

Under-Deposit Chloride-Induced Stress Corrosion Cracking in Austenitic Stainless Steels: Aspects Associated with Deposit Type, Size and Composition

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The UK's Intermediate Level radioactive Waste (ILW) is likely to be held for many decades in interim stores, in containers fabricated from types 304L and 316L austenitic stainless steels [1]. Containers located near marine environments will be subject to the deposition of chlorides from sea-salt aerosol and, as such, at risk of developing localized corrosion (pitting and/or crevice attack). Consequently, in areas of tensile stress a transition from sites of localized attack to what has become known as Atmospheric Chloride-Induced Stress Corrosion Cracking (AISCC) may occur [2]. Assessing the risk to container integrity from such degradation phenomena during interim storage will clearly require a means of predicting long-term corrosion behavior over a wide range of different environmental scenarios. Knowledge of the effects of changes in material and environmental variables on mechanistic and kinetic quantities such as the induction time (time to cracking) and crack growth rate will be crucial to developing accelerated testing methods and/or models to predict damage evolution in the storage condition over such long timescales.

Investigations pertaining to the occurrence of localized corrosion or AISCC in ILW container materials are often performed using a single salt, such as MgCl_2 , rather than sea-salt. This practice may not be altogether appropriate given that the thin layer electrolyte formed in the vicinity of chloride-containing deposits under realistic service conditions is likely to be of a far more complex chemistry which will depend strongly on the environmental Relative humidity (RH) and temperature. As sea-water becomes more concentrated solid phases will precipitate as their solubility is exceeded. The least soluble species will precipitate first, usually the calcium containing salts (CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4), followed by halite (NaCl) then the potassium and magnesium containing salts such as carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) and finally bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). At 25°C halite wets to form a saturated solution at around 75% RH, carnallite at 59% RH and bischofite at 33% RH [3], hence sea-salt deposits will remain wet to some degree over a large RH range. For example, at 25°C and above 33% RH the associated electrolyte will be composed of a rather complex mixture of solution species. Other environmental variables will also be important in terms of the development of localized corrosion phenomena, for instance the size and distribution of deposits and their organic content. In this work, we have sought to obtain kinetic data under various

environmental conditions to aid in the development of future experimental protocols or models for prediction of AISCC damage. In all the experiments described herein, U-bend specimens fabricated from both 304L and 316L stainless steels were used to supply a tensile stress and deposits of either sea-salt or MgCl_2 to produce an electrolyte under the chosen environmental conditions.

To investigate the effect of electrolyte composition, specimens laden with 3 mm diameter circular salt deposits (applied from a 5 μl aliquot of an artificial sea-water solution or 10.9 g dm^{-3} MgCl_2 solution) were exposed to RH values of 33, 50 and 75% at 70°C. At 33% RH both sea-salt and MgCl_2 deposits were found to produce a similar number of cracks with an induction time of around seven days. However, at 50% RH sea-salt appeared to be the more aggressive species, at least in terms of crack numbers; induction times and crack growth rates were similar. This RH value is close to the deliquescence point of carnallite and suggests it may be of importance in promoting AISCC under such conditions.

A parallel set of experiments was conducted at 80°C and 30% RH, to study the effects of deposit size on induction time and crack growth rates. In these experiments salt deposits were produced using a spray deposition technique. For specimens with sea-salt deposits both parameters correlated with changes in the average deposit size prior to environmental exposure. Induction times increased, and average crack growth rates decreased, with decreasing deposit size. MgCl_2 deposits produced via the spray application technique were beyond the resolution of the optical microscope employed. Both quantities were, however, seen to correlate with the nominal MgCl_2 deposition density, i.e. induction times were seen to increase and the extent of cracking to decrease with decreasing deposition density. It should be noted that the temperatures employed in the experiments were significantly higher, as are the deposit sizes, than those likely to be encountered by ILW containers in practice. There is, however, no reason to assume that similar trends will not be observed at lower temperatures or as the deposit size is progressively decreased.

To investigate the effect of organic matter on induction times and crack growth rates, experiments are currently in progress with 304L U-bend specimens contacted with organically enriched sea-salt, sea-salt or MgCl_2 deposits stored in an environmental chamber at a temperature of 50°C and RH of 30%. Results obtained to date indicate that organically-enriched seawater solutions delay the onset of cracking relative to sea-water and MgCl_2 solutions, yet lead to cracks of greater average length.

References

1. Nuclear Decommissioning Authority, Geological Disposal: Package Evolution Status Report, NDA RWMD 031 2010.
2. N.R. Smart, C.C. Naish, A.M. Pritchard, Corrosion principles for the assessment of stainless steel radioactive waste containers, Serco report SA/EIG14921/C010, 2006.
3. R.S. Lillard, D.G. Kolman, M.A. Hill, M.B. Prime, D.K. Veirs, L.A. Worl and P. Zapp (and references contained therein), Corrosion 65,175 (2009).