



Expected Impact of Chemical Effects on GSI-191 Risk-Informed Evaluation for South Texas Project

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This report is not safety related

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1. Introduction

Purpose

The purpose of this report is to 1) document the results of a literature review of testing that has been performed in support of generic safety issue (GSI) 191 chemical effects, 2) determine significant parameters relevant to chemical effects head loss, 3) develop a best-estimate evaluation for the real impact of chemical debris for South Texas Project (STP) based on available test data and plant-specific parameters, and 4) develop recommendations for more realistic, plant-specific experiments. The main objective of this effort is to support a risk-informed closure path for GSI-191. The risk-informed approach differs from the deterministic closure methodology followed by the industry for the last several years. In the deterministic setting, biased inputs are sought and uncertainty is ignored under the presumption that the bias is sufficient to bound the outcome. In a risk-informed approach, the best estimate of the distribution, including the extreme outcomes, is sought. In general, the mean of the best-estimate distribution is expected to differ significantly from the biased inputs used in deterministic analyses. Review of relevant literature indicates that in several areas, the industry-standard testing intended for deterministic analyses has produced overly-conservative estimates of head loss for debris beds that would be formed at a particular plant under the expected plant-specific conditions.

Overview

Chemical effects in a post-LOCA PWR containment environment involve complex phenomena with a wide variety of potentially significant parameters. The complexity of the chemical-effects issue has been one of the primary obstacles to fully resolving GSI-191.

The primary method that is currently used to address the chemical-effects issue by U.S. PWRs is to follow the approach recommended in WCAP-16530-NP (1; 2; 3; 4; 5; 6; 7), as approved by the NRC (8; 9; 10; 11; 12; 13). The basic plant-specific approach is to calculate the type and quantity of chemical precipitates that would form based on the quantity of aluminum, fiberglass insulation, Cal-Sil insulation, exposed concrete, and other chemically reactive materials in containment; the time-dependent temperature and pH; the duration of containment spray operation; and the buffer type. Based on this calculation, chemical surrogate materials are prepared per the guidelines in the WCAP. Bounding head-loss tests are performed using the limiting quantities of fiberglass and particulate debris that could be generated and transported to the strainer, and the chemical surrogate debris is added on top of the fiber/particulate debris bed. A similar method has also been used to simulate chemical effects for in-vessel testing.

Although the WCAP method is relatively easy to implement, many plants have found that it results in unacceptably high strainer head losses. It has also contributed to an unacceptably low fiber loading acceptance criterion of 15 g per fuel assembly (FA). Due to the severe impact of the WCAP method, a

best estimate approach needs to examine the conservatisms associated with the method and investigate alternatives. The following conservatisms and limitations are inherent in the WCAP method:

1. Material corrosion/dissolution rates are based on a limited data set. Confirmatory testing conducted by CNWRA showed significantly lower rates for almost all of the materials tested (14).
2. Material corrosion/dissolution rates are based on separate effects tests. Integrated testing and literature have shown that the presence of some materials will inhibit the dissolution/corrosion of other materials.
3. 100% of the dissolved aluminum is assumed to form a precipitate (sodium aluminum silicate and/or aluminum oxyhydroxide). Numerous tests (including the WCAP testing) have shown that significantly less than 100% of the aluminum will form a precipitate under prototypical conditions.
4. 100% of the dissolved calcium is assumed to form a precipitate (calcium phosphate) if the buffer is TSP. The WCAP testing showed that some of the calcium in solution did not precipitate when mixed with TSP (1).
5. The formation of chemical precipitates is assumed to occur at the same rate that the base constituents (Al, Si, or Ca) are released from their sources, without considering precipitation formation kinetics. Confirmatory testing conducted by ANL indicated that precipitation kinetics may significantly influence the timing of precipitate formation (15).
6. All precipitation is assumed to occur relatively early in the event (at the point of lowest strainer NPSH margin and highest required flow through the core), even though some of the material dissolution is calculated to occur later in the event. Several tests have shown that precipitates would not form until the pool cools down significantly. At this point, the strainer NPSH margin would generally be much higher, and the flow required to cool the core would be significantly lower.
7. The WCAP surrogate material is prepared in a form that causes large increases in head loss, but is not necessarily representative of the actual precipitates that would form after a LOCA (15). Alion integrated chemical effects tests have shown that chemicals precipitate as crystals on fiberglass fibers rather than forming a gelatinous mixture that would effectively coat and plug an entire debris bed (16).
8. The WCAP method provides a means of calculating the quantity of chemical precipitates for a variety of conditions, but requires individual tests to determine the corresponding impact on head loss for each case analyzed. Since it is not practical to run tests for every break scenario of concern, it is often necessary to unrealistically combine conservative parameters from different scenarios.

Most PWRs have attempted to resolve GSI-191 by following a deterministic approach as laid out in NEI 04-07 (17; 18). Each subject area related to GSI-191 (debris generation, debris transport, chemical

effects, ECCS strainer head loss, debris bypass, downstream effects, etc.) involves complex phenomena with significant uncertainty that make the issues difficult to evaluate. In deterministic evaluations, uncertainty is addressed through the use of conservatism to ensure that a bounding evaluation has been performed. Numerous tests and analyses (with varying success) have been performed in each subject area to better understand the physical phenomenon and reduce the level of conservatism in plant-specific evaluations.

South Texas Project (STP) is taking an alternative approach by leading an effort to address GSI-191 through risk-informed evaluations. Both the deterministic and risk-informed approaches attempt to address the physical phenomena as realistically as possible. However, the primary difference is that the deterministic approach analyzes bounding scenarios and addresses uncertainty with conservatism, whereas the risk-informed approach analyzes best-estimate conditions for the full spectrum of scenarios, taking probabilities into consideration and quantifying uncertainty as part of the evaluation.

A comprehensive review of literature has been performed, and conclusions of the review indicate that the effect of chemicals on pressure drop in debris beds at South Texas Project are overstated in industry standard testing. Analysis shows that more realistic testing under plant-specific conditions would more accurately estimate head loss at South Texas Project.

2. Background

Strainer performance issues for pressurized water reactor (PWR) nuclear power plants were initially evaluated in the early 1980s in response to unresolved safety issue (USI) A-43. Following a series of strainer clogging events at boiling water reactor (BWR) nuclear power plants in the early 1990s, all of the BWR plants in the U.S. performed detailed evaluations to assess strainer performance. After the issue was resolved for BWRs, the Nuclear Regulatory Commission (NRC) reopened the issue for PWRs as generic safety issue (GSI) 191, based on lessons learned from the BWR efforts. In February 2003, the Advisory Committee on Reactor Safeguards (ACRS) identified the potential for chemically induced corrosion products to exacerbate debris clogging. As part of an initial evaluation program conducted by the NRC, Los Alamos National Laboratory (LANL) and the University of New Mexico (UNM) conducted a limited-scope experimental study in 2003 to determine whether chemical effects was a significant concern (19). The following year, the NRC issued Generic Letter 2004-02 requiring licensees to provide information regarding the potential susceptibility for blockage in the flow paths for the emergency core cooling system (ECCS) and containment spray system (CSS) (20). This letter identified chemical effects as a potential concern that each licensee would need to address along with other aspects of debris generation, transport, and blockage.

From 2004 through 2006, the NRC conducted an extensive testing and analysis program to evaluate the impacts of chemical effects. The results of this research are published in a series of NUREGs. The Center for Nuclear Waste Regulatory Analyses (CNWRA) conducted experiments on corrosion rates for various metals and leaching rates for concrete and fiberglass. CNWRA also conducted thermodynamic simulations to determine important parameters for chemical effects and the most likely types of precipitates that could form. These results are documented in NUREG/CR-6873 (21). CNWRA conducted an evaluation of thermodynamic modeling software and concluded that if the initial water composition and material dissolution rates are well understood, and an adequate set of thermodynamic data is available for the precipitates that would be expected to form, thermodynamic modeling can be an effective predictive tool. This research is documented in NUREG/CR-6912 (22). ANL conducted a series of tests to investigate the potential effects of chemical precipitates on sump screen head loss in trisodium phosphate (TSP), sodium hydroxide (NaOH), and sodium tetraborate (NaTB) buffered solutions. They also conducted tests to measure Cal-Sil dissolution in TSP solutions and the settling rate of calcium phosphate precipitates, as well as benchmark tests in chemically inactive environments. The results of this testing are documented in NUREG/CR-6913 (23). LANL and UNM conducted an integrated chemical effects test (ICET) program, which included five 30-day tests with boron, lithium hydroxide, and hydrochloric acid; representative submerged and unsubmerged plant materials; a constant temperature of 140°F; a spray duration of 4 hours; and mixes of insulation and pH buffer systems as described in Table 1. The results of this testing are documented in NUREG/CR-6914, Volumes 1 through 6 (24; 25; 26; 27; 28; 29). LANL and UNM also conducted follow-on research and analysis of aluminum corrosion and precipitation based on the results of ICET Tests 1 and 5, a comprehensive literature review, and

additional experiments. One result of the additional experiments was the identification of the inhibitory effect of silicon on aluminum corrosion, which was caused by a coating of Al_2OSiO_4 on the aluminum surface. The results of this research are documented in NUREG/CR-6915 (30). In parallel with the testing activities, a peer review of the chemical-effects issue was conducted by the NRC and is documented in NUREG-1861 (31).

Table 1: Overview of integrated chemical effects tests

ICET Test Number	Controlling pH buffer system	Insulation (%)		Measured pH	Chemical byproducts	
		Fiberglass	Cal-Sil		Visible at test temperature	Visible upon cooling
1	Borate (NaOH)	100	0	9.3 - 9.5	No	Yes
2	Phosphate (TSP)	100	0	7.1 - 7.4	No	No
3	Phosphate (TSP)	20	80	7.3 - 8.1	Yes, only during first few hours	No
4	Borate (NaOH)	20	80	9.5 - 9.9	No	No
5	Borate (Borax)	100	0	8.2 - 8.5	No	Yes

In 2005 and 2006, the Pressurized Water Reactor Owners Group (PWROG) conducted a series of separate effects experiments to measure dissolution/corrosion rates and observe precipitation for various metals, concrete, and insulation materials typically found in U.S. PWRs under a range of pH and temperature conditions. The precipitates were characterized and filtration testing was performed in an attempt to compare the head loss properties for the various precipitates that formed. Based on the results of the testing, a model was developed to predict material dissolution/corrosion over time and the quantity of precipitates that would form based on plant-specific materials, pH history, temperature history, pool volume, and spray duration. This model was implemented using an Excel spreadsheet. A method was also developed for preparing surrogate chemical materials that can be used in ECCS strainer head-loss testing. This work is documented in WCAP-16530-NP (1) and the associated error notices (2; 3; 5; 6; 7). The WCAP was formally submitted to the NRC for review (4). As part of their review, the NRC sponsored confirmatory testing through CNWRA to evaluate the separate effects dissolution/corrosion rates measured by the PWROG (14). They also sponsored testing through ANL to evaluate the chemical surrogates recommended by the PWROG (15; 32). Following a series of NRC requests for additional information (RAIs) and PWROG responses (8; 9; 10; 11; 12), the NRC issued a formal safety evaluation (SE) for the WCAP (13). This method has been widely used by the industry to address chemical effects. However, due to the conservatism discussed in Section 1, this method often results in unacceptably high strainer head losses. The method provided in WCAP-16530-NP was extended to address incore blockage concerns as described in WCAP-16793-NP (33). This WCAP is currently being revised to address NRC concerns (34). However, the preliminary debris load acceptance criteria that have been provided

are so low that most plants will not be able to pass. The low acceptance criteria are due in part to the highly conservative treatment of chemical effects.

The PWROG also conducted testing in 2006 to evaluate alternative buffers that could be used by PWRs and would lower the impact of chemical effects. The results of this testing are described in WCAP-16596-NP (35).

To provide some relief on the level of conservatism in WCAP-16530-NP, the PWROG conducted additional testing in 2007 to allow for refinements to the WCAP model. The refinements investigated included 1) silicate inhibition of aluminum corrosion, 2) corrosion rates of various aluminum alloys, 3) phosphate inhibition of aluminum corrosion, and 4) solubility of sodium aluminum silicate, aluminum oxyhydroxide, and calcium phosphate precipitates. The corrosion rate of various aluminum alloys was found to be relatively close to pure aluminum, but the other refinement options significantly reduced the total quantity of precipitates. The results of this testing and methods for applying it to plant-specific evaluations are documented in WCAP-16785-NP and a corresponding letter to the PWROG plants (36; 37).

In 2008, the PWROG also completed a phenomena identification and ranking table (PIRT) evaluation of unbuffered boric acid mixing and transport in a reactor vessel under post-LOCA conditions (38).

In 2007 and 2008, Alion conducted integrated chemical effects testing at the VUEZ facility in Levice, Slovakia. The plants that participated in this test program included D.C. Cook, Three Mile Island, Beaver Valley, Turkey Point, St. Lucie, San Onofre, Indian Point, Waterford, and Vogtle. The testing simulated the prototypical chemical environment similar to the ICET experiments, but also included direct head loss measurements across a flat-plate¹ debris bed over the duration of the tests. The purpose of the tests was to determine a plant-specific bump-up factor that could be applied to the results of prototype strainer tank testing with standard fibrous and particulate debris. The test protocols that were used are documented within the proprietary ALION-I002 project files, and the test results are documented within plant-specific test reports. The chemical effects test results for Vogtle, which like STP is a TSP plant with mostly fiberglass insulation, are documented in ALION-REP-GENE-4777-100 (39). The VUEZ testing provides some excellent information on the impact of chemical effects. However, due to several NRC concerns that would have been very difficult to resolve without rerunning the tests, most plants that participated in the VUEZ tests ended up abandoning this effort. The NRC concerns are illustrated in the RAIs received by Vogtle (40).

Alion also performed chemical effects benchtop tests in 2007 and 2008, including 1) tests of aluminum and Nukon dissolution/corrosion in TSP (41), 2) tests of aluminum, zinc, Nukon, and mineral wool

¹ The test screen was actually rounded slightly to resolve issues with the accumulation of air below the screen. Additional testing for D.C. Cook was conducted with a small prototype strainer module.

dissolution/corrosion in TSP (42), 3) tests of aluminum, zinc, Nukon, Cal-Sil, and concrete dissolution/corrosion in TSP and NaTB (43), and 4) tests of unqualified alkyd coatings dissolution in TSP, NaOH, and NaTB (44).

ANL issued a series of test reports in 2008 describing studies on precipitate surrogates used by various head-loss test vendors (45), the long-term solubility of aluminum (46), and comparisons between the effects of aluminum surrogates and the aluminum actually dissolved from aluminum alloys (47).

In March 2008, the NRC issued the staff review guidance regarding plant-specific chemical effects evaluations (48). This document identifies the NRC's expectations regarding various chemical effects-related issues and provides a good summary of the knowledge base that existed at that time. The NRC also completed a PIRT evaluation of chemical effects in 2008, which is documented in NUREG-1918 (49). The PIRT panel identified several significant phenomena relevant to chemical effects in a post-LOCA environment. Also in 2008, the NRC sponsored additional analysis by Pacific Northwest National Laboratory (PNNL) to evaluate 10 topical areas related to chemical effects based on the work performed by the PIRT panel. The topical areas were 1) radiation effects, 2) carbonation of concrete, 3) alloy corrosion, 4) galvanic corrosion, 5) biological fouling, 6) co-precipitation and other synergistic solids formation, 7) inorganic agglomeration, 8) crud release effects, 9) retrograde solubility and solids deposition, and 10) organic material impacts. The results of this analysis are provided in NUREG/CR-6988 (50).

In 2009 through 2011, Alion performed high-temperature vertical loop chemical effects tests at the facility in Warrenville, IL. This testing has been used to provide plant-specific justification that chemical precipitates would not form until certain conditions (i.e., a low temperature) are reached. Alion also started developing a test program to determine the impact of chemical effects on BWRs for the Boiling Water Reactor Owners Group (BWROG) in 2011 (51).

In March 2011, the NRC issued an evaluation of 41 significant issues that had been identified by the PIRT panel in NUREG-1918. This evaluation was based on the current body of knowledge, and the NRC was able to show that each of the issues has been fully resolved either directly or through the use of conservatism in the plant-specific chemical effects evaluations (52). This document provides an excellent source of information on some chemical issues that have not been as extensively evaluated by the industry. Although the NRC considers each of the 41 issues to be fully resolved in the current chemical effects evaluations, some of the issues documented in this report will need to be revisited for the refined testing and analysis that will be conducted for STP.

3. Significant Contributors

Prior to refining the way that chemical effects tests or analyses are performed, it is important to understand the significant contributors to ensure that secondary parameters are not inadvertently ignored. As discussed in WCAP-16530-NP, the primary contributors to post-LOCA chemical effects are (1; 13):

- Time
- Buffer type
- Pool and spray pH
- Pool and containment temperature
- Pool volume
- Spray duration
- Types of insulation debris
- Exposed insulation debris quantities
- Exposed aluminum surface area
- Exposed concrete surface area
- Material dissolution or corrosion rates
- Inhibition of dissolution/corrosion of some materials by other materials
- Material solubility limits
- Reaction kinetics
- Precipitate types (silicates, hydroxides/oxyhydroxides, phosphates, borates)
- Physical characteristics of precipitates (form, size)

As discussed in WCAP-16530-NP (1; 13) and the NRC's evaluation of the PIRT results (52), important secondary contributors to chemical effects could include:

- Exposed surface area of other metals (copper, carbon steel, galvanized steel, nickel, lead, zinc coatings)
- Organic material (organic mastics, rubber, foam, phenolic resins, pressed wood, liquid hydrocarbons)
- Reactor coolant oxides
- Radiolysis products (hydrogen, oxygen, hydrogen peroxide, hydrochloric acid, nitric acid)
- Material aging
- Variations of reactor coolant system (RCS) chemistry conditions over fuel cycle (boron and lithium concentration, pH)
- Refueling water storage tank (RWST) chemistry conditions (boron and dissolved silica concentrations)
- Biological effects

- Effects of large temperature drop in heat exchangers
- Effects of large temperature increase in reactor vessel (retrograde solubility)

Although other potential chemical-effects contributors have been identified and discussed in NUREG-1918 (49), NUREG/CR-6988 (50), and the NRC's evaluation of the PIRT results (52), these issues are considered to be insignificant. The primary and secondary contributors are discussed in more detail below.

Time

Time is an important factor for many aspects of chemical effects: water is initially injected from the RWST for a relatively brief period prior to recirculation; sprays are often terminated after a relatively brief period; containment materials take time to dissolve; the containment and pool temperatures increase initially and then cool gradually; reaction kinetics dictate the rate of precipitate formation, which may result in precipitates forming later in the event when the pump NPSH margin is higher; and the ECCS must be operable for a mission time of 30 days. Therefore, a realistic evaluation of chemical effects must take into consideration time dependence.

Buffer Type

Three buffer types are used by U.S. PWRs: trisodium phosphate (TSP), sodium hydroxide (NaOH), and sodium tetraborate (NaTB). Certain combinations of buffers and containment materials can be particularly problematic with respect to chemical precipitation. TSP with high concentrations of calcium (due to dissolution of Cal-Sil, for example) can form significant quantities of calcium phosphate. Plants that use NaOH addition for buffering generally have a higher pH that can result in significantly more aluminum corrosion, which may lead to greater quantities of aluminum oxyhydroxide or other aluminum precipitates when the water cools. Also, ICET Test 5 buffered with NaTB showed a noticeable amount of precipitation upon cooling. Therefore, a realistic evaluation of chemical effects must take into consideration the buffer type.

Pool and Spray pH

Buffers are used by PWR plants to ensure that the containment pool has a pH greater than or equal to 7. For a TSP plant, the water injected from the RWST is initially acidic due to the high concentration of boric acid in solution. As the TSP in baskets on the containment floor dissolves, however, the pH in the pool will quickly rise to a value between 7 and 8. The spray pH will be identical to the RWST pH during the injection phase, and identical to the pool pH after the sprays are switched over to recirculation. Generally, higher pH will result in more severe chemical effects, since aluminum (one of the dominant contributors to chemical effects), has a higher corrosion rate in a more alkaline solution. Therefore, a realistic evaluation of chemical effects must take into consideration the pH.

Pool and Containment Temperature

The pool and containment temperatures will generally increase initially during the event to a maximum value around 270°F (for a large-break LOCA) and will then cool gradually as the decay heat is removed. The temperature of the containment sprays can be approximated by that of the containment atmosphere when the spray water impinges on various unsubmerged materials. Dissolution of non-metal materials, corrosion of metal materials, and aqueous chemical reactions generally occur more quickly at higher temperatures. Therefore, a realistic evaluation of chemical effects must take into consideration the pool and spray temperature.

Pool Volume

The pool volume will initially increase during the injection phase and will remain essentially constant during the recirculation phase. The pool volume depends on the volume of water in the RWST and whether the break is large enough for the safety injection tanks (or accumulators) to discharge. A portion of the water that is recirculated will be outside of the pool in the form of condensation on walls and as spray water falling or draining down through containment. Since dissolution for a particular material slows down as the dissolved concentration of the material increases, a larger pool volume would dilute the dissolution products and tend to maximize the overall dissolution. However, a smaller pool volume would tend to have higher concentrations of dissolved materials, which could result in the formation of more precipitates. Therefore, a realistic evaluation of chemical effects must take into consideration the pool volume.

Spray Duration

Containment sprays are used to control containment pressure and remove radioactive material from the atmosphere. Generally this can be accomplished relatively quickly and sprays can be secured within a few hours. However, some plants do not procedurally require the sprays to be secured, which leaves the possibility that spray flow could continue for the duration of the event. The majority of aluminum, structural steel, galvanized steel, concrete, and other containment materials are located above the containment pool. However, if materials that are susceptible to dissolution or corrosion are impacted by containment sprays, they may be affected similar to materials that are submerged in the pool. The corrosion or dissolution of these materials may continue as long as the sprays are in operation. Therefore, a realistic evaluation of chemical effects must take into consideration the spray duration.

Types of Insulation Debris

A variety of insulation materials are used in U.S. PWRs. Different combinations of these materials may be destroyed under different break scenarios. The insulation types include E-glass (fiberglass), RMI

(aluminum and stainless steel), microporous (Microtherm, Min-K), mineral wool, calcium silicate, aluminum silicate, and Interam. Each type of insulation can have a different impact on chemical effects based on the chemical composition of the material.

Exposed Insulation Debris Quantities

Insulation within the zone of influence (ZOI) of a pipe break can be destroyed in a range of sizes from fines to intact blankets. Some of this debris may be transported to upper containment, where it could get held up on grating or other structures; and some of it may be transported down to the containment pool, where it could transport to the sump strainer or settle in quiescent regions of the pool. The quantity of debris generated is generally estimated using assumptions intended to conservatively maximize debris quantities. Debris transport is generally estimated using assumptions intended to conservatively maximize transport to the pool and the sump strainer. Insulation debris in the pool (either on the strainer or settled in quiescent regions) would be subject to dissolution over the duration of the event. Insulation debris held up on structures above the pool would also be subject to dissolution over the duration of containment spray operation if the debris is in an area exposed to spray flow.

Insulation outside of the ZOI that is not damaged can generally be excluded from chemical effects considerations, since the canvassing or stainless steel jacketing would prevent any significant dissolution from the sprays. However, insulation without any type of jacketing may need to be considered, and aluminum jacketing on insulation would need to be included in the total quantity of aluminum considered for chemical effects.

Fiberglass debris that accumulates on the strainer would dissolve similar to fiberglass that settles in the pool. This decreases the fiber diameter and can result in increased debris bed compaction. This effect has been shown to cause steadily increasing head losses in long term tests as shown in Figure 1 (53).

Therefore, a realistic evaluation of chemical effects must take into consideration the exposed insulation debris quantities.

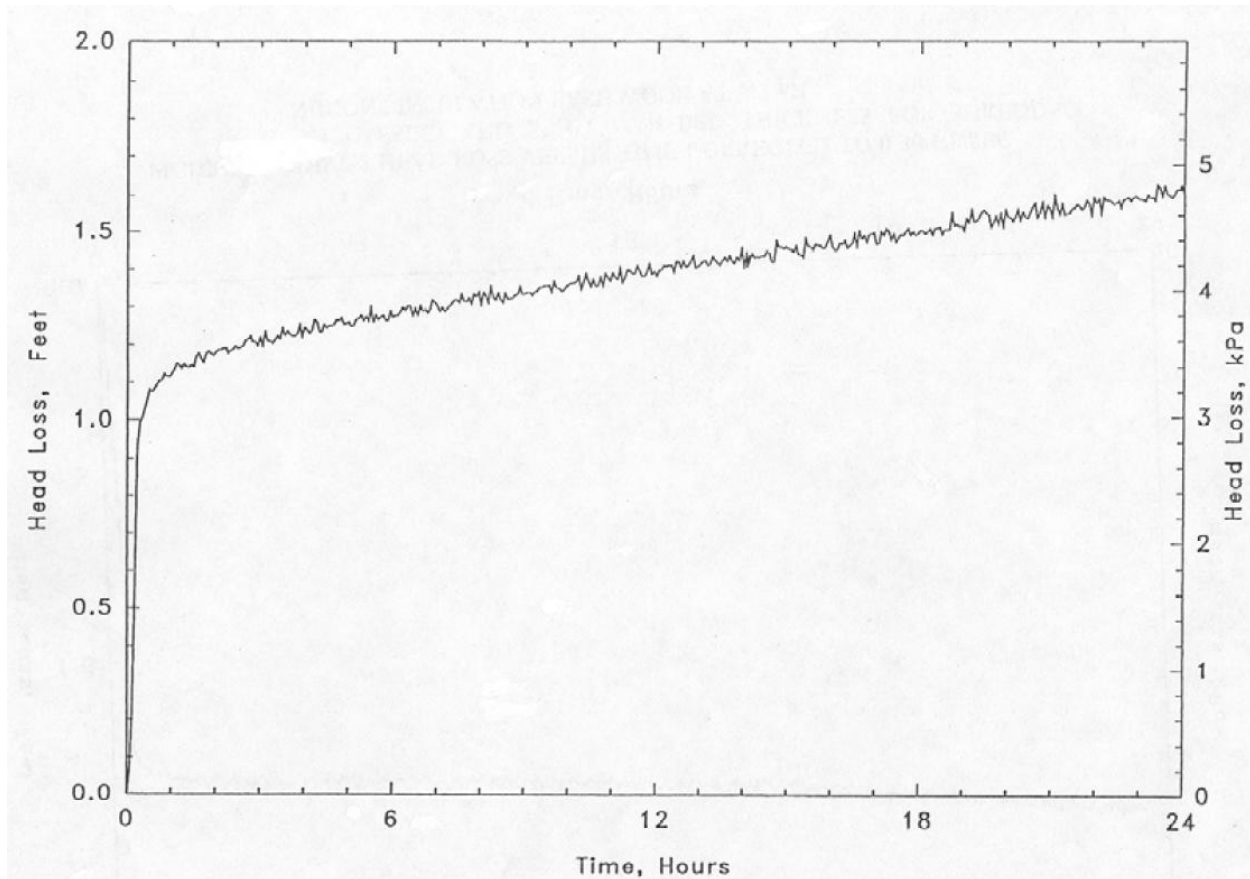


Figure 1: Increasing head loss due to Nukon dissolution (reproduced from NUREG/CR-6808 Figure 7-23)

Exposed Aluminum Surface Area

Sources of aluminum in containment include structures such as scaffolding, small components such as valves, aluminum RMI, aluminum jacketing on insulation, and aluminum coatings. Most of these materials would be above the containment pool elevation, but may be exposed to containment sprays. Both integrated and separate effects tests have shown that the corrosion of aluminum can be significant and may cause problematic precipitates. Therefore, a realistic evaluation of chemical effects must take into consideration the exposed aluminum surface area.

Exposed Concrete Surface Area

Most concrete surfaces in PWRs are coated. However, some uncoated surfaces could be exposed to the pool or spray water. Some concrete surfaces may be exposed due to direct jet impingement's stripping the coatings off of walls or floors within the ZOI. Also, some concrete surfaces with unqualified or degraded qualified coatings could be exposed if the coatings fail during the event. The WCAP-16530-NP testing indicated that the dissolution of concrete has a relatively minor impact on chemical effects, but

can leach calcium and silicon into the pool (1). Both elements are significant to chemical effects. Therefore, even though the contribution from concrete may be minor, a realistic chemical-effects evaluation should take into consideration the exposed concrete surface area.

Material Dissolution or Corrosion Rates

Tests results have shown that dissolution/corrosion of various materials can be significant in a post-LOCA environment. Generally, the dissolution/corrosion rates are higher at extreme pH (either acidic or basic) and are minimized in a neutral solution (pH of 7). Dissolution/corrosion rates are generally higher at higher temperatures as well. The presence of a dissolved element in solution will tend to slow the dissolution rate for materials containing that element. Also some materials such as silicates or phosphates in solution will inhibit the dissolution/corrosion of other materials such as aluminum. Since dissolution/corrosion is necessary for chemical precipitates to form, a realistic chemical-effects evaluation must take into consideration dissolution or corrosion rates for materials exposed to the pool or sprays.

Inhibition of Dissolution/Corrosion of Some Materials by Other Materials

As discussed previously, silicates and phosphates both tend to inhibit the corrosion of aluminum (36). Also, aluminum in solution may tend to inhibit the dissolution of fiberglass (32). Generally, the combination of more materials will tend to decrease the overall dissolution rates of the materials compared to single-effects tests, where the dissolution rate for an individual material is measured. Therefore, a realistic chemical-effects evaluation must take into consideration the inhibition of dissolution/corrosion of some materials by other materials.

Material Solubility Limits

The presence of dissolved materials does not necessarily lead to the formation of problematic chemical precipitates. If the concentration of dissolved material is less than the solubility limit, chemical effects could end up being insignificant. The methodology in WCAP-16530-NP conservatively neglects solubility limits (1). However, the testing described in WCAP-16785-NP showed that the solubility limit can significantly affect the total quantity of precipitates that form (36). Therefore, a realistic chemical-effects evaluation must take into consideration the material solubility limits.

Reaction Kinetics

Although thermodynamic simulations may predict that a precipitate will form given certain concentrations of dissolved materials, reaction kinetics can significantly affect the time required for precipitate formation (15). This implies that short-term tests may not be adequate to observe significant precipitate formation. However, a delay in precipitate formation is generally beneficial because the

NPSH margin is typically higher later in the event (due to the lower temperature), and precipitation that takes longer than 30 days can be neglected. Therefore, a realistic chemical-effects evaluation should take into consideration reaction kinetics.

Precipitate Types

The types of precipitates that can form depend on the pool chemistry. Generally the potential precipitate types that could form in a post-LOCA environment include silicates, hydroxides/oxyhydroxides, phosphates (in TSP-buffered plants), and borates (1). The precipitate types can be predicted by thermodynamic modeling. Since different precipitates may have different impacts on head loss, a realistic chemical-effects evaluation should take into consideration differences in the potential precipitate types.

Physical Characteristics of Precipitates

The physical characteristics of precipitates that form largely determines their potential effect on head loss. Chemicals may precipitate as an amorphous material, forming a gelatinous substance that can coat a fiberglass debris bed and cause very high head losses, as predicted by the WCAP-16530-NP surrogates (see Figure 2). Chemicals may also precipitate as crystals on the fiberglass within the debris bed as seen in the VUEZ integrated chemical-effects tests (see Figure 3).

The location for precipitate formation may be significant. In industrial processes involving precipitation, solutions are often “seeded” with crystals of the desired precipitate to cause precipitation to occur in the bulk solution. Without seeding, precipitation generally occurs on surfaces, which have the necessary nucleation sites. In the post-LOCA environment, suitable surfaces for precipitation may include corroded aluminum surfaces, which may already contain oxide layers, insulation fibers, or other rough surfaces throughout the containment. If precipitation readily occurs on these surfaces, the solubility limit may form an effective upper bound on the concentration of aluminum that can enter the solution as a result of corrosion, and may effectively prevent precipitation in the bulk fluid until the temperature decreases.

The size of chemical precipitates is also important. If the precipitates form as amorphous materials within the pool, they will tend to agglomerate and more effectively coat and block the flow paths in a fiber bed. If the precipitates form as crystals on the fibers, larger crystal formation will tend to obstruct flow in the debris bed more than small crystals.

Therefore, a realistic chemical-effects evaluation should take into consideration the physical characteristics of the precipitates.



Figure 2: Photograph showing WCAP-16530-NP chemical surrogate following a head-loss test for STP

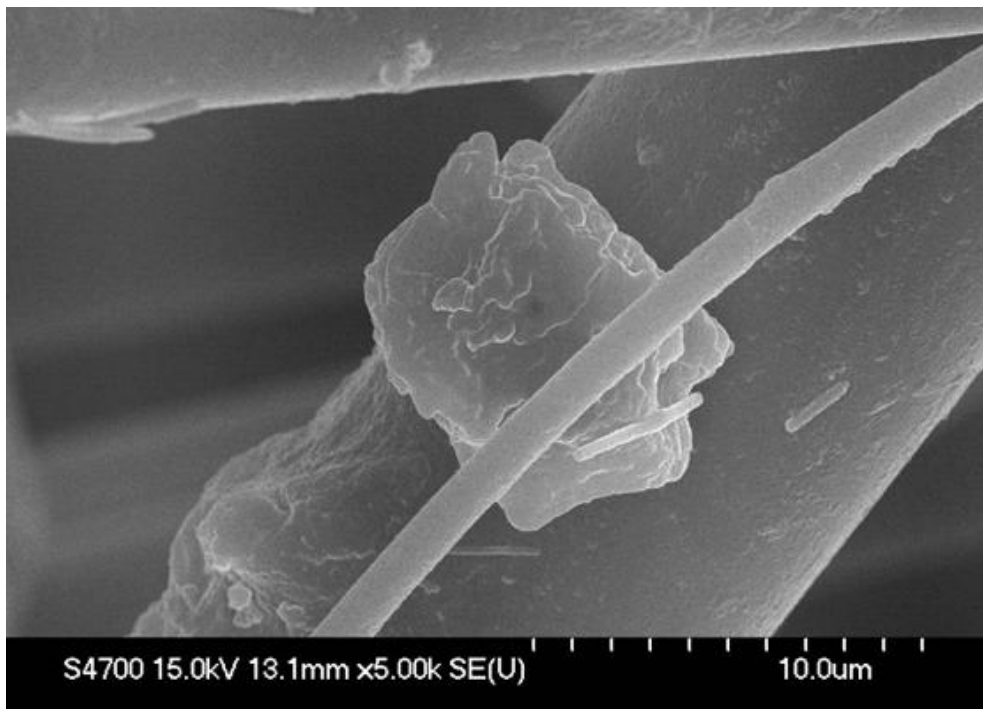


Figure 3: SEM photo showing precipitate within a fiber bed from VUEZ Testing

Exposed Surface Area of Other Metals

Although aluminum dissolution has been shown to be the most dominant with respect to chemical effects, other metals in containment may also be significant.

Copper may be present in containment in air coolers, motor windings, and grounding straps. Copper can inhibit corrosion by depositing and forming a passivation layer on other metals such as aluminum. However, copper can also enhance corrosion by forming a galvanic couple with other metals such as aluminum. The evaluation of the PIRT results concluded that the galvanic effects of copper can be neglected based on the conservatism in the WCAP-16530-NP aluminum corrosion rate. Although the corrosion of copper would likely be minor (1), a realistic chemical-effects analysis should probably take into consideration the potential corrosion inhibition or enhancement of copper.

Carbon steel is generally present in containment as structural supports. Carbon steel was included in the WCAP-16530-NP testing and was found to have a negligible corrosion mass of 6 mg compared to 1,580 mg for aluminum (1). Therefore, carbon steel can be reasonably neglected for a realistic chemical-effects analysis.

Zinc is typically found in containment in the form of galvanized steel and inorganic zinc (IOZ) coatings. Similar to the result for carbon steel, the WCAP-16530-NP testing showed that galvanized steel had a negligible dissolution mass of 8 mg released into solution, compared to 1,580 mg for aluminum. Therefore, galvanized steel can be reasonably neglected for a realistic chemical-effects analysis.

IOZ coatings could potentially be a more significant contributor than the galvanized steel. Some plants have large quantities of unqualified or degraded qualified IOZ coatings. If the coatings fail as particulate, which is likely for IOZ, the surface-to-volume ratio would be very high and may result in significant leaching of zinc into solution. Therefore, a realistic chemical-effects analysis should probably take into consideration the source of zinc from IOZ coatings.

Nickel could be present in the form of RCS crud. However, nickel is resistant to corrosion, and even if some nickel is in solution, it is not likely that any insoluble nickel compounds would be generated (1). Therefore, nickel can be reasonably neglected for a realistic chemical-effects analysis.

Lead may be present in containment in the form of permanent lead shielding blankets or lead wool insulation. Generally, the quantity of lead exposed to the pool or sprays would be low. However, lead corrosion was not tested in the WCAP or ICET experiments. If the quantity of exposed lead is significant, a realistic chemical-effects analysis should probably take into consideration potential lead corrosion and precipitation.

Organic Material

Organic material may be present in containment in a variety of forms such as organic mastics, rubber, foam, phenolic resins, pressed wood, and liquid hydrocarbons (e.g., RCP oil). Generally, the quantity of organic material in the containment pool would be relatively small. The effects of organic materials in containment have been addressed by the NRC in their evaluation of the chemical effects PIRT results. The presence of organic material could potentially have some influences on chemical effects (both beneficial and detrimental). However, the NRC concluded that these influences would in general be minor and would have an insignificant effect on head loss (52). Therefore, organic material can be reasonably neglected for a realistic chemical-effects analysis.

Reactor Coolant Oxides

During normal plant operation, iron and nickel oxides can build up on the inner surfaces of the RCS piping, fuel, and components. Some of this material is released as crud during normal plant shutdowns. Since a LOCA would create a much larger shock on the system, the quantity of crud released following a LOCA may be higher than the quantity released during a refueling outage. In the evaluation of the chemical-effects PIRT results, the NRC estimated that up to 400 kg of crud could be released (52). However, the NRC concluded that the potential transport for the crud would be minimal and the material itself would not significantly influence chemical effects. Therefore, reactor coolant oxides can be reasonably neglected for a realistic chemical-effects analysis.

Radiolysis Products

Radiolysis is the chemical decomposition of molecules by radiation. Radiolysis of water can produce H_2 , O_2 , H_2O_2 , OH , and other products. The NRC reviewed radiolysis as part of the evaluation of the chemical-effects PIRT results and concluded that the small concentration of these products would produce negligible effects on the dissolution or corrosion rate for other materials (52).

The radiolysis of electrical cables in containment can cause chloride ions to gradually leach into the pool and form hydrochloric acid (HCl) or other acids. Also, the nitrogen in the containment atmosphere can be broken down by radiolysis, resulting in the formation of nitric acid (HNO_3). The NRC concluded that the various acids that could form through radiolysis would have a relatively minor impact on chemical effects (52). However, since the acids that gradually form would tend to decrease the pH in the pool, and the dissolution/corrosion of various containment materials is pH dependent, a realistic chemical-effects analysis should take into consideration the slight decrease in pH due to the long-term formation of acids from radiolysis.

Material Aging

The effects of aging on concrete material in containment were addressed in the NRC evaluation of the chemical-effects PIRT results (52). Over time, carbonation can occur on the exposed surfaces of some components in cement. This can result in a higher calcium dissolution rate than would occur with fresh cement. This could be a significant concern, particularly for plants with a TSP buffer. Generally, however, most concrete surfaces in containment are coated, which would prevent carbonation. Therefore, for concrete surfaces exposed by the removal of coatings within the ZOI, it is not necessary to consider the effects of carbonation. However, a realistic chemical-effects analysis should take into consideration the effects of carbonation on uncoated concrete that is exposed to the pool or spray water.

Variations of RCS Chemistry Conditions over Fuel Cycle

The chemistry of the RCS varies during a normal fuel cycle. Specifically, the boron and lithium concentrations will diminish over time, and the pH will become less acidic. Although the RCS volume is smaller than the volume of water injected from the RWST, the initial concentration in the RCS will affect the final pool concentration. Therefore, a realistic chemical-effects analysis should take into consideration the effects of variations in the RCS chemistry over the fuel cycle.

RWST Chemistry Conditions

The initial chemistry conditions of the pool are largely defined by the RWST water. The RWST water generally has a high boron concentration and a low silicon concentration. Both materials are important parameters for chemical effects. Therefore, a realistic chemical-effects evaluation must take into consideration the RWST chemistry conditions.

Biological Effects

Biological growth can occur under extreme conditions. If significant quantities of bacteria or other microorganisms grew in a post-LOCA environment, the material could be transported to the strainer or the core and contribute to debris-bed head loss and blockage. This issue was addressed by the NRC in their evaluation of the chemical effects PIRT results (52). The NRC concluded that most microorganisms cannot survive under high temperature, low or no light, and high radiation conditions. They also concluded that it would be highly unlikely for any microorganisms that do survive to experience significant growth under the harsh post-LOCA conditions. Therefore, biological effects can be reasonably neglected for a realistic chemical-effects analysis.

Effects of Large Temperature Drop in Heat Exchangers

Water that is circulated through the ECCS sump passes through a heat exchanger with a temperature drop of approximately 30°F prior to being injected into the core. This drop in temperature may sufficiently reduce the solubility limit for dissolved materials to cause precipitation. The precipitates could contribute to incore clogging, and if the chemical species remain insoluble at the higher containment pool temperatures, they could contribute also to strainer clogging. Although the thermodynamic conditions are important, reaction kinetics is also important here because the period where the water is cooler (from the heat exchanger to the core) would be brief. If a particular species tends to precipitate slowly, the cooler temperature may not have any impact. Therefore, a realistic chemical-effects analysis should consider the potential for chemical precipitates to form downstream of the heat exchanger, based on both the thermodynamic conditions and the kinetics.

Effects of Large Temperature Increase in Reactor Vessel

At any point in the event, the water temperature will be highest in the core. Due to retrograde solubility, some chemical species may precipitate within the core. This could result in material buildup on hot surfaces such as the fuel rods. Also, precipitated solids or spall from the fuel can transport back to the containment pool, where they can contribute to strainer blockage or bypass the strainer to contribute to incore blockage. Therefore, a realistic chemical-effects analysis should consider the potential effects of the large temperature increase and retrograde solubility within the reactor vessel.

4. Plant Specific Parameters

As discussed in Section 3, many parameters need to be considered for a realistic chemical-effects analysis. Table 2 provides a summary of the plant-specific inputs for STP, including the normal range of values that could be expected. Some values are approximate and may be refined with additional analysis.

Table 2: STP chemical-effects input parameters

Parameter	Minimum Value	Nominal Value	Maximum Value	Reference(s)
Mission Time (days)	-	30	-	(54)
ECCS Switchover Time				
LBLOCA (min)	16.7	-	24.4	(55)
SBLOCA (min)	TBD	-	TBD	
Containment Sprays Secured	7.6	12	720	(56; 57)
Buffer Type	-	TSP	-	(58)

Expected Impact of Chemical Effects on GSI-191
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Parameter	Minimum Value	Nominal Value	Maximum Value	Reference(s)
RCS Initial Concentrations Boron (ppm) Lithium (ppm) Silica (ppm)	0-40 (EOC) 0.4 (EOC) <0.1 (EOC)	1,000 (Mid) 2.5 (Mid) 0.3-0.8 (Mid)	1,400 (BOC) 3.5 (BOC) 0.5-1 (BOC)	(59)
RWST Initial Concentrations Boron (ppm) Silica (ppm)	2,850 1	- -	2,975 6	(59)
Accumulator Initial Concentrations Boron (ppm) Silica (ppm)	2,700 TBD	- -	3,000 TBD	(60)
Containment Pool Initial Concentrations Boron (ppm) Lithium (ppm) Silica (ppm)	2,372 TBD TBD	- - -	2,878 TBD TBD	(60)
Containment pool pH before TSP dissolution	4.6	-	4.8	(61)
Containment pool pH following TSP dissolution	7.3 ²	-	7.9	(60)
Containment Atmosphere Temperature LBLOCA (°F) SBLOCA (°F)	120 TBD	- -	260 TBD	(62)
Containment Pool Temperature LBLOCA (°F) SBLOCA (°F)	126 TBD	- -	267 TBD	(62)
Heat Exchanger Temperature Drop ³ (°F)	≤39	-	93	(63)
Reactor Vessel Temperature	TBD	TBD	TBD	
Pool Volume LBLOCA (ft ³) SBLOCA (ft ³)	31,431 34,860	- -	89,350 -	(64; 65)
Insulation Debris Fiberglass (ft ³) Microtherm (penetrations) (ft ³) Stainless Steel RMI (reactor cavity) (ft ²)	0 0 0	- - -	2,385 4.3 24,493	(66; 58)
Coatings Debris Qualified Epoxy (lb _m) Qualified IOZ (lb _m) Qualified Polyimide Primer (lb _m) Unqualified Alkyd (lb _m) Unqualified IOZ (lb _m) Unqualified Baked Enamel (lb _m) Unqualified Epoxy (Reactor Cavity)(lb _m) Unqualified Epoxy (Other) (lb _m)	0 0 0 0 0 0 0 0	- - - - - - - -	23 553 10 247 843 268 1,714 294	(66)

² Minimum value does not include post-LOCA acid formation. One licensee calculated that radiolysis products could decrease the long term pH by 0.2 (48).

³ Heat exchanger outlet temperature is a function of the inlet temperature and the difference decreases with decreasing inlet temperature (min and max values correspond to 170°F and 267°F inlet temperatures respectively).

Parameter	Minimum Value	Nominal Value	Maximum Value	Reference(s)
Latent Debris				
Fiber (lb _m)	0	-	30	(66)
Dirt/Dust (lb _m)	0	-	170	
Concrete				
Submerged (ft ²)	0	-	0	(66)
Exposed to Sprays (ft ²)	0	-	5,700	
Aluminum ⁴ (ft ²)	-	5,567	6,600	(67)
Copper (ft ²)	TBD	TBD	TBD	
Lead (ft ²)	TBD	TBD	TBD	

Figure 4 shows the time-dependent pH history following initial dissolution of the TSP with minimum and maximum values based on conservative input parameters (61). Figure 5 shows the time dependent containment and pool temperatures for an LBLOCA (62).

⁴ Calculation CN-CSA-06-6 uses a total quantity of 7,000 ft² of aluminum with 10% assumed to be submerged and the remaining 90% assumed to be exposed to sprays (56).

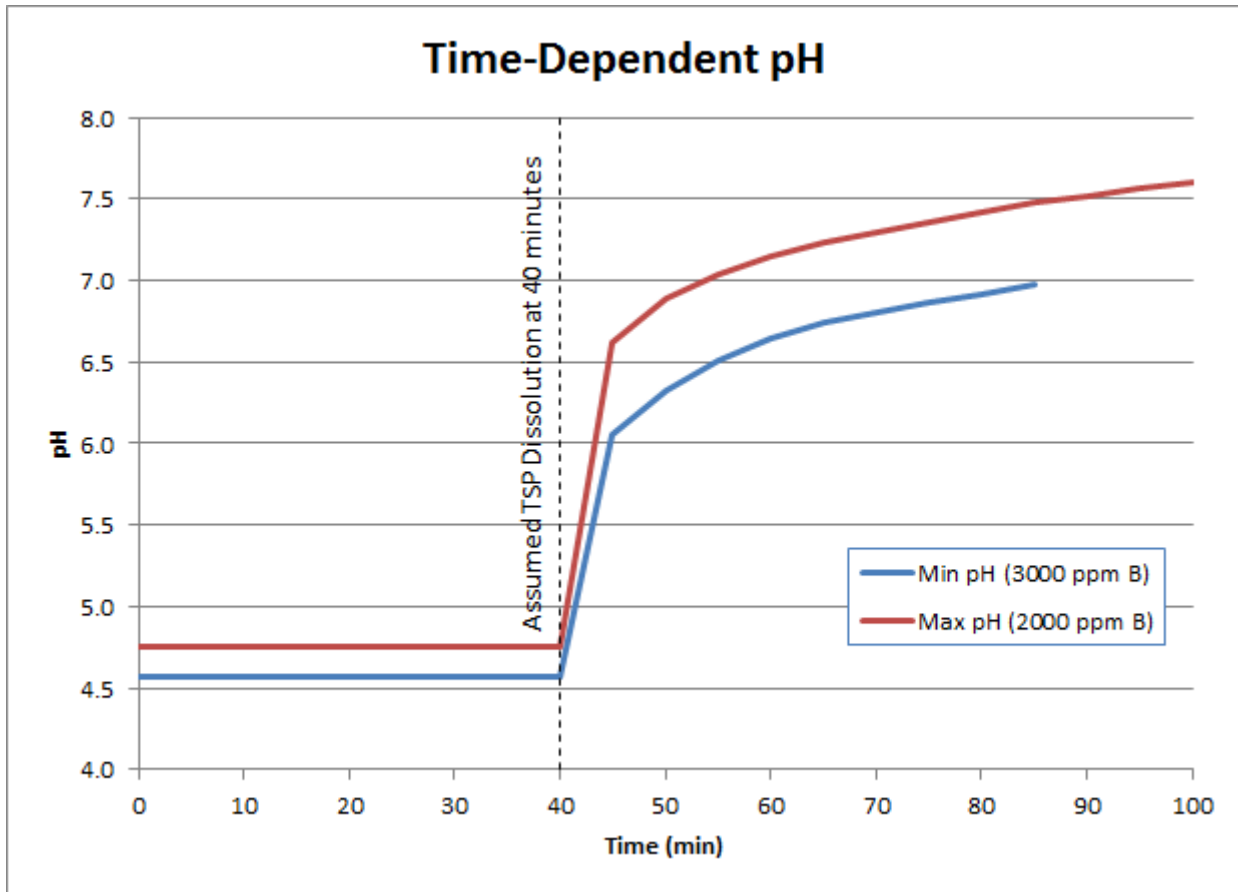


Figure 4: STP time dependent pH following initial dissolution of TSP

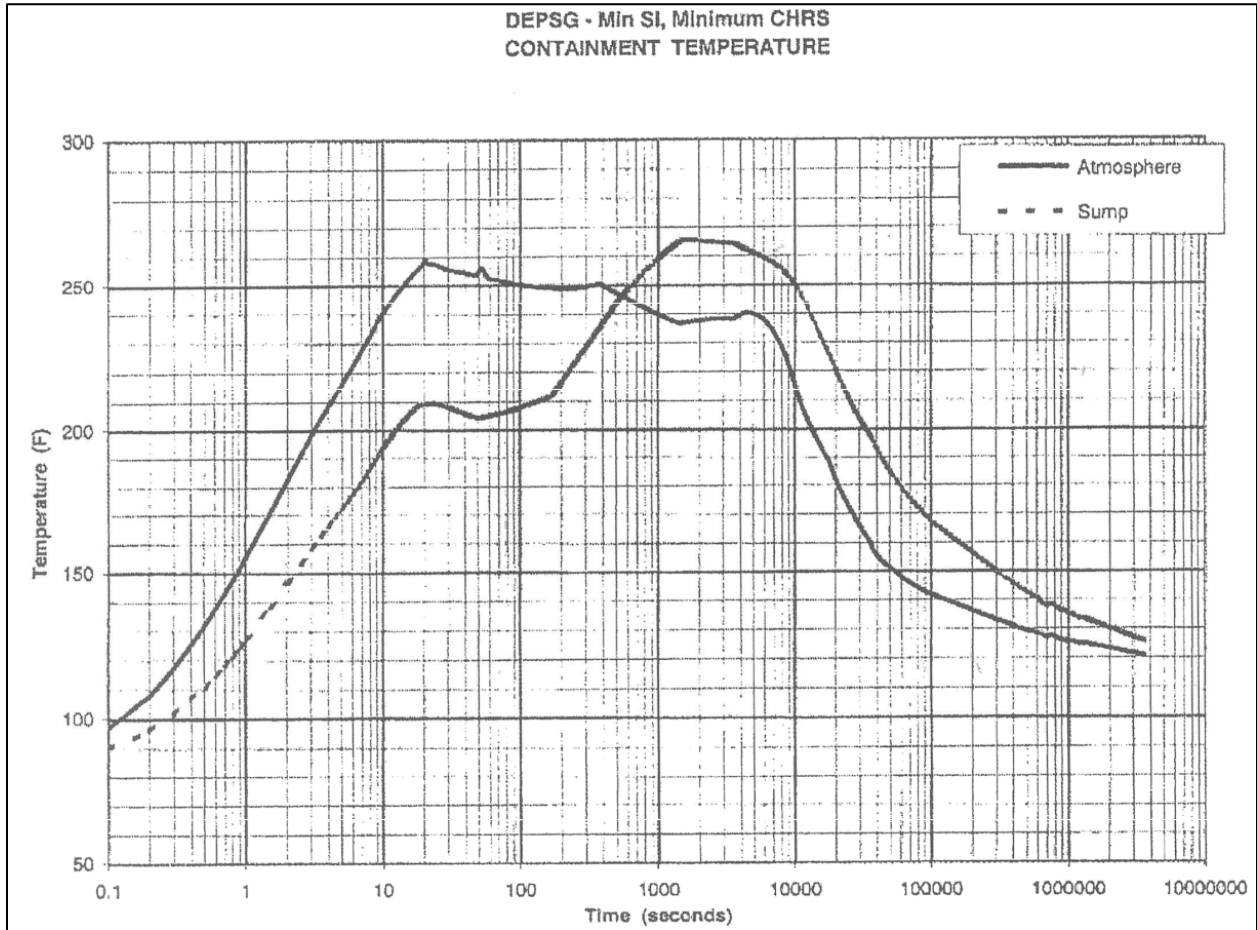


Figure 5: STP time dependent containment and pool temperature for an LBLOCA

5. Expected Plant-Specific Impact from Chemical Effects

The WCAP-16530-NP protocol has been used to predict quantities of aluminum, calcium, and silicon that would be released into solution during a LOCA, based on quantities of materials present in containment at the STP plant. The WCAP-16530-NP protocol is a conservative approach that may overestimate the potential for material release into solution and subsequent precipitation. The ICET and Alion tests provide perspective on the WCAP-16530-NP predictions and suggest possible areas where overpredictions may exist. Results of the ICET and Alion tests pertinent to chemical effects at STP are presented below.

The corrosion of aluminum coupons and concentration of aluminum in solution are consistent with the formation of chemical reaction products that may precipitate from solution. In ICET Tests 1 and 5, the submerged aluminum coupons lost significant mass, and aluminum was detected in solution. However, in Tests 3 and 4, the submerged aluminum coupons did not lose mass, and no aluminum was detected in solution. In Test 2, the submerged aluminum coupons lost a slight amount of mass (0.2%), but no aluminum was detected in solution. None of the unsubmerged aluminum coupons (exposed to the spray for four hours) lost any appreciable mass in any of the tests. Furthermore, the concentration of aluminum in solution was relatively consistent with the loss of mass from the submerged coupons, suggesting that the unsubmerged coupons did not contribute significantly to the formation of products in solution. The concentration of aluminum in solution over the duration of Tests 1 and 5 is shown in Figure 6. In Test 1, the aluminum concentration rose steadily until reaching a concentration of about 360 mg/L after 18 days and stayed at about that concentration for the remainder of the test. In Test 5, the aluminum concentration rose steadily to about 50 mg/L by the 14th day of the test and stayed close to 50 mg/L for the remainder of the test. In both cases, there was no significant concentration difference between filtered and unfiltered samples, which implies that the measured aluminum species in the solution were dissolved, as operationally defined by the filter pore size of 0.7, and that no precipitation in the bulk solution had taken place. Soluble aluminum concentrations were below the detection limit in Tests 2, 3, and 4.

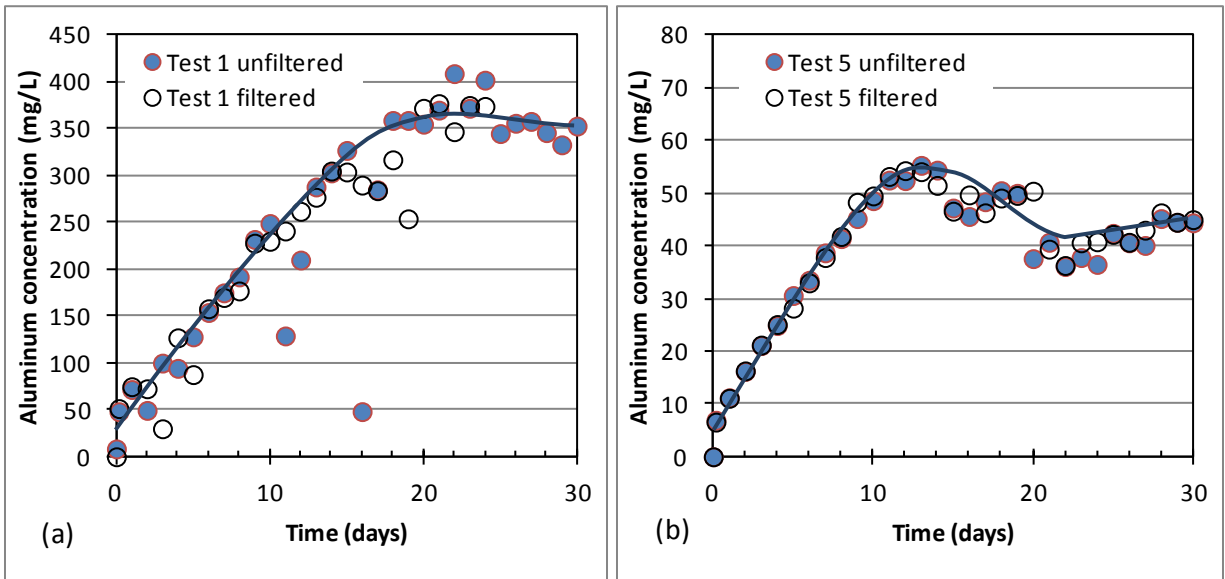


Figure 6: Concentration of aluminum in solution during ICET tests: (a) Test 1, and (b) Test 5

The trends in silicon concentration were the opposite of aluminum. Tests 2, 3, and 4 showed increasing concentrations of silicon in solution, reaching about 40 mg/L (as Si) in Tests 2 and 3 and 84 mg/L in Test 4. The silicon concentration was 6 mg/L (as Si) at the end of Test 1 and 3.5 mg/l at the end of Test 5. The concentration of silicon in solution during the ICET tests is shown in Figure 7.

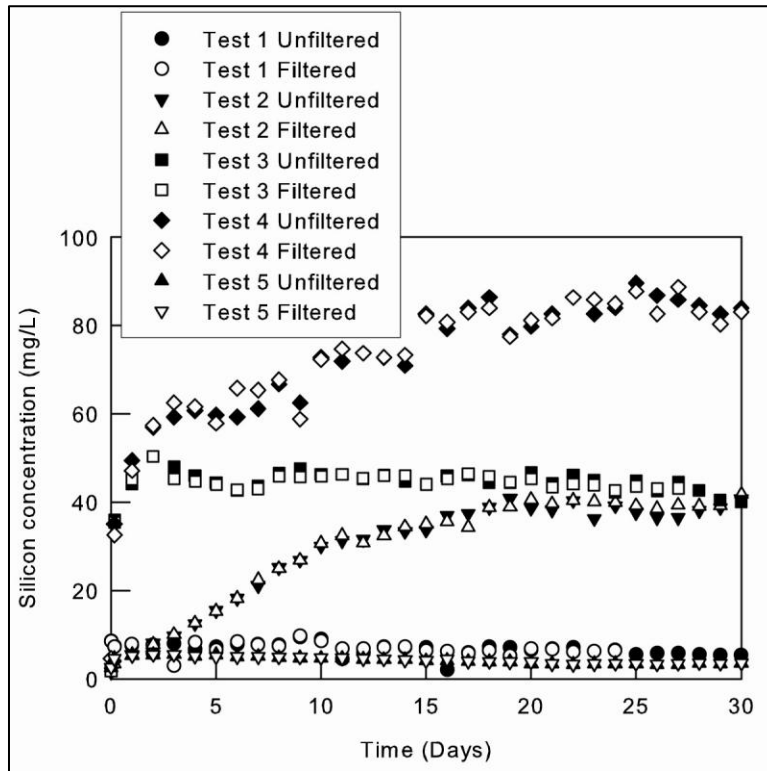


Figure 7: Concentration of silicon in solution during ICET tests

As a result of the ICET program, it was concluded varying amounts of chemical reaction byproducts could precipitate from solution under the conditions outlined in Table 1. Some byproducts were visually detected in test solution at varying temperatures (Tests 1, 3, and 5), whereas other byproducts were found only through microscopic analysis of the fiberglass beds (Tests 2 and 4). Analysis of the three visually detected precipitates revealed that the precipitates were largely composed of aluminum, sodium, and boron (Test 1), calcium, phosphorous, and oxygen (Test 3), and aluminum, sodium, boron and calcium (Test 5) (24).

The quantities of sodium aluminum silicate, aluminum oxyhydroxide, and calcium phosphate that would form in the containment of the STP plant as a result of a LOCA, as predicted by WCAP-16530-NP, are presented in Table 3 (58). Although WCAP-16530-NP used improved estimates for the actual type and quantity of plant-specific materials compared to the ICET program, the corrosion rate equations and precipitation predictions considered independent chemical effects. As a result, this approach may produce conservative results due to the exclusion of competing and simultaneous chemical reactions that influence the final chemical speciation equilibrium. The results from ICET Test 2, which was similar to STP plant conditions with respect to type of insulation and pH control, can be usefully compared to the results simulated for STP under the guidance of WCAP-16530-NP. The quantities of materials in the STP containment versus ICET Test 2 are compared in Table 4 (58; 26). The amount of aluminum available

to corrode into solution in the ICET test was approximately 23 times larger than in the STP containment, and the amount of fiberglass insulation was nearly 4 times the amount at STP. Although the WCAP-16530-NP calculation for STP resulted in large amounts of precipitates, no visible precipitates were formed in ICET Test 2 at test temperature or upon cooling at the completion of the test (although it should be noted that the ICET test was conducted at a constant temperature of 140°F).

Table 3: Quantities of precipitates formed in the STP plant based on WCAP-16530-NP (Base case, max volume, 30-day spray)

Material Released	Quantity (kg)
Sodium aluminum silicate [NaAlSi ₃ O ₈]	649.5
Aluminum oxyhydroxide [AlOOH]	35.7
Calcium phosphate [Ca ₃ (PO ₄) ₂]	162.7

Table 4: Comparison of quantities of materials in containment at STP and ICET Test 2 experimental conditions

Material Type	STP Quantities	Ratio of STP Quantities to Max Pool Volume	Ratio of ICET Test 2 Quantities to Tank Volume	Ratio ICET/STP
Aluminum submerged	700 ft ²	0.007834 ft ² /ft ³	0.179 ft ² /ft ³	22.8
Aluminum exposed to spray	6300 ft ²	0.070509 ft ² /ft ³	3.34 ft ² /ft ³	47.4
Fiberglass insulation submerged	2385.1 ft ³	0.026694 ft ³ /ft ³	0.103 ft ³ /ft ³	3.9
Marinite insulation submerged ⁵	15.2 ft ³	0.00017 ft ³ /ft ³	-	0.0
Microtherm insulation submerged	1.8 ft ³	2.01E-05 ft ³ /ft ³	-	0.0
Concrete submerged	5700 ft ²	0.063794 ft ² /ft ³	0.015 ft ³ /ft ³	0.2

The changes in pH during a LOCA were captured in the protocol for ICET Test 2. Before test initiation, the containment-solution pH was 4.3. At test initiation, the containment-solution pH rose to ~5.5 due to the addition of latent debris and concrete dust and remained at this pH for 30 minutes. The addition of the two batches of TSP began 30 minutes into the test and resulted in a rise of solution pH to 7.3. The pH drifted from a high of 7.3 at day one to ~7.1 by day four and returned to a value of 7.3 by day seven, where it remained for the duration of the test.

Throughout ICET Test 2, concentrations of aluminum, copper, iron and nickel in the test solution were below the detection limits. The concentration of zinc, the only transition metal measured in solution, peaked at 10 mg/L on the first day of testing and decreased below the detection limit by the fifth day,

⁵ Note that the marinite insulation (originally installed on the reactor vessel nozzles) has been removed. However, it is included in this table since the current STP chemical precipitate calculation still includes marinite as part of the chemical source term (58).

where it remained for the duration of the test. Soluble concentrations of calcium and sodium were relatively constant throughout the test, with average values of 8 mg/L and 900 mg/L, respectively. The soluble concentrations of magnesium and silicon increased from below detection concentrations at the start of the test to their respective maximum concentrations of 8 mg/L and 40 mg/L by Day 20. Turbidity and total suspended solids (TSS) measurements were at their highest values during the first day of testing and decreased to minimum values by the fifth day of testing, where they remained for the duration of the test.

Particles and/or precipitates were not visually observed in solution at test temperature or upon cooling of water samples, but white deposits were observed upon surfaces within the test structure. These deposits became visible during the first day of testing and appeared to increase during the first two weeks.

The submerged aluminum coupons were the only coupons in ICET Test 2 to lose mass. However, they lost only 2.7 g, or 0.2% of their combined mass, and the daily soluble concentration of aluminum was below detection limit over the entire test. Under the guidance of WCAP-16530-NP, which considered only independent chemical effects, the corrosion rate for the ICET Test 2 aluminum should have been approximately 10 times the measured corrosion rate, as shown in Figure 8. Although the conditions in ICET Tests 3 and 4 differed from those at the STP facility, WCAP-16530-NP overpredicts the corrosion rates observed in those tests by at least 100 times. Although the WCAP-16530-NP equation used to determine the aluminum corrosion rate was based on temperature and pH effects, excluding competing and/or simultaneous chemical reactions may cause this equation to predict an overly conservative corrosion rate.

The conservative nature of the WCAP-16530-NP equation may be due to the interactions between aluminum and silicon or between aluminum and phosphate in solution. An examination of ICET Test 2 indicates that the aluminum corrosion rate is below the prediction of the WCAP-16530-NP equation when the silicon concentration is higher than baseline (see Figure 7 and Figure 8). This suggests that silicon inhibited aluminum corrosion in the ICET tests. Also, silicon inhibition of aluminum corrosion, as well as phosphate inhibition on aluminum corrosion was demonstrated in WCAP-16785-NP (36).

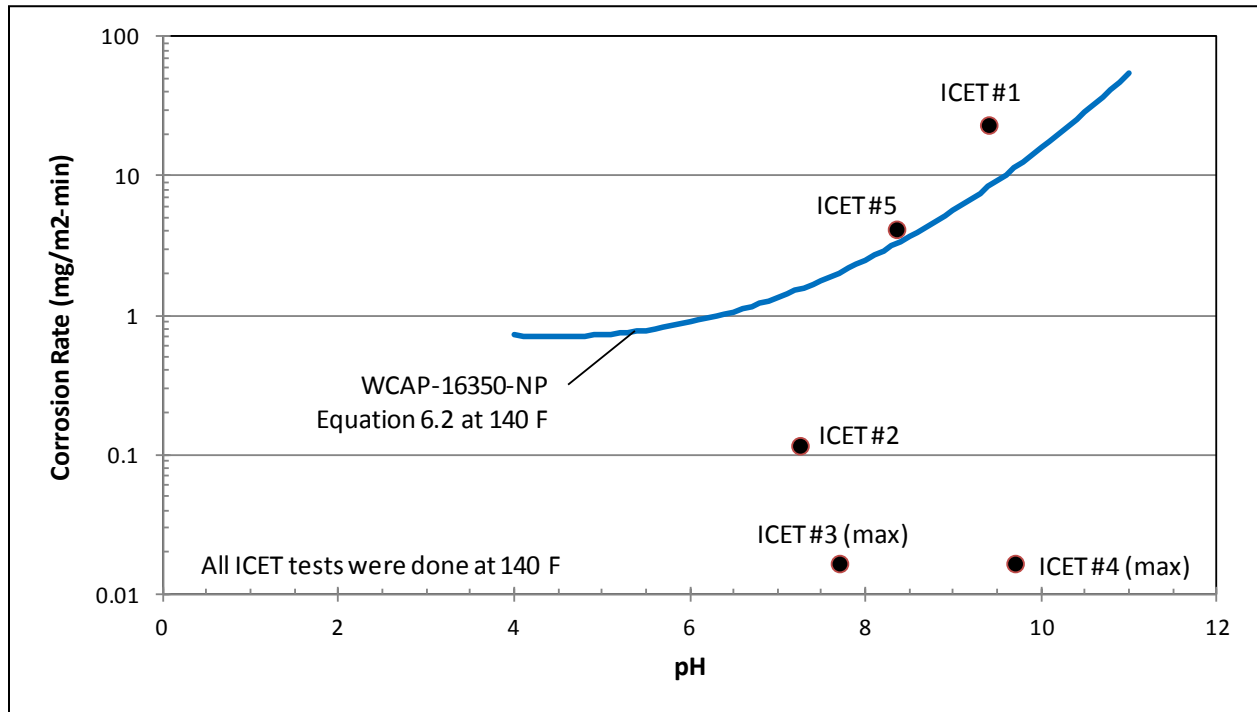


Figure 8: Simulated and experimentally observed aluminum corrosion rates (the rates shown for ICET #3 and #4 are maximum rates based on the limit of detection of the weight measurements, since no weight loss was detected for those tests)

WCAP-16785-NP developed additional inputs to the WCAP-16350-NP model (36). Provisions were allowed for silicon and phosphate inhibition of aluminum corrosion. Additionally, WCAP-16785-NP indicated that as precipitation progresses and the aluminum concentration in solution declines to the solubility limit, precipitation will cease. WCAP-16785-NP determined the aluminum solubility of both aluminum precipitates, sodium aluminum silicate and aluminum oxyhydroxide, to be 40 mg/L (1.48 mM) for a temperature range from 140 to 200°F. Tests for WCAP-16785-NP were conducted at pH = 8, but the report indicated that perturbations down to pH = 7 and up to pH = 9 had no effect on solubility. These results are not consistent with accepted trends of aluminum solubility.

Figure 9, which depicts the result of thermodynamic modeling, indicates that the solubility limit for aluminum prior to the precipitation of aluminum hydroxide is strongly dependent on both pH and temperature. The specification of aluminum solubility as 40 mg/L is conservative as pH rises above 8 and temperature rises above 140°F, but it is not necessarily conservative for pH values below 8. The latter point was noted in a review of WCAP-16785-NP, which stated “WCAP-16785-NP also states that perturbations in pH down to 7.0 did not affect these results. The test results reported here, that were based on longer term tests, show that the WCAP limits are not conservative for pH values as low as 7.0” (46). This is important for STP since the pH in containment during a LOCA ranges from 7.3 to 7.9 following dissolution of the TSP (see Table 2).

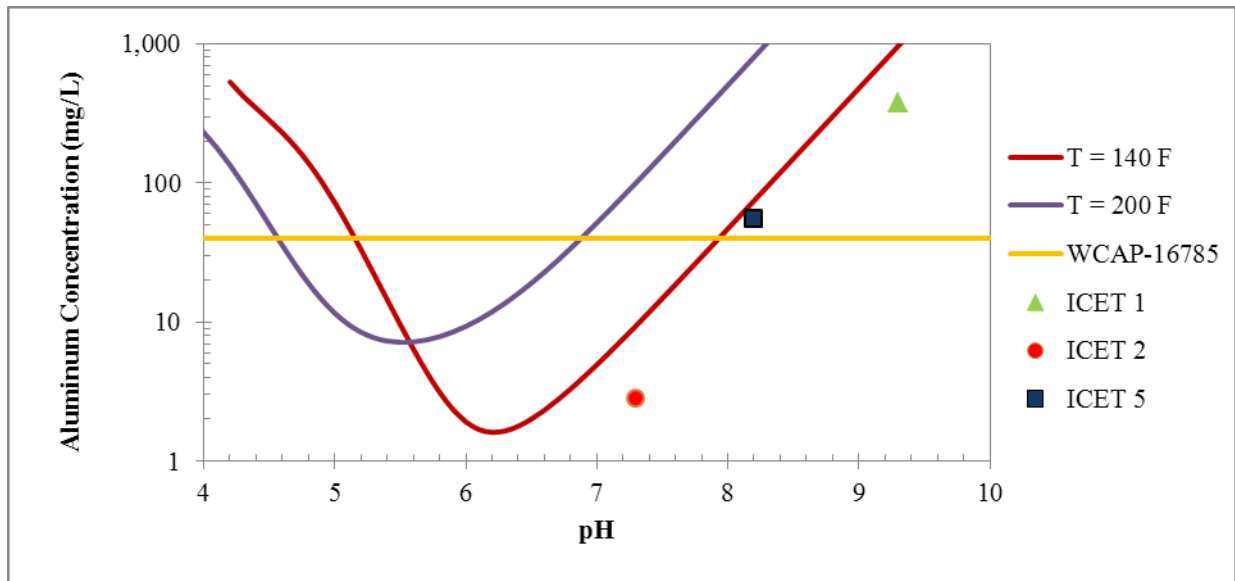


Figure 9: Aluminum solubility in borated water⁶

Also shown in Figure 9 is the aluminum concentration in solution at the end of ICET Tests 1, 2, and 5. The aluminum concentrations shown for these tests are measured values for Tests 1 and 5, and a calculated value for Test 2 (based on the mass lost from the submerged aluminum coupons and the tank volume) because the aluminum concentration was not detected during Test 2. The calculated aqueous aluminum concentration of ICET Test 2 was below the aluminum solubility defined by WCAP-16785-NP, but measured aqueous aluminum concentrations for ICET Tests 1 and 5 were at or above the limit of solubility as defined by WCAP-16785-NP, indicating that aluminum can exist in solution significantly above the WCAP-16785-NP solubility limit without precipitation occurring.

As shown in Figure 9, the maximum concentrations of aluminum in ICET Tests 1, 2, and 5 were all slightly below the solubility limit for aluminum based on the precipitation of aluminum hydroxide, even though no precipitation occurred in the bulk solution during the tests. As noted earlier, the concentration of aluminum rose steadily during the first portion of Tests 1 and 5 (18 days for Test 1 and 14 days for Test 5) but did not continue to rise for the remainder of the tests. Regardless of whether aluminum corrosion may have continued, it appears that the release of aluminum into solution ceased as the concentration approached the solubility limit. Thus, the solubility of aluminum hydroxide may act as an upper bound to the amount of aluminum that can enter solution via corrosion. A consequence of this upper bound is that it may not be possible for aluminum to become sufficiently supersaturated to precipitate in the bulk solution, provided pH and temperature do not shift to lower solubility conditions.

⁶ The lines labeled T = 140 and T = 200 are solubility limits for aluminum hydroxide based on thermodynamic modeling using Visual MINTEQ. The WCAP line is the solubility limit specified in WCAP-16785-NP (34), and the ICET points are the measured Al concentrations at the measured pH at the end of the 30-day tests (24).

Although the solubility limit might be an upper bound to the aluminum concentration at a given temperature, the solubility of aluminum hydroxide is strongly temperature dependent. The solubility of aluminum hydroxide for temperatures from 68 to 212°F is shown in Figure 10.

The existence of the solubility limit as an upper bound on the aluminum concentration in solution can be explained by surface reactions and precipitation kinetics at the surface of the aluminum coupons. When immersed in borated water, the aluminum coupons corrode and form a rough, non-protective oxide layer, which was seen in many SEM images during the ICET tests. The oxide layer has a chemistry similar or identical to the aluminum hydroxide precipitate, and therefore forms effective nucleation sites for precipitation to occur. Any aluminum ions released into solution from the metal surface have to pass through or near this oxide coating. If concentrations are near the saturation limit, the precipitation will occur on the previous oxide coating and not in the bulk solution.

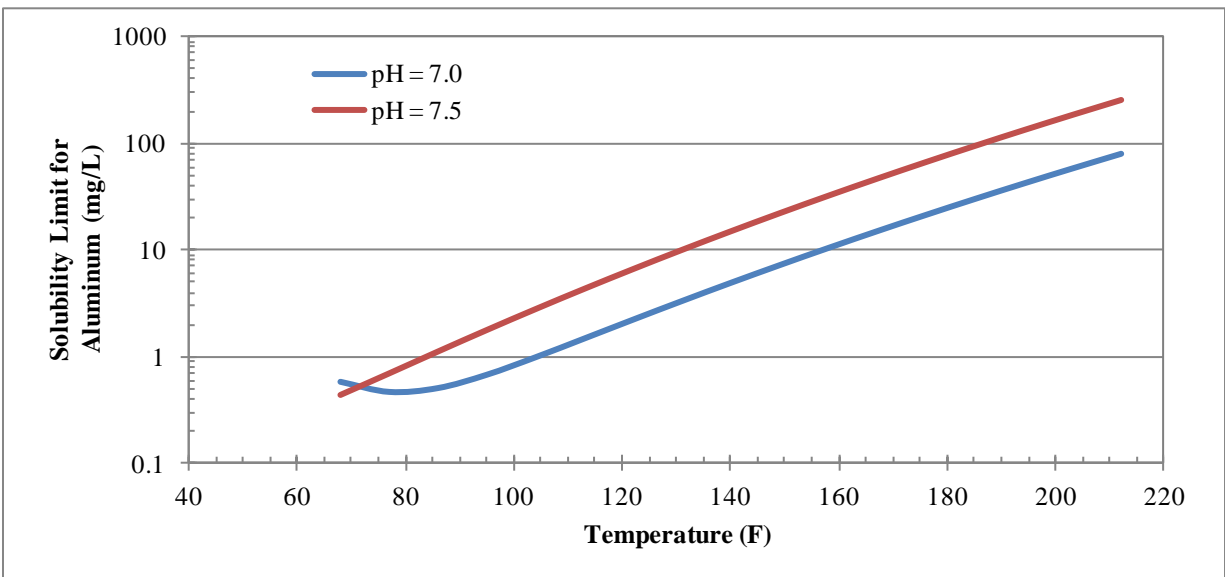


Figure 10: Solubility limit of aluminum based on precipitation/dissolution of aluminum hydroxide in borated water from thermodynamic modeling using Visual MINTEQ

Testing done by Alion for the Vogtle plant at the VUEZ facility appears to corroborate the ICET Test 2 results (39). A series of bench corrosion experiments were conducted to evaluate corrosion and material release when combinations of debris were evaluated together. When Nukon was present with aluminum in solution, the concentration of silicon was higher and the concentration of aluminum was lower than when Nukon was absent. This suggests that the release of silicon from the Nukon fibers had a passivating effect on the corrosion of aluminum. When the Nukon was absent, the aluminum concentration was higher but was bounded by the solubility limit of aluminum, as in the ICET tests. Furthermore, no visible precipitates were observed in solution, suggesting that if precipitation did occur,

it did so on surfaces (aluminum coupons or Nukon fibers). Integrated corrosion and headloss tests also showed similar results. At the end of each of the three integrated tests, the concentration of silicon was 25 mg/L or higher and the concentration of aluminum was below 1 mg/L.

Also, Alion high-temperature vertical loop testing has shown that aluminum precipitates would not form at higher temperatures for specific concentrations of aluminum and silicon in solution. A test series performed for Vogtle showed that aluminum precipitates would not form at temperatures higher than 128°F at a pH between 7.6 and 7.8 with a dissolved aluminum concentration of approximately 4 ppm and silica concentration of approximately 26 ppm (68). Similarly, a test series performed for Calvert Cliffs in 2009 showed that there would be no precipitation of 10 ppm dissolved aluminum and 60 ppm dissolved silicon in NaTB buffered and borated water at temperatures as low as 60°F with a pH of approximately 7.4 (69; 70).

The quantities of materials predicted to be generated in the STP plant are presented in Table 5. The materials precipitated were presented in Table 3. These values are predicted using the WCAP-16530-NP methodology, and a base case with the maximum pool volume and a spray duration of 30 days (58). The amount of aluminum predicted to be in solution is 33 mg/L, which is more than 10 times greater than what was observed in ICET Test 2 and greater than the predicted solubility limit for aluminum hydroxide. At 140°F and pH = 7.5, the solubility of aluminum is 15 mg/L. With the lower aluminum release rate that is suggested by ICET Test 2, the concentration of aluminum in the post-LOCA containment environment of STP might never exceed the solubility limit of aluminum hydroxide.

Table 5: Quantities of materials released in the STP plant based on WCAP-16530-NP (Base case, max volume, 30-day spray)

Material Released	Quantity (kg)
Calcium	63.06
Silicon	208.85
Aluminum	82.92

The precipitated quantities can be expected to be lower than given in Table 3. The calcium phosphate is based on quantities of calcium released from several materials, including marinite insulation. However, the marinite insulation has since been removed from containment, reducing the amount of calcium released into solution from 63.06 to 28.57 kg. As noted above, the amount of aluminum precipitates may be reduced by silicon or phosphate inhibition as demonstrated by the ICET tests, the Vogtle integrated-effects tests, and the WCAP-16785-NP single-effects tests. However, NRC staff have expressed reservations about the WCAP protocols with respect to these inhibitions since neither the ICET tests nor the WCAP-16785-NP tests contain both plant-specific inputs and integrated chemical effect. The Vogtle tests included plant-specific inputs, but the NRC staff expressed concern that the debris configuration in the test tanks may not have allowed the debris materials to interact with the test

fluid in a representative manner. Therefore, there is a need to experimentally demonstrate the inhibition on aluminum corrosion as a function of silicon and phosphate in an integrated chemical-effects test and correlate the final corrosion rates to expected precipitate formation. This should be done to reflect plant-specific conditions and the incorporation of the temperature and pH profiles of a containment sump during a LOCA.

In summary, the ICET tests suggest that several factors may lead to less precipitation than predicted by the WCAP-16530-NP protocol, including:

- Corrosion rates in Tests 2, 3, and 4 were 10 to 100 times lower than predicted by WCAP, possibly because of silicon or phosphate inhibition. The STP insulation and pH control is similar to that of ICET Test 2.
- The ICET tests suggest that the solubility of aluminum hydroxide may act as an upper bound to the concentration of aluminum that can occur in solution at a given pH and temperature. The WCAP predicts that the concentration of aluminum in containment at STP will reach 33 mg/L, which is above the solubility limit at 140°F.

6. Preliminary Ideas for Test Methodology

Risk-informing the GSI-191 chemical issue for STP is based on the development of a chemical module for the CASA Grande program. The CASA Grande chemical module will be intended to calculate the chemical precipitate(s) for each weld break location based on the break-specific debris sources (e.g., the debris from the ZOI), other materials (e.g., exposed aluminum, concrete), and parameters associated with the break (e.g., water level, spray duration, water temperature). The chemical module will need to be validated experimentally. There is also a need to develop an algorithm for implementation in the CASA Grande head-loss module to assess impact of chemical precipitates on head loss. Most experiments currently used to determine the chemical-effects impact on head loss are based on the WCAP-16530-NP formulation of amorphous chemical precipitate(s). As discussed elsewhere in this document, there are indications that the amorphous form of the surrogate chemical precipitate may not represent the actual chemical precipitate. There are limited single effects and integrated experiments that are directly applicable to the STP conditions, and almost no data to support the development of an algorithm to calculate the head losses due to chemical precipitates. This section addresses experiments that could be performed to obtain the necessary data to develop and validate a CASA Grande chemical module, and develop and validate a chemical-effects head-loss algorithm that can be implemented within the CASA Grande head-loss module.

Experimental Goal

The goal of risk-informing the chemical issue for STP is to realistically model chemical effects and validate the model by conducting experiments to obtain the necessary data for the CASA Grande chemical module and chemical-effects head-loss algorithm. The experiments need to be as prototypical as possible in order to develop realistic, applicable data. These goals suggest the conduct of integrated chemical-effects experiments performed with prototypical water chemistry, debris, plant materials submerged and exposed to spray, temperature profiles, and fluid flows.

Data Requirements

To develop and validate a chemical precipitate module, the experiments need to provide data to determine:

- The identity of the chemical precipitate(s)
- The total quantity and rate of formation of the chemical precipitate(s)
- The form of the precipitate(s) (i.e., crystalline or amorphous)
- The size and shape (if crystalline) and other characteristics of the precipitate(s)
- The site of formation of the precipitate(s) (i.e., the site of nucleation if crystalline)

To develop and validate a chemical-effects algorithm, the experiments need to provide data to determine:

- Head loss as a function of chemical precipitate quantity (and concentration)
- Head loss as a function of debris-bed thickness and composition
- Head loss as a function of flow and temperature

Experimental Objectives

The following are the primary objectives of an integrated chemical-effects experiment:

- Demonstrate and characterize aluminum corrosion in the presence of silica and phosphate at various temperatures
- Determine temperature, pH, and concentration of aqueous chemical constituents at the point of precipitation when constituents are introduced into solution through corrosion and dissolution processes instead of through the addition of metal salts
- Determine precipitate chemical composition by Nuclear Magnetic Resonance (NMR) analysis
- Determine whether the precipitate is amorphous or crystalline by X-Ray Diffraction (XRD) analysis
- Determine effects of temperature, pH, and aging on the precipitate after it is formed
- Determine the site of nucleation if the precipitate form is crystalline
- Determine the head loss across a STP specific debris bed exposed to prototypical fluid chemistry as a function of time and temperature

Experimental Apparatus Considerations

Integrated experiments that include both corrosion and head loss within a single apparatus are warranted to provide input data to the risk-informed closure path. Such integrated experiments should be run at suitable conditions to address the range of parameters and uncertainty necessary to apply the risk-informed approach. Variable temperature and pH are key parameters. In addition, the experiments can be designed to address the higher corrosion rates that occur during the initial periods of a LOCA, such as by including additional materials for corrosion during the first period of testing, operation at an intermediate temperature for a longer period, or titration of additional corrosion products into the experimental apparatus at a rate corresponding to the initial corrosion rates.

Three basic categories of apparatus are capable of performing integrated chemical and head-loss experiments:

- Vertical head-loss loop
- Chemical reaction tank with an associated head loss loop
- Chemical reaction tank with a full-scale strainer module

Vertical Head Loss Loop

The Alion high-temperature chemical vertical head-loss loop located in Warrenville, IL is representative of this type of apparatus. The Alion facility provides the ability to pass fluid through a debris bed formed over a horizontal perforated plate. The fluid temperature can be set anywhere from 60°F to 200°F. Degasification of the fluid can be done with a vacuum roughing pump for the conduct of head-loss testing at temperatures above 150°F. Ports are available for the introduction of chemicals and the removal of fluid samples. Instrumentation includes dP pressures sensors to monitor the head loss across the debris bed, and thermocouples to monitor and control the fluid temperature. The loop includes a flanged opening to allow introduction of the debris material onto the perforated plate and removal of the perforated plate. The bulk of the system consists of 316 or 304 stainless steel, and the interior of the sections around the perforated plate are transparent to allow for observation of the debris bed. The loop's design promotes debris transport and minimizes debris collection areas. Figure 11 and Figure 12 show a photograph and schematic of the Alion high-temperature vertical loop.

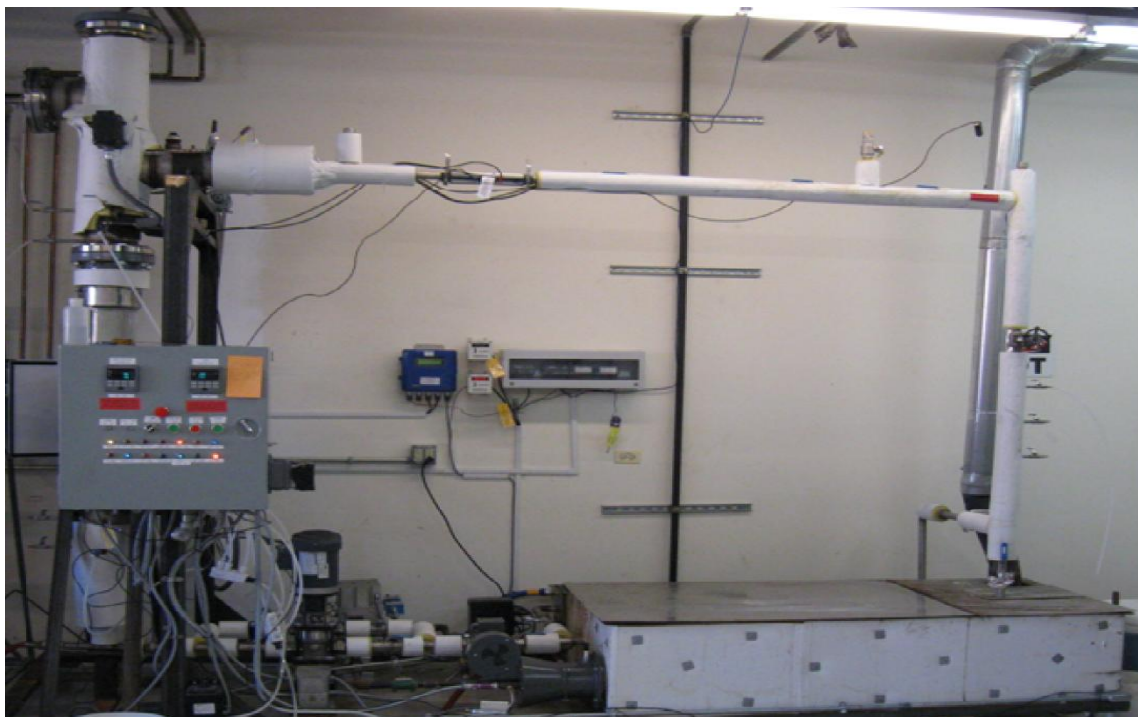


Figure 11: Photograph of Alion high-temperature vertical head-loss loop

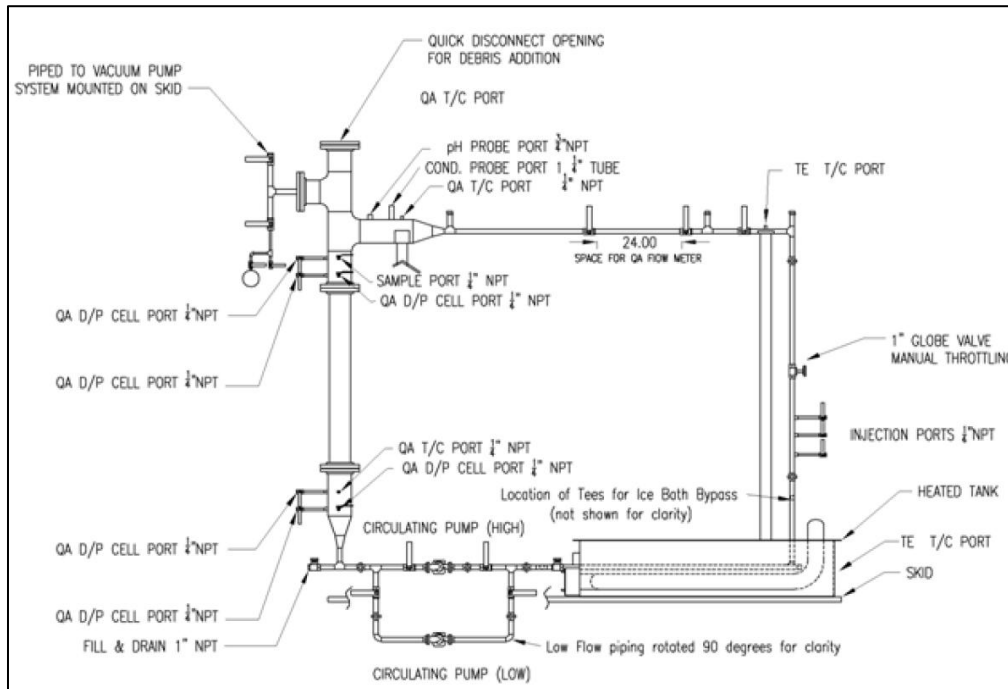


Figure 12: Flow diagram of Alion high-temperature vertical head-loss loop

Chemical Reaction Tank with an Associated Head Loss Loop

The ICET tank (if modified to include a vertical head-loss loop) is representative of this type of apparatus. The ICET tank, located at UNM in Albuquerque, provides sufficient volume and flow capabilities to address concerns about appropriate contact between insulation materials and sump fluids. Head loss can be evaluated by modifying the ICET tank system to include a recirculating head loss loop that directs the sump fluid in contact with the containment materials through an instrumented debris bed. Thermal cycling due to heat exchangers may also be accommodated in a modified ICET tank if deemed appropriate. Various materials (such as copper, zinc from IOZ coatings, and lead) can be incorporated into the experiment design. Variability in RCS and RWST chemistry can be incorporated to be representative of a LOCA rather than conservative bounding conditions. Figure 13 and Figure 14 show a photograph and schematic of the UNM ICET tank.



Figure 13: Photograph of UNM ICET tank

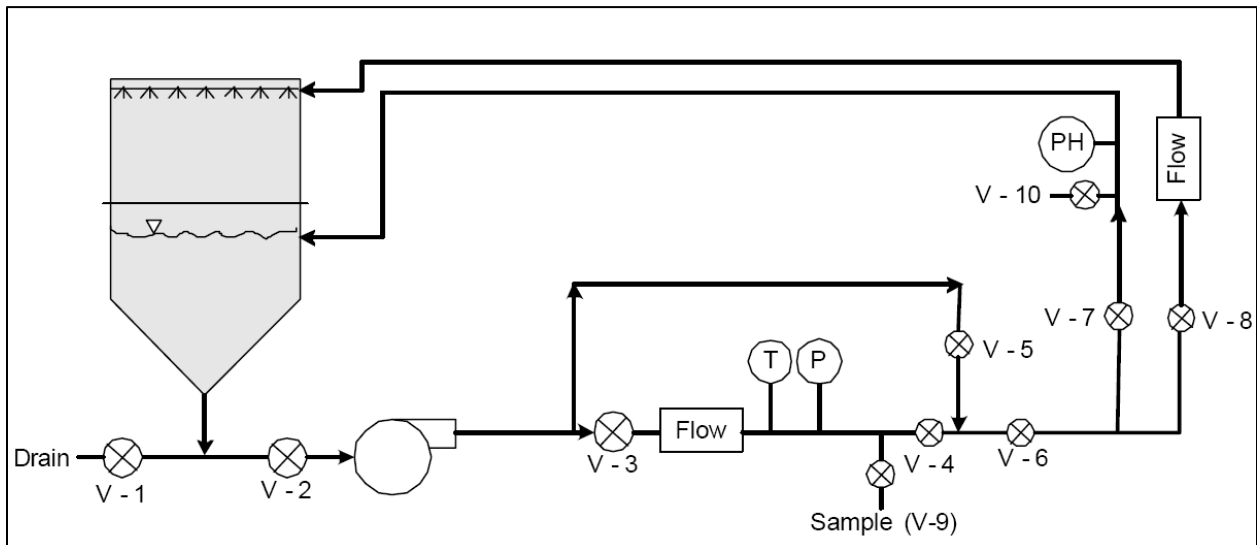


Figure 14: Flow diagram of UNM ICET tank

Chemical Reaction Tank with a Full-Scale Strainer Module

The VIKTORIA loop is representative of this type of apparatus. The VIKTORIA loop, located in Levice, Slovakia, was developed by the “Institut de Radioprotection et de Sûreté Nucléaire” (IRSN) and VUEZ to conduct integrated chemical experiments with a full scale strainer module. The VIKTORIA loop is a significant evolution of the ELISA loops used to conduct the Alion chemical-effects head-loss tests circa 2008. VIKTORIA was designed to address the concerns of the U.S. NRC, especially those associated with the debris bed formation in the ELISA loops. A full size strainer module can be placed in the VIKTORIA tank. The debris is introduced in a separate upstream tank and delivered to the strainer-module tank by a trough, allowing the debris to be prototypically deposited onto the strainer by the flow. The VIKTORIA loop was also designed to investigate downstream effects by incorporating the ability to expose fuel assemblies to the actual debris that bypasses the strainer. Figure 15 and Figure 16 show a CAD model and schematic of the VIKTORIA loop.

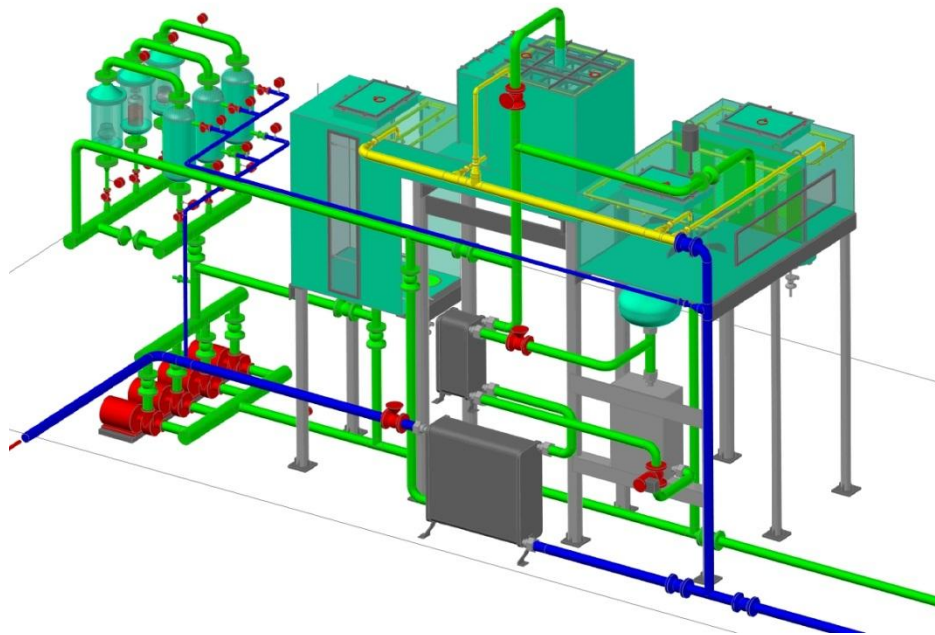


Figure 15: CAD model of VIKTORIA loop

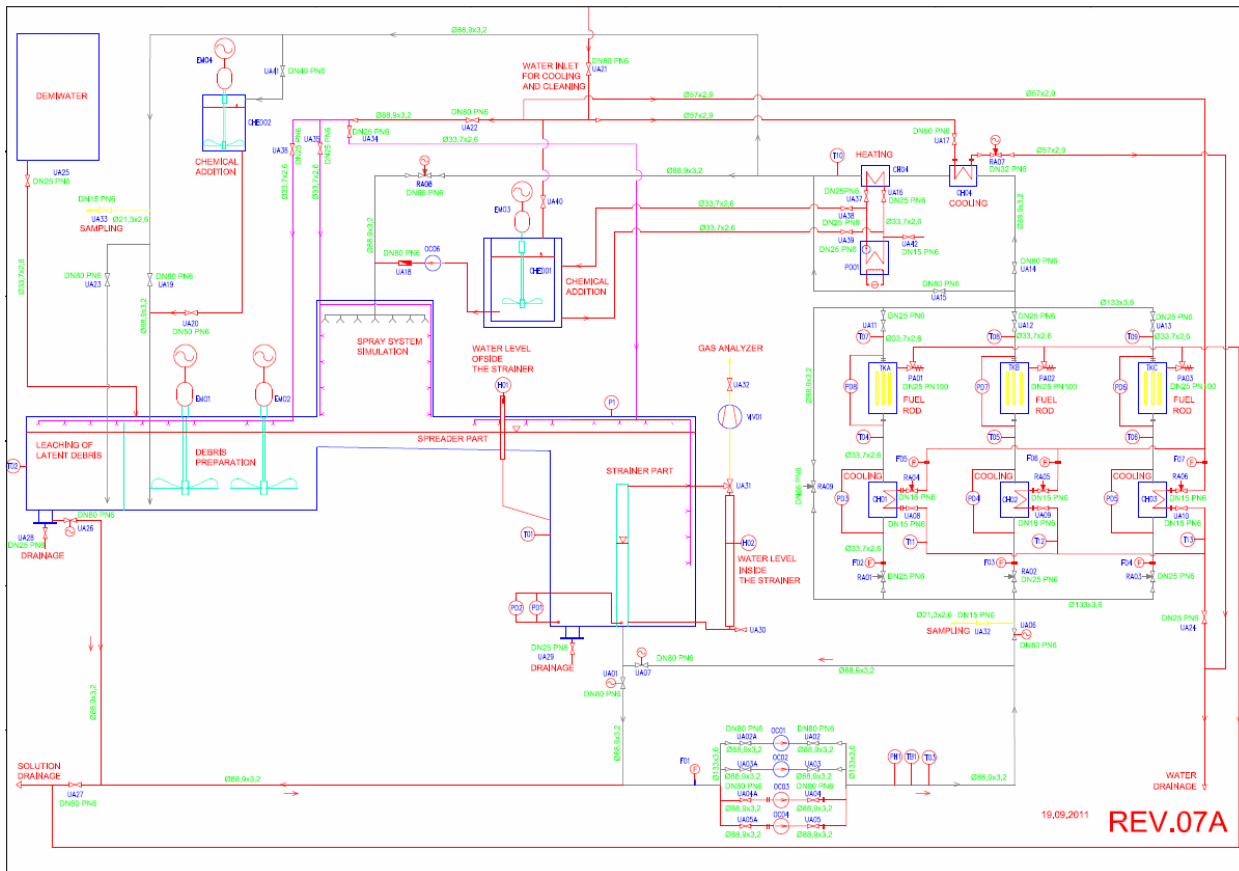


Figure 16: Flow diagram of VIKTORIA loop

Conduct of Integrated Chemical Effects Experiments

The following are some of the basic protocols used for integrated chemical-effects testing:

- Integrated chemical-effects experiments will be conducted in a vessel with metal and concrete test coupons that are scaled to provide a surface area to pool volume ratio that closely matches plant conditions.
- Representative insulation and other debris samples will be placed in the vessel, and all insulation material, concrete, and coatings debris will be constrained, within reason, in a chemically non-reactive mesh that allows water to flow in the region of the samples.
- Any material assumed to be un-submerged yet exposed to spray conditions will be positioned such that it is exposed to the appropriate spray, or submerged in the fluid for the specific period of time while the sprays are assumed to be engaged.
- Experiment conditions (i.e., material quantities and containment environment) will be within the range of conditions considered for the integrated plant analysis.

- The temperature of the simulated sump fluid will be held at the highest temperature limit for the experiment apparatus for such time until the plant specific profile goes below this temperature, at which point the time-temperature profile for the remainder of the experiment will be closely matched to the plant's estimated temperature profile.
- The initial solution within the tank will replicate that which is assumed to occur at the start of a post-LOCA event.
- Buffer will be added to the system at approximately the same rate as it is expected to be introduced into the containment environment.
- Once the scaled amount of buffer has been added, no further pH adjustment will be made (i.e., system pH will not be artificially maintained, but will be allowed to seek its own level due to corrosion, etc.), to be as indicative as possible of actual events in the post-LOCA environment.
- Depending on the experiment apparatus, a fiber debris bed will be formed to investigate the interaction of fiber with the fluid, and the pressure difference across the debris bed will be monitored.
- The fiber debris bed will also serve as a source of nucleation for crystalline particulate based on previous experience in the conduct of integrated chemical testing at VUEZ.

Test Plan Development

A variety of tests (e.g., integrated tank tests, benchtop experiments, and vertical loop tests) may be necessary to achieve the experimental goal, data requirements, and objectives discussed above. An STP-specific preliminary test plan will be developed to address this in more detail. The test parameters will be developed based on the results of thermodynamic modeling of STP specific plant parameters and debris types, and the preliminary test plan will establish the requirements of the experimental apparatus. Apparatus-specific test plan(s) will be developed that will include discussions on scaling and the conduct of the experiments.

As appropriate, bench-top or autoclave testing will be conducted to investigate the interactions of STP-specific chemistry and debris types. These experiments are useful for providing thermodynamic data and insights into the possible outcome of the integrated experiments.

Thermodynamic and kinetic modeling based on the test plans will be conducted to develop the expected results. Head-loss modeling of the fiber debris bed conditions and composition will provide the expected head-loss magnitude across the debris beds. Adjustments will be made to the test plan based on the results of the chemical and head-loss modeling.

Review and Comment Cycles

As with all aspects of the STP GSI-191 Risk-Informed Project there will be numerous comment and review cycles both internally and with the NRC. The intent is to ensure the achievement of a successful technical and licensing outcome for the integrated chemical-effects experiments.

7. Preliminary Ideas for Incorporating Chemical Effects in Risk-Informed Analysis

The proposed experimental work is expected to capture chemical information related to the corrosion rates of aluminum as a function of chemical inhibition resulting from an integrated test. pH and temperature will be important variables. The chemical structures (amorphous or crystalline), the chemical formulas, equilibrium coefficients, enthalpies, and kinetics of formation associated with the precipitates demonstrated to occur during a LOCA will also be determined, from either the experimental work or the literature. These parameters will capture the uncertainties of chemical effects that result from variable rates of aluminum corrosion and precipitate formation as a result of the temperature and pH variability expected in a LOCA. The captured chemical-effects uncertainties will be used in conjunction with uncertainties associated with bed formation on the screen, which will allow a probabilistic risk assessment analysis to be performed.

The STP chemical effects program is intended to incorporate chemical effects into the risk-based assessment by developing a module for the CASA Grande code that relies on output from a thermodynamic chemical-equilibrium and speciation model. Thermodynamic modeling is the computation of a series of chemical reactions to predict the chemical equilibrium for a system, given a set of chemical components. Although many thermodynamic modeling packages exist, such as PHREEQC (United States Geological Survey), Visual MINTEQ (J. Gustafsson), TITRATOR (S. Cabaniss), and Geochemical Workbench (Rockware, Inc.), the thermodynamic equilibrium prediction of a given system should be independent of the program chosen, because all programs operate on the same theoretical and mathematical principles. They use analytical and thermodynamic constraints to iteratively solve a mass balance to predict chemical species concentrations at equilibrium. Thermodynamic modeling provides a conservative approach for modeling chemical effects following a LOCA because the kinetic aspects related to the formation of chemical species is ignored by assuming that all reactions have come to completion regardless of time. To successfully use thermodynamic modeling to predict chemical effects in a containment sump under LOCA conditions, the system has to be adequately defined. To do this, the user must determine representative aqueous concentration of chemical components available to react and must provide a thorough database of reactions with the associated equilibrium coefficients and enthalpies that reflect the most current literature.

To build a thermodynamic model for evaluating chemical effects that occur in a containment sump under LOCA conditions, some basic parameters need to be better defined. Although chemical components such as calcium and aluminum have been identified as critical components to capture in a reaction matrix (due to the expected precipitation of their associated reaction products), the release rate of these species into solution is variable due to corrosion-inhibiting effects found in an integrated system. The uncertainties associated with the release of chemical components into solution are not well understood, but must be captured to adequately describe the chemical concentrations available to react. Moreover, although previous work has identified precipitates that could occur during an event,

these precipitates have yet to be detected in integrated tests. Therefore, the precipitates that are proven to occur in the integrated system must be thoroughly characterized to determine chemical composition and structure, providing confirmation of literature equilibrium coefficients and enthalpies. This will also provide insight regarding the completeness of the reaction database used by the model.

Once the uncertainties associated with the concentrations of available chemical components are captured, and the chemical composition and structure of precipitation products are confirmed, the thermodynamic modeling program can incorporate the chemical components available to react in solution into defined reaction equations, using the associated thermodynamic constraints to determine equilibrium speciation. For a given reaction product at a given solution pH, the program uses the associated equilibrium coefficient to determine the amount of chemical product formed. The associated enthalpy is used to correct the value of the equilibrium coefficient for temperature if it is different from the reference temperature. The program then uses the predicted concentration of a species in solution with the calculation of a saturation index to determine the amount of precipitation products that occur.

Understanding the precipitate composition and its chemical structure may allow for the incorporation of kinetic data into chemical modeling to predict chemical equilibrium at a given time frame. Incorporation of kinetic data allows the model to use the rate of formation of a precipitate product with the soluble species concentration to determine the amount of chemical product that will precipitate at a given time. If the kinetics associated with the formation of precipitates dictates that the products do not precipitate out of solution quickly, the chemical model may predict a lower mass of precipitate at various points in the event compared to the amount predicted by a thermodynamic model. The captured chemical-effects uncertainties will be used in conjunction with uncertainties associated with bed formation on the screen, which will allow a probabilistic risk assessment analysis to be performed.

8. Conclusions

This white paper summarizes the history and important documents related to the GSI-191 chemical issue; identifies the parameters significant to chemical effects; provides the range of relevant STP-specific conditions; and provides a best-estimate evaluation of the actual effects of chemical precipitation at STP in a post-LOCA environment.

The initial best-estimate evaluation will need to be refined and validated with additional tests and analysis, but experimental evidence from several sources suggests that the impact of chemical effects on head loss at STP would be far less severe than predicted by WCAP-16530-NP. Inhibition of aluminum corrosion by silicon and/or phosphate has been demonstrated in tests in support of WCAP-16350-NP, the ICET tests, and tests by Alion. The ICET tests also provided evidence that the corrosion rate for aluminum in conditions similar to the STP post-LOCA containment environment may be an order of magnitude lower than that predicted by the WCAP-16350-NP correlation. Furthermore, these tests indicated that the form of the chemical precipitate for STP is crystalline and not amorphous, as were the precipitates formed using the WCAP 16350-NP recipe.

This white paper supports two major conclusions with regard to the quantity and form of chemical precipitates at STP:

- The quantity of chemical precipitates at STP would likely be significantly less than the quantity calculated using the WCAP-16350-NP methodology.
- The STP chemical precipitates would likely be crystalline and not the amorphous form of WCAP-16350-NP precipitates.

These two major conclusions, in turn, support the following conclusions with regard to the impact of chemical effects at STP:

- The actual STP chemical effects strainer head losses would likely be significantly less than the head losses established by tests that were based on WCAP-16350-NP.
- The actual impact of chemical effects on fuel assembly head losses at STP would likely be significantly lower than the head losses established by tests that were based on WCAP-16350-NP. This conclusion suggests that the fiber limit would be significantly higher than the 15 g/FA acceptance criterion for STP—perhaps close to the limits for conditions without chemical effects.

The risk-informed approach to address the chemical issue for STP considers uncertainty and the probability of various break scenarios. For each break location the chemical precipitate quantity and form will be calculated using thermodynamic and, if possible, kinetic models. Unbiased estimations of

the additional head loss contribution at the strainer and at the fuel assemblies from chemical effects will be developed based on the quantity and form calculated by the chemical models.

Although single effects tests have been conducted to determine the corrosion rates of various materials and the head loss produced by various precipitates, there have been relatively few integrated tests. Furthermore, some of those integrated tests have been conducted at constant temperature and without integration between corrosion and head loss, or have been compromised by concerns about non-representative contact between insulation materials and sump fluids, or other factors. Currently available chemical-effects data from single-effect tests or limited integrated tests are not sufficient to support the risk-informed path to GSI-191 closure. The tests that are currently being considered for the risk-informed chemical-effects program include the following:

- Well-developed integrated chemical effects testing will likely be used to support the development and validation of thermodynamic and kinetic modeling.
- Benchtop and autoclave testing could be used to supplement the integrated chemical effects tests.
- Vertical loop head loss testing with realistic chemical precipitates based on the integrated chemical tests could be used to support the development of a chemical precipitate head loss correlation.
- An integrated chemical and head loss test using a full scale strainer module could be used to validate the overall chemical-effects head-loss model that is developed.

For each aspect of the risk-informed chemical-effects program, previous NRC concerns will be addressed, and the test protocol will be discussed with the NRC prior to running tests to ensure that any additional concerns are fully addressed.

6. References

1. **WCAP-16530-NP.** *Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191.* Revision 0 : 2006.
2. **WOG-06-102.** *Distribution of Errata to WCAP-16530-NP, "Method for Evaluating Post-Accident Chemical Effects in Containment Sump Fluids" (PA-SEE-0275).* March 17, 2006.
3. **WOG-06-107.** *PWR Owners Group Letter to NRC Regarding Error Corrections to WCAP-16530-NP (PA-SEE-0275).* March 21, 2006.
4. **WOG-06-113.** *Submittal of WCAP-16530-NP, "Evaluation of Post Accident Chemical Effects in Containment Sump Fluids to Support GSI-191" for Formal Review.* March 27, 2006.
5. **OG-06-255.** *PWR Owners Group Letter Releasing Revised Chemical Model Spreadsheet From WCAP-16530-NP (PA-SEE-0275).* August 7, 2006.
6. **OG-06-273.** *PWR Owners Group Method Description of Error Discovered August 16, 2006 in Revised Chemical Model Spreadsheet (PA-SEE-0275).* August 28, 2006.
7. **OG-06-378.** *PWR Owners Group Letter Issuing Revised Chemical Model Spreadsheet (PA-SEE-0275).* November 15, 2006.
8. **Office of Nuclear Reactor Regulation.** *Request for Additional Information Re: Westinghouse Owners Group (WOG) Topical Report WCAP-16530-NP, "Evaluation of Post Accident Chemical Effects in Containment Sump Fluids to Support GSI-191" (TAC No. MD1119).* October 4, 2006.
9. **OG-06-387.** *Responses to the NRC Request for Additional Information (RAI) on WCAP-16530, "Evaluation of Chemical Effects in Containment Sump Fluids to Support GSI-191".* November 21, 2006.
10. **Office of Nuclear Regulatory Research.** *Request for Additional Information Re: Pressurized Water Reactor Owners Group Topical Report (TR) WCAP-16530-NP, "Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191" (TAC No. MD1119).* March 23, 2007.
11. **OG-07-129.** *Responses to the NRC Second Set of Requests for Additional Information (RAI's) on WCAP-16530, "Evaluation of Chemical Effects in Containment Sump Fluids to Support GSI-191".* April 3, 2007.
12. **OG-07-408.** *Responses to NC Requests for Clarification Regarding WCAP-16530, "Evaluation of Chemical Effects in Containment Sump Fluids to Support GSI-191" (PA-SEE-0275).* September 12, 2007.
13. **Office of Nuclear Reactor Regulation.** *Final Safety Evaluation by the Office of Nuclear Reactor Regulation Topical Report WCAP-16530-NP "Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191" Pressurized Water Reactor Owners Group Project No. 694.* December 21, 2007.
14. **IM 20.12130.01.001.320.** *Supplementary Leaching Tests of Insulation and Concrete for GSI-191 Chemical Effects Program.* November 2006.
15. **Argonne National Laboratory.** *Technical Letter Report on Follow-on Studies in Chemical Effects Head-Loss Research; Studies on WCAP Surrogates and Sodium Tetraborate Solutions.* February 15, 2007 : s.n.

16. **ALION-REP-GENE-4777-100.** *Summary Report for Impact of Chemical Effects for Vogtle 1 & 2.* July 25, 2008 : Revision 0.
17. **NEI 04-07 Volume 1.** *Pressurized Water Reactor Sump Performance Evaluation Methodology.* Revision 0 : December 2004.
18. **NEI 04-07 Volume 2.** *Safety Evaluation by the Office of Nuclear Reactor Regulation Related to NRC Generic Letter 2004-02, Nuclear Energy Institute Guidance Report "Pressurized Water Reactor Sump Performance Evaluation Methodology".* Revision 0 : December 2004.
19. **NUREG/CR-6868.** *Small Scale Experiments: Effects of Chemical Reactions on Debris-Bed Head Loss.* March 2005.
20. **NRC Generic Letter 2004-02.** *Potential Impact of Debris Blockage on Emergency Recirculation During Design Basis Accidents at Pressurized-Water Reactors.* September 13, 2004.
21. **NUREG/CR-6873.** *Corrosion Rate Measurements and Chemical Speciation of Corrosion Products Using Thermodynamic Modeling of Debris Components to Support GSI-191.* April 2005.
22. **NUREG/CR-6912.** *GSI-191 PWR Sump Screen Blockage Chemical Effects Tests: Thermodynamic Simulations.* December 2006.
23. **NUREG/CR-6913.** *Chemical Effects Head-Loss Research in Support of Generic Safety Issue 191.* December 2006.
24. **NUREG/CR-6914, Volume 1.** *Integrated Chemical Effects Test Project: Consolidated Data Report.* December 2006.
25. **NUREG/C-6914, Volume 2.** *Integrated Chemical Effects Test Project: Test #1 Data Report.* December 2006.
26. **NUREG/CR-6914, Volume 3.** *Integrated Chemical Effects Test Project: Test #2 Data Report.* December 2006.
27. **NUREG/CR-6914, Volume 4.** *Integrated Chemical Effects Test Project: Test #3 Data Report.* December 2006.
28. **NUREG/CR-6914, Volume 5.** *Integrated Chemical Effects Test Project: Test #4 Data Report.* December 2006.
29. **NUREG/CR-6914, Volume 6.** *Integrated Chemical Effects Test Project: Test #5 Data Report.* December 2006.
30. **NUREG/CR-6915.** *Aluminum Chemistry in a Prototypical Post-Loss-of-Coolant-Accident, Pressurized-Water-Reactors Containment Environment.* December 2006.
31. **NUREG-1861.** *Peer Review of GSI-191 Chemical Effects Research Program.* December 2006.
32. **Argonne National Laboratory.** *Technical Letter Report on WCAP-16530-NP, Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191.* February 15, 2007.
33. **WCAP-16793-NP.** *Evaluation of Long-Term Cooling Considering Particulate, Fibrous and Chemical Debris in the Recirculating Fluid.* May 2007 : Revision 0.
34. **OG-11-265.** *Request for Review of DRAFT WCAP-16793-NP, Revision 2-A, "Evaluation of Long-Term Cooling Considering Particulate, Fibrous and Chemical Debris in the Recirculating Fluid," (PA-SEE-0312 Revision 2).* September 7, 2011.

35. **WCAP-16596-NP.** *Evaluation of Alternative Emergency Core Cooling System Buffering Agents.* July 2006 : Revision 0.
36. **WCAP-16785-NP.** *Evaluation of Additional Inputs to the WCAP-16530-NP Chemical Model.* May 2007 : Revision 0.
37. **LTR-SEE-I-07-14.** *Implementation of Refinements to WCAP-16530-NP.* June 22, 2007 : Revision 1.
38. **WCAP-16745-NP.** *Phenomena Identification and Ranking Table (PIRT) for Unbuffered Boric Acid Mixing/Transport in Reactor Vessel During Post-LOCA Conditions.* June 2008 : Revision 0.
39. **ALION-REP-GENE-4777-100.** *Summary Report for Impact of Chemical Effects for Vogtle 1 & 2.* July 25, 2008 : Revision 0.
40. **Office of Nuclear Reactor Regulation.** *Vogtle Electric Generating Plant, Units 1 and 2 - Request for Additional Information Regarding Generic Letter 2004-02, "Potential Impact of Debris Blockage on Emergency Recirculation During Design Basis Accidents at Pressurized-Water Reactors".* September 17, 2008.
41. **ALION-REP-LAB-2352-103.** *Test Report of Aluminum & NUKON Dissolution and Corrosion in TSP.* August 8, 2007 : Revision 1.
42. **ALION-REP-LAB-2352-104.** *Test Report of Aluminum, Zinc, NUKON and Mineral Wool Dissolution and Corrosion in TSP.* August 8, 2007 : Revision 1.
43. **ALION-REP-LAB-2352-219.** *Test Report: Aluminum, Zinc, Insulation, and Concrete Corrosion and Dissolution in TSP and NaTB.* September 4, 2007 : Revision 1.
44. **ALION-REP-LAB-2352-225.** *Test Report of Unqualified Alkyd Coatings Bench Top Testing.* February 13, 2008 : Revision 0.
45. **Argonne National Laboratory.** *Technical Letter Report on Evaluation of Chemical Effects; Studies on Precipitates Used in Strainer Head Loss Testing.* January 30, 2008.
46. —. *Technical Letter Report on Evaluation of Long-Term Aluminum Solubility in Borated Water Following a LOCA.* February 25, 2008.
47. —. *Technical Letter Report on Evaluation of Head Loss by Products of Aluminum Alloy Corrosion.* August 11, 2008.
48. **Office of Nuclear Reactor Regulation.** *NRC Staff Review Guidance Regarding Generic Letter 2004-02 Closure in the Area of Plant-Specific Chemical Effects Evaluations.* March 2008.
49. **NUREG-1918.** *Phenomena Identification and Ranking Table Evaluation of Chemical Effects Associated with Generic Safety Issue 191.* February 2009.
50. **NUREG/CR-6988.** *Final Report - Evaluation of Chemical Effects Phenomena in Post-LOCA Coolant.* March 2009.
51. **BWROG-ECCS-TA04-001.** *BWROG ECCS Strainer Chemical Effects Resolution Strategy Plan and Flowchart.* April 16, 2011 : Revision 0.
52. **Office of Nuclear Reactor Regulation.** *Evaluation of Chemical Effects Phenomena Identification and Ranking Table Results.* March 2011.
53. **NUREG/CR-6808.** *Knowledge Base for the Effect of Debris on Pressurized Water Reactor Emergency Core Cooling Sump Performance.* Final Report : February 2003.

54. **UFSAR Section 9.2.1.2.** *Essential Cooling Water System: Design Bases.*
55. **UFSAR Table 6.2.1.1-10.** *Accident Chronology for DBA LOCA Analysis.* : Revision 15.
56. **Email from Ernie Kee (STP) to Duane Gore (STP).** *RE: When turn off cont spray RE: Follow-up on this week's meetings.* October 5, 2011.
57. **Email from Ernie Kee (STP) to Kerry Howe (UNM), Tim Sande (Alion), et al. .** *Discussions of Containment Spray Operation.* October 5, 2011.
58. **CN-CSA-06-6.** *South Texas Project GSI-191 Chemistry Effects Evaluation.* August 16, 2007 : Revision 1.
59. **Email from Ernie Kee (STP) to Tim Sande (Alion) and Kerry Howe (UNM).** *Fwd: stp-specific chemistry.* October 18, 2011.
60. **MC-6480.** *Min & Max Sump pH.* July 12, 1999 : Revision 0.
61. **CN-CRA-97-094.** *Required Mass of TSP for LOCA Sump Solution pH Adjustment.* November 24, 2008 : Revision 1.
62. **NC-7032.** *Containment LOCA Pressure/Temperature Analysis.* March 1, 2005 : Revision 13.
63. **Email from Wes Schulz (STP) to Tim Sande (Alion).** *Heat Exchanger Temp Drop and RCS Temp RE: STP White Paper (nearly complete).* October 26, 2011.
64. **WES010-CALC-001.** *South Texas Project Post-LOCA Containment Water Level Calculation.* November 24, 2008 : Revision 0.
65. **MC-5033.** *Flooding Analysis - Reactor Containment Building.* August 17, 1999 : Revision 5.
66. **ALION-CAL-STPEGS-2916-002.** *GSI 191 Containment Recirculation Sump Evaluation: Debris Generation.* October 20, 2008 : Revision 3.
67. **MC-6477.** *Added Commodities Inside the RCB.* September 17, 2003 : Revision 4.
68. **ALION-CAL-SNC-7487-003.** *Vogtle High Temperature Vertical Loop Test Report.* December 23, 2009 : Revision 0.
69. **ALION-RPT-CCNPP-7651-001.** *Aluminum Precipitate Head Loss Considerations at the Cliffs Nuclear Power Plant.* October 15, 2009 : Revision 1.
70. **ALION-REP-CCNPP-7311-001.** *CCNPP Chemical Effects Vertical Loop Head Loss Test Report.* April 17, 2009 : Revision 2.