

## **Stress Corrosion Cracking of Type 304 Stainless Steel Exposed to Atmospheric Ammonium Nitrate and Sodium Chloride Mixtures**

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### **ABSTRACT**

In the United States, some spent nuclear fuel is stored in dry cask storage systems. Most dry storage systems use canisters fabricated from austenitic stainless steel. Canisters are exposed to the ambient atmosphere and literature data indicate that near regions of industrial, commercial, or agricultural activities, abundant airborne particulates may include sulfate, nitrate, and ammonium as well as a smaller amount of chloride. This study evaluated the stress corrosion cracking (SCC) susceptibility of as-received and sensitized Type 304 stainless steel exposed to ammonium nitrate mixed with sodium chloride salts. SCC tests were conducted at 45 °C-44% relative humidity using U-bend specimens coated with salt mixtures of ammonium nitrate and sodium chloride with mole ratios of 3 and 6. After a period of exposure of 1.5 months, examination of specimens showed that severe SCC occurred. The SCC severity is greater for specimens coated with ammonium nitrate and sodium chloride at mole ratio of 3. Previous work under this program showed that no SCC was observed on specimens exposed only to ammonium nitrate. The results indicate that chloride has a large effect on SCC initiation and nitrate did not inhibit SCC at the tested nitrate to chloride mixture mole ratios.

*Keywords: Type 304 stainless steel, stress corrosion cracking, U-bend, ammonium nitrate and sodium chloride mixture*

## INTRODUCTION

In the United States, some spent nuclear fuel is stored in dry cask storage systems (DCSS). Most DCSS designs use canisters fabricated from austenitic stainless steel, including Types 304, 304L, and 316L stainless steel.<sup>1,2</sup> The canisters are placed either horizontally or vertically inside a metal or concrete shielding structure with vents to allow airflow for cooling. Canisters may be exposed to airborne species that enter through the vents and deposit on the surface. A brine could then form by the process of deliquescence in high-humidity conditions. NRC has investigated whether austenitic stainless steel is susceptible to stress corrosion cracking (SCC) when exposed to deliquescent brines, given residual stresses that may be present at canister welds.<sup>3,4</sup> In previous work,<sup>3,4</sup> airborne species were generally categorized as being chloride-rich, for instance being representative of coastal regions near saltwater bodies, or as non-chloride, for instance being representative of regions where there is industrial, agricultural, or commercial activity. For SCC tests, simulated sea salt was selected to represent chloride-rich species, while ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>), and mixtures of NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> were selected to represent non-chloride salts, based on a literature review indicating that ammonium, nitrate, and sulfate are abundant species in airborne particulates. Crack initiation was observed for Type 304 stainless steel specimens exposed to deliquescent brines of simulated sea salt in the temperature range of 35 to 80 °C, even at relatively small salt quantities.<sup>3</sup> However, SCC initiation was not observed for Type 304 stainless steel exposed to deliquescent brines of the non-chloride species, even at much higher salt quantities.<sup>4</sup> Given that at some locations, spent fuel canisters may be exposed to chloride-rich salts or various non-chloride salts containing a small amount of chloride, additional SCC tests have been conducted using mixtures of these species, which are the subject of the present paper.

The majority of inorganic chlorine in the Earth's troposphere is found as chloride contained in sea salt aerosol generated from ocean–wind and ocean–turf interactions.<sup>5</sup> Recent studies indicate that sea salt aerosol can be transported to interior North America more than 1,000 km from any ocean water.<sup>5</sup> Another natural source of inorganic chlorine is particulate chloride contained in wind-blown soils from arid regions and hydrochloric acid (HCl) from active volcanoes. Anthropogenic sources of inorganic chlorine include biomass burning, agricultural burning, coal/wood combustions, wildfires, diesel exhaust, and waste incineration.<sup>6,7,8</sup> The principal chlorine-containing byproduct of these activities is HCl or particulate chloride.<sup>9,10</sup> Table 1 lists the global sources of tropospheric HCl. HCl can react with ammonia to produce NH<sub>4</sub>Cl (solid), which can accumulate in atmospheric particulate matter.

Source	Amount (Teragram Chloride/Year)
Dechlorination of Sea Salt Aerosols	50 ± 20
Via Acid Displacement	7.6
Coal Combustion	4.6 ± 4.3
Waste Burning	2 ± 1.9
Volcanoes	0.4–11
Biomass Burning	<6
Transport From the Stratosphere	0.3
Chlorocarbon Oxidation	~4.2

\*Sanhueza, E. "Hydrochloric Acid From Chlorocarbons: A Significant Global Source of Background Rain Acidity." *Tellus B*. Vol. 53. pp. 122–132. 2001.

To define the NO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>/Cl<sup>-</sup> mole ratios, the measured composition of particulate matter at five noncoastal sites monitored by the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network were downloaded from the IMPROVE database.<sup>11</sup> The IMPROVE network measures the concentrations of major components of atmospheric particulate matter at more than 160

sites throughout the United States. Figure 1 shows the locations of the IMPROVE monitoring sites (as of 2002) and the five sites selected are (i) Arendtsville, Pennsylvania; (ii) Bondville, Illinois; (iii) Great River Bluffs, Minnesota; (iv) Great Smoky Mountains National Park, Tennessee; and (v) Phoenix, Arizona. The five sites were selected to represent different, inland geographic regions of the United States.



**Figure 1: Locations of Monitoring Sites in the IMPROVE Network.<sup>11</sup> Arrows Show the Sites Selected for Determining Mole Ratios of  $\text{NO}_3^-/\text{Cl}^-$  and  $\text{SO}_4^{2-}/\text{Cl}^-$ : (i) Arendtsville, Pennsylvania; (ii) Bondville, Illinois; (iii) Great River Bluffs, Minnesota; (iv) Great Smoky Mountains National Park, Tennessee; and (v) Phoenix, Arizona.**

Table 2 lists the range and median values of the nitrate, sulfate, and chloride concentrations in fine particulates measured at the five sites during the period January 1, 2009, to December 31, 2010. Table 3 lists the mole ratios of nitrate to chloride, sulfate to chloride, and sulfate to nitrate calculated from the median concentrations given in Table 2. SCC tests were conducted only for a nitrate and chloride salt mixture because of interest in the potential inhibiting effects of nitrate. From the data in Table 3, the calculated  $\text{NO}_3^-/\text{Cl}^-$  mole ratios for the five sites are 2.6, 5.8, 12.1, 12.2, and 21.1. It was thought that a lower  $\text{NO}_3^-/\text{Cl}^-$  mole ratio would be more likely to cause cracking because of a relatively more abundant quantity of chloride. Therefore,  $\text{NO}_3^-/\text{Cl}^-$  mole ratios of 3.0 and 6.0 were selected for the SCC tests.

<b>Table 2. Nitrate, Sulfate, and Chloride Concentration in Fine Particulate Matter Collected at Five IMPROVE Monitoring Sites*</b>			
<b>Site Location</b>	<b><math>\text{NO}_3^-</math> Concentration Median and Range (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b><math>\text{SO}_4^{2-}</math> Concentration Median and Range (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b><math>\text{Cl}^-</math> Concentration Median and Range (<math>\mu\text{g}/\text{m}^3</math>)</b>
Arendtsville, Pennsylvania	0.53 (0.053 to 8.300)	2.27 (0.366 - 15.267)	0.025 (0.0002 to 0.3252)
Bondville, Illinois	1.16 (0.0662 to 8.919)	2.05 (0.4084 to 9.0997)	0.032 (0.0006 to 0.2855)
Great River Bluffs, Minnesota	0.49 (0.0145 to 16.11)	1.14 (0.1649 to 8.3342)	0.0229 (0.0001 to 0.61)
Great Smoky Mountains National Park, Tennessee	0.15 (0.0382 to 4.5818)	2.05 (0.1252 to 7.0209)	0.0145 (0.0007 to 0.17)
Phoenix, Arizona	0.38 (0.0638 to 5.9663)	0.78 (0.1761 to 8.3342)	0.0841 (0.0028 to 1.096)

\*IMPROVE. "Metadata Browser." Fort Collins, Colorado: Interagency Monitoring of Protected Visual Environments. 2013. <<http://vista.cira.colostate.edu/improve/Web/MetadataBrowser/metadatabrowser.aspx>> (January 10, 2013). Negative values in the database were excluded.

Site Location	NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup> Mole Ratio	SO <sub>4</sub> <sup>2-</sup> /Cl <sup>-</sup> Mole Ratio	SO <sub>4</sub> <sup>2-</sup> /NO <sub>3</sub> <sup>-</sup> Mole Ratio
Arendtsville, Pennsylvania	12.1	33.1	2.7
Bondville, Illinois	21.1	24.0	1.1
Great River Bluffs, Minnesota	12.2	18.3	1.5
Great Smoky Mountains National Park, Tennessee	5.8	52.2	8.9
Phoenix, Arizona	2.6	3.4	1.3

\*Based on median NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup> aerosol concentration listed in Table 2.  
 IMPROVE. "Metadata Browser." Fort Collins, Colorado: Interagency Monitoring of Protected Visual Environments. 2013.  
 <<http://vista.cira.colostate.edu/improve/Web/MetadataBrowser/metadatabrowser.aspx>>  
 (January 10, 2013).

## EXPERIMENTAL APPROACHES

Deliquescence and efflorescence tests were conducted to determine the temperature and humidity conditions at which the salt mixtures would deliquesce. The general approach for the stress corrosion cracking tests was to deposit pre-stressed austenitic stainless steel specimens with salts, then to expose those specimens in controlled temperature and humidity conditions for a period of weeks to months, after which they were examined for evidence of SCC initiation.

### Deliquescence and Efflorescence Tests

To understand the deliquescence behavior of the salt mixture, the deliquescence and efflorescence at 45 °C of NH<sub>4</sub>NO<sub>3</sub> and NaCl pure salts and mixtures of NH<sub>4</sub>NO<sub>3</sub> and NaCl were measured using beakers. Glass beakers containing the salt or salt mixture were placed inside the temperature–relative humidity (RH)–controlled chamber. The RH was incrementally increased to observe for evidence of water absorption by deliquescence, and then decreased to observe the drying of the salt by efflorescence. For the deliquescence and efflorescence tests at 45 °C, the RH was started from 10% and increased to 59% at 3% intervals, then subsequently decreased to 10% RH. The beakers were photographed after stabilization at each RH. The wetness or presence of liquid water by visual observation in the beaker indicates the absorption of moisture or deliquescence by the salt.

### Type 304 Stainless Steel and U-Bend Specimens

SCC tests were conducted using U-bend specimens of as-received and furnace sensitized Type 304 austenitic stainless steel. As-received material was selected to represent a typical base metal, while the furnace sensitized material was intended to represent the weld heat affected zone at the canister welds. The sensitization was conducted in a furnace open to air at 650 °C for 2 hours. The chemical composition of the as-received and sensitized specimens is shown in Table 4.

Material	C	S	Mn	P	Si	Cr	Mo	Ni	Cu	N	Fe
Type 304	0.046	0.003	1.06	0.021	0.5	18.41	0.01	8.23	0.04	0.050	Bal
Bal=Balance											

For both as-received and sensitized conditions, the U-bend specimens were fabricated in the same way as described in a previous paper.<sup>3</sup> Flat specimens were cut from sheet material, then polished to 320 grit before bending 180 degrees around a 1.90-cm diameter mandrill, in accordance with the ASTM G30–97, "Standard Practice for Making and Using U-Bend Stress-Corrosion Test Specimens."<sup>12</sup> The U-bend specimens were kept in the mandrill under stress while the Alloy C–276 stressing elements

were tightened to maintain specimen displacement. Each U-bend specimen was inspected using a microscope after bending to ensure that no cracks or fissures were present in the test specimen initially. The strain of the current U-bends calculated from ASTM G30–97<sup>12</sup> was 16.7 percent. It is uncertain whether this is representative of the material strain in the canisters, even at the welds. Because of this uncertainty, another series of tests were performed using C-ring specimens in which the strain was manually adjusted to set at a lower level than represented by the U-bend specimens. The results from the C-ring specimens are presented in another paper<sup>13</sup> under this test program.

#### U-Bend Specimen Salt Deposition

The SCC test protocol involved the deposition of salt mixtures onto the U-bend specimens prior to exposing them in environmental chambers.  $\text{NH}_4\text{NO}_3$  and  $\text{NaCl}$  salts were used to prepare the salt mixtures with  $\text{NO}_3^-/\text{Cl}^-$  mole ratios of 3.0 and 6.0. The dry salts were weighed and pre-mixed to make homogeneous solutions to ensure all the species are in intimate contact during drying and deliquescence. Specimens were deposited with salts prior to exposure rather than during test (e.g., by aerosol fog) to ensure that SCC would only be caused by the deliquescence of the already-present salt. Salts were deposited using spray bottles with specific solutions prepared from  $\text{NH}_4\text{NO}_3$  and  $\text{NaCl}$ . The solution compositions for the spray are shown in Table 5. Before depositing the salts, the U-bend specimens were preheated to 90 °C in an oven for at least 15 minutes. The salts were deposited by applying 10 squirts of the solution from a spray bottle and allowing the solution to evaporate for 5 minutes. The salt application was repeated 8 to 10 times. The surface salt amount on the U-bend specimens was determined by weighing a control  $2.5 \times 7.5\text{-cm}^2$  flat specimen before and after salt was deposited. In this manner, the estimated loading amounts per unit area on the specimens are shown in Table 6. Based on the molar ratio and the amount of total salt deposited, the  $\text{NaCl}$  loading amount per unit area was calculated to be between 5 and 8  $\text{g/m}^2$ , as shown in Table 6. This chloride amount is near the 10  $\text{g/m}^2$  simulated sea salt used in previous work focusing on chloride-rich salts.<sup>3</sup> Some specimens were microscopically examined after salt deposition but before environmental exposure. There were some stains on the surface, but no cracks were observed on any specimen surface.

Spray Solution for Salt Deposition			Calculated Deliquescence Brine pH at 45 °C and 44% RH
Composition	Measured pH at 20 °C	Calculated pH	
5 m $\text{NaCl}$ + 15 m $\text{NH}_4\text{NO}_3$ ( $\text{NO}_3^-/\text{Cl}^- = 3.0$ )	3.91	3.91	3.43
3 m $\text{NaCl}$ + 18 m $\text{NH}_4\text{NO}_3$ ( $\text{NO}_3^-/\text{Cl}^- = 6.0$ )	3.93	3.98	3.50

Specimen Type	Molar Ratio of $\text{NH}_4\text{NO}_3$ to $\text{NaCl}$	Amount of $\text{NH}_4\text{NO}_3$ and $\text{NaCl}$ Deposited ( $\text{g/m}^2$ )	Calculated Amount of $\text{NaCl}$ Deposited ( $\text{g/m}^2$ )
As-Received	3	54	6.4
	6	74	4.9
Sensitized	3	62	7.4
	6	83	5.5

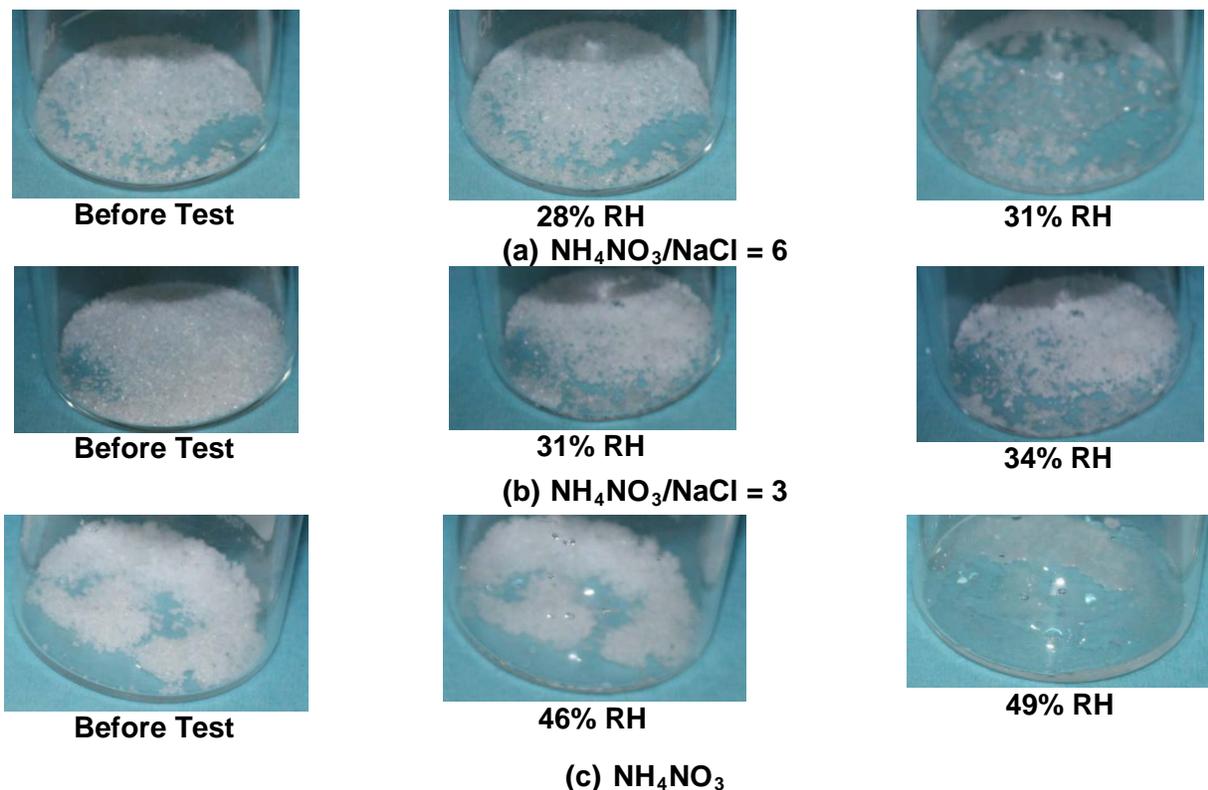
## Stress Corrosion Cracking Tests

For SCC testing, the U-bend specimens were exposed in environmental chambers at the temperature of 45 °C and relative humidity of 44% (approximately 30 g/m<sup>3</sup> absolute humidity). After the period of exposure, the specimens were removed from the test chambers to examine for visual and microscopic examination. The specimens were photographed, rinsed with deionized water, and dried with acetone or isopropyl alcohol. The surface of the apex on the U-bend specimen was first examined using a stereomicroscope with 50 to 1,000x magnification. If cracks were clearly observed from the surface, then the specimen examination was complete. For some specimens where cracking was not clearly visible on the surface, the region around the apex was cross sectioned into three to four pieces. The cross section was mounted in resin and polished to 1 μm for examination of cracking under the stereomicroscope with at least 50 to 1,000x magnification.

## RESULTS

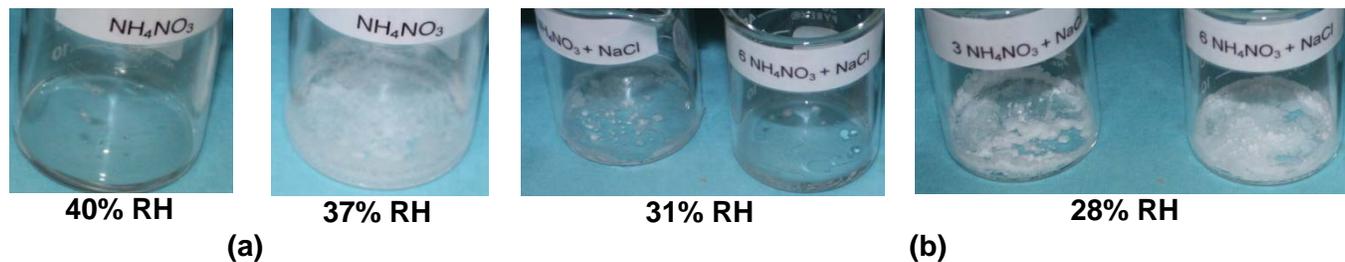
### Deliquescence and Efflorescence Tests at 45 °C

Figure 2 shows the beakers at several RHs where deliquescence was observed. Mixtures of NH<sub>4</sub>NO<sub>3</sub> and NaCl, with NO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> mole ratios of 3.0 and 6.0, deliquesced at 31% and 34% RH, respectively, as indicated by the wetness of the salt and the presence of liquid in the beakers. Pure NH<sub>4</sub>NO<sub>3</sub> deliquesced at 49% RH. Deliquescence was not observed for NaCl up to 59% RH, so photographs are not shown.



**Figure 2. Observation From Beakers at 45 °C for Deliquescence Tests at Increasing Relative Humidity: (a) NH<sub>4</sub>NO<sub>3</sub>/NaCl = 6, (b) NH<sub>4</sub>NO<sub>3</sub>/NaCl = 3, and (c) NH<sub>4</sub>NO<sub>3</sub>**

Figure 3 shows the beakers in the process of decreasing RH for efflorescence test.  $\text{NH}_4\text{NO}_3$  and the two mixtures effloresced at 37 and 28% RH, respectively. This suggests that the efflorescence relative humidity (ERH) of  $\text{NH}_4\text{NO}_3$  and NaCl mixtures is lower than that of  $\text{NH}_4\text{NO}_3$ , which is consistent with the deliquescence test.

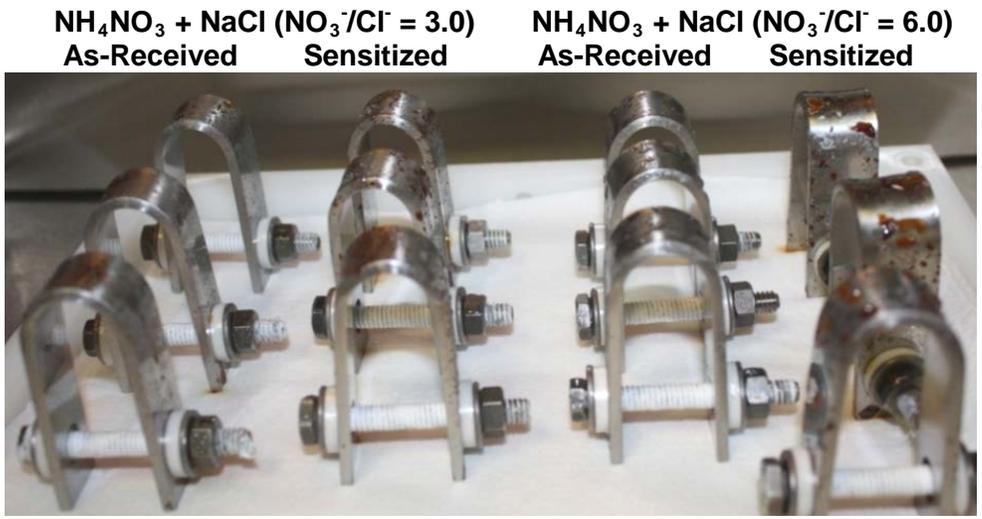


**Figure 3: Observation From Beakers at 45 °C for Efflorescence Tests at Decreasing Relative Humidity: (a)  $\text{NH}_4\text{NO}_3$  and (b) Mixtures  $\text{NH}_4\text{NO}_3/\text{NaCl} = 3$  and 6**

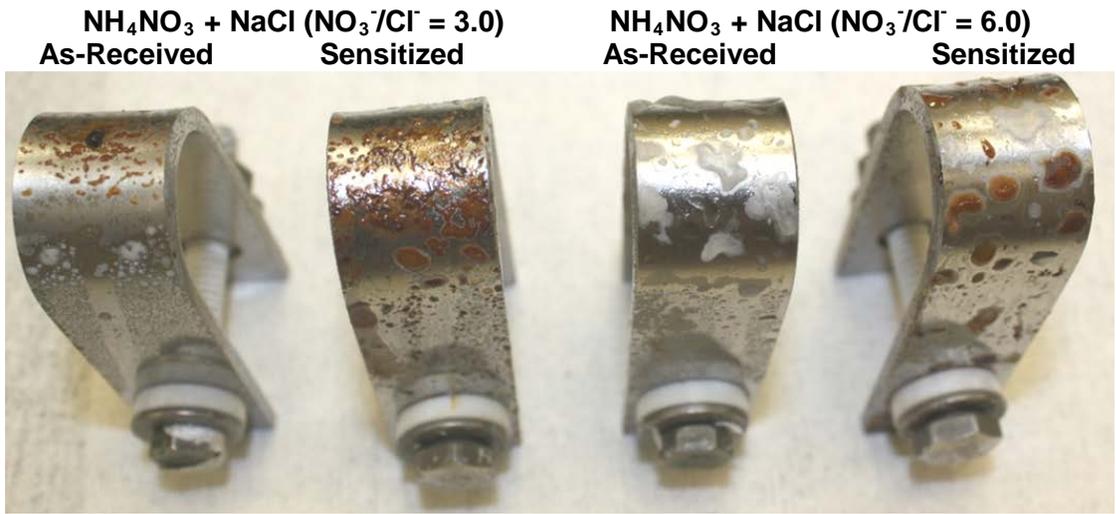
### Stress Corrosion Cracking tests

One as-received and one sensitized U-bend specimens were removed from the test chamber for each salt mixture after 47 days of exposure. Figure 4 shows the photos of all the specimens at 47 days and the four specimens removed from the chamber. Pitting corrosion was observed on all specimens, with large pits at the apex and more pits on the sensitized specimens compared to the as-received specimens. Extensive cracking was observed on the surface of the sensitized specimens from both tested solutions. Cracks were also observed from the cross section of the two sensitized specimens, as shown in Figure 5 for both mixture compositions, but not from the as-received specimens. The cracks appear to be intergranular. Because both sensitized specimens showed SCC-induced cracks, all the remaining sensitized specimens were removed from the chamber after a test duration of 8 weeks. The remaining as-received specimens were kept in the chamber for a 4-month duration as discussed later in this paper. The images of the sensitized specimens exposed for 8 weeks are shown in Figure 6. SCC is clearly evident on the surface. One specimen deposited with  $\text{NH}_4\text{NO}_3$  and NaCl salt mixture with  $\text{NO}_3^-/\text{Cl}^-$  mole ratio of 3.0 had a complete through-wall crack, as shown in Figure 6(a).

The remaining four as-received specimens were removed after a 4-month exposure at 45 °C and 44% RH. The images are shown in Figure 7. Pitting corrosion occurred on all of the specimens, but the specimens deposited with  $\text{NH}_4\text{NO}_3$  and NaCl salt mixture with  $\text{NO}_3^-/\text{Cl}^-$  mole ratio of 3.0 had more pits than those with the 6.0 ratio. Microscopic examination showed that SCC is clearly evident on the specimens deposited with a  $\text{NH}_4\text{NO}_3$  and NaCl salt mixture with a  $\text{NO}_3^-/\text{Cl}^-$  mole ratio of 3.0 [Figure 7(a)]. The specimens deposited with the  $\text{NH}_4\text{NO}_3$  and NaCl salt mixture with a  $\text{NO}_3^-/\text{Cl}^-$  mole ratio of 6.0 appear to show SCC initiation, as depicted in several images in Figure 7(b), but the crack features were located away from the apex and near the arc-to-leg transition area of the U-bend. The specimens were not cross sectioned for further examination, because the pitting on the specimens was very small and it would be very difficult to capture the small pits with a cross section.

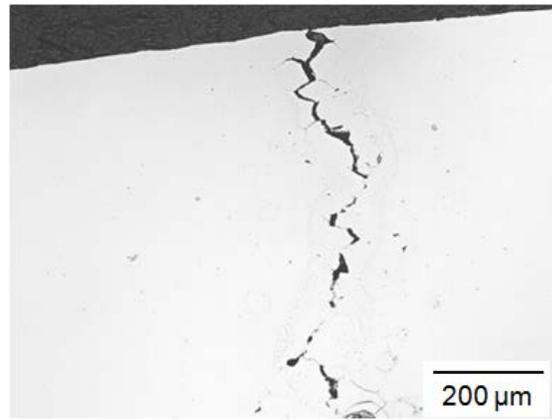
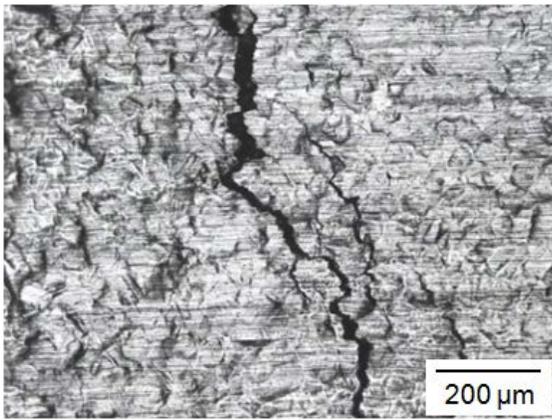


(a)

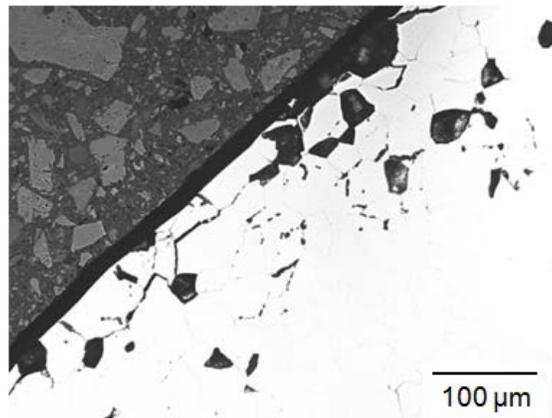
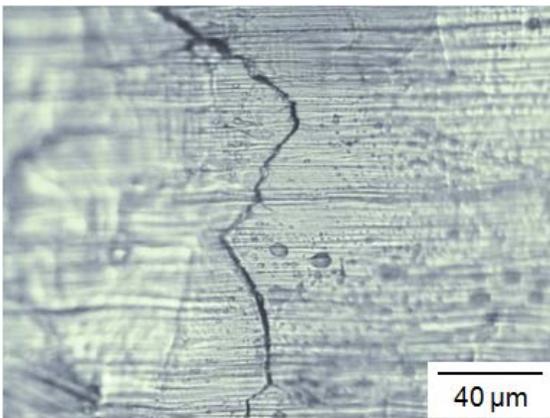


(b)

**Figure 4: (a) All Test Specimens after Exposure for 47 Days at 45 °C and 44% Relative Humidity and (b) Four Specimens After Exposure Removed from Chamber after 47 Days**



(a)



(b)

**Figure 5: Micrographs of Cracks Observed From Surface (left in figure) and Cross Section (right in figure) of Sensitized Specimens Deposited With (a)  $\text{NH}_4\text{NO}_3$  and NaCl Mixture ( $\text{NO}_3^-/\text{Cl}^- = 3.0$ ) and (b)  $\text{NH}_4\text{NO}_3$  and NaCl Mixture ( $\text{NO}_3^-/\text{Cl}^- = 6.0$ ) After Exposure at 45 °C and 44% Relative Humidity for 47 Days**

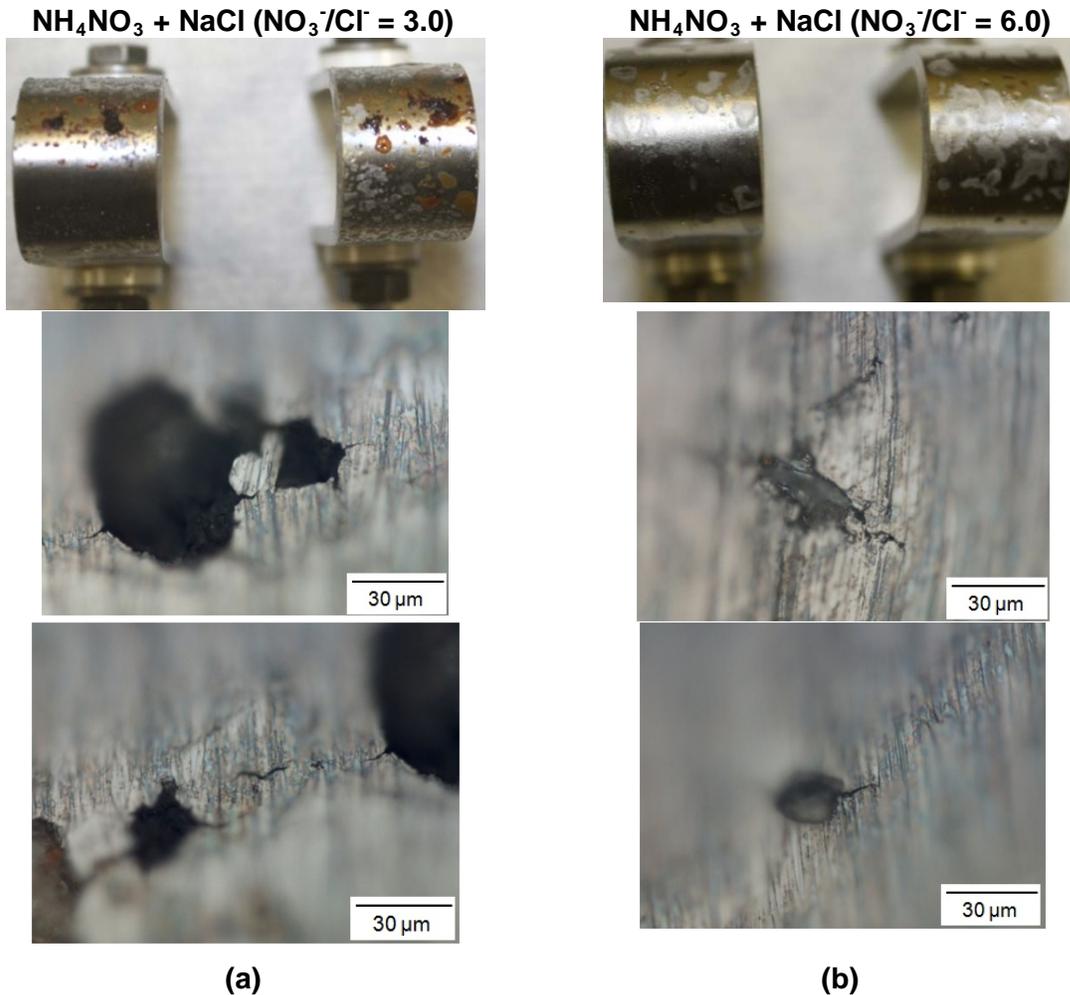
**$\text{NH}_4\text{NO}_3 + \text{NaCl}$  ( $\text{NO}_3^-/\text{Cl}^- = 3.0$ )**



**$\text{NH}_4\text{NO}_3 + \text{NaCl}$  ( $\text{NO}_3^-/\text{Cl}^- = 6.0$ )**



**Figure 6: Photographs of Sensitized Specimens Deposited With  $\text{NH}_4\text{NO}_3$ , NaCl Mixture ( $\text{NO}_3^-/\text{Cl}^- = 3.0$ ),  $\text{NH}_4\text{NO}_3$ , and NaCl Mixture ( $\text{NO}_3^-/\text{Cl}^- = 6.0$ ) Exposed at 45 °C and 44% Relative Humidity for 8 Weeks**



**Figure 7: Photographs and Micrographs of As-Received Specimens Deposited With (a)  $\text{NH}_4\text{NO}_3$  and  $\text{NaCl}$  Mixture ( $\text{NO}_3^-/\text{Cl}^- = 3.0$ ) and (b)  $\text{NH}_4\text{NO}_3$  and  $\text{NaCl}$  Mixture ( $\text{NO}_3^-/\text{Cl}^- = 6.0$ ) After a 4-Month Period of Exposure at 45 °C and 44% Relative Humidity**

## DISCUSSION

Previous work<sup>3</sup> showed that SCC initiation did not occur on Type 304 stainless steel U-bend specimens exposed only to  $\text{NH}_4\text{NO}_3$ . For tests in salt mixtures of  $\text{NH}_4\text{NO}_3$  and  $\text{NaCl}$ , with  $\text{NO}_3^-/\text{Cl}^-$  mole ratios of 3.0 and 6.0, however, SCC initiation was clearly observed in both compositions. The results suggest that the presence of chloride has a large effect on SCC susceptibility, which is expected based on various literature studies.<sup>14,15,16</sup> However, in published literature, nitrate has been shown to inhibit localized corrosion, including SCC, of stainless steels in chloride-containing solution. Brossia and Kelly<sup>17</sup> reported that both nitrate and sulfate inhibit crevice corrosion of Types 304 and 316 stainless steels. Uhlig and Gilman<sup>18</sup> reported that pitting of 18-8 stainless steel is inhibited by nitrate in ferric chloride solutions. El Dahan<sup>19,20</sup> reported that nitrate inhibited pitting corrosion of 316 stainless steel in phosphoric acid-chloride solutions at a concentration of 500 ppm in 30%  $\text{H}_3\text{PO}_4$  containing 15,000 ppm  $\text{Cl}^-$ ; this was accomplished by the ability of nitrate to be adsorbed on the electrode and to displace the aggressive ions from the surface, where the nitrate-to-chloride ratio is about 0.03. Tong and Swartz<sup>21</sup> reported that nitrate inhibits pitting and SCC for Type 316 stainless steel at the investigated concentration of 700 ppm in 35%  $(\text{NH}_4)_2\text{SO}_4$  solution containing 700 ppm chloride, where the ratio of

nitrate to chloride is 1. Uhlig and Cook<sup>22</sup> found that nitrate inhibits SCC of 18-8 stainless steel in MgCl<sub>2</sub> solution at 130 °C in the concentration of several percent.

The inhibiting effects of nitrate reported in the literature appear to conflict with the results of the tests observed in this work. The reported inhibiting concentration of nitrate in the literature is lower than the NO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> mole ratios of 3.0 and 6.0 used in this work. However, as mentioned previously, the inhibiting effect of nitrate on SCC reported in the literature was observed under immersion conditions. In contrast, in this work, SCC would be caused by deliquescent brines. During the test, it was observed that the salt mixture deliquesced without NaCl solid evident on the surface even though the test was conducted at an RH below the NaCl deliquescence RH (DRH). This suggests that the chloride was dissolved in the deliquescence solution.

Table 7 summarizes the measured DRH and ERH values shown in Figures 2 and 3 and the DRHs calculated using OLIAnalyzer Studio<sup>23</sup>. The data clearly show that the DRH of NH<sub>4</sub>NO<sub>3</sub> and NaCl mixtures is lower than either of the pure NH<sub>4</sub>NO<sub>3</sub> and NaCl constituents, which is consistent with the observation from the SCC tests. The beaker tests clearly show that the DRH of NH<sub>4</sub>NO<sub>3</sub> and NaCl mixtures is lower than either of the pure NH<sub>4</sub>NO<sub>3</sub> and NaCl constituents. Literature reports describe a deliquescence lowering effect for multicomponent mixtures. Based on the solution thermodynamic theory, it has been shown that the DRH of a multicomponent mixture is lower than the minimum DRH of each component.<sup>24,25,26</sup> This minimum RH is known as mutual DRH (MDRH) and “eutonic point”,<sup>27</sup> at which the mixture has a composition that minimizes water activity, thus it is thermodynamically favored. At the MDRH the aqueous phase is saturated with respect to all the salts. The MDRH has been demonstrated in numerous systems such as the atmospheric aerosols<sup>28</sup> and pharmaceutical systems.<sup>29</sup>

<b>Table 7. Measured and Calculated Deliquescence Relative Humidity and Efflorescence Relative Humidity of NH<sub>4</sub>NO<sub>3</sub> NaCl Pure Salts, and Mixtures of NH<sub>4</sub>NO<sub>3</sub> and NaCl at 45 °C</b>				
<b>Pure Salts and Salt Mixture</b>	<b>NH<sub>4</sub>NO<sub>3</sub></b>	<b>NaCl</b>	<b>NH<sub>4</sub>NO<sub>3</sub>/NaCl Mole Ratio</b>	
			<b>3</b>	<b>6</b>
Calculated DRH, %	50	75	35	35
DRH by Beaker, %	49	>59	34	31
ERH by Beaker, %	37	N/A	28	28
DRH = deliquescence relative humidity ERH = efflorescence relative humidity RH = relative humidity				

The measured DRH values are close to the calculated for the pure salt and salt mixtures. In addition to the lower DRH of the salt mixtures, the deliquescence brine solution would have low pH, which is calculated to be 3.43 and 3.5 at 45 °C using OLIAnalyzer Studio<sup>23</sup> for the salt mixture with mole ratios of 3 and 6, respectively. The pH values were included in Table 5. The pH is slightly lower compared to the spray solution. The low pH and DRH of salt mixtures could explain the occurrence of SCC at the tested conditions and the increase in extent of corrosion with chloride concentration observed in this study.

## SUMMARY

SCC tests were performed to evaluate the susceptibility of Type 304 stainless steel to SCC initiation caused by deliquescence of mixtures of NH<sub>4</sub>NO<sub>3</sub> and NaCl. In previous tests, SCC initiation was not observed on specimens exposed only to NH<sub>4</sub>NO<sub>3</sub>, but in this study, cracking was observed for specimens exposed to the mixtures with NO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> mole ratios of 3.0 and 6.0. The extent of SCC appeared to be higher at the higher chloride concentration. The results indicate that chloride has a

large effect on SCC susceptibility and that the presence of nitrate did not inhibit SCC at the tested  $\text{NO}_3^-/\text{Cl}^-$  mole ratios. SCC of Type 304 stainless steel in nitrate-chloride mixtures could be attributed to the low pH and dissolution of chloride in the deliquescence solution.

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