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December 19, 2007

U.S. Nuclear Regulatory Commission
Attention: Document Control Desk
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DOMINION NUCLEAR CONNECTICUT, INC. (DNC)
VIRGINIA ELECTRIC AND POWER COMPANY (DOMINION)
MILLSTONE POWER STATION UNITS 2 AND 3
NORTH ANNA AND SURRY POWER STATIONS UNITS 1 AND 2
NRC GENERIC LETTER (GL) 2004-02, POTENTIAL IMPACT OF DEBRIS BLOCKAGE
ON EMERGENCY RECIRCULATION DURING DESIGN BASIS ACCIDENTS AT
PRESSURIZED-WATER REACTORS
DRAFT BENCH-TOP TEST PLAN FOR DETERMINING CHEMICAL EFFECTS

A conference call was held on December 12, 2007 with the NRC staff, DNC, Dominion and Atomic Energy of Canada Limited (AECL) to discuss the bench-top testing plan that AECL has developed to perform chemicals effects testing for Millstone Power Station Units 2 and 3, North Anna Power Station Units 1 and 2, and Surry Power Station Units 1 and 2. The chemical effects testing is being performed to facilitate resolution of the containment sump performance issues identified in NRC Generic Safety Issue (GSI) 191, "Assessment of Debris Accumulation on PWR Sump Performance," and GL 2004-02. During the conference call, the NRC requested a copy of the bench-top testing plan, and Dominion agreed to provide the test plan for the NRC's information. Accordingly, a copy of the draft AECL bench-top testing plan entitled, *Bench-Top Tests in Support of Chemical Effects Testing*, is provided herein.

If you have any questions or require additional information, please contact Mr. Gary D. Miller at (804) 273-2771.

Sincerely,

A handwritten signature in black ink, appearing to read "C. L. Funderburk", with a horizontal line extending to the right.

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Director - Nuclear Licensing and Operations
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Commitments contained in this letter: None

Attachment

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ATTACHMENT

DRAFT AECL TEST PLAN

BENCH-TOP TESTS IN SUPPORT OF CHEMICAL EFFECTS TESTING

**MILLSTONE 2 AND 3
NORTH ANNA 1 AND 2
SURRY 1 AND 2**

**DOMINION NUCLEAR CONNECTICUT, INC.
(DNC)**

**VIRGINIA ELECTRIC AND POWER COMPANY
(DOMINION)**



Test Plan

**Bench-Top Tests in Support of
Chemical Effects Testing**

Dominion

**Millstone 2 and 3
North Anna 1 and 2
Surry 1 and 2**

**GNP-34325-TP-001
Revision D2**

2007 December

décembre 2007

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LIST OF ACRONYMS AND SYMBOLS

AECL	Atomic Energy of Canada Limited
ECCS	Emergency Core Cooling System
FTIR	Fourier Transform Infrared Spectroscopy
ICET	Integrated Chemical Effect Tests
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LOCA	Loss of Coolant Accident
MF	Mineral Fiber
MW	Mineral Wool
Nu	Nukon
SEM	Scanning Electron Microscopy
TTWP	Transco Thermal Wrap Fiber
TM	TempMat
TSP	Tri-sodium Phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$
XRD	X-ray Diffraction

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1. SCOPE

The purpose of the bench top tests described in this test plan is to:

- Demonstrate that the solubility behaviour of aluminum hydroxide and calcium phosphate¹ obtained from the literature are reproducible and conservative under the conditions expected at the Dominion plants (Sections 3 and 4).
- Confirm that precipitates with suitable properties (settling rate, particle size and filterability) can be produced, prior to producing these materials for reduced scale head loss testing. In addition, tests will be carried out to determine the optimum storage time for the precipitates (Section 5).
- Determine if the water chemistry that will exist during the chemical effects testing will have any effect on the properties of the walnut shells used in the tests as a paint surrogate (Section 7).

Precipitation of a calcium phosphate phase was observed in the Integrated Chemical Effects Tests (ICET) Test 3 when trisodium phosphate (TSP) was added to simulated sump water containing 80% CalSil and 20% fiberglass at pH 7, but no visual precipitation appeared in solution of ICET Test 2 in which only fiberglass was used. The precipitation of calcium phosphate either as a single phase or as a mixture with aluminum hydroxide was also found when TSP is used as a buffer at pH 8 in the test runs 35 and 38, containing CalSil and powdered concrete, respectively [1]. As some uncertainty exists as to whether sufficient calcium will be released from concrete and insulation materials under Millstone Units 2 and 3 post-LOCA² sump water conditions, some dissolution and precipitation testing using these materials will be performed under station-specific conditions.

“Solubility” refers to the mass of a substance dissolved in a given amount of solvent to form a saturated solution at a given temperature and pressure. The major factors that affect the solubility of a substance are:

- Temperature – generally, as the temperature increases, the solubility increases.
- Solution pH, which can increase or decrease the solubility.
- Ionic strength; in general increased ionic strength increases the solubility.
- The presence of common ions, which decrease the solubility.

It has been recognized that, while solubility is an equilibrium property, the kinetics of the precipitation process is very important in determining the phases that form and the time required for their formation under post-LOCA sump water conditions. These kinetic aspects will be examined in the bench top testing.

Aluminum can form various hydroxides or oxyhydroxides in weakly alkaline aqueous

¹ The actual identity of the precipitates produced under post-LOCA sump water conditions is typically not known. For convenience, when the actual phase is unknown, the precipitate formed from aluminum is denoted aluminum hydroxide, and the precipitate produced from calcium and trisodium phosphate is denoted calcium phosphate.

² Loss of Coolant Accident.

solutions, for example: gibbsite, boehmite, bayerite and diaspore. The solubilities of all of these species are similar. Gibbsite is the thermodynamically most stable phase and other less stable phases can be transformed to gibbsite. Amorphous aluminum hydroxide has much higher solubility than crystalline aluminum hydroxides and can form in highly supersaturated aluminum solutions.

Most of the studies of aluminum hydroxide precipitation carried out under Pressurized Water Reactor (PWR) post-LOCA sump water conditions have shown that the solubility of aluminum in these solutions is higher than the reported solubilities of the crystalline phases. This may be the result of the effect of boron on the precipitating phases and or because of the formation of amorphous phases. Figure 1 summarizes most of the available Al solubility data under PWR post-LOCA sump water conditions, as a function of solution pH. The graph has been divided into a "Precipitation" and a "No Precipitation" region based on the data. The data strongly suggest that, at a given pH, precipitation does not occur at Al concentrations in the "No Precipitation" zone. These solubility limits will be confirmed, and the experimental uncertainty evaluated, in the bench top testing outlined below.

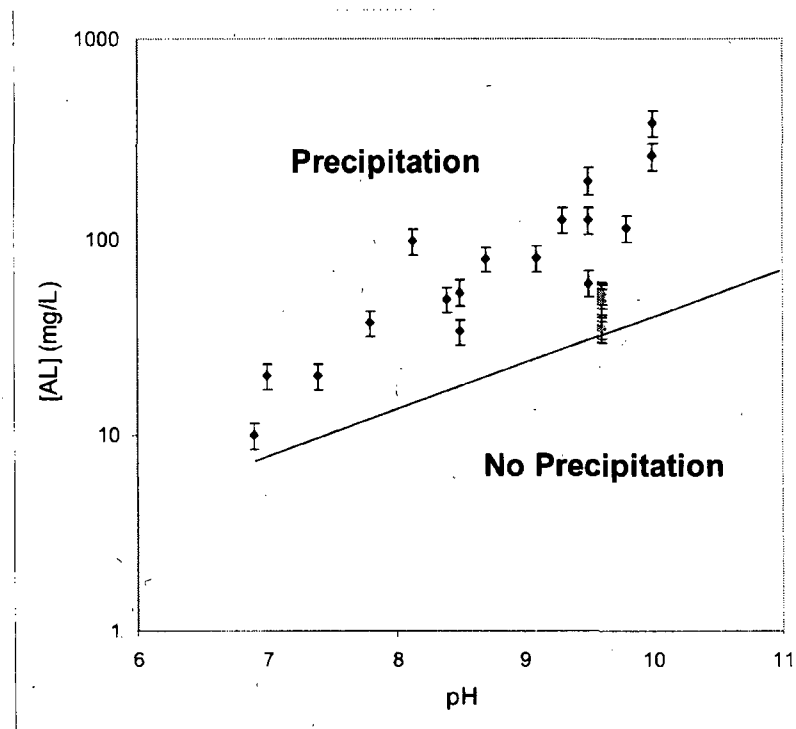


Figure 1: Summary of available solubility data for aluminum hydroxide under PWR post-LOCA sump water conditions as a function of solution pH.

It should be noted that, in contrast to the methodology described in WCAP-16530-NP [1], sodium aluminum silicate will not be used in the bench top or reduced scale tests. This

compound was never identified in the ICET test reports, in particular, the report on the results of ICET Test 1 [2]. Preliminary thermodynamic modeling [3], carried out before the first ICET results were available and using input values from peer-reviewed literature (corrosion and dissolution rates) and the ICET test plan (surfaces areas, water composition) predicted that various amounts of silicate species should have formed under the conditions of the ICET tests over time. However, silicate phases were not observed in the ICET tests, and it was noted that, while these silicates are the thermodynamically stable phases, their formation is kinetically slow. The thermodynamic simulations were repeated for ICET Test 1 with the formation of silicates suppressed [4] and reasonable predictions of the aluminum and calcium concentrations in solution were obtained for the first 720 h, after which the model overpredicted the concentrations of Al and Ca. This overprediction was attributed to the reduction in the Al release rate due to the passivation of the Al surfaces. As a result of these observations, it is not believed that sodium aluminum silicate will form under containment sump conditions.

For the subsequent reduced scale tests (1/200 scale tests), it is proposed to prepare the precipitates separately outside the test rig, and then add them to the test rig at the specified time. Therefore, in the bench top tests, the precipitates will be prepared under conditions identical to those to be used during the preparation for the reduced scale tests except precipitate concentrations. Because of the dilution that will occur during the addition to the test rig, the precipitates will be prepared at higher concentrations than the final reduced scale test concentration. The bench tests will therefore also identify any issues with this proposed addition strategy.

2. CHEMICAL ASSAYS

An assay of all chemicals purchased for use in the chemical tests will be performed to verify the composition of the chemicals. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) will be used to determine the concentrations of aluminium, sodium, silicon, calcium, phosphorus, and boron, plus any major impurities. If required, the concentrations of anions will be determined using ion chromatography. The service water (filtered river water) will be analysed for total dissolved solids (TDS), alkalinity, pH, and the concentrations of sodium, calcium, aluminium, chloride, sulphate, and silica.

3. CALCIUM DISSOLUTION AND CALCIUM PHOSPHATE PRECIPITATION TESTING

The purpose of the dissolution and precipitation testing is to:

- Confirm that the amount of calcium released from materials in Millstone Units 2 and 3 will not produce a mass of calcium phosphate precipitate sufficient to cause a significant increase in head loss. Calcium phosphate precipitation tests will not be performed for North Anna and Surry because TSP is not used in these stations.
- Demonstrate that the solubility limits of aluminium hydroxide shown in Figure 1 are reproducible and conservative under the conditions expected at the Dominion plants, Millstone Units 2 and 3, Surry Units 1 and 2, and North Anna Units 1 and 2.

3.1 Calcium Dissolution and Precipitation Tests

The purpose of these tests is to confirm that the amount of calcium released from materials in Millstone Units 2 and 3 will not produce a mass of calcium phosphate precipitate sufficient to cause a significant increase in head loss. To show this, a two-phase test will be performed for each station under specified conditions; the first phase will characterize calcium dissolution, and the second phase will characterize calcium phosphate precipitation. The design parameters in the test matrices are based on documentation provided by Dominion.

3.1.1 Dissolution Phase

The dissolution test matrix for Millstone Units 2 (M2-D) and 3 (M3-D) is shown in Table 1. In Test M2-D, representative quantities of concrete (as coupons), Nukon (Nu), Mineral Fibre (MF) and Mineral Wool (MW), will be placed in a 5 L flask containing 4 L of a solution of 1500 mg/L B at the appropriate pH. In Test M3-D, the insulation materials will be Transco Thermal Wrap Fiber and particulate Microtherm and a solution of 2500 mg/L B will be used. Tests will be carried out at pH values of 5, 6, 7 and 8, at a temperature of 90°C and the solution will stirred slowly using a magnetic stirring apparatus. The pH will be adjusted using NaOH or HNO₃ as required. Water samples will be withdrawn at regular intervals (once per hour for the first 6 h, less frequently after that) and analyzed for the concentrations of calcium, silicon, aluminum, sodium, magnesium, potassium and sulfur. The pH and conductivity of the solutions will also be measured, and the pH will be adjusted to the specified test value as required. The dissolution tests will be carried out for a total of four days. If the measured Ca concentration has not reached a plateau on Day 4, the dissolution period will be extended up to a maximum of 30 days.

TSP can affect calcium dissolution from concrete and insulation materials; calcium phosphate has very low solubility and the precipitation of calcium phosphate can decrease the dissolved calcium concentration. In the presence of TSP, the dissolved calcium concentration is controlled by the two reactions: calcium release from concrete and insulation materials, and precipitation of calcium phosphate. To quantify the effect of TSP on the Ca release rate, tests M2-C and M3-C will be repeated with 5000 and 6600 mg/L of TSP present, respectively.

3.1.2 Precipitation Phase

The precipitation test matrix for Millstone Units 2 (M2-P) and 3 (M3-P) is shown in Table 2. At the completion of the dissolution phase, 500 mL samples of the test solution will be removed, filtered through a 0.1 µm filter and used to fill 4×100 ml Nalgene bottles. A

representative amount of trisodium phosphate in M2-P and M3-P of Table 2 will be added to each of the test bottles and the solutions will be cooled to 80, 60, 50 and 25°C. The solutions will be examined visually for evidence of precipitation. Samples will be withdrawn after 1, 2, 3, 4, 12 and 24 hour and the turbidity measured. The solutions will be stirred for an additional six days. On Day 7, the solution turbidity will again be measured, and if the turbidity has stabilized, the solutions will be filtered through a 0.1 µm filter and the filter weighed to determine if any precipitate has formed. If the turbidity has not stabilized on Day 7, the duration of the precipitation test will be extended up to 30 days.

Table 1. Calcium Dissolution Test Matrix

Test Identifier	Duration (days)	Insulation Materials	Coupons ¹	[Boron] (mg/L)	[TSP] (mg/L)	pH	T (°C)	Sampling times (hours)	ICP-MS analysis ²
M2-D	4	75%Nu 16% MF 8.6% MW ¹	concrete	1500	0	5, 6, 7, 8.	90	1, 2, 3, 4, 5, 6, 10, 20, 30, 54, 78, 96	Ca, Si, Al, Na, K, S
M3-D	4	99.9%TT WF 0.1%PM ²	concrete	2500	0	5, 6, 7, 8.	90	1, 2, 3, 4, 5, 6, 10, 20, 30, 54, 78, 96	Ca, Si, Al, Na, K, S
M2-C	4	75%Nu 16% MF 8.6%MW ¹	concrete	1500	5000	5, 6, 7, 8	90	1, 2, 3, 4, 5, 6, 10, 20, 30, 54, 78, 96	Ca, Si, Al, Na, K, S
M3-C	4	99.9%TT WF 0.1%PM ²	concrete	2500	6600	5, 6, 7, 8.	90	1, 2, 3, 4, 5, 6, 10, 20, 30, 54, 78, 96	Ca, Si, Al, Na, K, S

¹ The numbers and dimensions of concrete coupons will be determined using sump water data.

² The solution will be filtered using 0.1 µm filters before ICP-MS analysis.

Table 2. Calcium Phosphate Precipitation Test Matrix

Test Identifier	Duration (days)	Starting Solutions	[TSP.12H₂O] (mg/L)	T (°C)	pH	Time of Turbidity Measurements¹ (h = hours, d = days)
M2-P	6	M2-D (96 hours)	5000	80, 60, 50, 25	5, 6, 7, 8	1(h), 2, 3, 4, 12, 24, 2(d), 3, 4, 5, 6, 7.
M3-P	6	M3-D (96 hours)	6600	80, 60, 50, 25	5, 6, 7, 8	1(h), 2, 3, 4, 12, 24, 2(d), 3, 4, 5, 6, 7.

¹ If the turbidity has not stabilized after 7 days, the test duration will be extended to a maximum of 30 days, with measurements being made every second day.

4. PRECIPITATION TESTING OF ALUMINUM HYDROXIDE

As noted above, the purpose of the precipitation testing is to determine if the Al solubility limits shown in Figure 1 are reproducible and conservative under the conditions expected at the Dominion plants, Millstone Units 2 and 3, Surry Units 1 and 2, and North Anna Units 1 and 2. The bench top precipitation tests (500 ml) will be carried out under conditions of temperature, pH, and concentration of Al and other additives (e.g., boron, phosphate) based on the sump water chemistry conditions provided by Dominion. In particular, testing will be carried out under the following conditions:

- Conditions representative of those expected at the highest Al or Ca concentrations reached.
- Conditions representative of those expected when the pH and temperature change rapidly, as these rapid changes may induce precipitation.

Preliminary testing shows that Al can precipitate on glassware surfaces. Therefore, all tests with aluminum solutions will be done in laboratory plasticware if possible.

4.1 Testing at Maximum Al Concentration

The water chemistry conditions on Day 30 of the post-LOCA mission time have been chosen for the tests at the maximum aluminum concentration (Table 3). Five possible cases were considered in AECL's analysis of aluminum release for both North Anna and Surry; the conditions listed in Table 3 are for the most conservative cases considered. These chemistry conditions are considered very conservative, since after 30 days the temperature of the sump water has decreased to a stable, low value, the pH is low and the dissolved aluminum concentration has reached its maximum value.

Table 3. Aluminum Precipitation Test Conditions

Parameter	Station			
	Millstone 2	Millstone 3	North Anna 1 and 2	Surry 1 and 2
Sump water pH (25°C)	8.2	8.1	9.5	9.5
Sump temperature (°F)	150	150	180	140
[TSP] (mg/L)	4789	6609	0	0
[Al] from NaAlO ₂ (mg/L)	4.1	38.3	44.2	74.6
[Li] from LiOH (mg/L)	0.044	0.02	0	0
[NaOH] (mg/L)	0	0	As required	As required
[B] from H ₃ BO ₃ or Na ₂ B ₄ O ₇ (mg/L)	1540	2545	2800	2800
Insulation debris	Nukon	TTWF	TTWF	TM
Times for turbidity (days)	0, 1, 2, 3, 5, 8, 11, 15, 18, 22, 25, 30.			

One liter of sodium aluminate stock solution at a concentration of 400 mg/L and boron at a concentration of 2500 mg/L will be prepared. Sufficient NaOH will be added to ensure that the starting pH is greater than 11 to avoid precipitation of aluminum hydroxide. This solution will be used to prepare 100 to 250 mL sub-samples at lower Al concentrations as specified in Table 3. Three HNO₃ stock solutions with concentrations of 0.1 M, 1.0 M and 5.0 M will be prepared for titrations.

For each condition, the pH of the sub-samples will be adjusted slowly (stepwise additions over several hours) to the target pH. The solutions will be stirred slowly using a magnetic stirring apparatus. The HNO₃ solution will be added in small aliquots to minimize changes in the solution volume that would lower the aluminum concentration in the solution. The acid concentrations and addition times will be chosen to avoid unrepresentative pH changes.

When the solution has reached the target pH, the solution will be allowed to stand for 30 days. The pH of the solution will be checked daily and adjusted as required to maintain the target pH. The turbidity of the solution will be measured immediately after preparation and at the times listed in Table 3.

The mass of any precipitate formed after 30 days will be determined by filtering the solution through a 0.1 µm pore size filter (Millipore Type VVLP), drying the filter and then weighing the dried filter. If a sufficient amount of precipitate is available, the chemical composition of the precipitate will be determined using ICP-MS, and an attempt will be made to use X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) to characterize the chemical phase(s) present. Samples of the filtrate will be taken for elemental analysis using ICP-MS or ICP-AES. These water samples will be split into two sub-samples; one sub-sample will be filtered through a 0.1 µm filter, and the other will be unfiltered.

4.2 Testing Under Changing Conditions of pH and Temperature

The solubilities of aluminium hydroxides (and oxyhydroxides) decrease with decreasing temperature and pH in alkaline solutions. Therefore, testing will also be performed to determine the pH and temperature at which the onset of precipitation occurs, and the stability of aluminum solutions at pH values 0.5 pH units above the onset value. The test matrix is shown in Table 4. Each test will be performed in the presence and absence of representative insulation debris. The debris will be enclosed in a mesh basket (made of an unreactive material) and suspended near the top of the test vessel to facilitate the measurement of the mass of any precipitate formed.

Table 4. Test Matrix to Determine the Effect of Temperature and pH on Aluminum Hydroxide Precipitation.

Test Identifier	Duration (days)	[Al] (mg/L)	[B] ¹ (mg/L)	Temperature (°C)	Debris Present? ²
ALD-pHT1-a	1	2.5	2500	60, 40, 25	N
ALD-pHT1-b	1	2.5	2500	60, 40, 25	Y
ALD-pHT2-a	1	5	2500	60, 40, 25	N
ALD-pHT2-b	1	5	2500	60, 40, 25	Y
ALD-pHT3-a	1	10	2500	60, 40, 25	N
ALD-pHT3-b	1	10	2500	60, 40, 25	Y
ALD-pHT4-a	1	20	2500	60, 40, 25	N
ALD-pHT4-b	1	20	2500	60, 40, 25	Y
ALD-pHT5-a	1	50	2500	60, 40, 25	N
ALD-pHT5-b	1	50	2500	60, 40, 25	Y
ALD-pHT5-c	1	75	2500	60, 40, 25	N
ALD-pHT5-d	1	75	2500	60, 40, 25	Y
ALD-pHT6-a	1	100	2500	60, 40, 25	N
ALD-pHT6-b	1	100	2500	60, 40, 25	Y
ALD-pHT6-c	1	100	2500	60, 40, 25	Y (Nukon)
ALD-pHT6-d	1	100	2500	60, 40, 25	Y (Temp Mat)
ALD-pHT7-a	1	100	2500	60, 40, 25	N
ALD-pHT7-b	1	100	2500	60, 40, 25	Y

H₃BO₃ and NaOH will be used in tests ALD-pHT1 to ALD-pHT6; Na₂B₄O₇ will be used in test ALD-pHT7.

²- debris will be Tranco Thermal Wrap Fiber in all tests unless indicated.

One liter of sodium aluminate stock solution at a concentration of 400 mg/L and boron at a concentration of 2500 mg/L will be prepared. Sufficient NaOH will be added to ensure that the starting pH is greater than 11 to avoid precipitation of aluminum hydroxide. This stock solution will be used to prepare 100 to 250 mL sub-samples at concentrations of 2.5, 5, 10, 20, 50, 75 and 100 mg/L Al. Three HNO₃ stock solutions with concentrations of 0.01 M, 0.1 M and 1.0 M will be prepared for titrations.

At each temperature, the pH of the sub-samples will be lowered **slowly** by adding acid at a rate of 0.5-1 ml/min from the starting pH (approximately 11) while the solution is stirred slowly using a magnetic stirring apparatus. The HNO₃ solution will be added in small aliquots to minimize changes in the solution volume that would lower the aluminum concentration in the solution. The acid concentrations and addition times will be chosen to avoid unrepresentative pH changes. The pH will be lowered until the onset of precipitation occurs; the turbidity of the solution will be measured to determine if precipitation has occurred, as this method is more sensitive than visual observation. The test will then be repeated, stopping the titration 0.5 pH units higher than the pH at which precipitation was noted. These solutions will be sampled daily for turbidity until a precipitate is noted or until 30 days has passed.

When the solutions are not being adjusted or sampled, the test vessels will be closed to minimize air ingress, as CO₂ ingress can rapidly lower the pH in an uncontrolled fashion. Samples of the solution will be taken at each temperature for elemental analysis using ICP-MS or ICP-AES. These water samples will be split into two sub-samples; one sub-sample will be filtered through a 0.1 µm filter, and the other will be unfiltered. The mass of any precipitate formed will be determined by filtering the solution through a 0.1 µm pore size filter (Millipore Type VVLP). If a sufficient amount of precipitate is available, the chemical composition of the precipitate will be determined using ICP-MS, and an attempt will be made to use X-ray diffraction and infrared spectroscopy to characterize the chemical phase(s) present.

At the conclusion of each test, the fibres will be removed from the test vessel, and, while still wet, be transferred to a microscope slide with a sample well, and sealed. The wet fibres will be examined by optical microscopy for evidence of precipitation on the fibre surfaces.

5. PRECIPITATE PREPARATION FOR REDUCED SCALE TESTING

Should it be determined that reduced scale testing is required, bench tests (4 L) will be performed prior to production of the precipitates for the reduced scale tests. The precipitates formed in these bench top tests will be characterized and the properties compared with those of the precipitates prepared in the tests described in Sections 3 and 4 of this Test Plan. The same chemicals (supplier, grade) that will be used in the precipitate production for the reduced scale testing will be used in these tests, and the concentrations of all solutions will be the same in the bench top and reduced scale head loss tests. The results of the bench top tests will be used to develop the method for production of the precipitates required for the strainer testing, once the masses of precipitate required are available.

The precipitates will be prepared in borated, deionised water to minimize interferences from inorganic or organic impurities in the service water that might alter the properties of the precipitates as they form, or as they are stored prior to introduction to the test apparatus. The boron concentration and pH of the test solutions will be chosen based on the technical specifications for each plant. It should be noted that the use of borated water differs from the method described in WCAP-16530-NP [1]. It is clear from the NRC and industry test data that boron species in solution have a significant effect on the properties of aluminum precipitates. It is therefore important that the precipitates be produced in the presence of representative concentrations of boron in solution.

No effort will be made to exclude ingress of carbon dioxide from the air into the test solutions; uptake of carbon dioxide by the tests solution may lower the solution pH. Therefore, the pH of the test solution will be monitored at 15-minute intervals during the mixing tests, and adjusted if required.

5.1 Preparation of Aluminum Hydroxide Precipitates

The aluminum hydroxide will be produced from a starting solution of sodium aluminate. The concentration of the sodium aluminate solution will be determined from the assessment of the expected concentration of aluminum and the relevant aluminum solubility data from the literature and bench top testing described in Sections 3 and 4. The mass of sodium aluminate added will be based on the assay results from the ICP-AES analysis to ensure that the correct aluminum concentration is obtained in the final solution. The precipitate will be formed by adjusting the pH to the target value using nitric acid. The rate of addition of the acid will be determined based on the results of the precipitation tests.

Since Millstone uses TSP while North Anna and Surry use NaOH to adjust the pH of sump water, aluminum hydroxide will be prepared separately in alkaline borated solutions with and without phosphate (PO_4^{3-}). It is expected that TSP will increase the ionic strength of solution and hence increase the solubility of aluminum hydroxide over that found in the absence of TSP at the same temperature and pH.

A portion of the product solution will be removed from the reaction vessel, added to a solution of borated service water, and the pH adjusted to the target value. The amount of the product solution added will be scaled to be representative of the amount to be added in the actual chemical effects tests. If required, the pH will be readjusted after the addition of the precipitates. After 1 h, a water sample will be taken, filtered to determine the particulate concentration, and the elemental composition of the precipitate and filtrate will be determined by ICP-AES. An attempt to determine the chemical phase will be made using XRD and or

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FTIR. This measurement will be used to determine if, during the actual chemical effects testing, the precipitate properties change upon addition to the test loop, which will contain service water.

6. PRECIPITATE CHARACTERIZATION

Four types of tests will be performed on samples of the precipitates formed in the precipitation and mixing tests to characterize the precipitate properties. The four types of tests are described below.

6.1 Precipitate Stability Test

Samples taken at three different times will be characterized; the first sample will be taken just after mixing of the solutions has been stopped, and the second and third samples will be taken after 1 and 2 days, respectively, to determine how the precipitate properties may change with time. The settling rate, size, and filterability will be measured. An attempt will be made to determine the chemical phase using FTIR and or XRD. Information on the precipitate stability is required to determine if precipitates must be prepared fresh for each addition, or if one batch can be made at the start of the tests.

6.2 Precipitate Settling Rate

The settling rates of the precipitates formed in the mixing tests will be measured using two methods:

- 10 mL of the shaken precipitate solution will be placed into a centrifuge tube and the visible volume of the precipitate will be measured after settling for 0.25, 1, 2, 3 and 4 hours.
- The turbidity of the solutions will be measured using a Hach DR2000 Direct Reading Spectrophotometer after any precipitate has been allowed to settle for 0.25, 1, 2, 3 and 4 hours. The instrument will be calibrated using a Turbidity Standard solution. The standard solution will be prepared by mixing 5 ml of solutions A and B (see below) in a 100 ml volumetric flask and allowing it to stand for 24 h, then diluting to 100 mL with distilled, deionized water. Solution A will be prepared from 1.0g of hydrazine sulfate in 100 ml of distilled deionized water. Solution B will be prepared from 10.0g of hexamethylenetetramine in 100 ml distilled deionized water.

6.3 Precipitate Particle Size Characterization

The particle size of the precipitates formed in the mixing tests will be analyzed using Scanning Electron Microscopy (SEM) on a sample of each precipitate after filtering through a 0.1 μm pore size filter and drying.

6.4 Precipitate Filterability

To characterize the filterability properties of the aluminum hydroxide precipitate, a simple filterability apparatus will be used. This apparatus consists of a 1.1 m long glass column with 7.32 cm in diameter. A removable sintered glass filter disk is attached to the bottom of the column. The column is drained through a wide orifice into a 4 L beaker. A constant 1 m water head is maintained on the system. The weight of the water flowing into the beaker over a fixed time interval (typically 10 seconds) is measured until 2-4 L of the test solution have passed through the filter. The flow rate through the column can be controlled by the resistance of a combination of the sintered glass frit and a filter paper placed on the frit. Filters of various pore sizes will be used to select the flow rate.

7. **DEPENDENCE OF WALNUT SHELL PROPERTIES ON CHEMISTRY**

Walnut shells are used as a paint surrogate in the AECL reduced scale testing. To ensure that there are no significant changes in the properties of the walnut shells in the chemical effects test solutions, two series of tests will be performed. In one series, the change in walnut shell particle size upon exposure to the proposed chemical effects solutions will be measured. A second series of tests will be carried out to determine if the walnut shells dissolve in the test solution. A chemical environment representative of the reduced scale tests will be produced using solutions from the chemical precipitate preparation, from which the precipitates have been removed by filtration. In this way, the effects of the chemicals on the walnut shells can be measured without interference from the physical effects of the precipitates.

The change in particle size will be measured by measuring the change in volume of a settled suspension of the walnut shells. To measure the volume change, a known mass of walnut shell powder will be added to each of five 2 mL graduated test tubes, and the test solution added. The powder volumes will be measured as a function of time (once per hour) for 4 hours, and then once again after 12 hours, at room temperature. A water sample from one of the test tubes will be taken and analyzed for carbon content, to determine if significant dissolution has occurred. The remaining four solutions will then be heated to the test temperature for five days, and the volumes measured three times per day.

To measure the walnut shell dissolution, a known mass of walnut shells will be added to the test solution, with a solution-to-volume ratio representative of the reduced scale tests. The solution will be heated to the test temperature and left for five days with constant stirring. At the end of the tests, the mass of the walnut shells will be measured and compared to the starting mass. A water sample will be taken at the end of the test and analyzed for carbon content.

8. QUALITY ASSURANCE

The quality assurance program for this work is in compliance with 10 CFR 50 Appendix B (Quality Assurance Criteria for Nuclear Power Plants) and 10 CFR 21 (Reporting of Defects and Noncompliance).

9. REFERENCES

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