

HYDROGEN ABSORPTION AND CREVICE CORROSION BEHAVIOR OF Ti GRADE 12  
DURING EXPOSURE TO IRRADIATED BRINE AT 150°C

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ABSTRACT

The Ti Grade 12 alloy is being considered for use as a corrosion-resistant overpack for high-level nuclear waste packages in a salt repository. Two experiments performed at Pacific Northwest Laboratory (PNL) were directed toward determining this material's resistance to hydrogen absorption and crevice corrosion during exposure to concentrated anoxic Na/Mg/K chloride brines at 150°C under conditions of gamma irradiation. At an irradiation intensity of  $2 \times 10^4$  rad/hr, the hydrogen absorption rate of Ti Grade 12 specimens was low, and appeared to stop entirely after six months. Grit-blasted specimens absorbed considerably more hydrogen than as-received sheet stock specimens. Crevice corrosion was observed between specimen spacers and between (purposefully) contacting specimens. The observed crevice corrosion susceptibility must be taken into account when considering the Ti Grade 12 alloy as a candidate waste package overpack material.

INTRODUCTION

The Salt Repository Project (SRP) of the U.S. Department of Energy has developed several conceptual designs for waste packages intended for use in the disposal of high-level nuclear waste in a salt repository. The design currently receiving primary emphasis utilizes a thick container made of low-carbon steel as the primary containment barrier (1,2). The steel container is expected to corrode in the presence of elevated-temperature brines, so a corrosion allowance is provided for the expected metal loss. An alternate waste package concept utilizes a relatively thin overpack of titanium alloy, considered to be highly corrosion resistant, surrounding the low-carbon steel container (3). The titanium alloy selected for this service, Ti Grade 12, was developed to exhibit a high degree of resistance to general corrosion and crevice corrosion in high-temperature brines. The hydriding and corrosion behavior of the Ti Grade 12 alloy is the subject of the present paper.

Titanium alloys have a high affinity for hydrogen. For example, some of the hydrogen resulting from the reaction of titanium alloys with water to form  $TiO_2$  is absorbed by the metal; and hydriding of the metal can be readily achieved either by making it the cathodic member in an electrochemical cell or by exposing it to high-purity hydrogen gas at elevated temperatures. Also, it has been shown that Ti Grade 2 and Ti Grade 12 can absorb hydrogen directly from an irradiated ( $2 \times 10^6$  rad/hr, maximum) low-ion-strength basaltic ground-

water environment at 250°C (4). Absorbed hydrogen tends to embrittle titanium alloys, with the extent of embrittlement being highly dependent on the amount of hydrogen absorbed, the composition and the microstructure of the alloy, the temperature of the mechanical tests, and the mechanical loading characteristics (i.e., static or dynamic, and if dynamic, the strain rate imposed). Also, should gross quantities of hydrogen be absorbed by the metal, the metal may be converted entirely to hydride phase, with consequent disintegration of the structure.

If the complete conversion of the structure, or parts of the structure, to hydride is considered improbable, then there are two major modes of embrittlement that are of concern: tensile embrittlement and sustained-load-cracking (hydrogen-induced delayed failure) (5). Tensile embrittlement may be separated into two components: embrittlement at high strain rates (during impact) and slow-strain-rate embrittlement. No published data are known to exist on the impact testing of Ti Grade 12 specimens charged with hydrogen. However, a significant amount of work has been performed using the slow-strain-rate test approach. Sorenson and Ruppen (6) tested notched tensile specimens in both air and Brine A (a Na/Mg/K chloride brine described in the Materials section of this report; its composition is given in Table I) at temperatures from 25° to 150°C. The specimens, precharged with hydrogen, contained various hydrogen concentrations between 24 and 975 ppm. Hydrogen concentrations to 445 ppm had little effect on the mechanical properties of the material under

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

slow-strain-rate test conditions. Significant embrittlement was found between 445 and 975 ppm hydrogen. Whether the reduction observed would be a significant consideration in the design of a nuclear waste package overpack is not known. Also, the effects of hydrogen concentration beyond 975 ppm were not explored. The same investigators cathodically polarized smooth tensile specimens of Ti Grade 12 in Brine A at 150°C and strained them to failure. At a cathodic current density of  $\sim 7 \text{ mA/cm}^2$  there was a dramatic drop in mechanical properties. Optical micrography of the sample revealed severe secondary cracking along the length of the gage section. The change in mechanical properties was attributed to hydrogen embrittlement.

The foregoing slow-strain-rate data indicate that the alloy is not particularly sensitive to hydrogen under conditions of slow plastic deformation, especially if the hydrogen concentrations in the metal do not exceed  $\sim 500$  ppm and if the results obtained to date are applicable to all fabricated forms of the alloy, including weldments. The hydrogen-induced failure mode of much more potential concern to the longevity of a Ti Grade 12 overpack is sustained-load cracking, or hydrogen-induced delayed failure. This failure mode is due to the growth of sub-critical cracks under a static load at stress intensities less than  $K_{IC}$ . Such crack growth is attributed to the formation of hydride phase in the highly stressed region near the crack tip, with the subsequent fracture of the hydride and advancement of the crack. Such cracking has been observed in alpha + beta alloys, and Ti Grade 12 is such a two-phase alloy (7). The effect has been observed at hydrogen concentrations  $< 50$  ppm in a Ti-6Al-4V alloy, so very little hydrogen is needed to cause degradation under the right circumstances. Unfortunately, as yet no results have been published on the effects of hydrogen on sustained-load cracking in the Ti Grade 12 alloy.

In spite of the uncertainty regarding the amount of hydrogen that can be tolerated by the Ti Grade 12 alloy, the studies addressed in the present paper were undertaken primarily to determine the rate of hydrogen absorption by Ti Grade 12 specimens exposed to irradiated hydrothermal brines. The effect of hydrogen on the mechanical properties of the material and any corrosion observations associated with the study were considered to be adjuncts to the primary objective. Irradiation was considered to be an important factor in the environment because use of a corrosion-resistant overpack is consistent with use of a relatively thin waste package container and overpack, and hence, relatively high radiation intensities at the surface of the package.

#### MATERIALS

Two brine compositions were used in the present studies: Brine A, a Na/Mg/K chloride brine formulation based on the composition of several brines from the potash-rich region overlying the Waste Isolation Pilot Plant (WIPP) site in New Mexico; and PBB3 (Permian Basin Brine No. 3), a formulation based on the composition of brines found in inclusions in a salt horizon representative of that targeted for the salt repository at the Deaf Smith site in Texas. The compositions of the brines are presented in Table I.

Two alloys, Ti Grade 12 and Ti Grade 2 (commercial purity titanium), each in sheet and plate form, were used in the present study. The sheet stock was used in the fabrication of U-bend and corrosion-coupon specimens, and the plate stock was used in the fabrication of Charpy impact and fracture toughness specimens. The compositions of the alloys are presented in Table II.

TABLE I  
Brine Compositions

Ion	Concentration, ppm	
	Brine A	PBB3
Na <sup>+</sup>	42,000	19,000
K <sup>+</sup>	30,000	8,700
Mg <sup>2+</sup>	35,000	44,000
Ca <sup>2+</sup>	600	12,000
Sr <sup>2+</sup>	5	--
Cl <sup>-</sup>	190,000	170,000
SO <sub>4</sub> <sup>2-</sup>	3,500	130
I <sup>-</sup>	10	--
HCO <sub>3</sub> <sup>-</sup>	700	--
Br <sup>-</sup>	400	2,000
BO <sub>3</sub> <sup>-</sup>	1,200	--

TABLE II  
Compositions of Titanium Alloys

	Element, wt%						
	N	C	H	O	Fe	Mo	Ni
<u>Ti Grade 12</u>							
0.79-mm sheet	0.008	0.021	0.005	0.13	0.12	0.30	0.67
12.7-mm plate	0.009	0.012	0.008	0.12	0.09	0.31	0.74
<u>Ti Grade 2</u>							
1.57-mm sheet	0.016	0.02	0.006	0.151	0.05	--	--
12.7-mm plate	0.013	0.013	0.006	0.14	0.13	--	--

#### EXPERIMENTAL

Two tests were performed. The first test utilized an environment of Brine A (Table I) at a temperature of 150°C, and, to provide an irradiation overtest, a maximum gamma (<sup>60</sup>Co) irradiation intensity of  $2 \times 10^6$  rad/hr was imposed on the system. The test contained specimens of both Ti Grade 12 and Ti Grade 2 materials in the form of plain corrosion-coupon specimens, U-bend specimens, Charpy impact specimens, and bolt-loaded compact-tension fracture toughness specimens pre-cracked and stressed to 22 MPa  $\sqrt{m}$ . The specimens were contained in an electrically heated Zr-2.5 Nb autoclave held in an access tube in an irradiation facility. The anoxic brine flowed through the autoclave on a once-through basis at a flow rate of 35 mL/hr. The system pressure was maintained at  $\sim 3$  MPa. Because of the length of the specimen rack relative to the length of the <sup>60</sup>Co sources, irradiation intensity was not uniform over all the specimens in test (see Fig. 1). The test duration was three months.

In the second test (Test 2) the irradiation intensity was reduced to  $2 \times 10^4$  rad/hr, a level much closer to that actually expected at the outside of a waste package [ $\sim 1 \times 10^3$  rad/hr for 10-year old spent fuel and a waste package container just thick enough to resist lithostatic pressures (2)].

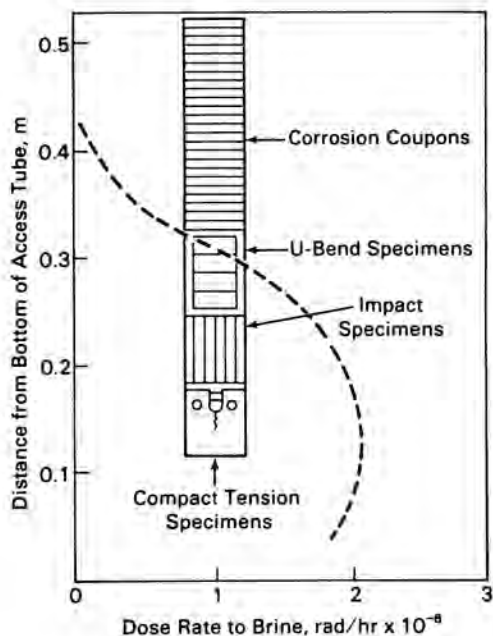


Fig. 1. Variation of Intensity of Gamma Irradiation over Specimen Array

The test was run in a static (unrefreshed) mode, with changes of brine at each specimen inspection. Only plain coupons of Ti Grade 12 material, 36-mm square, in both the as-received and SiC-grit-blasted conditions, were exposed in this test. Also, a number of specimens were allowed to contact each other closely as "crevice pair" specimens during the 10 1/2 months duration of their exposure (Fig. 2). The maximum exposure attained in this test was 18 months. As in Test 1, the autoclave was made of a Zr-2.5 Nb alloy, with the radiation being derived from  $^{60}\text{Co}$ . The system pressure was maintained at  $\sim 3$  MPa.

## RESULTS

### Test 1

Within approximately two months of test initiation, bubbles of hydrogen gas were being discharged from the exit tubing along with the effluent brine. When the autoclave was opened for specimen examination, certain test specimens had been greatly damaged (Fig. 3), with much particulate  $\text{TiH}_2$  and  $\text{TiO}_2$  in evidence. The primary damage occurred to the Ti Grade 2 Charpy impact specimens and the associated Ti Grade 2 rack structure, though damage was evident elsewhere, including the corners of the Ti Grade 2 and Ti Grade 12 fracture toughness specimens (no crack elongation was observed in these specimens) and the Ti Grade 12 band used to restrain the Charpy specimens. The U-bend specimens showed no signs of incipient failure. Hydrogen analyses on representative Ti Grade 12 specimens, done in quadruplicate, showed an average increase of 23 ppm by weight; and the impact specimen restraining band, which had failed during the test,

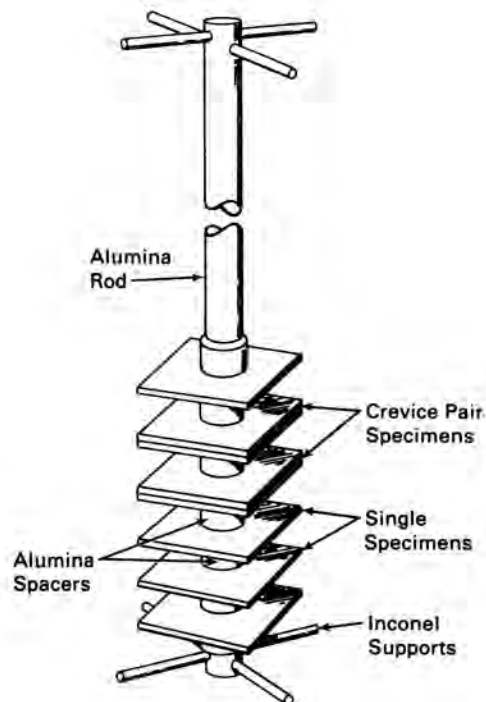


Fig. 2. Method of Mounting Specimens in Autoclave (Test 2)

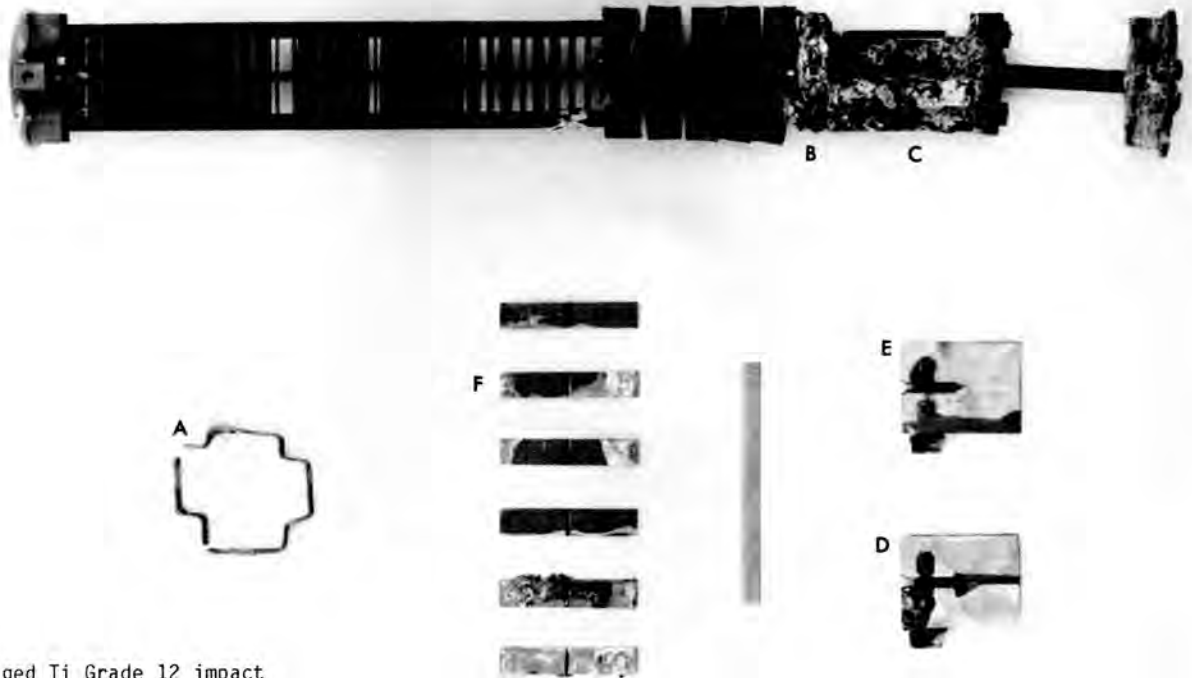
showed 2000 ppm. The Ti Grade 2 material absorbed hydrogen at approximately twice the rate of the Ti Grade 12 material.

The severe attack could have been initiated in either a crevice area (e.g., between Charpy specimens) or on a sharp machined corner of a specimen or rack component. Once started, hydriding and oxidizing reactions proceeded rapidly, with the attack spreading from specimen to specimen as the normally protective oxide film became breached and unable to re-passivate.

### Test 2

The specimens were first examined after 6 months. (No crevice pairs had yet been put in test.) At that time, it was noted that two of the twenty-one specimens in the test were forming thick layers of tenacious corrosion product, identified by x-ray-diffraction as  $\text{TiO}_2$ , on their surfaces. This oxide was apparently emanating from the crevice regions associated with the alumina spacers. The two specimens were cut in half, and the oxide was abraded from one half of each specimen with 180-grit emery paper. Classic crevice corrosion was found underneath the oxide on both specimens, with the maximum depth of attack being approximately 0.1 mm. One of the specimens is shown in Fig. 4.

At the conclusion of the test (a maximum exposure of 18 months for some specimens) all of the specimens were removed for analysis. All of the crevice-pair specimens (six pairs, both as-received and grit-blasted) showed some degree of corrosion where they contacted each other. These specimens had a total exposure of 10 1/2 months. Typical crevice pairs are



- A - Damaged Ti Grade 12 impact specimen retainment band
- B - Attack on Ti Grade 2 rack
- C - Attack on Ti Grade 2 impact specimens
- D - Attack on Ti Grade 2 specimen
- E - Attack on Ti Grade 12 specimen
- F - Undamaged Ti Grade 12 specimen

Fig. 3. Appearance of Specimens After Three-Month Test Exposure. Discoloration or presence of deposits does not necessarily indicate attack, as specimens were not cleaned prior to photograph. Rule is 96 mm long.

shown in Fig. 5. A specimen (R226X) exhibiting what appeared to be the most advanced corrosion was cleaned by light abrasion with emery paper. The sites of crevice corrosion attack under the  $TiO_2$  layer are shown in Fig. 6. The attack had proceeded to an average depth of  $\sim 0.07$  mm in several places on the specimen.

Specimens from this test were analyzed for hydrogen content. The results of these analyses are shown in Figures 7 and 8.<sup>(a)</sup> The hydrogen absorption rates found in this study were remarkably low, much lower, for example, than those reported by Schutz and Hall (8) or the previously described results obtained from Test 1. The hydrogen absorption appeared to stop after six months; and the crevice pairs (which were sampled away from areas of advanced corrosion) showed no enhanced hydrogen absorption. The reason for the low hydrogen pickup may be related to the oxygen fugacity in the irradiated system caused by brine radiolysis. That is, a relatively oxidic environment might be expected to be more resistant to hydrogen absorption

(because of "film healing") than in an anoxic environment such as the one employed by Schutz and Hall (8) or one brought about by gross metal reaction such as occurred in Test 1. There appeared to be little or no tendency for the metal specimens to absorb hydrogen directly from the irradiated environment, as previously reported (4); instead, the hydrogen appears to have come from the minimal reaction of the metal with water in forming the oxide tarnish film.

The observation that crevice corrosion will occur in the Ti Grade 12 alloy in brine environments under certain conditions is consistent with the findings of several other investigators (9,10,11,12), although some studies have found Ti Grade 12 to be free from crevice corrosion (8,13). The wide divergence of experimental results regarding crevice corrosion is difficult to explain. Griess (14), in his study of the crevice corrosion of unalloyed titanium, found no crevice corrosion in deaerated solutions, regardless of the pH. If oxygen, or some other oxidizing specie, is

(a) If it is assumed that the as-received Ti Grade 12 sheet stock is of constant hydrogen concentration (estimated at 25.1 ppm) throughout, then the 95% confidence interval associated with each data point in Figures 7 and 8 is 5.5 ppm. Each data point in Figures 7 and 8 represents the average of duplicate hydrogen-analysis results obtained from one test specimen.





Fig. 4. Specimen Showing Crevice Corrosion Attack After Six Months Exposure. Half of specimen (on right) has been abraded to reveal attack near hole. Specimen was originally 36-mm square, with a 9.6-mm-diameter hole.



Fig. 6. Sites of Crevice-Corrosion Attack Under Corrosion Product ( $TiO_2$ ) Layer. Areas of severe attack are noted.

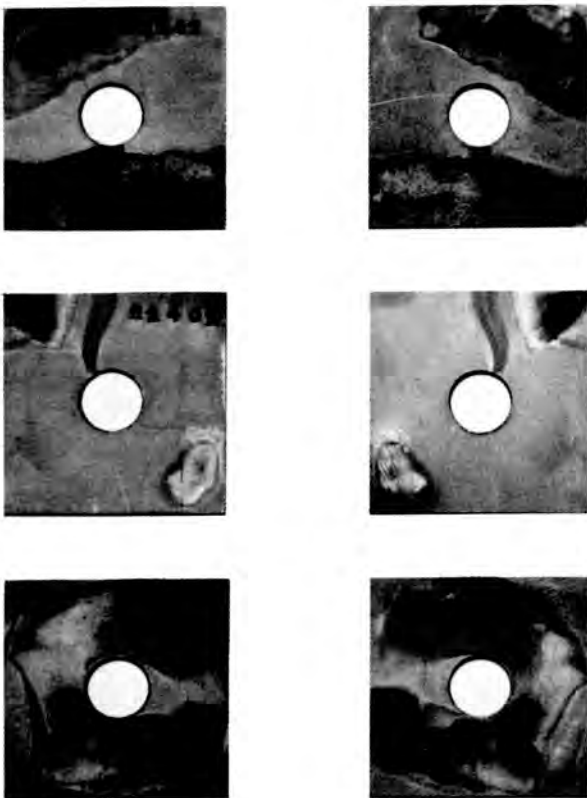


Fig. 5. Separated "Crevice-Pair" Specimens of As-Received Material, After 10-1/2 Months Exposure. Specimens are 36-mm square. Previously contacting surfaces are shown.

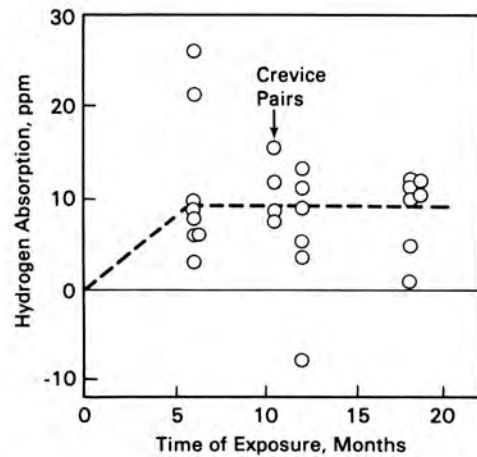


Fig. 7. Hydrogen Absorption Results, As-Received Specimens

## CONCLUSIONS

1. Ti Grade 12 exhibited more resistance to hydrogen absorption than Ti Grade 2 in an irradiated brine (Brine A) environment containing rapidly corroding titanium metal at 150°C and an irradiation intensity of  $2 \times 10^6$  rad/hr (maximum).
2. Ti Grade 12 specimens absorbed only small quantities of hydrogen over a time period of 18 months in a 150°C brine (PBB3) environment irradiated at a dose rate of  $2 \times 10^4$  rad/hr, with the absorption essentially stopping after six months. Grit-blasted specimens absorbed more hydrogen than as-received sheet stock.
3. Ti Grade 12 exhibited severe crevice corrosion in a 150°C PBB3 brine environment irradiated at a dose rate of  $2 \times 10^4$  rad/hr. Irradiation of the environment and the formation of oxidizing radiolysis products were not sufficient to maintain the metal in the crevice region in an oxidized, passive condition.

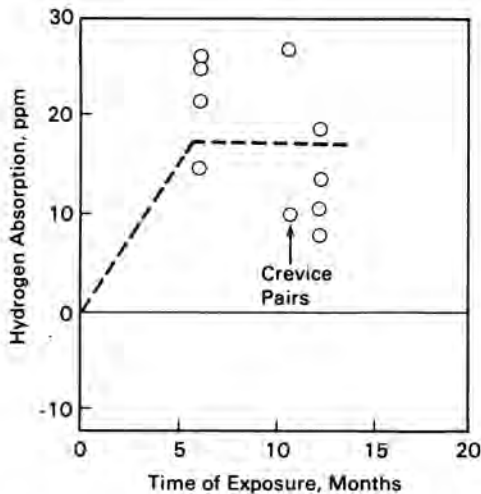


Fig. 8. Hydrogen Absorption Results, Grit-Blasted Specimens

required for the crevice corrosion of Ti Grade 12, it is not surprising that studies performed in chloride brines that are maintained in an anoxic condition (i.e., with free oxygen being rigorously excluded from the system) would not produce significant crevice corrosion. Some attack would be expected, however, because of the difficulty of completely excluding free oxygen from any corrosion test system, including that entrained in the initial brine charge. Thus, even an "anoxic" test would be expected to show some crevice corrosion, even if the attack is limited to very thin interference color oxide films. On the other hand, the presence of large amounts of oxidant could cause oxygen to permeate the entire system, even that area within the crevice, and thereby prevent the formation of the galvanic cell giving rise to crevice attack. This occurrence would explain the lack of attack reported by Braithwaite et al. (13), who exposed Ti Grade 12 specimens to Brine A containing 250 ppm  $O_2$  at temperatures to 300°C. It appears reasonable, from the foregoing considerations, that crevices of the size generally employed in experimental studies would be susceptible to initiation and promotion of crevice attack if the level of oxidant were maintained at some intermediate value, perhaps near that resulting from air saturation, i.e., about 1.5 ppm for PBB3. Interestingly, as the present PNL study clearly shows, irradiation cannot reliably provide an adequate concentration of oxidizing species inside the crevice to passivate the metal surface and prevent the initiation of crevice attack. Rather, it appears that the oxidizing species formed can participate strongly in the cathodic reaction without seriously impeding the anodic reaction within the crevice.

The fact that crevice corrosion has been observed, to some degree or other, by several investigators over a range of exposure conditions relevant to those that could exist in a salt repository must be taken into account when considering the candidacy of Ti Grade 12 as a waste package overpack material.

## ACKNOWLEDGMENTS

The authors wish to acknowledge the contribution of G. L. Jones, Westinghouse Hanford Company, who expedited the PNL experimental work at the gamma irradiation facility; the effort of M. C. Burt, Westinghouse Hanford Company, in performing the required hydrogen analyses; the programmatic assistance offered by D. J. Bradley, PNL, and J. A. Carr and J. S. Perrin, BPMD (Battelle Project Management Division); and the programmatic support provided by the Salt Repository Project of the U.S. Department of Energy.

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