Coastal Salt Effects on the Stress Corrosion Cracking of Type 304 Stainless Steel

Todd S. Mintz
Southwest Research Institute[®]
6620 Culebra Road
San Antonio, Texas 78238-5166
U.S.A

Xihua He
Southwest Research Institute[®]
6620 Culebra Road
San Antonio, Texas 78238-5166
U.S.A

Larry Miller
Southwest Research Institute[®]
6620 Culebra Road
San Antonio, Texas 78238-5166
U.S.A

Roberto Pabalan
Southwest Research Institute[®]
6620 Culebra Road
San Antonio, Texas 78238-5166
U.S.A

Yi-Ming Pan
Southwest Research Institute[®]
6620 Culebra Road
San Antonio, Texas 78238-5166
U.S.A

Leonardo Caseres
Southwest Research Institute[®]
6620 Culebra Road
San Antonio, Texas 78238-5166
U.S.A

Greg Oberson
U.S. Nuclear Regulatory Commission
Two White Flint North
11545 Rockville Pike
Washington, DC 20555
U.S.A

Darrell Dunn
U.S. Nuclear Regulatory Commission
Two White Flint North
11545 Rockville Pike
Washington, DC 20555
U.S.A

ABSTRACT

Some U.S. nuclear power plants are storing spent nuclear fuel in dry cask storage systems (DCSS). In many cases, the DCSS consists of a metal storage canister inside a concrete vault or overpack for radiation shielding. Most canisters are made of austenitic stainless steel, including UNS S30400 (304 SS). The concrete vault or overpack is vented to the atmosphere for passive cooling, allowing interaction between the canister and the ambient environment. In coastal environments, airborne salts could deposit and accumulate on the surface of the canisters over time. Deliquescence of these salts in a humid environment could create a chloride-rich brine on the canister surface. This, in addition to the presence of residual tensile stresses, could make the canister susceptible to chloride-induced stress corrosion cracking.

The objective of this work is to evaluate how salt concentration, temperature, and relative humidity affect stress corrosion cracking initiation for austenitic SS used for dry storage canisters. To that end, simulated sea salt in quantities between 0.1 and 10 g/m^2 was deposited on the surface of type 304 SS U-bend specimens. Three material conditions were used in this evaluation: as-received, sensitized, and welded with type 308 SS filler metal. Once the salt was deposited, the specimens were exposed to a range of temperatures and both cyclic and static humidity conditions to examine crack initiation. The results indicate that both as-received and sensitized 304SS are susceptible to crack initiation at all salt concentrations from 0.1 to 10 g/m^2, and that cracks initiate at temperatures between 35 and 80 °C.

Keywords: Stress Corrosion Cracking, Atmospheric Corrosion, Stainless Steel, Dry Storage Containers, Dry Cask Storage, Spent Nuclear Fuel

INTRODUCTION

At a number of operating and decommissioned nuclear reactor sites in the U.S., the U.S. Nuclear Regulatory Commission[1] (NRC) has issued licenses for independent spent fuel storage installations (ISFSIs). At the ISFSIs, spent fuel removed from the reactor may be placed into dry cask storage systems (DCCS) after cooling for several years in the spent fuel pool. The spent fuel is typically confined in canisters fabricated from austenitic stainless steel (SS) of the types UNS S30400 (304 SS), UNS S30403 (304L SS), or UNS S31603 (316L SS).[1,2] The steel canister is in turn emplaced in a concrete or metal overpack or vault for radiation shielding and physical protection. The overpack or vault is vented to the ambient external environment to allow airflow for passive cooling. Inspections of DCCS have shown evidence of water intrusion and dust or particulate matter on the canister surfaces.[3]

Some ISFSI sites are located in areas where the atmosphere could contain a relatively high concentration of airborne chloride-rich salts, including coastal regions, near salted roads, or near cooling towers.[4] Salts could deposit on the spent fuel canister surface via the external vents. Further, it is expected that residual tensile stresses on the canister from welding or other fabrication activities could be relatively high. It is known that in certain conditions, austenitic SS materials under tensile stress are susceptible to chloride-induced stress corrosion cracking (SCC).[5,6,7] Such occurrences have been reported for external tanks and piping systems at a number of nuclear power plant sites near the ocean. SCC could affect the function of dry storage canisters by allowing leakage of radionuclides through a confinement barrier or by compromising structural integrity. Given this concern, NRC has undertaken research projects to better understand the conditions that could lead to SCC initiation.

In a previous scoping study, 304, 304L, and 316L SS U-bend specimens deposited with simulated sea salt were observed to undergo SCC at a temperature of roughly 45 °C while cracking was not observed at either 85 °C or 120 °C. [8,9] It was determined from these tests that the SCC susceptibility of the stainless steel samples was related to the deliquescence of the deposited simulated sea salt. The deliquescence of the deposited salt is dependent upon the relative humidity at the surface of the sample. The testing also showed that the relative humidity at the surface of the sample is not the same as the bulk environment relative humidity, but rather the absolute humidity (dependent upon both the relative humidity and temperature) at the surface of the sample was the same as the bulk absolute humidity. The bulk absolute humidity in these previous tests was measured to be roughly 65 g/m^3. At an absolute humidity of 65 g/m^3, the relative humidity at the surface of the 45, 85, and 120 °C samples is calculated to be roughly 99, 18, and 6 percent respectively. The main components of sea salt are

sodium chloride and magnesium chloride which have deliquescence points at a relative humidity of roughly at 70 and 30 percent (dependent upon temperature), respectively. Due to the lower relative humidity at the surface of the 85 and 120 °C samples, no deliquescence could occur.

The applicability of scoping study test conditions to the actual condition of in-service canisters is uncertain. The tests used an absolute humidity of roughly 65 g/m^3, which is high compared to the natural environment humidity. A survey of absolute humidity measurements from coastal regions around the United States indicated a maximum of about 26 g/m^3.[8] In addition to this data, one of the highest recorded absolute humidity occurred in Sharjah, United Arab Emirates located on the western shore of the Persian Gulf.[10] The dew point was recorded as 34 °C [93.2 °F]. Depending upon the temperature, the absolute humidity would be around 35 g/m^3. Moreover, Japanese data for austenitic stainless steel indicated that SCC could initiate at surface chloride concentration as low as 0.3 g/m^2.[11] The scoping study used a significantly higher chloride concentration, approximately 20 g/m^2. While the actual salt deposition on in-service canisters has not been well-studied, it would be useful to know whether there is a minimum chloride concentration needed for SCC initiation.

Given the conservatisms associated with the scoping study, NRC is sponsoring a follow-on study to more systematically evaluate the parameters that could affect crack initiation, including temperature, humidity, salt content, and material condition. This paper presents some of the preliminary results.

EXPERIMENTAL PROCEDURE

Tests were conducted using welded and unwelded alloy 304 SS. Single U-bend samples were cut out of a 0.125 in (0.318 cm) thick alloy sheet with the sample length perpendicular to the rolling direction. The U-bend samples had dimensions of 5 in (12.7 cm) length and 0.75 in (1.9 cm) width. After cutting, some unwelded samples were sensitized in air at 650 °C for 2 hours to simulate the condition of the weld heat affected zone. The U-bend samples were bent around a 0.5 in (1.27 cm) diameter mandrill, following the procedures of ASTM[(2)] G30, "Standard Practice for Making and Using U-Bend Stress Corrosion Test Specimens."[12] The total strain on the outside of the U-bend specimen can be closely approximated as 17 percent. After bending, all samples were inspected to ensure no cracks or fissures were present prior to testing.

An ASME[(3)] Code Section IX qualified welder and procedure were used to prepare the welded specimens.[13] Welding of specimens was performed using a gas tungsten arc welding process. The weld was roughly 0.64 cm [0.25 in] wide and the welded U-bends had the same dimensions as the other U-bend samples. All welds were examined using radiographic testing[14] in accordance with ASME Section III and the acceptance criteria in ASME Section III WB-5000. Materials that passed the ASME criteria were then machined into U-bend specimens with the weld located at the apex of the specimen, following ASTM G58 procedure.[15] Similar to the as-received specimens, each welded specimens was inspected after bending to ensure no cracks or fissures were present prior to testing.

Two different types of tests were conducted with the first being a cyclic humidity test. In the cyclic testing the specimens were mounted on cylindrical heaters and placed in the test chamber as has been described previously.[9] The full test matrix for the cyclic tests is shown in Table 1. The temperature set points for the specimens exposed to cyclic conditions included 35, 45, 52, and 60 °C. Specimens at 35 and 45 °C were examined after 1 and 4 month exposure periods. Some had only been examined after 1 month exposure. The 60 °C specimens are yet to be examined in later stages of this project.

Different surface concentrations of simulated sea salt were deposited on the U-bend specimens. Past work by Shirai et al. indicated that the threshold for SCC to initiate is expected to be between 0.3 and 10 g/m^2.[11] As such, the tests described in this paper included specimens deposited with 0.1, 1, and 10 g/m^2 in an attempt to bound these conditions. The deposition was accomplished by placing the specimens in a chamber that was fogged using simulated sea water prepared per ASTM D1141-98.[16] During the deposition, all the specimens were maintained at 90 °C. The deposition procedure is shown in Table 2. The surface concentration was adjusted by increasing or decreasing the exposure time in the simulated sea salt fog. Once the salt was deposited, the specimens were heated to the appropriate temperature and the cyclic test was conducted. The cyclic test consisted of a high humidity cycle followed by a dry cycle. The high humidity was obtained by flooding the bottom of the environmental chamber and submerging heaters. Once the heaters were submerged, they were turned on to increase the humidity. The exposure condition maintained the absolute humidity below 30 g/m^3.

The second type of testing was performed under static environmental conditions. U-bend specimens were deposited with salt under the same procedure as previously described. Once deposited with salt, the U-bend specimens were placed in an environmental chamber with a constant temperature and relative humidity. In the static tests, only one surface salt concentration of 10 g/m^2 was used. The static test matrix is shown in Table 3. As can be seen from Table 3, specimens were exposed to 45, 60, and 80 °C. As will be explained later, some of the exposure conditions had an absolute humidity that exceeded 30 g/m^3.

After both the cyclic and static testing, the specimens were removed and examined with a stereomicroscope with at least 50 to 1000x magnifications. For some of the specimens, if cracks were observed, the samples were polished and etched to identify the type of cracking.

RESULTS

Cyclic Humidity Tests with Varying Surface Salt Concentrations

The preliminary results for the cyclic humidity testing at various surface salt concentrations are shown in Figures 1 through 3. As can be seen by Figure 1, the specimens deposited with 10 g/m^2 were extremely susceptible to SCC. Specimens held at 35, 45, and 52 °C were all observed to undergo SCC. The cracks observed in the welded specimens did not occur in the welded material but in the base material away from the weld. SCC susceptibility appears to be greater for sensitized specimens than as-received, with the welded specimens appearing to be the least susceptible. While cracks were observed to occur as early as 1-month after exposure, the cracking was much more severe at 4-months exposure as can be seen in Figure 1.

Figure 2 provides the results for the U-bend specimens deposited with 1 g/m^2 simulated sea salt. As can be seen from the figure, the specimens were susceptible to cracking at both 35 and 45 °C. In addition, the figure seems to show that the sensitized specimens are more susceptible than the as-received specimens; however both specimens showed cracking at the two temperatures when exposed for 4 months.

Figure 3 shows the results for the U-bend specimens deposited with 0.1 g/m^2 surface salt. As can be seen from this figure, the sensitized specimens were susceptible to cracking at both 35 and 45 °C. For the as-received samples, only the 45 °C samples were observed to undergo cracking and not the 35 °C samples. SCC initiated after 4 months of exposure suggesting that the amount of salt appears to affect the crack initiation time.

Figure 4 provides images of 4-month exposed U-bend specimens with different amounts of deposited salt. As can be seen in Figures 4a and 4b, the 10 and 1 g/m^2 specimens have a whitish color given the

quantity of salt deposited on the surface. Further, pitting corrosion is clearly visible on those specimens, though cracks cannot be seen at this magnification. For the 0.1 g/m^2 specimens shown in Figure 4c, the surface appears to be nearly pristine as the quantity of salt is very low and there is little evidence of pitting. Photomicrographs of the specimen surfaces and cross-sections, however, show SCC initiation at all of the surface salt concentrations, including 0.1 g/m^2. Figure 5 shows cracks on the surface at the apex of the U-bend specimens. It appears that cracks tend to grow between pits. In some cases, the pitting on the surface of the samples may mask visual observation of cracks so cross-sectional imaging is preferable for identifying cracking. Figure 6 shows the cross-section image of various U-bend specimens. Figures 6a, 6b, and 6c show cross-section images of U-bend specimens that were etched to reveal the grain boundaries. As can be seen in these three images, the cracks appear to have both transgranular and intergranular features.

Constant Humidity Tests

The results for the U-bend samples held at 45 °C and 45 percent relative humidity are not shown in a figure because only one test was conducted at this condition. The results indicate that the 304SS specimens exhibited SCC initiation in the static environmental conditions, which is consistent with the results of the cyclic test. At this temperature, both sensitized and as-received specimens cracked. The cross-sectional images of the U-bend specimens are shown in Figure 7. Similar to the cyclic testing the cracks appear to be of mixed mode with both intergranular and transgranular features.

Figure 8 provides the preliminary results for the U-bend specimens held at 60 °C. The results indicate that the sensitized and as-received 304 SS exhibited SCC initiation at a relative humidity above 25 percent. After 1-month exposure to 60 °C and 22 percent relative humidity, not only were there no cracks, but there was no observable pitting either.

Figure 9 provides the preliminary results for the U-bend samples held at 80 °C. The results indicate that the sensitized and as-received 304SS samples are susceptible to SCC at a relative humidity at or above 35 percent.

The images of the SCC for the U-bend specimens held at 60 and 80°C with different relative humidity are shown in Figures 10 and 11, respectively.

DISCUSSION

One of the main results observed in the testing was that the susceptibility for SCC tended to increase with increasing relative humidity. This can be rationalized by examining Figure 12, which is a plot of relative humidity versus temperature with constant absolute humidity lines plotted in black.   In addition, the plot shows the calculated lines for the deliquescence relative humidity of the significant constituents of simulated sea salt, including calcium chloride, magnesium chloride, and sodium chloride. The red dots represent the constant environment tests where cracking has been observed. Although sodium chloride is the most abundant constituent of sea salt, SCC occurred at humidity levels below its deliquescence relative humidity. Rather, SCC was observed as long as the test relative humidity was above the deliquescence relative humidity of magnesium chloride or calcium chloride. In natural conditions where the absolute humidity is limited to about 30 g/m^3, such a relative humidity could only be reached at temperatures below approximately 60 °C. This suggests that colder canisters are likely to be more susceptible to SCC.

In addition to evaluating how the constituents of sea salt affect the SCC susceptibility of 304 SS, the effect of salt concentration on SCC initiation was assessed. In certain temperature and relative humidity conditions, cracks initiated with a surface salt concentration as low as 0.1 g/m^2, where the

unmagnified surface appeared pristine and no significant pitting was observed. This weight includes not only chloride but also other cations in the total surface weight. This is a lower surface salt concentration than reported in previous work by Shirai et al., where the surface chloride concentration needed for SCC to occur was 0.3 g/m^2.[11] Much more extensive cracking, however, was noted on the specimens with 10 or 1 g/m^2 surface salt concentration. It should be noted that no cracks were observed in the weld material or along the heat affected zone for the welded samples. Cracks that did initiate in the welded samples were located in the base material. These cracks took longer to initiate than observed in the as-received samples. However, the stress is less in the base material for the welded samples because it is along the side of the U-bend samples.

CONCLUSION

The objective of this work was to evaluate the susceptibility of austenitic stainless steels typically used in nuclear waste dry storage containers for chloride SCC. Sea salt was deposited onto the surface of various U-bends held at 35, 45, 52, 60 and 80 °C. The samples were either exposed to cycling or constant relative humidity conditions. Samples were deposited with simulated sea salt at surface concentrations of 0.1, 1.0, or 10 g/m^2. The results showed that samples would undergo SCC between 35 and 80 °C as long as the relative humidity was maintained above the calcium chloride relative humidity deliquescence threshold. The results also indicated that SCC could initiate for surface salt concentration at or above 0.1 g/m^2.

ACKNOWLEDGMENTS

REFERENCES

1. U.S. Nuclear Regulatory Commission. "NAC International Inc., Safety Analysis Report for the UMS Universal Storage System – Docket No. 72-1015." ML003743531, U.S. NRC: Rockville, Maryland. 2003.

2. U.S. Nuclear Regulatory Commission. "Transnuclear Standardized Advanced Nuhoms® Horizontal Modular Storage System for Irradiated Nuclear Fuel Safety Evaluation Report." ML030100468, U.S. NRC: Rockville, Maryland. 2003.

3. Constellation Energy Nuclear Group. "Response to Request for Supplemental Information, RE: Calvert Cliffs Independent Spent Fuel Storage Installation License Renewal Application." ML12212A216, CENG: Baltimore, Maryland, 2012.

4. U.S. Nuclear Regulatory Commission. "Information Digest." NUREG-1350, Vol. 23, U.S. NRC: Rockville, Maryland. 2003.

5. Toshima, Y. and Y. Ikeno. "Long-Term Exposure Test for External Stress Corrosion Cracking on Austenitic Stainless Steels in Coastal Areas." Corrosion/2000, Paper Number 597, NACE International: Houston, Texas. 2000.

6. Huizinga, S., J.G. De Jong, W.E. Like, B. McLoughlin, and S.J. Paterson. "Offshore 22Cr Duplex Stainless Steel Cracking – Failure and Prevention." Corrosion/2009, Paper Number 05474, NACE International: Houston, Texas. 2005.

7. National Aeronautics and Space Administration. "Corrosion Study of Bare and Coated Stainless Steel." MAB 431-68, NASA: Kennedy Space Center, Florida. 1971.

8. Mintz, T.S. and D.S. Dunn. "Atmospheric Chamber Testing to Evaluate Chloride Induced Stress Corrosion Cracking of Type 304, 304L, and 316L Stainless Steel." Corrosion/2009, Paper Number 09295, NACE International: Houston, Texas. 2009.

9. Mintz, T.S., L. Caseres, D.S. Dunn, and M. Bayssie. "Atmospheric Salt Fog Testing to Evaluate Chloride Induced Stress Corrosion Cracking of Type 304, 304L, and 316L Stainless Steel." Corrosion/2010, Paper Number 10232, NACE International: Houston, Texas. 2010.

10. Salmela, H.A. and D.D. Grantham. "Diurnal Cycles of High Absolute Humidity at the Earth's Surface." AD-753 078, Air Force Cambridge Research Laboratories: Bedford Massachusetts. 1972.

11. Shirai, K. J. Tani, T. Arai, M. Wataru, H. Takeda, and T. Saegusa. "SCC Evaluation Test of a Multi-Purpose Canister." 13th International High-Level Radioactive Waste Management Conference. ANS: LaGrange Park, Illinois. 2011.

12. ASTM International. "Standard Practice for Making and Using U-Bend Stress Corrosion Test Specimens." ASTM G30–97. West Conshohocken, Pennsylvania: ASTM International. 1997.

13. American Society of Mechanical Engineers. "Rules for Construction of Nuclear Power Plant Components, Division 3, Containment Systems and Transport Packagings for Spent Nuclear Fuel and High Level Radioactive Waste." Section III. ASME Boiler and Pressure Vessel Code. ASME: New York City, New York. 2003.

14. American Society of Mechanical Engineers. "Welding and Brazing Qualifications." Section IX 2003 Addenda. ASME Boiler and Pressure Vessel Code. ASME: New York City, New York. 2003.

15. ASTM International. "Standard Practice for Preparation of Stress-Corrosion Specimens for Weldments." ASTM G58–85. West Conshohocken, Pennsylvania: ASTM International. 2005.

16. ASTM International. "Standard Practice for the Preparation of Substitute Ocean Water" ASTM D1141–98. West Conshohocken, Pennsylvania: ASTM International. 2003.

Table 1
Environmental Cycling Test Matrix

Temperature, (°C)	Salt Concentration, (g/m^2)	Fabrication
35	0.1, 10	As-Received, Sensitized, Welded
	1.0	As-Received, Sensitized
45	0.1, 10	As-Received, Sensitized, Welded
	1.0	As-Received, Sensitized
52	1, 10	As-Received, Sensitized

Table 2
Atmospheric Test Chamber Protocol During Salt Deposition Phase

Cycle #	Chamber Cycle	Time, minutes	Chamber Temp, °C	Comments
1	Salt fog	5	27	Deposit Salt on specimens
2	Hold	15	27	Dry specimens after fog cycle

Table 3
Static Environmental Test Matrix

Temperature	Relative Humidity	Fabrication
45	44	As-Received, Sensitized
60	22, 25, 30, 35, 40	As-Received, Sensitized
80	35, 40	As-Received, Sensitized
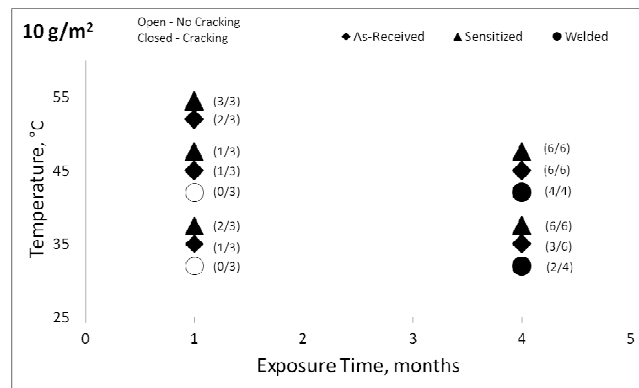
Figure 1: Cycling environment SCC susceptibility map for 10 g/m^2 simulated sea salt U-bend samples (number in brackets indicates number of specimens observed to have cracked versus the number that were inspected).
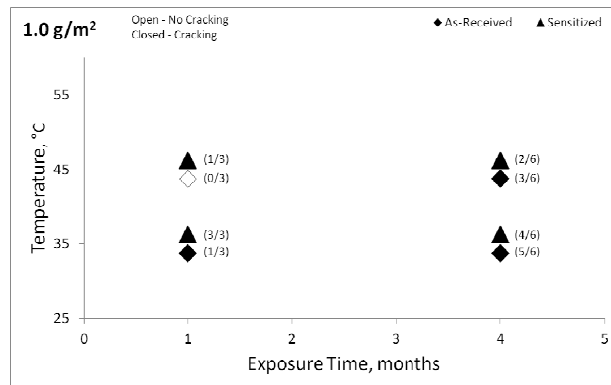
Figure 2: Cycling environment SCC susceptibility map for 1 g/m^2 simulated sea salt U-

bend samples (number in brackets indicates number of specimens observed to have cracked versus the number that were inspected).
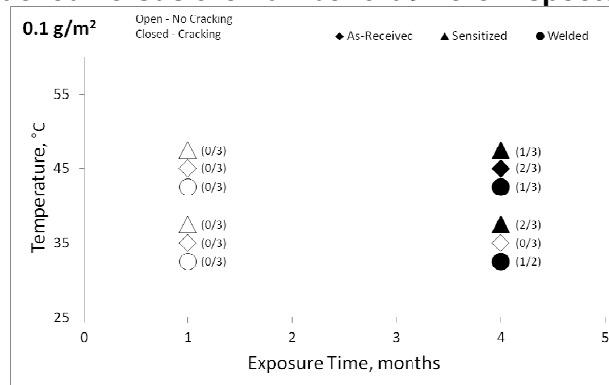

Figure 3: Cycling environment SCC susceptibility map for 0.1 g/m² simulated sea salt U-bend samples (number in brackets indicates number of specimens observed to have cracked versus the number that were inspected). Tests are still ongoing at this deposited salt level.
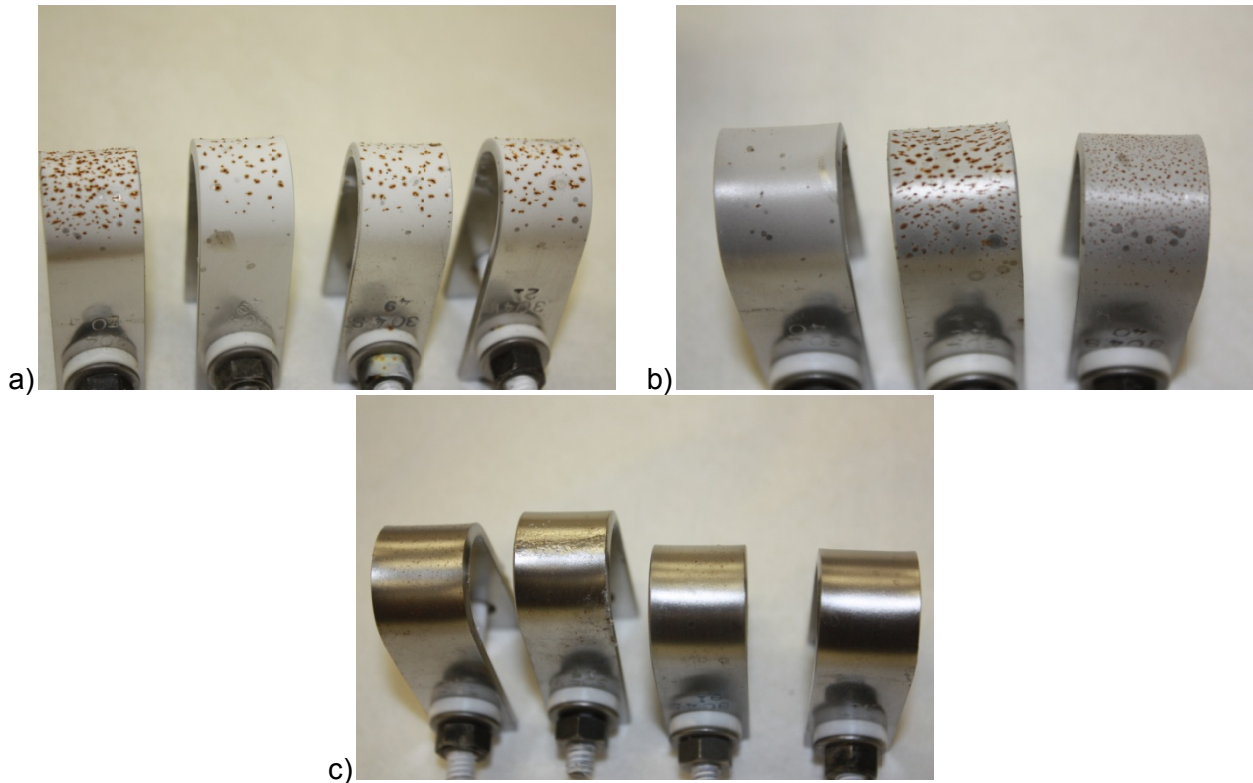

Figure 4: Visual observation of corrosion product developed after 4-month exposure to cycling conditions for a) 10 g/m² specimens, b) 1 g/m² specimens, and c) 0.1 g/m² specimens.
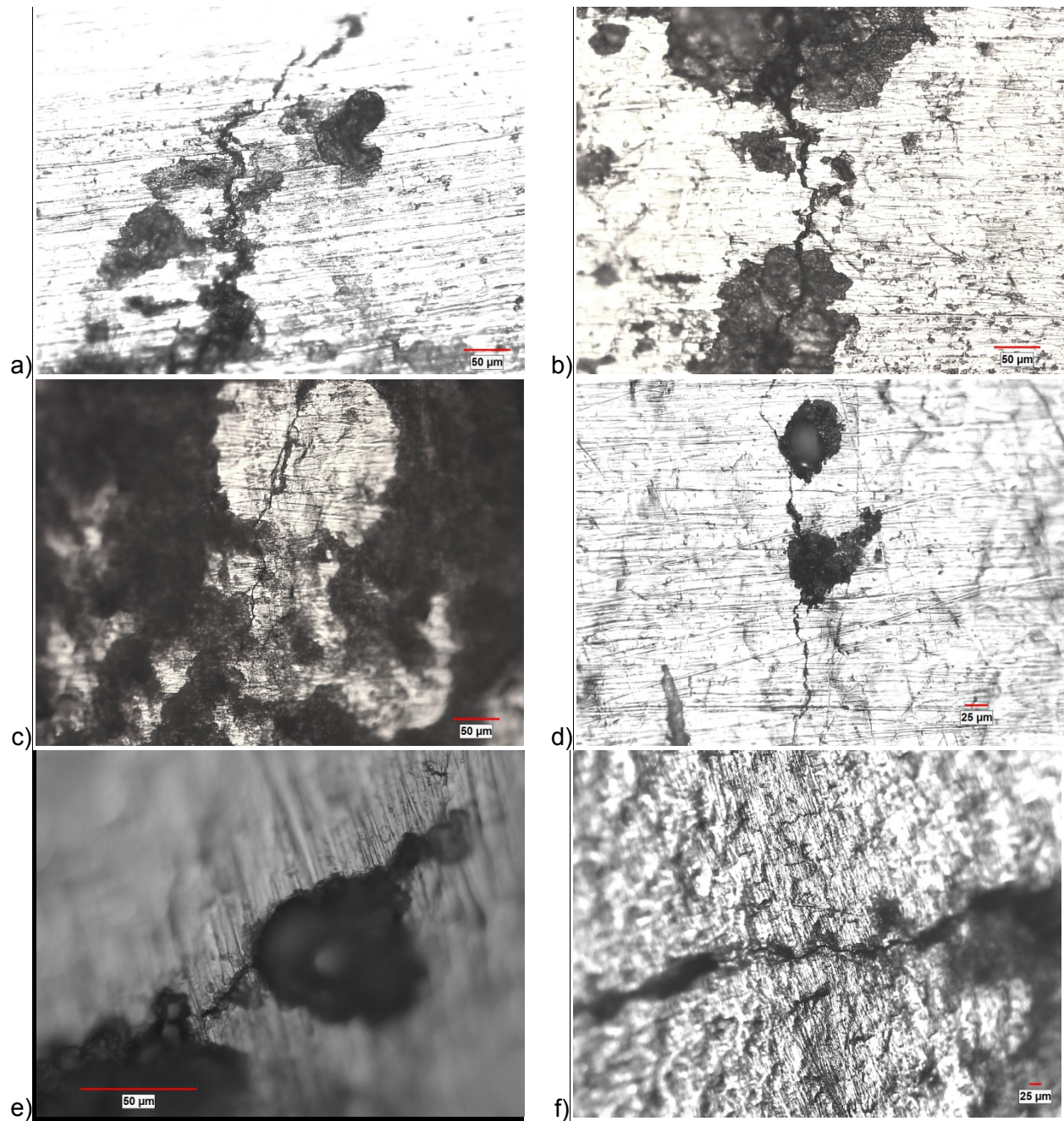
Figure 5: Top view of cracked U-bend specimens deposited with 10 g/m^2 of simulated sea salt including 35 °C a) as-received and b) sensitized. Top view of cracked U-bend specimens deposited with 1 g/m^2 of simulated sea salt including 45 °C c) as-received and d) sensitized. Top view of cracked U-bend specimens deposited with 0.1 g/m^2 of simulated sea salt including 45 °C e) as-received and f) sensitized.
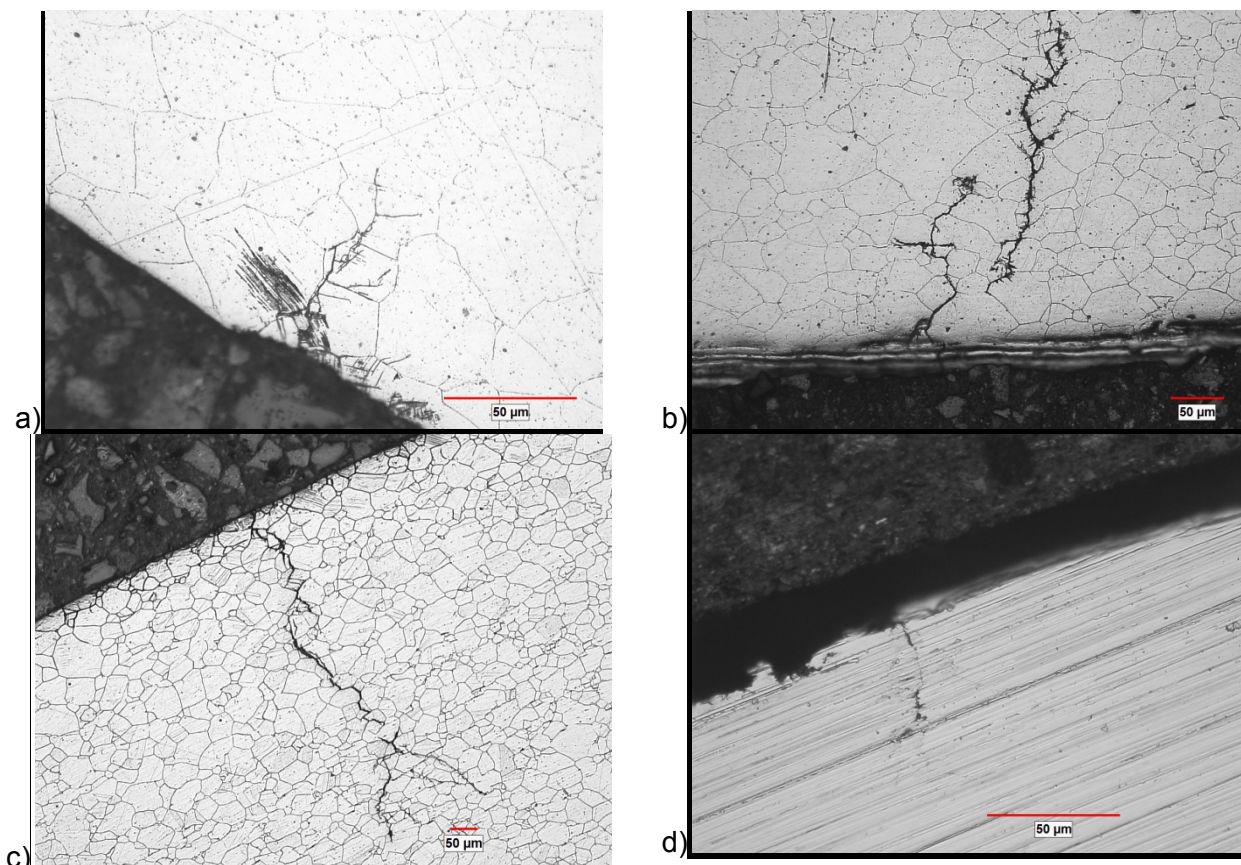
Figure 6: Cross-section view of cracked U-bend specimens deposited with 10 g/m^2 of simulated sea salt including a) 45 °C sensitized. Cross-section view of cracked U-bend specimen deposited with 1 g/m^2 of simulated sea salt including b) 35 °C sensitized. Cross-section view of cracked U-bend specimens deposited with 0.1 g/m^2 of simulated sea salt including c) 35 °C sensitized and d) 45 °C sensitized.
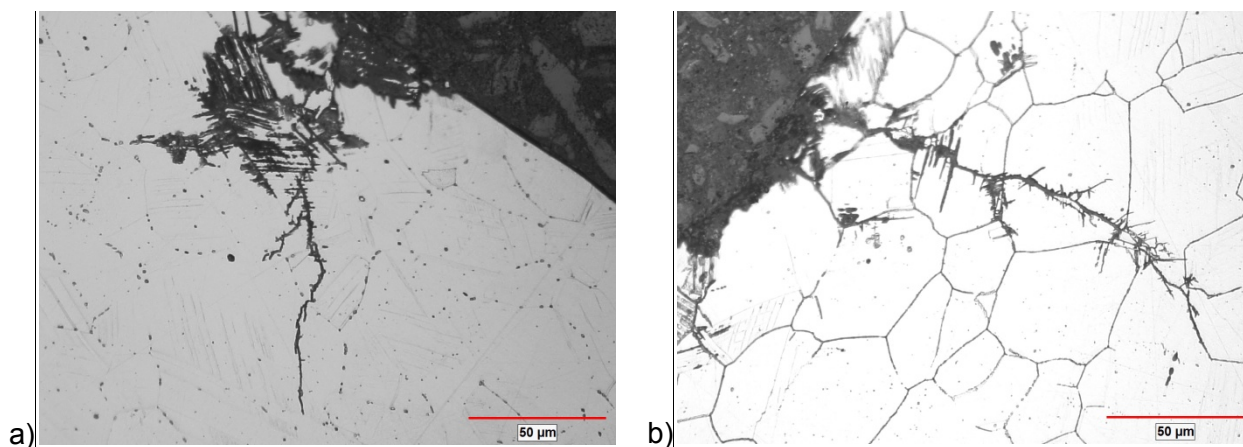

Figure 7: Images of cracked U-bends held at 45 °C and deposited with 10 g/m^2 of simulated sea salt. 45 percent relative humidity a) as-received and b) sensitized
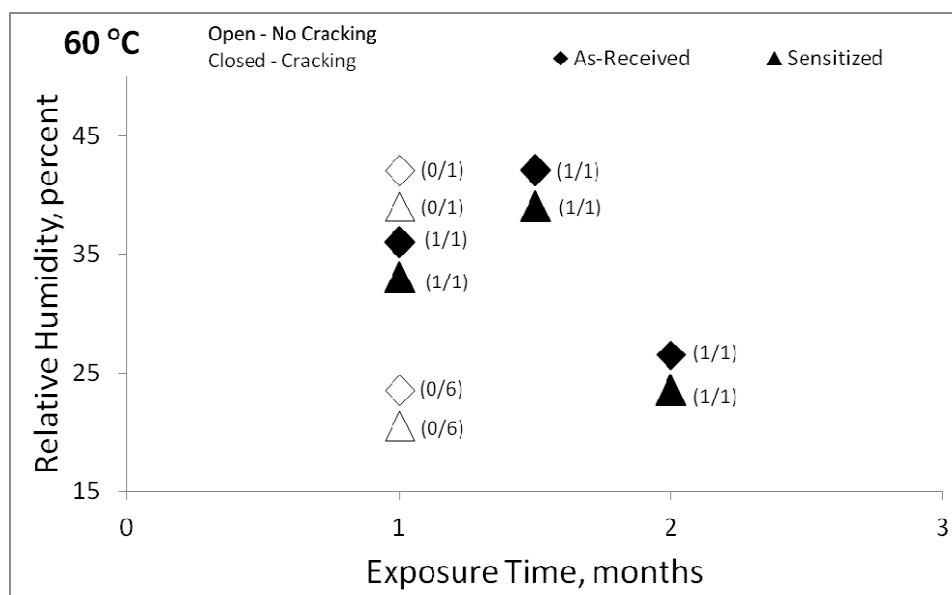
Figure 8: Static environment atmospheric stress corrosion cracking susceptibility map for 10 g/m² simulated sea salt U-bend specimens held at 60 °C (number in brackets indicates number of specimens observed to have cracked versus the number that were inspected).
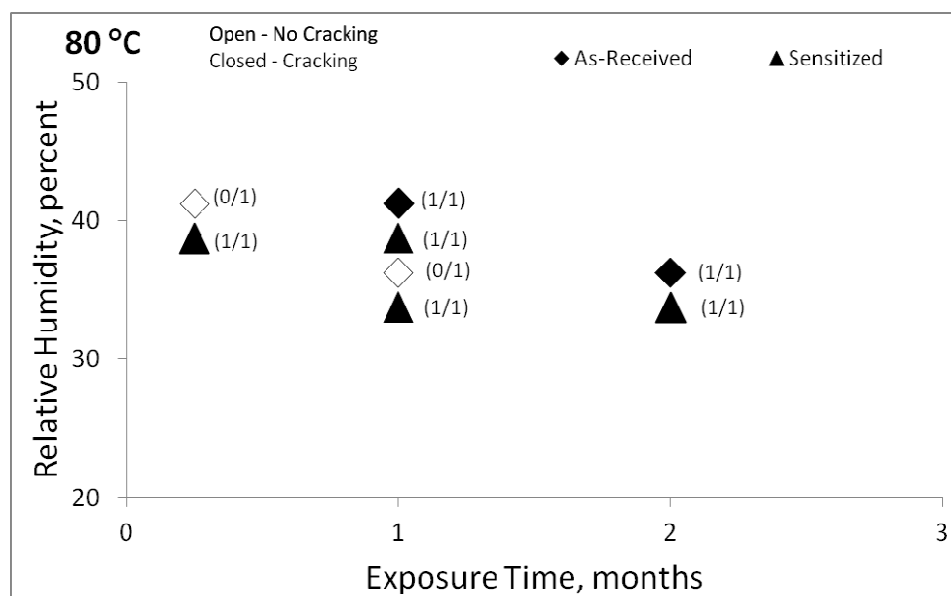

Figure 9: Static environment atmospheric stress corrosion cracking susceptibility map for 10 g/m² simulated sea salt U-bend specimens held at 80 °C (number in brackets indicates number of specimens observed to have cracked versus the number that were inspected). Tests are still ongoing for this temperature at a lower relative humidity.
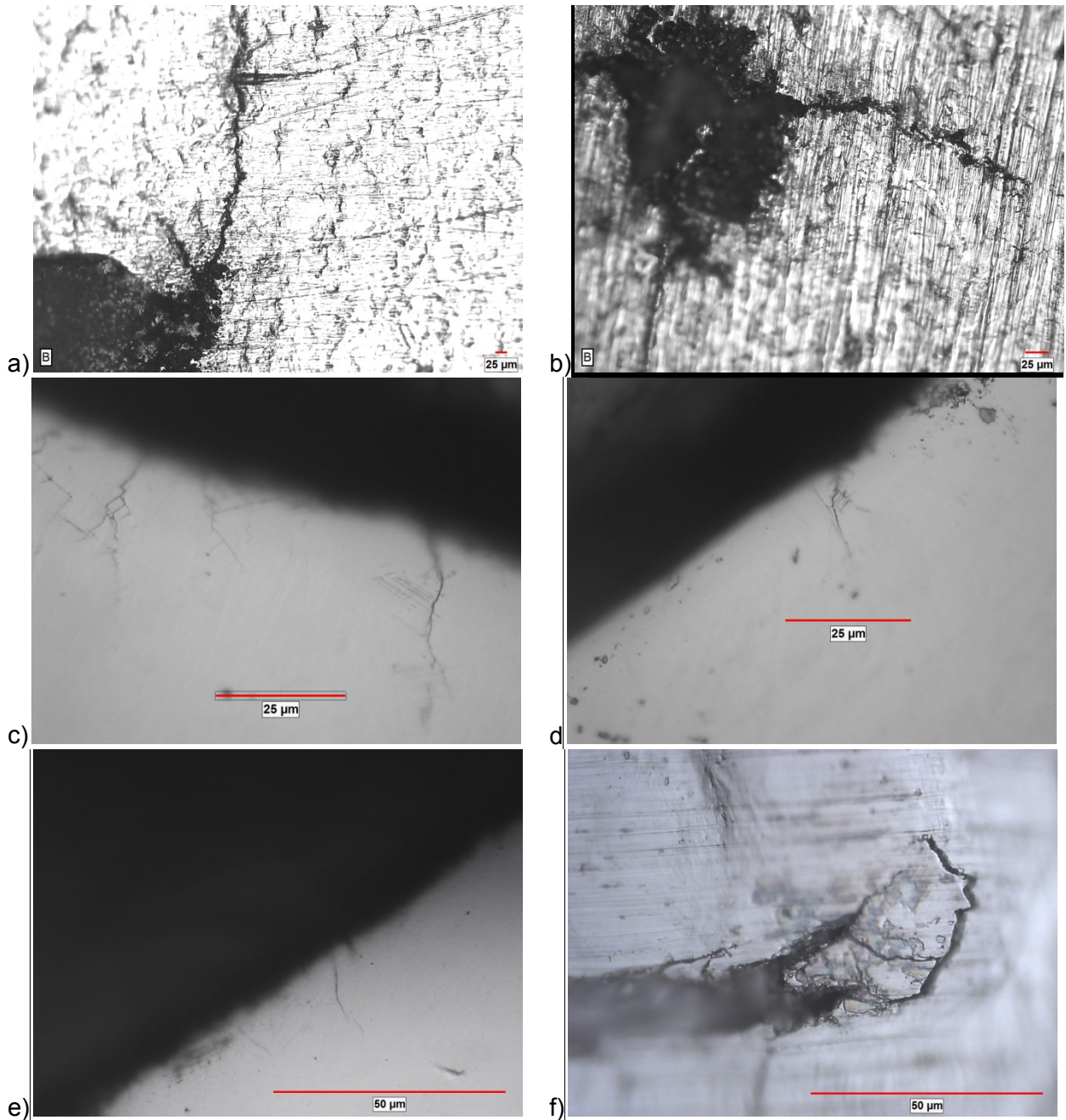
Figure 10: Images of cracked U-bends held at 60 °C and deposited with 10 g/m² of simulated sea salt. 40 percent relative humidity a) as-received and b) sensitized; 35 percent relative humidity c) as-received and d) sensitized; 25 percent relative humidity e) as-received and f) sensitized
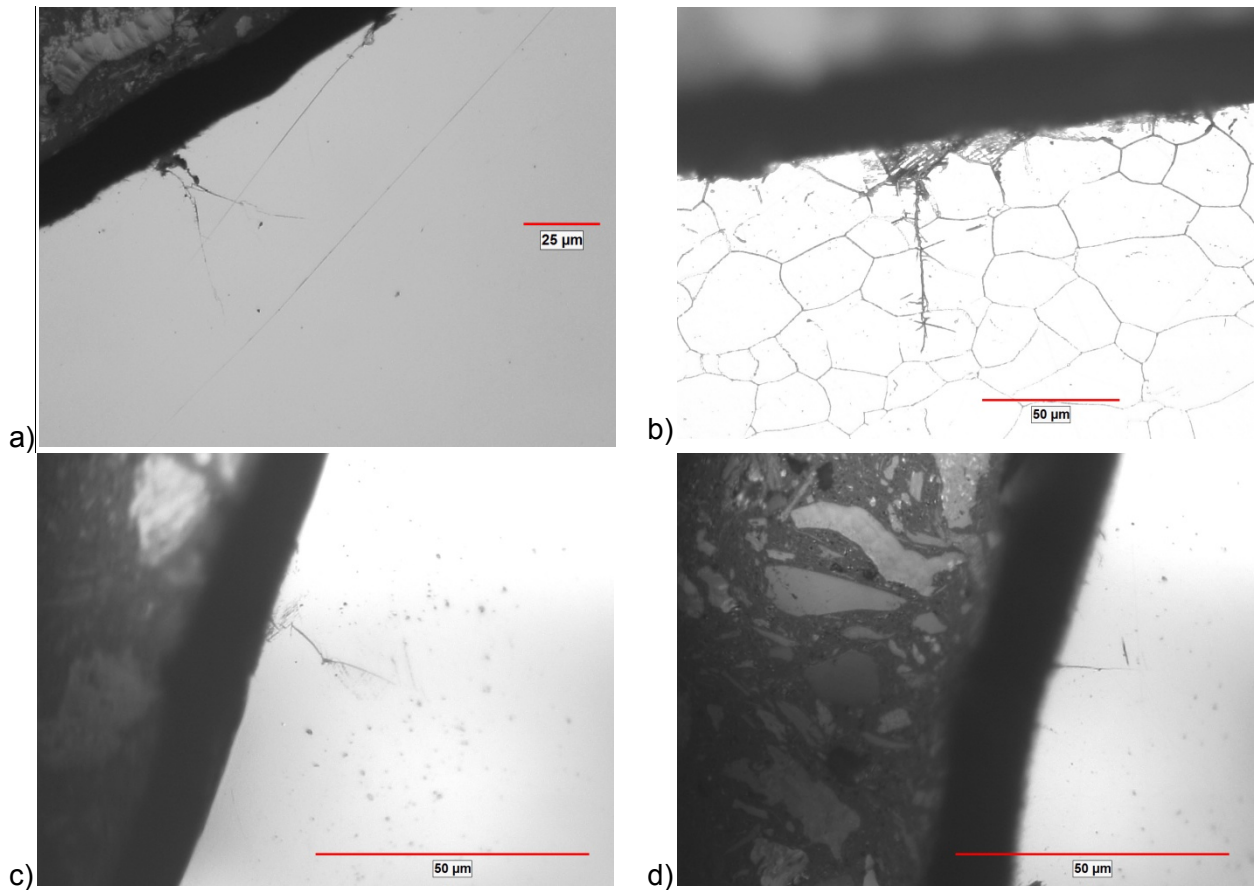
Figure 11: Images of cracked U-bends held at 80 °C and deposited with 10 g/m² of simulated sea salt. 40 percent relative humidity a) as-received and b) sensitized; 35 percent relative humidity c) as-received and d) sensitized
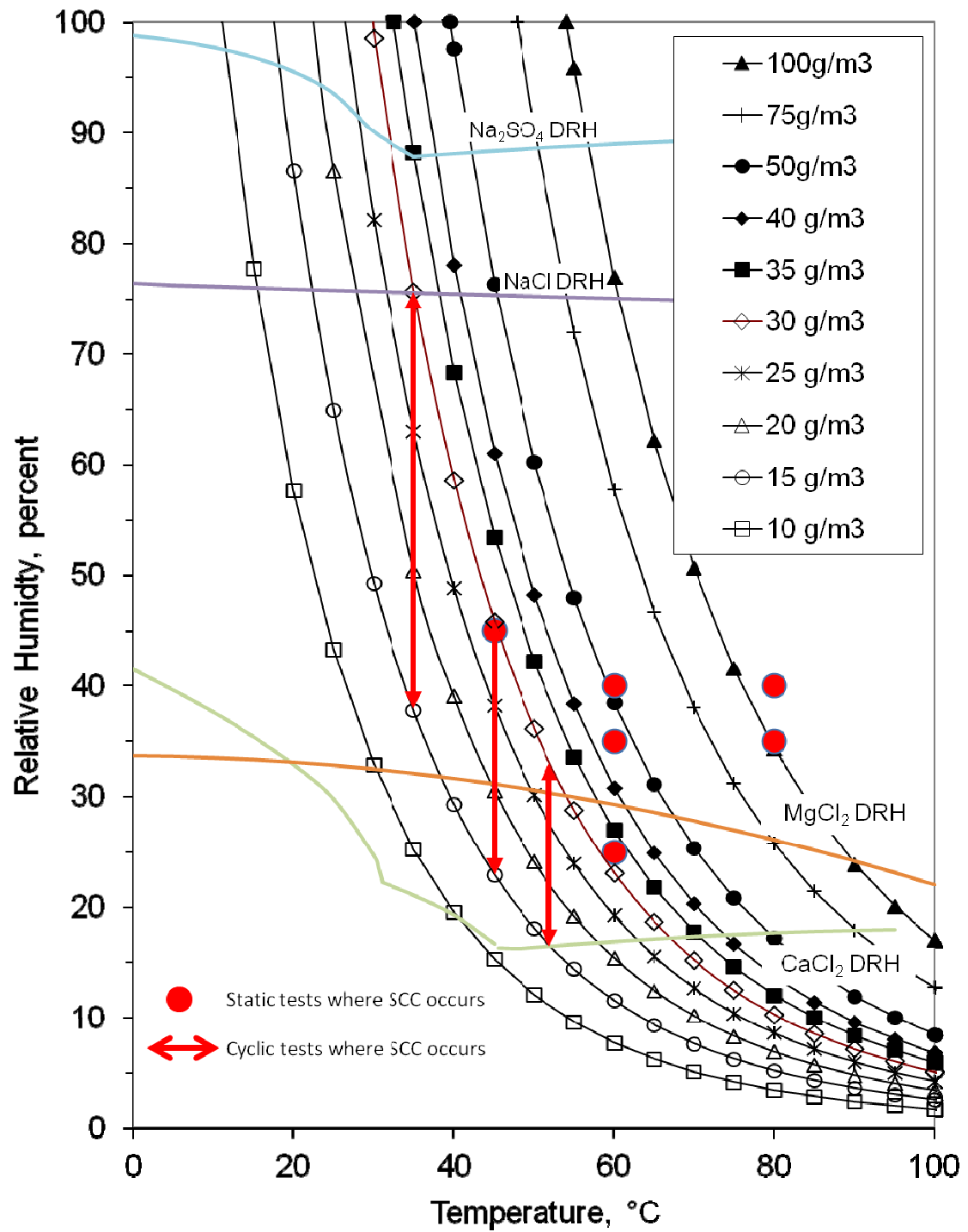
Figure 12: Test conditions relative to the salt deliquescent conditions necessary to form salt brine