Journal of Nuclear Materials 379 (2008) 42–47

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Stress corrosion cracking of stainless-steel canister for concrete cask storage of spent fuel

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ARTICLE INFO

PACS:
62.20.Mk
82.45.Bb
28.41.Kw

ABSTRACT

Resistance to external stress corrosion cracking (ESCC) and crevice corrosion were examined for various candidate canister materials in the spent fuel dry storage condition using concrete casks. A constant load ESCC test was conducted on the candidate materials in air after deposition of simulated sea salt particles on the specimen gage section. Highly corrosion resistant stainless steels (SS), S31260 and S31254, did not fail for more than 46000 h at 353 K with relative humidity of 35%, although the normal stainless steel, S30403 SS failed within 500 h by ESCC. Crevice corrosion potentials of S31260 and S31254 SS became larger than 0.9 V (SCE) in synthetic sea water at temperatures below 298 K, while those of S30403 and S31603 SS were less than 0 V (SCE) at the same temperature range. No rust was found on S31260 and S31254 SS specimens at temperatures below 298 K in the atmospheric corrosion test, which is consistent with the temperature dependency of crevice corrosion potential. From the test result, the critical temperature of atmospheric corrosion was estimated to be 293 K for both S31260 and S31254 SS. Utilizing the ESCC test result and the critical temperature, together with the weather station data and the estimated canister wall temperature, the integrity of canister was assessed from the view point of ESCC.

1. Introduction

In the dry storage of spent nuclear fuels using concrete casks, stainless-steel canisters act as an important barrier for encapsulating spent fuels and radioactive materials. According to the spent fuel storage concept, the decay heat of spent nuclear fuels dissipates through the canister wall by air cooling. Hence, the canister wall is in direct contact with air containing sea salt particles and is possibly contaminated by chlorides, because the interim storage facilities for spent nuclear fuels will be built in coastal regions in Japan and the expected service life of storage canisters is 40–60 years.

Stainless steels are widely used as structural materials for chemical and nuclear power plants because of their excellent general corrosion resistance, mechanical properties, and weldability. However, austenitic stainless steels are susceptible to stress corrosion cracking (SCC) in certain environments under tensile stress. The SCC induced by sea salt particles and chlorides, for example, has been observed on various structures of chemical plants built in coastal regions [1]. This type of SCC is referred to as external SCC (ESCC) or atmospheric SCC since the cracking starts from the outside of the equipment in air.

The ESCC manifests itself as intergranular or transgranular cracking depending on the material and environmental conditions. Intergranular SCC is commonly observed in sensitized parts of stainless-steel structures at approximately ambient temperature. On the other hand, transgranular SCC is observed regardless of the material's condition at relatively high temperatures above 327 K. As one environmental factor, moderate relative humidity (RH) is necessary to moisten the chlorides adhering to stainless-steel surfaces. The relative humidity at which ESCC easily occurs (RHp) is dependent on the type of chlorides. For example, Shoji et al. reported [2] RHp values of 60% for NaCl and 30% for $MgCl_2$. Another important factor for ESCC is a tensile stress, which is mostly derived from the residual stress as the result of welding or cold working.

Storage canisters have several welding lines on their wall and lid, which probably have high residual tensile stresses. Contamination by sea salt particles also is expected to occur during the long service life of such canisters, as mentioned earlier. Thus, ESCC susceptibility should be examined carefully to select candidate canister materials. The anticipated storage period of the spent fuel is 60 years, thus, the canister structural integrity must be maintained during this period to prevent the release of radioactive materials. As shown in Fig. 1, the environmental conditions for SCC are fulfilled when the RH around the canister surface is higher than the critical value (RH_L) to deliquesce sea salt particles adhered to the

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doi:10.1016/j.jnucmat.2008.06.005

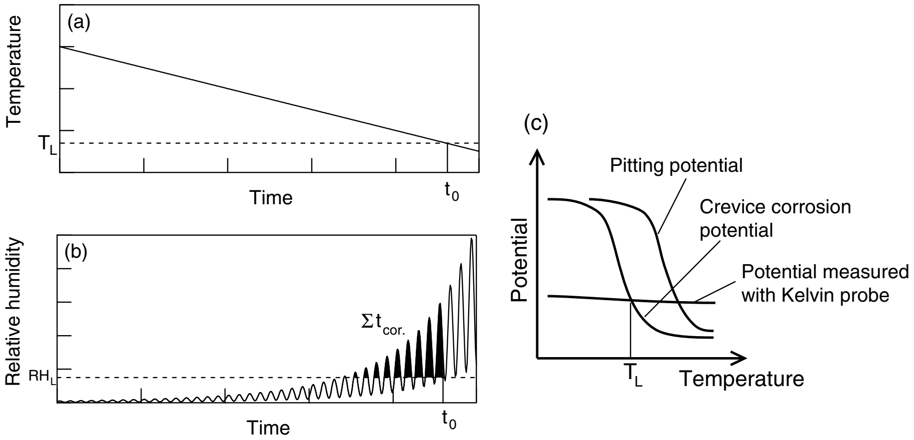


Fig. 1. Method for of evaluating canister integrity against SCC. (a) Decay heat of canister surface, T_L: lowest temperature for SCC, (b) relative humidity changes with time around canister surface, RH_L: lowest RH for SCC, (c) definition of T_L utilizing electrochemical properties of stainless steel, assuming crevice corrosion as crack initiation site.

canister surface. On the contrary, stainless steels become immune to SCC when the temperature decreases to a certain critical value (T_L) below which the anodic process of atmospheric corrosion is negligible. Thus, SCC may occur during the period corresponding to the sum of the shaded areas ($\sum t_{cor.}$) in Fig. 1(b). Hence, if the condition of $t_f > \sum t_{cor.}$ is fulfilled after comparing $\sum t_{cor.}$ with the SCC failure time (t_f) obtained from the constant-load test in an accelerated environment, we can assume that the canisters will survive without suffering from SCC during interim storage. An idea to determine the threshold temperature T_L is shown in Fig. 1(c). Both the crevice corrosion and the surface potentials are necessary to determine T_L. Tsujikawa suggested that SCC in a neutral chloride solution is initiated by crevice corrosion [3]. We also assume that the occurrence of crevice corrosion is necessary to initiate SCC on the surfaces beneath sea salt particles. Hence, the objective of this study is to obtain the SCC failure time of the candidate canister materials at 353 K by a constant-load test. The present test is a continuation of tests in our previous studies [4–7]. Updated data are shown in this report. Additionally, the temperature dependence of crevice corrosion potential also is examined by electrochemical potentiodynamic technique.

2. Experiment

2.1. Materials

Fifty-mm-thick welded joints of S31260 stainless steel (SS) and S31254 SS were prepared together with 2-mm-thick plates of S30403 SS and S31603 SS. Table 1 shows the chemical compositions of the test materials. The S31260 SS is dual-phase stainless steel. The S31254 SS is austenitic stainless steel of high chromium and molybdenum content. Both of these materials are candidate canister materials in Japan.

2.2. Constant-load test

A stress corrosion cracking test was conducted by a constant-load method using a coil spring for loading. Fig. 2 shows the shape and dimension of the constant-load-test specimen and a

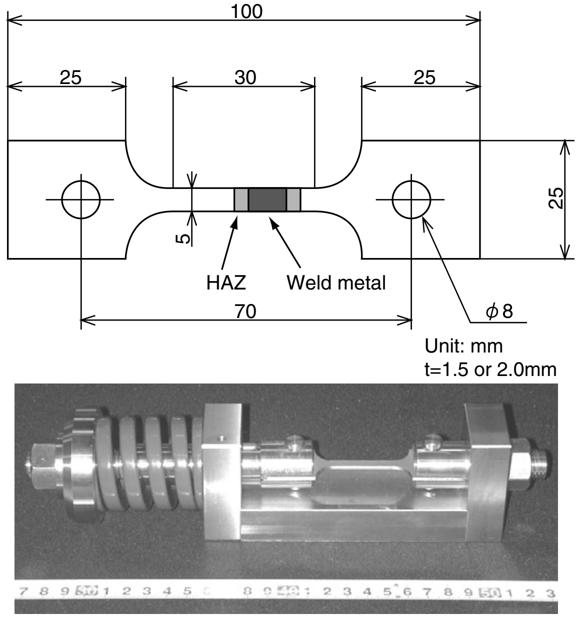


Fig. 2. Shape and dimension of specimen for constant-load test and loading apparatus for test.

Table 1
Chemical compositions of test materials

Material	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	W	N
S31260	0.01	0.41	0.45	0.024	0.001	0.49	6.88	25.67	3.33	0.4	0.23
Weld metal[a]	0.016	0.3	0.5	0.008	0.002	0.49	9.06	25.28	3.06	1.96	0.22
S31254	0.013	0.51	0.55	0.023	0.001	0.62	17.84	19.84	6.12		0.19
Weld metal[a]	0.02	0.13	0.11	0.009	0.001	0.14	55.88	21.59	8.34		
S31603	0.019	0.65	1.23	0.034	0.002		12.07	17.51	2.08		
S30403	0.02	0.67	1.34	0.032	0.002		9.69	18.13			
											Mass%

[a] Tensile specimens have a weld on their gage section.

photograph of the loading apparatus. From the welded joints, tensile specimens with a gage section of 1.5 mm (S31260) or 2 mm (S31254) thick, 5 mm wide, and 30 mm long were machined out so as to contain the welded part in the gage section. After machining, the specimens were polished by #600 emery papers, degreased with acetone, rinsed with deionized water, and then attached to the loading apparatus to apply stress. The stress applied to the SS ranged from $0.25\sigma_{0.2}$ to $1.75\sigma_{0.2}$ (where $\sigma_{0.2}$: 0.2% proof stress). Maximum stress is close to ultimate tensile stress of the test material. To deposit chlorides simulating sea salt particles on the gage section of the specimen, droplets (5×10 μl) of synthetic seawater were placed on the gage section using a micropipette and allowed to dry. The major ingredients of the synthetic seawater used were sodium chloride, magnesium chloride and sodium sulfate. The resultant surface chlorine concentration on the specimen was higher than 10 g m^{-2} as Cl. The loading apparatus with the specimen was placed in a constant-temperature/humidity chamber at 353 K with RH = 35%.

A crack initiation test was performed on the S30403 specimen in the same manner as the constant-load test. Stress was set to $1.1\sigma_{0.2}$, because half of yield stress is enough to initiate crack from the results of previous test. The chloride concentration on the gage section of the specimen was 10 g m^{-2} as Cl. The temperature was kept constant between 293 K and 313 K, and the test was terminated after 500 h. After the test, the chlorides and corrosion products on the gage section were removed, and the specimen surface was observed by a scanning electron microscope (SEM).

2.3. Corrosion test

A corrosion test was conducted to determine the lowest temperature at which corrosion to occur. Flat plates of 75 mm × 75 mm and 2–10 mm thick were prepared as specimens. The surface of the specimens was polished by #600 emery papers and degreased with acetone. Then synthetic seawater was sprayed on the specimens surface, and the chloride concentration of the specimen was adjusted to 10 g m^{-2} as Cl. The test temperature ranged from 273 K to 313 K. The RH was maintained at 35% for all measurements except at 273 K. The RH decreased from 35% to 5% at 273 K during the test. The test was terminated after 500 h. A photograph of the specimen taken after the test was analyzed by image processing software to obtain the rusted area ratio on the specimen surface. We assume that a rust on stainless steel correspond to localized corrosion such as pitting or crevice corrosion induced by chloride.

2.4. Measurement of repassivation potential for crevice corrosion

The repassivation potential for crevice corrosion was measured as the index of susceptibility to crevice corrosion potential. The S30403 SS, S31603 SS, S31260 SS and S31254 SS specimens were prepared for this test. Shape and dimension of the specimen and the crevice former are illustrated in Fig. 3 with an image of an assembled test piece. The surface of the specimens was polished by #600 emery papers and degreased with acetone. Synthetic seawater was prepared for use as the test solution whose pH was adjusted to 8.2 by sodium hydroxide addition. The temperature range was between 283 K and 353 K. The procedure for the repassivation potential measurement is illustrated in Fig. 4. Crevice corrosion occurs during the constant-current period of 2 h. When the current increased by 20 μA, the potential was decreased by 10 mV during the potentiostatic period. The measurement was terminated when the current showed no increase during the 2 h of constant potential period; the potential at that time was regarded as the crevice corrosion potential $E_{R,crev}$.

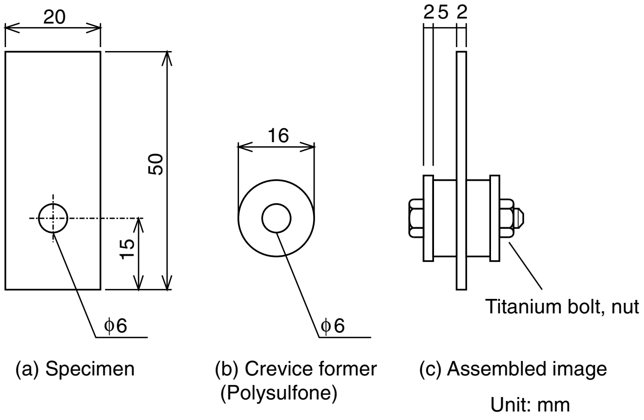


Fig. 3. Shape and dimension of specimens used for crevice corrosion potential measurement.

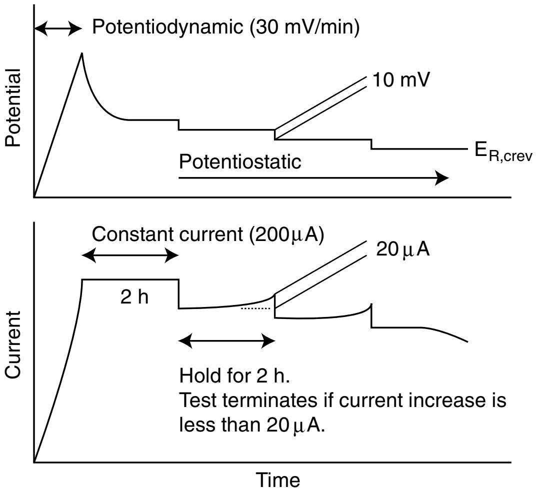


Fig. 4. Measurement of repassivation potential for crevice corrosion.

3. Results and discussion

3.1. Constant-load test

Fig. 5 shows the relationship between applied stress and failure time for the various stainless steels tested at 353 K with RH = 35%. The S31260 SS and S31254 SS specimens showed no failure for

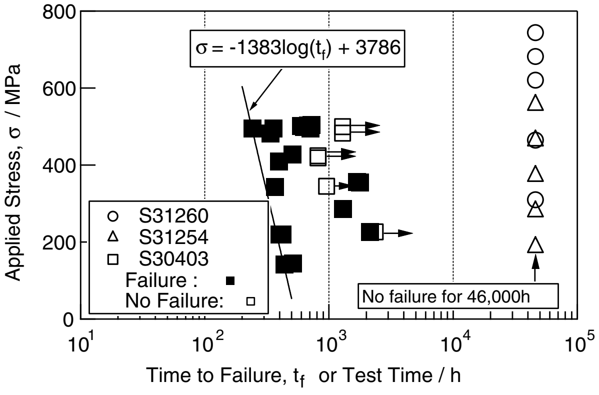


Fig. 5. Results of constant-load test at 353 K and RH = 35%.

46 000 h, whereas the S30403 SS specimens failed within 500 h under the same test conditions. Although each specimen of S31260 SS and S31254 SS had rust on the surface, no visible crack was found. There was no difference in corrosion properties between the weld and base metals in the gage section.

3.2. Corrosion test

The rusted area on the specimen surface decreased with decreasing temperature. Only a few rust spots were observed on the specimen of S31260 SS and S31254 SS tested at 298 K. No rust spot was observed on the specimen tested at 293 K for the same materials. The rusted area ratios of these specimens were obtained by analyzing photoimages of the specimens. The results are summarized in Fig. 6, showing the relationship between rusted area ratio and temperature. The S31603 SS specimens corroded even at 293 K, whereas the S31260 SS and S31254 SS specimens showed no corrosion at 293 K. The S31260 SS and S31254 SS specimens seemed to have a threshold temperature for corrosion at approximately 293 K.

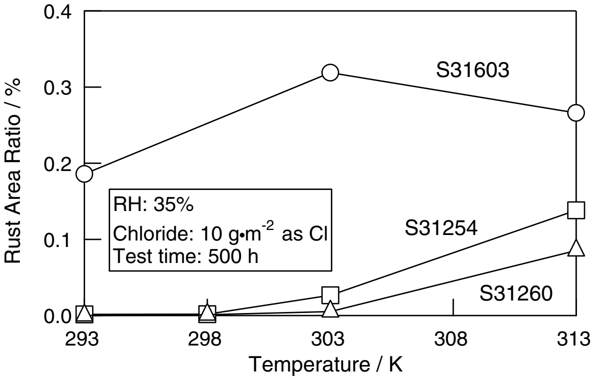


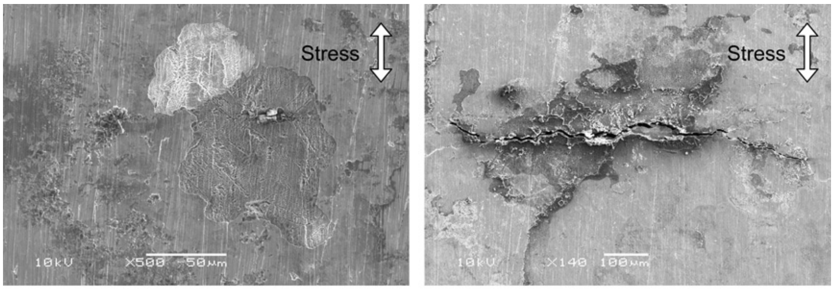
Fig. 6. Temperature dependence of rust area ratio for various stainless steels.

3.3. Crack initiation test

Fig. 7 shows SEM images of the constant-load-test specimen after the crack initiation test. The specimen is S30403 SS. Fig. 7(a) shows the SEM image of the specimen tested at 303 K for 500 h. Although several rust spots were observed on the specimen and shallow corrosion was observed under the rust spots, no crack was found in the corroded region. Fig. 7(b) shows the SEM image of the specimen tested at 313 K. Distinct cracks were observed on the specimen. Thus it was concluded that the threshold temperature for the cracking of S30403 SS was between 303 K and 313 K.

3.4. Crevice corrosion potential

Fig. 8 shows examples of raw data obtained by the repassivation potential measurement for crevice corrosion. Fig. 8(a) is the result for S30403 SS at 353 K, which showed the typical tendency of the measurement. Fig. 8(b) shows the result for S31260 SS at 293 K. Because of difficulty to initiate crevice corrosion at a low temperature for the high-corrosion-resistant stainless steel, the constant current (200 μA) was held for 2 h (10^4 s in Fig. 8(b)) at 333 K in this case and then the temperature was decreased to 293 K in the con-



(a) 303 K, RH=35%

(b) 313 K, RH=35%

Fig. 7. SEM images of constant-load-test specimen: S30403, 1.1$\sigma_{0.2}$, 500 h.

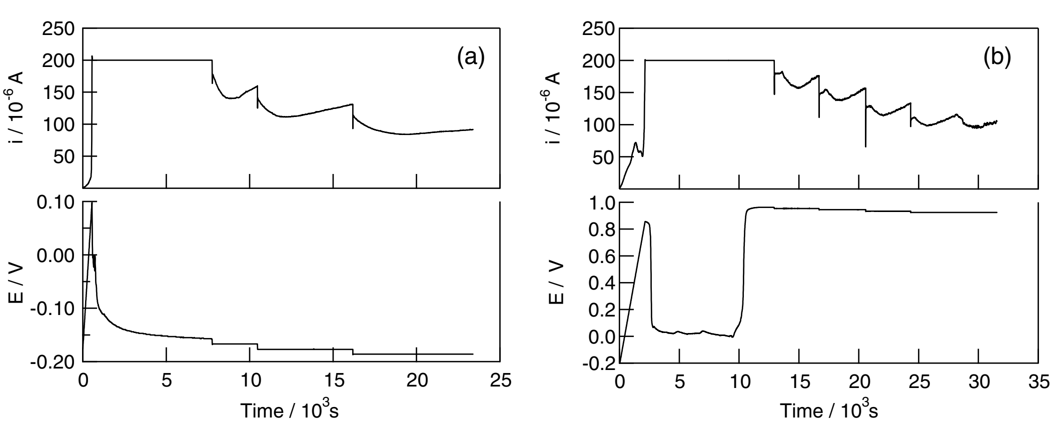


Fig. 8. Examples of crevice corrosion potential measurement. (a) S30403, 333 K; this is a typical result for this measurement. (b) S31260, 293 K; the temperature was kept at 333 K during the initial 2 h period of constant current and then decreased to 293 K. Potential increased with decreasing temperature.

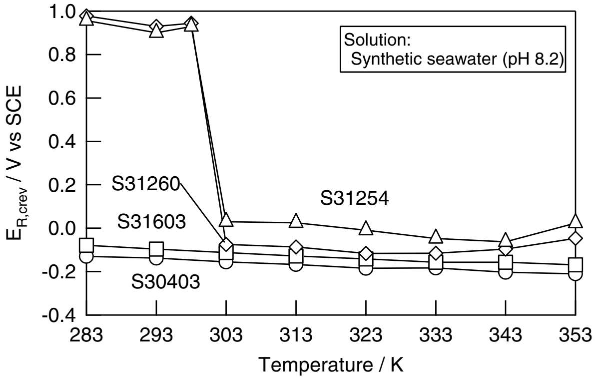


Fig. 9. Temperature dependence of crevice corrosion potential; $E_{R,crev}$ values for various stainless steels.

stant-current phase. The potential increased with decreasing temperature.

Fig. 9 shows the relationship between crevice corrosion potential and temperature. When the temperature was higher than 303 K, the difference in the potential among the specimens was small, although the potential depended on the SS types. The crevice corrosion potentials of S31260 SS and S31254 SS increased to a high value when the temperature decreased to 298 K. These potentials correspond well to the oxygen or chlorine evolution potential. The crevice corrosion potentials of S30403 SS and S31603 SS remained at the low values of less than 0 V vs. SCE even at temperature below 298 K.

Results of the crevice corrosion potential measurement, corrosion test and constant-load test are summarized in one graph for each kind of material. Fig. 10(a) shows the summary of the test results for S30403 SS. The S30403 SS corroded even at 273 K. The

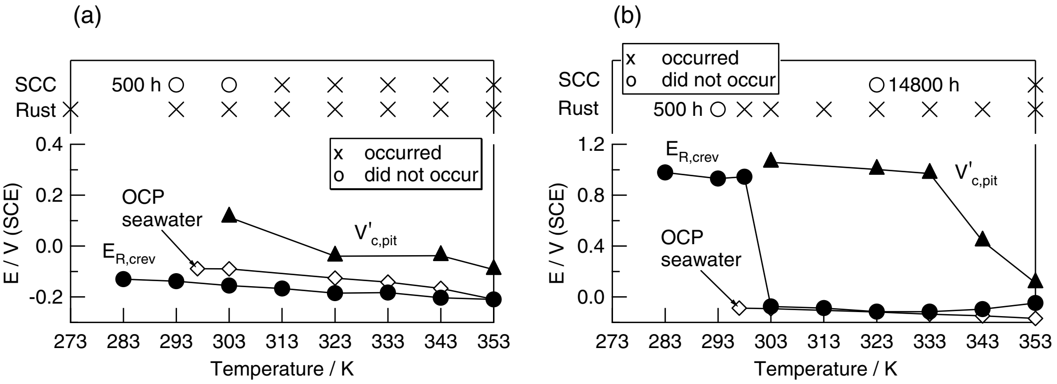


Fig. 10. Summary of temperature dependence of corrosion or cracking. (a) S30403, (b) S31260, SCC: results of constant-load-test (test termination time attached for good), rust: results of corrosion test, $V^{prime}_{c,pit}$: pitting potential, OCP: open circuit potential in aerated synthetic seawater, $E_{R,crev}$: crevice corrosion potential.

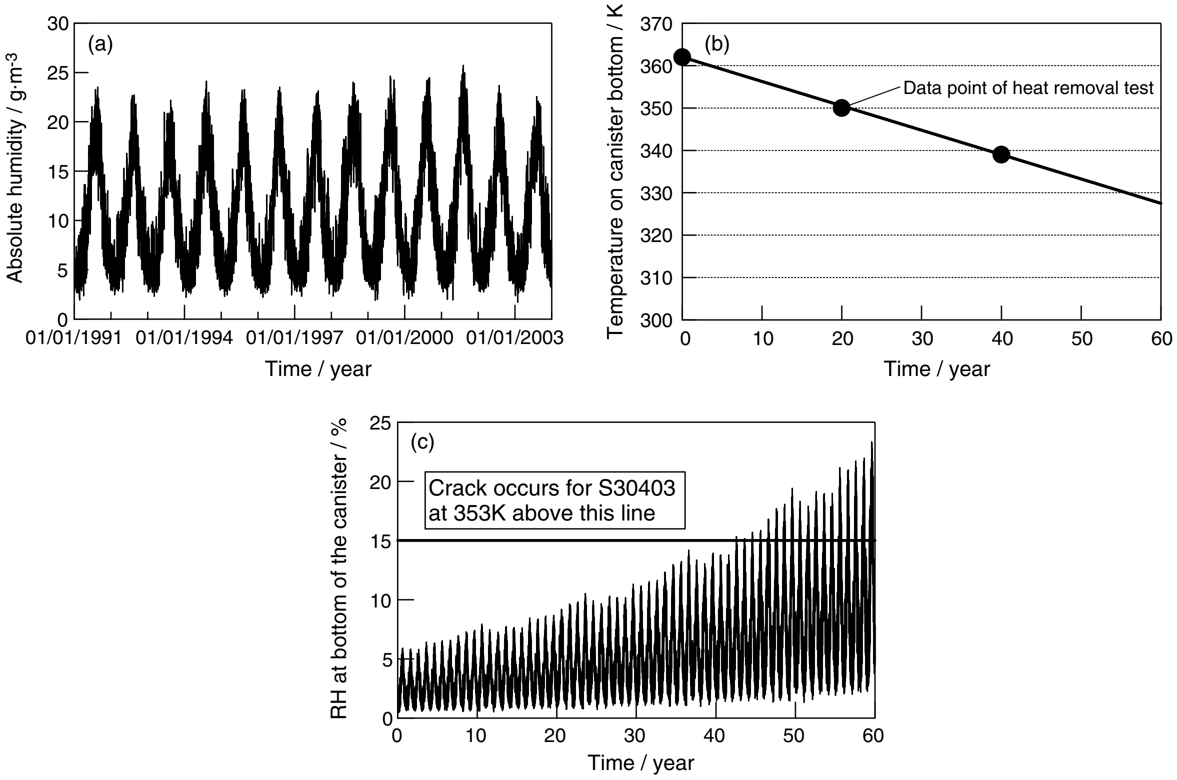


Fig. 11. Example of evaluation of canister integrity against SCC. (a) Hourly absolute humidity obtained from weather station in Japan; (b) result of heat removal test; and (c) RH changes with time for 60 years.

crevice corrosion potential is low even at 283 K, and corresponds reasonably well with the result of the corrosion test. The S31603 SS gave almost the same tendency as S30403 SS. For the S30403 SS, the threshold temperature for cracking was between 303 K and 313 K. The threshold temperature for cracking was higher than that for corrosion. Fig. 10(b) shows the summary of the test results for the S31260 SS. The threshold temperature for corrosion, which produces rust spots on the specimen surface, was approximately 293 K. The crevice corrosion potential increased to a considerably high value when temperature decreased to 298 K. The threshold temperature obtained from the corrosion test coincided with the threshold temperature for crevice corrosion obtained by the electrochemical measurement. Although the surface potential has not been determined yet, the threshold temperature for crevice corrosion seems to be approximately 298 K. We also conducted a constant-load test at 323 K, and no crack was found after exposure of 14800 h. The threshold temperature for cracking seems to be higher than the threshold temperature for corrosion. Almost the same results were obtained for S31254 SS.

3.5. Evaluation of canister integrity

An example of calculation, according to the method described in Section 1, to assess canister integrity is discussed in this section. As mentioned in the previous section, the critical temperature below which no SCC being expected has not been determined yet. However the storage period for interim spent fuels has been publicly announced to be 40–60 years in Japan, thus the termination time in the calculation is fixed to 60 years in this evaluation. Hourly absolute humidity data were obtained from the weather station data, as shown in Fig. 11(a). The change in the canister temperature was obtained from the experimental result of a heat removal test performed by a mock-up canister [8] as shown in Fig. 11(b). By combining both the data, the relative humidity change with time on the canister surface was calculated and shown in Fig. 11(c). In the figure, a line is drawn at RH = 15% as the critical of RH below which no SCC to occur. The critical RH, indicating the cracking threshold for S30403 SS at 353 K, is cited from a previous work [4]. The summation of time above this line is the time period in which SCC might be possible to initiate. This time is calculated as 15430 h, which is shorter than 46000 h, the test time for the constant-load test at 353 K for S31260 SS and S31254 SS. However the calculation suggested that the canisters are not likely to fail during the 60 years of storage.

4. Summary

A constant-load test was carried out to determine SCC failure time. The S31260 SS and S31254 SS specimens did not fail after 46000 h at 353 K with RH = 35% under deposition of 10 g m^{-2} chloride on the specimen gage section.

The S30403 SS and S31603 SS specimens corroded at 273 K with RH = 35%. The crevice corrosion potential of the S30403 specimens was about -0.1 to -0.2 V (SCE) between 283 K and 353 K. These results suggest that the conditions required for SCC initiation are satisfied at less than 283 K. No initial cracking was observed at 303 K, whereas distinct cracks were observed at 313 K.

The corrosion test specimens of S31260 SS and S31254 SS showed no rust at 293 K with RH = 35%. The crevice corrosion potential of S31260 SS and S31254 SS is more than 0.9 V (SCE) below 298 K while the crevice corrosion potential above 303 K is -0.1 to 0 V (SCE). These results suggest that the threshold temperature for SCC initiation is about 298 K.

The period in which the stainless-steel canister may suffer from SCC during the 60 year period was calculated from actual weather and decay heat test data as 15430 h, which is far less than the constant-load test time of 46000 h without SCC failure. The calculation suggests that the S31260 SS and S31254 SS canister can maintain the integrity for 60 years of storage.

Acknowledgements

Dr Gen Nakayama of IHI Corporation gave us helpful suggestions in the measurement of repassivation potential for crevice corrosion.

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