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CORROSION BEHAVIOR OF CARBON STEELS UNDER TUFF REPOSITORY ENVIRONMENTAL CONDITIONS

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ABSTRACT

Carbon steels may be used for borehole liners in a potential high-level nuclear waste repository in tuff in Nevada. Borehole liners are needed to facilitate emplacement of the waste packages and to facilitate retrieval of the packages, if required. Corrosion rates of low carbon structural steels AISI 1020 and ASTM A-36 were determined in J-13 well water and in saturated steam at 100°C. Tests were conducted in air-sparged J-13 water to attain more oxidizing conditions representative of irradiated aqueous environments. A limited number of irradiation corrosion and stress corrosion tests were performed. Chromium-molybdenum alloy steels and cast irons were also tested. These materials showed lower general corrosion but were susceptible to stress corrosion cracking when welded.

INTRODUCTION

This paper is concerned with the corrosion behavior of carbon steels and other ferrous metals under environmental conditions representative of a high-level waste repository in tuff. Lawrence Livermore National Laboratory (LLNL) is responsible for high-level nuclear waste package development as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. This project is part of the Department of Energy's Civilian Radioactive Waste Management (CRWM) Program, and is investigating the suitability of tuffaceous rocks at Yucca Mountain in Nye County, Nevada for high-level nuclear waste disposal. The waste package effort at LLNL is developing multi-barriered packages for safe, permanent disposal in a repository such as the one being considered at Yucca Mountain.

While the NNWSI project focuses on austenitic stainless steel as the containment materials for the conceptual design of high-level nuclear waste packages, carbon steel is of interest as the principal candidate material for borehole liners. Selection of candidate materials for the waste package canister and for borehole liners have been previously discussed [1]. The borehole liner is needed to facilitate emplacement of the waste package, and if required, to facilitate the retrievability of the waste package. Waste packages may be emplaced horizontally or vertically in the repository. In horizontal emplacement designs, multiple waste packages units are spaced along a horizontally mined borehole between parallel drifts. Horizontal borehole lengths of several hundred feet are proposed. Other repository designs call for vertical emplacement of single waste packages in boreholes mined along a drift floor. Vertical boreholes would be lined for the top several feet. Borehole liner thicknesses on the order of 1.25 cm are under consideration for both the horizontal and vertical emplacement conceptual designs. The retrievability period is 50 years after package emplacement. Therefore, the integrity of the liner material during this 50-year period is the reason for this investigation of corrosion rates and corrosion attack modes.

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LINER ENVIRONMENT

The reference horizon for a repository proposed for Yucca Mountain is about 150 meters above the static water level. Heat generated from the waste packages after emplacement converts moisture in the near-package environment to steam. Air and steam are the dominant environmental species during the retrievability period. Episodic intrusion of water into the package environment could occur through downward percolation of precipitation along rock fractures. The low annual precipitation in the Nevada desert should minimize the amount of possible water intrusion. Further, fractures in the rock below the repository should permit drainage from the package environment and minimize the time during which the borehole liner surface is in contact with an aqueous phase. A thermal analysis of several different waste package designs in both horizontal and vertical emplacement arrangements is available [2].

Because the corrosion rate of carbon steels is highest under wet conditions, the experimental program emphasizes these conditions since they are more limiting in establishing the minimum service length for a given grade of steel. As alternative materials to the carbon steel, different grades of cast irons and chromium-molybdenum alloy steels were tested; these materials often show greater corrosion resistance than carbon steels in aqueous environments, particularly when the environment is oxidizing. Representative water in the repository location is oxidizing. Water from near-by J-13 well is considered representative of vadose water which has percolated through the welded tuff layers in Yucca Mountain and has been conditioned by contact with this rock. The principal minerals present in the welded tuff layers are quartz, cristoballite, and alkali feldspar.

The corrosion tests reported in this paper were conducted in J-13 well water and, in some cases, in the vapor phase above this water. With regard to the corrosion behavior of the different metals tested, the significant chemical species present in J-13 well water are: dissolved oxygen (5-6 ppm); nitrate ion (5-10 ppm); chloride ion (6-8 ppm); fluoride ion (2-3 ppm); bicarbonate ion (110-130 ppm); sulfate ion (20-30 ppm); and sodium ion (40-50 ppm). The pH of the well water is between 7.1 and 7.5.

OUTLINE OF CORROSION TEST PROGRAM

In addition to the general corrosion rates of different candidate borehole liner materials, the resistance of these materials to localized and stress-assisted forms of corrosion is also an issue as these forms of corrosion could drastically shorten the service life of the liner. A severely pitted or cracked liner could hinder retrievability of the nuclear waste package.

The data reported in this paper were obtained over an approximate two-year period. When some of the tests were started, different conceptual designs were being pursued for the waste package and liner. For instance, at one point a self-shielded canister concept was pursued in which the nuclear waste would be contained in a thick cast iron canister (on the order of 30 cm thick) [3]. The present conceptual designs consider a much thinner canister section (on the order of 1 cm thick) of a more corrosion resistant austenitic stainless steel. Carbon steel or other iron-base material would be used as a borehole liner around the stainless steel canister. Some of the materials (for example, gray cast iron) whose corrosion resistance was investigated as possible self-shielded canister materials would probably not be suitable for fabricating long borehole liners. However, all of the available test results are reported here, because the effects of the different alloying constituents are instructive in understanding the corrosion behavior of this general class of materials.

Five different tests are discussed in this report: 1. A weight loss test to determine the general and localized corrosion rates of carbon steel and other Fe-base materials in J-13 water at different temperatures. The J-13 water was "conditioned" by contact with crushed tuff rock and air sparged to saturate the water with oxygen. 2. An electrochemical polarization test of the same alloys as the above to determine the corrosion potentials and currents as a function of temperature. 3. A general and localized corrosion test of unstressed specimens of carbon steels and other Fe-base materials exposed to J-13 water and saturated steam at 100°C. The purpose of this experiment was to discern the differences in corrosion rates and corrosion attack modes in the two different phases. 4. A bent-beam stress corrosion susceptibility test of welded specimens of 1020 carbon steel, nodular cast iron, and 9 Cr - 1 Mo alloy steel in 90°C J-13 water. Comparison between the stress corrosion susceptibilities of the welded zone, heat-affected zone and base metal is possible with this particular stress configuration. 5. Corrosion tests of specimens exposed to irradiated J-13 water in a gamma radiation facility were performed to determine the effect of radiation on corrosion rates.

MATERIALS TESTED

The actual chemical analyses of the different materials tested are presented in Tables I and II.

Table I Composition of Coupons Used in Weight Loss Corrosion Tests

	<u>Gray Cast Iron</u>	<u>A-36</u>	<u>1020</u>	<u>2 1/2 Cr-1 Mo</u>	<u>9 Cr-1Mo</u>
Si	2.68	0.03	--	0.27	0.71
Mo	--	--	--	0.94	0.96
Fe	bal	bal	bal	bal	bal
Cr	--	--	--	2.36	8.27
C	3.26	0.22	0.18	0.12	0.13
Mn	0.72	0.46	0.35	0.56	0.48
P	0.038	0.008	0.040	0.016	--
S	0.059	0.009	0.025	0.012	0.010

Table II Composition of Weld Plate and Weld Rod Used to Fabricate Bent Beam Stress Corrosion Specimens

	<u>1020 Plate</u>	<u>E7018 Rod</u>	<u>9Cr-1Mo Plate</u>	<u>502-18 Rod</u>	<u>Nod.Fe Plate</u>	<u>Ni-Rod 55 Rod</u>
Si	0.08	0.40	0.71	0.05	2.98	1.27
Ni	0.05	0.03	0.057	0.08	0.25	59.48
Cu	0.03	--	0.11	--	0.05	2.95
Mo	0.09	0.01	0.96	0.62	0.01	--
Fe	bal	bal	bal	bal	bal	bal
Cr	0.07	<0.01	8.27	4.96	0.01	0.10
Al	0.03	--	0.009	--	--	--
C	0.22	0.03	0.13	0.06	3.30	0.78
Mn	0.50	0.67	0.48	0.44	0.17	0.81
P	0.027	0.014	--	0.020	0.027	0.007
S	--	0.015	0.010	0.019	0.011	0.002

Blank space means not determined.

CORROSION TEST RESULTS

1. Weight Loss Tests in J-13 Water

The weight loss experienced by the coupons of carbon steel, cast iron, or alloy steel was determined by ASTM G-1 and G-31 test procedures at periodic intervals. The coupons were also examined for any evidence of localized attack, and the depth of localized attack was determined by a focusing microscope (ASTM G-46). Slotted Teflon washers were used as fasteners to hold the coupons to fiberglass mounting sticks. The slotted washers intentionally created a creviced area on the coupon so that localized corrosion attack would preferentially occur in this area. Nearly all of the materials tested showed some preferential crevice attack; many also showed some localized attack on the "bold" area of the coupon as well. Attack on the bold area outside the creviced area is termed "pitting attack" in this discussion. The "pitting" attack rate and the "crevice" attack rate are expressed on an annualized basis to make a direct comparison of the localized attack to the general attack. The ratio of pitting corrosion rate to general corrosion rate and the crevice corrosion rate to the general corrosion rate are called the "pit factor" and "crevice factor", respectively.

Table III summarizes the results from coupon tests of carbon steel, alloy steel and cast iron in 50-100°C J-13 water. These solutions were intentionally air-sparged to create highly oxidic conditions and establish a high but credible corrosion penetration rate for the different materials. These results represent the average of three replicate coupons for each alloy at each test temperature. The coupons were exposed for 1500 hours. 1020 carbon steel showed consistently the highest corrosion rates of the materials tested, while the 9 Cr - 1 Mo alloy steel exhibited corrosion rates which were considerably less than those for the other alloys. Maximum corrosion rates were attained at 70°C or 80°C with the rate decreasing at higher temperatures because of the decrease in oxygen solubility in the water. Localized corrosion observations on these exposed coupons are summarized in Table III.

The results indicate that while the 9 Cr-1 Mo alloy steel shows a low general corrosion rate in the J-13 water, the alloy is moderately susceptible to localized attack particularly in crevices. The localized susceptibility is highest at 70 and 80°C and lowest at 100°C. The lower localized corrosion susceptibility may be due to the lower solubility of oxygen at the higher temperatures and smaller differences between the concentration of O₂ in the crevice and that on the bold surface. This alloy steel appears to take on the characteristics of a "stainless steel" in the J-13 water with respect to its general corrosion, but the amount of alloying Cr and Mo is insufficient to confer a high degree of localized corrosion resistance. The O₂ contents were determined in the water at the different temperatures: 50°C (6.65 ppm O₂); 70°C (5.60 ppm); 80°C (4.50 ppm); 90°C (3.30 ppm); and 100°C (2.25 ppm).

2. Electrochemical Polarization Tests

As an analogue to the weight loss coupon tests, the corrosion rates of the different steels were determined by electrochemical methods. The linear polarization resistance method was used to determine the corrosion currents [4]. These results are summarized in Table IV. These results were obtained from single specimens of each material. Corrosion potentials were measured against a saturated calomel electrode (SCE). The corrosion potentials for the 9 Cr - 1 Mo alloy steel are substantially more anodic than those of the other materials tested. This observation is in agreement with the nearly stainless character of this alloy. The corrosion rates given in Table IV are in good agreement with the rates determined from the weight loss (Table III).

Table III General and Localized Corrosion Rates of Steels
in J-13 Water at Different Temperatures

Temp. (°C)	General Corrosion Rate (µm/yr)	Pitting Corrosion Rate (µm/yr)	Pitting Factor	Crevice Corrosion Rate (µm/yr)	Crevice Factor
<u>1020 Carbon Steel</u>					
50	401	380	0.95	413	1.03
70	505	1018	2.02	359	0.71
80	531	465	0.88	472	0.89
90	414	1046	2.52	563	1.36
100	320	1018	3.18	635	1.98
<u>Gray Cast Iron</u>					
50	359	203	0.57	98.2	0.42
70	422	392	0.94	138	0.43
90	357	79.6	0.22	305	0.35
90	323	27.9	0.09	14.6	0.05
100	318	0.0	0.00	232	0.69
<u>2-1/4 Cr - 1 Mo Alloy Steel</u>					
50	316	649	2.07	946	2.97
70	469	1448	3.07	1100	2.33
80	376	1089	2.90	1415	3.63
90	370	868	1.83	800	2.17
100	278	1352	4.87	781	4.50
<u>9 Cr - 1 Mo Alloy Steel</u>					
50	21.2	42.3	1.83	202	14.6
70	21.2	152	7.47	450	22.5
90	14.1	246	17.4	319	23.1
90	8.3	0.0	0.00	84.7	10.1
100	6.8	0.0	0.00	33.0	8.10

Table IV Corrosion Potentials and Currents of Steels in J-13 Water.

Material	Temp. (°C)	Corrosion Potential (mV, vs SCE)	Corrosion Current (µA/cm ²)	Corrosion Rate (µm/yr)
Gray Cast Iron	50	-593	32.8	366
	70	-582	21.0	233
	80	-595	28.5	318
	90	-584	40.4	452
1020 Steel	50	-691	81.2	856
	70	-690	50.1	559
	80	-691	75.2	841
	90	-678	67.0	749
2 1/4 Cr - 1 Mo Alloy Steel	50	-600	25.5	285
	70	-380	2.1	22.9
	80	-568	10.4	117
	90	-368	2.1	22.9
9 Cr - 1 Mo Alloy Steel	50	-318	2.4	27.9
	70	-381	3.6	40.6
	80	-380	4.7	53.3
	90	-335	1.8	20.3

3. Corrosion Coupon Tests in Water and Steam

Corrosion rates measured after 5000 hours of exposure to boiling J-13 water and to the saturated steam above the water are presented in Table V. These tests followed the same procedures as those reported in section 1 (weight loss tests in J-13 water). The data in Table V show that the corrosion rates are lower for the metals exposed in the vapor phase than in the liquid.

Table V Corrosion Rates of Steel Coupons Exposed 5000 Hours to J-13 Water and Steam at 100°C

Material	Corrosion Rate in Water ($\mu\text{m}/\text{yr}$)	Corrosion Rate in Steam ($\mu\text{m}/\text{yr}$)
1020 Steel	26.8	12.5
A-36 Steel	30.2	9.74
9 Cr - 1 Mo	0.70	-0.55 (wt. gain)

After 5000 hours, the maximum localized corrosion rates expressed in $\mu\text{m}/\text{yr}$ were: 1020 Steel (262 in the water and 185 in the steam); A-36 Steel (152 in water and 159 in steam). Both the general corrosion penetration rates and the localized corrosion rates decreased with an increase in exposure time. For example: after 3000 hours the general corrosion rate of the 1020 carbon steel was 41.6 $\mu\text{m}/\text{yr}$ in the water and 20.3 $\mu\text{m}/\text{yr}$ in the steam; while the maximum localized rates were 260 $\mu\text{m}/\text{yr}$ in the water and 331 $\mu\text{m}/\text{yr}$ in the steam. These tests are continuing to accumulate longer exposure periods.

4. Stress Corrosion Test Results

Specimens were prepared from welded 1/4-inch plates of the ferrous alloys. The compositions of the plate and weld rod are given in the blocks in Table II. These are the standard AWS filler materials recommended for these plate materials. The differences in alloy composition between plate and rod should be noted. A J-groove was machined into the plate stock, and the weld was made in one pass with a 1/8-inch shielded metal electrode. All welding of the 1020 steel was done at ambient temperature, but some of the nodular cast iron and the alloy steel plates were pre-heated to 150 or 200°C. After welding, the plates were machined to cross sections between 0.060 to 0.125 inch to provide defect-free weld areas. Nine bent beam specimens were machined from each welded plate. The bent beam specimens were loaded in a four-point fixture and then stressed to 90% of their respective yield strengths (ASTM G-39).

The stressed specimens were emplaced in 90°C J-13 water and inspected after 500 hours and in 1000-hr increments after that. The first sign of cracking occurred on two specimens of 9 Cr - 1 Mo which failed after 3500 hours of testing. Table VI gives a summary of the results from the bent beam specimen tests after 9000 hours of exposure. None of the 1020 carbon steel specimens have failed to date. It is suggested that a hydrogen embrittlement mechanism is responsible for the failures of the nodular cast iron and Cr-Mo alloy steel specimens. The compositional differences between the base and weld metal create microstructural differences. The fracture morphology of the cast iron and alloy steel specimens was similar in that both are intergranular and occurred in the weld metal. Galvanic differences between the weld and the base metal develop and the weld acts as a cathode to the base metal. This explanation was confirmed in a laboratory determination of the actual potential on the weld and on the base metal. Further, the weld metal was entirely martensitic; the high internal stress in martensite renders it more susceptible to hydrogen embrittlement. These tests are continuing.

Table VI Stress Corrosion Test Results on Bent Beam Specimens
Exposed to 90°C J-13 Water. 9000 Hours of Exposure.

Nodular Cast Iron	1 out of 9 specimens failed
9 Cr - 1 Mo	6 out of 9 specimens failed
1020 Steel	no specimens failed

5. Irradiation Corrosion Tests

A limited number of corrosion tests have been performed at 105°C in irradiated aerated J-13 water on 1025 wrought steel and on 9 Cr - 1 Mo alloy steel. Crushed tuff rock was placed in the test vessel so that some specimens were "embedded" in the rock + water "phase". These results are given in Table VII. These tests were performed in the gamma radiation facility at Pacific Northwest Laboratory. The calculated gamma dose rate was 3×10^5 rads/hr. The values given in Table VII are the averages of 6 or 7 coupons in each location. The corrosion rates in this irradiated environment are higher for both the carbon steel and the alloy steel than in a comparable non-irradiated environment (Table V at 100°C). This increase is undoubtedly due to the production of oxygen, hydrogen peroxide, and other oxidizing species by radiolysis of the water.

Table VII Corrosion of Steels in Irradiated J-13 Water at 105°C.
Exposure Period of 3 Months, Gamma Dose Rate of 3×10^5 rads/hr.

Material	"Phase"	Corrosion Rate ($\mu\text{m}/\text{yr}$)
1025 Wrought Steel	Water	36
	Water + Rock	45
9 Cr - 1 Mo	Water	15
	Water + Rock	21

CONCLUSIONS AND FUTURE WORK

The work indicates that AISI 1020-1025 or ASTM A-36 carbon steel should not suffer excessive corrosion in the tuff repository environmental conditions tested so far. These conditions include J-13 well water in the temperature range 50-100°C, saturated steam at 100°C, and irradiated J-13 water at 105°C. When the solutions are intentionally air sparged, the corrosion rate increases with the increase in oxygen content of the solution. The maximum corrosion rate occurs at 70-80°C, where the flux of oxygen to the steel surface is maximum. The maximum is determined by the increase in diffusion rate of oxygen with increasing temperature, and the decrease in oxygen solubility with increasing temperature. Carbon steels also appear to be resistant to stress corrosion in the modes so far tested. Some localized corrosion occurs, with the localized corrosion factor usually on the order of 1-3 times the general corrosion rate. The localized (crevice) corrosion rate can be as high as 15 times the general corrosion rate in wet steam conditions. A 1.25 cm thick borehole liner fabricated from carbon steel could attain a service life of more than 50 years according to projections of these data if continuously wet conditions do not dominate the environment. The anticipated environmental conditions at the Yucca Mountain repository are "dry" because of the low water percolation rate to the repository horizon. The test conditions used here were immersion of specimens in water and exposure to wet steaming conditions in order to give an upper limit. Additional testing time is needed to

substantiate these first results and projections. Possible galvanic effects between a carbon steel liner and a stainless steel canister needs to be addressed.

While the 9 Cr - 1 Mo alloy steel exhibits a lower corrosion rate than carbon steel, the high susceptibility of this material to hydrogen embrittlement (a form of stress corrosion cracking) in the welded condition makes it unsuitable for further consideration. While a post-weld heat treatment could temper the martensite and reduce the susceptibility, this extra operation in the installation of a liner would be impractical and costly. Perhaps, a low-carbon, high-alloy steel could combine the best features of corrosion resistance with better welding characteristics.

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