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STRESS CORROSION CRACKING, GALVANIC CORROSION, AND SELECTIVE LEACHING TEST REQUIREMENTS FOR TiCODE-12 HIGH LEVEL WASTE CONTAINERS

DRAFT REPORT

B. SISKIND

MANUSCRIPT COMPLETED AUGUST 1982

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Prepared for the U.S. Nuclear Regulatory Commission
Office of Nuclear Materials Safety and Safeguards
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NOTICE

ABSTRACT

In the context of the use of TiCode-12 as part of the high level nuclear waste overpack structure, we discuss the testing of this alloy for three corrosion modes: stress-corrosion cracking (SCC), galvanic corrosion, and selective leaching. We consider two broad categories of SCC tests: static and dynamic. We describe static testing in simulated repository environments using smooth-bar, pre-cracked, and residual stress specimens. In the dynamic test category, we describe the slow-strain rate and the fatigue-crack-growth rate methods. We recommend long term testing, on the order of years, for SCC in TiCode-12 using statically loaded specimens under expected repository conditions in parallel with the design and development of the waste package and repository in order not to delay the waste disposal program. We find that relatively little work has been done on either galvanic corrosion or selective leaching of titanium and its alloys. We recommend some long term testing for these failure modes using facilities already planned or constructed at DOE laboratories.

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1. INTRODUCTION

Titanium alloys have been identified as prime candidates for high level nuclear waste package applications in which relatively thin (<2 cm) corrosion-resistant sections are required. At least one of the current conceptual designs for a high level nuclear waste package incorporates a titanium alloy as part of the overpack structure.[1] In the present report, the testing of one of these alloys for three of the possible modes of corrosion is discussed; the particular alloy is TiCode-12 (ASTM Grade 12)[2] and the three corroson modes are stress-corrosion cracking (SCC), galvanic corrosion, and selective leaching. The composition of ASTM Grade 12 titanium nominally 0.3% molybdenum and 0.8% nickel, is given in Table 1.1. Of the three modes of corrosion addressed in this report, only SCC has been considered as a potentially significant failure mode,[3] and thus receives the most extensive treatment. The discussion of each of these corrosion modes begins with some general introductory remarks about the testing for that mode. Some examples of testing of titanium or its alloys for the particular corrosion mode are then given so that the reader may be given some idea of the current status of such testing; testing of TiCode-12 is emphasized when such information is available. Finally, recommendations are made for further testing of TiCode-12 for these modes of corrosion in the context of demonstrating that a TiCode-12 container is capable of containing radionuclides for 1000 years.

Table 1.1

Composition of ASTM Grade 12 Titanium[2]

Element	Composition, %
Nickel	0.6 to 0.9
Molybdenum	0.2 to 0.4
Iron, max.	0.30
Carbon, max.	0.08
Oxygen, max.	0.25
Hydrogen, max.	0.015
Nitrogen, max.	0.03
Residuals (each), max.[a]	0.1
Residuals (total), max.[a]	0.4
Titanium	remainder

[a]A residual is an element present in a metal or an alloy in small quantities inherent to the manufacturing process but not added intentionally.

2. TESTS FOR STRESS-CORROSION CRACKING OF TiCode-12

2.1 Introduction

Stress-corrosion cracking (SCC) is potentially one of the most significant of the failure modes which can compromise the integrity of the metallic components of the waste package.[3] This failure mode is difficult to quantify, and difficult to eliminate as a potential failure mode during the course of a short (in comparison with 1000 years) laboratory study, because there are two phases to the SCC process--crack initiation and crack growth--and each phase may be controlled by a different mechanism. A discussion of these mechanisms is given by Shao elsewhere in this program.[4]

Quantification of the time of penetration of the metallic barrier and, the elucidation of the mechanisms of SCC provide the rationale for the testing of a potential barrier material for SCC. Such predictions are necessary to demonstrate the compliance (or lack of compliance) with the 1000-year containment criterion. In this section, after some general introductory comments about SCC testing, the DOE's SCC testing program on TiCode-12 will be reviewed, and recommendations will be made for future work.

2.2 Real-Time Testing vs Accelerated Testing

There are several limitations on the use of laboratory data on SCC to predict the probability of 1000-year containment by a metallic barrier. Real-time data are limited by experimental constraints, e.g., the length of time a test can be conducted, the constancy of steady-state crack-growth rates, and the uncertainty in the threshold stress integrity for crack propagation . For example, the present experimental capability for measuring crack-growth rates (10^{-8} mm/sec or about 300 mm/1000 years) is insufficient for 1000-year life predictions.[5] Thus, attempts have been made to observe SCC in candidate metals by changing the value of some key environmental parameter in order to accelerate the SCC process. The validity of extrapolating such accelerated data back to the real-time conditions is open to question, however, if the real-time SCC mechanism cannot be shown to be the same as the accelerated SCC mechanism.*

Parameters which have been suggested by a Materials Characterization Center (MCC) workshop as suitable for accelerating SCC at constant temperature are pH, Eh (and O_2 concentration), stress, strain rate, and halide concentration.[5] Temperature was not considered a suitable accelerating parameter because temperature increases were deemed likely to introduce mechanisms not relevant to real-time SCC. As noted by the BNL group,[6] even for the isothermally accelerated testing it would be necessary to show that neither the metal nor the metal-solution interface would undergo any structural, physical, or chemical change that could alter the corrosion rate over the time

*Use of the term "real-time testing" is in no way meant to imply that there is anything "unreal" about accelerated testing.

period in question. In two of the tests to be discussed later in this report, the slow-strain rate (SSR) and the fatigue-crack-growth rate (FCGR) tests acceleration of the fracture process is attempted by varying the strain rate and the cyclic stress intensity, respectively, on the test specimens in order to induce a breakdown of any passivating surface film and thus expose fresh metallic surface to the environment.

As noted by the MCC, a testing program for SCC may be divided into two phases. In the first phase, the SCC resistance of a variety of candidate materials should be determined by surveying the literature and by performing relatively simple, inexpensive screening tests. Susceptibility to SCC is often evaluated by real-time testing using stressed corrosion coupons (e.g., U-bends or C-rings). Accelerated testing may also be part of the screening process.[3,5]

In the second phase of a SCC testing program, fracture mechanics testing should be conducted on those materials selected as a result of the screening phase of the program. Real-time testing may be performed on statically loaded, pre-cracked specimens (e.g., the wedge-opening-load test) in order to determine threshold stress intensities for crack propagation. As already noted, any crack-growth rates measurable in the laboratory on real-time test specimens would be too high for 1000-year barrier service. On the other hand, the threshold stress intensity for short term tests may be much larger than for longer term tests. Accelerated testing (e.g., the FCGR method) should also be part of this phase of the program. Fracture resulting from purely mechanical failure may be observed during these tests, but any environmentally enhanced cracking, i.e., any increase in crack-growth rate in a simulated repository environment over the rate in a reference environment (often referred to as an "inert" environment), usually air, may be indicative of the susceptibility of the material to SCC.[3,5] According to some workers,[7,8] only metallographic examination of the fractured surface (e.g., by scanning electron microscopy) can be used to unequivocally determine whether SCC is present.

In the present report, it is assumed that TiCode-12 has been selected as a material for further consideration as a result of the screening phase of the SCC testing program. For completeness, test methods from both phases of the testing programs will be described in the following sections. The test methods may be grouped into two broad categories, static and dynamic. In static testing, either smooth-bar or pre-cracked specimen geometries may be used. The former, in particular, are frequently used for screening purposes because of their relative simplicity. The pre-cracked fracture mechanics geometries in a sense provide for accelerated testing with stress intensity as the isothermal accelerating parameter and in some cases, e.g., wedge-opening load and cantilever beam, are also relatively simple and compact. The dynamic tests considered, SSR and FCGR, are conservative accelerated tests requiring complex external loading devices. In the following section, static SCC testing with smooth-bar and pre-cracked specimens and dynamic SCC testing by the SSR and FCGR methods are described with emphasis on SCC testing of TiCode-12 in a simulated nuclear waste repository environment.

2.3 Static Tests

Two types of static testing are considered to be conventional methods for evaluating the susceptibility of a material to SCC: static load using smooth-bar specimens and static load using pre-cracked specimens.[5] A statically loaded specimen which exhibits no cracking when exposed to simulated repository conditions is considered to have low susceptibility to SCC.[9] The use of pre-cracked static specimens provides a complementary test method which defines an experimentally determined threshold stress-intensity factor and a crack-growth rate which together can provide design-related data.[9]

There are four SCC specimen designs accepted for smooth-bar SCC testing: U-bend (ASTM G30-72)*, C-ring (ASTM G38-73), bent beam (ASTM G39-79), and direct tension (ASTM G49-76).[10] Two of these designs, the U-bend and the C-ring, have been adopted by the Materials Characterization Center as MCC-103S, SCC Susceptibility Test Method. These two specimen designs were selected because they are: (1) generally small so that many specimens can be tested in a restricted volume, (2) generally of simple design and therefore inexpensive to make, and (3) bolt loaded requiring no external fixture to apply the strain as is sometimes the case for direct-tension or bent-beam specimens.[9] A summary of the advantages and disadvantages is given with rough sketches of the specimen geometries in Figure 2.1 for each of these smooth-bar methods.

A companion fracture test method (MCC-104) is in preparation which can be used both to test resistance to crack propagation and to provide design-related data on threshold-stress intensities and crack-growth rates.[9] A MCC workshop has considered four types of pre-cracked specimens for SCC testing: cantilever, compact tension (ASTM E399),[10] wedge-opening load, (WOL) and cantilever beam. A summary of this is given with rough sketches of the specimen geometries in Figure 2.2 for each of these pre-cracked specimen methods.

In the present discussion of static testing, a description of some smooth-bar and pre-cracked fracture mechanics test methods will be given and their use in testing for SCC in TiCode-12 will also be considered. In addition, a brief comment will be made about residual stress specimen tests.

2.3.1 Smooth-Bar Tests: U-Bend and C-Ring

As noted in ASTM G 30-79,[10] the U-bend specimen may be used for any metal alloy sufficiently ductile to be formed into the U-shape without mechanically cracking. The specimen usually contains large amounts of elastic and plastic strain and thus provides one of the most severe tests available for smooth stress-corrosion test coupons. Because a wide range of stresses exist in a single stressed specimen, the U-bend geometry is not suitable for determining the effects of different applied stresses on SCC or for variables which have only a minor effect on cracking. The U-bend specimens, however,

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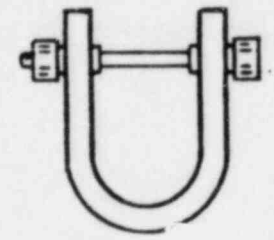
*Designations such as ASTM G30-72 refer to standard practices or standard test methods issued by the American Society for Testing and Materials, see Ref. 10.

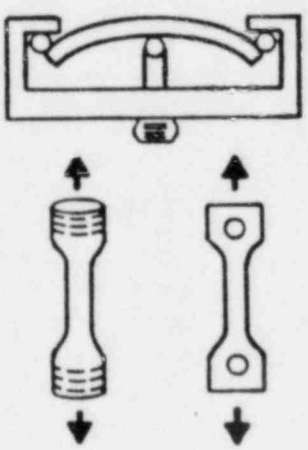


U-BEND (ASTM G30)

- QUALITATIVELY STRESSED
- SIMPLE, ECONOMICAL GEOMETRY
- USEFUL FOR DETECTING LARGE DIFFERENCES IN SCC RESISTANCE OF METALS

C-RING (ASTM G38)

- QUANTITATIVELY STRESSED
- SIMPLE, ECONOMICAL GEOMETRY
- SUITABLE FOR MAKING SHORT TRANSVERSE TESTS ON MATERIALS



BENT BEAM (ASTM G39)

- QUANTITATIVELY STRESSED
- SUITED FOR FLAT MATERIALS
- REQUIRES STIFF LOAD FIXTURE

TENSION SPECIMEN (ASTM G49)

- QUANTITATIVELY STRESSED
- VERSATILE TEST SPECIMEN
- REQUIRES STIFF LOAD FIXTURE

Figure 2.1 Smooth-bar specimens for SCC testing.[5]

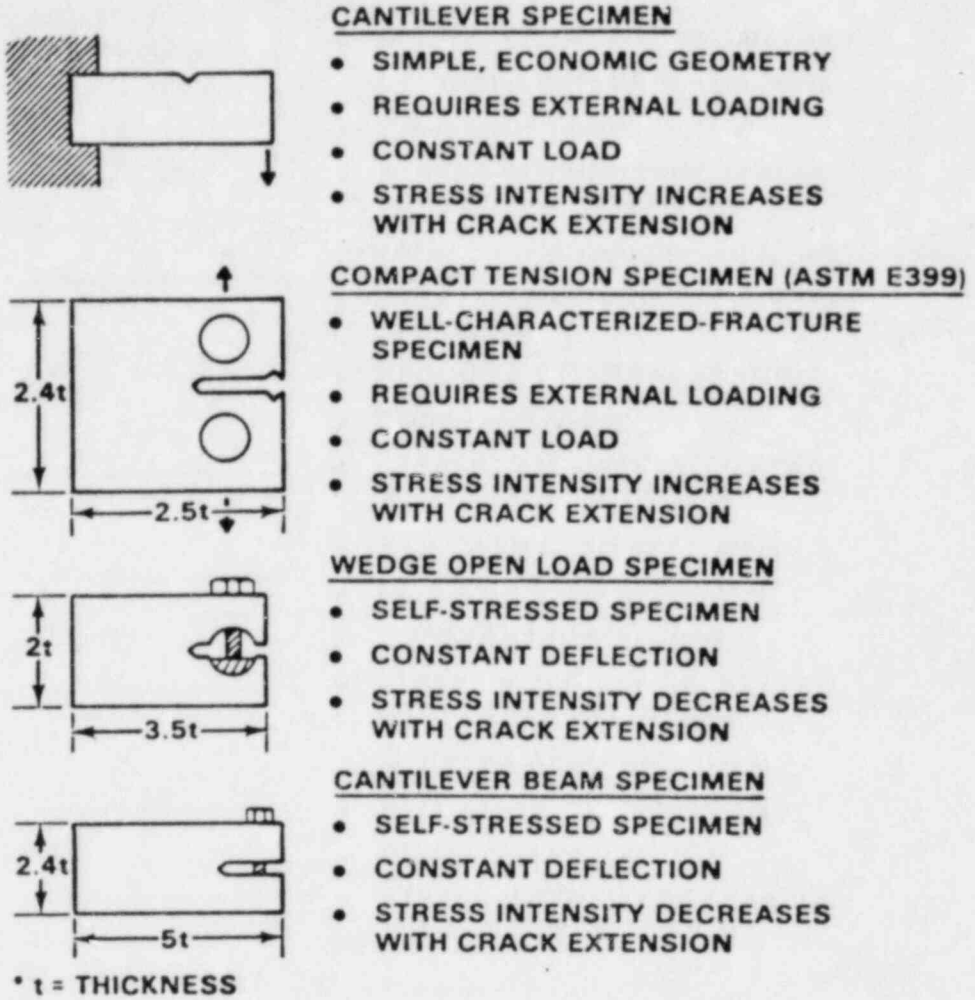


Figure 2.2 Pre-cracked specimens for SCC testing.[5]

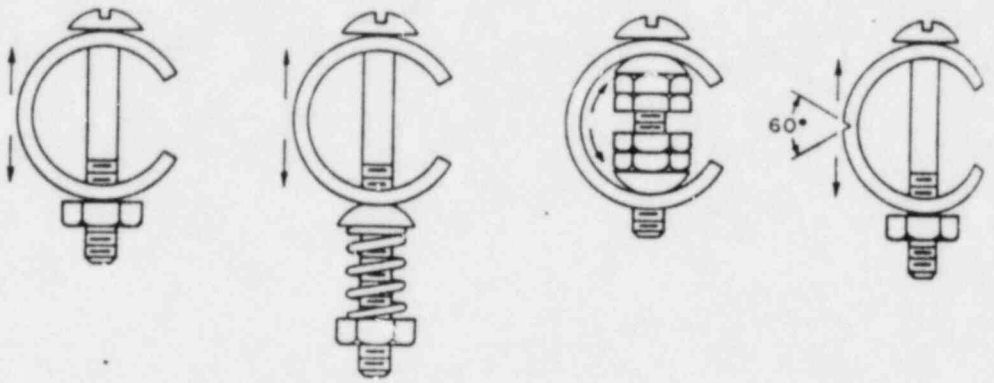
are simple and economical to make and use and are thus suitable for large scale screening to ascertain large differences in the SCC susceptibility of:

1. Different metals in the same environment
2. One metal in different metallurgical conditions in the same environment
3. One metal in several environments.

The U-bend specimen is most easily made from strip or sheet stock, but it is also possible to use plate, bar, castings, and weldments. The specimens may be cut from rolled stock material either transversely or longitudinally to the direction of rolling; since the SCC susceptibility may be anisotropic, the orientation of the test specimen must be defined.

The C-ring, as noted in ASTM G 38-73,[10] is another versatile, economical specimen for determining the susceptibility to SCC of alloys. It is particularly suited for making transverse tests of tubing and rod. The C-ring is usually used as a constant strain specimen with tensile stress produced on the

extension of the ring by tightening a bolt centered on the diameter of the ring. Other methods of stressing have been developed to produce a nearly constant load and to create a tensile stress on the inside surface (Figure 2.3). The C-ring specimens can be stressed with high precision and accuracy by application of a measured deflection, but the stress calculated from this deflection does not apply if cracking is initiated. The C-ring, because of its small size and simplicity, can be exposed to almost any kind of corrosion environment. The specimen should be electrically insulated from any other metals in the system to avoid galvanic effects, unless such effects on SCC are to be studied (see Section 3.3, below).



(a) (b) (c) (d)

Constant Strain Constant Load Constant Strain Constant Load

Figure 2.3 Methods of stressing C-rings. Note that for (d) a similar notch chould be used on the tension side of (b) or (c). (Adapted from Ref. 10.)

A screening study using specimens in the U-bend configuration was carried out at Pacific Northwest Laboratories (PNL).[11] A tungsten-inert gas welding torch was used to melt through the sheet material prior to fabrication and bending in order to create a weld bead. Two water chemistries were used in this study: a simulated Hanford basaltic groundwater and a simulated WIPP brine (Table 2.1). The requirement of total immersion of the specimens in an aqueous phase at a high test temperature (250°C) necessitated the use of a pressurized autoclave system. For the tests in the simulated basalt environment, a flow of simulated groundwater was maintained through a basalt rock layer in the bottom of the autoclave and over the corrosion specimens at rates of 30 to 300 mL/h (Figure 2.4). The tests in the simulated brine environment were run in a static brine solution.

2.3.2 Pre-Cracked Specimen Tests

There are two major objectives in performing SCC testing with fracture mechanics type pre-cracked specimens. First, the SCC threshold stress intensity for a specific material and orientation in a specific environment may be

Table 2.1

Brine Solution Composition and Synthetic Hanford Groundwaters Formulations[11]

Brine Solution			Synthetic Hanford Groundwaters Formulations				
				August 1979 to May 1980		May 1980 to July 1980	
Component	Makeup		Component or Property	Makeup, mg/L	Effluent Analyses,[a] mg/L	Makeup, mg/L	Effluent Analyses,[a] mg/L
Mg^{2+}	34.98	g/L	Al^{3+}	0	10	0	6
Na^{+}	41.34	g/L	Na^{+}	139	140	111	127
K^{+}	29.95	g/L	Mg^{2+}	0.5	0.05	0.5	0.05
Ca^{2+}	0.60	g/L	Ca^{2+}	1.6	0.1	2.5	0.1
Li^{+}	20	mg/L	K^{+}	13	55	13	21
Rb^{+}	20	mg/L	CO_3^{2-} (total)	167	210	167	240
Sr^{2+}	5.3	mg/L	SiO_2	36	210	36	331
Cs^{+}	0.8	mg/L	Cl^{-}	52	50	52	58
Cl^{-}	191.3	g/L	F^{-}	8	8	8	8
SO_4^{2-}	3.51	g/L	SO_4^{2-}	0.8	--	0.8	5
BO_3^{3-}	1.24	g/L	O_2	<1	--	<0.05	--
Br^{-}	0.39	g/L					
I^{-}	10	mg/L	pH	9.5	8.5	9.0	7.7
Fe^{2+}	2	mg/L	Conductivity, μMHo	475	55	630	600

[a]Sample was cooled before sampling. The water passed through a bed of crushed basalt at 250°C in the autoclave, which increased the Al and Si, and decreased pH, Ca, and Mg. The units of concentration (mg/L) do not apply to the pH or conductivity.

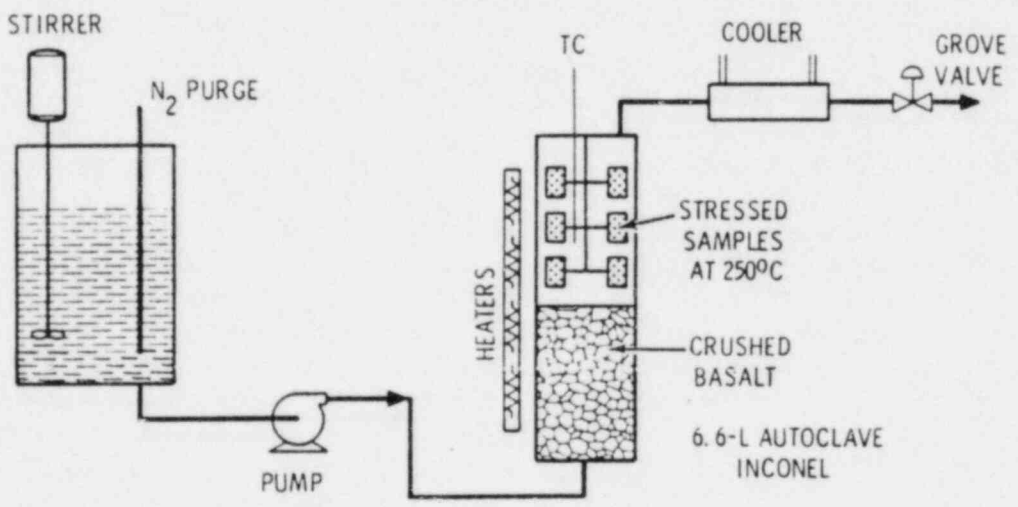


Figure 2.4 Autoclave facility used in Hanford groundwater corrosion tests.[11]

determined. As a second objective, the rate of SCC propagation, da/dt, as a function of the mechanical crack driving force may be determined under controlled test conditions.[12] The parameter "a" represents the length of the crack.

Two convenient types of specimen for determining SCC propagation rates are the double-cantilever beam (DCB) and the wedge-opening-loading (WOL) geometries (Figure 2.2). Both are loaded for a constant displacement (called "constant deflection" in Figure 2.2) to a stress intensity at or just below the critical stress intensity required for crack propagation. At high stress intensity, SCC will start quickly in highly susceptible materials. Since the displacement across the notch is held constant by a bolt or other loading device, crack propagation causes the loading on the specimen and thus the stress intensity at the crack tip to decrease. When stress corrosion crack growth stops, the stress intensity at the crack tip has dropped to the threshold value for SCC (K_{Iscc}). This stress intensity level associated with crack arrest can be computed.[12,13] Alternatively, a pre-cracked fracture mechanics specimen may have a constant load imposed upon it. Under a constant-load constraint, the stress intensity factor increases as the crack extends (if crack growth occurs).

At PNL, WOL specimens were used to evaluate the susceptibility of TiCode-12 to SCC.[11] A load-retaining wedge rather than a bolt was used to load the specimen (Figure 2.5). The external load was recorded during the wedge loading process so that the stress intensity could be determined. The crack length at the specimen surface was also recorded before the specimens were put into an autoclave. The specimens were exposed for 89 days at 250°C in a simulated Hanford groundwater repository environment.

At Sandia National Laboratories (SNL), a series of tests was conducted on pre-cracked fracture mechanics specimens of the compact tension geometry (Figure 2.6) using the constant displacement technique.[8] (This geometry, which is an ASTM standard described in E 399-81,[10] is considered by an MCC workshop[5] to be a constant load rather than constant displacement type of specimen.) The specimens were fatigue pre-cracked over a stress-intensity range of 2 to 11 $MN/m^{3/2}$ and exposed to the environment prior to loading. A heavy load ring with bolt-mounted clevises* across its diameter was used to load the specimen to 65 to 90% of the measured overload stress intensity (37 $MN/m^{3/2}$) in brine and dry salt plus 100% relative humidity air, for 1024 to 2000 hours. The specimens were electrically insulated from the clevises.

2.3.3 Residual Stress Specimen Tests

Many SCC problems are associated with residual stresses developed in the metal during heat treatment, fabrication, and welding.[14] As already noted above, a weld bead was produced on U-bend specimens as part of a screening study at PNL. In addition, residual stress specimens (Figure 2.7) were

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*A clevis is a U-shaped yoke at the end of a chain or rod, between the ends of which the specimen can be pinned or bolted. In the present case, two clevises are used to pull the "jaws" of the specimen apart.

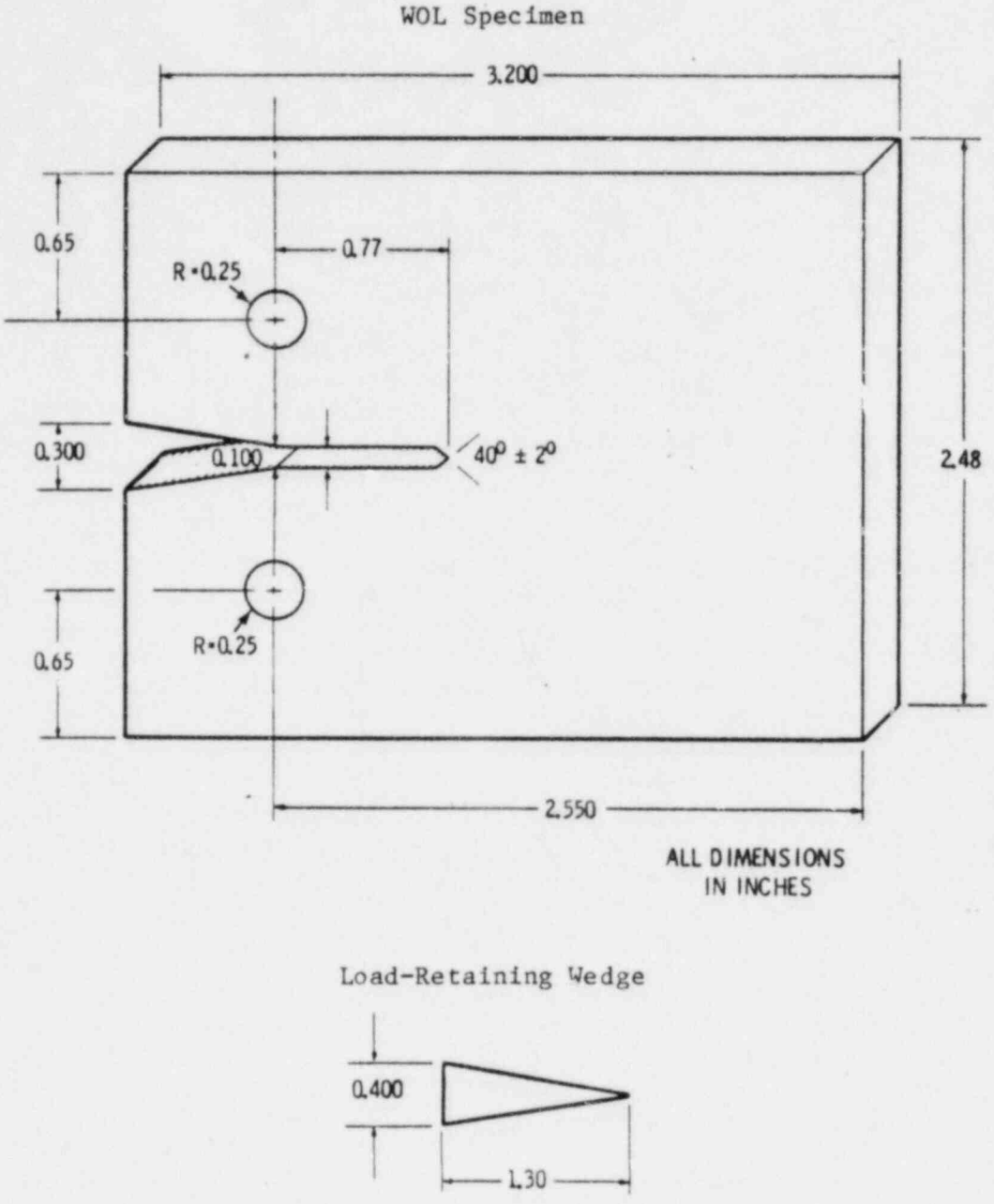

Figure 2.5 Wedge-opening load specimen used for stress-corrosion-cracking evaluation in autoclave tests.[11]

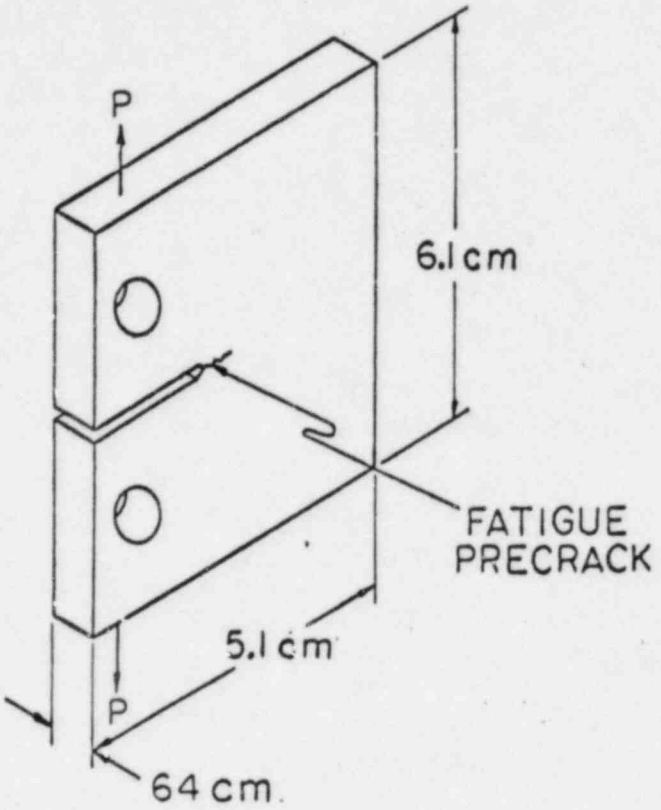

Figure 2.6 Pre-cracked fracture mechanics specimen with the compact tension geometry.[8]

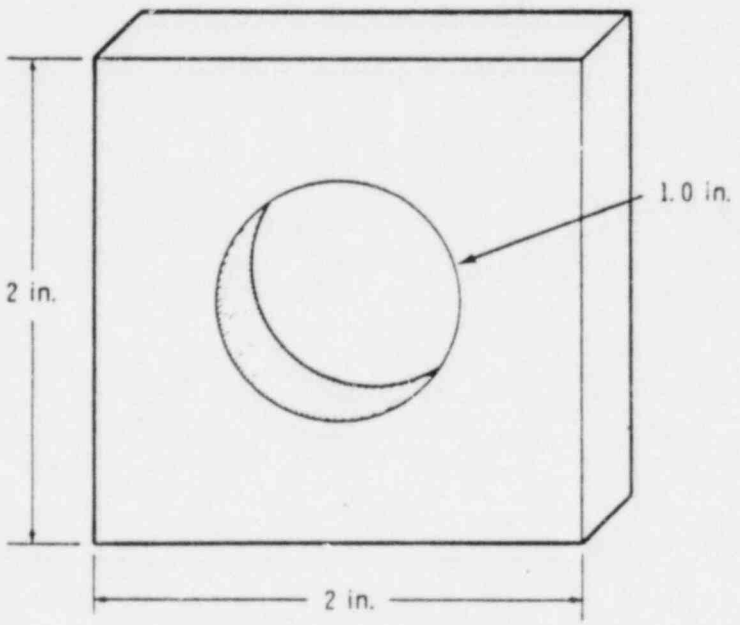

Figure 2.7 Residual-stress specimen used in SCC testing.[11]

included in autoclave tests. The specimens were plastically deformed in compression, then allowed to spring back, thus producing residual tensile stresses. The specimens were exposed for 89 days at 250°C to simulated basaltic groundwater.[11]

2.4 Dynamic Testing

2.4.1 Slow-Strain Rate Testing

The slow-strain rate (SSR) test is an accelerated test relative to statically loaded tests, but it is qualitative in nature. Data from SSR testing can be used to show susceptibility to SCC in a particular environment, but the data may not be useful in a quantitative sense for design.[3]

The SSR technique consists of subjecting a specimen to a slow, constant strain rate under controlled environmental conditions. Typically, strain rates range from 10^{-8} to 10^{-4} sec^{-1}. SCC will be promoted if the strain rate is within a critical range of values for which a balance is maintained at the crack tip between deformation, dissolution, film formation, and diffusion. (For a further discussion of the mechanism of SCC, see the BNL report by Shao.[4]) The SSR apparatus must provide reproducible, constant strain rates over the 10^{-8} to 10^{-4} sec^{-1} range.[7]

The slow-strain apparatus used at PNL consists of a gear-driven loading device with which constant extension rates are applied to the specimen (Figure 2.8). The load is measured in a load cell external to an autoclave containing the sample, and displacement is measured on a linear variable differential transformer (LVDT) between the autoclave and the loading rod. The load-displacement data were plotted for each test so that deformation characteristics could be determined.[3]

Tensile specimens fabricated from sheet metal material were used to conduct the SSR tests at 250°C (Figure 2.9). Simulated Hanford groundwater was passed into the bottom of an autoclave and through a layer of crushed basalt before reaching the specimen (Figure 2.8). The dissolved oxygen content was 6 ppm. The tests were performed at strain rates ranging from 10^{-7} to 10^{-4} sec^{-1}. The fracture surfaces were examined by scanning electron microscopy for evidence of SCC.[15,16]

For the purpose of evaluating the SCC (and hydrogen embrittlement) behavior of TiCode-12, an SSR testing program has been carried out at SNL.[8,17] The SSR tests were conducted on electrically insulated specimens (Figure 2.9) inside Hastalloy C-276 autoclaves. In the first series of tests, the specimens were subjected to initial strain rates ranging from 5×10^{-7} to 1×10^{-4} sec^{-1}, a temperature of 250°C, and an environment of air, dry salt, and saturated brine. Additional testing was carried out at a strain rate of 1×10^{-5} sec^{-1} at 250°C in oxygenated brine (~500 ppm O_2), deoxygenated dry salt (~0.003 ppm O_2 in any condensed solution) and dry salt plus 2% H_2O. In the second series of tests a constant strain rate from 10^{-7} to 10^{-4} sec^{-1} was maintained by means of a gear-reducer and electric motor coupled to the load cell so that recordings of applied load vs

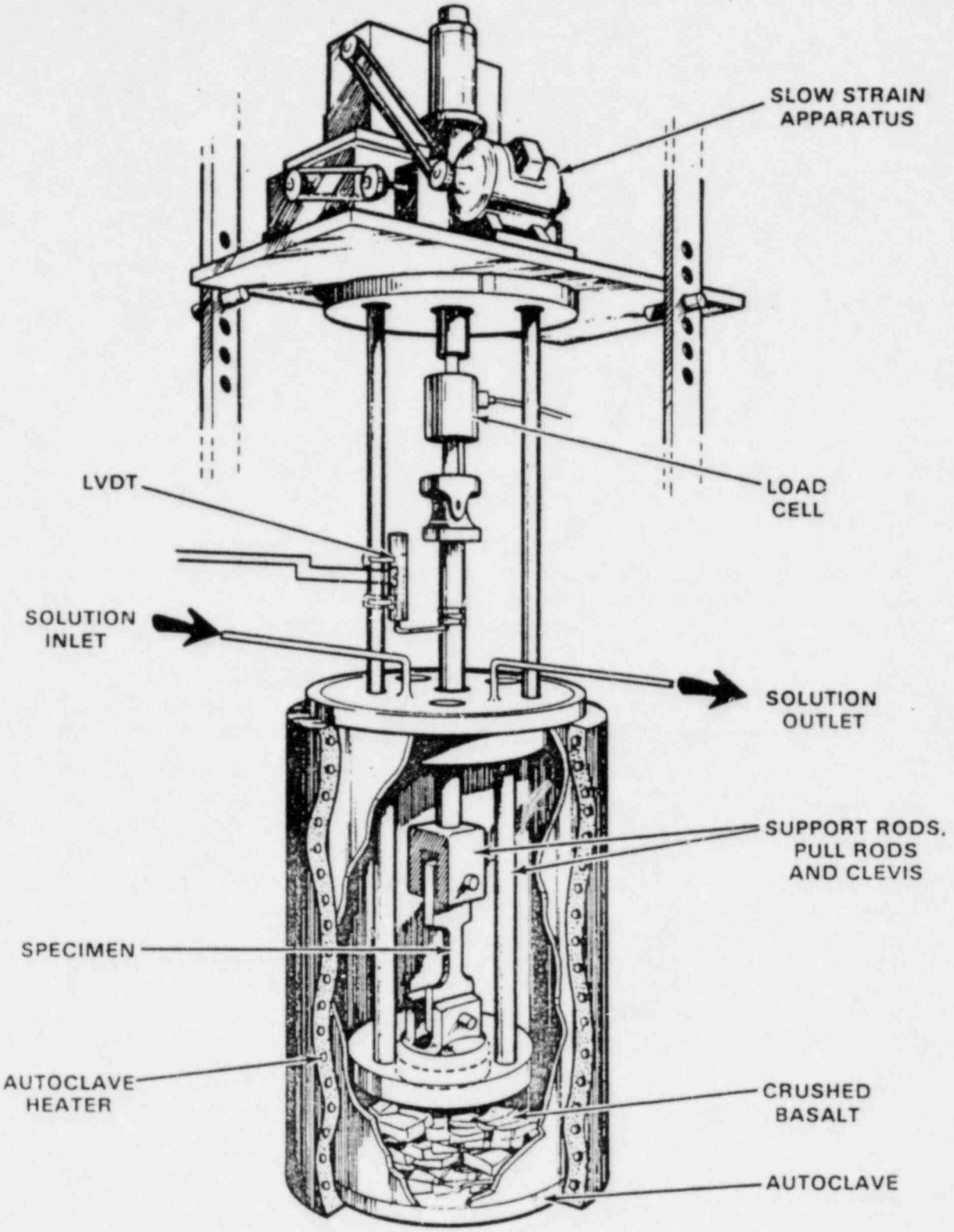

Figure 2.8 Slow-strain rate test system.[3]

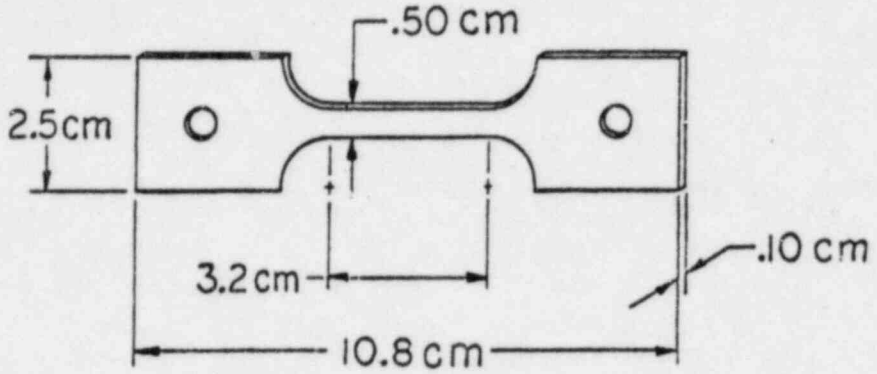

Figure 2.9 Slow-strain rate test specimen.[17]

time could be obtained. The testing environments were synthetic seawater and simulated WIPP brine solutions (Table 2.2). The testing solutions had been deaerated by bubbling argon through them for eight hours prior to testing in order to reduce the dissolved oxygen content to ~30 ppb.

Susceptibility to SCC was assessed by measuring time to failure (i.e., total strain at fracture), the ultimate tensile strength, and reduction in cross-sectional area. The resulting experimental data for these three parameters were then divided by the values obtained for the corresponding parameters in air, which is the reference environment; ratios significantly less than unity were to be taken as an indication of susceptibility to SCC. The results indicate that SCC is an unlikely failure mode for the test conditions used.

2.4.2 Fatigue-Crack-Growth Rate Testing

The FCGR method, as its name implies, is a technique to determine the growth rates of cracks produced as a result of metal fatigue. Fatigue cracking, however, is a mechanical failure mode of interest in assessing the failure of metal structures subjected to cyclic stresses, and these are not anticipated in the repositiitory environment. The FCGR method is of interest in the present context, however, because use of this method accelerates the SCC process in susceptible metals by the mechanical breakdown of the passivating film at the crack tip.

As noted by Pitman,[3] in FCGR testing, a crack is forced to grow by cycling the tension load on a notched, pre-cracked specimen and the rate of growth of this crack is measured. The new data are usually presented as crack extension per tension cycle (da/dn). The effects of a simulated repository environment on the crack-growth rate may be evaluated by the dependence of da/dn on the cyling frequency and by the acceleration of da/dn relative to its value in a reference environment (often referred to as an "inert" environment) such as air. An accelerated crack-growth rate may be indicative of SCC. In addition, the microscopic structure of the fracture surfaces should be examined for evidence of SCC.[7,8] FCGR data may be used with fracture

Table 2.2

Representative Solution Compositions Used for SSR Testing at SNL[8]
(Major Ions)

Ion	Seawater (ppm)[a]	WIPP Brine A (ppm)[a]	WIPP Brine B (ppm)[a]
Na^+	10,651	42,000	115,000
K^+	360	30,000	15
Mg^{2+}	1,272	35,000	10
Ca^{2+}	400	600	900
Sr^{2+}	13	5	15
Cl^-	18,980	190,000	175,000
SO_4^{2-}	884	3,500	3,500
I^-	0.05	10	10
HCO_3^-	146	700	10
Br^-	65	400	400
BO^{3-}	--	1,200	10
Total Dissolved Solids (g/L)	35	306	297
pH	8.1	6.5	6.5

[a]Except total dissolved solids and pH.

toughness data and anticipated stress levels to predict the growth of a crack under repository conditions.[11]

Crack-growth rates for Ti-6Al-4V plate have been found by Bania and Antolovich[18] to obey an Arrhenius-like relationship:

$$(da/dt)_{SCC} = A\, e^{-(Q_{SCC}/RT)}$$

where

$(da/dt)_{SCC}$ = crack extension rate

A = constant

Q_{SCC} = apparent activation energy

Note that Q_{SCC} is found to decrease linearly with K^2, where K is the stress intensity, and is thus only an apparent activation energy. Keeping in mind the possibility of failure mechanism changes under accelerated conditions,[6] data from the FCGR method could, in principle, be used to obtain crack-growth rates for SCC in TiCode-12, assuming that the resulting

crack-growth rate data as a function of temperature would also obey such an Arrhenius-like relationship. Also note that FCGR data are obtained under cyclic stressing and thus may be applicable to stress conditions which are much more severe than those reasonably expected in a repository environment. Further discussion of the SCC mechanism implied by the above Arrhenius-like relationship is presented in the original paper.[18]

FCGR testing at PNL was conducted both in air and in simulated basalt groundwater. Compact tension specimens (Figure 2.10) were used to characterize the FCGR of TiCode-12 plate in air at 20°C at a stress-cycling frequency of 10 Hz. Center-crack tension specimens (Figure 2.11) were used to evaluate the crack-growth characteristics of TiCode-12 sheet in air at frequencies of 5 and 10 Hz.

The first series of FCGR tests in a simulated repository environment was conducted at 87 to 90°C on sheet specimens of TiCode-12 (Table 2.3). A system was designed to circulate pre-heated simulated basalt groundwater solution through a chamber surrounding the cracked area of the specimen (Figure 2.12). The temperature of the specimen was maintained by the heating tapes and monitored for control by the thermocouple. The flowing environmental solution was pre-heated by wrapping the inlet tube around the heating elements. The composition of the simulated Hanford groundwater used in this series of tests is given in Table 2.4.

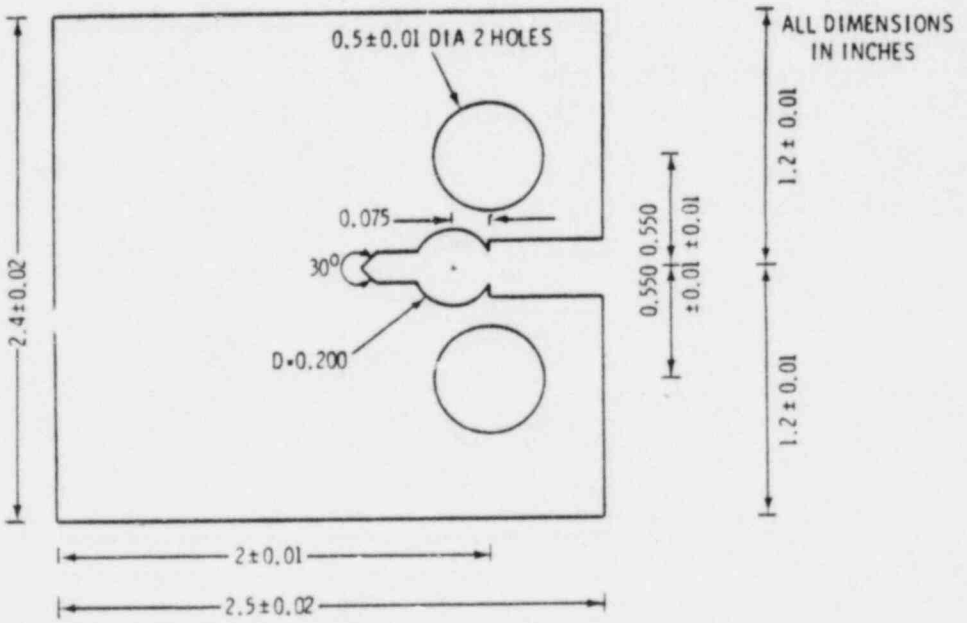

Figure 2.10 Compact tension specimen (ASTM E399) modified to accept a clip gauge for load-line displacement measurement.[11]

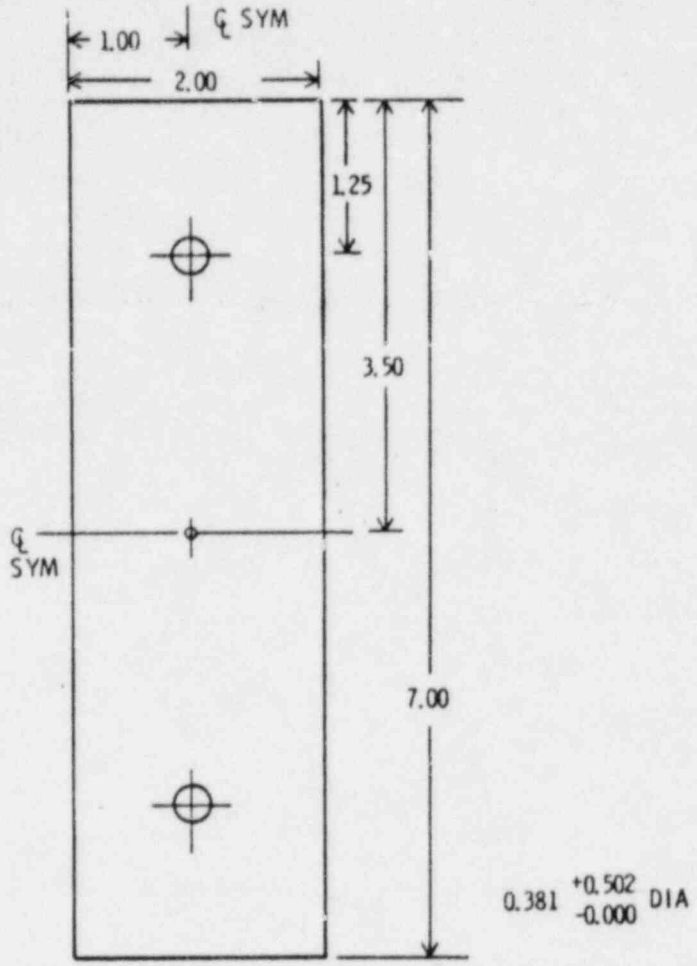

Figure 2.11 Center-cracked tension specimen (all dimensions in inches).[11]

Table 2.3

Summary of Environmental Fatigue-Crack-Growth Rates Tests at PNL[11]

Specimen Number	Material	Orientation[a]	Temperature (°C)
M267	Ti-12	LT	87 to 90
M268	Ti-12	TL	90
M269	Ti-2	LT	90
M270	Ti-2	TL	90
M271	Ti-2	TL	90
M272	Ti-12	TL	90
M273	Ti-2	TL	90

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

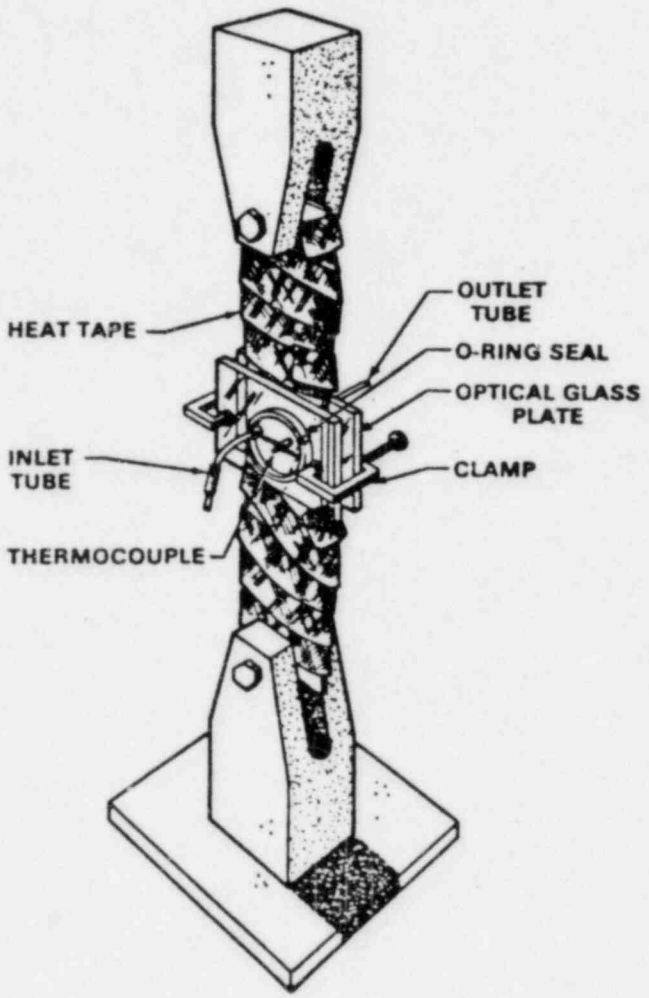

Figure 2.12 Environmental test system for fatigue-crack-growth rate testing using CCT specimens.[11]

Table 2.4

Chemical Analysis of Simulated Hanford Repository Water Used for FCGR Testing at PNL[11] (pH: 9.50; Conductivity (μMHo): 472)

Solution Makeup	Concentration (ppm)
HCO_3^-	139.8
CO^{2-}	22.0
SO^{2-}	1.2
F^-	6.7
Cl^-	43.9
Ca^{2+}	1.5
Mg^{2+}	0.63
Na^+	100
Si	0.2

A more elaborate version of the environmental chamber was developed at PNL for further FCGR testing (Figure 2.13).[3] A gravity feed system provides flowing solution to the chamber, and the flow rate is controlled using an in-line metering device. A once-through flow rate of approximately 10 ml/h is maintained. The solution in the chamber is heated to 90°C by pyrex-covered electrical resistance wire. The temperature is monitored for control by a thermocouple. No metal or conducting parts are in contact with the wet portion of the specimen. The composition of the simulated basalt groundwater is given in Table 2.5. (Note that in both series of FCGR tests, the simulated groundwater was exposed to air before and during the tests; no attempt was made to control the concentration of dissolved oxygen.) The tests were conducted at frequencies of 1.0, 0.1,[15,16] and 0.01 Hz, the last expected to be the most severe in the series.[19] The stress intensity was varied sinusoidally with the maximum and minimum stress intensities 554 and 55.4 kg, respectively.

2.5 Discussion

2.5.1 Advantages and Disadvantages of the Test Methods

The advantages and disadvantages of the various SCC test methods discussed above have been considered by a Workshop on Corrosion of Engineered Barriers[5] sponsored by the MCC:

U-Bend and C-Ring Tests

Advantages:

- Low-cost specimens
- Multiple specimens permitted in a single test
- Suitable for accelerated electrochemical tests

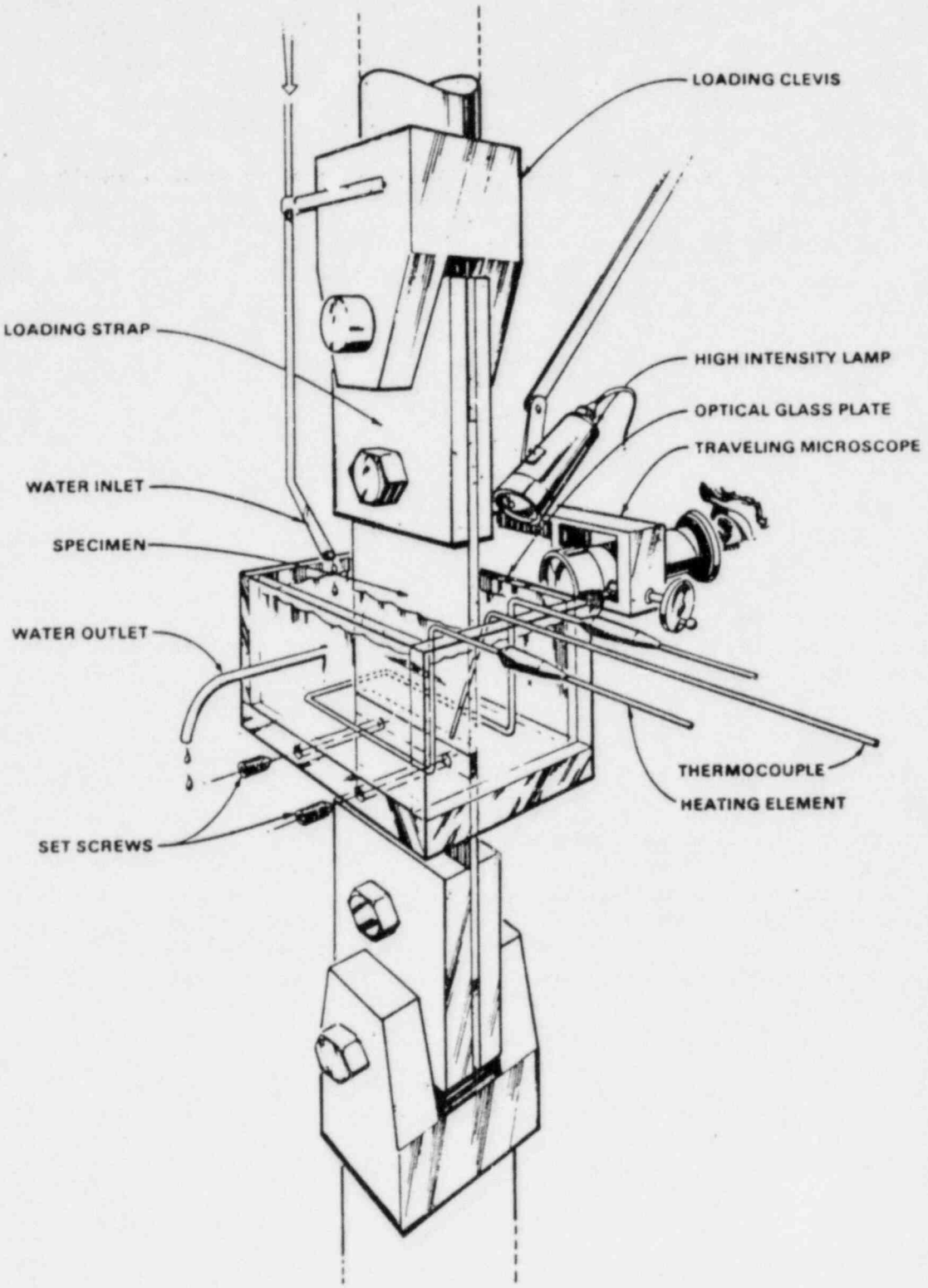

Figure 2.13 Environmental chamber used in fatigue-crack-growth rate tests.[3]

Table 2.5

Typical Inlet and Outlet Composition of
Simulated Basaltic Groundwater in SSR and FCGR at PNL[3]

Component	Concentration (ppm)[a] Inlet	Outlet
B	0.02	0.03
Ca^{2+}	1.2	0.4
K^{+}	3	42
Mg^{2+}	0.31	<0.05
Na^{+}	285	267
Si	63	173
Sn	0.1	0.1
SO_4^{2-}	115	112
F^{-}	37	37
Cl^{-}	153	162
pH	9.84	9.46

[a]Except pH.

- Sensitive to crack initiation
- Suited for autoclave and radiation tests
- ASTM standards for specimen geometry
- Good for evaluating the effects of pitting on SCC.

Disadvantages:

- Sensitive to surface preparation
- Questionable repeatability
- Uncertainty about the time a test should last to show SCC susceptibility
- Uncertainty in starting stress
- Stress gradient through the thickness.

Pre-Cracked Fracture Mechanics Tests

Advantages:

- Threshold stress intensity determined in these tests is useful for quality-assurance inspection of containers
- Good for evaluating both hydrogen embrittlement and stress corrosion
- ASTM standard for specimen geometry
- Good reproducibility
- Multiple WOL specimens permitted in a single test.

Disadvantages:

- Experimental limitations in extrapolating crack-growth rate results to 1000 years
- More costly than smooth-bar specimens
- The externally loaded, compact-tension specimens not suited for autoclave and gamma-radiation testing
- Doubt about results from accelerated electrochemical tests on precracked specimens
- The compact-tension specimen limited to single-specimen tests.

Slow-Strain-Rate Tests

Advantages:

- Potential accelerated test, although requires verification of applicability to various classes of material
- Good for screening, but examination needed for several parameters (strain rate in particular)
- Good for hydrogen embrittlement (external)
- Good for accelerated electrochemical tests
- ASTM standard for the tensile specimen geometry
- Good reproducibility.

Disadvantages:

- Any lifetime predictions will depend on modeling the appropriate failure mechanisms
- May be too severe a test since a large dislocation density is being introduced in the material
- Not well suited for testing in a radiation field.

Fatigue-Crack-Growth Rate Tests

Advantages:

- Generally considered to give a more conservative (lower value) stress-intensity threshold than do static methods
- Reproducible threshold values.

Disadvantages:

- Most difficult and costly of the tests considered
- Very few existing autoclave-fatigue-testing systems
- Uncertain effect of the loading wave form on SCC results
- Not well suited for testing in a radiation field.

2.5.2 Recommendations

The ideal test for SCC would yield data which could be used to predict the crack initiation time and the crack propagation rate under repository conditions, assuming that TiCode-12 is indeed susceptible to SCC under such conditions. As a practical matter, deriving such quantitative predictions from the experimental data is beset with difficulties. As noted by Wei, Novak, and Williams,[20] for example, the existence of an incubation period (a period of crack-growth rate much less than 10^{-6} in/min) and of a non-steady-state crack-growth period can lead to an underestimation of the steady-state rate of crack growth (and thus to an overestimation of the operating life of the barrier) as well as to erroneous values of K_{Iscc}.

We, therefore, recommend long term real-time testing of statically loaded specimens under expected repository conditions. "Long term" here means on the order of years. Such long term testing need not delay the progress of the waste disposal program, but can and should be carried out in parallel with the design and development of the waste package and repository.

As a result of such a long term testing program, data would be obtained on the crack initiation time and on the rate of crack growth for SCC of TiCode-12 under repository conditions (assuming that any measurable rate of SCC is found). Such data may be used to generate emperical predictive equations, from which extrapolations of the SCC data to 1000 years and confidence limits for the time to failure of a TiCode-12 containment barrier may be obtained. The work by Bania and Antolovich,[18] discussed in Section 2.4.2 above, provides an example of the use of SCC test data, in this case from short term dynamic testing, to generate predictive equations. There is, of course, no a priori reason to assume that long term static test data for TiCode-12 under repository conditions will necessarily obey the Arrhenius-like relationship found by these authors.

We further recommend that SCC testing of TiCode-12 be carried out under expected repository conditions in the presence of a radiation field so that any combined effects of both the repository environment and the radiation field may be observed. We note that PNL has constructed an autoclave test apparatus in a radiation facility[11,19] (shown schematically in Figures 2.14 and 2.15) and has undertaken a preliminary study of the effects of γ-irradiation on the chemistry of simulated basaltic groundwater.[15] Statically loaded specimens such as U-bend, C-ring, or WOL are the most appropriate specimen geometries for this type of facility. We particularly recommend that multi-year long term testing be carried out under the combined effects of the repository environment and the radiation field and that any crack surfaces which may develop be examined fractographically to check for microscopic evidence of SCC.

3. TESTS FOR GALVANIC CORROSION OF TiCode-12

3.1 Introduction

Galvanic corrosion results from the chemical reaction which occurs when two (or more) dissimilar metals are in physical or other electrical contact in

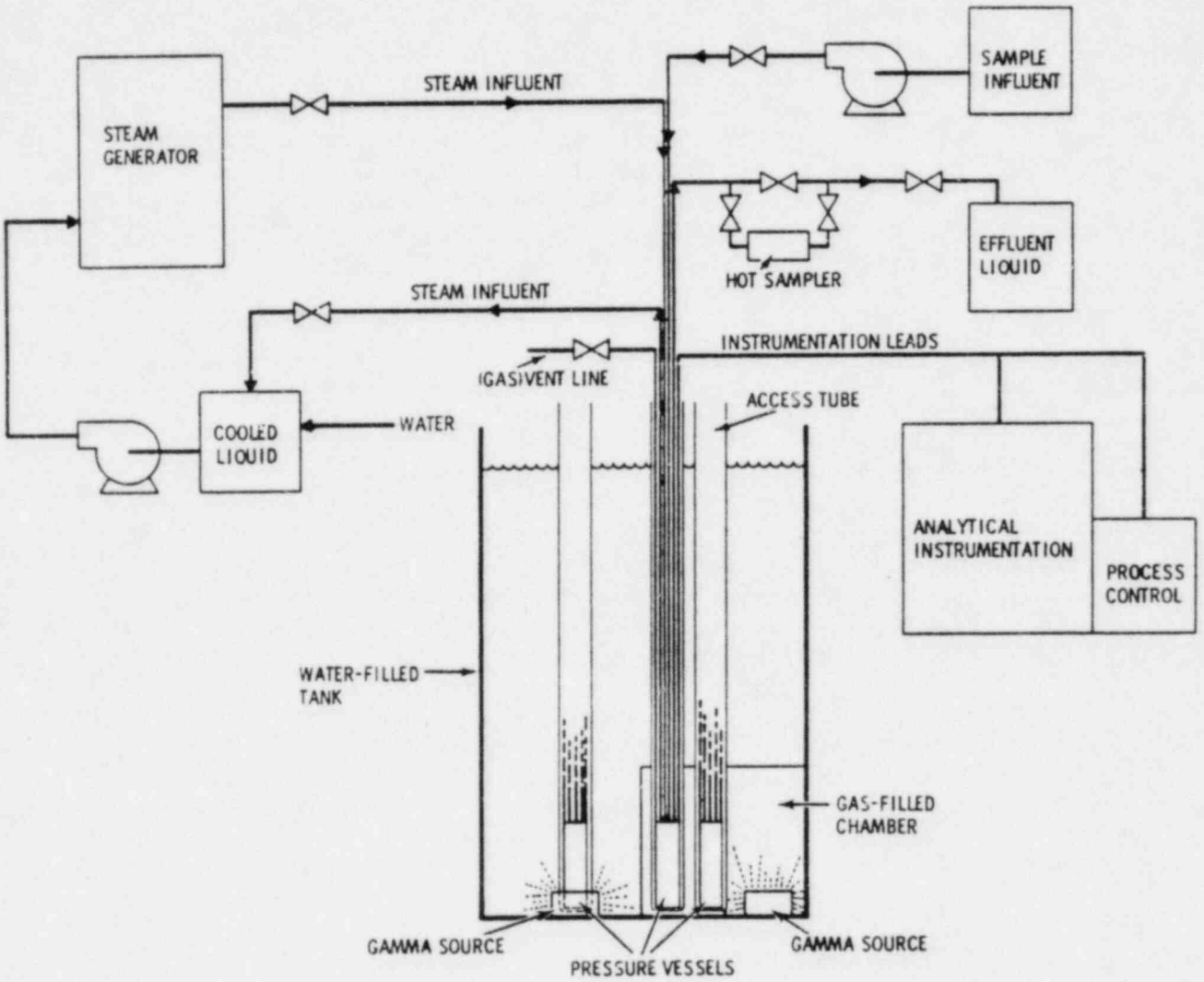

Figure 2.14 Radiation/corrosion test facility.[11]

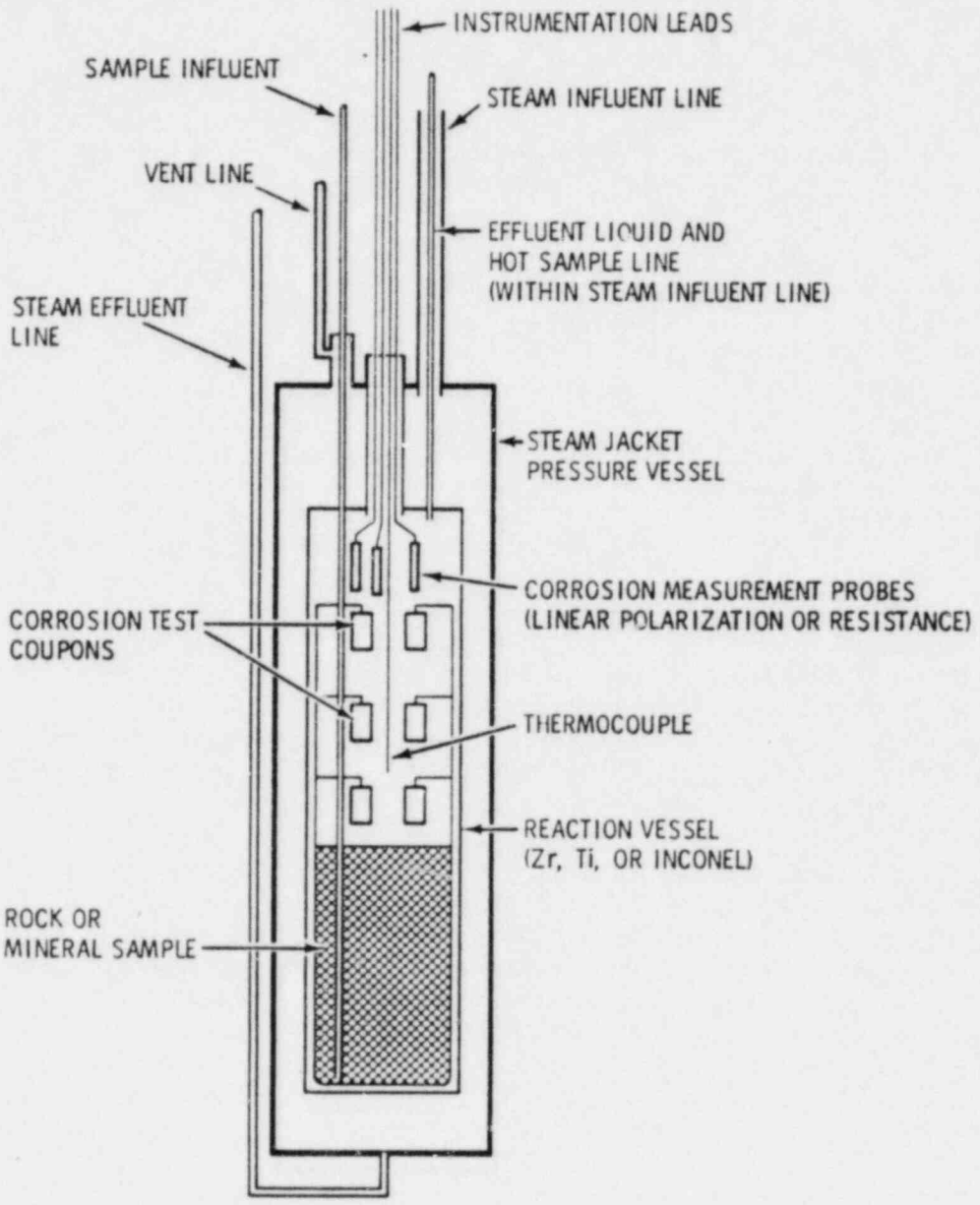

Figure 2.15 Reaction chamber for radiation/corrosion test facility.[11]

a conductive solution. Such a situation could arise in a repository if backfill is not used or if the position of the container shifts with time as a result of the cracking or liquefaction of the backfill material. In either case, TiCode-12 could come into contact with the emplacement sleeve. This mode of corrosion has not been considered significant in the context of nuclear waste package performance because it is considered likely that it can be avoided by proper materials selection.[6]

In contrast to stress-corrosion cracking, which, for TiCode-12 has been investigated at several DOE laboratories, very little work has been done on the galvanic corrosion of this alloy. For example, galvanic corrosion was not addressed (for any material) by a workshop on corrosion of engineered barriers sponsored by the MCC.[5] Nevertheless, some additional data requirements characterizing the galvanic corrosion behavior of TiCode-12 are suggested by Shao.[4] In the present report, a brief account will be given of galvanic corrosion test methods, in particular, those which have been used on titanium and its alloys coupled with other metals. The applicability of such test methods, suitably modified, to the above-mentioned data requirements will be considered.

3.2 Current Status of Galvanic Corrosion Testing

In order to measure galvanic corrosion, the two metals of interest are placed in electrical contact and the galvanic couple is them immersed in the electrolyte of interest under specified conditions. If the electrical contact is created by actual physical contact of the two specimens, then conditions which may be conducive to crevice corrosion must be avoided. Corrosion rates may be determined directly by measuring weight loss and indirectly, as well, by measuring the average galvanic current densities.

For example, Macki and Kochen[21] measured the galvanic corrosion behavior of a selected group of alloys (Table 3.1), including Ti-6Al-4V, in ocean water and hydrochloric acid by gravimetrically measuring the corrosion rates of galvanically coupled specimens and by measuring electrode potentials for these couples. The alloy specimens were disks 1 inch in diameter by 0.080 inch in thickness. After being machined, the disks were abraded (to ensure good contact between the electrically connected faces of the two disks in the galvanic couple), measured to the nearest 0.001 inch, cleaned with acetone, dried, and weighed to the nearest 0.1 mg. A pair of disks was then assembled into a galvanic couple by mounting the pair in an insulated nylon clamp (Figure 3.1). The exposed edges of the disks were coated with a silicone adhesive so only one face of each disk was exposed to the environment; the adhesive also isolated the circle of contact between the exposed edges of the two disks from any possible crevice corrosion. The electrical resistance of each couple was measured before and after exposure to the electrolyte in order to ascertain the degree of electrical contact between the disks. After exposure to the electrolyte (up to 96 hours in 0.1 N HCl) each couple was disassembled, the disks were cleaned in distilled water and acetone, dried, and reweighed to determine the weight loss, if any. A galvanic series for the alloys in each electrolyte was established by measuring the electrical poten-

Table 3.1

Alloys Used in Galvanic Tests by Macki and Kochen[21]

Tuballoy (depleted uranium)	U-10 wt% Mo
U-4.5 wt% Nb	7178 Al
U-6 wt% Nb	Ti-6Al-4V
U-8 wt% Nb	4340 steel
Mulberry (U-7.5 wt% Nb-2.5 wt% Zr)	Type 304 SS (passivated)

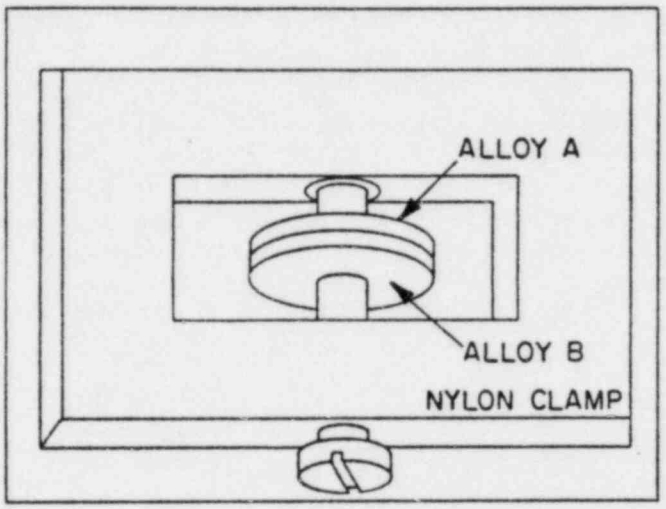

Figure 3.1. Apparatus used for gravimetric-galvanic corrosion tests.[21]

tials relative to a saturated calomel electrode generated by disks of each alloy immersed in the particular electrolyte (e.g., ocean water at 25°C).

Another discussion of the galvanic corrosion properties of titanium in NaCl and HCl solutions is given by Schlain.[22] In this series of experiments, the metal specimens were cut to size (10 cm x 2.5 cm x 0.13 cm for Ti), vacuum annealed at 900°C for two hours, and cleaned with solvent. The equipment used included an open two-liter beaker, a rotating specimen holder, and an aerator. The strips were fastened to the rotating holder, electrically coupled through a calibrated 0.62 ohm resistor, immersed in a 3% NaCl solution, and rotated at speeds up to 150 rpm. During the course of the test, voltage readings were taken across the calibrated resistor in order to estimate the size of the galvanic current. The weight loss of the specimens was also noted. All of these measurements were performed at room temperature (20-25°C).

Another study of the galvanic corrosion behavior of titanium was conducted by Shalaby.[22] Diagrams of the test system and corrosion cell used in this study are presented in Figures 3.2 and 3.3, respectively. The materials studied were 99.5% Ti and the four alloys described in Table 3.2. Measurements were taken, over a period of one month, of the corrosion current densities of the couples in a 32.7 g/l NaCl solution at 90°C with oxygen gas bubbled through the solution. Micrographs of the coupled specimens were compared with those of uncoupled specimens subjected to the same conditions.

Mansfield and others[24] studied the galvanic interactions between several aluminum alloys and various metals, including Ti-6Al-4V in air-saturated 3.5% NaCl solution by means of weight-loss measurements and continuous monitoring of the galvanic current in 24-hour tests. The test specimens were flat coupons which were mounted in a lucite holder so that an area of about 20 cm^2 of each specimen was exposed to the electrolyte. The corrosion potential of the two specimens, as yet uncoupled, was followed for 15 minutes after immersion. The specimens were then electrically connected via a zero-impedance ammeter, the output of which is proportional to the galvanic current. The ammeter output and the potential for the couple were monitored by recorder for 24 hours. Because the titanium alloy was considered to be more noble than the aluminum alloys, only the weight losses of the latter were noted when they were coupled with the titanium alloy.

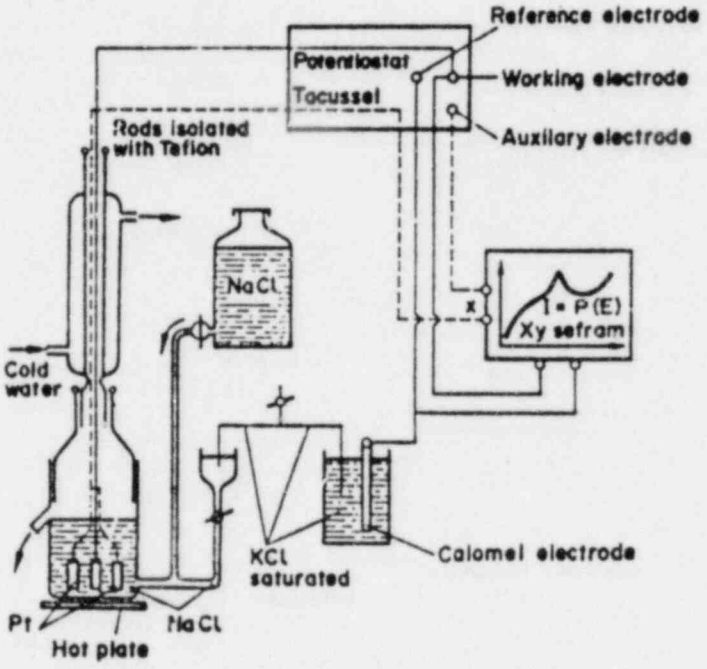

Figure 3.2 Galvanic corrosion test system used by Shalaby.[23]

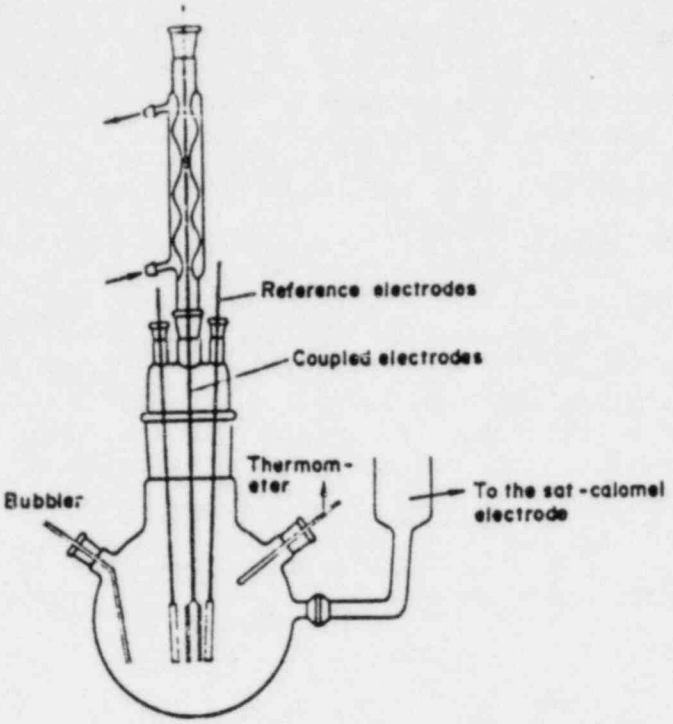

Figure 3.3 The corrosion cell used by Shalaby.[23]

Table 3.2

Four Alloys Investigated by Shalaby[23]

	Cu	Zn	Ni	Al	Fe	Mg	Sn	Si	As	Mn
Admirality brass	69-9	28-77	--	--	--	--	1-01	--	0-02	--
Al-brass	74-1	23-5	--	2-35	--	--	--	--	0-02	--
Cu-Ni	89-4	0-04	9-44	--	0-52	--	--	0-036	--	0-49
Ag-Mg	--	--	--	97-0	--	2-9	--	--	--	0-01

None of the above studies are directly applicable to the galvanic corrosion of TiCode-12 in a nuclear waste repository environment and are mentioned only to provide the reader with a general impression of the kind of galvanic corrosion testing which has been done on titanium and its alloys. In the context of the nuclear waste package program some work has been done by Westermann and others[15] on the corrosion of galvanic couples of cast iron and cast steel with titanium, although the focus seems to have been on the iron and steel. Simulated Hanford groundwater flowing through crushed basalt at about 35 ml/hr, was the electrolyte. The tests were run at temperatures of

150 and 250°C. The inlet oxygen concentration was kept between 6 and 8 ppm by sparging with a mixture of 20 % oxygen and 80% argon; the outlet oxygen concentration was about 1 ppm. Further discussion of the autoclave system and simulated groundwater composition are given elsewhere in this series of reports.

3.3 Recommendations for Future Work

As was noted in the previous section, there has been very little work applicable to a nuclear waste package on the galvanic corrosion of titanium or its alloys, probably because TiCode-12, the alloy under consideration, is expected to be more noble in a metallic sense than the other waste package components with which it is likely to couple galvanically. Nevertheless, some additional data requirements for the galvanic corrosion behavior of TiCode-12 have been suggested by Shao:[4]

- the extent of the galvanic corrosion on both couple components, including a determination of dissolution and film growth rates
- the cathode-to-anode ratio effect
- the galvanic series in brine and basalt groundwaters for TiCode-12 and the other waste package components
- the amount of hydrogen evolution during coupling.

All of these data requirements may be obtained by a continuation of the work on galvanic corrosion in simulated Hanford groundwater by Westermann and others[15] mentioned in the previous section. Galvanic couples of TiCode-12 and other likely metallic components of the waste package should be immersed in simulated basalt groundwater and brine under conditions expected in the repositories for periods of up to several years. This kind of experiment could be conducted using the autoclaves and auxiliary equipment described elsewhere in this program. The effect of radiation on galvanic corrosion would also be of interest and could be carried out in the radiation test facility also described elsewhere. The metal specimens comprising the galvanic couples should be weighed and their surfaces characterized at least by scanning electron microscopy and preferably by a combination of surface analysis techniques, both before and after exposure to the simulated repository environments; any weight changes of the specimen and the growth (or dissolution) of any surface films may be observed by these techniques. The testing of galvanic couples with several different area ratios should also be considered. The galvanic series for the metals and alloys likely to be used in a waste package under expected repository conditions in brine and basaltic groundwaters may be determined by potentiometric measurements of the single-electrode potential for each of these metals and alloys relative to some standard electrode such as the calomel electrode. Measurement of the hydrogen or other gas evolution at the low rates of galvanic corrosion expected is difficult and should not be conducted unless other evidence of galvanic corrosion is obtained. Placement of an inverted container or other collection device (possibly for several

years) over a galvanic couple of interest in an autoclave-simulated repository environment would be the most direct way to obtain evidence of hydrogen evolution, but this would not be an easy experiment to carry out. If a significant portion of any evolved hydrogen were to be retained by the metal, tests for hydrogen embrittlement, discussed elsewhere in this program, would be appropriate.

It has been recommended that consideration be given to the evaluation of possible galvanic effects on stress corrosion.[25] Such testing could be carried out through the use of double U-bend type specimens in which the appropriate dissimilar metals are placed in contact (see Section 2.3.1 above). Galvanic enhancement of the dealloying of nickel-aluminum bronzes by titanium has been reported;[26] galvanically enhanced dealloying of TiCode-12, while unlikely, should be examined during the course of galvanic corrosion studies on TiCode-12 (see Section 4.3 below).

4. TESTS FOR SELECTIVE LEACHING OF TiCode-12

4.1 Introduction

Selective leaching, or as it is often termed, dealloying, is a corrosion process by which one component of an alloy is preferentially removed from the alloy leaving an altered residual composition and structure.[27] As in the case of galvanic corrosion, dealloying has not been considered significant in the context of nuclear waste package performance because it is considered likely that it can be avoided by proper materials selection.[6] Selective leaching was addressed and dismissed by the MCC Workshop on Corrosion of Engineered Barriers as a form of localized corrosion encountered only with materials such as brasses, aluminum bronze, and gray cast iron, none of which are primary candidates for waste containment.[5] Additional data requirements, however, on the possible dealloying of TiCode-12 are suggested by Shao.[4] In this portion of the report, a brief account will be given of testing for selective leaching which has been done on titanium alloys. Recommendations for future investigation of selective leaching of TiCode-12 will then be made.

4.2 Current Status of Selective Leaching Testing of Titanium Alloys

Selective leaching is not an expected failure mode for titanium alloys[5] and for this reason it has generally not been the main focus of corrosion experiments on such alloys. Some evidence for dealloying has been observed during the course of testing for other modes of corrosion.

For example, Tomashov and co-workers[28] conducted a study of the passivation and corrosion behavior of titanium and some of its alloys by electrochemical, gravimetric, analytical, metallographic, and X-ray and electron diffraction methods. As part of this study, the dissolution of Ti-15 Mo alloys with different histories of heat treatment (and thus different crystalline microstructures) were carried out in 40% H_2SO_4 at 65 to 100°C. Chemical analyses of the solutions to which the specimens had been

exposed to determine the ratio of dissolved Ti to dissolved Mo were carried out as well as gravimetric determinations of the overall corrosion rates. The molybdenum content of the solution was only 3.3% of the dissolved metal, a result implying some kind of preferential dissolution of the titanium.

In the context of nuclear waste packages, at SNL an Auger depth profile was obtained for TiCode-12 which had been immersed in concentrated NaCl brine with a pH of 1 at 200°C for three weeks.[29] Evidence was obtained of nickel enrichment at the surface relative to the bulk metal concentration.

4.3 Recommendations

Additional data requirements for the selective leaching behavior of TiCode-12 have been suggested by Shao:[4]

- better definition of the range of conditions under which TiCode-12 and its welds will be prone to selective leaching
- further depth profiling studies using surface analytical techniques such as Auger spectroscopy
- better definition of the microstructure and examination of the stabilities of the phases making up this microstructure in order to evaluate the extent of selective texture attack
- further studies of the mechanisms which lead to near-surface composition gradients
- the effects of component enrichment or depletion or overall corrosion resistance
- determination of the mechanism of corrosion and any changes in these with time as the enrichment or depletion of components proceeds.

Surface analysis and metallographic examination of TiCode-12 specimens and, if possible, chemical analyses of the solutions to which these specimens were exposed, all of which could be conducted as part of the long term testing for uniform corrosion, would provide most of the above data and, in particular, would indicate whether TiCode-12 is susceptible to selective leaching under repository conditions. Uniform corrosion test methods are addressed in a BNL report by Jain.[30] We recommend that selective leaching be considered during the course of uniform corrosion testing of TiCode-12.

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