COATINGS BENCH-TOP AUTOCLAVE EXPERIMENT TEST PLAN for Calvert Cliffs Nuclear Power Plant

CCNPP-CHLE-007, Revision 0c
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REVISION HISTORY LOG

Revision	Description
a	Initial draft
b	Incorporate initial review comments
c	Incorporate 7/25 comments from CCNPP

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1.0 INTRODUCTION

Calvert Cliffs Nuclear Power Plant (CCNPP) is implementing a refined chemical effects test program to aid in resolving GSI-191. This refined chemical effects test program includes a number of experiments and tests to investigate different aspects of chemical effects. Included in this program are integrated chemical effects head loss tests intended to simulate temperature, pressure, fluid, and debris conditions in containment after a loss of coolant accident (LOCA).

CCNPP has a variety of potentially reactive materials in containment that must be considered in the refined chemical effects test program. Some of these materials may influence the dissolution or corrosion of other materials such that including them in the integrated tests can be considered non-conservative. Some materials may be sufficiently immune to dissolution and corrosion so that they can be excluded from the integrated tests.

The objective of this bench-top autoclave test plan is to investigate the dissolution and elemental release rates of coatings materials postulated to be delivered into the containment sump coolant pool post-LOCA. The results of this test will help determine which, if any, coatings material combinations are most appropriate for inclusion in the integrated chemical effects head loss tests for CCNPP.

2.0 PURPOSE

The purpose of this document is to describe a bench-top autoclave experimental plan for the CCNPP CHLE program. This plan presents the material combinations for the experiments, the thermal and chemistry conditions for each experiment, and the approach to analyzing the results.

3.0 JUSTIFICATIONS

3.1 Eliminate Epoxy From Planned Tests

Based on the commissioning dates for Calvert Cliffs Nuclear Power Plant Unit 1 [1975] and Unit 2 [1977], the “acceptable” and “un-acceptable” epoxy coatings applied to reactor containment systems, structures, and components were most probably Bisphenol A resin formulations. This is a formulation that was state-of-the-art in coating technology at that time, relatively easy to prepare and suitable for normal and accident reactor containment design conditions. (Reference 6)

Please note that the likely difference between an "acceptable" and "un-acceptable" coating formulation is the lack of complete QA/QC documentation for coatings in the "un-acceptable" category. In the early 1970’s, the basic epoxy resins were only available from a few manufacturers world-wide. The resin manufacturers did not then and do not now have nuclear quality assurance programs in effect in their facilities. Therefore, the probability is very high that the Bisphenol A epoxy resin in “acceptable” and “un-acceptable” coatings in the 1970’s are identical.

During design normal and accident conditions in a PWR reactor containment structure similar to or more severe than the Calvert Cliffs conditions, it has been determined that no organic compounds are released from Bisphenol A epoxy coating formulations (Reference 6).

The other component in a typical epoxy coating used on SSCs in a reactor containment is the pigment blend, which is comprised of fine (5 to 100 micrometer) solid particles which never dissolve during formulation and application of the coating material. In reactor containment coatings, the pigments are selected to provide a number of physical properties in the coating film, including:

1. color,
2. opacity, and
3. decreased permeability.

The test results documented in Reference 6 state " The dried residue from Sample KTA-2 (liquid smaple) was found to consist of mainly of calcium carbonate and silicate material. The brown material extracted from the filter was determined to consist of mostly china clay." China clay is one name for kaolinite, a source of alumino-silicate use in many industries. Calcium carbonate and aluminio-silicates are possible pigments in Bisphenol A epoxy coatings. These two compounds are generally considered to be crystalline, to have low solubility in water (but not zero solubility), and to be relatively chemically inert.

Mr. Jon Cavallo of UESI Nuclear Services reviewed the types of pigments which likely were used in the formulation of the reactor containment epoxy coatings, both “acceptable” and “un acceptable.” The only one of concern is aluminum (Reference 7), which might have been added to the coating in a flat or “leaf” form to provide decreased permeability. Aluminum in the post-DBA PWR environment in some containment pool chemistries can form aluminum-based precipitates which can adversely affect suction strainer performance, especially in debris covered conditions. Many plants, including CCNPP, have removed aluminum compounds from containment for this reason.

DBA testing of epoxies has indicated that no coatings debris smaller than 1/32 inch in face dimension is produced, no organic compounds are released, and the pigments that are released do not dissolve or leach (Reference 6).

3.2 Eliminate Irradiated Alkyd Coatings From Test

The alkyd coatings in containment at CCNPP have been exposed to radiation from the reactor for nearly 40 years. Therefore, one may reasonably expect that such exposure would cause some effects on detachment performance when such coatings would be exposed to post-LOCA conditions. However, EPRI performed extensive coatings tests (Reference 8) which included testing unqualified alkyd coatings. One feature of the test suite was to test irradiated and non-irradiated in post LOCA environments to determine the effects, if any, on the performance of the coatings to remain adhered to their substrate. Table 4-3 of the EPRI report is reproduced below with one additional column which notes the direction of change for detachment. It appears that radiation has no universal effect, some coating samples performed better after irradiation (3 out of 14 samples), some performed worse (5 out of 14 samples), and many showed no effect (6 out of 14 samples).

Based on the results of the EPRI tests, it is expected that the unqualified alkyd based coatings in containment at CCNPP would show similar range of performance. Therefore, we will not include irradiated samples in our tests.

Table 1: Table 4-3 from Reference 8 - Extent of Alkyd Coating Detachment After DBA Autoclave Testing

Component Identifier	Coating Type as Determined by FTIR	% Detachment After DBA		Net Effect of Radiation on Detachment
		Without Radiation	With Radiation	
01	Alkyd	50	5	decrease
18	Alkyd	1	1	none
19	Alkyd	95	95	none
20	Alkyd	10	55	increase
21	Alkyd	5	5	none
22	Alkyd	20	1	decrease
25	Alkyd	1	80	increase
26	Styrenated Alkyd	15	20	increase
31	Alkyd	20	98	increase
32	Alkyd	5	5	none
34	Alkyd	40	50	increase
35	Alkyd	10	5	decrease
36	Alkyd	5	5	none
37	Alkyd	50	50	none
Summary Average Detachment		**23.4**	**33.9**	6 = none 5 = increase 3 = decrease

3.3 Eliminate Inorganic Zinc Primer From Tests

CCNPP is performing other autoclave bench-top tests that include zinc. Those tests are intended to investigate the effects and interactions of zinc, including zinc from coatings, with other potentially reactive materials. Therefore, this coatings test will not include inorganic zinc coatings.

4.0 EXPERIMENTAL PLAN

The experimental plan consists of a series of dissolution experiments in which potentially reactive coatings materials are exposed to high temperature fluid simulating the post-LOCA fluid chemistry and temperature in containment for a 168 hour period. The identification and concentration of dissolution products and characterization of any precipitates will be compared to determine if significant dissolution and elemental release of potential precipitants occurs. Analysis of the results will provide recommendations on coatings materials to include in the integrated tests including the possibility of recommending no coatings be included.

The fluid chemistry will be similar to the initial post-LOCA pool chemistry expected at CCNPP. A scaled quantity of NaTB buffer will be dissolved in the test chamber fluid to simulate the buffer in the plant.

Materials used in the test will be representative of the coatings that are used in CCNPP's containment and that may be submerged in the containment pool or exposed to containment spray and which may be expected to dissolve and contribute to chemical effects. The material quantities will be scaled to approximate the ratio of the test fluid volume to the volume of the pool fluid times the surface area of the postulated failed alkyd coatings in the pool fluid.

CCNPP has a postulated pool volume of 64,360 cubic feet or 481,445 gallons of fluid in the pool and 7,534 square feet of alkyd coatings in containment. Assuming 100% of the alkyd coating fails and is submerged in the pool would create twice this exposed surface (front and back of the coating) in the pool. Therefore, the alkyd coating to be used in the autoclave shall be

$$\frac{7{,}534\ ft^2\ coating\ x\ 2}{481{,}445\ gallons} = 0.0313\ \frac{ft^2\ coating}{gallon}$$

5.0 EXPERIMENTAL PARAMETERS

5.1 Debris Quantities

Table 2: Debris Sample Quantities

Coatings Debris	Test Quantity	References
Qualified Epoxy from within the ZOI	0	Section 3.1
Qualified IOZ (primer for the above Epoxy)	0	Section 3.3
Qualified IOZ w/o topcoat exposed to spray	0	Section 3.3
Formerly Qualified Epoxy	0	Section 3.1
Unqualified Alkyd Coating	0.0313 ft^2 per gallon of test fluid	1, and 2

5.2 Chemistry Conditions

Table 3: Chemistry Conditions

Deionized Water with		Reference
Boron Concentration (H_3BO_3)	2800 ppm as boron[1]	4
Lithium Hydroxide	0.78 ppm as lithium	4
Initial pH	~5	5

5.3 Buffer

Include 3.78 grams per liter sodium tetraborate decahydrate (NaTB) buffer (Reference 5). The buffer shall be added after the other materials and not before the fluid temperature has reached 195°F during the initial solution heat-up.

[1] The 2800 ppm boron concentration is prior to the introduction of the NaTB buffer.

5.4 Temperature Conditions

The experiments will use the temperature profile presented in Table 4 and Figure 1±5°F [Reference 3].

Table 4: Solution Temperature Profile

Time (sec)	Temp (°F)		Time (sec)	Temp (°F)
0	280		28,800	224
400	280		43,200	195
800	279		64,800	191
1,000	279		86,400	187
3,600	274		115,200	181
7,200	266		144,000	176
14,400	252		172,800	170
			604,800	170

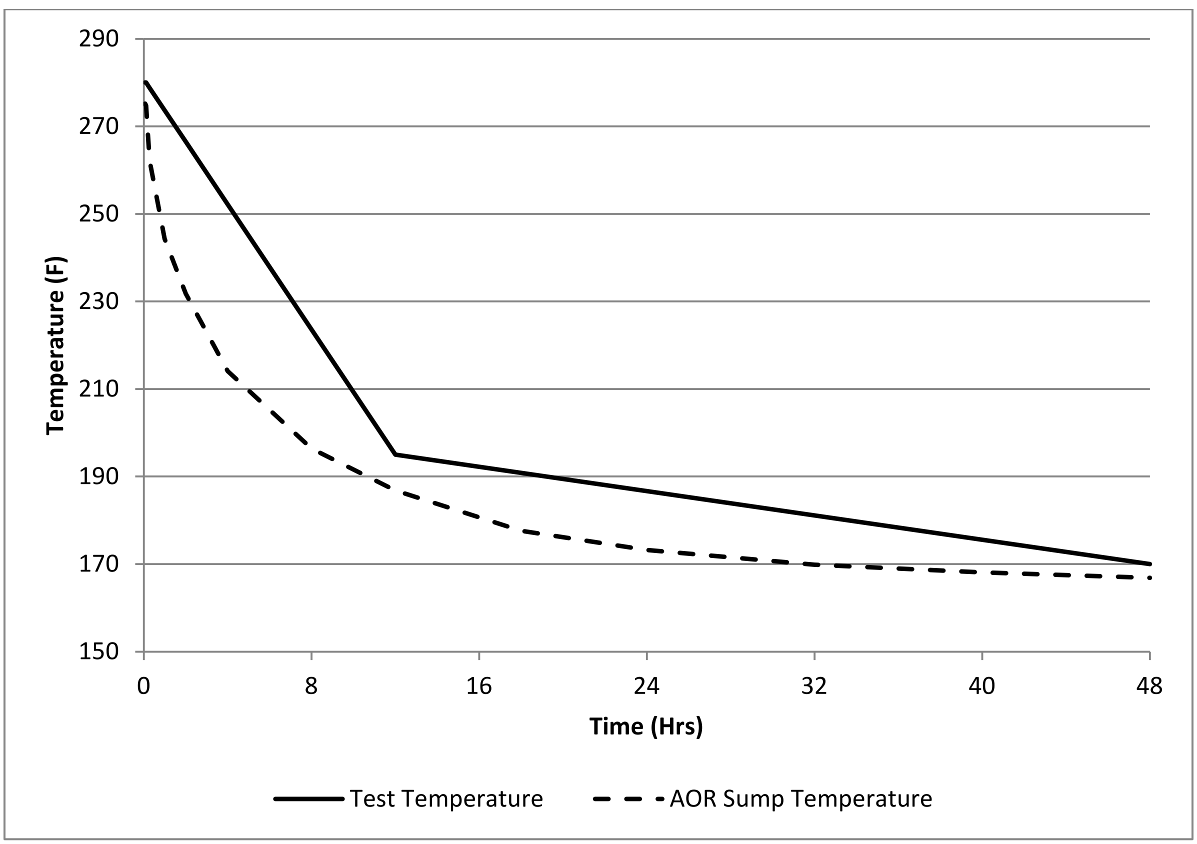

Figure 1: Solution & Sump AOR Temperatures

5.5 Solution Sampling

The fluid solution in the autoclave shall be sampled every 12 hours and at the conclusion of each experiment. The samples shall be stored in containers fabricated from non-reactive and corrosion resistant materials. Samples shall be adequate for post test chemical analysis (Gas Chromatography -Mass Spectrometry, Liquid Chromatography-Mass Spectrometry, or other) but limited in volume to avoid significantly affecting total volume of fluid remaining in the autoclave.

5.6 Agitation

The autoclave shall be agitated continuously throughout the experiment to facilitate fluid flow across the test materials.

5.7 Autoclave Materials

Wetted materials of the autoclave should be type 316 stainless steel or other very corrosion resistant material. No silicate glass products may be used.

6.0 TEST MATRIX

The experiment will be performed in accordance with the test matrix presented in Table 5. Please note that only alkyd coatings are included and that the test shall be repeated. Three simultaneous tests are acceptable.

Table 5: Test Matrix

Test No.	Coatings Included
	Unqualified Alkyd Coating
1	X
2	X
3	X

7.0 CHEMISTRY ANALYSIS

Mass spectrometry of the fluid used in the experiment shall be performed on the samples collected during the experiment. Potential methods of analysis to be used are:

- GC/MS (Gas Chromatography/Mass Spectrometry) - with organics, the gas chromatograph separates the organic compounds, and the mass spectrometer gives structural information about each;

- Hydrogen-1 or Carbon-13 Nuclear Magnetic Resonance (NMR) Spectroscopy - used to characterize carbon and hydrogen (quantity, number of hydrogen atoms attached to each carbon, etc.); and
- Infrared (IR) Spectroscopy - identifies functional groups.

The concentrations of the following elemental species or organic materials shall be reported:

1. Zinc
2. Titanium Dioxide
3. Calcium Carbonate
4. Organic Compounds
    a. polyesters
    b. phenolic compounds
    c. styrene
    d. vinyl toluene
    e. acrylic (monomers & polymers)
    f. urethane (monomers & polymers)
    g. formaldehyde
    h. polyepoxides
    i. Ethylbenzene
    j. Mineral Spirits

8.0 EXPERIMENTAL METHODS

Professional laboratory and safety practices shall be followed. Specific laboratory procedures used to implement the experiment shall be made available to Calvert Cliffs for review and comment.

The following specific experimental processes shall also be followed.

8.1 Material Preparation

Coatings coupons shall be prepared in accordance with the coatings manufacturer's instructions and spray coated both sides to the mid-range of the manufacturer's recommended dry film thickness. The coupons shall be minimum 1 inch by 6 inch stainless steel strips at least 16 gauge with surface preparation that conforms to SSPC-SP6/NACE 3 specifications or specific manufacturer's requirements if available. The samples shall be suspended in the autoclave and secured to remain submerged in the experimental fluid and protected from the agitation device but exposed to the flow of fluid produced by agitation.

Photographs of the coatings materials before preparation, after weighing or measuring, and contained in the mesh container shall be provided. Photographs documenting any post test degradation of the coatings debris shall be provided.

8.2 Visual Examination

A thorough visual examination of the autoclave and coatings material containers shall be performed. Any indications of precipitation or dissolution shall be documented.

9.0 REPORT

A formal report shall be provided documenting the performance of the experiment and the results of the experiment. The following topics shall be included in the report.

9.1 Introduction

A brief introduction to the report shall be presented

9.2 Experiment Description

A detailed description of the experiment shall be presented including at least the following sections.

9.2.1 Facility

A comprehensive description of the experimental facility shall be presented with photographs. This shall include:

1) Autoclave(s)
    a. Volume capacity
    b. Wetted materials
    c. Heating method
    d. Agitation method
2) Temperature controls
    a. Heat up rate
    b. Cool down rate
3) Instrumentation and analysis equipment
    a. Temperature
    b. pH
    c. Mass Spectrometry

9.2.2 Experiment Input Parameters

A detailed description of the input parameters for each experiment shall be presented.

9.2.3 Material Preparation

The methods and processes for preparing fluid solutions and coatings debris samples shall be described and the results presented with photographs.

9.2.4 Autoclave Setup and Control

The procedures used to setup the autoclave, control temperature conditions, take and store samples, and perform the chemistry analyses shall be described in detail.

9.3 Experimental Results

The results of each test shall be presented in individual sections. These sections shall include at least the following information.

1) Experimental parameters used
2) Actual temperature profile achieved
3) Results of chemical analysis of samples
4) Deviations and Nonconformance Reports
5) Results of visual examination
6) Photographs of notable observations as appropriate

9.4 Summary of Results and Conclusions

A summary of results comparing the individual tests if the experiment will be presented and any conclusion drawn presented.

9.5 References

Unique references used in the preparation of the report shall be presented. This test plan shall be included as a reference.

9.6 Appendixes

Appendixes shall be provided including as a minimum the following:

1) Test Logs
2) Calibration Certificates/Records
3) Standards Certificates
4) Photographs

10.0 REFERENCES

1. Design Calculation CA06938, Rev. 0001, Prediction of LOCA Coating Debris Loads on the Containment Sump Strainer.
2. Design Calculation CA07464, Rev. 0000, Prediction of LOCA Coating Debris Loads on the Containment Sump Strainer.
3. Design Calculation CA06774, Rev. 0002, Containment Response to LOCA and MSLB for Calvert Cliffs Units 1 and 2.
4. Design Calculation CA0xxx, Rev. 000y, MPR Calculation No. 0090-0267-01, Probabilistic Distribution of Boric Acid Concentration in Containment Building Sump Pool.
5. Calvert Cliffs Nuclear Power Plant Calculation CA06963, "Mass of Sodium Tetraborate Decahydrate Buffer Required for Post LOCA Containment Building Sump pH Control", Revision 1.
6. Keeler & Long Report 06-0413
   a. ML070230387 Comanche Peak Transmittal of Report on TXU Power Sponsored Coatings.
   b. ML070230390 report proper
   c. ML070230392 Report 06-0413 Chart 7.
   d. ML070230395 Report 06-0413 Chart 120-307.
   e. ML070230396 Report 06-0413 Chart 250-200.
   f. ML070230397 Report 06-0413 Chart 307-250.
   g. ML070230398 Report 06-0413 Chart End Test.
   h. ML070230401 Pre-DBAS and Post DBA Pictures
   i. ML070230402 Description of Pictures TXU Comanche Peak SES Report #06-0413.
7. ML080380214 NRC Staff Review Guidance Regarding Generic Letter 2004-02 Closure in the Area of Plant-Specific Chemical Effect Evaluations, Enclosure 3.
8. ML071130069 "Design Basis Accident Testing of Pressurized Water Reactor Unqualified Original Equipment Manufacturer Coatings". EPRI, Palo Alto, CA: 2005. 1011753.