

# Understanding the Environment on the Surface of Spent Nuclear Fuel Interim Storage Containers

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**Abstract:** A primary concern with dry storage of spent nuclear fuel is chloride-induced stress corrosion cracking, caused by deliquescence of salts deposited on the stainless steel canisters. However, limited access through the ventilated overpacks and high surface radiation fields impede direct examination of cask surfaces for CISCC, or sampling of surface deposits. Predictive models for CISCC must be able to predict the occurrence of a corrosive chemical environment (a chloride-rich brine formed by dust deliquescence) at specific locations (e.g. weld zones) on the canister surface. The presence of a deliquescent brine is controlled by the relative humidity (RH), which is a function of absolute humidity and cask surface temperature. This requires a thermal model that includes the canister and overpack design, canister-specific waste heat load, and passive cooling by ventilation. Brine compositions vary with initially-deposited salt assemblage, reactions with atmospheric gases, temperature, and the relative rates of salt deposition and reaction; predicting brine composition requires site-specific compositional data for atmospheric aerosols and acid gases. Aerosol particle transport through the overpack and deposition onto the canister must also be assessed. Initial field data show complex variability in the amount and composition of deposited salts as a function of canister surface location.

**Keywords:** Spent Nuclear Fuel, Interim Storage, Stress Corrosion Cracking, Waste Package Surface Environment.

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## 1. INTRODUCTION

Following initial cooling in pools, spent nuclear fuel (SNF) is transferred to dry storage casks for longer-term storage at the reactor sites. The storage cask systems are commonly welded stainless steel (304SS [1]) containers enclosed in ventilated concrete or steel overpacks. These cask systems are intended as interim storage until a permanent disposal site is developed, and until recently, were licensed for up to 20 years, and renewals also up to 20 years. In 2011, 10 CFR 72.42(a) [2] was modified to allow for initial license periods of up to 40 years, and also, license extensions of up to 40 years. However, the United States does not currently have a disposal pathway for SNF, and these containers may be required to perform their waste isolation function for many decades beyond their original design criteria. Of primary concern with respect to the long-term performance of the storage casks is the potential for canister failure due to localized corrosion. For most dry cask storage systems, passive ventilation is utilized to cool the casks within the overpacks, and large volumes of outside air are drawn through the system. Dust and aerosols within the air are deposited on the steel canisters, and as the casks cool over time, salts in the dust will deliquesce to form brine on the storage container surface. Under these conditions, localized attack can occur. Chloride-induced stress corrosion cracking (CISCC) of welded zones is of special concern, as it is a well-documented mode of attack for austenitic stainless steels (including 304SS and 316SS) in marine environments [3], and many reactors and the onsite interim storage locations are located in coastal areas.

In order to assess the probability of CISCC on a given cask, an understanding of the processes affecting the environment on the surface of the cask is required. In this paper, we discuss factors controlling the chemical and physical environment on the surface of SNF interim storage containers and how they will evolve through time. Important controls on the physical and chemical environment include the canister surface temperature and its evolution through time, the composition of

atmospheric aerosols entering the package, mineral decomposition reactions, reactions between deposited salts and reactive gases in the atmosphere, and processes affecting aerosol particle transport and deposition. Finally, preliminary data from dust sampling on the surfaces of in-service SNF interim storage canisters is presented. The data show wide variability in dust compositions over the surfaces of individual storage canisters, and illustrate the difficulties in developing a defensible predictive model for the chemical and physical environment at unique locations (e.g., welds) on interim storage casks.

## **2. ENVIRONMENT ON THE STORAGE CONTAINER SURFACE**

The majority of SNF in dry storage is stored in stainless steel (3041) storage containers which are enclosed in concrete or steel overpacks. The stainless steel casks are shielded from the weather by the overpacks, so the only likely mode of aqueous solution formation is by deliquescence of dusts deposited on the metal surface from air drawn through the passively ventilated overpack. Conditions for deliquescence are a function of the temperature and relative humidity at the metal surface and of the composition of deposited salts. The water content, or absolute humidity, of the air within the overpack will be the same as that of the ambient air outside the overpack, but the relative humidity at the container surface will vary with the temperature. At high container surface temperatures, corresponding to low relative humidities, salts cannot deliquesce and corrosion cannot occur [4]. The actual relative humidity at which deliquescence occurs is controlled by the salt assemblage that is present, and for sea salts, this corresponds to 80-85°C.

### **2.1. Temperature**

Detailed predictions of the temperatures on SNF storage container surfaces are rarely available. Storage system final safety analysis reports (FSARs) generally only report maximum container surface temperatures, and often, the calculations are conducted utilizing bounding thermal loads and ambient temperature values. For larger storage containers, maximum surface temperatures can exceed 200°C [5, 6]. Although deliquescence is limited to lower temperatures, understanding the temperature evolution of the storage system at higher temperatures may still be important, as it will impact airflow through the system and aerosol deposition, as well as potentially affecting the rate of salt mineral decomposition reactions.

For several reasons, determining the surface temperature on a storage container at any given time or surface location is difficult. The initial temperature of each container will vary with the initial activity and thermal load of the SNF it contains, and the surface temperatures evolve over time, as the radioactivity of the SNF decreases. Moreover, the temperature varies over the surface of the container, depending on the distribution of the heat generating waste inside the container and on the air flow over and around the container in the ventilated overpack. Recently, detailed thermal models have been developed for specific spent fuel dry cask systems at different Independent Spent Fuel Storage Installations (ISFSIs) around the U.S. [7,8]. These models evaluate a horizontal NUHOMS system (24PWR) and a vertical HOLTEC system (32PWR), and implement both radiative and conductive heat transfer as well as heat loss due to convective air flow through the overpacks. Predicted surface temperatures on the 24PWR storage container (which contains fuel removed from the reactor 25-30 years ago) varied over a range of 90°C, from 27°C to 122°C (the assumed ambient temperature was ~14°C). For this horizontally emplaced cask, the ends were coolest, and the lower surface, where the incoming air first contacted the package, was much cooler than the upper surface. The vertical HOLTEC canisters showed large variations in temperature from the bottom (near the inlet vents) to the top, from 30°C to 50°C depending upon the design and heat load. Moreover, the temperature profiles scale directly with the assumed ambient temperature, which will vary seasonally by 10-20°C or more. Although the actual temperatures and the range of temperatures will vary with the storage system design and the spent fuel load, it is apparent some regions of the storage container surface will cool sufficiently for deliquescence, and potentially SCC, years, perhaps decades earlier than other areas. Measured temperatures on HOLTEC storage canisters at Diablo Canyon, holding

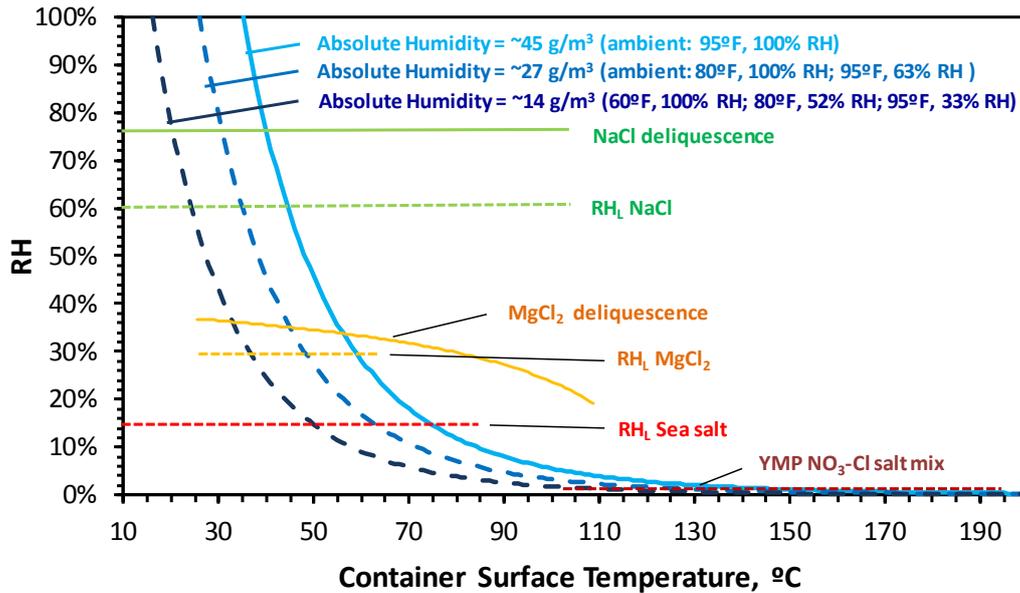
high-burnup fuel 6 years out of the reactor and after two years of storage, showed that the lower parts of the canister surface were already well within the temperature range for salt deliquescence.

Predicted waste package surface temperatures control the RH at the surface, and thermal histories can be used to estimate when deliquescence will initiate and persist. The resulting “time of wetness” model can be combined with measured corrosion penetration rates to estimate penetration over time. This approach has been used to estimate penetration on the bottom of a vertical storage cask emplaced on a concrete pad [9]. However, it is apparent that such a model would be very difficult to parameterize for storage containers across the nuclear waste complex, as it would not only require complex thermal modeling of each individual container and heat load (the number, history, and burnup characteristics of each assembly), but also would have to be specific to individual locations on the waste package surface corresponding to welds. The timing of initial deliquescence and total time of wetness for a longitudinal weld would vary not only with the circumferential location of the weld relative to the inlet and outlet vents, but also along the length of the weld, with deliquescence occurring sooner at the cooler regions. Modeling and field measurements show that the surface temperature drops below the nominal 85°C upper limit for deliquescence soon after emplacement at cooler regions on the canister. Also, because the actual locations of the canister welds are not recorded during emplacement into the overpack, these would have to be determined for any surface location-specific time-of-wetness model.

## 2.2. Relative Humidity

Relative humidity (RH) is the ratio of the partial pressure of water vapor in air ( $P$ ) to the saturated vapor pressure at the same temperature ( $P_{sat}$ ). As ambient air with a given water content (or absolute humidity,  $AH$ ) advects through a storage system and heats up,  $P$  does not change, but  $P_{sat}$  increases, so the RH drops. The RH at the container surface is controlled by the water content in the outside air and the temperature at the container surface. This is illustrated in Figure 1, for three different absolute humidities (the mass-per-unit-volume water content in the air). A reasonable upper bound for the water content in the ambient air is 45 g/m<sup>3</sup>, corresponding an RH of 100% at 95°F (35°C). In Figure 1, conditions to the left of this line are potentially accessible under interim storage conditions. Also shown on this figure are the deliquescence RH values for several potentially relevant salts or salt assemblages, including NaCl, MgCl<sub>2</sub>, and sea salts. It is important to note that experimentally, corrosion is observed at RH values significantly lower than the deliquescence RH, implying that even very thin adsorbed water films are sufficient to cause corrosion. The RH values at which corrosion occurs are referred to as the limiting RH (RH<sub>L</sub>). At values above the deliquescence RH, the activity of water in the brine is equivalent to the RH expressed as a unit value; as RH increases, solutions on the container surface become progressively more dilute. At RH values below the RH<sub>L</sub>, corrosion cannot occur; at sufficiently high RH values, the deliquesced solution is too dilute to support SCC.

It should be noted that experimental work for the Yucca Mountain Program showed that some nitrate-chloride salt mixtures deliquesce at very low relative humidities, and may never dry out, instead transitioning to molten salt mixtures as temperatures increase [10]. The potential relevance of these mixtures to interim storage conditions is not known; however, at inland sites, atmospheric salts are commonly nitrate-rich.



**Figure 1.** Relationship between RH, surface temperature, and conditions of deliquescence for potentially relevant salt assemblages [9, 10, 11].

### 2.3. Salt Composition

The composition of salts on a storage container is controlled by many processes and will vary with geographical location, but also with time, location on the canister, and surface temperature. The salt/brine composition and amount present at any given time is controlled not only by the rate of deposition of atmospheric aerosols, but also by the rate of exchange or reaction with reactive gases in the air flowing through the overpacks.

Models for aerosol deposition must consider that salt aerosols in the ambient air are likely to be deliquesced or partially deliquesced droplets. Particle mass, size, and aerodynamic properties will be a function of the relative humidity, and can vary widely over a single day. These properties will also change as the aerosol particle is drawn into the overpack, moves upward, evaporating as it is heated. Adherence properties with the canister surface will also change as the aerosol particle evolves from a droplet to a dried particle. If a partially deliquesced multicomponent aerosol grain of sea salt (mostly NaCl, but with small amounts of MgCl<sub>2</sub>, CaCl<sub>2</sub>, and other salts) is transported, perhaps preferential deposition of the most deliquescent salts (e.g., MgCl<sub>2</sub>, CaCl<sub>2</sub>) will occur, as the particles impact the canister surface and bounce off, transferring small amounts of brine to the surface. Moreover, the composition of aerosol particles commonly varies with particle size; sea salts are wave-generated, and are generally in the coarser (2.5-10 μm) fraction, while nitrate and sulfate salts are more abundant in the fine (<2.5 μm) fraction. If localized deposition on a canister varies with particle size, as is likely, then compositional variation will result. Adequate deposition modeling will require knowledge of site-specific aerosol compositions and concentrations in the ambient air, and an adequate model for thermally driven airflow through the overpack that includes changes in temperature, RH, and particle aerodynamic and adherence properties along the transport pathway.

Loss of salt components to the gas phase is due to salt-mineral decomposition reactions, which can occur prior to deliquescence, and reactions between the particles/brines and the atmosphere. Important reactions are a function of thermodynamic stability, and will vary with time and temperature, as initially dry salts deliquesce on the canister surface. Capturing the effect of these processes requires site-specific knowledge of the salt aerosols present and the concentrations of

reactive gases (e.g., NH<sub>3</sub>, HCl, HNO<sub>3</sub>, SO<sub>2</sub>) in the atmosphere. With respect to the corrosiveness of the brines, these reactions may be either beneficial or detrimental.

#### Deposited salts

The composition of the salts on the container surface will determine the temperature at which deliquescence will occur, and the corrosivity of the brine that forms. Chloride is generally the species of concern with respect to corrosion, although other industrial contaminants such as SO<sub>2</sub> are also important. For this reason, ISFSIs in near-marine environments are of greatest concern, and experimental work on SNF storage canister corrosion has largely focused on sea salt and its components, including magnesium chloride, which deliquesces at very low relative humidities and produces brines with high chloride contents. Since a mixture of salts will deliquesce at a lower RH than any single component within it, sea salt deliquesces at a lower RH than MgCl<sub>2</sub>. Moreover, as noted previously, the RH<sub>L</sub> for corrosion is even lower than the nominal deliquescence RH. For sea salts, RH<sub>L</sub> is generally taken to be about 15% [9].

Table 1 lists the composition of ASTM D1141-98 synthetic sea water [12], which is widely used in corrosion experiments to represent sea salt/spray. As can be seen, sea salt is dominantly a sodium-magnesium-chloride-sulfate assemblage. Several experimental studies indicate that stainless steel weld zones will corrode via CISCC in the presence of deliquesced sea salts [9, 11, 13, 14, 15]. It should be noted, though, that while sea water may represent the most important source of salts in near-marine environments, it is not the only one. Salts in rainwater and fog in near-marine environments are not pure sea salts, but contain variable but generally quite significant amounts of ammonium and nitrate, and are enriched in sulfate relative to sea salts [16]. For marine aerosols, reactions with atmospheric gases may greatly modify the composition of sea-salt particulates. Particle-gas conversion reactions with nitric acid and acidic sulfur compounds in the atmosphere act to convert sea salts to nitrate and sulfate compounds, accounting for the enrichment of these species in atmospheric aerosols in near-marine areas and even above the oceans. Sea-salt chloride in sea breezes on the west shore of the Iberian Peninsula is depleted by 67% and 24% for fine and coarse particles respectively, by the time the air mass reaches the coast [17]. Because chloride is the aggressive component in brines, it is conservative to assume that deposited salts will be sea salts.

At inland sites, atmospheric salts are largely derived from anthropogenic activities, terrestrial sources, and atmospheric reactions with marine salts [18, 19]. Typical National Airfall Deposition Program data from an inland site in Iowa [20] are shown in Table 1. Inland atmospheric salts are dominantly ammonium-calcium-nitrate-sulfates, with only minor chloride.

**Table 1: Composition of ASTM Ocean Water and Typical Inland Rainwater**

Species	Syn. ocean water, mg/L <sup>[12]</sup>	Iowa rainwater, µeq/L <sup>[20]</sup>
NH <sub>4</sub> <sup>+</sup>	—	29.22
Na <sup>+</sup>	11031	2.045
K <sup>+</sup>	398	0.511
Mg <sup>2+</sup>	1328	3.208
Ca <sup>2+</sup>	419	16.766
Cl <sup>-</sup>	19835	1.975
Br <sup>-</sup>	68	ND
F <sup>-</sup>	1	ND
SO <sub>4</sub> <sup>2-</sup>	2766	17.685
NO <sub>3</sub> <sup>-</sup>	—	15.565
BO <sub>3</sub> <sup>3-</sup>	26	ND
HCO <sub>3</sub> <sup>-</sup>	146	ND
pH	8.2	ND

### Processes affecting salts/brines on the container surface

Once deposited on the hot container surface, some salts or salt assemblages may decompose, or may form brines that will not persist stably over time. At high initial temperatures following emplacement, parts of the canister surface will be too hot for deliquescent brines to form, and particle-gas conversion reactions such as exchange of nitrate for chloride will not occur. However, some mineral phases will thermally decompose. As the SNF assemblies age and the heat load decreases, the containers cool and salts deliquesce; at this point, particle-gas conversion reactions and gas-brine exchange reactions occur, modifying the brine. With respect to the corrosivity of the brine, these processes may be either beneficial or harmful.

At container locations that are too hot for a stable deliquescent brine to form, important mineral decomposition reactions involve ammonium minerals, which are major components of inland aerosols but also contribute to coastal aerosols. Prior to deliquescence, ammonium salts decompose to generate ammonia and an acid gas, via reactions like the following:



Similar reactions apply to  $\text{NH}_4\text{NO}_{3(s)}$  and  $(\text{NH}_4)_2\text{SO}_{4(s)}$ . This results in loss of salts from the canister surface; because decomposition occurs directly from the solid, the loss of acid gases is stoichiometric—the identity of the ammonium mineral phase present determines which anionic species is lost. For atmospheric aerosols, most ammonium is associated with sulfate, and to a lesser degree, nitrate; ammonium chloride is generally a minor component [21]. Experiments with bulk salts show that ammonium nitrate and ammonium chloride decompose rapidly, even at only moderately elevated temperatures. At 100°C, the reaction is complete within days or weeks; even at 50°C, a large fraction of the minerals will be lost over years. Ammonium sulfate decomposition is much slower, but is complete in less than 1 year at 100°C [10]. For fine particulates, loss is rapid even at ambient temperatures—loss of nitrate due to volatilization of particulate ammonium nitrate from sampling filters is a widely recognized bias in atmospheric dust sampling [22, 23]. It is evident that ammonium salts deposited on a hot dry storage container will decompose rapidly, taking a significant fraction of acid gas anions with them. At inland sites, this may have a large effect on the salt load and the salt composition present at any given time.

Following deliquescence, many reactions with the atmosphere can affect the composition of the deliquesced brines. In general, hot brines will produce partial pressures of acid gas that are higher than concentrations in ambient air, and will tend to degas acid species, resulting in loss of the acid gas anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ) from solution. In the absence of buffering reactions, this causes the pH to rise and equilibrium acid gas partial pressures to drop. The reaction becomes self-limiting, ceasing when acid gas partial pressures become equal to those in the ambient air [10]. However, several different reactions can occur that will buffer the pH, permitting continued acid degassing. These include concomitant ammonia degassing, and adsorption of atmospheric acids or gas species that react with water to form acids.

If an assemblage of ammonium minerals deliquesces, or if ammonium minerals were to settle onto an existing brine and dissolve, then the brine will degas both ammonia and an acid gas species; because this reaction is pH-neutral, there is no pH rise, and degassing can continue. In this case, however, the brine will degas ammonia and acid gas cations in proportion to their equilibrium vapor pressure above the brine; the identity of the anion lost is no longer a function of the original ammonium mineral phase. For instance, dissolution of ammonium sulfate into a chloride/nitrate brine will result in preferential degassing and loss of  $\text{NH}_3$  plus  $\text{HCl}$  and/or  $\text{HNO}_3$ , and buildup of sulfate in the brine, because  $\text{H}_2\text{SO}_4$  is not as readily degassed. At inland sites, it is likely that the original deposited composition is similar to the Iowa rainwater composition in Table 1, and will be extensively modified by ammonia and acid gas loss over long time spans on the heated package surface. These reactions may not be beneficial—nitrate may be lost preferentially to chloride. In near-marine environments,

ammonia is a relatively minor component of the atmospheric salt load, but ammonia degassing may still have some role in modifying deposited dust compositions.

Other buffering reactions include the particle-gas conversion reactions discussed previously, in which adsorption of  $\text{HNO}_3$  or  $\text{SO}_2$  (which reacts with water to form  $\text{H}_2\text{SO}_4$ ) results in degassing of  $\text{HCl}$  and conversion of chloride salts to nitrates or sulfates. Another buffering reaction involves absorption of  $\text{CO}_2$  from the atmosphere and precipitation of carbonate [10]. For a sodium-rich brine, this reaction does little to promote acid degassing, because sodium carbonate does not precipitate until the pH has risen to  $>10$ , at which point degassing is negligible. For Mg-rich and Ca-rich brines, saturation with carbonates occurs at much lower pH (6-8), and degassing can continue until all Mg and Ca is precipitated as carbonates. This may occur at elevated temperatures, however, at lower temperatures, the opposite reaction can occur; carbonates in dust can scavenge acid gases from the atmosphere [24]. It is evident that the temperature variation on the canister surface may have a considerable effect on the brine composition at any given location.

A second buffering reaction for Mg-rich brines is precipitation of a  $\text{Mg}(\text{OH},\text{Cl})$  phase. This reaction does not require absorption of any component from the gas phase ( $\text{MgCl}_2 + \text{H}_2\text{O} = \text{MgOHCl} + \text{HCl}$ ), so it can occur rapidly under some conditions. At  $150^\circ\text{C}$ , deliquesced  $\text{MgCl}_2$  brine has been experimentally shown to rapidly convert to nondeliquescent  $\text{Mg}(\text{OH},\text{Cl})_2$ , resulting in brine dryout. However, the relevance of this reaction at lower temperatures is unknown.

The effect of acid degassing is always to raise the pH; if a buffering reaction such as precipitation of carbonate occurs such that the degassing reaction can go to completion, then dryout may also occur, as highly deliquescent Mg and Ca chlorides are converted to nondeliquescent carbonates [10]. The potential importance of these reactions has not been evaluated under conditions relevant to interim storage.

In field conditions, for salts deposited over a period of years or decades on a heated storage container experiencing exposure to high air flows, brine/atmosphere exchange reactions are likely to play an important role in determining the composition of salts deposited on the storage canister surface. As noted previously, accurate assessment of exchange reactions between the atmosphere and deposited materials, and their potential effect on chloride concentrations on waste package surfaces requires site-specific information that is not currently available. However, it may be possible to show that for some locations, specifically inland sites, brines containing chloride are not stable under a wide range of possible conditions; even should chloride be occasionally deposited on the package, it would rapidly be lost via reactions with atmospheric  $\text{HNO}_3$  or  $\text{SO}_2$ . Of course, the ultimate composition of deliquescent brines on the canister surface will be a function the steady state between influx and loss (solid particle deposition and loss, and atmospheric exchange).

#### Reactions with Other Dust Components (Organics, Minerals)

A large fraction of dusts is likely to be organic in nature, including plant materials (pollen, plant fibers) naturally occurring organic acids, and in industrial settings anthropogenic volatile compounds such as compounds in diesel fuel. Insoluble organic compounds do not appear to significantly affect the RH at which deliquescence occurs [25,26] but soluble organics, when added to an inorganic salt mixture, lower the deliquescence point of the mixture, and raise the water content at a given RH [27,28]. Thus, organic compounds may affect the temperature at which deliquescence occurs, and the salt concentration of the resulting brine. Organic compounds may also react with and consume nitrate in dust. Atmospheric dusts and dusts collected in the underground tunnels at the Yucca Mountain Site experienced order-of-magnitude losses in nitrate upon heating to  $180^\circ\text{C}$  [29,30]. The atmospheric dust concomitantly lost ammonium, suggesting that ammonium nitrate volatilization was responsible. However, the underground dusts were very low in ammonium, and the nitrate loss was attributed to reaction with organics in the dust. It is unlikely, however, that reactions between nitrates and organics would be kinetically favored once temperatures drop below the point of deliquescence.

Alteration or dissolution of low solubility minerals such as clays and other silicates potentially buffer the pH of deliquescent brines in dust to near-neutral values [10]. However, these reactions may be kinetically limited, occurring too slowly to effectively modify brine compositions.

#### **2.4. Field measurements of salts on in-service SNF storage canisters**

The relative importance of processes resulting in fractionation of deposited salts or alteration of salts/brines after deposition is not known. Until recently, there were no measured data on the composition of dust on SNF storage canisters. However, within the last two years, sampling of dust on in-service SNF storage casks has been carried out at three ISFSIs in coastal regions, at Calvert Cliffs MD, Hope Creek NJ, and Diablo Canyon CA. The Calvert Cliffs ISFSI is located ~½ mile from the shore of Chesapeake Bay, and the SNF is stored in NUHOMS horizontal cask storage systems. The Hope Creek site is on the Delaware River about 15 miles above Delaware Bay; and the Diablo Canyon ISFSI is ~1/3 mile from the Pacific Ocean. In the two latter cases, the SNF is stored in HOLTEC vertical cask systems. At each location, there was concern that marine salts would be present on the waste package surfaces, providing optimum conditions for CISCC. Sampling was done both using a wet method (a wick) to quantitatively extract soluble salts from a known surface area, to determine salt loadings per unit area, and a dry method employing a pad to collect both soluble and insoluble salts without dissolution. Only the wet samples have been analyzed to date.

At Calvert Cliffs, sampling was sparse, but it was visually determined that the dust load on the canister surface varied greatly from location to location, with the upper surface being heavily coated. Analysis of the samples collected indicated that the soluble anions present on the waste package surface were mostly sulfate, with only minor amounts of nitrate and chloride. Dominant soluble cations were  $\text{Ca}^{2+}$ , with lesser  $\text{Mg}^{2+}$  and  $\text{Na}^+$ .

At Hope Creek, the composition and amount of salts varied strongly over the surfaces of the two canisters sampled. The most abundant soluble ions in most samples were calcium, magnesium, sulfate, and nitrate. Sodium and chloride dominated on only a few of the 13 samples collected. Dominant soluble cations were  $\text{Ca}^{2+}$ , with lesser  $\text{Mg}^{2+}$  and  $\text{Na}^+$ . Highest dust and salt loads were on the flat upper surface of the canister, and corresponded to the highest sodium and chloride concentrations.

Two canisters were also sampled at Diablo Canyon. The surface temperatures of these recently emplaced canisters limited what areas could be sampled using the wet sampling method to only the lower sides of each container; the upper half of the canisters and the canister tops could not be sampled. Salt loads were very light, reflecting the short time in storage. As with the Hope Creek samples, and there was wide variability in the sampled salt compositions, and despite the proximity to the ocean, nitrate and sulfate were more abundant than chloride in some samples. High nitrate and sulfate concentrations correlated with high Ca concentrations. However, in most samples, abundant chloride was present, as composite grains of sodium chloride and magnesium sulfate.

While anions can be affected by exchange reactions with the atmosphere, cations are not; if the sampled dusts are dominantly sea salts, they should be Na-rich (See Table 1). The majority of the dust samples collected at Calvert Cliffs and Hope Creek are both Na and Cl poor, and appear to be mostly derived from continental salt aerosols. A small fraction of samples that are Na-rich (and generally chloride-rich) may be dominated by sea salts. Most salts at Diablo Canyon were sea salts. At both Hope Creek and Diablo Canyon, the relative proportion of continental and sea salts varies over the surface of each SNF canister sampled. We speculate that this variability represents size fractionation in the deposited salts, with the finer continental salts preferentially depositing on the vertical sides of the canister, and the coarser sea salts being preferentially deposited on the top of the package, where gravitational settling dominates the deposition process.

The observed variability in deposited salt amounts and compositions, not only from one ISFSI to another, but from location to location on individual canisters, demonstrates the difficulty in attempting to predict the chemical environment on SNF storage canisters and the potential for CISCC.

### 3. CONCLUSIONS

A primary concern with dry storage of spent nuclear fuel is chloride-induced stress corrosion cracking, caused by deliquescence of salts deposited on the stainless steel canisters. Because of difficulties in observing and sampling storage canister surfaces, predictive models for CISCC would be useful in assessing long-term risk associated with CISCC of interim storage canisters. An integral part of such a model would be the ability to assess chemical environment resulting from deliquescence of salts in dust on the canister surface. Parameterization of a model for the physical and chemical environment on the canister surface would require site-specific information on ambient air conditions, including temperature and RH, aerosol load and compositions, and concentrations of reactive gases in the atmosphere. An accurate thermal model accounting for canister and overpack design, canister-specific waste heat load, and passive cooling by ventilation, is also required. Aerosol particle transport and deposition processes must be assessed. Brine compositions vary with initially-deposited salt assemblage, reactions with atmospheric gases, temperature, and the relative rates of salt deposition and reaction, and will vary as a function of canister surface location. Preliminary data for canister surface salt compositions at three different ISFSI locations show wide variability in deposited salt amounts and compositions, and demonstrate the complexity in developing an adequate chemical environment model for the evolving surface conditions on SNF interim storage canisters.

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### References

- [1] B. Hanson, H. Alsaed, C. Stockman, D. Enos, R. Meyer, and K. Sorenson. “*Gap Analysis to Support Extended Storage of Used Nuclear Fuel*,” FCRD-USED-2011-000136 Rev 0, U.S. Department of Energy, 2012.
- [2] 10 CFR 72.42, *Licensing Requirements for the Independent Storage of Spent Nuclear Fuel and High-Level Radioactive Waste*, U.S. Nuclear Regulatory Commission, Washington, D.C.
- [3] R. M. Kain. “*Marine Atmospheric Stress Corrosion Cracking of Austenitic Stainless Steels*,” *Materials Performance* 29(12), 60 (1990).
- [4] L. Caseres and T.S. Mintz, “*Atmospheric Stress Corrosion Cracking Susceptibility of Welded and Unwelded 304, 304L, and 316L Austenitic Stainless Steels Commonly Used for Dry Cask Storage Containers Exposed to Marine Environments*,” NUREG/CR-7030, U.S. Nuclear Regulatory Commission, Washington, D.C., 2010.
- [5] Transnuclear, Inc., “*NUHOMS FSAR*,” Rev. 10, 2008.
- [6] Holtec International, “*HI-STORM FSAR*,” Rev. 8, 2010.
- [7] S. Suffield, J.A. Fort, J.M. Cuta, and H.E. Adkins, “*Thermal Modeling of NUHOMS HSM15 and HSM-1 Storage Modules at Calvert Cliffs Nuclear Power Station ISFSP*”, PNNL-21788, Pacific Northwest National Laboratory, 2012, Richland WA.
- [8] J.M. Cuta and H.E. Adkins, “*Preliminary Thermal Modeling of HI-STORM 100S-218 Version B Storage Modules at Hope Creek Nuclear Power Station ISFSP*”, PNNL-22552, Pacific Northwest National Laboratory, 2013, Richland WA.
- [9] K. Shirai, J. TaniI, T. Arai, M. Wataru, H. Takeda, and T. Saegusa, “*SCC Evaluation Test of a Multi-Purpose Canister*,” Proceedings IHLRWM Conference 2011, Albuquerque, NM April 10-14 (2011).

- [10] Sandia National Laboratories, “*Analysis of Dust Deliquescence for FEP Screening*,” ANL-EBS-MD-000074 Rev.01, Sandia National Laboratories, 2008, Albuquerque, NM.
- [11] J.-I. Tani, M. Mayuzumi, and N. Hara, “*Initiation and Propagation of Stress Corrosion Cracking of Stainless Steel Canister for Concrete Cask Storage of Spent Nuclear Fuel*,” *Corrosion* 65(3), 187-194 (2009).
- [12] ASTM International, “*D1141-98: Standard Practice for the Preparation of Substitute Ocean Water*,” ASTM International, 2008, West Conshohocken, PA.
- [13] T. Mintz, L. Caseres, X. He, J. Dante, G. Oberson, D. Dunn, and T. Ahn, “*Atmospheric Salt Fog Testing to Evaluate Chloride-Induced Stress Corrosion Cracking of Type 304 Stainless Steel*,” Presentation at CORROSION 2012, Salt Lake City, UT, March 11-15 (2012).
- [14] G. Nakayama, “*Atmospheric Stress Corrosion Cracking (ASCC) Susceptibility of Stainless Alloys for Metallic Containers*,” *Mat. Res. Soc. Symp. Proc.* 932 (2006).
- [15] T. Prosek, A. Iverson, C Taxén, and D. Thierry, “*Low-Temperature Stress Corrosion Cracking of Stainless Steels in the Atmosphere in the Presence of Chloride Deposits*,” *Corrosion* 65(2), 105-117.
- [16] Electric Power Research Institute, “*Climatic Corrosion Considerations for Independent Spent Fuel Storage Installations in Marine Environments*,” Report # 1013524, EPRI, 2006, Palo Alto, CA.
- [17] C.A. Pio and D.A. Lopes, “*Chlorine loss from marine aerosol in a coastal atmosphere*,” *J. Geophys. Res.-Atmos.* 103(D19), 25263-25272 (1998).
- [18] D.R. Hitchcock, L.L. Spiller, and W.E. Wilson, “*Sulfuric Acid Aerosols and HCl Release in Coastal Atmospheres: Evidence of Rapid Formation of Sulfuric Acid Particulates*,” *Atmospheric Environment* 14, 165-182 (1980).
- [19] M.J. Rossi, “*Heterogeneous Reactions on Salts*,” *Chemistry Reviews*, 103(12), 4823-4882 (2003).
- [20] National Atmospheric Deposition Program (NADP), National Trends Network, <http://nadp.sws.uiuc.edu/ntn/>, accessed 12/11/12.
- [21] J.H. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution*, John Wiley & Sons, 1986, New York, NY.
- [22] X. Zhang and P.H. McMurry, “*Evaporative Losses of Fine Particulate Nitrates during Sampling*,” *Atmospheric Environment*, 26A (18), 3305-3312 (1992).
- [23] M.C. Chang, C. Sioutas, S. Kim, H. Gong, and W.S. Linn, “*Reduction of nitrate losses from filter and impactor samplers by means of concentration enrichment*,” *Atmospheric Environment* 34(1), 85-98 (2000).
- [24] E.R. Gibson, P.K. Hudson, and V.H. Grassian, “*Physicochemical Properties of Nitrate Aerosols: Implications for the Atmosphere*,” *J. Phys. Chem. A.*, 11785-11799 (2006).
- [25] Y. Ming and L.M. Russell, “*Thermodynamic Equilibrium of Organic-Electrolyte Mixtures in Aerosol Particles*,” *AIChE Journal*, 48(6), 1331-1348 (2002).
- [26] M.T. Parsons, D.A. Knopf, and A.K. Bertram, “*Deliquescence and Crystallization of Ammonium Sulfate Particles Internally Mixed with Water-Soluble Organic Compounds*,” *J. Phys. Chem. A*, 108, 11600-11608 (2004).
- [27] C. Marcolli, B. Luo, and T. Peter, “*Mixing of the Organic Aerosol Fractions: Liquids as the Thermodynamically Stable Phases*,” *J. Phys. Chem. A*, 108, 2216-2224 (2004).
- [28] C. Marcolli, B. Luo, T. Peter and F.G. Wienhold, “*Internal mixing of the organic aerosol by gas phase diffusion of semivolatile organic compounds*,” *Atmos. Chem. Phys.*, 4, 2593-2599 (2004).
- [29] Z.E. Peterman, “*Effects of Temperature on the Compositions of Soluble Salts in Dust at Yucca Mountain*,” Presentation to the Nuclear Waste Technical Review Board, Las Vegas, NV, Jan. 16 (2008).
- [30] Z.E. Peterman, “*Thermal Experiments on Atmospheric and Subsurface Dust at Yucca Mountain, Nevada*,” Presentation to the Nuclear Waste Technical Review Board, Las Vegas, NV, Jan. 28 (2009).