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Understanding the Risk of Chloride Induced Stress Corrosion Cracking of Interim Storage Containers for the Dry Storage of Spent Nuclear Fuel: Evolution of Brine Chemistry on the Container Surface

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ABSTRACT

Although the susceptibility of austenitic stainless steels to chloride induced stress corrosion cracking is well known, uncertainties exist in terms of the environmental conditions that exist on the surface of the storage containers. While a diversity of salts is present in atmospheric aerosols, many of these are not stable when placed onto a heated surface. Given that the surface temperature of any container storing spent nuclear fuel will be well above ambient, it is likely that salts deposited on its surface may decompose or degas. To characterize this effect, relevant single and multi-salt mixtures are being evaluated as a function of temperature and relative humidity to establish the rates of degassing, as well as the likely final salt and brine chemistries that will remain on the canister surface.

INTRODUCTION

One criterion for SCC is a corrosive environment, an aqueous environment that contains an aggressive chemical component that promotes metal corrosion. In the context of interim storage canisters stored within overpacks, a persistent aqueous solution can only form by deliquescence of salts deposited on the canister surface from air circulating though the overpack, and the aggressive component in the brines is chloride. The composition of atmospheric salt aerosols varies from storage site to storage site, and the composition of deposited salts may vary from the atmospheric salts. However, the potential for deposition of chloride-containing salts, at least at some sites, is high. In near-marine environments, chloride rich sea salts comprise a significant fraction of the atmospheric salt load. At inland sites, salt aerosols are generally chloride-poor; however, chloride salts associated with cooling tower emissions or with road salting during inclement winter weather could be carried into the ventilated overpack and deposited onto the canister.

However, while chloride-containing salts may be deposited on the canister, a variety of reactions can occur that can modify the composition of the deposited salts potentially making them less deliquescent, or even less corrosive if the reactions result in loss of chloride to the atmosphere.

Atmospheric Aerosol Compositions

Atmospheric aerosol particles have a number of natural sources, such as windblown surface soils/dust, sea spray, volcanic emissions, biosphere emissions, and the condensation of atmospheric gases. In addition, a significant fraction of the modern aerosol loading of the atmosphere results from anthropogenic activities such as fuel combustion. The chemical and physical properties of aerosol particles vary globally. A large fraction of ISFSIs are located in coastal regions, while others are located inland. Typical atmospheric aerosols for the two environments differ. Aerosols in the atmosphere over or near the oceans contain a large proportion of sea-spray-derived salt; sulfates formed by oxidation of sulfide species emitted by marine plankton also contribute to the soluble salt load. The aerosols over continental landmasses generally contain a larger proportion of terrestrial dusts/soil particles, particles derived from reactions of sea salt with atmospheric gases, and particles that have anthropogenic origins (Seinfeld 1986).

Near-Marine Aerosols

In near-marine settings, chloride-rich sea salts generated by wave action and evaporation of sea-spray can comprise a large fraction of aerosols. These salts reflect the composition of sea water, a typical example of which is provided in

Table 1. Dominant ions in seawater are Na^+ and Cl^- with lesser amounts of Mg^{2+}, Ca^{2+}, K^+, and SO_4^{2-}. Sea spray evaporates to form salt aerosols, which upon deliquescence form highly concentrated chloride-rich brines (sea salt is approximately 55% Cl by weight). The predicted evolution of brine composition upon evaporation of sea water was modeled using the thermodynamic solubility and speciation modeling program EQ3/6 (Wolery and Jarek 2003) and the YMP Pitzer database (SNL 2007). In Figure 1a, solute concentrations are plotted against the activity of water in the brine, which is equivalent to the relative humidity, expressed as a unit value. Inflections in the concentration curves occur when a mineral phase begins to precipitate. In **Figure 1**b, the concentrations are given in terms of concentration factor, calculated as (original water mass)/(remaining water mass). The final concentration factor, at a RH of 28%, is 6060, meaning that 0.16 ml of water is left out of an original volume of 1 liter. On the concentration factor plot, solutes plot along a straight line as long as they are conserved in solution (do not precipitate out). Note that, while these plots show the evolution of seawater as it evaporates, deliquescence of sea-salts produces exactly the same fluid compositions as a function of RH. At low relative humidities, predicted deliquescent brine compositions are rich in Mg^{2+} and Cl^-, and somewhat less enriched in Br and B; these species plot as straight lines in **Figure 1**b, as they are conserved in solution—that is, no mineral containing them is predicted to precipitate. (it should be noted that the YMP database is not qualified for use to predict borate species and contains few borate salts, so the enrichment in B may not be real). Other seawater components have been removed by precipitation, and are minor in the remaining brine.

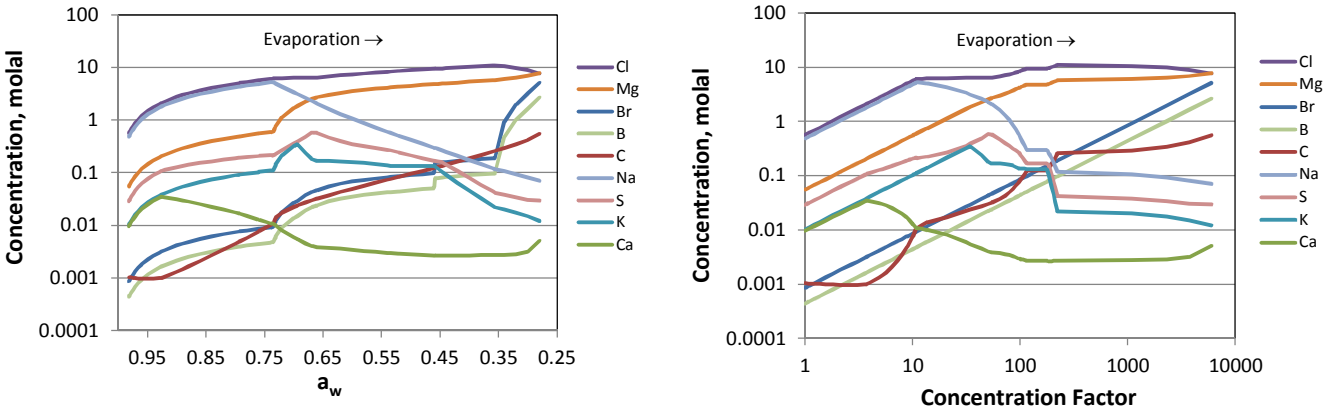

Figure 1: Evaporation of seawater. (a) Predicted brine composition as a function of a_w. (b) Predicted brine composition as a function of concentration factor.

Table 1. Typical composition of seawater

Species	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	Br^-	F^-	SO_4^{2-}	BO_3^{3-}	HCO_3^-	pH
µg/ml*	11031	398	1328	429	19835	68	1.4	2766	25.7	146	8.2

* ASTM D1141-98 (2008)

It is mineral precipitation that ultimately controls the relative proportion of species in the evaporating brine. Salt minerals that are predicted to precipitate out during evaporation are shown in Figure 2. In order of occurrence, calcite ($CaCO_3$) precipitates first, and then gypsum ($CaSO_4$:$2H_2O$), which converts to Anhydrite ($CaSO_4$) at a concentration factor of about 9. Halite (NaCl) precipitates at a concentration factor of about 11. Other minerals precipitate, and in many cases redissolve, as the seawater evaporates. The final salt assemblage at dryout consists mostly of halite, with minor amounts of Bischofite ($MgCl_2$:$6H_2O$) and Kieserite ($MgSO_4$:$2H_2O$) and trace amounts of Anhydrite, Carnallite ($KMgCl_2$:$6H_2O$), and Hydromagnesite ($Mg_5(CO_3)_4(OH)_2$:$4H_2O$). As sea-spray aerosols dry out, these salts are precipitated, and salts, or a mixture of salts and brine, may be deposited on the canister surface. As the RH rises over time, the salts redissolve and the composition of the deliquescent brine follows the path of evaporation in reverse order. It is the highly deliquescent $MgCl_2$:$6H_2O$ that is believed to control the deliquescence behavior of sea salts, determining when an aqueous phase is present.

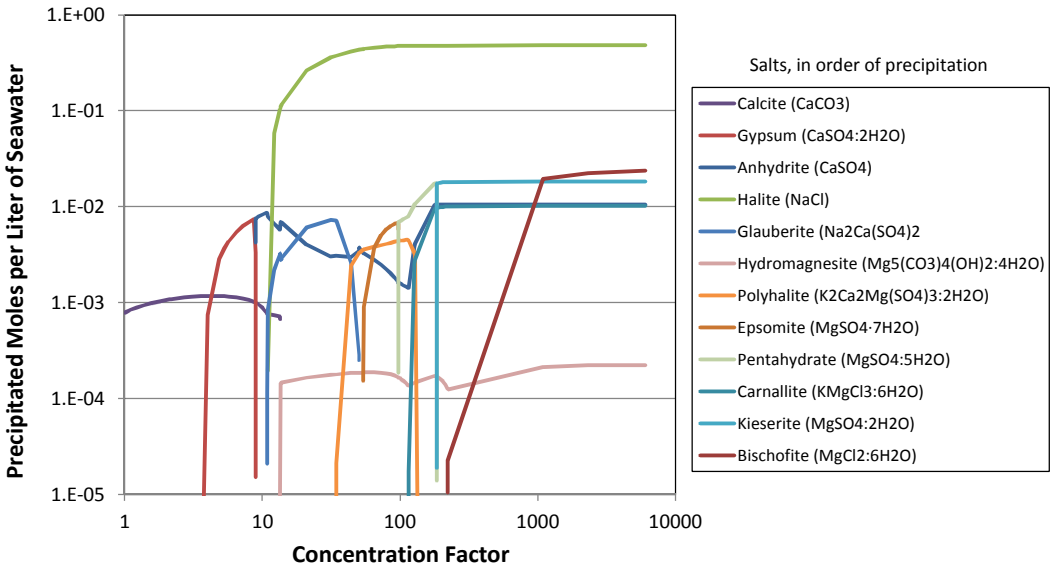

Figure 2: Evaporation of Seawater. Predicted salt phases as a function of concentration factor.

The occurrence of sea-salt aerosols on SNF dry storage canisters was recently confirmed, when sea-salt aggregates were observed in dust samples collected from canister surfaces at the Diablo Canyon ISFSI (Bryan and Enos, 2014).

Inland Aerosols

Nitrate and sulfate salts typically dominate the soluble fraction of atmospheric aerosols over continental landmasses, with the most common cations being ammonium and sodium (Seinfeld 1986; Malm et al. 2003; Rossi 2003). Most atmospheric ammonia is anthropogenic in origin, being produced by

hydrolysis of urea present in livestock wastes and by offgassing of ammonia from fertilizers used in agriculture; other significant anthropogenic sources include biomass burning, human wastes, chemical and industrial processes, and fossil fuel combustion (Seinfeld 1986; Aneja et al. 2001; Anderson et al. 2003). The primary natural sources are oceanic emissions and emissions from soil and vegetation. Like ammonia, atmospheric nitrate and sulfate currently have major anthropogenic sources, being emitted as acid gases, or reduced species that react with water to form acid gases, in power plant emissions. However, their anthropogenic emissions are decreasing in the U.S., due to pollution prevention programs. Atmospheric ammonia reacts readily with sulfate and nitrate acid gases in the atmosphere to form solid salts such as $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and NH_4NO_3 (Seinfeld 1986; Rossi 2003). Because the ammonia originates almost entirely from the surface, the abundances of ammonium salts are higher in the lower troposphere, are becoming less abundant in the upper troposphere, and are nearly absent in the stratosphere(Rossi 2003). Near the surface, $(NH_4)_2SO_4$ and NH_4NO_3 dominate. At higher altitudes, the more acidic $(NH_4)HSO_4$ becomes important, while in the stratosphere, sulfate and nitrate exists as sulfuric and nitric acids. Fine atmospheric particles (particles with diameters less than 2.5 microns, also referred to as the PM2.5 fraction) primarily originate from gas condensation reactions such as those involving ammonia and sulfuric and nitric acids. Thus, one would expect most of the $(NH_4)_2SO_4$ and NH_4NO_3 to be present in the fine fraction.

Atmospheric salt compositions have been characterized extensively by national sampling programs. The State and Federal Interagency Monitoring of Protected Visual Environments (IMPROVE) program provides compositional data for the PM2.5 aerosol size fraction at over 150 sites through the continental US. The database does not include all solute species, but provides data for the most abundant soluble anions in atmospheric dusts, including nitrate, sulfate, and chloride. Data for five typical sites across the US were summarized in NRC (2014, Table 4-2), and are given in Table 2. These data illustrate the relative abundances of the anion species in typical continental aerosols.

The National Atmospheric Deposition Program (NADP) (2015) provides wet deposition, or rainout, data across the U.S. Precipitation scavenges aerosols from the atmosphere, and is often used to evaluate atmospheric aerosol compositions. Wet deposition data from a typical site in Iowa is given in Table 3, and confirm that ammonium is the dominant cation species. At this inland site, far from the ocean, Ca is the second most abundant cation. Nearer to the ocean, Na-sulfate and Na-nitrate are commonly abundant, formed by reactions between chloride-rich sea salts and sulfuric and nitric acids in the atmosphere.

Table 2. Selected element concentrations in PM2.5 dust fractions from Five IMPROVE Sampling Sites.

Site	**NO_3^-, µg/m^3 Median (Range)**	**SO_4^{2-}, µg/m^3 Median (Range)**	**Cl^-, µg/m^3 Median (Range)**
Arendtsville, PA	0.5349 (0.0529 to 8.3000)	2.2702 (0.366 to 15.2673)	0.0253 (0.0002 to 0.3252)
Bondville, IL	1.1627 (0.0662 to 8.9192)	2.0517 (0.4084 to 9.0997)	0.0315 (0.0006 to 0.2855)
Great River Bluffs, MN	0.4869 (0.0145 to 16.106)	1.1351 (0.1649 to 8.3342)	0.0229 (0.0001 to 0.6104)
Great Smoky Mtns National Park, TN	0.1482 (0.0382 to 4.5818)	2.0497 (0.1252 to 7.0209)	0.0145 (0.0007 to 0.1657)
Phoenix, AZ	0.3837 (0.0638 to 5.9663)	0.7779 (0.1761 to 8.3342)	0.0841 (0.0028 to 1.0963)

Data from National IMPROVE network, summarized in NRC (2014), NUREG/CR-7170, Table 4-2.

Table 3. Composition of wet deposition from an Iowa NADP site.

Species	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}

Rain Conc., μeq/L	29.217	2.045	0.511	3.208	16.766	1.975	15.565	17.685

NADP (2015)

Processes Affecting Aerosol/Brine Compositions

Once deposited on the canister surface, several processes can affect the composition of deposited salts, or of the brine that can form when they deliquesce. Some of these can occur prior to deliquescence; others can only occur after a deliquescent brine has formed, or, at least, require the RH be sufficiently high that a thin adsorbed water film is present on the salt surface. Significant films of adsorbed water may be present below the deliquescence RH (RH_D) for a given salt, and probably explain why the limiting RH for corrosion (RH_L) is below the deliquescence RH for a given salt.

For purposes of the discussion here, it is assumed that the RH_L represents the humidity at which adsorbed water films on salt surfaces become significant enough to support chemical reactions between the salt and other solid or gaseous phases present, while the RH_D refers to a somewhat higher RH at which a salt or assemblage of salts is in equilibrium with a bulk saturated solution of that salt or assemblage.

Reactions occurring prior to deliquescence.

Some salts are not thermally stable and prior to deliquescence can decompose, emitting gas species and therefore being removed from the surface of the storage canister. The salts most susceptible to thermal decomposition are ammonium salts, which are abundant at inland sites. Prior to deliquescence, ammonium salts decompose via the following reactions:

$$NH_4Cl(s) \leftrightarrow NH_3(g) + HCl(g)$$

$$NH_4NO_3(s) \leftrightarrow NH_3(g) + HNO_3(g)$$

$$(NH_4)_2SO_4(s) \leftrightarrow 2NH_3(g) + H_2SO_4\ (g)$$

As ammonia degasses, there is concomitant loss of an acid gas species. Experiments with bulk salts show that ammonium chloride and ammonium nitrate reactions are very rapid even at moderately elevated temperatures (SNL 2008). At 100ºC, the reaction is complete within days or weeks; even at 50ºC, a large fraction of the minerals will be lost over years. Ammonium sulfate decomposition is much slower; it is complete in less than 1 year at 100ºC, but may persist with little loss at lower temperatures (SNL 2008). For fine particulates such as atmospheric aerosols, 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 (Zhang and McMurry 1992; Chang et al. 2000). 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. The ratio of cations removed is a function of the identity of the salt phases—for atmospheric aerosols, most ammonium is associated with sulfate, and to a lesser degree, nitrate (Seinfeld 1986); however, if the small amount of chloride present in inland aerosols is present as ammonium salts, it will also be lost over time. If the rate of loss is more rapid that the rate of deposition, then there can be no accumulation of ammonium chloride on canister surfaces. Because the previous experiments were performed on bulk salts (SNL 2008), and we anticipate that finely dispersed salts will degas much more rapidly, SNL has evaluated decomposition rates for ammonium minerals as a function of temperature under essentially dry conditions (RH = 11-13%).

Other than ammonium salts, most inorganic salts are thermally stable (with the exception of dehydration reactions) at temperatures anticipated to occur on interim storage canisters surfaces.

Reactions occurring after Deliquescence.

Once an aqueous solution is present either as a deliquescent brine or as an adsorbed water film, salts may react with gas phases in the atmosphere, or with other salt phases. Some of these reactions can result in degassing of chloride and other anionic components as mineral acids, and loss of those species from canister surfaces.

Possible exchange reactions with the atmosphere include acid degassing, equilibration with atmospheric CO_2, and coupled degassing of ammonium and acid gases. At low pH, concentrated, deliquesced brines will produce partial pressures of acid gases (HCl, HNO_3) that are higher than the concentrations in ambient air. The brines degas the acids, resulting in loss of Cl^- and NO_3^- from solution. The solution pH rises, and the acid gas partial pressures decrease until (1) they are equal to that of the ambient air and degassing ceases; or (2) a buffering reaction occurs which stabilizes the pH allowing continued acid degassing and loss of Cl^-/NO_3^-. One buffering reaction involves adsorption of CO_2 from the atmosphere and precipitation of carbonate. For a sodium-rich brine, this occurs only at high pH (>10), because of the high solubility of sodium carbonate phases. Because of the high equilibrium pH, acid degassing is likely to be inhibited before significant loss of anions occurs. For a magnesium-rich brine, saturation with magnesite and precipitation occurs between pH 6 and 7; at these values, acid gas partial pressures in equilibrium with the solution may still be higher than ambient values, and degassing will continue to occur. A second buffering reaction for Mg-rich brines is precipitation of Mg-hydroxy-chlorides. Because this reaction is internally buffered, it can occur rapidly under some conditions. At 150ºC, deliquesced $MgCl_2$ brine has been experimentally shown to rapidly convert to nondeliquescent $Mg(OH,Cl)_2$. While this temperature is excessive for long term interim storage, it does illustrate that acid degassing can potentially change brine compositions over the long term. 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 the composition of the salt assemblage has changed, and dryout may also occur (SNL 2008). In field conditions, for salts deposited over a period of years or decades in a storage container experiencing exposure to large volumes of circulating air, it is likely that degassing will limit brine pH, and may result in precipitation of non-deliquescent Mg carbonate or hydroxyl-chloride. Note that in a laboratory corrosion test setting, these effects are minimized by rapid deposition of relatively large amounts of salt, and low rates of air exchange. Proper experiment design is critical to understanding the effects of these processes.

Salt deposition continues to occur after deliquescence, but the role of ammonium salts changes. Once a deliquescent brine is present, ammonium minerals will dissolve into it, and coupled ammonium/ acid degassing will occur. However, the identity of the cation lost is no longer a function of the original ion association in the deposited mineral. Instead, the brine will degas ammonia and acid gas cations in proportion to their equilibrium vapor pressure above the brine. This means that chloride deposited as any chloride salt will be degassed, if ammonium, deposited as any ammonium salt is present. For instance, assume that NaCl and $(NH_4)_2SO_4$ are deposited on the canister. Once deliquescence occurs, the following reaction can occur:

$$2NaCl(s) + (NH_4)_2SO_4(s) \leftrightarrow Na_2SO_4(s) + 2HCl(g) + 2NH_3(g)$$

where ammonia and HCl are degassed and lost from the canister surface. Similar reactions can be written for Mg-Cl_2 or Ca-Cl_2 phases or the equivalent NO_3^- phases, or even carbonate phases, all result in loss of the mineral acid and ammonia from the canister surface. These reactions may be very important in limiting chloride accumulation at inland sites, where ammonium salts are the dominant components of atmospheric aerosols.

Other reactions that may be important in limiting chloride buildup on canisters at inland sites involve reactions of chloride and nitrate salts with atmospheric SO_2, or with sulfuric acid formed when SO_2 reacts with water, that result in degassing of HCl or HNO_3 and precipitation of a sulfate mineral. These reactions are likely to be most important in the mid Atlantic states, where atmospheric concentrations of SO_2 are elevated due to industrial activities. Evidence of these reactions has been observed in dust samples collected at the Hope Creek and Calvert Cliffs ISFIs (Bryan and Enos, 2014).

The soluble fraction of marine aerosols contains a significant amount of chloride (as might be expected, as sea salt is approximately 55% by weight Cl). However, even over the oceans, the composition of soluble aerosols has long been recognized to be deficient in chloride relative to sea salt (e.g., Hitchcock et al. 1980), implying the presence of a mechanism for the removal of chloride (or chlorine) from atmospheric particles. This is generally attributed to reactions of strong inorganic acids with sea salt, such as:

$NaCl(s, aq) + HNO_3(g) \leftrightarrow NaNO_3(s, aq) + HCl(g)$

$2NaCl(s) + H_2O + ½O_2 + SO_2(g) \leftrightarrow Na_2SO_4(s) + 2HCl(g)$

In addition, there are a number of photochemically-mediated reactions with nitrous oxides that can transfer chloride from the solid to the gas phase (Rossi 2003).

Because of these reactions, as sea-salt aerosols in near-marine settings are blown inland, they become progressively enriched in sodium salts of nitrate and/or sulfate, originating from reactions on primary particles of sea salt (Wall et al. 1988; Malm et al. 2003). These reactions can be very efficient; for instance, coastal aerosols in Spain lose 24% (coarse particles) to 67% (fine particles) of their chloride prior to reaching the shoreline, and continue to convert to nitrates and sulfates at a rate ~11% per hour thereafter (Pio and Lopes 1998).

One criterion for chloride-induced SCC of interim storage canisters is the accumulation of chloride on the canister surface. Accumulation will largely be controlled by the rate of chloride deposition relative to that of processes which result in chloride loss through degassing. If the chloride-loss reactions can be shown to be sufficiently rapid, then chloride is unlikely to accumulate. At some sites, particularly inland sites, this approach, when combined with validating site-specific aerosol or dust compositional data, may be a rationale for screening SCC, or at least, increasing SCC inspection intervals.

EXPERIMENTAL PROCEDURE

In order to evaluate salt and brine stability as a function of temperature and RH on a canister surface, SNL developed techniques to accurately deposit a finely dispersed coating of soluble salts on flat surfaces. These samples are exposed to controlled environments, and mass loss and compositional changes are monitored. As discussed above, for some salts, mass loss can occur by decomposition of the solid phase. For other salts, deliquescence, or at least the development of an adsorbed water film on the surface of the salts, is required before degassing, reaction with atmospheric gas species, or reaction with other salts contacting them can occur. These reactions may result in mass or compositional changes in the soluble salts or brine chemistry, or, if a salt species is completely converted or decomposed, changes in the RH_D, resulting in dryout.

To evaluate these processes, we first deposit salts in aqueous or alcohol-based solutions onto samples using an airbrush mounted to an automated X-Y stage. We simultaneously deposit salts onto a quartz-crystal microbalance (QCM) wafer and onto 2.5″ × 5″ metal coupons. The QCM wafers monitor the mass deposited, and are later used to monitor deliquescence and mass loss in the environmental chamber. The coupons have a much larger surface area, and are used to measure changes in salt composition due to exposure in the environmental chamber; this is done by leaching off the soluble salts and analyzing them by wet chemical methods.

Salt Deposition

Sea salt aerosols formed from evaporation of sea-spray are mostly in the >2.5 μm aerosol fraction, and can be up to ~20 μm in diameter. Continental salts, which generally form by condensation from atmospheric gases (e.g., ammonia and sulfuric acid) are commonly in the PM2.5 fraction. Because degassing and decomposition reactions will be strongly controlled by the surface area of the salt particles, it is important, when evaluating salt and brine stability, to evaluate the reactions using finely dispersed salts deposited on the surface of interest. An example of the salt coating produced using the spray system is shown in Figure 3. The deposited salts are present as dispersed particles, evenly coating the surface of the sample. Though not as small as most atmospheric aerosols, the deposited salts are in the range of 20-50 μm in diameter, and should be fine enough for use as analogs for atmospheric salt aerosols.

The salt deposition system is ideal for preparing samples for atmospheric corrosion testing, because it is capable of evenly depositing very thin films of salts over the surface of test coupons, at surface loads ranging from a few mg/m^2 to g/m^2.

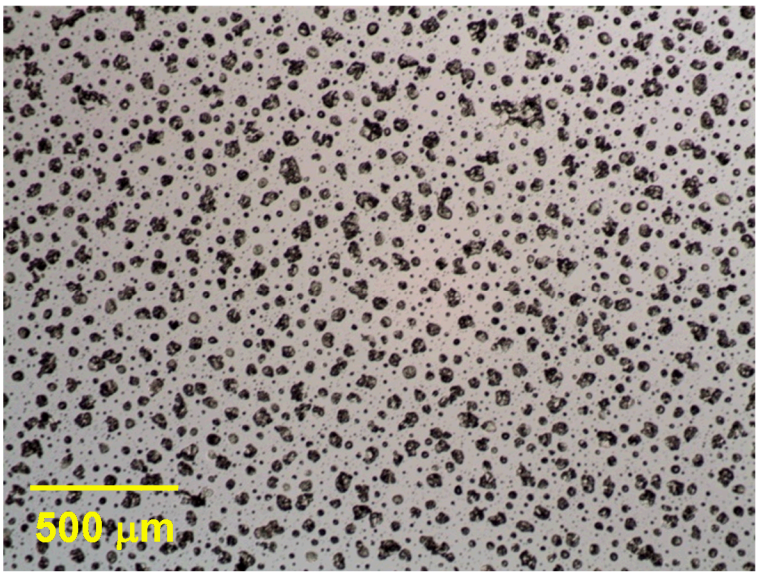

Figure 3: QCM wafer coated with 100 µg/cm^2 (1 g/m^2) of evenly dispersed $NaNO_3$.

Quartz Crystal Microbalance

The quartz crystal microbalance, or QCM, is a very sensitive mass measuring device. It was used to monitor the amount of salt surface loading (salt deposited per unit area) by the salt spray unit, but is also used in experiments evaluating salt and brine stability. Specifically, after coating QCM wafers with salts, they were exposed to controlled temperature and RH conditions in an environmental chamber, and mass changes were monitored. Mass changes occur because of degassing or decomposition of the dry salts, and this can be monitored directly by QCM. Once deliquescence occurs, the mass on the wafer cannot be measured for reasons discussed below. However, mass loss during the period of deliquescence can still be monitored, by measuring the mass of the initial dry salts, and then measuring the mass again, after drying the deliquesced brine out again.

To interpret the results of these experiments, a general understanding of how a QCM works is necessary. The heart of the QCM is a thin wafer of quartz, cut at a precise crystallographic orientation from a single crystal of quartz. The wafer has a gold electrode on each side (Figure 4a). Electrical contacts or leads are attached to the electrodes and an oscillator circuit is used to apply an oscillating current to the electrodes (Figure 4b). Because quartz is piezoelectric, the wafer vibrates in a direction parallel to the surface at a frequency corresponding to the fundamental frequency of the wafer (9MHz for the QCM used here). As mass is deposited onto the crystal, that fundamental frequency changes, and by monitoring the frequency change, the deposited mass can be measured (Figure 4c). Because changes in frequency of less than one Hz can be readily measured, QCMs offer an extremely precise method of measuring changes in mass on the wafer surface. The mass resolution for the 9 MHZ QCM used for these experiments is <1 ng/cm^2; corresponding to a thickness of NaCl on the surface less than 1/10 of a molecular monolayer thick.

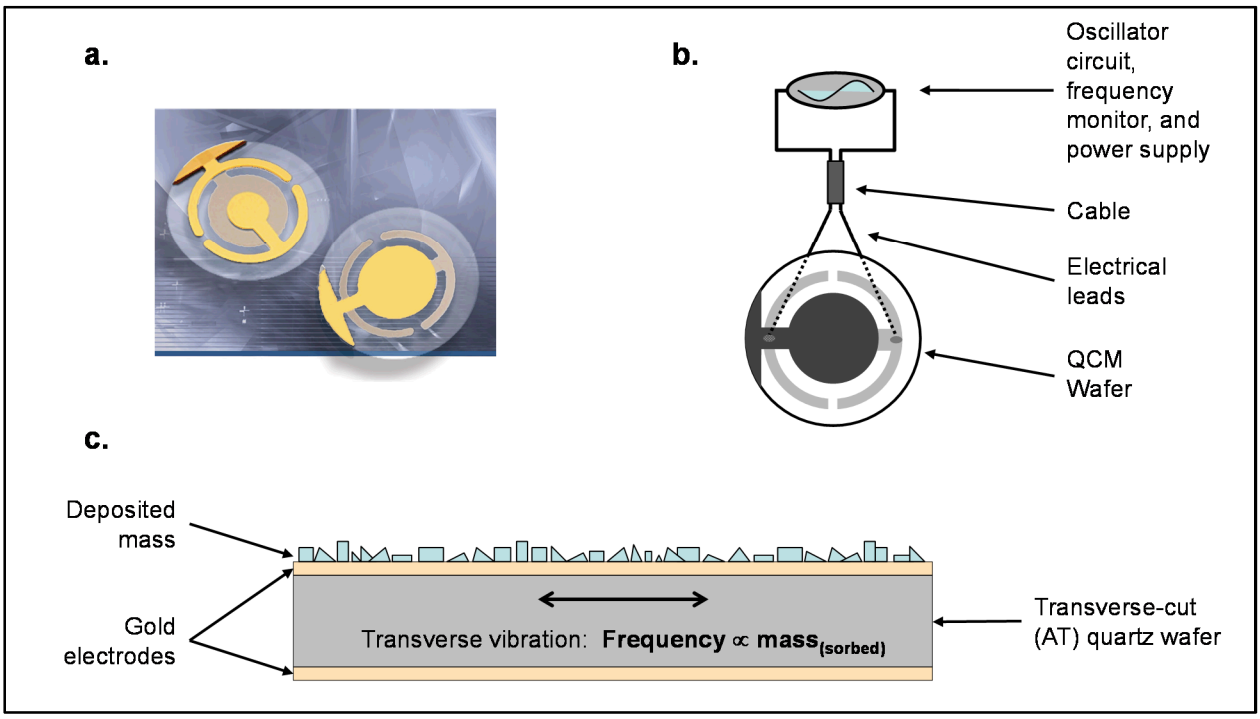

Figure 4: Operating principle of a QCM. Quartz wafers with gold electrodes (a) are connected to a control circuit that both piezoelectrically stimulates the wafer, and monitors the resulting frequency of vibration. The oscillating current creates a transverse vibration in the wafer, the frequency of which is a function of the mass deposited on the wafer (c).

The QCM can only accurately measure mass if the mass strongly couples to the surface of the wafer and vibrates with it as the wafer vibrates. If the mass is not strongly coupled—for instance, if it is present as a liquid (e.g., deliquescent brine) on the wafer surface, shear or slip will occur at the contact with the wafer, and the mass will appear to be less than it actually is. At the same time, the vibration will extend into the solution and exert a viscous drag on the vibrating wafer; this resistance to vibration does not affect the fundamental frequency, but instead affects the current necessary to achieve it; it is exactly equivalent to an increase in electrical resistance in the driving circuit. This means that the QCM cannot be used to measure the mass of liquid on the surface. In the experiments described here, QCM wafers are used to monitor the salt load deposited on the wafers, and are also used to monitor mass loss due to decomposition or degassing over the course of the experiment when the salts are in the solid state. The QCM can also be used to measure mass loss of deliquesced salts, however, by first measuring the mass of the dry salts, then raising the relative humidity and causing the salts to deliquesce for the test period, and then lowering the RH to dry the salts back out and measuring the mass a second time.

RESULTS AND DISCUSSION

To date, the stability of simple systems involving ammonium salts has been evaluated. These were chosen because they are the dominant soluble components at inland sites. Also, previous work has shown that they decompose relatively rapidly as bulk salts at higher temperatures (SNL 2008), and it was considered likely that finely dispersed, high surface area salts would decompose even more rapidly. If decomposition reactions are sufficiently rapid, then coexistence of ammonia and chloride on a canister surface is not possible, and the likelihood that SCC can occur at ammonium-rich inland sites may be small.

Existing data for ammonium salt decomposition rates can be found in SNL (2008). The data suggest that at temperatures below 100ºC on an interim canister surface, NH_4NO_3 and NH_4Cl can persist for days to years, or even years to decades at a temperature of 50ºC; lower temperatures were not tested. Moreover, the salts were dry, and the work did not evaluate whether deliquesced salts would degas as

efficiently as the dry salts decomposed. However, these data were collected using fairly coarse-grained salts; it is likely that decomposition and degassing rates are a function of salt surface area, and that fine grained, high surface area atmospheric aerosols will decompose even more rapidly. To test this, salt and brine stability experiments were performed with individual ammonium salts.

NH_4NO_3

In this experiment, 100 µg/cm^2 was deposited on a QCM wafer, the wafer was placed in an environmental chamber at the desired conditions, and decomposition and degassing were monitored by measuring the weight change over time. Because only one salt is present, the weight change correlates directly to amount of salt lost, and it was not necessary to coat and analyze metal coupons to evaluate changes in composition. First, conditions for deliquescence were evaluated. A temperature of 50ºC was used as a baseline. The sample was placed in a Thunder Scientific environmental chamber, and the minimum possible RH was used, corresponding to about 11% as measured by a Viasala RH probe placed adjacent to the QCM wafer in the center of the chamber. An unloaded QCM wafer was also placed in the chamber, as a blank. Then, the RH was ramped up in 5% increments. The results are shown in Figure 5. There was an overall decrease in mass over the course of the experiment, as NH_4NO_3 decomposed (dry salt) or degassed (deliquesced brine) from the wafer surface. The salt deliquesced between 40 and 45% RH (about 210 minutes into the experiment), and there was an apparent large loss in mass, along with a concomitant large increase in resistance as the brine decoupled from the wafer surface. However, when the RH was decreased to about 28%, below the deliquescence RH, the salts dried back out, and recoupled with the wafer. At this point, it was possible to accurately measure the mass load again. To verify that deliquescence had occurred, the RH was once again raised to above 40% (about 270 minutes into the experiment) and decoupling occurred once again.

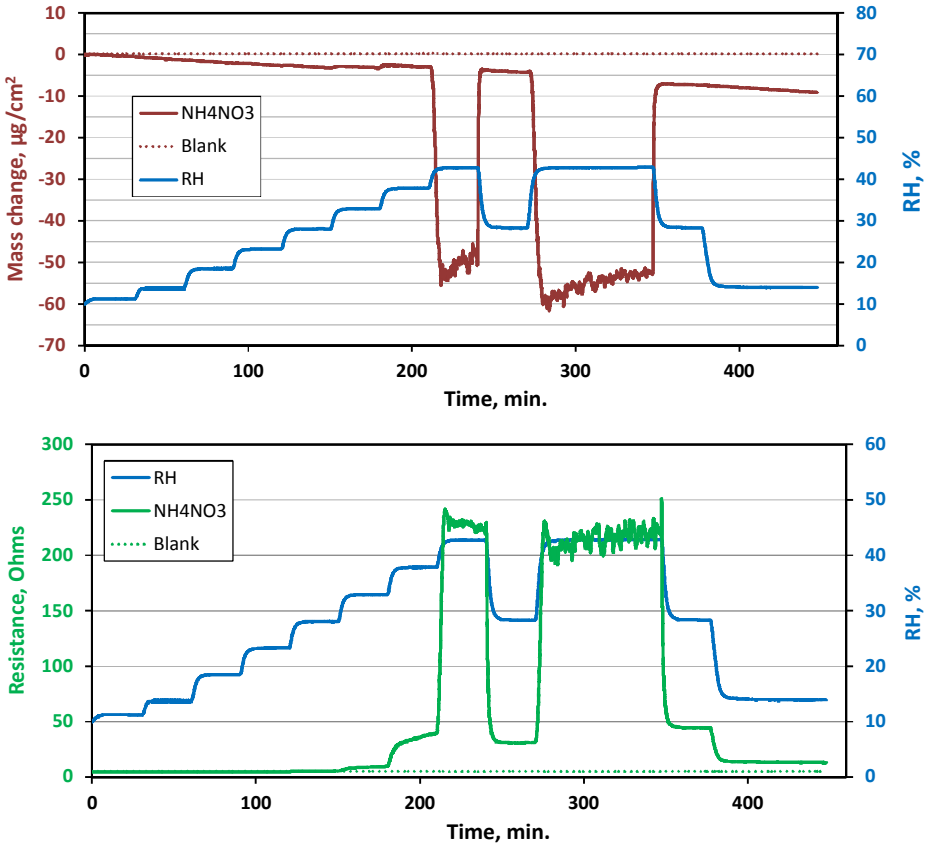

Figure 5: Changes in apparent mass loading (upper) and electrical resistance (lower) as a function of RH, for a QCM wafer loaded with 100 µg/cm$_2$ NH_4NO_3.

An expanded image of the upper part of Figure 5 is shown in Figure 6. An important feature of this image is that it shows that there are progressively larger increases in the mass loading on the wafer as the deliquescence RH is approached. These show that, while full deliquescence and conversion from a solid salt to a brine is sharply delineated, some water adsorption occurs below the deliquescence point. This is commonly observed for many deliquescent salts, including NaCl and $MgCl_2$ (e.g., Dai et al. 1997; Schindelholz et al. 2013), and is probably the reason why the threshold RH for corrosion (RH_L) is below the deliquescence RH. Thin adsorbed water films on the salt surface form initially at high-energy step sites, and then, with increasing RH, expand over the salt grain surface until they are sufficient to support corrosion. Corrosion has frequently been observed at RH values below the deliquescence point of $MgCl_2$, the most abundant component in sea-salt deliquescent brines at low RH. This has been attributed to the presence of a $CaCl_2$ hydrate, which deliquesces at lower RH values, in small amounts (NRC 2014). However, this is probably incorrect. Thermodynamic modeling shows that Ca concentrations in sea-salt deliquescent brines are controlled by precipitation of gypsum and anhydrite, and are extremely low at low RH. It is more likely that the development of adsorbed water films on the hydrated $MgCl_2$ mineral phase is the real cause.

In the next experiment, mass loss as a function of temperature was measured, first decomposition of the dry salt at ~13 % RH, and then degassing from the deliquesced brine, at a RH above the RH_D. Mass loss was measured directly under dry conditions. To measure mass loss from deliquesced brines, the surface load was first measured dry, then the salts were deliquesced for a time interval, and the dried out again, and a second reading taken. Dry and deliquesced degassing rates were measured at 50ºC, 40ºC, and 30ºC (Figure 7). The deliquescence RH of NH_4NO_3 is temperature-sensitive; at 50ºC and 40ºC, deliquescence occurred at about 40% RH, while at 30ºC, it was necessary to raise the RH to 50% to reach deliquescence. In this plot, the yellow lines are linear fits to the data for dry decomposition, and connect the measured masses under dry conditions before and after deliquescence for wet conditions. The slopes of the lines represent the rate of mass loss at each condition.

The mass on the QCM wafer decreased over the entire duration of the experiment, as the time was insufficient to result in complete loss of the ammonium nitrate. At the end of the experiment, the surface was examined with a microscope to verify that the recorded changes were not artifacts of the experimental method. Before and after images of the salt loading on the wafer are shown in Figure 8; it is clear that the majority of the salt has been lost from the wafer. The wafer was returned to the environmental chamber at 50ºC and 13% RH, and after additional ageing, the NH_4NO_3 decomposed completely. The rates of mass loss are summarized in Table 4. Finely dispersed NH_4NO_3 decomposes very rapidly even at low temperatures. A surface load of 1 g/m^2, which is quite heavy relative to measured salt loads on in-service canisters and would require years or decades to accumulate, would degas within days to a few weeks even at canister surface temperatures as low as 30ºC. It is clear that NH_4NO_3 accumulation cannot occur at temperatures above ambient.

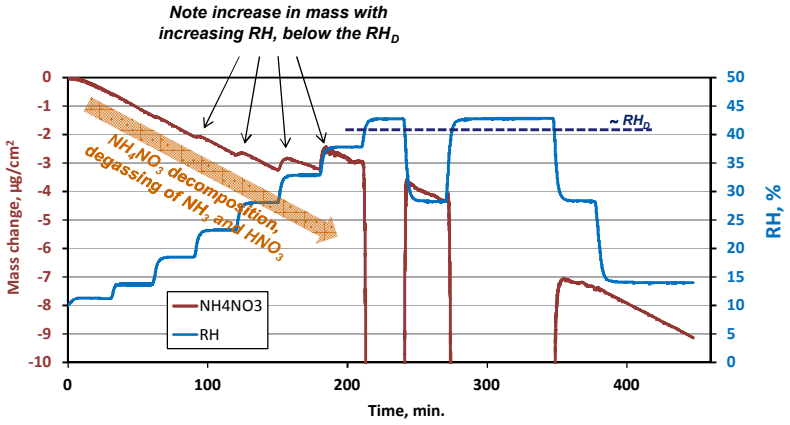

Figure 6: Expanded image of Figure 5, showing water adsorption by NH_4NO_3 prior to deliquescence.

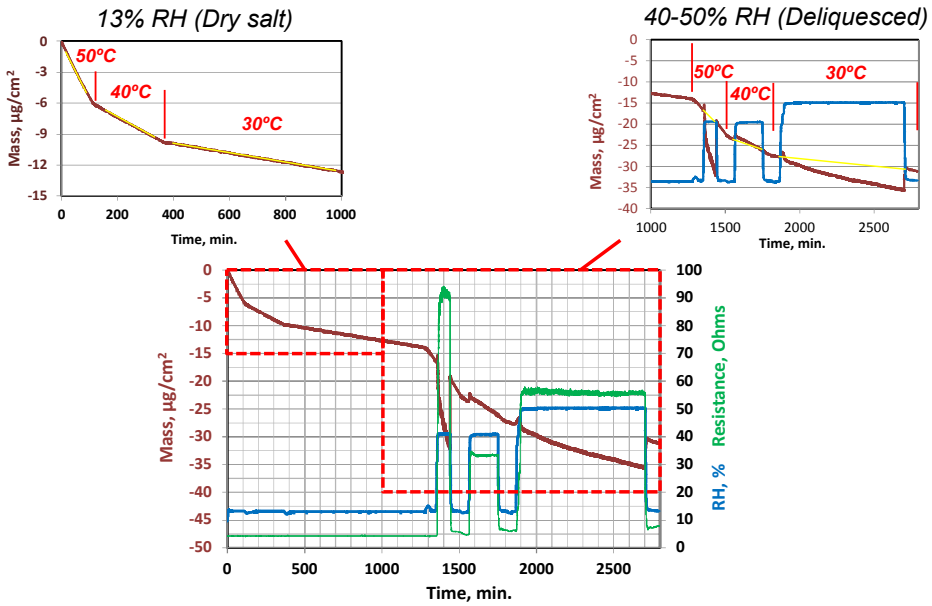

Figure 7: QCM measurements of NH_4NO_3 mass loss as a function of temperature, under dry and deliquesced conditions.

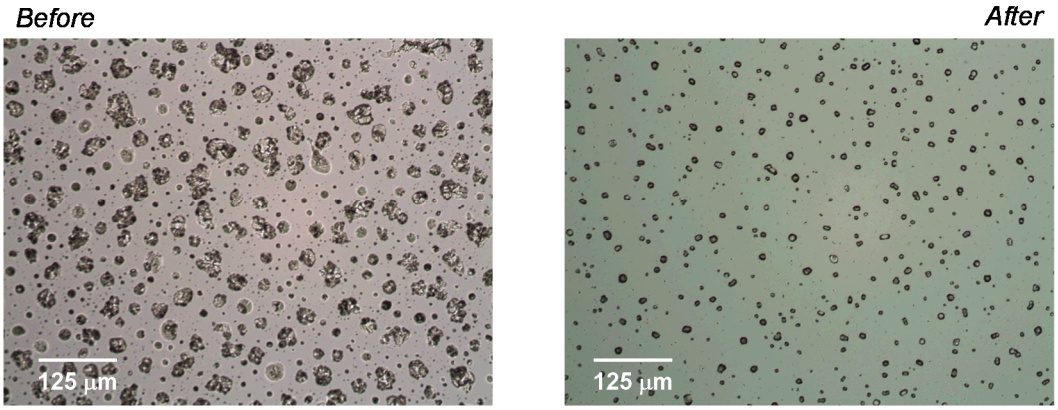

Figure 8: NH_4NO_3 loading on the QCM wafer, prior to and after testing.

Table 4. NH_4NO_3 degassing rates as a function of temperature.

Dry			
T, ºC	RH	Decomp. Rate, $mg/m^{-2}\ hr^{-1}$	Days to degas a load of 1 g/m^{-2}
49.7	13.2%	32.10	1.3
41.2	13.2%	8.78	4.7
30.6	13.0%	2.72	15.3

Deliquesced			
T, ºC	RH	Decomp. Rate, $mg/m^{-2}\ hr^{-1}$	Days to degas a load of 1 g/m^{-2}
50.3	41.2%	20.28	2.1
40.8	41.0%	8.56	4.9
31.2	50.3%	1.97	21.2

NH_4Cl

A second salt and brine stability test was conducted with NH_4Cl, following the same protocol as the NH_4NO_3 experiment. Degassing rates were measured at 50ºC, 40ºC, and 30ºC under both dry and deliquesced conditions. Because NH_4Cl is less soluble than NH_4NO_3, the RH required for deliquescence is higher. At 50ºC and 40ºC, NH_4Cl deliquesced between 65% and 70% RH, while at 30ºC, it occurred between 70% and 75% RH. The QCM measurements of mass loss are shown in Figure 9. NH_4Cl degassing and mass loss occurred rapidly for both the solid phase and the deliquesced brine. Rates for NH_4Cl mass loss are provided in Table 5, and are only slightly lower than the rates for NH_4NO_3. An NH_4Cl surface load of 1 g/m^2 would degas within days to perhaps one month, even at canister surface temperatures as low as 30ºC.

Activation energies for NH_4NO_3 and NH_4Cl degassing

The measured rate data for NH_4NO_3 and NH_4Cl were used to create linearized Arrhenius plots (ln(rate) versus 1/T), as shown in Figure 10. A best-fit line was fitted to each data set and the slope of the line was used to calculate the activation energy (E_a) for decomposition of the solid salt, or degassing of the deliquesced brine. For both salts, the values for degassing from the solid salt and the brine are very similar and probably within the uncertainty in the measurement. The E_a values for NH_4NO_3 are approximately 100 kJ/mol (104.1 kJ/mol dry and 100.2 kJ/mol deliquesced), while those for NH_4Cl are slightly lower, about 95 kJ/mol (96.4 kJ/mol dry, 95.5 kJ/mol deliquesced). These values are slightly higher than those reported in SNL (2008) which are, respectively, 91.5 and 89 kJ/mol.

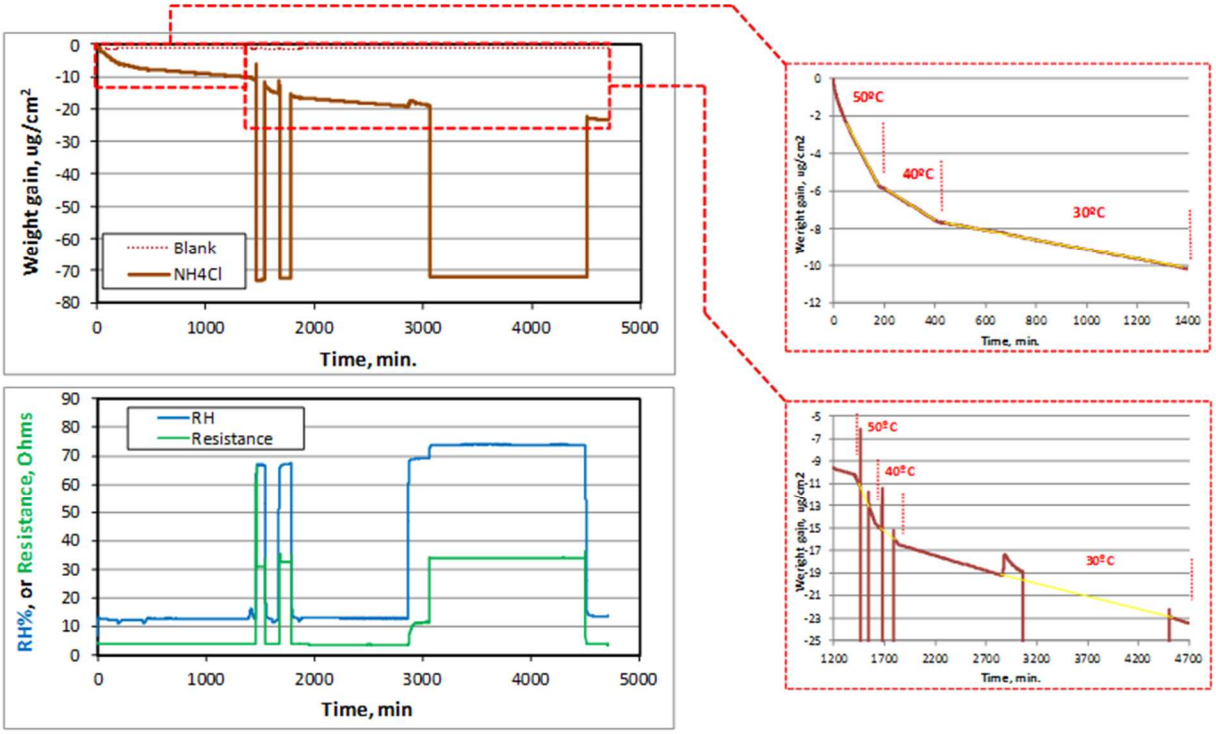

Figure 9. QCM measurements of NH_4Cl mass loss as a function of temperature, under dry and deliquesced conditions.

Table 5. NH_4Cl degassing rates as a function of temperature.

Dry			
T, ºC	**RH**	**Decomp. Rate, mg/m^{-2} hr^{-1}**	**Days to degas a load of 1 g/m^{-2}**
49.8	12.6	15.20	2.7
40.6	12.5	5.03	8.3
30.6	13.0	1.57	26.5

Deliquesced			
T, ºC	**RH**	**Decomp. Rate, mg/m^{-2} hr^{-1}**	**Days to degas a load of 1 g/m^{-2}**
50.2	63.9	12.98	3.2
40.4	62.1	4.26	9.8
30.7	72.9	1.33	31.4

$(NH_4)_2SO_4$

Only preliminary experiments have been carried out with $(NH_4)_2SO_4$. The results indicate that deliquescence occurs between 75% and 80% RH, but there is measurable water adsorption onto the salt surfaces as low at 55% RH. Degassing results at 50ºC seem to be consistent with those in SNL (2008). Over the course of a several-hour experiment, no measurable decomposition of the solid phase occurred. Degassing under deliquescent conditions was not evaluated. Longer duration experiments with $(NH_4)_2SO_4$ will be carried out in the future.

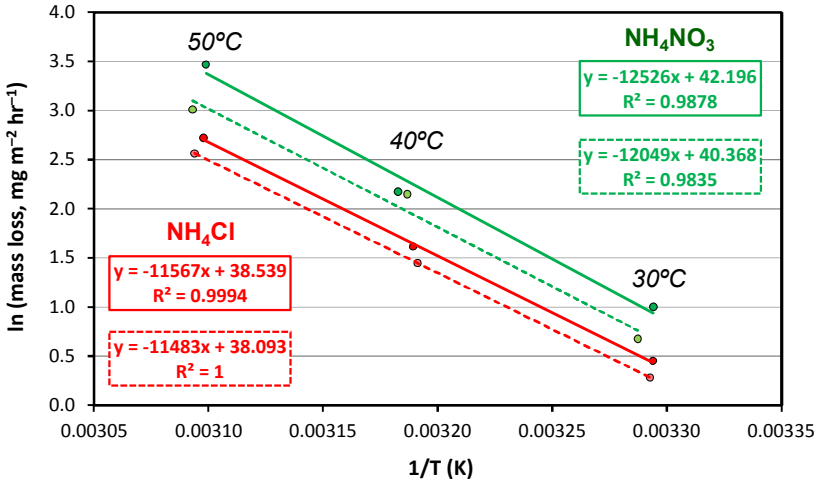

Figure 10. Arrhenius plots of mass loss data for NH_4NO_3 and NH_4Cl. Solid lines—dry conditions. Dotted lines—deliquesced conditions.

CONCLUSIONS

Preliminary experiments show that NH_4NO_3 and NH_4Cl decompose very rapidly in the solid phase, at even slightly elevated temperatures. Degassing from the deliquesced salt is also very rapid. It is not possible for these salts to persist or accumulate on the surface of interim storage canisters at temperatures above ambient. Preliminary data for $(NH_4)_2SO_4$ indicate it does not decompose rapidly, and will likely accumulate on canister surfaces at inland sites, where it is an important atmospheric aerosol.

It is important to recognize that ammonium chloride and ammonium nitrate will not persist on storage canisters at elevated temperatures, but the real goal of these experiments is to evaluate if chloride deposited as a different chloride salt at an inland site—perhaps NaCl in road salt—can deliquesce to form a corrosive brine on storage canister surfaces. It seems likely that this can only occur if the rate of nitrate and chloride deposition exceeds the rate of ammonium deposition (as sulfate, nitrate, or chloride), because once deliquescence occurs, the resulting brine will degas ammonia and chloride/nitrate until one or the other is consumed. Given that ammonium sulfate is the most abundant salt in inland aerosols and sulfate does not degas, it seems likely that ammonium will the component in excess, and chloride-rich brines will not form. Planned degassing experiments will evaluate the degassing of mixed salt assemblages to test this hypothesis. Additional experiments will evaluate the stability of sea salts, concentrating on potential reactions that convert magnesium chloride to less deliquescent salts.

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