

Dr. Charles G. Interrante, Program Manager
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National Bureau of Standards
U.S. Department of Commerce
Gaithersburg, MD 20899

Dear Dr. Interrante:

As followup to our recent discussions with respect to improving the usefulness of the NBS/NRC waste package data base, we are sending you a review of a document dealing with stress corrosion cracking as an illustration of the kinds of information we believe would be more immediately useful in dealing with questions arising at licensing time. Another use is in preparation of position papers and state of the art papers prior to licensing time.

We request that your staff review this illustrative document in preparation for an in-depth discussion of the elements of information in it. It is of interest to reach agreement shortly on what changes to the existing database format and content should be made.

Actions resulting from this letter are considered to be within the scope of FIN A-4171. No changes in costs or delivery of contracted products are authorized. Please notify me immediately if you feel this letter will result in additional costs or delay in delivery of contracted products.

Sincerely,



Charles H. Peterson, Project Manager
Materials Engineering Section
Technical Review Branch
Division of High-Level Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosure: As noted

cc: Dr. Neville Pugh, Director
Metallurgy Division

Dr. Dale Hall, Group Leader
Corrosion Group, Metallurgy Division

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WASTE PACKAGE DOCUMENT REVIEW

IDENTIFICATION

Title Stress Corrosion Cracking Tests on High-Level Waste Container Materials in Simulated Tuff Repository Environments
Organization BNL
Number NUREG/CR-4619; BNL-NUREG-51996
Published June 1986
Authors T. Abraham; H. Jain; P. Soo
Contract No. NRC FIN A3167
Availability NTIS

DESCRIPTION

Date Reviewed 3/31/87
Problem Stress corrosion cracking (SCC) of waste package materials
Purpose <To check the integrity of the NNWSI reference materials>
Contents 70 pages with 46 figures and 20 tables. Literature survey of SCC: 15 p. Geochemical conditions in tuff: 1 p. Test methods: 14 p. C-Ring test results: 25 p. Water chemistry measurements: 8 p. Discussion and Conclusions: 2 p.
Scope <Not stated>
Materials Tested Incoloy 825 and Types 304L, 316L, and 321 austenitic stainless steels
Method Stressed C-Ring specimens were exposed for 3 time periods (3, 6, and 12 months) to synthetic normal and concentrated J-13 water, refluxed at atmospheric pressure. All the specimens were surrounded by crushed tuff. The specimens in the lower half of the test vessels were immersed in liquid while those in the upper half were exposed to steam and air.

INFORMATION CONTENT

Literature Survey

1. Williams 1957: Austenitic stainless steels subjected to intermittent wetting and drying cycles in exposure to the steam phase of alkaline-phosphate-treated boiler water will fail by SCC even though the water has as little as 5 ppm each of oxygen and chloride ion.
2. Birchon 1964: For strains as low as 0.001 cm/cm in bent beam specimens of 304 and 321 SS held at 200° and 300°C in the steam phase above water containing 5 ppm chloride ion, failure <time to cracking> readily occurs within 40-100 hours.
3. Tashiro 1983: Tested 304, 304L, 304XL, and 3095 SS; also Incoloy 825, Inconel 600 and 625, and SMA 50. Used double U-bend <nested> specimens in boiling deionized water. <Table 2 is not printed clearly.> BNL states SCC obtained with 304 and 304L steels, usually on the inner specimen, but also on the outer specimens which had V-notches. Irradiation at 0.11 MR/h for 7 to 180 days was more damaging. <Not clear from Table 2>. BNL speculates that crevice corrosion may be involved.
4. Kowaka 1978: Tested 316ELC (<0.02% C), 304, 316, and 316L double U-bend specimens in nondeaerated pure water at 250°C for 500 h after sensitization by heating at 700°C for 10 h. Crack depth was shown to be an increasing function of carbon contents in the range <0.01 to 0.04% C.
5. Fujiwara 1978: Tested 304, 304L, 304ELC, 304 ELN, 321, 347, 316ELC, 316ELN, 316ELN-Nb, 304LMo, 304LP, 304HP, 304LSi, 304HSi, 304HS, and a Cr-Ni-Mo alloy in deionized water at 100° to 300°C after sensitization by heating for 24 h at 620°C. Cracking was observed only on the tension side of the inner of double U-bend specimens. Crack depth vs temperature showed maxima at 200°C. <Some inferences are given for the effect of C, N, P, Si, S, and Mo but study of Table 4 suggests these may not be warranted.>
6. Warren 1960: Type 304 SS U-bend samples failed by SCC when tested in 100°C water with 10 ppm chloride ion when the chloride is concentrated on the specimens by a porous medium <not explained>. Failures begin after about a month and all failed after about 9 months. With 100 ppm chloride, all failed in about 2000 h.
7. Staehle (1970) observed the time-to-breaking of wires for a wide variety of alloys including Types 304, 304ELC, and 316 SS, Incoloy 800 and 825, and Inconel 718. The wires were stressed to 90% of the 0.2% offset yield strength and exposed to boiling MgCl₂ solution at 154°C. More than 90% of

the specimens of 316 were broken within 3 hours while the Incolloys and the Inconel showed the same failure percentage within 30 hours.

8. McCright (1983, 1984) subjected 304L SS specimens <not described> to slow strain rates of $1E-4$ and $2E-7/s$ <36%/h and 0.072%/h> while exposed to air-sparged tuff-conditioned J-13 water at $150^{\circ}C$ <pressure?>. These were described by McCright as tuff repository conditions. The specimens were tested in the solution-annealed and in sensitized conditions. <Table 5 describes these conditions, but the description is unclear.> It was concluded that stress-assisted fractures were unlikely. <BNL commented that these were accelerated tests and did not address the very long term exposures that might be needed to initiate cracks. Nor were the effects of gamma radiolysis included.>
9. Juhas, McCright, et al (1984) are continuing the above study, using U-bend specimens in annealed and annealed-and-sensitized conditions that were then stressed beyond the yield strength. Test conditions were 50° and $90^{\circ}C$ under Co-60 irradiation in autoclaves. After 3 months, there was no evidence of pitting or other forms of non-uniform attack. A few of the Type 304 specimens cracked. In bent beam tests, specimens were heavily cold worked, welded, and some given a post-weld anneal, and some given a sensitizing treatment ($700^{\circ}C$ for 8 hours), and finally were stressed to 90% of the room temperature yield strength. No cracking was observed in 4000 h for the sensitized specimens or 2000 h for the unsensitized specimens, but the tests were continuing.

<Critique of Literature Survey

Good but not exhaustive. BNL concluded that the data surveyed suggested that stressed and sensitized SS are susceptible to SCC in pure water and in water containing very low concentrations of chloride ion.

Variables in the test programs included: specimen composition, specimen form, specimen shape, pretest cold work, sensitization by heat treatment, stress during testing, temperature, solution composition, radiation, and oxygen content of environment. In summary:

1. Austenitic SS with <0.01% C will fail by SCC in environments containing as little as 5 ppm each of oxygen and chloride ion.
2. In boiling water the failure occurs readily in times ranging from a few hours to several months.
3. Failures occur even at very low strains like 0.001 cm/cm. However, one worker concluded that stress-assisted fractures were unlikely.
4. Both sensitized and unsensitized specimens were susceptible to SCC.>

Geochemical Conditions

1. There is no information yet available on the composition of groundwater or steam that will be present in the proposed unsaturated zone of the tuff repository.
2. The groundwater is thought to be similar to J-13 well water, the reference composition for which is shown in Table 8. It will be saturated with oxygen from the surrounding air.

Experimental Method

Test Plan

4 Materials x 4 Test environments x 3 Test times x 2 Sample conditions x 3 Replicates = 288 Specimens.

Materials: 304L, 316, 321, Incoloy 825
 Environments: J-13 water, J-13 steam, concentrated J-13 water, steam from concentrated J-13 water.
 Test times: 3, 6, 12 months
 Sample conditions: Solution annealed (SA), SA + sensitized
 Specimen form: SS: 0.75-in OD x 0.125-in tubing
 Incoloy: 0.84-in x 0.109-in tubing

Materials Preparation

C-Rings: <Pieces of tubing were bent into a C-Ring shape, which was then a torus of unspecified diameter with a 60° sector left open. Stress was imposed by tightening a threaded bolt mounted on a diameter of the torus so as to pull the arms of the C together. A 60° notch was cut into the outside surface of the torus. No dimensions are given.>

For sensitized specimens, the tubing was heated at 600°C for 100 h followed by furnace cooling. Comparison of microstructures showed that the heat treatment had probably sensitized the steels.

<Critique: The document notes that the carbon contents were all at the low end of the permissible range (one-half to one-third of maxima), and that they were less likely to become sensitized. The above statement about "probably sensitized" means that the investigators were not confident they had achieved sensitization.

Also, they state that sensitization was slightly stronger near the surfaces of the specimens, as indicated by a greater degree of etching on treatment with oxalic acid. It is not obvious to this reviewer that this is shown in Figure 10. BNL then states that this preferential sensitization is most likely due to unavoidable contamination from lubricants during mill operations. It is not

clear that the sensitization was attempted after these mill operations. If it was, then could not the specimens have been cleaned more thoroughly? BNL speculates that <all> SS containers might become sensitized to SCC during production and handling.>

The elastic limit was determined for unnotched specimens of each of the 8 types of test specimens. The notched test specimens were then loaded to 90% of these values. However, local plastic deformation did occur because, when the stress was removed on selected specimens, the deflection was only partially recovered.

Tuff: Tuff was obtained from the Yucca Mountain site, crushed and sieved into two sizes for use in the tests. It was analyzed by X-ray spectrometry. and the results were normalized to silica, whose absolute concentration was not determined.

<Critique: The analytical results should have been worked up to show compositions adding up to 100%. No Mg, chloride, sulfate, or carbonate are shown.>

Synthetic Groundwater: J-13 well water is the reference test solution, in the absence of data on the actual groundwater at the site. A synthetic groundwater was prepared by BNL, as well as a more concentrated one, nominally 10 x the concentrations in J-13, by equilibrating 10 times the amounts of chemicals used to make the J-13 substitute at 100°C.

Apparatus and Procedure

The C-rings were stacked into Pyrex vessels in two layers and void spaces were filled with fine tuff. Water was added to cover the lower layer of rings. The vessels were heated electrically and boiloff was refluxed by condensers.

Oxygen Measurements

Since the vessels were open to the atmosphere, it was believed that there was an oxygen concentration gradient from the value in air to some lower value within the vessel because of the presence of steam. Also some of the oxygen would be consumed in corrosion reactions. Indirect measurements by chromatography indicated the ratio of oxygen to nitrogen was 0.494 within the upper layer of C-Rings vs 0.560 for laboratory air. BNL concluded there was appreciable consumption of oxygen.

<Critique: A more likely interpretation is that the difference is due simply to the partial pressure of water vapor.>

For the solution, samples analyzed by oxygen electrodes showed 2.8 and 2.9 ppm for J-13 and 10xJ-13 waters, respectively. BNL used Henry's Law data to calculate the equilibrium solubility of oxygen in water as 5.25 ppm.

<Critique: These observations are questionable. At the boiling point of pure water, the vapor pressure of water equals the total pressure. Below the boiling point, any dissolved gas contributes its partial pressure to the total pressure exerted by the solution. At the boiling point, there can be no contribution from a dissolved gas and hence its concentration in the solution is zero. If the total external pressure is less than a standard atmosphere, as for example at the elevated Yucca Mountain site, the boiling point of the solution will be somewhat less than the usual 100°C. If there are mineral solutes in the water, the boiling point will usually be raised somewhat.

The Henry's Law constant (H) is correctly stated as 7.01E04. However, since the partial pressure of the solute oxygen has to be zero, the concentration in solution is zero. By way of further clarification, H at 80°C is 6.87E04. The partial pressure of water is 0.467 atmospheres, so the partial pressure of oxygen is 0.533 atmospheres, and the concentration in solution is 7.75E-06 mole fraction. Since a liter of water contains 55.5 g-moles H₂O, there will be at equilibrium 13.8 ppm of dissolved oxygen.

BNL states that the calculated value is 5.25 ppm. Details of their calculation are not given so it is not clear whether they were using some lower temperature like 98°C. They also state measured values as 2.8 and 2.7 ppm. Considering the above analysis, the reviewer does not believe any conclusion can be drawn without some information on the accuracy of the measurements. There is also the question as to what is a significant level of oxygen for SCC.>

C-Ring Test Results

Type 304L SS

1. Two untested specimens showed no evidence of microcracks at the V-notch or on adjacent surfaces. Therefore, any microcracks observed on tested specimens would be nucleated as a consequence of a corrosion mechanism.
2. Table 15 shows no increase in cracking in going from 3 to 12 months exposure. Nor is there any clear effect of using more concentrated well water or using steam/air environment rather than water.

<Critique: The results are reported in terms of how many samples in each cell of the test matrix showed cracking out of the number

examined. Since at most two specimens were examined in each cell, the results are 0/2, 1/2, or 2/2. Some indication of the density of cracks, i.e., how many cracks per unit area, or how much cracked area per unit area was observed, might have permitted some discrimination as to the effect of test conditions.>

3. Figure 16 shows a forked crack propagating along a grain boundary in a non-sensitized specimen tested in steam/air over J-13 water for three months. Two other specimens, both sensitized, and over 10 x J-13 water, showed no cracking.

<BNL does not make clear how it determined that the cracking was along a grain boundary. Nor does it bring into this context the finding that at 6 months 2/2 specimens showed cracking in both the previous sets of test conditions. Thus, sensitization did not matter. At 12 months, 1/2 for J-13 water and 1/1 for 10xJ-13 water showed cracking, thus supporting this inference.>

4. Figures 17 to 20 show results for specimens tested for 6 months. In Figure 17, a crack in a sensitized specimen is shown, but the grain boundaries could not be revealed by etching. Figures 18 and 20 are offered as showing intergranular attack in an as-received specimen. Figure 19 shows several cracks at the root of the notch in a sensitized specimen, which BNL interpreted as showing that cold working made the specimen more susceptible to cracking.

<BNL notes, however, that only one specimen had crack initiation at the notch root, all others being at the outer surfaces of the specimens. The explanation offered is that cracks could be initiated at metal-tuff contact points where crevice-like conditions could give rise to more aggressive environments.>

Type 316L SS

1. Minute cracks <microcracks?> were observed in a single as-machined specimen. None were observed in any other specimen of 316L tested, or of any of the other materials.
2. For the six month tests, cracks initiated for all test conditions <but not for all specimens>.
3. For the one year tests, in one specimen, a crack was observed that led to a cavity beneath the surface of the tubing. BNL speculated that the metallographic procedure may have removed small grains from the specimen.

4. Again, no trend of severity of cracking with test conditions was evident. The maximum crack lengths at one year were the same order of magnitude as those at 6 months.

Type 321 SS

1. Two as-received untested specimens showed no cracks or pits in the V-notch or in the areas around the notch.
2. Again there was no pattern of cracking with test conditions. At 6 months, 4/4 as-received specimens showed cracking vs 0/3 at 12 months. For sensitized specimens, 2/12 showed cracking, both of which were on exposure to 10xJ-13 water.

Incoloy 825

1. Two as-received untested specimens showed no cracks or pits on the specimen surfaces or in the V-notch.
2. Only 1/11 specimens cracked. X-ray examination indicated depletion of Cr, Fe, and Ni inside the crack.

Salt Deposition

1. During the tests salts deposit on the specimens resulting in attachment of pieces of tuff to the specimens sometime after 3 months.
2. All C-Ring specimens tested in solution had a coating of salt and corrosion scale.
3. In steam, SS specimens showed patches of unreacted metal surrounded by a brown, rust-colored scale whereas Incoloy showed no scale.
4. A white substance was found on the vessel interior which was inferred to be amorphous silica.

Water Chemistry Measurements

1. Samples of tuff were equilibrated first with boiling distilled water for one month, then with a fresh quantity of boiling distilled water for second month, and after this treatment for one of two further treatments: (a) another seven weeks and (b) another four months and one week.

<Ion concentrations were 4 to 70 times those in J-13 water; silica was 95 ppm vs 61 in J-13 for the first treatment. Subsequent treatments all

showed lower concentrations except for sulfate ion. Thus, there is a limit on how much can be extracted from tuff. No explanation was given for how sulfate could increase to 530 ppm without an increase in some cation. The pH remained essentially constant at 8.5.>

2. No significant precipitation of solutes was observed. However, colloids containing silica may be present that can pass through filter paper. This is based on the finding that the silica contents in the test solutions from the 3-, 6-, and 12-month tests were in a narrow range (406 to 488 ppm), irrespective of the composition of the starting solutions. <BNL infers that> at the test temperature the solutions are saturated with silica and thus supersaturated when they are cooled to room temperature. Also, earlier work showed the solubility of silica in J-13 water was about 160 ppm at 120°C. Further, there was no significant difference in silica or other species between filtered and unfiltered solutions. However,

10xJ-13 water from a 12-month test cooled and contacted with tuff for three days, filtered and analyzed showed no change in composition except for a 40% decrease in silica. <Table 19 also shows a 40% drop in potassium ions, and a 60% drop in fluoride ions.>

3. For the extended duration tests, from three months to 12 months there are no large changes in concentrations of the ionic species except for calcium and sulfate, both of which decrease with time.

<This appears imprecise. Silica indeed is about the same throughout both the J-13 tests and the 10xJ-13 tests and the levels in each set are about the same. Sodium similarly remains about the same, although the level in the 10xJ-13 tests is about 800 ppm vs 480 for the normal J-13 water. Calcium does decrease from about 300 ppm at 3 months through 160 ppm at 6 months to about 115 ppm at 12 months.

However, sulfate decreases about 25% in 10x J-13 water but in J-13 water after an initial decrease it remains constant. Potassium at twelve months is about half that at 6 months. For J-13 water, chloride and nitrate decrease about 30% whereas in 10xJ-13 water they increase 20-30%. Stannous ion doubles in both waters, although its level is quite low (1 ppm). Fluoride increases 50% in J-13 water and 300% in 10xJ-13 water. Finally, the pH increases for both waters by 0.9 units, which is a decrease in hydrogen ion concentration by a factor of 8.

Unless BNL wishes to conclude that the variations observed between 6 and 12 months are within experimental error, these differences may warrant further study.

Conclusions

1. Both the sensitized and non-sensitized specimens may suffer from microcracking and intergranular attack.
2. Microcracking occurs in both aqueous as well as air/steam environments. The environments are equally aggressive based on similar numbers of cracked specimens in each environment. Microcracks appear at notches and in regions away from notches. There is no clear effect of stress on crack depth.
3. There does not appear to be a significant difference in the degree of cracking in J-13 and 10xJ-13 solutions. Possibly, this is because the two solutions quickly become similar due to interactions with the tuff.
4. The crack paths are usually difficult to determine but some are definitely intergranular and some are transgranular. Branched cracks are often observed.
5. Type 316L SS specimens used in this study are more susceptible to cracking than Type 304L. This is possibly due to the presence of very small cracks which could be present in some Type 316L specimens prior to testing. These cracks were probably formed at the mill and in some specimens were not removed by surface abrasion with silicon carbide paper during the C-Ring fabrication process. Nevertheless, some cracks in Type 316L, which were found at the notched region, were clearly formed during the test period.
6. More limited examination was carried out on Type 321 SS and Incoloy 825 specimens, but they also are susceptible to microcracking. They are, however, probably superior, to Types 304L and 316L SS.

<The above are mainly results, not conclusions. The report also states the following:>

- a. Types 304L, 316L, and 321 SS are susceptible to cracking (either intergranular corrosion, intergranular SCC, or transgranular SCC in aqueous environments at 100°C containing sufficient levels of chloride ion, oxygen, and other ionic species.
- b. Cracking also occurs at the same frequency in the steam/air phase above these boiling solutions.

- c. Incoloy 825 appears to be significantly more resistant to cracking under similar conditions.

<Critique: Conclusion 1 appears to say that sensitization has nothing to do with stress corrosion cracking. Conclusion 3 says the solution concentration over a factor of about 10 is also irrelevant. Even chloride ion, which was increased from 7.5 ppm in J-13 water to 10 times this level, showed no effect. A deficiency is that the actual ion concentrations for this concentrated synthetic J-13 water was not given in the report. Conclusion 4 throws doubt on whether any credence is to be placed on the statements that some cracks were intergranular and others were transgranular.

Perhaps the most significant conclusion is that some of the cracks were pre-existing. This suggests the possibility that all steels have some population of microcracks introduced by the mechanical stresses in processing in steel mills.

The findings on incidence of cracking also appear at variance with the information in the literature survey earlier in the document.

Recommendations

1. Selected steel specimens should be examined for pre-existing microcracks.
2. The experiments should be repeated using alloy steels with higher carbon contents to demonstrate SCC. Before such experiments are carried out, a more thorough literature search should be made to prepare a more definitive picture of the state of understanding of stress corrosion cracking.
3. The literature survey given in the document should be studied to identify consistent information.>

OFFICIAL CONCURRENCE AND DISTRIBUTION RECORD

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FROM: Charles H. Peterson, Project Manager
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