

EVALUATION OF CHEMICAL EFFECTS PHENOMENA IDENTIFICATION AND RANKING TABLE RESULTS

MARCH 2011

Prepared by:

Mechanical and Electrical Engineering Branch
Division of Engineering
Office of Nuclear Regulatory Research

and

Safety Issue Resolution Branch
Division of Safety Systems
Office of Nuclear Reactor Regulation

and

Steam Generator Tube Integrity and Chemical Engineering Branch
Division of Component Integrity
Office of Nuclear Reactor Regulation

TABLE OF CONTENTS

| | |
|---|----|
| INTRODUCTION | 1 |
| DISPOSITION OF OUTSTANDING CHEMICAL EFFECTS ISSUES | 11 |
| 1 UNDERLYING CONTAINMENT POOL CHEMISTRY | 11 |
| 1.1 Reactor Coolant System Coolant Chemistry Conditions at Break | 11 |
| 1.2 pH Variability | 12 |
| 1.3 Hydrogen Sources within Containment | 13 |
| 1.4 Containment Spray CO ₂ Scavenging and CO ₂ /O ₂ Air Exchange | 15 |
| 1.5 Emergency Core Cooling System Injection of Boron | 19 |
| 2 RADIOLOGICAL CONSIDERATIONS | 20 |
| 2.1 Radiolytic Environment | 20 |
| 2.2 Radiological Effects: Corrosion Rate Changes | 22 |
| 2.3 Hydrolysis | 24 |
| 2.4 Conversion of N ₂ to HNO ₃ | 25 |
| 2.5 Additional Debris Bed Chemical Reactions | 27 |
| 3 PHYSICAL, CHEMICAL, AND BIOLOGICAL DEBRIS SOURCE TERMS | 29 |
| 3.1 Crud Release | 29 |
| 3.2 Jet Impingement | 31 |
| 3.3 Debris Mix Particle/Fiber Ratio | 33 |
| 3.4 Effects of Dissolved Silica from Reactor Coolant System and Refueling Water Storage Tank | 34 |
| 3.5 Containment Spray Transport | 37 |
| 3.6 Initial Debris Dissolution | 39 |
| 3.7 Submerged Source Terms: Lead Shielding | 40 |
| 3.8 Submerged Source Terms: Copper | 42 |
| 3.9 Concrete Material Aging | 44 |
| 3.10 Alloying Effects | 45 |
| 3.11 Advanced Metallic Corrosion Understanding | 46 |
| 3.12 Submerged Source Terms: Biological Growth in Debris Beds | 47 |
| 3.13 Reactor Core: Fuel Deposition Spall | 50 |
| 4 SOLID SPECIES PRECIPITATION | 54 |
| 4.1 Polymerization | 54 |
| 4.2 Heat Exchanger: Solid Species Formation | 55 |
| 4.3 Reactor Core: Precipitation | 58 |
| 4.4 Particle Nucleation Sites | 60 |
| 4.5 Coprecipitation | 61 |
| 5 AGGLOMERATION AND SETTLING: CHEMICAL EFFECTS | 66 |
| 5.1 Inorganic Agglomeration | 66 |
| 5.2 Deposition and Settling | 67 |
| 5.3 Quiescent Settling of Precipitate | 69 |
| 5.4 Transport Phenomena: Precipitation and Coprecipitation | 70 |
| 6 ORGANICS AND COATINGS | 71 |
| 6.1 Break Proximity to Organic Sources | 71 |

| | | |
|-----|---|----|
| 6.2 | Organic Agglomeration | 73 |
| 6.3 | Organic Complexation | 75 |
| 6.4 | Coating Dissolution and Leaching | 76 |
| 7 | CHEMICAL EFFECTS ON DOWNSTREAM SYSTEM PERFORMANCE: PUMPS, HEAT EXCHANGERS, AND REACTOR CORE | 79 |
| 7.1 | Emergency Core Cooling System Pump: Seal Abrasion and Erosion or Corrosion | 79 |
| 7.2 | Heat Exchanger: Deposition and Clogging | 80 |
| 7.3 | Reactor Core: Fuel Deposition and Precipitation | 81 |
| 7.4 | Reactor Core: Diminished Heat Transfer | 84 |
| 7.5 | Reactor Core: Blocking of Flow Passages | 85 |
| 7.6 | Reactor Core: Particulate Settling | 86 |
| | CONCLUSION | 89 |
| | REFERENCES | 91 |
| | ABBREVIATIONS AND ACRONYMS | 97 |

INTRODUCTION

Background

The U.S. Nuclear Regulatory Commission (NRC) and the nuclear industry have sponsored research to provide information and develop guidance for evaluating the chemical effects following a loss-of-coolant accident (LOCA) in support of resolution of Generic Safety Issue (GSI)-191, "Assessment of Debris Accumulation on PWR Sump Performance." The NRC convened an external peer review panel to review the NRC-sponsored research conducted through the end of 2005 and to identify technical gaps that the original NRC-sponsored research either did not resolve or did not consider. NUREG-1861, "Peer Review of GSI-191 Chemical Effects Research Program" (Ref. 1) summarizes this review.

The NRC also conducted a phenomena identification and ranking table (PIRT) exercise between March 2006 and June 2006 to identify additional chemical effects that may affect the performance of the emergency core cooling system (ECCS). The PIRT panelists independently ranked the significance and current knowledge associated with the chemical phenomena most likely to (1) contribute to containment screen clogging, (2) affect downstream component performance, (3) impact core heat transfer, or (4) degrade structural integrity.

The PIRT process identified three types of issues: (1) issues that had been evaluated during the previous research activities, (2) remaining follow-on issues or questions stemming from the prior research, and (3) entirely new issues that the previous research did not address. The PIRT focused on identifying issues that could significantly affect ECCS performance and identified the state of knowledge associated with each issue to facilitate separation of the more mature, or known, issues from those that are not currently as well understood. While the PIRT focused on identifying potentially deleterious chemical effects, the process also identified and evaluated several advantageous, or potentially advantageous, chemical effects. NUREG-1918, "Phenomena Identification and Ranking Table Evaluation of Chemical Effects Associated with Generic Safety Issue 191" (Ref. 2), details the results of the PIRT exercise, including the final summary issue tables resulting from the PIRT.

The PIRT panelists identified and evaluated over 100 chemical effects phenomena. These phenomena pertain to the underlying containment pool chemistry; radiological considerations; physical, chemical, and biological debris sources; solid species precipitation; solid species growth and transport; organics and coatings; and downstream effects.

The PIRT phenomena fall into one of four different categories. The first category (Category I) represents those phenomena or issues that are generally known or have been demonstrated to be significant by prior research. The second category (Category II) includes phenomena or issues that either are expected to be significant by the PIRT panelists or have been demonstrated to be significant by prior research. However, their implications with respect to ECCS performance are not well known. The third category (Category III) includes phenomena that are potentially significant but are not well understood, and the ECCS performance implications are highly uncertain. The fourth category (Category IV) represents phenomena that have no engineering significance as determined by both the aggregate PIRT rankings and individual rankings and justifications.

After the PIRT was completed, the NRC staff conducted an initial evaluation of these phenomena to reduce the list to those phenomena that can be potential contributors to ECCS performance degradation, including those issues that needed additional study before their

significance could be determined. The final list consisted of the 41 items identified in Table 1. These 41 issues fall mostly in Categories II and III such that further evaluation is necessary to assess ECCS performance implications. The descriptions and possible implications associated with these 41 items as noted in Table 1 were extracted from NUREG 1918 (Ref. 2).

Objective

The objective of this report is to document the staff's subsequent evaluation of the implications of the 41 outstanding chemical effects phenomena (see Table 1) and the technical justification supporting the disposition of these phenomena.

Motivation

Since the PIRT was completed in 2007, the nuclear industry and the NRC have conducted additional research. The nuclear industry has developed various technical reports to provide guidance for the evaluation of post-LOCA chemical effects in the containment pool and within the ECCS. Specifically, the industry has developed Westinghouse Commercial Atomic Power (WCAP)-16530-NP-A, "Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191," issued March 2008 (Ref. 3) to provide plants with a methodology to perform plant-specific chemical effects evaluations. WCAP-16406-P-A, Revision 1, "Evaluation of Downstream Sump Debris Effects in Support of GSI-191," issued December 2007 (Ref. 4), evaluates the downstream impact (i.e., wear and blockage) of containment debris on the performance of the ECCS and containment spray system (CSS) components. WCAP-16793-NP, Revision 1, "Evaluation of Long-Term Cooling Considering Particulate and Chemical Debris in the Recirculating Fluid" (Ref. 5), addresses clogging within the reactor core. This WCAP report also examines the effects of chemical precipitates and debris on core cooling.

The NRC has sponsored research to confirm important aspects of the various WCAP reports. This research included leaching studies at Southwest Research Institute (SwRI) (Ref. 6) and various studies addressing surrogate precipitate characteristics, head loss by aluminum precipitates, and the appropriateness of the WCAP-16530-NP-A chemical model by Argonne National Laboratory (ANL) (Refs. 7, 8, 9, 10).

The various research programs summarized above have significantly advanced the understanding of chemical effects within the post-LOCA containment environment. In some cases, this additional research has further defined critical post-LOCA variables and parameters for specific phenomena. Therefore, evaluation of the implications of the 41 outstanding phenomena identified by the PIRT will consider the knowledge gained by this additional research.

Approach

The staff first identified those phenomena that could be evaluated using either prior knowledge or knowledge gained through the industry and NRC-sponsored research conducted since the PIRT was completed. The staff also identified those phenomena that required additional study to understand the chemical effects and their relevance before the practical generic or plant-specific implications could be determined. The staff grouped these phenomena into 10 topic areas (see Table 2) which Pacific Northwest National Laboratory (PNNL) subsequently evaluated. The PNNL study used past research findings, scoping calculations, and targeted numerical analyses to assess the significance of these phenomena. NUREG/CR-6988, "Final

Report—Evaluation of Chemical Effects Phenomena in Post-LOCA Coolant,” issued February 2009 (Ref. 11), documents the results of the PNNL study.

The NRC next assembled a team of staff with knowledge related to these issues to evaluate the significance of each issue. The staff used existing knowledge, results from the PNNL study, and the findings from the additional industry and NRC- sponsored research to evaluate the implications associated with each issue. In some topic areas, the staff conducted independent research to adequately understand and evaluate the implications of the chemical effects on ECCS performance. All team members reviewed the disposition of each issue. Additionally, an independent NRC staff person reviewed the draft disposition document. This final document reflects the modifications to address comments by the independent reviewer.

Table 1: Summary of Remaining 41 Chemical Effects Issues

| | PIRT Issue Number | Phenomenon | Description | Possible Implications |
|---|-------------------|---|---|---|
| 1. Underlying Containment Pool Chemistry | | | | |
| 1.1 | T1-2 | RCS coolant chemistry conditions at break | The RCS coolant chemistry varies over the fuel cycle. B concentrations \approx 2,000 - 4,000 ppm (beginning) to 50 ppm (end of fuel cycle) B/Li ratio \approx 100. The two-phase jet is at temperatures of \approx 315 °C to 120 °C upon cooling. | Initial reactor water chemistry spewing out of the break and forming the containment pool will have variable B concentration. The Li/B ratio is maintained approximately constant. |
| 1.2 | T1-3 | pH variability | pH at 25 °C at beginning of fuel cycle is acidic (pH 4), while closer to neutral (pH 7) at end of cycle. | Similar implications to issue 2; variable reactor and initial containment pool chemical environment. |
| 1.3 | T2-1 | Hydrogen sources within containment | H ₂ concentrations in vapor and containment pool include the RCS inventory, Schikorr reaction, and corrosion of metallic materials. | Containment pool redox potential is a function of dissolved hydrogen, which is established by the listed reactions. RCS evaporation may lead to equilibration with liquid, decreasing redox potential. |
| 1.4 | T2-8 | Containment spray CO ₂ scavenging and CO ₂ /O ₂ air exchange | Containment sprays cause CO ₂ absorption within containment pool and carbonate formation. | (1) Affect containment pool concentrations of CO ₂ . (2) Increase solid species in containment pool. |
| 1.5 | T2-2 | ECCS injection of boron | After pipe break, B (\approx 2,800 ppm) is injected into RCS to cool reactor. | Provides large B source which may affect chemical reaction products in containment pool. Specifically, the B source will serve as a pH buffer. |
| 2. Radiological Considerations | | | | |
| 2.1 | T3-6 | Radiolytic environment | Radiolysis reaction changes solution's redox potential; H ₂ , O ₂ , and H ₂ O ₂ balance; peroxide formation occurs after approximately 20 minutes. Radiolysis can cause changes in the redox potential either in the containment pool or in debris beds (on the sump screen). | Could affect chemistry in containment pool which affects species formation—most important for determining redox potential (e.g., the Hanford tank includes a mixture of different components at different phases). |
| 2.2 | T4-29 | Radiological effects: corrosion rate changes | Low doses and low temperature elevate the corrosion rate through formation of hypochlorite through radiolysis of Cl-bearing water. Could increase corrosion rates (especially pitting corrosion) of Al, SS, and Fe. | Corrosion rate increases could increase the amount of metallic and nonmetallic species in containment; alters chemical byproduct formation. |
| 2.3 | T2-14 | Hydrolysis | NiO becomes a catalyst for producing H ₂ from radiolysis. Expansion of issue after PIRT: The hydrothermal hydrolysis of various organic/inorganic coating and insulation materials will partially depolymerize polymeric materials, producing material | (1) Affects redox potential. (2) Affects solid species formation. |
| 2.4 | S-1 | Conversion of N ₂ to HNO ₃ | Radiolysis converts atmospheric N ₂ to HNO ₃ within containment pool. | pH in containment pool decreases due to HNO ₃ production. Buffering becomes ineffective. |
| 2.5 | T3-16 | Additional debris bed chemical reactions | Concentration of radionuclides (hundreds of curies available) within the sump screen acts as a "resin bed" or chemical reactor (altering the local chemical conditions). A number of possible reactions occur. | (1) Hydrogen peroxide forms. (2) Fe+2 \rightarrow Fe+3 increases due to increase in redox potential. (3) Organic materials decompose. (4) Possible coating of NUKON® to reduce solubility; glass embrittlement (shorter fiber). |

Table 1: Summary of Remaining 41 Chemical Effects Issues

| | PIRT Issue Number | Phenomenon | Description | Possible Implications |
|--|-------------------|---|---|--|
| 3. Physical, Chemical, and Biological Debris Source Terms | | | | |
| 3.1 | T1-1 | Crud release | Fe, Ni corrosion oxides ($\approx 125 \mu\text{m}$ layer) from the RCS piping are released due to hydraulic shock of the failure event. | The crud release creates a radiolytic environment on materials caught on the sump screens which could affect subsequent reactions. Also, the oxides add particulate mass to containment pool and may enhance coagulation. |
| 3.2 | T1-6 | Jet impingement | Water jet and fine debris within jet may impact surfaces and chip coatings. | Initiates metallic pitting, corrosion, and ablation of other materials (concrete, insulation). |
| 3.3 | T1-9 | Debris mix particle/fiber ratio | Breaks in different locations will create different debris characteristics: total mass, mixture constituents, compositions. | (1) Could alter the containment pool chemistry. (2) Could affect debris bed formation on the sump screen and increase variability of chemical product capture efficiency. |
| 3.4 | S-2 | Effects of dissolved silica from RCS and RWST | Silica in the water storage systems and the RCS affects chemical product formation. | (1) Silica in the water storage systems and the RCS can combine with magnesium, calcium, and aluminum and can form materials with retrograde solubility. (2) Silica can have an effect on the total mass of material precipitating. |
| 3.5 | T2-7 | Containment spray transport | Sprays wash latent debris, corrosion products, insulation materials, and coating debris into containment pool. | Affect on containment debris sources (types, amounts, compositions) and contributions to the chemical containment pool environment. |
| 3.6 | T2-9 | Initial debris dissolution | Debris dissolution begins. Initial (within first 20 minutes) expected products include Cal-Sil, cement dust, organic fiberglass binders, epoxy and alkyd coatings, uncoated concrete. | Indicate potential important contributors (if any) to chemical containment pool environment during first 20 minutes. Dissolution of other products will occur over longer timeframes. |
| 3.7 | T4-2 | Submerged source terms: lead (Pb) shielding | Any acetates present in containment pool will dissolve Pb, which could lead to formation of lead carbonate particulate. Lead blanketing to shield hot spots and covered with plastic coating, but coating likely destroyed. Several hundred pounds of lead in | Provides additional particulate loading within containment pool. |
| 3.8 | T4-3 | Submerged source terms: copper (Cu) | Concern stems not from Cu compounds, but the various effects that Cu may have on other corrosion processes. ICET program evaluated Cu concentrations; Cu comes from containment air coolers, motor windings, and grounding straps. | (1) By forming a galvanic couple, can facilitate attack of other metals (e.g., Al). (2) Cu ion deposition can occur which may inhibit corrosion. (3) Within an oxygenated environment, Cu can accelerate corrosion. |
| 3.9 | S-3 | Concrete material aging | The exposed concrete faces and dust in the containment building are aged and will be carbonated. | Aging could affect the solid species precipitates that are formed. |

Table 1: Summary of Remaining 41 Chemical Effects Issues

| | PIRT Issue Number | Phenomenon | Description | Possible Implications |
|---------------------------------------|--------------------------|--|---|---|
| 3.10 | S-3 | Alloying Effects | Corrosion rate data exhibit wide variability depending on the specific corrosion conditions and the alloy. | Alloying could affect dissolution/corrosion rates. |
| 3.11 | S-4 | Advanced metallic corrosion understanding | Need a better understanding of metallic corrosion in the containment pool environment, especially for Al. Some issues include understanding corrosion under the wide-ranging LOCA conditions (jet impingement—immersion), synergistic corrosion effects, the effect of hypochlorite on corrosion, and effects of phosphates/salts on corrosion. | This could substantially affect corrosion rates. |
| 3.12 | T4-22 | Submerged source terms: biological growth in debris beds | Bacteria grow in preexisting debris beds located on the sump strainer screen or elsewhere within the ECCS system. | Increased source term which can contribute to clogging or detrimental performance of pumps, valves, and other components. |
| 3.13 | T4-38 | Reactor core: fuel deposition spalling | Zn, Ca, Mg, CO ₂ -based deposits and films which form on the reactor core spall. | (1) Additional solid products which contribute to clogging within the reactor core. (2) Additional solid products which contribute to sump screen head loss. |
| 4. Solid Species Precipitation | | | | |
| 4.1 | T2-18 | Polymerization | Precursor to precipitation and agglomeration; metals/oxygen bonds ripen to form covalent bonds; grow until they qualify as ~nanometer particles size: Si, Al, Fe, boric acid are candidates | May be necessary to form large enough particles to result in tangible effects on ECCS performance. |
| 4.2 | T3-20 | Heat exchanger: solid species formation | Concentrations/species that are soluble at the containment pool temperature precipitate at lower ($\Delta T \sim 15\text{--}20$ °C) heat exchanger outlet temperature. Drop in temperature leads to the formation of solid species (e.g., AlOOH, FeOOH, amorphous SiO ₂). | (1) Species remain insoluble at higher reactor temperatures and affect ability to cool the reactor core. (2) Products could form that may clog reactor core and degrade heat transfer from fuel. |
| 4.3 | T3-27 | Reactor core: precipitation | ΔT increase (+70 °C from containment pool) and retrograde solubility of some species (e.g., Ca silicate, Ca carbonate, zeolite, sodium calcium aluminate) causes precipitation and additional chemical product formation. | (1) Products contribute to debris in reactor core which blocks flow passages and impedes heat transfer. (2) Additional precipitate could be created and transported to the sump screen. |
| 4.4 | T3-15 | Particulate nucleation sites | Particles within containment create nucleation sites for chemical precipitation. Examples include radiation tracks, dirt particles, coating debris, insulation debris, and biological debris. | Environment is created which fosters formation of solid species that could lead to ECCS degradation. |
| 4.5 | T2-19 | Coprecipitation | Method of precipitation/separation examples: Ni/Fe/Cr, Al/Si/B; Co/Fe systems. Precipitation of one species leads to precipitation of other species (below solubility limit); radioactive elements precipitate (at low concentrations), activation products: | More solid species form, which could lead to greater concentration of chemical products at the sump screen or downstream. |

Table 1: Summary of Remaining 41 Chemical Effects Issues

| | PIRT Issue Number | Phenomenon | Description | Possible Implications |
|--|-------------------|--|--|---|
| 5. Agglomeration and Settling: Chemical Effects | | | | |
| 5.1 | T2-21 | Inorganic agglomeration | Formation of larger clumps of smaller particulates depends on PZC; ionic strength (the higher the strength the smaller the distance for agglomeration); sensitive to many factors, including shape factors, and maximum particle size. | (1) May be necessary to form large enough particles to result in tangible effects on ECCS performance. (2) Can occur quickly if conditions are right. (3) Existence of organic species can increase or decrease likelihood. |
| 5.2 | T2-23 | Deposition and settling | Possibility that chemical products formed during this time period either settle within containment pools or are deposited on other surfaces. Chemical species which attach to or coat particulate debris may enhance settling. Examples are Al coating on Nu | Results in less particulate debris and chemical product transporting to and either accumulating on or passing through the sump screen. |
| 5.3 | T3-11 | Quiescent settling of precipitate | Quiescent flow regions within containment pool promote settling. | Little flow allows larger size, more stable particles/precipitates to form, which promotes settling. |
| 5.4 | T4-40 | Transport phenomena: precipitation/coprecipitation | Precipitation/coprecipitation and ripening of solid species within containment pool creates solid species that are less likely to transport. | Decreased transportability will result in less product migrating to or through the sump screen. |
| 6. Organics and Coatings | | | | |
| 6.1 | T1-7 | Break proximity to organic sources | RCP oil storage tank is made with ½-inch carbon steel with epoxy coating (250 gallons per pump, but tank may just contain leakage). | Tank failure timing: earlier in post-LOCA (jet impingement) vs. later in post-LOCA (corrosion). Organic sources to containment pool would alter chemistry (i.e., complexation, etc.). |
| 6.2 | T2-24 | Organic agglomeration | Formation of larger clumps of smaller inorganic particulates nucleating around organic acids or oil (such as soap coagulates dirt particles). | Coagulated particles can collect on sump screen, decreasing flow, or collect in other places to decrease the loading on the sump screen. |
| 6.3 | T2-15 | Organic complexation | Organic acids become absorbed on surfaces of solids and inhibit solid species growth (e.g., aliphatic acid). | Effectively enhances solubility limits. Solid species may precipitate, but remain relatively small in size (nanoscale). They do not agglomerate or grow to macroscopic sizes. |
| 6.4 | T4-17 | Coating dissolution and leaching | Dissolution/leaching of submerged epoxy, alkyd, or zinc-based coatings and primers occurs to contribute species to the containment pool. Other possible sources include Pb-based paints (older containment buildings), phenolics, PVC. | (1) Additional source terms (e.g., chlorides, fluorides, organics) for products affecting the containment pool chemistry. (2) Chlorides affect radiolysis and ion. |

Table 1: Summary of Remaining 41 Chemical Effects Issues

| | PIRT Issue Number | Phenomenon | Description | Possible Implications |
|---|-------------------|---|--|---|
| 7. Chemical Effects on Downstream System Performance: Pumps, Heat Exchangers, and Reactor Core | | | | |
| 7.1 | T3-19 | ECCS pump: seal abrasion and erosion/corrosion | Abrasive wearing of pump seals (e.g., magnetite—high volume/concentration of mild abrasive) creates additional materials that contribute to containment pool chemistry. Also, chemical byproducts cause erosion or corrosion of pump internals, especially tight to | (1) Additional particles may contribute to reactor core clogging. (2) Particles may add additional sump screen loading. (3) Particles may affect chemical species formation. (4) Pump performance degrades. |
| 7.2 | T3-21 | Heat exchanger: deposition and clogging | Solid species which form in the heat exchanger lead to surface deposition and/or clogging within close-packed heat exchanger tubes (5/8" diameter). | (1) Severe clogging/deposition causes flow to decrease through heat exchanger core and an inability to cool reactor core. (2) Less severe deposition may degrade heat transfer and degrade heat flow from the reactor core. |
| 7.3 | T3-22 | Reactor core: fuel deposition and precipitation | ΔT increase (+70 °C from containment pool) and retrograde solubility of some species (e.g., Ca silicate, Ca carbonate, zeolite, sodium calcium aluminate) causes scale buildup on reactor core. Zn, Ca, Mg, CO ₂ -based deposits, films, and precipitates may form at h | (1). Decreases heat transfer from the reactor fuel. (2). Localized boiling occurs due to insufficient heat removal. (3) Deposits spall off, creating additional debris source which could clog the reactor core or contribute to sump screen head loss. |
| 7.4 | T3-24 | Reactor core: diminished heat transfer | Insulation debris and chemical products mixed within water cause a reduction in the effective heat transfer capabilities of mixture. The precipitation of this material is initiated in RHR heat exchanger. | Ability to remove heat from the fuel is diminished. |
| 7.5 | T3-25 | Reactor core: blocking of flow passages | Chemical products, in combination with other debris, block primary flow passages for getting cooling water through core. | Heat transfer may be impeded; flow is forced to bypass the lower plenum debris screens. |
| 7.6 | T3-26 | Reactor core: particulate settling | Particulate settling occurs due to relatively low, upwards flow (for cold-leg injection) within reactor. | Compacted deposits form which may impede heat transfer and water flow, especially for lower portions of reactor fuel. |

Table 2: Topic Areas and Objectives of PNNL Study

| Topic | Objectives |
|--|---|
| Radiation effects | Study the effect of the post-LOCA radiation environment in the reactor vessel, containment pool, and contaminated sump strainer on the containment pool chemical constituents. |
| Carbonation of concrete | Evaluate the effect of carbonation or other concrete aging processes on the leaching rates and dissolved species from aged concrete and concrete dust and compare this with research programs that used relatively fresh concrete samples. |
| Alloy corrosion | Evaluate the effect of material alloy variability on the corrosion rate and dissolved species of important submerged containment pool metals. |
| Galvanic corrosion | Identify galvanic corrosion effects and specific galvanic configurations that could most significantly alter the amounts and types of chemical byproducts. |
| Biological fouling | Assess the potential for biological fouling of sump strainers caused by bacteria, algal, or other biological growth during the 30-day post-LOCA mission time. |
| Coprecipitation and other synergistic solids formation | Identify conditions that could significantly promote coprecipitation of chemical species or enable synergistic production of more or different solids than had been considered. |
| Inorganic agglomeration | Identify conditions affecting inorganic agglomeration in the post-LOCA coolant. |
| Crud release effects | Evaluate the quantities and chemical/radiation effects related to metal corrosion oxides (crud) within the RCS released during the post-LOCA time period. |
| Retrograde solubility and solids deposition | Identify likely chemical species and estimate quantities that could precipitate at the reactor core because of retrograde solubility. Also indicate which, if any, preexisting solid chemical species could be deposited onto the reactor fuel. |
| Organic material impacts | Identify the organic materials that could exist in significant quantities in the post-LOCA containment environment that have the most significant (either beneficial or detrimental) impact on chemical effects within the post-LOCA coolant environment. |

DISPOSITION OF OUTSTANDING CHEMICAL EFFECTS ISSUES

1. Underlying Containment Pool Chemistry

1.1 Reactor Coolant System Coolant Chemistry Conditions at Break

Description and Possible Implications

The reactor coolant system (RCS) coolant chemistry varies over the fuel cycle. Boron concentrations vary from approximately 2,000 to 4,000 parts per million (ppm) at the beginning of the fuel cycle to approximately 50 ppm at the end of the fuel cycle. Therefore, the initial reactor water chemistry spewing out of the break and forming the containment pool will have variable boron concentration while the ratio of lithium to boron is approximately constant. The two-phase jet emanating from the break is initially at 315 degrees Celsius (C) (599 degrees Fahrenheit (F)) and then cools to 120 degrees C (248 degrees F). The main concern raised by the peer reviewers relates to how variations in the initial RCS chemistry will affect the interaction with containment materials and whether these variations have been appropriately addressed. Variations may influence corrosion rates of metals, leaching of species from nonmetallic materials, formation of chemical precipitates, and ultimately, plant-specific chemical effects.

Discussion

Although the conditions within the RCS vary during the course of an operating cycle, RCS chemistry at the time of a LOCA will only influence material degradation for a very brief period relative to the ECCS system mission time. For example, the initial blowdown phase of a large-break LOCA is less than 1 minute compared to a typical ECCS mission time of 30 days. Longer term leaching of containment materials above the post-LOCA water level in containment can result from interaction with containment spray following the LOCA over a period of several hours.

The chemistry and pH of containment spray during the ECCS injection period, however, is governed by the refueling water storage tank (RWST) chemistry and any chemical additives to the spray and not the initial RCS chemistry conditions. Although the RCS conditions at the time of the break will influence post-LOCA containment pool conditions somewhat, the more dominant contributors to overall pool chemistry is the greater volume of borated water from the RWST and accumulator tanks and the chemical buffer used to maintain the pH of the post-LOCA equilibrium pool above 7.

Initially, the pool pH will be acidic (e.g., 4–5) and will increase to a pH greater than 7 as the buffering chemicals are added to the containment pool. Sodium hydroxide (NaOH) buffers are injected directly through the containment spray, while trisodium phosphate (TSP) or sodium tetraborate (STB) powders dissolve as water from the break fills the containment pool. The larger breaks that lead to containment spray actuation produce a bounding amount of debris, including chemical precipitate.

All licensees are required to adequately account for potential chemical precipitates during strainer qualification tests. This includes accounting for potential variability in post-LOCA chemistry, such as boron concentration and pH. For example, NUREG/CR-6915, "Aluminum Chemistry in Prototypical Post-LOCA PWR Containment Environment" (Ref. 12), discusses how boron adsorption can favor amorphous aluminum-hydroxide-type precipitates by impeding the

crystallization of aluminum compounds. Most licensees use the WCAP-16530-NP-A (Ref. 3) chemical model that considers the effects of containment pool pH variations with time. Licensees typically assume those conditions that maximize the amount of precipitate generated during the post-LOCA mission time. Since greater sump pool pH values result in more aluminum corrosion, which leads to the prediction of more precipitate, licensees typically make assumptions that maximize post-LOCA pH. Testing in support of WCAP-16530-NP-A, conducted by the Pressurized Water Reactor Owners' Group (PWROG), evaluated the effects of pH and boron and included tests over a range of pH and temperatures with a boron concentration that bounds the boron concentration identified by the peer review panel. Plants not using the WCAP-16530-NP-A spreadsheet to determine their chemical source term have performed plant specific tests in borated water buffered to the appropriate pH. Therefore, the chemical effects analysis performed by the licensees have adequately addressed variation in potential chemical effects related to initial RCS coolant chemistry.

Conclusion

Potential variability in the RCS chemistry at the time of a LOCA may affect the initial jet chemistry and the long-term post-LOCA pool conditions. Because of the very small amount of time that the jet interacts with plant materials, however, the potential variability in jet chemistry does not significantly affect the plant-specific chemical source term. The plant-specific chemical effects evaluations considered the variability in the RCS water chemistry at the time of the break, along with potential impacts to long-term pool conditions and chemical precipitate formation. Licensees typically assume conditions that cause the most chemical precipitate to be predicted. The NRC staff performs a detailed review of each licensee's overall chemical effects evaluation to verify its adequacy. Therefore, no additional research is needed to address this issue.

1.2 pH Variability

Description and Possible Implications

The normal operating pH of the RCS is typically in the range of 6.9–7.4. The pH adjusted to 25 degrees C (77 degrees F) changes during the course of the fuel cycle from acidic at the beginning of the cycle to closer to neutral by the end of a fuel cycle. There are implications similar to those discussed in Section 1.1 of this report with respect to how pH variations may affect the interactions between containment materials and the post-LOCA environment. These variations may influence corrosion rates of metals, leaching of species from nonmetallic materials, formation of chemical precipitates, and ultimately plant-specific chemical effects.

Discussion

This issue is similar to the concern identified in Section 1.1 regarding how the variability in RCS chemistry at the time of the break may influence potential chemical effects. Sections 1.5, "Emergency Core Cooling System Injection of Boron," and 2.4, "Conversion of N₂ to H₂NO₃," of this report also address the concerns identified by the PIRT panelists related to how changes to the post-LOCA environment could affect corrosion and leaching of plant materials. As previously discussed, the variability of the initial RCS chemistry during the operating cycle will influence somewhat the post-LOCA containment pool conditions. The water volume supplied by the RCS contents, however, typically provides less than one-fourth of the total pool volume following a large-break LOCA. Therefore, pH variations in the RCS water chemistry during the operating cycle have a significantly reduced influence on final pool conditions following a LOCA.

The more dominant factors affecting the containment pool chemistry will be the boron concentration from the RWST and accumulators (or safety injection tanks) and the chemical buffers (i.e., TSP, STB, or NaOH) used to ensure that the post-LOCA containment pool pH remains above 7.

Licensees are required to evaluate potential chemical effects, and their analysis considers the potential range of pH values that may result from differences in the RCS chemistry during the operating cycle and differences in the initial RWST boron concentrations. The NRC staff expects (Ref. 13) that, in order to perform acceptable chemical effects evaluation, licensees develop a thorough understanding of plant materials and the range of potential post accident environments (e.g., temperatures, spray and pool pH values, spray durations) and use this information to conservatively evaluate potential chemical interactions during the plant's ECCS mission time. Post-LOCA pH evaluations include consideration of the time for buffer chemicals to be dissolved in the pool or to be injected into the containment spray. To ensure a conservative evaluation, licensees analyze the possible range of pool pH following a LOCA and assume the pH values that maximize the amount of precipitate generated during the post-LOCA mission time.

Conclusion

Potential variability in the RCS pH at the time of a LOCA will influence somewhat the post-LOCA pool pH and plant-specific chemical source term. Licensees' chemical effects evaluations consider the variability in the RCS pH and the potential impact to chemical precipitate formation. The NRC staff performs a detailed review of each licensee's overall chemical effects evaluation to verify its adequacy. Since licensees assume pH values that maximize the prediction of chemical precipitates, no additional research is needed to address this issue.

1.3 Hydrogen Sources within Containment

Description and Possible Implications

Dissolved hydrogen may play a significant role in the containment pool water chemistry. Hydrogen sources within the containment include the RCS inventory; the corrosion of metallic materials, including the reactor fuel cladding; and the Schikorr reaction. Containment pool reduction-oxidation (redox) potential is a function of the dissolved hydrogen resulting from these sources. Higher H₂ concentrations may decrease the redox potential. However, containment conditions are expected to foster H₂ evaporation, which could raise the redox potential.

This issue could be important if H₂ concentrations have a significant effect on the redox potential in the post-LOCA containment water. The redox potential determines which materials will corrode or dissolve within the pool. A higher redox potential (i.e., more oxidizing) promotes metallic corrosion. As the concentration of dissolved constituents increases, so does the potential for solid species precipitation that could affect ECCS performance. The NRC or industry testing has not attempted to accurately simulate post-LOCA H₂ concentrations. However, the Schikorr reaction, by itself, may be beneficial by converting compounds that could form gelatinous-type chemical species into the mineral magnetite.

Discussion

At least one PIRT member strongly believed that an accurate accounting of dissolved H₂ concentrations is important for determining the underlying ECCS water chemistry (Ref. 2). The panelist contended that the redox potential is a function of the amount of dissolved H₂. Hydrogen sources within the containment include the RCS inventory; the corrosion of metallic materials, including the reactor fuel cladding; and the Schikorr reaction.

The following equation characterizes the Schikorr reaction:



The possible generation of H₂ from the Schikorr reaction and the related chemical transformations might contribute significantly to the H₂ inventory in containment immediately after a LOCA. However, additional H₂ in the containment pool caused by the Schikorr reaction is beneficial in one sense because it may decrease the redox potential and inhibit corrosion. This is the reason that H₂ is added to pressurized-water reactor (PWR) and boiling-water reactor (BWR) primary coolant systems. Another positive attribute of the Schikorr reaction is that it decreases gelatinous iron(II) hydroxide (Fe(OH)₂), which may react with other components (e.g., Si(OH)₄) to produce mixed oxides/oxyhydroxides and mixed hydroxides that may be more detrimental than Fe(OH)₂. One possible downside of this reaction is that magnetite (Fe₃O₄) is produced. However, Fe₃O₄ is expected to have a less deleterious chemical effect than Fe(OH)₂ because it has a higher density, which impedes transport, and it is a stable particulate that will not form gels. Therefore, on balance, additional dissolved H₂ within the post-LOCA containment water may be expected to decrease deleterious chemical effects.

However, other PIRT panelists argued that dissolved H₂ concentrations will have little effect on the post-LOCA chemical environment (Ref. 2). The injection of H₂ gas within the RCS actively maintains an H₂ overpressure to preserve reducing conditions and impede metallic corrosion. These initial H₂ concentrations are essentially evaporated during the blowdown period of the LOCA (Ref. 11). Therefore, the initial post-LOCA dissolved H₂ concentration within the RCS is small. Additional dissolved H₂ concentrations can result from radiolysis of water and through the corrosion of RCS metallic materials. NUREG/CR-6988 (Ref. 11) addresses the H₂ contribution from radiolysis. Calculations of the H⁺ and H₂ concentrations generated by the gamma radiolysis of water suggest that radiation will have a negligible contribution to the inventory of these species within the containment pool. The concentration of H⁺ produced by radiolysis in the RCS will quickly (~2 milliseconds) approach a saturation level of 1.8 parts per trillion (PPT). This concentration of H⁺ is small compared to the buffer capacity of the coolant and is not expected to have any noticeable effect on RCS chemistry in the coolant. Similarly, the concentration of H₂ produced by radiolysis will approach a saturation level of 10⁻⁶ moles per liter (moles/L) in the first 100 seconds and will remain at this level or lower for the remaining 30 days as the hydrogen establishes equilibrium with its partial pressure in air. Therefore, the expected production of H₂ resulting from radiolysis is negligible.

The largest sources of dissolved H₂ result from metallic corrosion of RCS components, including the reactor fuel cladding. However, the rate of H₂ production from these sources will decrease with time because of metallic surface passivation. More importantly, the NRC and industry-sponsored chemical effects testing has focused on these effects.

The H₂ production caused by the Schikorr reaction will also be limited by the dissolved Fe concentration. The integrated chemical effects test (ICET) series (Ref. 14) measured low Fe

concentrations in representative post-LOCA environments. Additionally, some plants use hydrogen igniters to limit the atmospheric hydrogen concentration within the containment building. These systems typically actuate when the hydrogen concentration reaches approximately 2 percent. These low hydrogen levels result in negligible dissolved H₂ within the containment pool to affect the redox potential (Ref. 2) and provide additional defense against H₂ accumulation for those plants that utilize igniters. Several PIRT panelists also argued that the remaining dissolved H₂ in containment was not significant because H₂ is not a very effective reducing agent in the absence of a catalyst (such as platinum metal) and H₂ partitioning into the containment building atmosphere renders it largely inert (Ref. 2).

Conclusion

The effect of H₂ on the post-LOCA chemical environment is not expected to be significant. Higher dissolved H₂ concentrations could actually be beneficial by decreasing the redox potential and reducing metallic corrosion. This could lead to less chemically induced solid species (or debris) that could degrade ECCS performance. However, the initial post-LOCA dissolved H₂ concentrations from the RCS overpressure are expected to evaporate, and the relatively low dose associated with the noncritical reactor fuel will limit the radiolytic production of dissolved H₂. Production of H₂ from the Schikorr reaction will also be limited because the Fe concentration is expected to be low. Additionally, some plants utilize hydrogen igniters, which provide an additional means of maintaining a low threshold of dissolved H₂ within the containment pool.

Therefore, the largest H₂ source is expected from the corrosion of RCS metallic components. Because the contribution of chemical species to the redox potential is proportional to concentration, the larger dissolved concentrations resulting from dissolution of post-LOCA debris and corrosion of RCS components are expected to govern the redox potential of the containment water. The NRC and industry-sponsored chemical effects testing has focused on determining the corrosion rates and ionic concentrations from corrosion of RCS metallic components. Therefore, previous chemical effects testing have explicitly considered the effect of H₂ on the chemical environment and redox potential. No additional research is needed to address this issue.

1.4 Containment Spray CO₂ Scavenging and CO₂/O₂ Air Exchange

Description and Possible Implications

Air entrainment within the containment pool beginning soon after the LOCA will cause carbon dioxide (CO₂) absorption within the containment pool. This entrainment increases the amount of CO₂, which could produce higher carbonate precipitate concentrations than would otherwise be present. These precipitates could also enhance nucleation and precipitation of other chemical species. Consequently, the air/liquid interactions within containment may increase the amount of chemical precipitates and degrade ECCS performance more than if these interactions were not considered.

Discussion

Air entrainment within the containment pool, caused by coolant water emanating from the break and pool turbulence in addition to atmospheric scrubbing from containment spray, will cause CO₂ absorption beginning soon after the LOCA, well before the onset of ECCS recirculation. It is worth noting that the ICET program did not simulate the large containment-air-to-pool-volume

ratio that exists in plants. With the dissolution of post-LOCA debris (e.g., calcium silicate (Cal-Sil), concrete, and fiberglass), Ca cations (Ca^{2+}) would build up in solution.

Because the pH-buffered recirculating cooling water eventually becomes alkaline (i.e., the pH is 7–10), the absorbed CO_2 would accumulate predominantly as the bicarbonate ion, which would, in turn, react with Ca^{2+} to precipitate CaCO_3 . Both the absorption of CO_2 and precipitation of CaCO_3 tend to further increase pH, which, together with the depletion of Ca^{2+} from solution, could enhance the continuing dissolution of insulation materials. However, the pH buffers in solution mitigate pH changes and may also suppress continued Ca^{2+} production. The eventual depletion of CO_2 in the air of the containment building limits the amount of calcite precipitation.

Scoping calculations by some of the PIRT panelists suggest that as much as approximately 300 pounds of finely divided CaCO_3 particulate may be produced through the uptake of atmospheric CO_2 in the largest containment buildings. However, the quantity of Ca that is converted into CaCO_3 represents less than 1 percent of the dissolved Ca produced by complete fiberglass dissolution in the ICET tests. Additionally, depending on the buffering chemical, the CaCO_3 may simply replace other finely divided Ca precipitates like hydrated lime ($\text{Ca}_3(\text{PO}_4)_2$) or calcium hydroxide ($\text{Ca}(\text{OH})_2$). The hydrated lime, calcium hydroxide, and calcite solids are physically similar and are unlikely to differ significantly in their effects on either sump screen flow or downstream ECCS performance (Ref. 1). Additionally, scrubbing of CO_2 from the atmosphere and mixing within the containment waters is less effective at higher temperatures (i.e., 80°C) than at ambient temperatures (i.e., 25°C). This suggests that in an actual LOCA, the dissolution of CO_2 and subsequent precipitation of CaCO_3 will likely be delayed until later in the post-LOCA scenario.

The chemical effect model developed in WCAP-16530-NP-A (Ref. 3) conservatively accounts for carbonate precipitation resulting from air entrainment in plants buffered with TSP because all dissolved concentrations of calcium that could form carbonate precipitates are already assumed to precipitate. This model assumes precipitate formation regardless of solubility considerations.

Additionally, all plants were required to conduct chemical effects testing to measure head loss for their specific debris types, debris concentrations and sump configuration. These tests proceeded until head loss did not substantially increase with continued test time. Quite often, the test configuration was open to allow continuous CO_2 uptake from the atmosphere to occur during the test. While the test pH did not always match post-LOCA plant conditions, the large available supply of atmospheric CO_2 is expected to result in a conservative concentration of CaCO_3 in tests open to the atmosphere, compared to the post-LOCA environment, since containment buildings are more leak tight.

Based on the above knowledge, staff expects that additional effects due to calcite formation is only a plant-specific consideration in the unlikely scenario that all of the following five conditions exist:

1. The plant does not adopt the WCAP-16530-NP-A model.
2. The plant-specific testing did not allow continuous CO_2 uptake.
3. Plant conditions do not foster $\text{Ca}_3(\text{PO}_4)_2$ precipitation.

4. Three hundred pounds of calcite carbonate is expected to be a significant percentage of the plant's debris loading (i.e., the plant's debris loading is less than a few thousand pounds).
5. The plant does not have significant open area on the sump strainer during the post-LOCA scenario.

It should be noted that conditions 3 and 4 above could only exist in plants with sufficient dissolved Ca concentrations (e.g., from Cal-Sil, exposed concrete, and fiberglass insulation) that use a buffer other than TSP. Plants with TSP buffering already contend with $\text{Ca}_3(\text{PO}_4)_2$.

Staff conducted a review of the Generic Letter (GL) 2004-02 supplemental responses to determine if any plant satisfies all five criteria above such that plant-specific evaluation of CaCO_3 precipitation may be required. This review concluded that only seven units needed additional evaluation to determine if calcite formation could be a significant influence on chemical effects. However, none of these plants satisfy all of the criteria 2 through 5 above for the following reasons:

1. Two units use TSP as the pH buffer and thus have adequately addressed $\text{Ca}_3(\text{PO}_4)_2$ precipitation. These plants do not satisfy criterion 3.
2. Four units have very similar designs. They use NaOH as the pH buffer. The containment buildings for these units have approximately 45% less free air space than the larger unit used for the scoping calculation that concluded an estimate of 300 lbs of CaCO_3 particulate was possible. Therefore, for these units, the estimated bounding quantity of CaCO_3 particulate is approximately 170 lbs. The smallest maximum debris load from fibrous insulation addressed in the analysis for these 4 units is approximately 1500 pounds and the smallest maximum coating and latent debris load is approximately 1000 pounds, for a total of 2500 pounds of debris. The additional CaCO_3 particulate is less than 7% of the total debris load. Therefore, this additional CaCO_3 particulate is not a significant consideration compared to the other debris sources and these plants do not satisfy criterion 4.
3. The 7th unit has a similar containment size to the 4 units discussed above and also uses NaOH for the pH buffer. Therefore, the estimated quantity of CaCO_3 particulate, assuming that the formation is limited by the available CO_2 , is 170 lbs. The analysis for this unit accounted for a maximum insulation debris load of approximately 800 lbs, mainly from Cal-Sil based mineral wool type insulation. The analysis considered a maximum coatings and latent debris load of approximately 1900 lbs and 100 lbs, respectively, such that the total debris is 2800 lbs. The additional maximum CaCO_3 particulate is approximately 6% of the total debris load. Therefore, this additional CaCO_3 particulate is a not significant consideration compared to the other debris sources and this unit also does not satisfy criterion 4. It should also be noted that the strainer for this unit has a design margin of approximately 2.5 psi pressure drop across the strainer which provides additional assurance that CaCO_3 precipitation is not a significant concern for this unit.

Additionally, the PIRT panelists indicated that CaCO_3 could assume a secondary role by serving as a site for heterogeneous nucleation and growth of other chemical phases (e.g., Al phosphates and silicates) early in the post-LOCA cooling cycle. This effect is not likely to increase the final concentration of these other chemical phases, but it could accelerate their

formation below the solubility limit. Thus, although the concentration of calcite formed from atmospheric CO₂ may not be an important additional consideration (as demonstrated above), its effect on precipitation kinetics could be more significant.

For this reason, a few PIRT reviewers recommended that the relative impact of CO₂ absorbed from the air and the effect of subsequent calcite formation be further assessed. However, the accurate assessment of these implications requires consideration of plant-specific debris sources, dissolved Ca levels, containment environmental conditions, and the quantity of fresh air in containment that replenishes the CO₂ supply that may have been exhausted by carbonate precipitation. The WCAP-16530-NP-A model conservatively accounts for these effects by assuming that chemical precipitates form from all dissolved species at the beginning of the post-LOCA scenario (Ref. 3). Also, the inefficient scrubbing of CO₂ at higher temperature implies that any enhancement of heterogeneous nucleation and growth due to CaCO₃ is likely delayed until later in the post-LOCA scenario when ECCS operating margins are much greater. Therefore, staff expects that the analyses used within the GL 2004-02 supplemental responses are sufficiently conservative and robust to address the possible accelerated formation of other chemical species due to CaCO₃ precipitation without explicit plant-specific evaluation of this effect.

Conclusion

The chemical effects model in WCAP-16530-NP-A conservatively assumes that the concentrations of dissolved cationic species form chemical precipitates at the beginning of the post-LOCA scenario. This approach sufficiently addresses the effect of air entrainment of CO₂ on the formation of both CaCO₃ precipitates and acceleration of other precipitates within the containment pool. Therefore, this issue is not a consideration for plants that adopt the WCAP-16530-NP-A model.

Staff performed a detailed review of the licensees' chemical effects evaluations in the GL 2004-02 supplemental responses for the seven plants that required additional evaluation. Two plants adequately address debris loading due to calcium-based precipitates by assuming that they are calcium phosphate. Calcium phosphate is a representative surrogate for accounting for debris loading effects due to CaCO₃. The remaining five plants do not have a significant concentration of CaCO₃ precipitate compared to the concentration of other debris sources within the containment pool. Therefore any additional debris loading from CaCO₃ particulate produced through the uptake of atmospheric CO₂ does not need to be explicitly considered.

The effect of calcite precipitation on the accelerated precipitation of other chemical phases (e.g., Al phosphates and silicates) is also not expected to be a significant consideration for the seven plants that do not adopt the WCAP-16530-NP-A model because these effects are not likely to be significant until the containment pool approaches ambient temperatures. At this point in the post-LOCA scenario, the ECCS margin is much greater and it is expected to be sufficient to account for any additional precipitate loading due to this effect. Therefore, the post-LOCA effects resulting from air entrainment of CO₂ require no further generic or plant-specific evaluation.

1.5 Emergency Core Cooling System Injection of Boron

Description and Possible Implications

After a pipe break, RWST inventory with a boron concentration of approximately 2,800 ppm is injected into the RCS to cool the reactor core. This provides for a large boron source, which may affect chemical reaction products in the containment pool. Specifically, the boron source will serve as a pH buffer. This may influence corrosion rates of metals, leaching of species from nonmetallics, and ultimately formation of chemical precipitates.

Discussion

Boron can affect chemical reactions in the post LOCA containment pool by influencing precipitation reactions or by influencing the containment pool pH. For example, NUREG/CR-6915 (Ref. 12) discusses the potential role of boron adsorption in the aluminum precipitation process in a simulated post-LOCA environment. Industry chemical effects evaluations have also considered potential effects related to boron. The ICET tests (Ref. 14) initially used to screen for potential chemical effects included 2,800 ppm of boron for the tests with TSP and NaOH buffers. The ICET STB test contained a boron concentration of 2,400 ppm to better simulate ice condenser plants. All of the PWROG-sponsored tests summarized in WCAP-16530-NP-A (Ref. 3) used a boron concentration of 4,400 ppm. Therefore, the chemical analysis procedure used by most licensees to determine their plant-specific chemical precipitate load is based on testing that was performed using a range of boron concentrations which represent the boron concentrations that may exist following a LOCA. Licensees that did not rely on the WCAP-16530-NP-A methodology to determine their chemical source term performed plant-specific tests in borated water. Licensees' chemical effects evaluations also consider the range of plant-specific pH values resulting from possible variations in boron concentration and account for the plant-specific amount of buffering chemical used to ensure that a long-term equilibrium pH following a LOCA remains greater than 7. Plants typically select those parameters that result in the greatest amount of predicted chemical precipitate.

Conclusion

The industry's chemical effects evaluations already consider the potential effects of boron, since the plant-specific analysis considers the range of possible pH values in the post-LOCA containment pool and the testing that provides the technical basis for chemical effects evaluations was performed with water containing appropriate boron concentrations. Therefore, no additional research is needed to address this issue.

2. Radiological Considerations

2.1 Radiolytic Environment

Description and Possible Implications

Radiolysis is the dissociation of molecular chemical bonds by a high energy radiation flux. The largest source of this radiation flux is the gamma radioactive decay of the reactor fuel. When the ECCS fluid passes through the reactor core, it is subjected to this radiation flux. Radiolysis reactions may change the pH of the ECCS containment pool, the fluid's redox potential, or both. Hence, chemical species which differ from those evaluated may form or the fluid may be more corrosive than that evaluated in all previous chemical effects testing.

Discussion

Radiolysis of water will form H_2 , O_2 , H_2O_2 , hydroxyl radicals (OH), and a number of other minor products. The post-LOCA heat and agitation of the containment pool will remove the H and O gaseous products, leaving the H_2O_2 and OH radicals. These radicals can cause changes in the pH and redox potential either in the containment pool or in the fibrous debris bed on the sump screen strainer. The effect of radiolysis in the containment pool chemistry is the issue of interest in this evaluation. Section 2.5 of this report discusses the effect on the fibrous debris bed.

Changing the relative amounts of H, O, and H_2O_2 present affects the pH and redox potential of the water. Some of the PIRT panelists believed that radiolysis would form a significant amount of H_2O_2 . Therefore, the redox potential could be significantly altered. Sections 3.1 through 3.7 of NUREG/CR-6988 (Ref. 11) discuss the conservative bounding scoping calculations for radiolysis effects on pH and redox potential. Section 3.2 evaluates the formation of H_2O_2 . H_2O_2 could begin to form soon after the ECCS recirculation phase begins, when the coolant is passing through the core region. The analysis evaluated the formation of H_2O_2 , as well as its destruction by radiolysis. H_2O_2 is destroyed by interaction with other radiolytically produced species and by disproportionation to form H_2O and O_2 . This evaluation concluded that H_2O_2 equilibrium would be established fairly quickly, and the equilibrium concentration would range between 0.3 to 6 ppm. The 0.3-ppm value is considered a reasonable estimation of H_2O_2 concentration within the reactor core, while the 6-ppm value represents an upper limit based on measurements of H_2O_2 in several spent fuel pools. Regardless, the effect of this low concentration of H_2O_2 on pH is insignificant. The buffer available in the containment pool will readily neutralize the H_2O_2 ; thus, the H_2O_2 will not have a significant effect on the formation of corrosion products.

Additionally, even if the buffering system did not operate as expected and the acidic containment fluids were not neutralized by the buffer, the potential for increased corrosion would be limited to the flooded portions of containment. Approximately 95 percent of the aluminum and 66 percent of the carbon steel in a typical containment building is above the flooded area and would not be subjected to increased corrosion from H_2O_2 . The increase in corrosion products from the small fraction of submerged material would not add an appreciable amount of particulate debris to what is already postulated to form. Therefore, because of the low concentration of H_2O_2 and the limited quantities of submerged materials, accelerated material corrosion from H_2O_2 should be insignificant.

However, NUREG/CR-6988 recommends that mixed potential modeling analyses be performed to confirm that the acids will be neutralized, as predicted in the scoping calculations. To adopt this recommendation, a radiolysis model would first be constructed to speciate the fluid system under post-LOCA conditions; in particular, one would calculate the concentrations of redox species, such as H_2 , O_2 , H_2O_2 , OH , and H . The concentrations of these species would then be used in a mixed potential model to estimate both the redox potential and the corrosion potential for a specific metal or alloy. Evaluations using mixed potential modeling like this have been performed successfully for operating BWRs in a closed-loop reactor coolant system to study water chemistry effects on intergranular stress-corrosion cracking. This is a very controlled environment where water volumes and initial water chemistry are known and strictly controlled. However, this modeling has never been applied to post-LOCA water chemistry conditions for a PWR. In the open post-LOCA environment, there would be a high degree of mixing of gases and vapors between the containment pool and the containment atmosphere. Such mixing would necessitate the use of assumptions as to the chemical interactions that occur. The results would therefore be subject to substantial uncertainty unless tests were performed to validate the model. Therefore, such modeling is not expected to result in additional insights and is not currently warranted.

In addition to the evaluations contained in NUREG/CR-6988, the PWROG evaluated radiolysis-induced changes in redox potential in its response to requests for additional information (RAIs) related to WCAP-16530-NP (Refs. 15, 16, 17). The PWROG reached the same conclusion as NUREG/CR-6988. The concentration of H_2 , O_2 , and H_2O_2 that is produced from radiolysis is relatively small (i.e., less than 1 ppm) and would not measurably influence corrosion rates. In addition, any acids formed by radiolysis will be neutralized by the buffer present and would have little effect on pH.

WCAP-16793-NP, Revision 1 (Ref. 5), also evaluated the redox potential in response to an RAI. This evaluation concluded the following:

[The OLI StreamAnalyzer™ calculation in Appendix F (Ref. 5)] includes representative concentrations for oxygen and hydrogen in the containment liquid. The oxygen and hydrogen are allowed to partition between the liquid and vapor phases as appropriate. Changes in the Oxidation-Reduction Potential (ORP) of the solution, either by oxygen and hydrogen from radiolysis or through other potential radiolysis products (hydrogen peroxide or nitrate), could slightly decrease the solubility of some of the predicted precipitates.

However, because subsequent analyses already assume 100-percent precipitation of all solutes present in the liquid, the final results would not change.

The NRC staff considers the OLI StreamAnalyzer™ database to be acceptable for this analysis because it provides predictions for complex mixed-chemistry environments over a wide range of solute concentrations. It was specifically used to identify the most likely precipitate species and to verify the assumption that 100 percent of the dissolved species are available for precipitation. While the OLI database does not include all possible species available for precipitation, it does include a large number of relevant species (i.e., oxides, hydroxides, aluminum-containing silicates, nonaluminum-containing silicates, and borates). The PWROG considered it unlikely that a precipitated species, which was not included in the thermodynamic database, would have characteristics that differ significantly from those evaluated.

Licenseses have performed other analyses that provide additional insights into pH changes related to radiolysis. The ECCS could contain chloride compounds created by the radiolytic breakdown of electrical cable insulation or from leaching of protective coatings and other organic material. These chlorides could form strong acids, such as hydrochloric acid, which may alter the pH and redox potential. Analyses performed for alternate source term (AST) (Refs. 18, 19) license amendments and GSI-191-related buffer change license amendments for several licensees (Refs. 20, 21, 22) account for the formation of strong acids due to radiolysis. These analyses demonstrated that the quantity of buffer addition needed to counteract pH changes resulting from strong acid formation is small. In some cases, more buffering chemicals have been added to counteract predicted pH changes due to acid formation, and in other cases the change in pH, without an increase in buffer, was determined by analysis. For example, one licensee demonstrated that the change in pH due to radiolysis would be approximately 0.2 pH units. As part of preparing its safety evaluations (SEs) for these amendment requests, the staff typically reviewed and verified the licensees' analyses.

Therefore, for the reasons identified in this section, the staff does not expect radiolysis-induced pH changes and accelerated materials corrosion resulting from radiolysis to add a significant quantity to the total debris load in containment over the 30-day mission time.

Conclusion

Radiolysis of water will form H_2 , O_2 , H_2O_2 , OH , and a number of other products. The post-LOCA heat and agitation of the containment pool will remove the H and O gaseous products, leaving the H_2O_2 and OH radicals. These radicals can cause changes in the pH and redox potential in the containment pool. However, evaluations by both industry and the NRC staff have concluded that these changes are not expected to add a significant quantity of precipitate to the containment pool over the 30-day mission time. Further, the buffer available in the post-LOCA containment environment will neutralize the H_2O_2 and other strong acids formed by radiolysis of the fluids and electrical cables in containment; thus, the acids will not have a significant effect on the containment pool pH. The technical basis discussed above is sufficient to provide adequate assurance that radiolysis will have a minimal effect on post-LOCA chemical products formation. Therefore, no additional research related to this issue is necessary.

2.2 Radiological Effects: Corrosion Rate Changes

Description and Possible Implications

Radiolysis of water bearing the chloride ion (Cl^-) can elevate the post-LOCA corrosion rate through formation of hypochlorite (ClO^-) or hypochlorous ($HOCl$) acid. The presence of these acids could increase the corrosion rate of metallic and nonmetallic species in containment, which in turn could alter the chemical byproducts formed. Hence, the chemical precipitates that form could differ from those previously evaluated. These different precipitates could subsequently affect ECCS performance in a manner that has not been considered previously.

Discussion

Chloride is a constituent of the post-LOCA coolant resulting primarily from the radiolytic breakdown of electrical cable insulation due to radiolysis. Section 5.2.1 of NUREG-1918 (Ref. 2) initially evaluated the effect of corrosion rate changes caused by Cl^- radiolysis. The PIRT panelists generally expected that the impact would be modest because the containment pool Cl^- concentrations are expected to be low and would be neutralized by the buffer, as

discussed above in Section 2.1. The ICET tests, documented in NUREG/CR-6914 (Ref. 14), were conducted with initial Cl⁻ concentrations of 100 ppm. This concentration was selected to conservatively bound the Cl⁻ concentration from degradation of electrical cable insulation (Ref. 23). Radiolysis testing of water containing sodium chloride performed in Germany in 2004 (Ref. 24) also supports the selection of this concentration. The evaluation of these tests (Ref. 11) concluded that the formation of Cl⁻ ions as a result of radiolysis is expected to be less than 100 ppm after 30 days of exposure.

While the ICET program explicitly evaluated the effect of 100 ppm of Cl⁻ on material corrosion rates, tests were not conducted without Cl⁻ to determine whether the corrosion rate was affected. However, other tests have evaluated the effect of Cl⁻ on aluminum corrosion (Ref. 25). These tests were performed in water with a temperature of 80 degrees C (176 degrees F) which contained 100 ppm Cl⁻ and 100 ppm H₂O₂. The researchers observed no enhanced corrosion rate due to Cl⁻. Therefore, as long as Cl⁻ concentrations remain less than 100 ppm, then the corrosion rate effects are not significant and have been addressed. Further, as previously discussed, this quantity of Cl⁻ will be neutralized by the buffer present in containment and will also have a negligible impact on pH.

License amendments for AST evaluations, buffer change amendments, and WCAP-16530-NP-A also provide supporting evidence of the bounding Cl⁻ concentrations evaluated in prior testing and the insignificant effect of Cl⁻. When a licensee applies for an AST or buffer change amendment, one of the evaluations required is to assess the post-LOCA containment pool pH changes caused by radiolysis. The pH changes can occur by the radiolytic formation of hydrochloric acid (HCl), the radiolytic conversion of N₂ to HNO₃ (see Section 2.4 of this report), and other phenomena, as described in NUREG/CR-5950, "Iodine Evolution and pH Control" (Ref. 26). The radiolytic breakdown of certain types of electrical cable insulation provides the major source of HCl in a post-LOCA environment; thus, the quantity of HCl generated will be plant specific. A review of several these license amendments showed that the quantity of HCl generated varied from 6.2 ppm to 58.2 ppm, but in all cases reviewed, it was less than the 100-ppm concentration assumed in the ICET tests.

Another potential source of Cl⁻ is from coatings within containment. The PWROG evaluated chloride leaching from protective coatings in WCAP-16530-NP-A (Ref. 3). In that topical report, the PWROG conservatively determined that the maximum expected chloride concentration in the containment pool resulting from the leaching of design-basis-accident (DBA)-qualified epoxy coatings would be less than 8.6 ppm. Hence, qualified coatings will have only a minor contribution to Cl⁻ levels and an insignificant effect on pH. The staff accepted this evaluation in the SE (Ref. 27).

Unqualified protective coatings are judged to leach chlorides at a rate similar to the qualified epoxy coatings and are also not expected to be significant source of Cl⁻ in the containment pool. This expectation is based on the following tests:

1. Alion Science and Technology evaluated alkyd coatings in 2008 (Ref. 28). No detected chloride concentrations were reported. Keeler and Long performed DBA testing of an unqualified epoxy coating for a licensee in 2006. The liquid residue from the autoclave was analyzed after the test was completed. No epoxy resins or chlorides were reported.
2. NSF-61 leaching tests of unqualified epoxy coatings, (Refs. 29, 30) did not report any chlorides.

Additionally, a survey of unqualified coatings by Electric Power Research Institute (EPRI) (Ref. 31) indicates that unqualified coatings are a small percentage of the total quantity of protective coatings in containment. Therefore, even if previously untested coatings release chlorides, they are not expected to result in a significant chloride concentration within the post-LOCA containment pool.

Conclusion

As discussed in Section 1.2 above, the licensees' chemical effects evaluations consider the variability in the RCS pH both with (see Section 2.1 of this report) and without radiolysis effects, as well as its potential impact on chemical precipitate formation. The combined chloride formation from electrical cable insulation breakdown and leaching from protective coatings has been calculated to affect pH by 0.2 pH units or less. Sufficient buffering agent is available in containment pools to counteract the formation of strong acids, such as HCl. ICET and other testing have also demonstrated that the effect of chloride concentrations expected within the post-LOCA containment pool or material corrosion rates is insignificant. Therefore, radiolysis will have little effect on the pH or resultant corrosion products formed in the post-LOCA environment. Hence, no additional research is needed on this issue.

2.3 Hydrolysis

Description and Possible Implications

Nickel oxide (NiO), as well as other oxides, resulting from the corrosion of stainless steel and Alloy 600 metals can become a catalyst for producing H₂ from radiolysis of water. This process occurs more readily at higher water temperatures (i.e., hydrothermal environments). The hydrothermal hydrolysis of various organic/inorganic coating and insulation materials could partially depolymerize polymeric materials, producing materials ranging from small molecules to colloids. The colloids could subsequently aggregate into larger particles and gels. If this were to occur, the aggregated depolymerized materials may be more likely to transport to the sump strainer and affect pump performance or create chemical precipitates with different characteristics than those evaluated.

Discussion

Hydrolysis is a chemical reaction during which one or more water molecules are split into hydrogen and hydroxide ions, which may then go on to participate in further reactions. Hydrothermal hydrolysis occurs in hot water (generally above the boiling point). NiO from corrosion of stainless steel or Alloy 600 series steels can serve as a catalyst for hydrolysis.

Section 5.6.2 and Appendix F of NUREG-1918 (Ref. 2) and Appendix E of NUREG-1861 (Ref. 1) briefly discuss this issue. If NiO (or other oxides) catalyze the production of hydrogen from the radiolysis of water, it could alter the redox potential. However, the stoichiometry of the overall reaction is such that catalysis should also result in the production of oxidizing species that would scavenge excess hydrogen.

In addition, the elevated temperatures necessary for this phenomenon (hydrothermal hydrolysis) to occur exist for only a relatively brief period of time. The temperature of the water in the containment pool is typically expected to be above 200 degrees F for just a few hours (Ref. 23). If NiO acting as a catalyst, does result in a net increase in the production of H₂, it would proceed at a slow rate and occur for just a few hours. Therefore, the production of any excess H₂ is

expected to have a minimal net effect on the organic materials in the containment pool. Subsequently, any increase in the quantity or nature of the post-LOCA debris is therefore expected to be minimal over the mission time required for ECCS operation and is bounded by the large quantity of post-LOCA debris generated by the LOCA and containment spray actuation. The effects of any excess H₂ are also evaluated in Section 1.3.

Conclusion

This issue is concerned that hydrolysis could form additional deleterious chemical precipitates more readily at the high post-LOCA containment pool temperature than have been previously considered in the chemical effects testing and evaluations. Effects due to hydrolysis are more significant at higher temperatures, generally above the boiling point of water. However, the post-LOCA containment pool temperatures are above 200 degrees F for a relatively short period of time. Also, the net production of H₂ from NiO catalysis, should it occur, is also expected to proceed slowly. Therefore, it is unlikely that hydrolysis will significantly increase precipitate concentrations compared to those generated during the post-LOCA ECCS mission time or detrimentally alter the nature of these precipitates. Therefore, additional research on this phenomenon is not warranted.

2.4 Conversion of N₂ to HNO₃

Description and Possible Implications

One panelist was concerned about the effects of nitric acid (HNO₃) formed in the containment pool due to radiolysis of dissolved nitrogen (N₂). This panelist was mostly concerned that the HNO₃ concentration may overwhelm the buffering capacity and cause the containment pool pH to drop precipitously to a range within 1–3. If the containment pool pH were this acidic, the redox potential becomes strongly oxidizing and corrosive and would lead to significant metallic corrosion and leaching of inorganic ions from other materials (e.g., concrete). Most previous NRC and industry-sponsored research has evaluated the chemical effects and their implications associated within the neutral-to-alkaline pH range (i.e., 7–10) that is expected within the buffered post-LOCA containment pool. Therefore, if the containment pool pH were highly acidic (i.e., 1–3), the chemical effects that would occur may differ significantly from those previously evaluated. The implications of these effects on ECCS performance would also be largely unknown.

Discussion

The panelist who raised this concern postulated the following scenario. Radiolysis converts N₂ into HNO₃ within the containment pool. The HNO₃ acts to decrease the pool pH. The HNO₃ concentration increases with dose rate such that the rate of decrease in pH also increases with dose rate. If the radioactive dose rate is sufficiently high in the containment pool, it could overwhelm the buffering capability provided by the lithium hydroxide concentrations within the RCS (Ref. 1). This panelist also conducted an initial scoping evaluation to support the postulated scenario. This evaluation predicted, for dose rates within the reactor pressure vessel (RPV) which are representative of the post-LOCA radiation levels (10⁵–10⁶ rads per hour (rad/h)), the pH after the LOCA could drop to approximately 4.5 after 1 day, 3 after 1 month, and 2 after 1 year. At lower dose rates, longer times are required to reach these pH values (Ref. 1). This panelist further predicted that such a precipitous pH drop would lead to significant corrosion of structural materials (Ref. 1). However, it is important to note that this scoping

evaluation did not consider the effect of the post-LOCA buffering chemicals on the containment pool pH.

As part of the AST analysis (Ref. 19), plant licensees are currently required to account for radiolysis, including that of N_2 , in evaluating the containment pool's post-LOCA buffering system. NUREG/CR-5950 (Ref. 26), also describes a method for calculating pH to account for this effect and other radiolytic phenomena (e.g., hypochlorite formation, as discussed in Section 2.2 of this report). These calculations (Refs. 20, 21, 22) typically demonstrate that the bulk of the buffer mass (e.g., greater than 90 percent) is needed to adjust the pH to greater than 7.0, and only a small amount is necessary to buffer the acids created by radiolysis (including HNO_3).

The AST calculations are not explicitly required to consider the effects on pH from all of the various debris types existing in the post-LOCA containment pool (Appendix B to Ref. 2). However, the AST pH calculations are sufficiently conservative to provide confidence that the buffering system should adequately account for post-LOCA debris effects and variations in the concentration of acids formed by radiolysis as a function of temperature, as discussed in Section 2.1 of this report. In addition, the ICET experiments (Ref. 14) directly evaluated the effect of the insulation and containment debris on the pH of the post-LOCA containment pool. These tests demonstrated that the containment pool pH is not strongly affected by continued dissolution and corrosion of post-LOCA containment debris. The buffering provided by TSP, STB, or NaOH is sufficient to ensure that the pH remains above neutral (i.e., pH greater than 7.0) during the entire 30-day post-LOCA scenario in the presence of representative quantities of post-LOCA debris and radiolytic HCl.

NUREG/CR-6988 (Ref. 11) also evaluated the effect of HNO_3 formed by the radiolysis of atmospheric N_2 on the containment pool pH. As described in this report, the production rate (G value) for HNO_3 in neutral water at a dose rate of 600,000 rad/h is estimated to be approximately 0.007 molecules per 100 electron volts (eV) (Refs. 26, 32). This dose rate is between the dose rate expected within the RPV (i.e., 10^6 rad/h) and the average dose rate within the circulating containment pool water (i.e., approximately 8×10^4 rad/h). This G value, which assumes that HNO_3 is only formed by the radiolysis of N_2 dissolved in water, is low because the solubility of N_2 in water is low. The G value decreases as pH increases. Thus, in 2.8×10^{-2} moles/liter (M) potassium hydroxide (pH ~12.4), nitrite (NO_2^-) rather than nitrate (NO_3^-) is formed (Ref. 33). The G value of 0.007 molecules of HNO_3 per 100 eV is equivalent to 5.80×10^{-7} moles/L-h of HNO_3 for the average containment pool radiation field of 80,000 rad/h. This yield could lead to an HNO_3 concentration of 4.18×10^{-4} moles/L in 30 days. It should be noted that this G value is consistent with the value used in the AST calculations (Refs. 20, 21, 22).

The pH for 4.18×10^{-4} moles HNO_3 /liter solution in unbuffered water is 3.38 and corresponds well with the scoping calculations performed in NUREG-1861. However, NUREG/CR-6988 also considered the effect of the containment pool buffering compound (i.e., either NaOH, TSP, or STB). Based on the industry surveys conducted for the ICET experiments (Ref. 14), the NaOH concentration is approximately 0.2 moles/L, the TSP concentration is approximately 0.01 moles/L, and the STB concentration is approximately 0.025 moles/L. The NaOH reacts with a 1:1 stoichiometric ratio with HNO_3 , while the TSP and STB reacts on a 2:1 ratio. There is approximately a factor of 450 excess NaOH ($0.2/0.00042$), a factor of 45 excess TSP ($0.02/0.00042$), and a factor of 120 excess STB ($0.025/0.00042$) compared with the concentration of HNO_3 . Therefore, the HNO_3 concentration is negligible compared with the concentration of

the containment pool buffering compounds. This result is also consistent with the AST calculations.

In addition, because the HNO₃ is generated over the 30-day, post-LOCA period, most HNO₃ is formed well after the introduction of the buffering compounds which occurs within the first few hours following the LOCA. Because of the excess buffering caused by the NaOH, TSP, or STB additions early in the LOCA and the relatively slow generation of the radiolytic HNO₃, the containment pool pH does not significantly decrease because of the radiolytic generation of HNO₃ (Ref. 11). It should also be noted that exposed submerged concrete provides additional buffering in the form of calcium carbonate. However, the buffering capacity from this source has not been estimated.

Conclusion

The radiolytic conversion of atmospheric nitrogen N₂ into HNO₃ does not create an acidic pH (i.e., ≈ 3) in containment pool water over the approximately 30 days mission time of the ECCS. The plants' buffering systems have been demonstrated to maintain the containment pool pH above 7 when accounting for the effects of radiolysis of N₂. Further evaluation, as summarized in NUREG/CR-6988, also demonstrates that these buffering systems are sufficient to ensure that the effect of HNO₃ on the containment pool pH is negligible. Therefore, no additional research of this phenomenon is required.

2.5 Additional Debris Bed Chemical Reactions

Description and Possible Implications

The concentration of radionuclides, postulated to be hundreds of Curies, available within the sump strainer fiber bed acts as a "resin bed" or chemical reactor potentially altering the local chemical conditions, such as pH. A number of possible radiolytic reactions could occur which may directly alter the chemical byproducts formed. This effect may lead to the formation of different, or a larger quantity of, chemical products than those evaluated, which could have a different impact on head loss than that considered.

Discussion

NUREG-1918, Section 5.2.1, and NUREG/CR-6988, Section 3.8, discuss the phenomenon of radiolytic-induced chemical reactions in the fiber bed. The concern is that, if radionuclides are transported to the containment strainers and collect on the debris bed, then the radiation field may affect chemical reactions currently considered in the testing and chemical effects analyses. These radionuclides would be activation products of metals present in the core and within the primary system that are dislodged during the LOCA. If they do not settle within the containment pool, the concentration of these particulates could add to the debris load of the fiber bed that forms on the sump strainer. The resulting radiation field on the fiber bed could then produce locally higher levels of H₂O₂, which would then affect the pH or increase the corrosion rate and produce more precipitates.

The local pH in the fiber bed is not expected to differ significantly from the bulk pH in the containment pool as a whole because the ECCS flow through the fiber bed on the strainers will effectively flush the fiber bed out, keeping the pH relatively stable. Any acids, such as of H₂O₂, that might be formed locally in the fiber bed would also be swept through the strainers by the ECCS flow. As previously discussed in Sections 2.1 and 2.2 of this report, there is sufficient

excess buffer available to neutralize the acids in the bulk containment pool. As a result, significant local concentrations of acids or pH differences are not expected.

Burns and Moore (Ref. 34) also studied the effect of radiolysis on the pH of water. The radiolysis rates were estimated at beta/gamma ($\beta\gamma$)-irradiation intensities of 1, 5, and 10 Watts per gram (1 watt per gram = 3.6×10^8 roentgen per hour (R/h.)) by computational methods based on known radiolytic species yields and reaction rates. It was determined that the effect of irradiation on water pH is negligible up to approximately 10^6 R/h.

The PIRT panelists also concluded that this phenomenon would not have a significant effect on the already high oxidation state within the containment pool. Because both the oxidation rate and pH will not be affected, the panelists concluded that the corrosion rates or precipitant species of inorganic material would not be substantially different than those observed in the ICET tests (Ref. 14).

The PIRT panelists further noted that this phenomenon may only be significant for organic materials within, or passing through, the fiber bed. The most probable effect would be an increase in radiolytic degradation of insulation or silica precipitation, or both. However, any localized production of strong acids like HNO_3 and HCl would be at concentrations that are too small to overcome the buffers present and, as discussed previously, these acids will be swept from the fiber bed by the ECCS flow. Therefore, radiolysis is expected to have negligible influence on the degradation of insulation debris. The NUREG/CR-6988 analysis also evaluated the effects of the fiber bed radiation field on precipitation of silica. The radiation fields in the fiber bed were estimated to be on the order of 1,000 rad/h. At this exposure rate, any increase in precipitation of silicate corrosion products was judged to be negligible.

The PWROG also evaluated this phenomenon and reached a similar conclusion in responding to RAI #15 (Ref. 15) for WCAP-16530-NP. The PWROG noted that borosilicate materials, chemically similar to fiberglass insulation, are routinely used as a filtration media for high activity particulate, implying that this type of material would not be used if it were susceptible to radiolytic degradation. The PWROG subsequently concluded that the presence of highly oxidizing free radicals is not expected to have a significant effect on the dissolution of inorganic materials such as insulation, since dissolution does not occur by oxidation. The staff accepted the response to the RAI in the SE (Ref. 27).

Conclusion

The effect of any accumulation of radionuclides on the strainer fiber beds, which could alter the chemical species, will be mitigated by the buffering agents present in the containment pool and by the ECCS flow through the strainers. The ECCS flow through the fiber bed will keep the fiber bed flushed out and will tend to equalize the acid concentration and pH throughout containment. Therefore, a significant difference between the local pH and the pH of the bulk containment pool is not expected. The excess capacity of the containment buffering agents will also ensure that the containment pool pH remains stable. Therefore, the accumulation of radionuclides will not be significant enough to alter the chemical reaction byproducts resulting from either radiolytic-induced insulation degradation and silica precipitation or locally higher levels of acidic corrosion. The ICET series of tests documented in NUREG/CR-6914 (Ref. 14) and the chemical models based on WCAP-16530-NP-A will remain largely representative of the post-LOCA environment at the strainers. No additional research is warranted on this topic.

3. Physical, Chemical, and Biological Debris Source Terms

3.1 Crud Release

Description and Possible Implications

A PIRT panelist postulated that iron and nickel corrosion oxides up to 125 microns thick may exist on the interior of the RCS piping, fuel, and components. These oxides could be released by the hydraulic shock of the LOCA event. After release, the reduced Fe and Ni ions can be dissolved in the RCS (aided by radiolysis) and, when combined with air, can form oxides of hematite, maghemite, and magnetite. The crud release can create a localized radiolytic environment on materials caught on the sump screens, which could affect subsequent chemical reactions. The crud particles would also add to the debris concentration within the containment pool.

Discussion

This evaluation addresses three processes which ultimately determine the effects of crud on ECCS performance: crud formation and release, crud transport, and radiolytic effects.

(1) Crud Formation and Release

Crud is the term used to designate the corrosion products that spall from the fuel and reactor component internal surfaces. NUREG-1918, Section 5.3.2, and NUREG/CR-6988, Section 10, evaluate this phenomenon. The NUREG/CR-6988 evaluation focused on the crud existing before the LOCA occurs. As discussed in Section 10.1 of this NUREG, because of the relatively slow rate of corrosion product generation, little additional crud formation is expected during the 30-day, post-LOCA mission time. The crud is principally Fe and Ni oxide particulates, with some Co and Cr ions included. This material consists of finely divided and poorly soluble oxide particulates that have typical densities ranging from 5.2 to 8.9 grams per cubic centimeter (g/cm^3) (324 to 555 pounds per cubic foot (lb/ft^3)). This material loosely adheres to the surface and can be mobilized by thermal or hydraulic shocks, pH changes, and large temperature changes.

Crud thicknesses vary greatly and are plant-specific. Localized crud thicknesses up to 140 microns (5.5 mils) have been observed on fuel surfaces, but the average crud thickness is much lower. From plant surveys documented in NUREG/CR-6988, 4 to 7 kilograms (kg) of Ni are common quantities of crud removed by the purification system at the beginning of a refueling outage. The NUREG evaluation conservatively estimated that approximately 700 to 1,000 kg of crud could potentially be released during a LOCA. This is substantially greater than the amount of crud produced during a plant shutdown. However, as discussed in NUREG/CR-6988, this estimate assumed that all of the wetted RCS surfaces would have a uniform crud thickness of 20 microns and that all of the crud is released during the LOCA. This crud thickness is conservative for internal piping surfaces and steam generator tubes that have lower surface temperatures than the fuel clad. The NUREG went on to state that a more realistic thickness for these lower temperature surfaces would be on the order of 1 to 2 microns, and the lower temperature surfaces areas would be 66 to 75 percent of the total wetted surface area. Thus, using these more realistic thicknesses, the potential quantity of crud would be approximately 400 kg.

The PWROG, in WCAP-16530-NP, also evaluated the effects of crud in its reply to several RAIs related to this topical report (Refs. 15, 16, 17). The evaluation was based on the crud concentrations released during normal operational events, such as startups and shutdowns. The crud released from the RCS after a LOCA is considered to be comparable to that released during a normal shutdown because the chemistry changes (pH and temperature) in the coolant are similar and the hydraulic transient/shock of a LOCA was considered to be similar to a reactor coolant pump (RCP) stop and start. Based on these assumptions, The PWROG initially estimated that, on the order of 189 kg of oxides could be present on the RCS wetted surfaces, but only a fraction would be released. Crud buildup models were developed to estimate the fraction that could be released during a LOCA. The models included the amount released from shear forces and the amount from chemical dissolution. The estimates suggested that between 12 and 25 kg of oxides from Inconel surfaces, with a specific gravity of 3.8 to 6.4 g/cm³, could be released. The upper bound estimate of 25 kg of material was later increased to 36 kg of material to account for corrosion products on the stainless steels. The PWROG compared these results to operating experience from crud releases during refueling outages and from primary-side chemical decontamination projects and concluded that the results were appropriate. The staff believes the pressure and temperature transients associated with a LOCA are likely to be more severe than during a shutdown, such that more crud could be released than estimated in WCAP-16530-NP and observed from operating experience. Therefore, it might be reasonably expected that between 100 and 400 kg of crud could be dislodged and be released into the containment pool as a result of the LOCA. The effect of this amount of crud release is discussed below.

(2) Crud Transport

The assumption in NUREG/CR-6988 that the majority of the crud inventory is released in the LOCA and is available in the containment pool is considered conservative. Some of the compounds formed, such as monoclinic zirconium oxide (ZrO₂) on the fuel clad, have poor solubility in the fluid environment. This NUREG also noted that because of the crud's high particle density, most of the material would settle in quiescent areas and not likely transport under the low flow conditions in the containment pool (assuming the pipe break location is distant from the strainer)

The PWROG evaluation of crud transport is based on the crud concentrations released during normal operational events, such as startups and shutdowns. The PWROG also considered the particle size analysis of the oxides released during refueling shutdowns and concluded that approximately 75 percent of the material is dense particles larger than 10 microns that would not transport readily to the strainers. Based on their estimates that as much as 36 kg of crud could be released, the PWROG concluded that less than 0.1 ft³ of the crud oxide would actually transport to the strainers, and the subsequent increase in head loss would be negligible. If the total amount of crud released was an order of magnitude higher to be consistent with up to 400 kg of crud released as discussed above, there could be up to 1 ft³ transported to the strainers. That amount is still considered negligible when compared to the total quantity of debris.

The staff, in its SE accepted the PWROG's conclusion that the amount of crud released during a LOCA would be insignificant compared to the other more readily transportable debris already included in strainer head loss testing. Thus, the staff concluded that it is acceptable to exclude crud as a head loss testing source term.

(3) Radiolytic Effects

The NRC staff evaluated the potential for crud accumulation on the strainer fiber bed to create a localized radiolytic environment by performing a simplified scoping calculation. RCS crud is rich in nickel from Inconel corrosion, with Ni-63 being one of the higher energy isotopes in the crud film. Assuming that 25 kg of Ni-63 accumulates on the strainers over the 30-day mission time, the resulting incremental dose rate in the fiber bed is approximately 1 rad/h. This minimal increase is considered insignificant when compared to the 1,000 rad/h already evaluated in Section 2.5. As discussed in Section 2.5, the effect on chemical species formation or behavior due to this much greater radionuclide concentration on the strainer fiber beds is not expected to be significant.

Conclusion

A release of primary system corrosion products (i.e., crud) during a LOCA could potentially generate dense oxide particulate material, which could add to the debris source term for particulate debris accumulating on the strainer fiber bed. The PWROG evaluated this additional potential debris in WCAP-16530-NP-A and found that it would add an insignificant amount of potential debris. The NRC staff accepted these findings and thus does not require the additional potential debris to be included as a specific head loss source term. In addition, the staff notes that strainer head loss tests typically incorporate a conservative amount of particulate due to plant debris assumptions as has been discussed elsewhere in this report. Furthermore, scoping calculations determined that the increase in radiation dose on the strainers from any crud that did transport to the strainers would not significantly affect chemical species formation or behavior. Therefore, no additional research is warranted on this issue.

3.2 Jet Impingement

Description and Possible Implications

The two-phase jet, and fine debris within the jet, will impact surfaces and could chip coatings, cause metallic erosion, or ablate materials like concrete. This phenomenon will govern the contributions of these materials in the early post-LOCA time period, before corrosion and leaching become important. Jet impingement could also initiate pitting corrosion, which could accelerate the corrosion of normally passivated materials like stainless steel. Most of the discussion from the peer review panel describes the jet interaction with materials as the primary source for post-LOCA debris. Jet impingement could result in a potential chemical effects debris source term that is greater than currently anticipated.

Discussion

The jet associated with a LOCA will interact with a number of containment materials that may include coatings, fibrous insulation, metals, and concrete. The plant-specific chemical effects evaluations account for interactions between a LOCA jet and containment building materials in various ways that are discussed below. Additionally, it should be noted that instantaneous chemical interactions between the jet and the various plant materials will be of a very short duration and that plant buffering chemicals in the containment spray or containment pool will quickly alter the chemistry for the duration of the ECCS mission time.

Coatings within the containment building are classified into two categories, qualified and unqualified. All qualified coatings within the zone of influence (ZOI) from the break are assumed

to fail as fine particulates. Qualified coatings outside the ZOI are assumed to remain intact. Industry has performed two-phase jet testing to validate the qualified coatings ZOI and has also performed testing on some unqualified coatings. The NRC staff has evaluated the industry tests and has issued guidance concerning coating evaluations (Ref. 35). Unless justified by the licensee, all unqualified coatings within containment are assumed to fail as 10-micron particulate. Therefore, from a coatings perspective, the industry is conservatively evaluating the potential consequences of jet impingement since industry-sponsored tests showed that not all unqualified coatings fail as a particulate.

Industry ZOI values for the various insulation materials and fire barrier materials have been established by jet testing, by selecting a ZOI for a similar tested material, or by using a conservative default ZOI as discussed in the staff's SE (Ref. 36). A detailed technical staff review is performed in the debris generation area for each plant to verify that the ZOI values selected by the licensee are acceptable to the staff. Therefore, the plant-specific evaluations account for the LOCA jet interactions with insulating materials and fire barrier materials.

The plant-specific calculation of debris materials does not consider metallic erosion or ablation of concrete. However, the quantity of metal eroded during the short-term blowdown following a large-break LOCA is expected to be insignificant as compared to the debris source term from the subsequent interactions of metallic components and the post-LOCA environment during the ECCS mission time following a LOCA. Similarly, the amount of concrete that may be ablated by the jet is expected to be insignificant compared to the source term contributions from latent debris (i.e., concrete dust) and leaching from submerged concrete resulting from long-term (i.e., 30 day) interaction with the post-LOCA containment pool.

Determination of the source term also does not consider the possibility that jet impingement could act to initiate pitting corrosion of some metals, such as stainless steel. Jet interaction is of such short duration that it is unlikely that significant pitting would initiate during the RCS blowdown phase. Even if pitting were to initiate, most of the metallic surfaces in the containment building are above the post-LOCA containment pool height and remain unsubmerged during the post-LOCA period. Pitting is also a localized corrosion mechanism that typically results in relatively small areas of attack on a metallic surface. Accumulation of corrosion products (i.e., oxides) within the pit restricts the amount of metallic ion exchanged with the bulk fluid. Considering the large volume of water contained in a post-LOCA pool, and the limited amount of extra dissolved metallic ions that could be added to the containment pool by a localized pitting mechanism, any pitting initiated by jet impingement is likely to be insignificant compared to the total chemical species developed from debris within the containment pool and submerged materials during the ECCS mission time.

Conclusion

The two-phase jet, and fine debris within the jet, will impact surfaces and create debris that could affect ECCS and CSS performance. Plant-specific evaluations account for jet interactions with coatings and other containment materials, such as insulation. Since the NRC staff performs detailed technical reviews of plant-specific debris generation evaluations, no additional work is needed in this area. The NRC staff also concludes that no additional work is needed to address metallic erosion, concrete ablation, or metallic pitting induced by jet interaction since the amount of metallic species released by these mechanisms, if they were to occur, is judged to be insignificant compared to the overall calculated plant-specific debris load. Therefore, no additional research is needed to address this issue.

3.3 Debris Mix Particle/Fiber Ratio

Description and Possible Implications

Breaks in different locations will create different debris characteristics with respect to the total mass of debris, debris constituents, and the ratio of particulates to fiber. Depending on the specific break location, significantly different types and quantities of debris (e.g., Cal-Sil and fiberglass insulations) can alter the type and quantity of chemical effects. Ultimately, the debris bed characteristics determine the chemical product capture efficiency and the total pressure drop across the sump screen strainer.

Discussion

Although it is not practical to test every possible combination of debris generated by different pipe break locations, NRC staff guidance (Ref. 36) directs the licensee to analyze and demonstrate that the sump strainers can accommodate the break location and size that produces the maximum amount of head loss. Therefore, plant-specific evaluations consider breaks at many locations to determine the amounts and types of debris that would produce the maximum head loss. Thus, plant-specific test cases include a strainer debris bed with variable amounts of fiber saturated with particulate (i.e., a “thin bed”) and a bed with a maximum amount of fiber and particulate.

With respect to chemical effects evaluations, licensees that use the base model described in WCAP-16530-NP-A (Ref. 3) to determine the amount of chemical precipitate for head loss testing typically find that the breaks that generate the most nonchemical debris also produce the most chemical precipitate. The PWROG sponsored additional testing to evaluate plant-specific refinements to the base chemical model which are discussed in WCAP-16785-NP (Ref. 37). The NRC’s chemical effects review guidance (Ref. 13) comments on these additional inputs. Since the total chemical precipitate is sensitive to the pipe break location for some of these refinements, the NRC staff expects licensees to perform tests based on the conditions that produce the greatest head loss, including chemical effects. The following excerpt from the chemical effects review guidance provides the NRC staff’s position:

Licensees should discuss why the debris from the break location selected for plant-specific head loss testing with chemical precipitate yields the maximum head loss. For example, plant X has break location 1 that would produce maximum head loss *without consideration of chemical effects*. However, break location 2, with chemical effects considered, produces greater head loss than break location 1. Therefore, the debris for head loss testing with chemical effects should be based on break location 2.

Since a LOCA could generate many different combinations of debris depending on the break location, the plant-specific head loss test objective is to demonstrate that adequate net positive suction head (NPSH) margin exists for the breaks that produce the most challenging head loss. NRC staff guidance for strainer head loss testing (Ref. 38) also explains the staff’s expectation that the licensee will conduct its debris addition sequence in a way that produces conservative head loss results.

Conclusion

Although there are many combinations of debris that could be produced based on the plant-specific conditions and the pipe break location, licensees are required to perform testing for those conditions that produce the greatest amount of head loss. Plant-specific tests identify whether a thin debris bed or maximum fiber scenarios produce the greater head loss. The NRC technical staff has performed detailed reviews of debris generation, debris transport, head loss, and chemical effects to assess whether each licensee's testing assumed break locations that produce the greatest head loss. Therefore, no additional research is needed to address potential variations in plant-specific LOCA debris quantities and types.

3.4 Effects of Dissolved Silica from Reactor Coolant System and Refueling Water Storage Tank

Description and Possible Implications

Dissolved silica is present in the water storage systems and the RCS during normal operation. This silica can react with other chemical constituents (most prominently magnesium, calcium, and aluminum) that form as a result of material dissolution or corrosion, or both, within the containment pool after the LOCA occurs. This reaction may result in a greater concentration of the chemical precipitates than would otherwise exist. The reaction may also alter the nature of the chemical precipitates by creating amorphous materials or gels or precipitates with retrograde solubility (i.e., they become more insoluble as temperature increases). The creation of additional chemical precipitates, amorphous materials, and retrograde soluble species could degrade ECCS performance by increasing head loss at the sump strainer or decreasing in the heat transfer rate from the reactor fuel if significant quantities of silica-containing precipitates are formed.

Discussion

The ICET (Ref. 14) testing included many materials that leach silica under conditions that are representative of the post-LOCA environment. Prominent materials that leached silica in the ICET tests included fiberglass insulation (specifically NUKON®), Cal-Sil, concrete, and a latent debris mixture consisting of concrete particulate, sand, and clay. The silica concentrations measured during the ICET series were approximately 10 ppm (2×10^{-4} M) for tests 1 and 5, 100 ppm (2×10^{-3} M) for tests 2 and 3, and 200 ppm (4×10^{-3} M) for test 4. It should be noted that initial analyses using thermodynamic equilibrium models predicted much larger silica concentrations for ICET tests 1 and 5. In addition, the Westinghouse chemical effects testing (Ref. 3) considered other classes of silica-containing insulation materials that would be expected to leach silica in the post-LOCA environment, including aluminum silicates, Cal-Sil, E-glass, Interam E Class, amorphous silica, and mineral wool. Some coating systems, especially alkyds, also contain silica that may leach into the containment pool.

The impact of dissolved silica from these various sources has been evaluated. Testing conducted at ANL examined the head loss associated with aluminum precipitates that contained silica, such as sodium aluminosilicate (Ref. 7), and demonstrated that substantial head loss can occur under certain conditions. Dissolved silicon can also have a beneficial head loss effect as demonstrated by testing conducted by Alion (Ref. 39). Alion conducted head loss tests with 10 ppm aluminum both with and without 60 ppm of dissolved silicon. The tests containing higher silicon concentrations had less head loss. WCAP-16793-NP, Revision 1 (Ref. 5) also considers the effect of sodium aluminosilicate on the heat transfer rate from the reactor fuel. As stated in

WCAP-16793-NP, “the most insulating material that could deposit from post-LOCA coolant impurities would be sodium aluminum silicate.”

However, the assessment of the implications associated with silica and silica-containing precipitates did not consider the contribution of preexisting silica within the RCS and RWST. One of the PIRT panelists estimated that the concentration of silica in the RWST may be as high as 3 ppm, while the silica concentration in the RCS will be in the range of 0.3 to 3.0 ppm (Ref. 1). Therefore, as much as 3 ppm of dissolved silica may exist within the containment water after the RWST has drained. As demonstrated in NUREG/CR-6988, silica in combination with Mg, Ca, and Al can form materials with retrograde solubility. The dissolved silica could also react with other species leading to the formation of secondary precipitates. Therefore, the total silica concentration within the containment pool can affect the total mass of chemical precipitate that forms.

Because NRC and industry-sponsored testing has evaluated the effect of silica, it is only necessary to consider effects from the additional silica (approximately 3 ppm) contained within the RCS and RWST. The chemical model in WCAP-16530-NP-A (Ref. 3) can be used to assess plant-specific effects resulting from silica, including the initial RCS and RWST contribution. The WCAP chemical model was determined from leaching tests on materials that were grouped to represent common classes of post-LOCA debris material (e.g., fiberglass insulation, mineral wool). McMurry and He (Ref. 6) evaluated the Westinghouse leaching tests and the model. This evaluation considered both materials similar to those used in the Westinghouse study and additional materials within several classes. The evaluation found that the Westinghouse tests leached significantly more silica (i.e., greater than 3 ppm in every case) for the same materials or for other materials grouped within the same class (Ref. 6). Additionally, the dissolution is conservatively assumed to occur at the onset of the LOCA instead of the actual situation where leaching will occur according to the dissolution rate associated with the various insulation materials. Therefore, the WCAP-16530-NP-A chemical model conservatively models the silica concentrations that leach into the post-LOCA containment pool from debris sources and incorporates a margin of at least 3 ppm to account for silica from RCS and RWST contributions. Additionally, plants that use this model have already addressed effects related to the initial silica concentration in the RCS and RWST.

It is also informative to consider an estimated concentration of silica that may be present in the containment pool. For fiberglass (or other similar insulations), it can be conservatively assumed that at least 50% of its mass is silicon. It is further assumed (based on strainer bypass testing which demonstrated that 1 ft³ of fiber per 1000 ft² of strainer screen area bypasses the screen) that 10% of the insulation bypasses the strainer and that complete dissolution of the insulation due to radiolysis occurs. Then, the amount of silicon per pound of insulation can be determined as follows:

$$Si = \frac{(454 \times 10^3 \text{ g})(0.10)(0.50) \left(\frac{60 \text{ amu SiO}_2}{28 \text{ amu Si}} \right)}{(5 \times 10^5 \text{ gal}) \left(3.785 \frac{\text{L}}{\text{gal}} \right)} = 0.0257 \frac{\text{ppm}}{\text{lb insulation}}$$

where the containment pool volume of 5x10⁵ gallons represents the median of all of the maximum containment pool volumes reported for plants in WCAP-16530-NP-A (Ref. 3). Therefore, approximately 0.03 ppm of Si per pound of insulation is a reasonable estimate of the dissolved Si from insulation in the containment pool. If a plant has at least 1000 pounds of fiberglass-type or Cal-Sil insulation in containment, the additional 3 ppm from the RCS and

RWST inventories will be less than 10% of the total dissolved silica inventory from the other insulation and will not be significant.

Conversely, it can be assumed that all of the silica from the RCS and RWST inventories forms sodium aluminum silicate ($\text{AlNa}_{12}\text{SiO}_5$). This precipitate is assumed because it is particularly detrimental in terms of both head loss and insulation properties (Ref. 10). The molecular weight of $\text{AlNa}_{12}\text{SiO}_5$ is 411 g/mol. If a containment volume of 5×10^5 gallons is again assumed, the mass of $\text{AlNa}_{12}\text{SiO}_5$ that can form from 3 ppm of silica is

$$\text{AlNa}_{12}\text{SiO}_5 = \frac{(0.003 \text{ g/L})(5 \times 10^5 \text{ gal}) \left(3.785 \frac{\text{L}}{\text{gal}} \right) \left(\frac{411 \text{ amu AlNa}_{12}\text{SiO}_5}{28 \text{ amu Si}} \right)}{454 \frac{\text{g}}{\text{lb}}} = 185 \text{ lbs}$$

Therefore, 185 lbs is a reasonable upper bound for the maximum amount of precipitate that can result from 3 ppm of RCS and RWST silica. If the total debris loading is greater than approximately 1,800 lbs, then this additional contribution is also insignificant.

In summary, the 3 ppm concentration of silica from the RCS and RWST inventories is not expected to be a significant consideration for plants that (1) apply the WCAP-16530-NP-A chemical model, (2) account for more than 1000 lbs of fiberglass-type or Cal-Sil-type insulation in their ECCS design, or (3) account for more than 1,800 lbs of total debris (i.e., physical and chemical) in their ECCS design.

Staff conducted a review of the GL 2004-02 supplemental responses to determine how many plants satisfy any of three criteria above such that additional silica contribution from the RCS and RWST are not a significant consideration. This review concluded that most plants use the WCAP-16530-NP-A model and hence meet criterion (1) above. The remaining units were evaluated against the other two criteria above. All of these plants satisfy at least one of these criteria as summarized below:

1. Two units accounted for approximately 1500 pounds of fiberglass insulation debris and 1000 pounds of coating debris, for a total of 2500 pounds of total debris. Therefore, these units satisfy both criteria (2) and (3).
2. Two units accounted for approximately 1200 pounds of Cal-Sil/asbestos and temp mat insulation. These insulation materials contain silica. These units also considered approximately 1000 pounds of coating debris so that the total debris is approximately 2200 pounds. Therefore, these units satisfy both criteria (2) and (3).
3. Two units accounted for approximately 3000 pounds of NUKON and Claremont fiberglass insulation debris which are well above the requirements in criteria (2) and (3). Therefore, these units also satisfy both criteria (2) and (3).
4. One unit expects only a small quantity (i.e., less than 100 lbs) of debris from fiberglass insulation. However, this unit accounted for approximately 790 pounds of Cal-Sil based mineral wool insulation debris and more than 1100 pounds of latent and coating debris. The total debris loading considered in the analysis was therefore in excess of 2000 pounds. Therefore, this unit satisfies criterion (3).

Therefore, staff expects that the analyses used within the GL 2004-02 supplemental responses are sufficiently conservative and robust to address the possible effects due to additional silica inventories within the RCS and RWST that were not explicitly addressed within the plant-specific evaluations.

Conclusion

The water from the RWST and RCS contains less than 3 ppm of silica which will be present within the containment pool during the beginning of the post-LOCA scenario, before the onset of ECCS recirculation. The NRC-sponsored and industry-sponsored research has considered the silica contributions from post-LOCA debris and other materials within the containment pool, such as fiberglass and Cal-Sil insulation, mineral wool, E-glass, concrete, and latent debris. Additionally, these studies have generally considered the effect of silica on containment screen clogging and heat transfer from the reactor fuel. Some tests have even indicated that additional dissolved silica has a beneficial effect with respect to head loss. Therefore, no additional research is necessary to understand the effect of silica on ECCS performance due to debris within the post-LOCA containment environment.

The additional silica concentration from the RCS and RWST is not expected to be a significant consideration for plants that (1) apply the WCAP-16530 chemical model, (2) account for more than 1000 lbs of fiberglass-type or Cal-Sil-type insulation in their ECCS design, or (3) account for more than 1,800 lbs of total debris (i.e., physical and chemical) in their ECCS design. Only seven units did not follow the WCAP 16530-NP chemical model. Staff performed a detailed review of the licensees' chemical effects evaluations in the GL 2004-02 supplemental responses for these seven plants. It was determined that all of these plants accounted for either a sufficient quantity of silica or a sufficient quantity of total debris loading from other sources in their responses to meet at least one of the above criteria. Therefore, staff expects that the analyses conducted by all plants for the GL 2004-02 supplemental responses are sufficiently conservative and robust to address the possible effects due to additional silica inventories within the RCS and RWST that were not explicitly addressed within the plant-specific evaluations. Therefore, no further generic or plant-specific evaluations are required to address this issue.

3.5 Containment Spray Transport

Description and Possible Implications

Following a LOCA, the containment spray will tend to wash latent debris, corrosion products, insulation materials, and coating debris into the containment pool. This changes the containment debris sources (types, amounts, compositions) and chemical species reaching the containment pool environment which could affect the sump strainer debris bed and the formation of chemical precipitates.

Discussion

With respect to nonchemical debris, the NRC staff's guidance contained in the SE to Nuclear Energy Institute (NEI) 04-07, Revision 0, "PWR Sump Performance Evaluation Methodology" (Ref. 40), is intended to conservatively predict debris transport to the strainers. Therefore, this guidance typically tends to over predict the transport of debris to the containment pool. For example, in the baseline guidance summarized in Table 3-4 of the SE (Ref. 36), the initial blowdown distribution of debris between upper and lower containment is conservatively biased to lower containment, despite the fact that most of the containment free volume resides in the

upper containment. The baseline guidance also assumes 100-percent wash down for any fiber fines and small pieces of debris which are assumed to be blown initially from the upper containment. Appendix VI to the SE (Ref. 36) permits more realistic methods for assessing debris transport and retention within containment, although methods in Appendix VI were still based on a conservative application of experimental debris transport results. For example, experimental results for debris capture on gratings and wetted surfaces can be credited in this analysis rather than assuming 100% washdown of debris into the containment pool. However, the majority of licensees followed baseline SE positions related to debris transport, which result in a conservative amount of debris reaching the containment pool. Only a minority of licensees did not follow the SE guidance for some or all types of debris and these licensees typically attempted to credit debris retention on gratings for some fraction of debris that was larger than or of approximately the same size as the openings of plant gratings. Credit for retention of fine debris that is exposed to containment sprays is not accepted by the staff. The staff is cognizant of the issues involved with debris retention in upper containment and is performing a detailed technical evaluation of plants for which the wash down assumptions deviate from SE recommendations on a case-by-case basis to ensure that their assumptions are prototypical or conservative. Therefore, staff will have reasonable assurance that the plant-specific evaluations performed by licensees appropriately consider the transport of nonchemical debris by the containment spray.

Plant-specific evaluations also require transport of all debris by containment spray of species that may affect chemical precipitation. These evaluations consider containment spray transport of chemical species in several ways. First, plant-specific debris, including debris transported to the containment pool by spray as discussed above, is added as an input to the chemical model contained in WCAP-16530-NP-A. In addition, dissolved aluminum terms representing both submerged aluminum and nonsubmerged aluminum subject to spray are considered. This is important because tests have shown aluminum contributes the greatest mass to post-LOCA chemical precipitates. Finally, licensees typically introduce margin into the chemical effects evaluation which conservatively addresses transport by assuming some or all of the following:

- Upper bound estimates of the amount of aluminum in containment.
- Containment spray times are greater than expected following a LOCA, with spray pH values biased high to promote greater corrosion of aluminum.
- No corrosion products are retained on the aluminum.
- All dissolved aluminum forms a precipitate.

Therefore, plant-specific evaluations appropriately consider transport of physical debris and chemical species that ultimately result in the consideration of conservative concentrations of chemical precipitates within the containment pool.

Conclusion

The plant-specific evaluations performed by licensees adequately consider wash down of plant debris by containment spray actuation following a LOCA and the potential impacts on chemical effects. Most licensees follow guidance that conservatively predicts the amount of physical debris that reaches the containment pool. Plant-specific evaluations also require transport of all physical debris by containment spray of species that may affect chemical precipitation. In

addition, the chemical source term is conservative and includes contributions from non-submerged aluminum that corrodes and is transported by containment spray. Plant-specific evaluations that credit lesser amounts of physical debris or chemical species are reviewed by staff to ensure that their assumptions and approach are representative or conservative. Therefore, no additional research related to this issue is necessary.

3.6 Initial Debris Dissolution

Description and Possible Implications

Typical debris generated by the LOCA (within the first 20 minutes) includes Cal-Sil insulation, cement dust, organic fiberglass binders, and protective coatings. Initial debris dissolution could indicate potential important contributors to the chemical containment pool environment. It is possible that the dissolved, ionic species could react and precipitate to form new, solid phases that were not originally in the containment pool.

Discussion

Sections 3.2 and 3.3 of this report also address the initial debris generation and debris mix. Staff agrees that different quantities of material (e.g., Cal-Sil and fiberglass insulation) can fundamentally alter the chemical effects (Section 3.3). Debris dissolution and metallic corrosion begin just after the LOCA as materials are impacted by the jet (Section 3.2) and then immersed within the containment pool. This is the principal scenario for creating the ionic species within the containment pool. The dissolved, ionic species may subsequently react and precipitate to form new solid species in the containment pool. Therefore, corrosion or dissolution, or both, as well as subsequent reactions, will determine both the total inventory and the type of solid material in the containment pool resulting from chemical effects.

The ICET program has evaluated the importance and effects associated with metallic corrosion and debris dissolution for representative long-term (i.e., after 1–2 days) post-LOCA environments (Ref. 14). In addition, the PWROG has conducted testing to quantify corrosion and dissolution rates of debris in support of WCAP-16530-NP-A, which most licensees use to evaluate chemical effects. Tests were performed with pH values of 4.1, 8, and 12 to bound the pH values expected in the post-accident containment pool. Test temperatures of 190 degrees F and 265 degrees F were used to evaluate leaching of containment material to simulate the high initial temperature in containment. The NRC staff reviewed the test methods and results from the WCAP-16530-NP leaching tests and determined that the values selected for pH and temperature were acceptable, as documented in the staff SE (Ref. 27). In addition, the NRC sponsored supplementary leaching studies at the Southwest Research Institute (Ref. 6). This evaluation considered both materials similar to those used in the Westinghouse study and additional materials within several classes. For leaching tests with comparable times, temperatures, and pH, the concentration of elements in the Southwest tests were similar to or less than the concentration from the Westinghouse tests. Therefore, the WCAP-16530-NP-A chemical model, developed from the results of the bench testing, conservatively models the initial debris dissolution in the post-LOCA containment pool.

Plants not using the WCAP-16530-NP-A spreadsheet conduct plant-specific testing to evaluate chemical effects. Plant-specific materials are tested to determine the types and concentrations of the chemical species that form. These tests are conducted in borated water which is buffered to the appropriate pH. The water temperature also appropriately represents the sump temperature during the ECCS mission time. The effects of these chemical species are

subsequently evaluated to determine the associated sump strainer head loss and/or downstream effects.

Conclusion

As discussed above, initial debris dissolution is expected to be an important factor in the formation of solid species within the post-LOCA environment. Both the NRC and industry testing have addressed the effect of debris dissolution to conservatively determine dissolution and corrosion rates for debris types. The results of the testing were used to develop the WCAP-16530-NP-A chemical model which most licensees use to evaluate chemical effects on ECCS sump performance. Plants not using the WCAP-16530-NP-A spreadsheet to determine their chemical source term have performed plant specific tests in borated water buffered to the appropriate pH. Therefore, the implications associated with initial debris dissolution have been addressed and additional research to gain a better knowledge of realistic initial debris dissolution is not required. In addition, the NRC staff performs a detailed review of each licensee's overall chemical effects evaluation to verify that debris dissolution has been addressed. Therefore, no additional research related to this issue is necessary.

3.7 Submerged Source Terms: Lead Shielding

Description and Possible Implications

Acetates present in the containment pool will corrode any submerged lead existing in containment, which could lead to formation of lead carbonate particulate or dissolved lead within the containment pool. Lead blanketing or lead wool is used to shield radiation hot spots during refueling outages and may remain in the containment building during the fuel cycle. In addition, several plants may still use small quantities of lead wool for insulation.

Lead carbonate contributions would provide additional particulate loading within the containment pool that could contribute to head loss at the sump strainer screen. Dissolved lead could also lead to cracking of submerged stainless steel structural components within containment. Neither the testing conducted to date nor do the licensee evaluations of ECCS performance consider these contributions. These omissions are potentially non-conservative if significant quantities of lead carbonate or dissolved lead are formed.

Discussion

Lead blanketing or lead wool is used to shield radiation hot spots during containment outage operations. One panelist estimated that several hundred pounds of lead may be used in these shielding blankets. Although the blankets are usually covered with a protective plastic coating, at least one PIRT panelist expects that the coating will be penetrated in many places as a result of normal operational wear and tear. However, most of these blankets should be removed after an outage. The only other likely source of significant quantities of lead in containment is from lead wool insulation, which may still exist in a small number of plants.

As indicated, testing used to address chemical effects within the post-LOCA environments has not studied the effects of lead. There were no lead sources evaluated within the ICET testing (Ref. 14) or the Westinghouse testing, which considered both the materials used in the ICET testing and additional containment materials (Ref. 3). Further, licensees have not been requested (Refs. 36, 40) to assess the effects of lead corrosion in their evaluations to demonstrate the acceptability of their ECCS.

Two possible effects of lead have been identified. The first effect is that dissolved lead could lead to cracking of submerged stainless steel structural components within containment. A bounding calculation of the concentration of dissolved lead within the containment pool can be determined by estimating a bounding concentration of acetate and then assuming that the acetate forms a complex with only lead, and no other metallic species, to keep the lead dissolved. Acetate will be present in containment from the addition of zinc acetate to reduce crud transport in the reactor coolant system during the operating cycle. However, only 5 to 10 ppb of zinc is added as zinc acetate which results in a molar concentration of acetate of 6.2×10^{-8} M after assuming representative volumes for the reactor coolant system (10^5 gallons) and the post-LOCA containment pool (5×10^5 gallons).

This concentration of acetate is insignificant compared to the concentration derived from other organic materials that may be present in containment. If it is conservatively assumed that 250 gallons of oil is released due to the failure of the RCP lube oil systems (i.e., the jet from the pipe break or other debris created during LOCA damages RCP lube oil systems such that all the oil leaks into the containment pool), the high radiation field in the reactor will break down the organic material that passes through the core into formic and acetic acid¹ (Refs. 41, 42). If 10% of the organics are assumed to convert to acetic acid, then approximately 6.8×10^{-4} M, or approximately 40 ppm, of acetic acid will form. Because lead complexes with acetate in a 1:2 ratio, the amount of lead that could be dissolved by this acetic acid concentration is 3.4×10^{-4} M or approximately 70 ppm.

It is important to note that 70 ppm is a bounding calculation assuming that there is a relatively large concentration of acetate, and that all the acetate complexes with lead. Other metal ions such as calcium, aluminum, iron (III), and nickel will also complex with acetate and reduce the concentration available to complex with lead. The amount of dissolved lead in containment is also expected to be limited by the protective coating applied to the lead shielding sheets. While this coating may be damaged in certain areas, it will effectively cover most of the exposed lead surface. Finally, sulfates, phosphates, carbonates, oxides, and sulfide present in containment would cause surface passivation such that the lead remains insoluble at the neutral pH values within the containment pool (Ref. 43). These corrosion layer compounds are much more insoluble than acetate has complexing capability. Therefore, under realistic post-LOCA containment conditions, actual lead dissolution is expected to be low (on the order of parts per billion to a few ppm) (Ref. 44).

This relatively low lead concentration will not induce cracking in stainless steel components within the 30-day mission time typically assumed for ECCS operability requirements. Timeframes much longer than 30 days would be required to generate cracking that would challenge the structural integrity of such components. This issue is also minimized by the low expected lead concentration and the neutral or alkaline (i.e., non acidic) pH of the post-LOCA containment pool. Therefore, lead-induced cracking of stainless steel is not expected to degrade ECCS performance such that the ability to provide long-term cooling is challenged, or accelerate the corrosion of other materials within the containment pool over the post-LOCA time period such that ECCS performance is affected.

¹ The formation of acetate and formate ions in radiation fields comes from PWR experience with organic amines in the secondary plant. The organic amines such as methoxypropylamine and ethanolamine undergo radiolytic decomposition in the steam generators yielding measureable quantities of acetate and formate ions.

The second possible effect of lead is that lead carbonate solids precipitate and provide additional particulate loading within the containment pool that could contribute to head loss at the strainer screen. However, the most likely place for lead carbonate to form is *in situ* on the established corrosion layer on the lead metal. That would prevent transport of the carbonate to the sump strainer. Even if the carbonate did form within the containment pool and not on the corrosion layer, the concentration of dissolved lead, as previously discussed, is expected to be low. The PIRT panelists largely agreed that as long as the dissolved lead concentration is low, lead carbonate precipitates will not be a significant contributor to the debris source term.

Conclusion

It is unlikely that lead will significantly affect either the post-LOCA containment chemistry or ECCS performance. Although some submerged lead may be present in containment, most lead sources are removed after an outage and lead shields contain a protective coating that is expected to be largely intact following a LOCA. More importantly, significant acetate sources are not expected within containment to accelerate lead corrosion. In fact, several species (i.e., silica) expected in the post-LOCA containment pool can actually hinder lead corrosion.

Because lead corrosion is not expected to be significant, the precipitation of lead carbonate solids is also not expected to appreciably contribute to the debris loading within the containment pool. Additionally, the low concentrations of dissolved lead should not induce cracking of stainless steels or other submerged containment metals, especially over the relatively short mission time required for ECCS operability. Therefore, no research is necessary to address the unlikely event that both lead and acetate are present in sufficient quantities within the post-LOCA environment.

3.8 Submerged Source Terms: Copper

Description and Possible Implications

Copper present in containment can accelerate or inhibit corrosion of other metals. One way in which Cu can alter the corrosion rate of other materials is by forming a galvanic couple. Galvanic effects can accelerate corrosion of less noble material while inhibiting corrosion of more noble materials. Dissolved copper can also enhance the rate of corrosion of other metals within an oxygenated environment. Different corrosion rates can impact the amount of corrosion products formed and therefore could have different effects on ECCS sump head loss.

Discussion

A galvanic couple is created when a structural material and Cu are in electrical contact and submerged within an ionic solution. A less noble metal than Cu can then preferentially corrode through anodic dissolution. NUREG/CR-6988 (Ref. 11) evaluated this issue and found it to be insignificant because of the limited surface area that may be subject to galvanic effects. The most likely galvanic couple occurs between the copper grounding straps used for large equipment within containment and the connected steel structures that become submerged in coolant waters under post-LOCA conditions. Because the grounding straps are cathodic with respect to carbon steel, the carbon steel will form corrosion products in a local region around the strap connection points. To evaluate the effects of galvanic corrosion, NUREG/CR-6988 conservatively assumed an affected region of 1 square meter on each carbon steel surface surrounding the anchoring point of the grounding strap and a total of 100 grounding straps, resulting in an affected area of 100 square meters. Assuming a corrosion rate of 100 mils per

year, the quantity of corroded steel was estimated to be less than 60 liters (Ref. 11). This estimated quantity is judged to be insignificant compared to other chemical byproducts from corrosion (e.g., from metallic alloys) or dissolution (e.g., from insulation debris).

Cu can inhibit corrosion of other metals by depositing onto the surface of other materials to create a passivation layer. Copper ion deposition was observed on Al coupons in ICET tests 2 and 3, and the measured Al solution concentration was below the detection limits in these tests. While this effect would reduce the chemical concentration of species like aluminum, it is currently not credited within the plant-specific evaluations required by GL2004-02.

Dissolved copper can also enhance the rate of corrosion by forming local galvanic cells on the metal surface. For the prominent containment materials, the materials ranked by decreasing nobility are as follows: Cu, Fe, Zn, and Al. Thus, Al is more likely to corrode than other materials if a galvanic coupling is present. Therefore, this effect would potentially be most significant for aluminum.

Based on the Westinghouse response to RAI #12 to WCAP-16530-NP (Ref. 15), this mechanism may be most significant later in the post-accident phase when minor amounts of copper may be present and rapid aluminum corrosion caused by extremes in temperature and pH has ceased. Under these conditions, aluminum would be less susceptible to general corrosion because of the more neutral pH within the containment pool, the lower temperature of the pool, and potential inhibition resulting from silicates from silica-containing debris. The staff accepted the response to the RAI in the SE (Ref. 27). In addition, the WCAP-16530-NP-A chemical model assumes a conservative aluminum corrosion rate over the entire 30-day mission time and that because acceleration effects are most important once this rate slows down, this conservative assumptions bounds any secondary rate effects attributable to Cu.

Furthermore, even if Cu did enhance the Al corrosion rate, compared to the WCAP model, the net effect is not expected to be significant because (1) this galvanic effect would not apply for corrosion of non-submerged aluminum which accounts for most of Al in containment, and (2) other conservative assumptions in the chemical model (Ref. 3) account for any secondary corrosion effect of Al due to Cu such as no credit for inhibition of aluminum corrosion by silicates and phosphates.

Conclusion

Copper present in containment can accelerate or inhibit corrosion of other metals because of galvanic effects. The surface areas affected by galvanic effects are limited, leading to a limited corrosion product contribution from this process to sump strainer clogging. Corrosion inhibition through Cu ion deposition is beneficial, although it is currently not credited in the evaluations of ECCS performance. Although dissolved copper can enhance the rate of corrosion of other metals, the impact is considered insignificant due to conservative assumptions in the chemical model and the potential effect of corrosion inhibition due to Cu. The potential differences in corrosion rates, mechanisms, and surface areas associated with the presence of Cu would have little impact on the sump strainer loading. Therefore, no additional research related to this issue is necessary.

3.9 Concrete Material Aging

Description and Possible Implications

The PIRT panelists raised questions about the effect of aging on the leaching process for nonmetallic materials such as concrete. Neither the exposed concrete faces nor concrete dust in the containment building is likely to be fresh. After 30 years of exposure to the atmosphere, a substantial fraction of both the exposed calcium silicate hydrate (C-S-H) gel and the portlandite ($\text{Ca}(\text{OH})_2$) constituents of the concrete would have been carbonated. Carbonation or other aging processes of concrete could affect the leaching rates and dissolved species as compared to relatively fresh concrete samples used in the ICET experiments and other research programs.

Discussion

Chapter 4 of NUREG/CR-6988 (Ref. 11) evaluated concrete and aging chemistry. This NUREG reviewed the technical and engineering literature to investigate the effects of carbonation. The literature shows that the $\text{Ca}(\text{OH})_2$ present in Portland cement converts to CaCO_3 to force the ensuing decomposition of C-S-H gel (Ref. 11). The outer carbonated layer of concrete which contains CaCO_3 , protects the inner noncarbonated concrete from leaching. The net effect is that carbonation very quickly forces the concrete surface chemistry to be controlled by CaCO_3 .

Based on the carbonation rates found in the technical literature, NUREG/CR-6988 evaluated the predicted effects of using 30 to 40-year-old concrete coupons in the ICET experiments instead of the 3-to-11-month-old coupons actually used to determine whether the ICET results would have been significantly altered. The calcium concentrations observed in the ICET tests were a factor of ~10 lower than the calcium concentrations expected if dissolution resulted solely from $\text{Ca}(\text{OH})_2$ as would be the case for unaged concrete.

Instead, the Ca concentrations observed in both ICET test 1 and ICET 5 were within a factor of ~2 to 4 of the concentration expected if dissolution resulted solely from CaCO_3 as would be expected for 30 to 40-year aged coupons. This relatively small difference in the dissolved Ca concentrations between actual and fully-aged samples is not expected to significantly affect solution pH or alter the types and concentrations of chemical species or precipitates observed in the ICET experiments. Therefore, the anticipated net impact of using the relatively fresh coupons in the ICET experiments, instead of using coupons that were 30 to 40 years old (and therefore more carbonated), is minimal.

Conclusion

The NUREG/CR-6988 evaluation concluded that carbonation or aging of the concrete samples used in the ICET series to more represent current plant conditions would have a negligible effect on calcium availability and concentration, as well as on solution pH measured in these tests. Therefore, the effect of using aged concrete coupons would not have significantly altered the types and concentrations of chemical species and precipitates present within the ICET testing. Because of the representative nature of the ICET testing and the additional generic and plant-specific testing conducted to address chemical effects, it is also not expected that considering the effects of aged concrete will significantly affect the results of the plant-specific licensee evaluations related to GL 2004-02. Therefore, no additional research on this issue is necessary.

3.10 Alloying Effects

Description and Possible Implications

Another issue raised by the PIRT is the effect of different alloys on the quantity of corrosion products. Corrosion rate data exhibit wide variability depending on the specific corrosion conditions and the nature of the alloy being subject to corrosion. Alloying could affect dissolution and corrosion rates, thereby affecting the solid species precipitates that are formed.

Discussion

The ICET experiments (Ref. 14) studied the impact of coolant solution chemistry on containment material surfaces. With the exception of aluminum, little metallic corrosion was exhibited during the ICET experiments. The presence of other corrosion products containing iron, copper, nickel, and zinc is very small (less than 1 percent). Therefore, for most metals used within the containment, except aluminum, the potential differences in corrosion rates and alloying effects would have an insignificant impact on the amount of debris generated. For carbon steel, the corrosion resistance is essentially the same for various low alloy steels (Ref. 45). For zinc and zinc alloys, studies indicated that there is less than a 10-percent difference between the corrosion rate of galvanized iron, zinc die castings, and three grades of rolled zinc (Ref. 45).

General corrosion rates observed in the ICET experiments and industry-sponsored testing were greatest for aluminum. It has been postulated that other aluminum alloys may have different corrosion rates than the 3003 aluminum alloy used in the ICET experiments. The PWROG conducted testing to evaluate the corrosion rates of three aluminum alloys: 3003, 5005, and 6061 (Ref. 37). The corrosion tests were performed for 12 hours and 24 hours at a temperature of 200 degrees F in 2,500 ppm boron at a pH of 8.0. The corrosion rates for the 3003, 5005, and 6061 alloys were 79 to 92 percent of the rates observed for the commercially pure aluminum. It was concluded that the difference in corrosion rate of aluminum alloys as compared to aluminum metal was negligible. In addition, an evaluation documented in NUREG/CR-6988, Section 5.2, based on a review of the literature and other testing also concluded that the impact of alloy composition, with respect to the amount of aluminum corrosion product, is not significant. This finding is consistent with testing conducted at ANL which confirmed that a release rate equation based on test data derived using 1100 and 3003 Al alloys (Ref. 8) is a good predictor of the Al release rate of 6061 Al alloy. In addition, testing conducted by the PWROG, as documented in WCAP-16785-NP (Ref. 37), concluded that the difference in corrosion rate of aluminum alloys as compared to aluminum metal was negligible.

Conclusion

With the exception of aluminum, little metallic corrosion was exhibited during the ICET experiments. Therefore, for most metals used within the containment except aluminum, the potential differences in corrosion rates, mechanisms, and surface areas occurring in the 30-day post-LOCA window would have little impact on the total solids loading of the sump strainers. This assertion is supported by the insignificant difference in corrosion rates seen in prior testing and in results found in the literature. The various aluminum alloys also have corrosion rates that are similar to the 3000 series used in the ICET experiments so that the aluminum corrosion rates observed in ICET and other test programs are expected to be representative. Therefore, alloy variation is not expected to cause significant differences in ECCS performance and no additional research related to this issue is necessary.

3.11 Advanced Metallic Corrosion Understanding

Description and Possible Implications

The PIRT panel raised several other issues related to the understanding of metallic corrosion in the post-LOCA environment. These issues include enhanced Al corrosion caused by hypochlorite or other catalytic effects (e.g., jet impingement), synergistic effects on corrosion, and corrosion inhibition. These effects could substantially affect corrosion rates and therefore could have different effects on ECCS sump head loss.

Discussion

The containment pool could contain chloride compounds created by the radiolytic breakdown of electrical cable insulation or from leaching of protective coatings (paints) and other organic materials. Radiolysis of this solution has the potential to form chlorate, hypochlorite, and hypochlorous acid, which could alter the pH and redox potential. NUREG/CR-6988 (Ref. 11) evaluated the formation of hypochlorite (ClO^-), which Sections 2.1 and 2.2 of this report also addressed. As indicated in these sections, the effect of hypochlorite on containment pH and Al corrosion is expected to be insignificant because of the low hypochlorite concentration ($\sim 3 \times 10^{-6}$ to 10^{-5} moles/L at a pH of 7 to 10). The combined chloride formation from electrical cable insulation breakdown and leaching from protective coatings has been calculated to affect pH by 0.2 pH units or less. Containment pools contain sufficient buffering agent to counteract the formation of strong acids, such as HCl. As a result, there will be little effect on the pH or resultant corrosion product formation.

Jet impingement could also initiate pitting corrosion, which could accelerate the corrosion of normally passivated materials like stainless steel. However, the PIRT panelists generally recognized that corrosion, erosion, and ablation caused by jet impingement (see Section 3.2 of this report) will likely be inconsequential because of the short time duration of the jet (i.e., approximately 30 seconds) (Ref. 2) and the relatively small affected volume relative to the rest of the materials submerged within the containment pool or wetted by containment sprays. Even if pitting were to initiate, most of the metallic surfaces in the containment building are above the post-LOCA containment pool height and remain unsubmerged during the post-LOCA period. Pitting is also a localized corrosion mechanism that typically results in relatively small areas of attack on a metallic surface. Considering the large volume of water contained in a post-LOCA pool, and the amount of extra dissolved metallic ions that could be added to the containment pool by a localized pitting mechanism, any pitting initiated by jet impingement is likely to be insignificant compared to the total chemical species developed from debris within the containment pool and submerged materials during the ECCS mission time.

The ICET program demonstrated the importance of metallic corrosion and debris dissolution for representative post-LOCA environments containing multiple plant materials and debris generated by the water jet (Ref. 14). However, it's not possible to simulate all the plant-specific material and debris combinations within a reasonable generic testing program such as the ICET series. Therefore, it was not possible for the ICET testing to address all the complex interactions between dissolution processes of multiple materials or second-order effects resulting from variations in the trace chemicals of the containment water. However, several principal effects related to these issues were observed. For example, synergistic dissolution rate effects observed in the ICET series include the inhibition of NUKON® fiber leaching by dissolved Al, inhibition of Al corrosion by dissolved silica, and inhibition of Al corrosion by Cu

deposition. It is important to note that all the synergistic effects apparent in the ICET series resulted in less corrosion than would be expected from single-material (i.e., single-effect) testing.

In its response to a question about possible synergistic effects, the PWROG stated that important synergistic effects were also considered in the development of the WCAP-16530-NP-A chemical model. These effects are discussed more fully in Section 4.5. The PWROG also stated that these synergistic effects generally tend to result in reduced metallic corrosion rates. This statement concurs with the observations made in the ICET series. The staff accepted the response to this question in the SE associated with WCAP-16530-NP-A (Ref. 27). The dissolution and precipitation evaluations in the WCAP-16530-NP-A chemical model were primarily developed through single-effects testing and synergistic effects which reduce metallic corrosion rates are not credited. Therefore, although single-effects testing results may differ from those obtained through integrated or multiple-material testing, the results are expected to conservatively account for synergistic effects. Most licensees followed the WCAP-16530-NP-A model which results in conservative concentrations of chemical precipitates in the containment pool. Plants not using the WCAP-16530 model to determine their chemical source term also contain conservation assumptions, such as using an adjusted pH to ensure that a conservative concentration of chemical precipitate forms. Additionally, the nuclear industry has performed head loss testing with multiple plant materials, including aluminum, and the amounts of precipitate that formed in these tests were less than the WCAP-16530-NP-A chemical model predicted.

Conclusion

As discussed above, the effect of hypochlorite on containment pH and Al corrosion is expected to be insignificant because of the low hypochlorite concentration. The effect of jet impingement, as discussed above and also in Section 3.2 of this report, is also expected to be insignificant since the amount of metallic species released by this mechanism, if it were to occur, would be much less than the total plant-specific debris load. The ICET and industry-sponsored testing identified several important synergistic effects that generally reduce metallic corrosion rates. The chemical effects model developed by industry conservatively addresses these effects by basing corrosion rates on single-effect testing which do not credit corrosion inhibition due to the interaction among multiple materials. Subsequent integrated head loss testing has confirmed the efficacy of this model. In addition, the guidance for licensees to evaluate the effect of these species on ECCS performance is sufficiently conservative. Therefore, no additional research related to this issue is necessary.

3.12 Submerged Source Terms: Biological Growth in Debris Beds

Description and Possible Implications

The PIRT considered the propensity for bacteria or other biota to grow in preexisting debris beds located on the sump strainer screen or elsewhere within the ECCS system. Significant bacterial growth may be important if it creates additional debris that contributes to sump screen clogging or detrimental performance of downstream components like pumps and valves.

Discussion

In the post-LOCA period, the conditions expected in the nuclear reactor containment environment (i.e., high borate, high initial temperature, high radiation flux, transiently high pH,

absence of light, and low nutrient availability) are not generally favorable for biological growth, especially during the 30-day period following the accident.

High temperatures (i.e., greater than 100 degrees C) are expected initially in the post-LOCA containment pool. This initial high temperature would likely kill most bio-organisms, minimizing the likelihood of significant biofouling growth. Organisms that can survive at temperatures up to 121 degrees C are known (Ref. 11). However, an organism has a defined temperature range within which it is capable of growing, and, if a temperature is too high or too low, significant growth will not occur (Ref. 46). For example, some organisms have an optimal temperature range of 80–110 degrees C and are unable to grow at temperatures below 60 degrees C, while some are unable to grow at temperatures below 80 degrees C (Ref. 46). Some organisms may survive the initial large temperature increase by sporulation, but would effectively be inactive and unable to germinate until the temperature decreased (Ref. 46).

Most thermo-tolerant microbes require essential nutrients to survive, and the post-LOCA environment is expected to be very low in these nutrients. Under severely oligotrophic (i.e. lacking nutrients) conditions, it is unlikely that microbial growth would be significant within the ECCS containment pool during the 30-day mission time, since biomass accumulation is proportional to the amount of carbon present (Ref. 11). In addition, radiation within the post-LOCA containment environment is expected to kill most microorganisms. While various bacteria have been found in low-nutrient, high-radiation conditions in spent fuel storage pools, the growth rate of these bacterial was slow under these conditions (Ref. 11). Therefore, while certain species of microbes can survive under very low nutrients and high radiation conditions, extensive growth within the 30-day mission time typically assumed for ECCS operability is unlikely.

Photosynthetic microbes such as algae and cyanobacteria could also grow under low fixed carbon and nitrogen situations (Ref. 11). In the case of cyanobacteria (blue-green algae), many species are able to grow in the absence of fixed carbon or nitrogen if sufficient light is available. However, there is little or no lighting in the post-LOCA containment such that the growth of photosynthetic microbes is not expected to be significant.

Microorganisms typically also have a pH range within which growth is possible, and each usually has a well-defined pH for optimal growth. Most bacteria thrive in neutral pH environments. While a pH greater than 10 inhibits the growth of many microbe species, there are alkaline tolerant and alkalophilic organisms that can grow at high pH. Some species grow at a pH as high as 12 (Ref. 11). Alkaline tolerant organisms show optimal growth in the pH range of 7–9, but cannot grow above pH 9.5, and alkalophilic organisms show optimal growth between pH 10.0–12.0, but some cannot grow below pH 8.5–9.0 (Ref. 46). Depending on the buffering system, the final steady-state containment pool pH can vary between 7 and 11 (Ref. 2). Organisms that thrive in a neutral environment may not survive when the pH is greater than 10; similarly, organisms that thrive in high pH may not survive in a neutral environment.

Microbiological modeling has been performed to evaluate the potential quantities and impact of microorganisms on the geochemistry of the area adjacent to and within nuclear waste packages in the proposed Yucca Mountain repository. A number of simplified calculations have been performed using the Microbial Impacts to the Near-Field Environment Geochemistry (MING) codes (Ref. 47). The results showed a maximum biomass production of 10 to 12 grams per year per meter of repository based on the nutrients and energy in the large mass of mild steel that would be emplaced. Biomass production based on the nutrients in the other constituents (concrete, C-22 alloy, and J-13 ground water) varied from 1 to 0.01 grams per year per meter

(Ref. 46). The MING code was designed to function within parameters that have been shown to directly affect microbial activity, including nutrient availability, salinity, pH, water activity, radiation, temperature, and redox conditions coupled with relevant metabolic processes (Ref. 47). Although the conditions expected in the post-LOCA containment environment are not the same as Yucca Mountain, they do share some similarities, such as high temperature, high radiation flux, and low nutrients. The temperature in the vicinity of the waste package is expected to exceed 100 °C for more than 100 years (Ref. 46). Temperatures in excess of 100°C are also expected in the initial post-LOCA containment pool and moderately high sustained temperatures just below 100 °C are expected for most plants during the 30-day mission time. The environment at Yucca Mountain, similar to the post-LOCA environment, is also expected to be oligotrophic (i.e., lacking nutrients) with respect to the supply of nutrients needed to sustain most bacteria growth. With respect to radiation exposure, depending on waste package design, exposure could vary from negligible to 0.06 Gy/min (360 rad/h). This upper limit is comparable to the radiation field expected in the post-LOCA containment. Therefore, because relatively low biomass is expected in the Yucca Mountain repository, there is no reason to believe that significant amounts of biomass will be present in the post-LOCA containment pool within the 30-day mission time.

The PIRT report (Ref. 2) indicates that significant biological debris was found in the Three Mile Island (TMI), Unit 2, post-LOCA containment when it was opened. It was not clear when this observation was made and how the conclusion was drawn. The references cited in the PIRT report were vague with regard to microbial growth and would not by themselves suggest that significant growth of various microbes was possible in a post-LOCA situation. One reference is the analytical chemistry report from Oak Ridge National Laboratory (ORNL) that evaluated samples extracted from TMI containment water after the accident. The containment water samples were taken several months after the LOCA occurred and river water was mixed with the RCS and ECCS water in the samples (Ref. 2). The report noted the observation of precipitate in the bottom of the sample solution which was flocculent in appearance, gelatinous, and a dirty green color. This observation may have resulted from the introduction of organic material and microbes from river water, or it could have been sediment or sludge imported from the river water. The observation of a greenish flocculent material in these samples suggests that biological growth may have occurred in TMI, Unit 2, but it does not provide any concrete evidence that significant biological growth is possible in expected post-LOCA environments. The inclusion of river water, which leaked from Service Water System relief valves (Ref. 48), is not representative of the conditions expected in most post-LOCA environments and only biological growth within the 30-day mission time is considered.

Conclusion

While the research reported in the literature indicates that microbial growth may be possible under post-LOCA containment conditions, the ability of any microorganism to not only survive, but to undergo the significant growth required to pose a risk to the ability of coolant waters to pass through the sump strainers over the 30-day ECCS mission time, is highly unlikely. The initial high temperature, variation in pH, high radiation flux, absence of light, and low nutrient availability in this environment is not conducive to survival or growth of most bio-organisms. The observation of biological materials in the post-LOCA TMI, Unit 2 environment is not expected to be representative of expected post-LOCA conditions. Furthermore, microbiological modeling performed for the Yucca Mountain repository showed that only a small amount of biomass is expected. Since the conditions expected in the post-LOCA environment are similar to the Yucca Mountain repository, there is no reason to believe that significant amounts of

biomass will be present in the post-LOCA containment pool. Based on the above discussion, no additional research related to this issue is necessary.

3.13 Reactor Core: Fuel Deposition Spall

Description and Possible Implications

Spall of reactor fuel cladding oxides (ZrO_2) and deposited chemical products could be a potential source of activated materials that could affect chemical reactions in the post-LOCA containment pool. Also, precipitates of post-LOCA chemical products (organics, Al, B, Ni, Fe, Zn, Ca, Mg, silicates (SiO_3^{2-} and SiO_4^{4-}), and CO_3^{2-} -based products) could deposit on the fuel clad and spall, contributing either to clogging within the reactor core, or head loss across the sump strainer.

Discussion

The downstream effect evaluations used by licensees is provided in WCAP-16793-NP, Rev 1 (Ref. 5). The chemical source term used in this WCAP is conservatively determined from the WCAP-16530 model. WCAP-16793-NP, Revision 1 also includes a calculation tool, the LOCA Deposition Analysis Model (LOCADM), which is used by licensees of PWRs to predict the post-LOCA buildup of chemical deposits on fuel rods. The LOCADM model assumes all chemical species that are dissolved in the sump pool following a LOCA remain dissolved and deposit only on the fuel rods. All precipitates that are predicted to form are assumed to pass through the strainers and into the reactor. Therefore, no credit is taken for chemical precipitates that settle, for precipitates that are trapped in fiber bed on the suction strainers, or for precipitates retained within any other area in the plant. In reality, any precipitates that collect in fiber beds on the suction strainers, on the core inlet nozzles, or deposit in other areas are not available to form deposits on the core and subsequently spall. This is a conservative assumption. Licensees are required to address the effect of these deposits in their evaluations.

This evaluation of clogging caused by spallation of these precipitates is presented in two sub-topics—clogging within the reactor core by spall of chemical deposits from reactor fuel, and clogging of the sump strainer by chemical-deposit spall released from the reactor fuel. The effects of spall from fuel cladding and other metallic surfaces within the primary pressure boundary (cumulatively described as “crud”) are discussed in Sections 2.5 and 3.1 of this report.

(1) Clogging of the Reactor Core by Spall from Chemical Deposits from Reactor Fuel

Although WCAP-16793-NP does not consider this effect, in reality, the quantity of chemical precipitates deposited on fuel rods following a LOCA, the potential of these precipitates to spall, and the potential for the spall to obstruct coolant flow within the core is influenced by the location of the pipe break—upstream or downstream of the core with respect to the direction of ECCS flow.

If the pipe break occurs on the cold-leg (upstream) side of the reactor core in a typical PWR (other than a 2-loop Upper Plenum Injection (UPI) Westinghouse PWR), the coolant flow into the core equals the quantity required to replenish boil-off (typically 3 gallons per minute (gpm) per fuel assembly at the onset of recirculation). The coolant entering the core exits the vessel as steam, leaving behind all suspended and dissolved solids. As boil-off continues, debris and dissolved solids (including boric acid) concentrate in the vessel. To prevent the boron concentration from reaching its solubility limit (typically 4 to 6 hours after the initiation of the

event), flow of coolant to the reactor vessel is reversed by initiating flow through the hot-leg, thus flushing suspended and dissolved solids from the reactor vessel. The transients induced by boiling and flow reversal may be expected to make spallation from the reactor fuel more likely.

During the period prior to hot-leg injection, spall of deposits from fuel would either be kept in suspension by the robust boiling within the core or would settle out onto the tops of spacer grids or the top of the core inlet nozzle. This debris layer is expected to remain sufficiently porous to permit adequate flow of coolant throughout the core. This expectation is based on numerical analyses prepared by the PWROG and documented in WCAP-16793-NP, Revision 1 that demonstrates that there is significant margin in the flow rate required to cool the core if debris blockage were to occur as long as a relatively small open area (i.e., a single unobstructed area or porosity within a uniform debris bed) is present. These analyses show that adequate flow to the core can be achieved with over 99 percent of the core inlet area blocked and the fuel cladding temperature can be maintained at an acceptable level with the gap between the fuel rod and the grid-strap completely filled with debris. Independent analysis performed by the NRC staff confirmed that adequate flow can be maintained with a small open area at the core inlet. The staff is reviewing the grid strap blockage analysis as part of the WCAP-16793 review and has no further questions related to that analysis.

Further, fuel assembly testing conducted by the PWROG will be used to establish limits on the quantity of fibrous debris that can enter the core without forming a debris bed that can trap sufficient concentrations of particulate and chemical precipitates to cause insufficient coolant flow within the core. These fiber limits are intended to ensure that flow will reach the core, irrespective of the quantity of particulate and chemical-precipitate entrained in the coolant.

Using these limits, fuel assembly tests performed by the PWROG, simulating cold leg break conditions (Ref. 49) demonstrated that nearly all of the fiber introduced into the fuel assembly is captured by the first grid strap in the inactive fuel region at the core inlet, leaving the interior of the core free of fiber that could interact with spall to form a compact, flow-restricting debris bed. The PWROG testing also demonstrated that fiber is a necessary component to form an impenetrable debris bed. Without the formation of a fiber-bed, particulate and chemical precipitate debris readily passed through the core in these tests. A flow test conducted using AREVA-designed fuel (Ref. 50) showed that the fiber debris bed formed on the upstream side of the grid strap could be easily dislodged by reverse flow, suggesting that a debris bed formed at the core inlet would not present an obstruction to flow upon initiation of hot-leg injection. These tests and analyses demonstrate that under cold-leg break flow conditions, insufficient concentrations of fiber are expected within the core region to trap chemical precipitate spall such that a non-porous debris bed is formed that would prevent adequate core cooling.

For pipe breaks occurring on the hot-leg side of the core in a typical PWR (other than a 2-loop UPI Westinghouse PWR), the ECCS coolant is pumped directly through the core at a rate equal to ECCS pump capacity (typically 6 to 45 gpm per fuel assembly). At this flow rate, boiling in the core would be reduced and the bulk of any particulate or precipitate that could form would be carried out of the reactor vessel by the coolant; diminishing the opportunity for deposits to form on the fuel pins. Also, the more uniform flow conditions may make spallation less likely than for cold-leg pipe breaks. If sufficient fiber is deposited on the grid straps, spall could be captured by these fibrous debris beds. However, the fiber limit previously set by WCAP-16793-NP, Revision 1 (Ref. 5) on the quantity of strainer bypassed fiber that may reach the core inlet assures that spall, in combination with fiber, would not form non-porous debris bed at the grid straps. The additional spall that could be trapped at the grid straps is not expected to increase

the pressure drop. This conclusion is supported by flow tests completed by the PWROG, using simulated hot leg break conditions, showing that ECCS debris concentration of low particulate to fiber ratios yielded the highest pressure drop across the fuel assembly. Therefore, the spall, by itself, would not form an impenetrable debris bed that could prevent adequate core cooling.

Note: The above discussion is also applicable to 2-loop Westinghouse UPI PWRs except that the conditions for the hot-leg and cold-leg breaks are reversed.

As mentioned above, the PWROG tests and analyses considered in the deposition of this issue are documented in WCAP-16793-NP, Revision 1 (Ref. 5). The WCAP report is currently under NRC staff review. Staff observations of the fuel assembly test are documented in trip reports (Refs. 50, 50), as noted.

Spall of chemical deposits from fuel will not form a debris bed in the reactor vessel that could prevent adequate coolant flow to the core. This conclusion is based on staff observations of testing performed by the PWROG to determine the maximum quantity of the various types of sump strainer bypassed debris that may reach the core inlet while maintaining adequate coolant flow to the core, and staff review of analyses completed by the PWROG to demonstrate that (1) adequate core cooling can be achieved even with over 99 percent of the core inlet blocked and (2) fuel clad temperature can be maintained within acceptable limits even if the gap between fuel rods within the grid straps is filled with debris.

(2) Clogging of the Sump Strainer by Spall of Chemical Precipitates Deposited on Fuel

Spall of chemical deposits from fuel would not increase the debris load on the ECCS sump strainer beyond the quantity of debris the strainers are qualified for because the sump strainers are tested by licensees using the maximum expected debris loads to ensure that strainers are capable of passing the required ECCS flow. The additional particulate that may be created by spall of chemical precipitates is bounded by the conservative assumptions made by licensees for particulate debris sources. For example, licensees assume all unqualified coatings in the containment building fail as 10 micron particulate. Licensee's chemical effect evaluations also contain other conservative assumptions to account for uncertainties such as additional source material (e.g. spall). For example, licensees typically assume that additional aluminum is present in the plant, calculate aluminum corrosion using the highest possible post-LOCA pool pH, and then assume all the dissolved aluminum precipitates without regard to solubility to provide margin for additional chemical precipitates that may form due to other mechanisms and in other locations. These conservative, plant-specific debris loads are typically developed in accordance with WCAP-16530-NP-A and they are used in the sump strainer tests to demonstrate acceptable performance. Plants with appreciable calcium concentrations may be more likely to have scale form and spall from the fuel rods following a LOCA because many calcium precipitates have retrograde solubility. However, these plants have also performed sump strainer tests with particulate concentrations that bound the maximum possible quantity of calcium silicate insulation debris within the plant. Therefore, conservative assumptions in the amount of chemical and particulate debris used in sump strainer tests are adequate to account for additional material from spalled chemical deposits from fuel rods.

Conclusion

The potential for spall of chemical deposits from fuel to prevent adequate flow through the reactor core is unlikely because the post-LOCA conditions in the core are not conducive to forming an impenetrable fibrous debris bed that can trap particulate debris and chemical

precipitates such that adequate coolant flow within the core is not achieved. This is demonstrated by testing and analysis documented in WCAP-16793-NP, Revision 1 (Ref. 5). While the staff has not yet approved this WCAP, ongoing testing will establish the limiting amount of debris within the core to ensure adequate coolant flow and acceptable peak clad temperatures will exist over the entire post-LOCA mission time.

The potential for solid species to precipitate in the reactor, deposit on the fuel cladding, spall, and contribute to clogging of the sump screen is addressed by the conservatism in the chemical debris source term, and by testing strainers using particulate and chemical debris loads that bound the potential additional debris concentrations created by spallation of chemical precipitates from the reactor core. Therefore, no additional research related to this topic is necessary

4. Solid Species Precipitation

4.1 Polymerization

Description and Possible Implications

The PIRT panelists expect polymerization to occur after molecular precipitation as a precursor to solid species agglomeration in post-LOCA environments. Molecular precipitation refers to the formation of bonds between metallic species and oxygen to form monomers. Polymerization is the ripening of these bonds to form covalent bonds and the growth of the monomers through one of many types of polymerization reactions. Chain polymerization, which is the most common, consists of initiation and propagation reactions and may include termination and chain transfer reactions (Ref. 51). Step-growth and condensation polymerization are two additional mechanisms. Polymerization occurs until approximately nanometer-sized particles have formed. These particles can then continue to grow to larger sizes through agglomeration mechanisms.

The PIRT panelists expect polymerization is needed to form large enough particles to tangibly affect ECCS performance. The fact that chemical precipitates have formed during testing to simulate post-LOCA conditions (Refs. 3, 14, 52) provides evidence that polymerization is likely occurring. The issue is important only if the differences in polymerization mechanisms in the simulated and actual post-LOCA environments are significant enough to alter head loss or downstream effects associated with the chemical precipitates.

Discussion

Inorganic polymerization is the process by which hydrolyzed cations link together, generally through oxo (-O-) bridges and dehydration, to form chains and networks. With sufficient growth, colloidal particles will result. Condensation polymerization occurs when the covalent bonds are rearranged such that monomers (the basic building blocks) are connected and water is expelled. The PIRT panelists expect this process to be a component of the primary mechanism for forming solids in the post-LOCA containment pool, as demonstrated in the ICET testing (Ref. 14). This process may also be necessary, along with agglomeration mechanisms, to form particles that are large enough to significantly affect ECCS performance. The PIRT panelists hypothesized a scenario describing this process, which the following paragraphs summarize.

Polymerization may begin early in the post-LOCA scenario (within 20 minutes of the initiating event) as cations are introduced in the containment pool. Any of the cations that can induce precipitation in the post-LOCA environment are candidates for polymerization, including Al, Fe, Si, Zn, Cu, Ca, and boric acid. Extensive knowledge of the hydrolysis and precipitation of solids from solutions containing simple cations, such as Al^{3+} and Fe^{3+} , exists, but there is less understanding for more complex systems (e.g., precipitation of aluminosilicates).

The conditions leading to polymerization are a function of the ionic species and concentrations, time, temperature, and pH. Specifically, variations in the degree of polymerization and the polymerization mechanisms may be affected by temperature variations in the post-LOCA fluid caused by the cooling of the ECCS water at the heat exchanger (see Section 4.2 of this report) and heating within the RPV (see Section 4.3 of this report). Therefore, additional study could clarify the details associated with the role of polymerization on the formation of solid species in either representative or plant-specific environments.

However, the formation of macroscopic solid species during the ICET testing and other testing (Refs. 3, 52) that conservatively represent the pH, time, containment pool temperature, and ionic species concentrations of the post-LOCA environment (see Sections 1.1 and 1.2 of this report) provides evidence that polymerization can occur in these environments. The effects of temperature variations on solid species formation have also been studied (Refs. 3, 52) over a range of conditions that appropriately represent the post-LOCA environment (see Sections 4.3 and 4.4 of this report). This research has demonstrated that chemical precipitates may contribute to head loss and potentially affect ECCS performance downstream of the sump strainer. The implications associated with these findings are more significant than a detailed understanding of the physical polymerization processes that occur in the post-LOCA environment. Because chemical effects, and specifically chemical precipitation, have been studied over a wide-range of conditions that are either conservative or representative of actual post-LOCA conditions, staff does not expect the implications associated with polymerization processes to differ significantly between the simulated and actual post-LOCA environments. Additionally, guidance has been provided for licensees (Ref. 13) to conservatively assess the effect of chemical precipitates (and hence the implications associated with these polymerization processes) within their plants after a LOCA.

Conclusion

As discussed, polymerization is expected to be an important process in the formation of solid species within the post-LOCA environment. While the role of polymerization is not fundamentally understood, prior research has effectively considered the significance of the solid species that arise, partially as a result of polymerization. The prior research explored a wide range of conservative and representative conditions so that significant differences between the implications associated with the simulated and actual post-LOCA conditions are not expected. The guidance for licensees to evaluate the effect of these species on ECCS performance is also sufficiently conservative. Therefore, the implications associated with polymerization have been addressed, and additional research to gain a fundamental understanding of the role of polymerization is not required to ensure that ECCS performance will be acceptable.

4.2 Heat Exchanger: Solid Species Formation

Description and Possible Implications

Chemical species having normal solubility profiles may be dissolved in the containment pool at higher temperatures. However, these chemical species may precipitate in the heat exchanger because of a drop in temperature of approximately 30 degrees F. Some possible solid species that could form include $\text{Al}(\text{OH})_3$, FeOOH , and amorphous SiO_2 . The lower temperature at the heat exchanger outlet could also facilitate the development of macroscale coatings or suspended particulates, or both, that can continue to transport in the circulating fluid. Possible implications of this scenario include (1) species remain insoluble at higher reactor temperatures and affect the ability to cool the reactor core, (2) solid species formed may clog the reactor core and degrade heat transfer from the fuel, (3) species remain insoluble at higher containment pool temperatures and cause additional head loss upon recirculation, and (4) particulates act as nucleation sites for other compounds to precipitate.

Discussion

This evaluation is presented in four sub-topics in the order defined above.

(1) Species Remain Insoluble at Higher Reactor Temperatures, Affecting the Ability of the ECCS Coolant to Remove Decay Heat from the Reactor Core.

In the course of preparing their downstream effects evaluations using the guidance in WCAP-16406-P-A (Ref. 4), licensees have conservatively estimated, through testing, the combined concentration of fiber, particulate, and chemical precipitate debris that may bypass the ECCS sump strainers is less than 1000 ppm by weight. As demonstrated by testing, and confirmed by a scoping calculation discussed below, this concentration of precipitates and particulates in the circulated coolant is not expected to significantly affect the ability of the water to remove heat from the core. A scoping calculation was performed to evaluate the change in specific heat capacity due to 1000 ppm of debris in coolant. The specific heat capacity of a solution (i.e., slurry) can be estimated by calculating the weighted average of the heat capacity of the individual elements. The debris is assumed to consist mainly of aluminum, calcium, silica, and iron oxide materials. The specific heat, C_p , of these elements is approximately equivalent. For the purpose of the evaluation, a value of 5.3 BTU/lb-m per degree F was used for the debris and 1.0 for the water (Refs. 53, 54). The results of this calculation show less than a 1% change in heat capacity which is not sufficient to affect the ability of the water to remove heat from the fuel rods for a hot-leg break. As discussed in Section 3.13, for hot-leg breaks (cold-leg breaks for UPI plants), the bulk of the ECCS flow is pumped through the core and exits the vessel mainly as debris-laden water. Therefore, much of the debris that enters the core will be flushed from the reactor vessel, minimizing the concentration of solids and dissolved chemicals in the core region. Therefore, less than 1000 ppm of debris is expected under this scenario.

For cold-leg breaks (hot-leg breaks for UPI plants), coolant cannot be pumped directly into the core. Therefore, the core is initially cooled by boiling off the inventory of coolant in the core. The only coolant flow into the core is that required to replenish what is boiled off. Because the flow exiting the core is steam, the concentration of dissolved and suspended solids increases with time. However, under this condition, the flow of coolant to the core is much reduced and, therefore, the quantity of debris entering the core is also reduced. It is possible, under this scenario, that the debris concentration could exceed 1000 ppm before reverse flow is initiated. However, the heat removal mechanism during this break scenario is by boiling and the earlier scoping calculation demonstrates that the boiling point and specific heat of the coolant (water) are not significantly affected by the relatively diluted concentrations of suspended solids. Therefore, adequate heat transfer from the fuel cladding to the coolant is expected to be maintained.

The increasing concentration of boric acid in the core is of greater concern because it potentially has the most significant affect on heat transfer by increasing the viscosity and boiling point of the coolant. However, this condition is addressed in the plant design basis calculations and the PWROG currently has a test program to validate those calculations (see Section 7.4). Further, to reduce the concentration of boron in the core, reverse ECCS flow into the core is initiated within a predetermined time interval, flushing the concentrated boron and debris from the core.

(2) Solid Species Formed Could Clog the Reactor Core and Degrade Heat Transfer from Fuel.

The PWROG has performed flow testing on full-scale cross-section, one-third height fuel assemblies to determine the maximum quantities of fibrous, particulate, and chemical precipitate debris that can reach the core inlet and still maintain adequate flow to the core. These tests demonstrated that chemical precipitates and particulate debris without the presence of a fiber bed had negligible effect on pressure drop across the test assembly. The test also

showed that fibrous debris was readily captured by the grid straps within the fuel assemblies and that the fiber bed captured particulate and chemical precipitate debris. Absent chemical precipitates, the fiber/particulate debris bed remained relatively porous. However, with chemical precipitates present, a thin fibrous debris bed deposited on the grid straps was sufficient to block flow. Therefore, the PWROG is developing limits for the quantity of fiber that may bypass the ECCS sump strainer. Once debris limits are identified by the PWROG and accepted by the NRC staff, licensees will need to demonstrate that their strainer bypassed fibrous debris are less than these limits. Licensees who do not apply the WCAP-16793-NP method for evaluating the downstream effects of ECCS sump strainer bypassed debris on the reactor vessel and core will need to demonstrate to NRC staff that bypassed fiber will not impede adequate flow to the reactor core.

(3) Species Remain Insoluble at Higher Containment Pool Temperatures and Cause Additional Head Loss Upon Recirculation

The industry-developed WCAP-16530-NP-A (Ref. 3) examines the interactions between the PWR post-LOCA containment environment and containment materials that may produce corrosion products, gelatinous material, or other chemical reaction products that are capable of affecting head loss across the sump strainer or blocking flow through components located downstream of the sump strainers. Licensees may use the methods described in WCAP-16530-NP-A to perform plant-specific chemical effects evaluations to characterize their chemical precipitates. The information from these evaluations can serve as the basis for the sump strainer testing or to determine the chemical source term for in-vessel downstream effects evaluations. When calculating the available precipitate in the containment pool for strainer head loss testing, WCAP-16530-NP-A does not rely on the precipitate mass measured during precipitation testing to determine the amounts of plant-specific precipitate, but conservatively assumes that all dissolved aluminum precipitates and all dissolved calcium in phosphate solutions precipitates in the sump pool and are included in strainer head loss tests. Licensees who use an alternate to the WCAP-16530-NP-A method either inject chemicals into the strainer test or test with a simulated post-LOCA environment using an adjusted pH to ensure precipitation of a conservative concentration of solids.

While sump strainer testing is performed with a conservative amount of chemical precipitate, the LOCADM methodology used for in-vessel analysis in WCAP-16793-NP, Revision 1 assumes that all species remain dissolved until reaching the reactor core. In other words, in-vessel analysis using LOCADM assumes no precipitates form in the sump pool and no precipitates are trapped on the strainer debris bed or in other locations such as in heat exchangers. Moreover, tests that have included rapid temperature drops to simulate a heat exchanger have not produced additional precipitation (Ref. 7). Therefore, no additional precipitates that are considered to be effective at blocking flow through a fibrous debris bed are attributable to precipitation in the RHR heat exchanger.

(4) Particulates Act as Nucleation Sites for Other Compounds to Precipitate

As more fully discussed in Section 4.4, differences in the types and concentrations of nucleation sites between testing and actual post-LOCA environments are not expected to affect the types and concentrations of chemical precipitate formation. Therefore, no further research is required on this issue.

Conclusion

The effect of chemical species that may precipitate in the RHR heat exchanger because of a drop in temperature of approximately 30 degrees F could facilitate the development of additional solid species but is not expected to significantly affect (1) the ability of the ECCS to cool the core, (2) the flow of coolant to the core, (3) the flow of coolant through the sump strainer, or (4) the creation of additional nucleation sites that may increase the rate of precipitate formation. Licensees address the effects of these precipitates on sump strainer performance and on the reactor vessel and fuel on a plant-specific basis following the guidance in WCAP-16530-NP-A and WCAP-16793-NP, Revision 1. While the staff has not yet approved WCAP-16793-NP, Revision 1 (Ref. 5), ongoing testing will establish the limiting amount of debris within the core that will ensure adequate flow to provide acceptable peak clad temperatures. Therefore, no additional research related to this issue is necessary.

4.3 Reactor Core: Precipitation

Description and Possible Implications

The increased temperature in the reactor vessel (i.e., 70 degrees C higher than the containment pool) and retrograde solubility of some species (e.g., Ca silicate, Ca carbonate, zeolite, sodium calcium aluminate) causes precipitation and additional chemical product formation. This could result in the following: (1) additional precipitate could be created and transported to the sump screen that would then contribute to head loss and (2) precipitate or spall (see Section 3.13 of this report) passing through the sump screen may degrade the performance of ECCS components downstream from the screen.

Discussion

This evaluation is presented in two sub-topics in the order defined above.

- (1) The Retrograde Solubility of Some Species Could Cause Additional Precipitate that Could be Transported to the Sump Screen and Contribute to Head Loss.

Testing and evaluation requirements contained in NRC staff-approved guidance are sufficiently conservative to account for the effect of precipitates that may form on hot surfaces such as the fuel rods because:

- a) Debris quantities used in strainer tests are developed assuming that most dissolved material precipitate and are filtered at the strainer,
- b) Concentrations of dissolved solids used in in-vessel testing and analyses are based on the assumption that no dissolved material in the ECCS coolant precipitates until it reaches the reactor vessel, and
- c) The LOCADM model used to calculate fuel cladding deposition thickness and clad temperature assumes that all dissolved species that are transported to a location of boiling on the fuel rod deposit on the surface of the fuel rod.

Licensees of PWRs are implementing the NRC-approved guidance and procedures to predict the types and quantities of precipitates that may form and to examine the effects of these

precipitates on sump strainer performance, core inlet blockage, fuel blockage, and fuel fouling as described below.

Licensees are applying the industry-developed WCAP-16530-NP-A (Ref. 3) or alternate methods to estimate the types and quantities of deleterious precipitates that may form in their respective containment pools. The WCAP examines the interactions between the PWR post-LOCA containment environment and containment materials that may produce corrosion products, gelatinous material, or other chemical reaction products (including products of Ca) that are capable of affecting head loss across the sump strainer or blocking flow through components located downstream of the sump strainers. Licensees may use the methods described in WCAP-16530-NP-A to perform plant-specific chemical effects evaluations to characterize their chemical precipitates. The information from these evaluations can serve as the basis for the sump strainer testing or in-vessel downstream effects evaluations.

When calculating the available precipitate in the containment pool for strainer head loss testing, WCAP-16530-NP-A does not rely on solubility considerations to determine the amounts of plant-specific precipitate, but conservatively assumes that all dissolved aluminum precipitates and all dissolved calcium in phosphate solutions precipitates. Any aluminum (and calcium in phosphate solutions) that remains in solution provides margin to account for additional chemical precipitates that may form due to all other possible chemical species. Additionally, because the aluminum and calcium precipitates have the most deleterious properties of the possible precipitates formed, the types and concentrations of the chemical precipitates used in strainer head loss testing and reactor core blockage is considered conservative. Alternate methods to the WCAP-16530 approach also contain conservative assumptions, such as using an adjusted pH to ensure that a conservative concentration of chemical precipitate forms. Therefore, the precipitate loading in strainer testing conservatively accounts for precipitation whether the precipitate forms in the sump pool prior reaching the sump strainer or in the reactor vessel due to retrograde solubility.

- (2) Precipitated solids or spall from fuel passing through the sump screen could degrade the performance of ECCS components located downstream from the screen.

All licensees are implementing NRC-approved guidance and procedures in the industry-developed WCAP-16406-P-A (Ref. 4) to address blockage and the wear of ECCS components caused by debris that bypasses the sump strainers. The WCAP report provides guidance and a consistent approach for PWR licensees to evaluate the downstream impact of particulate and fibrous debris suspended in circulated fluid downstream of the strainers. However, the WCAP does not consider for the effects of chemical precipitates on wear or blockage of flow. Therefore, NRC staff investigated the potential for the precipitates occurring most commonly and in significant quantities to affect downstream component performance. In this evaluation (Ref. 55), staff concluded that although chemical precipitates in the circulated sump fluid could significantly affect pressure drop across a fiber bed formed on the sump strainer or fuel grid straps, it would not significantly affect other downstream components. The bases for staff's conclusions were:

1. In-vessel fuel blockage tests conducted at Westinghouse and AREVA using particulate, fiber and aluminum oxyhydroxide precipitate demonstrated that any flow resistance created by these substances was significantly less than the pump head that is available in the ECCS and CSS piping systems. The test loop low-head pumps, throttle valves, differential-pressure gages and flow meters did not experience blockage or visible wear. Therefore, components

downstream of the sump strainers are not expected to become clogged with debris and chemical precipitate such that blockage of flow occurs.

2. Of the many plant-specific strainer head loss qualification tests observed by NRC staff, not a single case occurred where WCAP-16530-NP-A surrogate precipitates, in combination with particulate and fibers, obstructed flow through the test loop (other than across the strainer debris bed).

3. Chemical precipitates by themselves do not appear to have high shear strengths. Precipitate from ICET 1 that had agglomerated following weeks of post-test storage sloughed off a stirring rod and readily broke apart when stirred. Calcium phosphate precipitate, by itself, was not able to build a sustainable bed on a test screen during vertical loop head loss tests conducted at ANL (Ref. 52).

4. In all the strainer and in-vessel flow testing there is no evidence to suggest that aluminum-oxyhydroxide, calcium phosphate, or similar chemical precipitates can be a major contributor to erosive or abrasive wear in ECCS and CSS components. Further, the abrasive properties of the debris (sand, glass chards and coating chips) used in the WCAP-16406-P-A (Ref. 4) wear evaluations of downstream components are much more aggressive than that of aluminum oxyhydroxide or calcium phosphate precipitates.

Conclusion

Testing and evaluation requirements contained in NRC staff-approved guidance are sufficiently conservative to account for the effect of precipitates that may form on hot surfaces such as the fuel rods. The debris quantities used in strainer tests are developed assuming that most dissolved material precipitate and are filtered at the strainer. Further, the concentrations of dissolved solids used in in-vessel testing and analyses are based on the assumption that no dissolved material in the ECCS coolant precipitates until it reaches the reactor vessel. Also, the fuel cladding deposition thickness and clad temperature are calculated assuming that all dissolved species are transported to a location of boiling on the fuel rod and deposit on the surface of the fuel rod. Finally, the guidance in WCAP-16406-P-A for evaluating the potential for wear of downstream components is based on debris concentrations and abrasive properties that bound the effects of precipitates and spall that could be formed. Therefore, no additional research related to this issue is necessary.

4.4 Particulate Nucleation Sites

Description and Possible Implications

Particles within containment create the nucleation sites required for chemical precipitation. Examples of particles that could serve as nucleation sites include irradiated particles, dirt particles, coating debris, insulation debris, biological debris, and other materials within the post-LOCA containment pool. These particles then grow through polymerization (see Section 4.1 of this report) and agglomeration (see Sections 5.1 and 6.2 of this report) into solid species that are large enough to possibly degrade ECCS performance.

This issue identifies a fundamental aspect of the formation of solid species. Implications only arise if the nucleation sites in the post-LOCA environment are not appropriately simulated in testing. That is, the quantities and types of nucleation sites used in testing should be

representative of the post-LOCA environment to ensure that solid species formation is not suppressed.

Discussion

Precipitation is enabled by the existence of heterogeneous nucleation sites within the containment pool. Conversely, a dearth of these sites could delay precipitation. A wide variety of materials could serve as nucleation sites, including dirt particles, coating debris, insulation debris, and biological debris. The PIRT panelists all agreed that the post-LOCA containment environment would contain a plethora of heterogeneous nucleation sites to enable precipitation. The panelists noted that standard laboratory environments and simulations should also contain sufficiently representative types and amounts of nucleation sites unless extreme cleanliness is practiced. Therefore, although these sites are the necessary first step in forming solid species that may affect ECCS performance, they exist naturally in both laboratory and post-LOCA environments.

Both ANL (Ref. 52) and Westinghouse (Ref. 37) conducted tests with increased concentrations of nucleation sites to examine the effects on solid species formation. ANL added alumina nanoparticles to two tests to determine whether they affected the solubility of the solution and subsequently the measured head loss of any precipitates that formed. The tests were run for approximately 6 days after the addition of the nanoparticles to allow ample time for precipitation. No significant effects were observed on either head loss or solution solubility as a result of the addition of the alumina nanoparticles. Westinghouse also performed tests in which stainless steel powder was added to aluminum-containing solutions to determine whether additional nucleation sites encouraged aluminum oxyhydroxide precipitation during 30-day solubility testing. These additional nucleation sites did not initiate precipitate formation. These results substantiate that the absence of precipitation was not because of a lack of nucleation sites within the test solution.

Conclusion

Particulate nucleation sites must exist for precipitation to occur. However, a sufficient number of nucleation sites will exist in most environments except those that are extremely clean. Special measures are required to achieve a level of cleanliness that would significantly reduce the number of nucleation sites to a level that could affect precipitation. Post-LOCA containment environments, standard laboratory test environments, and scaled-strainer testing environments should contain sufficient nucleation sites to enable precipitation. Placing additional nucleation sites within test environments was not observed to significantly affect either precipitation or head loss induced by aluminum precipitates. Thus, differences in the types and concentrations of nucleation sites between testing and the actual post-LOCA environments are not expected to affect precipitation, and this issue has been addressed. Therefore, no further research on this issue is required.

4.5 Coprecipitation

Description and Possible Implications

Coprecipitation occurs when a normally soluble ion becomes either included or occluded into the crystalline structure of a particle of insoluble material. Precipitation of one species could lead to increased precipitation of another species (which, if taken separately, are each below their solubility limit). Thus, more solid species could form, which could lead to a greater

concentration of chemical precipitates at the sump strainers or downstream of the strainers. Additionally, the species that form could differ in size from those observed in the ICET tests (i.e., 1 to 100 microns) such that they affect the head loss at the sump strainer more significantly.

Discussion

In the context of this evaluation, precipitation is the creation of small (submicrometer size) particles suspended within the ECCS coolant. Precipitation occurs when the solubility of a specific solid phase is exceeded in solution. Coprecipitation occurs when a normally soluble ion becomes either included or occluded into the crystalline structure of the insoluble material.

In NUREG-1918 (Ref. 2), the PIRT panelists disagreed about the significance of this phenomenon. Some panelists believed that coprecipitation would not likely be significant since leaching of nonmetallic materials would occur over a long period of time. However, others believed that it is not possible to accurately predict coprecipitation since it is not a thermodynamic property and the post-LOCA containment environment is so complex.

NUREG/CR-6988 (Ref. 11) evaluated the coprecipitation of various materials in more detail. Painted surfaces release organic compounds slowly over time. The evaluation of coatings in NUREG/CR-6988 is based, in part, on testing performed by the National Sanitation Foundation (NSF) (Refs. 29, 30, 56). The NSF tests materials to be used in potable water systems for leaching of different compounds. Testing of epoxy coatings used in potable water systems, typical of the DBA-qualified type used in nuclear power plants (NPPs), indicates that very low levels of leached organic compounds would be expected. The water soluble organic species that are formed from the compounds require sufficient time to form. Meanwhile, these compounds would undergo radiolysis in the reactor core and break down to carbon dioxide. As a result, the water soluble organic species are not expected to contribute significantly to coprecipitation. Other aspects of organic material impacts on chemical effects are evaluated in Section 6 of this report.

Aluminum and iron species are also expected to be present in the post-LOCA environment. However, both of these species have very low solubility for the long-term pH ranges under consideration (near 7) for most plants. Thus, coprecipitation effects would not significantly affect the concentration of precipitates that form from these species. At higher pH levels, which are possible (i.e., 9.5), aluminum solubility increases. However, the WCAP-16530-NP-A (Ref. 3) chemical model already assumes that all aluminum precipitates. This eliminates the concern that coprecipitation of aluminum could create additional debris material.

WCAP-16530-NP-A evaluated another aspect of this phenomenon—synergistic interactions. In the WCAP report, the PWROG responded to a question about possible synergistic effects (Ref. 15). In its response, the PWROG stated that material interactions were considered in the development of the chemical model, which included key interactions. The synergistic effects of material combinations overwhelmingly tend to reduce material release. Thus, a decision not to perform testing on material combinations is conservative. The following section discusses key material interactions and how the WCAP-16530-NP-A chemical model addresses them.

(1) Precipitation Reactions

The chemical effect of most significance is the combination of dissolved species to create chemical precipitates (solids) that could potentially increase sump screen head loss. Based on the chemical composition of the containment materials and coolant additives, the predominant

classes of precipitates expected would be metal hydroxides and oxyhydroxides, aluminum silicates, and metal phosphates (for plants using TSP buffering). Based on the results from the ICET program (Ref. 14), the PWROG testing to support WCAP-16530-NP-A, and NUREG/CR-6873, "Corrosion Rate Measurements and Chemical Speciation of Corrosion Products Using Thermodynamic Modeling of Debris Components to Support GSI-191," issued April 2005 (Ref. 57), the specific precipitates expected to predominate would be aluminum oxyhydroxide, sodium aluminum silicate, and calcium phosphate.

The WCAP chemical model assumes that all dissolved aluminum precipitates as either sodium aluminum silicate or aluminum oxyhydroxide (AIOOH). All dissolved silicon is assumed to precipitate as sodium aluminum silicate. For plants using TSP buffering, all calcium is assumed to precipitate as calcium phosphate. The results of the ICET program (Ref. 14) and other testing (Refs. 58, 59, 60) showed that some fraction of the dissolved species does not precipitate but remains in solution such that head loss is not affected. Thus, the assumption of complete precipitation is conservative.

In practice, some fraction of the available aluminosilicates would precipitate with other cations rather than sodium (e.g., calcium aluminum silicate). However, since all of the aluminum is assumed to precipitate (i.e., as either sodium aluminosilicates or AIOOH), formation of other metal aluminosilicates does not significantly affect the total precipitate concentration.

In addition, metals present in solution, other than Al and Ca, may precipitate as phosphates or hydroxides (e.g., zinc phosphate or iron hydroxide). However, based on the results of the ICET and the PWROG programs, the concentration of other dissolved metals is less than 1 percent of the concentration of the predominant metals that are currently present within the plants (aluminum and calcium). Thus, the net effect of ignoring these interactions is less than 1 percent. The aluminum precipitates that are assumed to form, and are used in head loss testing, are considered conservative for determining head loss effects.

(2) Common Ion Effect

For any chemical reaction, the reaction rate is dependent on the concentration of the reacting materials and the resulting products, according to LeChatlier's Principle. As the concentration of the reaction products increases, the reaction slows. This is true regardless of whether the reaction product actually comes from the reaction of interest or is introduced from another source. In practice, for the dissolution of post-LOCA debris, the rate of dissolution depends on the concentration of the dissolved species in the containment pool fluid, irrespective of the source. In cases in which an element of interest is released from more than one material, the dissolution rates would be interdependent. For example, calcium may be released from dissolution of calcium silicate, concrete, and mineral wools. As a consequence, the release rate of calcium from the individual materials is slower in the presence of the other materials than it would be if a single material were to be present. This is true in both the short and long term. Therefore, single-effects testing, as in the WCAP report, should conservatively account for this effect. It is also noted, based on staff observations of chemical effects head loss tests at the various vendor facilities, the tests using the WCAP chemical model results are more conservative, when compared tests that rely on natural corrosion of suspended coupons. The tests with suspended compounds may exhibit the common ion effect.

(3) Loss because of Precipitation

As a corollary to the common ion effect, the rate of dissolution reactions may increase if a dissolved reaction product combines with other elements or compounds in solution and precipitates as a solid (i.e., coprecipitation). For example, loss of aluminum because of precipitation as sodium aluminum silicate would tend to increase the dissolution rate of Kaowool and other materials containing aluminum silicate. This effect is not significant during the beginning of the post-LOCA period when rapid material release occurs.

Ion loss due to precipitation is expected to have the largest effects later on the post-LOCA period and on the dissolution rates of calcium-bearing materials in the presence of TSP because calcium phosphate precipitation is relatively rapid. However, because of the high net release rates for calcium used by the WCAP-16530-NP-A chemical model (as based on single effects testing), it is not expected that the common ion effect will result in significantly higher release rates. In fact, the net dissolution rate of these materials as predicted by the WCAP model is in excellent agreement with the results from the ICET program and other published data. Therefore, it is not necessary to consider the common ion effect as part of the WCAP model as its inclusion would not be expected to substantially alter the predicted chemical precipitant concentrations.

(4) Silicate Inhibition of Corrosion

Silicate is a well-known inhibitor of corrosion of most metals. Silicate inhibition occurs from formation of insoluble metal silicates on the metal surface. Although there is a significant source of silicate from dissolution of silicate insulation materials, the baseline chemical model did not include this effect. Of most concern for containment materials is aluminum corrosion. Omission of silicate inhibition of aluminum corrosion introduces additional conservatism in the evaluation. However, licensees with high silicate loadings have the option to consider inclusion of silicate inhibition if supporting data are available from plant-specific testing performed outside of the scope of the work reported in WCAP-16530-NP-A. .

(5) Effects of Dissolved Metals on Corrosion

Dissolved metals, such as copper, may enhance the rate of corrosion of more active metals because of the formation of local galvanic cells on the metal surface. For containment materials, this effect would potentially be most significant for aluminum in the presence of dissolved copper (Section 3.8 also evaluates dissolved Cu). This galvanic effect would not apply for corrosion of nonsubmerged aluminum, and most aluminum is above the water level and not submerged. This mechanism would be expected to be most significant later in the post-accident phase when minor amounts of copper may be present and rapid aluminum corrosion resulting from extremes in temperature and pH has ceased. However, under these conditions, aluminum would be less susceptible to corrosion because of the more neutral pH, lower temperature, and the effect of silicate inhibition. Additionally, based on results from the ICET program and data reported in the literature, the release rate of more noble metals, such as copper, is expected to be low under post-accident containment conditions. On the basis of the above discussion, the effect of dissolved active metals on corrosion is judged to be insignificant.

Conclusion

As discussed above, a net increase in the solids quantity caused by coprecipitation or related synergistic interactions is not expected. A significant quantity of organic material leaching from

the containment coatings is also not expected. Organics which leach out will do so over time and will be broken down by radiolysis in the reactor core into carbon dioxide. Therefore, organics are not expected to contribute significantly to coprecipitation. The WCAP-16530-NP-A chemical model, which the staff accepted, also conservatively predicts precipitation of dissolved aluminum. Therefore, consideration of synergistic interactions would have no effect on Al precipitation for plants adapting the WCAP methodology.

Integrated chemical effects head loss tests that either used an ICET type environment or were based on the WCAP 16530-NP-A chemical model already account for potential effects due to co-precipitation as a result of the conservative types and concentrations of chemical species in these tests. Further, the chemical sources are all present in the test rig at the beginning of the tests and are not prevented from interacting with each other such that co-precipitation can occur naturally. Therefore, any co-precipitation that occurs is accounted for in the test results. As a result of these considerations, no additional research related to this issue is required.

5. Agglomeration and Settling: Chemical Effects

5.1 Inorganic Agglomeration

Description and Possible Implications

Inorganic agglomeration is the formation of larger clumps of smaller particulates. This phenomenon depends upon the pH of the point of zero charge (PZC) of the species and the ionic strength (the higher the ionic strength, the smaller the distance for agglomeration) of the fluid. This phenomenon is sensitive to many factors, including particle shape factors, and maximum particle size. Inorganic agglomeration of small particles into larger sized particulates could degrade strainer performance.

Discussion²

Section 9.1 of NUREG/CR-6988 (Ref. 11) partially evaluated this phenomenon. Inorganic agglomeration denotes the physical-chemical interactions between established solid particles within the suspending fluid. In the context of this evaluation, inorganic agglomeration refers to the potential clumping of individual inorganic solid particles of corrosion products, latent debris, and insulation debris. Particles of opposite electrical charge may coagulate to form macroscopic precipitates. This electrostatic agglomeration occurs when the pH of the fluid is between the PZC of the different particles. For agglomeration to affect ECCS performance, it would be necessary to form particles of just the right size to fill the gaps in the fiber debris mats forming on the strainer surfaces. If the agglomerated particles are relatively large and dense, they will sink to the containment floor; if they are very small and transportable to the sump screen, they will pass through the fiber mat.

The ICET testing (Ref. 14) included the appropriate ranges of the parameters affecting this phenomenon, such as types of containment materials, solution pH, and solution buffering chemicals. In addition to the ICET testing, site-specific chemical effects head loss testing performed by licensees has spanned the applicable ranges of many of these parameters. If any agglomeration occurred during the licensee tests, it would be demonstrated in the test results, even if there were no specified criteria to monitor for it.

Many licensees already assume that 100 percent of the solids will transport and do not credit settling. Applicable staff guidance documents for head loss testing (Refs. 13, 38) state that licensees should discuss in the GL 2004-02 response whether the head loss testing required debris agitation or whether near field settlement was credited for the testing. If agitation was used, the licensee should document to what degree it was successful (i.e., the percentage of debris reaching the strainer). If near field settlement was credited, the debris characteristics, preparation, and introduction become more critical. Licensees should verify that turbulence within the test facility does not significantly affect debris bed formation and that debris transport during the test was representative of what would occur in the plant. As noted in Section 5.2 of this report, licensees have generally not attempted to credit debris settlement.

Head loss testing at ANL (Ref. 52) with chemical precipitates considered representative of those that would form from NUKON® and Cal-Sil insulation in a TSP-buffered containment pool (i.e., ICET-3 type environment) showed that calcium precipitates can agglomerate and will settle

² Note that the presence of organic materials can also affect inorganic agglomeration. These interactions are addressed in Section 6.2.

more quickly than nonagglomerated precipitates. The testing also showed that the agglomeration occurs more readily in low flow areas (i.e., velocities in the range of 0.01 feet per second (fps)). On the basis of a review of licensee submittals, the staff notes that all strainer approach velocities are less than approximately 0.022 fps and most are less than 0.01 fps.

Other tests by ANL (Ref. 52) and Los Alamos National Laboratory (LANL) (Ref. 12) in an ICET-1 type environment with NUKON® insulation, NaOH as the buffer, and a source of aluminum demonstrated that aluminum-based precipitates can be very effective in producing high head losses. The behavior of these aluminum-based precipitates and the potential for agglomeration is more complex and variable than the calcium precipitates (i.e., behavior is a function of pH, aluminum concentration, temperature, and other factors) (Refs. 8, 9, 10). The aluminum precipitates remain small (in the nanosize range) even with agglomeration and are therefore readily transported to the sump strainer such that settling is not expected. Therefore, the effects of any agglomeration of aluminum-based precipitates, while not explicitly measured, are sufficiently and conservatively addressed within licensee specific head loss testing.

Conclusion

NRC-sponsored testing (Refs. 12, 14, 52), staff guidance (Refs. 13, 38) and site-specific testing by licensees have addressed this phenomenon. These tests included representative or conservative variations in pH buffering systems, latent debris, coating debris, insulation debris, and chemical reaction byproducts. Testing has demonstrated that increases in the amount of inorganic agglomeration would increase the likelihood of settling of calcium-based precipitates, but is not expected to have a significant effect on settling of aluminum-based precipitates. However, since most licensees do not credit debris settling, most licensee testing protocols are representative or conservative.

For testing that credits settling, the staff has specified more stringent chemical precipitate properties and the validation that flow streams in the testing are prototypical (Refs 13, 38). This additional guidance is required to ensure that the precipitate used in these tests settle no more rapidly than would be expected in the projected plant environment. Therefore, the potential for debris settling during strainer head loss testing is adequately controlled to represent plant conditions, and no additional investigation is required.

5.2 Deposition and Settling

Description and Possible Implications

Chemical products formed in the post-LOCA containment environment could either settle within the containment pool or be deposited on other surfaces. Chemical species which attach to or coat particulate debris may enhance settling. Examples are aluminum coating on NUKON® fiber shifting the PZC or formation of a hydrophobic organic coating. This could result in less particulate debris and chemical product transporting to the sump screen and either accumulating on or passing through it. The possible implications of this issue are that the chemical precipitates added to the plant-specific chemical effects tests could result in increased settling during the tests compared to actual plant conditions.

Discussion

The PIRT panel raised the issue that some chemical products may either settle within containment pools or enhance settling of other debris within the containment pools. Either of

these issues would reduce the amount of debris available for transport to the strainer and thus be a beneficial phenomenon. That is, any excessive settling would be expected to reduce head loss across the strainer and downstream effects in the plant. Licensees have generally not attempted to credit this phenomenon during testing.

The staff expects licensees to conduct head loss testing using procedures that provide either realistic or conservative debris transport to the test strainer. The majority of tests utilizes stirring to enhance the transport of all types of debris to the strainer. Testing that uses stirring is reviewed to ensure that the stirring provides conservative transport of debris during testing. For testing that uses stirring, it is not likely that enhanced settling would result in a significant reduction in the amount of debris transported to the strainer. Therefore, these test results should be conservative compared to the actual plant conditions with respect to this issue.

Some vendors do credit near-field settlement of debris during testing. The staff evaluates the methodology that the vendor uses to compare the plant-flow parameters to those in the test flume. The purpose of the evaluation is to ensure that the transport that occurs during testing is representative or conservative with respect to that expected in the plant. If the addition of chemicals to the test resulted in enhanced settling for this type of test, it is possible that a significant portion of debris that would not normally settle could settle before reaching the strainer. Settling is more likely during a test than in the plant because the concentration of debris is much higher in most test tanks. However, strainer vendors that allow settling require either a minimum number of pool turnovers or require that head loss be stable after the nonchemical debris is added and before the addition of the chemical debris. Either of these requirements provides adequate assurance that a majority of the transportable debris will reach the strainer before the addition of chemical debris. Therefore, a significant reduction in debris transport as a result of enhanced settling is not expected to occur for tests that credit near-field settling. The staff has issued industry guidance which addresses strainer testing that credits near-field settlement and discusses the issues cited above (Ref. 38).

The NRC staff reviews each licensee's test program as part of the GL 2004-02 closeout process. This review includes the evaluation of debris transport in the test flume. The review is intended to ensure that testing was conducted in a manner that produces representative or conservative debris transport to the strainer. For licensees that do not credit reduced transport, tested head loss values are not reduced, and the application of these values would be conservative if the settling phenomenon actually occurred in the plant.

One mechanism of chemically induced settling that could result in higher head loss would be if fibrous debris were to settle, thereby reducing transport of the fiber. The result could be a higher particulate to fiber ratio, or thin bed, in the plant. However, staff guidance (Ref. 38) recommends that plants test for a thin bed using a high particulate to fiber ratio as part of their strainer testing program. The staff put this guidance in place because reduced fiber amounts on the strainer could be caused by a phenomenon other than enhanced settling. Because thin-bed testing purposely searches for the maximum head loss caused by a debris bed consisting of a high particulate to fiber ratio, the potential for chemically enhanced settling of fibrous debris is not a concern.

Although settling downstream of the strainer has generally not been quantified, it has been postulated that settling could occur in the reactor lower plenum. The postulated settling was noted as a potential positive because any debris that settles in this area would not transport to the reactor core. Any enhanced settling in this area would reduce the amount of debris

available to enter the core and add to head loss at the fuel inlet or at the fuel spacer grids. Therefore, enhanced settling would be beneficial.

Conclusion

Because licensees have generally not credited enhanced settling of debris during debris generation and transport evaluations or strainer testing, and they have tested for thin-bed head losses, the possibility of enhanced, chemically induced settling has generally been conservatively addressed. The sole phenomenon that could significantly affect head loss evaluations would occur during strainer testing that credits near-field settling. However, chemicals are not added to head loss tests until almost all of the non-chemical debris has been transported to the strainer and a stable head loss resulting from non-chemical debris has been attained. Therefore, enhanced settling should also not adversely affect these tests. Therefore, licensees' evaluations of the acceptability of their ECCS also conservatively address chemically induced settling.

5.3 Quiescent Settling of Precipitate

Description and Possible Implications

Quiescent flow regions within the containment pool promote settling. The low flow rate within most of the containment pool also allows larger size, more stable particles and precipitates to form, which promotes settling. Settling of nonchemical debris and precipitate could be beneficial with respect to the pressure drop across the sump strainer.

Discussion

Some settlement of chemical precipitates may occur, particularly in regions with quiescent flow. The peer review panel considered this to be a potentially beneficial effect because precipitates that settle in the containment pool are not transported to the strainer surface and will not contribute to pressure drop across the strainer debris bed. Most vendor head loss tests use mechanical or hydraulic agitation to ensure that chemical precipitates and other test debris are transported to the test strainer (as discussed in Section 5.2 of this report). If a vendor test method allows for near-field settlement of debris, including chemical precipitate, the NRC staff requires that flow parameters in the test be conservative or representative of the plant, such that precipitate used during testing will not settle more rapidly than precipitate that is formed following a LOCA. See Sections 5.1 and 5.2 for additional discussion associated with testing that credits near-field settlement. Also, as discussed in Section 5.2, any settling in quiescent areas of the containment pool would reduce the amount of debris available to enter the core and contribute to head loss at the fuel inlet or at the fuel spacer grids. Therefore, enhanced settling would be beneficial to downstream effects as well.

Conclusion

As discussed in Sections 5.1 and 5.2, most sump strainer head loss tests are designed to ensure that all precipitate is transported to the test strainer. For tests that are designed to credit near-field debris settlement, the NRC staff expects licensees to control test flow parameters to prevent precipitates from settling prematurely during testing. Since settlement of precipitates within the containment pool is potentially beneficial to ECCS performance, no further action is needed to investigate this item.

5.4 Transport Phenomena: Precipitation and Coprecipitation

Description and Possible Implications

Precipitation or coprecipitation and ripening of solid species within the containment pool would create solid species which are less likely to transport. Decreased transportability will result in less product migrating to or through the sump screen.

Discussion

As summarized in Section 4.5, coprecipitation occurs when a normally soluble ion becomes either included or occluded into the crystalline structure of a particle of insoluble material. Precipitation of one species could lead to increased precipitation of another species below its individual solubility limit. Hence, more solid species could form, which could lead to a greater concentration of chemical precipitates at the sump strainers or downstream of the strainers. Section 4.5 of this report addresses the effects of precipitation and coprecipitation on head loss and downstream effects.

This particular issue focuses solely on the effect of precipitation (or coprecipitation) and ripening on solid species transport. Precipitation and ripening of solid species, in general, results in larger solids through aging and agglomeration. This mechanism would increase the settling rates of both chemical solids and debris within the containment pool as discussed in Sections 5.2 and 5.3 above. Thus, these phenomena would reduce the amount of debris that is transported to the strainer, which would be expected to reduce both head loss across the strainer and downstream effects in the plant. However, NRC guidance (Refs. 13, 38) for conducting head loss testing, in general, does not allow for crediting settling through this mechanism, as discussed in more detail in Sections 5.1 and 5.2 of this report. For testing that credits settling, the staff has specified more stringent chemical precipitate properties and the validation that flow streams in the testing are prototypical (Refs. 13, 38). This additional guidance is required to ensure that the precipitate used in these tests settle no more rapidly than would be expected in the projected plant environment. These conservative positions eliminate the need to more fully address this complex issue to make more realistic predictions of solid species transport.

Conclusion

Precipitation generally will inhibit solid species transportation and reduces the solid species concentration both at the containment sump strainers and downstream of the strainer. It is also a complex phenomenon that is affected by plant-specific conditions such as pH and debris type which makes it difficult to realistically evaluate its significance on a generic basis. However, the NRC guidance (Refs. 13, 38) for conducting head loss testing does not generally allow for crediting settling through this mechanism. In addition, most licensees do not credit settling through this phenomenon to reduce the debris that must be considered when evaluating sump strainer head loss and downstream effects. For licensees that credit settling, the staff has specified the use of more stringent chemical precipitate properties and the validation that flow streams in the testing are prototypical in the plant-specific testing (Refs. 13, 38) to ensure representative or conservative settling rates. Hence, no additional research or evaluation is required to address this issue.

6. Organics and Coatings

6.1 Break Proximity to Organic Sources

Description and Possible Implications

The pipe break location plays an important role in debris generation. If the break occurs in close proximity to organic sources, it could introduce a significant amount of organic materials into the containment pool. Organic sources could then affect the nature, properties, and quantities of chemical byproducts that form in the post-LOCA containment environment. The scenario evaluated by the PIRT considered failure or leakage of oil and other organics from either the RCP oil collection tanks or lube oil systems resulting from LOCA-induced damage. If the pipe break occurs in close proximity to the organic sources, up to approximately 250 gallons of oil may be released to the containment pool (Ref. 2). If this should occur, head loss and downstream effects may be altered, either beneficially or negatively, by these organic materials.

Discussion

During normal operation, potential organic sources may include coatings, insulation debris (e.g., fiberglass and Cal-Sil), RCP motor oil, and greases. The quantity of organic material from coating dissolution and leaching is expected to be very small, as discussed in Section 6.4 of this report. The ICET experiments included any organics that leached from fiberglass and Cal-Sil insulation. Both the fiberglass and Cal-Sil were heat treated before the experiments to simulate temperature profiles existing in service and some of the organic resins were representatively baked off. However, dissolved organic materials were likely present in the ICET solution based on the pigmented solution color (yellowish to rust colored) observed in each test (Ref. 14). The organics were attributed to decomposition products of the phenol formaldehyde resin-based polymer that coats the fiberglass insulation tested in the ICET program. ICET test 2 measured the total organic content. The baseline measurement at the onset of testing was 0.2 milligram per liter (mg/L), increasing to 7.3 mg/L by day 15, and then more slowly increasing to 7.9 mg/L by the end of the test at day 30 (Ref. 14). These measurements show that the quantity of organic material from insulation debris is relatively small. These measurements were not conducted for the other ICET tests.

Because ICET considered organics from fiberglass and Cal-Sil insulation, the scenario evaluated in the PIRT considered the overflow, failure, or leakage of oil and other organics from either the RCP oil collection tanks or lube oil systems. This scenario was not evaluated in the ICET testing. The oil collection tanks are the most likely to fail due to a pipe break in close proximity because they are fabricated from approximately ¼ inch carbon steel. However, these tanks only typically contain a few gallons of residual oil. The RCP lube oil systems contain bigger sources of oil, but these systems are less likely to fail unless there is direct impact from the piping failure that initiates the LOCA sequence. The panelists agreed that a relatively large release of oil cause by an RCP oil system failure may affect containment pool chemistry. The oil could alter metallic corrosion, precipitation, or coprecipitation (see Section 4.5 of this report); agglomeration (see Section 6.2); or complexation (see Section 6.3); or some combination of all of these.

However, one licensee evaluated the impact of oils and greases on ECCS strainer head loss. The licensee conducted a 30-day integrated chemical effects strainer flow test using the Vuez large Eliza apparatus (Ref. 61), which is similar to the ICET tank used in the NUREG/CR-6914 testing. The volume of oil representing the loss of oil from one RCP motor was added to the

test loop, along with a quantity of grease representing exposed surface areas of the polar crane components. This resulted in an organic concentration of approximately 550 ppm in the test setup, based on the average minimum containment pool volume of 60,809 ft³. (Using the nominal containment pool volume of 75,123 ft³ would result in a concentration of 435 ppm.) Note that this concentration is nearly an order of magnitude greater than the organic concentration present in ICET #2.

This licensee's main ECCS strainer, at 900 square feet (ft²), is one of the smaller replacement strainers for the PWRs. The total surface area for the main strainer plus the backup strainer is approximately 3,000 ft², but just the main strainer area was modeled for this test (a more typical replacement strainer is at least 3,000 ft²). This assumption results in a potential organic material concentrations that is higher than would be present for larger strainers, assuming the volume of one RCP motor, and is therefore considered very conservative.

The test sequence began with aluminum, galvanized steel, copper, and unpainted carbon steel coupons placed in the tank to allow natural corrosion product formation instead of using the chemical surrogates recommended in WCAP-16530-NP-A. The post-LOCA debris mixture (fibers + particulates) was then introduced as a slurry in the test apparatus in front of the strainer pockets once recirculation flow was established. Once the head loss reached a steady state value, the organic grease-oil mixture was added. The mixture was observed to emulsify within minutes after it was added to the test flume with no obvious indications that it had been added. The licensee also noted that the head loss did not change due to the addition of this organic mixture.

The licensee's post-test observations of the test tank pool identified bubbles of petroleum-based material on the pool water surface along with a slight film on the hard surfaces of the test fixture. It was noted by the licensee's observer that this observation was made after the test had ended and there was no recirculation flow in the test loop. The petroleum material appeared to be coated with very fine debris from the test tank. The petroleum material was also visible on the galvanized steel panels, again covered by very fine debris. Following the completion of the test, the test tank was drained and the test strainer section was removed from the tank. The surface of the debris bed inside the strainer pockets showed some evidence of a slight petroleum material sheen.

Based on these observations, the organic materials did not appear to significantly impact the head loss measured in this test. The organics may affect material transport (Section 6.2), but because they were introduced after the debris mixture was circulated through the screen for multiple cycles such that settling is precluded, the effect on transport in these tests is insignificant. The observation that the oil and grease adhered to the solid surfaces could potentially reduce the release rate of the affected metals (Ref. 61) if present during an actual LOCA event. Therefore, staff does not expect these materials will significantly degrade ECCS performance more detrimentally than has been evaluated in the plant-specific head loss testing.

Conclusion

The quantity of organic material from coating leachate, insulation debris, RCP motor oil, and lubricating greases is expected to be relatively small. The ICET experiment (Ref. 14) did address the effects of organics stemming from fiberglass and Cal-Sil insulation. Additionally, one of the licensees evaluated the effects of conservative amounts of oil and grease on the measured head loss. Based on the observations by the licensee in this test, staff does not expect the impact of oil and grease to significantly degrade ECCS performance more

detrimentally than has been evaluated in the plant-specific head loss testing. Therefore, no additional research is needed to address this issue.

6.2 Organic Agglomeration

Description and Possible Implications

Organic agglomeration is the process of small organic colloidal particles (1 to 100 nanometers in size) joining together, or coagulating, to form larger particles and precipitates. Coagulated particles can collect on sump strainers, decreasing ECCS flow; they could also collect on other wetted surfaces, such as walls or structural steel, and decrease the debris loading on the sump screen. Hence, head losses and downstream effects could differ from those evaluated during plant-specific testing.

Discussion

Section 9.2 of NUREG/CR-6988 (Ref. 11) initially evaluated the phenomenon of organic agglomeration. The issues are similar, in some regards, to those associated with inorganic agglomeration discussed previously in Section 5.1 of this report. As discussed in NUREG/CR-6988, the primary sources of organic compounds that may be a concern in a post-LOCA environment are from lubricating oils and greases on equipment (see Section 6.1 of this report) and decomposition of protective coatings (see Section 6.4). These organic compounds, like the inorganic particles discussed in Section 5.1, are electrically charged and may act as either coagulants, and promote agglomeration of colloidal particles, or as dispersants and cause the particles to disperse.

Organic agglomeration of colloidal solutions can occur by changing the pH (usually decreasing). The acid groups are protonated (i.e., the repulsive surface charge on the particles is overcome, and then the attractive Van Der Waal forces allow particles to agglomerate). This is a complex, but understood, process when the environment is controlled. Van der Waal forces are weaker at higher temperatures (near boiling point) than they are at room temperature. Hence, agglomeration is promoted at elevated temperatures.

Once organic molecules form, interaction between inorganic and organic species is possible. One possible phenomenon is that floating organic compounds in the containment fluid combine with inorganic particulates to form buoyant particulates. This interaction of dispersed organics with inorganic solids could decrease the density of the combined solids, thus making them more transportable to the suction strainer and increase the particulate loading on the strainers.

There has been some limited investigation of this phenomenon. As noted above in Section 6.1 of this report, one licensee performed an integrated chemical effects head loss test with a large quantity of organic material (i.e., RCP motor oil, grease and ethylene glycol). The volume of oil representing the loss of motor oil from one RCP motor was added to the test loop, along with a quantity of grease representing exposed surface areas of the polar crane components. The grease was added by coating a steel panel and suspending it into the test loop. Ethylene glycol was also added to simulate the concentration that would be present in the containment pool due to a ruptured ice coolant pipe. The debris mixture (fibers + particulates) was introduced as a slurry into the test loop at the beginning of the test. The head loss due to this debris was then allowed to stabilize. The head loss was stable after approximately 45 minutes. Next the ethylene glycol and motor oil were slowly poured in. There was no indicated change in head loss due to the addition of either of these organic liquids.

At the conclusion of the test, the licensee observed bubbles of petroleum-based material on the pool surfaces in the test tank, along with a slight oil film. The petroleum material appeared to be coated with very fine debris from the test tank. The bubbles were also visible on the galvanized steel test coupons, again covered by very fine debris. Later, when the test tank was being drained for disassembly and cleaning, the licensee observed that what appeared to be bubbles on the surface of the galvanized steel test coupons was actually petroleum material captured on the coupon. It was also noted that the location of the petroleum product on the galvanized steel test coupons was only on the upper quarter of the plates. When the water level decreased sufficiently to allow the buoyancy of the petroleum material to break through the debris layer, the petroleum material rose to the surface. In some cases, the petroleum material brought part of the debris with it. Some petroleum material/oil bubbles were also observed on the debris fiber bed after the test. None of the oil seemed to have penetrated into the fiber bed. However, the fiber bed was not dissected for a more detailed evaluation. This petroleum material was not observed on the other test coupons (aluminum, copper, zinc, carbon steel, concrete, etc) in the submerged portion of the test tank during draining and subsequent removal from the test tank for drying.

These observations imply that the organic materials interacted with the test coupons, insulation debris, and possibly inorganic chemical species present during the test and may have had some effects on agglomeration and transport, or settling of the debris and precipitates that were not captured on the sump strainer screen before the organic materials were introduced. The total head loss due to all debris and chemical source terms was measured during the test. However, the head loss did not change as a result of the addition of these organic materials.

Another evaluation of the effects of organic material on agglomeration of aluminum precipitates is contained in NUREG/CR 6915 (Ref. 12). The NUREG stated that as little as 0.0125 mg/L (0.12 ppm) of fulvic acid is sufficient to increase the solubility of aluminum and prevent formation of aluminum precipitate. Fulvic acid is an organic acid found in soil from water leaching through organic material such as humus. While the presence of fulvic acid is unlikely in the containment pool, there are other weak carboxylic organic acids formed from the degradation of the RCP motor oil or other lubricants and greases that would have the same effect. As discussed in Section 6.1, small concentrations of these organics may be present in containment, especially if there is a rupture or leak of the oil collection system that is either preexisting or induced by the LOCA. Oils continually react with atmospheric oxygen to produce organic oxidation products that are acidic in nature. At ambient temperature, this reaction is very slow and has little effect upon oil conditions. The Acid Number (AN) is the measurement of weak carboxyl acid formation in the oil. The higher the AN, the more acidic constituents are present in the oil. After 1 or 2 operating cycles it is not unusual to have the acid number increase from about 0.4 to about 1 indicating an increase in the quantity of organic acids.³

Therefore, in an unlikely situation where the LOCA causes a release of the RCP motor oil, it can have both positive and adverse affects. There will be a large increase of organic material (oil) in the containment pool which may interact with other test debris to affect agglomeration and transportation to the sump strainer, but there will also be a small increase in organic acids, which could prevent aluminum ions from precipitating. The net effect, as indicated by the head loss tests discussed above, is that the presence of RCP oil may have some impact on organic/inorganic agglomeration and transport of fine debris, but it is not expected to significantly increase sump strainer screen head loss. The licensee head loss testing is

³ Verbal communication with an oil test laboratory, Herguth Laboratories.

conducted such that fine debris remains suspended during the test and organic materials would not result in greater transport of these fine materials during an actual LOCA. In addition, other conservatisms used as the basis of licensee head loss testing accounts for the other possible detrimental effects due to organic materials that have been discussed.

Conclusion

The quantity of organic material available is plant-specific and pipe-break specific. A plant with very little unqualified coatings or a pipe break that would not result in a release of RCP oil or ethylene glycol would have very low levels of organic compounds available. The observations by one licensee in their head loss tests suggest that the overall impact of organic material from coatings and lubricants did not significantly affect head loss. While organic material may affect debris agglomeration, debris bed formation and head loss during a LOCA, the conservative nature of the head loss testing ensures that any detrimental effects that may result from organic materials are appropriately accounted for within the results. It should also be noted that many licensees do not credit settling of debris and assume that 100 percent of the solids transport to the strainers therefore any organic/inorganic agglomeration that promotes settling of larger pieces is conservatively neglected. Therefore, no additional research is warranted.

6.3 Organic Complexation

Description and Possible Implications

Organic complexing agents act to inhibit agglomeration either by adsorption onto solid surfaces or by interaction in solution with metal ions. Organic surface complexation occurs if organic molecules (i.e., amines, acids, and heterocycles) adsorb on surfaces of ions or solids and inhibit the subsequent precipitation or growth of those species. The implications of organic complexation are counter to those associated with organic agglomeration. Organic complexation could reduce the effects associated with chemical precipitates and therefore may be beneficial to ECCS performance if this phenomenon is not credited or addressed during plant-specific testing.

Discussion

Complexation by organics arising from the decomposition of paints, plastics, and lubricants in the post-LOCA containment environment also might alter the distribution of the polyvalent activation products to the solid phases. The organic complexants are alcohols, simple organic acids, and perhaps aldehydes. None of these, however, are highly potent complexing agents, particularly at the neutral to alkaline pH of the post-LOCA coolant at which hydrolysis would be important (Ref. 11).

Organic complexation is expected to have limited influence because of low complexation strength compared with hydrolysis and the presence of calcium in the post-LOCA containment pool. The calcium ion (Ca^{2+}) is present in relatively high concentration in the coolant and possesses high propensity for organic complexation. Therefore, Ca^{2+} is a formidable competitor for any organic complexants and would serve to decrease their impact on redistribution of the polyvalent radioactive activation and limited fission products (Ref. 11). The Ca^{2+} also would occupy the organic complexants and prevent their surface complexation with fixed or less mobile inorganic solids (Ref. 11).

Organic complexation would effectively enhance the solubility limits of affected inorganic solids. Solid species may precipitate, but they remain relatively small in size (nanoscale) because of the inhibition caused by the adsorbed organics (Ref. 2). These species therefore are less likely to agglomerate or grow to macroscopic sizes that could result in head loss at the sump screen or lead to deleterious downstream effects. Therefore, if it were to occur, organic complexation would be beneficial to ECCS performance by reducing the effects associated with chemical precipitates.

Conclusion

Organic complexation is expected to have limited influence because of low complexation strength and the presence of calcium in the post-LOCA containment pool. However, if it were to occur, organic complexation may be beneficial to ECCS performance by enhancing solubility limits and reducing the effects associated with chemical precipitates. Therefore, no additional research is needed to address this issue.

6.4 Coating Dissolution and Leaching

Description and Possible Implications

Coatings existing within containment represent possible additional physical debris sources. Generally conservative guidance for considering the effects of physical coating debris is provided for the evaluation of ECCS performance. However, dissolution and leaching of coatings can impact the chemical effects that occur within, or are transported to, the ECCS cooling water. Both inorganic (e.g., zinc-based) and organic (e.g., epoxy-based) coatings exist within containment. One concern is that these coatings leach chemicals as a result of being submerged in the containment pool environment after the LOCA. Coatings may create additional chemical species (e.g., chlorides or organics) within the containment pool that could potentially increase sump screen head loss or promote more deleterious downstream effects.

Discussion

Coatings within the containment building are classified into two categories, qualified and unqualified. All qualified coatings within the ZOI from the break are assumed to fail as fine 10-micron particulates. Qualified coatings outside the ZOI are assumed to remain intact. Unless justified by the licensee, all unqualified coatings within containment are assumed to fail as 10-micron particulates. Therefore, from a coatings perspective, the industry is conservatively evaluating the physical effects associated with coating debris. However, chemical effects associated with the dissolution and leaching of coatings may create additional debris source terms.

NSF testing of epoxy coatings used in potable water systems, typical of the type qualified for use in nuclear power plants, indicate that very low levels of leached organic compounds would be expected in the post-LOCA environment. These tests were performed in accordance with NSF Standard 61 "Drinking Water System Components - Health Effects" (Ref. 56) in room temperature water (23 degrees C) at pH levels of 5, 8, and 10. Less than 1.0 ppm total organic compounds leached into solution under these conditions (Refs. 29, 30). Similar tests conducted at elevated temperature (60 degrees C) showed slightly greater than 1.0 ppm of organic compounds leached into solution. Negligible concentrations of inorganic compounds were measured under all conditions. While these tests were conducted at room temperature for a period of 24 hours, it is reasonable to conclude that the leaching of organic compounds from

epoxy coatings occurs slowly over a range of applicable pH values, even at the post-LOCA elevated temperatures over the 30-day mission time.

The nuclear industry has also performed testing and evaluation of coating dissolution within the post-LOCA environment. In support of WCAP-16530-NP-A, the PWROG evaluated chloride leaching from epoxy coatings. The PWROG estimated that the maximum chloride concentration in the containment pool leached from DBA-qualified epoxy coatings would be less than 8.6 ppm (Ref. 62). This calculation assumes that the submerged epoxy coating in the containment will leach up to 700 ppm of chlorides per kg of coatings. The Cl concentration is then divided by the minimum mass-volume of the smallest PWR containment sump to arrive at 8.6 ppm. These estimates are expected to be conservative because the assumed leachable chloride concentration bounds test results on leaching within qualified topcoats materials (Ref.16). This calculation demonstrates that coatings will have only a minor contribution to Cl levels. Unqualified coatings are judged to leach chlorides at a rate similar to the qualified epoxy coatings and would not be a significant source for additional chloride in the containment pool as discussed in Section 2.2.

The NRC has also sponsored research to evaluate the effects of coating dissolution from epoxy coatings. PNNL, in NUREG/CR-6988 (Ref. 11), estimated the mean organic concentration from paint leaching to be 1.87×10^{-3} M (~22 ppm) by considering the mean painted area and mean liquid volume of the containment pool. This estimate is conservative because it is based on the mean painted area within containment and assumes that all the coating area will be immersed during the LOCA.

However, unqualified coatings such as alkyds would be expected to break down in a post-LOCA environment. Alkyd coatings are considered to be the most susceptible type of unqualified coating used in nuclear power plants. An evaluation by Alion indicated that alkyds soften and release organic solvents when submerged under conditions similar to the post-LOCA PWR containment pool (i.e., 200 degrees F, pH buffered, and borated water) (Ref. 28). Alkyds are readily attacked by alkaline hydrolysis, also known as "saponification," which causes the polymer and cross-linking bonds to break.

A study by EPRI evaluated the different types and locations of DBA-unqualified coatings at nuclear power plants (Ref. 31). The study showed that many plants (i.e., 25 of the 27 plants that responded to the survey) do have some alkyd coatings. The quantity, however, varies greatly from 0 ft³ to 1.43 ft³ (Ref. 31). The upper value of 1.43 ft³ represents only approximately 2 percent of all the coatings in the containment. In addition, the survey data also show that a majority of the alkyd coatings are on components that are above the flood level and are therefore not as likely to undergo degradation due to immersion as reported by Alion, unless they failed or disbonded and were transported by containment spray to the containment pool.

Assuming that all 1.43 ft³ of alkyd coatings end up in the containment pool and break down completely as organic materials, approximately 23.5 ppm of organic material would be available in the water based on the average minimum containment pool volume of 60,809 ft³. This is a very conservative concentration because it assumes that the organic material is available at the beginning of the post-LOCA event and that all alkyd coating is fully immersed, and that these coatings break down completely as organic materials. In reality, the leaching process occurs over several days and most of the alkyds coating will be above the containment pool water level. Therefore, the actual organic concentration would be much less at any given time.

Therefore, 3 different estimates of leaching from epoxy coatings have been calculated based on testing and evaluations performed by NSF, the nuclear industry, and NRC-sponsored research. The estimates predict that between 1 to approximately 25 ppm of organic compounds could result from coatings leaching. Differences among these values result from the various assumptions made in the calculations, but all are intended to be conservative. Estimates of leaching from alkyd coatings demonstrate that these coatings contribute, at most, approximately 25 ppm of organic compounds. Therefore, less than 50 ppm of organic material from coatings is expected to present in the containment pool. As discussed previously in Section 6.1, organic concentrations resulting from the breakdown of insulation resins were approximately 10 ppm in the ICET testing. Further, the ICET testing added 100 ppm Cl to simulate cable breakdown. This concentration is significantly higher than the expected contribution due to leaching from coating materials. In addition, one licensee conducted head-loss testing with approximately 550 ppm of oil and grease. The maximum additional organic contribution from coatings does not significantly contribute to the organic concentrations that have been considered in these other tests.

In addition, studies have been conducted to investigate leaching and radiolysis of organics from containment coatings and iodine interactions with organics within containment during a LOCA (Ref. 63). These studies indicate that organics that are leached from the paints decompose as a result of the high dose rates expected in the reactor core during the post-LOCA period. Radiolysis will readily oxidize those organics as they pass through the reactor core to products that are more soluble in water (i.e., phenolics and carboxylic acids) and then eventually to CO₂ (Ref. 63). Based on ECCS recirculation rates, the complete decomposition of organics to CO₂ is expected within days. Therefore, decomposition will reduce any significance of organic compounds as the post-LOCA 30-day mission time progresses.

Conclusion

The NRC guidance in the area of coating evaluations (Ref. 35) conservatively considers the effects of physical coating debris. NSF testing of epoxy coatings used in potable water systems, typical of the type qualified for used in nuclear power plants, indicate very low levels of leached organic compounds. Industry-sponsored testing of qualified coatings supports the NSF results. Similarly, evaluations by the staff and PNNL expect a low concentration of leached organics from both qualified epoxy and unqualified coatings (i.e., mainly alkyds). Therefore, the quantity of organic material from coating dissolution and leaching is expected to be within the range considered in ICET and head-loss testing from one licensee. Further, those organics that are dissolved and pass through the reactor core will undergo radiolysis that is likely sufficient to fully decompose continually recirculating organics to CO₂ within days. Based on this evidence, leaching from coatings is not expected to have a significant impact on ECCS strainer performance and no additional research is required for this issue.

7. Chemical Effects on Downstream System Performance: Pumps, Heat Exchangers, Reactor Core

7.1 Emergency Core Cooling System Pump: Seal Abrasion and Erosion or Corrosion

Description and Possible Implications

Abrasive wearing of pump seals (e.g., magnetite—high volume or concentration of mild abrasive) creates additional materials that contribute to containment pool chemistry. In addition, chemical byproducts cause erosion or corrosion of pump internals, especially close-clearance components (e.g., bearings, wear rings, impellers). The possible implications of these phenomena are (1) additional particles could contribute to reactor core clogging, (2) particles could add additional sump screen loading, (3) particles could affect chemical species formation, and (4) pump performance degrades, possibly to the point of being inoperable.

Discussion

This evaluation is presented in four sub-topics in the order defined above

(1) Additional Particles Generated by Pump Wear Could Contribute to Reactor Core Clogging

The quantity of suspended debris that may be added to the containment pool as a result of pump wear and erosion is insignificant in comparison to the quantity of fiber, particulate, and chemical precipitates that are assumed to be present within the containment pool. This has been shown by the PWR licensees in their wear evaluations of ECCS pumps using the guidance in WCAP-16406-P-A. The wear evaluations show that wear would be negligible over the 30-day mission time of the component, thus contributing little to the debris mix. As an example, the maximum expected diametric wear in the wear-rings of a 10-stage safety injection pump is 40 mils. With a 6 in² wear area per ring, the total volume of material added to the containment pool by all 10 wear rings would be less than 2.5 in³. Pump seals would also not contribute significant quantities of debris to the containment pool because the volume of material in the wear surfaces of the seals is less than the volume of materials in the wear rings. With only 4 to 6 pumps circulating coolant from the containment pool, the quantity of metallic material added by the wear of all pump seals would be insignificant.

(2) Particles Could Add Additional Sump Screen Loading

As stated above, the quantity of suspended debris that may be added to the containment pool as a result of the wear and erosion of pump components exposed to the ECCS coolant is insignificant in comparison to the quantity of fiber, particulate, and chemical precipitates that are assumed to be present within the containment pool and evaluated by licensees to demonstrate that adequate head across the sump screen exists.

(3) Particles Could Affect Chemical Species Formation

As with issues (1) and (2), particulate generated by pump seal degradation or pump internal corrosion/erosion would not exist in sufficient quantities to significantly alter chemical species formation. Further, pump components exposed to the ECCS coolant are designed to be corrosion resistant; therefore, chemical contributions due to corrosion are expected to be

insignificant. Any abraded material (including pump seal material) would not chemically interact with other chemicals in the containment pool.

(4) Pump Performance Degrades, Possibly to the Point of Being Inoperable

Licensees of PWRs are required to demonstrate that their ECCS systems are capable of performing their design functions over the specified equipment mission time. All licensees have elected to apply the guidance in WCAP-16406-P-A for their downstream effect evaluations. WCAP-16406-P-A (Ref. 4) provides an acceptable method for determining the expected degradation in pump dynamic and hydraulic performance and pump seal wear using plant-specific debris loading and debris characteristics. Although this WCAP does not specifically address the effects of chemical products, the impact of chemical products on pump degradation is not expected to be significant as discussed in Section 4.3. The potential for these additional solid species to affect pump performance is indirectly addressed in WCAP-16406-P-A by evaluating components for wear and blockage using debris concentrations and abrasive properties that bound the effects of precipitates and spall that could be formed.

Conclusion

The quantity of abraded material from ECCS pumps is negligible when compared to the quantity of debris assumed to be in the containment pool from other sources. Therefore, these sources are not expected to affect reactor core clogging, sump screen loading, or chemical species formation. Additionally, licensee testing and evaluation of the effects of debris on pump performance evaluates conservative concentrations of debris that are harder and therefore potentially more detrimental to pump performance. Therefore, no further research on this issue is required.

7.2 Heat Exchanger: Deposition and Clogging

Description and Possible Implications

Solid species which form in the heat exchanger lead to surface deposition or clogging, or both, within close-packed heat exchanger tubes (5/8-inch in diameter). This could cause decreased flow through the heat exchanger core or diminished heat transfer between the ECCS and heat exchanger cooling water, or both. Diminished cooling of the ECCS water could ultimately decrease the capacity of the ECCS water to remove heat from the reactor core.

Discussion

The RHR heat exchanger tube diameter is sufficiently large that tube plugging within the mission time of the heat exchanger (30 days) is unlikely. However, deposits that precipitate as a result of cooling as they pass through the heat exchanger tubes may, with time, form on the tube inside surfaces and diminish heat transfer. Aluminum based precipitates are not expected to form immediately after the break because it will take some time for the chemicals to go into solution, reach the saturation limit, and begin to precipitate upon cooling. Other precipitates that could occur sooner, such as calcium phosphate precipitate, may be filtered by the debris bed on the sump strainer surface. As discussed in the PWROG response to WCAP-16793-NP RAIs, precipitates that pass downstream of the strainer are not expected to have sufficient shear strength to form a thick enough coating on the wall of the heat exchanger tubes to create a blockage in the heat exchanger under ECCS flow rates (Ref. 64). A thin film of calcium deposits was observed on the inside surface of the circulation loop piping during ICET Test 3 (Ref. 14),

but these deposits provided no significant flow impediment over the 30-day run time of this test which is consistent with this expectation. Therefore, the relatively high flow velocity through the RHR heat exchanger (2.5 to 5 fps) should be sufficient to keep chemical deposits such as these to a minimum (Ref. 64). Particulate suspended in the coolant would further enhance the removal of deposits from the tubes. Further, the RHR pumps can generate a high pressure differential (>300 psi) which also helps remove deposit buildup so that it does not become significant (Ref. 64). Therefore, precipitates, if formed because of temperature decreases in the RHR heat exchanger, will likely be transported to the containment pool rather than cause blockages in the RHR heat exchanger. Only thin films of chemical deposits are expected over the 30-day mission time

A thin film of precipitates on the inside diameter of heat exchanger tubes would not prevent the RHR heat exchanger from performing its design function because RHR heat exchangers are sized to bring the plant to cold-shutdown conditions under normal conditions within a relatively short amount of time (i.e., from approximately 350°F to 140°F within 24 hours). Following a LOCA, the temperature of the water in the containment pool is typically expected to decrease to approximately 200°F within a few hours (Ref. 23). At this temperature, the heat transfer requirement following a LOCA is significantly reduced compared to during normal plant cooldown. Therefore, the heat exchangers have excess capacity for removing decay heat after a LOCA. Furthermore, the decay heat load diminishes rapidly (from 2 percent of operating power after 1 hour to 0.5 percent of operating power after 1 day to 0.3 percent of operating power at 11 days following a LOCA), providing additional excess heat exchanger capacity for long-term core cooling. Therefore, although a thin film of precipitates on the heat exchanger tubes could impact the local heat transfer coefficient and heat transfer efficiency, the overall heat transfer capacity required for the RHR heat exchanger is not expected to be challenged due to the excess capacity and the reduced heat load. In addition, heat exchangers are typically designed with excess margin to account for fouling or other degradation. For example Information Notice 2007-28 (Ref. 65) describes severe fouling in one plant's essential water (i.e., shutdown cooling) heat exchangers due to poor chemistry control of the water. The licensee's evaluation concluded that even with approximately 20% degradation below the design capacity, the heat exchanger was still capable of performing its safety function.

Conclusion

The formation of solid species that may deposit in the RHR heat exchanger tubes and significantly reduce the heat exchanger efficiency is unlikely because most precipitates will form later in the post-LOCA scenario when temperatures have decreased and the required heat transfer capacity for the RHR exchangers has ample margin. Precipitates that form soon after the pipe break are only expected to form, at most, thin deposit films on the heat exchanger tubes. Deposit thicknesses are limited by scrubbing from particulate in the coolant as well as the relatively high flow rate and pressure differential associated with the ECCS system. In addition, operating experience has demonstrated that heat exchangers can adequately perform even with significant fouling. Therefore, no further research is necessary on this issue.

7.3 Reactor Core: Fuel Deposition and Precipitation

Description and Possible Implications

The increased temperature (+70 degrees C from containment pool) and retrograde solubility of some species (e.g., Ca silicate, Ca carbonate, zeolite, sodium calcium aluminate) causes scale buildup on the reactor core. Zn, Ca, Mg, and CO₂-based deposits, films, and precipitates may

form at higher temperatures within the reactor core. This may lead to (1) a decrease in heat transfer from the reactor fuel, (2) localized boiling due to insufficient heat removal, and (3) spallation of deposits, creating additional debris sources which could clog the reactor core or contribute to sump screen head loss.

Discussion

This evaluation is presented in three subtopics in the order defined above

(1) Decreased Heat Transfer From Reactor Fuel

As discussed in Section 3.13, the quantity of chemical precipitates deposited on fuel rod during a LOCA is most limiting for cold-leg breaks (hot-leg breaks for UPI plants) because, for these breaks, core cooling is accomplished by boiling off the coolant in the core. The deposition of precipitates on reactor fuel due to boiling, and its effects on core cooling, are addressed in WCAP-16793-NP, Revision 1 (Ref. 5). Among other analyses, the WCAP report includes a generic calculation demonstrating that for a representative PWR post-LOCA containment pool chemistry, the deposits thickness on fuel rods will not exceed an allowable thickness of 50 mils and the cladding temperature will not exceed the allowable post-quench temperature of 800 °F. The WCAP also includes a calculation tool, LOCADM, which can be used by licensees of PWRs to predict the post-LOCA buildup of chemical deposits on fuel rods in their PWRs using their plant-specific containment pool chemistry. The staff has evaluated the LOCADM methodology used in the WCAP for the generic calculations and in the licensee evaluation and has no additional questions concerning LOCADM due to the conservative assumptions used by this methodology. For example, it is assumed that the entire chemical source term determined by WCAP-16530-NP-A (which is conservative, see Section 3.13) remains dissolved until it reaches the reactor core and then all of this source term deposits on the fuel rods. In addition, a limiting value of thermal conductivity is assumed for all deposits. The source of the chemical products is the interaction of debris and other materials submerged in the containment pool or exposed to containment spray. LOCADM predicts both the deposit thickness (including the cladding oxide layer) and cladding surface temperature as a function of time at a number of core locations or nodes. Licensees' GL 2004-02 responses typically report cladding temperatures in the 400 to 500°F range when using LOCADM. The WCAP report is currently under NRC staff review. Although a final SE of WCAP-16793-NP, Revision 1 has not been issued by the NRC, staff has no outstanding issues related to the adequacy of the LOCADM evaluation method.

(2) Localized Boiling Due to Insufficient Heat Removal

As discussed in Section 3.13, the primary mode of initial core cooling during a cold-leg break (hot-leg break for UPI plants) is through boiling off the coolant in the core such that primarily steam exits the core. Significantly less boiling will occur during a hot-leg break (cold-leg break for UPI plants) as flow is sufficient to keep the core submerged. Therefore, boiling during a cold-leg break is the mode of heat transfer that is potentially most affected by debris buildup. As stated above, the thickness of deposits due to boiling and the effect of the deposits on core cooling have been evaluated in WCAP-16793-NP, Revision 1 and each licensee ensures that adequate core cooling is retained considering their plant-specific debris sources and concentrations.

(3) Spall of Deposits Creates Additional Debris Sources Which Could Clog the Reactor Core or Contribute to Sump Screen Head Loss

The potential for spall or precipitated solid species to affect ECCS components located downstream from the sump screen is discussed in Section 4.3 which concluded that the guidance in WCAP-16406-P-A (Ref. 4) for evaluating downstream components is sufficiently conservative such that the effects of chemical precipitates and spall do not need to be explicitly considered. This issue is concerned with the effects that this spall may have on clogging the reactor core or significantly contributing to sump screen head loss.

As discussed in Section 3.13, the PWROG has demonstrated through numerical analyses and flow testing with representative debris concentrations that, within specified debris limits, debris ingested into the ECCS that deposits on the reactor fuel will not form sufficient spall to either (a) clog the reactor core or (b) clog the sump strainer to an extent that would prevent the ECCS from maintaining long-term core cooling.

Fuel assembly testing, in support of WCAP-16793-NP, using chemical precipitates in combination with particulate and fibrous debris demonstrates that a significant debris bed will not form and the required flow can be maintained through the core provided total debris transported to the reactor vessel is within specified debris limits. These debris limits are determined by this same series of testing. Also, through numerical analyses, the PWROG has shown that, even if a debris bed were to form, (1) adequate coolant will reach the core with over 99 percent of the core inlet blocked, and (2) the fuel clad temperature can be maintained below 800°F even if the space between grid straps is filled with debris. Analysis of the grid strap blockage was conservative because it assumed complete blockage of the grid strap (i.e., no flow through the grid strap) and heat conduction in the radial direction only (i.e., no axial heat conduction). As discussed in Section 3.13, for cold-leg breaks, a fuel blockage test has also shown that the debris bed that formed in this test could be easily dislodged by reverse flow. For hot-leg breaks, the WCAP-16793-NP limits on the amount of fiber that can enter the core ensure that adequate flow rates through the reactor core will be maintained.

As also discussed in Section 3.13 of this report, spall of chemical deposits from fuel would not increase the debris load on the ECCS sump strainer beyond the quantity the strainers are qualified for because the sump strainers are tested by licensees using the maximum expected debris loads to ensure that strainers are capable of passing the required ECCS flow. The chemical debris loads used in the tests are specific to each plants design conditions and are developed in accordance with WCAP-16530-NP-A. The dissolved aluminum and calcium concentrations used in the testing are typically determined from the WCAP-16530-NP-A analysis and all concentrations are assumed to precipitate. Therefore, as discussed previously, these precipitate concentrations and type conservatively account for chemical debris loading that may be present in the post-LOCA containment pool.

Conclusion

The deposition of precipitates on reactor fuel due to boiling and its effects on heat transfer from the fuel are evaluated in WCAP-16793-NP, Revision 1 (Ref. 5). As part of the ongoing WCAP-16793 review, the staff has evaluated the WCAP LOCADM methodology for predicting the post-LOCA buildup of chemical deposits and has no additional questions concerning LOCADM due to the conservative assumptions used by this methodology. The WCAP concludes that adequate long-term core cooling can be achieved provided the quantity of fiber entering the core is limited, by design, to that demonstrated to be acceptable in fuel assembly testing. This

testing and numerical analyses also provides assurance that spall does not lead to clogging within the reactor core such that acceptable coolant flow rates are not achieved. Where these evaluations indicate that the estimated quantities of chemical, fibrous, or particulate debris loads could lead to exceeding the allowable fuel cladding temperature or the sump strainer head-loss, corrective actions are required of the licensee(s) to bring the debris quantities within acceptable limits. While the staff has not yet approved WCAP-16793-NP, Revision1 (Ref. 5), ongoing testing will establish these limiting debris concentrations to ensure adequate flow through the reactor core and acceptable peak clad temperatures.

Also, the potential for deposits to spall and contribute to clogging of the sump screen is addressed by testing strainers using particulate and chemical debris loads based on conservative assumptions. The tested concentrations account for uncertainties such as the concentration of spall transported from the reactor vessel such that this source of chemical precipitates does not have to be explicitly considered in the testing. Therefore, no additional research is needed to address this issue.

7.4 Reactor Core: Diminished Heat Transfer

Description and Possible Implications

Physical and chemical solid debris within the ECCS coolant water could diminish the fluid's heat transfer capacity and degrade the ability of the coolant to remove heat from the core.

Discussion

Section 7.3 addresses the effect that chemical precipitates deposited on the fuel has on the heat transfer from the fuel. Section 4.2 addresses the effect of chemical species that precipitate due to lower temperatures at the RHR heat exchanger outlet on the heat transfer capacity of the ECCS coolant. This section addresses the effects of chemical species on the heat transfer capacity of the ECCS coolant. These species may have precipitated or spalled at any location within the primary coolant circuit or in containment that are transported with the ECCS coolant.

During the initial phase of sump recirculation, cooling of the reactor fuel is accomplished primarily by boiling of the water surrounding the fuel. For a cold-leg break (hot-leg break on UPI plants), the driving head for flow into the core is the manometric difference between the liquid level in the downcomer and the collapsed liquid level in the core. The coolant exits the core as steam. This LOCA poses the most challenging condition for core cooling because (1) there is limited flow to the core and (2) the boric acid, other dissolved species, and suspended solids become more concentrated as the accident progresses. As suspended solids become more concentrated, the ratio of solids to water would increase, leaving less water in the core for evaporation. However, as demonstrated in Section 4.2, the boiling point and heat of vaporization of water in the core are not significantly affected by relatively dilute concentrations of suspended solids within the ECCS coolant. Therefore, suspended solids would not significantly affect the rate of boiling and thus, the rate of heat removal. The increasing concentration of the dominant solute, boron, is a design consideration that is already addressed in plant accident analyses. Based on these analyses, the LOCA accident mitigation procedures call for the initiation of hot-leg injection (cold-leg injection for UPI plants) within 3 to 6 hours of the initial break, to introduce forced coolant flow through the core to flush the concentrated boric acid and debris from the core, thus preventing the precipitation of boron in the reactor vessel.

Note: To respond to NRC concerns regarding boron precipitation in the core, the PWROG initiated a program in 2004 to refine the methods used to analyze post-LOCA boric acid build-up in the core for cold-leg break scenarios. In 2006, NRC staff and the PWROG concluded that effects of strainer bypassed debris on core cooling and boric acid precipitation issues were interrelated and, therefore, decided that strainer bypassed debris needed to be considered in the boron precipitation evaluations. Therefore, a decision was made to address the effects of sump strainer bypassed debris on boric acid concentration in the PWROG Boric Acid Precipitation Evaluation Project. The evaluation will consider the significant chemical effects phenomena identified in NUREG 1918 (Ref. 2) and will study the effects of these chemicals/precipitates on the physical and heat transfer properties of highly concentrated boric acid solutions.

For a hot-leg break (cold-leg break for UPI plants), the entire ECCS flow is pumped through the core, supplying excess coolant flow and preventing any significant buildup of precipitates or solids. Compared to a cold-leg break, the coolant flow rate is substantially increased and boric acid concentrations are much lower. The corresponding margin associated with hot-leg breaks is therefore also much greater. PWROG testing in support of WCAP-16793 shows the limiting amount of fiber for a hot leg break flow condition is greater than for a cold leg break. The percentage of fiber passing downstream of the sump strainer that reaches the core, however, is also greater for hot leg breaks. Therefore, the PWROG tested both flow conditions to determine the limiting amount of fiber permitted to reach the core to maintain adequate cooling flow. As demonstrated in Section 3.13, for both cold leg and hot-leg breaks, the limits placed on the amount of fiber that can enter the core in WCAP-16793-NP ensures that adequate coolant flow is maintained during the post-LOCA mission time.

Conclusion

Debris concentration limits based on testing of fuel assembly mockups will establish allowable bypassed debris concentrations and the ECCS design and evaluation will demonstrate that these threshold concentrations are not exceeded. Thus, the effect of physical and chemical debris contained within the core is not a concern because the debris concentration expected to enter the core will not be sufficient to prevent the coolant from circulating and removing decay heat. Therefore, there is no additional research required in this area. However, the effect of concentrated boric acid in the core on coolant circulation within the core is being addressed by the PWROG in a separate program to be concluded by 2015. Therefore, research in this area is ongoing and is being monitored by NRC staff.

7.5 Reactor Core: Blocking of Flow Passages

Description and Possible Implications

Fuel deposition products and precipitated retrograde soluble chemical species spall and settle within the reactor vessel. Settling can be potentially deleterious if flow passages to the fuel elements are either globally or locally impeded. Reduced flow within the RPV, if significant, has the potential to diminish heat transfer from the fuel.

Discussion

As discussed earlier in Sections 3.13 and 7.3, spall from fuel would not form a debris bed in the reactor vessel that could prevent adequate coolant flow to the core. This conclusion is based on (1) staff observations of testing performed by the PWROG to determine the maximum

quantity of the various types sump strainer bypassed debris that may reach the core inlet and not impede adequate long-term core cooling, and (2) staff review of numerical analyses completed by the PWROG to demonstrate that adequate core cooling can be achieved with over 99 percent of the core inlet blocked and that the fuel clad temperature can be maintained within acceptable limits with the gap within the grid straps filled with debris. In both the tests and analyses, conservative concentrations of chemical precipitates are considered. As discussed in Section 3.13, other conservatisms exist in the testing and analysis as well. WCAP-16793-NP analyses demonstrate that the limits placed on the amount of fiber that can enter the core provide assurance that adequate coolant flow is maintained during the post-LOCA mission time. These tests and analyses are documented in WCAP-16793-NP, Revision 1 (Ref. 5). While the staff has not yet approved WCAP-16793-NP, Revision 1 (Ref. 5), ongoing testing will establish the limiting amount of debris within the core that will ensure adequate flow to provide acceptable peak clad temperatures. Further, the NRC staff has reviewed the overall methodology contained in the WCAP and has no additional questions about the test method. Staff observations of the testing are documented in trip reports as noted in Section 3.13.

Conclusion

The effect of debris settling on the grid straps to block flow and prevent heat transfer from the fuel cladding is evaluated in WCAP-16793-NP, Revision 1. The WCAP concludes that adequate long-term core cooling can be achieved provided the quantity of fiber entering the core is limited, by design, to that demonstrated to be acceptable in fuel assembly testing. Once debris limits are identified by the PWROG and accepted by the NRC staff, licensees will need to demonstrate that their strainer bypassed fibrous debris are less than these limits. Licensees who do not apply the WCAP-16793-NP method for evaluating the downstream effects of ECCS sump strainer bypassed debris on the reactor vessel and core will need to demonstrate to NRC staff that bypassed fiber will not impede adequate flow to the reactor core. Therefore, this issue is being adequately addressed and no additional research is necessary on this issue.

7.6 Reactor Core: Particulate Settling

Description and Possible Implications

Relatively low, upwards flow (for cold leg injection) within the reactor causes particulates to settle. Compacted deposits form and may impede heat transfer and water flow, especially for lower portions of reactor fuel.

Discussion

As discussed in Section 3.13, the quantity of debris carried into the core is determined by the location of the pipe break. If the break occurs upstream of the core, coolant flow into the core is low (less than 3 gpm per fuel assembly). Therefore, the quantity of debris entering the core is relatively small. For this break location, the cooling of the core is accomplished by boiling. Therefore, the fluid conditions in the core are expected to be very turbulent, thus preventing the settling of significant quantities of debris at the grid straps or core inlet. As discussed in Section 3.13, a fuel assembly test was performed to demonstrate the effects of reverse flow simulating hot-leg injection initiation. During that test, the reverse coolant flow dislodged the debris bed that had formed on the grid straps (Ref. 50).

If a break occurs on the downstream of the core, the flow of coolant through the core is greater (6 to 44 gpm per fuel assembly). At this flow rate, strainer bypassed particulate debris is readily

transported out of the core. Fuel assembly testing observed by NRC staff (Refs. 49, 50) demonstrated that absent fiber, debris would not be captured in the fuel assemblies. However, with fiber present, particulate could be captured within the fiber bed. Therefore, to prevent blockage of flow to the core, WCAP-16793-NP places limits on the quantity of fiber that may be transported to the core inlet. Licensees are required to ensure that their strainer bypass quantities do not exceed these limits.

Further, to demonstrate defense in depth, the PWROG performed numerical analyses that demonstrate that adequate core cooling can be achieved with over 99 percent of the core inlet blocked and that the fuel clad temperature can be maintained within acceptable limits with the gap within the grid straps filled with debris. Independent analysis performed by the NCR staff confirmed that adequate flow can be maintained with a small open area at the core inlet. The staff is reviewing the grid strap blockage analysis as part of the WCAP-16793 review and has no further questions related to that analysis.

Conclusion

The potential for particulate settling on the grid straps to block flow and prevent heat transfer from the fuel cladding is evaluated in WCAP-16793-NP, Revision 1. The WCAP concludes that adequate long-term core cooling can be achieved provided the quantity of fiber entering the core is limited, by design, to that demonstrated to be acceptable in fuel assembly testing. Licensees of PWRs are expected to ensure that sump strainer bypassed fiber quantities reaching the core are within the specified limit. While the staff has not yet approved WCAP-16793-NP, Revision 1 (Ref. 5), the staff has not identified any outstanding issues associated with this planned approach. Therefore, this issue is being adequately addressed and no additional research is necessary on this issue.

CONCLUSION

This report documents the staff's evaluation of the implications of the outstanding chemical effects phenomena and the technical justifications supporting the disposition of these phenomena. The staff used the existing knowledge and the additional research sponsored by the industry and the NRC to determine the significance and implications associated with each issue. Sections 1 through 7 in this report summarize the results of this evaluation. The staff's evaluation of the outstanding issues concluded that the implications of these issues are either not generically significant or are appropriately addressed within the guidance associated with assessing chemical effects on ECCS performance in response to GL 2004-02. Although several issues associated with downstream in-vessel effects remain, the staff does not anticipate the need for additional research in these areas since ongoing testing will establish the limiting amount of debris within the core that will ensure adequate flow to provide acceptable peak clad temperatures. The remaining issues that will be resolved by this testing and/or analysis are summarized below:

- The deposition of precipitates on reactor fuel and its effects on core cooling (Section 7.3).
- The effect of physical and chemical debris contained within the core on the ability of the coolant to remove heat from the core (Section 7.4).
- The effect of debris settling on the grid straps to block flow and prevent heat transfer from the fuel cladding (Section 7.5).
- The potential for particulate settling on the grid straps to block flow and prevent heat transfer from the fuel cladding (Section 7.6).

The NRC staff will review the licensee's in-vessel effects evaluation to ensure these issues are adequately addressed. Additionally, the effect of sump strainer bypassed debris on boric acid concentration (Section 7.4) is being addressed by the PWROG in a separate program to be concluded by 2015. Therefore, research in this area is ongoing and is being monitored by NRC staff. The resolution of this issue will be documented separately once this research is complete and the implications are understood.

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ABBREVIATIONS AND ACRONYMNS

| | |
|---|-------------------------------|
| Al | aluminum |
| Al(OH) ₃ | aluminum hydroxide |
| AlOOH | aluminum oxyhydroxide |
| ANL | Argonne National Laboratory |
| AST | alternate source term |
| | |
| B | boron |
| BWR | boiling-water reactor |
| | |
| C | Celsius |
| Ca | calcium |
| Ca(OH) ₂ | calcium hydroxide |
| Ca ₃ (PO ₄) ₂ | hydrated lime |
| CaCO ₃ | calcium carbonate |
| Cal-Sil | calcium silicate |
| CL | cold leg |
| Cl | chlorine |
| Cl ⁻ | chloride ion |
| ClO ⁻ | hypochlorite |
| Co | cobalt |
| CO ₂ | carbon dioxide |
| Cr | chromium |
| C-S-H | calcium silicate hydrate |
| CSS | containment spray system |
| Cu | copper |
| | |
| DBA | design-basis accident |
| | |
| ECCS | emergency core cooling system |
| eV | electron volt |
| | |
| F | Fahrenheit |
| Fe | iron |
| Fe(OH) ₂ | iron(II) hydroxide |
| Fe ₃ O ₄ | magnetite |
| FeOOH | iron oxyhydroxide |
| fps | feet per second |
| ft ² | square foot or feet |
| ft ³ | cubic foot or feet |
| | |
| g/cm ³ | gram per cubic centimeter |
| GL | generic letter |
| gpm | Gallons per minute |
| GSI-191 | Generic Safety Issue 191 |
| | |
| H | hydrogen |
| H ₂ | hydrogen molecules |
| H ₂ O | water |

| | |
|-------------------------------|--|
| H ₂ O ₂ | hydrogen peroxide |
| HCl | hydrochloric acid |
| HL | hot leg |
| HNO ₃ | nitric acid |
| HOCl | hypochlorous acid |
| ICET | integrated chemical effects test |
| kg | kilogram |
| LANL | Los Alamos National Laboratory |
| lb/ft ³ | pound per cubic foot |
| Li | lithium |
| LOCA | loss-of-coolant accident |
| LOCADM | LOCA Deposition Analysis Model |
| mg/L | milligram per liter |
| MING | Microbial Impacts to the Near-Field Environment Geochemistry |
| Moles/L | moles per liter |
| N ₂ | atmospheric nitrogen |
| NaOH | sodium hydroxide |
| Ni | nickel |
| NEI | Nuclear Energy Institute |
| NiO | nickel oxide |
| NO ₂ ⁻ | nitrite |
| NO ₃ ⁻ | nitrate |
| NPP | nuclear power plant |
| NPSH | net positive suction head |
| NRC | U.S. Nuclear Regulatory Commission |
| NSF | National Sanitary Foundation |
| OH | hydroxyl radicals |
| ORP | oxidation-reduction potential |
| Pb | lead |
| pH | hydrogen ion concentration |
| PIRT | phenomena identification and ranking table |
| PNNL | Pacific Northwest National Laboratory |
| ppm | parts per million |
| PWR | pressurized-water reactor |
| PWROG | Pressurized Water Reactor Owners' Group |
| PVC | polyvinyl chloride |
| PZC | point of zero charge |
| R/h | roentgen per hour |
| rad/h | rad per hour |
| RAI | request for addition information |
| RCP | reactor coolant pump |
| RCS | reactor coolant system |
| redox | reduction-oxidation |

| | |
|---------------------|--------------------------------------|
| RHR | residual heat removal |
| RPV | reactor pressure vessel |
| RWST | refueling water storage tank |
| SE | safety evaluation |
| Si | silicon |
| Si(OH) ₄ | silicic acid |
| SiO ₂ | silicon dioxide |
| SS | stainless steel |
| STB | sodium tetraborate |
| SwRI | Southwest Research Institute |
| TMI | Three Mile Island |
| TSP | trisodium phosphate |
| UPI | upper plenum injection |
| WCAP | Westinghouse Commercial Atomic Power |
| Zn | zinc |
| ZOI | zone of influence |
| ZrO ₂ | zirconium oxide |