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Irradiation-Corrosion of Iron-Base Alloys in Hanford Grande Ronde Groundwater

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Abstract

The corrosion behavior of four iron-base alloys was investigated in a gamma radiation field (~3×10^5 rad/hr) to time exposures of up to 13 months. Synthetic Grande Ronde groundwater was pumped through a bed of crushed basalt in the bottom of an autoclave operating at 250°C prior to contacting the specimens. All alloys exhibited acceptably low uniform corrosion rates. The highest steady-state rate observed was 11μm/yr (0.43 mil/yr) based on linear corrosion kinetics. A cast steel containing chromium and molybdenum generally exhibited the greatest resistance to corrosion.

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IRRADIATION-CORROSION OF IRON-BASE ALLOYS IN HANFORD GRANDE RONDE GROUNDWATER

Submitted to

Basalt Waste Isolation Project
Rockwell Hanford Operations

by
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July 1983

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BACKGROUND

The Structural Barriers Materials Study being performed at Battelle-Northwest for the Basalt Waste Isolation Project (BWIP) has as its objective the characterization and recommendation of metallic materials that have the ability to contribute to the long-term (to 1000 years) waste-containment function of high-level nuclear waste packages. During this period of time the canister materials will be exposed to elevated-temperature groundwaters that have been modified by irradiation emanating from the waste contained within the packages. An empirical determination of the effects of irradiation on the corrosion processes is necessary, as it is difficult to predict the effects of radiolysis on metal corrosion rates a priori. The gamma irradiation intensity used in the present study (~3 x 10^5 rad/hr) is considered to be conservatively high, compared with that expected from spent-fuel waste packages; and the test temperature of 250°C is higher than that expected over the major part of the required container lifetime. These assumed overstress conditions provide data that should allow conservative estimates of corrosion behavior for canister materials development purposes. Also, the potential corrosion-mitigating effect of a packing material has not been taken into account in the present studies.

The investigation of general (uniform) corrosion has been emphasized in the series of tests reported herein. Stress-corrosion-cracking, crevice corrosion, and weldment corrosion have not yet been specifically addressed under irradiated test conditions but are the focus of future studies.

EXPERIMENTAL

All of the irradiation-corrosion studies were performed using a refreshed autoclave system installed in a ^{60}Co radiation facility. The synthetic Grande Ronde groundwater was pumped to the autoclave at ~35 ml/hr from a storage reservoir continuously sparged with an Ar-20% O_2 mixture. The water containing 6-8 ppm O_2, entered the autoclave at the bottom and flowed upward through a bed of crushed basalt rock 3-5 cm (1-2 in.) deep prior to contacting the specimens. The effluent from the autoclave was not recycled. The system was held at 250°C for all tests. An Inconel 600 autoclave was used in the tests. The oxygen concentration and groundwater flow rate in these tests are much higher than anticipated in the repository and are expected to result in higher corrosion rates than actual canisters would experience in a nuclear waste repository.

At the conclusion of the desired exposure, selected specimens were removed from the autoclave and stripped of their surface films by means of light abrasion and immersion in formaldehyde-inhibited HCl. Specimens were generally not reinserted after stripping, though it was occasionally done. Stripped specimens did not appear to corrode at a rate appreciably different from specimens that had not undergone a stripping operation. The results presented here represent exposure periods of up to 13 months; exposure times will be extended to 17 months before termination of the test.

A more detailed description of the experimental procedure has been published elsewhere[1].

MATERIALS

Early screening studies[2] revealed the possibility of using relatively inexpensive iron-base alloys under the conditions expected in a repository constructed in a basalt formation, and subsequent studies have tended to support the early findings[1]. To date, a total of four iron-base materials have been tested: a cast ductile iron, a 2 1/2% Cr, 1% Mo cast steel; a 1025 cast steel; and a 1020 wrought steel. The compositions of the materials are presented in Table 1.

Each of the first three materials listed were tested in the as-cast condition. The specimens of cast ferrous material were obtained from castings each weighing ~160 kg (350 lb) with a minimum dimension of 130 mm (5.0 in.). Specimens were cut so that an edge would lie on the surface of the casting. The 1020 wrought steel was supplied in the form of hot-rolled, de-scaled sheet nominally 1.5 mm (0.060 in.) thick.

The ductile cast iron is representative of a large group of cast irons with good impact and low ductility properties relative to the still-cheaper gray irons. The low-alloy cast steels are more expensive than the cast irons but have superior mechanical properties. The low level of chromium/molybdenum in one of the cast steels represents an attempt to learn what beneficial effects, if any, such modest alloy additions might have on the corrosion resistance of cast ferrous materials.

Prior to corrosion testing, the cast steel specimens were ground with an aluminum oxide wheel to produce a surface finish of 32 to 63 μm rms. The same wheel produced a surface finish of 8 μm rms on the ductile iron specimens. The wrought steel sheet was surface ground with a 50-grit disc prior to corrosion testing.

The approximate composition of the basalt rock[3] and the Hanford Grande Ronde (basalt) groundwater[4] used in the study are given in Tables 2 and 3. The basalt was obtained from a surface outcrop of the Umtanum Flow, Grande Ronde formation, near the Hanford Site. The groundwater was made up to simulate the water contained in flow tops in the Grande Ronde basalts.

RESULTS AND DISCUSSION

The corrosion rates of the four candidate iron-base materials have been determined in 250°C synthetic Grande Ronde groundwater at an irradiation intensity of ~3×10^5 rad/hr. The rates obtained are plotted in Figure 1, based on a linear-kinetics interpretation. Presently available data obtained from nonirradiated tests performed in the same environment are included in the form of a shaded band for comparison. The irradiation-corrosion data presented in Figure 1 represent individual corrosion specimens. These are tabulated in Table 4. The corrosion rates show an increase in progressing from the one-month test duration to the three-month exposure. The ductile iron sample showing the highest corrosion rate at three months exposure exhibited nonuniform corrosion, which was not apparent in the other samples. The attack consisted of a mass of closely-spaced, shallow pits, covering about two-thirds of one sample surface. The six-month corrosion-rate data are somewhat higher than those of the nonirradiated system, but they are much lower than the three-month irradiated system rates. Between the one-month and three-month data analysis points, the autoclave operated in the vapor phase for several days, apparently because of a reduced back pressure and slightly elevated temperature. It is possible that this operational anomaly had a bearing on the increased corrosion rates measured at three-months. Also, the three-month specimens selected for penetration determinations were

TABLE 1. Composition of Iron-Base Alloys

Material	Element, wt %						
	C	Mn	Si	P	S	Mo	Cr
2 1/2% Cr, 1% Mo Cast Steel	0.116	0.57	0.57	0.020	0.004	1.02	2.46
1025 Cast Steel (ASTM A-27, Grade 60-30)	0.240	0.60	0.49	0.012	0.018	-	-
Ductile Cast Iron (ASTM A536-77, Grade 60-40-18)	3.53	0.31	2.51	0.05	0.004	-	-
1020 Wrought Steel	0.19	0.36	-	0.029	0.043	-	-

TABLE 2. Composition of Umtanum Flow Basalt(3)

Constituent	wt%
SiO_2	54.9
Al_2O_3	14.3
FeO	13.2
CaO	7.2
MgO	3.4
Na_2O	2.6
TiO_2	2.2
K_2O	1.6
P_2O_5	0.4
MnO	0.2

TABLE 3. Composition of Hanford Grande Ronde (Basalt) Groundwater(4)

Chemical Species	Concentration, mg/l
Na^+	250
K^+	1.9
Ca^{+2}	1.3
Mg^{+2}	0.40
CO^{-2}	27
HCO_3^-	70
OH^-	1.4
$H_3SiO_4^-$	103
Cl^-	148
SO_4^{-2}	108
F^-	37

pH = 9.8–10

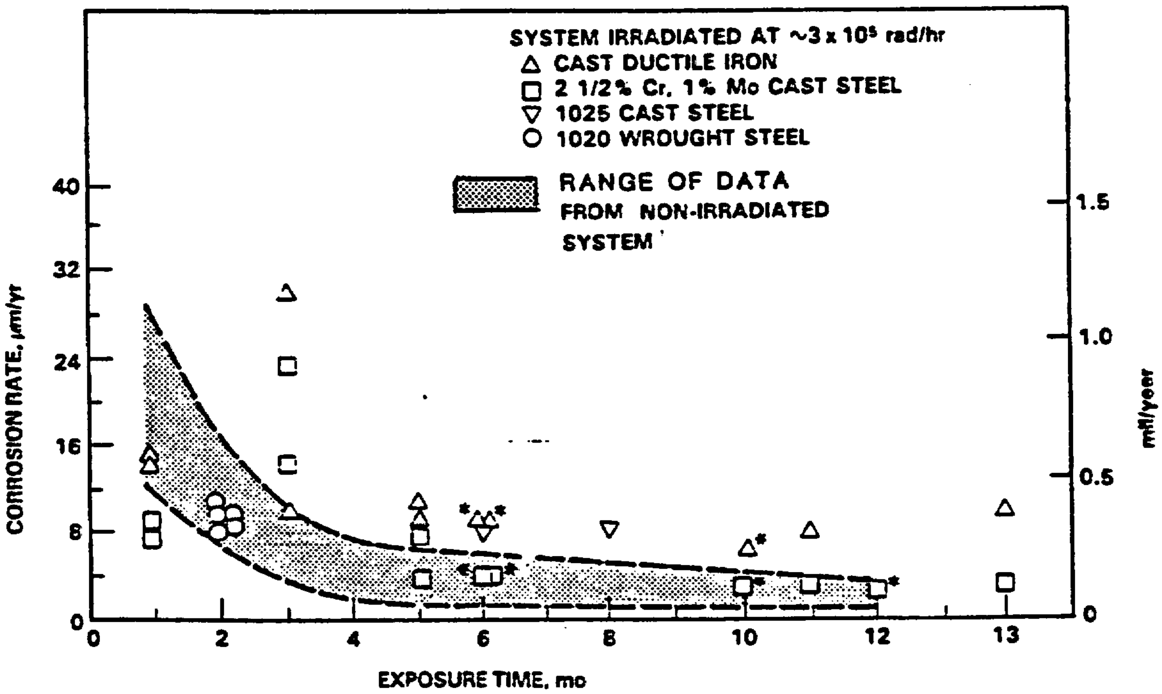

FIGURE 1. Corrosion of Iron-Base Alloys Exposed to Synthetic Hanford Grande Ronde Basalt Groundwater at 250°C and ^{60}Co γ Irradiation Intensity of ~3 x 10^5 rad/hr. Asterisks Signify Specimens Stripped Once Prior to Exposure Shown.

TABLE 4. Summary of Iron-Base Alloy Irradiation-Corrosion Data

Hanford Grande Ronde Basalt Groundwater
250°C, ~ 3 x 10^5 rad/hr

Material	Exposure Time, mo.	Penetration, µm/yr (mils/yr)	Remarks
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)	Previously stripped
	10	6.4 (0.25)	Previously stripped
	11	9.1 (0.36)	
	13	9.7 (0.38)	
2 1/2% 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)	Previously stripped
	10	3.8 (0.15)	Previously stripped
	11	3.3 (0.13)	
	12	2.8 (0.11)	Previously stripped
	13	3.0 (0.12)	
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)	

taken from a region of the specimen holder where the most serious apparent corrosion, was visually detected, namely, the region near the inlet, whereas the other specimens were taken from positions uniformly spaced along the holder. In general, the position of a specimen was not found to exert a significant effect on its measured corrosion, other than at the three-month sampling point.

After three months, the rates appear to have become approximately constant with time, with the maximum rate observed being 11 μm/yr (0.43 mil/yr). As has been frequently observed in past studies, the Cr-containing steel corrodes at a rate that is generally less than the mild steels and cast irons. The corrosion rates observed under irradiation conditions are generally 2-3 times higher than those obtained on similar materials under non-irradiated conditions as shown in Figure 1.

Aside from the pitting attack already noted at three months on a cast ductile iron specimen, little non-uniform attack has been observed in the tests. The cast iron samples have routinely exhibited a surface roughness, attributed to an expected galvanic attack between the cathodic graphite nodules and the matrix; and the 2 1/2% Cr, 1% Mo steel specimens began to show light, isolated pitting at the 13-month exposure time. The cast steel specimen at 8 months exposure shows about one-fifth of one surface lightly marred by intergranular attack, and there are signs of crevice corrosion effects on all samples where they contact the specimen support rack. Conclusions cannot be drawn at the present time with regard to anticipated non-uniform attack of canisters fabricated from these iron-base alloys, as expected conditions at the canister surface include contact with a basalt-bentonite packing mixture and a much lower oxygen concentration, than was present in these experiments.

The film on the surface of a specimen of ductile iron removed from the irradiation-corrosion test after a one-month exposure consisted entirely of nontronite, $(Fe, Al)Si_2O_5(OH).nH_2O$. After the three-month exposure, X-ray diffraction analysis of a ductile iron specimen revealed large amounts of analcime, $NaAlSi_2O_6.H_2O$, and hematite, Fe_2O_3.[a] No nontronite was present. A specimen of 2 1/2% Cr, 1% Mo steel, examined after 3 months of exposure, also showed evidence of analcime and hematite.[a] Also, some areas of the specimen were covered only with a film of magnetite, Fe_3O_4. Again, no nontronite was present. After five months exposure, the ductile iron showed the presence of acmite, $NaFe(SiO_3)_2$, along with nontronite; no magnetite was observed. The 2 1/2% Cr, 1% Mo alloy, on the other hand, showed weak indication of both acmite and magnetite; no nontronite was present. No systematic corrosion-product pattern is yet emerging in these studies. Further surface analyses are planned at the conclusion of the test (October 1983).

The relatively high corrosion rates found at the third month of exposure prompted a statement of concern[1] regarding the use of iron-base alloys in irradiated basaltic groundwaters. Subsequent testing has mitigated these concerns somewhat; however, the occurence of significant non-uniform attack is an ever-present possibility. Continued long-term testing under a variety of temperature, radiation, and environmental conditions (such as presence of packing material) will be necessary to assure the continued uniformity of

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

attack. If non-uniform corrosion is found to occur under certain testing conditions, it does not necessarily signify the need to reject that particular material, as the pit depth may remain constant with time once a maximum depth is attained. These aspects of the corrosion problem remain to be defined in future tests, along with corrosion of weldments, crevice corrosion, and stress corrosion cracking.

CONCLUSIONS

- Iron-base alloys exhibited a general corrosion rate a factor of 2-3 higher when exposed to 250°C synthetic Grande Ronde groundwter in the presence of ^{60}Co (γ) irradiation of ~3×10^5 rad/hr than when the radiation is absent. The four iron-base alloys tested corroded at similar rates, i.e., they differed at most by a factor of ~2. The cast steel containing chromium and molybdenum generally exhibited the greatest resistance to corrosion.

- The highest steady-state corrosion rate (beyond three-month exposure times) observed in the present study was 11 μm/yr (0.43 mil/yr). Thus, barring possible corrosion-accelerating factors (such as might be brought about by lower temperatures, thick surface films, etc.) and the occurence of aggressive non-uniform attack, stress corrosion cracking, or unusual corrosion susceptibility of weldments, iron-base alloys appear to exhibit acceptably low corrosion rates under conditions expected to be conservatively severe relative to anticipated waste package environments in a nuclear waste repository constructed in basalt. Additional irradiation-corrosion testing is required to more fully characterize the effects of gamma radiation under conditions anticipated in a repository constructed in basalt.

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