#### **Calvert Cliffs Nuclear Power Plant**

1650 Calvert Cliffs Parkway Lusby, Maryland 20657



CALVERT CLIFFS NUCLEAR POWER PLANT

June 14, 2013

U. S. Nuclear Regulatory Commission Washington, DC 20555

ATTENTION: Document Control Desk

SUBJECT:

Calvert Cliffs Nuclear Power Plant Independent Spent Fuel Storage Installation Material License No. SNM-2505, Docket No. 72-8 Response to Request for Additional Information, RE: Calvert Cliffs Independent Spent Fuel Storage Installation License Renewal Application (TAC No. L24475)

**REFERENCES:** 

- (a) Letter from G. H. Gellrich (CCNPP) to Document Control Desk (NRC), dated September 17, 2010, Site-Specific Independent Spent Fuel Storage Installation (ISFSI) License Renewal Application
  - (b) Letter from Mr. J. Goshen (NRC) to Mr. G. H. Gellrich (CCNPP), dated October, 31, 2012, Third Request for Additional Information for Renewal Application to Special Nuclear Materials License No. 2505 for the Calvert Cliffs Site Specific Independent Spent Fuel Storage Installation (TAC No. L24475)
  - (c) Letter from G. H. Gellrich (CCNPP) to Document Control Desk (NRC), dated April 24, 2013, Response to Request for Additional Information, RE: Calvert Cliffs Independent Spent Fuel Storage Installation License Renewal Application (TAC No. L24475)

N/MSD26 N/MSS

In Reference (a), Calvert Cliffs Nuclear Power Plant, LLC, submitted a license renewal application to the U.S. Nuclear Regulatory Commission for the Calvert Cliffs site-specific independent spent fuel storage installation. In Reference (b), the Nuclear Regulatory Commission issued a request for additional information to support their review of Calvert Cliffs' license renewal application. In Reference (c) Calvert Cliffs provided a response to one of the request for additional information (RAI E-3). Attachment 1 contains Calvert Cliffs responses to the two remaining request for additional information (RAI E-1 and E-2) along with the accompanying Enclosures 1 through 10.

The calculations in Enclosures 1, 3, 4, and 5 include proprietary information from Transnuclear, Inc. Enclosure 6 contains an affidavit signed by Transnuclear, Inc. requesting withholding of the proprietary information. The Affidavit sets forth the basis on which the information may be withheld from public disclosure by the Commission, and addresses, with specificity, the considerations listed in 10 CFR

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2.390(b)(4). Accordingly, it is requested that the information that is proprietary to Transnuclear, Inc. be withheld from public disclosures. Enclosures 7 through 10 contain the non-proprietary versions of the calculations.

This letter contains a regulatory commitment as listed in Attachment (2).

Should you have questions regarding this matter, please contact Mr. Douglas E. Lauver at (410) 495-5219.

I declare under penalty of perjury that the foregoing is true and correct. Executed on June 14, 2013.

Very truly yours,

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Mark D. Flaherty Plant General Manager

MDF/KLG/bjd

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Attachments: (1) Calvert Cliffs Response for RAIs

- Enclosures: 1 Outer Surface Weld Temperature of the NUHOMS<sup>®</sup> 24P and 32P DSCs Stored at CCNPP ISFSI Site Proprietary
  - 2 Computing Surface Soluble Salt Density from Conductivity Measurements
  - 3 Calvert Cliffs Nuclear Power Plant (CCNPP) ISFSI: Canister Cask Stress Corrosion Cracking Review for License Renewal -Proprietary
  - 4 Summary of SCC Assessment of SS Welds in 24P and 32P NUHOMS<sup>®</sup> Dry Storage Casks Proprietary
  - 5 To Determine Time Limit for Exposure of the Fuel Cladding to Oxidizing Atmosphere for the 24P and 32P DSCs Stored at the CCNPP ISFSI Site - Proprietary
  - 6 Transnuclear, Inc. Affidavit
  - 7 Outer Surface Weld Temperature of the NUHOMS<sup>®</sup> 24P and 32P DSCs Stored at CCNPP ISFSI Site Non-Proprietary
  - 8 Calvert Cliffs Nuclear Power Plant (CCNPP) ISFSI: Canister Cask Stress Corrosion Cracking Review for License Renewal – Non-Proprietary
  - 9 Summary of SCC Assessment of SS Welds in 24P and 32P NUHOMS<sup>®</sup> Dry Storage Casks – Non-Proprietary
  - 10 To Determine Time Limit for Exposure of the Fuel Cladding to Oxidizing Atmosphere for the 24P and 32P DSCs Stored at the CCNPP ISFSI Site – Non-Proprietary
- (2) Regulatory Commitment

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#### cc: J. M. Goshen, NMSS

(Without Enclosures 1, 3, 4, 5) N. S. Morgan, NRC W. M. Dean, NRC Resident Inspector, NRC

S. Gray, DNR C. Haney, NMSS

# **ATTACHMENT (1)**

# **CALVERT CLIFFS RESPONSE FOR RAIs**

By letter dated September 17, 2010, as supplemented February 10, March 9, and June 28, 2011; and July 27, 2012, Calvert Cliffs Nuclear Power Plant, LLC (CCNPP) submitted a license renewal application to the U.S. Nuclear Regulatory Commission (NRC) for the CCNPP site-specific independent spent fuel storage installation (ISFSI). The NRC staff has reviewed the July 27, 2012, supplement to your application and has determined that additional information is required to complete its detailed technical review.

#### **REQUEST FOR ADDITIONAL INFORMATION (RAI)**

#### Appendix E: Component Specific Aging Management

**E-1** Provide an evaluation that demonstrates that the loaded Dry Storage Canisters (DSCs) in horizontal storage modules at the CCNPP ISFSI currently maintain design-basis confinement integrity in order to satisfy the regulatory requirements of 10 CFR Part 72.

An evaluation should include, but is not limited to: Consideration of current applicable industry experience, along with an analysis of the DSC's condition (e.g., thermal profile, surface salt concentration, etc.). If the evaluation includes commitments to periodic monitoring and inspections in the future, detailed justification should be provided for the acceptability of these processes. As a minimum, a discussion of inspector qualification, inspection techniques, acceptance criteria, along with inspection frequencies should be provided for evaluation.

The report provided to the staff following the examination of the DSC exterior on July 27, 28, 2012, did not provide sufficient information for evaluation. For instance, the methods to examine the DSC may not be sensitive enough to identify stress corrosion cracking (SCC) of the DSC. Therefore the staff was unable to perform a technical evaluation of CCNPP's application to determine that the DSCs can safely perform their design basis function for the duration of the requested license renewal period.

NUREG/CR-6860 "An Assessment of Visual Testing," emphasized that "inspection reliability of the various VT systems, calibration standards, and procedures is not well characterized." NUREG/CR-6943, "A Study of Remote Visual Methods to Detect Cracking in Reactor Components," states that detection of cracks that have openings typically associated with intergranular SCC with radiation-hardened video cameras under field conditions are "strongly dependent on the camera magnification, lighting, inspector training, and inspector vigilance."

This information is required to evaluate compliance with 10 CFR 72.128(b), (c), (h) and 10 CFR 72.128(h)(5).

#### CALVERT CLIFFS RESPONSE E-1:

The response to RAI E-1 will address the request for an evaluation that demonstrates that the loaded dry shielded canisters (DSCs) in horizontal storage modules (HSMs) at the CCNPP ISFSI currently maintain design-basis confinement integrity. This evaluation will be subdivided into analysis of the likelihood that Chloride Induced Stress Corrosion Cracking (CISCC) will cause penetration of the DSC confinement boundary during the renewal period, and the potential consequences for compliance with 10 CFR 72.122(b), (c), (h), (h)(5), and 10 CFR 72.236(d) if such a penetration were to occur. The response to the portion of RAI E-1 which deals with the adequacy of various inspection methods and future inspection plans for aging management of the DSC is deferred to the response to RAI E-2.

#### Likelihood of Through-Wall CISCC During the License Renewal Period

The likelihood of CISCC resulting in a penetration of the confinement barrier is evaluated in two steps: 1) time to achieve the environmental conditions necessary to initiate CISCC, and 2) time for a CISCC crack to grow through-wall once initiated. Chloride induced stress corrosion cracking of austenitic

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stainless steel can occur when three major critical conditions for initiation are met. These conditions include (i) susceptible material (e.g., sensitized areas such as a weld and its heat affected zone), (ii) corrosive environment (e.g., temperature, humidity, sufficient chlorides), and (iii) relatively high residual tensile stress present on the metal surface. This evaluation assumes the first condition is present and focuses primarily on the time required to achieve the environmental and stress conditions necessary for initiation of CISCC. The evaluation includes the requested thermal profile analyses, analysis of residual stresses to support CISCC initiation and crack growth analyses, and chemical analysis of actual deposits collected from the surface of a DSC at Calvert Cliffs.

#### <u>Thermal Analysis</u>

Enclosure 1 provides a thermal analysis using ANSYS FLUENT to determine temperatures on the outer surface of the NUHOMS<sup>®</sup> 24P and 32P DSCs for various heat loads, to identify the heat load at which the confinement weld temperatures on the outer surface of the DSCs is at 80°C. Dry shielded canisters may be susceptible to CISCC initiation between 30 and 80°C (The basis for this range is discussed in Enclosure 3). The evaluation was done for the design basis normal ambient condition of 70°F.

The thermal evaluation shows that at least one portion of the longitudinal weld located close to the top cover plate, which faces the back wall of the HSM, remains below 80°C for all heàt loads between 2 kW and 19 kW. The temperature at this location is 80°C for a heat load of approximately 23.9 kW based on the linear fitting of the data. The maximum design basis heat loads of the DSCs in use at Calvert Cliffs are 15.84 kW for the 24P DSC, and 21.12 kW for the 32P DSC. Even maximum DSC shell temperatures fall below 80°C for the highest heat load 24P DSC in service at Calvert Cliffs (Loading 48 in 2005) after 19.5 years of storage, and after 35.5 years of storage for the highest heat load 32P DSC in service to date (Loading 66 in 2010). Thus, DSC shell temperature alone cannot be used to rule out CISCC for any of the canisters during their service life.

#### Additional Analysis of Surface Deposits from a DSC at the Calvert Cliffs ISFSI

As discussed in Reference 1-1, there was a discrepancy noted between the SaltSmart field conductivity reading obtained during the June 2012 inspection using the wet collection method, and the offline laboratory analysis of the dry samples. Enclosure 2 provides a quantitative analysis on how this could credibly result from an inaccurate assumption about the salt composition of the deposits on the surface of the DSC (i.e., use of sea salt rather than an actual sample of the material present to perform the calibration of the SaltSmart). The results suggest that salt concentrations within a factor of a few of those obtained last summer using the wet collection method could be obtained even in the absence of significant amounts of chloride. In addition, the SaltSmart results together with the additional analysis performed in Enclosure 2, support a conclusion of a chloride ion surface density consistent with those seen in dry samples and well below 100 mg/m<sup>2</sup>, even considering an extreme and unlikely worst case scenario of substantial chloride ion volitization prior to laboratory analysis.

#### Time to Achieve the Environment Needed for Initiation of CISCC

Enclosure 3 evaluates the environmental conditions required for initiation of CISCC, and determines when these conditions would occur in the storage life of a DSC at the CCNPP ISFSI. The key environmental conditions are a threshold concentration of chloride salts deposited on the canister surface, and conditions of surface temperature (taken from Enclosure 1) and relative humidity where the salts will absorb moisture from the air to form a slurry (deliquesce). The review of published research indicates that a conservative critical concentration of chloride in salt to initiate CISCC is 100 mg/m<sup>2</sup> (Reference 1-2 recommends a critical salt concentration for initiating CISCC as high as 800 mg/m<sup>2</sup>) and the canister surface temperature range of concern is from 30 to 80°C. Deliquescence has usually been observed at the deliquescence relative humidity of magnesium chloride, MgCl<sub>2</sub>, about 30%, but the deliquescence relative humidity of calcium chloride, CaCl<sub>2</sub>, 15%, is conservatively used in this evaluation. All three conditions must be met before an environment capable of initiating CISCC is considered to be present.

Dry shielded canister salt accumulation as a function of time, temperature, and airborne salt concentration is determined using an equation that was developed from laboratory and field test results on vertical storage canisters in Japan (Reference 1-3). A range of airborne concentrations of salt are evaluated from 0.1 to 40  $\mu$ g/m<sup>3</sup> (the latter value bounds the range of maximum values reported for the ocean coast in Japan, while the former is the inferred airborne concentration based on the chloride measurements on Calvert Cliffs DSCs from Enclosure 2 and the Reference 1-3 deposition rate). Based on linear extrapolation of the Calvert Cliffs DSC surface measurements from Reference 1-1, the critical chloride concentration for CISCC would not be reached until about 120 years from the beginning of storage. Taking a more conservative approach, the report shows that the chloride deposition on the Chesapeake Bay is much less than that on the Atlantic Ocean coast (the Bay is approximately one third to one half the salinity of the ocean at the location of CCNPP), but nonetheless assumes an airborne chloride concentration of 10  $\mu$ g/m<sup>3</sup>, account for any uncertainties in predicting chloride deposition rate on the actual DSC surface inside of the HSM (due mainly to lack of empirical data on airborne salt concentrations at the CCNPP ISFSI) and uncertainties related to the limited salt concentration measurements performed to date. Using this approach, the report concludes that the combination of surface temperature, 15% relative humidity and surface chloride concentration needed for initiation of CISCC would at the earliest be reached 30 years following the beginning of storage of a DSC.

#### Time for CISCC Crack to Grow Through-Wall Once Initiated

Enclosure 4 provides a finite element calculation of the residual weld stresses in the 24P and 32P shell welds, based on data from the fabrication records for these canisters. The longitudinal and circumferential shell welds for both canister designs were of a double V groove design, with welding sequence being: root, fill inner, grind outside of root, and fill outer. Both longitudinal and circumferential welds were analyzed. At the outer surface of the weld, tensile stresses parallel to the weld joint were in the vicinity of yield as expected. Additionally, these stresses parallel to the joint remain tensile through the full thickness. These are equivalent to hoop stress in a circumferential weld, or axial stress in a longitudinal weld. The significance is that only cracks oriented perpendicular to the weld (with the length of the cracks limited to the width of the weld and the adjacent heat affected zone region) will have tensile stresses to propagate them through the full thickness. The potentially significant longer cracks oriented parallel to the weld could be arrested by compressive stresses before penetrating through the entire thickness.

The report conservatively assumes that once the environmental conditions for CISCC are reached, a properly oriented crack will initiate and propagate at a constant rate without crack arresting. The constant crack growth rate (9.6  $\times$  10<sup>-12</sup> m/s based on the mean of SCC propagation rates in Figure 6 of Reference 1-4) used is that observed in naturally occurring CISCC, and penetrates the 0.625 inch thick canister wall in 48 years from the time of initiation.

#### Conclusions Regarding the Likelihood of Through-Wall CISCC During the License Renewal Period

The analyses discussed above indicate that some, but not all, of the conditions needed to initiate CISCC on DSCs in storage at Calvert Cliffs are currently present. The calculated residual tensile stresses in the confinement boundary welds of the 24P and 32P DSCs are greater than the threshold for crack initiation and propagation through the entire thickness of the shell. Similarly, some locations on the DSC shell welds are at temperatures that could support CISCC for even the most recent higher heat load DSCs.

However, the chloride concentrations on the DSC surface do not appear to have reached the critical concentration needed to initiate CISCC at this time.

Analyses performed to identify the possible timing for when all of the required environmental conditions for CISCC initiation could occur indicate that time ranges from 30 to 120 years after the start of storage of a DSC at the CCNPP ISFSI (with 30 years based on conservative assumptions on airborne salt concentrations for locations near the ocean). From the time of crack initiation, the calculated time to propagate through the full shell thickness is 48 years with a constant propagation rate and no crack arrest. Based on the above results, the earliest time for crack initiation added to the time for crack propagation through the shell is 30+48 = 78 years from the start of storage to penetration of the confinement boundary.

Therefore, it is considered unlikely that CISCC has initiated on any of the DSCs at this time, and even less likely that penetration of the confinement barrier has occurred on any DSC.

#### **Consequences of CISCC During the License Renewal Period**

The potential consequences for compliance with 10 CFR 72.122(b), (c), (h), (h)(5), and 10 CFR 72.236(d) if a CISCC induced penetration of the confinement boundary were to occur were also considered as part of this evaluation. The above mentioned regulations can be summarized into four main requirements: 1) the fuel clad must be protected against degradation that leads to gross rupture, 2) doses must be maintained within 10 CFR 72.104 and 72.106 requirements, 3) the fuel must be retrievable, and 4) design functions must be maintained during credible design basis events. The sections below discuss the conditions under which such a CISCC induced penetration of the confinement boundary would not result in an immediate or catastrophic loss in the ability to meet these requirements. This argument is supported by both analysis, and direct evidence from a cask owned by the U.S Department of Energy which contains Zircaloy clad fuel and has had a failed confinement boundary since August 2005 [the REA-2023 cask at the Idaho National Engineering Laboratory (INEL) as discussed in Reference 1-5]. The purpose of this section is not to justify the acceptability of an unremediated CISCC induced penetration of the confinement boundary for the extended life of the ISFSI. The intent is to provide information that will allow for a more risk-informed approach to the frequency of inspections for CISCC and timing of the response or remediation activities to such a penetration if one were ever discovered.

#### Protect the Fuel Cladding Against Degradation Leading to Gross Rupture

Even if a canister were to lose its internal inert helium environment as a result of CISCC, the fuel cladding would be expected to present a further barrier to any release of radioactive material for some period of time after introduction of air given the amount of time required for CISCC initiation and penetration to occur. The CCNPP ISFSI Technical Specifications do not allow loading of fuel with known cladding defects greater than a pinhole leak or hairline crack. In addition, CCNPP uses various methods (vacuum canister sipping, review of cycle chemistry data, etc...) to provide high confidence that fuel loaded into the DSC has no known through-wall cladding defects. There have also been no Kr-85 releases during vacuum drying of the presently loaded DSCs as would be expected if cladding with pinhole leaks or hair line cracks had been loaded. While a helium atmosphere remains in the DSC no significant degradation of the fuel is expected to occur.

A review of cladding failure mechanisms in both inert and oxidizing environments is summarized in Reference 1-6. Mechanisms of specific concern for exposure to oxidizing environments are oxidation of the cladding, and oxidation of the fuel pellets. The general oxidation rate of Zircaloy cladding exposed to an oxidizing environment is reported as being negligible over a 40 year period for temperatures below 250°C (penetration of the DSC by CISCC during the initial 20 year license was identified as highly

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unlikely above). Oxidation of fuel pellets is a potential concern for cladding integrity if a through-wall cladding defect exists. Oxidation would convert the  $UO_2$  fuel pellets to less dense  $U_3O_8$  at a rate dependent on time exposed to air at elevated temperature. This oxidation induced swelling of the fuel would place additional stress on the cladding, and potentially cause small pinholes or hairline cracks to become gross ruptures. In addition to allowing release of radionuclides contained in the fuel, if such gross failure of the cladding occurred it would also likely create difficulty in retrieval of the fuel from the DSC, as well as unanalyzed conditions for criticality safety.

The NRC provides a method for determining the allowable time that fuel may be exposed to an oxidizing atmosphere in ISG-22 without concern for gross rupture of the cladding (Reference 1-7). Reference 1-7 indicates that "for fuel with burnup below ~45 GWd/MTU and Zircaloy cladding, the time-at-temperature (TT) curves developed to date (RE Einziger and RV Strain, "Oxidation of Spent Fuel at Between 250 and 360°C" EPRI Report NP-4524, 1986 for example) can be used to determine the allowable exposure duration to an oxidizing atmosphere if the fuel temperature is known." While Reference 1-7 is specifically written to address use of oxidizing atmospheres during the DSC loading process, the Electric Power Research Institute (EPRI) report cited (Reference 1-8) was specifically written to identify the time when maintenance of an inert environment inside of a cask would no longer be necessary. Reference 1-7 also indicates that "data between 30 and 45 GWd/MTU, shows a decrease in the oxidation rate due to the presence of certain actinides and fission products that are burned into the fuel. There is no reason that this should not continue at higher burnups, but the strength of the effect may change with burnup." A concern is also expressed that this reduced oxidation rate may be counteracted at burnups greater than 55 GWd/MTU by formation of a fine grained (high surface area) rim at the edge of the pellets. This should not be a concern for fuel currently in storage at the Calvert Cliffs ISFSI as Technical Specifications currently limit burnup to  $\leq$  52 GWd/MTU, and as is shown in Figure 3-1 in the response to RAI E-3 (Reference 1-1), the burnup of fuel loaded in the DSCs with the longest storage time is generally much less than 45 GWd/MTU.

Enclosure 5 provides the thermal analyses to determine peak fuel temperatures as a function of DSC heat load for the 24P and 32P DSCs. Uniform assembly heat loads are assumed. The resulting peak fuel cladding temperatures are then utilized, along with the data from Figure 3-9 of Reference 1-8, to determine the incubation time for a small through-wall cladding defect to become a gross rupture as a function of DSC heat load. The results of this analysis are summarized in Table 1-1 below. It should be noted that the times to gross rupture are conservatively calculated in Reference 1-8 (p. 4-4) suggests that the time exceeds 100 years for fuel temperatures below 230°C based on the same data. An exponential fit to the indicated time to incubate a gross rupture in air as a function of DSC heat load, or for a 32P DSC with a heat load slightly below 6 kW. All of the currently loaded 24P and 32P DSCs would be expected to fall below these heat loads before even the conservatively estimated minimum time for CISCC to initiate and penetrate a DSC (78 years assuming a correctly oriented crack and airborne chloride concentrations more than 10 times higher than expected for the CCNPP ISFSI site). This indicates that CISCC would be unlikely to result in a loss of the DSC confinement boundary's function to prevent gross cladding rupture.

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DSC DSC Heat		Peak Fu Tempera	el Cladding atures in Air	Incubation Time For Small Cla Breach to Become Gross Ruptu		
Туре	Load (kW)	°F	°C	on Air Exposure (years)		
240	6	447	231	2.9		
241	4	354	179	571		
220	6	399	204	38		
32P	4	306	152	14,399		

#### Table 1-1

As discussed above, the REA-2023 cask at INEL also provides some indirect evidence that at low cask heat loads, loss of the confinement boundary will not result in gross cladding breach of even known failed fuel rods. Reference 1-9 indicated that the REA-2023 cask contained 52 GE BWR 7x7 assemblies from the Cooper Nuclear Station, however discussions with INEL staff indicate that fuel was replaced by various remnants of fuel rods and fuel assemblies from the Test Area North pool in the 2002 timeframe. Reference 1-10 (p. 40) indicates that the cask had calculated heat loads of 918 watts in 2002 and 826 watts in 2007. However gas temperature measurements in 2007 also suggest that the heat load may be as low as 180 watts. The REA-2023 cask began to leak at a high rate in August 2005 after a quick disconnect fitting and pressure transducer were installed to allow internal pressure data to be obtained remotely. Reference 1-11 indicates that the cask had an estimated leak rate of 0.11 cc/sec at standard temperature and pressure in 2006 and 0.04 cc/sec in 2007. Reference 1-10 indicates that maintenance to tighten the leaking fitting in 2007 reduced the leak rate to an estimated 3E-3 cc/sec at standard temperature and pressure. Gas sampling results in Table 3 of Reference 1-12 show that the nitrogen, oxygen, and argon contents of the cask internal atmosphere were all approaching their atmospheric composition by April 2007 (oxygen content went from 0 to 16.3% in ~20 months). Reference 1-5 (Section 2.1.4) indicates, and discussions with INEL staff have confirmed, that the REA-2023 cask contains known failed fuel rods. As would be expected given the presence of failed fuel, internal gas sampling identifies the presence of Kr-85, and Kr-85 releases from REA-2023 were estimated to be 0.3 mCi/year based on the leak rate estimated after the fitting was tightened. However, cask fittings that were surveyed prior to cask sampling in October 2008 did not indicate contamination (Reference 1-12, p. 10), and none of the gas sampling discussed in References 1-5, 1-10, 1-11, 1-12, and 1-13 indicate the presence of any radionuclides other than Kr-85 in the REA-2023 gas samples (note that only gamma analysis of samples was performed), or signs of external contamination. This suggests that either no gross cladding rupture has occurred as a result of exposure to an oxidizing environment (as would be expected given the low heat load) or the combination of the release fraction and leak path factors is low enough to reduce particulate releases below detectable levels (a leaking fitting of the magnitude indicated above would be expected to provide a less tortuous release pathway than a CISCC induced penetration). Additional data may be generated in the coming years if the U.S. Department of Energy implements the recommendation in Reference 1-5 to inspect the fuel in REA-2023 in order to determine if long term exposure to an oxidizing environment has had any deleterious effect.

#### Maintain Doses within 10 CFR 72.104 and 72.106 Requirements

An assessment of dose at the site boundary from a hypothetical failure of both a DSC and 100% of the fuel cladding contained therein has already been evaluated as one of the design basis accidents for the current Calvert Cliffs ISFSI licensing basis. This assessment is summarized in ISFSI Updated Safety Analysis Report Section 8.2.8 for the 24P DSC and Section 12.8.2.8 for the 32P DSC, and involves a non-mechanistic instantaneous (puff) release to the environment of the gap inventory of Kr-85 fission gas from all fuel rods contained in a single design basis canister (1.39E3 Ci for 24P, 8.54E3 Ci for 32P). The resulting calculated doses for the 24P are 0.1 mrem and 17.8 mrem for the maximum off-site whole body and skin doses, respectively. The calculated whole body and skin doses for the 32P DSC are 0.65 and

109.6 mrem, respectively. Since Kr-85 has a half-life of 10.8 years, a simple exponential decay indicates these design basis accident doses would decrease by 72% after 20 years of storage, 98% after 40 years of storage, and 99.9% after 60 years of storage.

As part of a response to a recent NRC RAI on the ISFSI License Renewal Application (Reference 1-14), CCNPP submitted a revised dose assessment on December 15, 2011 (Reference 1-15) that meets the current expanded source term requirements of Table 5-2 of Reference 1-16. Only the 32P DSC was evaluated since the source term bounds that of the 24P DSC. Normal, Off-Normal, and Accident total effective dose equivalent were 67 mrem, 16 mrem, and 2.12 rem, respectively. Substituting in the same source term with additional decay time from Reference 1-17, these doses would decrease by 16% after 20 years of storage, and 27% after 40 years of storage (a source term with 60 years of decay was not available in Reference 1-17).

Both assessments show that the unlikely event of coincident failure of the DSC and all fuel cladding confinement boundaries would not lead to doses exceeding 10 CFR 72.104 and the 10 CFR 72.106(b) dose limits. The experience of the REA-2023 cask discussed above suggests that the current licensing basis confinement dose calculations in Updated Safety Analysis Report Sections 8.2.8 and 12.8.2.8 which release only Kr-85 may be a more realistic representation of the doses from a CISCC induced penetration of such a DSC in storage with all fuel rods failed. As discussed above, Calvert Cliffs has high confidence that none of the rods loaded into the currently loaded DSCs were failed at the time of loading. However, if failures were present and releases similar to the REA-2023 cask occurred at Calvert Cliffs, total effective dose equivalent doses at the site boundary would be less than a  $\mu$ rem assuming accident X/Qs and only Kr-85 release.

#### Fuel Must Be Retrievable

Reference 1-18 identifies two aspects of fuel retrievability: 1) the ability to retrieve a sealed DSC from its HSM, and 2) the ability to unload the fuel from the DSC if either the fuel or the DSC is not suitable for transport off-site (neither the 24P or 32P DSCs in use at Calvert Cliffs are presently licensed for transport off-site).

Chloride induced stress corrosion cracking would have no impact on the ability to retrieve the DSC from the HSM during the time frame required to reach the environmental conditions necessary for initiation (30 to 120 years as discussed above). Once a crack initiates from CISCC, the existing stress analyses provide some insight on the amount of crack growth that could be tolerated without further analysis. The current design basis stress analyses for both the 24P and 32P DSCs assume a minimum shell wall thickness of 0.55 inches versus the nominal thickness of 0.625 inches. Stresses are evaluated for dead weight, pressure, thermal, handling, seismic, and drop loads. Of most interest for retrievability of the DSC are stresses associated with withdrawal of the DSC from the HSM and re-flood of the DSC. The DSC shell stress intensities for the off-normal jammed DSC condition bound both of these normal activities, and are less than 70% of the allowable stress intensity for the minimum shell wall thickness indicated above for both DSC types for individual Level B loads and load combinations. Based on the CISCC crack growth rate cited above (and in Enclosure 4), a CISCC crack would require at least 6 years to grow from the nominal to the minimum shell thickness assumed in the DSC shell stress analyses, at which point substantial additional margin likely remains. Attempts to quantify this margin based on existing analyses were not made due to the conservative nature of the method normally used to combine stresses for comparison against code allowables. A future analysis to access retrievably of the DSC will be performed using a critical flaw calculation assuming a crack has propagated through DSC shell. Since only cracks which are oriented perpendicular to the weld will propagate through the full thickness of a DSC shell, cracks in the hoop direction will be evaluated for axial stresses and cracks oriented in the axial direction will be evaluated for hoop stresses. The initial length of all cracks evaluated will be limited to the thickness of the location of the respective weld. While DSC retrievability remains an open item, this limited review indicates that substantial time remains, after the point where the environmental conditions necessary to initiate CISCC are reached, before the ability to retrieve the DSC would be impacted.

The ability to retrieve fuel from a DSC by normal means (i.e., with crane and grapple) is primarily controlled by the ability of the fuel assembly hardware to continue to perform its structural function. As described in Table 3.2-1 of Reference 1-19, there are no aging effects requiring management while the fuel assembly hardware remains in an inert environment. Following a hypothetical penetration by CISCC and depressurization of the DSC, the internal environment would initially still be helium at atmospheric pressure. However, diurnal temperature variations would cause expansion and contraction of the remaining fill gas and begin slowly allowing entry of air. The experience with the REA-2023 cask at INEL suggests that the process of replacing the inert environment with air could take as long as 2 years. However, the fuel assembly hardware is fabricated from corrosion resistant materials such as Zircaloy, Inconel, and stainless steel, which would not suffer significant corrosion from air exposure during the license renewal period. In addition, even if the confinement boundary were penetrated by CISCC, the DSC would still provide considerable shelter for the fuel hardware in addition to that provided by the HSM. Potential contaminants such as chlorides would be expected to take even longer to build up on fuel hardware to the CISCC initiation concentration than was required for the DSC. Finally, Reference 1-18 indicates that the addition of special tooling or modifications to the assembly to make the assembly suitable for lifting with crane and grapple does not preclude the handling from being considered "normal means." Therefore, it is considered unlikely that a hypothetical CISCC penetration of a DSC would render fuel incapable of being handled by normal means during the time frame being considered for license renewal.

#### Design Functions Must be Maintained During Design Basis Events

This section addresses the possible impact of a CISCC induced penetration of the confinement boundary on the other design functions of the DSC.

- Criticality The helium fill gas does not directly support the criticality control function of the DSC. Criticality is not evaluated for the DSC in the HSM due to the fact that the sealed DSC provides moderator exclusion. A CISCC induced penetration would not be expected to allow significant quantities of rainwater dripping onto the DSC from the outlet vent to enter the DSC, and rain water was only noted as contacting a small area near the top end of the DSC during the June 2012 inspection. Flooding of the ISFSI site is not a credible event for the Calvert Cliffs ISFSI. It is also noted that the 24P DSCs do not credit soluble boron for criticality control in the spent fuel pool.
- Thermal The helium fill gas has higher thermal conductivity than air, which will cause temperatures to increase when it is replaced by air as demonstrated for the cladding in Enclosure 5. However, the DSC heat load will decay far below the design basis values in the time required for CISCC initiation and penetration to occur. The magnitude of increase in temperatures as a result of replacing helium with air is more than compensated for by the reduced decay heat, and thus no DSC components would be expected to exceed their design temperatures as a result of a CISCC induced loss of helium. This argument would apply to both normal conditions and the design basis Forest Fire accident.
- Structural The DSC basket structure is fabricated from corrosion resistant materials such as stainless steel, aluminum, or aluminum coated carbon steel, which would not suffer significant

corrosion from air exposure during the license renewal period. In addition, even if the confinement boundary were penetrated by CISCC, the DSC would still provide considerable shelter for the basket in addition to that provided by the HSM. Potential contaminants such as chlorides would be expected to take even longer to build up on the DSC basket to the CISCC initiation concentration than was required for the DSC.

The DSC shell response to design basis accident loads given the presence of a CISCC induced crack remains an open item. As discussed under the Retrievability section, based on the minimum DSC shell wall thickness utilized in the stress analyses, there is minimal concern for the first 6 years following initiation of a CISCC crack based on existing analyses. As with DSC retrievability, quantification of the effects of through-wall CISCC cracks oriented perpendicular to the weld on DSC response to design basis accident loads will require a critical flaw evaluation, which will be performed at a later date.

Shielding – The helium in the DSC provides no contribution to the shielding function of the DSC. The lead in the shield plugs at the top and bottom of the DSC is fully encased in stainless steel and does not contact the internal atmosphere in the DSC, and would therefore be unaffected by loss of the helium inside of the DSC.

#### Conclusions Regarding the Consequences of Through-Wall CISCC During the License Renewal Period

The review of consequences above indicates that through-wall CISCC would not represent a catastrophic failure of a DSC to perform the safety functions attributed to the confinement boundary. Neither the protection of cladding from gross rupture or off-site dose functions would be expected to be significantly impacted given the time required for CISCC to occur. Similarly, the loss of the inert environment would not impact the system performance for many design basis events. The one open item remaining is the impact of a CISCC induced penetration on DSC retrievability and response to structural design basis events (i.e., hairline DSC crack does not become a gross DSC rupture). This information is utilized in the response to RAI E-2 as part of the process to develop the type and frequency of aging management activities for CISCC, and the timing of response to such a penetration.

It should also be noted that despite the expected low consequence of a CISCC induced penetration, discovery of such a penetration would still elicit an in-depth response from the site. In addition to being a potential violation of the ISFSI Technical Specification 3.2.2.2 requiring a licensee event report, the Calvert Cliffs Emergency Response Plan would require declaration of an Unusual Event upon the discovery of any failure of the DSC confinement boundary (Reference 1-20). In the absence of a concurrent radiological release from the ISFSI, the response would not be upgraded to higher Emergency Action Levels. However, the result would be that the NRC would be involved almost immediately in the response to a positive confirmation of through-wall CISCC.

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- 1-15. Calvert Cliffs Nuclear Power Plant Calculation CA07718, "2011 Update of ISFSI USAR DSC Leakage Dose Analyses," NRC ADAMS Accession Number ML11364A025
- 1-16. U.S. Nuclear Regulatory Commission, NUREG-1536, Revision 1, Standard Review Plan for Spent Fuel Dry Storage Systems at a General License Facility, July 2010
- 1-17. Calvert Cliffs Nuclear Power Plant Calculation CA06721, "Source Terms for ISFSI 32P Burnup Extension," NRC ADAMS Accession Number ML091680542
- 1-18. U.S. Nuclear Regulatory Commission, Interim Staff Guidance 2, dated February 22, 2010, Revision 1, "Fuel Retrievability"
- 1-19. Letter from G. H. Gellrich (CCNPP) to Document Control Desk (NRC), dated September 17, 2010, Site-Specific Independent Spent Fuel Storage Installation (ISFSI) License Renewal Application
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E-2 Provide a revised proposed aging management plan that considers the potential for SCC at the CCNPP ISFSI.

Publicly available research has indicated that SCC may occur in regions of strained, sensitized austenitic stainless steel when atmospheric chlorides are present (ADAMS Accession Number: ML12128A133). The thermal and strain conditions of the canister and internal HSM atmosphere are not completely understood, and it is unclear whether SCC could result in degradation of the confinement integrity during the renewal period without a sufficient monitoring and mitigation program.

The applicant should develop a process for periodically incorporating on-going SCC evaluations and knowledge gained by the industry's generic program to identify designs and conditions susceptible to SCC and associated mitigation recommendations. The aging management program may also need to consider interim measures to verify the DSC time-limited aging analyses and confinement integrity during the requested license renewal period.

This information is required to evaluate compliance with 10 CFR 72.128(b), (c), (h) and 10 CFR 72.128(h)(5).

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The original Calvert Cliffs ISFSI License Renewal Application did not identify any aging effects for the DSC that required aging management (Reference 2-1, Table 3.3-1). This conclusion was consistent with the NRC approval of the license renewal for a NUHOMS<sup>®</sup> ISFSI of similar design for a 40-year license renewal period slightly more than one year prior to the Calvert Cliffs submittal (Reference 2-2, Section 3.2.4). The Reference 2-2 approval is indicated to be based on the fact that "*Each DSC is placed into an HSM and, thereafter, exposed to only a mild ambient environment. There are no aging effects requiring management of the stainless steel or lead subcomponents of the DSC's because of the corrosion-resistant materials of construction, double seal-welded closure, and the environments to which each DSC is exposed." However, Calvert Cliffs understands that CISCC may be a special concern due to the possibility of chlorides in the environment as a result of its proximity to a body of brackish water (i.e., the Chesapeake Bay). Based on the analysis and inspection results discussed in the response to RAI E-1, we believe that the aging management program for the effects of CISCC should be done using a phased approach similar to that recommended in Reference 2-3. Figure 2-1 summarizes the proposed phased aging management program for the Calvert Cliffs DSC's to address the potential effects of CISCC.* 

#### Selection of DSC's for Inspection

The inspections will initially include the two DSCs and HSMs inspected in June 2012. However, as was discussed in our February 2011 RAI Response (Reference 2-4), Calvert Cliffs may add additional DSCs for subsequent inspections as it is expected that the integrated thermal and radiological source terms of the more recently loaded 32P canisters will surpass that of the 24P canisters inspected in June 2012 before the next inspection. Inspections and surface sampling would be done on DSCs with at least 15 years of storage time to both allow sufficient time for chlorides to accumulate, and ensure that occupational doses during the inspection can be kept as low as reasonably achievable.

#### Visual Inspection

Calvert Cliffs will continue to perform visual inspections of the DSCs during the interior visual inspection required for aging management of the HSMs. We will perform this inspection on a 10-year frequency in a manner of equal or better quality to that performed in June 2012. We believe this may still be a valuable general aging indicator for the exterior of the DSC. Both the accelerated aging CISCC tests in high chloride environments in References 2-3 and 2-5 show areas of high density localized rust spots in

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areas that were later shown by destructive testing to have experienced CISCC. Calvert Cliff's personnel and/or contractors who perform the inspection shall be visually certified according to applicable station procedures.

<u>Environmental Monitoring for Chlorides</u> – The results of the June 2012 inspections and the analyses discussed in the response to RAI E-1 suggest that chloride concentrations on the oldest Calvert Cliffs DSCs still appear to be well below the proposed 100 mg/m<sup>2</sup> initiation threshold for CISCC indicated by laboratory results, and that they would be expected to remain so for many years. As such, we believe it is premature to begin detailed DSC surface inspections for the effects of CISCC. We believe that the more prudent and dose sensitive approach is to first obtain additional data on the chloride concentration on the DSC surface via both wet and dry sample collection methods similar to that performed in June 2012. We would propose to perform this sampling on different positions on the canister surface to represent a spatial variation of the chloride concentration. We would perform this sampling on a 5-year frequency (starting from the June 2012 inspection) for the first 10-years, after which the frequency would be increased to 10 years to coincide with the timing of visual inspections of the HSM provided trending indicates the threshold concentration would not be exceeded within 10 years.

In addition, we would propose to establish a monitoring program for airborne chlorides in the vicinity of the ISFSI. We are exploring whether the filters presently being used in the airborne particulate monitors SFA3 and SFA4 credited for the Radiological Environmental Monitoring Program can be utilized to characterize the airborne chloride concentration (several years worth of these filters are currently archived). An alternative or supplemental option may be to deploy monitoring stations specific to airborne chloride measurement. The intent would be both to validate the RAI E-1 response expectation of low airborne chloride content in the vicinity of the ISFSI, as well as to support validation of the correlation between airborne chloride content and DSC surface chloride concentration. We would commit to establishing this airborne chloride monitoring capability in some form within 5 years of renewal of the Calvert Cliffs ISFSI license. After 10 years, the continuance of the program would be reevaluated. If the existing correlation with DSC surface chlorides is validated, or a new site-specific correlation developed, the airborne chloride monitoring may be continued in place of the surface chloride sampling discussed above. Otherwise, the airborne chloride monitoring program may be discontinued since surface sampling would be more representative of the actual chloride concentration present on the DSC.

<u>Inspection for the Effects of CISCC</u> – Once the proposed environmental monitoring program identifies confirmed chloride concentrations on the surface of a DSC which exceed the proposed 100 mg/m<sup>2</sup> limit for initiation, Calvert Cliffs would propose to perform an inspection to look for the effects of CISCC on the surface within 5 years, with subsequent inspections performed on a 10-year frequency thereafter. The initial 5-year period is based on the fact that flaw growth rate calculation in Enclosure 4 suggests that a CISCC induced crack would not grow farther than the minimum DSC shell thickness assumed in stress analyses and the 10 year frequency is substantially below the 48-year time to propagate through-wall determined in Enclosure 4.

The inspections could take one of two forms: 1) a surface inspection to look for cracking in the DSC shell, or 2) an inspection to look for indication that the helium inside the DSC has been lost via nondestructive means if the DSC heat load is less than 5 kW for a 24P DSC, or 6 kW for a 32P DSC (with the heat loads based on the results of Enclosure 5 and the consequence discussion in the RAI E-1 Response). The methods for the former option will utilize appropriate available nondestructive examination techniques for identifying CISCC remotely on high dose rate DSCs in-situ, as directed by a Calvert Cliffs site Non-Destructive Evaluation Level 3 qualified individual. Research and development by NRC, U.S. Department of Energy, EPRI, and Industry on nondestructive examination tooling for such inspections has only begun recently and it is therefore premature to specify which technique will be utilized at this time. Reference 2-6 suggests that both eddy current testing (a surface/near surface inspection technique) and ultrasonic testing (a volumetric inspection technique) are current technologies that may be suitable but will require further development to customize them for this application.

The latter method would be available only for DSCs where the DSCs heat loads were low enough to allow fuel exposure to air without consequence for times much longer than the proposed inspection interval. Furthermore, for this optional inspection method to be utilized, the CISCC crack acceptance criteria analysis to be discussed shortly would have to identify that the presence of through-wall CISCC would not impact the retrievability of the DSC, or its ability to withstand design basis events. Preliminary follow on work from that discussed in Reference 2-7 suggests that one such method for a 24P DSC design may involve changes in the DSC surface temperature profile that would occur if the internal helium environment were replaced with air. Calvert Cliffs is currently planning an additional inspection during the summer of 2013 to determine if thermography via a periscope deployed down the rear outlet vent can be utilized to obtain a temperature profile that could be utilized in conjunction with such analyses to positively confirm the presence of helium in a 24P DSC. Other non-destructive means may be available to confirm the presence of helium, however further research on those methods will also be needed.

Both techniques will require an acceptance criterion to determine whether the depth of any CISCC observed represents a potential loss of the structural function of the confinement boundary. This acceptance criterion will be based on a critical flaw calculation assuming a crack has propagated through DSC shell. Since Enclosure 4 demonstrates that only cracks which are oriented perpendicular to the weld will propagate through the full thickness of a DSC shell, cracks in the hoop direction will be evaluated for axial stresses and cracks oriented in the axial direction will be evaluated for hoop stresses. The initial length of all cracks evaluated will be limited to the thickness of the location of the respective weld. Calvert Cliffs will commit to perform this evaluation within 5 years of approval of the ISFSI License Renewal.

If the presence of CISCC exceeding the acceptance criterion is confirmed, a repair or replacement plan for the DSC will be implemented, with timing commensurate with the consequences of through-wall CISCC.

#### **REFERENCES**

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#### Figure 2-1. Proposed DSC Aging Management Program for the Effects of CISCC

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# **ENCLOSURE 2**

**Computing Surface Soluble Salt Density from Conductivity Measurements** 

# Computing Surface Soluble Salt Density From Conductivity Measurements

Delivered to Constellation Energy Nuclear Group by Paul D. Gossen, LLC

Report Revision Date: 10 June 2013

#### **1** Executive Summary

This short technical white paper demonstrates how to develop calibration equations that relate conductivity to salt concentration for dilute aqueous solutions of strong electrolytes.

The application for this paper is computing a surface soluble salt density from a conductivity measurement of a solution extracted from the sample surface. The methodology is to generate candidate calibrations from standard tables of ionic conductivities. This work supports interpreting results of a SaltSmart<sup>™</sup> surface salt measurement from a spent fuel dry storage cask (DSC) at Calvert Cliffs in June 2012.

In that test, surface soluble salt density was computed from a SaltSmart sample extraction device with a field conductivity sensor calibration that was based on sea salt solutions. The field result measured was:

$$\rho_{A.sea \ salt} = 510 \text{ mg/m}^2 \text{ total salt}$$

Subsequent laboratory analysis of salts extracted from that SaltSmart device revealed that the soluble salts on the Calvert Cliffs DSC were not typical of sea salt. Those analytical results found predominantly calcium and sulfate ions, plus they had a deficit of anion charge that forces making an assumption about the missing anion species to compute a new conductivity calibration. Rather than select a single model salt solution, this report computes a separate conductivity calibration for four plausible missing anions, giving a range of interpretations of the SaltSmart field conductivity reading.

Salt Solution Model	Anion used to balance charge	Conductivity calibration constant, $c_2$ [g·cm <sup>-2</sup> ·S <sup>-1</sup> ]	$\rho_{A_2} = \rho_{A,sea \ salt} \cdot \frac{c_2}{0.48}$ [mg/m <sup>2</sup> total salt] with new Salt Solution Model calibration		
Table 7	Hydroxide (OH)	0.103	110		
Table 8	Carbonate $(CO_3^{2-})$	0.187	199		
Table 9	Nitrate (NO <sub>3</sub> <sup>-</sup> )	0.244	259		
Table 10	Chloride (Cl <sup>-</sup> )	0.183	194		

SaltSmart Total Surface Salt Readings from Conductivity Calibrations consistent with Calvert Cliffs DSC Sample Analytical Test Results

Of these models, the hydroxide case represents an assumption that the SaltSmart sample has a basic pH, and the other three represent an assumption of an acidic sample.

1

Each composition model used to compute a conductivity calibration has a chloride ion mass concentration in its respective model. Each model can therefore give its own estimate of surface salt chloride ion concentration by multiplying the total surface salt density computed from the SaltSmart reading by that model's chloride ion mass concentration with. Those calculations yield the following results:

Salt Solution Model	Anion used to balance charge	Chloride Ion (CI) mass % in the Salt Solution Model	$\rho_{A_2} = \rho_{A,sea \ salt} \cdot \frac{c_2}{0.48}$ [mg/m <sup>2</sup> total salt]	$\rho_{A_2,Cl^-}$ [mg/m <sup>2</sup> chloride ion, Cl <sup>-</sup> ]
Table 7	Hydroxide (OH <sup>-</sup> )	1.42%	110 mg/m <sup>2</sup> total salt	$1.6 \text{ mg/m}^2 \text{Cl}^2$
Table 8	Carbonate $(CO_3^{2-})$	1.18%	199 mg/m <sup>2</sup> total salt	$2.4 \text{ mg/m}^2 \text{Cl}^2$
Table 9	Nitrate $(NO_3)$	0.84%	259 mg/m <sup>2</sup> total salt	$2.2 \text{ mg/m}^2 \text{Cl}^-$
Table 10	Chloride (Cl <sup>-</sup> )	43.03%	194 mg/m <sup>2</sup> total salt	83.7 mg/m <sup>2</sup> Cl <sup>-</sup>

Surface Density of Chloride Ion Computed from Model Salt Solutions combined with SaltSmart Field Conductivity Reading

Note that these results are based on a model that combines a field SaltSmart sample, a field conductivity measurement of that SaltSmart device, later off-line laboratory analysis of the SaltSmart contents, and then some educated guessing about the concentrations of missing anions in that sample. The range of chloride ion results presented here depends more on an assumption about the model salt solution than it does on the actual field conductivity measurement of the SaltSmart. It is better characterized as a model calculation exercise than an analytical result. This analysis is intended for technical guidance only and is not presented as the definitive measurement of the surface soluble salt density.

## 2 Surface Soluble Salt Density from a Conductivity Sensor

This section explains how surface salt contamination is assessed using conductivity measurements. The symbols and nomenclature are the same as those used in ISO 8502-9 *Field method for the conductometric determination of water-soluble salts* (ISO, 1998).

#### 2.1 Using Conductivity to Measure Surface Salt Concentration

The total surface salt density  $\rho_A$  of the salts is defined as:

$$\rho_A = \frac{m}{A}$$

where

*m* is the mass of soluble salts in the sample area;

A is the area of that sample area.

All field analytical techniques that measure soluble salts on a surface use some solvent to extract salt from a defined sample surface area, A, into a known volume of solvent, V.

If the mass of salt, m, inside the area A is extracted from the surface into a volume V of solution, then the conductivity of the solution is related to its salt concentration<sup>1</sup> by:

$$\frac{m}{v} = c \cdot (\gamma - \gamma_0) \tag{2}$$

where

c is a calibration constant that depends on the salt species in the extract;

*V* is the volume of water;

 $\gamma$  is the conductivity of the extract water on the addition of *m* salt.

 $\gamma_0$  is the conductivity of the clean extract solvent plus conductivity contributed by the test device.

Consider now a test device that extracts a mass of salt, m, from an area, A, into a volume, V, and then measures its conductivity, the governing calibration equation for surface salt density is a combination of (1) and (2) above:

$$\rho_A = \frac{m}{A} = c \cdot \frac{v}{A} \cdot (\gamma - \gamma_0) \tag{3}$$

#### 2.2 Shifting between calibrations for different salt solutions

In the present case, we have a situation where surface salt density was computed with one value of c, say  $c_1$ , based on calibration with sea salt. So, from Equation (3):

$$\rho_{A_1} = c_1 \cdot \frac{v}{A} \cdot (\gamma - \gamma_0) \tag{4}$$

But now, we would like to compute the surface salt density based on a calibration with some new value of c based on some different type of salt solution, say  $c_2$ :

$$\rho_{A_2} = c_2 \cdot \frac{v}{A} \cdot (\gamma - \gamma_0) \tag{5}$$

(1)

<sup>&</sup>lt;sup>1</sup> The linear relationship between concentration and conductivity is an approximation that is valid at solution concentrations below 400 mg/L (see Bresle, 1995). SaltSmart operates in this dilute salt concentration range.

For any one data point from one test device, the term  $[V/A \cdot (\gamma - \gamma_0)]$  doesn't change, so comparing Equations (4) and (5) yields:

$$\frac{\rho_{A_2}}{c_2} = \frac{\rho_{A_1}}{c_1}$$
 (6)

Or

$$\rho_{A_2} = \rho_{A_1} \cdot \frac{c_2}{c_1} \tag{7}$$

#### 2.3 Computing the conductivity calibration constant, c

The choice of the constant, c, depends on the salt species in the extract solution and is best determined experimentally. Common values of  $c \operatorname{are}^2$ 

 $c = 5.0 \text{ kg} \cdot \text{m}^{-2} \cdot \text{S}^{-1}$  mathematically derived for a mixture of chloride and sulfate "mixed corrosion products on steel" and used in ISO 8502-9; and,

 $c = 4.6 \text{ kg} \cdot \text{m}^{-2} \cdot \text{S}^{-1}$  for pure NaCl solution and used for IMO PSPC MSC.215(82)

These values were derived by Bresle (1995) from standard tables of ionic conductivities. The rest of this section demonstrates that calculation. Consider again Equation (2) rewritten for a single conductivity value:

$$\frac{m}{v} = c \cdot \gamma \tag{8}$$

where

c is a calibration constant that depends on the salt species in the extract;

*V* is the volume of salt solution;

*m* is the mass of salt in the salt solution;

 $\gamma$  is the conductivity of the salt solution.

Dividing by the molar mass of the salt, M, yields:

$$\frac{m}{M \cdot V} = \frac{c}{M} \cdot \gamma = \frac{1}{\Lambda} \cdot \gamma$$

$$\gamma = \Lambda \cdot \frac{m}{M \cdot V}$$

$$c = \frac{M}{\Lambda}$$
(9)
(10)

or

and

where

 $\Lambda$  is the ionic conductivity of the salt species in the solution; and the term  $\frac{m}{M \cdot V}$  is simply the molar concentration of ions in solution.

4

<sup>&</sup>lt;sup>2</sup> Values are from A. Bresle, "Conductimetric Determination of Salts on Steel Surfaces", Materials Performance, June 1995 but converted to SI units used in ISO 8502-9. The ISO 8502-9 standard allows for any value of c, but the value c=5 is used as an example in ISO 8502-9 and in general practice this has become a standard for the protective coatings industry. Except for the IMO PSPC, which called out ISO 8502-9 as the test method, but required the result to be reported "equivalent to NaCl". Commercial surface salt contamination devices, therefore, often include both calibrations.

Surface soluble salt test methods mostly yield test solutions that can be considered as dilute solutions of strong electrolytes. In this case, the ionic conductivity of the solution can be calculated from standard tables of zero-concentration ionic conductivities like Table 1 below. Values of this table are used with Kohlrausch's law of independent conductivities, which states that for a solution of electrolyte  $v_+A^{z^+}v_-B^{z^-}$  the zero-concentration ionic conductivity can be computed from the zero-concentration ionic conductivity of the constituent ions:

$$\Lambda^0 = \nu_+ \cdot \Lambda^0_+ + \nu_- \cdot \Lambda^0_- \tag{11}$$

For example, for sodium chloride, NaCl:

$$\nu_{+}A^{z^{+}}\nu_{-}B^{z^{-}} = (1 \cdot Na^{+})(1 \cdot Cl^{-}), \text{ so:}$$
  
 $\Lambda^{0}_{NaCl} = 1 \cdot \Lambda^{0}_{Na} + 1 \cdot \Lambda^{0}_{Cl}$   
 $\Lambda^{0}_{NaCl} = 50.15 + 76.35$   
 $\Lambda^{0}_{NaCl} = 126.50 \text{ S} \cdot \text{cm}^{2} \cdot \text{mol}^{-1}$ 

From Equation (10) above, dividing the molar mass of by NaCl (58.35 g/mol) by this value yields:

 $c = 0.46 \text{ g}\cdot\text{cm}^{-2}\cdot\text{S}^{-1}$ , which is the value in Bresle's 1995 paper for NaCl, or in SI units  $c = 4.6 \text{ kg}\cdot\text{m}^{-2}\cdot\text{S}^{-1}$ 

A second example calculation for calcium chloride, CaCl<sub>2</sub>, shows how to deal with the mole-equivalents units of the standard tables:

$$\nu_{+}A^{z^{+}}\nu_{-}B^{z^{-}} = (1 \cdot Ca^{2+})((2 \cdot Cl^{-})), \text{ so:}$$

$$\Lambda^{0}_{CaCl_{2}} = 1 \cdot \Lambda^{0}_{Ca} + 2 \cdot \Lambda^{0}_{Cl}$$

$$\Lambda^{0}_{CaCl_{2}} = 1 \cdot (2 \cdot \Lambda^{0}_{1/2Ca}) + 2 \cdot \Lambda^{0}_{Cl}$$

$$\Lambda^{0}_{CaCl_{2}} = 2 \cdot 59.50 + 2 \cdot 76.35$$

$$\Lambda^{0}_{CaCl_{2}} = 271.7 \text{ S} \cdot \text{cm}^{2} \cdot \text{mol}^{-1}$$

Again, dividing the molar mass of CaCl<sub>2</sub> (110.98 g/mol) by this value yields:

 $c = 0.41 \text{ g} \cdot \text{cm}^{-2} \cdot \text{S}^{-1}$ , which is the value in Bresle's 1995 paper for CaCl<sub>2</sub>, or in SI units  $c = 4.1 \text{ kg} \cdot \text{m}^{-2} \cdot \text{S}^{-1}$ 

For the general case of a solution of multiple strong electrolytes  $v_{i+}A_i^{z+}v_{i-}B_i^{z-}$  each present in  $y_i$  mole fraction:

$$\Lambda^{0} = \sum_{i} y_{i} \cdot (v_{i+} \cdot \Lambda^{0}_{i+} + v_{i-} \cdot \Lambda^{0}_{i-})$$
(12)

and the value of c is then computed using the bulk molar mass of solutes in solution.

		a wakal	$\Lambda^0$ , zero-concentration ionic conductivity
aniana	huravida	Symbol	
anions	nyroxide	UH T	197.60
	sulfate	1/2SO4	93.80
	phosphate	⅓PO <sub>4</sub>	93.80
	bromide	Br	78.17
	chloride	Cl	76.35
	nitrate	NO <sub>3</sub> <sup>-</sup>	71.44
	carbonate	½CO3	69.30
	fluoride	F	55.40
cations	hydronium	$H_3O^+$	349.85
	potassium	K+	73.50
	ammonium	NH3 <sup>+</sup>	73.40
	iron III	⅓Fe <sup>+++</sup>	68.00
	titanium	½Ti <sup>++</sup>	67.00
	chromium	%Cr <sup>+++</sup>	67.00
	calcium	1⁄2Ca <sup>++</sup>	59.50
	copper	1⁄2Cu <sup>++</sup>	56.60
	nickel	1⁄2Ni <sup>++</sup>	54.00
	manganese	½Mn <sup>++</sup>	53.50
	iron II	1/2Fe <sup>++</sup>	53.50
	magnesium	½Mg <sup>++</sup>	53.06
	zinc	1⁄2Zn <sup>++</sup>	52.80
	sodium	Na⁺	50.15
	lithium	Li <sup>+</sup>	38.64

Table 1: Zero-Concentration Ionic Conductivities

[from R. Parsons, Handbook of Electrochemical Constants, Butterworth, London, 1952 as reproduced in J. Robbins, 1979]

## **3** Conductivity Calibration for the Calvert Cliffs DSC

#### 3.1 Conductivity Calibration with Sea Salt Solutions

The calibration constant that was developed for the June 2012 Calvert Cliffs DSC field trial was developed using solutions of sea salt dissolved in deionized water. The concentration-to-conductivity relationship of that solution is given in Figure 1 below. Its proportionality constant, c = 0.48 g·cm<sup>-2</sup>·S<sup>-1</sup> by least squares fit, falls between that of pure NaCl and the ISO 8502-9 value. This is expected because all of these values represent solutions comprising predominantly NaCl.



#### Figure 1: Calibration of Aqueous Sea Salt Solution Concentration from Conductivity

## 3.2 Conductivity Calibration Computed from Models of Salt in Calvert Cliffs DSC Samples

Analysis of a deionized water extraction from the SaltSmart device from the Calvert Cliffs DSC revealed a composition very different from sea salt (see Table 2).

	ICP conc'r			
constituent	control	used	net	mass %
fluoride	0	9.0	9.0	0.64%
chloride	2.7	29.7	27.0	1.91%
sulfate	0	429.8	429.8	30.38%
phosphate	0	95.0	95.0	6.71%
sodium	2.5	148.5	146.0	10.32%
ammonium	0	5.9	5.9	0.42%
potassium	0	91.4	91.4	6.46%
magnesium	0	77.8	77.8	5.50%
calcium	6.29	539.3	533.0	37.67%

Table 2: ICP of deionized water extraction of SaltSmart [EPRI March 25, 2013 letter to Ron Seagraves, CCNPP]

Rather than characteristics of deposits from sea salt mist, these salt deposits are more characteristic of industrial pollution (sulfates), agricultural fertilizer (ammonium, phosphate) and concrete dust (calcium, magnesium).

A SaltSmart calibration computing surface salt concentration from conductivity based on sea salt solutions is invalid if the actual test solution is the one in Table 2 above. But, there is a simple way to compute a new value for surface salt concentration for a different salt solution. Use Equations (12) and (10) with the methodology of the previous section to compute a new value for the calibration constant,  $c_2$ , and then use Equation (7) above

7

to convert any surface salt density value computed with the sea salt calibration curve to this new calibration:

$$\rho_{A_2} = \rho_{A,sea \,salt} \cdot \frac{c_2}{0.48} \tag{13}$$

Unfortunately, there is a complication with the ICP data presented above. The accounting of anions and cations does not match. The molar equivalents, i.e. the charge, of anions and cations in solution should match, but instead there is a shortage of anions. Table 3 shows the calculations and results.

		and the second design of the s					
			mass ions		mol ions for		
		1	for 1 g solute	molar mass	1 g solute		mol
	ion	mass %	[g]	[g/mol]	[mol]	charge	equivalents
anions	fluoride	0.64%	0.0064	19.00	0.0003	1	0.0003
	chloride	1.91%	0.0191	35.45	0.0005	1	0.0005
	sulfate	30.38%	0.3038	96.07	0.0032	2	0.0063
	phosphate	6.71%	0.0671	94.97	0.0007	3	0.0021
				tota	al anion equiv	alents ==>	0.0093
cations	sodium	10.32%	0.1032	22.90	0.0045	1	0.0045
	ammonium	0.42%	0.0042	18.04	0.0002	1	0.0002
	potassium	6.46%	0.0646	39.10	0.0017	1	0.0017
	magnesium	5.50%	0.0550	24.31	0.0023	2	0.0045
	calcium	37.67%	0.3767	40.08	0.0094	2	0.0188
				tota	total cation equivalents ==>		
			diffe	rence (cation -	anion) equiv	alents ==>	0.0204

Table 3: Molar Equivalents of Anions and Cations in ICP Analysis of SaltSmart

## 3.3 Choosing Anions to Balance Charges in the Model Salt Solution

For an example calculation of the conductivity calibration equation we must first balance the charges in the model salt solution by postulating some anions consistent with the sample environment that, upon dissolution, drying and storage of the SaltSmart device are either volatile enough to disappear or are not detected by ICP.

X-ray diffraction analysis of the used SaltSmart extraction wick [EPRI March 25, 2013 letter to Ron Seagraves, CCNPP] found the following constituents of concrete:

- Al(OH)<sub>3</sub>; Gibbsite (Aluminum Hydroxide)
- MgO; Periclase, syn (Magnesium Oxide)
- CaCO<sub>3</sub>; Calcite, Calcium Carbonate
- CaMg(CO<sub>3</sub>)<sub>2</sub>; Dolomite (Calcium Magnesium Carbonate)

So, two plausible candidate anions to make up the charge imbalance in calculations are carbonate  $(CO_3^{2^-})$  and hydroxide  $(OH^-)$ . Hydroxide would be an obvious choice if the sample solution had a basic pH. The hydroxide in a basic SaltSmart solution would be masked by the large amounts of water used to extract the SaltSmart sample for ICP analysis. If, on the other hand, the SaltSmart sample solution were acidic, calcium carbonate becomes soluble, but that carbonate could volatilize to  $CO_2$  gas on drying of the SaltSmart device after field sampling and field reading of conductivity (see EPRI report 1013524 for a discussion of this mechanism).

The discussion in EPRI report 1013524 *Climatic Corrosion Considerations for Independent Spent Fuel Storage Installations in Marine Environments,* also postulates that chloride (Cl<sup>-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) anions could off-gas from evaporating acidic solutions as HCl and HNO<sub>3</sub> gas, respectively (page 2-30 of that report).

Comparing deionized water extractions of the SaltSmart device with those of two dry samplers does not give a conclusive answer as to which of these four anions  $(CO_3^{2^2}, NO_3^{2^2}, Cl^- \text{ or } OH^-)$  is the best choice to balance the charges in a model salt solution.

On the one hand, ICP analyses of deionized water extracts of dry samplers also have an anion charge deficit (Tables 4 and 5 below). This is consistent with the hypothesis that all DSC samples had a basic pH with the anion charge deficit from OH<sup>-</sup>.

		the second s					
			mass ions for		mol ions for		
			1 g solute	molar mass	1 g solute		mol
	ion	mass %	[g]	[g/mol]	[mol]	charge	equivalents
anions	fluoride	0.00%	e e	19.00	-	1	0.0000
	chloride	1.72%	0.0172	35.45	0.0005	1	0.0005
	nitrite	0.00%		46.01	-	1	0.0000
	nitrate	9.46%	0.0946	62.01	0.0015	1	0.0015
	sulfate	36.90%	0.3690	96.07	0.0038	2	0.0077
	phosphate	0.00%		94.97		3	0.0000
				te	otal anion equ	ivalents ==>	0.0097
cations	lithium	0.86%	0.0086	6.94	0.0012	1	0.0012
	sodium	4.30%	0.0430	22.90	0.0019	1	0.0019
	ammonium	4.26%	0.0426	18.04	0.0024	1	0.0024
	potassium	0.00%	-	39.10	÷.	1	0.0000
	magnesium	5.08%	0.0508	24.31	0.0021	2	0.0042
	calcium	37.42%	0.3742	40.08	0.0093	2	0.0187
				to	tal cation equ	ivalents ==>	0.0271
			dif	ference (catio	n - anion) equ	ivalents ==>	0.0174

Table 4: Molar Equivalents of Anions and Cations in ICP Analysis of Filter [Derived from test results in EPRI March 25, 2013 letter to Ron Seagraves, CCNPP]

			mass ions for		mol ions for		
			1 g solute	molar mass	1 g solute		mol
	ion	mass %	[g]	[g/mol]	[mol]	charge	equivalents
anions	fluoride	0.00%	-	19.00	-	1	0.0000
	chloride	2.66%	0.0266	35.45	0.0007	1	0.0007
	nitrite	0.47%	0.0047	46.01	0.0001	1	0.0001
	nitrate	12.95%	0.1295	62.01	0.0021	1	0.0021
	sulfate	40.17%	0.4017	96.07	0.0042	2	0.0084
	phosphate	1.66%	0.0166	94.97	0.0002	3	0.0005
				to	otal anion equ	ivalents ==>	0.0118
cations	lithium	0.00%	-	6.94	-	1	0.0000
cations	sodium	7.97%	0.0797	22.90	0.0035	1	0.0035
	ammonium	1.33%	0.0133	18.04	0.0007	1	0.0007
	potassium	9.96%	0.0996	39.10	0.0025	1	0.0025
	magnesium	2.93%	0.0293	24.31	0.0012	2	0.0024
	calcium	19.92%	0.1992	40.08	0.0050	2	0.0099
				to	tal cation equ	ivalents ==>	0.0191
			dif	ference (catio	n - anion) equ	ivalents ==>	0.0073

Table 5: Molar Equivalents of Anions and Cations in ICP Analysis of Scotch-Brite [Derived from test results in EPRI March 25, 2013 letter to Ron Seagraves, CCNPP] On the other hand, one observation consistent with the hypothesis of an acid solution environment in the SaltSmart device is the absence of nitrates in the SaltSmart. Nitrates are present in the dry samplers. The salts on the dry samplers did not go through a cycle of dissolution and drying of salt like the SaltSmart sample, so presumably the off-gas of acid gases  $CO_2$ , HCl or HNO<sub>3</sub> would not occur with the dry samplers even if it occurred with the SaltSmart sample.

Table 6 below compares the anion concentrations from the two dry sample methods (Filter and Scotch-Brite) with the SaltSmart. The left half of Table 6 shows values in the units reported by the ICP analysis. On the right half of Table 6, the mass concentration of each anion is divided by the sulfate concentration in that sample. This analysis shows that chloride (Cl<sup>-</sup>) is present in a consistent ratio to sulfates in all samples, but nitrate (NO<sub>3</sub><sup>-</sup>) is not, which argues for adding nitrate to the list of anions to consider for balancing charges in a model salt solution.

	ICP connet	onc'n in [ppb = of (Used - Cor	µg/kg] htrol)	Concentration Ratio to Sulfate				
	Filter	Scotch-Brite	SaltSmart	Filter	Scotch-Brite	SaltSmart		
Fluoride F-	0.00	0.00	8.99	0.000	0.000	0.021		
Chloride Cl-	4.0	8.0	27.0	0.047	0.066	0.063		
Nitrite (NO2)-	0.00	1.41	0.00	0.000	0.012	0.000		
Nitrate (NO3)-	22.00	39.00	0.00	0.256	0.322	0.000		
Sulfate (SO4)2-	85.79	121.00	429.79	1.000	1.000	1.000		
Phosphate (PO4)3-	0	5	95	0.000	0.041	0.221		

Table 6: Anions in ICP of deionized water extract of salt samplers from Calvert Cliffs DSC

[Derived from test results in EPRI March 25, 2013 letter to Ron Seagraves, CCNPP]

At this stage, of the 4 most likely anions to choose to balance charges in a model solution, there is some evidence in the analytical data to support using  $OH^-$  for a basic pH case, and  $CO_3^{2^-}$  or  $NO_3^-$  for an acidic pH case. It was therefore decided to add chloride, Cl<sup>-</sup>, as a potential worst case scenario for the acidic pH case and compute conductivity calibrations for four model salt solutions, one for each of these candidate anions for balancing the charge in the model salt solution.

Details of those model salt solutions and their computed molar conductivity are in Tables 7 through 10 below. In each of these tables, the molar mass of the solute ions is computed by dividing the sum of the "mass ions" column by the sum of the "mol ions" column.

	new	total mass:	1.35		molar mass			ma	olar conductivity		
		ICP basis:	1.00			31.19			301.37		
	ion	ICP mass %	mass ions for 1 g ICP solute [g]	mass % for model salt solution	molar mass [g/mol]	mol ions for 1 g solute [mol]	charge	mol equivalents	molar conductivity [S cm <sup>2</sup> mol <sup>-</sup> 1]	concentration weighted molar conductivity contribution [S cm <sup>2</sup> mol <sup>-1</sup> ]	
anions	fluoride	0.64%	0.0064	0.47%	19.00	0.0003	1	0.0003	55.40	0.62	
	chloride	1.91%	0.0191	1.42%	35.45	0.0005	1	0.0005	76.35	1.38	
	sulfate	30.38%	0.3038	22.55%	96.07	0.0032	2	0.0063	187.6	39.92	
	phosphate	6.71%	0.0671	4.98%	94.97	0.0007	3	0.0021	281.4	20.08	
	carbonate		-	0.00%	60.01	-	2	0.0000	138.60	0.00	
	hydroxide		0.3470	25.76%	17.01	0.0204	1	0.0204	197.60	135.65	
					tota	l anion equi	valents ==>	0.0297			
cations	sodium	10.32%	0.1032	7.66%	22.90	0.0045	1	0.0045	50.15	7.61	
	ammonium	0.42%	0.0042	0.31%	18.04	0.0002	1	0.0002	73.4	0.57	
	potassium	6.46%	0.0646	4.79%	39.10	0.0017	1	0.0017	73.5	4.09	
	magnesium	5.50%	0.0550	4.08%	24.31	0.0023	2	0.0045	106.12	16.16	
	calcium	37.67%	0.3767	27.97%	40.08	0.0094	2	0.0188	119	75.29	
					total	cation equi	valents ==>	0.0297			
				1.00							

 

 difference (cation - anion) equivalents ==>
 0.0000

 Table 7: Molar Conductivity for Model DSC Surface Salt with Hydroxide (OH<sup>-</sup>) Added

 to Balance Anions.

	new	v total mass:	1.61			molar mass			ma	olar conductivity
		ICP basis:	1.00			48.86				260.87
	ion	ICP mass %	mass ions for 1 g ICP solute [g]	mass % for model salt solution	molar mass [g/mol]	mol ions for 1 g solute [mol]	charge	mol equivalents	molar conductivity [S cm <sup>2</sup> mol <sup>-</sup> <sup>1</sup> ]	concentration weighted molar conductivity contribution [S cm <sup>2</sup> mol <sup>-1</sup> ]
anions	fluoride	0.64%	0.0064	0.39%	19.00	0.0003	1	0.0003	55.40	0.62
	chloride	1.91%	0.0191	1.18%	35.45	0.0005	1	0.0005	76.35	1.38
	sulfate	30.38%	0.3038	18.84%	96.07	0.0032	2	0.0063	187.6	39.92
	phosphate	6.71%	0.0671	4.16%	94.97	0.0007	3	0.0021	281.4	20.08
	carbonate		0.6121	37.97%	60.01	0.0102	2	0.0204	138.60	95.14
	hydroxide		-	0.00%	17.01	-	1	0.0000	197.60	0.00
					tota	l anion equi	valents ==>	0.0297		
cations	sodium	10.32%	0.1032	6.40%	22.90	0.0045	1	0.0045	50.15	7.61
	ammonium	0.42%	0.0042	0.26%	18.04	0.0002	1	0.0002	73.4	0.57
	potassium	6.46%	0.0646	4.01%	39.10	0.0017	1	0.0017	73.5	4.09
	magnesium	5.50%	0.0550	3.41%	24.31	0.0023	2	0.0045	106.12	16.16
	calcium	37.67%	0.3767	23.37%	40.08	0.0094	2	0.0188	119	75.29
					total	cation equi	valents ==>	0.0297		
				differe	nce (cation -	anion) equi	valents ==>	0.0000		

Table 8: Molar Conductivity for Model DSC Surface Salt with Carbonate  $(CO_3^{2-})$  Added to Balance Anions.

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	new	total mass:	2.27			molar mass			ma	lar conductivity
		ICP basis:	1.00			52.44				214.76
	ion	ICP mass %	mass ions for 1 g ICP solute [g]	mass % for model salt solution	molar mass [g/mol]	mol ions for 1 g solute [mol]	charge	mol equivalents	molar conductivity [S cm <sup>2</sup> mol <sup>-</sup> <sup>1</sup> ]	concentration weighted molar conductivity contribution [S cm <sup>2</sup> mol <sup>-1</sup> ]
anions	fluoride	0.64%	0.0064	0.28%	19.00	0.0003	1	0.0003	55.40	0.62
	chloride	1.91%	0.0191	0.84%	35.45	0.0005	1	0.0005	76.35	1.38
	sulfate	30.38%	0.3038	13.41%	96.07	0.0032	2	0.0063	187.6	39.92
	phosphate	6.71%	0.0671	2.96%	94.97	0.0007	3	0.0021	281.4	20.08
	nitrate		1.2650	55.85%	62.01	0.0204	1	0.0204	71.44	49.04
	carbonate		-	0.00%	60.01	-	2	0.0000	138.60	0.00
	hydroxide		-	0.00%	17.01	-	1	0.0000	197.60	0.00
					tota	l anion equi	valents ==>	0.0297		
cations	sodium	10.32%	0.1032	4.56%	22.90	0.0045	1	0.0045	50.15	7.61
	ammonium	0.42%	0.0042	0.18%	18.04	0.0002	1	0.0002	73.4	0.57
	potassium	6.46%	0.0646	2.85%	39.10	0.0017	1	0.0017	73.5	4.09
	magnesium	5.50%	0.0550	2.43%	24.31	0.0023	2	0.0045	106.12	16.16
	calcium	37.67%	0.3767	16.63%	40.08	0.0094	2	0.0188	119	75.29
					total	cation equi	valents ==>	0.0297		
				differe	nce (cation -	anion) equi	0.0000			

Table 9: Molar Conductivity for Model DSC Surface Salt with Nitrate (NO<sub>3</sub><sup>-</sup>) Added to Balance Anions.

	new total mass:		1.72	molar mass		molar conductivity				
	ICP basis:		1.00		39.90				218.04	
	ion	ICP mass %	mass ions for 1 g ICP solute [g]	mass % for model salt solution	molar mass [g/mol]	mol ions for 1 g solute [mol]	charge	mol equivalents	molar conductivity [S cm <sup>2</sup> mol <sup>-</sup> 1]	concentration weighted molar conductivity contribution [S cm <sup>2</sup> mol <sup>-1</sup> ]
anions	fluoride	0.64%	0.0064	0.37%	19.00	0.0003	1	0.0003	55.40	0.62
	chloride	1.91%	0.7409	43.03%	35.45	0.0209	1	0.0209	76.35	53.70
	sulfate	30.38%	0.3038	17.64%	96.07	0.0032	2	0.0063	187.6	39.92
	phosphate	6.71%	0.0671	3.90%	94.97	0.0007	3	0.0021	281.4	20.08
	carbonate		-	0.00%	60.01	-	2	0.0000	138.60	0.00
	hydroxide		-	0.00%	17.01	-	1	0.0000	197.60	0.00
					tota	l anion equi	valents ==>	0.0297		and the second
cations	sodium	10.32%	0.1032	5.99%	22.90	0.0045	1	0.0045	50.15	7.61
	ammonium	0.42%	0.0042	0.24%	18.04	0.0002	1	0.0002	73.4	0.57
	potassium	6.46%	0.0646	3.75%	39.10	0.0017	1	0.0017	73.5	4.09
	magnesium	5.50%	0.0550	3.19%	24.31	0.0023	2	0.0045	106.12	16.16
	calcium	37.67%	0.3767	21.88%	40.08	0.0094	2	0.0188	119	75.29
				total cation equivalents ==>			0.0297			
				difference (cation - anion) equivalents ==>				0.0000		

Table 10: Molar Conductivity for Model DSC Surface Salt with Chloride (Cl<sup>-</sup>) Added to Balance Anions.

The new calibration constant  $c_2$  is then computed using Equation (10) by dividing the molar mass by the molar conductivity. Those results are in Table 11 below.

Salt Solution Model	Anion used to balance charge	Conductivity calibration constant, $c_2$ [g·cm <sup>-2</sup> ·S <sup>-1</sup> ]		
Table 7	Hydroxide (OH)	0.103		
Table 8	Carbonate $(CO_3^{2-})$	0.187		
Table 9	Nitrate (NO <sub>3</sub> <sup>-</sup> )	0.244		
Table 10	Chloride (Cl <sup>-</sup> )	0.183		

Table 11: Conductivity Calibration Constants for Model Salt Solutions

These values of  $c_2$  are used with Equation (13), repeated here, to shift the SaltSmart reading from the sea salt calibration to one of these new calibrations:

$$\rho_{A_2} = \rho_{A,sea \,salt} \cdot \frac{c_2}{0.48} \tag{13}$$

Consider now the actual SaltSmart field test from the June 2012 trial. Below is a screen capture of the SaltSmart device conductivity trace immediately after the test:



In the nomenclature of this report, this result means:

$$\rho_{A,sea \ salt} = 510 \text{ mg/m}^2 \text{ total salt}$$

Using Equation (13) with this value and the set of calibrations from Table 11 yields the following surface salt readings:

Salt Solution Model	Anion used to balance charge	Conductivity calibration constant, $c_2$ [g·cm <sup>-2</sup> ·S <sup>-1</sup> ]	<i>P<sub>A,sea salt</sub></i> [mg/m <sup>2</sup> total salt] with sea salt calibration	$\rho_{A_2} = \rho_{A,sea \ salt} \cdot \frac{c_2}{0.48}$ [mg/m <sup>2</sup> total salt] with new Salt Solution Model calibration	
Table 7	Hydroxide (OH <sup>-</sup> )	0.103	510	110	
Table 8	Carbonate $(CO_3^{2-})$	0.187	510	199	
Table 9	Nitrate (NO <sub>3</sub> <sup>-</sup> )	0.244	510	259	
Table 10	Chloride (Cl <sup>-</sup> )	0.183	510	194	

 Table 12: SaltSmart Total Surface Salt Readings from Conductivity Calibrations consistent with Calvert Cliffs DSC Sample Analytical Test Results

The salt solution models that assume an acidic sample (carbonate, nitrate, chloride) give results half or less than the calibration based on sea salt solutions because the Calvert Cliffs model solution is predominantly calcium and sulfate, which have higher ionic conductivities than the sodium and chloride that dominate sea salt conductivity.

The high-hydroxide model for a sample solution with basic pH gives a result that is half again of the acidic solution model because of the extremely high ionic conductivity of the hydroxide ion.

Of particular interest for this field test is the chloride ion concentration on the DSC steel surface. For the composition models proposed in Tables 7 through 10, each one shows a chloride ion mass concentration computed for its respective model. Each model can therefore give its own estimate of surface salt chloride ion concentration by combining

Salt Solution Model	Anion used to balance charge	Chloride Ion (Cl <sup>-</sup> ) mass % in the Salt Solution Model	$\rho_{A_2} = \rho_{A,sea \ salt} \cdot \frac{c_2}{0.48}$ [mg/m <sup>2</sup> total salt]	$\rho_{A_2,Cl^-}$ [mg/m <sup>2</sup> chloride ion, Cl <sup>-</sup> ]
Table 7	Hydroxide (OH)	1.42%	110 mg/m <sup>2</sup> total salt	$1.6 \text{ mg/m}^2 \text{ Cl}^-$
Table 8	Carbonate $(CO_3^2)$	1.18%	199 mg/m <sup>2</sup> total salt	$2.4 \text{ mg/m}^2 \text{ Cl}^-$
Table 9	Nitrate (NO <sub>3</sub> <sup>-</sup> )	0.84%	259 mg/m <sup>2</sup> total salt	$2.2 \text{ mg/m}^2 \text{Cl}^2$
Table 10	Chloride (Cl <sup>*</sup> )	43.03%	194 mg/m <sup>2</sup> total salt	83.7 mg/m <sup>2</sup> Cl <sup>-</sup>

that model's chloride ion mass concentration with the total surface salt density computed from SaltSmart conductivity in Table 12. That calculation yields the following results

 Table 13: Surface Density of Chloride Ion Computed from Model Salt Solutions combined with SaltSmart Field Conductivity Reading

When interpreting the results of Table 13, note that the range of results depends more on an assumption about the model salt solution than it does on the actual conductivity measurement from the SaltSmart in the field. Table 13 is therefore better characterized as a model calculation result than an analytical result. Also, summarizing the prior discussions in this report, the "Table 10" case with the highest chloride ion concentration is the case that is the least consistent with the analytical test results, but was included to give a complete range for possible conductivity calibrations.

## **4** References

Åke Bresle, Conductimetric Determination of Salts on Steel Surfaces, Materials Performance, June 1995, p. 35.

ISO 8502-9:1998(E), Preparation of steel substrates before application of paints and related products – Tests for the assessment of surface cleanliness – Part 9: Field method for the conductometric determination of water-soluble salts. International Organization for Standardization, Genève, Switzerland, 1998.

J. Robbins, Ions in solution (2); an introduction to electrochemisty. Oxford University Press, London, 1979

Climatic Corrosion Considerations for Independent Spent Fuel Storage Installations in MarineEnvironments, EPRI, Palo Alto, CA: 2006. 1013524.

Keith Waldrop letter to Ron Seagraves, CCNPP, Calvert Cliffs Canister Inspection Chemical Analysis Results of Samples Collected, EPRI, letter dated March 25, 2013

# **ENCLOSURE 6**

Transnuclear, Inc. Affidavit

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#### AFFIDAVIT PURSUANT TO 10 CFR 2.390

Transnuclear, Inc.	)
State of Maryland	) SS.
County of Howard	)

I, Paul Triska, depose and say that I am a Vice President of Transnuclear, Inc., duly authorized to execute this affidavit, and have reviewed or caused to have reviewed the information which is identified as proprietary and referenced in the paragraph immediately below. I am submitting this affidavit in conformance with the provisions of 10 CFR 2.390 of the Commission's regulations for withholding this information.

The CENG-CCNPP License Renewal support documents for which proprietary treatment is sought listed below:

- Transnuclear, Inc. document- Engineering Evaluation # 10955-EE-00, Revision 0, "Calvert Cliffs Nuclear Power Plant (CCNPP) ISFSI: Canister Cask Stress Corrosion Cracking Review for License Renewal".
- Transnuclear, Inc. document- Thermal calculation 10955-0401, Revision 1, "Outer Surface Weld Temperature of the NUHOMS<sup>®</sup> 24P and 32P DSCs Stored at CCNPP ISFSI Site".
- Transnuclear, Inc. document- Thermal calculation 10955-0402, Revision 1, "To Determine Time Limit for Exposure of the Fuel Cladding to Oxidizing Atmosphere for the 24P and 32P DSCs Stored at the CCNPP ISFSI Site".
- AREVA document # 86-9203390-001, "Summary of SCC Assessment of SS Welds in 24P and 32P NUHOMS<sup>®</sup> Dry Storage Casks".

These documents have been appropriately designated as proprietary.

I have personal knowledge of the criteria and procedures utilized by Transnuclear, Inc. in designating information as a trade secret, privileged or as confidential commercial or financial information.

Pursuant to the provisions of paragraph (b) (4) of Section 2.390 of the Commission's regulations, the following is furnished for consideration by the Commission in determining whether the information sought to be withheld from public disclosure, included in the above referenced document, should be withheld.

- 1) The information sought to be withheld from public disclosure involves details and analyses related to Transnuclear, Inc.'s CENG-CCNPP ISFSI License Renewal documents, which are owned and have been held in confidence by Transnuclear, Inc.
- 2) The information is of a type customarily held in confidence by Transnuclear, Inc. and not customarily disclosed to the public. Transnuclear, Inc. has a rational basis for determining the types of information customarily held in confidence by it.
- 3) Public disclosure of the information is likely to cause substantial harm to the competitive position of Transnuclear, Inc. because the information consists of details and analyses related to Transnuclear, Inc.'s CENG-CCNPP ISFSI License Renewal documents. The availability of such information to competitors would enable them to modify their product to better compete with Transnuclear, Inc., take marketing or other actions to improve their product's position or impair the position of Transnuclear, Inc.'s product, and avoid developing similar data and analyses in support of their processes, methods or apparatus.

Further the deponent sayeth not.

Paul Triska

Vice President, Transnuclear, Inc.

Subscribed and sworn to me before this 7<sup>th</sup> day of June, 2013.

Lewis G. Puedeno

Notary Public My Commission Expires 03 1251 2014



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