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Analysis of Samples Collected from the Surface of Interim Storage Canisters at Calvert Cliffs in June, 2017: Revision 01

Charles R. Bryan
Eric J. Schindelholz

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

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Analysis of Samples Collected from the Surface of Interim Storage Canisters at Calvert Cliffs in June, 2017

Charles R. Bryan
Department 8845, Storage and Transportation Technologies
Sandia National Laboratories
P. O. Box 5800
Albuquerque, New Mexico 87185-MS0779

Eric J. Schindelholz
Department 1852, Materials Reliability
Sandia National Laboratories
P. O. Box 5800
Albuquerque, New Mexico 87185-MS0889

Abstract

In June 2017, dust and salt samples were collected from the surface of Spent Nuclear Fuel (SNF) dry storage canisters at the Calvert Cliffs Nuclear Power Plant. The samples were delivered to Sandia National laboratories for analysis. Two types of samples were collected: filter-backed Scotch-Brite™ pads were used to collect dry dust samples for characterization of salt and dust morphologies and distributions; and Saltsmart™ test strips were used to collect soluble salts for determining salt surface loadings per unit area. After collection, the samples were sealed into plastic sleeves for shipping. Condensation within the sleeves containing the Scotch-Brite™ samples remobilized the salts, rendering them ineffective for the intended purpose, and also led to mold growth, further compromising the samples; for these reasons, the samples were not analyzed. The SaltSmart™ samples were unaffected and were analyzed by ion chromatography for major anions and cations. The results of those analyses are presented here.

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EXECUTIVE SUMMARY

In June 2017, dust and salt samples were collected from the surface of spent nuclear fuel dry storage canisters at the Calvert Cliffs independent spent fuel storage installation. The goal of this sampling effort was to characterize the distribution and morphology of dust on the canister surface, with specific focus on the composition and distribution of soluble salts. Two types of samples were collected:

- Soluble salt samples were collected using SaltSmart™ test strips, which were then shipped to Sandia National Laboratories for disassembly, leaching and analysis. These samples provide the composition and abundance (concentration per unit area) of soluble species on the canister surface.
- Dry dust samples were collected using vacuum line with an attached sampling tool. The tool consisted of a steel head with a filter-backed abrasive Scotch-Brite™ pad, which was rubbed across the surface to collect dry dust. The dry dust samples provide information of the size and morphology of dust and salt particles on the canister surface.

After collection, both types of samples were sealed into plastic sleeves and placed into an insulated chest with an ice pack for shipping to Sandia National Laboratories for characterization. However, high humidities at the time of sampling compromised the dry dust samples, causing condensation and mold growth within the sleeves containing the dry dust sampling heads and ruining the samples. No attempt was made to analyze those samples. The SaltSmart™ samples appeared to be unaffected—no mold growth was observed—and were analyzed by ion chromatography for major anions and cations. In addition to the canister samples, SaltSmart™ blanks and control samples with a known amount of salts were also provided and analyzed.

The six SaltSmart™ samples from the storage canister all had similar chemistries, with the cations being dominated by Ca^{+2} and Na^+ . Cation mass abundances for all samples followed the order $\text{Ca}^{+2} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{+2} > \text{NH}_4^+$. Anions were dominantly SO_4^{-2} and NO_3^- ; mass abundances followed the order $\text{SO}_4^{-2} > \text{NO}_3^- > \text{Cl}^- \approx \text{PO}_4^{-3}$. These compositions are consistent with the soluble salts being a mixture of continental aerosols and sea-salt aerosols. All charge balances for the canister samples were poor, indicating a deficiency of anions. This is consistent with all previously-measured canister soluble salt compositions and indicates that carbonate species are a large component of the soluble salts. Carbonate/bicarbonate species require special sample handling and measurement techniques for accurate analysis, and the sampling technique and very small masses did not allow separate analysis for these species.

Finally, charge balance errors for the carbonate-free control samples were excellent (<1%), and measured concentrations were close to the anticipated values, indicating that disassembly of SaltSmart™ test strips, followed by leaching and analysis by IC, is an effective method of measuring soluble salt loads and compositions on metal surfaces.

NOMENCLATURE

Abbreviation	Definition
DOE	Department of Energy
EPRI	Electric Power Research Institute
DI	deionized [water]
IC	ion chromatography
ISFSI	independent spent fuel storage installation
NRC	Nuclear Regulatory Commission
SCC	stress corrosion cracking
SNF	spent nuclear fuel
SNL	Sandia National Laboratories

1. INTRODUCTION

In June 2017, dust and salt samples were collected from the surface of Spent Nuclear Fuel (SNF) dry storage canisters at the Calvert Cliffs independent spent fuel storage installation (ISFSI). Interim storage systems at the site are NUHOMS horizontal storage modules, consisting of a concrete overpack, into which a stainless steel (304L) storage cask is placed horizontally. The system is passively ventilated via air inlet vents at the base of the unit, and outlet vents on the top. Decay heat from the waste drives convective airflow through overpack, cooling the container. Over time, dust, drawn into the overpacks with the circulating air, is deposited on the surfaces of containers within the storage systems. Salts within the dust will deliquesce as heat production declines over time and the packages cool, and it is possible that deliquescence-induced corrosion of the 304L waste container could lead to penetration of the container walls by chloride-induced stress corrosion cracking (SCC). To address this concern, the Nuclear Regulatory Commission (NRC) has mandated that periodic canister inspections be carried out. Canisters at Calvert Cliffs were first examined and dust samples were collected for analysis in June, 2012; the results of those analyses are given in EPRI (2014). The current inspection is the second, carried out 5 years after the first.

The goal of this sampling effort was to characterize the distribution and morphology of dust on the canister surface, with specific focus on the composition and distribution of soluble salts present. Two types of samples were collected.

- Dry dust samples: an abrasive tool was used in an attempt to sample loose dust on the container surface. This device consisted of a steel head with an abrasive Scotch-Brite™ sponge backed with a filter pad for capturing >5 μm particles. The sampler was attached to a vacuum line and a long rod, and was inserted into the overpack through the annulus around the package at the front entrance. The sampler head was designed such that, when rubbed over the container surface, dust dislodged by the abrasive sponge would be pulled through the sponge and collected on the filter.
- Soluble salt samples: SaltSmart™ test strips were used to collect soluble salts from the canister surface. These test strips are designed to leach soluble salts off the surface using a wet wick, and to provide a direct reading of the conductivity of the salts thus removed. However, this standard approach does not distinguish between different soluble salts, so a modified approach was used here. Following sampling, the Salt-Smart™ test strips were disassembled and the soluble salts leached from the wick and internal reservoir sponge and then analyzed by wet chemical methods.

After collection, the samples were sealed into plastic sleeves and placed into an insulated chest with an ice pack for shipping to Sandia National Laboratories (SNL) for characterization. Unfortunately, condensation within the sleeves containing the Scotch-Brite™ samples remobilized the salts, rendering them ineffective for the intended purpose of characterizing salt morphologies, compositions and distributions within the dust. Moreover, although the samples were placed within a desiccator immediately upon receipt, over the next few days, significant mold growth occurred,

further compromising the samples. For these reasons, the Scotch-Brite™ samples were not analyzed. The SaltSmart™ samples appeared to be unaffected and were analyzed by ion chromatography (IC) for major anions and cations. The results of those analyses are presented here. The samples that were received by Sandia and the analytical methods used to analyze them are described in Section 2 of this report. Results are presented and discussed in Section 3, and a summary is provided in Section 4.

2. SAMPLES AND METHODS

2.1. Samples

Following collection at Calvert Cliffs, the SaltSmart™ samples and the dry dust samples were prepared for shipping. Each Salt-Smart test strip was placed into a plastic sleeve and sealed, and then placed into a compartmentalized polypropylene box. Each steel sampling head used for the dry dust sampling, with the Scotch-Brite™ pad and the paper filter backing still attached, was treated similarly, sealed into a plastic sleeve and placed into a compartmentalized polypropylene box. The samples were then placed into a Yeti® ice cooler with a single Blue Ice pack and packing materials, and shipped via overnight express to Sandia. The packaging is shown in Figure 1.



Figure 1. Packaging of SaltSmart™ samples delivered to SNL. Dry dust sampling heads (not shown) were packaged in the same manner.

Upon receipt at SNL, the cooler was opened and the samples extracted. It was immediately noted that the “dry dust” sampling heads were no longer dry. Condensation had formed within the sealed plastic sleeves, in some cases in sufficient quantity to actually pool in the bottom of the bags. It was clear that any salts present would have been remobilized by the condensation. As the purpose of the “dry dust” samples was to evaluate the size, morphology, composition, and distribution of salts in the dust on the canister surface, the samples were no longer acceptable for their intended use. The Scotch-Brite™ pads also displayed a patchy discoloration, which initially was interpreted as moist dust adhering to the pad. In an effort to preserve the samples from further damage, the plastic sleeves were cut open and the samples were placed within a desiccator with Drierite™ desiccant (calcium sulfate). Although visible moisture was removed, after four days, the patchy discolorations had evolved

into heavy mold growth (Figure 2). At this point, the decision was made not to pursue further analysis of the Scotch-Brite™ samples.



Figure 2. Mold growing on one of the dry dust sampling heads, after four days in a desiccator.

Unlike the “dry dust” samples, it had been anticipated that the SaltSmart™ samples would be damp and could be affected by biological activity over long-term storage, so preparations had been made for immediate analysis of the SaltSmart™ test strips, and this was done. There was no evidence of mold growth on the SaltSmart™ samples, although there was sufficient water in the samples to form condensation within the sample sleeves, and the surfaces of the SaltSmart™ test strips were discolored with dust. It is not believed that the SaltSmart™ samples were affected by biological activity.

The samples delivered to SNL are listed in Table 1. A total of 10 used SaltSmart™ test strips were sent, including 6 SaltSmart™ samples from the canister surface, two blanks that had been treated with deionized water, and two control samples, that had been exposed to a metal surface coated with 500 mg/m² NaCl. Five dry-dust samples were sent, each consisting of the steel sampling head, with the Scotch-Brite™ pad and paper filter still attached.

Photographs of the SaltSmart™ samples after removal from their plastic sleeves are shown in Figure 3. All samples that contacted the canister were heavily discolored with dust which in some cases was nearly dry, and in other cases (Samples #1 and #6) was formed a muddy coating on the wick of the SaltSmart™. As shown in Figure 3, the wick to Sample #4 was damaged. It is not known if this occurred during insertion of the tool or during removal; if it occurred during insertion, then the test strip probably did not function as designed, and the results for this sample may not be valid. The blank and control samples (not shown in Figure 3) had no discolorations on the wicks of the test strips.

Table 1. Calvert Cliffs Samples Delivered to SNL

Sample Number	Description upon delivery
SaltSmart™ Samples	
#1 6-8-17/11:30	Wick heavily coated with moist, silty, brown dust
#2 6-8-17/11:45	Wick discolored with silty dust
#3 6-8-17/12:00	Wick lightly discolored with silty dust.
#4 6-8-17/12:10	Wick discolored with silty dust; wick damaged
#5 6-8-17/13:20	Wick discolored with silty dust
#6 6-8-17/13:36	Wick heavily coated with moist, plastic, dust/mud
DI H ₂ O Control (A)	No discoloration on wick
DI H ₂ O Control (B)	No discoloration on wick
500 mg NaCl/m ² Dosed (A)	No discoloration on wick
500 mg NaCl/m ² Dosed (B)	No discoloration on wick
Dry Dust Samples	
#1 6-8-17/10:20	Heavy mottled discoloration on Scotch-Brite™ pad
#2 6-8-17/10:24	Mottled discoloration on Scotch-Brite™ pad
#3 6-8-17/10:29	Minor discoloration on Scotch-Brite™ pad
#4 6-8-17/10:34	Mottled discoloration on Scotch-Brite™ pad
#5 6-8-17/10:38	Mottled discoloration on Scotch-Brite™ pad

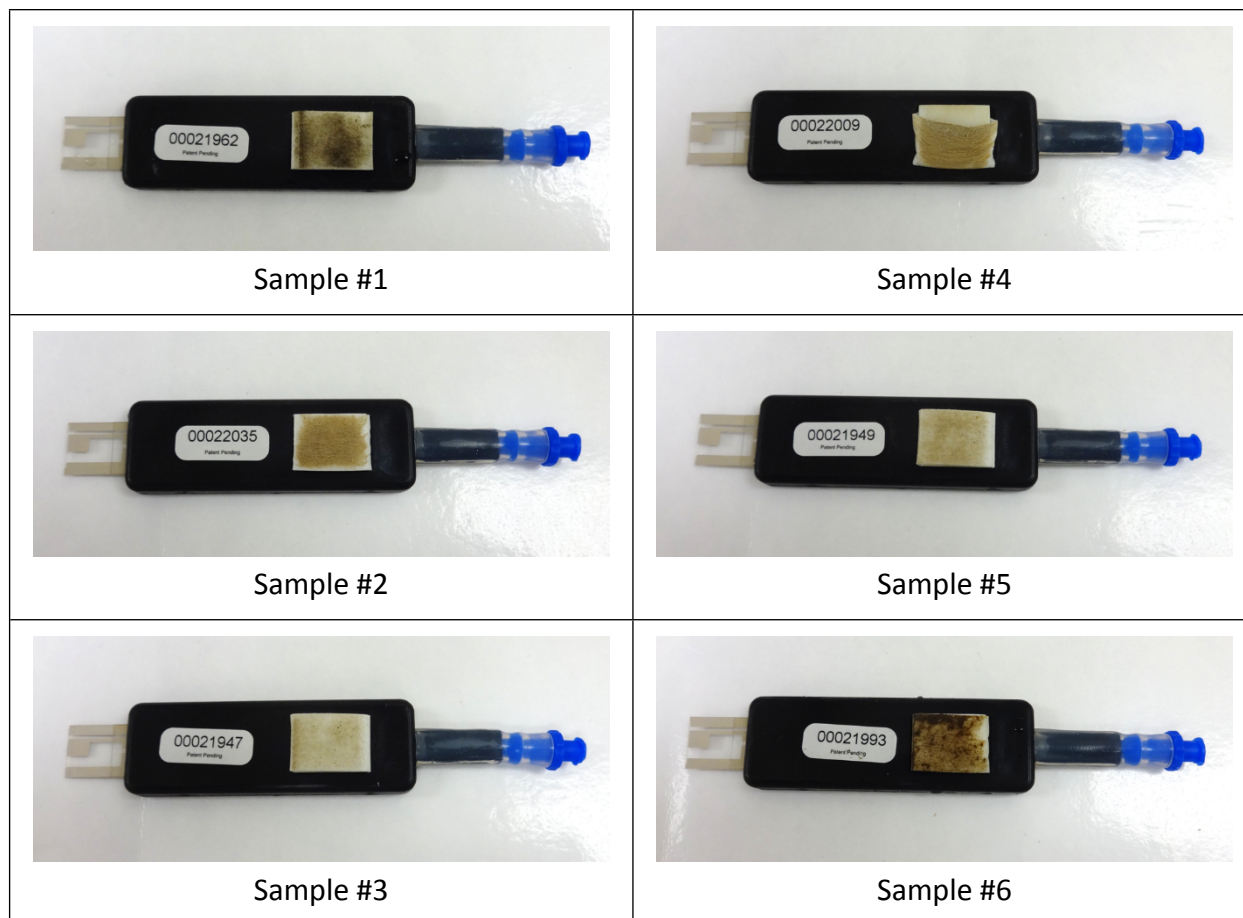


Figure 3. Photographs of SaltSmart™ test strips used to collect samples from the canister surface.

2.2. Methods

Once at Sandia, the SaltSmart™ test strips were disassembled and the soluble salts were extracted with DI water for chemical analysis. Then the salt compositions, including chloride concentration, were measured directly by cation/anion IC.

For analysis, the SaltSmart™ sensors were removed from the sealed plastic sleeves then had been shipped in and split open along the seam with a small chisel. The component parts of each sensor are shown in Figure 4. The wick and the reservoir pad inside the SaltSmart™ device were removed and transferred to a pre-weighed 50 ml polypropylene screw-cap sample tube. The internal pieces and the shells were rinsed with deionized water (DI) (>18M Ω) and the water transferred to the polypropylene sample tubes containing the wicks and pads. The original plastic sleeves used for shipping the samples commonly contained condensate, and these were also rinsed into the polypropylene sample tubes, along with any moist dust remaining in the sleeves. Additional DI water was added, to achieve a total water volume of ~15 ml per sample; the exact volume was determined by the weight difference between the empty and filled vials, after subtracting the weights of a dry wick and reservoir pad. The samples

were placed on a shaker table overnight to leach the salts in the wick and pad into the solution. Finally, the reservoir pads and wicks were removed, compressing to drive out retained water. The solutions were filtered through 0.45 μm syringe filters and 5 ml aliquots were immediately transferred to sample vials for analysis by IC.

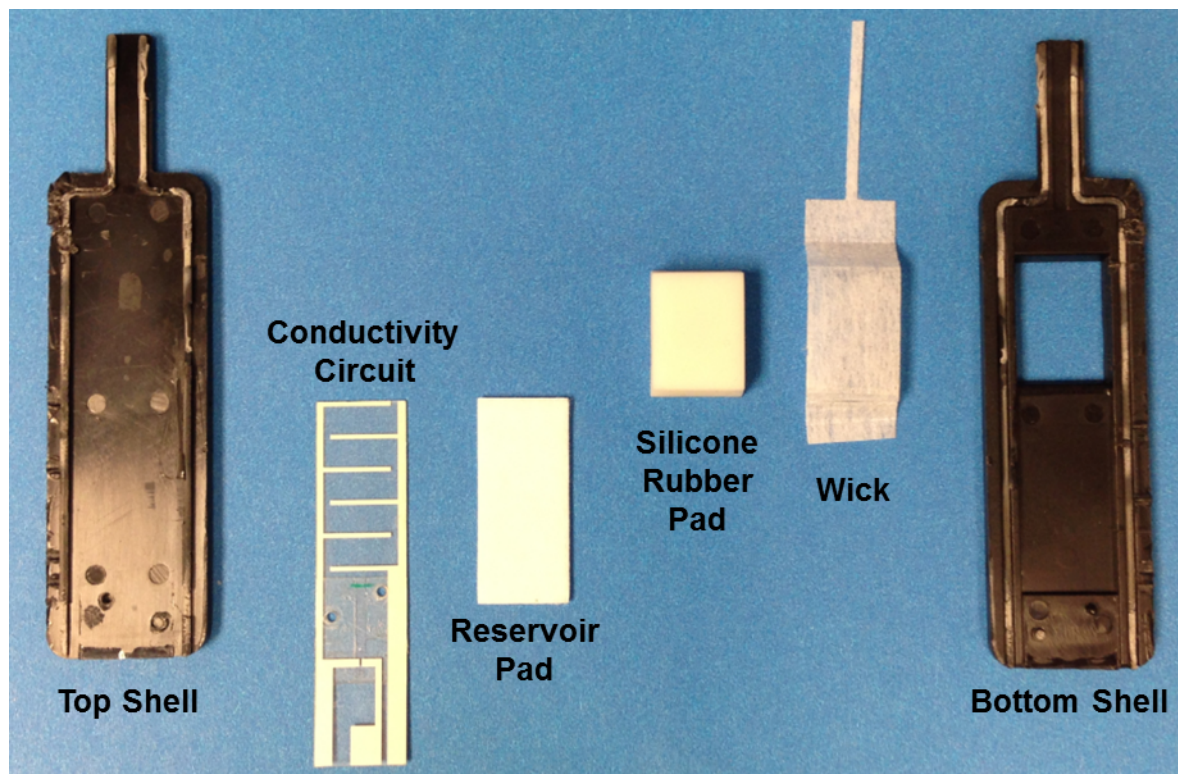


Figure 4. Disassembled SaltSmart™ Device.

IC analyses were done with a Dionex ICS-1100 RFIC ion chromatograph. Anionic analytes were F^- , Cl^- , Br^- , NO_2^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} ; however, no signal for Br^- and NO_2^- was detected in any sample, and those species are not included here. Analyses were done with a 4 mm Dionex Ionpac AS-23 RFIC column and AG-23 guard column, and a Dionex AERS 500 suppressor. Blanks were run after every sample to minimize carryover, but little was observed. Five standards and a blank were made by dilution of stock Dionex IC anion standards. Sample concentrations were estimated using a subset of the standards (never less than three and a blank), excluding those which were higher than necessary to constrain the sample concentration. This was done because the calibration curves were based on the least squares method, which over-weights higher-concentration standards, potentially resulting in larger errors for values in the lower part of the range. Cationic analytes were Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{+2} , and Ca^{+2} . IC analyses were done with a Dionex Ionpac CS-12A column and CG-12A guard column, and a CERS 500 suppressor, all 4 mm in diameter. As with the anions, blanks were run after every sample to minimize

carryover, but little was observed. The standards were made by dilution of stock Dionex IC cation standards. As with the anions, five standards and a blank were made, but only a bounding subset of the standards (never less than three and a blank) was used to determine the sample concentrations. All standards and eluents were purchased for this analysis, and were will within their expiration dates.

The effectiveness of the leaching and analysis procedure used here has previously been confirmed by ambient-temperature testing of SaltSmart™ test strips at Sandia. Testing at Sandia using metal coupons with known deposited salt loadings showed that SaltSmart™ sensors are efficient at removing soluble salts from metal surfaces, and that the disassembly and leaching procedure described here is effective, with experimental salt recoveries in the range of 80-100% (Memo from C. Bryan to L. Zsidai dated Nov. 13, 2013; SAND#2013-9948P).

Also during disassembly, the condition of the wick and the saturation state of the reservoir pad were recorded. In previous tests with the SaltSmart™ test strips, the reservoir pads inside the sensors are completely saturated after use, indicating that water flow was adequate through the sensor. However, for these samples, It was observed that the inner components of the SaltSmart™ test strips appeared to be dry, or nearly dry. This was true for al samples, controls and blanks, except for sample #6, the inside of which was fully saturated. This raises a concern that the SaltSmart™ test strips may have been misapplied during testing at Calvert Cliffs, and may not have quantitatively leached salts from the surfaces sampled. However, as will be discussed below, recovery for the two control samples did match the expected values, suggesting that the use was appropriate.

It should also be noted that some of the wicks on the test strips were very dirty, and one actually had a thick “muddy” deposit adhering to the surface. It is unlikely that the dust retained on the wicks represented all material that was present on the surface contacted by the test strip. Moreover, no testing has been done to show that the SaltSmart™ strips effectively leach all salts from surfaces covered with a thick layer of dust.

In light of the heavy dust loads on the sampled surfaces, and the unusually dry inner components of the test strips, the soluble salt loads provided here may represent minimum values, rather than accurate estimates of the soluble salt surface loads.

3. RESULTS AND DISCUSSION

3.1. Canister surface samples

The methods used for chemical analysis of the SaltSmart™ test strips are described in Section 2.2. As discussed in that section, the soluble salts were extracted from the SaltSmart™ test strips by disassembling them and leaching the components in deionized water. The dissolved salts were then analyzed by IC. Ten test strips were analyzed, consisting of the six canister surface samples, the two controls, and the blanks. All were analyzed using the identical procedure, with the same equipment, chemicals, and IC analytical setup. In the data tables below, analytical uncertainties were estimated by running calibration standards as unknowns, and unless otherwise indicated are in the range of $\pm 5\%$. Values in gray text are $\pm 10\%$, while gray, italicized values are qualitative, representing analytes for which a clear peak was present, but which are below the limit of quantitation—defined as the value of the lowest calibration standard used.

The amounts of each ionic species present in the samples, controls, and blanks are given in $\mu\text{g}/\text{sample}$ Table 2. The deionized water blank values are very small compared to the measured sample values for all elements except for lithium, for which the blank values are commensurate with sample values. This suggests that Li is not present in the samples, but is being leached from the components of the SaltSmart™ test strips. It is also possible that Li is not present at all, but that an organic compound with a similar elution time as Li^+ is being released by the test strips. In either case, it is assumed that measured Li values are experimental artifacts, and that Li is not present in the samples; Li is not considered further. The two deionized water control samples yielded very consistent values for the other ions present, and the average of those values has been subtracted from the measured sample values in Table 3. These “blank-subtracted” values represent soluble salts collected from the metal surface by the SaltSmart™ test strips.

Table 4 shows the ion concentrations in micro-Equivalents (μEq), where $\mu\text{Eq} = \mu\text{moles} * \text{ion charge}$. By normalizing to the molecular weight, this unit allows better evaluation of the relative contribution of each ion to the total ion load on the canister surface.

The canister surface samples all display a consistent chemistry. For all six samples, Ca^{+2} is the dominant cation by mass and Na^+ is the second most abundant. Smaller amounts of K and Mg are present, and minor ammonium. For all samples, the relative mass abundance of the cations is as follows: $\text{Ca}^{+2} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{+2} > \text{NH}_4^+$. The same trend is shown in the μEq data, except that the relative abundances of Mg and K are reversed. The most abundant anions are SO_4^{-2} and NO_3^- respectively; Cl^- and PO_4^{-3} are also present, in lower concentrations.

The ion concentrations in μEq are also to calculate the charge balance error:

$$\text{Charge balance error, \%} = \frac{\Sigma\text{Cations}(\mu\text{Eq}) - \Sigma\text{Anions}(\mu\text{Eq})}{\Sigma\text{Cations}(\mu\text{Eq}) + \Sigma\text{Anions}(\mu\text{Eq})} * 100$$

Acceptable charge balance errors are in the range of $\pm 5\%$, or as high as $\pm 10\%$ for small volume or dilute samples. As been previously observed for soluble salt analyses at Calvert Cliffs, Hope Creek, and Diablo Canyon (Enos et al., 2013; Bryan and Enos, 2014; EPRI, 2014; Bryan and Enos, 2015b; Bryan and Enos, 2016), the charge balance errors for the canister SaltSmart™ samples are large, ranging from 32% to 55%, and summed anion μEq values are much less than cation μEq values, indicating a deficiency of anions in the analyses. This has previously been attributed to unmeasured carbonate species, because carbonate minerals have been commonly observed in SEM analyses of canister dust samples (Enos et al., 2013; Bryan and Enos, 2014; EPRI, 2014; Bryan and Enos, 2015b; Bryan and Enos, 2016). The analyses indicate that more than half the total anionic charge must consist of carbonate species.

The salt compositions from the sampled locations suggest that the soluble salts are a combination of both sea-salts (rich in Na, Cl, and Mg), and salts derived from continental sources, rich in NH_4 , K, Ca, NO_3 , and SO_4 (NADP, 2013) although NH_4 was not observed here. It is reasonable to assume that most of the chloride was deposited as sea-salts because chloride is only a trace component in continental aerosols. However, in seawater (and in initially-formed sea-salt aerosols), the molar ratio of chloride to sodium is equal to 1.16. In these samples, Cl/Na ratios range from 0.15 to 0.25. If the chloride was deposited as sea-salts, then the salt particles have partially undergone particle-gas conversion reactions prior to or after deposition. Such reactions have been discussed in Bryan and Enos (2015), and convert chloride-rich sea-salts to nitrate and sulfate minerals. By reducing the chloride load on the canister surface, these reactions reduce the risk of canister SCC.

Because the SaltSmart™ test strips sample a known surface area (3 cm^2), the measured salt compositions can be used to calculate salt surface loads on the metal surface. The measured surface loads in mg/m^2 are given in Table 5. Total soluble salt loads vary from $500 \text{ mg}/\text{m}^2$ to nearly $1500 \text{ mg}/\text{m}^2$ and this does not include carbonate, which was not measured. Including carbonate would push the highest total solute loads above $2000 \text{ mg}/\text{m}^2$. However, concentrations of chloride, the aggressive component in the salts, were $50 \text{ mg}/\text{m}^2$ or less, representing only a tiny fraction of the total solutes present.

3.2. Control samples

The control samples were collected from a surface coated with $500 \text{ mg}/\text{m}^2$ NaCl and as expected, and consisted almost entirely of NaCl, although trace quantities of other soluble species were detected in one of the two samples (Table 4). Moreover, charge balances for these two samples, which do not have significant carbonate or hydroxide, are very good, with errors of less than 1%. The total NaCl present for sample A was $451 \text{ mg}/\text{m}^2$, while that for sample B was $486 \text{ mg}/\text{m}^2$. Although Sample A is about 10% below the expected value, these values sufficiently close to the nominal value of $500 \text{ mg}/\text{m}^2$ to indicate that the SaltSmart™ test strips were properly applied. The charge balance errors of $<1\%$ and the match to the expected value for salt load also confirm that the SaltSmart™ disassembly, leaching and analysis procedure used at Sandia is an effective method of measuring the soluble salts on metal surfaces.

Table 2. Measured Soluble Ion Concentrations ($\mu\text{g}/\text{sample}$) in the Calvert Cliffs SaltSmart™ Samples

Sample	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Mg ⁺²	Ca ⁺²	F ⁻	Cl ⁻	NO ₃ ⁻	PO ₄ ⁻³	SO ₄ ⁻²
#1 6-8-17/11:30	0.031	41.8	4.0	17.0	8.7	88.3	0.86	13.9	93.3	9.4	76.4
#2 6-8-17/11:45	0.030	36.2	2.9	21.4	9.6	117.5	0.36	8.3	26.0	13.9	114.7
#3 6-8-17/12:00	0.018	13.3	2.5	8.9	3.8	45.1	0.27	4.8	36.4	5.0	37.7
#4 6-8-17/12:10	0.020	43.1	3.8	30.2	12.2	145.1	0.66	15.7	39.7	15.7	149.5
#5 6-8-17/13:20	0.019	10.9	1.9	8.0	4.0	69.7	0.23	4.2	29.6	3.4	39.8
#6 6-8-17/13:36	0.031	20.4	4.1	18.4	9.5	157.3	0.69	6.9	31.7	14.1	87.2
DI H ₂ O Control (A)	0.019	0.53	0.39	0.33	0.53	4.6	0.26	0.52	4.9	n.a.	2.2
DI H ₂ O Control (B)	0.011	0.56	0.37	0.28	0.08	4.7	0.27	0.85	5.3	n.a.	n.a.
500 mg NaCl/m ² (A)	0.012	54.1	0.21	0.22	0.09	3.7	0.22	82.6	5.2	n.a.	n.a.
500 mg NaCl/m ² (B)	0.031	58.8	0.15	0.56	0.31	6.0	0.22	88.2	7.6	n.a.	4.1

Table 3. Blank-Subtracted Soluble Ion Concentrations, µg/sample

Sample	Na ⁺	NH ₄ ⁺	K ⁺	Mg ⁺²	Ca ⁺²	F ⁻	Cl ⁻	NO ₃ ⁻	PO ₄ ⁻³	SO ₄ ⁻²
#1 6-8-17/11:30	41.3	3.6	16.7	8.3	83.7	0.60	13.2	88.2	9.4	75.3
#2 6-8-17/11:45	35.6	2.5	21.1	9.3	112.9	n.a.	7.6	21.0	13.9	113.5
#3 6-8-17/12:00	12.8	2.2	8.6	3.5	40.5	n.a.	4.1	31.3	5.0	36.6
#4 6-8-17/12:10	42.5	3.5	29.8	11.8	140.4	0.39	15.0	34.6	15.7	148.4
#5 6-8-17/13:20	10.4	1.5	7.7	3.7	65.1	n.a.	3.5	24.5	3.4	38.7
#6 6-8-17/13:36	19.8	3.7	18.1	9.2	152.6	0.42	6.2	26.6	14.1	86.1
500 mg NaCl/m ² (A)	53.5	n.a.	n.a.	n.a.	n.a.	n.a.	81.9	n.a.	n.a.	n.a.
500 mg NaCl/m ² (B)	58.2	n.a.	n.a.	n.a.	1.4	n.a.	87.5	2.5	n.a.	3.0

Table 4. Blank-Subtracted Soluble Ion Concentrations, µEq/sample

Sample	Na ⁺	NH ₄ ⁺	K ⁺	Mg ⁺²	Ca ⁺²	F ⁻	Cl ⁻	NO ₃ ⁻	PO ₄ ⁻³	SO ₄ ⁻²	Sum. Cat.	Sum An.	Chrg. Bal. %
#1 6-8-17/11:30	1.80	0.20	0.43	0.69	4.18	0.03	0.37	1.42	0.30	1.57	7.29	3.69	32.7
#2 6-8-17/11:45	1.55	0.14	0.54	0.77	5.63	n.a.	0.21	0.34	0.44	2.36	8.63	3.36	44.0
#3 6-8-17/12:00	0.55	0.12	0.22	0.29	2.02	n.a.	0.12	0.51	0.16	0.76	3.20	1.54	35.0
#4 6-8-17/12:10	1.85	0.19	0.76	0.97	7.01	0.02	0.42	0.56	0.50	3.09	10.8	4.59	40.3
#5 6-8-17/13:20	0.45	0.08	0.20	0.30	3.25	n.a.	0.10	0.39	0.11	0.80	4.28	1.41	50.6
#6 6-8-17/13:36	0.86	0.21	0.46	0.76	7.62	0.02	0.18	0.43	0.45	1.79	9.91	2.87	55.1
500 mg NaCl/m ² (A)	2.33	n.a.	n.a.	n.a.	n.a.	n.a.	2.31	n.a.	n.a.	n.a.	2.33	2.31	0.4
500 mg NaCl/m ² (B)	2.53	n.a.	n.a.	n.a.	0.07	n.a.	2.47	0.04	n.a.	0.06	2.60	2.57	0.5

Table 5. Blank-Subtracted Soluble Ion Concentrations, mg/m².

Sample	Na⁺	NH₄⁺	K⁺	Mg⁺²	Ca⁺²	F⁻	Cl⁻	NO₃⁻	PO₄⁻³	SO₄⁻²
#1 6-8-17/11:30	138	12.0	56	28	279	2.0	44	294	31	251
#2 6-8-17/11:45	119	8.4	70	31	376	n.a.	25	70	46	378
#3 6-8-17/12:00	43	7.2	29	12	135	n.a.	14	104	17	122
#4 6-8-17/12:10	142	11.5	99	39	468	1.3	50	115	52	495
#5 6-8-17/13:20	35	5.0	26	12	217	n.a.	12	82	11	129
#6 6-8-17/13:36	66	12.5	60	31	509	1.4	21	89	47	287
500 mg NaCl/m ² (A)	178	n.a.	n.a.	n.a.	n.a.	n.a.	273	n.a.	n.a.	n.a.
500 mg NaCl/m ² (B)	194	n.a.	n.a.	n.a.	4.5	n.a.	292	8.4	n.a.	10.1

4. CONCLUSIONS

In June 2017, dust and salt samples were collected from the surface of spent nuclear fuel dry storage canisters at the Calvert Cliffs independent spent fuel storage installation. The goal of this sampling effort was to characterize the distribution and morphology of dust on the canister surface, with specific focus on the composition and distribution of soluble salts. Two types of samples were collected:

- Soluble salt samples were collected using SaltSmart™ test strips, which were then shipped to Sandia National Labs for disassembly, leaching and analysis. These samples provide the composition and abundance (concentration per unit area) of soluble species on the canister surface.
- Dry dust samples were collected using vacuum line with an attached sampling tool. The tool consisted of a steel head with a filter-backed abrasive Scotch-Brite™ pad, which was rubbed across the surface to collect dry dust. The dry dust samples provide information of the size and morphology of dust and salt particles on the canister surface.

After collection, both types of samples were sealed into plastic sleeves and placed into an insulated chest with an ice pack for shipping to Sandia National Laboratories for characterization. However, high humidities at the time of sampling compromised the dry dust samples, causing condensation and mold growth within the sleeves containing the dry dust sampling heads and ruining the samples. No attempt was made to analyze those samples. The SaltSmart™ samples appeared to be unaffected—no mold growth was observed—and were analyzed by ion chromatography for major anions and cations. In addition to the canister samples, SaltSmart™ blanks and control samples with a known amount of salts were also provided and analyzed.

The six SaltSmart™ samples from the storage canister all had similar chemistries, with the cations being dominated by Ca^{+2} and Na^+ . Cation mass abundances for all samples followed the order $\text{Ca}^{+2} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{+2} > \text{NH}_4^+$. Anions were dominantly SO_4^{-2} and NO_3^- ; mass abundances followed the order $\text{SO}_4^{-2} > \text{NO}_3^- > \text{Cl}^- \approx \text{PO}_4^{-3}$. These compositions are consistent with the soluble salts being a mixture of continental aerosols and sea-salts aerosols. All charge balance errors for the canister samples were large (32% to 55%), and all indicated a deficiency of anions. This is consistent with all previously-measured canister soluble salt compositions and indicates that a carbonate species, not included in the analysis, are a large component of the soluble salts. Carbonate/bicarbonate are not readily measured by ion chromatography, and the sampling technique and very small masses did not allow separate analysis to determine them.

Finally, charge balance errors for the carbonate-free NaCl-coated control samples were <1%, and measured concentrations were close to the anticipated values, indicating that disassembly of SaltSmart™ test strips, followed by leaching and analysis by IC, is an effective method of measuring soluble salt loads and compositions on metal surfaces. The results for the controls provide confidence in the use of the SaltSmart™ strips in the field at Calvert Cliffs, and in the measured values for the unknowns.

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