PROGRESS REPORT

**General Corrosion, Irradiation-
Corrosion, and Environmental-
Mechanical Evaluation
of Nuclear Waste Package
Structural Barrier Materials**

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Pacific Northwest Laboratory
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SUMMARY

The disposal of high-level nuclear wastes in deep underground repositories may require the development of a waste package that will keep the radioisotopes completely contained for time periods up to 1000 yr (proposed NRC Regulation 10CFR60). The primary candidate geologic media being considered for repository siting are basalt formations underlying the Hanford Site; tuff deposits on the Nevada Test Site; and a salt site that has not yet been selected. If the structural barrier elements of a waste package (e.g., canister, overpack, or hole sleeve) are expected to contribute to the long-term containment of the radioisotopes, they must be fabricated from materials that will resist the anticipated major degradation modes associated with the individual repository environments for the required time period.

As part of the Waste Package Program, sponsored by the Department of Energy through the Office of Nuclear Waste Isolation, Pacific Northwest Laboratory is studying the general corrosion, irradiation-corrosion, and environmentally enhanced crack propagation of five candidate materials in high-temperature aqueous environments simulating those expected in basalt and tuff repositories. The materials include three cast ferrous materials (ductile cast iron and two low-alloy Cr-Mo cast steels) and two titanium alloys, titanium Grade 2 (commercial purity) and Grade 12 (a Ti-Ni-Mo alloy).

The general corrosion results are being obtained by autoclave exposure of specimens to slowly replenished simulated ground water flowing upward through a bed of the appropriate crushed rock (basalt or tuff), which is maintained at the desired test temperature (usually 250°C). In addition, tests are being performed in deionized water. Metal penetration rates of iron-base alloys are being derived by stripping off the corrosion product film and weighing the specimen after the appropriate exposure time. The corrosion of titanium alloy specimens is being determined by weight gain methods. The irradiation-corrosion studies are similar to the general corrosion tests, except that the specimen-bearing autoclaves are held in a ^{60}Co gamma radiation field at dose rates up to 2×10^6 rad/h. For evaluating the resistance of the candidate materials to environmentally enhanced crack propagation, three methods are

being used: U-bend and fracture toughness specimens exposed in autoclaves; slow strain rate studies in repository-relevant environments to 300°C; and fatigue crack growth rate studies at ambient pressure and 90°C.

The preliminary data suggest a 1-in. corrosion allowance for iron-base barrier elements intended for 1000-yr service in basalt or tuff repositories. No evidence has yet been found that titanium Grade 2 or Grade 12 is susceptible to environmentally induced crack propagation or, by extension, to stress corrosion cracking.

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INTRODUCTION

The Terminal Isolation activity of the U.S. Commercial Waste Management Program is responsible for identifying and exploring candidate geologic repository sites. Three areas, basalt deposits underlying the Hanford Site, tuff deposits on the Nevada Test Site, and a yet-to-be-determined salt site, are considered the prime repository candidates. In each repository, the waste form would be enclosed in a waste package incorporating one or more of the following components: canister, overpack, and hole sleeve. Any of these components would be considered structural barriers if they were expected to perform a long-lived waste containment function, i.e., containment extending beyond the 100-yr retrievability period.

The most stringent waste package performance criterion is the requirement that all radionuclides be contained for 1000 yr (Proposed Rule 10CFR60, Subpart E), as structural barriers are susceptible to a number of failure modes that could compromise their effectiveness over this time period. Some of the potentially important degradation phenomena are general (uniform) corrosion; nonuniform corrosion (pitting, crevice corrosion); stress corrosion cracking; hydrogen embrittlement; aging reactions; and mechanical overload.

Currently, programs are under way at several laboratories, primarily Pacific Northwest Laboratory (PNL), Sandia National Laboratory (SNL), Rockwell Hanford Operations (RHO), and Lawrence Livermore National Laboratory (LLNL), to address the selection and validation of materials for waste package structural barriers. These programs are being sponsored by the Department of Energy (DOE) through the Office of Nuclear Waste Isolation (ONWI). PNL's role involves selecting, characterizing, and recommending structural barrier materials for basalt and tuff repository applications. This progress report documents the work accomplished through September 1982 under Task 2 of the ONWI-funded PNL Waste Package Program (WPP). Included are details of the technical approach, materials, specific tests, and results.

Three types of tests are being conducted: general (uniform) corrosion, irradiation-corrosion, and environmental-mechanical effects. The materials

being evaluated include a ductile cast iron, two low-alloy Cr-Mo cast steels, and two titanium alloys (Grade 2, a commercial purity material, and Grade 12, a Ti-Ni-Mo alloy).

General corrosion tests are being conducted at temperatures to 250°C in flowing (refreshed) autoclave systems, in simulated basalt ground water, tuff ground water, and deionized water. The maximum test duration attained to date is 6 months.

The irradiation-corrosion testing utilizes flowing autoclaves installed in a ^{60}Co radiation facility, at radiation intensities as high as 2×10^6 rad/h and temperatures of 250°C. Irradiation-corrosion tests have been performed only on basalt ground water; the maximum test duration attained is 6 months.

The intent of the environmental-mechanical tests^(a) is to determine the susceptibility of candidate materials to environmentally enhanced fracture propagation. Static tests to 250°C, slow strain rate tests to 300°C, and fatigue crack growth rate tests to 90°C have been performed.

(a) Environmental-mechanical testing determines whether an environment has an effect on the propagation of a pre-existing flaw. It includes that aspect of stress corrosion cracking that follows crack initiation. Because flaw initiation is presumed to have taken place, the testing approach is, by definition, conservative.

CONCLUSIONS

1. Based on 6-month corrosion data in oxic Hanford basalt ground water at 250°C and 150°C, and the assumption of linear corrosion kinetics, cast iron or cast steel appear to be suitable materials for a basalt repository structural barrier, with a 1000-yr corrosion allowance of only ~1/2 in. However, 250°C irradiation-corrosion data indicate that this corrosion allowance may not be adequate. Until the effect of irradiation is resolved, a conservative approach would utilize a 1-in. corrosion allowance.
2. Short-term (1-month) corrosion studies of cast ferrous materials in unirradiated, 250°C oxic tuff ground water show relatively low corrosion rates. These low rates suggest that a corrosion allowance of 1/2 in. would be satisfactory for a 1000-yr barrier in a tuff repository.
3. Corrosion studies of cast ferrous materials in oxic deionized water at 250°C indicate a corrosion rate approximately the same as that found in the basalt water studies, despite significant differences in corrosion products formed on the sample surfaces.
4. Irradiation-corrosion studies of titanium Grade 2 and Grade 12 in 250°C basalt ground water show that the general corrosion of the Grade 2 alloy is affected by radiation to a much greater extent than the Grade 12 material. However, the corrosion of the Grade 2 material observed is not significant from a waste package design standpoint. During irradiation-corrosion test exposure, both the Grade 2 and the Grade 12 alloys have been found to absorb hydrogen to an extent greater than that which can be attributed to the corrosion reaction alone.
5. Titanium Grade 2 and Grade 12 have been exposed as U-bend and bolt-loaded compact tension specimens in irradiated basalt ground water at 250°C; as tensile specimens in slow strain rate tests in basalt ground water to 300°C; and as pre-flawed sheet specimens in normal

and enhanced-fluoride fatigue crack growth rate tests at 90°C. Environmental enhancement of crack growth has not yet been positively observed. It appears that these materials would be extremely resistant to stress corrosion cracking in a basalt repository environment.

TECHNICAL APPROACH

This section describes the objectives of the three principal testing methods being used in this study.

GENERAL CORROSION TESTING

General corrosion testing is useful for preliminary screening of candidate materials because materials vary so greatly in their corrosion response to a given aggressive environment. These tests act first as an initial material selection/rejection tool, and secondly, when done in a repository-relevant fashion, as a preliminary basis for longevity predictions. In addition to providing data on uniform corrosion, the tests are expected to provide information on the susceptibility of materials to pitting and intergranular corrosion.

IRRADIATION-CORROSION TESTING

Irradiation-corrosion testing is essential because, unless special precautions are taken, the surface of the outermost structural barrier will be exposed at some time to ground water modified by gamma irradiation emanating from the waste form. Predicting the effects of radiolysis on metal corrosion rates is difficult a priori. For example, in pure water, radiolysis produces strong oxidizing agents such as peroxides. Peroxides can increase the corrosion rate of metals by facilitating the cathodic process, i.e., by acting as cathodic depolarizers. This process could enhance the corrosion rates of iron-based alloys, for example. On the other hand, peroxides can lead to anodic passivation, which decreases the corrosion rate relative to the nonirradiated environment. Such uncertainties make experimental determination of corrosion essential. [In general, it is believed that metals that possess a protective, adherent oxide film, such as titanium alloys, should be little affected by the oxidizing radiolysis products.⁽¹⁾] In addition to the effects on general corrosion induced by radiation, it is also important to determine the disposition of the liberated hydrogen when the candidate barrier element material, e.g., titanium or zirconium, is known to have a high affinity for hydrogen.

The radiation intensity at the surface of the barrier is difficult to estimate, as it depends on time, thickness of the barrier element, barrier material, waste loading in the waste form, age of the waste, composition of the waste, etc. Some calculations (by D. J. Bradley, PNL) indicate that a dose rate lying in the range 10^5 – 10^6 rad/h is the probable maximum that would be expected at the surface of a thin canister containing 10-yr-old commercial high-level waste.^(a)

ENVIRONMENTAL-MECHANICAL TESTING

Environmentally enhanced propagation of cracks from existing flaws can occur with little or no warning, i.e., in the absence of general corrosion and with relatively low net-section stresses in susceptible systems. Because the results of these failures are potentially catastrophic and unpredictable, a major portion of this project is devoted to environmental-mechanical testing. The approach involves exposing statically loaded specimens (U-bend and bolt-loaded fracture toughness specimens) in autoclaves; slow strain rate testing; and fatigue crack growth rate testing.

In the slow strain rate test, a specimen is loaded in the presence of the service environment and strained to failure. A range of low displacement rates is often used so that strain rate effects can be investigated. The straining of any metal in tension increases the surface area and continually breaks up the corrosion product film so that unoxidized material is continuously exposed. Deformation mechanisms accommodate the strain within the metal. Slip planes emerging at the surface provide sites for environment-metal interaction. Environmentally enhanced fracture is often found to be influenced by strain rate. At high strain rates, time to failure is so fast that influence of the

(a) The calculations assume a canister 12 in. in diameter made of 304 stainless steel with a Schedule 40 wall; a burnup of 33,000 MWD/MTU, with 0.5% loss of U and Pu; a 6-month time before processing; a waste loading in a glass waste form of 15.6 wt% fission product oxides and 5.6 wt% actinide oxides; a glass density of 3.0 gm/cc; and an effective glass atomic mass equivalent to 5% U, 16% Ni, and 79% Al (for shielding calculations).

The dose rate at the surface of a structural barrier element can be reduced, if desired, by making the element thicker. Two inches of iron, for example, will provide approximately a factor of 10 attenuation, 4 in. a factor of 100, etc.

environment on the metal is minimal. At very low strain rates, damage from the environment is limited by continual reformation of the oxide film. Thus, intermediate loading rates are often found to cause the lowest ductility.

Slow strain rate tests indicate susceptibility of metals to environmentally enhanced cracking in three ways:

1. loss of ductility relative to an inert environment
2. ductility diminution at particular slow strain rates relative to other strain rates
3. fractographic evidence of embrittlement.

Loss of ductility and dependence of ductility on strain rate are the most readily observed signs of environmentally enhanced fracture; however, strengthening or embrittlement mechanisms may also cause these phenomena. When loss of ductility occurs, the fracture surfaces are examined to determine the mode of failure. If evidence of environmentally enhanced failure modes is not present, the ductility diminution cannot be attributed to environmentally enhanced fracture.

In the fatigue crack growth rate test, a crack is forced to grow by cycling the load on a specimen and measuring the rate of crack growth. Crack growth rate is found to be a function of cyclic stress intensity. Stress intensity is, in this case, a function of applied stress and crack length. When the tests are conducted in an environment representative of the service environment, the data can be used to compare the susceptibility of various materials to environmentally enhanced cracking or to provide information useful in designing barrier elements so they will not be susceptible to cracking over the design lifetime.

There are two ways of qualitatively evaluating the effects of an environment on fatigue crack growth rate: 1) frequency dependence and 2) accelerated crack growth rate relative to an inert environment. Environmental interactions are time-dependent; therefore, there is some high frequency at which the fatigue crack growth rate is independent of environment (analogous to higher

strain rates in the slow strain rate test). At lower frequencies, the crack growth rate may be advanced or retarded due to the effects of the particular environment on the crack tip. Environmental fatigue crack growth rate tests are usually considered conservative, rigorous measures of resistance to environmentally enhanced cracking, as they combine the effects of notch chemistry with a triaxial stress state and forced exposure of fresh, unoxidized materials.

MATERIALS

Early screening studies⁽²⁾ revealed the possibility of using relatively inexpensive and abundant iron-base materials in oxic^(a) Hanford basalt ground water. The excellent corrosion resistance of titanium alloys, shown both in PNL screening studies and in SNL brine investigations,⁽³⁾ qualified these materials in addition as primary candidates for waste package applications. Accordingly, five materials were chosen for the basalt/tuff repository barrier studies:

- ductile (nodular) iron (cast)
- 1-1/4% Cr, 1/2% Mo steel (cast)
- 2-1/2% Cr, 1% Mo steel (cast)
- Ti Grade 2 (wrought sheet and plate)
- Ti Grade 12 (wrought sheet and plate).

The compositions of the alloys studied and their mechanical properties are presented in Tables 1 through 3.

The ductile cast iron is representative of a large group of cast irons with good impact and ductility properties relative to the still-cheaper gray irons. The low-alloy cast steels are more expensive than the cast irons but have superior mechanical properties. The low levels of chromium and molybdenum in the cast steels represent an effort to learn what beneficial effects, if any, such modest alloy additions might have on the corrosion resistance of cast iron base materials. The specimens of cast ferrous material were obtained from castings each weighing ~350 lb, with a minimum dimension of 5 in.

Titanium Grade 2 is a commercial purity titanium alloy. Titanium Grade 12, a Ti-Ni-Mo alloy, was developed for superior high-temperature corrosion resistance to crevice corrosion, and is outstanding in brines representative of salt repositories.⁽³⁾ The titanium alloys were obtained in sheet stock, 0.050 in. thick and 0.062 in. thick (Grade 2) and 0.031 in. thick (Grade 12); and plate stock, 0.50 in. thick (both alloys). The 0.050-in.-thick

(a) In the context of this report, "oxic" refers to ground water having a dissolved oxygen content approximately equivalent to that which would be expected if the water were equilibrated with air under ambient conditions.

TABLE 1. Composition of Iron-Base Alloys

Iron-Base Alloy	Element, wt%						
	C	Mn	Si	P	S	Mo	Cr
2-1/2% Cr, 1% Mo	0.116	0.57	0.57	0.020	0.004	1.02	2.46
1-1/4% Cr, 1/2% Mo	0.117	0.76	0.59	0.018	0.001	0.49	1.31
Ductile Cast Iron, (ASTM A 536-77, Grade 60-40-18)	3.53	0.31	2.51	0.05	0.004		

TABLE 2. Composition of Titanium Alloys with ASTM Nominal Compositions for Comparison

Titanium Alloy	Element, wt%						
	N	C	H	O	Fe	Mo	Ni
Grade 2, sheet, 0.050 in., actual	0.009	0.011	0.005	0.12	0.12	-	-
Grade 2, sheet, 0.062 in., actual	0.016	0.02	0.0039- 0.0079	0.151	0.05	-	-
Grade 2, plate, 0.50 in., actual	0.013	0.013	0.006	0.14	0.13	-	-
Grade 2, ASTM Nominal(a)	0.030	0.100	0.015	0.250	0.300	-	-
Grade 12 sheet, 0.031 in., actual	0.008	0.021	0.005	0.13	0.12	0.30	0.67
Grade 12 plate, 0.50 in., actual	0.009	0.012	0.008	0.12	0.09	0.31	0.74
Grade 12, ASTM nominal(a)	0.03	0.08	0.015	0.25	0.30	0.2-0.4	0.6-0.9

(a) Maximum elemental levels, except as noted, per ASTM B-265-78.

TABLE 3. Room-Temperature Mechanical Properties of Materials

Material	Yield Strength, ksi (MPa)	Tensile Strength, ksi (MPa)	Elongation, %
Ti Grade 2, sheet, 0.050 in., L ^(a)	51 (351)	74 (497)	29
Ti Grade 2, sheet, 0.050 in., T ^(a)	57 (393)	72 (517)	28
Ti Grade 2, sheet, 0.062 in., L	51 (352)	65 (448)	25
Ti Grade 2, sheet, 0.062 in., T	-	-	-
Ti Grade 12 sheet, 0.031 in., L	62 (427)	87 (600)	22
Ti Grade 12 sheet, 0.031 in., T	87 (600)	101 (696)	18
Ti Grade 2 plate, 0.50 in., L	46 (317)	78 (538)	28
Ti Grade 2 plate, 0.50 in., T	54 (372)	79 (545)	28
Ti Grade 12 plate, 0.50 in., L	50 (345)	80 (552)	22
Ti Grade 12 plate, 0.50 in., T	74 (510)	92 (634)	22
2-1/2% Cr, 1% Mo ^(b)	73.5 (506)	92.0 (634)	25
1-1/4% Cr, 1/2% Mo ^(b)	71.5 (492)	90.5 (623)	27
Ductile cast iron ^(c)	44.9 (309)	67.6 (466)	20

(a) L = longitudinal (parallel to rolling direction); T = transverse (perpendicular to rolling direction).

(b) Nominal compositions. Materials are low-alloy cast steels.

(c) ASTM A 536-79, Grade 60-40-18 nodular iron.

Grade 2 and 0.031-in.-thick Grade 12 sheet materials were used in the slow strain rate and fatigue crack growth portions of the environmental-mechanical testing. The 0.062-in.-thick Grade 2 and 0.31-in-thick Grade 12 materials were used in the U-bend and corrosion coupon specimens of the irradiation-corrosion test. The 0.50-in.-thick plate material was used in the fabrication of Charpy V-notch and bolt-loaded fracture toughness specimens.

Prior to corrosion testing, the cast steel specimens were ground with an aluminum oxide wheel to produce a surface finish of 32 microns rms in the grinding direction and 63 microns rms in the transverse direction. The same wheel produced a surface finish of 8 microns rms in both directions on the ductile iron specimens. The titanium sheet stock was tested in the as-received (mill annealed and pickled) condition.

TESTING METHODS AND EQUIPMENT

Each area of investigation requires special test methodology and test equipment.

GENERAL CORROSION

All general corrosion tests are performed in refreshed (flowing) autoclave systems. A schematic diagram of a typical general corrosion test facility is displayed in Figure 1. A reservoir contains simulated ground water, either made up to a specified composition or obtained directly from a representative aquifer. A positive displacement pump delivers influent water to the autoclave at ~35 ml/h. The water flows upward through a bed of crushed rock (basalt or tuff) 1 to 2 in. deep as it attains the test temperature to "fine-tune" the water chemistry prior to its contacting the specimens. Of course, true equilibrium between the rock and the water is not ever actually attainable under these dynamic conditions.

FIGURE 1. Schematic Diagram of Typical Refreshed Autoclave System Used in General Corrosion Study

The autoclaves are operated at a pressure several hundred psi higher than the vapor pressure of water at the given test temperature, e.g., 800 to 1000 psi when the test temperature is 250°C.

The inlet ground water is equilibrated in all cases in its reservoir with an argon-oxygen mixture containing 20% oxygen. Thus, the inlet water contains 6 to 8 ppm dissolved oxygen when it enters the autoclave. It is unclear what the dissolved oxygen level will be, as a function of time, in a repository after closure. In the present study, oxic tests have been emphasized rather than anoxic tests since oxic tests are usually more severe, and conservative tests are performed whenever possible.

A bed of crushed basalt rock alone in the autoclave will decrease the oxygen level of the effluent water to levels as low as 0.3 ppm at 250°C. This effect is attributed to the reducing action of large amounts of divalent iron present in the basalt rock. The tests are still considered oxic, however, as the level of oxygen present in the autoclave represents a large oxygen fugacity compared with that expected to eventually exist in equilibrium with basalt rock after the repository is sealed. The effect of tuff rock on the level of oxygen present in the water is not known.

When the desired test duration has been achieved, the specimens are removed and visually examined. Selected specimens of iron-base alloys, generally duplicates, are stripped of their corrosion product films by a combination of gentle abrasion and immersion in formaldehyde-inhibited HCl. The specimens are then weighed, and the weight loss exhibited is converted to a metal penetration. The data in this report are derived from specimens that have been stripped only once, i.e., for one reported weight change (or metal penetration).

The approximate composition of the basalt rock and the basalt ground water used in the study are given in Tables 4 and 5. The basalt was obtained from an Umtanum surface flow outcrop near the Hanford Site. The ground water is made up to simulate the water contained in the aquifer lying just beneath the proposed Hanford Site repository horizon.⁽⁵⁾ The composition of the basalt ground water used in the tests differs somewhat from the composition now considered to define the reference basalt ground water.⁽⁶⁾ The slightly different chemistries are not expected to affect observed corrosion kinetics.

TABLE 4. Composition of Umtanum Flow Basalt⁽⁴⁾

<u>Constituent</u>	<u>wt%</u>
SiO ₂	54.9
Al ₂ O ₃	14.3
FeO	13.2
CaO	7.2
MgO	3.4
Na ₂ O	2.6
TiO ₂	2.2
K ₂ O	1.6
P ₂ O ₅	0.4
MnO	0.2

TABLE 5. Composition of Hanford Basalt Ground Water⁽⁵⁾

<u>Chemical Species</u>	<u>Concentration, mg/l</u>
Na ⁺	250
K ⁺	1.9
Ca ⁺²	1.3
Mg ⁺²	0.40
CO ₃ ⁻²	27
HCO ₃ ⁻	70
OH ⁻	1.4
H ₃ SiO ₄ ⁻	103
Cl ⁻	148
SO ₄ ⁻²	108
F ⁻	37

pH = 9.8-10

The approximate composition of the tuff rock and the composition of the tuff ground water used in the study are given in Tables 6 and 7. The tuff rock was obtained from an outcropping of the Bullfrog horizon on the Nevada Test Site. The composition of the specific lot of rock used in the present study has not been determined, but it is expected to lie within the composition ranges shown in the table. The water used in the test was obtained directly from well J-13, Jackass Flats, Nevada Test Site. The J-13 well water composition noted in Table 7 may or may not correspond closely to the composition of the water lying near the ultimate tuff repository location, but it is considered to be reasonably typical of the ground waters in the region. [An independent PNL analysis of the J-13 well water obtained for use in the corrosion studies was in substantial agreement with the results shown in Table 7.]

TABLE 6. Composition Range of Welded Silicic Tuff⁽⁷⁾

<u>Constituent</u>	<u>Typical Range (wt%)</u>
SiO ₂	68-75
TiO ₂	0.0-0.4
Al ₂ O ₃	10-17
Fe ₂ O ₃	0.1-2.0
FeO	0.1-2.0
MnO	0.0-0.2
MgO	0.1-1.5
CaO	0.5-2.5
Na ₂ O	1.0-6.0
K ₂ O	2.0-7.0
P ₂ O ₅	0.0-2.0
S	0.0-2.0
H ₂ O ^(a)	1.0-5.0

(a) Does not include pore water.

TABLE 7. Composition of Water from Well J-13, Jackass Flats,
Nevada Test Site^(7,8)

<u>Constituent</u>	<u>Concentration, mg/l</u>
Li	0.05
Na	51
K	4.9
Mg	2.1
Ca	14
Sr	0.05
Ba	0.003
Fe	0.04
Al	0.03
SiO ₂	61
F ⁻	2.2
Cl ⁻	7.5
CO ₃ ⁻²	0.0
HCO ₃ ⁻	120
SO ₄ ⁻²	22
NO ₃ ⁻	5.6
PO ₄ ⁻³	0.12

pH = slightly basic (7.1)
Eh = mildly reducing

IRRADIATION-CORROSION

In order to study irradiation effects on the corrosion and hydriding of candidate structural barrier materials under repository-relevant conditions, an existing ⁶⁰Co irradiation facility^(a) was modified to accept three high-pressure, high-temperature refreshed autoclaves. Figure 2 is a schematic diagram of the facility. The electrically heated autoclaves lie within dry access tubes in the water pool. Each autoclave has an independent water inlet, sampling, and effluent system. The system is capable of exposing specimens to

(a) The irradiation facility is administered by Westinghouse Hanford Company.

FIGURE 2. Schematic Diagram of Irradiation-Corrosion Test Facility

flowing simulated ground-water environments at a maximum temperature of 300°C and a maximum radiation dose rate to the specimens' aqueous environment of $\sim 2 \times 10^6$ rad/h.

As in the unirradiated specimen tests, a layer of the appropriate crushed rock ~2 in. deep is placed in the bottom of the autoclave to "fine-tune" the water chemistry as the ground water passes upward through the rock bed into the region of the autoclave occupied by the specimens. The autoclaves are ~1 liter volume. The usual flow rate (refreshment rate) is ~35 ml/h. The iron-base specimens currently are being exposed in an autoclave made of Inconel 600, a corrosion-resistant, nickel-base alloy. The titanium specimens are in a titanium Grade 2 autoclave. The autoclaves are operated at ~700 psi to maintain the water in the liquid phase during 250°C operation.

ENVIRONMENTAL-MECHANICAL

The environmental-mechanical tests consist primarily of slow strain rate testing and fatigue crack growth rate testing. A diagram of a typical slow strain rate testing apparatus is shown in Figure 3. The specimen is strained to failure at a fixed rate while it is immersed in a repository-relevant environment. The approach is similar to that used in the corrosion screening studies; i.e., simulated ground water is pumped through a bed of crushed rock lying in the bottom of the autoclave. The water flows upward, attains the test temperature, passes over the specimen, then flows out to the drain through a pressure-control valve on a once-through basis. The specimen load and strain are continuously monitored. Strain rates of $10^{-4}/s$ to $2 \times 10^{-7}/s$ are routinely employed.

A diagram of the ambient-pressure, fatigue crack growth rate apparatus is given in Figure 4. In this apparatus, a pre-flawed specimen is cyclically loaded at a controlled load and cycling rate while it is submerged in a bath of simulated ground water. Because of the ambient pressure constraint, temperatures in this facility are limited to $\sim 90^{\circ}C$. The small tank of simulated

FIGURE 3. Typical Slow Strain Rate Test System

FIGURE 4. Fatigue Crack Growth Rate Test System

ground water surrounding the specimen is continually refreshed on a once-through basis. The water is allowed to equilibrate with the surrounding air. A traveling microscope is used to determine crack extensions. The ambient pressure constraint on this apparatus clearly prevents the attainment of repository-relevant conditions surrounding the specimen. To correct this testing deficiency, facilities are currently under construction that will be capable of housing the specimen and the surrounding environment in special high-pressure, high-temperature autoclaves.

RESULTS AND DISCUSSION

This section gives the results of the material degradation studies, along with the implications of these data.

GENERAL CORROSION

The experimental matrix for evaluating the general corrosion behavior of three Fe-base materials is given below:

<u>Materials</u>	<u>Aqueous Medium (oxic)</u>	<u>Test Temperature</u>	<u>Maximum Test Duration Reported</u>
●Cast ductile iron	Basalt Ground Water	$\left. \begin{array}{l} 250^{\circ}\text{C} \\ 150^{\circ}\text{C} \end{array} \right\}$	6 months 6 months
●Cast 2-1/2% Cr, 1% Mo steel	Tuff Ground Water	250°C	1 month
●Cast 1-1/4% Cr, 1/2% Mo steel	Deionized Water	250°C	3 months

More data have been obtained on specimens exposed to the basalt ground water than on specimens exposed to the other media. For this reason, the basalt data are used for comparing general corrosion data and irradiated-corrosion data throughout this discussion.

Basalt Ground Water

The general corrosion of the candidate ferrous materials in basalt ground water at 250°C is shown in Figure 5. The rate of penetration is expressed as a linear rate (mil/yr or in./1000 yr), based on the metal penetration determined at the end of a given autoclave run. The rate of penetration is clearly decreasing with time of exposure, indicating that the corrosion product film has some ability to protect the substrate from attack. After 6 months of exposure, a maximum rate of only 0.30 mil/yr (0.30 in./1000 yr) is observed for all of the materials. In general, the ductile iron corrodes more rapidly than the low-alloy steels. Of the low-alloy steels, the higher chromium alloy corrodes at the lowest rate. No gross pitting attack, or other evidence of significant

FIGURE 5. General Corrosion of Cast Ferrous Materials in Hanford Basalt Ground Water at 250°C. Based on Linear Corrosion Kinetics.

nonuniform corrosion, was seen on any specimen after 6 months exposure. Pitting attack is a potentially serious form of barrier degradation, and any tendency of a candidate barrier material to show such nonuniform attack must be taken into account when barrier elements are being designed.

The 150°C basalt ground-water corrosion data are superimposed on the 250°C data in Figure 6. The same general trends are observed as with the 250°C data, except that the corrosion rates are lower. After 6 months, all of the data lie under a rate of 0.20 mil/yr (0.2 in./1000 yr). Although no gross pitting of the specimens is evident after 6 months, the ductile iron specimens present a much rougher appearance under microscopic inspection than the steel specimens. This roughness may be a prelude to pitting.

The corrosion data presented in Figures 5 and 6 suggest that ferrous materials offer promise as waste package structural barrier elements in a basalt

FIGURE 6. General Corrosion of Cast Ferrous Materials in Hanford Basalt Ground Water at 150°C and 250°C. Based on Linear Corrosion Kinetics.

repository for time periods up to 1000 yr. Of course, possible effects of radiation and the possible interaction of environmental and mechanical considerations, as in stress corrosion cracking, are not addressed in these general corrosion results.

Understanding the corrosion mechanism would be extremely valuable for data extrapolation to very long times. A procedure commonly used as a starting point in ascertaining the operative mechanism is to determine, at a given temperature, whether the corrosion data can be expressed in terms of a time rate law, i.e., (penetration) = $f(t)$. In Figures 7 and 8 the weight loss exhibited by the specimens is plotted against exposure time. The 250°C data (Figure 7) show no correlation with a continuous function of time, as the specimen weight loss does not change appreciably with time after 1 month. The 150°C data (Figure 8), on the other hand, show a fairly good adherence to a linear rate law. The data of Figures 7 and 8 represent only a preliminary attempt to fit the existing short-term data to a tractable mathematical expression.

FIGURE 7. Specimen Weight Loss Shown as a Function of Exposure Time in Hanford Basalt Ground Water at 250°C

FIGURE 8. Specimen Weight Loss Shown as a Function of Exposure Time in Hanford Basalt Ground Water at 150°C

The next logical step involves characterizing the corrosion product layer that forms on the sample surface. The corrosion product layer on the surface of a specimen of ductile iron, exposed to 250°C basalt ground water for 5 months, was analyzed by x-ray diffraction. A strong indication of analcime, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, was found. Microscopic examination revealed discrete "islands" of crystals of this compound scattered over the specimen surface. The principal corrosion product on the surface of the specimen, however, was found to be nontronite $(\text{Fe, Al})\text{Si}_2\text{O}_5(\text{OH}) \cdot n\text{H}_2\text{O}$. The diffraction pattern was diffuse, indicative of a weakly organized crystal structure. No indication was found of hematite, Fe_2O_3 , or magnetite, Fe_3O_4 .

A photomicrograph of the corrosion product film cross section is shown in Figure 9. A notable feature of the film is the numerous small crystallites incorporated in it that have apparently been derived from the basalt in the bottom of the autoclave. Otherwise, the film appears to be of uniform structure. Further characterization of specimens in this study is planned after 12 months of exposure.

FIGURE 9. Photomicrograph of Cross Section of Corrosion Product Film on Ductile Iron Specimen After 5 Months Exposure in Hanford Basalt Ground Water at 250°C. Note Basalt Crystallites Contained in Film.

Tuff Ground Water

Only a limited amount of data are available on the general corrosion of iron-base materials in tuff ground water. One-month data, once again conservatively expressed in terms of a linear rate, are shown in Figure 10. For comparison, these data are superimposed on the basalt ground-water corrosion data scatter band. These preliminary results suggest a corrosion penetration behavior that is somewhat less than that exhibited by the basalt ground water.

The 1-1/4% Cr, 1/2% Mo data point lying above the data point cluster represents a specimen that lay partly in the vapor phase for ~1/2 day following a rupture disc failure on the inlet line to the autoclave.^(a) During this time

FIGURE 10. General Corrosion of Cast Ferrous Materials in Tuff Ground Water at 250°C Compared with Rates Found in Hanford Basalt Ground Water. Based on Linear Corrosion Kinetics.

- (a) The inlet line is prone to plugging because a calcium carbonate deposit forms where the line becomes heated as it penetrates the autoclave head. (Both calcite and aragonite make up the carbonate plug.) The plug tends to retain the contents of the autoclave after failure of the inlet rupture disc.

the autoclave remained pressurized (560 psi) and at temperature. It is not known whether the vapor phase is more corrosive than the liquid phase, hence the cause of the relatively high weight gain. The "water line" is definitely visible on the specimen, however, and a visual observation suggests a higher corrosion rate on the vapor-phase end of the sample.

A ductile iron specimen having a "water-line" was examined by x-ray diffraction. Both nontronite $(\text{Fe, Al})\text{Si}_2\text{O}_5(\text{OH}) \cdot n\text{H}_2\text{O}$ and magnetite (Fe_3O_4) were found both below and above the water line. Below the line magnetite predominated; above the line nontronite yielded the stronger pattern. A 2-1/2% Cr, 1% Mo specimen from the test having no "water line" showed only magnetite on its surface. A 1-1/4% Cr, 1/2% Mo specimen, also without a water line, showed both magnetite and nontronite.

Deionized Water

The general corrosion of the candidate cast ferrous materials is being determined in oxic deionized water to provide a corrosion data base obtained in the absence of the normal ground-water constituents. It is anticipated that this data base will provide insights into the effect of certain ground-water constituents on the corrosion process, i.e., which corrosion products form and the rate at which they form, and so assist in elucidating the corrosion mechanisms.

In Figure 11, the 1-month and 3-month data obtained at 250°C in oxic deionized water, expressed in terms of linear kinetics, are superimposed on the basalt ground-water data scatter band. The figure demonstrates that the corrosion rates found in deionized water lie entirely within the basalt data scatter band, suggesting that deionized water is approximately as corrosive as the basalt ground water toward the candidate ferrous materials. The corrosion product found on the surface of a ductile iron specimen exposed for 3 months test duration consisted, not surprisingly, only of magnetite (Fe_3O_4). This corrosion product apparently is as protective as the corrosion product layers formed on the specimens in the basalt ground-water study. It is more difficult to strip the corrosion products from the specimens exposed to deionized water than from specimens exposed to the basalt or tuff ground waters preparatory to sample weighing.

FIGURE 11. General Corrosion of Cast Ferrous Materials in Deionized Water at 250°C Compared with Rates Found in Hanford Basalt Ground Water. Based on Linear Corrosion Kinetics.

IRRADIATION-CORROSION

Because of the great difficulty in predicting theoretically the effects of radiation-altered environments on the degradation of candidate barrier materials, experimental results must be obtained that combine the effects of radiation with the high-temperature aqueous environment. The experimental irradiation-corrosion test matrix is presented below:

Materials	Aqueous Medium	Test Temperature	γ Dose Rate, rad/h (max)	Maximum Test Duration Reported
<ul style="list-style-type: none"> ● Cast ductile iron ● Cast 2-1/2% Cr, 1% Mo steel 	Oxic basalt ground water	250°C	$\sim 2 \times 10^5$	5 months
<ul style="list-style-type: none"> ● Ti Grade 2 ● Ti Grade 12 	Oxic basalt ground water	250°C	$\sim 2 \times 10^6$	6 months

Ferrous Materials

The corrosion rates of the cast ferrous materials in oxic basalt ground water, based on a linear-kinetics data interpretation, are shown in Figure 12. The data are superimposed on the data band from the nonirradiated, but otherwise equivalent, system for comparison. The corrosion rates show a substantial increase in progressing from the 1-month test duration to the 3-month exposure. The ductile iron sample showing the highest corrosion rate exhibited nonuniform corrosion, which was not apparent in the other samples. The attack consisted of a mass of closely-spaced, shallow pits, covering about two-thirds of one sample surface. The 6-month corrosion-rate data are somewhat higher than those of the nonirradiated system, but they are much lower than the 3-month irradiated-system rates. Between the 1-month and 3-month data analysis points, the autoclave operated in the vapor phase for several days, apparently because of a slightly elevated temperature. It is possible that this operational anomaly had a bearing on the increased corrosion rates observed. Also, the 3-month specimens selected for penetration determinations were taken from a region of

FIGURE 12. General Corrosion of Two Cast Ferrous Materials in Basalt Ground Water at 250°C, With and Without Radiation. Based on Linear Corrosion Kinetics.

the specimen holder where the most serious corrosion was observed, namely, the region near the inlet, whereas the 6-month metal-penetration specimens were taken from positions uniformly spaced along the holder.

✓X
product // The corrosion product on the surface of a specimen of ductile iron removed from the irradiation-corrosion test after a 1-month exposure consisted entirely of nontronite, $(\text{Fe, Al})\text{Si}_2\text{O}_5(\text{OH}) \cdot n\text{H}_2\text{O}$. After the 3-month exposure, x-ray diffraction analysis of a ductile iron specimen revealed large amounts of analcime, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, and hematite, Fe_2O_3 .^(a) No nontronite was present. A specimen of 2-1/2% Cr, 1% Mo steel, examined after 3 months of exposure, also showed evidence of analcime and hematite.^(a) Also, some areas of the specimen were covered only with a film of magnetite, Fe_3O_4 . Again, no nontronite was present. After 5 months exposure, the ductile iron showed the presence of acmite, $\text{NaFe}(\text{SiO}_3)_2$, along with nontronite; no magnetite was observed. The 2-1/2% Cr, 1% Mo alloy, on the other hand, showed weak indication of both acmite and magnetite; no nontronite was present. No systematic corrosion-product pattern is yet emerging in these studies.

The relatively high corrosion rates found in the irradiation-corrosion test raises some questions regarding the stability of iron-base alloys in the irradiated basalt ground-water environment. Further testing is needed to resolve the validity of the observations and the potential implications to the design of ferrous waste package barrier elements.

Titanium Alloys

Titanium Grade 2 and Grade 12 materials are being exposed to the irradiated oxic basalt ground-water environment in four different specimen configurations: corrosion coupons; U-bend specimens; Charpy V-notch impact

(a) It is possible that the Fe_2O_3 deposits formed on the corrosion specimens during the time period between test shutdown and specimen recovery from the autoclave. This time period was unusually long, i.e., several days, after the 3-month exposure; and during this time the specimens were in a warm, moist environment.

specimens; and compact tension fracture toughness specimens bolt-loaded to a stress intensity level of $\sim 20 \text{ ksi}\sqrt{\text{in}}$. The fully-loaded specimen holder is illustrated in Figure 13.

The radiation intensity is not uniform throughout the autoclave holding the titanium specimens. The approximate variation of radiation intensity with the position of samples in the sample holder is shown in Figure 14. Note that the corrosion coupons are exposed to a maximum radiation intensity of about $1 \times 10^6 \text{ rad/h}$, with the maximum occurring at the bottom of the coupon holder. The minimum radiation intensity (at the top of the holder) cannot be accurately estimated, but it is thought to be no more than $1 \times 10^4 \text{ rad/h}$.

After an exposure of 6 months, no stress-corrosion cracking failures were observed in the U-bend specimens, and no crack extension was observed in the bolt-loaded compact tension specimens.

Corrosion coupon specimens of both Grade 2 and Grade 12 alloys were removed from the sample holder for surface analysis after 3 months and 6 months exposure. After 3 months exposure no TiO_2 was found on the sample surfaces--only titanite, CaTiSiO_5 , was observed. After 6 months exposure, however, anatase (TiO_2) was found on specimens of both Grade 2 and Grade 12 corrosion coupons (Table 8).

TABLE 8. Six-Month Analysis of Ti Grade 2 and Grade 12 Corrosion Coupons

<u>Material</u>	<u>Radiation Intensity</u>	<u>Film</u>	<u>X-Ray Diffraction Intensity</u>	
			<u>CaTiSiO_5</u>	<u>TiO_2</u>
Grade 2	low	fairly thick, black	medium	weak
Grade 2	high	black, thick	strong	very weak
Grade 12	low	thin, purple	very weak	weak
Grade 12	high	thin	weak	very strong

The qualitative summary of Table 8 suggests that the relatively slowly corroding Grade 12 material may have a tendency to form an anatase corrosion product, while the Grade 2 may have a tendency to form the titanite phase.

FIGURE 13. Sample Holder Containing Titanium Alloy Specimens for Irradiation-Corrosion Study. Holder contains 32 corrosion coupons, 8 U-bend specimens, 12 notched Charpy impact specimens, and 2 compact tension specimens.

FIGURE 14. Variation of Local Radiation Intensity with Position of Specimen in Holder

The corrosion coupons were all weighed after 3 months and 6 months exposure. The weight change varied significantly with the position of the specimen in the sample holder, presumably due to radiation effects (Figure 15). The Grade 2 material corrodes at a much more rapid rate than the Grade 12 alloy in the irradiated environment. However, if the corrosion product film is assumed to be completely composed of titanite, the Grade 2 material is corroding at a maximum rate of only ~ 0.03 in. in 1000 yr. Therefore, the radiation effect observed would probably not be considered particularly important to a waste package designer.

Metallographic cross sections of the corrosion-product films on Ti Grade 2 and Ti Grade 12 specimens after 6 months exposure in the high-radiation-intensity region of the irradiation-corrosion test are shown in Figure 16. The films are strikingly nonuniform in thickness, but the attack is reasonably uniform in nature; i.e., no gross pitting attack or intergranular attack is evident. No metallographic evidence could be found in either alloy for hydride phase.

FIGURE 15. Effect of Sample Position on Weight Change Observed, Hanford Basalt Ground Water Environment. Maximum Radiation Intensity: 1×10^6 rad/h. Temperature: 250°C

FIGURE 16. Metallographic Cross Sections of Specimens of (a) Ti Grade 2 and (b) Ti Grade 12 After 6 Months Exposure to 250°C Hanford Basalt Ground Water and $\sim 1 \times 10^6$ rad/h Gamma Irradiation. Weight gain of Ti Grade 2 is 667 $\mu\text{g}/\text{cm}^2$; of Ti Grade 12, 80 $\mu\text{g}/\text{cm}^2$.

Hydrogen embrittlement of titanium alloys is a potentially serious structural barrier element degradation mode. Titanium alloys exposed to a high-temperature ground-water environment in the presence of gamma-irradiation-induced radiolysis products could possibly absorb hydrogen via two distinct mechanisms: 1) direct absorption of hydrogen atoms produced by radiolysis and/or 2) by absorbing a portion of the hydrogen produced as a byproduct of the (radiation-enhanced) corrosion reaction(s), e.g.,

or

In order to determine whether hydrogen absorption was taking place during the irradiation-corrosion test exposure, selected specimens from the high- and low-radiation-intensity ends of the specimen holder, along with as-received specimens of the titanium alloy sheet stock, were analyzed for hydrogen. The results are presented in Table 9.

These preliminary data show a tendency of the titanium alloys to pick up hydrogen from the test environment, notably in the high-radiation region of the specimen holder. The hydrogen absorbed by the metal could be derived from the corrosion reaction, or it could come from direct absorption of H or H⁺ produced by radiolysis. The direct reduction of water by titanium to form TiO₂ and hydrogen is an efficient hydrogen-producing corrosion reaction. If it is assumed that TiO₂ is the major corrosion product, the maximum weight gain of the Ti Grade 2 specimens is equivalent to ~120 ppm of hydrogen at 6 months exposure. Thus, absorption of ~30% of this hydrogen could explain the hydrogen concentrations observed. In the Grade 12 material, an absorption of ~100% of such corrosion product hydrogen would be required to explain the levels observed in the metal. If the corrosion product is not primarily TiO₂, but titanite, then it is impossible to invoke corrosion product hydrogen as being

TABLE 9. Hydrogen Concentration in Titanium Alloy Specimens Exposed to Irradiation-Corrosion Test Conditions: Hanford Basalt Ground Water, 250°C; 1 x 10⁶ rad/h Gamma Irradiation (maximum)

As-Received Material		Hydrogen Concentration, ppm ^(a)			
		Irradiation-Corrosion Test Specimens			
		3-Month Exposure		6-Month Exposure	
Grade 2	Grade 12	Grade 2	Grade 12	Grade 2	Grade 12
32 (18) ^(b)	32 (18)	48 (6)H ^(c)	39 (6)H	71 (3)H	79 (3)H
		37 (3)L	33 (3)L	38 (3)L	47 (3) L

(a) The hydrogen analyses were supplied by J. A. Ruppen, Sandia National Laboratories, Albuquerque, New Mexico.

(b) Number in parentheses denotes number of individual hydrogen analyses performed. Three individual analyses, at a minimum, are run on each sample. The hydrogen concentration presented represents the average of these individual runs.

(c) "H" designates the high-radiation-intensity end of the specimen holder, "L" the low-radiation-intensity end.

the total source of the hydrogen observed, as it is difficult to envision a titanite-forming reaction as an efficient hydrogen producer. As titanite is the major corrosion product formed on the Grade 2 material, and is present to some extent on the Grade 12 material, some hydrogen must be absorbed directly from the environment. A more extensive investigation of the hydrogen absorption process is planned at the next run termination date, i.e., at ~10 months total exposure. An improved statistical base of hydrogen concentration data is obviously required before substantive conclusions can be drawn.

ENVIRONMENTAL-MECHANICAL

The environmental-mechanical studies primarily have sought to determine the susceptibility, if any, of titanium Grade 2 and titanium Grade 12 alloys to environmentally enhanced fracture in Hanford basalt ground water. Two major test methods have been used: slow strain rate testing and fatigue crack growth rate testing. In this report only a small, but representative, portion of the results obtained to date are presented, i.e., the effect of strain rate and the effect of temperature on ductility of Grade 2 and Grade 12 materials by slow strain rate methods, and the crack growth rate of Grade 2 and Grade 12 materials in basalt ground water and inert environments by fatigue crack growth rate test methods. More detailed descriptions of these test results have been published elsewhere. (2,9,10)

Slow Strain Rate Results

Susceptibility of a material to environmentally induced fracture frequently appears as a ductility reduction in a strain rate range between the relatively rapid strains that do not allow the environment sufficient time to interact with the metal specimen and the very slow strain rates that allow a specimen time to re-passivate through relatively long contact with the environment. Slow strain rate tests of titanium Grade 2, LT^(a) orientation were made in 250°C basalt ground water and 250°C air. Results are given in Figure 17.

(a) The first letter refers to the direction of loading, i.e., longitudinal (rolling direction) in this example; the second letter refers to the direction of crack propagation, in this case transverse (perpendicular to the rolling direction).

FIGURE 17. Results of Slow Strain Rate Testing of Titanium Grade 2, LT Orientation, in Hanford Basalt Ground Water and Air at 250°C

The ductility is described in terms of both reduction of area^(a) and elongation^(b) and plotted as a function of the strain rate. The ductility of the Grade 2 material is slightly lower at lower strain rates, but there is no ductility "minimum" in the strain rate range investigated. The ductility measured in the air tests is approximately the same as that measured in the ground-water tests. As air is considered to be inert (in a crack-enhancement sense) to titanium Grade 2, the material does not appear to be susceptible to crack propagation enhancement in the basalt ground water.

-
- (a) The difference between the smallest cross-sectional area of a specimen after fracture and the original cross-sectional area expressed as a percentage of the original area.
 - (b) The permanent elongation (plastic strain) of the gage section of the specimen expressed as a percentage of the original gage length.

The titanium Grade 12 material, LT orientation (Figure 18) is clearly affected by strain rate. Once again, there is no ductility "minimum," and there appears to be no difference between the results of the ground-water tests and the air tests. As before, this result indicates that the lack of ductility is not caused by the ground-water environment but by an embrittling phenomenon, perhaps a strain-aging process, operating within the metal. The lack of environmentally associated effects indicates that the ability of the metal to accept deformation without cracking is not likely to undergo significant changes over time. The results of similar tests, except on the TL orientation of titanium Grade 12, are given in Figure 19. The data of Figure 19 show an even more profound effect of strain rate on ductility, but once again the air data and the basalt ground-water data agree quite closely. Comparing Figures 18 and 19 reveals the strong effect of orientation on the mechanical properties of titanium alloys. An analysis of the fracture surfaces of Grade 12 specimens, TL orientation, tested at the highest and lowest strain rates in 250°C basalt ground water, is presented in Figure 20. The fracture surfaces are very similar, suggesting an internal strengthening mechanism not an environmentally induced failure.

The ductility of titanium Grade 2, at a constant strain rate of 10^{-4} /s, is presented as a function of temperature in Figure 21. Ductility, expressed in terms of reduction of area, is not adversely affected over the temperature range (20° to 300°C) investigated; ductility in terms of elongation does, however, show a modest reduction with reduced test temperature. The fracture surfaces of specimens tested at each temperature were observed with a scanning electron microscope. No significant differences were observed between specimens; microvoid coalescence, typical of ductile rupture, was found to be the fracture mode in all cases.

Fatigue Crack Growth Rate Results

Fatigue crack growth rate tests of titanium Grade 2 and Grade 12 have been run in basalt ground water, fluoride-ion-enhanced basalt ground water, and high-purity water at 90°C, with low cyclic loading frequencies of 5, 1, 0.1 and 0.01 Hz. Low frequencies and high fluoride ion concentration are considered to represent relatively severe "accelerated" test conditions.

FIGURE 18. Results of Slow Strain Rate Testing of Titanium Grade 12, LT Orientation, in Hanford Basalt Ground Water and Air at 250°C

FIGURE 19. Results of Slow Strain Rate Testing of Titanium Grade 12, TL Orientation, in Hanford Basalt Ground Water and Air at 250°C

FIGURE 20. Typical Fracture Surfaces of Titanium Grade 12 Specimens, TL Orientation, Strained to Failure at (a) $10^{-4}/s$ and (b) $2 \times 10^{-7}/s$ in Hanford Basalt Ground Water at $250^{\circ}C$

Lower frequencies allow relatively long times for the environment to act on the advancing crack tip during each loading cycle, thus potentially increasing the environmentally induced crack growth occurring per cycle. Under certain circumstances fluoride ion can break down the passivating film on titanium alloys, thereby allowing environmental attack.

In the test data presented in Figures 22 and 23, low frequencies and enhanced fluoride ion content (220 ppm instead of the normal 37 ppm) were employed in an effort to make the tests relatively severe. Titanium Grade 2 (Figure 22) was unaffected by loading frequency and by the high fluoride ion content. Results of the two tests shown in this figure do not cover the same stress-intensity range; however, these data points also closely match those of tests conducted in air (not shown). The results indicate that acceleration of fatigue crack growth rate due to environmental effects was not present.

FIGURE 21. Slow Strain Rate Test Results, Titanium Grade 2, LT Orientation, Strain Rate 10^{-4} /s. Effect of Temperature on Ductility at Constant Strain Rate.

Tests analogous to those shown in Figure 22 were performed on titanium Grade 12 (LT orientation). As shown in Figure 23, neither lower frequency (0.1 Hz relative to 1 Hz) nor increased fluoride ion content (from 37 to 220 ppm) increased the crack growth rate at 90°C.

So far, the environmental-mechanical investigations of titanium Grades 2 and 12 using slow strain rate tests to 300°C in normal basalt ground water and fatigue crack growth rate tests at 90°C in normal and fluoride-enhanced basalt ground water have revealed no positive proof of crack environmentally assisted fracture or growth rate enhancement attributable to environmental affects alone.

FIGURE 22. Fatigue Crack Growth Rates of Titanium Grade 2, TL Orientation, in High-Fluoride (220 ppm F-) and Normal Basalt Ground Water at 90°C

FIGURE 23. Fatigue Crack Growth Rates of Titanium Grade 12, LT Orientation, in High-Fluoride and Normal Basalt Ground Water at 90°C

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