minute period after the debris was added to the loop, but it is not clear when that period started. Thus, for ICET-3-6, it looks as if the balance of the TSP was metered in between 30 and 60 minutes after the start of the test. But for the ICET-3-10 procedure, it merely states that the remaining TSP was metered in "…after introduction of the debris".

p. 18 1st par. It seems that a direct graphical comparison between ICET-3-6 and ICET-3-10 would be better than those with ICET-3-11 in Figures 17a and 17b.

p.18 2nd par. The strongly non-linear relationship observed due to stepwise additions of CaCl2 in ICET-3-9 suggests a relatively high degree of sensitivity to screen clogging due to small increases in Ca once a critical calcium phosphate concentration is reached. Several factors may be involved; the degree of supersaturation with respect to calcium phosphate before nucleation is induced, the relative growth rate of calcium phosphate particles, the Ca2+ and PO43-saturation concentration with respect to calcium phosphate, the extent of Ca borate complexing, and the conditions needed to induce coagulation. These factors suggest that the test may not be reproducible, unless great care is taken to control all parameters. Because ICET-3-9 has unearthed this issue, which could be very important in predicting the behavior of screen clogging in a PWR, further testing and characterization work may be needed.

p. 19 It is pointed out that the effect of cal-sil loading, even without the effect of calcium phosphate precipitates is to cause head loss to increase "…very rapidly to a high level". Yet this head loss is only 40% of that due to calcium phosphate precipitation.

p. 23 Hydroxyapatite is highly unlikely to form, as noted elsewhere, when discussing the work of McMurry et al. (2006). Indeed, these authors indirectly demonstrate that hydroxy apatite could not form without seriously depressing the pH of the solution, a phenomenon that is not observed in ICET #3.

Table 2 The experiments conducted respectively at 1.5 g/L and 0.5 g/L cal-sil are not identified.

p. 24 The rate of cal-sil dissolution is discussed, and the conclusion is made that the experimental work being reported supports an earlier assumption that the cal-sil dissolution rate is not too strongly dependent on the [Ca] concentration [in solution]. How do these findings compare with the cal-sil dissolution studies reported by Mcmurry et al. (2006) in their Appendix A?

p. 25 The observation that some of the tests could not be completed as planned, because of excessive head losses, raises the questions as to what should be done next. It is tempting to fiddle with the test parameters so that quantifiable results can be obtained within the range where head losses are less than 100 %, i.e. when substantially complete blockage of the screen has occurred under conditions comparable to that would exist in a PWR. However, how would such results be used to modify existing plant design, or how does the resulting information bear on modified sump screen changes that have already been implemented at operating PWRs?. Will any additional changes be required? How will this be demonstrated using the results of current and ongoing testing?

### 4.2.2 Supplementary Studies Characterizing Dissolution of Debris and Precipitation: Oral Presentations, October 18, 2005

#### 4.2.2.1 Park et al. (2005)

This presentation includes some experimental results regarding the dissolution of cal-sil in borated water at pH = 4, in borated water adjusted with NaOH to pH = 7.14, and in water containing dissolved STP. Information was also provided on a simulated short-term test of the ICET #1 aluminum chemistry, designed to mimic the conditions involving precipitation on cooling. This work is interesting and should be pursued with the goal of generating temperature dependent kinetic data on cal-sil dissolution, and aluminum hydroxide nucleation and precipitation from pH = 10 borate solutions.

#### 4.2.2.2 Klasky (2005)

In this presentation, the major observations of ICET #1 were summarized, and a number of issues identified for more detailed exploration. In general, the reviewer concurs with the objectives, the issues raised, the approach and the methodology. A commentary follows regarding specific issues.

Particulate Nature of Precipitates. Slides 6 and 7, representing TEM images of 15-day and 30-day high volume filtrates indicate that the material is made up of clusters of sub-equant particles (See comments to p. 50 of ICET #1). It seems likely that the particles, once nucleated from a supersaturated solution, were inhibited from further growth by the adsorption of boron (as B(OH)3 or B(OH)4-) on the surface. Sorption of B on amorphous aluminum oxides approaches a maximum at pH = 8.5 – 9.0, but falls off steeply above pH = 9, so that the amount adsorbed at pH = 10, is less than 50% of that at maximum adsorption at pH ≈ 8.5. (Goldberg et al., 2001). In another paper, Goldberg et al. (2004) have successfully modeled B adsorption on soils using a constant capacitance model:

$$SOH + B(OH)_3(aq) = SH_3BO_4^- + H^+$$

Thus, $B(OH)_3$ adsorption would be favored with increasing pH until $B(OH)_3$(aq) itself dissociates in solution at pH ≈ 8.6. At still higher pH values, the $B(OH)_4^-$ would tend to be repelled from the hydroxylated surface, thus causing borate adsorption to decline. The solid state $^{11}B$ NMR spectrum of the ICET #1 precipitate (Slide 20) indicates that B is present in both tetragonal and trigonal coordination, raising the question whether B is adsorbed in more than one way on the precipitate.

$B(OH)_3$(aq) adsorption could not only stabilize the $Al(OH)_3$ particles, but also inhibit Ostwald ripening. In other words, a suspension of borate-coated particles is thermodynamically metastable. However, it is possible that certain cluster configurations, consisting of 6 – 20 particles, may be slightly more stable than the individual particles, and that particle adhesion can overcome the repulsive effects of the adsorbed B(OH)3. Thus, the multi-modal particle size distribution shown in slides 25 and 26, may reflect the stable formation of such multi-particle assemblages or clusters. An extensive literature exists on the thermodynamic stability of clusters, e.g., Sciortino et al (2004), which might be relevant to the problem at hand It is suspected, however, that adhesion between the particles is generally weak in the system under consideration, and that turbulence would limit aggregation to form a gel.

The small size of the discrete particles (≈ 2–5 nm) approaches in size some of the larger polynuclear Al complexes, which have been identified in solution, and have been reviewed by Casey et al. (2001),. The fact that most of the Al present in the precipitates is octahedrally coordinated, with only a small proportion in tetrahedral coordination (see 27Al NMR, Slide 19) is consistent with the coordination state of Al in the Keggin molecule, which has 12 Al in octahedral coordination and one in tetrahedral coordination (Casey et al., loc. cit.)

The reviewer endorses additional bench-top solubility studies on the observed precipitates (Slides 35 and 36), and concurs in the use of the MINTEQ codes for evaluation of, and comparison with the solubility products of known precipitates. However, the thermodynamic data used in MINTEQ may be neither up to date, nor sufficiently comprehensive for the problem under study. Therefore a literature study should complement the ongoing experimental studies, and the results of both be used to augment the thermodynamic database.

### 4.3 Head Loss Simulation Testing and Analysis: Questions and Answers

Answers are provided below to the questions posed to the Peer Review Group by NRC.

**Q.** *Is the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?*

**A.** The general impression gained is that the current head loss testing facility is insufficiently flexible for evaluation of multiple chemical environments or replication of tests to establish reproducibility. A better approach would be to use replicate small bench-scale facilities that could be run simultaneously, with stepped variations in critical parameters, so that the sensitivity and magnitude of potentially adverse conditions could be rapidly mapped out as a function of these parameters. The rapid acquisition of results would also facilitate focusing the experimental program on important issues as they are recognized. Factorial design experiments might be considered if parameter interactions are poorly understood and unpredictable. The current test loop should be reserved for confirmatory “demonstration” tests, based on the results of small-scale scoping studies.

**Q.** *What is the best method for incorporating time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?*

**A.** This is a very broad and non-specific question, without a simple answer. Clearly, with the variability in individual PWR designs and differing operating histories, there is a need to concentrate on the most critical parameters and efficiently study their effects through small-scale bench tests. Thus, for example, the impact of cal-sil carbonation during aging could be investigated through field sampling from operating PWRs followed by mineralogical and bench-scale leaching studies. Once the degree of variability and its importance has been established, then small-scale loop and head-loss tests could be conducted on a suitable range of variably aged samples. Similarly, the effect of temperature could also be studied through small bench-scale tests followed by limited small-scale loop and head-loss tests. Only after the impact of all relevant parameters has been assessed, should confirmatory tests be conducted using the present facilities. Even confirmatory tests are limited in what they can accomplish. For example, it would be difficult to conduct, or analyze the results of a non-isothermal test simulating post-LOCA cooling history.

A second approach is to develop a sufficiently powerful chemical modeling simulator that the consequences of material aging and evolving chemical environments can be studied in simulation mode. Simulations would allow multiple complex non-isothermal cases to be run that would be difficult, expensive, or impractical using current facilities For this approach to be successful requires active ongoing coordination between the modeling group at SW Research Institute and the experimental investigators at ANL and LANL on an experiment by experiment basis This is not happening at present.

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**Q.** *What metrics are most appropriate for evaluating the results of simulated chemical products with those that formed during the ICET program?*

**A.** By "metrics" the reviewer presumes that this is to mean measurement methods. By "simulated chemical products", it is assumed that the investigator is attempting to simulate conditions in the laboratory that would permit the formation of similar or identical products that formed during the ICETs, and that are also likely to form under actual conditions in a PWR. The purpose of such studies is to identify the processes taking place, quantify certain parameters under controlled conditions, and characterize the chemical and physical properties of any precipitates that form. Such investigations should take advantage of all instrumental techniques that are currently available. It appears that the scientific staff is already well versed as to what should be done. The reviewer's primary concern is that there appears to be little if any attempt to coordinate experimental studies with model developers. At present this is a serious limitation, as it leaves the investigator conducting bench-scale tests without the needed focus, or incentive to tailor his work to the requirements of a model that encompasses the diverse range of conditions expected in current operating plants.

**Q.** *Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical by-product are known?*

**A.** The reviewer has limited experience in this particular area, but is confident, that even if correlations are currently unavailable, they could be developed, and could predict the associated head loss if the physical properties of a given precipitate are known. There must be a huge literature concerning filtration technology that could be readily adapted to the problem at hand. This should be initiated promptly. One could conceive of the development of a post-LOCA coolant circulator simulator, which would utilize as input, the precipitation conditions generated by a chemical simulator module alluded to in the reviewer's response to the preceding question. With such an integrated simulator, critical screen blockage scenarios could be defined, and system modifications tested for effectiveness.

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# Appendix B

## Final Assessment Report

Chemical Effects in PWR Sump Pool Environments
Peer Review

Wu Chen

## Abstract

This report evaluated the results of the project work for investigating the chemical effect on the sump screen head loss at the post LOCA sump environment. The evaluation was done from the view point of filtration. Once particles are formed in the post LOCA sump environment, the key information to look at are if these particles can reach the sump screen and how many (represented by the total suspended solid value) and what kind of particle (characterized by particle size and morphology). Based on the ICET runs by LANL and loop tests by ANL, there is a high possibility that the sump screen will encounter head loss problems during the post LOCA recirculation.

## Executive Summary

This report is the results of the Chemical Effect Peer Review. The project was to investigate the possible scenarios of chemical effect in the sump during a post LOCA situation. It was a concern that the particles generated in the post LOCA sump environment might cause the increase of head loss at the sump screen and reduce or stop the flow of the recirculating cooling water.

The investigation was conducted by Los Alamos National Laboratory (LANL) and Argonne National Laboratory (ANL) and the results were discussed in two peer review meetings and team communications.

In this report, the assessment of the results from the project work was evaluated from the filtration perspective as the head loss in the sump screen is a filtration process.

Once particles are formed in the post LOCA sump environment, the key information to look at is

(1) Will these particles reach the pump screen?
(2) How many (represented by the total suspended solid value)?
(3) What kind of particle (characterized by particle size and morphology)?

Based on the ICET runs by LANL and loop tests by ANL, it is a highly possible that the sump screen will encounter head loss during the post LOCA recirculation.

## Contents

## 1. Introduction

This report is the results of the Chemical Effect Peer Review. The project was to investigate the possible scenarios of chemical effect in the sump pool during a post LOCA situation. There was a concern that the particles generated in the post LOCA sump environment might cause the increase of head loss at the sump screen and reduce or stop the flow of the circulating cooling water.

The investigation was conducted by LANL (Los Alamos National Laboratory) and ANL (Argonne National Laboratory) and the results were discussed in two peer review meetings and team communications.

In this report, the assessment of the results from the project work was focused on the filtration aspect as the head loss in the sump screen is a filtration process.

## 2. Integrated Chemical Effects Testing (ICET)

This work was conducted by LANL. Excellent work has been done to investigate the potential chemical effects in the sump pool under the post-LOCA environment. The experimental parameters were derived from surveys of operation nuclear power plants and should be representative. The type and quantity of coupon material, degree of submergence were thoroughly considered. Advanced tools and analytical methods were used to analyze the chemical species generated under each condition.

The Phenomenon Identification and Ranking Table (PIRT) process conducted at the end of the 2nd review meeting and the teleconference afterward were very useful in identifying additional potential post-LOCA scenarios which can be investigated in future work. Perhaps PIRT process can be conducted at the beginning or the early phase of the project to guide the research plan.

The head loss process in the sump screen during post-LOCA is the same as the pressure drop development across the filter medium in any filtration process. The pressure drop in a filtration process can be caused by either a cake build up or the clogging of the filter medium. In either case, the rate of pressure drop increase can be affected by particle concentration, particle size, particle shape, particle charge, particle-particle interactions (such as coagulation and flocculation), liquid viscosity, and chemical reaction around the filter medium. Among these factors, particle concentration and particle size have the most profound impact on the head loss of the post-LOCA sump screen.

### 2.1 Total suspended solids (TSS)

Total suspended solid (TSS) is the key parameter to quantify the amount of particles generated in different sump environments. It is also important to monitor TSS as a function of time to determine if the rates of chemical effects change.

Based on the Integrated Chemical Effect Testing (ICET) reports, TSS data were collected during ICET runs. As these results are the most important information toward the assessment of sump screen plugging and head loss tendencies, TSS data were reported and discussed during both review meetings. It is recommended that the TSS data and procedure used for measuring them be reported in the final project report. These data are the key information for finding solutions for the sump screen head loss challenges. The head loss tests at Argonne National Laboratory (ANL) simulated the ICET conditions. Although it probably made no difference on the final conclusion in this case but the common practice is to match the TSS values to ensure the testing conditions are the same.

The primary sources of particles are the insulation material (fiberglass and/or calcium silicate) and particulates generated by chemical effects in the sump pool. It is expected that the insulation material will get into the recirculation water during LOCA and most of the particles from chemical effect won't be present until a few hours or a few days later. The filtration process at the post-LOCA sump screen can be divided into two stages, the first stage is the filtering of insulation material with cake build up (it is a cake filtration process). Later, the particles from chemical effect will be filtered by the insulation cake and most particles are caught inside the cake (depth filtration process). These two mechanisms will be the reasonable approach for post-LOCA filtration simulation if so desired. Although it is unlikely, in this author's opinion, the chemical effects can also occur inside the debris cake and grow solids to generate more resistance to water flow.

In the building of insulation material cake, it is important to know the amount of insulation material suspended in the sump water. There was a good estimate of insulation material per unit sump water (0.137 $ft^3/ft^3$). It will be helpful to estimate how much of this insulation material remains in the suspension during recirculation. The 268 mg/l initial value in ICET #3 may refer to this information but it was not clear. It is expected that all the suspended insulation materials will end up in the cake on the sump screen. Even those particles which escape the initial filtration will be caught once the cake builds up. Therefore, it is recommended that the suspended portion of the insulation material for each ICET test run be clearly quantified. With these numbers, the cake thickness and its depth filter capacities can be estimated.

The amount of insulation material remains in the suspension vs. those settle depends on the recirculation rate. For the ICET's, 25 gpm recirculation rate and 0.3 cm/s cross flow velocity were mentioned. It is important to ensure this rate simulate the actual sump water recirculation rate.

Presume all the data presented in the ICET runs are due to chemical effects, a summary of these TSS data is shown in the following table. Based on these results, sump environment under the conditions of Test #1 and #4 will have the tendency of generating more particulate materials and causing severe head loss (by plugging the insulation material cake). Conditions simulated by Test #3 will have the lowest risk of plugging the insulation cake.

|  | TSS (mg/l) |
|---|---|
| ICET #1 | 30~15~30 |
| ICET #2 | 35 - 10 leveled to 10 |
| ICET #3 | 14 stable |
| ICET #4 | 30~40 stable |
| ICET #5 | 25~15 leveled to 15 |

Table 1 Total Suspended Solid (TSS) in ICET runs

It is understood that during the TSS measurement, the sample was filtered but not washed. As there are dissolved solids in the water and will show up as solid after being dried, the TSS numbers may be a few mg/l higher than the actual solid concentration.

The higher the particle concentration, the more head loss is expected. In industrial applications, the impact of TSS can be semi-quantitatively classified as the following. The sump screen with insulation debris cake can be considered as a deep bed filter.

|  |  |
|---|---|
| < 1 mg/liter | a deep bed filter can last for over a month |
| 1~10 mg/liter | a deep bed filter can last for a week |
| 10~ 30 mg/liter | a deep bed filter needs to be regenerated within 1-3 days |
| 30~70 mg/liter | a deep bed filter can only run for hours |
| 70~100 mg/liter | deep bed filters are struggling and cake starts to form on top of filter media |
| 100~500 mg/liter | expect very fast deep bed plugging and cake forming on top of filter media |
| >500 mg/liter | cake filtration |

Bed height, inter-particle porosity of the bed, and size of the particles in the suspension can affect above assessment to a small degree. Nevertheless, it provides a good rule of thumb of what to expect of the head loss in the sump screen with insulation material cake. Based on the ICET data, the sump screen can be plugged in a few days no matter which sump condition we are considering.

As mentioned, particle size distribution and gelatinous properties can also impact the filtration. These will be discussed in the following sections.

The project team did a good job in TSS measurement by considering the temperature effect and avoided the additional precipitation of solids during cooling down process. As a filter sample is dried to measured the amount of solid collected on the filter, the dissolved solids in the liquid will also precipitate (this is a similar but different phenomena from the precipitation due to cooling) and add to the solid mass. The common practice for the correct TSS measurement is to wash the filter cake with pure liquid (purified DI water in this case) to wash off any dissolved solids before drying. The alternative method is to analyze the amount of total dissolved solids and then mathematically subtract (not direct subtraction) it from the measured TSS value. A procedure of the TSS measurement is shown in Appendix A.

Turbidity values are also used in the filtration industry to quantify the content of solids particles and filtration effectiveness. As turbidity is affected by liquid colors and does not always reflect solid concentration well, turbidity data are not as useful as TSS values for evaluating a filtration system.

### 2.2 Particle size

The particles need to be retained by the sump screen (and anything that got caught on the screen) before they can contribute to the head loss. Small particles (<1 micron) have good chances of passing through all barriers without being caught. On the other hand, higher particle concentration enhances the bridging effect and makes the particles easier to be filtered. Therefore, the effectiveness of filtration is determined by the combined effect of particle size and total suspended solids.

For solid/liquid separation applications, the particle size measurement needs to be conducted in the mother liquor. Any modification (dilution, drying, and additives) to the particle suspension should be avoided as it can change the particle size distribution. For the purpose of post-LOCA environment, the best particle size measurement methods are optical microscope and laser diffraction particle size analyzer (such as Horiba LA-910 or Coulter LS-13-320). Particle counters (like Particle Size System Accusizer or Hiac particle counters) can be used if the TSS is below 20 mg/l as it is very dilute and may be difficult for the laser diffraction particle size analyzer to work. Taking particle photos with an optical microscope allows a visual comparison of particle size, shape, and agglomerateion/flocculation characteristics under different simulated environment. A laser diffraction particle size analyzer (or a particle counter) will generate the particle size distribution.

Sometimes, dilution is necessary for particle size analyzer to work. It needs to be noted that pure water should be avoided as the dilution agent since it may dissolve some fine particles and the change of ionic strength in the solution will change the agglomeration state. The standard procedure is to filter the particles out of some suspension to obtain the particle free mother liquor for dilution.

Limited particle size data were presented in the report and during review meeting. It is recommended that the project team re-evaluate the particle size information and present data for all ICET runs in the final report.

### 2.3 Gel particles

These types of particles were reported in the first review meeting but later investigation by the LANL team discovered that was due to measurement issues.

In case gel particles become an issue, some understandings of the impact of these types of particles are useful. There are two distinct gel particles behaviors which can affect filtration. Some gel particles can be easily torn apart by hydrodynamics forces (during recirculation) and very difficult to be caught by any filters. This property is to the favor of the sump screen and will not cause head loss problems. Another type of gel particles can be sticky and easily plug up filter media even at very low TSS. If this type of gel is present in the post-LOCA sump pool, fast head loss can be encountered in the sump screen.

The only method to understand the impact of these gelatinous coating materials to the sump screen filter is by experiments. A cake of insulation material can be formed based on the estimated amount (as discussed earlier) and a sample suspension containing the gel material be poured through this cake. By measuring the presence of gel in the filtrate and the head loss of the filter, a qualitative to semi-quantitative measurement of the effect of this kind of gel to the sump screen can be evaluated.

## 3. Head Loss Simulation Testing

This work was conducted by ANL. A very good test loop was constructed at ANL and suitable for the intended head loss test. The challenges seemed to be on the confirmation of the representative type and amount of material used for testing. The test suspension should match the environment in the ICET runs and the actual post-LOCA sump pool.

### 3.1 Test suspensions

It is important to match the particle size and concentration from the ICET findings. It is difficult to generate exactly the same materials given the time and scale of tests. As long as the particle size and concentration are matched, the head loss experiment will generate useful information about the screen plugging tendencies.

Head loss test #1 mimics the condition of ICET #3. ICET#3 reported a stable TSS of 14 mg/l. The "cloud" and the fast pressure drop increase encountered in head loss test #1 right after $CaCl_2$ was added indicted the TSS must be higher than 14 mg/l and could be in 200 mg/l range. It would be useful if the TSS data were collected during the head loss test to document the test conditions.

There are more opportunities for solids to settle in the ICET tank as the cross flow rate is not uniform throughout the whole system and some stagnant portion cannot be avoided. The flow loop in ANL is easier for maintaining a uniform cross flow velocity so fewer particles can settle and most of them will be caught by the filter.

### 3.2 Laboratory filtration tests

It is time and efforts consuming to run the big test flow loop. Valuable information can be obtained by running simple laboratory filtration test or a smaller flow loop. One example is shown in Figure 1.

As the first step in a post LOCA sump recirculation is the build up of a cake by the insulation material, it is important to understand the filtration behavior of the insulation material. Tests can be conducted with different amount of insulation material to build a correlation of the pressure drop as a function of cake height. It may not be linear. This correlation allows the assessment of the risk of sump screen plugging right after LOCA (without any chemical effect) for different insulation materials.

Conducting tests with same amount of insulation material but under different pressures can detect the compressibility of the insulation material cake. Compressible cakes can be compacted by the flow during the post LOCA recirculation and generate more head loss.

The material generated from chemical effects can then be added to the system to understand their impacts on the insulation cake.

A small filter device allows the project team to evaluate filtration behaviors under different conditions with less effort. With information from small scale tests, the design of experiments for the large flow loop can be conducted more effectively and relevant data can be obtained.

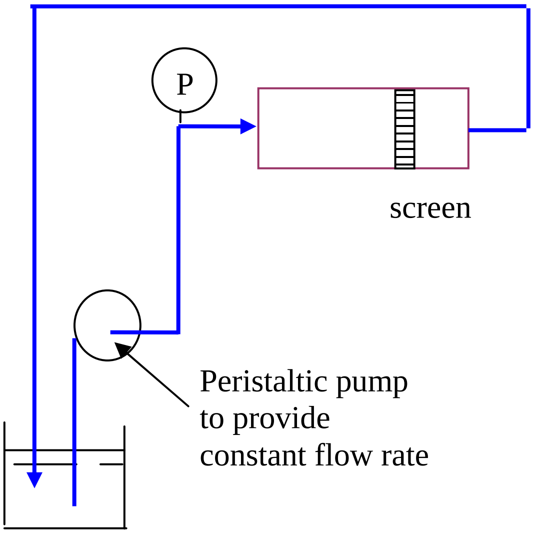

Figure 1 A constant rate filter device

## 4. Conclusion

Once particles are formed in the post LOCA sump environment, the key information to look at is
(1) Will these particles reach the pump screen?
(2) How many (represented by the total suspended solid value)?
(3) What kind of particle (characterized by particle size and morphology)?

Based on the ICET runs by LANL and loop tests by ANL, it is highly possible that the sump screen will encounter head loss during the post LOCA recirculation.

## Appendix 1 Total Suspended Solid (TSS) Measurement Proceudre

### A1.1 Measure solid concentration by drying

For cakes, very thick suspensions or difficult to filter suspensions, it is impractical to run a filtration to measure solid concentration. Oven drying should be used.

| | |
|---|---|
| **Equipment:** | Weighing dishes<br>Balance<br>Oven |

**Procedure:**

1. Put a proper amount of sample in a weighing dish and weigh it.
2. Put the sample and dish into the oven to dry.
3. Measure the weight of the dried solids.
4. Calculate according to the following formula.

Sometimes there are solids (like salt) dissolved in the liquid and need to be accounted for.

$$\text{Weight of liquid} = \frac{\text{weight of initial sample} - \text{weight of dried solids}}{1 - \%\ \text{total dissolved solid}}$$

$$\text{Weight of true solid} = \text{weight of initial sample} - \text{weight of liquid}$$

$$\text{Weight}\,\% = \frac{\text{weight of true solid}}{\text{weight of initial sample}}$$

$$\text{Volume}\ \% = \frac{\dfrac{\text{weight of true solid}}{\text{solid density}}}{\dfrac{\text{weight of true solid}}{\text{solid density}} + \dfrac{\text{weight of liquid}}{\text{liquid density}}}$$

## A1.2 Measure solid concentration by Filtration (with wash)

This method is good for dilute suspension or fairly easy to filter materials.

**Equipment:** Weighing dishes, Buchner vacuum filter,
Filter media (the selected filter medium need to be chemically compatible and capable of catching all the particles)
Volumetric pipets (50 ml, 20 ml, and 5 ml with large tip to prevent plugging)
Balance, Oven

**Procedure:**

1. Set up the vacuum filter and select a proper filter medium. Weigh the filter medium.
2. Keep the slurry well mixed.
3. Use volumetric pipet to move slurry to the filter.
4. Filter as much slurry as possible until the filter start to show the sign of plugging. Record the total volume of slurry filtered.

[Steps 3 & 4 can be replaced by filtering a known amount (volume or weight) of slurry.]

5. If there is too much solid in the filtrate, the test needs to be re-run with another medium.
6. Use clean liquid to wash the cake. This step is to remove any dissolved solids (like salt) in the mother liquor. The amount of wash liquid varies but use sufficient amount to ensure the cake is well washed.
7. Remove the filter cake with filter medium and dry them in the oven.
8. Measure the density of the filtrate.
9. Measure the weight of the dried cake.
10. Measure the density of the solids (use the dried cake for measurement).
10. Calculate according to the following formula.

$$\text{weight of liquid} = (\text{total volume filtered} - \frac{\text{weight of dried solid}}{\text{solid density}}) \times \text{liquid density}$$

$$\text{Weight \%} = \frac{\text{weight of dried solids}}{\text{weight of solid} + \text{weight of liquid}}$$

$$\text{Volume \%} = \frac{\frac{\text{weight of dried solids}}{\text{solid density}}}{\text{total volume filtered}}$$

$$\text{Total Suspended Solids} \qquad \text{ppm} = \frac{\text{mg}}{\text{liter}} = \frac{\text{weight of dried solids}}{\text{total volume filtered}}$$

### A1.3 Measure solid concentration by Filtration (without wash)

This method is used cake washing is difficult due to cake cracking or low filtration rate.

**Equipment:** Weighing dishes, Buchner vacuum filter,
Filter media (the selected filter medium need to be chemically compatible and capable of catching all the particles)
Volumetric pipets (50 ml, 20 ml, and 5 ml with large tip to prevent plugging)
Balance, Oven

**Procedure:**

1. Set up the vacuum filter and select a proper filter medium. Weigh the filter medium.
2. Keep the slurry well mixed.
3. Use volumetric pipet to move slurry to the filter.
4. Filter as much slurry as possible until the filter start to show the sign of plugging. Record the total volume of slurry filtered.

[Steps 3 & 4 can be replaced by filtering a known amount (volume or weight) of slurry.]

5. If there is too much solid in the filtrate, the test needs to be re-run with another medium.
6. Remove the filter cake with filter medium and measure the wet weight of the cake
7. Dry the cake in the oven.
8. Measure the density and the total dissolved solids in the filtrate.
9. Measure the weight of the dried cake.
10. Measure the density of the solids (by measuring the dried cake). If there are dissolved solids in the liquid, this measurement should be done with a washed cake.
11. Calculate according to the following formula.

$$\text{Weight of liquid in the cake} = \frac{\text{weight of wet cake} - \text{weight of dried cake}}{(1 - \%\ \text{total dissolved solid})}$$

$$\text{Weight of solid in the cake} = \text{weight of wet cake} - \text{weight of liquid in the cake}$$

$$\text{Weight}\ \% = \frac{\text{weight of solid}}{\text{weight of solid} + \text{weight of liquid}}$$

$$\text{Volume}\ \% = \frac{\dfrac{\text{weight of dried solids}}{\text{solid density}}}{\text{total volume filtered}}$$

$$\text{Total Suspended Solids} \qquad \text{ppm} = \frac{\text{mg}}{\text{liter}} = \frac{\text{weight of solids}}{\text{total volume filtered}}$$

## A1.4 Measurement of dissolved solid

**Equipment:** Weighing dish, Balance, and Oven

**Procedure:**

1. Remove all the suspended solid from the liquid by a Buchner vacuum filter or a laboratory centrifuge.
2. Measure the weight of an empty dish ($W_{dish}$).
3. Put some liquid in the dish and measure the weight ($W_{dish+liquid}$).
4. Dry the sample in the oven.
5. After drying, measure the weight of dish plus the remaining non-volatile. ($W_{dish+nonvolatiles}$).
6. Calculate according to the following formula.

$$\text{Total dissolved solids} = \frac{W_{dish+non\,volatile} - W_{dish}}{W_{dish+liquid} - W_{dish}}$$

# Appendix C

# CHEMICAL EFFECT PEER REVIEW: ASSESSMENT OF TEST FACILITIES AND PROGRAMS TO INVESTIGATE CONCERNS RELATED TO CHEMICAL EFFECTS IN PRESSURIZED WATER REACTOR EMERGENCY CORE COOLING SYSTEMS

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# SUMMARY

The Generic Safety Issue 191 was formulated by the Nuclear Regulatory Commission (NRC) to evaluate the potential for and phenomena associated with debris accumulation on sump screens located upstream of pressurized water reactor pumps used in the emergency core cooling system following a loss-of-coolant accident (LOCA). To help understand the phenomena and the magnitudes of debris generation and accumulation, the NRC commissioned the performance of three technical studies – “Integrated Chemical Effects Testing,” “Chemical Speciation Prediction,” and the “Accelerated Chemical Effects Head Loss Testing.”

The “Integrated Chemical Effects Testing” experiments endeavored to re-create the post-LOCA environment in five engineering scale tests. The test conditions, following both chemical and temporal evolution of the post-LOCA, included reactor building containment spray-down, corrosion of both spray-wetted and immersed reactor containment test coupons, insulation materials, and recirculating solution. The “Integrated Chemical Effects Testing” apparatus and experimental design thus were devised to provide an approximate scale model of the post-LOCA reactor and containment environment and endeavored to encompass the primary material and environmental conditions present in the post-LOCA PWRs.

In doing these extensive and complicated tests, the ICET matrix provided much valuable information on material phase behavior and interaction. On one hand it was learned that many of the materials in the test matrix, including many of the metals, had little, if any, effect on solids formation either by direct contribution or by secondary interactions. On the other hand, the following materials had larger effects on solids formation:

- Hydrogen and hydroxide ion concentration (pH)
- Dissolved boron from borate buffers and burnable poisons
- Dissolved phosphate from trisodium phosphate pH buffer
- Aluminum metal (largely present as temporary structural material)
- Fiberglass thermal insulation material
- Cal-Sil, a calcium silicate thermal insulation material
- Concrete.

The “Chemical Speciation Prediction” work was accomplished by assessing the ability of geochemical and process chemical thermodynamic modeling software to replicate the solute concentrations and reaction sequence in the post-LOCA coolant system. The task ensured that each candidate model contained a sufficient thermochemical database. For this, the presence of boron aqueous solutes and compounds was a key discriminator. The models also needed to be valid for temperatures up to about 110°C and ionic strength up to 0.5 molal. Four chemical / geochemical models met these and other criteria:

- OLI “StreamAnalyzer”, version 2.0
- Lawrence Livermore National Laboratory “EQ3/6”, version 7.2b
- RockWare, Geochemist’s Workbench7, REACT, version 5.0
- US Geological Survey “PHREEQC”, version 2.8.

Each model then was tested for seven different starting solution conditions representative of the post-LOCA environment. It was found that EQ3/6 was the most robust, avoiding the convergence problems that the other codes suffered. The EQ3/6 code was selected, with the

OLI StreamAnalyzer, to predict the outcomes of the five ICET experiments and the results compared with the results actually found by ICET. Small scale experiments to determine the dissolution rates of insulation materials and the corrosion rates of aluminum in post-LOCA solution environments also were performed under the “Chemical Speciation Prediction” task and the results provided support to improving the accuracy of the chemical models. The small scale tests gave valuable insights into chemical behaviors of the complex post-LOCA solid/solution mixtures. The modeling refinements might be nearing the point that compositions in non-tested solid/solution conditions can be predicted.

The “Accelerated Chemical Effects Head Loss Testing” simulated the loading of the sump screen with debris materials and solids produced by chemical precipitation under recirculating coolant conditions. The test apparatus created seemingly the most severe pump screen geometry, perpendicular to stream flow, to provide the most definitive (conservative) test conditions. The testing focused on the chemical conditions studied in the one (of the five) “Integrated Chemical Effects Testing” experiments that produced finely divided calcium phosphate precipitates. The testing showed the severity of sump screen blockage that could occur even with relatively low debris loads and small amounts of calcium phosphate precipitate.

Some small scale tests also were performed under the “Accelerated Chemical Effects Head Loss Testing” to determine the dissolution of Cal-Sil and the subsequent precipitation of calcium phosphate under simulated sump pool conditions. It was found that the Cal-Sil dissolution is sufficiently rapid, even in the presence of trisodium phosphate (which inhibits Cal-Sil dissolution), to precipitate significant amounts of calcium phosphate within a few hours and engender prohibitive pressure drops in the debris bed.

The results of these three studies were presented to a group of five peer reviewers in technical reports, and in workshop meetings in October 2005 and March 2006, by the NRC and the studies’ researchers. The reviewers, with reactor, nuclear, industrial, and academic credentials, were charged by the NRC to review test approaches and results, recommend improvements to the testing and analysis, and to identify any important but overlooked technical issues for additional consideration or, perhaps, experiments. The evaluations of the author, one of the five peer reviewers, are presented in this report.

As seen, the three technical studies provided substantial information to understanding to the effects of various factors in the post-LOCA environment germane to Generic Safety Issue 191. The scope of the post-LOCA conditions in the many PWR configurations, however, forced certain simplifications in the experimental design. The results of the studies also suggested potential avenues of further investigation. The following additional investigations are suggested based on the evaluations made during review of the three technical studies:

- Further parametric studies could be performed both to understand the observations from the completed rounds of experiments and to investigate the roles of temperature variation, temperature gradient (heated and cooled surfaces), boron concentration variation, radiolysis, and organic materials. Because of the large size of the “Integrated Chemical Effects Testing” apparatus and resulting large quantity of required materials, the execution of more large scale tests under more widely varying conditions may be inefficient. Instead, the testing should be done on a smaller scale to gain, at lower cost, most of the pertinent information.

- The influence of organic materials to act as glues to accrete solid particles could be great. Therefore, determination of the behavior of electrical insulations, plastic coatings, and paints when treated to steam and hot liquid water should be done to investigate their coalescence and ability to collect inorganic solids as they cool.

- Kilorad ($10^3$ Rad) per hour fields may exist away from the reactor core in the post-LOCA coolant system while megarad ($10^6$) Rad per hour fields may exist around the core. Tests of the effects of radiolysis, particularly for organic materials, should be performed. The organic materials, besides providing radiolysis products that contribute additional chemical effects to the solution, can act as radiolytic radical scavengers and impose reducing conditions to the system.

- The effects of high temperature and low temperature heat transfer surfaces and heat cycling should be studied. The test approach perhaps could use a recirculation loop in which simulated post-LOCA coolant slurries, containing the dissolved and undissolved solids, would be exposed to surfaces at temperatures representative of the hotter fuel and cooler heat exchangers.

- Aluminum metal surface analysis by x-ray diffractometry may be useful to determine the competing or complementary effects of calcium ion, silicate, or both on inhibiting aluminum corrosion. The effects of phosphate and borate species on aluminum corrosion also might be monitored in this fashion. In a like manner, surface analyses could be done to assess the effects of the various solutes, particularly aluminum, on fiberglass or other silicates corrosion.

- The accelerated head loss test apparatus appears to be too large to encourage multiple tests. A smaller test loop perhaps would allow more of the needed tests to be performed with the same resources. The test conditions could include temperatures that ramped down with time, exposed high temperature surfaces (as provided in the post-LOCA system by the exposed fuel rods), and exposed lower temperature surfaces.

- The redox conditions and concentrations of water radiolysis products, such as hydrogen peroxide, in the post-LOCA waters should be estimated taking into account the particularly high radiation fields imposed by the core.

- The potential presence of hypochlorite from radiolysis of chloride ion in the aqueous post-LOCA coolant should be investigated. If hypochlorite is present, its effect on metal corrosion under post-LOCA conditions should be investigated.

- The potential for hot sodium tetraborate or boric oxide to act as a flux to attack and perhaps dissolve the magnetite oxide layer from the reactor vessel wall or the cladding from fuel should be examined.

- The relative impact of the quantity of the solids formed by reaction of the mineral tobermorite (from Cal-Sil) with carbonic acid from absorption of atmospheric carbon dioxide to form calcite and amorphous silica, though likely to be small, should be assessed.

- The potential for algae and other biological growth in the post-LOCA water recirculation system should be investigated either through examination of the technical literature or through testing. The boron concentration in the post-LOCA water (~0.2 molar) may prove to be sufficiently high to preclude biological activity.

# CONTENTS

## Appendices

## Tables

# ABBREVIATIONS

| | |
|---|---|
| ANL | Argonne National Laboratory |
| CNWRA | Center for Nuclear Waste Regulatory Analyses |
| ECCS | emergency core cooling system |
| GSI-191 | Generic Safety Issue 191 |
| ICET | Integrated Chemical Effects Testing |
| LANL | Los Alamos National Laboratory |
| LOCA | loss-of-coolant accident |
| NRC | Nuclear Regulatory Commission |
| PSD | particle size distribution |
| PWR | pressurized water reactor |
| SwRI | Southwest Research Institute |
| TSP | Trisodium phosphate |
| UNM | University of New Mexico |
| XRD | x-ray diffractometry |

# 1 INTRODUCTION

During a loss-of-coolant accident (LOCA) in a pressurized water reactor (PWR) operating at full load power, the primary coolant will be lost rapidly from the reactor pressure vessel and heat exchangers. The superheated water, at nominally 250-330°C temperature, will escape from the pressurized coolant system, flash off as steam as it attains normal atmospheric pressure, and scour the region surrounding the break, removing thermal insulation, paint, and even concrete. Immediately after the LOCA event, alkaline water jets near the top of the reactor containment dome will spray down within the containment building with the purpose of scrubbing radionuclides from the air space. Within about 30 minutes after the LOCA, emergency cooling water will be injected into the cooling system.

The condensed primary cooling water, the spray water, and the emergency cooling water will flow downward in the containment building, through sump screens, and into a pump located at the physical low point in the containment building. There, the water will be collected and, once the emergency cooling water is exhausted, pumped to the reactor pressure vessel, over the core, and through the cooling circuit breach where it will again flow down to the sump. This recirculating water system, which serves to cool the reactor core and reactor vessel in the post-LOCA period, is called the emergency core cooling system (ECCS).

The Generic Safety Issue 191 (GSI-191) was formulated to evaluate the phenomena associated with debris creation and bed accumulation on the sump screens located upstream of the PWR sump pump for the ECCS following a LOCA. The GSI-191 was engendered by the observation of gelatinous material in the containment building of the reactor, Three Mile Island–2, some time after its accident. The Nuclear Regulatory Commission (NRC) has defined the impacts of the pump blockage in Bulletin 2003-01 and in Generic Letter 2004-02 (NRC 2003 and NRC 2004).

As part of the resolution of GSI-191, three areas of technical investigation were undertaken at the behest of the NRC to define the nature and magnitude of the debris formation which would serve to block the sump screens.

The first area of investigation, the “Integrated Chemical Effects Testing” (ICET), was conducted by researchers at the Los Alamos National Laboratory (LANL) and the University of New Mexico (UNM). The ICET experiments endeavored to re-create the post-LOCA environment, including spray-down conditions, corrosion of reactor containment test coupons under both spray-wetted and immersed conditions, degradation of thermal insulation materials, and recirculating of coolant solution at a selected nominal temperature (60°C) in 30-day tests. The test scale was 250 gallons (~946 liters). Five different combinations of insulation materials and reactor solution compositions, thought to be broadly representative of the conditions in United States PWRs, were investigated. The results of the five tests were reported both formally (Dallman et al. 2005a-2005e) and during review meetings held October 18-19, 2005, at the Argonne National Laboratory (ANL) and March 27-29, 2006 at the Southwest Research Institute (SwRI). Follow-up testing and analysis by this same group is underway.

The second area of investigation was “Chemical Speciation Prediction”. This work was performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) of the SwRI. Geochemical and process chemical thermodynamic modeling software was used to attempt to replicate the solute concentrations and reaction sequence in the post-LOCA coolant system. Initial evaluations used starting conditions postulated for post-LOCA environments. The studies were informed by the results from metal corrosion rate laboratory studies and insulation material dissolution rate experiments performed by SwRI staff and by the results of the LANL/UNM ICET experimental series as they became available. The results of the experiments and the model testing and development are provided by formal reports (Jain et al. 2004, Jain et al. 2005, and McMurry et al. - draft) and by presentations during the October 2005 and March 2006 review meetings.

The third area of investigation, “Accelerated Chemical Effects Head Loss Testing,” is being performed by ANL researchers. The objective of the head loss testing is to create a simulation of the loading of the sump screen. The tests are conducted with debris solids (primarily arising from insulation materials) and precipitating solids in a recirculating loop containing flowing simulated coolant. The differential pressure across the 6-inch (~15-cm) diameter model sump screen, consisting of a plate perforated with holes of 3/16-inch (~0.4-cm) diameter, was measured as the flow continued to circulate. The test conditions to date have been based on variations of the third ICET experiment. Results of the experiments have been presented in two informal “quick look” reports (Oras et al. 2005 and Oras et al. 2006) and by presentations during the October 2005 and March 2006 review meetings.

A technical peer group, comprised of five members with reactor, nuclear, industrial, and academic credentials, was convened by the NRC to review the three sponsored activities related to understanding the post-LOCA PWR sump pool environments and the GSI-191. The peer review group also was charged to recommend improvements to the testing and analysis approaches in the three activities and identify any important but overlooked technical issues for additional consideration or, perhaps, experiments.

The NRC requested judgments from the peer reviewers on the technical soundness and potential shortcomings of the “ICET,” the “Chemical Speciation Prediction,” and the “Accelerated Chemical Effects Head Loss Testing.” The evaluations of the present report author (Cal Delegard), one of the five peer reviewers, are presented in this report. The specific questions posed by the NRC guidance to the peer reviewers and the author’s responses are given in Section 2 of this report. Some areas for new or expanded work to help understand effects not yet investigated by the existing program are proposed and discussed in Section 3. Technical references are given in Section 4.

The author’s credentials (*curriculum vitae*) are summarized in Appendix A. Brief comments and questions on the research results provided to the NRC by the author in a preliminary assessment report dated November 30, 2005 are found in Appendix B. Some further questions on ICET experiments, and the answers obtained from the researchers, are given in Appendix C. These questions were raised in an e-mail message on May 7, 2006.

## 2 PRINCIPAL TECHNICAL QUESTIONS

Three areas of investigation were pursued in the studies conducted to help resolve the impact of GSI-191, concerned with the potential for debris to accumulate on the sump screens located upstream of the PWR sump pump for the ECCS following a LOCA. The three investigation areas are called “Integrated Chemical Effects Testing” (dubbed ICET), “Chemical Speciation Prediction”, and “Accelerated Chemical Effects Head Loss Testing”. A technical peer group was convened by the NRC to review the three sponsored activities. As part of the review, a set of Principal Technical Questions was posed to the review panel by the NRC.

The questions posed to the review panel are:

- Integrated Chemical Effects Testing
    - *Have the principal sump pool variables which affect chemical by-product formation in the post-LOCA environment been adequately simulated?*
    - *Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?*
    - *What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects) and how should their effect be characterized by testing or analysis?*
    - *Were the methods used within the ICET program to characterize and analyze chemical by-products sufficient?*
- Chemical Speciation Prediction
    - *Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?*
    - *Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?*
    - *What is the most appropriate way to measure the uncertainty associated with these codes?*
- Accelerated Chemical Effects Head Loss Testing
    - *Is the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?*
    - *What is the best method for incorporating for time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?*
    - *What metrics are most appropriate for evaluating the results of simulated chemical products with those that formed during the ICET program?*
    - *Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical by-product are known?*

The responses to the principal technical questions are addressed, in the order given above, in this section of the report.

## 2.1 Integrated Chemical Effects Testing

The ICET experiments consisted of an ambitious set of five relatively large scale tests. The test matrix, given in Table 1, attempted to encompass the various water chemistry and materials environments present in the PWRs of the US and to emulate, on an engineering laboratory scale, the evolution of the post-LOCA situation with spray-down sequences, periods of little flow, and then active pumping. Each test had present a number of metallic coupons (galvanized steel, zinc primer coating, aluminum, copper, and carbon steel), crumbled and massive concrete, and thermal insulation materials. Two primary insulation types were considered. The first, Nukon®, is a fiberglass material with some included organic binder. Because of its widespread use, this insulation type was part of the constituents in all five tests. The second insulation type is a foamed calcium-silicate material called Cal-Sil. The Cal-Sil was included in two of the five tests. With the goal of emulating the distribution of exposed surfaces in the reactor containment, some of the coupons were submerged while others were in the vapor space and exposed to liquid only during the brief spray-down phase and to what was very little condensation.

**Table 1.** ICET Matrix

| Test | Temp, °C | Buffering Agent | Initial pH | Boron (ppm) | Comment |
|---|---|---|---|---|---|
| 1 | 60 | NaOH | 10 | 2800 | 100% fiberglass insulation, high pH, NaOH concentration determined by pH |
| 2 | 60 | Trisodium phosphate | 7 | 2800 | 100% fiberglass insulation, lower pH, TSP concentration determined by pH |
| 3 | 60 | Trisodium phosphate | 7 | 2800 | 80% Cal-Sil/20% fiberglass insulation, lower pH, TSP concentration determined by pH |
| 4 | 60 | NaOH | 10 | 2800 | 80% Cal-Sil/20% fiberglass insulation, high pH, NaOH concentration determined by pH |
| 5 | 60 | Sodium Tetraborate | 8.0 – 8.5 | 2400 | 100% fiberglass insulation, pH determined by achieving target boron concentration. |

The tests used 250 gallons of water (949 liters) and were conducted isothermally at 60°C for 30 days during which the solutions were monitored for pH and the solutions sampled for analysis. After the 30 days of testing, the test apparatus was opened, the coupons measured and photographed, and the solution and solids analyzed.

The ICET campaign was ambitious, attempting to re-create the post-LOCA environment for five conditions broadly representative of the various PWR insulation and ECCS water compositions. To ensure that the conditions in all PWRs were represented, an extensive survey of the PWRs was conducted such that the five tested conditions covered the various PWR environments.

The scale of the test apparatus was sufficiently large ensure that surface area – to – volume ratios followed those of the genuine reactor containments. The tests also followed the temporal sequence of events and conditions in the post-LOCA situation. Test control was excellent, with little deviation from the planned temperature or other test conditions.

To ascertain the key factors controlling the potential sump screen blocking phenomena, a broad suite of analyses was performed over the course of the testing and especially after the testing. Examinations of the metallic, concrete, and insulation (Nukon® and Cal-Sil) test coupons, by weighing and scanning electron microscopy, and analyses of the test solutions provided key information on the evolution of solid phase formation. The wide-ranging testing helped identify potential reactions or conditions that might lead to sump screen blockage in the post-LOCA system and provided key information for the activities in the Chemical Speciation Prediction and the Accelerated Chemical Effects Head Loss Testing activities.

### 2.1.1 Principal Sump Pool Variables and Constant Variables

The first two questions for the Integrated Chemical Effects Testing are closely related and, for simplicity, are addressed together.

> *Have the principal sump pool variables which affect chemical by-product formation in the post-LOCA environment been adequately simulated?* and *Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?* The ICET experiments considered only five post-LOCA situations while within these five situations, certain parameters were held constant for simplicity. These simplifications may have caused significant parameters to be overlooked.[a]

The test program was designed to provide an approximate “scale model” of the post-LOCA reactor and containment environment and endeavored to encompass the primary material and environmental conditions present in the post-LOCA PWRs. In doing these extensive and complicated tests, the ICET matrix provided much valuable information on material phase behavior and interaction. On one hand it was learned that many of the materials in the test matrix had little, if any, effect on solids formation either by direct contribution or by secondary interactions. On the other hand, the following materials had profound effects on solids formation:

- Hydrogen and hydroxide ion concentration (pH)
- Dissolved boron
- Dissolved phosphate
- Aluminum metal
- Fiberglass
- Cal-Sil
- Concrete.

In preparing the testing matrix, some system simplifications were required that may have masked effects perhaps present under actual post-LOCA conditions. Such simplifications are:

1. Test temperature. The static 60°C temperature was selected to minimize the difficulties in operating the tests at temperatures ranging from ~100°C (boiling) to ~40°C. Hence, the influence of temperature variation is not known. For example, higher temperature would accelerate corrosion rates and the rates of other reactions, and could increase or decrease the solubilities of various salts.
2. Boron concentrations. High and static total boron concentrations (2400-2800 ppm) were used during the testing. The concentration was near the maximum used in the primary coolant circuit of a freshly refueled reactor. However, the boron concentration decreases to as low as ~50 ppm by neutron capture over the fueling cycle. The ECCS water, constituting about 3 to 4-times the volume of the primary coolant, was introduced

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[a] The original questions posed by the NRC are given in *italics*. The bases of the question as perceived by the author are stated and expanded, in ordinary font, after the original NRC questions.

about 20-30 minutes after the LOCA. Because the boron solution concentration in the ECCS also is ~2400-2800 ppm, the boron concentration in the first part of the LOCA could vary widely from ~50 ppm to ~2000 ppm, for a reactor near the end of its cycle, to little variance, for a reactor near the beginning of its cycle. This wide boron concentration variation effect was not examined in the ICET experiments.

3. Heat transfer. The tests did not model well the cyclic steep temperature transients the recirculating coolant will experience in passing by the reactor core, where the fluid slurry will heat, and the heat exchanger, where the fluid slurry will cool. In a related way, the tests also did not model the extremely hot fuel cladding and pressure vessel surfaces, where dissolved and suspended solids plating and scale formation might occur, or the colder surfaces at the heat exchangers, where solids deposition and scale formation also can occur.
4. Radiation fields. Though testing on the magnitude of ICET experiments could only be performed non-radioactively, no supporting small-scale tests were performed to investigate the effects of radiation.
5. Organic materials. Aside from the organic materials present with the Nukon® fiberglass insulation, no organic materials (for example, from electrical insulation or paint except for that in zinc primer coating) were present in the testing.

Further parametric studies could be performed both to understand the test observations obtained from the ICET #1-#5 experiments and to investigate the roles of temperature variation, temperature gradient (heated surface and cold surface), boron concentration variation, radiolysis, and the presence of organic materials. Because of the large size of the test apparatus and resulting large quantity of required materials, the execution of more large scale tests under more widely varying conditions may be prohibitively expensive. However, the testing could be done on a smaller scale to gain, at lower cost, most of the pertinent information.

### 2.1.2 Variables or Materials of Most Importance But Not Considered by ICET

> *What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects) and how should their effect be characterized by testing or analysis?* The ICET testing may have overlooked chemical, physical, or mechanical effects that might prove to be key contributors to sump screen blockage.

It is surmised that the variables and materials of most importance to the post-LOCA coolant blockage but not simulated by the ICET are the presence of organic materials, the effects of radiolysis, and the effects of hot and cold heat transfer surfaces.

The effects of organic coatings such as paints and electrical insulation (coatings) were intentionally overlooked in the ICET experiments. The severity of this simplification is not immediately evident without a reasonable estimate of the quantities of coatings involved, their properties, and the secondary effects of radiation and hydrothermal reactions (reactions with hot water) on the organic materials. The organic coatings mobilized by the LOCA and post-LOCA conditions and added to the coolant system likely would do so by being melted and blasted from their substrates (note – the area near a LOCA would be treated to a virtual steam cleaning, an effective means to remove paint). This area of influence, however, would not encompass the total of the coatings present in the containment and, in any case, the quantities should be relatively small compared with the quantities of the fiberglass and Cal-Sil thermal insulation materials.

However, the influence of such organic materials to act as glues to accrete and grow solid particles could be great. Therefore, it would be worthwhile, in a set of small scale tests, to determine the behavior of various broadly representative electrical insulations, plastic coatings, and paints when treated to steam and hot liquid water. A steam cleaner, as alluded above, may provide a suitable test apparatus. The tests also could investigate the ability of the water-treated organic materials to coalesce and collect inorganic solids (primarily the thermal insulation materials) as they cool, thus simulating their transport away from the LOCA blow-down region.

The organic materials also are more susceptible to radiolysis than the remaining inorganic matrix, aside from water. Therefore, the organic paints and coatings might be expected to break down in the kilorad ($10^3$ Rad) per hour fields of the post-LOCA coolant system and in the megarad ($10^6$ Rad) per hour fields near the reactor core. Because the oxygen and hydrogen gaseous radiolysis products will be quickly removed from solution by heat and agitation, radiolysis of unconfined water is expected to lead to increasing concentrations of hydroxyl radicals, $\cdot OH$, and hydrogen peroxide, $H_2O_2$. Small scale testing of the effects of radiation on the various organic materials in representative post-LOCA environments should be performed.

The effects of high temperature and low temperature heat transfer surfaces on the collection and dissolution of solid phases were not studied in the ICET experiments. Such tests could be performed in a recirculation loop in which the post-LOCA coolant slurries, containing the dissolved and undissolved solids, would be exposed to surfaces at temperatures representative of the fuel and heat exchangers. Examination of the hot and cold surfaces during and after the testing then would be performed to determine the importance of surface deposition.

### 2.1.3 Sufficiency of ICET Analysis Methods

> *Were the methods used within the ICET program to characterize and analyze chemical by-products sufficient?* Analytical methods used to characterize the ICET experiments may not be adequate or appropriate; other analysis methods may yield more or better insight.

The ICET experiments generally used accepted methods to identify and quantitate the starting and product solutions and solids. The magnitude of the tests left no shortage of sample for analysis. It has been proposed (see Appendix B) that the aluminum metal coupon surface analyses be augmented by x-ray diffractometry (XRD). The XRD technique seems to be well suited to understanding surface compound formation on the corroding metal and has been used in other areas to identify corrosion films on mild steel, copper, zirconium, uranium, and aluminum.

The surface appearances and XRD of the aluminum coupons might show the presence of boehmite (AlOOH) for the tests without added Cal-Sil. It was noted that though ICET #1 and ICET #4 were run at pH 10, aluminum corrosion for ICET #4, which contained Cal-Sil, had much lower aluminum corrosion than ICET #1, which had no Cal-Sil. As noted in the March 2006 presentation on ICET results at the peer review meeting held at the SwRI, research is underway to investigate the possibility that the lower rate in the presence of Cal-Sil is caused by surface deposition of silicate onto the aluminum and the resulting formation of a protective film.

It is noted that surface precipitation of calcium aluminate phases (as tricalcium aluminum hydroxide [$Ca_3Al_2(OH)_{12}$] and hydrocalumite [$Ca_2Al(OH)_7 \cdot 2H_2O$]) onto aluminum metal has been found from tests of grouting of aluminum with portland cement and from reaction with calcium hydroxide [$Ca(OH)_2$] slurries.[b] Such coatings also can suppress aluminum corrosion and should be investigated. Surface examination of the aluminum metal coupons after ICET #1 and #4 by XRD and other methods would help determine the relative roles of calcium and silicate to suppress aluminum corrosion. Surface analyses also might be done for fiberglass and for other silicates including concrete and Cal-Sil.

Analyses of particle size distribution (PSD) during the evolution of the ICET experiments would have been useful. However, measurement of the PSD without performing new experiments would not be valid because of alterations, with time, of the particles. If other smaller scale experiments were to be performed, an on-line assay of PSD would be a useful complement to the other analytical approaches as used in the original ICET experiments.

## 2.2 Chemical Speciation Prediction

The Chemical Speciation Prediction task was performed at the Center for Nuclear Waste Regulatory Analyses (CNWRA) of the Southwest Research Institute. Chemical speciation algorithms were run to attempt to model the post-LOCA coolant conditions, as observed in the ICET experiments, and to use the developed model or models to predict the post-LOCA conditions (particularly, types and quantities of precipitates) based on input values germane to reactors operating under conditions not exactly represented by the five ICET conditions. To do this, geochemical and process chemical modeling software was tested for robustness and accuracy in predicting ICET observations. Some laboratory testing also was performed to measure dissolution and corrosion rates to provide input data to test the models.

The Chemical Speciation Prediction task screened the available modeling software, first taking care that each model had present a sufficient thermochemical database. For this, the presence of boron aqueous solutes and compounds was a key discriminator. The models also needed to be valid for temperatures up to about 110°C and ionic strength up to 0.5 molal. The CNWRA selected four chemical/geochemical models that met these and other criteria:

- OLI “StreamAnalyzer”, version 2.0
- Lawrence Livermore National Laboratory “EQ3/6”, version 7.2b
- RockWare, Geochemist’s Workbench7, REACT, version 5.0
- US Geological Survey “PHREEQC”, version 2.8.

and then compared their performances in modeling post-LOCA solutions and solids.

Each code was tested for seven different starting solution conditions representative of the post-LOCA environment. It was found that the code EQ3/6 was the most robust, avoiding the convergence problems that the other codes suffered. The EQ3/6 code was selected, with the OLI StreamAnalyzer, to predict the outcomes of the five ICET experiments. The predicted experimental results of both EQ3/6 and StreamAnalyzer for ICET then were compared with the results actually found by ICET. Modeling simulations were also run for post-LOCA conditions involving metal corrosion and for interactions of the post-LOCA fluids with the fiberglass insulation, Cal-Sil, and concrete.

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[b] See Short and Parker (2005) for a description of the results of reacting aluminum metal with $Ca(OH)_2$ aqueous slurry and with portland cement grout.

Finally, the CNWRA performed laboratory tests to investigate the static leaching (dissolution) rates of the fiberglass insulation and Cal-Sil insulation and the corrosion rate of aluminum in small scale tests under a variety of conditions (containing borated solution) relevant to the post-LOCA environment. The experimental conditions and some rate observations are summarized in Table 2 (from Table A-5 of McMurry et al., to be issued).

**Table 2.** Dissolution and Corrosion Rate Measurement Results

| **Component** | | | | **Rate Observations** |
|---|---|---|---|---|
| **Nukon®** | **Cal-Sil** | **Aluminum** | **pH Buffer** | |
| Yes | No | No | 7, TSP* | $\text{Rate}_{\text{Si}}$ = 0.79 mg Si/L-hr; simulated ICET #2 |
| Yes | No | Yes | 7, TSP | $\text{Rate}_{\text{Si}}$ = 0.76 mg Si/L-hr; Al does not affect Nukon® leach rate; Al corr. rate not measured |
| Yes | No | No | 10, NaOH | $\text{Rate}_{\text{Si}}$ = 35 mg Si/L + 0.73 mg Si/L-hr |
| Yes | No | Yes | 10, NaOH | $\text{Rate}_{\text{Si}}$ = 14 mg Si/L + 0.14 mg Si/L-hr; Al inhibits Nukon® leaching; $\text{Rate}_{\text{Al}}$ = 1.16 g/$m^2$-hr; simulated ICET #1 |
| No | Powder | No | 7, TSP | $\text{Rate}_{\text{Si}}$ = 5.61 x P mg Si/L + 1.27 mg Si/L-hr; calcium silicate reaction with TSP observed; simulated ICET #3 |
| No | Solid | No | 7, TSP | $\text{Rate}_{\text{Si}}$ = 5.61 x P mg Si/L + 3.02 mg Si/L-hr; calcium silicate reaction with TSP observed |
| No | Powder & Solid | No | 10, NaOH | $\text{Rate}_{\text{Si}}$ = 51.6 mg Si/L + 0.87 mg Si/L-hr;<br>$\text{Rate}_{\text{Ca}}$ = 32.2 mg Ca/L + 0.13 mg Ca/L-hr;<br>simulated ICET #4 |
| No | No | Yes | 10, NaOH | $\text{Rate}_{\text{Al}}$ = 0.986 g/$m^2$-hr (electrochemical)<br>$\text{Rate}_{\text{Al}}$ = 1.31 g/$m^2$-hr (weight loss) |
| No | No | Yes | 7, TSP | $\text{Rate}_{\text{Al}}$ = 0.0039 g/$m^2$-hr |
| No | Yes | Yes | 7, TSP | $\text{Rate}_{\text{Al}}$ = 0.028 g/$m^2$-hr |
| No | Yes | Yes | 10, NaOH | $\text{Rate}_{\text{Al}}$ = 0.80 g/$m^2$-hr |
| * TSP is trisodium phosphate. | | | | |

These experiments provided fundamental concentration and kinetic data useful for the model testing effort, corroborative data to the ICET results, and helped in understanding the key reactions of the most active solid phase reactants (Nukon®, Cal-Sil, and aluminum) and their interactions with each other and with the key solution parameters (pH and presence of TSP).

### 2.2.1 Credibility of Product Predictions

> *Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?* Chemical speciation prediction by the presently available codes may not be adequate to predict sump environment products.

For many but not all solutes, the modeling software made reasonable predictions of solute concentration and pH based on comparison with experimentally derived values. At the level of model development available in March 2006, the results of the analytical simulation still seemed to follow, rather than lead, the observations made in the experimental testing and thus required further refinement. For example, some of the observed precipitating phases [e.g., $Ca_3(PO_4)_2$ and silica, $SiO_2$, for calcium/phosphate and silicon, respectively] were not the equilibrium phases predicted by the software [e.g., apatite, $Ca_5OH(PO_4)_3$, and albite, $NaAlSi_3O_8$, respectively]. In addition, amorphous (poorly crystalline) phases generally are not part of the model databases but may be the compounds controlling the concentrations of many of the solutes in the relatively short 30-day time frames of the post-LOCA systems.

It was observed that concessions to the seeming lack of the role of $CO_2$ to form low solubility carbonates had to be made. Reaction rates (kinetics) also are not handled well by the modeling software; the models thus may not reflect the evolving concentration profiles. As the models are refined, they should provide closer matching of the observed ICET concentrations, the concentrations observed in the supplemental CNWRA testing described in Table 2, and ultimately the concentrations in systems not exactly mimicked in the ICET experiments.

Of the software modeling codes tested, the StreamAnalyzer® by OLI seemed best, likely because of its industrial pedigree and ability to handle the higher solute concentrations. It would be useful for the purposes of GSI-191 if the modeling could predict, with more certainty, the chemical precipitation behaviors at the higher and lower post-LOCA temperatures in addition to the conditions not yet investigated by ICET or other testing. It is not evident from the results to-date that the predictions would be successful.

### 2.2.2 Code Benchmarking by Tests

> *Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?* Other methods may exist that are better in calibrating and determining the adequacy of the thermodynamic modeling codes.

The small-scale testing is a valid approach to gain more information on the kinetic and equilibrium behaviors of the key solutes and solid phases. From the present results, it seems that benchmarking these codes is constructive because it reveals where gaps exist in the data. Further small-scale testing, as is being done under this activity to validate the code predictions, likely will be useful.

### 2.2.3 Measuring the Code Uncertainties

> *What is the most appropriate way to measure the uncertainty associated with these codes?* The ability of the codes to predict behaviors accurately for chemical regimes having no experimental results may not be adequate.

Comparison of the code predictions against the results of targeted small-scale tests is a feasible way to strengthen the codes and to identify and measure their uncertainties. Again, however, the codes seem to be following, rather than leading, the chemical testing. Predicting the behaviors and evolutions of the complicated and rapidly changing post-LOCA coolant systems may be beyond the sophistication of present geochemical and industrial chemical modeling codes. However, the models are approaching the ability to predict compositions at non-tested conditions.

## 2.3 Accelerated Chemical Effects Head Loss Testing

The objective of Accelerated Chemical Effects Head Loss Testing is to simulate the loading of the sump screen by recirculating dissolved and suspended solids generated in the post-LOCA system. This is done by directing the simulated coolant flow containing suspended debris solids, primarily arising from insulation materials and precipitating solids, through a screen in a recirculating loop. The quantity of cake that ultimately forms on the screen is measured; the rate of cake formation and the cake’s flow properties also are measured.

The Head Loss Testing focused on the environments for which trisodium phosphate (TSP) buffering is used to control pH and Cal-Sil insulation is present. These conditions, found in ICET #3, lead to the precipitation of finely particulate calcium phosphate with the calcium arising from dissolution of the Cal-Sil. The effects of the degree of Cal-Sil dissolution, amount of fiberglass and Cal-Sil debris (which is adjusted to match the areal mass loading on the screen), and the relative arrival times of the debris and the calcium phosphate precipitates were studied. The effects of the Nukon® fiberglass and Cal-Sil insulation debris beds alone and the debris beds with the calcium phosphate precipitate were compared.

Some small scale tests also were performed to determine the dissolution of Cal-Sil and the subsequent precipitation of calcium phosphate under simulated sump pool conditions. It was found that the Cal-Sil dissolution is sufficiently rapid, even in the presence of TSP (which inhibits Cal-Sil dissolution), to precipitate significant amounts of calcium phosphate within a few hours and engender flow-prohibitive pressure drops in the debris bed.

### 2.3.1 Adequacy of the Head Loss Testing Approach

> *Is the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?* Perhaps other, more efficient, or more definitive methods are available to test head loss effects.

The accelerated head loss test apparatus and associated reagent requirements as practiced in the testing to-date (Oras et al. 2005 and 2006) has produced a large foundation of data germane to the those reactors having both TSP buffering and Cal-Sil insulation and thus having the prospect of calcium phosphate solids generation in the post-LOCA coolant. Such conditions are exemplified by ICET #3. The calcium phosphate, in concert with the debris from remaining undissolved Cal-Sil and fiberglass insulation, produce significant pressure drops across the prototypical screen bed. Note that it would be valuable to determine if the calcium leached or rinsed from concrete alone and without the Cal-Sil (i.e., ICET #2 conditions) would be sufficient to produce enough calcium phosphate to create a significant pressure drop in the prototypical screen bed.

The testing approach demonstrably provides valuable information on the behavior of the mixed debris and precipitate bed formed in a dead-end screen loop. Nonetheless, the test apparatus seems overly large. The apparatus also forces all solution to go, in a parallel flow, through the screen. This design would seem to be the most prone to blockage and may have been chosen in the test design for this reason. In some of the sump screen designs being created for reactor application, the screens are vertical and the solution would pass through the debris bed only near the screen bottom. The debris bed depth would decrease with screen height with the more easily suspended precipitates flowing over the top without encountering significant fiberglass or remaining solid Cal-Sil debris.

Because of the large scale of the tests, fewer tests can be performed than would be performed if tests were at smaller scale. This limitation decreases the information that could otherwise be obtained to characterize the multiple chemical environments of the post-LOCA coolant. A smaller apparatus might accomplish the needed testing and generate much less waste per test thus encouraging more and more varied testing. A smaller apparatus might also be designed to model the operation of a vertical screen rather than the tested perpendicular dead-end screen.

A smaller test loop also would make possible, or make easier, testing at temperatures that vary (ramp down) with time and might allow exposed high temperature surfaces (as provided in the post-LOCA system by the cooling fuel rods) and exposed lower temperature surfaces (at the heat exchangers) to be examined more economically.

### 2.3.2 Methods for Observing Time-Dependent Effects

> *What is the best method for incorporating for time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?* The simulation of head loss effects in laboratory testing can involve shortcuts in creation of the cake on the screen to overcome slowly evolving reactions and environments. The adequacy of this approach is questioned.

The evolution over time of TSP and Cal-Sil dissolution and the accumulation of a solids debris bed in an actual post-LOCA event are unknown. Therefore, various modes of creating the debris and calcium phosphate precipitate bed were emulated in the testing program. The test results indicated the approximate quantities of solids necessary to provoke bed blockage. Because the only way to incorporate time-dependent effects is to run the experiments over time, the testing program endeavored to recreate the evolution of the debris bed. As shown in the following section, the solids created in some post-LOCA environments were unlikely to have been adequately recreated by certain chemical shortcuts.

### 2.3.3 Evaluation of Simulated Chemical Products

> *What metrics are most appropriate for evaluating the results of simulated chemical products with those that formed during the ICET program?* Chemical products created to simulate those created during the ICET experiments are used in some of the head loss testing. The adequacy of the simulated products to perform like the genuine products must be measured to determine their legitimacy.

The ICET experiments generated aluminum corrosion products from the actual corrosion of aluminum. However, in the filtration / head-loss testing, the aluminum corrosion product was introduced by neutralization of $Al(NO_3)_3$ with NaOH. This method is not representative of the way aluminum solids arise in the post-LOCA cooling water system. This introduction method also may have caused the non-prototypical so-called “snowfall” behavior. At a minimum, the aluminum nitrate method introduces nitrate, an anion not otherwise present in the real post-LOCA system. It is proposed that the aluminum be introduced in another manner, either by corroding a coupon of aluminum in NaOH (simulating the actual conditions, but potentially difficult to achieve under experimental conditions) or by adding sodium aluminate solution, $NaAl(OH)_4$. Sodium aluminate is what is initially dissolved from the corroding aluminum metal by the NaOH and is available as a solid material through chemical supply houses or can be made by dissolving $Al(OH)_3$ in hot excess NaOH.

Similarly, several of the head loss tests used calcium chloride ($CaCl_2$) solution addition to simulate the dissolution of Cal-Sil. Use of $CaCl_2$ provides chloride at concentrations overwhelming the small chloride concentrations normally present in the post-LOCA environment. Besides giving an unrealistically high chloride concentration, the addition of $CaCl_2$ in place of Cal-Sil fails to provide other solutes (e.g., sodium, silicate, some carbonate) and solid phases (e.g., amorphous silica) gained by dissolving the Cal-Sil. It is proposed that dissolved Cal-Sil (as used in many of the tests), rather than $CaCl_2$, provide the desired dissolved Cal-Sil addition.

To be consistent with the ICET experiments, the head loss testing emulated the ICET solids generation sequence. However, it is more important that the simulated chemical products created in the head loss testing emulate the products arising in the containment building during the 30-day post-LOCA interval. The testing performed for the ICET program has shown the importance of pH, Cal-Sil dissolution, borate, aluminum corrosion, phosphate, the Nukon fiberglass, and perhaps concrete on solids formation. The head loss testing could focus on varying these components, plus study the effects of temperature differentials and hot and cold surfaces, to create the solids present in the post-LOCA environment.

### 2.3.4 Identifying Key Physical Parameters to Predict Head Loss Performance

> *Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical by-product are known?* Certain key physical parameters, such as particle size and shape, might be useful to predict the filtration/screening behavior of fluids bearing such suspended solids.

Methods to predict head loss or filtration behavior based on physical properties may or may not exist. Therefore, in such an effort, it likely would be useful to consult experts, including experts in the review panel, with backgrounds in water treatment, wastewater treatment, mineral mining and milling, or similar process industries for correlation methods.

However, even if such parameters could be identified and measured, the coolant solutes and the suspended solids continue to react as shown by ICET and other testing. Thus, chemical interactions of the various particles and the coolant solutes themselves (e.g., borate, phosphate) can influence head loss due to material corrosion, surface precipitation, self-cementation, or other chemical and even radiolytic effects.

# 3 UNEXAMINED AND LITTLE EXAMINED CONDITIONS

In Section 3, certain post-LOCA conditions are identified that require more examination. Discussions of these important post-LOCA conditions and some possible avenues of research are presented in this section. The phenomena being examined are radiolysis, solution composition effects on metal (particularly aluminum) corrosion, material deposition and spallation, atmospheric contributions, and biological activity. Recommendations for additional testing and analysis are presented for each topic.

## 3.1 Radiolysis and Its Effect on Metal Corrosion

The effects of radiolysis on water and its subsequent effects on the corrosion of vulnerable metals such as aluminum (Al; present in scaffolding and ladders) and zinc (Zn; present on galvanized metal), were not examined in any of the testing. The current studies show that aluminum can be one of the primary contributors to solids loading in the post-LOCA recirculating coolant waters. The behavior of aluminum and other metals as influenced by water radiolysis remains to be studied.

The review panel, in the meetings held March 27-29, 2006, at the SwRI, discussed the radiolytic conditions of the cooling water as the LOCA event evolves. Under operating reactor conditions, water radiolysis produces primarily hydrogen ($H_2$), diatomic oxygen ($O_2$), and hydrogen peroxide ($H_2O_2$). These components recombine, however, under the pressurized conditions in the PWR. The concentrations of these three species at full reactor power, where the dose rate is taken to be $10^4$ gray/second (~$3.6\times10^9$ rad/hour) at 280°C, are ~$10^{-5}$ moles per liter in $H_2$ and $H_2O_2$ and ~$10^{-6}$ moles per liter in $O_2$ (Ishigure et al. 2006). At the same time, corrosion of the reactor steel pressure vessel exposed to the water imposes reducing conditions by being oxidized to magnetite ($Fe_3O_4$) and related spinel phases. These reactions chemically reduce water to produce $H_2$. A $H_2$ overpressure is also actively maintained by injection of $H_2$ gas within the primary coolant system to preserve reducing conditions and impede metal corrosion. This overpressure gives much higher $H_2$ concentrations than those produced by radiolysis.

During a LOCA, however, the confining overpressure is released and the gaseous $H_2$ and $O_2$ constituents are flashed from the liquid water and lost to the air. And though nuclear fission ceases during the LOCA, water radiolysis continues by fission and activation product decay to produce the estimated megarad-per-hour fields in the core. Though the gaseous $H_2$ and $O_2$ constituents continue to be created but escape readily from the hot irradiated solution, the hydroxyl radical, ·OH, continues to be formed but is retained by the solution. Two ·OH radicals combine to form $H_2O_2$ which likewise stays dissolved in solution.

The $H_2O_2$ can build in the solution to give conditions more oxidizing than deaerated or even oxygenated water. This effect may be augmented by the radiolysis of chloride ion, $Cl^-$, dissolved in water to produce hypochlorite ($OCl^-$) or hypochlorous acid (HOCl), both strong oxidants. The ICET experiments #1-#5 contained 100 ppm HCl (~$2.7\times10^{-3}$ moles $Cl^-$ per liter). On the other hand, organic compounds present in the recirculating water from post-LOCA cooling water, from paint, plastic, the organic coating on the fiberglass insulation, or other sources, can act as scavengers of the radiolytically generated oxidants. This scavenging can, in itself, engender reducing conditions. As a result of these conflicting effects, the reduction/oxidation, or redox, conditions extant in the post-LOCA recirculating water are not immediately evident.

*Recommendation: It is suggested that the redox conditions and concentrations of radiolysis products, such as hydrogen peroxide, in the post-LOCA waters be defined taking into account the radiation fields imposed by the core.*

It was recognized early in the design of nuclear reactors that the effects of radiolytically-generated $H_2O_2$ on engineering materials must be considered. The role of aluminum in metallic uranium fuel cladding and in reactor fuel tubes led to much early work on the durability of aluminum in radiolytic conditions. For expediency, instead of studying aluminum performance under radiolysis, initial studies simply tested aluminum in the presence of $H_2O_2$. In these tests, the $H_2O_2$ was added to water in concentrations expected during reactor operations. These early tests showed that $H_2O_2$ had very little effect on aluminum corrosion. Subsequent tests of aluminum performance in water by direct irradiation under reactor conditions showed enhanced aluminum corrosion rates. Because of the higher corrosion observed under direct exposure, it was thought that the primary but transitory oxidizing radiolytic products – free hydroxyl or atomic oxygen – rather than the subsequent $H_2O_2$ or dissolved diatomic oxygen, $O_2$, were responsible (Goldsmith 1953). These findings were confirmed in subsequent studies (Richman 1958).

Such direct irradiation of aluminum should not occur under the postulated post-LOCA situation in which the fuel is defined to remain intact and radiolysis only to occur on the recirculating coolant. Hence, the effects of radiolysis should be confined to the secondary reactions of the irradiated water, and its contained solutes and entrained solids, on the corroding metals.

## 3.2 Solution Composition Effects on Metal Corrosion

Continued parametric testing of the susceptibility of aluminum to corrosion caused by typical water constituents was conducted (Troutner 1957). The results of these studies are very germane to the present considerations of aluminum durability in the post-LOCA environment. The constituents whose effects were studied included chloride, nitrate ($NO_3^-$), sulfate ($SO_4^{2-}$), bicarbonate ($HCO_3^-$), hydrogen peroxide, acetate ($CH_3CO_2^-$), oxalate ($C_2O_4^{2-}$), citrate [$C_3H_4OH(COO)_3^{3-}$], arsenate ($AsO_4^{3-}$), phosphate ($PO_4^{3-}$), silicate ($HSiO_4^{3-}$), dichromate ($Cr_2O_7^{2-}$), molybdate ($Mo_7O_{24}^{6-}$), and mixtures of these ions. Individual tests, run at 92°C (~198°F) with 100 ppm of the respective constituents, showed that only citrate increased corrosion, and phosphate decreased corrosion.

Significantly, again hydrogen peroxide had no effect on aluminum corrosion rate. Though the effects of hypochlorite were not studied, chloride even up to 10,000 ppm concentration (~0.28 moles of chloride per liter) also had no effect on uniform corrosion rate. In addition, tests containing both chloride and hydrogen peroxide, even up to 100 ppm $Cl^-$ and 100 ppm $H_2O_2$ (~$3\times10^{-3}$ moles per liter) showed no enhanced corrosion.

*Recommendation: It is suggested that the potential presence of hypochlorite in the post-LOCA coolant be investigated. If present, its effect on metal corrosion under post-LOCA conditions should be investigated.*

As noted in the ICET testing, pH had a significant effect on aluminum corrosion rates with much higher rates observed at pH ~10 than at pH ~7. In the tests by Troutner (1957), minimum corrosion rates were exhibited at pH ~6 with rates increasing steeply above and below this pH.

Further study of the corrosion of aluminum (Troutner 1957) showed that measurable inhibition occurred with as little as 5 ppm (~0.0005 M) phosphate. It was postulated that the inhibition occurred because of the surface deposition of a protective layer of aluminum phosphate.

Subsequent X-ray diffraction studies of the surface of aluminum exposed to 5 ppm phosphate at 195°C (383°F) for 24 days showed the formation of the aluminum phosphate compound augelite, $Al_2PO_4(OH)_3$, on the metal surface and is even formed on aluminum at 0.5 ppm phosphate (Groot 1957). Such deposits might be postulated to form on the aluminum coupons in the ICET experiments 2 and 3 having the phosphate buffer at pH 7.

*Recommendation: It is suggested that further post-test XRD examination of the corroded metal coupon surfaces be conducted, especially for aluminum, and to examine the role of phosphate in coupons prepared during the ICET and other testing.*

Some salts including chromates, dichromates, silicates, and borates are reported to inhibit aluminum corrosion (Shreir et al. 1994). Borates are common additives to automotive antifreeze formulations and can encounter aluminum parts. The formation of perborates, $BO_3^-$, from the reaction of sodium metaborate, sodium hydroxide, and hydrogen peroxide, also should be considered to be possible under radiolytic conditions (p. 980, Wiberg 2001). Perborates are used as bleaches and thus indicate that they are oxidizing.

*Recommendation: Compare the effects of sodium tetraborate and perborate on aluminum corrosion.*

### 3.3 Spallation of Deposits from the Hot Fuel Cladding and Reactor Vessel

The LOCA event produces a rapid alteration in the pressure, temperature, and local chemical conditions on the fuel cladding and reactor vessel walls. In the initial moments of the LOCA, the pressure within the vessel drops to atmospheric, the vessel itself undergoes mechanical shuddering attendant to the loss of coolant, and the temperature of the fuel fluctuates as the coolant supply and condition varies. Under such thermal and mechanical transients, the magnetite corrosion layer in the reactor vessel, though nominally adherent, may vibrate loose and report to the recirculating coolant. The fuel itself, generally clad in zirconium alloy, may spall its metal oxide outer layer (in this case, zirconium oxide, $ZrO_2$) though this is much less likely than magnetite spallation from the reactor vessel. Note, however, that thick ~50-µm films of $ZrO_2$ have been observed under certain conditions (Johnson 1989).

Deposits of "crud" from stainless steel and nickel hardware in the primary coolant circuit also occur on fuel cladding. In one study, the crud deposits from operating PWRs were less than one mil (~0.025 mm) thick, were composed of a nickel-substituted magnetite (formula $Ni_xFe_{3-x}O_4$ with $0.45<x<0.75$) spinel, and were more highly concentrated on fuel having lower power (Solomon and Roesmer 1976; Sandler 1979). Chromium also was found in some cruds, substituting for iron in the spinel structure to give the composition $Cr_yNi_xFe_{3-x-y}O_4$. Other contaminants found in the crud included aluminum and silicon, which were not incorporated in the spinel but apparently formed amorphous aluminosilicates, and carbonaceous material, postulated to arise from ion exchange resin (Sandler 1979). In both reactor vessel and fuel cladding cases, the spalled solids would report to the recirculating coolant and then travel to the sump and sump screens where they would contribute to the solids loading and may impede coolant flow.

*Recommendation: Tests should be conducted to examine the possibility and extent of corrosion product spallation from reactor vessel walls and from fuel cladding surfaces under conditions that would occur under LOCA thermal and mechanical shock conditions.*

It is more likely that solids spallation from reactor vessel and fuel cladding surfaces will occur from cyclic deposition onto and spallation from hot surfaces during the subsequent recirculating coolant flow. The deposition would occur by the transport of the dissolved and suspended boric acid ($H_3BO_3$), sodium tetraborate ($Na_2B_4O_7$), trisodium phosphate (TSP; $Na_3PO_4$), Cal-Sil insulation, aluminum corrosion products [e.g., $Al(OH)_3$, AlOOH, aluminum phosphate phases], calcium phosphate, fiberglass fibers, concrete particles, and other suspended debris to the hot fuel cladding and reactor vessel surfaces. The characterization of crud found on PWR fuel cladding from operating reactors (Sandler 1979) informs this hypothesized post-LOCA scenario in that organic and aluminosilicate deposits were found in addition to nickel ferrites.

Note that most of the suspended solids, by virtue of being transported into the reactor vessel and past the sump screen, would be in the form of fine particulates. The coolant water, bearing the dissolved and suspended solids, would flash away as it encountered the hot fuel cladding and reactor vessel surfaces and leave its solids load behind. There, the deposited solids could undergo higher temperature hydrothermal reactions and likely undergo self-cementation. With time, as the deposits thickened, thermal shock and mechanical vibration caused by the recirculating water would loosen the deposits and transport the caked, dried, and matted solids to the sumps and sump screens. Overall, the fine particulates and dissolved salts could agglomerate and become cemented to create much larger particles that would present greater barriers to fluid flow.

The solid deposits likely would be shaped by the depositional surfaces and take the form of curved flakes. As such, they could be both easily transported by the flowing coolant and be readily caught upon, and thus clog, the sump screens. Much of the deposit would arise from drying of dissolved salts. The dried salts (e.g., sodium tetraborate, sodium phosphate) may easily re-dissolve in hot water and with agitation once they were re-introduced to the water flow after spallation. However, the phosphate and borate salts themselves also undergo polymerization upon heating to produce polyphosphates and polyborates that resist re-dissolution.

In addition, sodium tetraborate dehydrates on heating to 350-400°C (662-752°F) to form $Na_2B_4O_7$ and, if heated to the 878°C melting point of $Na_2B_4O_7$, can act as a fluxing agent to dissolve zirconium oxide, $ZrO_2$, from the cladding and transition metal oxides (such as the magnetite coating on the reactor pressure vessel; Bock 1979). Boric acid ($H_3BO_3$) and its dehydrate, $B_2O_3$, also can act as fluxes. The sodium tetraborate and boric acid thus might act as an additional vector to displace iron and nickel from the reactor vessel and zirconium from the fuel cladding and direct them to the cooling water where they would precipitate as fine hydroxides. More importantly, attack by the hot boron compounds might compromise the zirconium and, more so, any stainless steel fuel cladding to expose the irradiated fuel to the flowing coolant.

The solids might also cling tenaciously to the fuel cladding and compromise the heat transfer meant to occur during the post-LOCA period. If such deposition occurs, it might sufficiently impede the desired heat transfer as to lead to fuel cladding failure due to thermal stresses.

*Recommendation: The behavior of recirculating coolant, bearing dissolved and suspended solids, upon encountering reactor fuel and vessel surfaces heated to the immediate post-LOCA temperatures should be investigated. Of particular interest are examination of solids deposition, spallation, shape, re-dissolution or re-suspension, and the resistance of the solids to transport. The formation of tenaciously held deposits on the fuel surfaces is of high impact because of its effect on heat transfer. The potential effect of hot sodium tetraborate or boric oxide to act as* *fluxes to dissolve the magnetite oxide layer from the reactor vessel wall or the clad fuel should be examined in separate tests.*

## 3.4 Atmospheric Contributions

The alkaline post-LOCA spray-down of the reactor containment building will scrub carbon dioxide ($CO_2$) from the air to contribute from ~25 to 170 kg of $CO_2$ to the coolant solution.[c]

Accounting of the solids budget due to $CO_2$ absorption shows that the effect may be minor. For $CO_2$ to have an effect, it must first be absorbed by water to form carbonic acid, $H_2CO_3$. The formation of $H_2CO_3$ would move the pH towards ~5.5, either up or down depending on the starting pH imposed by the other solution components. The carbonic acid would react with calcium with the calcium source most likely being from the dissolution of Cal-Sil insulation. Water attack of concrete, another potential source of calcium, would provide little soluble calcium; the calcium would already be in stable solid phases including $CaCO_3$.

The Cal-Sil insulation contains both $CaCO_3$ and tobermorite, $Ca_{2.25}(Si_3O_{7.5}(OH)_{1.5})\cdot H_2O$ (Dallman et al. 2005c). The reaction of solid tobermorite with $CO_2$ dissolved in water produces solid $CaCO_3$, solid amorphous silica, $SiO_2$, and releases some water:

$$4\ Ca_{2.25}(Si_3O_{7.5}(OH)_{1.5})\cdot H_2O_{\ (s)} + 9\ CO_{2\ (g)} \rightarrow 9\ CaCO_{3\ (s)} + 12\ SiO_{2\ (am)} + 4\ H_2O_{\ (l)}$$

The parent tobermorite, without reacting with carbonic acid, forms amorphous silica and hydrated lime, $Ca(OH)_2$, by reaction with water:

$$4\ Ca_{2.25}(Si_3O_{7.5}(OH)_{1.5})\cdot H_2O_{\ (s)} + 2\ H_2O_{\ (l)} \rightarrow 9\ Ca(OH)_{2\ (s)} + 12\ SiO_{2\ (am)}$$

It is seen that the difference between the two reactions of tobermorite is the replacement of the $Ca(OH)_2$ product from reaction with water with the $CaCO_3$ from the reaction with $CO_2$. The net effect is that the hydrated lime from tobermorite reacts with $CO_2$ to produce calcite and water:

$$Ca(OH)_{2\ (s)} + CO_{2\ (g)} \rightarrow CaCO_{3\ (s)} + H_2O_{\ (l)}$$

The $10^7$ $ft^3$ (~280,000 $m^3$) volume of the largest containment building holds about 171 kg of $CO_2$. Therefore, the net increase in solids weight, caused by the reaction of $Ca(OH)_2$ with $CO_2$, would be ~100 kg. The weight increase for other containment buildings would be lower by about a factor of 4. These quantities likely are negligible contributors to the total suspended solids budget in the coolant system. For both reactions, finely divided solids, consisting of amorphous silica and either hydrated lime or calcite, would form. The solids in either case are physically similar and are unlikely to be significantly different in affecting sump screen flow.

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[c] According to the presentation, “Principal Attributes of the LOCA Accident Sequence”, made on March 27, 2006, during the second peer review meeting, the air volumes in one of the PWR containment buildings is about 10 million cubic feet. The remaining 29 PWR containment buildings have volumes around 1.5-3 million $ft^3$. Because the concentration of $CO_2$ in air is about 330 parts per million on a mole basis, the quantity of $CO_2$ present in $10^7$ $ft^3$ of air is

$$10^7\,\text{ft}^3\text{air} \times \frac{28.3\ \text{liters}}{\text{ft}^3} \times \frac{0.00033\ \text{liters CO}_2}{\text{liter air}} \times \frac{\text{mole}}{24\ \text{liters gas}} \times \frac{0.044\ \text{kg}}{\text{mole CO}_2} = 171\,\text{kg CO}_2\,.$$

*Recommendation: The relative impact of the quantity of the solids formed by reacting tobermorite from Cal-Sil with carbonic acid from $CO_2$ absorbed from the air to form calcite and amorphous silica, though likely to be small, should be assessed.*

## 3.5 Biological Activity

Temperatures during the immediate post-LOCA period will not be sufficiently high to sterilize the interior of the reactor containment building. As a result, as the reactor and surroundings cool, warm moist conditions, augmented in many cases by phosphate buffer, will be conducive to growth of algae and perhaps other life forms. With time, the algae and other growths may develop mats and help block flow through the sump screens.

However, it is noted that boron is an effective algaecide and may be a sufficient biocide to thwart growth of biota in the coolant water system. Therefore, the presence of boric acid ($H_3BO_3$) in all tests and sodium tetraborate in Test #5 may be adequate to block growth in any situation.

The total boron concentrations in Tests #1-#4 was 2800 ppm, or about 0.26 moles of boron per liter, and 2400 ppm in Test #5, about 0.22 moles boron per liter. These high boron concentrations may be toxic and preclude biologic growth. Though boron is consumed by neutron capture during irradiation and its concentration decreases to ~50 ppm towards the end of the fueling cycle, its concentration is quickly restored to near starting levels within about 30 minutes after LOCA by the injection of 3- to 4-fold volumes of emergency cooling water containing ~2800 ppm boron.

*Recommendation: The potential for algae and other biological growth in the post-LOCA water recirculation system should be investigated either through testing or through examination of the technical literature. The ~2000 ppm boron concentration in the post-LOCA coolant may be sufficiently high to preclude biological activity.*

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# APPENDIX 1

## Curriculum Vitae – Calvin H. Delegard

### Professional Activities

Twenty-six years (1970; 1972-1976; 1979-1987; 1992-present) in applied/process chemistry and nuclear materials safeguards at the Hanford Site.

- Plutonium process and waste chemistry (speciation, separation, purification, processing)
- PUREX and Plutonium Finishing Plant process chemistry
- Environmental chemistry of radionuclides (Co, Sr, Tc, Cs, U, Np, Pu, Am)
- Technical liaison with the Institute of Physical Chemistry, Russian Academy of Sciences, on chemistry of the actinides and technetium in alkaline media, on K Basin sludge treatment/disposal, chromium phase dissolution, and uranium metal corrosion
- Hanford tank waste chemistry (bulk and radionuclide components)
- Tank farm evaporator chemistry (concentration and crystallization)
- Organic decomposition reactions in tank waste (e.g., gas generation in 101-SY)
- Tank waste treatment chemistry (ozonation, electrolysis, calcination/dissolution, leaching/sludge washing)
- Material corrosion; Zr and other metals in nitric acid; copper and mild steel in basalt groundwater
- Chemical characterization, processing, and U metal corrosion of K Fuel Storage Basins sludge
- Domestic (234-5) and design of int'l. (Hanford, RFES, SRS) nuclear materials safeguards
- Development and qualification of plant calorimeters for international safeguards
- Development of prompt gamma analysis for Pu materials characterization
- Plutonium materials stabilization for storage.

Eight years (1976-79; 1987-92), nuclear materials safeguards at the International Atomic Energy Agency, Vienna, Austria.

- International nuclear material safeguards inspection execution
- Subsidiary arrangements, design information, and facility attachments preparation
- Destructive and non-destructive nuclear materials verification methods development.

### Technical Publications

Contractor and National Laboratory Documents

- Atlantic Richfield Hanford Company
- Rockwell Hanford Operations
- Westinghouse Hanford Company
- B&W Hanford, Duke ESH, B&W Protec, Numatec Hanford
- Los Alamos National Laboratory
- Brookhaven National Laboratory
- Pacific Northwest National Laboratory

Symposium Proceedings

- Institute of Nuclear Science, Boris Kidrič, Vinča, Yugoslavia
- American Nuclear Society
- American Society Metallurgical Engineers
- Institute of Nuclear Materials Management
- American Chemical Society
- European Safeguards Research and Development Association

- Minerals, Metals & Materials Society
- Russian Conference on Radiochemistry
- NATO Advanced Research Workshop
- Waste Management
- Materials Research Society
- International Atomic Energy Agency

Scientific Journals

- Radiochimica Acta
- Radiochemistry
- Nuclear and Chemical Waste Management
- Journal of Alloys and Compounds
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## Education

BS, Chemistry, with distinction, Phi Beta Kappa, Washington State University, 1970; Graduate course work at the University of Colorado (1970-72) and Washington State University (1973-2001).

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## APPENDIX 2

## Preliminary Assessment Report

To: Robert Tregoning, US Nuclear Regulatory Commission

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Date: November 30, 2005

Subject: Peer Review Preliminary Assessment Report

Thank you for the opportunity to participate in the Chemical Effect Peer Review of the PWR sump pool chemistry. The following comments are based on the peer review meeting at Argonne National Laboratory, October 18-19, 2005, the associated view graph materials, and listed reports.

The comments are provided in fulfillment of the obligation to provide a “Preliminary Assessment Report” of the Chemical Effects studies by November 30, 2005. The comments are grouped in five sections according to general remarks and the major areas of investigation:

1. General Questions and Comments
2. Integrated Chemical Effects Testing (ICET)
3. Modeling
4. Chemical Effects Head Loss Testing
5. Chemical Effect on the Sump Water.

I look forward to the follow-on review meeting in January 2006.

### 1. General Questions and Comments

- The overall testing approach is comprehensive, ambitious, and sound. Many of the questions, comments, and suggestions given below arise from the fact that much of the work still is in progress. However, some areas of investigation may still need to be done. The suggested additional work is noted within the following questions and comments.
- Was chemical and physical characterization done of the sump materials from the TMI-2 and Barsebäck-2 LOCAs?[d] If so, what were the findings? How do they compare with the ICET and other experimental results?
- Flashing of the cooling water bearing dissolved and entrained mineral solids and the retrograde solubility of calcite ($CaCO_3$), calcium phosphate [$Ca_3(PO_4)_2$], and perhaps other minerals may leave solids deposited on the hot fuel and vessel surfaces. What is the influence of this caking on the fuel rods and the heat transfer that the post-LOCA

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[d] I was not able to find the reference by Hermannson and Erixon (SKI Report 98:12) cited in NUREG/CR-6873 and in LA-UR-03-6415 *Small-Scale Experiments: Effects of Chemical Reactions on Debris-Bed Head Loss*, by R.C. Johns et al., nor a description of the TMI-2 solids (reference 7 in LA-UR-03-6415).

recirculation is designed to achieve? For the purposes of the present task, spallation of the deposits from the fuel cladding surfaces also would be expected. These spalled crusts would contribute to the solids loading in the cooling cycle and likely would adopt curled shapes imparted by the fuel pin surface. Therefore, tests might be proposed to test for this potential effect and, if operant, project the type and characteristics of the spalled materials.

- Some interesting discussion arose during the first day's meeting regarding the spallation of the protective magnetite ($Fe_3O_4$) corrosion layer from within the stainless steel pressure vessel due to the abrupt thermal and pressure shocks in a LOCA. I do not know the thickness of the protective film nor to what degree this spallation might occur but perhaps some industry experts could be consulted.[e] The magnetite spallation, if it should happen, would contribute to the solids load that must be considered in the post-LOCA cooling cycle.
- The same discussion also provoked speculation on the rapid corrosion of the internal surface of the pressure vessel under high temperature oxic water to produce dissolved $Fe^{2+}$ that would air oxidize to give fine $Fe(OH)_3$ particles. Again, some industry experts might have insight on the amount of corrosion that would occur.

## 2. Integrated Chemical Effects Testing (ICET)

The Integrated Chemical Effects Testing (ICET) results were presented in five separate reports, one for each of the five tests in the series. The first three tests were described in full reports (the third one in draft version), and the fourth and fifth in ~10-page "quick look" reports. ICET results also were summarized in presentations by Bruce Letellier ("Integrated Chemical Effects Tests – Design and Operations" and – "Survey of Results") and Marc Klasky ("Chemical Product Analysis and Simulation") of LANL at the "Chemical Effects Peer Review Kick-off Meeting," October 18-19, 2005. Observations, suggestions, and critiques on the ICET laboratory investigations are provided.

- The ICET experiments must cover the range of anticipated chemical and physical (primarily temperature) conditions, and combinations of conditions, which might occur for the US PWRs. It would be useful in the presentation of the ICET results to assign the various PWRs to the conditions encompassed by the 2x2 test matrix (i.e., high/low pH, presence/absence of Cal-Sil) plus the fifth test for the sodium tetraborate ice melt (i.e., Tests #1 through #5). Such assignment would ensure that all of the US PWRs were represented by at least one of the five test conditions.
- The close proximities of the metallic test coupons may have influenced their respective behaviors as noted in the surmised plating of copper on the aluminum (ICET #2, LA-UR-05-6146, page 21; ICET #3, Bruce Letellier presentation, page 56). Could the close metal coupon proximities also have affected their corrosion rates? It is evident from the experimental results (and also what would be expected) that the biggest metallic corrosion contributor is aluminum followed distantly by zinc. Therefore, the influence of copper on potentially decreasing or increasing the corrosion rate of aluminum is of concern and may be profound.
- Related to the above question, what was the arrangement of coupons in the test racks (e.g., Al-Cu-GS-US etc.)? According to the photos of the test racks (e.g., Figures 11 and 18 of LA-UR-05-0124), it seems that the metals were placed in groups. Were the aluminum and

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[e] I did not find mention of this phenomenon in the report *Development of a Phenomena Identification and Ranking Table (PIRT) for Thermal-Hydraulic Phenomena During a PWR Large-Break LOCA*, R. A. Shaw, S. Z. Rouhani, T. K. Larson, and R. A. Dimenna, NUREG/CR-5047, Idaho National Engineering Laboratory, Idaho Falls, ID (1988). However, I am not conversant in the literature. Is magnetite spallation from the inside of the reactor vessel a credible outcome from a large break LOCA?

copper coupons always or mostly adjacent to each other? Were any systematic differences noted in the weight loss observations for the immersed aluminum coupons? For example, were the greatest or least losses of aluminum weight consistently observed for coupons closest to copper?

- What was the aluminum alloy that was tested? Is it representative of aluminum used in scaffolding or in other equipment exposed to the spray and sump water?
- More detail on the compositions of the other metals also should be provided in the ICET reports for completeness.
- Results of the surface examinations of the metallic test coupons (particularly aluminum and particularly in Test #1) would be useful to sort out the corrosion rates and the effects of borate and other agents on passivation/activation. Surface examinations could include x-ray diffractometry. The diffraction pattern of the corrosion product (likely boehmite, γ-AlOOH; see Oxides and Hydroxides of Aluminum by K. Wefers and C. Misra, 1987, Alcoa Laboratories) should be evident even though the diffraction pattern may also disclose the underlying aluminum metal pattern. Some scoping tests might be useful here.
- Both Test #1 and Test #4 were run at pH 10. However, Test #4 seemed to have much lower aluminum corrosion than Test #1. Why? Note that Test #4 had the Cal-Sil and Test #1 did not. Do the surface appearances (or XRD) of the aluminum coupons give any hints (e.g., calcium aluminate as tricalcium aluminum hydroxide [$Ca_3Al_2(OH)_{12}$] and hydrocalumite [$Ca_2Al(OH)_7 \cdot 2H_2O$]) deposit on the surface)? See *Potential for Generation of Flammable Mixtures of Hydrogen from Aluminum-Grout Interaction in the K Basins During Basin Grouting*, S. M. Short and B. M. Parker, 2005, PNNL-15156 (http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15156.pdf) for a description of the results of reacting aluminum metal with $Ca(OH)_2$ and with portland cement grout. Bruce Letellier (LANL) speculated that $CaCO_3$ passivation layer formed (page 49 of October 18 viewgraphs) but these calcium aluminates also should be considered.
- The concentration of calcium observed in Test #3 (Figure 3-9) is about 110 mg/liter or ~0.0028 M. This is near the solubility of calcite, $CaCO_3$, in pH 8 water. The large amount of Cal-Sil in the system may indicate that $CaCO_3$ (if present in Cal-Sil) is the solubility-controlling phase for this test. On the other hand, the calcium concentration in Test #4 is about 45 mg/liter or ~0.0011 M, at pH ~9.9. This concentration is too high to be controlled by $CaCO_3$ and may indicate that $Ca(OH)_2$ (or something else) is controlling the calcium concentration (also see note below in discussion of head loss testing).
- The incipient boehmite phase also would be forced to crystallization by heating. Some useful discussion on the formation of gelatinous boehmite, the influence of anions to retard further crystallization, and the influence of temperature on boehmite solubility are in the excerpt (provided separately) from the monograph, Oxides and Hydroxides of Aluminum by K. Wefers and C. Misra of Alcoa (1987). The excerpt also gives some information on the boehmite corrosion layer formed in water on aluminum (see page 4 and pages 66-68 from the excerpt). This monograph is available in printed form from Alcoa (Nickolas C. Kotow, Senior Information Scientist, Alcoa, 724 337-5704).
- There should be more description of the “dirt” added to the ICET experiments to establish that these “dirt” components are representative of what might be found in the reactor containment. What is the source of the dirt; what is its composition? I recall montmorillonite (or bentonite) being mentioned as a component.
- For completeness, there should be some description of the aggregate incorporated into the concrete used in the testing. The contribution of the aggregate to the dissolved and suspended solids is probably minor but this should be stated. Also, the aggregate used to construct the various PWRs may vary (for example, most of the crushed rock in this area is basalt; other areas may use river rock from granite).

- One of the other reviewers, Wu Chen, suggested that the particle size distribution and particle concentration be measured for the ICET runs. The physical characteristics of the solids are important in selecting the solid/liquid separation equipment and media to be used upstream of the containment sump. The technique of small angle x-ray scattering (SAXS; http://www.mri.psu.edu/mcl/techniques/saxs.asp) could be used to discern the particle sizes of the microcrystallites in the 1-100 nm particle size range. However, one should be wary of the particle size data if measured on the ICET #1-#5 slurries that have now aged for several months. Some new, small scale, tests are needed to create materials for characterization.
- What is the reason for the abrupt spike (though only to 0.06 to 0.11 and one at 0.19 mg/liter) in aluminum concentration shown in Figure 3-8 in Test #3? Is this a case of having detectible concentrations for these samples and the non-detectible concentrations being plotted as zero?

## 3. Modeling

The modeling work, conducted by Vijay Jain and colleagues at the Center for Nuclear Waste Regulatory Analyses (CNWRA), is presented in "Chemical Speciation, Using Thermodynamic Modeling, During a Representative Loss-of-Coolant Accident," CNWRA[f] 2004-07, and in "Corrosion Rate Measurements and Chemical Speciation of Corrosion Products Using Thermodynamic Modeling of Debris Components to Support GSI-191," NUREG/CR-6873. The findings were reviewed in the October 19, 2005, presentation "GSI-191 Chemical Effects: Modeling and Experiments," by Vijay Jain.

- The postulated $NaAlSi_3O_8$ phase (albite) seems to be plausible for the alkaline (pH 10) systems with aluminum and silica (Tests #1 and #4). Similar phases are found in Hanford Site waste tanks.
- The apatite phase, $Ca_5OH(PO_4)_3$, postulated by CNWRA for the Test #3 system having high calcium and phosphate, seems more reasonable than the $Ca_3(PO_4)_2$ phase postulated by Shack and colleagues at ANL in their head loss tests. Apatite has very low solubility.
- Carbonation of concrete and Cal-Sil (i.e., formation of $CaCO_3$) is to be expected and seems to have occurred in the Cal-Sil that was characterized by CNWRA. Some limited amount of carbonation also will occur during spraydown of the containment building atmosphere but that contribution should be relatively minor. $CaCO_3$ has retrograde solubility (becomes less soluble as temperature increases) and thus is prone to plate out on hot surfaces such as the irradiated core fuel and the pressure vessel. Other minerals also have retrograde solubility and could plate out. As noted by Bruce Letellier (LANL) on page 21 of his October 18 presentation, an internal pipe coating by calcium silicate was thought to be a concern for heat conduction from fuel.
- The characterization of the Cal-Sil (8th slide of October 19 presentation) showed a loss on ignition (LOI) of 35.2 wt%. According to follow-up questions, this LOI was done to ~1000°C. This temperature is too high to distinguish the loss of water, typically occurring below 200°C, from the decomposition of $CaCO_3$ or other carbonates, which occurs 600-850°C for $CaCO_3$. It would be useful to perform a thermal analysis [e.g., "Determination of Free Lime and Carbonate in Calcium Silicate Hydrates by Thermobalance," F. M. Biffen, *Analytical Chemistry*, 28(7):1133-1136, 1956; more recent references certainly exist] or use some alternative method to find out how much $CO_2$ as carbonate is present in the Cal-Sil. The actual condition of the Cal-Sil in the operating plants then must be considered as one would expect the Cal-Sil composition to change with aging.

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[f] Note that the document number is given as C<u>WN</u>RA 2004-07 on the cover page.

## 4. Chemical Effects Head Loss Testing

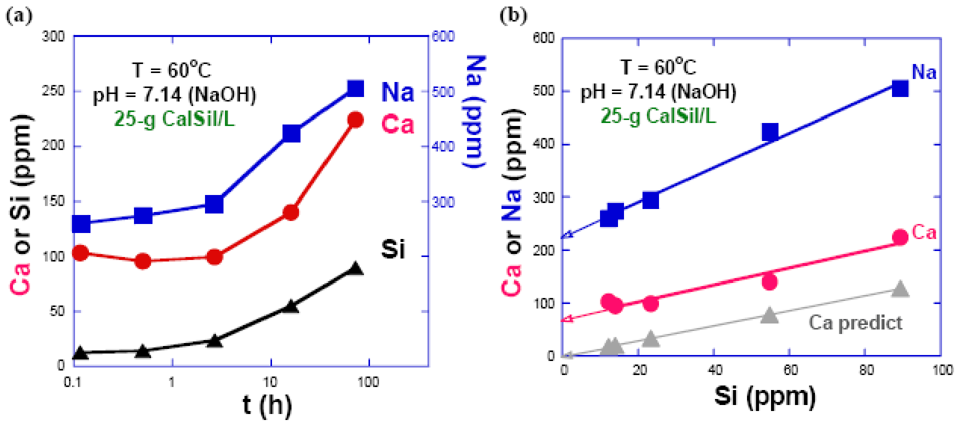
The chemical effects head loss testing was conducted by Bill Shack, J. Oras, and colleagues at ANL. Their results were given in “Chemical Effects / Head-Loss Testing Quick Look Report, Tests 1 & 2” and in the October 19 viewgraphs, “Chemical Effects Head Loss Tests”.

- The introduction of the aluminum phase to the filtration / head-loss testing, accomplished by neutralization of $Al(NO_3)_3$ with NaOH, is not representative of the way aluminum is introduced to the post-LOCA system (and may have caused the so-called non-prototypical snowfall behavior). For one thing, it introduces nitrate, an anion otherwise not present. It is proposed that the aluminum be introduced in another manner, either by corroding a coupon of aluminum in NaOH (simulating the actual conditions, but potentially difficult under experimental conditions) or by adding sodium aluminate solution, $NaAl(OH)_4$. Sodium aluminate is what is initially dissolved off the corroding aluminum metal by the NaOH. Sodium aluminate is available as a solid material through chemical supply houses (https://www1.fishersci.com/Coupon?catnum=NC9365903) or can be made by dissolving $Al(OH)_3$ in hot excess NaOH.
- The calcium concentration dependence on pH given by Cal-Sil dissolution tests (Figure 1 of “Quick Look” report) is interesting in that it is practically flat – i.e., the calcium concentration decreases only about a factor of 10 for a pH increase of 6. Most minerals would become less soluble by about a factor of 100 per increase of one pH unit. Has the solid phase(s) been identified?

## 5. Chemical Effect on the Sump Water

The “Chemical Effect on the Sump Water” presentation describes work by J. H. Park and colleagues of ANL. Perhaps some of their findings also were given in the “Small Scale Dissolution Test” section in the “quick look” report by J. Oras and colleagues of ANL.

- The Cal-Sil dissolution information (below) shows increasing dissolution with time. Does this increase continue with time? What do the solids look like?



Elements in the solution as a function of time (a) and Ca and Na vs. Si (b)

- The experiments using $Al(NO_3)_3$ to introduce the aluminum (slides 8-10 of the presentation) again are not representative of the system being studied (which contains no nitrate). Suggest repeating the tests using sodium aluminate.

## APPENDIX 3

## Informal Comments on ICET Reports to B. Letellier – May 7, 2006
## And Responses – May 10, 2006 (*in italics*)

- Will an ICET comparison report be prepared? It would be useful to see, in one report, a side-by-side comparison of the various tests and their outcomes. *A comparison report is being prepared.*
- It would be useful to provide a more detailed description of the inorganic zinc / coated steel coupons. For example, they are called (I think) cold galvanizing spray paints and they contain high, ~93%, zinc concentrations. Is this what is meant? *Yes, paint containing high metallic zinc content is what is meant.*
- Please describe if more or different deposits were observed on the heat exchanger surfaces. This might give some information on what may be expected for the potential for deposits on hot fuel in the post-LOCA reactor. *The deposits on the heat exchanger surfaces did not appear to be materially different from the recirculating solids and were not present in noticeably higher concentrations.*
- Was any biological activity noticed in any ICET bath? This might be the presence of green slimes or some checking with a microscope. The presence or lack of biological activity should be noted, whatever the case. *No particular microscopic study looking for algae or other biota was done; however, no apparent "green slimes" were observed.*
- When RO water was added on Day 8 of Test #3 (p. 21), and cloudiness observed, was it because of temperature drop? If so, how much did the temperature drop? *The cloudiness is thought to be due to turbulence that moved previously deposited solids when the water was added.*
- In Figure 3-5 of the Test #3 report, (p. 26), what is the label on the y-axis? What was the average NTU, excluding the potentially spurious day #1 and day #15 results? *The label will be remedied in future reports.*
- Also check y-axis label on Figure 3-7 of Test #3 report. *The label will be remedied in future reports.*
- How was chloride analyzed? Was it by ICP or instead by ion chromatography? *Ion chromatography was used to analyze chloride concentration.*
- In the proposed overview report, it would be useful to compare Ca concentrations with respect to phosphate concentrations (for example, in the Test #3 report, compare Figures 3-16 (phosphate) with Figure 3-9 (Ca). *The direct comparison could be done, as suggested, or another means used to correlate the data.*
- In Figure 3-8 of Test #3, the Al concentrations look anomalous around days 8-15 inclusive. Is this a minimum detection limit phenomenon in which "real" values were found on days 8-15 and the other days had "less-than" values? *As suspected, this is an artifact of the minimum detection limit.*
- In Figure 3-39 of the Test #3 report, was EDS (energy dispersive spectroscopy) done on the large flat fibers to identify the elements present? What is their origin? Were the large flat fibers observed in the original fiberglass insulation? *The large flat fibers were postulated to come from the cal-sil materials, as noted on page 47 of the report.*
- On p. 56 of the ICET #3 report, is there further substantiation of the identification of the $Ca_3(PO_4)_2$ phase? *This identification is based on EDS data, not on XRD. Therefore, the speculation that the phase is* $Ca_3(PO_4)_2$ *is not supported.*
- Suggest X-ray diffraction be done to identify phases on metal coupons though your XPS and surface infrared analyses might give other complementary information. *This suggestion is acknowledged.*
- In the Summary of the test #3 report, at the bottom of p. 97, identify the "crystalline substances". *The crystalline substances were identified earlier in the report (e.g., p. 81 and Figure 3-117) as tobermorite,* $Ca_{2.25}(Si_3O_{7.5}(OH)_{1.5})(H_2O)$.
- In test #4, p. 20, did the RO water addition and cooling cause precipitation? *As in the Test #3 result, this is probably from loosening of solids deposits caused by turbulence.*
- On p. 99 of the test #4 report, and as you indicated in one of the presentations at the SwRI, aluminosilicate surface precipitation may be occurring. This is also suggested by comparison of the Test #1 and Test #4 conditions, which differ in that Test #4 has Cal-sil and Test #1 does not; both at pH 10. However, on slide #22 of Jude McMurry's presentation of March 27 (excerpted below), little change in corrosion rate found between the pH 10 tests with and without Cal-sil. *The tests done at*

*SwRI measured initial corrosion rates, so may not have benefited from the formation of a passive layer.*

| Test Conditions | Method | Corrosion Rate g/m$^2$-h [mil/yr] |
|---|---|---|
| Aluminum in borated alkaline containment water (pH 10) | Electrochemical | **0.986**<br>[126] |
| Aluminum in borated alkaline containment water (pH 10) **with Nukon** glass fiber insulation | Weight loss | **1.31**<br>[168] |
| Aluminum in borated alkaline containment water (pH 10) with Nukon glass fiber insulation | Chemical analysis | 1.16<br>[148] |
| **Aluminum in borated trisodium phosphate containment water (pH 7)** | Electrochemical | **0.0039**<br>**[0.5]** |
| **Aluminum in borated trisodium phosphate containment water (pH 7) with calcium cilicate insulation** | Electrochemical | **0.028**<br>**[3.61]** |
| Aluminum in Borated Alkaline Containment Water (pH 10) with Calcium silicate Insulation | Electrochemical | 0.80 [103] |

- In Test #5, why the daily pH spikes -- see Figure 3-1 on page 21? *This phenomenon was noted during the data collection for this meter installed with the tank system. Efforts to locate the cause of the spikes were not successful. However, the pH data for record are those from samples taken daily and measured using a pH meter that was calibrated for each use. The tank system pH meter was used for indication only.*
- Thank you for showing how $H_2$ tracks with Al concentration in your summary presentation at the SwRI. This explanation also should be given on p. 22 of the Test #5 report. *Acknowledged.*

Appendix D

# EVALUATION OF INTEGRATED CHEMICAL EFFECTS TESTING

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## Abstract

The potential formation of gels, as a result of containment materials interacting with reactor coolant fluid following a large break loss of coolant accident (LOCA), was studied under various conditions. The principal concern is that formation of gels, or other insoluble materials, could block the screens on the containment recirculation sumps of pressurized water reactors (PWR). A series of experimental chemical simulations were performed by Argonne National Laboratory (ANL), Los Alamos National Laboratory (LANL) and Southwest Research Institute (SwRI) to determine if the chemicals resulting from reactor coolant system post-LOCA containment spray reacting with Reactor Coolant System (RCS) insulation and other materials in containment (metals and concrete) could be identified, and if the containment recirculation sump screens would, in fact, become blocked due to formation of these chemicals.

This report reviews the fidelity of these simulations, and addresses how the simulations can be further refined to address more closely all significant, potential factors in the complex mixture of materials that are exposed to RCS liquid during a large break LOCA.

# CONTENTS

# ABBREVIATIONS

| | |
|---|---|
| CBS | Containment Building Spray |
| CRUD | A term used to identify insoluble corrosion products present in the Reactor coolant system and located on the piping |
| ICET | Integrated Chemical Effects Test |
| ICP | Inductively Coupled Plasma Spectrometry |
| LOCA | Loss of Coolant Accident |
| pH | The negative logarithm (base 10) of the $H^+$ concentration |
| PWR | Pressurized Water Reactor |
| RHR | Residual Heat Removal |
| RCS | Reactor Coolant System |
| SAT | Spray Additive Tank |
| SEM | Scanning Electron Microscopy |
| SG | Steam Generator |
| TSP | Trisodium Phosphate |
| TSS | Total Suspended Solids |
| XRD | X-ray Diffraction |

# **Executive Summary**

The Integrated Chemical Effects Test (ICET) Program was implemented to assess the effects that certain chemical constituents of post-LOCA materials, particularly insulation, latent debris and the chemicals found in a PWR containment spray environment, would have on recirculation sump flow in a PWR should a LOCA occur. The tests examined the principal parameters, which could affect transport of water flow into the containment sump. The principal parameters examined were:

- pH
- RCS chemicals
    - Boric acid
    - Lithium hydroxide
- pH control agent
    - Sodium Hydroxide
    - Trisodium Phosphate
    - Sodium Tetraborate
- Insulation Materials
    - Fiberglass
    - Calcium Silicate
    - Reflective Metal
- Latent Debris generated *in situ* as a result of the LOCA
    - Concrete fines
    - Miscellaneous Organics from insulation and paint
    - Paint chip particulates
    - Halide ions resulting from the destruction of electrical cable insulation
- Materials of construction of different components found in containment
    - Aluminum
    - Zinc
    - Copper
- Temperature

This document reviews the work to date and identifies parameters which have yet to be accounted for, and conditions of significant conservatism in the modeling.

Overall the tests show that the formation of insoluble chemicals will occur in all cases of containment spray interacting with insulating materials and metals used in PWR containment buildings. Each combination of spray additives and insulation forms different types of precipitates. These precipitates may cause an impediment to water flow to different degrees based on the types of precipitates and the types of materials that may be transported to the debris screens at the containment sump area.

## Summary of Key Points

The ICET tests provide information regarding the chemical environment of the liquid in the containment sump following a large break LOCA. The time period involved is from the onset of sump recirculation to containment spray headers, through the termination of spray (approximately 4 hours) and to the 30-day mark. The elements of these tests that are of significance with regards to containment sump screen blockage are:

- The pH values used are representative of the long term recirculation pH values in the three different types of PWR containment spray systems
- The chemical concentrations used approximate the PWR post LOCA RCS chemicals.
- The materials used as latent debris and as accident generated debris, although limited in scope, are representative of some of the PWR materials
- The predominant metals that can undergo significant corrosion are included as coupon materials during the tests
- Significant masses of compounds are precipitated as a result of the interaction with the RCS post LOCA chemicals and plant materials such as insulation, uncoated metals and general debris
- The compounds that are precipitated in the presence of TSP are generally amorphous. These compounds will adhere to fragmented pieces of insulating materials and can impede complete flow of water when this debris is embedded against engineered screens.
- The precipitate that forms from the interaction of TSP and Cal-Sil forms the greatest impediment to flow of the materials tested.

Certain physical and chemical parameters were not addressed in these tests. Those of greatest significance are:

- A radiation field for the debris bed was not simulated (this can have a significant effect on the species of precipitate material as well as its ability to agglomerate
- The effects of two temperature gradients in the post-LOCA environment: RHR heat exchanger and the passage of the RCS over the reactor core
- The effects of the core radiation field on the formation of radicals and reactive compounds, and in particular hydrogen peroxide.
- The rate of the settling of the insulating material and precipitates during their transport to the containment sump screens is not effectively modeled by the settling tests performed.

## Introduction

The objective of the Integrated Chemical Effects Test is determine if during a Loss of Coolant Accident (LOCA) in a PWR chemical reactions may occur with materials already in containment, which may form insoluble compounds that can block containment recirculation sump screens. This review will examine the key parameters used to establish the test conditions, the implementation of those conditions and the analytical techniques used to measure the chemical effects.

## Discussion

The discussion section of this final assessment is divided into three parts. Part I addresses the tests conducted using tri-sodium phosphate, sodium hydroxide and sodium tetraborate on containment materials and if all major parameters that could affect the results have been considered. The specific materials examined were fiberglass insulation, Cal-Sil insulation, concrete debris, non-metallic jacketed insulation and combinations of these materials. Specific questions were posed to the peer review group that serves as the structure for Part I.

Part II discusses individual test results and their potential impact on the blockage of containment sump screens

Part III identifies plant specific configurations that will have an impact (either mitigation or exacerbation) on the applicability of these test results, and need to be considered on a plant-by-plant basis.

## **Part I.**

1. Did the ICET tests have the principal sump pool variables that could affect chemical by-product formation in the post-LOCA environment properly simulated?

   The concentrations of chemicals used during the operation of a PWR are approximately in the range of anticipated chemical concentrations.
   The concentration of boron is slightly higher than would be expected. Based on a beginning of life (BOL) boron concentration of 1200-1400 ppm the final B concentration would only reach about 2200-2600 ppm. It is not expected that this will result in any significant difference in the results.
   The lithium concentration used in some of the tests was as high as 3.5 ppm. The maximum post-LOCA lithium concentration would be 0.3 ppm. This overestimate of lithium concentration will have a small effect on changing the final pH of the test solutions.

   The concentrations of NaOH or TSP in the final sump volume are appropriate for the post-LOCA environment model.

   The types of materials that are present in containments of PWRs have been appropriately selected. The ratios of these materials exposed to the liquid in the test loop likewise are in the correct proportions as would be expected within a containment building. These components susceptible to leaching and dissolution contain the elements Zn, Al, Mg Ca, Si in addition to those materials of construction elements of Fe and Cu. In at least one test (#3) it appears that the mass of Cal-Sil insulation, which would come into contact with the RCS, is greater than would be expected following a LOCA.

   Chemical constituents that have not been simulated are:
   - initial RCS silica concentrations up to 1 ppm (and in the refueling storage tanks of several PWRs this concentration may be as high as 5-10 ppm),
   - CRUD concentrations (which will contain mixtures of nickel ferrite, magnetite, nickel oxide and hematite) of up to 100 ppm from the thermal/hydraulic transient caused by the LOCA,
   - the presence of hydrogen peroxide resulting from the gamma radiation field of the core,
   - Miscellaneous containment materials like other forms of insulation, the presence of organic matter, and bacteria.

   The first three together have the potential for altering the outcome of the test program. The fourth is estimated to have a relatively minor effect over 30 days.

2. Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?

   Chemical Constituents:
   Of the chemical constituents used, variation in their equilibrium concentration would not produce significantly different effects. However incorporation of the

chemical constituents not included which will most certainly be part of a real post-LOCA environment, will have significant impacts on the test results.

It is likely that as time after the LOCA progresses the mass of $Fe(OH)_3$ present will increase. This material has a significant effect on coagulating and precipitating other materials. Its effect has not been modeled.
The instantaneous, high concentration of TSP used at the start of the ICET tests, in combination with the precipitating agent calcium (from Cal-Sil) is unrealistic for the manner in which the materials would initially mix in the sump.

Physical Parameters:
Temperature has a significant effect on solubility and the types of compounds that will form with the mixture of ionic constituents present. The two temperature gradients that are critical to the formation of scales and other insoluble compounds (such as flocculants like AlOOH) <u>are not</u> incorporated into the design of the test loop.

The first of these temperature gradients is the fuel surface. The temperature at the clad surface will cause materials with retrograde solubility (calcium carbonate, sodium-aluminosilicates, etc.) will precipitate out and bind to these surfaces. This may have secondary precipitation effects (i.e. other materials being flocculated or trapped by this primary precipitate), as well as fuel decay heat removal effects (heat transfer is reduced potentially leading to other fuel clad concerns). Once water that has passed through the core exits at a higher temperature, it can dissolve additional ions from containment materials. This will lead to more precipitate being formed from the mixture of materials (i.e., the equilibrium initially established will be pushed to yield more precipitate).

The second temperature gradient is at the RHR system heat exchangers. These heat exchangers use service water or a closed loop cooling system to maintain less than the maximum design temperature of the water leaving the heat exchanger. No effort is made to control this output temperature as long as it remains less than the design temperature. Since the ultimate heat sink for this system is water from a river, lake or ocean, this temperature will vary over the course of days. Chemicals with normal solubility profiles will precipitate in this heat exchanger due to the temperature drop.

How these two heat exchange surfaces affect these test results is not easily predicted. The main reason is that in both cases there are co-precipitation effects that cannot be modeled (co-precipitation is a non-thermodynamic parameter). A modified design, which incorporates these heat sources and sinks, would be important to the overall understanding of the formation of insoluble materials that may have a deleterious effect on the recirculation flow path.

Another physical parameter not modeled in this design is radiation fields. This is a difficult aspect to model. However the effect of <u>high-level</u> radiation fields (in the core in the mega-rad range, if material is caught on the sump screens this would most likely be in the kilo-rad range) on chemical characteristics cannot be ignored. A specific example is the chemical state of silica. This element in water may form the following: $SiO_3^{2-}$, $HSiO_3^{1-}$, $H_2SiO_3$, $SiO_2$, and poly-silicate compounds. The spent fuel pools at PWR sites have been plagued with decomposition of their Boraflex®by the radiation fields from the spent fuel. This decomposition has led to concentrations of reactive silica (usually as $HSiO_3^-$, or reactive silica) as high as 100 ppm. Contrary to this phenomenon, reactive silica in solutions from pH 3-9 has been known to form poly-silicates (in the absence of radiation) that are highly insoluble. One possible resolution to this issue may be to take the solids formed from the ICET Test Runs and expose them to high radiation doses for several days, then re-examine their morphology. This would help to assess if there is any effect by the high intensity radiation fields within the coolant system.

3. What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects) and how should their effect be characterized by testing or analysis?

   The effect of the liquid coming into contact with fuel in the reactor vessel will have considerable impact. There are two missing variables here: heat and radiolytic effects. Heat at the fuel surface will be several hundred degrees Fahrenheit. This will have an affect as the materials with retrograde solubility, the scale formers, will concentrate on this surface and not be available to form other precipitates. [See additional notes on this effect above].

   The presence of suspended solids from the reactor coolant system, which will have a very high iron and nickel content were not considered as one of the solution constituents. Specifically, magnetite, nickel ferrite, bonaccordite, nickel oxide and nickel metal are materials that would be produced in large amounts (10-500 ppm) following a LOCA. Over the course of a thirty-day test these materials will change their chemical form, including the formation of ferric hydroxide (a strong flocculating material).

   Another variable not simulated is the presence of silica in the water storage systems and the RCS. The concentration of silica in the storage tanks may be as high as 1 ppm and in the RCS the silica concentration will be in the range of 0.3 ppm to 3.0 ppm. Since silica in combination with magnesium, calcium and aluminum can form materials with retrograde solubility; silica can have an effect on the total mass of material precipitating.

4. Were the methods used within the ICET program to characterize and analyze chemical by-products sufficient?

   The analytical techniques used for characterizing the chemical by-products were:

   A. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP_AES): Method for determining the elemental content qualitatively and quantitatively present in the solutions produced by the tests. Although it does not identify oxidation state or molecular environment it will identify all elemental components in the percent to the ppb range. The concentration ranges used for analysis were appropriate for the concentrations expected in the simulated post-LOCA environment.

   B. Scanning Electron Microscopy (SEM):

A microscopic technique used to identify the topography of a solid material. This aids in identifying, qualitatively, whether a material is crystalline or amorphous. It is limited to materials that have been pre-dried and can only view the surface molecules/atoms. This morphological characteristic of a solid is important to its ability to act as a gel. This technique is very useful in characterization of the solid materials produced during the ICET program.

C. Energy Dispersive Spectroscopy (EDS):
Another elemental analysis tool that can aid in assessing the composition of the material at the surface of the substrate. However it does not identify molecular structure or oxidation state. This technique is supplemental to SEM and can non-destructively determine element concentration in solids

D. Transmission Electron Microscopy (TEM):

A microscopic technique designed to view solids at the atomic level. General structure and arrangements of atoms can be determined, but this may only be semi-quantitative due to the unusual nature of the solids we are examining. However it cannot discriminate between the surface material and sub-strata. This technique also suffers from the sample preparation that requires loss of water in order to provide an appropriate sample medium. It does provide important structural information regarding the materials that form during the tests.

E. X-Ray Fluorescence (XRF).
An elemental technique based on the generation of x-rays by the elements in the sample matrix using particles from the instrument source. In matrices of the type we are examining this technique will be semi-quantitative since the duplication of a standard geometry is very difficult.

F. X-ray Diffraction (XRD):
A technique used to determine the crystalline structure of materials. Its shortcoming is that amorphous materials cannot be analyzed and if present will interfere with the diffraction pattern of minor crystalline components. Based on the type of crystalline material one can infer an oxidation state of the elements. This is a very important technique in helping to identify specific molecular species that may play an important part in potential clogging issues.

G. Wet Chemical Techniques, Kinematic Viscosity, Turbidity, pH, Total Suspended Solids and Temperature:
These techniques are all applicable to the parameters that we are trying to assess. They will be helpful in determining the general physical characteristic of the post-accident fluid. None of the methods is material or compound specific. However in these circumstances, the instrumental methods noted above will be able to identify the major and minor contributors to the overall make-up of the fluid.

The analytical techniques used to characterize the chemical compounds that were formed are complementary. Taken as a whole they are the most extensive analytical tools that could be used for this assessment and are adequate to address changes that would be observed during the ICET program.
The only additional test that might be of value would be FTIR of the colored materials/solution to identify the chemical identity of those colored materials. It should be noted that in a strong radiolytic field that most color-bearing organic materials would be transformed to carbon dioxide and water.

The one analytical test that yields very little useful information is the mass determination of the coupons before and after the tests. These coupons should be used for qualitative observation of the mechanism of corrosion and deposition of other insoluble compounds. XRD may be useful in assessing the types of compounds not related to the coupon material that may be formed on its surface, and TEM may provide qualitative insight as to the materials present. Unless a total mass balance is attempted using the interior system surfaces as well as the coupons, the actual mass of the coupons will not provide any significant information.

5. Analytical Simulation. Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?

   The average temperature and concentration ranges used for the ICET program do simulate the bulk water, average temperature and concentrations of constituents (with the exceptions noted in A1 (above).

   However, two important temperature profiles and two physical effects are not part of the ICET simulation. The increase in temperature as the water passes over the hot fuel surface will cause scale to form at that surface, potentially scavenging the gel formers from the solution. The decrease in temperature as the water passes from the containment sump to the residual heat removal system can also cause precipitation of materials on the inlet tubesheet and tube surfaces of the heat exchanger (this particular effect was seen in Test#1 with turbidity see Figure 29 of test report).

   The two physical effects not modeled are the radiation field from the fuel, and the layer of corrosion products on the interior surface of the reactor coolant system. The radiation field will promote the formation of radicals that can expand the potential number of mineral products that can be formed. The presence of corrosion products on the interior surface of the system can provide a mechanism for removal of some contaminants. The corrosion products released during he LOCA can contribute to the settling rate of other insoluble compounds of lower density prior to reaching the containment sump. The exact location of this settled material would need to be modeled in a future experiment.

6. Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?

   It would be appropriate to use the codes to help bound the characteristics that we expect to observe. However, it is important to note that not all of the important physical and chemical parameters present in the post-LOCA environment have been appropriately modeled in the ICET tests. Thus using the models with the existing data can give us limited information.

7. What is the most appropriate way to measure the uncertainty associated with these codes?
   Not within the reviewer's area of expertise.

8. Was the Head Loss Simulation Testing & Analysis for the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?

   One of the difficulties in this testing mechanism is that the concentrations of several of the potential fouling species will increase over time. The effects of aging of the insoluble materials are that they generally will increase in size and crystalline character, increasing density. The test loop does not provide the same type of stagnant environment that would be encountered in the submerged portion of the containment building. The relatively lower flow rate would promote better agglomeration of particulate material due to the effect of relatively high concentration of the precipitants at the surface of the insulation. This will promote settling that will not be modeled in these tests.

   The test loop as designed does not allow for insoluble materials to drop out, as would occur during transit along the containment floor following a LOCA. The relatively long flow paths and impediments to flow caused by structural components are not simulated. These provide 'drop out' areas for insoluble/suspended materials before they can approach the screens. Thus there is a bias towards a rapidly increasing pressure across the filtering media, which does not depict the actual mechanism of transport in the containment.

   Furthermore the test loop design has forced impingement, vertically down on the filter screen. In containment sump the flow of water is horizontal, and the water is not confined to a pipe. If the surface area of the screen at, and below the water level is clogged, the water will rise to a higher level where the screen is not clogged. This type of 'overflow effect' cannot be realized in the current design. A proposed modification where the effect of long term clogging could be more realistically evaluated is shown in Attachment I.

9. What is the best method for incorporating for time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?

   The techniques that have been used by the test groups thus far seem to be the most appropriate.
   The only exception is the preparation of the stainless steel surface of the test loop. In a PWR the interior surfaces of all the metals will be covered with relatively thick oxide coatings (100-250 microns, compared to the test loop which is most likely only about 10 microns). The stainless steel will visibly be black,

and several hundred microns thick. Although this is an initial material condition, it goes to the heart of developing the right conditions of materials to supply accurate data for simulations.

10. What metrics are most appropriate for evaluating the results of simulated chemical products with those that formed during the ICET program?
    Not within the reviewer's area of expertise.

11. Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical by-product are known?

    Models that predict head-loss cannot account for the effects of gelatinous or amorphous materials. At least one reason is the secondary effect of coprecipitated or agglomerated materials. Flow rate-∆P curves for specific filtration media have been developed by filter manufacturers. These relationships are almost all made for closed systems, where flow is impacted on a constant filtration area, and a specific well-characterized material is used for the tests. In the early stages of the event this type of curve would not be representative of what would occur in containment. Additionally should the entire screen become covered with debris and the level of water should rise above the screen level, buoyant effects for the solid debris may come into play and change the effected area of blockage.
    Although the preliminary data provides some information regarding head loss due to a certain type of compound, there is insufficient information to make valid predictions of head-loss based on physical or chemical characteristics of the containment mixture of materials.

## Part II.

In this portion of the report, the individual tests and their results are evaluated.
Three parameters not included in the test conditions that will have a significant effect on the conclusions reached are:

- Radiation Field (a flux of approximately $10^{12}$ $e^-/cm^2$-sec in the fuel vicinity) in addition to the gamma flux from the fuel (mega rad level)
- Presence of magnetite as an insoluble material which would be present in concentrations of upwards of 50 ppm in the post LOCA environment
- Presence of several ppm of hydrogen peroxide due to air-saturated-water radiolysis in the fuel area

These conditions would favor the formation of an agglomerated precipitate that would have a large density compared to the precipitates measured in these tests, and would settle or be filtered more easily. The only way to determine whether the test represents the post-LOCA condition is to add these additional items as test parameters.

The above comments apply to all five ICET programs.

### Test#1.

The introduction of chemicals into the loop simulates the containment spray initiation process when NaOH would be used. The pH attained in the bulk fluid is representative of what would be expected in this situation. In this test, 100% of the insulation was fiberglass.

In section 4.3 SEM examined the effects of the test solution on the fiberglass insulation. However it does not appear that a control was run for this experiment, i.e., demineralized water soaking of the fiberglass that would assess whether the same type deposits would form. This is relatively important since in containment the humidity is about 100% saturation during operation. This means that fiberglass will be moisture saturated while in service. It would be important to distinguish what is caused post-LOCA and normal operations.

Section 4.4 describes the grinding of concrete into dust prior to introducing it into the test loop. This technique appears to be overly conservative. Although it is possible for concrete to be ground up by a water jet during the LOCA, it would be rather limited due to the short duration of the blowdown period and the relatively small surface area that would be scoured. Once the material settled (and it most certainly would during the first four hours) the concrete would begin to “heal” over, forming a protective coating of $CaCO_3$ over the open scar and over any deposited material. This would take place in aerated waters in particular due to the enhanced solubility of $CO_2$ in the post-LOCA basic pH.

In Figure 43 the solubility of aluminum is plotted as a function of time. It is noted that filtration through a 0.7 micron filter did not affect the filtered vs. non-filtered results so that all samples after day 25 were not filtered. The solubility of $Al(OH)_3$ at pH 7.0 is 0.14 ppb, but increases substantially above pH 9.0 due to the formation of the complex $Al(OH)_4^{-1}$. These compounds when heated will have waters of hydration removed and condense to AlO(OH) [boehmite] or $Al_2O_3$ [alumina] depending upon the temperature.

The conditions to promote the formation of these materials will exist at the fuel surface, which is at a much higher temperature than the titanium immersion heaters. ICET#1 has the highest concentration of aluminum in solution as a direct result of the high pH yielding a soluble aluminate complex.

One conclusion of the test was, “Most of the aluminum remained in solution and passed through the 0.45 µm filter at 60 ºC, e.g., the aluminum did not settle.” This conclusion is consistent with the results of Test #1 conditions. It is important to note that once the solution cooled, that a significant solubility effect was observed. The reheating of the precipitated material during this test did not completely re-dissolve the precipitate. This is an important effect for this combination of materials, since the post-LOCA sump water is passed through a heat exchanger that will significantly lower the temperature of the solution. This will cause precipitation to occur in both the heat exchanger and other portions of the RCS, that precipitate will then not completely redissolve. This precipitated material may then act to trap or coprecipitate other species.

Qualitatively, the SEM photographs show that the precipitated material forms bridges between the fiberglass fibers. These precipitates are somewhat structured, but this is a very qualitative observation. The amount of material seen in these photographs may have an effect on flow, but this would need to be specifically measured versus a clean filter bed to determine any quantitative effects.

Test#2.

The test conditions were targeted for a pH of 7.3 using $Na_3PO_4$ (TSP).
The TSP is immediately injected into the test line, which flows over the test coupons in the tank. This condition does not simulate the containment environment during the initial 4 hours. Immediately following the break, water to the spray header and the RCS will be supplied by the RWST. This is borated water at a pH of approximately 4.2. TSP is contained in baskets in the sump or surrounding the sump and slowly dissolves as the volume of water from the break depletes the RCS and RWST inventory. Once the inventory is depleted, containment recirculation phase begins. At this point (~30 minutes later, depending upon the size of the LOCA) the pH 7.3 solution will come into contact with the bulk of the materials in containment.
During the initial phase of containment spray for TSP based plants the pH of the spray will be closer to 4.5 (due to the presence of some $Li^+$ in the RCS). This will mean that more dissolution of metals contacted will occur during that 30-minute period when the TSP is not buffering the containment spray.

The non-detectable concentration of aluminum in the solution for Test #2 is consistent with the presence of a mixture of very insoluble aluminum hydroxide and calcium phosphate precipitates. As noted in the Test#1 discussion, the solubility at pH 7.0 is approximately 0.14 ppb for aluminum hydroxide. This is much less than the detection level for the ICP-AES analysis of 50 ppb. The limiting reagent in this test was the phosphate as calcium and magnesium were found in solution as a soluble species.

The deposits on the aluminum metal coupons were found to be predominantly $Al(OH)_3$, with insoluble calcium, magnesium, sodium and silica materials. These additional compounds were most likely coprecipitated with the aluminum hydroxide. Although the appearance of the coupons indicates significant weight gain due to precipitate deposition, generally speaking, the weight loss/gain by the coupons is going to be of little analytical value. The real value is in identifying the qualitative nature of the deposits (see pages 45-50 in the ICET #2 Report). The amorphous, precipitated material attached well to the fiberglass fibers and appears that it would provide significant impedance to water flow through a debris bed comprised of these fibers.

A significant quantity of white precipitate consisting of calcium phosphate and aluminum hydroxide were found in the bottom of the test tank. Although this material precipitated within the first day, its amorphous nature, density and attachment to fiberglass materials make it a concern for flow through sump screens.

### Test#3.

Test#3 had an initial pH of ~4.2 and used a mixture of 80% Cal-Sil and 20% fibrous insulation, as well as “latent debris”. Based on the amount of concrete dust added (21.3 g) and the surface are of exposed concrete (solid) it is surprising that the pH did not initially rise to close to 9.0. The concrete dust and soil that were added as “latent debris” are may not be representative of what is present in the reactor containment building. Those materials from concrete would provide a significant alkaline environment for water in contact with them even over short period of time.

This starting condition is out of synchronization with the LOCA starting sequence. At the onset the high velocity jet that would impinge the insulation would be closer to a pH of 5-6.0 rather than 4.2. This is because the boric acid concentration during the blowdown phase will be dominated by the ambient RCS boron concentration (1-1600 ppm) and not the much higher (2300+ ppm) in the storage tanks.

As the leak progresses and the water collects in the sump the water washing over the insulation is maintained at that pH. Until the containment recirculation spray initiates. At that time a swing in pH from about 5.0 to about 8.0 then back to about 7.1 will occur over the next 30 minutes to 4 hours as the water in the containment begins to mix to equilibrium concentrations. During the time period prior to recirculation the insulation would be lying in a stagnant pool of water on the containment floor or caught on another component.

Table 2-1 shows the ratio of mass or ft$^3$ of contaminant per ft$^3$ of sump water. The ratio of Cal-Sil to water mass (0.137 ft$^3$/ ft$^3$), in particular, seems very high. If this is scaled up to the PWR case, the mass of insulation that would be getting soaked is about 7,400 ft$^3$. This particular parameter should be revisited to determine if the long-term recirculation solution would contact this significant a mass of Cal-Sil.

The introduction of the TSP as a concentrate directly into the wetted insulation matrix does not simulate what would happen in the containment situation. The concentration of TSP would be far more dilute before it initially contacted the insulation due to dilution with the remaining volume in the RCS and containment floor. Additional tests within the ICETTest#3 matrix was performed which varied the concentrations of insulation used with the matrix. The purpose was to ascertain if there would be significant differences in the measured head loss when the solution is pumped through the *in situ* debris bed. The results show that even though with lower concentrations of Cal-Sil insulation that less head loss was initially experienced, the head loss continued to increases for the duration of the test (approximately one hour). One variation of this test used the test solution without the introduction of TSP. The purpose was to ascertain what the direct effect of the TSP-Calcium precipitate had on head loss. Although an initial pressure increase of ~2.8 pounds was measured, it stabilized at that value and did not change for the remainder of that test.

The concentration of boron in the test loop increased by ~18% during the 30 day trial. The reason for this is most likely leaching from the fiberglass insulation. It is possible that this would occur in the post-LOCA environment since the much of the containment insulation would eventually become wetted. It would be important to determine if this is the case (note this also happened in Test #4; a boron concentration increase of about 21%).

The results from Test #3 show that significant mass of precipitate can form in the presence of TSP and the Cal-Sil insulation. The data presented indicate that this is a mixture of $Ca_3(PO_4)_2$ and some other amorphous materials that either co-precipitate with the calcium phosphate or are innately insoluble. The SEM/EDS results provide evidence that at least part of the precipitated material is a carbonate. This is also significant in that it adds to the mass of precipitate that will be formed from the carbon dioxide that is 'scrubbed' from the containment air. The TEM results were not able to provide conclusive evidence for a specific type of crystalline material being formed.

### Test#4.

The solution for Test #4 was made up to pH 10 using NaOH with a mixture of Cal-Sil (80%) and Fiberglass (20%) insulation.
The high pH and presence of Cal-Sil yielded solution samples that had high TSS values and turbidity, but low aluminum. A significant mass of precipitate was collected from the screen at the tank bottom at the test conclusion. Although analysis of this precipitate did not detect aluminum, a small quantity must be present form the initial solution measurements. The precipitates of (calcite) $CaCO_3$, Lime ($Ca(OH)_2$)and tobermorite ($CaSiO_3$), most likely coprecipitated any aluminum from the fiberglass insulation. It is also likely that the aluminum coupon was coated with a thin film of the tobermorite that inhibited the further dissolution of the aluminum metal. The significant decrease in turbidity over the first day identifies the flocculent nature of this mixed precipitate.

Additionally, the precipitate would 'stick' to surfaces like fibers of insulating material, but it could not be found on materials like the nylon bag used to hold the unfractured insulation pieces. This is most likely due to the 'common ion' effect (decreasing localized solubility) that exists at the surface of the insulating materials (containing one of the precipitate ions) while in other materials this cannot occur. This is also seen in the metal test coupon photographs taken at the end of the 30-day period. The amount of deposited material is minimal because of this lack of 'common ion' effect.

As compared toTest#3 the precipitated material in Test#4 was more crystalline. Crystalline precipitates are less likely to cause attract significant amounts of other materials and block flow, than are amorphous, hydrated gels.

Test#5.

This test used sodium tetraborate as the chemical additive for the spray system. Only fiberglass insulation was used for the test. In general, very little mass of precipitated material was observed over the 30-day test. These materials were composed of sodium aluminum and silicates.

Borax was added before the spray phase began. Borax is a constituent in "ice-condensers", and would only be added into the mix after the spray phase had initiated. Thus the initial interaction of the 'blowdown" liquid with containment materials would be with acidic borated solution. The addition of boric acid with the components in the initiation of the test is out of sequence with actual LOCA conditions. It would take at least 2 hours for the pH to approach 8.0 in the containment sump. Thus the interaction of the RCS with the containment metallic components would yield additional metal ions in solution (lower pH generally will favor more significant dissolution of the metallic components).

The step decreases in aluminum on days 14 and 21, and the step increase in calcium on day 25, appear to be unrelated. This type of behavior is not expected in a system, which has solid material in excess with a soluble counterpart (i.e., a saturated solution). These changes do not appear to correspond to system changes during those time periods that have been noted in the report thus far.

The significant change in appearance of the coupon materials and the general weight loss is evidence for corrosion occurring in this chemical environment. The qualitative analysis of the aluminum coupons shows deposition of some iron and zinc corrosion products. The exception to this was for the concrete 'coupon' which showed a large weight gain. This is presumably from the deposition of sodium-alumino-silicates.

The rise in aluminum concentration over the first 14 days is consistent with the small amount of hydrogen gas generation during that same period. The continued presence of aluminum in solution, and the lack of additional hydrogen generation after day 18, suggests that the corrosion film that was observed on its surface has mitigated the aluminum corrosion.

Copper and iron corrosion played a part in the inhibition of the aluminum corrosion. The copper concentration in solution was constant after about 8 days at 0.7 ppm. The iron concentration either in the filtered or unfiltered solution was undetectable.

The qualitative effect of the precipitated material was that it formed a more structured solid on the fiberglass surfaces than was observed in previous tests (especially ICET#3). The mass of material observed was significantly smaller. Both of these observations generally support the notion that flow through the debris bed on a screen would be less impeded with this chemical combination in the post-LOCA environment.

## Conclusions

The ICET test clearly shows that there are a variety of different chemical environments formed when containment spray is initiated and interacts with materials within the containment building. The effects observed which are of note are:

- In all cases insoluble precipitates are formed as a result of the containment spray chemicals reacting with insulation and metallic components in the containment building
- The precipitated materials are different depending upon the type of spray chemical and the type of insulation.
- Aluminum metal corrosion contributes most significantly to the dissolved metal concentration of the post-LOCA environment
- Significant concentrations of magnesium, silica and calcium may be leached from the two insulating materials used in these tests
- The corrosion of metal coupons (with the exception of aluminum) used in these tests show that in the 30-day trial that their contribution to the metal loading in solution is small, but that they can provide a surface for the adherence of precipitated materials

Plant specific characteristics will impact how the results of these tests can be used to assess the acceptability of current sump and screen designs.

It is important to note that although the different classes of post-LOCA spray have been identified, not all containment materials have been tested in these programs. Each PWR will need to carefully examine all materials that could potentially come into contact with post-LOCA spray, and assess the effects of leaching, precipitation of leached ions and coprecipitation of ionic substances on these plant specific materials.

The most significant impacts on post-LOCA sump chemistry occur with systems that have both TSP and Cal-Sil type insulation. The formation of amorphous calcium phosphate and the apparent coprecipitation of other materials create a significant impediment to forced water flow in the system used in the ICET programs.

The information in the ICET programs provides plant personnel with a direction for focusing any testing that they may need to perform if modifications to their sump screens are going to be made. Each plant should use their plant specific information as part of test program for assessing feasibility of design. The methods of analysis used in the ICET programs that should be considered as part of the design testing are:

- SEM
- XRD
- TSS
- Turbidity
- Metal concentration (by an ICP or related spectroscopic technique)
- EDS

These analyses will help to characterize the precipitated materials and establish specific bases for flow testing.

# Recommendations

1. Chemical constituents that have not been simulated are:
    a. Initial RCS silica concentrations up to 1 ppm (and in the refueling storage tanks of several PWRs this concentration may be as high as 5-10 ppm),
    b. CRUD concentrations (which will contain mixtures of nickel ferrite, magnetite, nickel oxide and hematite) of up to 100 ppm from the thermal/hydraulic transient caused by the LOCA, and
    c. The presence of hydrogen peroxide resulting from the gamma radiation field of the core.

    Consideration should be given to include these parameters in the experimental simulations.

2. The relatively high concentration of TSP used at the start of the ICET tests, is very conservative compared to the manner in which the materials would finally mix in the sump. Consideration should be given to inject the TSP into the loop at a lower concentration over a longer period of time to simulate more closely actual post-LOCA condition.

3. Temperature profiles of the reactor coolant system have not been modeled. The temperature profiles will have a significant effect on the rate and type of precipitate that is formed, and also where the precipitates will be formed. This may have a significant effect on the head loss modeling. These temperature profiles should be included in the test loop.

4. Radiation fields from the nuclear fuel also have not been modeled. Free radical formation will have a significant effect on the type of compounds that can be formed and where they will precipitate. One possible resolution to this issue may be to take the solids formed from the ICET Test Runs and expose them to high radiation doses for several hours, then re-examine their morphology. This would help to assess if there is any effect by the high intensity radiation fields within the coolant system.

5. The analytical techniques used to characterize the chemical compounds that were formed are complementary. Taken as a whole they are the most extensive analytical tools that could be used for this assessment and are adequate to address changes that would be observed during the ICET program.
    The only additional test I could recommend would be FTIR of the colored materials/solution to identify the chemical identity of those colored materials. It should be noted that in a strong radiolytic field, most color-bearing organic materials would be transformed to carbon dioxide and water.

6. The mass determination of the coupons yields little quantitative information (if any). I would recommend deleting this part of the coupon analysis unless a total mass balance approach is performed. Coupons should be used strictly for qualitative assessment of what transformations of the coupon materials occur and what insoluble products are formed or precipitate on these surfaces.

7. The test loop as designed does not allow for insoluble materials to drop out, as would occur during transit along the containment floor following a LOCA. The

relatively long flow paths and impediments to flow caused by structural components are not simulated. Recommend using the modification as shown in Attachment 1.

8. The interior surface of the test loop does not simulate the conditions of the interior surfaces of a PWR. Recommend that the test loop internal surfaces that are designed to mimic the internal PWR surfaces be treated with the initial test solution at $550^0$F and 2200 psig before additional testing is performed.

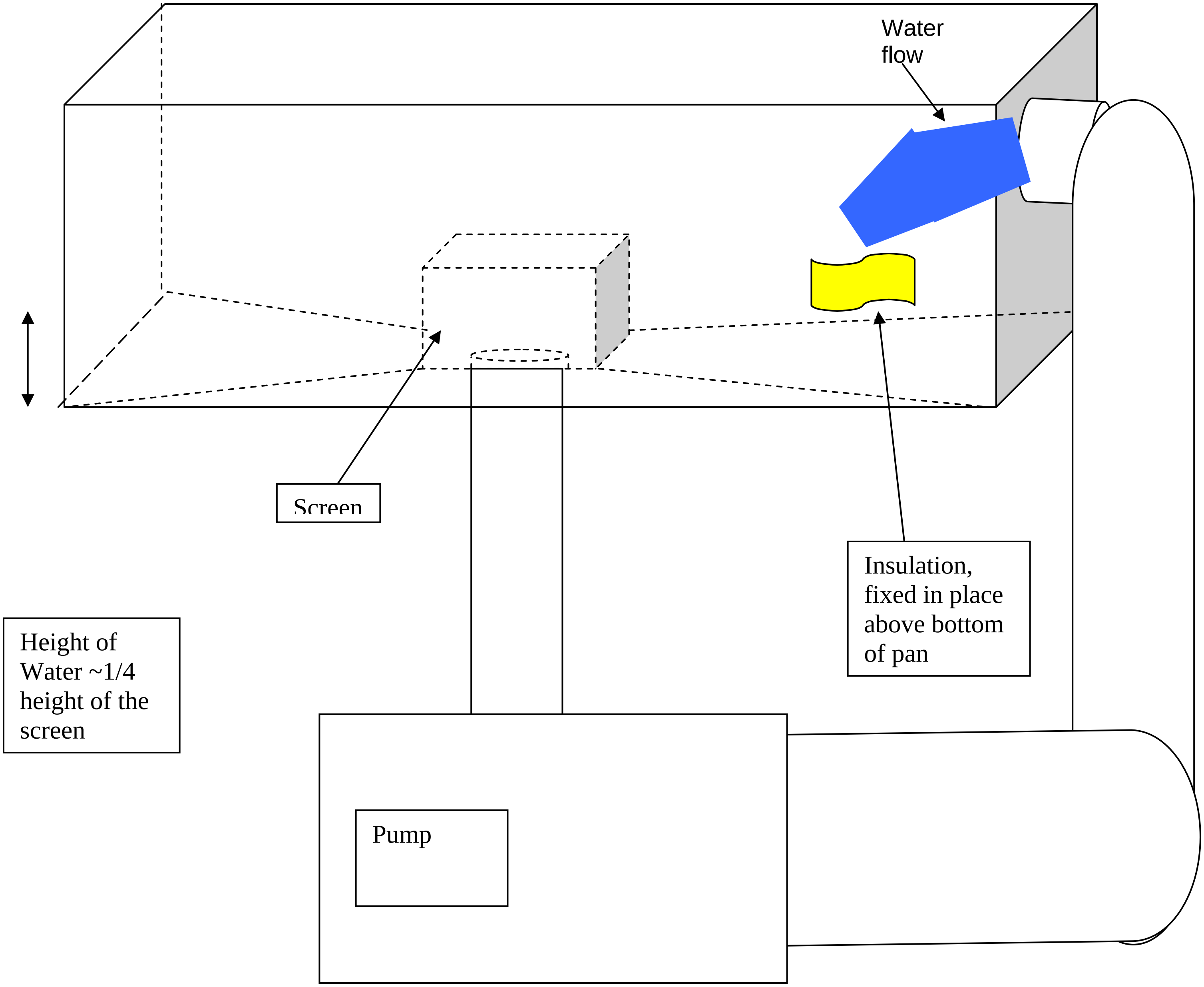
9. The concentration of boron in the test loop, in Tests 3 and 4 increased by ~18% and 21% respectively, during the 30 day trial. The reason for this may be leaching from the fiberglass insulation. It is important to determine if this is the source of the increase, or if not where the increase is coming from.

10. In Test 5, Borax was added before the spray phase began. Borax is a constituent in “ice-condensers”, and would only be added into the mix after the spray phase had initiated. This is out of sequence with actual LOCA conditions. This should be corrected in a subsequent run of this test.

11. The ICET tests did not include all combinations of materials (i.e., insulation) in the reactor containment buildings. If additional tests are performed, other materials should be put into the mix to help assess the extent of materials that may be precipitated.

12. The submerged mass/volume of Cal-Sil insulation involved in the long-term testing is greater than expected during a post-LOCA recovery. Although this is a conservatism in the ICET programs, it would be beneficial to identify more realistic submerged materials and their effect compared the existing information.

# Attachment 1



# Appendix E

## Final Report

# Characterization of Chemical and Corrosion Effects Potentially Occurring Inside a PWR Confinement Following a LOCA

By

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# Abstract

A review is presented of the fundamental physico-electrochemistry of those processes that are reckoned to contribute to the evolution of the chemical properties of the containment pool after a LOCA (Loss of Coolant Accident) in a Pressurized Water Reactor (PWR). The processes and issues considered include the establishment of the redox and corrosion properties of the environment, due to the radiolysis of water and the presence of hydrogen from the PWR primary coolant and the oxygen contained within containment; the impact of the redox potential on the chemistry of the pool in a post-LOCA environment; co-precipitation of other species with FeOOH, AlOOH, etc; Ostwald ripening; the Schikorr reaction and the generation of hydrogen *in situ*; the pH of zero charge (PZC) and coagulation; $\gamma$-AlOOH formation; precipitation on fibers; thermal hydrolysis of organic material; the maximum particle size that can be tolerated; the reason(s) why a bimodal distribution exist might exist in particle size; and the corrosion of aluminum. These are all issues that figure prominently in the generation of solid products that have the potential for clogging the sump pump screens that are designed to enable recirculation of the coolant ejected from the primary circuit upon a LOCA, the injection of emergency core coolant into the core, and the functioning of the building spray system that is designed to remove the fission product, iodine. The purpose of this report is not to provide a time-line for the events that occur during a LOCA, but rather to identify and articulate some of the fundamental processes involved. This process does, however involve an assessment of how well the Integrated Chemical Effects Tests (ICETs) and the analytical simulations were able to reasonably reproduce the effects that might occur in an actual LOCA. It is concluded that the ICETs and analytical simulations have serious shortcomings, because redox potential effects and the impact of radiolysis were not taken into account. For example, the redox potential, which arises from non-equilibrium processes, cannot be simulated analytically using current chemical modeling codes, because they lack an effective mixed potential model. The redox potential determines the driving force for the transition between different oxidation states. Possibly, of much greater importance, is the radiolytic conversion of nitrogen from the ambient containment air into nitric acid, because preliminary modeling work indicates that, if the dose rate is sufficiently high in the pool, the production of nitric acid may overwhelm the buffering capacity of the boric acid/lithium hydroxide in the pool. If this were the case, the pH would drop precipitously and the conditions would lie well outside those simulated in the ICETs and in the analytical modeling performed to date. Indeed, if the pH drops by the amount predicted for a high (but realistic) gamma-photon dose rate ($10^6$rad/h), massive corrosion of structural materials might be expected, which, in turn, might have unforeseen consequences for the operation of vital systems that maintain effective cooling of the core. Therefore, it is recommended that radiolytic acidification of the pool and changes in the redox properties be explored to determine the exact impact that they might have on pool chemistry.

# Executive Summary

A review is presented of the fundamental physico-electrochemistry of those processes that are reckoned to contribute to the evolution of the chemical properties of the containment pool after a LOCA (Loss of Coolant Accident) in a Pressurized Water Reactor (PWR). Eleven critical issues were identified: (1) The evolution of the electrochemical properties of the containment pool, and scoping calculations were performed using the radiolysis/corrosion potential code, FOCUS, and variants thereof, that was developed to model electrochemical phenomena in the primary coolant circuits of Boiling Water Reactors (BWRs) and PWRs; (2) Co-Precipitation of Other Species with FeOOH, AlOOH, etc.; (3) Ostwald Ripening, which transforms newly precipitated phases into thermodynamically more stable phases; (4) the Schikorr reaction and the *in situ* generation of hydrogen; (5) the pH of zero charge (PZC) and its role in coagulation; (6) $\gamma$-AlOOH formation; (7) precipitation of solid particles and corrosion products on fibers; (8) degradation of organic materials; (9) whether there is a particle size that can be tolerated; (10) possible reasons why a bimodal distribution exists in the particle size; and (11) the corrosion of aluminum. Additionally, an assessment was made of the effectiveness of the experimental programs that were supported at various national laboratories (ANL, LANL) and at the Center for Nuclear Waste Regulatory Analysis (CNWRA) at the Southwest Research Institute in San Antonio, Texas, in addressing vexing issues and in simulating the chemical processes that might occur in a containment pool after a PWR LOCA.

The processes and issues considered include the establishment of the redox and corrosion properties of the environment, due to the radiolysis of water and the presence of hydrogen from the PWR primary coolant and the oxygen contained within containment, and the impact of the redox potential on the chemistry of the pool in a post-LOCA environment. This issue is judged to be particularly important, because the redox potential controls the oxidation states of all components in the pool and the valency of dissolved species. The production of hydrogen peroxide via the radiolysis of water is expected to raise the redox potential substantially, thereby promoting precipitation of oxides, oxyhydroxides, and hydroxides through the formation of more highly charged cations ($Fe^{3+}$ versus $Fe^{2+}$). The second overriding issue arises from the tendencies of surfaces to acquire electrical charge through the protonation (at low pH) or ionization (at high pH) of surface hydroxyl groups to yields positive and negative charges respectively. The pH at which the net charge is zero is known as the “pH of zero charge” (PZC). If a multi-component system contains particles of opposite charge, the particles will coagulate to form macroscopic precipitates. Even if the particles are not oppositely charges, increasing the ionic strength of the medium will cause the electrical double layers to shrink to the extent that the attractive van der Waal forces will overcome electrostatic repulsion and coagulation will occur, as in the Alum water clarification technology. The third, principal issue that is addressed is corrosion, particularly the corrosion of aluminum. This phenomenon is expected to be a significant source term for solid materials in the containment pool after a LOCA. It is noted that the theory of corrosion is highly developed and that meaningful predictions of corrosion rate can be made if the corrosion evolutionary path can be defined (i.e., the path in terms of various parameters that the system travels after the LOCA). The important point is that these are all issues that figure prominently in the generation of solid products that have the potential for clogging the sump pump screens and pumps that are designed to recirculate the coolant ejected from the primary circuit upon a LOCA, the emergency core coolant, and the building spray that is designed to remove the fission product, iodine, through the core to remove decay heat. The purpose of this report is not to provide a time-line for the events that occur during a LOCA, but rather to identify and articulate some of the fundamental processes that require attention and analysis, if a reasonably accurate picture of the post-LOCA environment in a PWR is to be developed.

A number of recommendations were formulated that might advance the technology of predicting the evolution of the containment pool environment after a LOCA. The principal recommendations are as follows:

Equilibrium models must be used with great caution, because the environment produced by a LOCA is unlikely to be at equilibrium, at least during the initial stages. Furthermore, the processes that occur during corrosion, precipitation, and ripening are generally slow, as has been shown in some of the work carried out by ANL. The kinetics of many of these processes are such that the system may still be far from equilibrium as it enters the recirculation system. Accordingly, equilibrium calculations need to be bench-marked to the greatest extent possible against experiment to assess the reliability of the thermodynamic equilibrium codes.

Given the likelihood that equilibrium models may not be appropriate, emphasis should be placed on developing kinetic models for the precipitation and ripening (coagulation) processes. These models must recognize the most important driving force for coagulation; the charge (sign and magnitude) that develops on the surfaces of particles, as characterized by the zeta potential and the PZC (pH of zero charge). None of the commercial codes employed by SwRI appear to have the necessary sophistication to effectively model non-equilibrium precipitation phenomena.

The possible generation of hydrogen from the Schikorr reaction

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O$$

and related chemical transformations should be explored, as they might contribute significantly to the inventory of hydrogen in containment immediately after a LOCA and to the inventory of magnetite ($Fe_3O_4$) in the system.

Realistic and viable models for the corrosion of aluminum, iron, and zinc, and of the dissolution of concrete and polymeric materials in contact with hot coolant under high mass transfer rate conditions (e.g., due to impinging jets) need to be developed that are capable of predicting corrosion rates under LOCA environmental conditions.

The hydrothermal hydrolysis of various organic/inorganic coating and insulation materials needs to be explored under conditions that realistically simulate a LOCA. It is expected that hydrothermal hydrolysis will partially de-polymerize polymeric materials, producing materials ranging from particles to gels. These materials need to be screened for their physical and chemical properties and, in particular, for their tendencies to “set” into more resilient forms.

The models that are produced to predict corrosion rates and phase properties must be, to the greatest extent possible, deterministic in nature. Thus, a deterministic model is one whose output (prediction) is constrained by the natural laws to that which is physically viable. These constraints are generally the conservation laws, such as the conservation of mass, charge, energy, and momentum.

Development of a radiolysis code specifically for a containment pool is absolutely essential, since the redox potential controls the speciation within the pool. This model should incorporate boric acid/LiOH + TSP (tri-sodium phosphate) models for estimating the pH. The model should be calibrated and evaluated against laboratory experiments to establish efficacy.

A thorough analysis should be carried out to estimate the likely γ-dose rates in the containment pool as a function of time after a LOCA in a PWR. The contribution of α-dose rate from fission products also needs to be evaluated. The latter is completely ignored in the present analysis and the former ($\gamma$-dose rate) is little more than a guess. No information of guidance on this subject could be found in the open literature.

A better database for the kinetics of the hydrogen electrode reaction, the oxygen electrode reaction, and the hydrogen peroxide electrode reaction needs to be established. Some of the "raw" data are already in the literature, but the information is incomplete and the data are generally not in a form that is readily interfaced with radiolysis/redox potential models. In some cases, however, the required data must be experimentally measured.

It is concluded that the ICETs and analytical simulations have serious shortcomings, because redox potential effects and the impact of radiolysis were not taken into account. For example, the redox potential, which arises from non-equilibrium processes, cannot be simulated analytically using current chemical modeling codes, because they lack an effective mixed potential model. The redox potential determines the driving force for the transition between different oxidation states. Possibly of much greater importance is the radiolytic conversion of nitrogen from the ambient containment air into nitric acid, because preliminary modeling work by the author indicates that, if the dose rate is sufficiently high in the pool, the production of nitric acid may overwhelm the buffering capacity of the chemicals in the pool. If this were the case, the pH would drop precipitously and the conditions would lie well outside those simulated in the ICETs and in the analytical modeling performed to date. Furthermore, if the pH drops to the extent predicted by preliminary scoping calculations, massive corrosion of structural materials might be expected with unforeseen consequences for the operation of vital systems that maintain effective cooling of the core.

# Contents

# Figures

# Tables

# 1. Introduction

By any metric, a loss of coolant accident (LOCA) in a Pressurized Water Reactor would be a catastrophic event, potentially resulting in the over-heating of the core to the extent that a "melt-down" might occur. Such a possibility has been anticipated, of course, and the coolant system has been designed to provide for emergency core cooling via a gravity-fed supply of water that can be used to flood the core and remove the heat from the continuing fission and decay processes. However, the supply of emergency coolant is limited and it is insufficient to remove the decay heat from the core that continues to be generated well after the fission process has been shut down. Accordingly, the system relies upon the recirculation of the coolant that has been injected from the LOCA onto the containment floor, together with the emergency core coolant from the same location, to remove the decay heat. The free flow of the coolant from the containment floor through the pumps, screens, and filters is vital for the success of this strategy.

The occurrence of a LOCA, with water from the pipe break being directed onto a variety of surfaces, including concrete, steel, plastic (polymer, including coatings and paints), and aluminum, will result in a complex mixture of compounds that could further react to produce a veritable "soup". The high temperature of the water is assumed to result in significant dissolution and corrosion, resulting in the formation of precipitates and gelatinous material that, potentially, might block filters and screens and hence impede flow in the recirculating system. Thus, the goal of this program is to provide critical analysis and review of experiments that are being carried out at various national laboratories or affiliated units to identify the reaction products that may form by hydrothermal hydrolysis and other processes, resulting from the impingement of high temperature coolant [boric acid + lithium hydroxide solution] on the structural materials. The exact conditions (temperature and chemical composition) of the impinging coolant are somewhat uncertain, because of adiabatic expansion and flashing of the coolant from the break lowers the temperature and because much of the resulting chemistry remains unknown or not understood.

# 2. Charge to the Reviewers

The charge to the reviewers was presented by the Nuclear Regulatory Commission (NRC) (Paulette Torres and Robert L. Tregoning) in the kick-off meeting that was convened at the Argonne National Laboratory on August 18-19, 2005. The charge comprises specific tasks and issues that are best summarized by adopting, *verbatim*, the material presented by the NRC, as follows:

## 2.1. Peer Review Objectives

Review technical adequacy of RES-sponsored activities related to chemical effects in PWR sump pool environments. The Technical Review Areas (TRAs) are listed as follows:

- Integrated Chemical Effects Testing (ICET): LANL
- ICET Follow-up Testing and Analysis: LANL.
- Chemical Speciation Prediction: CNWRA.
- Accelerated Chemical Effects Head Loss Testing: ANL.

### 2.2. Principal Technical Questions

- **ICET**
  - Have the principal sump pool variables which affect chemical by-product formation in the post-LOCA environment been adequately simulated?
  - Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?
  - What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects) and how should their effect be characterized by testing or analysis?
  - Were the methods used within the ICET program to characterize and analyze chemical by-products sufficient?

- **Analytical Simulation**
  - Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?
  - Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?
  - What is the most appropriate way to measure the uncertainty associated with these codes?

- **Head Loss Simulation Testing & Analysis**
  - Is the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?
  - What is the best method for incorporating for time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?
  - What metrics are most appropriate for evaluating the results of simulated chemical products with those that formed during the ICET program?
  - Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical by-product are known?

### 2.3. Motivation

- NRC Policy
  - Encourage formal and independent peer review of research products consistent with the nature, importance, and timeliness of the information to be disseminated.
  - The results of peer reviews should be made visible.

- Sump Pool Chemical Effects: Logical Peer Review Topic.
  - Relatively new research area (2003) with an aggressive resolution schedule (2007).
  - Technical area is sufficiently complex to warrant independent assessment and consultation.
  - Research could significantly affect resolution path.

# 3. Reviewer's Expertise

The author of this report is an electrochemist/corrosion scientist who has 30+ years of technical experience in the nuclear industry. In particular, the author has been extensively involved in the modeling of the chemistry and electrochemistry of heat transfer circuits in BWR, PWR, and CANDU reactors. This modeling work has resulted in the prediction of the accumulated damage due to pitting corrosion, stress corrosion cracking, and corrosion fatigue using deterministic models whose outputs (predictions) are constrained by the natural laws (conservation of mass, charge, etc). The author has also developed the Point Defect Model and Damage Function Analysis, which provide the most current view of the phenomena of passivity and passivity breakdown and the accumulation of localized corrosion damage, which are critical issues in the present study. Finally, the author has spent three decades studying the properties of high temperature aqueous solutions and has been instrumental in developing methods for measuring pH (at a maximum temperature of 528$^o$C), [$H_2$], [$O_2$], and redox and corrosion potential at temperatures exceeding the critical value (374.15$^o$C). A resume for the author is appended to this report.

# 4. Review of Simulations

An important function of the review was to assess the effectiveness of work carried out at the Argonne National Laboratory (ANL), Los Alamos National Laboratory (LANL), the Center for Nuclear Waste Regulatory Analysis (CNWRA) at the Southwest Research Institute (SwRI), San Antonio, Texas, and at the University of New Mexico to address some of the issues related to chemical effects in the containment pool post LOCA. This work was performed to support resolution of Generic Safety Issue (GSI)-191, which addresses the potential for post LOCA debris accumulation on PWR pump screens to interfere with the emergency-core-cooling-system (ECCS). The specific task was to address the role that might be played by chemical processes ("chemical effects") in the interference.

Both experimental work and thermodynamic simulations have been performed to provide a broad basis for predicting chemical processes in the pool as a function of time after a LOCA. While these data provide a basis for predicting what might develop in the pool they are, by themselves, insufficient to develop a thorough understanding of the chemical processes that might occur, because: (1) The processes that are expected to occur in the pool are much more complex than can be reasonably simulated in "ideal" laboratory experiments; (2) Assumptions made in the simulations (e.g., equilibrium in the case of thermodynamic calculations) may not hold in practice, or: (3) Certain phenomena [e.g., radiolysis due to fission products ($\gamma$- and $\alpha$-emitters)] may be difficult or even impossible to accurately reproduce in the laboratory and may not be incorporated in current, commercially-available codes. Nevertheless, selected experiments provide the means of checking expected behavior and hence of building confidence in the predictions of pool behavior as the containment environment evolves after a LOCA.

ICETs (Integrated Chemical Effects Tests) were designed to address certain aspects of the evolution of the chemistry of the containment pool after a LOCA. These tests sought to reasonably simulate the chemical properties of the pool, so that the responses of certain materials (e.g., fiberglass insulation, concrete, electrical insulation, and various metals and alloys) could be assessed. These tests were carried out with an initial chemical environment containing 2800 mg/L of boron as boric acid, 100 mg/L of HCl, and 0.7 mg/L of lithium as LiOH. The tests were generally carried out over 30 days at a temperature of 60$^o$C, and pH control was affected by the addition of NaOH, TSP (tri sodium phosphate), or TSB (tetra sodium borate). The principal analyses that were performed were chemical (total concentrations of elements), physical (e.g., pressure drop, viscosity, total suspended solids, and turbidity measurements), and microscopic/visual examination. Thermodynamic simulations, including speciation calculations, were also performed.

### 4.1. Integrated Chemical Effects Testing (LANL)

In this first ICET (ICET # 1), pH control was affected by the addition of NaOH with a target pH of 10. The pH was found to decrease during that test, such that after 30 days the pH was about 9.4. The drop in pH corresponds to the consumption of protons by metal corrosion and oxide dissolution (concrete, fiberglass), even though the solution is strongly buffered. The materials exposed to the environment were scaled amounts of thermal insulation (NUKON$^{TM}$ fiberglass), 373 metal coupons, and one concrete sample. The metals included representative amounts of aluminum, copper, carbon steel, and zinc. Representative amounts of concrete dust and other latent debris were added to the system to simulate in-service conditions. Parameters that were measured included pH, turbidity, total suspended solids, kinematic viscosity, and shear dependent viscosity. The test incorporated an initial, 4-hour spray phase to simulate the LOCA. Apparently, no attempt was made to reproduce the redox conditions, through the addition of hydrogen, and through the addition of hydrogen peroxide to simulate the impact of radiolysis.

The solution apparently remained clear during the test, but a precipitate formed upon cool-down. The concentration of aluminum in the solution was found to build-up to approximately 350 mg/L over the 30-day exposure period. The most important finding of this test was the formation of a web-like precipitate that spanned individual fibers. This precipitate grew more expansive with time and could represent a significant impediment to flow through the screen. Finally, an increase in the viscosity of cooled samples was detected after four days. The increase in viscosity is almost certainly due to polymerization of hydrolyzed cations in a precursor step to coagulation and precipitation.

In the opinion of this reviewer, ICET # 1 was carefully planned and provided a reasonable simulation of the pool without the involvement of TSP or TSB, yet contained representative amounts of many of the solid phases of interest. The results demonstrate the importance of precipitation processes and indicate that polymerization, coagulation, and precipitation are far from instantaneous process and, indeed, are irreversible processes that are far from equilibrium. This finding has important implications for the modeling of the pool using thermodynamic equilibrium models (see below). However, as in all of the ICETs, the failure to realistically simulate the redox conditions is considered to be a significant shortcoming.

ICET # 2 was generally similar to ICET # 1, except that pH control was affected by TSP (tri sodium phosphate) with a target pH of 7. This test appeared to differ from ICET # 1 in that no aluminum was detected in the solution, but significant amounts of Si, Ca, Mg, and Zn were found. Furthermore, large amounts of white deposits (nominally 0.125 to 0.250 inches thick) were found to form on the submerged galvanized steel, aluminum, and zinc specimens. These results indicate that the TSP inhibits the corrosion of aluminum (not a surprising result), but also that it inhibits the dissolution of aluminates (e.g. calcium aluminate?) from concrete and other phases, most probably by forming a metal phosphate of lower solubility on the surface. Again, the greatest objection to ICET # 2 is the apparent lack of appreciation of the role played by the redox potential in determining the solution chemistry in the pool and the lack of appreciation of the role of radiolysis with respect to establishing the redox potential and pH.

The third ICET (ICET # 3) was similar to ICET # 2, except that the target pH (established with TSP) was 7.0. Process control comprised monitoring on-line recirculation flow rate, solution temperature, and pH. The flow rate and temperature were controlled at 25gpm and 140$^o$F (60$^o$C), respectively. The pH of the solution initially rose to 7.32 four hours after the addition of the TSP and the experiment ran uninterrupted for 30 days. No corrosion products were visible in the solution at either the test temperature or at room temperature. However, chemical analysis of the solution revealed the presence of Al, but of only trace amounts of Ca, Si, and Na. Examination of the fiberglass specimens revealed chemical products and the web-like material spanning the fibers. Shear-rate dependent viscosity measurements showed that the solution behaved as a Newtonian fluid, indicating the lack of significant amounts of hydrolytic polymers that are precursors to precipitation. Again, no attempt was made to control the redox potential or to simulate the impact of radiolysis.

ICET # 4 was generally similar to ICET # 1, in that NaOH was used to control the pH. The sodium hydroxide (6.65N) was added during the spray cycle, causing the pH to rise to 9.92 (in-line pH probe) at the end of the 4-hour cycle. Thereafter, the pH declined to 9.79 after 30 days of operation. The turbidity declined over the 4-hour spray period from about 130NTU to a little less than 40NTU, indicating the agglomeration of colloidal particles into larger species and eventually into precipitates. Thereafter, the turbidity remained constant at a very low value for the remainder of the test. This finding is consistent with a similar variation observed in the total suspended solids (TSS), indicating that the formation and settling of solids occurs primarily during the spray period. No significant changes were detected in the viscosity of the solution in this test at either the test temperature (60$^o$C) or at 25$^o$C. Finally, the concentration of dissolved aluminum remained low (< 1mg/L), but those of Ca (40 – 55mg/L), silica (0 – 200mg/L), and sodium (6,000 – 12,000mg/L) were high (note that the initial concentration of $Na^+$ was due to the added NaOH, but, nevertheless, the sodium concentration doubled over the term of the experiment). The concentrations of zinc and copper were found to remain low (< 1mg/L) throughout the entire ICET # 4. These results all indicate that, because of the high pH, the principal source of dissolved species is the concrete (sample and dust) with a possible contribution from the fiberglass. However, and again, no attempt was made to simulate the redox properties or the impact that radiolysis might have on this important parameter or on the pH.

In ICET # 5, the pH of the initial solution (6.48kg of boric acid + 10kg of borax + 0.284g of LiOH) was modified by the addition of HCl to achieve a value of 8.2 – 8.4. The in-line pH probe gave a value of 8.5±0.1 while the bench-top probe gave values that are slightly lower at 8.25±0.15 over the same period, possibly because of solution of carbon dioxide from ambient air during the sampling procedure. In this case, the turbidity during the initial spray period decreased slightly from 14NTU to about 12.5NTU; a much smaller decrease than in ICET # 4 at a higher pH. This is a consistent finding and indicates that cation hydrolysis, polymerization, agglomeration, and precipitation become more prevalent as the pH increases. At longer times, the turbidity measured at 25$^o$C was found to be consistently higher than that measured at the test temperature of 60$^o$C with the difference increasing with time. These data are indicative of continued formation of colloids over the entire period of the test, particularly upon cool-down. This finding is also consistent with the measured TSS (total suspended solids), which remained constant at 15 – 30mg/L over the entire test. The viscosity at 25$^o$C and at 60$^o$C remained constant during this test. The concentration of aluminum was found to build-up to about 50mg/L over the term of the experiment, while the concentrations of Ca and $SiO_2$ ranged over a few tens of mg/L. The concentrations of Cu, Zn, and Mg remained low (< 1mg/L), while that of sodium remained constant at 1150 – 1400mg/L. These data are consistent with enhanced corrosion of the aluminum metal coupons, probably because of the lower pH than employed in some other experiments. Finally, the initiation of this test resulted in significant turbidity and precipitation, resulting in the fouling of an in-line flow meter. Precipitates continued to form throughout the entire test, particularly from solution samples removed from the system. Also, the submerged metal samples appeared to be coated with a white precipitate. In this test, the rate of hydrogen generation was monitored, but no attempt was made to relate the hydrogen concentration to the redox conditions.

### 4.2. ICET Follow-up Testing and Analysis (LANL)

The issues raised in this follow-up analysis have been largely dealt with in the material presented above.

### 4.3. Chemical Speciation Prediction (CNWRA)

Extensive thermodynamic simulations of chemical effects associated with PWR sump screen blockage have been carried out by the Center for Nuclear Waste Regulatory Analyses at the Southwest Research Institute in San Antonio, TX. [J. McMurray, et.al., "GSI-191 PWR Sump Screen Blockage Chemical Effects Tests – Thermodynamic Simulations", Report NUREG/CR-XXXX (Working Draft)], These studies were performed using four widely-available chemical modeling programs, including the OLI System's StreamAnalyzer, EQ3/6 (LLNL), Geochemist's Workbench REACT (distributed by Rockware, Inc.), and PHREEQC (US Geological Survey). All four programs are largely equilibrium in nature and hence are significantly restricted in their ability to simulate the dynamic conditions that exist in the pool as the conditions evolve with time after a LOCA. However, the latter two (Geochemist's Workbench REACT and PHREEQC) also have the capability of simulating kinetically controlled (including irreversible) and mass transfer processes. None have the ability to simulate radiolysis phenomena, nor do the have the capability of calculating the redox potential via a mixed potential model, and these limitations are judged by the author to be severe. In this regard, it is also important to note that, in the geochemical literature, the $E_h$ that is commonly referred to as the "redox potential" is, in fact, an equilibrium potential that is calculated for a specific charge transfer reaction. The term, redox potential, as used in electrochemistry (from which it originates), is a *mixed potential that reflects the occurrence of two or more charge transfer reactions occurring simultaneously at a metal surface*. The mixed potential not only reflects the equilibrium properties of the individual reactions (through their equilibrium potentials), but is also determined by their kinetics (through the exchange current densities or rate constant and through the transfer constants) and by mass transfer processes. Because the exchange current densities, rate constants, and the transfer coefficients for the individual redox reactions depend upon the substrate, the redox potential is substrate specific. Thus, the value obtained for platinum will differ from that calculated for carbon, for example. If one or more of the redox reactions that occur at the surface involves oxidation of the substrate itself (e.g., dissolution and/or oxide formation), the potential is termed the "electrochemical corrosion potential" (ECP), which is a quantity of great importance in corrosion science. Thus, it is evident that the true redox potential that characterizes the oxidizing/reducing power of an environment is not the same as that commonly defined in geochemistry as $E_h$ and that it cannot be calculated by equilibrium thermodynamics. This issue is discussed at greater length later in this report.

The predictions of the four codes were compared by simulating identical containment water after 30 minutes of exposure at temperatures of 110°C, 90°C, and 60°C. The four codes generally produced identical results for the major component elements that exhibit a single oxidation state and hence that are not susceptible to changes in the redox conditions. For those elements that have multiple, accessible oxidation states the comparison is quite poor. The authors of the report attribute the discrepancies to the listing of different sets of solid phases in the data bases and, presumably, inconsistent thermodynamic data among these phases. However, the general lack of recognition of the importance of redox effects may also be an important, contributing factor. Furthermore, the lack of the ability of these codes to simulate radiolytic effects must, however, be judged a serious shortcoming in simulating actual pool conditions, in light of simulations discussed elsewhere in this report that predict significant acidification of the pool water due to the radiolytic generation of nitric acid from nitrogen in the ambient air.

Nevertheless, comparison with ICET data from the University of New Mexico (obtained in the absence of radiolysis) show generally fair (qualitative to semi-quantitative) agreement between theory (thermodynamic calculation) and experiment, as might be expected when modeling complex, kinetically-controlled chemical systems using equilibrium models. Combining this limitation with the lack of radiolysis modeling and the lack of viable modeling of redox effects raises serious doubts in the reviewer's mind of the viability of employing "off the shelf" codes to model a unique system such as the containment pool after a LOCA.

### 4.4. Accelerated Chemical Effects Head Loss Testing (ANL)

Head loss testing, which provides a measure of the likelihood of clogging of the screens during a LOCA, was performed during the ICETs by monitoring the pressure drop across, and the volume flow rate through, the screen. Precipitation was found to clog the screen, particularly in the presence of a debris bed of fiber glass and other material. In particular, the injection of $Ca^{2+}$ in the presence of TSP (e.g., in ICET #3) led to the precipitation of $Ca_3(PO_4)_2$, which effectively blocked the screen. Accordingly, the ICETs have effectively confirmed that the clogging of pump screens is a practical reality and they have defined the general conditions under which it may occur.

### 4.5. Limitations of the Current Tests

In Section 2.2, "Principal Technical Questions", the reviewers were asked to comment on the appropriateness and the effectiveness of the ICETs, analytical simulation, and head-loss testing work in accurately resolving various "chemical" issues related to clogging of the sump screens after a LOCA. These issues are addressed below in the order that they are presented in Section 2.2.

- ICET
    - *Have the principal sump pool variables which affect chemical by-product formation in the post-LOCA environment been adequately simulated?* No. The lack of consideration of redox effects and radiolysis, particularly upon the pH, due to the production of nitric acid, and upon the redox potential are serious shortcomings that need to be addressed. During the course of this study, the author and his colleagues modified radiolysis/corrosion models to predict the production of highly oxidizing $H_2O_2$ and highly acidic $HNO_3$. These simulations are important, because both the redox potential and pH are of great importance

with regard to corrosion processes and chemical speciation in the pool. It is predicted that, if the LOCA results in the release of copious amounts of fission products from damaged fuel, with dose rates exceeding $10^5$ – $10^6$ rad/hr, the problem may be severe, because radiolysis may overwhelm the buffering capacity of the pool. In that case, the pH could easily drop to values (1 – 3) at which the corrosion of metals and the leaching of inorganic ions from concrete (for example) would become severe.

  - *Many ICET variables were held constant during the experiments. How would changes in the most important constant variables affect chemical product formation?* As an initial approach, I would use the radiolysis/ECP (redox potential) models to bound the values of the redox potential and pH that might be experienced in the pool, post LOCA, and then simulate these effects by injecting hydrogen peroxide and $HNO_3$ into the solution at formation rates that are predicted by the radiolysis codes.
  - *What variables or materials not simulated by the ICET testing may have the most impact on chemical product formation (e.g., coatings, free insulation, flow through sediment and other materials on sump screen, galvanic effects) and how should their effect be characterized by testing or analysis?* The most important omission from the current tests is simulation of the production of $H_2O_2$ (which, along with hydrogen, essentially determines the redox potential) and production of $HNO_3$, which lowers the pH, by radiolysis.
  - *Were the methods used within the ICET program to characterize and analyze chemical by-products sufficient?* No. Probes (Pt electrodes) should have been incorporated in the tests to measure the ECP (redox potential) and (in retrospect, because the effects apparently had not been predicted when the experiments were planned) injections of hydrogen peroxide and nitric acid should have been made to simulate radiolysis effects. The measurements that have been made effectively characterize the physico-chemical, not the electrochemical, properties of the system.

- **Analytical Simulation**
  - *Is the speciation analysis expected to provide reasonable predictions of chemical product formation over a range of possible sump environments?* No. Again, none of these codes (to my knowledge) accurately predict redox effects, because the redox potential is a non-equilibrium phenomenon that can only be predicted using a mixed potential model. Thus, in a post LOCA environment, non-equilibrium concentrations of radiolysis products (and even species in the absence of radiolysis) render the system far from equilibrium, which cannot be addressed by the four codes chosen [OLI System’s StreamAnalyzer, EQ3/6 (LLNL), Geochemist’s Workbench REACT (distributed by Rockware, Inc.), and PHREEQC (US Geological Survey)].
  - *Is the plan for benchmarking these codes using small-scale testing and the ICET results appropriate?* Yes, provided that the actual processes are accurately simulated (see above).
  - *What is the most appropriate way to measure the uncertainty associated with these codes?* Sensitivity analysis on empirical or deterministic models.

- **Head Loss Simulation Testing & Analysis**
    - *Is the accelerated head loss testing approach viable for evaluating the effects of multiple chemical environments quickly?* Yes, again, only provided that the relevant processes are simulated (see above).
    - *What is the best method for incorporating for time-dependent effects (e.g., material aging, evolving chemical environments) in simulation testing?* Kinetic models, coupled with thermodynamic codes. However, the codes MUST accurately simulate radiolysis and redox effects.
    - *What metrics are most appropriate for evaluating the results of simulated chemical products with those that formed during the ICET program?* Speciation and concentration. However, if equilibrium models are to be used, they must involve a global Gibbs energy minimization algorithm to predict the existence of stable and meta-stable phases (and their relative stabilities). Because I do not have access to the source codes for OLI System's StreamAnalyzer, EQ3/6 (LLNL), Geochemist's Workbench REACT (distributed by Rockware, Inc.), and PHREEQC (US Geological Survey, it is not possible for me to ascertain their capabilities with regard to this issue. Furthermore, the codes would only be effective if they incorporate effective means of handling redox effects in highly non-equilibrium systems.
    - *Are correlations available, or can they be developed, which can predict the associated head loss if important physical characteristics of a chemical by-product are known?* This is a difficult problem that could only be treated by a kinetic model for hydrolysis, polymerization, coagulation, and precipitation in a highly non-equilibrium environment, coupled with codes for. To my knowledge, none of the present codes [OLI System's StreamAnalyzer, EQ3/6 (LLNL), Geochemist's Workbench REACT (distributed by Rockware, Inc.), and PHREEQC (US Geological Survey)] have this capability.

## 5. Issues

Review of the documents supplied to the review team and review of the presentations that were made by NRC, ANL, LANL, SwRI, and EPRI personnel raised a number of issues that should be addressed in developing an understanding of the chemical processes that might occur in containment during a LOCA and for developing predictive models. In the opinion of this reviewer, certain aspects of the chemistry and the electrochemistry of the system are not adequately covered or understood. Accordingly, it is recommended that the NRC request the contractors involved in the program to address the issues raised in this report through analytical assessment or by experiment. The issues are summarized below:

### 5.1. Electrochemical Properties of the Containment Pool

Upon the occurrence of a LOCA, it is likely that a significant amount of radioactive material will be released into containment. This material will arise from two principal sources; (1) Fission products from failed fuel, and (2) Neutron activated corrosion products and deposits that form on the fuel and coolant circuit surfaces. More than a hundred fission product isotopes exist, with some of the more prominent that are expected to be released from the fuel being $^{131}I$,

$^{134}$Cs, $^{137}$Cs, and $^{90}$Sr, among others. The isotopes of iodine ($^{131}$I, $^{134}$I, etc) are particularly dangerous, because they are gaseous and are readily absorbed by the human thyroid gland, resulting in carcinomas. Iodine is removed by the building spray system within containment. Neutron activated corrosion products contain $^{60}$Co, Co$^{58}$, Zn$^{65}$, Fe$^{59}$, Fe$^{55}$, and Ni$^{63}$, together with many other radio nuclides, all of which are $\gamma$-photon emitters, and hence all of which, depending upon their activity and photon energies, will contribute to greater or lesser extents to the radiolysis of water in the containment pool. Many of the fission products are $\alpha$-particle emitters, which also cause the radiolysis of water and should be taken into any account in any analysis of the radiolysis issue.

The radiolysis of water in Water Cooled Nuclear Reactor (WCNR) heat transport circuits has long been recognized as a potential source of corrosive, oxidizing species, such as $O_2$, $H_2O_2$, OH, etc., and for this reason hydrogen is added to PWR primary coolant circuits, and, in more recent years, to BWR coolant circuits, to suppress their radiolytic generation of oxidizing species and/or to displace the corrosion potentials of structural components in the coolant circuits in the negative direction. This has been accomplished in the case of PWR primary coolant by adding large amounts of hydrogen to the coolant [20 – 70cc(STP)/kg, $8.93\times10^{-4}$ – $3.13\times10^{-3}$m, respectively], seemingly with the philosophy that "if a little is good, a lot more must be better. In the case of BWRs, the Intergrannular Stress Corrosion Cracking (IGSCC) of sensitized Type 304SS primary coolant components (particularly the recirculation piping system, but more recently in-vessel components) has been linked to excessively high corrosion potentials, resulting from the generation of oxidizing species ($O_2$, $H_2O_2$ due to the radiolysis of water), and to a sensitized microstructure, due to either thermal sensitization or neutron irradiation above a certain fluence (accumulated dose > $10^{21}$n/cm$^2$, energy > 1MeV). That the Electrochemical Corrosion Potential (*ECP*) is the prime parameter in determining the accumulation of corrosion damage has been slowly accepted in the power reactor community, possibly because electrochemistry is seldom, if ever, included in Mechanical and Nuclear Engineering curricula at universities. The impact that ECP has on crack growth rate is roughly exponential [D. D. Macdonald and M. Urquidi-Macdonald, Corr. Sci., **32**, 51 (1991). D. D. Macdonald and M. Urquidi-Macdonald, "An Advanced Coupled Environment Fracture Model for Predicting Crack Growth Rates", *Proc. TMS Parkins Symp. Fund. Aspects Stress Corros. Crack.*, pp. 443-455, Oct. 20-24, 1991, Cincinnati, OH, (TMS, Warrendale, PA, 1992). D. D. Macdonald, P.C. Lu, M. Urquidi-Macdonald, and T. K. Yeh, Corrosion, **52**, 768 (1996). D. D. Macdonald, Corr. Sci., **38**, 1033 (1996). X. Zhou, I. Balachov, and D. D. Macdonald, "The Effect of Dielectric Coatings on Sensitized Type 304 SS in High Temperature Dilute Sodium Sulfate Solution", Corr. Sci., **40**, 1349 (1998). D. D. Macdonald and L. Kriksunov, "Flow Rate Dependence of Localized Corrosion Processes in Thermal Power Plants" *Adv. Electrochem. Sci. Eng.*,**5**, 125, (1997) [John Wiley & Sons, New York, N.Y.]. M. P. Manahan, Sr., D. D. Macdonald, and A. J. Peterson, Jr., Corr. Sci., **37**, 189 (1995)], if the ECP is above a critical potential for IGSCC ($E_{IGSCC}$), although the rate also depends upon the stress intensity, the extent of cold-working of the substrate, the conductivity of the environment, and the flow velocity of the coolant across the surface [D. D. Macdonald, and G. Cragnolino. "The Critical Potential for the IGSCC of Sensitized Type 304 SS in High Temperature Aqueous Systems". *Proc. 2nd Int'l. Symp. Env. Deg. Mat. Nucl. Power Syst. - Water Reactors*. (September 9-12, 1985). Monterey, CA., ANS]. Note that in much of the discussion that follows, the focus is on the primary coolant circuits of operating reactors, but the author emphasizes that the same principles apply to the containment pool post-LOCA.

As noted above, the redox potential ($E_{redox}$) and the *ECP* (the redox potential is simply the *ECP* of an inert substrate) are the key parameters in describing the susceptibility of reactor coolant circuit components to corrosion damage. The direct measurement of *ECP* in reactor coolant circuits has proven to be very difficult, notwithstanding the monumental efforts of researchers and plant operators worldwide [M. E. Indig and J. L. Nelson, Corrosion, **47**, 202 (1991)]. The major challenge in in-reactor *ECP* measurements has been to devise a reference electrode that can withstand the harsh environmental conditions that exist within a reactor pressure vessel (RPV).

Electrochemists will recognize that the $E_{redox}$ and *ECP* are both mixed potential, the values of which are determined by the balance of the oxidizing and reducing species in the environment and the kinetics of dissolution (corrosion) of the substrate. In order to calculate $E_{redox}$ and *ECP*, then, it is important, in principle, that the concentrations of all of the radiolytic species be determined, since all of these species are electroactive. However, theory shows that the contribution that any given species makes to the these potentials is determined by its concentration, so that only the most prevalent electroactive species in the system determine the *ECP*. This is a fortunate finding, because the various radiolysis models that are available for calculating species concentrations do not determine the concentrations of the minor species accurately, nor are there available electrochemical kinetic data for most of these highly energetic species.

In order to calculate the species concentrations, the combined effects of the radiolytic yield of each species due to the absorption of ionizing radiation by water, and the changes in concentration due to chemical reactions and fluid convection, must be taken into account. This problem reduces to one of solving as many stiff, coupled, simultaneous first order differential equations as there are species in the system. One of the major problems in describing the radiolysis of water is to devise efficient algorithms for performing that task. Details of the calculations may be found in the literature [T. K. Yeh, D. D. Macdonald, and A. T. Motta, Nucl. Sci. and Eng., **121**, 468 (1995). T. K. Yeh, D. D. Macdonald, and A. T. Motta, Nucl. Sci. and Eng., **123**, 295 (1996). T. K. Yeh, D. D. Macdonald, and A. T. Motta, Nucl. Sci. and Eng., **123**, 305 (1996). D. D. Macdonald, et al., “Estimation of Corrosion Potentials in the Heat Transport Circuits of LWRs,” *Proceedings of the International Conference on Chemistry in Water Reactors: Operating Experience & New Developments*, Nice, France, Apr. 24-27, 1994. D. D. Macdonald and M. Urquidi-Macdonald. Corrosion, **46**, 380 (1990). C. P. Ruiz, et al., “Modeling Hydrogen Water Chemistry for BWR Applications”, *EPRI-NP-6386*, Electric Power Research Institute, June 1989. K. Ishigure, Rad. Phys. Chem., **29**, 195 (1987). E. Ibe, J. Nucl. Sci. Tech., **24**, 220 (1987)].

Below is presented a brief (but incomplete) review of the current state-of-the-art in modeling the radiolysis and electrochemistry of PWR and BWR primary coolant circuits. The material is presented, so that the reader may appreciate the level of sophistication that has been achieved and to indicate the techniques that might be used to model radiolysis and electrochemical effects in the containment pool subsequent to a LOCA.

### Radioytic Yield

The rate at which any primary radiolytic species is produced is given by

$$R_i^y = \left( \frac{G_i^\gamma \Gamma^\gamma}{100 N_V} + \frac{G_i^n \Gamma^n}{100 N_V} + \frac{G_i^\alpha \Gamma^\alpha}{100 N_V} \right) \tilde{F} \rho \qquad (1)$$

where the rate of production of species "*i*", $R_i^y$, has units of mol/cm$^3$.s, $G^n$, $G^g$, and $G^\alpha$ are the radiolytic yields for neutrons, gamma photons, and alpha particles, respectively, in number of particles per 100eV of energy absorbed, $N_v$ is Avogadro's number, $\tilde{F}$ equals 6.25x10$^{13}$ (the conversion factor from Rad/s to eV/gram.s), and $\rho$ is the water density in g/cm$^3$. $\Gamma^\gamma$, $\Gamma^n$, and $\Gamma^\alpha$ are the gamma photon, neutron, and α-particle energy dose rates, respectively, in units of rad/s.

**Table 1.** Radiolytic Yields (*G* Values) for Primary Radiolytic Species

| Species No. | Species | $G^\gamma$ (No./100eV) | $G^n$ (No./100eV) | $G^\alpha$ (No./100eV) |
|---|---|---|---|---|
| 1 | $e^-$ | 2.66 | 0.61 | 0.06 |
| 2 | H | 0.55 | 0.34 | 0.21 |
| 3 | OH | 2.67 | 2.02 | 0.24 |
| 4 | $H_2O_2$ | 0.72 | 0.65 | 0.985 |
| 5 | $HO_2$ | 0.00 | 0.05 | 0.22 |
| 6 | $HO_2^-$ | 0.00 | 0.00 | 0.00 |
| 7 | $O_2$ | 0.00 | 0.00 | 0.00 |
| 8 | $O_2^-$ | 0.00 | 0.00 | 0.00 |
| 9 | $H_2$ | 0.45 | 1.26 | 1.3 |
| 10 | $O^-$ | 0.00 | 0.00 | 0.00 |
| 11 | O | 0.00 | 0.00 | 0.00 |
| 12 | $O_2^{2-}$ | 0.00 | 0.00 | 0.00 |
| 13 | $OH^-$ | 0.01 | 0.00 | 0.00 |
| 14 | $H^+$ | 2.76 | 0.00 | 0.06 |

Values for the radiolytic yields for various species considered in the author's radiolysis model for PWR coolants are listed in Table 1. A review of the literature reveals a wide variance in the G-values, even from the same author. The current *G*-values should be regarded as being little more than rough estimates.

The third term in Equation (1) accounts for the radiolysis of water by α-particles ($^4He_2$ nucleus), which are produced by the $^{10}B_5(^1n_0,^4He_2)^7Li_3$ reaction in PWR primary coolant environments, but this nuclear reaction does not occur on BWR environments, because of the absence of boron (specifically $^{10}B_5$). The importance of α-particle radiolysis in PWR cores has been recently assessed and it was concluded that the contributions from α-radiolysis to the concentrations of the radiolytic species are small, when compared with those from neutrons and γ-photons at the prevailing dose rates. Nevertheless, in a PWR primary coolant circuit, there are regions where α-particle radiolysis contributes significantly to the formation of the radiolytic species (> 10 %), and hence the third term in Equation (2) is necessary. In the case of BWR cores, the radiolysis models have tended to be based on that originally proposed by Burns and Moore, with modification being made in light of the later studies by Elliot. The models used by the author and his colleagues for modeling BWR primary coolant circuits contains 34 reactions, as discussed further below.

A word of caution is needed at this point; the radiolytic yields employed in radiolysis modeling should be the *primary* yields corresponding to events that occur within the time of scission of a bond within a water molecule. These values are impossible to measure, because no techniques are available for sampling the concentrations of primary radiolysis products in the sub-femto second time frame. Thus the radiolytic yields that are used to devise water radiolysis models are strictly not the values that are appropriate or needed. However, as with many physico-chemical models, values for various parameters are often selected, such that the original observations are reproduced. A major problem in radiolysis modeling is that there are many more unknown parameters than there are experimental observations, so that the values assigned to the models are not unique and they should not be transferred from model-to-model. Nevertheless, the models have proven to be quite robust, in the sense that reasonable values for the calculated concentrations of the various major radiolysis products are obtained. (However, it should be noted that the concentrations of minor radiolysis products are seldom measured and compared with those that are predicted).

### Chemical Reactions

The chemical reactions occurring in the system essentially determine the species concentrations. The reaction set used previously by Urquidi-Macdonald and Macdonald for modeling PWR primary coolant circuits has 48 reactions describing the interactions between the 14 species listed in Table 2, along with the rate constants and the activation energies.

**Table 2.** Reaction set used in the PWR radiolysis model

| *Reaction No. | Rate Constant, k (l/mol.s) | Activation Energy (kcal/Mol) | Reaction |
|---|---|---|---|
| 1 | 1.6D+1 | 3.0D0 | $e^- + H_2O = H + OH^-$ |
| 2 | 2.4D+10 | 3.0D0 | $e^- + H^+ = H$ |
| 3 | 2.4D+10 | 3.0D0 | $e^- + OH = OH^-$ |
| 4 | 1.3D+10 | 3.0D0 | $e^- + H_2O_2 = OH + OH^-$ |
| 5 | 1.0D+10 | 3.0D0 | $H + H = H_2$ |
| 6 | 2.0D+10 | 3.0D0 | $e^- + HO_2 = HO_2^-$ |
| 7 | 1.9D+10 | 3.0D0 | $e^- + O_2 = O_2^-$ |
| 8 | 5.0D+9 | 3.0D0 | $2e^- + 2H_2O = 2OH^- + H_2$ |
| 9 | 4.5D+9 | 3.0D0 | $OH + OH = H_2O_2$ |
| 10 | 1.2D+10 | 3.0D0 | $OH + HO_2 = H_2O + O_2$ |
| 11 | 1.2D+10 | 3.0D0 | $OH + O_2^- = OH^- + O_2$ |
| 12 | 2.0D+7 | 3.0D0 | $OH^- + H = e^- + H_2O$ |
| 13 | 4.5D+8 | 3.0D0 | $e^- + H + H_2O = OH^- + H_2$ |

| | | | |
|---|---|---|---|
| 14 | 6.3D+7 | 3.0D0 | $e^- + HO_2^- + H_2O = OH + 2OH^-$ |
| 15 | 1.44D+11 | 3.0D0 | $H^+ + OH^- = H_2O$ |
| 16 | 2.6D-5 | 3.0D0 | $H_2O = H^+ + OH^-$ |
| 17 | 2.0D+10 | 3.0D0 | $H + OH = H_2O$ |
| 18 | 3.4D+7 | 4.6D0 | $OH + H_2 = H + H_2O$ |
| 19 | 2.70D+7 | 3.4D0 | $OH + H_2O_2 = H_2O + HO_2$ |
| 20 | 4.4D+7 | 4.5D0 | $H + H_2O_2 = OH + H_2O$ |
| 21 | 1.9D+10 | 3.0D0 | $H + O_2 = HO_2$ |
| 22 | 8.0D+5 | 3.0D0 | $HO_2 = O_2^- + H^+$ |
| 23 | 5.0D+10 | 3.0D0 | $O_2^- + H^+ = HO_2$ |
| 24 | 2.7D+6 | 4.5D0 | $2HO_2 = H_2O_2 + O_2$ |
| 25 | 1.7D+7 | 4.5D0 | $2O_2^- + 2H_2O = H_2O_2 + O_2 + 2OH^-$ |
| 26 | 2.0D+10 | 3.0D0 | $H + HO_2 = H_2O_2$ |
| 27 | 2.0D+10 | 3.0D0 | $H + O_2^- = HO_2^-$ |
| 28 | 1.3D+8 | 4.5D0 | $e^- + O_2^- + H_2O = HO_2^- + OH^-$ |
| 29 | 1.8D+8 | 4.5D0 | $OH^- + H_2O_2 = HO_2^- + H_2O$ |
| 30 | 1.9973D-6 | 14.8D0 | $2H_2O_2 = 2H_2O + O_2$ |
| 31 | 1.04D-4 | 3.0D0 | $H + H_2O = H_2 + OH$ |
| 32 | 1.02D+4 | 3.0D0 | $H_2O + HO_2^- = H_2O_2 + OH^-$ |
| 33 | 1.5D+7 | 4.5D0 | $HO_2 + O_2^- = O_2 + HO_2^-$ |
| 34 | 7.7D-4 | 7.3D0 | $H_2O_2 = 2OH$ |
| 35 | 7.88D+9 | 3.0D0 | $OH + HO_2^- = O_2^- + H_2O$ |
| 36 | 1.28D+10 | 3.0D0 | $OH + OH^- = O^- + H_2O$ |
| 37 | 6.14D+6 | 3.0D0 | $O^- + H_2O = OH + OH^-$ |
| 38 | 3.97D+9 | 3.0D0 | $e^- + HO_2^- = O^- + OH^-$ |
| 39 | 6.42D+14 | 3.0D0 | $O_2^- + O_2^- + H^+ = HO_2^- + O_2$ |
| 40 | 2.72D-3 | 15.0D0 | $H_2O_2 = H_2O + O$ |
| 41 | 2.84D+10 | 3.0D0 | $O + O = O_2$ |
| 42 | 1.1D+6 | 3.0D0 | $O_2^{2-} + H_2O = HO_2^- + OH^-$ |

| | | | |
|---|---|---|---|
| 43 | 1.3D+10 | 3.0D0 | $e^- + O_2^- = O_2^{2-}$ |
| 44 | 0.5D0 | 3.0D0 | $H_2O_2 + HO_2 = H_2O + O_2 + OH$ |
| 45 | 0.13D0 | 3.0D0 | $O_2^- + H_2O_2 = OH + OH^- + O_2$ |
| 46 | 2.56D-8 | 3.0D0 | $H_2O_2 = H^+ + HO_2^-$ |
| 47 | 1.39D+10 | 3.2D0 | $e^- + HO_2 + H_2O = H_2O_2 + OH^-$ |
| 48 | 1.39D+10 | 3.2D0 | $e^- + O_2^- + H_2O = HO_2^- + OH^-$ |

This reaction set includes hydrogen peroxide decomposition. The impact of including $H_2O_2$ decomposition in a radiolysis, which has been used extensively in our BWR modeling work and which has been extensively evaluated against BWR plant data, is unknown, because no independent check on specie concentrations is currently available *for a PWR primary circuit or for a containment pool.* This is due to the fact that the concentration of oxygen, which is monitored on a routine basis in a BWR, is so low in a PWR primary circuit that it is not measured. Furthermore, the hydrogen that is present in a PWR primary circuit is primarily the result of hydrogen additions and not radiolysis, so that $[H_2]$ measured in the circuit is not a good indication of the state of radiolysis. Finally, the ECP, which is now measured on a routine basis in BWRs, is not monitored in any PWR primary circuit, to the authors' knowledge, even on an experimental basis, although some measurements have been made in VVER 440 reactors.

Other radiolysis mechanisms were examined during the development of models to describe radiolysis in reactor coolant circuits, and the codes that have been developed by the author have been written to facilitate, to the greatest extent possible, the inclusion of new mechanisms. As expected, insertion of different reaction sets requires considerable reprogramming of the code.

The rate of change of each species at a given location is given by reaction rate theory as

$$R_i^c = \sum_{s=1}^{N} \sum_{m=1}^{N} k_{sm} C_s C_m - C_i \sum_{s=1}^{N} k_{si} C_s \qquad (2)$$

where $k_{sm}$ is the rate constant for the reaction between Species *s* and *m*, $k_{si}$ is the rate constant for the reaction between Species *s* and *i*, and $C_i$, $C_m$, and $C_s$ are the concentrations of Species *i*, *m*, and *s*, respectively. N is the number of reactions in the model (i.e., N = 48). Explicit expressions for the gain and the loss of each species are included in the algorithm.

The rate constant, $k_j$ is a function of coolant temperature. Since the temperature throughout the heat transport circuit is not constant, the actual rate constant for each chemical reaction must be calculated for each specific position using Arrhenius' law

$$k = k_o \exp[\frac{E_a}{R}(\frac{1}{T_o} - \frac{1}{T})] \qquad (3)$$

where $k_o$ is the rate constant at temperature $T_o$, $E_a$ is the activation energy, $R$ is the universal gas constant, and $T$ is the temperature in Kelvin. The rate constant for hydrogen peroxide decomposition (Reaction # 30) was calculated separately using an experimentally derived relationship:

$$k_{30} = 1.9973e - 6.e^{-(14800/RT)} \qquad (4)$$

Table 1 lists the species considered and the number assigned to them. Note that $[H^+]$ and $[OH^-]$ are calculated from the pH and the speciation that is afforded by the chemistry of the coolant.

### Convection

As in all of the radiolysis models of reactor coolants, convection is considered to be the only mode of transport (i.e. diffusion and electro-migration are neglected). In both PWR and BWR *primary* coolant circuits, single-phase (water) flow is assumed to exist in all regions of the circuit, except in the core channels of a BWR, where boiling produces the steam that carries the energy directly to the turbines. Boiling results in the transfer of volatile species ($O_2$ and, in particular, $H_2$) to the steam, which in turn reduces their presence in the liquid phase. This transfer significantly modifies the radiolysis processes in the liquid, with the result that the coolant becomes more oxidizing in nature, because of the higher rate of loss of $H_2$ compared with $O_2$ or $H_2O_2$. In the case of PWRs, nucleate boiling within the power-producing channels, where the local saturation vapor pressure exceeds the prevailing hydrostatic pressure, has a much less effect on the coolant chemistry than does the sustained boiling in the fuel channels of a BWR, because the volatile species are returned to the liquid phase when the bubbles collapse. In nucleate boiling, the steam bubbles that form on the fuel collapse when they detach from the surface. Accordingly, any volatile radiolysis species that transfers to the steam phase is immediately returned to the primary coolant (liquid phase), so that the net effect of nucleate boiling on the bulk concentrations is expected to be small, if it exists at all. This situation contrasts with that in a BWR, where a continuous steam phase is formed that leaves the primary coolant. In this case, the irreversible transfer of volatile species ($H_2$, $O_2$) to the steam has an enormous impact on the electrochemistry of the primary circuit.

### General Solution of the Equations

The approach used in our work to solve the set of coupled ordinary differential equations (ODEs) for modeling PWR primary coolant circuits makes use of a publicly available subroutine (DVODE), which was developed by Hindmarsh at the Lawrence Livermore National Laboratory in California [www.netlib.gov]. This algorithm is designed to solve first degree, *stiff* ODE equation sets. Our system of equations is coupled throughout via the concentrations of the 14 species considered. To solve the $i$-coupled differential equation ($i$ = number or species), the DVODE subroutine needs to have the set of equations and the corresponding Jacobians described. The calculation begins by assuming that the coolant is an incompressible fluid $\left(\overline{\nabla} \cdot \overline{v} = 0\right)$ and that the flow is turbulent (efficient mixing). Accordingly, the flux of each dissolved species is given by

$$\overline{N}_i = -Z_i U_i F c_i \overline{\nabla}\phi - D_i \overline{\nabla} C_i + C_i \overline{v} \qquad (5)$$

flux = migration + diffusion + convection

Because of efficient mixing and in the absence of an electric field, we may ignore diffusion and migration, respectively, and hence the material balance can be written as

$$\frac{\partial C_i}{\partial t} = -\overline{\nabla} \cdot \overline{N}_i + R_i \qquad (6)$$

(accumulation = net input + production), where $R_i$ is the rate of production of the species in the fluid due to homogeneous reactions.

The primary coolant circuit of a water-cooled reactor (including BWRs and PWRs) has several loops, including the main coolant loop, a core heat removal system, and a reactor water clean-up system. However, it is convenient, for computational purposes, to differentiate between the *main* loop, which has a high flow fraction and the secondary loops, for which the flow fractions are small. The species concentrations and electrochemical potential (ECP) are solved for in the main loop and the values at the entrance to the secondary loop are used as the initial conditions for solving the system of equations for the secondary loops of interest. Mass balance is applied at each point where more than one section comes together.

By adopting the rates of change of species mass from the various sources discussed above, we write the total rate as

$$R_i = \left(\frac{G_i^{\gamma}\Gamma^{\gamma}}{100N_V} + \frac{G_i^{n}\Gamma^{n}}{100N_V} + \frac{G_i^{\alpha}\Gamma^{\alpha}}{100N_V}\right)\tilde{F}\rho + \left[\sum_{s=1}^{N}\sum_{m=1}^{N} k_{sm}C_sC_m - C_i\sum_{s=1}^{N} k_{si}C_s\right] \qquad (7)$$

The equations must be solved iteratively until satisfactory convergence is obtained. Note that, because the mass flow rate (*dm/dt*) in a single (un-branched) channel is constant at all points, the linear flow rate is given by $v = (dm/dt)/\rho A$, where A is the cross-sectional area of the channel.

By solving Equation (6) numerically, we are able to calculate the concentrations of each species at any point in a reactor heat transport circuit. In the actual numerical simulation, all of the parameters, except the flow velocity, circuit geometry, and temperature can be found in the published literature.

Transients during operation, for example those that result from a sudden increase in power or from a step change in feedwater oxygen level, may be modeled as a series of steady-states, with the initial conditions reflecting the progressive changes in the reactor operating parameters.

The above approach describes the method used by Macdonald and Urquidi-Macdonald in modeling PWR primary coolant circuits, but that employed by Yeh, Motta, and Macdonald and others for modeling BWR primary coolant circuits is somewhat different, but yields similar results. The reader is referred to the original literature for details.

### Mixed Potential Model and the Redox and Electrochemical Corrosion Potentials

After the concentration of each radiolysis species is calculated, the corrosion potential of the component can be estimated using a mixed potential model (MPM) [D. D. Macdonald, Corrosion, **48**, 194 (1992)]. The MPM is based on the physico-electrochemical condition that charge conservation must be obeyed at the corroding interface. Because electrochemical reactions transfer charge across a metal/solution interface at rates measured by the partial currents, the following equation expresses the charge conservation constraint

$$\sum_{j=1}^{n} i_{R/O,j}(E) + i_{corr}(E) = 0 \tag{8}$$

where $i_{R/O,j}$ is the partial current density due to the *j*-th redox couple in the system and $i_{corr}$ is the metal oxidation (corrosion) current density. These partial currents depend on the potential drop across the metal/solution interface.

In the current version of the MPM, which was developed for modeling the ECP of Type 304 SS in BWR primary circuits, the steel oxidation current density, $i_{corr}$, was modeled as an empirical function of voltage,

$$i_{corr} = \frac{e^{(E-E_o)/b_f} - e^{-(E-E_o)/b_r}}{384.62e^{4416/T} + X} \tag{9}$$

where

$$X = \frac{e^{(E-E_o)/b_f}}{2.61x10^{-3}e^{-4416/T+0.523(E-E_o)^{0.5}}} \tag{10}$$

and

$$E_o = 0.122 - 1.5286x10^{-3}T \tag{11}$$

In these expressions, $b_f$ and $b_r$ are the forward and reverse Tafel constants, respectively, for the metal dissolution reaction, with values of 0.06 V being assumed for both. In actual fact, they are empirical constants that were assumed *a priori* in fitting Equation (9) to the current/voltage data. It is important to note that Equation (9) applies strictly to Type 304 SS in near neutral solutions and hence that this expression may not be a good empirical model for stainless steels in PWR primary circuits or for metals and alloys in a containment pool. More recently, the Point Defect Model [D. D. Macdonald, Pure Appl. Chem., **71**, 951 (1999)] has been used as the basis for calculating the corrosion current density of the metal substrate.

**Metal** | **Barrier Layer** | **Solution/Outer Layer**

**(1)** $m + V_M^{\chi'} \xrightarrow{k_1} M_M + v_m + \chi e^-$

**(4)** $M_M \xrightarrow{k_4} M^{\Gamma+}(aq) + V_M^{\chi'} + (\Gamma - \chi)e^-$

**(2** $m \xrightarrow{k_2} M_i^{\chi+} + v_m + \chi e^-$

**(5** $M_i^{\chi+} \xrightarrow{k_6} M^{\Gamma+}(aq) + (\Gamma - \chi)e^-$

**(3)** $m \xrightarrow{k_3} M_M + \frac{\chi}{2} V_O^{\bullet\bullet} + \chi e^-$

**(6** $V_O^{\bullet\bullet} + H_2O \xrightarrow{k_6} O_O + 2H^+$

**(7)** $MO_{\chi/2} + \chi H^+ \xrightarrow{k_7} M^{\Gamma+}(aq) + \frac{\chi}{2} H_2O + (\Gamma - \chi)e^-$

**Figure 1.** Summary of the defect generation and annihilation reactions envisioned at the interfaces of the barrier oxide layer on a metal, according to the Point Defect Model (PDM). $V_M^{\chi'}$ ≡ cation vacancy in the film; $v_m$ ≡ vacancy in the metal substrate; $M_i^{\chi+}$ cation interstitial; $V_O^{\bullet\bullet}$ ≡ oxygen (anion) vacancy; $M^{\Gamma+}(aq)$ ≡ cation in solution; $M_M$ cation in cation site on the metal sublattice; $O_O$ oxide ion in anion site on the oxygen sublattice; and $MO_{\chi/2}$ ≡ stoichiometric barrier layer oxide. Note that Reactions 1, 2, 4, 5 and 6 are lattice conservative processes (they do not result in the movement of the interface) whereas Reaction 3 and 7 are non-conservative [D. D. Macdonald, Pure Appl. Chem., **71**, 951 (1999)].

The PDM yields the passive current density in the form

$$I_{ss} = \Gamma F\left[k_2^0 e^{\alpha_2 \alpha \gamma V} e^{-\alpha_2 \alpha \varepsilon \gamma L_{ss}} + k_4^0 e^{\alpha_4 \alpha \gamma V} e^{\alpha \beta \gamma pH} + k_7^0 \cdot C_{H^+}^n\right] \qquad (12)$$

where the film thickness is given by

$$L_{ss} = \frac{1-\alpha}{\varepsilon} V + \frac{1}{\varepsilon}\left\{\frac{2.303n}{\alpha_3 \chi \gamma} - \beta\right\} pH + \frac{1}{\alpha_3 \chi K} ln\left(\frac{k_3^0}{k_7^0}\right) \qquad (13)$$

[D. D. Macdonald, Pure Appl. Chem., **71**, 951 (1999)]. The parameters in these equations are as follows: $\chi$, $\alpha$, $\beta$, and $n$ are the oxidation state of the cation in the barrier layer; the polarizability of the film/solution interface (i.e., the dependence of the potential drop across the film/solution interface on the applied voltage); the dependence of the potential drop across the film/solution interface on the pH; and the kinetic order of the film dissolution reaction with respect to hydrogen ion concentration; respectively. Note that, in deriving Equations (12) and (13), the oxidation state of the cation in the barrier layer ($\chi$) is set equal to the oxidation state of the same cation in the solution/outer layer. The standard rate constants, $k_i^0$, and $\alpha_i$ correspond to the reaction shown in Figure 4, $\varepsilon$ is the electric field strength, $\gamma = F/RT$, and $K = \varepsilon\gamma$. The three terms on the right side of Equation (12) arise from the transmission of cation interstitials, the transmission of cation vacancies, and the transmission of oxygen vacancies (or dissolution of the film), respectively. Values for these parameters are readily obtained by optimizing the PDM on electrochemical impedance spectroscopic (EIS) data.

Because electrochemical kinetic data are available only for the hydrogen electrode reaction (HER, $H_2/H^+$), the oxygen electrode reaction (OER, $O_2/H_2O$), and the hydrogen peroxide electrode reaction (HPER, $H_2O_2/H_2O$), only $H_2$, $O_2$, and $H_2O_2$ are considered as the redox species in the MPM. The redox reactions of interest are therefore written as:

$$H^+ + e^- \rightarrow 1/2H_2 \qquad \text{or} \qquad H_2O + e^- \rightarrow 1/2H_2 + OH^- \tag{14}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad \text{or} \qquad O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{15}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad \text{or} \qquad H_2O_2 + 2e^- \rightarrow 2HO^- \tag{16}$$

depending upon the pH. For pH values of less than about 4, the acid forms of the reactions prevail (left side), while at higher pH values the base forms predominate. The exact form of the reaction has an important impact on the MPM, because it determines the reaction order with respect to the concentration of hydrogen ion in the expression for the exchange current density.

The current density ($i_{R/O}$) for a redox couple (e.g. $O_2/H_2O$, $H^+/H_2$, $H_2O_2/H_2O$)

$$R \Leftrightarrow O + ne \tag{17}$$

(where *R* is the reduced species and *O* is the oxidized species) can be expressed in terms of a generalized Butler-Volmer equation as

$$i_{R/O} = \frac{e^{(E-E^e_{R/O})/b_a} - e^{-(E-E^e_{R/O})/b_c}}{\dfrac{1}{i_{0,R/O}} + \dfrac{1}{i_{i,f}} e^{(E-E^e_{R/O})/b_a} - \dfrac{1}{i_{i,r}} e^{-(E-E^e_{R/O})/b_c}} \tag{18}$$

where $i_{0,R/O}$ is the exchange current density, $i_{l,f}$ and $i_{l,r}$ are the mass-transfer limited currents for the forward and reverse directions of the redox reaction, respectively, and $b_a$ and $b_c$ are the anodic and cathodic Tafel constants. $E^e_{R/O}$ is the equilibrium potential for this reaction, as computed from the Nernst equation:

$$E^e_{O/R} = E^0_{O/R} - \frac{2.303RT}{nF}\log\left(\frac{a_R}{a_O}\right) \tag{19}$$

where $a_R$ and $a_O$ are the thermodynamic activities of R and O, respectively, and $E^0_{O/R}$ is the standard potential. Limiting currents are calculated using the equation:

$$i_{l,O/R} = \pm 0.0165 nFDC^b_{O/R} Re^{0.86} Sc^{0.33} / d \qquad (20)$$

where the sign depends on whether the reaction is in the forward (+) or reverse (-) direction, *F* is Faraday's number, *D* is the diffusivity of the redox species, $C^b_{O/R}$ is the bulk concentration of *O* or *R*, as appropriate, *Re* is the Reynolds number ($Re=Vd/\eta$), Sc is the Schmidt number ($Sc=\eta/D$), d is the channel diameter, *V* is the flow velocity, and $\eta$ is the kinematic viscosity.

An important point that needs to be emphasized again is that the maximum contribution that any given radiolytic species can make to the *ECP* is roughly proportional to its concentration. Thus, in BWR simulations the concentrations of $H_2$, $O_2$, and $H_2O_2$ are calculated to be orders of magnitude greater than any other radiolytic species and hence only these three need be considered. In the case of PWR primary HTCs, our previous modeling work suggests that aquated electrons, H atoms, and OH radicals may be significant species in regions of very high-energy dose rate (e.g. near the fuel). However, no electrochemical kinetic data exist for these reactions and hence they cannot be incorporated at this time.

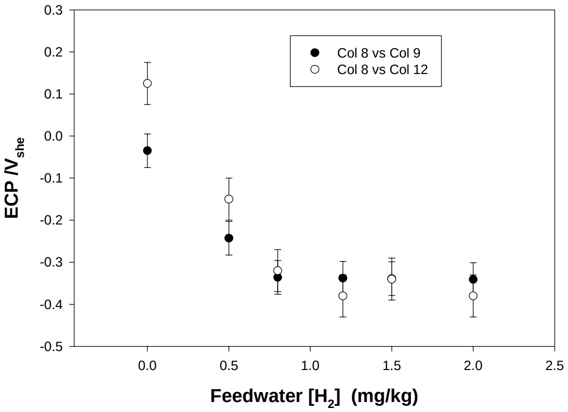

**Figure 2.** Comparison of calculated and measured *ECP* for the Leibstadt BWR. The "measured" data were acquired in a test cell attached to the recirculation piping.

The accuracy of the Mixed Potential Model has been evaluated by comparing calculated *ECP* values for Type 304 SS against measured BWR plant data [D. D. Macdonald, Corrosion, **48**, 194 (1992)]. While modeling of the *ECP* in BWR primary coolant circuits will be discussed at length later in this section, a brief discussion of some of the data is appropriate at this point. Thus, the most comprehensive comparison is probably that which employed data obtained during a Hydrogen Water Chemistry (HWC) mini-test at the Leibstadt BWR in Switzerland (Figure 2). The reactor water chemistry modeling and the prediction of the *ECP* was carried out in a “double blind” manner (i.e., we did not have access to the plant [$O_2$], [$H_2$], or *ECP* data prior to submission of our calculations and the contractor did not have access to our calculations while performing the mini-test). We were, of course, provided with the flow velocity, hydrodynamic diameter, and temperature data for the test system. The calculated and measured (plant)

*ECP* data for this case are summarized in Figure 2. Excellent agreement is obtained in systems to which hydrogen had been added, with the measured and calculated *ECP* values agreeing within the combined uncertainty levels. In the normal water chemistry case ($[H_2] = 0$), the measured *ECP* is significantly higher than the calculated value. This is almost certainly due to the presence of hydrogen peroxide in the coolant, which was not measured by the personnel conducting the HWC mini-test. Accordingly, we were unable to input a value for $[H_2O_2]$ into the MPM. However, if we use the calculated values for $[H_2]$, $[O_2]$, and $[H_2O_2]$ obtained from RADIOCHEM, excellent agreement is obtained.

At this point, it is of interest to explore the impact that oxygen and hydrogen peroxide are predicted to have on the *ECP* under typical PWR primary circuit conditions. This is done in Figure 9 for the system parameter values as summarized in the caption. In the case of both oxygen and hydrogen peroxide, the *ECP* is predicted to be displaced in the positive direction for $[O_2]$ or $[H_2O_2]$ greater than 0.001 mg/kg (1 ppb). Below this concentration, the *ECP* is dominated by the hydrogen electrode reaction. At high oxidant concentrations (> 0.1 mg/kg), the stronger oxidizing power of $H_2O_2$ becomes evident, in that the *ECP* is progressively displaced to more positive values compared with that for oxygen as the oxidant concentration is increased. The critical oxidant concentration of 1μg/kg (1ppb) at which the *ECP* is displaced from the hydrogen electrode behavior is in good semi-quantitative agreement with experimental data obtained from laboratory studies by Bertuch, et.al. [A. Bertuch, J. Pang, and D. D. Macdonald, "The Argument For Low Hydrogen and Lithium Operation in PWR Primary Circuits", *Proc. 7th Int'l. Symp. Env. Deg. Mat. Nuc. Pwr. Sys. – Water Reactors*, **2**, 687-697 (August 1995)].

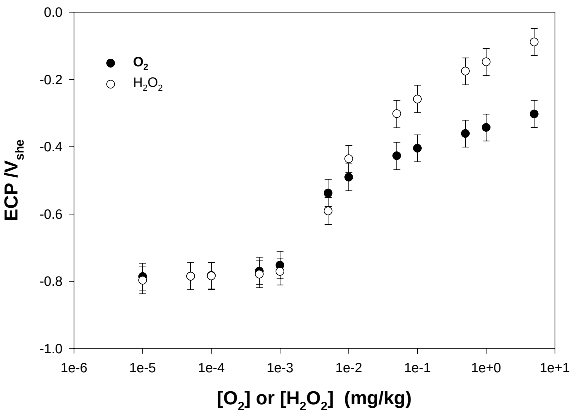

**Figure 3.** Calculated *ECP* vs. $[O_2]$ or $[H_2O_2]$ for a simulated PWR coolant system. T = 320 °C, $[H_2]$ = 25cc(STP)/kg($H_2O$), [B] = 1000 mg/kg, [Li] = 2 mg/kg, pH = 7.36, flow velocity = 100 cm/s, channel hydrodynamic diameter = 100 cm.

Finally, we note that, at least for BWR coolant conditions, and possibly for PWR primary conditions, also, when the *ECP* is not "clamped" by the hydrogen electrode reaction, the corrosion potential is a sensitive function of the hydrodynamic conditions in the channel. This sensitivity to flow arises because the hydrodynamic conditions control the rate of mass transport of the redox species to the metal surface. This is an extremely important issue when comparing the calculated *ECP* with laboratory and plant data, because the measurements are seldom carried out in a channel that is well characterized hydrodynamically. Indeed, a well-characterized channel should be a prerequisite for performing measurements of this type.

### Impact of Radiolysis in the Containment Pool

The computer code FOCUS, which was developed to describe the radiolysis of water and the accumulation of damage due to stress corrosion cracking in Boiling Water Reactors (BWRs) and which is outlined above, was modified to calculate the concentrations of oxygen, hydrogen peroxide, and hydrogen in the containment pool as a function of γ-dose rate, pH, and temperature. While this is a "stop gap" measure, given the lack of resources available to develop a code designed to specifically model the pool, it does yield useful information that provides a qualitative indication of the likely impact of radiolysis on the chemistry of the containment pool after a LOCA. Scoping calculations are summarized in Table 3, in which the concentrations of hydrogen peroxide, oxygen, and hydrogen are calculated for a temperature of $30^oC$ as a function of the ambient oxygen concentration (that concentration that would exist due to equilibrium with the ambient atmosphere in the absence of radiolysis), pH, and γ-dose rate. Calculations were also carried out at temperatures of $60^oC$ and $90^oC$ with broadly similar results. In the interest of brevity, they will not be presented at this time.

**Table 3**. Preliminary calculation of the generation of hydrogen peroxide, oxygen, and hydrogen in water at $30^oC$ as a function of ambient oxygen concentration (concentration in the absence of radiolysis), pH, and γ-dose rate.

| **$O_2$ Conc** (ppm) | **pH** | **γ-Dose Rate** (rad/s) | **$[H_2O_2]$** (ppb) | **$[O_2]$** (ppb) | **$[H_2]$** (ppb) |
|---|---|---|---|---|---|
| 0.1 | 8 | 10 | 44.00518 | 73.38579 | 1.91507 |
| | | 100 | 58.57714 | 85.27291 | 4.34055 |
| | | 1000 | 83.31808 | 116.1293 | 9.83723 |
| | | 10000 | 129.3054 | 168.6386 | 21.76393 |
| | | 100000 | 756.4755 | 862.5814 | 151.4454 |
| | 9 | 10 | 43.90286 | 73.38271 | 1.91325 |
| | | 100 | 58.43296 | 85.26128 | 4.33657 |
| | | 1000 | 83.13144 | 116.0977 | 9.83043 |
| | | 10000 | 137.4481 | 181.3297 | 22.55719 |
| | | 100000 | 756.297 | 863.5652 | 151.582 |
| | 10 | 10 | 43.89336 | 73.38182 | 1.91308 |
| | | 100 | 58.41952 | 85.25942 | 4.3362 |
| | | 1000 | 83.11398 | 116.0935 | 9.82978 |
| | | 10000 | 129.0472 | 168.6263 | 21.75823 |
| | | 100000 | 756.278 | 863.6576 | 151.595 |
| | 11 | 10 | 43.89242 | 73.38173 | 1.91306 |
| | | 100 | 58.41819 | 85.25923 | 4.33616 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
|  |  | 1000 | 83.11225 | 116.0931 | 9.82972 |
|  |  | 10000 | 137.4217 | 181.3244 | 22.55634 |
|  |  | 100000 | 756.276 | 863.6668 | 151.5963 |
| 1 | 8 | 10 | 214.5571 | 720.4191 | 3.60908 |
|  |  | 100 | 401.6951 | 677.9821 | 9.53419 |
|  |  | 1000 | 483.1018 | 722.171 | 20.17785 |
|  |  | 10000 | 576.0389 | 834.347 | 43.23481 |
|  |  | 100000 | 1171.148 | 1504.855 | 205.1361 |
|  | 9 | 10 | 214.5038 | 720.2722 | 3.60841 |
|  |  | 100 | 401.4674 | 677.7833 | 9.5308 |
|  |  | 1000 | 482.7655 | 721.9559 | 20.16937 |
|  |  | 10000 | 575.5655 | 834.1186 | 43.2132 |
|  |  | 100000 | 1170.635 | 1505.187 | 205.1646 |
|  | 10 | 10 | 214.4986 | 720.256 | 3.60835 |
|  |  | 100 | 401.4446 | 677.7611 | 9.53047 |
|  |  | 1000 | 482.7322 | 721.9315 | 20.16856 |
|  |  | 10000 | 575.515 | 834.0901 | 43.21096 |
|  |  | 100000 | 1170.584 | 1505.218 | 205.1673 |
|  | 11 | 10 | 214.498 | 720.2544 | 3.60834 |
|  |  | 100 | 401.4424 | 677.7588 | 9.53044 |
|  |  | 1000 | 482.7288 | 721.9291 | 20.16848 |
|  |  | 10000 | 575.5104 | 834.0874 | 43.21076 |
|  |  | 100000 | 1170.579 | 1505.221 | 205.1676 |
| 8 | 8 | 10 | 390.266 | 6020.668 | 4.60369 |
|  |  | 100 | 1884.806 | 5619.741 | 20.20714 |
|  |  | 1000 | 3166.904 | 5229.377 | 47.54566 |
|  |  | 10000 | 3579.936 | 5380.753 | 91.93316 |
|  |  | 100000 | 4627.551 | 6649.682 | 398.6037 |
|  | 9 | 10 | 390.2369 | 6020.403 | 4.60325 |
|  |  | 100 | 1884.622 | 5619.026 | 20.20429 |
|  |  | 1000 | 3166.315 | 5228.681 | 47.53422 |
|  |  | 10000 | 3579.17 | 5380.175 | 91.89964 |
|  |  | 100000 | 4626.253 | 6648.662 | 398.4206 |
|  | 10 | 10 | 390.2337 | 6020.374 | 4.60321 |
|  |  | 100 | 1884.603 | 5618.949 | 20.20402 |
|  |  | 1000 | 3166.254 | 5228.605 | 47.53312 |
|  |  | 10000 | 3579.093 | 5380.112 | 91.89642 |
|  |  | 100000 | 4626.123 | 6648.559 | 398.4024 |

| | | | | | |
|---|---|---|---|---|---|
| | 11 | 10 | 390.2334 | 6020.371 | 4.6032 |
| | | 100 | 1884.601 | 5618.941 | 20.20399 |
| | | 1000 | 3166.248 | 5228.598 | 47.53301 |
| | | 10000 | 3579.085 | 5380.106 | 91.8961 |
| | | 100000 | 4626.11 | 6648.549 | 398.4006 |

Of particular interest is the hydrogen peroxide concentration, because this species is a strong oxidizing agent. The calculations indicate that the $H_2O_2$ concentration is a very strong function of the γ-dose rate and ambient oxygen concentration, as expected, but is predicted to be insensitive to pH. At high ambient oxygen concentration (8ppm) and high γ-dose rate (100,000rad/s), the hydrogen peroxide concentration is predicted to exceed 4ppm. Likewise, the concentrations of oxygen and hydrogen are also predicted to be sensitive functions of the γ-dose rate (in particular) and oxygen concentration, but not of pH. One interesting prediction is that as the ambient oxygen concentration is increased, the concentration of hydrogen is also found to increase, which is counter-intuitive. We currently do not know whether this latter prediction is "real", in that it arises from the radiolysis mechanism, or whether it is an artifact that is produced by attempting to apply a model to describe a scenario for which it was never intended.

Assuming that the predictions are qualitatively correct, it is evident that radiolysis can have a major impact on the chemistry of the containment pool, if γ-dose rate can rise to the $10^4$ to $10^5$rad/s level through entrapment of neutron-activated corrosion products and fission products from failed fuel in the debris bed of the pool. The concentration of $H_2O_2$ is sufficiently high that the redox potential is expected to be correspondingly high. Unfortunately, the code FOCUS does not yield the redox potential of the solution, only the corrosion potential of stainless steel in contact with the environment is calculated. While both the redox potential and the corrosion potential (*ECP*) are mixed potentials, their values in the same environment can be greatly different, depending upon the kinetics of the charge transfer reactions that occur at the surfaces of platinum (the substrate that is normally used for defining the redox potential) and the steel, respectively. Thus, an unequivocal resolution of this issue will require the following:

- Development of a radiolysis code specifically for a containment pool. This model should incorporate boric acid/LiOH + TSP (tri-sodium phosphate) +TSB (tetra-sodium borate) modules for estimating the pH. The model should be calibrated/evaluated against laboratory experiments to establish efficacy.
- A thorough analysis should be carried out to estimate the likely γ-dose rates in the containment pool as a function of time after a LOCA in a PWR. The contribution of α-dose rate from fission products also needs to be evaluated. The latter is completely ignored in the present analysis and the former (γ-dose rate) is little more than a guess. No information of guidance on this subject could be found in the open literature.
- A better database for the kinetics of the hydrogen electrode reaction, the oxygen electrode reaction, and the hydrogen peroxide electrode reaction needs to be established. Some of the "raw" data are already in the literature, but the information is incomplete and the data are generally not in a form that is readily

interfaced with radiolysis/redox potential models. In some cases, however, the required data must be experimentally measured.

Given the above, it is useful at this point to speculate on the likely chemical effects that radiolysis might have on the containment pool chemistry. Thus, the solubility of species that are electroactive themselves (e.g., $FeOOH$) or yield species that are electroactive ($Fe^{2+}$, $Fe^{3+}$) generally depend upon the redox conditions of the environment. Thus, we may write as the solubility reactions for $FeOOH$ as

$$FeOOH + 3H^+ = Fe^{3+} + 2H_2O \qquad (21)$$

which clearly is not an electrochemical reaction and hence does not depend upon the redox conditions, but if the environment is sufficiently reducing, such that $Fe^{2+}$ is stable, the reaction becomes

$$FeOOH + 1/2H_2 + 2H^+ = Fe^{2+} + 2H_2O \qquad (22)$$

The equilibrium concentration of $Fe^{2+}$ may be written as

$$[Fe^{2+}] = p_{H_2}^{1/2}[H^+]^2 e^{-\Delta G_2^0/RT} \qquad (23)$$

where $p_{H_2}$ is the partial pressure of hydrogen and $\Delta G_2^0$ is the change in standard Gibbs energy for Reaction (22). Clearly, as written, the solubility of $FeOOH$ depends upon the hydrogen partial pressure and pH and, since the coolant in a LOCA contains hydrogen [approx. 25 cc/kg ($H_2O$) in the virgin coolant], the partial pressure of hydrogen after the LOCA becomes important (as does the pH), if the solubility is to be accurately calculated. However, when the hydrogen is released in a LOCA, the gas space presumably contains a mixture of $H_2$ and $O_2$, with $[H_2]$ being below the explosive limit, such that the solubility cannot be defined by Equation (3), because the system is not at equilibrium. Instead, the system is non-equilibrium in nature and a different approach must be used to estimate the solubility.

The dissolution Reaction (22) may be written in slightly different form as:

$$FeOOH + 3H^+ + e^- = Fe^{2+} + 2H_2O \qquad (24)$$

for which the concentration of $Fe^{2+}$ can be written as:

$$[Fe^{2+}] = [H^+]^2 e^{F(E_{24}^0 - E_h)/RT} \qquad (25)$$

In this expression, $E_{24}^0 = -\Delta G_{24}^0 / F$ is the standard potential for Reaction (24), $\Delta G_{24}^0$ is as previously defined, $F$ is Faraday's constant, $R$ is the universal gas constant, and $T$ is the Kelvin temperature. The parameter $E_h$ is the redox potential. This potential cannot be calculated from equilibrium thermodynamics, because the system is not at equilibrium, as noted above, due to the simultaneous generation of $H_2$, $O_2$, and $H_2O_2$, among other products, by the radiolysis of water. If the system was at equilibrium, the partial pressures of oxygen and hydrogen would satisfy

$$p_{H_2} p_{O_2}^{1/2} = e^{\Delta G^0_{H_2O}/RT} \tag{26}$$

where $\Delta G^0_{H_2O}$ is the standard Gibbs energy of formation of water. At 25°C (298.15 K), $\Delta G^0_{H_2O}$ = -237,178J/mol. Thus, substituting this value for $\Delta G^0_{H_2O}$ into Equation (26) and noting that, $p_{O_2}$ = 0.21atm and $R$ = 8.314J/K.mol, I obtain the hydrogen partial pressure as $p_{H_2}$ = 6.12x10$^{-42}$atm, which is the partial pressure of hydrogen in equilibrium with atmospheric oxygen and liquid water under the stated conditions. This partial pressure of hydrogen is orders of magnitude lower than that in the confinement volume, post-LOCA, from which we must conclude that hydrogen and oxygen are present simultaneously in the system at highly non-equilibrium concentrations, even though they may be present at well below the explosive limit. The message is that it is not possible to use equilibrium thermodynamic codes to estimate the solubility of electroactive components in non-equilibrium systems, such as that which must exist immediately after a LOCA in a PWR confinement. It is equally clear that calculation of the solubility requires knowledge of the redox potential, $E_h$. The redox potential may be estimated using the Mixed Potential Model (MPM) that was originally developed for calculating corrosion potentials of components in reactor coolant circuits [D. D. Macdonald, A. C. Scott, and P. Wentrcek. "Redox Potential Measurements in High Temperature Aqueous Systems". J. Electrochem., Soc., **128**, 250-257 (1981), D. D. Macdonald, "Viability of Hydrogen Water Chemistry for Protecting In-Vessel Components of Boiling Water Reactors". Corrosion, **48**(3), 194-205 (1992)], as described above. For calculating $E_h$ it is important to note that the potential corresponds to that which would exist when the net current due to all of the redox reactions occurring at a surface is zero. For the $j^{th}$ redox reaction, $R_j = O_j + n_j e^-$, in the system, the partial current density can be represented by the generalized Butler-Volmer equation as (repeated here for convenience):

$$i_j = \frac{e^{b_{a,j}\eta_j} - e^{-b_{c,j}\eta_j}}{\frac{1}{i_{0,j}} + \frac{e^{b_{a,j}\eta_j}}{i_{f,l,j}} - \frac{e^{-b_{c,j}\eta_j}}{i_{r,l,j}}} \tag{27}$$

where $\eta_j = E - E_j^e$ is the overpotential, and $E_j^e$, $b_{a,j}$, $b_{c,j}$, $i_{0,j}$, $i_{f,l,j}$, and $i_{r,l,j}$ are the equilibrium potential, the anodic Tafel constant, the cathodic Tafel constant, the exchange current density, the forward mass transfer-limited current density, and the reverse mass transfer-limited current density, respectively. The equilibrium potential is calculated from the composition of the system with respect to each redox reaction using the Nernst equation, the Tafel constants and the exchange current density must be measured for the reaction of interest, and the mass transfer-limited current densities can be calculated from the mass transfer correlations for the system. Thus, for the net current at the surface of an inert electrode being zero, the following equation results

$$\sum_j \frac{e^{b_{a,j}(E_h-E_j^e)} - e^{-b_{c,j}(E_h-E_j^e)}}{\frac{1}{i_{0,j}} + \frac{e^{b_{a,j}(E_h-E_j^e)}}{i_{f,l,j}} - \frac{e^{-b_{c,j}(E_h-E_j^e)}}{i_{r,l,j}}} = 0 \qquad (28)$$

Equation (28) must be solved for the redox potential, $E_h$. This normally is done by direct substitution or by using the Newton-Raphson iterative technique. It is important to note that, in applying Equation (28), the summation must be made over all redox reactions in the system. Thus, in the present case, the summation should be carried out over $Fe^{3+}/Fe^{2+}$ in addition to $O_2/H_2O$, and $H_2/H_2O$, and possible even over reactions involving various radiolytic species, such as $H_2O_2/H_2O$, if their concentrations are significant. An important conclusion from many years of modeling the redox potential and corrosion potential properties of a wide range of physico-electrochemical systems is that the contribution that any given species makes to the redox or corrosion potential is roughly proportional to its concentration. That is why, in modeling nuclear reactor coolant circuits, all radiolysis species except $O_2$, $H_2$, and $H_2O_2$ can be ignored. The same principle holds for a LOCA environment.

It may be argued that, if there is sufficient hydrogen in the water that $Fe^{2+}$ is the predominant dissolved species and that the stable phase is not $FeOOH$, but is $Fe_3O_4$ or even $Fe(OH)_2$ (see Issue 4 below), then the reaction of interest should be

$$Fe(OH)_2 + 2H^+ = Fe^{2+} + 2H_2O \qquad (29)$$

This argument would be valid, if the system was at equilibrium but, as shown above, we are dealing with a system that is far from equilibrium. Thus, in my opinion, the only rational way of modeling the chemistry of the system is in terms of the non-equilibrium redox potential and not in terms of equilibrium concepts.

There are a number of points that need to be made at this point:

- Precipitation, particularly if it occurs by rapid cooling and/or flashing, rarely results in an equilibrium product. Instead, the precipitate that forms is that which is least hindered kinetically in its formation and not that which is thermodynamically the most stable.
- For any given set of conditions, the most unstable solid exhibits the highest solubility. Thus, from the Second Law of Thermodynamics, the least stable form will dissolve to form a super saturated solution with respect to the more stable form, resulting in the precipitation of the latter. On the other hand, the least stable form may convert to the more stable form via a solid state reaction, although these are generally very slow at the temperatures of interest in this analysis.
- To ensure that a system is at equilibrium, the solubility should be approached from both sides of an independent variable (e.g., redox potential, pH, temperature). Furthermore, before any equilibrium model calculations can be believed or

accepted, the models must be bench marked against appropriate experiments to determine efficacy.

While this report was being prepared, the author and his colleagues prepared a radiolysis/ECP code that incorporates a boric acid/lithium hydroxide solution chemistry module and a radiolysis model that incorporates reactions for the oxidation of ambient air nitrogen to nitric acid and other nitrogen species in solution, in addition to the water radiolysis model outlined above. The code also incorporates the mixed potential model described above for calculating the corrosion potential (*ECP*) of stainless steel, using kinetic parameters that had been previously developed for modeling the electrochemistry of Boiling Water Reactor primary coolant systems.

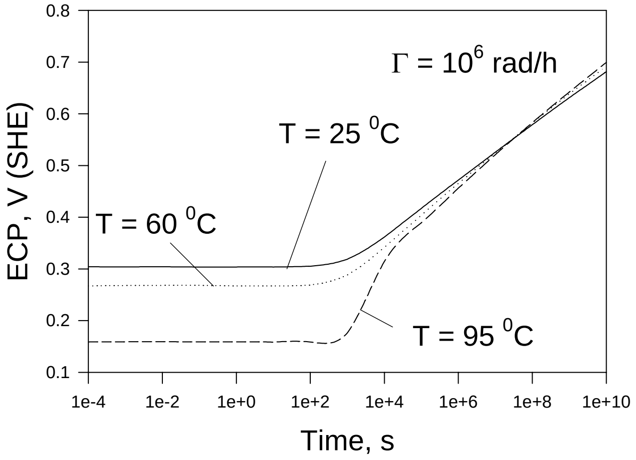

**Figure 4.** Predicted corrosion potential (*ECP*) for stainless steel as a function of time and temperature for a gamma photon dose rate of $10^6$rad/hr. Solution composition: [B] = 2800ppm, [Li] = 2ppm, $p_{O2}$ = 0.2atm, $p_{N2}$ = 0.8atm, $[H_2]_{init}$ = 0ppm, and $[H_2O_2]_{init}$ = 0ppm.

Scoping calculations using this code are summarized in Figures 4 to 6 for a solution of 2800mg/L boron (as boric acid) + 2mg/L lithium (as LiOH) in equilibrium with ambient air (0.2atm $O_2$ + 0.8atm $N_2$) as a function of irradiation time, temperature, and gamma-photon dose rate. The initial concentrations of hydrogen and hydrogen peroxide were assumed to be zero. As shown in Figure 4, for a dose rate of $10^6$rad/hand for all temperatures the ECP begins to increase after about 1000s (17 minutes) due to the initial production of $H_2O_2$ and subsequent acidification of the solution. Note that, at shorter times, the ECP is predicted to become more negative with increasing temperature. This is a well-established trend in corrosion science. Note also that, at long times, the ECP is insensitive to temperature. In this case, the ECP is dominated by the hydrogen peroxide formed by radiolysis and the nitric acid that results from the radiolytic oxidation of nitrogen from the ambient air.

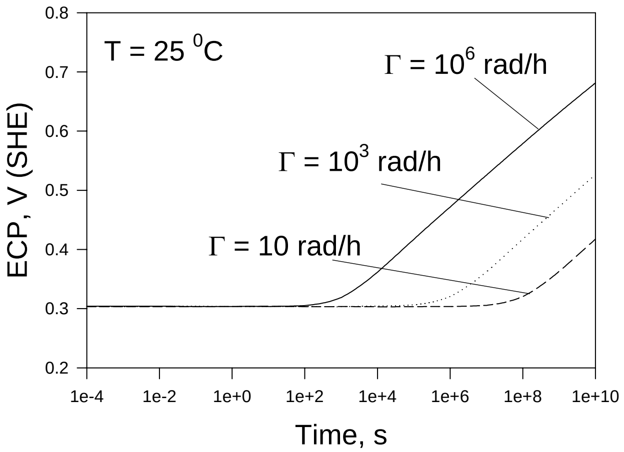

**Figure 5.** Predicted corrosion potential (ECP) for stainless steel as a function of time and gamma photon dose rate for [B] = 2800ppm, [Li] = 2ppm, $p_{O2}$ = 0.2atm, $p_{N2}$ = 0.8atm, $[H_2]_{init}$ = 0ppm, and $[H_2O_2]_{init}$ = 0ppm. T = 25°C.

As expected, the time at which the ECP is predicted to increase is a sensitive function of the dose rate, as shown in Figure 5. Thus, for a dose rate of $10^6$rad/h, the ECP at 25°C is predicted to increase after about 100s, but for a dose rate of 10rad/h no change is predicted until after about one year. Interestingly, for long times, the rate at which the ECP increases is predicted to be insensitive to the dose rate, a finding whose origin is not immediately apparent.

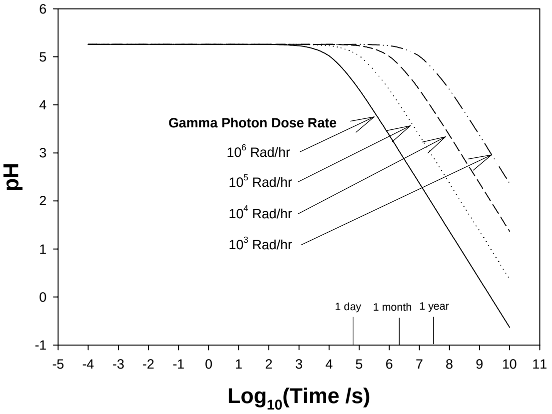

**Figure 6.** Predicted pH as a function of time and gamma photon dose rate for [B] = 2800ppm, [Li] = 2ppm, $p_{O2}$ = 0.2atm, $p_{N2}$ = 0.8atm, $[H_2]_{init}$ = 0ppm, and $[H_2O_2]_{init}$ = 0ppm. T = 25°C.

As noted above, the model predicts that the containment pool solution will become acidified due to the radiolytic oxidation of dissolved nitrogen from the atmosphere to nitric acid, a process that can be written in overall form as

$$N_2 + H_2O + 5[O] \rightarrow 2HNO_3$$

where the species in square brackets represents an oxidizing species derived from the radiolysis of water. The model predicts that, even in the presence of strongly buffering 2800mg/L of boron as boric acid + 2mg/L of lithium as lithium hydroxide, radiolytic production of nitric acid overwhelms the buffer in a time that is as short as a few tens of minutes, provided that the dose rate is sufficiently high. At lower dose rates, longer times are required to overwhelm the buffer, but it is predicted to be overwhelmed within times that are relevant to PWR LOCA analyses, even for dose rates as low as 1000rad/h.

Although the model does not incorporate other buffer systems that exist in containment (TSP, TSB) or captures the complexity of the containment pool chemistry, it does demonstrate that radiolytic effects can not and should not be ignored. Furthermore, the changes predicted in the ECP for stainless steel reflect large changes in the redox properties of the pool that will surly have an important impact on pool chemistry.

### 5.2. Co-Precipitation of Other Species with FeOOH, AlOOH, etc.

Co-precipitation is a phenomenon that can have a profound impact on the composition of a precipitated phase. Indeed, great use is made of this phenomenon in separation science, particularly in radiochemistry. Thus, it is possible that the precipitation of *AlOOH* will co-precipitate *FeOOH*, and vice versa, even though conditions are not right for the precipitation of the co-precipitated phase alone. To my knowledge, no thermodynamic equilibrium code is capable of predicting co-precipitation phenomena and, hence, this phenomenon needs to be explored experimentally. This topic is discussed further below.

### 5.3. Ostwald Ripening

Once a precipitate forms, usually as a floc, Ostwald Ripening may occur, in which the precipitate densifies by losing water and larger crystals grow from smaller crystals, because the latter have higher solubility. Fundamentally, this latter effect is due to the Gibbs-Thompson effect, which stipulates the dependence of the surface free energy ($\mu_r^0$) on the radius of curvature (*r*) as:

$$\mu_r^0 = \mu_\infty^0 + \frac{A}{r} \tag{30}$$

where A is a constant and $\mu_\infty^0$ is the Gibbs surface free energy of a flat surface (infinite radius of curvature). Thus, as *r* decreases, the Gibbs energy of the surface becomes larger and the equilibrium concentration of dissolved products increases. Thus, the solution becomes super-saturated with respect to a surface of larger radius, *r*, and hence precipitation occurs on that surface via the dissolution of the smaller particles. That is, larger particles tend to grow at the expense of smaller particles. Additionally, precipitates frequently become more mechanically resilient after Ostwald Ripening, with the result that they are easier to filter. However, the same property causes the precipitate to be more effective at blocking filters, which is the concern in a LOCA scenario. Ostwald Ripening of the precipitated phases in a LOCA needs to be clearly understood when designing and evaluating filters.

One other process plays an important role in “Ostwald ripening” and that is chemical reaction to form a new phase. For example, Ostwald ripening of a mixed precipitate, such as $Fe(OH)_2$ and $Ni(OH)_2$ will generally result in the formation of the mixed oxide, $NiFe_2O_4$, which has the structure of magnetite (i.e., a spinel) with Fe(II) being replaced by Ni(II). A huge number of reaction examples of this type exist, and indeed they are used to synthesize a wide range of materials, usually under hydrothermal conditions to obtain rapid reaction rates.

### 5.4. Schikorr Reaction Generates Hydrogen *In Situ*.

The Schikorr reaction describes the conversion of ferrous hydroxide, which is the immediate precipitated product of $Fe^{2+}$ hydrolysis, results in the conversion of $Fe(OH)_2$ into magnetite ($Fe_3O_4$):

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O \qquad (31)$$

This reaction not only forms a hard, crystalline deposit of black magnetite, but it produces one mole of hydrogen for every mole of magnetite formed. The hydrogen can have a profound impact on the redox potential of the system, and hence upon the solubility of those phases that are electroactive (i.e., dissolve with a change in oxidation state) – see Issue 1, above. This reaction has been recognized for many decades as being of great importance in boiler water chemistry and corrosion phenomena and, indeed, evidence suggests that the hydrogen that is produced is responsible for the hydrogen embrittlement of steels. Calculations need to be made as to how much hydrogen may be generated and what the consequences of that hydrogen may be for the redox potential assuming realistic values for $Fe^{2+}$ [and hydrolyzed Fe(II) ions] in the coolant at the point of a LOCA. The author wishes to stress that there are many reactions that exist in the $Fe/H_2O$ system (and indeed in the $Ni/H_2O$ and $Cr/H_2O$ systems) that are "Schikorr-like" and that may result in the conversion of hydroxides into oxides with the concomitant generation of hydrogen. These reactions need to be defined within the LOCA context and included in any discussion of chemical effects.

### 5.5. PZC and Coagulation

Certain aspects of the precipitation and coagulation of particles in aqueous environments are well understood, including the role played by the zeta potential and the PZC (pH of zero charge). Thus, all oxide/oxyhydroxide/hydroxide surfaces are amphorteric; that is, they undergo acid/base reactions to produce a surface charge. Thus, at sufficiently low pH (sufficiently high $H^+$ activity), surface hydroxide groups are protonated, $S—OH + H^+ \rightarrow S—OH_2^+$, whereas at a sufficiently high pH, deprotonation occurs, $S—OH + OH^- \rightarrow S—O^- + H_2O$, where S designates the surface. Thus, at some pH value, there will be equal populations of protonated and deprotonated hydroxyl groups on the surface or all groups will be the charge neutral, S—OH. In either case, the surface will have a net zero charge. This pH is known as the PZC (pH of zero charge). Thus, for pH < PZC, the surface will be positively charged, but for pH > PZC, the surface is negatively charged. The variation of the surface charge with pH for two different surfaces (A and B) is shown schematically in Figure 1. The true variation is sigmoid in shape (without the sudden changes in slope as shown) and the PZC is indicated by the pH at which the curve crosses the horizontal axis ($\sigma = 0$). The charge saturates at high and low pH, because there is a fixed density of adsorption sites on the surface, corresponding to the density of S—OH groups. A rough estimate of the density of sites is $1nmol/cm^2$, giving a charge density at saturation of $97\mu C/cm^2$.

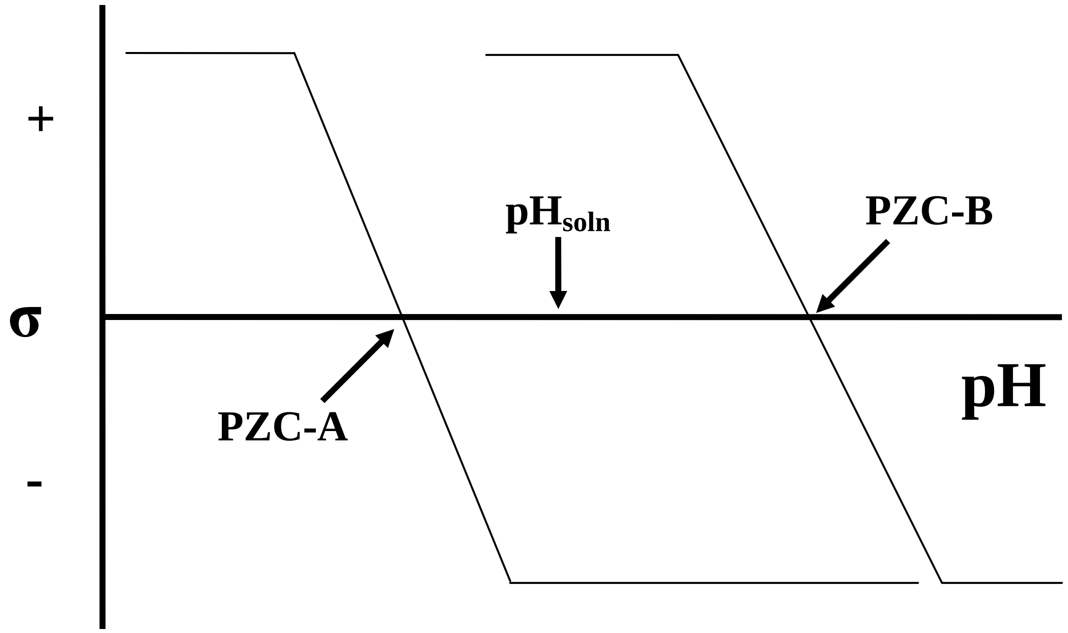

**Figure 7:** Schematic plot of surface charge density versus pH for two surfaces in contact with the same aqueous solution.

The importance of the surface charge that forms spontaneously on an oxide surface is that: (1) An electrical double layer forms in the solution side of the interface, such that the excess charge in the double layer is equal, but opposite in sign, to that on the surface. (2) The PZC of any given surface depends upon the identity of the substrate, such that different surfaces in an aqueous solution of a given pH may be oppositely charged (Figure 7, where the surface charge of A at $pH_{soln}$ is negative while that on B at the same pH is positive. Thus, the excess charge in the double layer on A is positive, while that on B is negative. Clearly, in this case, a coulombic attraction exists between the surfaces and, if the surfaces are those of particulates, the particles will coagulate. If, on the other hand, the system comprises like particles, such that all have the same charge (including sign),or if the pH of the solution containing unlike particles lies outside of the region defined by PZC-A ↔PZC-B, Figure 1, the electrical double layers repel one another and the dispersion is stable and precipitation will not occur. However, if the distance from the surface over which the double layer exists can be shrunk, the particles may approach one another to sufficiently small distances that van der Waal forces overcome the electrostatic repulsion and coagulation occurs.

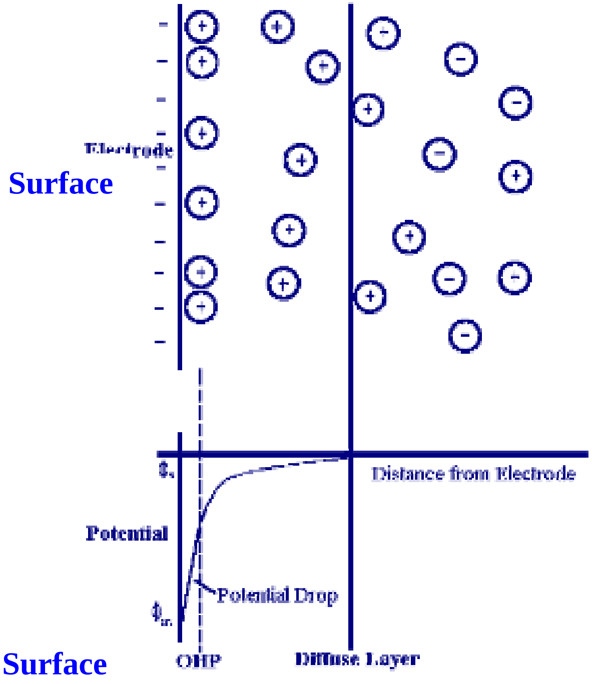

**Figure 8:** Schematic representation of the electrical double layer in the solution side of an oxide/solution interface.

The double layer comprises two layers (actually, three, but two is sufficient to facilitate the present discussion). In this simplified picture, closest to the surface, there exists an adsorbed layer of hydrated ions have a charge that is opposite to that due to the ionized or protonated hydroxyl groups, which is determined by the pH. In the case shown, this layer of adsorbed ions, the centers of which define the Outer Helmholtz Plane (OHP), only partially neutralizes the negative charge on the hydroxyl groups, so that the potential at the OHP is less than that in the bulk solution, $\varphi_s$. Outside of this plane, the relative concentrations of positive and negative ions is determined by electrostatic interaction and thermal randomization. Solution of Poisson’s equation yields a roughly exponential (actually a hyperbolic sine) dependence of electrostatic potential on distance in the “diffuse layer”, as indicated in Figure 8. The characteristic length is the distance from the surface to the point where the potential drop across the diffuse layer has decayed to *1/e* of the value at the OHP.

The characteristic length of the diffuse layer depends inversely upon the square root of the ionic strength of the medium, which is defined as

$$I = 0.5\sum_i z_i^2 c_i \qquad (32)$$

where $z_i$ is the charge number of the ion $i$, and $c_i$ is its concentration, with the summation being carried out over all ions in the system. If the solution is 0.1 M NaCl, for example, Equation (1) yields an ionic strength of 0.1 M. On the other hand, if the electrolyte is 0.1 M $Al_2(SO_4)_3$ (Alum), the ionic strength becomes 1.5, fifteen times that of a NaCl solution of equivalent concentration. The characteristic length of the diffuse layer is then reduced by a factor of nearly 4 and this reduction is sufficient to cause coagulation and precipitation of colloidal particles (e.g., clay, organic matter, and polymeric hydrolyzed ions), due to van der Waal attraction, followed by Ostwald ripening. Additionally, the hydrolysis and polymerization of Al(III) produces a gelatinous precipitate that co-precipitates other matter (ions, colloids, or even particles), as discussed in Issues 2 and 3 above and further discussed below. The above is nothing more or less than the Alum process for clarifying domestic and industrial water supplies and has been practiced for more than 140 years.

An important consequence of coagulation via surface charge effects is the phenomenon of co-precipitation and/or co-coagulation, in which the hydroxides and or oxyhydroxides and oxides of different metals may coagulate together to form, after ripening, mixed oxides, hydroxides and oxyhydroxides. Indeed, this is a well-established route for the synthesis of such materials. If the starting system is a colloidal mixture, then the charges (sign and magnitude) on the different material particles play key roles in determining the form and extent of the co-precipitates. Because the charge (again, the sign and magnitude) are determined by the activity of hydrogen ion in the solution, the pH is a key variable in determining the nature of the product. After a LOCA, it is envisioned that various oxides, oxyhydroxides, and hydroxides of elements, such as Al, Zn, Fe, Si, and Ca, will be present in the system. These oxides, oxyhydroxides, and hydroxides have widely differing PZC values, so that the relative charges on the different particles may change drastically as the pH of the medium is changes. Clearly an understanding of the dynamics of co-precipitation and co-coagulation requires a thorough characterization of the surface charge characteristics of all components in the system.

These concepts must be used to develop an understanding and, eventually, a predictive model for precipitation and coagulation post LOCA. This model should then be combined with a model for Ostwald ripening to provide a quantitative tool for predicting the identities and yield of solid precipitates in a LOCA. The combined model should be capable of predicting the temperature and pH at which precipitation occurs (see Issue 6, below) and the rate of particle growth. The process should begin by first collecting the extensive data that exist in the literature for the PZCs of the materials that are expected to come into contact with water and with one another; if the data are not available, they should be measured using standard techniques. The critical ionic strengths for coagulation should then be measured for the various colloidal systems, from which the van der Waal parameters may be estimated. From there, the rate of precipitation can be modeled as a Brownian motion problem (see collisional theory for gases) by assuming a sticking probability of one. Little attention seems to have been paid to these important factors in the analysis to date, but they provide guidance as to the rate of precipitate formation and may allow formulation of strategies to control the precipitation, so as to avoid clogging of the filters.

## 5.6. γ-AlOOH formation

The hydrothermal formation of boehmite, γ-AlOOH, from $Al^{3+}$ solutions has been studied [see D. D. Macdonald, P. Butler, and D. Owen. "Hydrothermal Hydrolysis of $Al^{3+}$ and Precipitation of Boehmite from Aqueous Solution". J. Phys. Chem., **77**(20), 2474-2479 (1973)], and this work provides useful data on the buffering capacity of that reaction as the precipitate forms. The reader will note that, as the temperature increases, the pH of the solution becomes independent of the initial concentration of $Al^{3+}$ in the system. This may have important implications in modeling the precipitation process. The paper also provides a model for the speciation of the principal polymeric ionic species in the system as hydrothermal precipitation of boehmite ($\gamma$-AlOOH) occurs. For example, starting with a solution of 0.038m $Al^{3+}$ in 1.0 m KCl at an initial pH of 2.59, the principal hydrolysis product is predicted to be the dimer, $Al_2(OH)_2^{4+}$, over the entire temperature range (25°C – 150°C). However, at temperatures above about 125°C, the highly polymerized species, $Al_{14}(OH)_{34}^{8+}$, is predicted to become significant, coincident with the precipitation of boehmite. Thus, this study shows that the hydrothermal precipitation of boehmite, for example, proceeds by the progressive formation of more highly hydrolyzed cationic species with the ratio of O to Al converging onto the ratio that exists in the precipitate (ratio = 2), with some species being preferred for structural reasons. Finally, this paper contains a model, which after updating with later data for the hydrolysis of $Al^{3+}$, should allow accurate simulation of the formation of the oxyhydroxides of aluminum in a LOCA environment.

Similar models have been developed for the precipitation of the oxyhydroxides of iron, but the author is not aware of similar treatments for the thermal hydrolysis of $Zn^{2+}$ and $Ca^{2+}$, for example.

### 5.7. Precipitation on Fibers

I believe that an explanation for the initial precipitation of $\gamma$-AlOOH onto glass fibers might be found in an analysis of the PZCs of the fiber and the precipitating material, with respect to the pH of the solution, and in the impact of ionic strength on the critical lengths of the diffuse layers and their impact, in turn, on the rate of particle agglomeration, as discussed in Issue 5. The viability of this mechanism might be tested by studying the rate of growth on different surfaces (and hence of different surface charge) and from solutions of different ionic strength using a quartz crystal microbalance. This technique is capably of detecting mass changes of nano-grams per square centimeter, is readily applied *in situ*, and can be used over a range of temperatures. The principal challenge will be in obtaining low mass fiber glass samples mounted on the silicon oscillator. Nevertheless, QCM would allow a high throughput in the experiments and would permit the determination of quantitative data for deposit growth rate.

### 5.8. Thermal Hydrolysis of Organic Material

Considerable organic material exists in confinement in a PWR, ranging from paint to plastic insulation. Some of this material would be partially pulverized and rendered into a colloidal form by hydrothermal hydrolysis. The reader should note that the PZC concept also applies to organic particles, so that PZC values for the organic colloids that are produced by the thermo-hydrolysis of the organic materials need to be determined. Thus, organic colloids need to be included in the list of particles that should be explored under Issue 6. It is most important to note that the hydrothermal hydrolysis of organic materials results not only in depolymerization, and hence in the production of particles of micro- to nano-meter dimension, but also in surfaces that are partially oxidized to produce alcoholic (-OH), ketonic (C=O), and acidic (-COOH) moeties, which contribute to defining the acid/base properties of the surfaces and hence the PZC.

Organic species also have an important effect of modifying surfaces by adsorption. In doing so, they may change the surface charge characteristics completely, causing precipitation or inhibiting coagulation. Many of these effects are currently very poorly defined and understood and, hence, are very difficult, if not impossible, to predict from first principle calculation. Those systems that have been studied at any depth tend to be "simple systems", that are of only marginal value to the problem of interest in this work.

### 5.9. Is There a Particle Size That Can Be Tolerated?

Accepting that clogging of the filters most likely would result from the initial formation of colloidal particles followed by coagulation and Ostwald ripening, the question arises: Is there a particle size that can be tolerated? A closely related question concerns the impact of flow velocity and fluid shear rate on the particle size distribution. This issue needs to be explored under realistically simulated LOCA conditions, because presumably there exists a particle size below which the particles will pass through the filter and hence will not impede flow. The formation of larger particles would be discouraged by the high shear rate that tends to inhibit coagulation. However, the current information on this process is very qualitative in nature, whereas quantitative information is required in order to synthesize predictive models. The models would then be used to assess the risk of clogging of the filters (and the pump) for different pump speeds. However, it is doubtful that such a model would yield a definitive answer without calibration using a full mock-up of the pump and filter system.

### 5.10. Why Does a Bimodal Distribution Exist in Particle Size?

A bimodal distribution in particle size commonly indicates parallel growth processes from a common population of nuclei, with the two growth processes occurring at different rates. The different growth rates may reflect different Ostwald ripening rates or a bimodal distribution in the nuclei with regard to surface charge (and hence with respect to agglomeration rate). The latter should be detectable by measuring the particle mobility electrophoretically, in which case a bimodal distribution in mobility should be found. Another method that might be tried is to fractionate the sample using centrifugation at different rotation speeds and then use each fraction as seeds for further growth. If there are two preferred sizes for growth, they might be detected in the final particle size distribution.

### 5.11. Corrosion of Aluminum

The corrosion and passivity of aluminum has been studied extensively and space does not exist here for me to summarize all that is known. Aluminum is a very active metal, particularly at elevated temperature, as indicated by the potential-pH diagram [D. D. Macdonald and P. Butler. "The Thermodynamics of the Aluminum-Water System at Elevated Temperatures". Corros. Sci., **13**, 259-274 (1973)]. The potential-pH diagram displays a large predominance region for the oxyanion aluminate, $Al(OH)_4^-$ that becomes larger with respect to that for $Al^{3+}$ as the temperature increases (reflecting a lower surface charge density for the former than for the latter). At intermediate pH values, there exists a stability region for the oxide, $Al_2O_3$, which passivates the surface.

The formation of passivating oxide films on metal surfaces is well understood in terms of the Point Defect Model (PDM) [D. D. Macdonald, Pure Appl. Chem., **71**, 951 (1999)]. Briefly, the film forms as a bi-layer structure, comprising a defective oxide barrier layer adjacent to the metal and an outer, precipitated layer of $Al(OH)_3$ adjacent to the solution. A point defect model for the passive layer in acidic solutions, where $Al^{3+}$ is the predominant species, is presented below, assuming that the mobile cation in the barrier layer is the metal interstitial. A similar model is easily formulated for the passive film on any metal under the conditions of interest.

The validity of the PDM for describing passivity and the corrosion of passive metals has now been demonstrated by the author and other researchers. The model is capable of accounting for not only the properties of the passive state, but also the transition to the transpassive state, passivity breakdown, and depassivation phenomena. When combined with the generalized Butler-Volmer equation for the cathodic reduction of oxygen and hydrogen evolution, and after imposing the conservation of charge, the resulting mixed potential model (MPM) is capable of calculating the corrosion potential and corrosion rate quantitatively, as has been demonstrated by the author's extensive modeling of corrosion processes in the heat transport circuits of water-cooled nuclear power reactors.

By using a two-component brick wall analogy (red bricks for cations and cation vacancies and blue bricks for oxygen ions and oxygen vacancies), and noting that the minimum unit of the barrier layer is one red brick and one blue brick in adjacent positions, it is apparent that Reactions (1), (3), and (4), Figure 3, are lattice conservative processes (i.e., the barrier layer boundaries do not move with their occurrence), whereas Reactions (2) and (5) are lattice non-conservative processes. Note that the entity $Al_{Al} + \frac{3}{2}V_O^{\bullet\bullet} \equiv \frac{1}{2}Al_2(V_O)_3$ is equivalent to $\frac{1}{2}Al_2O_3$, because vacancies can be regarded as being real species. Experimentally, we know that the barrier layer on a metal achieves a steady-state thickness and, hence, there must exist two non-conservative reactions at the barrier layer interfaces; specifically, the other must be at the barrier layer/outer layer interface. That reaction is Reaction (5), which describes the dissolution of the barrier layer. Thus, in the steady-state, the rates of Reactions (2) and (5) must be equal. The formation of the outer layer is due to precipitation of $Al(OH)_3$ from a super-saturated solution of $Al^{3+}$ that forms via dissolution from thermodynamically less stable sources; namely, aluminum metal via interstitials in the barrier layer and the defective barrier layer, itself, $Al_{1+x}O_{1-y}$. In any event, the outer later forms by precipitation and may contain substantial quantities of other species, such as borate, that are present in the solution.

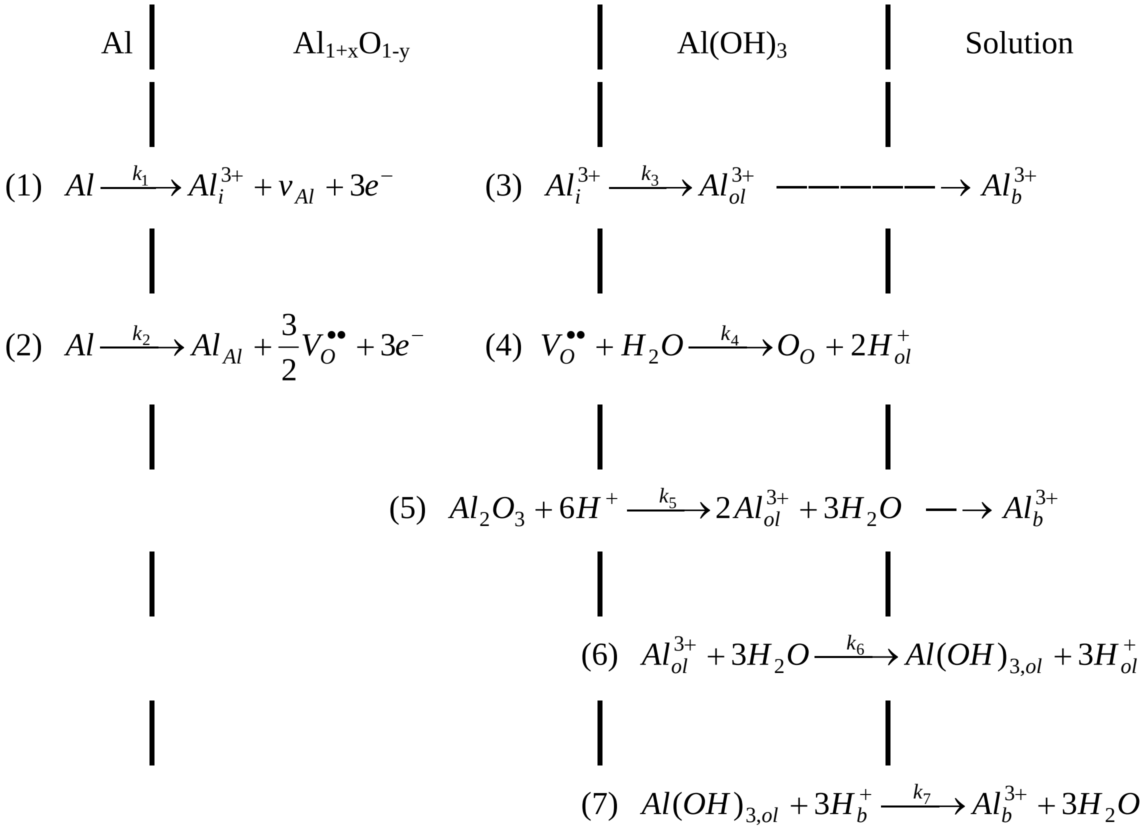

**Figure 9:** Point defect model for the anodic oxidation of aluminum in aqueous solution. The species $Al$, $Al_i^{3+}$, $v_{Al}$, $Al_{Al}$, $V_O^{\bullet\bullet}$, $Al^{3+}$, and $O_O$ represent aluminum metal, an aluminum cation interstitial, a vacancy in the metal substrate, an aluminum cation on the cation sublattice of the barrier layer, an oxygen vacancy on the anion sublattice of the barrier layer, an aluminum cation in solution, and an oxygen anion on a normal anion site on the anion sublattice, respectively. The subscripts "*ol*" and "*b*" designate outer layer and bulk solution locations.

When the outer layer comprises a hydroxide, such as $Al(OH)_3$, which is a good proton conductor, the phenomenon of passivity can be attributed to the barrier layer alone. However, under some conditions, the outer layer forms as a porous oxide, $Al_2O_3$, with the pores being oriented normal to the surface in a more-or-less regular array. In this case, the outer layer may contribute substantially to the interfacial impedance. The pores may be sealed, most commonly by boiling the specimen in water, in which case the outer layer acts as an impervious coating and may completely dominate the corrosion resistance of the substrate. The formation of such a film most commonly occurs under anodizing conditions and sealing is performed to enhance the corrosion resistance of the surface.

The corrosion rate of aluminum is due to Reactions (1) and (2), Figure 3, and may be written as

$$CR = \Omega_{Al}(k_1 + k_2) \quad \text{(cm/s)} \tag{33}$$

where $k_1$ and $k_2$ are the rate constants (mol/cm$^2$.s), as indicated in Figure 3, and $\Omega_{Al}$ is the molar volume of aluminum metal. The corrosion rate may also be expressed in terms of mass per unit area per unit time as:

$$CR = M_{Al}(k_1 + k_2) \quad \text{(g/cm}^2\text{.s)} \tag{34}$$

where $M_{Al}$ is the atomic weight of aluminum. Regardless of which expression is used, it is necessary to determine the rate constants $k_1$ and $k_2$. Partial charge transfer theory and activated complex theory show that the rate constants may be written in more fundamental form as

$$k_1 = k_1^{00} e^{a_1 V} e^{-b_1 L} e^{c_1 pH} \tag{35}$$

and

$$k_2 = k_2^{00} e^{a_2 V} e^{-b_2 L} e^{c_2 pH} \tag{36}$$

where the coefficients *a*, *b*, and *c* are functions of still more fundamental parameters, including the electric field strength, the polarizability of the barrier layer/outer layer interface, and the transfer coefficients for the interfacial reactions, among others, *V* is the voltage (the corrosion potential, in this case), and *L* is the thickness of the barrier layer. Values for these parameters are readily determined by using electrochemical impedance spectroscopy (EIS) [D. D. Macdonald, A. Sun, Priyantha, N., P. Jayaweera, "An Electrochemical Impedance Study of Alloy 22 in NaCl Brine at Elevated Temperature:II. Reaction Mechanism Analysis", J. Electroanal. Chem., **572**, 421-431 (2004)], and hence the corrosion rate may be calculated.

In highly alkaline solutions, corrosion is believed to occur in the transpassive state, in which the metal has been depassivated by the loss of the barrier layer. In this case, the corrosion rate is controlled by the dissolution of the metal in the presence of the precipitated outer layer, which offers only moderate resistance to corrosion. This case has been studied extensively under the DOE program in the 1980s that aimed at developing fuels for aluminum-air batteries for automotive application [D. D. Macdonald, K. H. Lee, A Moccari, and D. Harrington, "Evaluation of Alloy Anodes for Aluminum/Air Batteries I. Corrosion Studies". Corrosion, **44**, 652-657 (1988); S. Real, M. Urquidi-Macdonald, and D. D. Macdonald, "Evaluation of Alloy Anodes for

Aluminum/Air Batteries II. Delineation of Anodic and Cathodic Partial Reactions". J. Electrochem. Soc., **135**(7), 1633-1636 (1988); D. D. Macdonald, S. Real, and M. Urquidi-Macdonald. "Evaluation of Alloy Anodes for Aluminum-Air Batteries III. Mechanisms of Activation, Passivation, and Hydrogen Evolution", J. Electrochem. Soc., **135**(10), 2397-2409 (1988); D. D. Macdonald, S. Real, S. I. Smedley, and M. Urquidi-Macdonald, "Evaluation of Alloy Anodes for Aluminum-Air Batteries IV. Electrochemical Impedance Analysis of Pure Aluminum in 4M KOH at 25°C", J. Electrochem. Soc., **135**(10), 2410-2414 (1988)]. That work produces a model for aluminum dissolution in highly alkaline solutions that involves the stepwise electrochemical discharge of OH onto the metal surface followed by the chemical dissolution of $Al(OH)_4^-$ from the surface. The key question concerns which model to adopt (with or without a barrier layer) for the conditions that prevail in a LOCA.

In my opinion, a quantitative model for calculating the corrosion rate of aluminum, or of any other metal or alloy, could be developed and used to estimate the inventory of aluminum corrosion products in confinement as a function of time during a LOCA. This would require an EIS study of aluminum in various environments as a function of voltage, pH, and temperature, followed by optimization of the Point Defect Model (Figure 3) on the experimental data, in order to extract values for various model parameters. Work on developing a PDM for the corrosion of aluminum has been initiated in the author's laboratory with a visiting student from Spain. The results of this work will be made available to NRC/ANL as they become available.

Similar models may (and in some cases, have been) formulated for the other metals of interest, including iron and zinc. The models are readily available in the literature published over the past twenty years.

## 6. Recommendations

In the light of the issues identified above, a number of recommendations have been formulated that, in the author's opinion, will significantly aid in developing a quantitative understanding of, and a predictive capability for, the chemical processes that might occur during and after a LOCA in confinement of a PWR. The recommendations are supported by a number of publications that are cited in this report, but it is to be understood that the literature review was not exhaustive.

- Equilibrium models must be used with great caution, because the environment produced by a LOCA is unlikely to be at equilibrium, at least during the initial stages. Furthermore, the processes that occur during corrosion, precipitation, and ripening are generally slow, as has been shown in some of the work reviewed during the Kickoff Meeting at ANL. The kinetics of many of these processes are such that the system may still be far from equilibrium as it enters the recirculation system. Accordingly, equilibrium calculations need to be bench-marked to the greatest extent possible against experiment to assess the reliability of the thermodynamic equilibrium codes. This has been done to a significant extent in the present program, but the results are hampered by the lack of consideration of radiolysis and redox effects.

- Given the likelihood that equilibrium models may not be appropriate, emphasis should be placed on developing kinetic models for the precipitation and ripening (coagulation) processes. These models must recognize the most important driving force for coagulation; the charge (sign and magnitude) that develops on the surfaces of particles, as characterized by the zeta potential and the pzc (pH of zero charge). PZC and zeta potential data should be experimentally measured, although many of the required data may be obtained from the enormous literature that exists on the subject. Certainly, extensive data are available for the oxides and oxyhydroxides of iron and aluminum, but data may not be available for various organic entities.

- The possible generation of hydrogen from the Schikorr reaction

  $$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O$$

  and related chemical transformations should be explored, as they might contribute significantly to the inventory of hydrogen in containment immediately after a LOCA and to the inventory of magnetite ($Fe_3O_4$) in the system. On the positive side, the Schikorr reaction will decrease the inventory of gelatinous $Fe(OH)_2$, which may react with other components [e.g., $Si(OH)_4$] to produce mixed oxides/oxyhydroxides, and even mixed hydroxides that may be even more troublesome. This issue can probably be resolved by calculation, using data given in the literature.

- Realistic and viable models for the corrosion of aluminum, iron, and zinc, and of the dissolution of concrete and polymeric materials in contact with hot coolant under a wide range of mass transfer conditions (ranging from impinging jets to quiescent pools) need to be developed that are capable of predicting corrosion rates under realistic LOCA environmental conditions. The models for the metals must incorporate passive dissolution, transpassive dissolution, and active dissolution, as well as delineation of the conditions under which each occurs, as all three processes may occur in a LOCA environment. The models for metallic corrosion must also incorporate the appropriate cathodic partial processes (reduction of oxygen and the evolution of hydrogen). Note that any hydrogen evolved during corrosion must be added to the inventory generated by the Schikorr reaction and to that which was present in the virgin coolant. While estimates have been made of the corrosion rates of various materials, it is unclear that the empirical models used are comprehensive in their coverage of the relevant conditions.

- The hydrothermal hydrolysis of various organic/inorganic coating and insulation materials needs to be explored under conditions that realistically simulate a LOCA. It is expected that hydrothermal hydrolysis will partially de-polymerize polymeric materials, producing materials ranging from particles to gels. These materials need to be screened for their physical and chemical properties and, in particular, for their tendencies to “set” into more resilient forms. The physical properties that need to be explored include the iso-electric points (PZC), zeta potentials, and rheological properties. The propensity for interactions between the various components produced by hydrothermal hydrolysis among themselves and with other materials in the system must be clearly defined.

- The models that are produced to predict corrosion rates and phase properties must be, to the greatest extent possible, deterministic in nature. Thus, a deterministic model is one whose output (prediction) is constrained by the natural laws to that which is physically viable. These constraints are generally the conservation laws, such as the conservation of mass, charge, energy, and momentum. The equivalence laws, such as Faraday's law of the equivalence of mass and charge, or Joule's law of the equivalence of heat and work, are generally part of the constitutive equations of a model. Importantly, in the art of prediction, it is not sufficient for a model to be "mechanism based"; it must be implicitly constrained by the conservation laws, which are a summation of scientific experience. Thus, the researchers working on this program, and who are involved in the process of model building, are urged to ensure that their models are deterministic within the context stated above.

- Development of a radiolysis code specifically for a containment pool is absolutely essential, since the redox potential controls the speciation within the pool. This model should incorporate boric acid/LiOH + TSP (tri-sodium phosphate) + TSB (tetra-sodium borate) modules for estimating the pH. The model should be calibrated/evaluated against laboratory experiments to establish efficacy.

- A thorough analysis should be carried out to estimate the likely γ-dose rates in the containment pool as a function of time after a LOCA in a PWR. The contribution of α-dose rate from fission products also needs to be evaluated. The latter is completely ignored in the present analysis and the former (γ-dose rate) is little more than a guess. No information of guidance on this subject could be found in the open literature.

- A better database for the kinetics of the hydrogen electrode reaction, the oxygen electrode reaction, and the hydrogen peroxide electrode reaction needs to be established. Some of the "raw" data are already in the literature, but the information is incomplete and the data are generally not in a form that is readily interfaced with radiolysis/redox potential models. In some cases, however, the required data must be experimentally measured.

- Possible acidification of the pool by radiolysis is a matter of essential importance and must be explored to ascertain whether unacceptable conditions may develop due to the radiolytic generation of nitric acid from nitrogen in the ambient air. Of all of the recommendations given above, this recommendation and that on including redox effects is by far the most important.

# Appendix 1.

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**EDUCATIONAL BACKGROUND**

B.Sc. (1965) and M.Sc. (1966) in Chemistry, University of Auckland (New Zealand);
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**PROFESSIONAL EXPERIENCE** (past 35 years)

Distinguished Professor of Materials Science and Engineering, 6/2003 – present.
Chair, Metals Program, Penn. State Univ., 6/2001 – 6/2003
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Laboratory Director, Chemistry Laboratory, SRI International, Menlo Park, CA, 3/84 – 4/87
Director and Professor, Fontana Corrosion Center, Ohio State University, 3/79 – 3/84
Sr. Metallurgist, SRI International, Menlo Park, CA, 3/77 – 3/79.
Sr. Research Associate, University of Calgary, Canada, 3/75 – 3/77.
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Integrated Design Technologies
OLI Systems
Electric Power Research Institute
SRI International
Stone & Webster Engineering Co.
Science Applications International Corp.
Framatome
Metallic Power Inc.

Los Alamos National Laboratory

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## PROFESSIONAL ASSOCIATIONS AND HONORS

- Selector of the Kuwait Prize for Applied Sciences, 1985.
- Research Award, College of Engineering, Ohio State University, 1983.
- The 1991 Carl Wagner Memorial Award from The Electrochemical Society.
- The 1992 Willis Rodney Whitney Award from NACE International.
- Chair, Gordon Research Conference on Corrosion, New Hampshire, 1992.
- Member, Board of Visitors, Office of Naval Research.
- W.B. Lewis Memorial Lecture by Atomic Energy of Canada, Ltd., 1993, “in recognition of [his] contributions to the development of nuclear power in the service of mankind”.
- Elected Fellow, NACE-International, 1994.
- Member, USAF Scientific Advisory Board, Protocol Rank: DE-4 (Lieutenant General equivalent), 1993-1997
- Elected Fellow, The Electrochemical Society, 1995.
- Elected Fellow, Royal Society of Canada, 1996. (“National Academy” of Canada).
- Wilson Research Award, College of Earth and Minerals Sciences, Pennsylvania State University, 1996.
- Elected Fellow, Royal Society of New Zealand, 1997. (“National Academy” of New Zealand).
- H. H. Uhlig Award, The Electrochemical Society, 2001.
- U. R. Evans Award, The British Corrosion Institute, 2003.
- Appointed Adjunct Professor, Massey University, New Zealand, 2003.
- Appointed Adjunct Professor, University of Nevada at Reno, 2003.
- Elected Fellow, World Innovation Foundation, 2004.
- Elected Fellow, ASM International, 2005.

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11. ABSTRACT *(200 words or less)*

The NRC and RES has a policy of initiating formal peer reviews for research programs that are on the cutting-edge of technology and will influence important regulatory decisions. Such is the case for the series of research projects that RES has sponsored to resolve GSI-191, "Assessment of Debris Accumulation on PWR Sump Performance," and to inform the NRC's regulatory decisions regarding the potential for chemical by-products to clog sump screens in the post LOCA environment in PWRs.

This report describes the peer review assessment process and summarizes its significant findings. It is important to mention that this peer review is not a consensus review. Each reviewer was asked to provide an individual evaluation based on their particular area of expertise. The research projects addressed by the peer review included integrated chemical effects testing (ICET) conducted at Los Alamos National Laboratory, chemical speciation prediction conducted through the Center for Nuclear Waste Regulatory Analyses at Southwest Research Institute, and accelerated chemical effects head loss testing conducted at Argonne National Laboratory. The peer review evaluated the technical adequacy and uncertainty associated with the RES-sponsored research results, and identified outstanding chemical effects issues. The final assessment reports from the peer reviewers are included as appendices to this report.

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