

SUPPORTING DOCUMENT		Number <i>Copy</i> SD-BWI-TI-159	Rev. Ltr./ Chg. No. Rev 0-0	Page 1 1 of 35 Total Pages 35
PROGRAM: Basalt Waste Isolation Project		Baseline Document <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		
Document Title: Preliminary Corrosion Models for BWIP Canister Materials		WES No. or Work Package No. L234 CEI 002		
Key Words: Low Carbon Steel, Fe9Cr1Mo Steel, Corrosion Model, Waste Package Doc. Type:2070 Subject Code:W300		Prepared by (Name and Dept. No.) RL Fish (Engineered Barriers) RP Anantatmula (Engineered Barriers)		Date: 9/30/83

THIS DOCUMENT IS FOR USE IN PERFORMANCE OF WORK UNDER CONTRACTS WITH THE U.S. DEPARTMENT OF ENERGY BY PERSONS OR FOR PURPOSES WITHIN THE SCOPE OF THESE CONTRACTS. DISSEMINATION OF ITS CONTENTS FOR ANY OTHER USE OR PURPOSE IS EXPRESSLY FORBIDDEN.

Abstract
Waste package development for the Basalt Waste Isolation Project (BWIP) requires the generation of materials degradation data under repository relevant conditions. These data are used to develop predictive models for the behavior of each component of waste package. The component models are exercised in performance analyses to optimize the waste package design. This document presents all repository relevant canister materials corrosion data that the BWIP and others have developed to date, describes the methodology used to develop preliminary corrosion models and provides the mathematical description of the models for both low carbon steel and Fe9Cr1Mo steel. Example environment/temperature history and model application calculations are presented to aid in understanding the models. The models are preliminary in nature and will be updated as additional corrosion data become available.

Distribution	Name	Mail Address
*	M. K. Altenhofen	MO-407/200E
*	R. P. Anantatmula(5)	MO-407/200E
*	W. J. Anderson	MO-407/200E
*	L. G. Clayton	MO-407/200E
*	D. R. Drewes	MO-407/200E
*	R. L. Fish (5)	MO-407/200E
*	L. R. Fitch	PBB/1100
*	T. B. McCall	MO-407/200E
*	E. L. Moore	MO-407/200E
*	M. F. Nicol	PBB/1100
*	E. H. Randklev	MO-407/200E
*	P. F. Salter	MO-407/200E
*	M. J. Smith	2101M/200E
*	W. F. Todish (org)	1135J/1100
*	BWIP Library	PBB/1100
*	Records Retention P. F. Reder	1135J/1100

INFORMATION COPY
THIS COPY WILL NOT BE REPLACED AND MAY BE CHANGED WITHOUT NOTICE

B501070591 B41116
PDR WMRES EECAEROS PDR
A-4165

BASALT

*COMPLETE DOCUMENT
(No asterisk, title page/summary of revision page only)

Release Stamp **10** **C-0**
OFFICIALLY RELEASED
1984 JAN -4 11:58

Prepared By: Engineered Barriers Design Development and Analysis Group/BWIP
Used By: Engineered Barriers Design Development and Analysis Group/BWIP

Refer to #
172

PRELIMINARY CORROSION MODELS FOR
BWIP CANISTER MATERIALS

R. L. Fish
R. P. Anantamula

1983

Basalt Waste Isolation Project
Rockwell Hanford Operations
Richland, Washington

TABLE OF CONTENTS

1.0	Introduction	5
2.0	Applicable Data	6
2.1	Sealed Pressure Vessel Tests	7
2.2	Refreshed Autoclave Tests	9
2.3	Refreshed Autoclave Tests in the Irradiation Facility	10
3.0	Corrosion Models	12
3.1	Model Development Methodology	12
4.0	Corrosion Models for Canister Materials	21
5.0	Concluding Remarks	28
6.0	References	29
	Appendix A	A-1
Tables:		
	Table I. Summary of BMRL Corrosion Data on Ferrous Alloys Exposed to Synthetic Grande Ronde Groundwater with Packing Under Anoxic Conditions	8
	Table II. Summary of Iron-Base Alloy Corrosion Data Hanford Grande Ronde Basalt Groundwater	11
	Table III. Summary of Iron-Base Alloy Irradiation Corrosion Data	13
	Table IV. Nomenclature for Corrosion Equations	22
	Table V. Optical Metallography Measurements of Pit Depths of Selected Low Carbon Steel Specimens	25

PRELIMINARY CORROSION MODELS FOR BWIP CANISTER MATERIALS

1.0 INTRODUCTION

Development of a waste package is an integral part of the effort to assess the feasibility of constructing a high-level nuclear waste repository in a basalt formation. Waste package design and performance assessment activities require mathematical models for each component of the package that describe any active degradation processes over the range of conditions anticipated in the repository. An extensive testing effort is planned to investigate potential canister material degradation modes to provide the basis for development of canister corrosion and crack growth models. These models will be used to extrapolate canister materials behavior to time periods over which the waste package is expected to provide containment (300 yr to 1,000 yr). The data generated by this canister materials test program will be analyzed to develop a mechanistic understanding of the degradation processes and to provide a statistical description of the materials behavior as an integral part of the predictive model development. Preliminary models of canister materials behavior will be required as data are generated to help guide the waste package development and design efforts.

The canister materials studies have progressed through the initial testing and selection of a reference and a backup canister material: low carbon steel and Fe9Cr1Mo alloy steel, respectively. While these materials have been selected on a preliminary basis, renewed attention will be given to more

expensive alloys with higher corrosion resistance if the reference and backup materials prove unsatisfactory in meeting canister reliability requirements. Only corrosion test results are available at this time. Crack growth data generated under conditions simulating a nuclear waste repository constructed in basalt (NWRB) will become available starting in FY 1984. The preliminary corrosion models presented herein for low carbon steel and backup Fe9Cr1Mo steel canister materials are based on an analysis of all currently available corrosion data for these and similar materials generated under conditions close to those anticipated in a repository constructed in basalt. The canister corrosion models have been developed at this time to support performance assessment and advanced conceptual design activities. The models will be updated as new data become available to provide input to future design activities.

2.0 APPLICABLE DATA

Corrosion data have been generated on iron-base alloys in synthetic Hanford Grande Ronde basalt groundwater in three different facilities: (1) sealed pressure vessels in the Basalt Materials Research Laboratory (BMRL) at Rockwell Hanford Operations (Rockwell), (2) refreshed autoclaves at Pacific Northwest Laboratory (PNL), and (3) an irradiation-corrosion test facility with a refreshed autoclave at PNL. Corrosion data on Fe9Cr1Mo have been generated in synthetic Hanford Grande Ronde groundwater at the BMRL only. These results represent only a minor portion of the total information that will have to be generated for licensing purposes. An extensive canister materials testing program is planned and is currently in progress to generate the data that will be needed.

A summary of the test techniques and corrosion test results from each of the laboratories generating relevant data to date is provided in the following subsections.

2.1 SEALED PRESSURE VESSEL TESTS

Corrosion studies have been performed at the BMRL on low carbon steel under conditions closely representing those anticipated in the repository (i.e., with specimens in direct contact with the packing material). Three low carbon steels were selected for this purpose, e.g., AISI 1006, 1020, and 1025. The steels were procured in sheet form (0.10-0.15 cm thick) in the hot-rolled condition from which 1.27 cm square specimens were cut. Synthetic Grande Ronde groundwater was prepared according to established procedures (Jones, 1982) and the pH of the water was adjusted to 9.75 at room temperature. The water was sparged with argon gas prior to mixing it with packing material (75 wt% basalt + 25 wt% bentonite). These early experiments were performed in Teflon-lined pressure vessels (23 mL volume). The current testing is done only in unlined titanium pressure vessels (125 mL volume). The pressure vessels were loaded in an argon glove box by submerging the specimens in a groundwater-saturated packing mixture. The corrosion tests were performed under static, anoxic conditions (<0.1 mg/L O_2 measured by colorimetric techniques) at 100°, 150°, 200°, and 250°C for periods of up to six weeks. A limited number of corrosion tests were conducted on Fe9Cr1Mo. The corrosion data generated on low carbon steel and Fe9Cr1Mo in sealed pressure vessels at the BMRL are presented in Table I. The corrosion rates in the table were calculated by dividing the corrosion penetration by the exposure time. The corrosion penetration was the same for

TABLE I. Summary of DMRL Corrosion Data on Ferrous Alloys Exposed to Synthetic Grande Ronde Groundwater with Packing Under Anoxic Conditions**

Material	Exposure Time (Weeks)	Corrosion Rate, $\mu\text{m}/\text{yr}$ (mils/yr)			
		250°C	200°C	150°C	100°C
AISI 1020	2	10.7*(0.42), 12.7*(0.5), 12.1*(0.48), 14(0.55), 15(0.59), 14(0.55), 13(0.51)- \bar{x} =13.1, σ =1.4	10.9(0.43), 11.9(0.47), 10.2(0.4)- \bar{x} =11, σ =0.9	14*(0.55), 13.5*(0.53), 10.9*(0.43), 11.7*(0.46)- \bar{x} =12.5, σ =1.5	
	4	6.9(0.27), 7.1(0.28), 7.1(0.28), 8.4†(0.33), 7.5†(0.3), 8.1†(0.32), 8.5†(0.34), 8.2†(0.32), 8.5†(0.33), 8.5†(0.34), 8.8†(0.35), 9.0†(0.35), 7.6†(0.3), 9.6†(0.38), 7.3†(0.29), 7.3†(0.29), 7.7†(0.3), 7.3†(0.29), 8.3†(0.33), 9.2†(0.36), 8.6†(0.34)- \bar{x} =8.1, σ =0.8			66.3(2.61), 64.7(2.54), 67.4(2.65)- \bar{x} =66.1, σ =1.4
	6	6(0.23), 5.5(0.22), 6.4(0.25)- \bar{x} =6, σ =0.5			
AISI 1006	2	13.9*(0.55), 12.1(0.40), 9.4*(0.37)- \bar{x} =11.8, σ =2.3		11.1*(0.44), 12.8*(6.5), 13.9*(0.55)- \bar{x} =12.6, σ =1.4	
AISI 1025	2	10.8*(0.42), 15.3*(0.6), 13.7*(0.54)- \bar{x} =13.3, σ =2.3		10.9*(0.43), 11.2*(0.44), 12.2*(0.48)- \bar{x} =11.4, σ =0.7	
Fe9Cr1Mo	4	1.7(0.07), 1.8(0.07), 2(0.08)- \bar{x} =1.8, σ =0.2			3.2(0.13), 2.4(0.09), 2.9(0.11)- \bar{x} =2.8, σ =0.4

*Experiments performed in AISI 303 PARR pressure vessels with Teflon liners.

†Groundwater composition experiment.

** \bar{x} and σ are mean and standard deviation in $\mu\text{m}/\text{yr}$, respectively.

all three low carbon steels (AISI 1006, 1020, and 1025) at 150° and 250°C under anoxic conditions with packing, within experimental error. Therefore, under anoxic conditions in contact with packing material the corrosion was independent of the carbon composition of the low carbon steels. The probable reason that no apparent increase in corrosion occurred at 250°C over that at 150°C is that a very adherent layer of iron-rich clay formed on the surface of the steel at 250°C which tended to reduce the rate at which corrosion proceeded. The significantly higher corrosion rate exhibited by the low carbon steel at 100°C as compared to its behavior at 150°, 200°, and 250°C is attributed to a slower rate of formation of the protective iron-rich clay at the lower temperature. X-ray diffraction data from the low carbon steel specimens under anoxic conditions with packing indicated the formation of magnetite on the surface at both 150° and 250°C.

The Fe9Cr1Mo alloy steel specimens exhibited a significantly lower corrosion rate than the low carbon steel at both 100° and 250°C. Pitting was not detected in any of the specimens.

2.2 REFRESHED AUTOCLAVE TESTS

Corrosion data were generated at PNL to an exposure of five months on AISI 1020 (wrought) and 1025 (cast) steel (Westerman, 1963a) in refreshed autoclaves (35 ml/hr) under oxic (argon-20% oxygen sparge) groundwater conditions. The synthetic Grande Ronde groundwater was modified by contact with crushed basalt at test temperatures of 150° and 250°C prior to contact with the specimens. The groundwater O₂ concentration at the autoclave outlet was -0.3 ppm in the 250°C test. Although these conditions (i.e., no packing material, high flow rate and oxic groundwater) are not representative of the

anticipated waste package environment, the test provided low carbon steel data to compare with other ferrous alloy (cast ductile iron, 2-1/2Cr1Mo, and 1-1/4Cr1/2Mo) data generated under the same conditions at time periods of up to 17 months by PNL. The corrosion data generated by PNL in refreshed autoclaves are presented in Table II. The corrosion rates were calculated by dividing the corrosion penetration by the exposure time.

For exposure times of five months and beyond, the corrosion data appear to exhibit a nearly linear time dependence. Specimens that deviated from linearity beyond five months exposure were found to exhibit a degree of pitting. The corrosion behavior exhibited by the low carbon steel was very similar to that exhibited by the other ferrous materials at both 250° and 150°C. Three wrought 1020 steel specimens exhibited pitting in exposures up to five months at 150°C, but pitting is not likely to occur this soon nor to this extent in the repository since the experimental groundwater oxygen concentration was very high relative to the anticipated waste package environment. Pit growth rate studies are planned under conditions more representative of the waste package to describe pitting behavior under conditions anticipated in the repository. It is anticipated that early saturation of the packing material that results in groundwater contact with the canister at elevated temperature ($T > 125^{\circ}\text{C}$) would result in protective film formation and canister protection at subsequent lower temperatures ($T \leq 125^{\circ}\text{C}$).

2.3 REFRESHED AUTOCLAVE TESTS IN THE IRRADIATION FACILITY

Irradiation corrosion tests were conducted by PNL in a ^{60}Co irradiation facility using the same refreshed autoclave approach and synthetic Grande Ronde groundwater (80% Ar-20% O_2 sparge) environment as described in the

TABLE II. Summary of Iron-Base Alloy Corrosion Data
Hanford Grande Ronde Basalt Groundwater Under Oxidic Conditions*

Material	Exposure Time, mo	Corrosion Rate, $\mu\text{m}/\text{yr}$ (mil/yr)	
		250°C	150°C
1 1/4% Cr, 1/2% Mo Cast Steel	1	14(0.54), 25(0.98)	2.0(0.080), 2.0(0.078)
	3	7.4(0.29) ^(a) , 4.3(0.17)	2.5(0.10), 3.6(0.14) ^(a)
	6	5.8(0.23), 1.8(0.067)	2.4(0.096), 3.1(0.12)
	12	1.3(0.050), 1.4(0.055), 1.6(0.064)	2.5(0.10), 1.4(0.055), 1.8(0.072), 5.6(0.22) ^(b)
	17	1.8(0.071), 2.8(0.11)	3.3(0.13), 2.4(0.095)
2 1/2% Cr, 1% Mo Cast Steel	1	14(0.56), 15(0.59)	3.3(0.13)
	3	3.6(0.14) ^(a) , 4.1(0.16)	1.4(0.056) ^(a) , 2.0(0.078)
	6	2.8(0.11), 1.5(0.059)	2.5(0.099), 1.2(0.048)
	12	1.3(0.050), 1.2(0.046), 1.2(0.047)	3.3(0.13), 2.8(0.11), 3.3(0.13)
	17	20(0.80) ^(b) , 13(0.52) ^(b)	8.6(0.34) ^(b) , 8.6(0.34) ^(b)
Cast Ductile Iron	1	25(1.0), 23(0.91)	8.9(0.35), 7.1(0.28)
	3	8.4(0.33) ^(a) , 7.9(0.31)	3.8(0.15), 4.3(1.7) ^(a,b)
	6	6.9(0.27), 4.8(0.19)	3.6(0.14), 3.6(0.14)
	12	2.5(0.099), 3.1(0.12), 2.5(0.097)	3.6(0.14), 3.8(0.15), 3.8(0.15)
	17	3.8(0.15), 6.1(0.24)	2.8(0.11), 12(0.46) ^(b)
1025 Cast Steel	3	5.1(0.20), 5.3(0.21)	6.9(0.27), 6.3(0.25)
	5	2.5(0.10), 3.0(0.12), 2.8(0.11) 3.6(0.14)	9.6(0.38), 11(0.44)
1020 Wrought Steel	2		14(0.55), 13(0.53), 38(1.5) ^(b) Deepest Pit = 0.0065 in.
	3	5.3(0.21), 5.6(0.22)	5.8(0.23), 3.6(0.14), 71(2.8) ^(b) Deepest Pit = 0.0110 in.
	5	3.0(0.12), 3.3(0.13), 3.6(0.14) 4.6(0.18)	8.1(0.32), 7.6(0.36), 46(1.8) ^(b) Deepest Pit = 0.0115 in.

*80% Ar-20%O₂ sparge gas; [O₂] = 0.3 mg/L at autoclave outlet

(a) Specimen stripped once before final exposure.

(b) Specimen significantly pitted.

\bar{x} = 5 $\mu\text{m}/\text{yr}$ and σ = 6.6 $\mu\text{m}/\text{yr}$ calculated for penetration at \geq 5 months. Includes data at the two temperatures.

previous subsection (Westerman, 1983b). Groundwater oxygen concentration at the autoclave outlet was measured at ~ 0.3 mg/L. The same ferrous alloys (cast ductile iron, low carbon steel and 2-1/2Cr1Mo) were exposed at 250°C for periods of up to thirteen months at a gamma dose rate of 3×10^5 rad/hr. The corrosion data generated by PNL in the irradiation facility in the refreshed autoclave are presented in Table III. Examination of the data generated at time periods beyond 5 months for cast 1020 steel, cast ductile iron and 2-1/2Cr1Mo in Tables II and III provide a basis for a gamma radiation field effect. Calculation of the uniform corrosion gamma field enhancement factor for these materials after equivalent time periods results in factors of 1.6 to 3.5. The average radiation field enhancement factor is ~ 2.5 under the stated test conditions. No pitting was observed in any of the low carbon steel specimens that were exposed for time periods of up to eight months.

3.0 CORROSION MODELS

3.1 MODEL DEVELOPMENT METHODOLOGY

The development of corrosion models for canister materials is constrained at the present time by a relative lack of applicable data. Because of this data constraint, models for degradation of the canister materials require many assumptions. Most of these assumptions will not be required in the future as the planned test program generates the needed data and the preliminary models are subsequently refined. Specific areas where directly applicable data are not presently available include the operational period air/steam environment, the post-closure air/steam environment and the pitting behavior

TABLE III. Summary of Iron-Base Alloy Irradiation-Corrosion Data Under Oxidic Conditions

Hanford Grande Ronde Basalt Groundwater at 250°C with 80% Ar-20% O ₂ Sparge Gas ~3 x 10 ⁵ rad/hr, [O ₂] ~0.3 mg/L at Outlet		
Material	Exposure Time, mo.	Corrosion Rate μm/yr (mils/yr)
Cast Ductile Iron	1	12 (0.49), 14 (0.56)
	3	9.6 (0.38), 30 (1.2)
	5	9.1 (0.36), 11 (0.43)
	6	9.6 (0.38), 9.1 (0.36)
	10	6.4 (0.25)
	11	9.1 (0.36)
	13	9.7 (0.38)
2½% Cr, 1% Mo Cast Steel	1	8.9 (0.35), 7.6 (0.30)
	3	14 (0.56), 22 (0.86)
	5	4.8 (0.19), 8.1 (0.32)
	6	4.1 (0.16), 4.1 (0.16)
	10	3.8 (0.15)
	11	3.3 (0.13)
	13	2.8 (0.11)
1025 Cast Steel	6	8.1 (0.32)
	8	7.9 (0.31)
1020 Wrought Steel	2	9.4 (0.37), 7.6 (0.30)
		8.9 (0.35), 8.9 (0.35)
		10.7 (0.42)

$\bar{x} = 6.7 \mu\text{m/yr}$ and $\sigma = 2.8 \mu\text{m/yr}$ calculated for exposure times ≥ 5 months.

under hydrothermal conditions. Testing to be initiated in FY 84 will generate data in these areas and reduce the number of assumptions needed in the models.

The degradation models for both low carbon steel and Fe9Cr1Mo predict corrosion behavior under four distinct conditions: (1) repository operational conditions under which the canister is exposed to an air/steam (high humidity) environment, (2) repository post-closure conditions under which the canister is exposed to a steam environment and a diminishing oxygen supply (due to consumption by the packing and canister), (3) potential high temperature ($>125^{\circ}\text{C}$) hydrothermal environment after saturation of the packing material, and (4) a relatively low temperature ($\leq 125^{\circ}\text{C}$) hydrothermal environment. Inherent in the selection of these conditions are the assumptions that the waste packages will include canisters to hold the waste form, that the canisters will be emplaced without packing material in boreholes vented to repository drifts for a period of time prior to packing material emplacement, that the repository will be sealed to the atmosphere after packing material is placed around the canisters, and that groundwater will eventually saturate the packing material and contact the canister as a liquid phase aqueous environment (hereafter referred to as aqueous phase).

The penetration by corrosion under each of the conditions described above is assumed to occur without any protective effect from previously developed corrosion product films. This is equivalent to assuming that corrosion proceeds under each condition as though the metal surface is fresh with no previously developed corrosion product. This assumption allows for simple additive combination of the penetrations from each of the individual environmental conditions. The assumption of simple additive contributions is conservative in that protection may be afforded by films formed by exposure

to higher temperatures and/or previous environments. If planned tests provide enough information to quantitatively describe the protective effects of films formed at a prior higher temperature exposure, these will be incorporated into the models at a later date. One exception was taken to the "no protection" assumption in the present modeling effort, where a protective effect was specifically measured in the case of aqueous corrosion behavior at low temperature subsequent to a higher temperature exposure.

As can be seen from Table II, a significant aqueous corrosion data base has been generated at PNL for the BWIP on iron-base alloys (cast ductile iron, 2-1/2Cr1Mo and 1-1/4Cr1/2Mo) to exposure times of 17 months (test temperatures = 150° and 250°C). These data provide a basis for describing the time-dependence of the degradation of iron-base alloy canisters. Data generated on low carbon steel under the same conditions for times of up to five months at PNL (See Table II) exhibited similar behavior. Thus, the assumption was made that under aqueous conditions and temperatures of 150° and 250°C and for periods of five months and beyond, low carbon steel exhibits the same corrosion rate and time-dependence as the remaining iron-base alloys tested at PNL. Some of the iron-base alloy specimens exhibited anomalously high corrosion rates as presented in Table II. These are indicated with a (b) superscript in the table and are associated with specimens that experienced a significant degree of pitting. The pitting is believed to be the result of relatively high dissolved oxygen concentration levels in the test groundwater. Therefore, only uniform corrosion behavior was used to compare corrosion behavior of the low carbon steel with the other iron-base alloys. Testing was also conducted on two iron-base alloys (cast ductile iron and 2-1/2Cr1Mo steel) as well as low carbon steel in a gamma radiation field (3×10^5 rad/hr)

at 250°C. The behavior of the low carbon steel was sufficiently similar to the other iron-base alloys in the radiation field to allow the assumption of a similar radiation enhancement factor also.

For the purpose of the preliminary corrosion models, all aqueous corrosion behavior was assumed to have a linear time dependence. The equivalent corrosion rates in $\mu\text{m}/\text{yr}$ were calculated from the weight-loss data at each exposure time for each temperature. The PNL data for irradiated and unirradiated conditions for five months and beyond were averaged to obtain an average corrosion rate in $\mu\text{m}/\text{yr}$ and this rate was assumed to remain constant. On the other hand, the BMRL data for the longest times at each temperature were averaged to obtain an average corrosion rate in $\mu\text{m}/\text{yr}$ and the rate was then assumed to be linear from that time onwards. Aqueous corrosion data generated at the BMRL on three different low carbon steels show essentially no differences in corrosion behavior. These results should allow the use of corrosion data generated on low carbon steels in other programs [i.e., Lawrence Livermore National Laboratory (LLNL)] for making assumptions of relative canister material behavior under conditions anticipated in an NWRB. As the corrosion data base on low carbon steel and Fe9Cr1Mo steel is developed, most of these assumptions will not be necessary and more direct quantification of low carbon steel and Fe9Cr1Mo corrosion behavior will be possible.

In order to model the corrosion behavior of the canister materials (low carbon steel and Fe9Cr1Mo) under the repository operational conditions of an air/steam environment, one must rely on other sources of data, since information has not been generated to date on either material under basalt-relevant conditions. However, data on these materials have been generated with saturated steam at atmospheric pressure and aqueous environment

conditions, both at 100°C, by LLNL. These were six-week tests on triplicate specimens of each material. Since the BMRL has 100°C aqueous environment data on these same canister materials after four-week exposure, the relative corrosion rates under basalt-relevant air/steam conditions can be estimated at 100°C by multiplying the average BMRL 100°C aqueous corrosion rate by the ratio of air/steam to aqueous condition rates measured by LLNL. The air/steam corrosion rate calculated in this manner provides the basis for the repository operational condition corrosion behavior for both canister materials.

Specific time and temperature dependence under these conditions can be based on corrosion data for iron or low carbon steel in air from the literature.

The repository post-closure condition is characterized by corrosion mechanisms similar to the operational condition. However, the presence of the packing material (75% crushed basalt and 25% bentonite) in combination with the sealed repository results in a very limited supply of oxygen. Thus, corrosion rates are anticipated to be very low during this post-closure period prior to groundwater saturation of the packing. Since no corrosion data have been generated for either low carbon steel or Fe9Cr1Mo steel under this condition (air/steam/packing environment), it is assumed, for the purpose of this preliminary model, that corrosion rates are one-half of those estimated for the operational condition. The temperature dependence of corrosion rate is assumed to be the same as that estimated for the operational condition.

Aqueous corrosion of low carbon steel at temperatures of 150°, 200°, and 250°C under anticipated repository conditions has been observed to be essentially independent of temperature (Anantatmula et al., 1983). Aqueous corrosion of low carbon steel at 100°C, without prior higher temperature exposure, exhibits a significantly higher corrosion rate. Thus, a 125°C conditional temperature for describing aqueous corrosion behavior was

determined to be appropriate. At temperatures $>125^{\circ}\text{C}$, the long-term (≥ 5 months) steady-state corrosion rates (based on linear kinetics) reported by PNL at 150° and 250°C were determined to provide the strongest basis for uniform corrosion rates of low carbon steel. The PNL iron-base alloy corrosion rate data (no gamma field) at both 150° and 250°C for exposure times ≥ 5 months were averaged to calculate a single corrosion rate to apply to the aqueous corrosion behavior at $>125^{\circ}\text{C}$ for low carbon steel.

Approximately constant corrosion rates with time were observed at exposure periods beyond five months. Thus, a linear time-dependence assumption is justified for the aqueous corrosion behavior of low carbon steel. The Fe9Cr1Mo steel aqueous corrosion behavior at temperatures $>125^{\circ}\text{C}$ was estimated by applying the ratio of Fe9Cr1Mo to low carbon steel corrosion rates measured at 250°C at the BMRL to the corrosion rate established for low carbon steel at temperatures $>125^{\circ}\text{C}$ as described above.

Aqueous corrosion of low carbon steel at temperatures $\leq 125^{\circ}\text{C}$ is dealt with in this preliminary model from two different perspectives:

- (1) behavior with packing saturation occurring after the canister temperature drops below 125°C , and
- (2) behavior with packing saturation occurring before the canister temperature drops below 125°C .

If saturation of the packing does not occur until the canister temperature falls below 125°C , the corrosion rate for low carbon steel is expected to be significantly higher (about a nine-fold enhancement based on BMRL data) than the higher temperature rate. Therefore, for the purpose of this preliminary

model, an estimate can be made for the low temperature ($\leq 125^{\circ}\text{C}$) corrosion rate of low carbon steel by modifying the high temperature corrosion rate ($> 125^{\circ}\text{C}$, calculated using the PNL data) by the ratio of the 100° to 250°C low carbon steel corrosion rates measured in the four-week tests at the BMRL.

It was found that corrosion rates measured for low carbon steel at 100°C were significantly lower if the specimen experienced exposure to a high temperature aqueous/packing environment prior to the 100°C exposure. The lower rate can be attributed to the protective nature of an iron-rich clay surface film that forms at the higher temperatures. Longer-term exposures at temperatures below 125°C may also result in a surface film with an equally protective nature, but data presently do not exist to support this idea. Thus, data recently generated at the BMRL in tests conducted at 250°C followed by 100°C will be used to estimate corrosion rates for low carbon steel for the condition of aqueous corrosion at low temperature ($\leq 125^{\circ}\text{C}$) preceded by higher temperature exposure to groundwater saturated packing. Sequential temperature test data are not available on Fe9Cr1Mo at the lower temperature ($\leq 125^{\circ}\text{C}$) to differentiate corrosion behavior on the basis of prior exposure to higher temperatures. Thus, aqueous corrosion rates at temperatures $\leq 125^{\circ}\text{C}$, for the purpose of this preliminary model, were estimated by applying the ratio of 100° to 250°C Fe9Cr1Mo corrosion rates (based on linear kinetics) generated at the BMRL to the corrosion rate established for Fe9Cr1Mo at temperatures $> 125^{\circ}\text{C}$.

All of the data used to estimate corrosion rates under the conditions described above were generated in the absence of a gamma radiation field. It is anticipated that gamma irradiation of the canister environment prior to groundwater saturation of the packing will not significantly affect canister corrosion. However, the aqueous corrosion data generated on the iron-base

alloys at PNL in the ^{60}Co gamma radiation field definitely reflected an enhancement in corrosion rates relative to those measured on the same materials, under the same conditions in the absence of gamma radiation. Therefore, a factor of 2.5, based on the PNL data, was incorporated to account for the enhanced aqueous corrosion rate in the gamma field for all aqueous environment conditions. This factor was decreased as a function of time to account for the decay in gamma dose rate expected from the radioactive waste forms. It was assumed that enhancement of the corrosion rate due to gamma radiation becomes negligible at 300 years after waste canister emplacement. The same enhancement factor was assumed to be applicable for both low carbon steel and Fe9Cr1Mo steel canister materials.

Since pit initiation and growth in low carbon steel requires a differential aeration cell in an aqueous liquid phase environment, it was assumed that pitting will not occur in high temperature ($>100^\circ\text{C}$ at 1 atm) air/steam environments. Pitting has been observed in low carbon steel specimens only after exposure to high flow rate, oxidic groundwater at 150°C . Exposure times for the specimens that exhibited pitting in the aqueous environment were two, three, and five months. Metallographic examination of these specimens was conducted to measure the maximum pit depth on each specimen. Measured maximum pit depths were 0.17, 0.28 and 0.29mm (6.5, 11.0, and 11.5 mils) for the specimens exposed to successively longer times. Based on these limited data, a power law relationship of penetration as a function of time was developed for estimating maximum aqueous pitting penetration in low carbon steel. No data are available on which to base a pitting temperature dependence. Therefore, it was assumed, for the purpose of this preliminary model, that pitting behavior is independent of temperature. There are no data available to suggest that pitting will occur

in Fe9Cr1Mo steel under the conditions anticipated at the waste canister surface. Therefore, it is assumed in the present model that pitting will not occur in this material. The pitting relationship for low carbon steel under aqueous conditions should not be used for calculating canister corrosion thickness allowances for design since pitting is a localized phenomenon and does not result in a significant reduction of overall load-carrying capabilities. However, the low carbon steel pitting behavior description can be used to estimate canister lifetimes based on additive contributions from uniform and pitting corrosion penetration. The pitting relationship can also be used as an overcheck on the final canister design thickness to ensure that pitting penetration does not exceed the structural allowance portion of the canister wall for the design life of the canister.

Statistical treatment of the data used in development of these preliminary corrosion models only includes calculation of standard deviation values for each discrete environmental condition. Sufficient data exist to calculate these for the aqueous conditions only. As additional data become available and the models are refined to reflect new information, appropriate statistical treatment of the data will be performed and integrated within the models to aid in design and reliability analyses.

4.0 CORROSION MODELS FOR CANISTER MATERIALS

Using the corrosion modeling methodology presented in the previous section, preliminary models were derived for low carbon steel and Fe9Cr1Mo. These are presented in the following sub-sections. The nomenclature used in

TABLE IV. Nomenclature for Corrosion Equations

<u>Symbol</u>	<u>Definition</u>	<u>Units</u>
P_{AS}	Corrosion penetration in the operational period air/steam environment	mm
P_{PCAS}	Corrosion penetration in the post-closure air/steam environment	mm
P_{AQ1}	Corrosion penetration in the aqueous environment above 125°C	mm
P_{AQ2}	Corrosion penetration in the aqueous environment at $\leq 125^\circ\text{C}$ with aqueous conditions achieved at $\leq 125^\circ\text{C}$	mm
P_{AQ3}	Corrosion penetration in the aqueous environment at $\leq 125^\circ\text{C}$ with aqueous conditions achieved at $> 125^\circ\text{C}$	mm
P_u	Total uniform corrosion penetration	mm
P_{pit}	Maximum pit depth penetration	mm
P_t	Total corrosion penetration	mm
T	Temperature	$^\circ\text{K}$
F	Irradiation enhancement factor	----
\bar{x}	Mean	$\mu\text{m}/\text{yr}$
σ	Standard Deviation	$\mu\text{m}/\text{yr}$
t	Time	years
t_{aq}	Time from canister emplacement at which aqueous conditions are achieved above 125°C	years
t_{AS}	Time period during which the canister is in the operational period air/steam environment	years
t_{PCAS}	Time period during which the canister is in the post-closure air/steam environment	years
t_1	Time period during which the canister is in the post-closure aqueous environment at $> 125^\circ\text{C}$	years
t_2	Time period during which the canister is in the post-closure aqueous environment at $\leq 125^\circ\text{C}$ with aqueous conditions achieved at $\leq 125^\circ\text{C}$	years
t_3	Time period during which the canister is in the post-closure aqueous environment at $\leq 125^\circ\text{C}$ with aqueous conditions achieved at $> 125^\circ\text{C}$	years
t_{pit}	Time period during which the canister is in the aqueous environment	years

the mathematical expressions is described in Table IV. Sample calculations are presented in Appendix A to illustrate the use of the models in calculating corrosion penetration.

Equations for Low Carbon Steel

The corrosion penetration in the operational period air/steam environment is described in Equation (1) as a function of time and temperature. For this purpose, corrosion data for iron in air (Uhlig, 1948) in the temperature range 252° to 385°C, LLNL's aqueous corrosion and air/steam environment data and BMRL's 100°C aqueous corrosion data were utilized. Thus,

$$P_{AS} = 269 t^{0.2} \exp(-2900/T) \quad (1)$$

with t varying from 0 to t_{AS} .

As mentioned in Section 3.0, the corrosion penetration in the post-closure air/steam environment, P_{PCAS} , is assumed to be half as much as P_{AS} . Thus,

$$P_{PCAS} = 134.5 t^{0.2} \exp(-2900/T) \quad (2)$$

with t varying from 0 to t_{PCAS} .

The corrosion penetration in the aqueous environment above 125°C, P_{AQ1} , is derived from PNL's 150° and 250°C data beyond five months indicating constant corrosion rate and is

$$P_{AQ1} = 5.03 \times 10^{-3} t_1 \quad (3)$$

The corrosion penetration in the aqueous environment at $\leq 125^{\circ}\text{C}$ with aqueous conditions achieved at $\leq 125^{\circ}\text{C}$, P_{AQ2} , is derived by using the ratio of the BMRL short-term data at 100° to that at 250°C multiplied by PNL's high temperature data. The penetration is

$$P_{AQ2} = 46.71 \times 10^{-3} t_2 \quad (4)$$

The corrosion penetration in the aqueous environment at $\leq 125^{\circ}\text{C}$ with aqueous conditions achieved at $> 125^{\circ}\text{C}$, is derived from the BMRL sequential temperature test data and PNL's high temperature data. The penetration is

$$P_{AQ3} = 12.13 \times 10^{-3} t_3 \quad (5)$$

The irradiation enhancement factor, F , is assumed to be applicable only for aqueous conditions above 125°C . At 300 yr after canister emplacement, the temperature of the canister is assumed to reach 125°C . On this basis and also according to Section 3.0, F is obtained as,

$$F = (1.75 - 0.0025 t_{aq}) \text{ for } t < 300 \text{ and } T > 125^{\circ}\text{C} \quad (6)$$

$$= 1 \quad \text{for } t \geq 300 \text{ or } T \leq 125^{\circ}\text{C}$$

According to the above approach, only P_{AQ1} will be increased by the factor F . In Equation 6, t_{aq} is the time from canister emplacement at which aqueous conditions are achieved above 125°C .

The pitting penetration, P_{pit} for the maximum pit depth as a function of time, is derived from PNL's optical metallography data of pit depths (Table V) in a fairly conservative manner. The maximum pit penetration is described as a corrosion depth beyond the uniform corrosion penetration. The penetration is obtained as,

$$P_{pit} = 0.49 t_{pit}^{0.61} \quad (7)$$

Equations for Fe9Cr1Mo

The corrosion penetration during the operational period air/steam environment is derived on the same basis as that for the low carbon steel.

$$P_{AS} = 2.76 t^{0.2} \exp(-2900/T) \quad (8)$$

As for the low carbon steel, P_{PCAS} is assumed to be half as much as P_{AS} .

$$P_{PCAS} = 1.38 t^{0.2} \exp(-2900/T) \quad (9)$$

P_{AQ1} is derived from P_{AQ1} of the low carbon steel (Equation 3) and the ratio of BWIP corrosion rate data of low carbon steel and Fe9Cr1Mo at 250°C.

$$P_{AQ1} = 1.31 \times 10^{-3} t_1 \quad (10)$$

It is assumed here that $P_{AQ2} = P_{AQ3}$ for Fe9Cr1Mo in the absence of data from sequential temperature experiments. The corrosion behavior at $\leq 125^\circ\text{C}$ is assumed to be the same with and without prior aqueous conditions at $>125^\circ\text{C}$. The ratio of BMRL data for Fe9Cr1Mo at 100°C to that measured at 250°C was

TABLE V. Optical Metallography Measurements of Pit Depths of Selected Low Carbon Steel Specimens

Test Time (Months)	Deepest Pit Depth (μm)
2	165
3	279
5	292

applied to the corrosion rate established for Fe9Cr1Mo for temperatures >125°C (P_{AQ1}) in formulating the equation for P_{AQ2} as follows:

$$P_{AQ2} = P_{AQ3} = 2.03 \times 10^{-3} t_2 \quad (11)$$

The irradiation enhancement factor, F , is assumed to be the same as that for the low carbon steel:

$$F = (1.75 - 0.0025 t_{aq}) \text{ for } t < 300 \text{ or } T > 125^\circ\text{C} \quad (12)$$

$$= 1 \quad \text{for } t \geq 300 \text{ or } T \leq 125^\circ\text{C}$$

As stated earlier, pitting is assumed to be absent in Fe9Cr1Mo. Therefore,

$$P_{pit} = 0.$$

Summary of Equations

The preliminary corrosion models are summarized for both low carbon steel and Fe9Cr1Mo by the following expressions:

If packing saturation occurs above 125°C, the total uniform corrosion penetration can be described as:

$$P_u = P_{AS} + P_{PCAS} + F \cdot P_{AQ1} + P_{AQ3} \quad (13)$$

If packing saturation occurs below 125°C, the total uniform penetration can be described as:

$$P_u = P_{AS} + P_{PCAS} + P_{AQ2} \quad (14)$$

The total penetration by corrosion can be described as:

$$P_t = P_u + P_{pit}$$

5.0 CONCLUDING REMARKS

The preliminary models discussed here are an initial attempt at describing the corrosion behavior of the reference low carbon steel and the backup material, Fe9Cr1Mo. The models and the sample calculations (Appendix A) illustrate the several underlying assumptions and the need for more detailed experimental investigations. In addition to the assumptions involved in the model, there is a fair amount of conservatism built into the uniform corrosion penetration calculations. For example, the longer-term data for aqueous corrosion above 125°C were obtained under conditions more severe than those anticipated in the repository. Although the pit depth correlation for low carbon steel is derived on a conservative basis from the available data, the measured pit depths may not be very conservative since the flow rates expected in the repository are quite slow. Thus, long-term pitting data under experimental conditions anticipated in the repository become very important in accurately describing the corrosion behavior of low carbon steel. Based on the present simplified assessment, the low alloy steel, Fe9Cr1Mo, displays excellent corrosion behavior which could lead to a considerable reduction in the required design corrosion thickness allowance. Although pitting has not been observed in this material in the short-term tests, the long-term pitting studies on the material may indicate pitting behavior that will need to be incorporated into the corrosion model.

In conclusion, the present models will be upgraded as sufficient data become available to provide a more detailed description of the functional relationship of uniform and non-uniform corrosion penetration with respect to time and temperature. Such an effort will require additional data from the experimental test program. As more data are generated, many of the

assumptions used to develop the models will not be needed and more realistic corrosion models can be developed with lower uncertainties in the predicted behavior. In addition, more refined models, describing the effects of other variables (e.g., Eh, dissolved gasses, etc.) will be developed as appropriate data are generated. The models can then be used to provide input to the preliminary and final design efforts and performance assessment analyses.

6.0 REFERENCES

- Anantatmula, R. P., Delegard, C. H., and Fish, R. L., 1983, "Corrosion Behavior of Low Carbon Steels in Grande Ronde Basalt Groundwater in the Presence of Basalt-Bentonite Packing," Proceedings of Materials Research Society Meeting, Boston, Massachusetts, November 1983.
- Anderson, W. J., 1983, "Conceptual Designs of Waste Packages for a Nuclear Repository in Basalt," SD-BWI-CDR-004, Rockwell Hanford Operations, Richland, Washington.
- Jones, T. E., 1982, "Reference Material Chemistry-Synthetic Groundwater Formulation," RHO-BW-ST-37 P, Rockwell Hanford Operations, Richland, Washington.
- Uhlig, H. H., 1948, "The Corrosion Handbook," John Wiley, New York, New York.
- Westerman, R. E., 1983a, "Elevated Temperature Corrosion of Iron-Base Alloys in Hanford Grande Ronde Groundwater," SD-BWI-TI-151, Rockwell Hanford Operations, Richland, Washington.

Westerman, R. E., 1983b, "Irradiation-Corrosion of Iron-Base Alloys in Hanford Grande Ronde Groundwater," SD-BWI-TI-140, Rockwell Hanford Operations, Richland, Washington.

APPENDIX A
SAMPLE CALCULATIONS

APPENDIX A

Sample Calculations

The following scenario was used for the purpose of the sample calculations of the corrosion behavior of canisters in an NWRB: (1) the post-closure period starts at 50 yrs after the initial emplacement of the canister in the repository, (2) water saturation of the packing material occurs at 100 yrs after emplacement, and (3) the waste contained is CHLK. Thus according to SD-BWI-CDR-004, the temperature of the canister varies from a maximum of 250°C to 185°C in the operating period air/steam environment. During the post-closure air/steam environment period the temperature of the canister drops from 185°C to -150°C, when the water saturation is assumed to occur. From the start of the hydrothermal conditions, the temperature of the canister steadily decreases from 150°C to -125°C at 300 yrs after emplacement of the canister. Based on this scenario, the penetration in mm for both low carbon steel and Fe9Cr1Mo for a 1000 yr containment can be calculated as follows:

Low Carbon Steel. For the first 50 yr there is an air/steam environment. The penetration is given by Equation (1). This equation can be integrated for times from 0 to 50 yr and temperatures from canister emplacement to the time of repository sealing. The exponential term in temperature, upon integration, yields a power series, which can only be solved more precisely by means of a computer. Therefore, for purposes of the sample calculation, a constant temperature of 250°C is assumed throughout the 50 year period to simplify the calculation as well as retain the conservatism in the calculation. Then the penetration during the first phase, $P_{AS} = 2.30$ mm.

During the second phase, the environment is air/steam under post-closure conditions for 50 years. Assuming a constant temperature of 185°C, similar to Phase I, the penetration during this period, from Equation 2, is,

$$P_{PCAS} = 0.52 \text{ mm}$$

At the start of the third phase, hydrothermal conditions are achieved with canister temperature at >125°C. Since gamma radiation is present, Equation 3 in combination with Equation 6 is used to yield:

$$F \cdot P_{AQ1} = 1.51 \text{ mm}$$

The fourth and final phase also presents hydrothermal conditions with $T \leq 125^\circ\text{C}$ for 700 yr to complete a 1000 yr containment period. The penetration during this phase is:

$$P_{AQ3} = 8.49 \text{ mm}$$

Therefore, the total uniform corrosion penetration for a 1000 yr containment for the conditions described in this sample calculation for low carbon steel is,

$$P_U = 12.82 \text{ mm}$$

For the present sample calculation, a hydrothermal environment exists for a period of 900 yr during the 1000 yr containment, which translates into a maximum pit depth for low carbon steel (Equation 7) of

$$P_{\text{pit}} = 31.07 \text{ mm}$$

This maximum pit depth of 31.07 mm is expected to be localized and can be easily accommodated within the reference waste package design structural thickness allowance for CHLW of 41 mm.

Ee9Cr1Mo. Utilizing the same simplifying assumption of constant temperatures of 250°C and 185°C during Phase I and Phase II respectively as for low carbon steel, the penetration is obtained from Equations 8 and 9 as:

$$P_{\text{AS}} = 0.02 \text{ mm}$$

and

$$P_{\text{PCAS}} = 0.01 \text{ mm}$$

With the initiation of hydrothermal conditions and the presence of gamma radiation, the penetration during the third phase from equations 10 and 12 is:

$$F.P_{\text{AQ1}} = 0.39 \text{ mm}$$

The penetration during the fourth and final phase is

$$P_{AQ2} = P_{AQ3} = 1.42 \text{ mm}$$

With the assumption of no incidence of pitting during the containment period, the total corrosion penetration is

$$P_u = 1.84 \text{ mm}$$

The total penetration for Fe9Cr1Mo is, therefore, a factor of 7 lower than the uniform corrosion penetration for the low carbon steel. This leads to a substantial reduction in required canister thickness with a consequent decrease in canister cost for Fe9Cr1Mo.