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ABSTRACT

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Short-term experiments which studied the effect of gamma radiation on the waste package components of a basaltic repository were completed. Experimental parameters were similar to those expected during the saturated post-closure period of the repository, i.e., a temperature of 200°C and a hydrostatic pressure ≥70 bar. The waste package components included low carbon steel pressure vessels, GR4, CH4, basalt or packing, and low carbon steel coupons.

It was found that gamma radiation at a dose rate of 104 rad/hr for a duration of one and two months increased the H₂ yield in all tests. Increases in the organic carbon yield, the sulfate ion concentration, and the corrosion rate of the coupon were observed in some of the tests. These latter results varied with the combination of waste package components included in the tests. Evidence for the quench effect was observed in tests which included basalt.

INTRODUCTION

The Basalt Waste Isolation Project's (BWIP) function is to investigate the suitability of Hanford basalts as a site for a high-level nuclear waste repository. The emplacement of nuclear waste containers increases the temperature of the waste package environment and subjects the repository environment as well as the components of the waste package to ionizing radiation. The primary type of ionizing radiation, outside the container, during the saturated post-closure period (defined below) is gamma radiation. Much of BWIP's effort has, therefore, been directed towards studying the effects of gamma radiation on the waste package components in a hydrothermal, basaltic environment. Some of the questions which are currently being addressed are:

1. What is the effect of repository conditions on the yield of primary radiolytic species?
2. What effect will gamma radiation and hydrothermal conditions have on CH₄ which has been found in some sections of the proposed repository?
3. What are the long-term effects of gamma radiation on the environment of the waste package? Specifically, is there a radiolytic enhancement of container corrosion?

These questions have been examined previously but have not been answered completely.

Much work has been reported on the radiolysis products of gamma irradiated water [1,2]. However, much of this work was done with "pure" water. Little is known about the radiolysis of aqueous systems containing primarily Cl⁻, and possibly CH₄, in a complex geochemical hydrothermal environment.

The effects of irradiating basalt groundwater that contains methane has also been investigated previously [3,4]. The primary effect reported has been the formation of high molecular weight polymers. However, in these experiments, the pressure was achieved with a CH₄ atmosphere and the dose rate was relatively high. This work also showed that the addition of

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other waste package components would alter the results [3,4]. For instance, it was found that sodium bentonite inhibited the production of polymers. Another interesting result reported was that polymer formation occurred in irradiation tests of groundwater, low carbon steel, and CH₄ but that corrosion rather than polymerization predominated when basalt was added to the tests.

Previous work concerned with corrosion in irradiation tests found that gamma radiation increases the corrosion rate of soft iron in NaCl solutions by large factors [5]. On the other hand, it has also been reported that corrosion of low carbon steel in basalt groundwater is inhibited in the presence of basalt/bentonite packing in hydrothermal experiments [6].

The experiments proposed below will measure the effects of irradiating groundwater containing limited amounts of CH₄ at a dose rate $\leq 10^4$ rad/hr. It is important to identify the synergistic relationship between the various components of the waste package. The matrix of experiments described below add the waste package components one by one to irradiation experiments in an effort to identify the interactions between the waste package components. The matrix was designed so that it should be possible to establish the effect of irradiation on (1) the yield of the primary radiolytic species, H₂, (2) the extent of polymer formation when CH₄ is present, and (3) the corrosion rate of mild steel.

This paper is primarily concerned with the above issues during the saturated post-closure period of the repository. This is the time period which begins at full saturation of the repository and ends at the time of container failure. The parameters which characterize the saturated post-closure period are temperatures in the range of 60-200°C, hydrostatic pressures ca 90 bar, a reducing redox environment, a pH of 7-9, and dissolved gas concentrations of 0-1100 ppm CH₄, 25-75 ppm N₂, 0-6 ppm O₂, and trace levels of H₂. It is expected that the gamma dose rate during this time period will be < 120 rad/hr.

It is important when studying material interactions expected in the repository to replicate as many of these parameters as possible. For the initial experiments the temperature was set at 200°C, the hydrostatic pressure was 270 bar, and the dose rate was 10 krad/hr. The experiments were divided into sets, each set was defined by its composition of waste package components. The waste package components are GR4, a synthetic basaltic groundwater, basalt or packing (75% basalt, 25% sodium bentonite), low carbon steel (LCS) in the form of coupons (A27 cast sheets), and low carbon steel pressure vessels (SA36). Methane was also included in some experiments. The four sets of experiments were as follows.

Set I: GR4, LCS coupon and vessel

Set II: GR4, LCS coupon and vessel, 270 ppm CH₄

Set III: GR4, LCS coupon and vessel, 270 ppm CH₄, and basalt

Set IV: GR4, LCS coupon and vessel, 270 ppm CH₄, and packing

Each set consisted of three separate tests--two tests were irradiated and were duplicates, the third test was a blank, i.e., it was subjected only to hydrothermal conditions. The tests are being run for various durations, from one to six months. When this initial matrix is completed, the dose rate will be lowered to 1 krad/hr and finally to 0.1 krad/hr so that the effects of dose rate and total dose can be determined. When these tests are completed, the effects of variations in temperature, pressure, and methane concentration will be examined.

EXPERIMENTAL

The test vessels are Parr General Purpose Autoclaves, Model #4751. The vessels were fabricated of SA36 low carbon steel and had an approximate volume of 27 cc. SA36 was chosen as the material for the test

vessels because low carbon steel is currently the material of choice for the waste package container. Another advantage of using SA36* for the vessels is that there is less potential for contaminating the system. Each vessel was irradiated at a dose rate of 10 krad for 24 hours before use. The GR4 was made according to BWIP's standard formulation [7]. The low carbon steel coupons were cut to size from A27** cast carbon steel sheets. They were polished using a 600 grit abrasive, cleaned and weighed. The basalt used in Set III tests was crushed, wet sieved, and air dried, -1/2 to +1/4 fraction size, reference Cohassette Entablature Basalt, RCE-4 unwashed. The packing used in Set IV tests was 75% basalt crushed, wet sieved, and air dried, two equal quantities of two fraction sizes -16 to +60 and -120 to +230 reference Cohassette Entablature Basalt, RCE-4, unwashed and 25% sodium bentonite, ca 400 mesh provided by Baroid Industries. For each gram of packing 0.237 g of GR4 was added. The LCS coupon and the basalt or the packing were inserted into the test vessel at room temperature. The vessels were then evacuated and flushed several times with argon or methane to assure that there were no impurities, such as O₂. Methane was added after the last evacuation for those tests that required methane, otherwise the vessels were left evacuated. The vessels were then placed in an oven and connected to the water transfer line as shown in Fig. 1. A temperature compensated pressure transducer was also connected to the manifold in order to measure the hydrostatic pressure within the vessels. The internal temperature of the vessels was also monitored. This was accomplished by placing a similar vessel containing a thermocouple into the oven with the vessels to be loaded. The oven's temperature was then adjusted to 200°C and monitored with a thermometer. The next step was the evacuation of the water transfer line and the high pressure reservoir. The high pressure reservoir is Parr's High Pressure Autoclave, Model #4651. It was heated separately from the oven using a bench top heater and temperature controller. The high pressure reservoir was connected to an Enerpak Hand Pump, Model #11-100. The reservoir on the hand pump was filled with GR4 which was sparged with either argon or methane to remove all dissolved gases from the GR4. After being sparged for a minimum of 30 minutes, the GR4 was transferred from the hand pump's reservoir to the high pressure autoclave.

The temperature controller for the high pressure autoclave was activated. When the temperatures of the vessels in the oven and the GR4 groundwater in the high pressure autoclave were ~200°C, the GR4 was transferred from the high pressure reservoir to the vessels via the hand pump. When the pressure in the vessels was approximately 150 bar, the vessels were closed and removed from the water transfer line. It is known from preliminary experiments that there is a loss in the initial pressure of about 50% as the system equilibrates. After loading, the vessels were transferred using a heated insulated container that maintained the vessels' temperature between 190-200°C, either to another oven maintained at 200°C for the hydrothermal tests or to a specially modified oven placed in the gamma field (also maintained at 200°C) for the irradiation-hydrothermal tests. This step assured that the experiments maintained their integrity as repository-relevant tests.

At the conclusion of the test, the test vessels that were in the gamma facility were transferred to the hydrothermal test oven using a heated insulated container as above. The vessels were held in the hydrothermal test oven at 200°C until they were sampled. Sampling was done at

*Composition of SA36 as supplied by the vendor is: 0.18% C, 0.72% Mn, 0.009% P, 0.019% S, 0.20% Si, 0.16% Cu, 0.09% Ni, 0.17% Cr, 0.04% Mo, 0.014% Sn, 0.004% Nb, 0.002% V, with the balance Fe.

**Composition of A27 is 0.209% C, 0.66% Mn, 0.019% P, 0.015% S, and 0.50% Si.

Figure 1. Schematic of Water Transfer Line to Autoclaves

two different temperatures--185-200°C and room temperature. Previous hydrothermal studies of basalt-GR4 systems [8] indicated that solution composition and pH depend on the temperature of the sampled liquid. It was important to know if these changes, known as the quenching effect, would also be seen in irradiation/hydrothermal tests.

These earlier hydrothermal studies used Dixon autoclaves which facilitated sampling at the temperature and pressure of the test. This type of equipment is not readily adaptable to gamma irradiation experiments nor is it practical for batch type tests. In order to sample the test vessel at the temperature of the test, an alternate method was devised. This procedure was based on one developed previously [9]. The test vessel was removed from the oven and immediately placed in an insulated, heated container. The vessel was then connected to the sampling apparatus which consisted of a micrometering valve and a plastic syringe.

Sampling was generally completed within seven minutes with the gas and liquid samples collected simultaneously. Approximately 5 mL of solution were obtained.

The solution collected at 185°C and the autoclave were allowed to cool to room temperature. The gas sample was immediately analyzed with a Varian 330 Gas Chromatograph.

The autoclave was opened after it reached room temperature. The liquid was removed with a pipette and placed in a small polyethylene bottle. Each test, therefore, has two liquid samples--one from a sample obtained at the elevated temperature and the other obtained at room temperature.

Approximately 2 mL of each of these solutions was used to measure pH. Since preliminary experiments showed that the pH measurement did not affect the Cl^- concentration, the solution used to measure pH was also used for the anion analysis. A small aliquot from each sampling was used for the total carbon and total organic carbon measurements. The remainder of the solution was filtered (if necessary) and acidified with Ultrex HNO_3 and used for the cation analysis. The pH for both types of liquid samples was measured at room temperature. Organic and inorganic/purgeable carbon was measured for some of the tests where sufficient solution was available. F^- , Cl^- , SO_4^{2-} , and NO_3^- were determined using a Dionex Ion Chromatograph. It was not possible to determine NO_2^- because of potential interferences with the Cl^- . The cations were determined using inductively coupled plasma (ICP) spectroscopy.

After removal of the liquid, the other test components were removed from the vessel. The coupons were dried and stored in a non-reactive atmosphere. If particles of packing material adhered to the coupons, they were removed using an established BWIP procedure [10]. From each set of tests there were three coupons--two (one from the hydrothermal test and one from the irradiation test) were used to measure the corrosion rate and the remaining one was examined using surface analytical techniques such as scanning electron microscopy, x-ray energy dispersive spectroscopy, and x-ray diffraction. The two coupons used in the corrosion studies were cleaned after the test using 1.7M HCl inhibited by 0.26 wt % formaldehyde. Weight loss was measured according to procedures approved by BWIP [10].

RESULTS AND DISCUSSION

The data are presented in Tables I and II. A comparison of a given result can be made within a set to determine the effect of radiation and between sets to determine the effect of a different combination of waste package components. The effect of time can also be seen for some of the tests.

Effect of Gamma Radiation on the Gaseous Components

The results of the GC analyses are summarized in the gas analysis sections of Tables I and II. There was a pronounced effect of gamma irradiation on the amount of H₂ produced. The yield of H₂ is reported in two ways: (1) the amount of H₂ detected in the volume of the sample loop of the GC, and (2) an estimate of the total volume of H₂ collected. The latter is reported as an estimate because there is an uncertainty of about 10% in the measurement for the total volume of gas collected. For the Set I tests containing GR4, the yield of H₂ was ten times larger for the irradiated test than for the non-irradiated test. Set II tests included GR4 and CH₄, and the H₂ yield in the irradiated test was about 18 times larger. Set III tests included GR4, CH₄, and basalt, and the H₂ yield was about 12 times larger in the irradiated tests. The absolute value of the H₂ yield in the Set III tests was about 50% of the yield in the Set II tests. There are two possible explanations. One is the smaller volume of water and the other is the presence of the basalt. Additional testing is required to determine the predominant cause of the lower H₂ yield. The Set IV tests substituted packing for the basalt. The ratio of the yield in the irradiated tests vs. the non-irradiated test was about 220. This ratio was large because the amount of H₂ produced in the non-irradiated test was much smaller than in the other non-irradiated tests, while the yield of H₂ in the irradiated tests was comparable to that in the Set II tests.

Most of the methane was unreacted. The gas chromatograph showed that methane, when included in the test, was the largest constituent. The Set I tests also showed a very small peak due to either CO or CH₄. The CH₄ could be formed from the decarburization of the low carbon steel. A comparison of the one-month and two-month tests showed that there was an approximate doubling of the H₂ yield in the two-month tests.

Effect of Gamma Radiation on Solution Chemistry

The liquid phase was sampled at the test temperature and at room temperature. The pH, organic and inorganic/purgeable organic carbon measurements, and anion and cation analyses were made when possible on both samplings. Insufficient solution precluded some of the measurements.

Table I
Radiation Effects on Systems Typical of a BWTP Repository
(Irradiation Time, One Month)

Test	GR4	Set I			Set II			Set III			Set IV		
		1	2	3	4	5	6	7	8	9	10	11	12
Duration		31 days			31 days			31 days			31 days		
Radiation Dose (Mrad)		0	7.4	7.4	0	7.4	7.4	0	7.4	7.4	0	7.4	7.4
Components		LCS Coupon GR4			LCS Coupon GR4, CH ₄			LCS Coupon GR4, CH ₄ Basalt Rock-to-Water Ratio - 1 to 2			LCS Coupon GR4, CH ₄ Packing Packing-to-Water Ratio - 1 to 10		
GAS ANALYSES													
Moles of H ₂ Detected in 0.25 g of Sample x 10 ³		0.48	3.8		0.25	4.5		0.11	1.5	1.3	0.018	3.9	4.3
Estimated Total Number of Moles of H ₂ x 10 ³		4	38		10	180		5	72	57	0.09	160	170
$\frac{\text{H}_2}{\text{H}_2}$ (Irradiation Test Hydrothermal Test)			10	-		18	-		14	12		213	230
LIQUID ANALYSES*													
Anions (ppm)**													
Cl ⁻	419	538	450	578	387	477	448	421	411	439	424	436	424
F ⁻	20	26	23	30	14	27	29	14	14	20	17	20	28
SO ₄ ²⁻	4	9	7	9	8	6	7	18	35	55	97	144	119
Cations (ppm)***													
Na	344	480	418	488	376	385	397	267	267	274	393	386	387
K	14	17	15	18	14	14	14	93	98	93	62	60	57
Ca	2	<1	<1	<1	<1	<1	<1	8	9	8	5	5	4
Si	41	50	47	50	38	39	43	232	224	236	173	188	221
Fe	-	1	<1	2	4	4	4	<1	21	4	6	2	2
Al	-	<1	<1	<1	<1	<1	<1	<1	4	<1	3	1	4
Mg	-	<1	<1	<1	<1	<1	<1	<1	3	1	2	<1	<1

* The two solutions were mixed for cation and anion analyses for comparison with previous work.

** Accuracy is ±5% for anion analyses. NO₃⁻ in all samples is less than 1 ppm.

*** Accuracy is ±3-10% for cation analyses.

Table I (Cont'd)

LIQUID ANALYSES

	GR4	Set I			Set II			Set III			Set IV		
		1	2	3	4	5	6	7	8	9	10	11	12
pH, 185-200°C Sampling		8.42	8.40	-	8.89	8.35	8.09	7.02	6.80	6.65	7.41	7.26	7.36
pH, 25°C Sampling	9.6	11.32	11.05	11.52	9.98	10.49	10.52	8.34	8.54	8.27	8.71	8.72	8.54
Organic Carbon (ppm) 185-200°C Sampling		6.0	3.5	-	14.4	(31)*	(21)*	10.3	14.7	10.0	14.5	15.5	12.8
Organic Carbon (ppm) 25°C Sampling	0.5	5.3	3.8	3.8	10.7	(30)*	(18)*	9.1	13.0	11.8	-	19.1	-
Inorganic/Purgeable Carbon (ppm) 185-200°C Sampling		33.0	35.8	-	47.0	45.7	40.0	15.6	11.4	13.4	47.7	37.4	37.5
Inorganic/Purgeable Carbon (ppm) 25°C Sampling	18.7	11.6	14.2	13.2	27.3	20.9	38.1	6.4	5.4	2.3	-	36.8	-
Total Carbon (ppm) 185-200°C Sampling		39.0	39.3	-	61.4	(77)*	(61)*	25.9	26.1	23.4	62.2	52.9	51.3
Total Carbon (ppm) 25°C Sampling		16.9	18.0	17.0	38.0	(51)*	(56)*	15.5	18.4	14.1	58.5	55.8	44.4

ANALYSES OF LOW CARBON STEEL COUPON**

Components	GR4			GR4, CH ₄			GR4, CH ₄ , Basalt			GR4, CH ₄ , Packing			
Constituents of Reacted Surface	Fe, Cl, Si, Na			Fe, Cl, Si			Si, Fe			Si, Al, Mg, Ca, Fe			
Weight Charge After Test, Before Cleaning	0.00006	0.00005	0.00006	0.00011	0.00002	0.00001	0.00501	0.00596	0.00978	0.00138	0.00175	0.00147	
Weight Loss of Coupon (g)	0.00144	0.00151		0.00182	0.00181		0.00414		0.00670	0.00036			0.00076
% Weight Loss	0.038	0.045		0.044	0.043		0.10		0.16	0.011			0.018

* Filter may have added 10 ppm organic carbon. Accuracy is $\pm 5\%$ for carbon analyses.

** Duration of cleaning procedure was approximately the same for all coupons.

Table II
Radiation Effects on Systems Typical of a BWIP Repository (Irradiation Time, Two Months)

Test	Set I			Set II			Set III			
	13	14	15	16	17	18	19	20	21	
Duration	62 days			62 days			62 days			
Radiation Dose (Mrad)	0			0			0			
Components	LCS Coupon GR4			LCS Coupon GR4, CH ₄			LCS Coupon GR4, CH ₄ Basalt Rock-to-Water Ratio - 1 to 2			
GAS ANALYSES										
H ₂ (Irradiation Test)										
H ₂ (Hydrothermal Test)							14	18	≤39	≤43
Moles of H ₂ Detected in 0.25 cc of Sample x 10 ⁷	-	5.7	7.4	0.5	7.0	8.8	(0.08)*	2.3	2.6	
Estimated Total Number of Moles of H ₂ x 10 ⁷		57	59	24	340	400	(3)*	110	120	
LIQUID ANALYSES										
High Temperature Sampling										
Anions										
Cl	-	301	318	418**	339	326	355	339	341	
F	-	20	20	22	24	22	13	12	14	
SO ₄	-	5	5	9	5	5	18	44	39	
Cations										
Na	-	299	289	471	342	322	233	220	216	
K	-	10	11	18	11	11.6	103	93	92	
Ca	-	0.3	0.5	<0.2	0.2	0.4	1.2	1.9	1.7	
Si	-	32	33	42	34	25	305	247	251	
Fe	-	0.6	0.4	1.9	0.6	0.6	0.7	0.9	1.0	
Room Temperature Sampling										
Anions										
Cl	-	422	422	409**	439	446	413	454	484	
F	-	25	23	25	25	23	16	14	16	
SO ₄	-	6	7	6	5	6	19	57	54	
Cations										
Na	-	424	424	396	410	418	280	310	308	
K	-	15.7	15.7	15.2	15.2	15.6	95.5	108	103	
Ca	-	0.2	0.1	<0.05	0.1	0.3	4.9	6.6	6.0	
Si	-	42.1	43.7	41.0	41.2	41.0	165	149	186	
Fe	-	0.1	0.2	0.9	0.1	0.1	0.1	0.1	0.2	

*Packing on micrometering valve failed during sampling.

**Solution also contained between 12-15 ppm PO₄.

Table II (Cont'd)

		Set I			Set II			Set III		
	GR4	13	14	15	16	17	18	19	20	21
LIQUID ANALYSES										
pH, 185-200°C Sampling			7.78	7.94	8.97	8.44	8.60	7.08	6.98	7.17
pH, 25°C Sampling	9.6		10.76	10.78	10.11	10.34	10.55	8.54	8.39	8.75
Organic Carbon (ppm) 185-200°C Sampling			5.7	5.3	10.7	32.2	24.7	15.5	20.5	21.0
Organic Carbon (ppm) 25°C Sampling	0.5		3.9	3.8	7.9	42.2	34.4	13.7	18.5	21.2
Inorganic/Purgeable Carbon (ppm) 185-200°C Sampling			35.4	36.9	35.9	37.5	45.4	22.2	22.6	20.2
Inorganic/Purgeable Carbon (ppm) 25°C Sampling	18.7		18.2	16.5	21.1	14.1	24.6	6.2	2.3	2.1
Total Carbon (ppm) 185-200°C Sampling			41.1	42.2	46.6	69.7	70.1	37.7	43.1	41.2
Total Carbon (ppm) 25°C Sampling	19.2		22.1	20.3	29.1	56.3	59	19.9	20.8	23.3
ANALYSES OF LOW CARBON STEEL COUPON										
		Set I			Set II			Set III		
Test		13	14	15	16	17	18	19	20	21
Components	GR4				GR4, CH4			GR4, CH4, Basalt		
% Weight Loss					0.062		0.067	0.16	0.22	

All analyses were made at ambient temperature, and the results are shown in the liquid analyses section of Tables I and II. Gamma radiation had only a minimal effect on solution chemistry.

The pH values for the high temperature sampling were consistently lower than the values for the room temperature sampling. Of particular interest was the value for the pH for the Set III tests containing basalt. The average value for the high temperature sampling using the one- and two-month results was 7.0. A pH value of 8.3 was measured by Moore et al. in their hydrothermal experiments using basalt and synthetic groundwater [8]. Their experiments were somewhat different in that the reaction was carried out in Dickson autoclaves with a gold sample cell. Further studies should elucidate what effect the vessel's composition has on pH, if any.

The organic carbon content was measured for both samplings of the liquid phase. The effect of gamma radiation was not significant except in the Set II tests containing GR4 and CH₄. There was a two- to four-fold increase in organic carbon content in the irradiated, Set II, two-month tests compared to the corresponding non-irradiated test. Gamma radiolysis of aqueous methane has been studied previously [11]. Possible reactions include the following:

It would be expected then that the addition of methane and its subsequent irradiation would increase the organic content by increasing the yield of higher, more soluble, hydrocarbon homologs and their derivatives. No milky white precipitate was observed in any of the test solutions so polymerization reactions were not extensive. The data for the Set II, one-month tests, were not conclusive (the irradiated solutions were filtered with Millex GS filters which may have added 7-10 ppm carbon). Data for the basalt-containing tests were also inconclusive with respect to the effect of gamma radiation. In both the one- and two-month tests, the values for organic carbon content were similar for both the irradiated and the non-irradiated tests.

The inorganic/purgeable organic carbon measurements are also included in Tables I and II. It was not possible to separately measure the two components because of insufficient solution. Generally, there was little, if any, effect of irradiation on the inorganic/purgeable organic carbon content. There was also no significant increase in tests which included CH₄ compared to those which did not. For these reasons, it would seem that the inorganic/purgeable organic carbon is primarily a measurement of inorganic carbon. Another anomalous feature of these results was the lower value for the tests which contained basalt. A possible explanation is that small amounts of O₂ were added to the vessel during the loading procedure. Under the hydrothermal conditions of the tests, the O₂ reacted with the carbon in the steel forming CO₂. For the tests which contained the basalt, the O₂ was either not present or was consumed preferentially by the ferrous ion in the basalt. This is being studied further.

The results of the anion and cation analyses for the two-month tests for the high temperature and the room temperature samplings are shown in Table II. The Set III tests containing basalt showed a radiation effect as well as evidence of the quench effect. The SO₄⁻² concentration was significantly higher in the irradiated tests than in the non-irradiated test. The cation analysis for the high temperature sampling showed a decrease in sodium concentration and an increase in silica concentration.

These changes in the solution composition were accompanied by the lowering of the pH. Both phenomena have been seen previously in hydrothermal tests and are collectively referred to as the quench effect [8,12]. It was reported that when the basalt/GR4 system was subjected to hydrothermal conditions (temperatures of 100, 200, and 300°C and a hydrostatic pressure of 300 bar) sodium concentration fell while the concentrations of silica, potassium, aluminum, fluoride, and sulfate increased. Changes in fluoride concentration were not observed in the Set III tests herein and insufficient solution precluded the analysis for aluminum.

Effect of Gamma Radiation on the LSC Coupon

The results of the low carbon steel coupon analyses are shown in Tables I and II. The effect of gamma radiation depended on which waste package components were included in the test. Irradiation increased the % weight loss by 60% for the one-month Sets III (GR4, CH₄, basalt) and IV (GR4, CH₄, packing) tests, by 20% for the one-month Set I tests (GR4), and negligibly for the one-month Set II tests (GR4, CH₄). Irradiation increased the % weight loss by approximately 40% for the two-month Set III tests and by 8% for the two-month Set II tests.

The absolute value of the % weight loss also depended on the composition of the test. It was particularly low for the one-month packing tests. The smaller % weight loss is probably attributable to the strongly adherent character of the clay-rich layer that was deposited on the coupon. This has been seen previously [6].

The remaining coupons from each set were examined visually. The four coupons were very different in appearance. This is shown in Fig. 2. These coupons were then examined using scanning electron microscopy and energy dispersive x-ray spectroscopy. The micrographs for the coupons are shown in Figs. 3, 4, 5, and 6 for Sets I, II, III, and IV respectively. The primary constituents on the altered surface of the coupons were Fe, Cl, Si, and Na in Set I; Fe, Cl, and Si in Set II; Si in Set III; and Si, Al, Mg, Ca, and Fe in Set IV. The nature of these products is being further examined using x-ray diffraction techniques.

CONCLUSIONS

The effects of gamma radiation on the components of the waste package have been obtained for the following conditions: T = 200°C, P ≥ 70 bars hydrostatic, total dose = 7.4 and 15 Mrad, low carbon steel pressure vessels. The gamma radiation affected the gas, liquid, and solid (low carbon steel coupon) phases of the various tests.

The composition of the gas phase was altered by the irradiation. The H₂ yield increased by factors of 10 to 200. The amount of increase varied with the components of the test. The two mechanisms which contributed to the production of H₂ were the radiolysis of water and CH₄.

The liquid phase was not as sensitive to gamma radiation. The only change observed in the two-month irradiated tests was an increase in SO₄²⁻ concentration for tests containing basalt. The other changes observed in the solution chemistry were changes in pH and solution composition. These were controlled primarily by the components of the test, (i.e., whether or not basalt or packing were present), by hydrothermal conditions and by the sampling temperature. The effect of adding CH₄ to GR4 and irradiating the test solution was to increase the organic carbon concentration from about 8 ppm (non-irradiated) to about 33 ppm. This is believed to be due to the formation of more soluble higher hydrocarbon homologs and possibly alcohol, etc., from the various radiolysis reactions of CH₄ and ground-water. The effect of the addition of CH₄ to tests containing GR4 and

SET I
Test Components
GR4 LCS coupon

SET II
Test Components
GR4 LCS coupon CH₄

SET III
Test Components
GR4 LCS coupon
CH₃ basalt

SET IV
Test Components
GR4 LCS coupon
CH₃ packing

Figure 2. Photographs of Corrosion Coupons from Irradiation Tests

Figure 3. Photomicrograph of Corrosion Coupon from Irradiation Test with GR4 Water and Coupon

Figure 4. Photomicrograph of Corrosion Coupon from Irradiation Test with GR4 Water, Coupon, and CH₄.

Figure 5. Photomicrograph of Corrosion Coupon from Irradiation Test with GR4 Water, Coupon, CH₄, and Basalt

Figure 6. Photomicrograph of Corrosion Coupon from Irradiation Test with GR4 Water, Coupon, CH₄, and Packing Material

basalt or packing was not as decisive as above. There was only a slight increase in organic carbon content, but the increase was similar in both the irradiated and non-irradiated tests.

Radiation increased the corrosion rate of the low carbon steel coupon significantly in tests which contained basalt or packing, and to a lesser extent in tests which contained only GR4 or GR4 and CH₄.

Longer term tests have been initiated. These should clarify and strengthen many of the observations, but it is readily apparent that radiation at dose rates of 10^4 rad/hr alters the gas, liquid, and solid phases in tests which contain various combinations of waste package components.

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