Westinghouse Non-Proprietary Class 3

WCAP-17211-NP
Revision 0

August 2011

Sump Debris Chemical Effects Relating to LOCA Long-Term Cooling In-Vessel Precipitation Evaluation Models

Westinghouse

WESTINGHOUSE NON-PROPRIETARY CLASS 3

WCAP-17211-NP
Revision 0

Sump Debris Chemical Effects Relating to LOCA Long-Term Cooling In-Vessel Precipitation Evaluation Models

Robert S. Fournier*
System and Equipment Engineering II

Lauren D. Helstosky*
System and Equipment Engineering II

August 2011

William A. Byers*	Materials and Corrosion Technologies
Brett E. Kellerman*	LOCA Integrated Services II
Kyle S. Shearer*	LOCA Integrated Services II
Susan L. Baier*	Systems and Equipment Engineering I
David J. Fink*	LOCA Integrated Services II

Approved: Dawn M. Crytzer*, Manager
LOCA Integrated Services II

This work was performed under PWR Owners Group Project Number PA-ASC-0264

*Electronically approved records are authenticated in the electronic document management system.

Westinghouse Electric Company LLC
1000 Westinghouse Drive
Cranberry Township, PA 16066

LEGAL NOTICE

COPYRIGHT NOTICE

DISTRIBUTION NOTICE

This report was prepared for the PWR Owners Group. This Distribution Notice is intended to establish guidance for access to this information. This report (including Proprietary and Non-Proprietary versions) is not to be provided to any individual or organization outside of the PWR Owners Group program participants without prior written approval of the PWR Owners Group Program Management Office. However, prior written approval is not required for program participants to provide copies of Class 3 Non-Proprietary reports to third parties that are supporting implementation at their plant, and for submittals to the NRC.

PWR Owners Group
Member Participation* for Project/Task PA-ASC-0264 Rev. 2

Utility Member	Plant Site(s)	Participant	
		Yes	No
AmerenUE	Callaway (Westinghouse)	X	
American Electric Power	D.C. Cook 1 & 2 (Westinghouse)	X	
Arizona Public Service	Palo Verde Unit 1, 2, & 3 (CE)	X	
Constellation Energy Group	Calvert Cliffs 1 & 2 (CE)	X	
Constellation Energy Group	Ginna (Westinghouse)	X	
Dominion Connecticut	Millstone 2 (CE)	X	
Dominion Connecticut	Millstone 3 (Westinghouse)	X	
Dominion Kewaunee	Kewaunee (Westinghouse)	X	
Dominion VA	North Anna 1 & 2, Surry 1 & 2 (Westinghouse)	X	
Duke Energy	Catawba 1 & 2, McGuire 1 & 2 (Westinghouse), Oconee 1, 2, 3 (B&W)	X	
Entergy	Palisades (CE)	X	
Entergy Nuclear Northeast	Indian Point 2 & 3 (Westinghouse)	X	
Entergy Operations South	Arkansas 2, Waterford 3 (CE), Arkansas 1 (B&W)	X	
Exelon Generation Co. LLC	Braidwood 1 & 2, Byron 1 & 2 (Westinghouse), TMI 1 (B&W)	X	
FirstEnergy Nuclear Operating Co.	Beaver Valley 1 & 2 (Westinghouse), Davis-Besse (B&W)	X	
Florida Power & Light Group	St. Lucie 1 & 2 (CE)	X	
Florida Power & Light Group	Turkey Point 3 & 4, Seabrook (Westinghouse)	X	
Florida Power & Light Group	Pt. Beach 1 & 2 (Westinghouse)	X	
Luminant Power	Comanche Peak 1 & 2 (Westinghouse)	X	
Omaha Public Power District	Fort Calhoun (CE)	X	
Pacific Gas & Electric	Diablo Canyon 1 & 2 (Westinghouse)	X	
Progress Energy	Robinson 2, Shearon Harris (W), Crystal River 3 (B&W)	X	
PSEG – Nuclear	Salem 1 & 2 (Westinghouse)	X	
Xcel Energy	Prairie Island 1 & 2 (Westinghouse)	X	

Note:

* Project participants as of the date the final deliverable was completed. On occasion, additional members will join a project. Please contact the PWR Owners Group Program Management Office to verify participation before sending this document to participants not listed above.

PWR Owners Group
Member Participation* for Project/Task PA-ASC-0264 Rev. 2 (cont.)

Utility Member	Plant Site(s)	Participant	
		Yes	No
Southern California Edison	SONGS 2 & 3 (CE)	X	
South Carolina Electric & Gas	V.C. Summer (Westinghouse)	X	
So. Texas Project Nuclear Operating Co.	South Texas Project 1 & 2 (Westinghouse)	X	
Southern Nuclear Operating Co.	Farley 1 & 2, Vogtle 1 & 2 (Westinghouse)	X	
Tennessee Valley Authority	Sequoyah 1 & 2, Watts Bar (Westinghouse)	X	
Wolf Creek Nuclear Operating Co.	Wolf Creek (Westinghouse)	X	

Note:

* This is a list of participants in this project as of the date the final deliverable was completed. On occasion, additional members will join a project. Please contact the PWR Owners Group Program Management Office to verify participation before sending documents to participants not listed above.

PWR Owners Group
International Member Participation* for Project/Task PA-ASC-0264 Rev. 2

Utility Member	Plant Site(s)	Participant	
		Yes	No
British Energy	Sizewell B	X	
Electrabel (Belgian Utilities)	Doel 1, 2 & 4, Tihange 1 & 3	X	
Hokkaido	Tomari 1 & 2 (MHI)	X	
Japan Atomic Power Company	Tsuruga 2 (MHI)	X	
Kansai Electric Co., LTD	Mihama 1, 2 & 3, Ohi 1, 2, 3 & 4, Takahama 1, 2, 3 & 4 (Westinghouse & MHI)	X	
Korea Hydro & Nuclear Power Corp.	Kori 1, 2, 3 & 4 Yonggwang 1 & 2 (Westinghouse)	X	
Korea Hydro & Nuclear Power Corp.	Yonggwang 3, 4, 5 & 6 Ulchin 3, 4 , 5 & 6 (CE)	X	
Kyushu	Genkai 1, 2, 3 & 4, Sendai 1 & 2 (MHI)	X	
Nuklearna Electrarna Krško	Krško (Westinghouse)	X	
Nordostschweizerische Kraftwerke AG (NOK)	Beznau 1 & 2 (Westinghouse)	X	
Ringhals AB	Ringhals 2, 3 & 4 (Westinghouse)	X	
Shikoku	Ikata 1, 2 & 3 (MHI)	X	
Spanish Utilities	Asco 1 & 2, Vandellos 2, Almaraz 1 & 2 (Westinghouse)	X	
Taiwan Power Co.	Maanshan 1 & 2 (Westinghouse)	X	
Electricité de France	54 Units	X	

Note:

* This is a list of participants in this project as of the date the final deliverable was completed. On occasion, additional members will join a project. Please contact the PWR Owners Group Program Management Office to verify participation before sending documents to participants not listed above.

ACKNOWLEDGEMENTS

We hereby acknowledge the participation and cooperation of the many internal and external expert reviewers cited in this report. Their patience, insight, and commitment to the understanding of the very technical aspects of mixing/transport and precipitation modes phenomena are greatly appreciated.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS, ABBREVIATIONS, AND TRADEMARKS

ANL	Argonne National Lab
B&W	Babcock and Wilcox
BA	boric acid
BWR	boiling water reactor
BACCHUS	Mitsubishi Heavy Industries Boric Acid Concentration Core Mixing Tests
CE	Combustion Engineering
CENPD	CE Technical Report number prefix
CL	cold leg
CSS	containment spray system
DBA	design basis accident
ECCS	emergency core cooling system
EDS	electron dispersive spectroscopy
EDTA	ethylenediaminetetraacetic acid
FA	fuel assembly
GSI	Generic Safety Issue
HL	hot leg
HLSO	hot leg switchover
ICET	Integrated Chemical Effects Test
ICP	inductively coupled plasma
ID	inside diameter
LBLOCA	large-break LOCA
LOCA	loss-of-coolant accident

LIST OF ACRONYMS AND ABBREVIATIONS, AND TRADEMARKS (cont.)

LOCADM	loss-of-coolant accident deposition model
LTC	long-term cooling
MHI	Mitsubishi Heavy Industries
NPSH	net positive suction head
NRC	Nuclear Regulatory Commission
OEM	Original Equipment Manufacturer
PIRT	phenomena identification and ranking table
PWR	pressurized water reactor
PWROG	Pressurized Water Reactor Owners Group
RAI	Request for Additional Information
RCP	reactor coolant pump
RCS	reactor coolant system
Redox	reduction oxidation
REWET-II	Lappeenranta University of Technology test facility built to investigate the phenomena during the reflood phase of a loss-of-coolant accident
RTU	Westinghouse Research and Technology Unit
RV	reactor vessel
RVVV	reactor vessel vent valve
SE	Safety Evaluation
SEM	scanning electron microscope
SI	safety injection
SMB	sodium metaborate
SGlu	sodium gluconate

LIST OF ACRONYMS AND ABBREVIATIONS, AND TRADEMARKS (cont.)

SOK	State of Knowledge
STB	sodium tetraborate
STPP	sodium tripolyphosphate
TMI	Three Mile Island
TSP	trisodium phosphate
VEERA	Lappeenranta University of Technology test facility built for large-scale studies of the mixing and precipitation of boric acid during extended core boil-off accidents
WCAP	Westinghouse Technical Report number prefix (formerly Westinghouse Commercial Atomic Power)

Trademarks

Armaflex is a registered trademark of Armacell LLC.

Benelex is a registered trademark of Masonite Corp.

Fiberfrax and Durablanket are registered trademarks of Unifrax I LLC.

Interam and Thermalog are trademarks or registered trademarks of 3M.

Koolphen is a registered trademark of Kingspan Holdings (IRL) Limited Co.

Microtherm is a registered trademark of Microtherm nv.

Min-K is a registered trademark of Thermal Ceramics Inc.

NUKON is a registered trademark of Performance Contracting Inc.

EXECUTIVE SUMMARY

Following a loss-of-coolant accident (LOCA) in a pressurized water reactor (PWR), the reactor coolant system (RCS) begins to depressurize, and for all but the smallest breaks, significant boiling occurs in the core. The emergency core cooling system (ECCS) injects borated water into the reactor vessel to keep the core fuel temperatures at acceptably low levels to prevent fuel melt, cladding oxidation, and cladding embrittlement concerns. All three U.S. PWR nuclear plant designs (Westinghouse, Combustion Engineering [CE], and Babcock and Wilcox [B&W]) have ECCS features that, with or without operator action, initiate a core dilution mechanism to prevent the core region boric acid concentration from reaching the precipitation point. Long-term cooling (LTC) concerns regarding particulate, fibrous, and chemical debris have been well established in the Generic Safety Issue (GSI)-191 downstream effects issue resolution. Chemistry issues, both in the containment sump and downstream in the ECCS, are particularly complex due to the number of chemical constituents, the various states of the debris solutions, and the plant-specific nature of the debris mix and level of loading.

As part of the GSI-191 evaluation process, the Nuclear Regulatory Commission (NRC) Research funded a phenomena identification and ranking table (PIRT) exercise to better evaluate chemical phenomena and issues. The goal of the resulting PIRT and subsequent evaluation was to identify and resolve existing knowledge gaps so that eventually a more accurate chemical effects evaluation could be performed. Because the driver for this effort was GSI-191, primarily focused on sump solutions and nominal downstream solutions (i.e., the phenomena associated with the coolant solutions entering the reactor coolant system (RCS)), there was little discussion of the phenomena associated with high concentrations of solutions that would result from prolonged core boil-off with no core dilution flow. Typical plant post-LOCA scenarios could result in core region debris concentration multipliers of 20 or more as compared to nominal downstream ECCS coolant debris concentration.

Shortly after the NRC Research PIRT was published, NRC requested the Pressurized Water Reactor Owners Group (PWROG) to review it as part of an ongoing boric acid precipitation analysis methodology development program. Section 1 of this report provides additional background information related to this PWROG program. Section 2 discusses the purpose of this document, summarized as follows:

1. To review the relevance of the NRC Research PIRT (Reference 16) from the perspective of LOCA long-term cooling in-vessel precipitation.
2. To review or establish the state of knowledge (SOK) pertaining to the behavior of high-concentration solutions and the potential for the precipitation of solids.
3. To evaluate the phenomena and rankings in Reference 16 relevant to long-term cooling in-vessel precipitation evaluation models with consideration for the current SOK.
4. To present conclusions and make recommendations for the development of LOCA long-term cooling in-vessel precipitation evaluation models.

Section 3 provides a summary of key points of the NRC Research PIRT (Reference 16) and subsequent evaluation (Reference 19) focusing on those phenomena considered to be medium to high significance issues. Section 4 provides a summary of prior research, or research performed by or in conjunction with the PWROG that relates to the buildup of chemicals, primarily boric acid.

Section 5 provides an analysis of the key findings of high significance and limited SOK from the NRC Research PIRT summary and the Section 4 review, and identifies recommended resolutions for existing discrepancies. The conclusions of this report and resulting recommendations are provided in Section 6, summarized as follows:

1. Many of the concerns detailed in the NRC Research PIRT do not directly pertain to LOCA LTC in-vessel precipitation evaluation model.

2. Some of the concerns detailed in the NRC Research PIRT warrant additional investigation and should be considered in LOCA long-term cooling in-vessel precipitation evaluation model development.

To determine the impact of combined boric acid and buffer solutions with respect to bounding predictions that result from GSI-191 chemical loading and sump debris, the following recommendations are made:

3. The LOCA long-term cooling in-vessel precipitation evaluation model should focus on the precipitation characteristics of un-buffered and buffered boric acid solutions.

4. LOCA long-term cooling in-vessel precipitation model considerations for thermal and physical characteristics in the reactor vessel including boric acid mixing and transport may be impacted by the downstream effects of GSI-191 related issues. Vessel mixing tests are recommended to determine the impact of in-vessel debris on globally static, locally dynamic regions in the core. Future testing should also consider potential deposition on heated surfaces above the two-phase mixture level.

5. Additional testing should be considered to capture the effect of sump debris in the concentrated un-buffered and buffered boric acid solutions relative to heat removal capability.

6. GSI-191 downstream effect analyses can provide conservative boundary conditions for evaluating the effects of sump debris on in-vessel precipitation.

1 INTRODUCTION

The Pressurized Water Reactor Owners Group (PWROG) is funding a program to develop a loss-of-coolant accident (LOCA) boric acid precipitation control analytical approach, applicable to all pressurized water reactor (PWR) designs that would be acceptable to the Nuclear Regulatory Commission (NRC) staff. Since it was desirable to obtain generic NRC approval, the PWROG program was structured in phases consistent with NRC guidance on safety analysis evaluation model development. The NRC guidance (Reference 22) identified the first two steps when developing and assessing an evaluation model: *1) Determine requirements for the evaluation model* and *2) Develop an assessment base consistent with the determined requirements.* In order to carry out Steps 1 and 2, it was necessary to develop appropriate phenomena identification and ranking tables (PIRTs) including the current state of knowledge (SOK) for relevant phenomena. Given the diversity of post-LOCA scenarios, when considering boric acid mixing and transport in the reactor vessel, separate considerations for un-buffered boric acid solutions, buffered boric acid solutions, and buffered boric acid solution with debris are warranted. Note that the latter introduces new phenomena or impacts on phenomena associated with particulate, fibrous, and chemical debris. Chemistry issues, both in the containment sump and downstream in the emergency core cooling system (ECCS), are particularly complex due to the number of chemical constituents, the various states of the debris solutions, and the plant-specific nature of the debris mix and quantity.

As part of the Generic Safety Issue (GSI)-191 evaluation process, the NRC conducted a PIRT exercise to better evaluate chemical phenomena and issues. The goal of the resulting PIRT (Reference 16) and subsequent evaluation (Reference 19) was to identify and resolve existing knowledge gaps so that eventually a more accurate chemical effects evaluation could be performed. Because the driver for this effort was GSI-191, it focused primarily on sump solutions and nominal downstream solutions (i.e., the phenomena associated with the coolant solutions entering the reactor coolant system (RCS)). There was little discussion of the phenomena associated with high concentrations of solutions that would result from prolonged core boil-off before operators took action to dilute the core. Typical plant post-LOCA scenarios could result in core region debris bulk concentrations of 20 or more times higher than the nominal ECCS coolant debris concentrations directly downstream of the sump strainers.

Shortly after Reference 16 was published, the NRC requested the PWROG to review Reference 16 as part of the boric acid precipitation analysis methodology development program. The desired objective is to relate GSI-191 chemistry issues to phenomena that directly affect the potential for LOCA long-term cooling in-vessel precipitation against the current SOK. This process is to decide the phenomena that must be considered in full height testing and ultimately developing an evaluation model.

2 PURPOSE

The purpose of this document is fourfold. First, this report will review the relevance of the NRC PIRT (Reference 16) and subsequent evaluation (Reference 19) from the perspective of LOCA long-term cooling in-vessel precipitation evaluation models. These models are to analyze the potential effects of the precipitation of solids in the reactor vessel. Long-term cooling analyses have typically considered boric acid precipitation as the limiting condition precipitant. While References 16 and 19 focused primarily on sump solutions and nominal downstream solutions (i.e., the phenomena associated with the coolant solutions entering the RCS), there was little discussion of the phenomena associated with high concentrations of solutions that would result from prolonged core boil-off with no core dilution flow. However, this is to be considered in developing the in-vessel precipitation evaluation model.

Second, this report will review and update the SOK pertaining to the behavior of high-concentration solutions and the potential for precipitation of solids. The bulk of knowledge regarding the potential for in-vessel precipitation comes from a handful of industry and vendor tests that address boric acid precipitation and provide only limited insights into relevant phenomena. This database is supplemented by Westinghouse and PWROG funded tests that studied the boiling behavior and heat transfer characteristics of un-buffered and buffered boric acid solutions. Additional PWROG tests that focus on the boiling behavior and heat transfer characteristics of sump debris solutions are in progress.

Third, this report will evaluate the phenomena and rankings in References 16 and 19 relevant to long-term cooling in-vessel precipitation evaluation models with consideration for the current SOK pertaining to high-concentration solutions and the potential for the precipitation of solids.

Finally, this report will draw conclusions and make recommendations for moving forward with the development of LOCA long-term cooling in-vessel precipitation evaluation models.

3 SUMMARY OF NRC PIRT

The NRC Research PIRT (Reference 16) is divided into multiple time frames described below:

- T1: 0 to 30 seconds,
- T2: 30 seconds to 20 minutes,
- T3: 20 minutes to 24 hours,
- T4: 24 hours to 15 days, and
- T5: 15 to 30 days.

Since the focus of this report is in-vessel precipitation, only the time frames concerning this phenomenon are relevant. For U.S. PWR designs, 24 hours after the LOCA is considered a relevant time frame. It is expected that boric acid precipitation control measures (active or passive core dilution) would be in place within 24 hours following the design basis accident. Therefore, phenomena specific to time frames T4 and T5 from Reference 16 are generally neglected.

In addition to providing a review of the NRC Research PIRT, this report will be used to provide guidance for additional testing with respect to in-vessel precipitation. Since additional testing is warranted for those items with both high significance and low SOK, the NRC Research PIRT summary will focus on the phenomena or issues classified as Category II and Category III in Reference 16. Category II phenomena are characterized in Reference 16 as "either expected to be significant by the PIRT panelists or have been demonstrated to be significant by prior research [...]." However, the implications of these phenomena with respect to ECCS performance are not well known." Category III phenomena are characterized as "potentially significant, but are not well understood, and the ECCS performance implications are highly uncertain. These issues require more research, analysis, or evaluation within the context of specific post-LOCA plant environments to accurately consider the effects."

Figure 3-1 provides a process-level outline of events postulated to follow a design basis LOCA in Reference 16. These events have been identified in Reference 16 to be either (1) not understood well enough to model generically and conservatively, or (2) having a potential significant impact on chemical effects in the long-term cooling scenario. This process map is helpful in showing the relationships among many of the effects that occur in multiple time frames following the design basis accident. By providing a process map, it is possible to identify the major effects of interest and determine an early response to eliminate downstream consideration of the effect.

Tables 3-1 through 3-3 provide a summary of all of the phenomena as reported in Reference 16 for the first 24 hours of long-term cooling (time periods T1 through T3). Table 3-4 is a construct that condenses the information reported in Tables 3-1 through 3-3 to a more manageable number of effects. The rankings provided in Table 3-4 represent a limiting condition for both SOK and importance for the collected phenomena. It should be noted all table references in Table 3-4 refer to Reference 16 numbering. These effects are further condensed into 10 topical areas, shown in Table 3-5, which the NRC identified and evaluated against current experimental studies and research in Reference 19 based on phenomena raised in Reference 16. The issues raised in Reference 19 are classified by importance (high, medium, or low) based on those that deserve additional consideration to verify post-LOCA chemical effects and those that have been sufficiently addressed.

Following these tables, an in-depth exploration of the event is provided. The phenomena of importance identified in References 16 and 19 are diverse and, in many cases, interdependent. For convenience, they are divided into five major categorical sections. These sections include thermal-hydraulics, precipitation, chemical matrix formation, reaction types, and corrosion effects. A sixth minor category for biological effects is included for completeness.

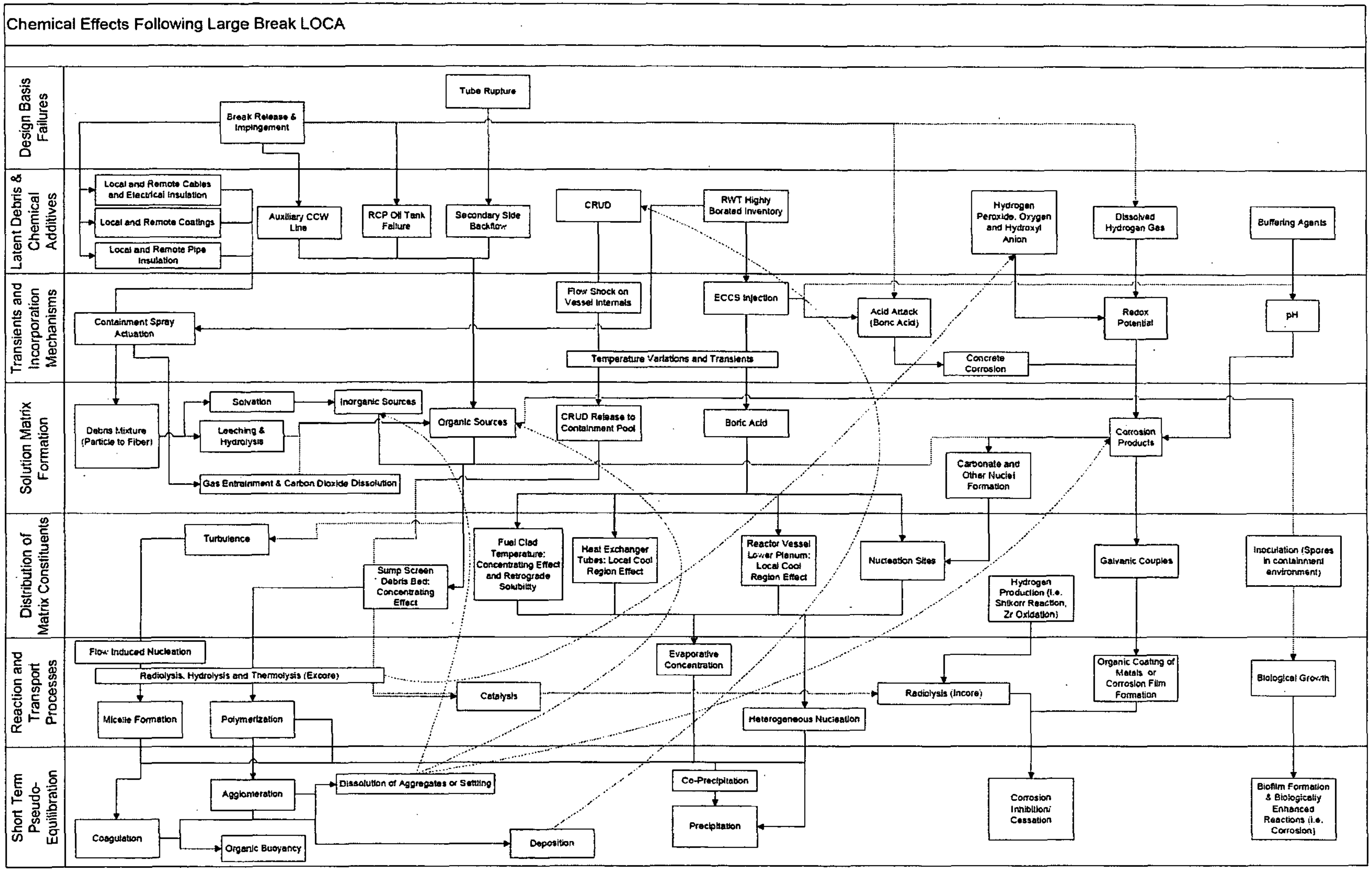

Figure 3-1 NRC PIRT (Reference 16) Chemical Effects Process Map

Table 3-1 NRC PIRT (Reference 16) Summary of T1 Phenomena and Rankings

Item Number	From Reference 16 Table 7	Description	Average Importance	Average Knowledge	Category
T1-1	Crud Release	Hydraulic shock dislodges crud and exposes fresh metals. Thermal fluctuations could exacerbate this process causing cyclical releases.	2.4	1.6	3
T1-2	RCS Coolant Conditions at Break Site	Temperature, pressure, and boron concentration are all highly variable and may need to be addressed on a plant by plant basis. Hot acidic material has a great deal of chemical activity.	2.4	1.4	2
T1-3	pH Variability	pH is initially low in containment pool, raised as buffering agents are added. Equilibration occurs 1 - 4 hours following event.	2.4	1.4	2
T1-4	Localized boron concentration in jet	At break site, the spraying action causes a high concentration boric acid aerosol.	1.9	1.8	3
T1-5	RCS fluid creates "oxidizing environment"	Hydrogen gas release influences chemical potential for H+ in the RCS fluid; therefore, increasing the oxidation state of the environment.	1.6	1.6	3
T1-6	Jet impingement	Two phase flow emanating from broken pipe impinges containment material and creates a debris load that is carried to the sump screen.	2.2	1.8	2
T1-7	Break proximity to organic sources	Source quantity and location is a major factor in determining amount of organics included in the pool following LOCA.	1.9	2.0	3
T1-8	Break proximity to secondary systems	The break proximity with respect to cooling systems could result in failure of lines containing compounds (e.g. Freon).	1.2	2.2	4
T1-9	Debris mix particle/fiber ratio	It is recognized that a variety of conditions may exist based on sequestration of constituents and this may influence the limiting condition.	2.6	1.6	2
T1-10	Hydrogen peroxide effects	Corrosive compounds, such as hydrogen peroxide can be generated due to increasingly oxidizing conditions in the sump pool chemistry.	1.4	1.4	4
T1-11	Nuclei formation	Rapid subcooling of water from the break location droplets could lead to precipitation of compounds.	1.2	2.0	4

Table 3-2 NRC PIRT (Reference 16) Summary of T2 Phenomena and Rankings

Item Number	From Reference 16 Table 8	Description	Average Importance	Average Knowledge	Category
T2-1	Hydrogen sources within containment	Several sources of hydrogen including the Schikorr reaction (magnetite formation), RCS inventory and corrosion of metals, including fuel clad, lead to an increasingly reducing environment.	1.2	1.6	3
T2-2	ECCS injection of boron	ECCS injection contributes to the addition of boron, and also participates in the buffering process.	2.2	1.4	2
T2-3	Containment spray corrosion	Corrosion of metals due to spray of un-submerged materials contributes to metal ion population in pool.	1.6	1.2	4
T2-4	NaOH pH control	Injection of NaOH through the containment spray system increases the dissolved content in the pool.	2.2	1	1
T2-5	STB pH control	STB is released by ice melting or dissolution of STB powder. This compound is fairly benign based on ICET test data	1.6	1	1
T2-6	TSP pH control	TSP is dissolved from the containment floor baskets and contributes calcium to the dissolved content in the pool.	2.2	1	1
T2-7	Containment spray transport	Post LOCA generated debris is propagated by spray. Submerged insulation debris is the primary contributor to chemical species.	2.4	2	2
T2-8	Containment spray CO_2 scavenging	Containment sprays cause CO_2 absorption within containment pool and carbonate formation.	1.9	1.2	1
T2-9	Debris dissolution begins	Debris dissolution and corrosion are the major mechanisms for creating the initial containment pool chemistry.	2.2	1.4	2
T2-10	Carbonate concentration	CO2 absorbed from air forms particulate debris. This is a negligible mass contribution; however, it could impact precipitation chemistry.	1.7	1.6	3
T2-11	Containment pool mixing	Mixing is limited to the region where flow is entering the pool, otherwise it is quiescent.	2	1.7	2
T2-12	Boric acid corrosion of exposed concrete	Concentrated boric acid contact with concrete generates precipitants and may decrease pool pH.	1.4	2.2	4

Table 3-2 NRC PIRT (Reference 16) Summary of T2 Phenomena and Rankings (cont.)

Item Number	From Reference 16 Table 8	Description	Average Importance	Average Knowledge	Category
T2-13	Fe and Ni radiological reaction	Hot boric acid or STB could dissolve crud increasing the exposure rate of surface metal resulting in an increased rate of metal dissolution. See Table 3-1, Item T1-1.	2	1.8	3
T2-14	Hydrolysis	Nickel oxide catalyzed hydrolysis results in de-polymerization of constituents which could result in additional aggregates.	1.2	2.2	3
T2-15	Organic complexation	Organic components can complex with inorganic compounds resulting in agglomeration. See Table 3-2 Item T2-21.	1.7	2	3
T2-16	Organic sequestration	Organo-metallic compounds form reducing metal ion concentrations.	1.6	2.2	4
T2-17	Auxiliary component cooling line failure	Failure of this component could result in the release of many chemicals into the containment environment.	1.7	2.2	4
T2-18	Polymerization	The formation of inorganic and organic polymers, which act as precursors to precipitation.	2.5	1.8	2
T2-19	Co-precipitation	ICET testing indicates low importance, but the nature of this effect is plant specific and may require additional testing.	1.7	1.8	3
T2-20	Radiolytic environment	Post LOCA radiolysis of water in the presence of metal ions generates hydroxyl radicals, perborate and hydrogen peroxide which are oxidizing agents. Radiolysis is expected to occur quickly during ECCS injection phase since hydrogen control is lost. Fe, Ni, Co and Al will oxidize readily precipitating various oxide products. See also, Table 3-2 Item T2-1.	2	1.8	3
T2-21	Inorganic agglomeration	Particle size distr bution is a function of the environmental conditions. Larger particles settle more; however, are also more detrimental.	2.2	1.6	2
T2-22	Galvanic effects	Dissimilar metals contacting in an electrolyte form a circuit. Current travels and causes the oxidation - reduction reaction of the metals. Cu, Fe, Zn and Al are susceptible.	1.6	1.8	3
T2-23	Deposition and settling	Generally a beneficial chemical phenomenon, except at the heat transfer boundaries.	2.3	2.2	2
T2-24	Organic agglomeration	Organic components can coagulate, trapping inorganic components forming larger agglomerates. See Table 3-2 Item T2-21.	2.3	2.6	3

Table 3-3 NRC PIRT (Reference 16) Summary of T3 Phenomena and Rankings

Item Number	From Reference 16 Table 9	Description	Average Importance	Average Knowledge	Category
T3-1	TSP pH control	See Table 3-2, Item T2-6	1.8	1.2	1
T3-2	NaOH pH control	See Table 3-2, Item T2-4. Also, in longer time frame, high pH contributes to more metal corrosion	2.2	1.0	1
T3-3	STB pH control	See Table 3-2, Item T2-5.	2.2	1.0	1
T3-4	NaOH injection	See Table 3-2 Item T2-4	1.7	1.6	4
T3-5	Cable degradation	Chloride is released due to radiolysis of solubilized material from cable insulation.	1.5	1.8	4
T3-6	Radiolytic environment	See Table 3-2, Item T2-20	2.3	1.8	3
T3-7	Fiberglass leeching	Si, Al, Mg, Ca etc are leached from fiberglass can form gels.	2.0	1.0	1
T3-8	Secondary system contamination	A tube rupture could lead to secondary side chemicals being added to containment pool.	1.5	1.8	4
T3-9	Flow-induced nucleation	Various types of phase separations caused by flow related phenomena could result in increased precipitation rates.	1.3	2.0	4
T3-10	Turbulent mixing	Turbulent mixing could reduce precipitation by reducing stagnant volume or could increase chemical load by reducing settling. (Table 3-3, Items T3-9 and T3-11)	1.5	2.2	4
T3-11	Quiescent settling of precipitate	Low flow conditions are expected in most PWRs for recirculation phase. These low flow rates increase settling of debris and chemical species.	2.4	2.2	3
T3-12	Electrostatic scavenging	Constituents may be removed by exposed material surfaces based on the galvanic series.	1.4	2.2	4
T3-13	Chemically induced settling	Chemical species which coat debris change the solubility parameters and chemical potential resulting in settling phenomena.	1.7	1.8	3
T3-14	Agglomeration and coagulation	See Table 3-2 Item T2-21	2.3	1.8	2
T3-15	Particulate nucleation sites	Many nucleation sites are available to foster precipitation.	1.8	2.2	1
T3-16	Additional debris bed chemical reactions	Radionuclide transport and accumulation within the sump screen debris bed which results in a local effect and an increasingly oxidizing environment.	1.9	2.4	3

Table 3-3 NRC PIRT (Reference 16) Summary of T3 Phenomena and Rankings (cont.)

Item Number	From Reference 16 Table 9	Description	Average Importance	Average Knowledge	Category
T3-17	Sump screen: high localized chemical concentrations	Due to gel formation and material accumulation at the sump screen, significant chemical concentrations may be present and result in different reactions than found in the remainder of the RCS.	1.6	2.2	4
T3-18	Sump screen: fiberglass morphology	Participation of fiberglass and dissolved metal results in debris bed compression and increased head loss.	1.6	2.0	4
T3-19	ECCS pump: seal abrasion	Downstream impact of ingested material on ECCS pumps. The seal material may be dislodged and generate additional chemicals in fluid.	2.0	2.0	3
T3-20	Heat exchanger: solid species formation	Local temperature gradients may induce precipitation.	2.4	1.6	3
T3-21	Heat exchanger: deposition and clogging	Precipitate formed by Table 3-3 Item T3-20 may form deposits on colder heat exchanger tubes reducing flow.	2.1	1.6	3
T3-22	Reactor core: fuel deposition	Spallation of deposited chemical products is a source for activated material.	2.1	1.6	3
T3-23	Reactor core: hydrogen increases	As fuel clad is oxidized, hydrogen is formed which results in risk hydrogen embrittlement and hydrogen deflagration. Also, oxidation - reduction potential and other previously identified chemical processes should be considered.	1.5	1.5	3
T3-24	Reactor core: diminished heat transfer	Deposition of material on fuel rods contributes to reduction in heat transfer coefficients.	2.1	1.8	3
T3-25	Reactor core: blocking of flow passages	Deposition of material within the vessel contributes to flow path occlusion and subsequent heat removal capability reduction.	2.3	2.0	3
T3-26	Reactor core: particular settling	Debris settling in the bottom of the core contributes to a reduction of the fluid's heat removal capability.	2.1	2.0	3
T3-27	Reactor core: precipitation	See Table 3-3, Item T3-22	2.3	2.0	3

Table 3-3 NRC PIRT (Reference 16) Summary of T3 Phenomena and Rankings (cont.)

Item Number	From Reference 16 Table 9	Description	Average Importance	Average Knowledge	Category
T3-28	Exposed, uncoated concrete dissolution	Leaching concrete elements into containment fluid as well as pH implications.	1.4	1.4	4
T3-29	Coatings dissolution	The inorganic and organic coatings found in containment are submerged and leach chemicals into the pool.	1.6	2.4	3
T3-30	Boric acid corrosion	See Table 3-2, Item T2-12. Continued effect with broader range of target materials.	1.7	1.8	4
T3-31	Carbon dioxide and carbonate radiolysis	Radiolysis of carbon dioxide and carbonates could form organic acid ligands. These could form metal complexes.	1.0	2.0	4

Table 3-4 Summary of NRC PIRT (Reference 16) Chemical Effects

Item Number	Phenomena Description	GSI 191 NRC PIRT Location	Maximum Score						Category 2 or 3?
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
1	Hydraulic shock within the RV dislodges deposits on the fuel pins. This could result in local changes in heat transfer coefficients. It is also feasible a cycle could be established between precipitation and shock induced releases.	Table 7, Item 1	2.4	N/A	N/A	1.6	N/A	N/A	3
2	Thermal and chemical conditions at the break site may differ significantly from those conditions in the bulk.	Table 7, Items 2, 4 and 6	2.4	N/A	N/A	1.8	N/A	N/A	2
3	pH within containment as well as within the RV varies significantly during stages of the accident. Such variations impact the chemistry (thermodynamics and kinetics of reaction or precipitation) within those locations.	Table 7, Item 3	1.9	N/A	N/A	2.0	N/A	N/A	2
4	Oxidizing conditions within the RCS influences chemical conditions.	Table 7, Items 5 and 10	1.6	N/A	N/A	1.6	N/A	N/A	3
5	The location of the break contributes significantly to the chemical makeup of the refueling cavity.	Table 7, Items 7 and 8	1.9	N/A	N/A	2.2	N/A	N/A	3
6	The physical and chemical makeup of the debris has downstream impact on the chemical makeup of the refueling pool. This is especially true of fiberglass and electrical insulation which contribute additional chemical species (e.g. silica, aluminum). This can result in gel formation and contribute to flow restriction at the sump screen resulting in unexpected chemical product formation.	Table 7, Item 9; Table 9, Items 5, 7, 17 and 18	2.6	N/A	2.0	1.6	N/A	2.2	2
7	Formation of particulate nuclei enhancing precipitation.	Table 7, Item 11; Table 9, Item 15	1.2	N/A	1.8	2.0	N/A	2.2	N/A
8	Reductive conditions in either refueling cavity or RCS proper.	Table 8, Item 1	N/A	1.2	N/A	N/A	1.6	N/A	3
9	ECCS chemical contributions and impact as well as impact of chemistry on ECCS.	Table 8, Item 2; Table 9, Item 19	N/A	2.2	2.0	N/A	1.4	2.0	2
10	Corrosion product formation from un-submerged material.	Table 8, Item 3	N/A	1.6	N/A	N/A	1.2	N/A	N/A
11	Impact of various buffering systems.	Table 8, Items 4, 5 and 6; Table 9, Items 1, 2, 3 and 4	N/A	2.2	2.2	N/A	1.0	1.2	N/A
12	Transport of material from containment to the refueling cavity.	Table 8, Item 7	N/A	2.4	N/A	N/A	2.0	N/A	2
13	Dissolution of submerged material to generate chemical composition of refueling cavity.	Table 8, Items 9 and 12; Table 9, Items 28, 29 and 30	N/A	2.2	1.6	N/A	2.2	2.4	2
14	The formation of carbonate compounds.	Table 8, Items 8 and 10; Table 9, Item 31	N/A	1.9	1.0	N/A	1.6	2.0	3

Table 3-4 Summary of NRC PIRT (Reference 16) Chemical Effects (cont.)

Item Number	Phenomena Description	GSI 191 NRC PIRT Location	Maximum Score						Category 2 or 3?
			Importance			Knowledge			
			T1	T2	T3	T1	T2	T3	
15	Mixing conditions within refueling cavity and impact on chemical content of pool.	Table 8, Item 11	N/A	2.0	N/A	N/A	1.7	N/A	2
16	Impact of radiation on chemical reaction matrix and rates (includes radiolysis reactions). Radiation can be sourced within the core or within the refueling cavity, and may concentrate within gels and fibers coagulated at the sump screen.	Table 8, Items 13 and 20; Table 9, Items 6 and 16	N/A	2.0	2.3	N/A	1.8	2.4	3
17	Metal catalyzed chemical reactions including hydrolysis.	Table 8, Item 14	N/A	1.2	N/A	N/A	2.2	N/A	3
18	Organic materials present impact reaction matrix and rates.	Table 8, Items 15 and 16	N/A	1.7	N/A	N/A	2.2	N/A	3
19	Auxiliary component cooling line break chemical contributions and impact.	Table 8, Item 17	N/A	1.7	N/A	N/A	2.2	N/A	N/A
20	Polymerization (inorganic or organic) impact on precipitation rates.	Table 8, Item 18	N/A	2.5	N/A	N/A	1.8	N/A	2
21	Co-precipitation: impact of chemical species interaction on precipitation rates and solubility limits.	Table 8, Item 19	N/A	1.7	N/A	N/A	1.8	N/A	3
22	Agglomeration: impact of inorganic or organic agglomeration on refueling cavity chemical content.	Table 8, Items 21 and 24; Table 9, Item 14	N/A	2.3	2.3	N/A	2.6	1.8	2
23	Galvanic couples: points of dissimilar metal contact within an aqueous salt solution create a circuit which results in points of oxidation and reduction. Products of these reactions can be solubilized in the refueling cavity pool.	Table 8, Item 22; Table 10, Item 6	N/A	1.6	N/A	N/A	1.8	N/A	3
24	Deposition, coating or settling: removal of chemical species from the refueling cavity.	Table 8, Item 23; Table 9, Items 11, 12 and 13	N/A	2.3	2.4	N/A	2.2	2.2	2
25	Secondary system inflow due to tube rupture or other causes. Chemical contributions and impact.	Table 9, Item 8	N/A	N/A	1.5	N/A	N/A	1.8	N/A
26	Flow induced effects including nucleation or turbulent scouring.	Table 9, Item 9; Table 10, Item 41	N/A	N/A	1.3	N/A	N/A	2.2	N/A
27	Turbulent mixing.	Table 9, Item 10	N/A	N/A	1.5	N/A	N/A	2.2	N/A
28	RHR/SDC HX: Chemistry within heat exchanger differs from bulk due to thermal gradients. HX serves as chemical source term.	Table 9, Items 20, 21and 35	N/A	N/A	2.4	N/A	N/A	1.6	3
29	Chemistry within the reactor vessel differs from bulk due to thermal gradients.	Table 9, Items 22, 23, 24, 25, 26 and 27	N/A	N/A	2.3	N/A	N/A	2.0	3

Table 3-5 Summary of NRC Chemical Effects Topical Areas (Reference 19)

Item Number	From Reference 19 Tables S.1, S.2	Description	State of Knowledge and Further Study	Importance
1	Radiation Effects	The effect of post-LOCA radiation environment and radiolysis in the reactor vessel, containment pool, and contaminated sump strainer on the containment pool chemical constituents.	Radiation effects on pH were minor in comparison with pH buffering effects. Assessment of redox effects requires mixed potential modeling, similar to that performed for boiling water reactors.	Medium
2	Carbonation of Concrete	The effect of carbonation or other aging processes of concrete on the dissolution rates from aged concrete as compared to tested fresh concrete samples.	The carbonation in tested concrete coupons sufficient to have negligible effect compared with outcome had aged coupons been used. No additional evaluation is required.	Low
3	Alloy Corrosion	The effect of material alloy variability on corrosion and dissolution rates of important submerged containment pool materials.	Aluminum is the major metal of concern for corrosion. Testing of variable aluminum alloys did not demonstrate significantly different corrosion rates. Further evaluation is not recommended.	Low
4	Galvanic Corrosion	Effects of galvanic corrosion and configurations that could significantly alter the amounts and types of chemical by-products.	Galvanic corrosion only affected limited metal surface area to yield negligible additional corrosion product quantities. Additional literature and testing of anodic reversal phenomenon for galvanized steel under post-LOCA conditions could be performed.	Low
5	Biological Fouling	Effects of growth of biota (potential fouling of sump strainers) in coolant waters with low light, low nutrient, high boron, high temperature and radiation field in 30-day post-LOCA mission time.	Growth rates of microbes under stressor combinations are not known. Green flocculent solids found in TMI waters provide evidence for growth over long periods. Inoculation tests of various microorganisms under post-LOCA coolant conditions are suggested.	Medium

Table 3-5 (cont.) Summary of NRC Chemical Effects Topical Areas (Reference 19)

Item Number	From Reference 19 Tables S.1, S.2	Description	State of Knowledge and Further Study	Importance
6	Co-precipitation and Other Synergistic Solids Formation	Effects of co-precipitation, organic complexation, and inorganic/organic agglomeration on solids formation in the post-LOCA system.	No net effect of solids quantity is anticipated solely from inorganic constituents. Limited organic complexation expected due to expected degradation due to hydrolysis and chemical masking by calcium in post-LOCA waters. Organic-mineral-aggregates expected of inorganic solids with organic paint and lubricants and solid mobilization. This effect to be considered in combination with Items 7 and 10.	High
7	Inorganic Agglomeration	Effects of soluble organics and their decomposition products on inorganic agglomeration in the post-LOCA coolant.	Effects of organics and organic degradation materials on inorganic agglomeration are not reliably predicted. Effects are small as most soluble organics will pass into the core to be destroyed by radiolysis. Inorganic agglomeration should be pursued in combination with Item 6, following Item 10 testing.	Low
8	Crud Release Effects	Chemical and radiation effects related to metal corrosion oxides (crud) in the RCS released during the post-LOCA time period.	LOCA events will have conditions favorable for "crud burst." Crud solids are expected to be near 1000 kg. These quantities are small as compared to cal-sil insulation solids, but could be significant for systems with limited particulates.	Low

Table 3-5 (cont.) Summary of NRC Chemical Effects Topical Areas (Reference 19)

Item Number	From Reference 19 Tables S.1, S.2	Description	State of Knowledge and Further Study	Importance
9	Retrograde Solubility and Solids Deposition	Effects of retrograde solubility and solids deposition on fuel assemblies and reactor vessel.	Retrograde solubility has been observed for calcium bearing solids, but effect on solids loading is small due to low calcium solubility. Borate salt depositions on fuel assemblies above boiling temperatures may be corrosive, may add to the solids load, and could impair heat transfer from the fuel. Further literature or laboratory study may help determine magnitude of this effect.	Medium
10	Organic Material Impacts	Effects of physical and radiolytic degradation of organic materials in the containment environment on chemical effects on post-LOCA coolant.	Many paints undergo hydrolytic decomposition and may contribute to load in coolant. Dissolved and suspended organics may undergo radiolysis by passing through the core, which could fully decompose recirculating organics to carbon dioxide within days. Organics above sump strainers may interact with solids as described in Items 6 and 7.	High

3.1 THERMAL-HYDRAULIC PHENOMENA

The goal of long-term cooling analysis is to demonstrate that sufficient heat removal capability is provided by the ECCS to remove decay heat produced by the core following the design basis accident (DBA). The chemical effects associated with GSI-191 can affect this capability in several ways. Precipitation in the core or at heat exchange locations can reduce heat transfer coefficients at fuel, block flow at inlet locations or in regions of restrictive geometry, and possibly change the heat transfer characteristics of the coolant. In Reference 16, specific instances of these types of phenomena are identified by the authors where it is believed that insufficient knowledge of highly significant issues may still exist. A summary of concerns and recommendations as described in Reference 16 follows.

First, it was determined in Reference 16 that thermal conditions at any heat exchange site could promote precipitation locally. Specifically, the cooler heat exchanger outlet temperature could cause the formation of solid species (Reference 16, Table 9, Item T3-20) and eventual surface deposition. This could result in different thermal conditions in the circulating fluid due to reduction in flow or heat transfer. This same category of effect could occur due to temperature gradients caused by reactor vessel (RV) heat transfer within the core. The pertinent chemical effects related specifically to heat exchanger performance are deposition and clogging (Reference 16, Table 9, Item T3-21). A conservative analysis of deposition may be sufficient to determine if adequate heat exchanger design margins remain. The precipitation kinetics could be studied to determine if solid species concentrations at these lower temperatures are less than assumed from either aqueous concentrations or solubility considerations. Evaluation of the flow conditions at tube inlet locations may also provide information to evaluate the propensity for heat exchanger or core inlet clogging.

The subsequent impact of the physical and solid chemical debris formed within or transported to the core is considered. This type of debris loading can impact the heat transfer capabilities of the coolant, including the heat capacity of the fluid, as well as flow blockages at the reactor core inlet nozzle or along the fuel elements. While these impacts have been investigated previously, Reference 16 provides recommendations to investigate additional issues such as quantification of the debris loading acceptance criterion given a variety of chemical compositions and precipitation distributions. Additional regions for flow blockage should be considered via testing and evaluation. It is possible that operator action may contribute significantly to maintaining acceptable fuel heat transfer.

Another major concern from Reference 16 is that evaluation of these chemical effects will result in predicted changes in coolant characteristics such that temperature and flow changes would be anticipated for the accident. Since the thermal conditions of the coolant are critical in determining the chemical reaction matrices, it is important to incorporate the synergistic effects and carry such changes throughout the downstream impacts. This may require substantial investigation and iterative processes before conservative conditions are truly identified. Figure 3-1 has been constructed to summarize the various effects and associated impacts as outlined in Reference 16.

Similarly, the deposit thickness and heat transfer implications of the chemical precipitant results in thermal changes. This influences the hydraulic conditions and can induce shock, resulting in spalling of such components. The physical, chemical and radiological consequences of such interdependent events need to be evaluated to ensure conservatism is maintained in the eventual long-term cooling strategy.

3.2 PRECIPITATION PHENOMENA

Boric acid precipitation is the chemical effect pertinent to existing strategy for long-term cooling following LOCA. Significant issues arise should precipitation in the reactor vessel present a possible challenge to fuel integrity. Precipitation is also investigated due to the high likelihood of the reactor vessel acting as a concentrator for chemical constituents in the early stages of long-term cooling following the LOCA. The NRC Research PIRT (Reference 16) indicates that while boric acid precipitation has been investigated to some extent, insufficient knowledge exists regarding the effect of high concentrations of un-buffered or buffered boric acid solutions. In general, the impacts of thermodynamic conditions and other chemicals on the precipitation of boric acid as well as the possibility of other compounds participating actively in precipitation of chemicals other than boric acid should be considered.

The NRC Research PIRT (Reference 16) notes that regardless of prevention or termination of a precipitation event, increasing boric acid concentration following LOCA is expected. The corrosive nature of concentrated boric acid salts on ferritic materials is a well known phenomenon in the industry. It is posited that the scope of existing knowledge does not adequately address (1) the reaction rate and subsequent degree of corrosion associated with the expected locations, quantities and concentrations of boric acid on the impacted materials in the post-LOCA environment, and (2) the feedback contribution of the degradation of these materials to the containment pool chemistry (Reference 16, Table 9, Item T3-30).

Should the available reaction pathways be narrowed down and mapped adequately, it is important to be able to determine either conservatively or on a plant-specific basis the likely chemical reaction scenarios leading to any precipitation event. This requires that plant-specific temperature and pH profiles be considered in conjunction with various debris mixtures. These conditions impact both thermodynamics and kinetics and should be understood well from the perspective of sensitivity. Reference 16, Table 7, Item T1-3 describes how pH variability exists in the sump fluid, and consequently in the long-term cooling flow, and implies the downstream impact of this variability.

Several factors influence the generation of solid precipitate. The reaction inputs, including both the variability of the chemical composition of the solution, as well as the thermodynamic and kinetic parameters, including temperature, pH, time, and ionic conditions, must be evaluated to determine the sensitivity of the distribution of both the types of precipitates and the particle sizes in the final solution to the initial conditions. These results are critical in determining the higher-level effects including polymerization and particle aging processes. This investigation is necessary to determine whether a bounding analysis can be constructed or whether plant-specific analysis is required. Consideration of co-precipitation is also recommended by Reference 16. This effect can occur as a result of solution thermodynamic changes for one chemical species caused by the presence of other species and can result in precipitation below the solubility limit (Reference 16, Table 8, Item T2-19).

Following precipitation, other effects considered in Reference 16 include the agglomeration of inorganic particles (Reference 16, Table 8, Item T2-21 and T2-19, Table S.2, Topic 7) and organic particles (Reference 16, Table 9, Item T3-24 and Reference 19, Table S.2, Topic 10). This effect could result in the formation of large beds of material on the sump screen or elsewhere. It is recognized in Reference 16 that this type of effect can reduce the available content of various chemical species. This reduction is also recognized to result from transport phenomena such as settling or deposition. It is posited that these effects (Reference 16, Table 8, Item T2-23) could influence the composition of the sump fluid. These effects are impacted by phenomena including quiescent flow fields (Reference 16, Table 9, Item T3-11), electrostatic scavenging (Item T3-12), and chemical settling (Item T3-13). These can influence the distribution and quantity of chemical species within the debris load. Retrograde solubility and solid deposition on hot core and fuel structures (Reference 19, Table S.2, Topic 9) may also add to the solids load and impair heat transfer from the fuel.

3.3 CHEMICAL MATRIX

The high-significance factors in determining the extent of the precipitation events described previously in Sections 3.1 and 3.2 are the thermodynamic conditions in the solution of interest, the chemical composition of the solution, and the available reaction pathways. The NRC Research PIRT (Reference 16) indicates that the thermodynamic conditions in the post-LOCA environment can be predicted in a conservative fashion; however, it also indicates the current research did not clearly define the chemical constituents likely to be involved in the precipitation events. Several compounds are readily found in most containment environments, and the significant impact associated with a LOCA-type accident could liberate many of these compounds for incorporation into the containment pool. Several mechanisms for this incorporation are provided and listed below.

A possible mechanism for dissolution of carbon dioxide in the containment pool is provided by gas entrainment within the spray flow (Reference 16, Table 8, Item T2-8). The formation of carbonate compounds (Reference 16, Table 8, Item T2-10) from atmospheric carbon dioxide should be evaluated on a plant-specific basis. This should include debris sources, dissolved calcium concentrations, and sump environmental conditions. These variables impact solid species inventory and precipitation kinetics. Also, radiolysis of carbonate compounds or dissolved carbon dioxide could result in the formation of organic acid ligands. This could lead to the formation of organo-metallic complexes, which could increase the solubility of metal ions, especially calcium.

The primary subgroups of coatings evaluated in Reference 16 are metallic and organic coatings. Either of these coatings could impact the chemical composition of the post-LOCA containment pool following incorporation into the chemical matrix. The mechanism for incorporation of the metal coatings is dissolution or leeching due to submergence in the containment pool. The rate for incorporation from the metal coatings depends on conditions in the pool including the chemical composition, pH, and temperature. Organic coatings are resistant to this form of incorporation; however, pathways are available via thermolytic and radiolytic decomposition. To determine the possible downstream effects associated with these constituents, it is first necessary to evaluate a conservative or realistic (plant-specific) model for incorporation of these materials into the pool.

A realistic plant-specific assessment should be performed to determine likely sources of organic material. Such sources could be stored at sites near postulated break points (Reference 16, Table 7, Item T1-7) or at the boundaries of secondary or auxiliary systems that may be breached during the LOCA, such as the auxiliary component cooling line (Reference 16, Table 8, Item T2-17). Debris coated by organic materials may have increased buoyancy and therefore a reduced likelihood of settling (Reference 16, Table 10, Item T4-16). It should be noted, this phenomena would be most prevalent in the T4 and T5 time frames, which are outside the time frame considered in this report for boric acid precipitation effects.

3.4 REACTION TYPES

The subtle form of codependency between parameters is discussed throughout Reference 16. For instance, the next significant point made is that the impact of the concentrated boric acid on the types, amounts, and properties of chemical precipitates that form in the reactor vessel should be considered during future studies. This is based on the supposition of several phenomena identified in Reference 16 including the aforementioned ferritic corrosion effect and corrosion of other susceptible materials such as concrete. Also, the requirement to develop extensive reaction matrices to account for boric acid interplay with the inorganic and organic sources found in containment including coatings, insulations, buffering systems, as well as corrosion products from ferritic materials, concrete and fuel clad (Reference 16). Co-precipitation and synergistic solids formation could increase the transportability of solids to sump strainers by interactions between organic and inorganic particulates and should be considered in conjunction with inorganic agglomeration and organic material effects due to physical and radiolytic degradation (Reference 19).

The NRC Research PIRT (Reference 16, Table 7, Item T1-1) describes neutron activated product release due to thermal shock as a possible source term for radioactive particle transport. Following the release of existing crud, precipitation and/or deposition of material on the vessel walls, fuel clad, or other internals may occur. This material would continue to be subjected to gamma fields following termination of active fission. Spallation of initial crud provides a mobile source for radioactive material, which would likely concentrate in the region of the sump screen, providing an ex-core radiation source of sufficient magnitude to influence the chemical reaction matrix. Gamma radiation fields can directly impact the chemical thermodynamics and kinetics as well as the oxidation-reduction potential where they occur (Reference 16, Table 8, Item T2-13 and Item T2-20, Table 9, Item T3-6). Likely locations for gamma radiation fields include the core, the containment pool, as well as the sump screen, where concentration of activated material within a debris bed is expected to occur (Reference 16, Table 9, Item T3-16). While only initial spallation introduces mobile activated material which could collect in the sump, gamma radiation induced chemical effects on subsequent in-vessel deposits are expected. However, this effect results in changes to the debris loading, which is considered to be outside the scope of this evaluation.

The containment pool model is also questioned given the lack of justification for certain assumptions. Additional evaluation is recommended to specifically address composition-driven corrosion kinetics. Several containments contain particularly broadly applicable constituents, which may act in a catalytic fashion in corrosion reactions. Specific examples of copper, citrate, and other hydroxyl organic acid anions are given, as these compounds are known to accelerate typical corrosion reactions. Additional study is also recommended to determine whether other catalysts would be found in the containment pool, and whether compounds commonly found in containment may act to inhibit such reactions.

Hydrolysis as a reaction mechanism should be evaluated specifically with respect to the conditions in the post-LOCA environment. If found to be a plausible mechanism, the most susceptible coatings and insulation materials should be evaluated to determine the possible reaction products as well as the second-order reactions and products that could occur, having included the other constituents of the post-LOCA pool.

3.5 CORROSION EFFECTS

Hydrogen production from sources such as cladding oxidation (Reference 16, Table 9, Item T3-23) or the Schikorr reaction (Reference 16, Table 8, Item T2-1) should be assessed to determine whether substantial production rates exist and whether these result in increased levels of dissolved hydrogen in the RCS. If this effect is not negligible, an assessment should be performed to determine the impact on precipitation.

Further discussion regarding the impact of causal agents for corrosion inhibition includes the products of material aging. A key point described is that existing testing may not have evaluated aging products that may be available in the post-LOCA environment. The presence of these components, specifically phosphates, chromates, dichromates, silicates, and borates inhibits the corrosion of aluminum surfaces. The effect of aged concrete coupons on carbonations was found to need no additional evaluation (Reference 19, Table S.2, Topic 2). The presence of dissimilar metals that are higher in the galvanic series can result in electroplating-type events, such as copper deposition on aluminum surfaces, which also can impact corrosion kinetics. As these impacts are highly interdependent, the resulting sensitivity to initial conditions is significant and requires plant-specific analysis to determine the final impact. Reference 16 recommends that the galvanic couples in plant-specific environments should be evaluated with respect to electroplating and the impact on relative concentrations of specific metal types (Reference 16, Table 8, Item T2-22). In Reference 19, galvanic corrosion was shown to affect only limited metal surface area; however, evaluation of the anodic reversal phenomenon for galvanized steel under post-LOCA conditions was not addressed. Also, Reference 16 recommends considering the extent to which corrosion or erosion characteristics of these or other chemical constituents result in pump seal and pump component degradation (Reference 16, Table 10, Item T4-14). It should be noted, this phenomena would be most prevalent in the T4 and T5 timeframes, which are outside the time frame considered in this report for boric acid precipitation effects.

Several events occur during the early stages of a LOCA that may contribute to significant changes in the oxidation-reduction potential of the sump fluid. Liberation of hydrogen gas from the superheated spray at the break site yields an increased oxidation-reduction potential (Reference 16, Table 7, Item T1-5). The oxidizing environment leads to the generation of hydrogen peroxide and other oxidizing agents, which results in changes in the core and pool chemistry (Reference 16, Table 7, Item T1-10).

3.6 BIOLOGICAL EFFECTS

The possibility of biological growth in containment should be evaluated within reasonable time frames. Microbe growth rates under low-light, low-nutrient, high-boron, high-temperature, and high-radiation stressors are not known. Downstream impacts of biological growth could be biofilm formation (Reference 16, Table 10, Item 19), biologically enhanced corrosion (Reference 16, Table 10, Item 20), biologically enhanced hydrogen embrittlement (Reference 16, Table 10, Item T4-21), biological growth in debris beds (Reference 16, Table 10, Item T4-22), and fouling of sump strainers (Reference 19, Table S.2, Topic 5). It should be noted, phenomena due to biological effects would be most prevalent in the T4 and T5 timeframes, which are outside the time frame considered in this report for boric acid precipitation effects.

4 UPDATE TO CURRENT STATE OF KNOWLEDGE: SUMMARY OF PWROG FINDINGS

The PWROG has funded a research program to investigate chemical effects in the post-LOCA containment sump environment to address GSI-191 concerns. The purpose of this program is to provide a consistent approach for utilities to evaluate and address the chemical effects that may impact fluids circulating in the containment sump and reactor vessel in the post accident scenario. This program includes first principles testing that addresses the knowledge gap regarding the properties of buffered and un-buffered boric acid solutions, especially the impact on convective boiling heat transfer, surface tension, density, solubility limit, and viscosity. The results of these tests are described in several PWROG and Westinghouse documents and are summarized below. The information relating to the PWROG testing has been grouped as follows: physical property chemistry (Section 4.1), core channel boiling (Section 4.2), PWR vessel mixing (Section 4.3), chemical reactions (Section 4.4), generic PWR chemical model (Section 4.5) and addendum to generic chemical model (Section 4.6), alternate buffering agents (Section 4.7), in-vessel effects (Section 4.8) and precipitation/mixing PIRT (Section 4.9).

In addition to investigating chemical effects in the post-LOCA containment sump, the PWROG sponsored a program to analyze the effects of debris and precipitates on core cooling for PWRs when the ECCS is realigned to circulate coolant from the containment sump (Section 4.8). In support of this effort, the PWROG initiated prototypical fuel assembly testing to establish limits on the debris mass that could bypass the containment sump screen and not cause unacceptable head loss that would impede core inlet flow and challenge LTC. This program and subsequent request for additional information (RAI) responses are documented in References 14, 20 and 24.

4.1 PHYSICAL PROPERTY CHEMISTRY

The chemical makeup of the post-accident coolant is primarily determined by the boric acid content of the source fluid and the plant-specific buffering system. The impact of the buffering system on post-accident coolant was investigated to provide additional details on possible chemical matrices in the post-accident environment. The presence of pH control agents in sump solutions could impact precipitation thermodynamics and kinetics as well as the general solution properties. The purpose of Reference 1 is to increase the SOK relative to the physical properties that play a large role in precipitation control and should be further investigated in full height testing. This is accomplished by determining key physical properties of buffered and un-buffered boric acid solutions under similar conditions to those expected during the LTC phase following a LOCA. The four physical properties addressed in Reference 1 for both buffered and un-buffered boric acid solutions are viscosity, density, surface tension, and solubility limits. These physical properties were found to differ between buffered boric acid solutions, un-buffered boric acid solutions, and water. This finding was mostly consistent with boiling channel testing funded by Westinghouse.

There are three alkaline pH control agents currently used in PWR plants including sodium hydroxide (NaOH), trisodium phosphate (TSP, $Na_3PO_4 \cdot 12H_2O$), and sodium tetraborate (STB, $Na_2B_4O_7 \cdot 10H_2O$). Sodium hydroxide is introduced into the coolant through the containment spray system (CSS). TSP is used at some PWR plants for pH control and is contained in baskets in containment. Following a LOCA, the TSP is dissolved by coolant exiting the break into containment and carried into the reactor upon recirculation. STB is another pH control agent used at some PWR plants. It is either added to the coolant via baskets on the containment floor, like TSP, via manual batching or contained in an ice reservoir in containment (with plants that have ice condensers) that remains frozen at normal operating conditions but melts under accident conditions. The solutions tested included a control solution of un-buffered boric acid and three test solutions of boric acid, each buffered with one of the three buffering agents described above.

4.1.1 Physical Property Test Procedure

The results presented in Reference 1 were derived from testing performed by Fauske & Associates as documented in Reference 2. Fauske & Associates performed bench scale tests to measure fluid properties and solubility data. Properties were obtained at atmospheric pressure, to be consistent with low-pressure, post-LOCA conditions. Atmospheric pressure is representative of lower bound containment pressures for large break scenarios where the RCS would quickly depressurize, as well as intermediate and small-break scenarios in which reactor operators would take actions to cool down and depressurize the RCS (Reference 1, Section 1.3, pg. 1-5). The temperature range for the properties was 150° to 212°F. This temperature range is expected to cover the bulk conditions in the boiling region and lower plenum of the reactor vessel (Reference 1, Section 1.3, pg. 1-5).

Concentration and pH were varied for the solutions during each property testing, by selecting values representative of post-LOCA containment sump conditions. For the NaOH – H_3BO_3 system, pH values of 7 and 10 were chosen to bound the expected conditions for the coolant prior to evaporative concentration in the core. A low pH value of 7 is a reasonable criterion since the ECCS is designed to achieve this minimum pH to meet regulatory requirements for iodine retention. A high pH value of 10 is consistent with maximum sump pH used by the industry and NRC for LTC testing. Extremes in pH were not tested for STB and TSP since the pH in these buffered systems is not likely to vary greatly. This is justified since these pH control agents are weak bases and form good buffers with weak acids, such as boric acid. Concentrations of boric acid and the buffering agents were chosen to represent expected ECCS concentrations directly following LOCA, as well as following approximately 10 to 20 times evaporative concentration.

4.1.2 Density

Density measurements were within expectations and support density-driven convection between the core and lower reactor vessel region as a mechanism that reduces the risk of bulk precipitation in the core. Density is shown to increase with increasing concentration of boric acid and/or weak base and decrease with increasing temperature for all solutions (Reference 1, Table 2-1). Densities of the concentrated pH buffered solutions at 212°F were higher than those of the corresponding dilute solutions at 150°F and, in some cases, densities of the concentrated buffers were quite high (Reference 1, Table 2-1). Such high densities can provide a force for circulation of the core volume with the lower plenum following a cold leg break. This provides a mechanism for core dilution and may provide more margin to precipitation prevention than would otherwise be predicted if lower plenum mixing was ignored.

4.1.3 Viscosity

The viscosity of each boric acid solution was determined using an Ubbelohde viscometer (Reference 1, Figure 3-10). Average viscosity measurements did not indicate any highly viscous solutions that might inhibit free flow and mixing in the core (Reference 1, Table 3-1). There was little difference in viscosity between the different solutions at 2500 ppm boron concentration at both temperatures tested (Reference 1, Figure 3-1). Viscosity increased at higher concentrations, with moderate differences between the different chemical systems (Reference 1, Figure 3-1).

4.1.4 Surface Tension

To measure surface tension, a tensiometer was used with an ethylene glycol bath (Reference 1, Figure 4-1). The average surface tension values for all the solutions, with and without a pH agent, were lower than that of pure water at the same temperature (Reference 1, Table 4-1). Surface tension also consistently decreased with increasing concentration of the un-buffered or buffered boric acid solution (Reference 1, Table 4-1). Decreases in surface tension promote boiling nucleation, so in the presence of boric acid or buffered boric acid, improved nucleate boiling heat transfer within the core, as compared to water, is expected.

4.1.5 Solubility Limits

The solubility limits of 10 different boric acid solutions were determined in Reference 1. The term "solubility limit" is defined as the concentration of solute at which precipitation is observed to occur and the solid and dissolved species are in equilibrium. It should be noted that the solubility limits determined in the testing performed in Reference 1 were measured using a procedure that minimized supersaturation. The test data show that the solubility of boric acid is increased by the presence of those compounds used to buffer pH in the post-LOCA containment pool (Reference 1, Table 5-1). Therefore, the amount of evaporative concentration that can be tolerated before precipitation would be greater for all the buffered solutions than for boric acid alone. As a result, there is conservatism inherent to using the solubility for un-buffered boric acid solutions in LTC post-LOCA analyses. The results of this report should be conservative, without the implications of chemical reactions between the simulated coolants and coolant impurities. This latter effect may either increase or decrease solubility limits.

[

]^{a,c}

[

]^{a,c}

4.2 CORE CHANNEL BOILING

There was a knowledge gap regarding the impact of concentrated boric acid solutions upon chemical precipitates, properties, and amounts that form within the core in post-LOCA environments. Westinghouse, as a result, investigated the convective boiling heat transfer behavior of buffered and un-buffered boric acid solutions in core channel geometry under conditions simulating those expected during the LTC phase following a LOCA in Reference 4. The research had two main objectives. First, nucleate boiling heat transfer tests were performed to determine the ability of sump chemical solutions to provide adequate boiling heat transfer from a simulated fuel rod without irreversible precipitation or irreversible depositions in a boiling channel configuration. The second objective was to assess fuel cladding integrity with concentrated un-buffered and buffered boric acid solutions and any deposits that might form due to the solutions.

Testing of convective boiling heat transfer of buffered and un-buffered boric acid solutions in a vertical channel was needed to confirm that pH control agents did not unfavorably alter heat transfer within the core. Concerns induced by buffering agents include boiling point elevation and boric acid solubility. Boiling point elevation may occur with the addition of any solute to a solvent. The presence of a solute (in this case the buffering agent), especially a less volatile solute, reduces the ability of solvent molecules at the surface of liquid-vapor interface to escape, reducing the vapor pressure of the solvent for a given temperature. As a result, a higher solution temperature is required to reach an appropriate vapor pressure such that boiling occurs. This can be improved via agitation and/or increased nucleation near the liquid-vapor interface. In addition, solubility curves for buffered boric acid solutions suggest the possibility of a lower limit at a higher pH. Also, if the turbulent bubble behavior in the nucleate boiling regime is reduced, boiling heat transfer from the fuel rod could be reduced at higher concentrations of solution. This would be due to the degraded circulation to bring liquid in contact with the rod surface.

4.2.1 Core Channel Boiling Test Procedure

Because of the concerns discussed above, three rounds of tests were performed by the Westinghouse Research and Technology Unit (RTU) in Reference 4. The three rounds of testing evolved from improvements made to the previous round of testing. The purpose of each round of testing is summarized below.

- Round 1: Investigated buffered boric acid with sodium hydroxide (to form sodium borate solution) at intermediate and low levels of pH.

- Round 2: Investigated buffered boric acid with sodium hydroxide (sodium borate) at high levels of pH, buffered boric acid with TSP, and boric acid without buffering agents.

- Round 3: Investigated boric acid buffered with STB and confirmed previous observations with an improved apparatus more prototypic of post-LOCA core boiling conditions.

The three rounds of boiling channel tests looked at the following characteristics of the buffer solutions as compared to water including:

- Boil-off rate
- Heat transfer from a heated rod
- Formation of solids
- Bubble characteristics

[

]^{a,c}

[

]^{a,c}

4.2.2 Results of Channel Testing

Observations were made at the rod bottom, center, and top for each round of testing. The collected evaporation rates and thermal data were found to not differ significantly between buffered boric acid solutions, un-buffered boric acid solutions, and water. [

]^{a,c}

The topical report prepared by Westinghouse (Reference 4) concluded that boiling channel tests show that for decay heat removal, boric acid solutions and boric acid solutions buffered with either sodium hydroxide, TSP, or STB were capable of adequately cooling a fuel rod at post-LOCA decay heat levels, over the concentration range expected prior to initiation of a means of active dilution such as a hot leg recirculation. Also, all boric acid solutions were capable of adequately cooling a fuel rod at post-LOCA decay heat levels without precipitation in the boiling region and without irreversible deposition just above the two-phase mixture level. There was potential for boric acid and buffered boric acid solutions to produce reversible deposition of solute further above the mixture level on heated surfaces via evaporation or boiling. As a result of this testing, it was shown that concentrated sodium borate solutions were effective in removing post-LOCA core decay heat (relative to pure water and un-buffered boric acid) and consequently did not invalidate Westinghouse LOCA clad heat up and post-LOCA decay heat removal assumptions. This boiling channel testing incorporated the importance of geometry, materials, and local thermal conditions on boric acid precipitation.

This report (Reference 4) did not address the following listed issues:

- Multi-component boiling (such as buffered boric acid with hydrocarbons)
- Impact of sump debris on core cooling
- Potential deposition on heated surfaces above the two-phase mixture level

4.3 PWR VESSEL MIXING

LTC considerations include decay heat removal, boric acid precipitation control, and the assurance of subcriticality in the core. The prevention of boric acid precipitation is usually assured by providing an active dilution mechanism to halt and reverse the concentration of boric acid prior to reaching the solubility limit. LOCA long-term cooling scenarios are typically defined by the break location and safety injection (SI) injection point. Three main break scenarios include (1) a cold leg (CL) break with CL injection (boric acid precipitation scenario), (2) a hot leg (HL) break with HL injection (hot leg switchover (HLSO) cycling requirement), and (3) a HL break with HL injection realignment with a dilute sump (potential for core recriticality). The credibility of these scenarios and ensuring effective dilution of the highly concentrated boric acid residing in the reactor vessel depends on the assumptions made regarding liquid mixing in the reactor vessel. The main mechanisms for vessel mixing include convection due to boron concentration gradients, convection due to thermal gradients, and turbulence due to boiling. Testing is needed to support the validity of the long-term cooling assumptions made with respect to these mixing mechanisms in the various LOCA scenarios.

4.3.1 CE, VEERA, and REWET-II Tests

The current and historical approach to in-vessel precipitation has been based on the assumption of limiting bulk precipitation mode in the RV. Test data on reactor vessel mixing behavior after a LOCA can defend assumptions typically used in long-term cooling analyses. [

]^{a,c}

[

]^{a,c}

For the PWR plant vessel and boiling channel mixing tests, boric acid precipitation was found to be a time-dependent effect throughout the upper and lower portions of the vessel, with the buildup proceeding gradually. The simplified methodologies currently used to evaluate PWRs should be conservative with respect to HLSO time and the potential for boric acid precipitation for un-buffered boric acid solution at typical PWR concentrations. Future studies could consider modeling decaying power level, axial and radial power distributions, concentrated un-buffered and buffered boric acid concentrations with and without sump debris, and higher-temperature coolant.

4.4 CHEMICAL REACTIONS

Westinghouse described the most important chemical reactions possible in a post-LOCA environment and why each might be important for core cooling to finalize a PIRT that integrates all the processes occurring after a LOCA that might impact LTC of the reactor core in Reference 5. Both important reactants and possible reactions are discussed. Reactants of the ECCS would include the coolant, materials contacted by the coolant and materials dissolved or suspended in the coolant. The reactive materials were ranked by available mass and surface area. [

]^{a,c} The possible reactions that occur are expected to be dominated by the reactants in greatest abundance, mainly boric acid and the plant-specific buffering agent. [

]^{a,c}

[

]^{a,c}

Inclusion of pH control agents has been shown to increase the solubility of boron compounds, as discussed previously. Properties of viscous solutions, instead of crystalline boric acid deposits, need to be considered when properties are significantly different from water. Polymeric borate species in solution at high concentrations would lead to increases in viscosity, not expected from simple salts. Boiling point elevations may also be high. Flow dynamics within the core may need to be addressed, including boiling pot scenario and reestablishment of flushing flow with the core. The flow may even be non-Newtonian. At worst case, sodium borates from bubbly masses could "puff" to form low-density solids. Changes in surface tension affect bubbles and boiling regimes, but have been shown to be favorable for nucleate boiling (Reference 1). Additional chemicals from corrosion and insulation dissolution make the situation complex. Interaction of containment organics with borate solutions is an area where little work has been done. These effects are discussed in subsequent sections.

4.5 GENERIC PWR CHEMICAL MODEL

A consistent approach for plants to evaluate the chemical effect that may occur post-accident in containment sump fluids is needed to address issues posed in Reference 16 and elaborated in Reference 19. Topical Report WCAP-16530-NP-A (Reference 10) establishes a method for utility engineers to perform a plant-specific evaluation of potential post-accident chemical effects in containment sump fluids to support their response to GSI-191. Version "-A" is the NRC-accepted non-proprietary version of Reference 10 that contains historical review information, including the NRC RAIs and Safety Evaluation (SE). The chemical precipitate amounts for the GSI-191 sump screen testing determined in Reference 10 is assumed to be a conservative bounding debris related chemical loading for in-vessel precipitation.

Each plant, given their plant-specific containment material concentrations, pH, and temperature post-accident can use this topical report to determine the type and amounts of chemical precipitates which may form and be transported to the sump screen. In order to meet this purpose, the topical report (Reference 10) discusses the following:

- Containment materials
- Rate of dissolution of materials
- Precipitate formation due to cooling and chemical reactions
- Development of a chemical model to predict dissolution and precipitate formation
- Use of particulate generator to produce representative precipitates for screen testing

For this summary, the work of Reference 10 is grouped into seven key areas listed below. Each of these is discussed in further detail including important points from the topical report and the NRC SE. The areas include:

1. Containment Materials
2. Dissolution Testing
3. Precipitation Testing
4. Chemical Model
5. Particulate Generator
6. Limitations and Conditions
7. Plant-Specific Application

Important issues raised by the NRC review of Reference 10 are included in the appropriate topic area from the list above.

4.5.1 Containment Materials

In order to select the materials and their representative amounts for the testing designed to support the topical report, plant surveys were collected delineating the types and quantities of material present in containment. The topical report (Reference 10) provides a compilation of containment materials based on a survey of all 69 operating U.S. PWRs. The base material of each containment material was determined from published information. Reference 10, Table 3.2-1 lists the base compositions of the containment materials. Ratios of plant material to water volume are determined conservatively, with maximum amount of material and minimum water volume. Table 3.2-2 classifies the materials based on their composition into 15 types. Tests were not performed on five material classes determined to have no significant interactions with the environment or having an insignificant amount of material in containment. Ten of the fifteen material classes were determined to have the potential to cause chemical effects in the containment sump including:

1. Aluminum

2. Aluminum silicate
3. Calcium silicate
4. Carbon steel
5. Concrete
6. E-glass
7. Amorphous silica
8. Interam® E-Class
9. Mineral wool
10. Zinc

Copper was not tested as it was found that the corrosion rate of copper and its alloys is low enough in the alkaline borate solution to be of no practical concern. Nickel was not included because the total quantity of nickel expected was small compared to other materials.

The NRC found the containment material types and amounts to be reasonable in the SE. The NRC had not verified the survey results in Reference 10, Section A. A RAI addresses the assumption that the amount of RCS oxides was not significant enough to be included in the testing of Reference 10. However, after the RAI was addressed, the NRC concluded that it was acceptable that RCS oxides were not included in the head loss testing source term. The amount of crud released during a LOCA would be insignificant compared to the other debris included in strainer head loss testing. Due to conservatism in other parts of the chemical model and the amounts of other particulate debris included in strainer testing, the amounts and effects of RCS oxides can be considered insignificant. The NRC also sponsored tests to confirm the selections of representative materials for the various nonmetallic material classes.

4.5.2 Dissolution and Precipitation Testing

Dissolution testing was performed in Reference 10 to determine the dissolution rates of various containment materials when contacted with simulated coolant solutions. Dissolution testing of containment materials of interest was measured as a function of pH and temperature. Interactions between dissolved materials to form precipitates were measured before and after cooling. The test data, in conjunction with the precipitation results, was used to construct a chemical model that considers plant-specific containment material mixes and conservatively predicts amounts and character of precipitates that form for a large-break LOCA (LBLOCA). Detailed material information chosen for dissolution testing can be found in Reference 10, subsection 5.1.2.1. Table 5.1-2 provides a breakdown of element weight percents for each material tested obtained through scanning electron microscope (SEM) and electron dispersive spectroscopy (EDS) scans. Material addition was scaled to the chemical reactor volume to maintain material-to-coolant volume ratios. Only concrete was added in a distorted ratio, being conservatively large. Specific amounts added per 100 mL chemical reactor volume are listed in Reference 10, Table 5.1-4. Tested materials for dissolution, chosen to represent the 10 material classes, included:

1. Aluminum sheet
2. Concrete
3. Cal-sil
4. NUKON® fiberglass
5. High-density fiberglass
6. Mineral wool

7. Min-K®
8. Fiberfrax Durablanket®
9. Interam
10. Galvanized steel
11. Uncoated carbon steel

Copper was not included since corrosion resistance is similar to that of carbon steel or galvanized steel. Amounts of released dissolved material and suspended solids from the RCS are expected to be similar to those in a normal PWR shutdown. As such, nickel was not included since the quantity is expected to be small compared to other materials (Reference 10, Figure 5.1-1).

Reference 10, Figures 5.2-1 through 5.2-9 show the bench test schematics and equipment. The dissolution test matrix is found in Table 4.2-1. The pH levels tested (4.1, 8.0, and 12.0) spanned the pH range expected in the sump after a LOCA. The maximum temperature value of 265° ±5°F bounds most industry survey values. Sampling times were at 30, 60, and 90 minutes. Short-term dissolution rates are expected to bound long-term corrosion rates, since most corrosion/dissolution reactions slow with time. Short sampling times also ensure measurement of dissolution rates before saturation occurs. Dissolution rates were measured for each containment material individually. These rates are expected to be conservative as the dissolution of one material will have either no effect or an inhibiting effect on the dissolution of other materials. With integrated testing using complex mixtures of materials, dissolution and precipitation occur simultaneously, making weight loss and gain information minimally useful. Integrated tests, while realistic, produce complex mixtures of products that are difficult to analyze. As such, single-effects testing was performed in Reference 10.

Reference 10 concluded the elements having the highest dissolved concentrations were Al, Si, Ca. These elements are the most likely to form precipitates. Appendix A of Reference 10 gives concentrations of dissolved chemical species, release rates, and sample mass measurements for dissolutions test runs. Sixty-six tests were used to complete the 'design matrix tests' and 22 tests were used for repeatability to aid in error estimations and improve confidence intervals for model predictions. Inductively coupled plasma (ICP) mass spectrometry analysis was performed for key elements including: Al, Ca, Si, Mg, P, S, Fe, Zn, and Ti. Reference 10, Table 5.2-1 and Figure 5.2-10 show the results obtained for total mass of each element at all time points, temperatures, and pH levels tested. Al, Ca, and Si dominated as the released elements. The elements P, Mg, and Ti were negligible in dissolved solution. Table 5.2-2 and Figure 5.2-11 show the total mass release from each tested material. Metallic Al had the highest potential for mass release into solution. Figure 5.2-12 shows the effect of pH upon release of Ca and Al. The higher the pH, the more Al was released. In contrast, the lower the pH, the more Ca was released.

The NRC reviewed the test methods and results for the dissolution testing and found them to be acceptable. The NRC determined the selection of pH and temperature was acceptable. The pH tested bounded the pH values that may be experienced by plant materials following a LOCA. The temperatures were acceptable since greater dissolution is expected to occur at elevated temperatures. The NRC also found the use of ICP analysis to determine the concentration of elements that leached into solution to be acceptable since this is a standard quantitative analytical method for determining the amount of a given element in solution.

At the end of 1.5 hours in the dissolution reaction vessels, the remaining solutions were placed in settling cones to measure any precipitation caused by cooling as documented in Reference 10. Reference 10, Figure 5.2-13 in the report shows the settling cone equipment setup. Reference 10, Table 5.2-3 provides the precipitation test matrix. Dissolution material was cooled to 80°F to test for chemical precipitate formation. This temperature is a typical long-term equilibrium pool temperature. The pH of boric acid solutions was adjusted to a pH of 8.0 using STB and TSP in separate tests. Characteristics of the precipitates were measured included mass, settling rate, settled precipitate volume, and precipitate filterability. Screening tests measured potential interactions between different containment materials to produce precipitates. Results of dissolution test and literature data guided selection of which solutions to combine.

Varying amounts of precipitate were observed for individual dissolution tests, as shown in Reference 10, Figures 5.2-14 and 5.2-15. Twenty-five of 60 experiments produced precipitates; however, only 13 produced measurable precipitations (listed in Reference 10, Table 5.2-4) with mass, volume, and estimated density. For simplicity in modeling, all aluminum released is assumed to form a precipitate and all calcium released in phosphate solutions is assumed to form a precipitate. Compositions of filtered precipitates analyzed by SEM are listed in Reference 10, Table 5.2-5.

Precipitates formed by cooling and by combining solutions were placed in centrifuge tubes to determine settling rates based on 10 mL of solution. Visible volume of the precipitate was measured at varying time intervals up to 4 hours and presented in Reference 10, Table 5.3-1. Precipitates did not settle quickly and cannot be discounted as a concern for sump screen performance. SEM analyses (found in Reference 10, Appendix B) of 13 precipitates showed constituent particles to be less than 20 microns and larger agglomerations of particles to be greater than 20 microns.

Precipitate filterability tests were performed to determine the overall filter cake coefficients (K_f) for the various precipitates formed to develop a filtration model. Chemically induced precipitates produced solids that had an average $K_f = 0.0034 \pm 0.0022$. Aluminum and silicate precipitates formed upon cooling had a value of $K_f = 0.0032 \pm 0.00202$. A small data set was used to generate these coefficients. The lower values may be used to make an initial guess for calculating maximum pressure drops. A filtration model was developed and can be found in Reference 10, Section 5.4.2 and the test procedure for filterability in Reference 10, Section 5.4.3. The pressure drop is a function of the flow rate, flow area, viscosity of the liquid in the slurry, and filter cake coefficient. Reference 10, Table 5.4-1 summarizes the results of the filter cake coefficients. The delta-P versus flow data are presented for each run in Reference 10, Appendix C.

In conclusion, 13 of 60 tests formed precipitates. Ten formed precipitates after exposure to simulated coolant with a reduction in temperature. Precipitates were predominantly aluminum oxyhydroxide, calcium aluminum silicate, or sodium aluminum silicate. No precipitates settled rapidly and would not be expected to settle before being transported to the sump screen.

The NRC questioned some of the filterability model assumptions and the conclusion that relative filterability of aluminum oxyhydroxide and sodium aluminum silicate surrogate precipitates was similar. Precipitate mass, used to calculate the filter cake coefficient, was obtained after the test was completed by drying the hydrated precipitate collected on the test filter. Differences in degree of hydration between precipitates or batches could contribute significant error. These tests were not accepted by the NRC;

however, they were performed to permit comparison of the different surrogate precipitates. These filterability test results are not factored into the chemical model predictions.

The NRC also recognized, as did Reference 10, that amorphous, hydrated precipitates are difficult to characterize. The surrogate precipitates created in Reference 10 cannot be considered identical to those in the ICET for the following reasons:

- Limitations in the EDS technique used to identify the precipitates.
- Prediction of sodium aluminum silicate precipitate formation in Reference 10 is based on thermodynamic calculations in part.
- Surrogate precipitate preparation sequence adds aluminum nitrate before adjusting the pH with sodium hydroxide. However, the surrogate precipitate filterability and settlement characteristics were adequate to represent post-LOCA chemical precipitates in strainer head loss tests.

The chemical model prediction of the total amount of precipitate (that all dissolved aluminum precipitates) was acceptable to the NRC since this assumption results in a conservative amount of precipitate. Testing of Reference 10 showed the surrogate precipitate mixing tank concentration affected the settling properties. As a condition on the use of Reference 10, the additional settlement criteria provided in Section 4.0 of the SE must be followed.

The NRC stated the chemical model of Reference 10 may not accurately predict the relative amounts of aluminum oxyhydroxide and sodium aluminum silicate precipitates that could form in a plant-specific environment. Testing confirmed that small quantities of each surrogate precipitate produced significant pressure drop across a NUKON fiber bed. Since the effects of the two surrogate precipitates are similar, the predicted amount of precipitates was deemed acceptable and small quantities of each precipitate are effective at producing significant head loss across a fiber bed.

4.5.3 Chemical Model

The chemical model of Reference 10 consists of a spreadsheet that contains algorithms based on the leaching and precipitation tests and uses linear sums of the individual test results to determine the total amount of material that is dissolved and precipitated. Plant-specific information is entered into the spreadsheet in several steps. The output of the model is presented in a results table that shows the time-dependent amounts of aluminum, calcium and silicon released. The amounts of each precipitate predicted are also provided as a function of time. Individual pages on the spreadsheet indicate the elemental release and the precipitate formation on a plant-specific material basis to allow the user to determine the potential benefits gained by reduction or removal of certain materials from their plant. The following discussion presents the work conducted to develop this model.

The predominant precipitates expected are aluminum oxyhydroxide, sodium aluminum silicate, and calcium phosphate (for plants using TSP as a buffering agent) based on dissolution/precipitation testing of Reference 10. Other minor silicate materials may also precipitate. The chemical model only considers the release rates of aluminum, calcium, and silicate. A justification for exclusion of zinc and iron is given in Reference 10, pages 97 and 98. Reference 10 Table 6.2-2 shows the predicted integrated zinc release for

30 days post-LOCA by Reference 10 Equation 6-3 to be relatively small. Justification for the exclusion of nickel and copper is given in Reference 10, Section 5.1.2 and was summarized above.

The primary source of aluminum is from the corrosion of aluminum alloys. Minor contributions of aluminum result from degradation of insulation and concrete, which contain aluminum silicate and other aluminum salts. The release rate of aluminum from these materials decreases with time as the solubility limit is approached. Aluminum corrosion is not affected by the mode of solution exposure, so the same equation is used for aluminum submerged in the sump pool and for aluminum exposed only to containment spray solution.

The primary sources of calcium are concrete and calcium silicate insulation. Minor contributors include fiberglass and mineral wools. Silicate is an effective inhibitor for the corrosion of aluminum alloys, but evaluation of this effect was not performed as part of this single-effect test program and is not included in this model.

Regression analysis on concentration data generated during the bench testing at specific chemistry conditions was used to develop release rate equations as a function of temperature, pH, and concentration of the given species. These equations can be found in Reference 10, Section 6.2 along with model verification.

Two equations are developed for the aluminum release rate. Equation 6-1 of Reference 10 is fitted to the bench scale testing data, while Equation 6-2 of Reference 10 is fitted to both the bench scale testing and data from Reference 26. Reference 26 data is for analyses concerning post-LOCA containment hydrogen generation. At intermediate times (less than 30 days), Equation 6-2 will under-predict the release rate. The cumulative 30-day integrated aluminum product release predicted by Equation 6-2 should be used for screen testing. Reference 10, Section 6.2.4 provides the equations developed to predict silicates, aluminum, and calcium release from insulation materials based on temperature and pH. The chemical effects dissolution model was verified for aluminum dissolution by comparing the aluminum corrosion predictions to those of the computer code GENNY, used to calculate hydrogen produced from aluminum corrosion. Good agreement was obtained, as shown in Reference 10, Table 6.2-5. Predictions for dissolution of cal-sil were verified against prediction of calcium release rate in the Argonne National Laboratory (ANL) cal-sil dissolution tests, and the results are given in Reference 10, Table 6.2-6. The model performance for calcium silicate dissolution is conservatively high.

The types of precipitates generated are dependent on plant sump chemistry as well as sump materials. It is conservatively assumed that all of the dissolved aluminum will form precipitates upon cooling in the chemical model of Reference 10. Since the solubility of calcium silicate increases at lower temperatures, dissolved calcium would remain in solution in the absence of phosphate.

The chemical model eliminates the influence of temperature upon precipitation by the assumption that all aluminum and calcium in the presence of phosphate forms precipitates in the chemical model of Reference 10. The quantity of key precipitates is based on stoichiometry based on the buffering agent used by the plant.

A sensitivity study was performed in Reference 10, Section 6.5 using sample inputs from a cal-sil plant. A base case was run on a cal-sil plant with input parameters set at levels expected from a large break LOCA.

After the base runs, key inputs were varied and changes in the prediction of precipitation amounts evaluated for sensitivity to the input.

The amount of precipitate generated increased with increased pH, as shown in Reference 10, Figure 6.5-5. The slope increased with increasing pH as well. Reference 10 Figure 6.5-6 shows that with increasing temperature, the total precipitation mass increases at a relatively linear rate. Reference 10 Figure 6.5-7 shows that the precipitation mass is cut to about half by replacing buffering agent TSP with borax. Reference 10 Figure 6.5-8 shows the effect of changing buffering agent on precipitate type. Reference 10 Figure 6.5-9 shows that with increasing exposed concrete surface area, the total precipitate increases slightly.

The predominant precipitates, aluminum oxyhydroxide, aluminum silicate, and calcium phosphate (for plants using TSP for pH control), are included in the model. The first step predicts the rate of dissolution and solubility limits for Al, Ca, and Si elements at selected times post-LOCA. All the material dissolved is conservatively assumed to form precipitates. The main precipitate types and potential mass are calculated as a function of time.

4.5.4 Particulate Generator

The purpose of the particulate generator of Reference 10 is to create prototypical surrogate solid chemical products for sump screen performance testing at vendor test facilities. Representative precipitate properties may not be achieved by the use of similar chemical formula solid material. Addition of commercially manufactured particulates with similar chemical compositions was not assumed to provide an adequate simulation of the chemical precipitates. Reference 10, Section 7 includes a proof-of-principle and qualification testing for the particulate generator.

The system used to generate surrogate particles generally consists of one or more chemical reaction tanks+, one or more precipitate transfer pumps, a precipitate mix holding tank, and interconnecting hoses, piping and valves. The system is intended to use normal potable water at ambient temperature. Filtration and settling behaviors of key precipitates are influenced by the amorphous and hydration properties of the materials.

Testing of the particulate generator showed that simulated particulates could be successfully generated for use in sump screen testing. The quality and temperature of the water used to prepare the particulates is shown not to be critical. The most critical parameter is the limitation on the concentration of particulates in the mixing tank.

Precipitate concentration in the mixing tank was evaluated. It was observed that precipitate solutions prepared at higher concentrations settled at atypically high rates, even after subsequent dilution. High concentrations favor formation of precipitate with faster settling properties. The maximum concentrations of aluminum oxyhydroxide and sodium aluminum silicate in the mix tank should not exceed 11 g/L. The maximum mist tank concentration for the calcium phosphate precipitate should not exceed 5 g/L.

Maximum acceptable 1-hour precipitate settlement values prevent atypical settling of the surrogate precipitate. The acceptable precipitate 1-hour settled volume criterion is greater than 4 mL for all three surrogate precipitates.

In summary, representative particulates for the precipitates formed during the bench testing and predicted using the chemical model could be generated for use in sump screen head loss testing. The chemical precipitates should be treated as another class of inert debris for strainer testing purposes. The quality and temperature of the water in which the particulates are generated is not critical, although the concentration of particulates in the mixing tank is critical. If large quantities are required, the particulates may need to be prepared in multiple batches or additional mixing tanks.

For the particulate generator, the NRC questioned whether the 1-hour settled volume criterion was sufficient. A batch of aluminum oxyhydroxide prepared for head loss testing displayed changes in properties over time, even though the 1-hour settlement values met the acceptance criteria. In addition, a modified strainer head loss testing approach has been proposed by some licensees. This test is different from an approach that intentionally uses agitation to keep chemical precipitate suspended to ensure it reaches the test strainer. Two acceptability criteria are presented for both scenarios by the NRC in Reference 10, Section A, pg. 10.

4.5.5 Limitations and Conditions

Limitations and conditions are placed on the results of Reference 10 by both the topical report itself and the NRC in the SE. Additional analyses or other results obtained during resolution of remaining peer review panel issues could affect the conclusions in this evaluation (i.e., potential influences of organic materials on chemical effects). This SE does not address Reference 12 and comments will be provided separately. In addition, a separate SE will evaluate Reference 14. Chemical effects in the reactor vessel are not addressed in Reference 10 or in the SE. If strainer head loss tests with surrogate precipitates are performed and apply time-based pump net positive suction head (NPSH) margin acceptance criteria, the chemical model must use the aluminum release rate that does not under predict the initial 15-day aluminum concentrations in ICET 1. Head loss test acceptance criteria are presented on pg. 17–18 of Reference 10. For strainer head loss testing that uses sodium aluminum silicate (Reference 10) and is performed in deionized water, the total amount of sodium aluminum silicate added to the test shall account for the solubility of sodium aluminum silicate in this environment.

4.5.6 Plant-Specific Application

Reference 10, Section 8.0 allows each plant to use their plant-specific post-accident containment material concentrations, pH, and temperatures to determine the types and amounts of chemical precipitates that may form and be exposed to the sump screen. A spreadsheet containing the chemical model allows for plant-specific prediction of precipitate formation. This section provides guidance for utility engineers to input plant-specific containment material amounts, recirculation water volume, post-accident sump and spray pH transients, post-accident sump and spray temperature transients, and to indicate if TSP is used as a buffering agent. Once the input is supplied, the chemical model predicts the types and amounts of precipitates formed. The main chemical precipitates of concern per the chemical effects testing are aluminum oxyhydroxide, sodium aluminum silicate, and calcium phosphate. The chemical model output yields types and amounts of chemical precipitates that should be included in plant-specific testing of replacement sump screens.

4.6 ADDENDUM TO GENERIC CHEMICAL MODEL

Additional plant-specific inputs to the chemical model of Reference 10 were evaluated in Reference 12. It should be noted the NRC has not issued a safety evaluation on Reference 12 at the time this report was issued, as such, arguments made by utilities based upon Reference 12 may not be accepted by the NRC. The chemical precipitate formation may be decreased by addressing conservatisms in the previous generic model. The areas of conservatism chosen for testing were silicate/phosphate inhibition of aluminum corrosion, the variability of corrosion rates between aluminum alloys, and the solubility limits of key precipitates. Initial scoping tests were performed to estimate the potential benefit of each plant-specific input. Follow-up parametric testing was then performed to quantify the effects over the temperature and chemistry conditions if specific criteria were met in the scoping tests. The temperature and pH ranges selected are expected to bound the long-term equilibrium conditions applicable for the participating plants. The majority of precipitates are formed under these conditions. Eight conclusions for the generic chemical model are listed in Reference 12, Section 6 regarding the results of the testing presented in Section 5. Reference 12, Section 3 outlines the test plan, and Section 4 describes any changes or additions made to the original test plan. Tasks included for exploration in the test plan include:

- Silicate inhibition of aluminum corrosion
- Corrosion rates of various aluminum alloys
- Phosphate inhibition of aluminum corrosion
- Solubility of aluminum and calcium precipitates:
  - Sodium aluminum silicate
  - Aluminum oxyhydroxide
  - Calcium phosphate

Changes to the original scoping and parametric testing outlined in Section 3 included increasing the long-term solubility observation period, sensitivity tests on precipitate solubility to evaluate changes to pH and temperature, and testing to evaluate increased nucleation and seed material upon aluminum precipitation.

Section 6, Item 1 of Reference 12 provides an amended aluminum release rate equation from that of Reference 10. For plants with predicted silicon concentrations in excess of 75 ppm threshold, the aluminum release rate equation may be used once the silicon concentration reaches a specified threshold value. The equation is valid over a pH range of 6.55 to 11.0 and at temperatures below 200°F. Outside these conditions, the Reference 10 aluminum release equation should continue to be used. The validity of the equation is independent of the buffering agent used. To account for conservatism in the quantity of silicon predicted to be released, consideration may be given to the use of a silicon threshold higher than the 75 ppm value determined in the Task 1 testing. Limited silicate inhibition may be credited at moderate temperatures (below 200°F) and pH (7 to 9).

Reference 12, Item 2 states that a generic corrosion rate for all aluminum alloys based on the corrosion rate of commercially pure aluminum (Alloy 1100) is sufficient. There is no benefit to the development and implementation of alloy-specific aluminum release rate equations, based on aluminum alloy testing under Task 2, relative to the corrosion rate of commercially pure aluminum. The corrosion of alloys tested was 68 to 82 percent of the corrosion measured on Alloy 1100 coupons. Dissolved aluminum in the test solutions for the alloys range from 79.2 to 92.1 percent of that measured for the Alloy 1100 control. Given that none of the alloys tested is the only type of aluminum present at any of the participating plants, the net reduction in aluminum precipitate generation that would result from including alloy-specific corrosion rates in the chemical model would be low. The results for specific alloys may be used to calculate reduced aluminum release under moderate temperature and pH.

Reference 12, Item 3 provides the aluminum release rate for plants that use TSP as a buffering agent. For plants that use TSP, the aluminum release rate equation may be used once the temperature is below 200°F. The equation is valid for pH levels 4.5 to 9.0 and temperatures from 150° to 200°F.

Reference 12, Item 4 states the effects of silicate and phosphate inhibition are applicable to aluminum metal. The effects of silicate inhibition and phosphate inhibition are applicable to both submerged and un-submerged aluminum metal. Both silicate and phosphate form conversion coatings that impart corrosion resistance. Both spray and bath applications of such coatings are common industrial practices for preparation of metal components. In these applications, the spray duration is 1 hour or less, so inhibition of un-submerged aluminum metal corrosion is applicable as long as the sprays have been on for 1 hour.

Reference 12, Item 5 states sodium aluminum silicate should be treated as insoluble in sodium hydroxide, STB, and sodium metaborate buffered solutions.

Reference 12, Item 6 provides the solubility limit of sodium aluminum silicate in TSP buffered solutions. The solubility limit of sodium aluminum silicate in TSP solutions is 40 ppm aluminum, with a corresponding silicon concentration of 119 ppm, valid at temperatures above 140°F. The aluminum concentration may be reduced by 40 ppm and the silicon concentration may be reduced by 119 ppm prior to calculation of the quantity of sodium aluminum silicate generated in the chemical model of Reference 10.

Reference 12, Item 7 provides the solubility limit of aluminum oxyhydroxide for all currently used and alternative buffering agents identified in Reference 13. The solubility limit of aluminum oxyhydroxide is 40 ppm aluminum. This limit is valid at temperatures from 140° to 200°F. Above 200°F, the solubility limit is 98 ppm aluminum. To implement this limit, the aluminum concentration may be reduced by 40 ppm prior to calculation of the quantity of aluminum oxyhydroxide generated in the chemical model of Reference 10. This solubility limit is applicable to all currently used buffering agents as well as alternative buffering agents identified in Reference 13.

Reference 12, Item 8 states that calcium phosphate should be treated as insoluble in TSP buffered solutions.

4.7 ALTERNATE BUFFERING AGENTS

An evaluation of alternative buffering agents for use in PWR ECCS, which may decrease chemical precipitate formation following a LOCA, was performed in Reference 13. The replacement of currently used buffering agents could reduce potential post-accident chemical effects in containment sump fluids, in-vessel precipitation, and sump screen plugging due to formation of chemical products. The results of the ICET program and the PWROG sponsored Chemical Effects Bench Testing (Reference 10) indicate two main contributors to precipitate formation following a LOCA. The high pH of sodium hydroxide buffered sump solution post-LOCA may cause significant metal corrosion, resulting in oxide particulate corrosion products and the potential for the formation of metal silicates. Also, the reaction of TSP with dissolved metals may form metal phosphate precipitates. Recent tests performed at ANL demonstrate that chemical products, specifically calcium phosphate precipitates, may contribute significantly to head loss across simulated sump screen debris beds. A reduction in the potential for chemical precipitate formation may allow plants to more easily demonstrate design margin for new or existing sump screens and in-vessel precipitation. Three primary classes of potential alternatives included:

- Borates
- Polymeric phosphates
- Chelating agents

Borates include salts of tetraborate, metaborate, and octaborate. Polymeric phosphates include salts of tripolyphosphate, pyrophosphate, and metaphosphate. Chelating agents are chemicals capable of capturing metal ions, such as ethylenediaminetetraacetic acid (EDTA).

Reference 13, Table 3-1 provides properties of the candidate ECCS buffering agents. Candidate replacement buffering agents for TSP and sodium hydroxide in PWR ECCS that were tested included:

- Sodium tetraborate decahydrate (STB)
- Sodium metaborate tetrahydrate (SMB)
- Sodium tripolyphosphate (STPP)
- Sodium gluconate (SGlu)

Important properties of all candidate buffers must be similar to those of those chemicals currently used at PWR plants. These properties include the quantity required to adjust pH to target value, the dissolution rate in water at post-LOCA sump temperatures, lack of toxic effects, no adverse affect on the solubility of boric acid, resistance to degradation from radiation, resistance to degradation from elevated temperatures and humidity, lack of significant release of metal oxide deposits, non-hazardous material, affordability, and ready availability of the chemical. Seven phases of tests were performed in Reference 13 to determine the acceptability of the selected candidates with these properties in mind. The test plan of each is provided in Reference 13, Section 4. Test results of each are provided in Reference 13, Section 5. The evaluation of the buffering agent criteria was rated as excellent, good, or poor for each phase of testing and summarized in Reference 13, Table 6-1. These phases included:

1. Dissolution testing
2. pH adjustment of boric acid solutions
3. Dissolution in boric acid as a function of temperature
4. Aluminum and calcium addition
5. Corrosion testing
6. Environmental effects testing
7. Boric acid solubility testing

SGlu was eliminated due to its inability to achieve a target pH of 8.0. STPP provided the best results in the precipitation testing and formed the smallest amount of precipitate with the addition of aluminum and calcium. However, during corrosion testing, STPP may cause significant release of iron and aluminum from containment structural materials. STB and TSP maintained their form during testing at elevated temperature for 30 days. STB and SMB buffers are the most comparable alternatives to TSP and sodium hydroxide, when comparing the tests phases. STB would be recommended over SMB due to the results of the environmental effects test, in which SMB dissolved. STB is currently used in ice condenser PWR plants. SMB in solution, however, would be a suitable replacement for sodium hydroxide.

STB is the best alternative to TSP for plants with high loadings of calcium-bearing materials in containment. For plants without a high loading of calcium-bearing materials, TSP would be the better candidate. For high-calcium plants, use of STB would eliminate concerns with precipitation of calcium phosphate (with precipitate reduction greater than 40%). In addition, STB provides the following attributes: comparable buffering capacity as compared to TSP, no new types of precipitate formation at a pH of 8.0 or less (irrespective of calcium loading), similar corrosion to steel structural materials compared to TSP, increased solubility of boric acid as with TSP, and STB has been evaluated for other potential chemical effects as part of the PWROG and ICET programs. The results of Reference 13 also show SMB in solution to be a suitable replacement for sodium hydroxide solution. The change to SMB with a target pH of 7.5 would reduce the total precipitate formation by about 50 percent, and the more moderate pH of SMB would reduce aluminum corrosion during the first few hours post-LOCA. SMB with boric acid has a higher buffering capacity than NaOH, allowing sufficient margin for a lower target pH for the final sump chemistry conditions and the decrease in release of aluminum and silica from containment materials. Sodium hydroxide and SMB provide similar increase in solubility of boric acid, comparable corrosion of carbon steel, and once dissolved, chemistry similar to buffered solutions with boric acid.

4.8 IN-VESSEL EFFECTS

Concerns have been raised about the potential for debris ingested into the ECCS, which may affect LTC when recirculating coolant from the containment sump. During operation of the ECCS to recirculate coolant from the containment sump, debris in the recirculating fluid that passes through the sump screen may collect throughout the fuel assemblies (FAs) causing resistance to flow through this path. The collection of sufficient debris is postulated to impede flow into the FA and core. Other concerns have been raised with respect to the collection of debris and post-accident chemical products within the core itself. Specifically, the debris has been postulated to either form blockages or adhere to the cladding, thereby reducing the ability of the coolant to remove decay heat from the core. Similarly, chemical precipitates have been postulated to plate out on fuel cladding, again resulting in a reduction of the ability of the coolant to remove decay heat from the core.

The PWROG undertook a program, Reference 14, to provide additional analyses and information on the effect of debris and chemical products on core cooling for PWRs when the ECCS is aligned to recirculate coolant from the containment sump. As part of this program, a methodology to predict chemical deposition on fuel cladding due to the transport of debris and chemical products into the RCS and core region was developed. This methodology is referred to as the loss-of-coolant accident deposition model (LOCADM). Additionally, FA testing was conducted to establish limits on the debris mass that could bypass the reactor containment building sump screen.

Actions are required of utilities to demonstrate LTC with debris and chemical products in the recirculating fluid. Plants will have to perform plant-specific LOCADM evaluations and prove the plant conditions are bounded by the debris load acceptance criteria.

4.8.1 LOCADM

LOCADM is a calculation tool that can be used to conservatively predict the build-up of chemical deposits on fuel cladding after a LOCA. The source of chemical products is the interaction of the fluid inventory in the reactor containment building sump with debris and other materials exposed to and submerged in the sump fluid. LOCADM predicts both the deposit thickness and cladding surface temperature as a function of time.

Plants must use the LOCADM calculation tool to demonstrate the following acceptance criteria are met:

1. The maximum clad temperature shall not exceed 800°F.
2. The thickness of the cladding oxide and the fuel deposits shall not exceed 0.050 inches in any region.

4.8.2 Debris Load Acceptance Criteria

As previously stated, the PWROG sponsored FA testing to establish limits on the debris mass that could bypass the reactor containment building sump screen. Testing was conducted by Westinghouse and AREVA and the test results are summarized in References 9 and 23, respectively. Upon issuance of these test reports, the NRC issued RAIs which resulted in additional FA testing.

Both Westinghouse and AREVA refined the debris load criteria presented in Section 10 of Reference 14. Both fuel vendors have simplified the debris load criteria to a single debris source – fiber. That is, the only debris that will have a limit is the fibrous insulation. Westinghouse and AREVA have submitted revised fiber limits to the NRC (References 24 and 25). Utilities are tasked with comparing plant-specific debris loads against the revised fiber limits. Plants that have bypass fiber loadings that are within the limits of the maximum allowable fiber load are bounded by the tests. At this time, the fiber limits are still under review and will not be included in this document until the NRC issues a draft SE on Reference 14.

4.9 PRECIPITATION/MIXING PIRT

The purpose of Reference 11 was to create a PIRT to identify and rank phenomena of the most plausible precipitation modes that lead to initiation of sustained net growth of solid phase precipitants in the steam generator, hot legs, and various regions of the reactor vessel. Reference 11 also identifies and ranks phenomena that impact transport and mixing in the reactor vessel prior to precipitation. These PIRT considerations may be useful in the development of analytical mixing models and scaled testing for a boric acid control plant evaluation model. Figure 4-1 depicts the factors the PIRT considered when predicting precipitation in the RV.

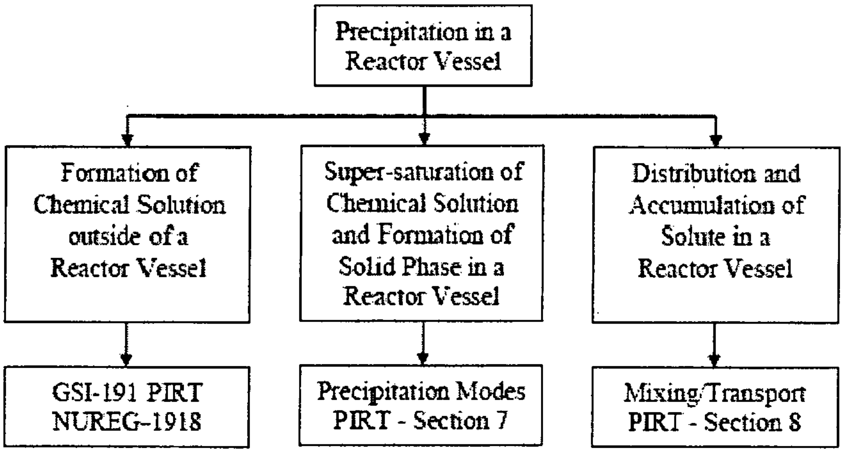

Figure 4-1 Precipitation PIRT Tree (Figure 6-1 from Reference 11)

The Precipitation Modes PIRT for un-buffered/buffered boric acid solutions addresses the possibility of multiple precipitation modes or limits in various regions of the reactor vessel that depend on different factors including supersaturation, liquid entrainment, and nucleation.

A bulk precipitation mode in a reactor vessel is not likely to occur or initiate before other precipitation modes. Bulk reactor vessel precipitation has not been seen or reported in any of the available precipitation tests. Precipitation was reported primarily in the high void region of the core/upper plenum region with less significant precipitation reported in the cooler sections of the lower plenum. The reactor vessel volume is not expected to be at uniform concentration and temperature. The local solubility limit is expected to vary as a function of local/regional temperature in the reactor vessel volume. Other precipitation modes have been observed in available precipitation tests. Local precipitation and growth have been seen in the presence of foreign surfaces and local supersaturation due to evaporating or cooling of the solution.

High-ranked precipitation modes involve interaction between buffered or un-buffered boric acid solution and various surfaces within the reactor vessel where supersaturation and favorable surface energy conditions exist for precipitation. Local or regional supersaturation is likely to be brought about by heated or cooled surfaces to initiate sustainable nucleation and growth. The following summarizes the highly ranked modes for initiation of boric acid precipitation:

- Precipitation (amorphous solid with voids) associated with rapid evaporation (boiling) and supersaturation of entrained liquid solution on heated surfaces above two-phase mixture level (core boiling region during core uncovery only and steam generator region)

- Precipitation on boiling surfaces in high void, two-phase mixture level associated with bubble film (microlayer film at base of bubble) evaporation and supersaturation (core boiling region)

- Precipitation on walls and structures above two-phase mixture level associated with liquid film or droplet evaporation (non-boiling) and supersaturation (core boiling region during core uncovery only, upper plenum region, barrel or baffle region during core uncovery only)
- Precipitation on cooled surfaces or walls and structures in single-phase liquid region associated with local supersaturation and heterogeneous nucleation (lower head region and core support region)

These highly ranked precipitation modes are consistent with test experience of the boiling channel tests funded by Westinghouse as well as the VEERA and REWET-II tests. These tests recorded crystallization after several hours of boiling at the core top near the two phased mixture level, and where supersaturation was reached by a fast reduction in pressure, crystallization took place in the whole upper part of the core. Crystallization was also observed in the lower plenum. Boric acid precipitation was determined to be time-dependent through the upper and lower portions of the PWR vessel with buildup proceeding gradually. BACCHUS tests did not report precipitation, but these tests were not conducted with the objective of discovering precipitation modes.

A second PIRT was generated to identify and rank phenomena that impact transport and mixing in the reactor vessel prior to precipitation. Initiation of active dilution measures during LOCA long-term cooling is expected to prevent precipitation. The PIRT rankings reflect the importance of mixing and transport phenomena with respect to their impact on the "Figure of Merit," which concerns the solute concentration in the liquid mixing volume relative to the solubility limit for un-buffered or buffered boric acid solutions in the reactor vessel. The highly ranked phenomena important to boric acid mixing and transport in a reactor vessel following a LOCA included:

- Boric acid accumulation due to decay heat boil-off.
- Turbulent convection or dispersion of boric acid due to void motion in the core region.
- Natural convection mixing and transport of boric acid due to boric acid concentration gradient between the core region and other regions in the reactor vessel such as the baffle-barrel region, core support region, and lower head region.
- Turbulent mixing and transport throughout the reactor vessel.
- Transport of lower-concentration boric acid liquid in excess of make-up for boil-off from downcomer to inner reactor vessel liquid mixing volume regions.
- Natural circulation transport of boric acid from upper plenum or core to downcomer via hot leg nozzle gap or reactor vessel vent valves (RVVVs) (B&W plant).
- Transport of boric acid due to circulation or communication between core, upper plenum, and hot leg regions of liquid mixing volume.
- Natural circulation transport of boric acid in core region due to "chimney effect" of hot power channel.
- Transport or mixing and unsteady liquid entrainment due to unsteady or oscillatory flow resulting from reactor vessel/loop system interaction effects.

5 ANALYSIS OF NRC PIRT AND PWROG PERSPECTIVES

The summarized findings of both the NRC and PWROG are compared to determine any differences in expectations between the two organizations. The key findings of high significance and limited SOK common to both organizations are identified. Testing to close the knowledge gap is either presented if available or recommended if not. Areas of work performed by the PWROG that supply a suitable response to NRC concerns within the Research PIRT include chemical matrix effects pertaining to coolant characteristics, chemical reactions, and chemical product formation (Section 5.1), vessel mixing and transport effects (Section 5.2), and precipitation/deposition effects (Section 5.3).

Table 3-4 is updated considering the information presented in Table 5-1 with description of the condition evaluated. The importance and SOK of each item, 1 through 29, is re-evaluated considering the new information and alternative viewpoints. A new category is then assigned using the same considerations as applied in Reference 16. This new category is based on an interpretation of the same system used by the PIRT panelists in Reference 17 and includes values of I, II, III and IV.

In this case, the definition of state of knowledge remains consistent with that used in Reference 16 although is interpreted from the perspective of boric acid precipitation. Importance, however, is interpreted as a measure of the relative sensitivity of boric acid precipitation to the effect in question. Therefore, if updated research provides a clearer means of capturing the effect in the model, the ranking will be shifted toward a I ranking, whereas, if research has indicated that the phenomena does not impact boric acid precipitation, the ranking will be shifted toward a IV. Those items whose updated ranking are either a II or a III will be targeted in upcoming research to better support the final precipitation model.

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
1	Crud release due to hydraulic shock in the RV following an LBLOCA has been determined to be insignificant in comparison to other debris released (for strainer head loss testing) per RAI Response 14 of Reference 10 and in Reference 19. In addition, based on measured releases of crud during intentional coolant oxidation routinely conducted as part of normal plant shutdown, the magnitude of this release is expected to introduce a negligible quantity of material into the sump under accident conditions. These conclusions indicate that the amounts of released RCS oxides are expected to be small and have a minimal impact on the overall in-vessel precipitation effects within the first 24 hours.	4.5.1	Decreased	N/A	N/A	Improved	N/A	N/A	IV
2	This evaluation is concerned with the bulk chemical effects in the RV within the first 24 hours following an LBLOCA. Surface thermal and chemical conditions at the break site are not expected to impact in-vessel chemistry conditions. Conservatisms with respect to precipitate formation included in the chemical model of Reference 10 and LOCADM analysis tool of Reference 14 are expected to bound any change in bulk chemical effects due to various break sites and thermal conditions.	4.5 and 4.8	Decreased	N/A	N/A	No Change	N/A	N/A	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
3	PWROG precipitation and physical property testing has been performed at pH ranges expected to bound those conditions following an LBLOCA. Testing pH ranges were based on the presence of boric acid and applicable buffering agents. Thermodynamic properties of all buffered boric acid solutions in simulated core geometry at a bounding pH range were found to not differ significantly from those of water per Reference 4. The pH range in the RV in conjunction with turbulent mixing, concentrated buffered and un-buffered boric acid solution, and sump debris are evaluated concurrently.	4.1 and 4.2.1	Decreased	N/A	N/A	Improved	N/A	N/A	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
4	Although no direct data are available, it is not expected that the presence of highly oxidizing free radicals would strongly affect the dissolution of inorganic containment materials such as insulation since the dissolution does not occur by oxidation. The 800°F temperature acceptance criterion of Reference 14 was chosen based on autoclave data that demonstrated oxidation and hydrogen pickup to be manageable and the reduction in cladding small. In addition, oxidation/reduction reactions, which typically occur slowly over time, are not expected to significantly impact the containment pool chemistry in the 24-hour period following an LBLOCA. Therefore, the expected reactive species in the containment sump pool are expected to be mostly inorganic and in dilute concentrations. Oxidizing conditions in the RCS are not expected to affect RV precipitation, and the results of the chemical model developed in Reference 10 and the LOCADM analysis tool of Reference 14 should remain bounding.	Reference 10, RAI 15 Response	Decreased	N/A	N/A	Improved	N/A	N/A	IV
5	Break location and size are not expected to significantly impact the bulk chemical conditions in the RV. The results of LOCADM, based on the chemical model developed in Reference 10, conservatively predict deposition of precipitates in the RV based on bounding amounts of reactive materials in containment following an LBLOCA, which were based on plant-specific chemistry and thermal conditions. See Response to Item 2 of Table 3-4.	4.5 and 4.8	Decreased	N/A	N/A	Improved	N/A	N/A	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
6	The chemical model of Reference 10 evaluated dissolution of 10 containment material classes evaluated to be potentially reactive. The primary species of interest, found to have the highest dissolved concentrations with the highest potential to form precipitates, included Al, Si, and Ca. Precipitation testing provided a basis for determining bounding predicted precipitate amounts for sump screen head loss testing. Reference 14 evaluated the impact of chemical debris upon heat transfer in the RV to determine acceptable debris loading based on testing including blockage at the core inlet, fuel grids, and between the fuel cladding. The testing recorded in References 9, 14 and 23 was conducted with the intent of defining a debris limit that would not impede coolant flow through the fuel assemblies. The presence of certain compounds in fiber beds containing sodium borate to form gelatinous beds has not been evaluated.	4.5.2, 4.5.3, and 4.8	Decreased	N/A	Raised Additional Questions	Improved	N/A	Improved	III
7	PWROG bench scale and core channel testing per Reference 1 and Reference 4, respectively, indicated the pathway for precipitation was dominated by thermal differences as compared to particulate nucleation sites. Precipitation is more likely to occur in areas of heat exchange; therefore, precipitation due to debris nucleation is not expected to be the dominant pathway for in-vessel precipitation following a LBLOCA.	4.1.5 and 4.2.2	No Change	N/A	Decreased	Improved	N/A	Improved	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
8	Reductive conditions in either the refueling cavity or RCS are not expected to impact the RV chemistry coolant conditions within the time period of interest, 24 hours following the LBLOCA. See Response to Item 4 of Table 3-4.	N/A	N/A	Decreased	N/A	N/A	Improved	N/A	IV
9	ECCS chemical contributions and impact as well as impact of chemistry on the ECCS are to be evaluated using GSI-191 and are not expected to impact the conservative results of the chemical model or LOCADM. The ECCS is expected to contribute water, boric acid, and the plant-specific buffering agent already considered to be part of the RV coolant for the chemical model and LOCADM.	N/A	N/A	No Change	No Change	N/A	Increased	Increased	II
10	LOCADM (Reference 14) includes conservative predictions of debris dissolution and corrosion product release from system materials, and dissolved corrosion products. All such released material that is transported to fuel cladding surfaces by boiling is assumed to deposit.	4.8	N/A	Decreased	N/A	N/A	Improved	N/A	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
11	PWROG testing considered the following pH buffering agents currently used in the operating fleet: sodium hydroxide, trisodium phosphate, and sodium tetraborate. Boric acid buffered with these pH agents was evaluated in physical property testing (Reference 1); in core channel geometry thermal property and precipitation testing (Reference 4), and development of the post-LBLOCA chemical model (Reference 10). Reference 1 determined buffered boric acid solutions have lower surface tension and higher solubility limits as compared to boric acid alone. These two properties reduce the potential for precipitation, indicating conservatisms in current analysis methodologies. Reference 10 determined the thermodynamic properties of all buffered boric acid solutions not to be significantly different from those of water. Reference 13 evaluates current and possible alternative pH buffering agents as compared to sodium hydroxide.	4.1, 4.2, and 4.5	N/A	No Change	No Change	N/A	Improved	Improved	II
12	The chemical precipitate amounts determined for GSI-191 sump screen testing in Reference 10 are bounding with respect to dissolution testing. For dissolution testing of Reference 10, representative concentrations expected in an LBLOCA environment were determined and tested.	N/A	N/A	Decreased	N/A	N/A	No Change	N/A	III

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
13	The chemical model of Reference 10 evaluated dissolution of 10 containment material classes evaluated to be potentially reactive based on relative amounts in containment and chemical composition. The primary species of interest, found to have the highest dissolved concentrations, included Al, Si, and Ca. These species, therefore, have the highest potential to form precipitates in the post-LBLOCA coolant. The chemical model of Reference 10 predicts the amount of generated precipitate based on plant-specific inputs, including temperature, pH range, buffering agent, and containment material masses.	4.5.2 and 4.5.4	N/A	No Change	No Change	N/A	Increased	Increased	II
14	The closed-vessel tests performed in Reference 10 to determine dissolution rates of materials did not have representative levels of carbon dioxide. For metals, the presence of higher levels of carbon dioxide could potentially reduce corrosion due to formation of protective metal carbonates; therefore, material release determinations in a carbon dioxide depleted atmosphere are conservative. During precipitation testing, the solutions were exposed to carbon dioxide from the air for 24 hours, so reaction with atmospheric carbon dioxide to form metal carbonate precipitates was possible. Since all Al in solution is assumed to precipitate, there is no net effect on precipitate quantity even if metal carbonates were to form. In addition, aluminum carbonate has better filtration characteristics as compared to Al silicate/oxyhydroxide, so not considering precipitation of carbonates in this model is conservative.	Reference 10, RAI 3 Response	N/A	Decreased	No Change	N/A	Increased	Increased	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
15	Mixing within the sump does not significantly impact the high concentration effects associated with boric acid precipitation. Poor mixing of the high concentration solution leaving the vessel with the lower concentration sump solution provides a positive impact which is not typically credited due to the effects described by the PIRT panelists. However, mixing within the vessel is highly pertinent. This effect is addressed in this item below. PWR vessel mixing tests with un-buffered boric acid solution to simulate post-LBLOCA conditions indicated the buildup of boric acid precipitate occurred at the coldest region of the reactor vessel, the inside surface of the vessel lower head. This is similar to the observations of the core channel geometry small-scale mixing testing of Reference 4. In addition, the mixing volume may credit the core region and part of the lower plenum based on PWR mixing testing. For a PWR plant, boric acid precipitation was found to be a time-dependent effect throughout the upper and lower portions of the vessel with the buildup proceeding gradually. Further testing to characterize, model, and quantify mixing/transport phenomena in the reactor vessel is recommended.	4.3.1	N/A	No Change	N/A	N/A	No Change	N/A	III

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
16	Inorganic containment materials are predominantly resistant to breakdown by radiolysis; therefore, direct contact by high-specific-activity oxides would be negligible. Although no direct data are available, it is not expected the presence of highly oxidizing free radicals would strongly affect the dissolution of inorganic containment materials such as insulation since dissolution does not occur by oxidation. As with possible radiolysis effects, it should be recognized that similar materials, such as calcium and aluminum silicates, (boiling water reactor (BWR) primary coolant environment) are present in crud and would be subject to high concentrations of free radicals generated from radiolysis of water. Organic coating materials are not expected to be subjected to radiation levels that would cause degradation within the first ~24 hours following the accident.	Reference 10, RAI 15 Response, Reference 14, RAI 45 Response and Reference 17	N/A	No Change	Decreased	N/A	Increased	Increased	III
17	Metal-catalyzed chemical reactions including hydrolysis would occur slowly in a post-LBLOCA containment sump environment, and are not expected to impact precipitation or deposition in the RV within the first 24 hours but may have a larger impact during the T4 and T5 time frames.	N/A	N/A	No Change	N/A	N/A	Increased	N/A	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
18	Reference 10 identified two organic material classes: organic mastics and other organic materials. These two classes were determined to occur in insignificant amounts in containment and be unlikely to break down to produce precipitate-forming species. Therefore, organic materials were excluded from bench scale testing of Reference 10. Reference 14 determined organic coating materials would not degrade or adhere to heat transfer surfaces.	4.5.1 and 4.8	N/A	Decreased	N/A	N/A	Increased	N/A	IV
19	Auxiliary component cooling line break chemical contributions and impact are to be evaluated using GSI-191 and are not expected to impact the conservative results of the chemical model or LOCADM.	N/A	N/A	Decrease*	N/A	N/A	No Change	N/A	IV*
20	During the first 24 hours following the LBLOCA, polymerization (inorganic or organic) impact on precipitation rates is considered negligible. Polymerization reactions are not expected to affect the overall predicted precipitates due to the conservative assumptions in the chemical model and LOCADM.	N/A	N/A	Decreased	N/A	N/A	No Change	N/A	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
21	Dissolution and precipitation evaluations of Reference 10 are based on single effects testing. Co-precipitation effects (i.e., Al corrosion inhibition from leachable Si) should be considered; however, the conservatisms within the chemical model were determined to bound this uncertainty. These conservatisms include: all Al in solution is assumed to precipitate, no credit is taken for phosphate inhibition of Al corrosion in TSP environments, and no credit is taken for inhibition of Al corrosion by silicates. Reference 12 further evaluates the conservatisms in the chemical model of Reference 10 with multiple-effects testing to determine silicate and phosphate inhibition of aluminum corrosion, the solubility of predicted precipitates, and corrosion rates for various aluminum alloys.	4.5.4	N/A	No Change	N/A	N/A	Increased	N/A	III
22	Reference 10 performed filterability tests upon surrogate precipitates and the agglomeration of these particulates was determined. Particulate agglomerations were approximately less than 20 microns. The contributions of organics and organic degradation products on inorganic agglomeration are not reliably predicted.	4.5.4	N/A	Decreased	Decreased	N/A	Increased	No Change	III
23	Galvanic couples corrosion products are not expected to have a significant impact on the refueling cavity pool in the time period of interest. See Item 4 response of Table 5-1.	N/A	N/A	Decrease	N/A	N/A	No Change	N/A	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
24	The precipitate particulate generator of Reference 10 was evaluated for sensitivity with respect to temperature, pH, and concentration upon the precipitate type and size in the final solution. The precipitates formed were amorphous, had slow settling behavior, and poor filterability. As a result, these particulates cannot be discounted as a concern for sump screen performance.	4.5.4	N/A	Raised Additional Questions	Raised Additional Questions	N/A	Increased	Increased	II
25	The chemical contributions and overall impact of secondary system inflow due to tube rupture or other causes are to be evaluated by GSI-191 and are not expected to impact the conservative results of the chemical model or LOCADM.	N/A	N/A	N/A	No Change	N/A	N/A	No Change	IV*
26	Flow-induced effects including nucleation or turbulent scouring are to be evaluated using GSI-191.	N/A	N/A	N/A	Decreased	N/A	N/A	No Change	IV
27	Turbulent mixing is expected in the RV, as supported by core channel testing of Reference 4. Turbulent mixing in the containment pool is to be evaluated by GSI-191.	N/A	N/A	N/A	Decreased	N/A	N/A	Increased	IV

Table 5-1 Updated Condensed PIRT

Table 3-4 Item No.	Description of PWROG State of Knowledge	Supporting Section	PWROG Score Delta						PWROG Category
			Importance			Knowledge Score			
			T1	T2	T3	T1	T2	T3	
28	While the precipitation path way in heat exchange areas will differ from the bulk solution due to thermal gradients, the model being developed will assume appropriate limits to bound heat exchange and geometry considerations for concentrated buffered and un-buffered boric acid solutions. More significantly, the boric acid precipitation pathway has been shown to be dominated by the higher concentration solutions generated in the core rather than the reduced concentrations observed in the recirculated coolant.	4.1.5 and 4.2.2	N/A	N/A	Decreased	N/A	N/A	Increased	IV
29	The core channel boiling tests of Reference 4 indicated concentrated buffered boric acid solutions provided adequate decay heat removal of a fuel rod at post-LOCA decay heat levels over a concentration range expected prior to initiation of a means of active dilution such as HLSO. No precipitation occurred in the boiling region without irreversible deposition just above the collapsed two-phase level. There is a potential boric acid and buffered boric acid solutions could produce irreversible deposition of solute further above the two-phase level on heated surfaces via evaporation or boiling. Future RV mixing testing should focus on areas where irreversible deposition may occur or where higher concentration material may accumulate at temperature gradients.	4.2.2	N/A	N/A	Raised Additional Questions	N/A	N/A	Increased	II

* **These conditions may refer to passive failure conditions that lie outside the scope of the design basis analysis that considers boric acid precipitation. Comparison of the relatively minor effects of failures in these systems to other limiting failures clearly supports this position. For plants where failures in these systems are not passive, i.e. system failure can be induced by pipe-whip or other kinetic effects in containment as a part of the design basis accident, more detailed consideration may be required.**

5.1 CHEMICAL MATRIX

Chemical constituents present in the post-LOCA coolant may impact its thermophysical characteristics as well as the kinetics and thermodynamics of precipitation related phenomenon. Chemical loading based on the resolution of GSI-191 issues as well as extensive chemical reaction matrices developed in Reference 10, and later extended in References 12 and 14, establish a basis for expected coolant composition. This basis accounts for interactions of boric acid solutions with inorganic and organic materials, insulation, buffering agents, and corrosion products. It is clear in these investigations (References 10 and 12) that specific chemical products are present in significant concentrations while others are scarce and therefore of lesser concern with respect to in-vessel precipitation. Therefore, it is recommended that the LOCA long-term cooling in-vessel precipitation evaluation model be based on the thermophysical and precipitation characteristics of un-buffered and buffered boric acid solutions when establishing concentration limits since these related constituents dominate the composition of the post-LOCA coolant. Investigations documenting the resulting thermophysical properties and precipitation characteristics of such coolant have been considered in References 1, 4, and 10. The coolant characteristics and reaction types expected for the post-accident containment environment as impacted by GSI-191 are discussed in additional detail below.

5.1.1 Coolant Characteristics

Coolant physical characteristics for concentrated buffered and un-buffered boric acid solutions have been determined at a range of temperatures and pH (Reference 1). In-vessel precipitation and heat transfer is either improved or is not affected by the presence of buffer (References 1 and 4). Un-buffered boric acid and solutions of boric acid buffered with sodium hydroxide, TSP, or STB were investigated to empirically determine viscosity, density, surface tension, and solubility limits at various boric acid concentrations as detailed in Reference 1. First, no highly viscous solutions capable of inhibiting free flow and mixing in the core were observed (Reference 1, Table 3-1). Investigations also demonstrated that a driving force for core mixing is present due to variations in density with concentration of boric acid and/or buffering agent and solution temperature (Reference 1, Table 2-1). In addition, the surface tension for all solutions were lower than that of pure water which promotes boiling nucleation and improved nucleate boiling heat transfer (Reference 1, Table 4-1). Finally, the solubility of boric acid was observed to increase in the presence of pH buffering agents indicating an increased tolerance for evaporative concentration prior to precipitation (Reference 1, Table 5-1). All properties observed for boric acid solutions indicate coolant mixing in the core would be either neutral or improved as compared to water. In addition, since all plants use pH buffering agents, current boric acid solubility limits are conservatively low.

Boiling tests were performed using a test rig simulating some aspects of a reactor vessel core as documented in Reference 4. These boiling channel tests demonstrate that buffered and un-buffered boric acid solutions are capable of adequately removing post-LOCA decay heat over the expected concentration range prior to initiation of active dilution mechanisms, such as a hot leg recirculation in the event of a cold leg break. Also, all boric acid solutions tested were capable of adequately cooling a simulated fuel rod at post-LOCA decay heat levels without precipitation in the boiling region and without irreversible deposition just above the two-phase mixture level (Reference 4). As a result of this testing it was shown concentrated sodium borate solutions were equally capable of removing post-LOCA core decay heat when compared to pure water. Additional testing is recommended to determine the impact of sump debris and chemical loading on these results. It is noted that the relatively small contributions of chemicals other than boric acid and sodium borates are not expected to significantly impact the thermophysical characteristics of the coolant.

5.1.2 Chemical Reactions

The chemical makeup of the post-accident coolant is primarily determined by the boric acid content of the source fluid and the plant-specific buffering system. There are three pH control agents currently used in PWR plants including sodium hydroxide, TSP, and STB. Boric acid precipitation is typically considered in LOCA safety analyses for the case of pool boiling scenario where the coolant boric acid concentration increases. This neglects the impact of the buffering system. It is also feasible to consider the less limiting case of precipitation of buffered sodium borates rather than un-buffered boric acid. Such best-estimate methods will be considered during development of the in-vessel precipitation model where appropriate justification for coolant composition is available.

Precipitation of either boric acid or sodium borate is expected to initiate at phase interfaces, especially at solid surfaces that are cooler than the bulk coolant. The concentration at which the solubility limit is reached is a function of temperature, pH, buffering agent, and concentration. The impact of the buffering system on post-accident coolant was investigated in References 1 and 4 to provide additional details on possible chemical matrices in the post-accident environment.

Second-order or higher chemical reaction products, such as metal-catalyzed reactions like hydrolysis (Table 3-4, Item 17), oxidation and reduction (Table 3-4, Items 4 and 8) due to radiolysis (Table 3-4, Item 16), and polymerization of inorganic and organic particulates (Table 3-4, Item 20), are predicted to be negligible in comparison to contributions of primary constituents and debris for the time frame of interest for in-vessel precipitation.

A bias is expected due to the concentration dependence for various effects. The rates of chemical interactions, such as reaction, deposition, or precipitation, are highly dependent on the concentrations of all interacting species. If two or more particles must interact to generate a product, low concentrations of the reactants will significantly limit the rate of reaction. Surface interaction effects such as deposition are also concentration-dependent. However, such effects are only dependent on the concentration of the species of interest in the vicinity of the deposition site. Given the highly turbulent flow streams in the vessel, mixing is nearly ideal and the local concentration at the deposition site will be maintained at near bulk concentrations. Conversely, higher-order reactions are dependent on the interaction of two disparate particles, and therefore at least an order of magnitude less likely in low-concentration environments. Finally as particles interact to form new constituents, the reaction products may also participate in deposition. As such, elimination of a potential reactant by deposition reduces the pool of constituents for additional reactions, while reaction does not fundamentally alter the likelihood of deposition. These conditions justify the use of a simplifying model of ubiquitous mass deposition for low-concentration solute constituents on the hotter fuel for the time frame of interest for in-vessel precipitation.

It is important to note several exceptions to these assumptions, such as for those larger-concentration constituents such as boric acid and buffering agents, or regions of significant flow restriction such as debris beds, which may form in the lower regions of the fuel assemblies. Also, an exception for those species that are particularly soluble in the post-LOCA coolant will be considered to ensure that the coolant decay heat removal capability is conservatively modeled. Consideration of the thermal and hydraulic consequences for this type of deposition on in-vessel precipitation will need to be incorporated in the evaluation model. An example of a possible platform for these considerations is the LOCADM (Reference 14), which is currently under review for application in GSI-191 evaluations.

As a result, released crud solids (Table 3-4, Item 1), galvanic corrosion products (Table 3-4, Item 23), carbonate compounds (Table 3-4, Item 14), corrosion products from un-submerged material (Table 3-4, Item 10), metal-catalyzed reaction products (Table 3-3, Item T3-17), oxidation and reduction corrosion products (Table 3-4, Items 4 and 8), polymerization agglomerates of inorganic and organic particulates (Table 3-4, Item 20), and biological growth solids (Table 3-5, Item 5) are projected to be of lesser importance when compared to boric acid, sodium borates, aluminum hydroxide from aluminum corrosion, and calcium and phosphate silicates from cal-sil reactions within the applicable time frame for in-vessel precipitation evaluation.

5.1.3 Chemical Products

5.1.3.1 Significant Product Formation

5.1.3.1.1 ECCS Coolant

The chemical makeup of the post-accident coolant is primarily determined by the boric acid content of the source fluid and the plant-specific buffering system (NaOH, TSP, STB). As previously noted, the boric acid and sodium borate (and sodium phosphates for plants using TSP) precipitation solids are the main concern of the in-vessel precipitation model development when determining concentration limits for LOCA LTC. The contributions of chemicals other than boric acid and sodium borates are not expected to significantly impact the thermophysical characteristics of the coolant.

Thermal and chemical conditions at the break site (Table 3-4, Items 2 and 5), possible secondary system inflow due to steam generator tube rupture (Table 3-4, Item 25), and possible auxiliary component cooling line break contributions (Table 3-4, Item 19) are not expected to significantly impact bulk chemical conditions of the coolant and consequentially will not significantly impact in-vessel precipitation within the first 24 hours following the accident. It is expected that the evaluation model for in-vessel precipitation following a LOCA will be based on boundary conditions provided by resolution of GSI-191 issues and will bound these possible conditions.

5.1.3.1.2 Chemical Precipitates

The research conducted in Reference 10 helped clearly define the chemical constituents that are present in containment and may have the potential to participate in precipitation events. A compilation of containment materials based on an industry survey is presented in Reference 10 and then these materials are placed into 15 classes based on their composition (Reference 10, Table 3.2-2). Ten of the fifteen material classes were determined to have potential to cause chemical effects in the containment sump and were included in dissolution or precipitation testing. Reference 10, Section 6.4 discusses significant product formation in the presence of concentrated un-buffered and buffered boric acid solutions. In dissolution tests performed in Reference 10 with those selected material classes expected to cause chemical reactions, elements having the highest dissolved concentrations were Al, Si, and Ca. These elements were found to be the most likely to form precipitates. In precipitation testing documented on

Page 78 of Reference 10, 13 of 60 tests formed measurable precipitates. Ten formed precipitates after exposure to simulated coolant with a reduction in temperature. Precipitates were predominantly aluminum oxyhydroxide, calcium aluminum silicate, or sodium aluminum silicate. No precipitates settled rapidly and would not be expected to settle before being transported to the sump screen. The predominant precipitates expected based on dissolution or precipitation of Reference 10 included in the chemical model are aluminum oxyhydroxide, sodium aluminum silicate, and calcium phosphate, which may be a concern for plants using TSP as a buffering agent. The primary source of aluminum is from corrosion of aluminum alloys. Minor aluminum contribution results from aluminum silicate and other aluminum-bearing minerals in insulation and concrete. The primary sources of calcium are concrete and calcium silicate insulation. Other minor contributors include fiberglass and mineral wools. Silicate is an effective inhibitor for corrosion of aluminum alloys, but evaluation of this effect was not performed as part of this single-effect test program and is not included in Reference 10, but is addressed in Reference 12. The method developed in Reference 10 was extended in Reference 14 to predict chemical deposition on fuel cladding due to the transport of debris and chemical products. This new method relies on the LOCADM calculation tool, which conservatively predicts the buildup of chemical deposits on fuel cladding after a LOCA. Appendix E of Reference 14 provides a complete description and qualification of this method.

5.1.3.1.3 Sump Debris

Fuel assembly tests were performed in References 9, 14, and 23 to define the limits on the mass of debris that may bypass the sump screen and still provide for a sufficient flow pressure drop across the fuel assembly such that sufficient flow is provided to ensure that LTC requirements are satisfied. The following debris types were evaluated: fiber, chemical precipitate, microporous insulation, calcium silicate, and particulate debris.

Additional testing and evaluation are recommended to determine the impact of combined boric acid and buffer solutions with respect to the bounding predictions resulting from GSI-191 chemical loading and sump debris to determine the coolant heat removal capability. Compounds other than highly concentrated and highly soluble chemical constituents, such as sodium borates or sodium phosphates, should be included in the evaluation based on deposition on the higher-temperature surfaces following the design basis accident rather than precipitation. Conservative boundary conditions to evaluate the effects of sump debris on potential in-vessel precipitation will be drawn from the GSI-191 conclusions. Conservative bounding debris load criteria applicable to all PWR designs are still under review by the NRC. These values will be updated prior to finalization of this work, but it is expected that the debris load will be provided as a boundary condition as regards to boric acid precipitation. It should be noted that GSI-191 determined debris and chemical loading may be representative of time frames that exceed the applicable time frame for in-vessel precipitation model development and additional evaluation may be required to determine appropriate initial conditions.

5.1.3.2 Low-Concern Product Formation

5.1.3.2.1 Crud Solids

Released dissolved material and suspended solids from the RCS are expected to be similar to a normal PWR shutdown. The crud solids released (Table 3-4, Item 1) are expected to be small in comparison to other solids, such as boric acid/sodium borate precipitates, aluminum corrosion products, and calcium/phosphate silicates. As such, the amount of RCS oxides was considered not significant enough to be included in the testing of Reference 10 and further investigation of the impact of crud solids is not necessary (Reference 19). Conservatisms in the chemical model (Reference 10) and GSI-191 limiting predicted amounts of sump debris are expected to bound any possible RCS oxide contributions.

5.1.3.2.2 Radiolysis Products

All radiolysis reactants and products transported to the fuel surface will be assumed to undergo deposition as previously indicated. This assumption diminishes the importance of coolant impurities, chemical reactions and radiochemical reactions in model development and is justified as limiting constituent mass deposition will be bounding of such scenarios. Organic coating materials are not expected to experience radiation levels that would cause degradation and subsequent transfer onto heat transfer surfaces (Reference 14, pg. 7-5). Mixed potential modeling, similar to that performed at boiling water reactors may be used to assess radiolysis effects on oxidation or reduction potential in post-LOCA coolant (Reference 19); however, corrosion products are not expected to have a significant impact on in-vessel precipitation within the applicable time period.

5.1.3.2.3 Galvanic and Redox Corrosion Products

Corrosion of ferritic materials in contact with concentrated boric acid solutions is a well known phenomenon in the industry. Dissolution and precipitation testing in Reference 10 helps to close the knowledge gap by providing a basis for evaluating the reaction rate and subsequent degree of corrosion occurring in high probability locations and materials given the quantities and concentrations of boric acid expected in the post-LOCA environment. Also testing in Reference 10 identifies the subsequent feedback contribution of the degradation of these materials to the containment pool chemistry.

Galvanic corrosion (Table 3-4, Item 23), the corrosion of un-submerged material (Table 3-4, Item 10) and oxidation and reduction reactions (Table 3-4, Items 4 and 8) are projected to contribute non-significant quantities of chemical product compared to other corrosion processes such as aluminum corrosion and cal-sil reactions for the time frame of interest for in-vessel precipitation. First, while the presence of dissimilar metals that reside higher in the galvanic series can result in electroplating type events, galvanic corrosion was shown to only affect limited metal surface areas yielding negligible corrosion product quantities in Reference 19. Anodic reversal at elevated temperature with enhanced steel corrosion has not been evaluated per Reference 19, but is not expected to create significant corrosion products that effect in-vessel precipitation within the applicable time period. Any solids loading due to the corrosion of un-submerged containment materials is expected to be minimal in comparison to precipitates due to high concentration constituents in the coolant. The oxidation-reduction potential of the sump fluid is impacted by several postulated events in the post-LOCA environment, such as liberation of hydrogen gas from the superheated spray at the break site and subsequent generation of oxidizing agents. These higher order chemical reactions are not kinetically favored when compared to precipitation and deposition for the time frame of interest and are therefore bound by these results.

5.1.3.2.4 Aging and Alloying Corrosion Products

Material aging and alloying effects (Table 3-5, Items 2 and 3) on solid product formation were both determined to be negligible through research and first principle testing (References 10 and 19). Therefore, the contribution to in-vessel solid load and precipitation due to these two effects are expected to be bounded by conservative reactor vessel solid loads determined by GSI-191 (References 14, 9, and 23) and predicted deposition. Further investigation for other metal alloys is not recommended based on low likelihood and existing evaluation.

5.1.3.2.5 Carbonate Formation Products

Reactive gases in containment in a post-LOCA LTC environment include oxygen, hydrogen, and carbon dioxide (Reference 5). Dissolution of carbon dioxide in the containment pool could occur by gas entrainment in the spray flow. The formation of carbonate compounds from atmospheric carbon dioxide and the resulting chemical effects has been determined to be insignificant within the applicable time period for in-vessel precipitation (References 10 and 19).

5.1.3.2.6 Organic Products

The containment material survey of all 69 operating PWR plants in the U.S. (Reference 10, Table 3.2-1) and subsequent containment material classification (Reference 10, Table 3.2-2) provides a realistic plant-specific assessment to determine likely sources of organic material. Two of the 15 containment material classes of Reference 10 that were not included in bench scale testing contain organics. Organic mastics include all mastic coatings that contain inorganic materials in organic binders. Containment materials in this class include CP-10 and Thermalog™ 330-1. The inorganic components of these compounds are encased in polymeric materials (vinyl for CP-10 and epoxides for Thermalog™) and would not be exposed to sump fluids. Other organic materials include rubber, foam rubber, phenolic resins, pressed wood products, and liquid hydrocarbons. The containment materials in this classification include Armaflex®, Benelex 401, Koolphen®, and reactor coolant pump motor oil. As in the ICET program, these organic materials were excluded from bench scale testing as they were judged unlikely to break down to produce precipitate-forming species under the temperature and chemistry conditions tested. The organic materials also occur in small amounts as compared to other containment material classes.

Co-precipitation (Table 3-4, Item 21), agglomeration (Table 3-4, Item 22), and other organic material related phenomena (Table 3-4, Item 18) and the impact on coolant composition and in-vessel precipitation have been considered based on the underlying synergism between these effects. It is recognized that organic-mineral aggregates can pass through the sump strainer and undergo radiolysis in the core. The role of organics and decomposition products to form inorganic agglomerates has not been studied. However, organic materials and coatings have been shown to occur in insignificant amounts in containment in comparison to inorganic materials. Also, while no net solids increase due to inorganic particulates is expected, the effect due to organic material degradation from coatings and lubricants within the time frame of interest could be considered in conjunction with inorganic agglomeration. While dissolution and precipitation testing (Reference 10) did not address multiple effects, other conservatisms in the chemical model based on single-effect testing are expected to be bounding for these scenarios. There is also an underlying expectation that many of the components, aside from the sodium-based buffering agents and boric acid, occur in quantities so small or are so quickly bound to the fuel clad that their participation in in-vessel boric acid precipitation is limited.

The primary subgroups of coatings evaluated in Reference 14 are metallic and organic coatings. These coatings were determined to have minimal impact on the chemical composition of the post-LOCA containment pool following incorporation into the chemical matrix. Coating dissolution or leeching due to submergence in the containment pool was evaluated in Reference 14. The rate for incorporation is a function of the conditions in the pool including the chemical composition, pH, and temperature. Organic coatings should be resistant to this form of incorporation; however, possible pathways are available via thermolytic and radiolytic decomposition.

The protective coatings used inside a PWR can be grouped into three categories: zinc-rich primers, epoxies, and non-epoxies. These three categories of coatings were evaluated to have negligible effect on the generation of precipitate (Reference 14). The amount of non-epoxy coatings used inside a PWR is small and therefore has a negligible contribution to post-LOCA PWR chemistry effects (Reference 14, pg. 6-4). Non-epoxy coatings, such as alkyds, urethane, and acrylics, are used on selected original equipment manufacturer (OEM) supplied equipment and estimated to a few thousand square feet or less (Reference 14, pg. 6-1). Non-epoxy coatings are also as a class chemically benign and are not expected to react with post-LOCA sump fluid. PWROG testing in Reference 10 demonstrated zinc contributes little to the generation of corrosion products post-LOCA and therefore, zinc-rich primers have negligible contribution to post-LOCA PWR chemistry effects (Reference 14, pg. 6-4). Most PWR containment buildings have a significant amount of epoxy coatings. However, chemical resistance testing has demonstrated that epoxy coating systems are chemically inert and contribute only a small amount of leachate to the recirculating coolant (Reference 10, Section D, response to RAI 2) and epoxy coatings will retain their structural integrity at temperatures up to 350°F (Reference 14, pg. 6-2). Therefore, epoxy coatings are evaluated to have negligible contribution to post-LOCA PWR chemistry effects (Reference 14, pg. 6-4).

5.2 VESSEL MIXING AND TRANSPORT

The goal of a long-term cooling analysis is to demonstrate that sufficient heat removal capability is provided by the ECCS to remove decay heat produced by the core following a design basis accident. The chemical effects associated with recirculated ECCS coolant from the containment sump can affect this capability in several ways. The chemical reactions and/or the precipitation of solids in the core or at heat exchange locations might reduce heat transfer coefficients, block coolant flow, and change the thermal-hydraulic characteristics of the coolant. An evaluation of long-term cooling with particulates and chemical debris in the recirculating fluid entering the core and possible deposition in the core was performed in support of GSI-191 analyses (References 9, 14, and 23). This work, in conjunction with the convective boiling channel tests performed by Westinghouse (Reference 4), provides a basis to address possible thermal and flow geometry effects caused by chemical effects in the coolant.

5.2.1 Flow Geometry and Transport

5.2.1.1 Precipitate Debris Settling

Transport phenomena of precipitate particulates have been studied in References 10 and 14 to determine settling and deposition rate of chemical materials. These transport effects can influence the distribution and quantity of chemical species within the debris load. Chemical precipitates that may form may be transported to the core and influence the pressure drop of debris accumulation at the core inlet or spacer grids. This effect on LTC is addressed in References 14 and 9. Testing documented in Reference 10 showed slow settling behavior of amorphous precipitates. The settling behavior of precipitates formed from the precipitate generator was shown to be dependent on the mixing tank concentration. The testing showed the surrogate precipitate mixing tank concentration affected the settling properties.

Fuel assembly tests were performed in References 9, 14 and 23 to define the limits on the mass of debris (fiber, particulate, and chemical) that may bypass the sump screen and reach the FA. The acceptance of these limits is based on a sufficiently low pressure drop across the FA, such that LTC requirements are satisfied.

The chemical model of Reference 10, in conjunction with Reference 12, conservatively determines on a plant-specific basis the likely chemical reaction scenarios leading to precipitation and precipitate generation. This chemical model requires plant-specific temperature and pH profiles in conjunction with various containment material amounts as input. These plant-specific inputs impact both thermodynamic and kinetic conditions and the inputs have been evaluated for sensitivity (Reference 10). In addition, the inputs into the particulate generator have been evaluated for sensitivity upon the types of precipitates and the particle sizes in the final solution (Reference 10).

Filtration and settling behaviors of key precipitates are influenced by amorphous and hydration properties of the materials. The precipitates formed in Reference 10 were amorphous and had slow settling behavior and poor filterability and, as a result, cannot be discounted as a concern for sump screen performance. SEM analyses (found in Reference 10, Appendix B) of 13 precipitates showed constituent particles to be less than 20 microns and larger agglomerations of particles to be 20 microns. The influence of temperature on precipitation was eliminated by the assumption that all aluminum and calcium in the presence of phosphate formed precipitates. The quantity of key precipitates is based on stoichiometry, considering the buffering agent used by the plant in the chemical model (Reference 10).

Representative particulates for the precipitates formed during the bench testing and predicted using the chemical model could be generated for use in sump screen head loss testing. The chemical precipitates should be treated as another class of inert debris for strainer testing purposes. Testing of the particulate generator in Reference 10 showed that simulated particulates could be successfully generated for use in sump screen testing. The quality and temperature of the water used to prepare the particulates is shown not to be critical. The most critical parameter is the limitation on the degree of concentration of particulates in the mixing tank. The surrogate precipitate filterability and settlement characteristics were adequate to represent post-LOCA chemical precipitates in strainer head loss tests. The chemical model prediction of the total amount of precipitate was acceptable. Testing in Reference 10 confirmed that small quantities of each surrogate precipitate produced significant pressure drop across a NUKON fiber bed. Since the effects of the two surrogate precipitates are similar, the predicted amount of precipitates was deemed acceptable by the NRC in the SE of Reference 1 and small quantities of each precipitate are effective at producing significant head loss across a fiber bed. These results are critical in determining the higher-level effects, including polymerization and particle ripening processes. The agglomeration of inorganic and organic particles results in the formation of large clumped material that can collect on the sump screen or elsewhere.

5.2.1.2 Flow Blockages

The flow blockages at the reactor core inlet nozzle or along the fuel elements were investigated in References 9, 14 and 23. The PWROG fuel assembly test results of References 9, 14, 23 updated with

RAI responses: References 24 and 25 demonstrate acceptable LTC in which sufficient flow will reach the core to remove core decay heat using fiber load acceptance criteria bounding and applicable to all PWR plant designs (Westinghouse, CE, and B&W). Westinghouse and AREVA have defined the maximum fiber loading that the fuel can withstand and not impede core cooling. This value is fuel-vendor-specific and is currently under review with the NRC.

5.2.1.3 LOCADM

A method to calculate the amount of chemical products generated in a post-LOCA environment was developed in Reference 10. Plant-specific inputs include pH values, sump fluid temperature histories, and specific alloys of reactant materials. The fuel cladding integrity within the concentrated sump chemical solutions was assessed and any deposits that might form, as cited in Reference 14. The method developed in Reference 10 was extended to predict chemical deposition on fuel cladding due to the transport of debris and chemical products into the RCS and the core region by the coolant circulated from the containment sump. LOCADM assumes chemical product transport occurs by (1) containment materials corroding and/or dissolving, (2) some of the dissolved material precipitates and does not settle, (3) all the dissolved material and suspended particles pass through the sump screen and into the core. LOCADM models deposits of chemical products that are dissolved or suspended in solution throughout the core in proportion to the amount of boiling in each core node. If there is no boiling, the chemical products are distributed according to heat flux at an empirically derived rate. All chemical material that is transported to the fuel surface by boiling is assumed to deposit and uses a deposit thermal conductivity and density expected to be bounding. The inputs into LOCADM include time, materials, material conversion, and core data parameters. The methodology presented in Reference 14, Section 7 is meant to provide plant-specific method to evaluate core deposition that meets the NRC requirements for predicting post-LOCA deposit formation on the core. It is expected that most plants using this methodology will be able to demonstrate acceptable LTC in the presence of core deposits (Reference 14, pg. 7-5).

5.2.2 Vessel Mixing

PWR vessel mixing test results documented in References 15 and 21 resulted in crystallization after several hours of boiling at the two phase mixture level interface in the two-phase region. Rapid pressure reduction was shown to result in significant crystallization throughout the entire upper portion of the core, while general crystallization was observed throughout the lower plenum. In-vessel precipitation was determined to be time-dependent through the upper and lower portions of the PWR vessel with buildup proceeding gradually.

The relatively small contributions of chemicals other than boric acid and sodium borates are not expected to impact the thermophysical characteristics of the coolant. However, while some limited vessel mixing tests have been performed, these considered only boric acid solutions without sump debris. Vessel mixing tests that consider concentrated un-buffered and buffered boric acid solutions with sump debris loads as determined by GSI-191 analyses are recommended. Such tests could be designed to determine thermal and pH gradients in the reactor vessel at post-LOCA conditions for the time period of interest. Particulate nuclei-enhanced precipitation (Table 3-4, Item 7) could also be investigated in such tests; however, this is not required since bench scale testing has indicated the precipitation pathway due to temperature gradients is dominant (References 7 and 8).

5.3 PRECIPITATION AND DEPOSITION

5.3.1 Precipitation

The precipitation of solids in the core or at heat exchange locations may reduce heat transfer coefficients, block coolant flow, and change the thermal-hydraulic characteristics of the coolant. Due to the relatively high concentrations of boric acid in the ECCS coolant before and after sump recirculation, boric acid precipitation has historically been considered the limiting condition precipitant in the reactor vessel after a LOCA. In reality, buffered boric acid is the predominant solute in the coolant. The potential for, and nature of, precipitants in buffered boric acid solutions are quite different than for un-buffered boric acid solutions, so the precipitation of both boric acid and sodium borates should be considered in the in-vessel precipitation model.

Secondary precipitants must be considered from containment materials in the post-LOCA environment. Dissolution testing of Reference 10 showed elements Al, Si, and Ca having the highest dissolved concentrations. Bulk boiling is assumed to occur following ECCS recirculation when coolant temperatures rise. These constituents are the most likely to remain in solution rather than deposit on the fuel rods in the initial stages of the event and are therefore those most likely to be available to participate in precipitation. Precipitation testing of Reference 10 reported aluminum oxyhydroxide, sodium aluminum silicate, and calcium phosphate (for plants using TSP as a buffering agent) as the predominant precipitates.

5.3.1.1 Thermal Gradients

The thermal conditions at the site of heat exchange provide locations for precipitation that may cause deposition and clogging, thus altering flow fields. Processes that could result in small temperature reductions will influence the boric acid crystallization processes. From the observations of References 4, 7 and 8, behavior causing the onset of precipitation appears to be more closely associated with areas of heat exchange between phase interfaces than foreign particles. Unless the solution is concentrated to the limit, foreign particles such as fibers/debris in the sump should not have a significant influence on the precipitation of boric acid. Precipitation of boric acid crystals on the surface of the water pool is likely due to the small temperature difference that exists as a result of limited surface vaporization. Crystallization did not occur on the magnetic stirrer or on the thermocouple in both References 7 and 8, but did occur at the liquid/vapor surface upon cooling. Boric acid precipitated in the lower plenum region of the vessel in Reference 4, where a slightly lower temperature was observed as compared to surrounding areas. These observations indicate the system is essentially in equilibrium and other foreign objects do not promote crystallization. Evaluations of the flow conditions and thermal gradients in the reactor vessel are needed to validate in-vessel precipitation modeling.

5.3.1.2 Co-Precipitation

In multi-constituent chemical systems, the solution thermodynamics may be changed for one chemical species by the presence of other species and could result in precipitation below the solubility limit. Some consideration is provided for co-precipitation in precipitation testing of References 10 and 12. Dissolution and precipitation evaluations of Reference 10 are based mostly on single-effects testing. Some screening tests in Reference 10 measured potential interactions between different containment materials to produce precipitates. Results of dissolution tests and literature data guided selection of which solutions to combine and the test matrix used is provided in Reference 10, Table 5.2-3. Although single-effects testing results in greater uncertainty compared to integrated testing, the NRC decided the single-effects testing of Reference 10 was acceptable since other conservative assumptions in the chemical model offset uncertainties associated with single-effects tests. These conservatisms include the assumption that all aluminum in solution forms a precipitate, and phosphate inhibition of aluminum corrosion in TSP environments, and inhibition of aluminum corrosion by silicates are not credited. Testing in Reference 12 evaluated additional plant-specific inputs to the chemical model of Reference 10 including silicate or phosphate inhibition of aluminum corrosion. Aluminum release rate equations are provided in Reference 12 that account for aluminum corrosion inhibition by both silica and phosphate.

5.3.2 Deposition

It has been recognized that constituents other than boric acid and the plant-specific buffering agent occur in low concentrations relative to un-buffered and buffered boric acid solutions. Those compounds other than highly concentrated and highly soluble chemical constituents, such as sodium borates or sodium phosphates, should be included in evaluations based on deposition on the higher-temperature surfaces following the design basis accident rather than precipitation. Testing and evaluation developed to address GSI-191 related concerns should therefore be based on boric acid solutions but include bounding consideration for these secondary effects. LOCADM is a preliminary tool for predicting deposition results for all but the most soluble chemical constituents discussed in Reference 16 following the design basis accident. Pending NRC acceptance of LOCADM, this or a similar analysis tool could be used to provide a conservative pathway for modeling in-vessel precipitation while neglecting many of the multi-constituent effects described in Reference 16 such as co-precipitation or multi-component agglomeration with regard to boric acid precipitation. In addition, this approach may be found to adequately address the precipitation of low-concentration chemicals, which may therefore be neglected when establishing concentration limits for LOCA long-term cooling in-vessel precipitation evaluation models.

6 CONCLUSIONS AND RECOMMENDATIONS

The PWROG is funding a program to develop a LOCA boric acid precipitation control evaluation model following the guidance in Reference 22. Evaluation model requirements and the establishment of an appropriate assessment base require a review and understanding of the chemical effects. After evaluating chemical effect concerns discussed in Reference 16 and 19 against the current SOK and relative importance of each effect, the following conclusions and recommendations are made.

6.1 CONCLUSIONS

1. *Many of the concerns detailed in the NRC Research PIRT (Reference 16) do not directly pertain to LOCA long-term cooling in-vessel precipitation evaluation model development* due to the time period of interest, typically no longer than 24 hours following the accident. Within this time frame, certain source terms are projected to have a limited impact in comparison to the primary source terms, which include boric acid, sodium borates, aluminum hydroxide from aluminum corrosion, and calcium and phosphate silicates from cal-sil reactions. The source terms of limited impact include released crud solids, material aging and alloying products, non-aluminum galvanic and oxidation-reduction corrosion products, carbonate compounds, metal-catalyzed reaction products, polymerized agglomerates of inorganic and organic particulates, and biological growth solids. These items are expected to be of low concern due to their occurrence at low concentrations in this short time frame. Such dilute species will also have a higher probability of deposition on high-temperature surfaces in the vessel than undergoing reaction or precipitation due to interactions with other constituents. Such reasoning is not applicable to the larger-concentration constituents, as previously mentioned, nor does it apply to regions of significant flow restrictions, such as debris beds.

2. *Some of the concerns detailed in the NRC Research PIRT (Reference 16) warrant additional investigation and may need to be included in LOCA long-term cooling in-vessel precipitation evaluation model development.* In-vessel precipitation evaluation should include consideration of bounding or plant-specific chemistry considerations, including buffering agents, containment materials, coolant pH, reactor vessel mixing, sump debris, and thermal gradients. These items should be considered for a time period that bounds the time period of interest. Deposition and precipitation should be determined based on the phenomena discussed throughout this report. Additional testing and evaluation for the impact of these items on in-vessel precipitation is recommended as discussed in Section 6.2 based on preliminary results for chemical loading and sump debris for GSI-191.

6.2 RECOMMENDATIONS

1. *The LOCA long-term cooling in-vessel precipitation evaluation model should focus on the precipitation characteristics of un-buffered and buffered boric acid solutions* when establishing concentration limits for the evaluation model. This is based on the recognition in Conclusion 1 that the other constituents occur in low concentrations relative to un-buffered and buffered boric acid solutions. As discussed, those compounds other than highly concentrated and highly soluble chemical constituents, such as sodium borates or sodium phosphates, should be included in the evaluation based on deposition on the higher-temperature surfaces following the design basis

accident rather than precipitation. Testing and evaluation developed to address GSI-191 related in-vessel precipitation concerns should therefore be based on un-buffered and buffered boric acid solutions but include bounding consideration for these secondary effects, such as deposition upon high temperature surfaces.

2. *LOCA long-term cooling in-vessel precipitation model considerations for thermal and physical characteristics in the reactor vessel including boric acid mixing and transport may be impacted by the downstream effects of GSI-191 related issues.* In-vessel flow rates and thermal gradients may be impacted by the deposition considerations described in Recommendation 1 and this should be considered during the evaluation model development process. Also, in-vessel debris at the fuel grids or other locations may impact local chemistry, coolant characteristics, flow rates, and temperature distributions and should be considered. *Vessel mixing tests are recommended to determine the impact of in-vessel debris on globally static, locally dynamic regions in the core where higher-concentration material may accumulate at different temperatures.* The mixing insights from these tests can eventually be applied to specific plant designs to establish the appropriate assumption for lower plenum mixing. This testing is the natural extension of the vertical channel precipitation testing documented in Reference 4. Future testing should also consider potential deposition on heated surfaces above the two-phase mixture level.

3. *Additional testing should be considered to capture the effect of sump debris in the concentrated un-buffered and buffered boric acid solutions relative to heat removal capability.* Previously, concentrated un-buffered and buffered boric acid solutions have been shown to be capable of removing decay heat in a test rig simulating core geometry for the post-LOCA scenario (Reference 4). Further insights will be gained from the in-progress sump debris boiling and heat transfer tests. These results will be used to evaluate the potential for in-vessel precipitation during core boiling on decay heat removal as well as the effect of sump debris on decay heat removal by the concentrated un-buffered and buffered boric acid solutions. Also, measurements of thermo-physical properties related to heat removal capability such as density viscosity and surface tension are in progress. These investigations will provide insight into possible impacts on the coolant second order properties including bubble nucleation, bubble detachment and surface rewetting.

4. In order for the LOCA long-term cooling in-vessel precipitation evaluation model to address sump debris issues, assumptions regarding ECCS coolant debris loading are necessary. *GSI-191 downstream effect analyses can provide conservative boundary conditions for evaluating the effects of sump debris on potential in-vessel precipitation.* Debris load criteria, conservative with respect to core pressure drop and applicable to all PWR designs, are currently under review with the NRC. Upon finalization of these values, it is recommended that the updated debris load be used as a boundary condition for boric acid precipitation. As discussed in Conclusion 1, this debris load will be very conservative since GSI-191 considers debris generation over an expanded time frame. As such, it may be necessary to reevaluate the GSI-191 debris load criteria should the impact of additional debris load accumulation beyond the time frame of interest become too restrictive.

7 REFERENCES

1. Westinghouse Report WCAP-17021-NP, Rev. 1, "Summary of Tests to Determine the Physical Properties of Buffered and Un-buffered Boric Acid Solutions," January 2010.

2. Fauske & Associates Calculation Note FAI/08-117, Rev. 0, "Evaluation of Boric Acid and Buffered Boric Acid Chemical Solution Fluid Properties and Solubility Data," August 2008.

3. Westinghouse Report WCAP-16317-P, Rev. 0, "Review and Evaluation of MHI BACCHUS PWR Vessel Mixing Tests," November 2004.

4. Westinghouse Report WCAP-17040-P and WCAP-17040-NP, Rev. 0, "Small Scale Un-buffered and Buffered Boric Acid Nucleate Boiling Heat Transfer Tests with a Single Fuel Rod in a Vertical Channel," July 2009.

5. Westinghouse Letter STD-MCE-07-53, Rev. 0, "Reactor Coolant Chemistry After a LOCA and Issues with Core Cooling," September, 2007.

6. Not used.

7. Fauske & Associates Calculation Note FAI/05-67, Rev. 1, "Test Results for Boric Acid Solubility Limits in the Presence of Sodium Hydroxide," June 2005.

8. Fauske & Associates Calculation Note FAI/05-13, Rev. 0, "Solubility of Boric Acid in Water with TSP Added," February 2005 (Input into EDMS as FAI-05-13).

9. Westinghouse Report WCAP-17057-P and WCAP-17057-NP, Rev. 0, "GSI-191 Fuel Assembly Test Report for PWROG," March 2009.

10. Westinghouse Report WCAP-16530-NP-A, "Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191," March 2008.

11. Westinghouse Report WCAP-17047-NP, Rev. 0, "Phenomena Identification and Ranking Tables (PIRT) for Un-Buffered/Buffered Boric Acid Mixing/Transport and Precipitation Modes in a Reactor Vessel During Post-LOCA Conditions," May 2009.

12. Westinghouse Report WCAP-16785-NP, Rev. 0, "Evaluation of Additional Inputs to the WCAP-16530-NP Chemical Model," May 2007.

13. Westinghouse Report WCAP-16596-NP, Rev. 0, "Evaluation of Alternative Emergency Core Cooling System Buffering Agents," July 2006.

14. Westinghouse Report WCAP-16793-NP, Rev. 1, "Evaluation of Long-Term Cooling Considering Particulate, Fibrous and Chemical Debris in the Recirculating Fluid," April 2009.

15. CE Report LOCA-75-127-P and LOCA-75-127-NP, "Post LOCA Boric Acid Mixing Experiment," October 1975.

16. U.S. NRC NUREG-1918, "Phenomena Identification and Ranking Table Evaluation of Chemical Effects Associated with Generic Safety Issue 191," February 2009. (ML090780090)

17. 2007 International LWR Fuel Performance Meeting INL/CON-07-12181, "Phase Identifications in Crud from Commercial Boiling Water Reactors at the Idaho National Laboratory by Transmission Electron Microscopy," September 2007.

18. Not Used.

19. U.S. NRC NUREG/CR-6988, "Final Report – Evaluation of Chemical Effects Phenomena in Post-LOCA Coolant," March 2009.

20. Westinghouse Report WCAP-16406-P-A, Rev. 1, "Evaluation of Downstream Sump Debris Effects in Support of GSI-191," March 2008.

21. J. Tuunanen, et al., "Long-Term Emergency Cooling Experiments with Aqueous Boric Acid Solution with the REWET-II and VEERA Facilities," *Proc. Int. ENS/ANS Conf. on Thermal Reactor Safety*, Vol. 4, Avignon, 1988.

22. U. S. NRC Regulatory Guide 1.203, "Transient and Accident Analysis Methods," U.S. NRC, Office of Nuclear Regulatory Research, December 2005 (ML053500170).

23. AREVA Proprietary Report 51-9102685-000, "GSI-191 FA Report for PWROG," March 2009.

24. Westinghouse Letter LTR-SEE-I-10-22, Revision 0, "Transmittal of RAI Responses for GSI-191 Fuel Assembly Test Report (WCAP-17057-P, Revision 0)," February 2010. (Proprietary)

25. OG-10-213, "PWROG Revised Response to Request for Additional Information Regarding PWROG Topical Report 51-9102685-000, Revision 0, 'GSI-191 FA Test Report for PWROG,' (PA-SEE-0479)," June 2010.

26. Westinghouse Report WCAP-7153-A, "Investigation of Chemical Additives for Reactor Containment Sprays," April 1975.