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November 1983

Walter J. Gray

Prepared for Rockwell Hanford Operations,
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Walter J. Gray
Pacific Northwest Laboratory
P. O. Box 999
Richland, Washington

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Rockwell International

Rockwell Hanford Operations
Energy Systems Group
P.O. Box 800
Richland, Washington 99352

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GAMMA RADIOLYSIS EFFECTS ON GRANDE RONDE BASALT GROUNDWATER

W.J. GRAY
Pacific Northwest Laboratory, P. O. Box 999, Richland, WA 99352

ABSTRACT

Gamma radiolysis of reference Grande Ronde Basalt groundwater containing 700 mg/L methane produces a milky liquid that is a suspension of fine particles of organic polymers similar to polyethylene. The amount and nature of these polymers does not vary much over the range of conditions tested. Differences in the radiolytic products that are formed may occur when host rock and engineered-barrier materials are present. This possibility is currently being investigated as is the potential for interactions between radionuclides and the products of radiolysis.

INTRODUCTION

Basalt formations within the Hanford Site, in the state of Washington, are being considered as possible geologic host media for disposal of high-level radioactive waste. The effects of alpha and gamma radiation on groundwater present within the basalt are being investigated by the Basalt Waste Isolation Project (BWIP) as part of an overall program to design and evaluate nuclear waste packages. Groundwater within the several candidate basaltic horizons has been found to contain methane in concentrations up to 700 mg/L. Early results from a study of gamma radiolysis effects on a synthetic formulation of reference Grande Ronde Basalt groundwater are presented in this paper.

BACKGROUND

Alpha and gamma irradiation of pure water or dilute aqueous solutions results principally in the generation of the following free radical, ionic, and molecular products [1]:

$$H_2,\ H,\ e^-_{aq},\ H^+,\ H_2O_2,\ OH,\ HO_2$$

These so-called primary products interact with themselves and with other species present in solution to yield secondary products. For example, the radiolysis of pure water produces only a very small equilibrium H_2 concentration because of the rapid back reaction,

$$H_2 + OH \rightarrow H_2O + H$$

If so-called scavenger ions such as Cl^- are present, they compete with H_2 for the OH radical, thereby raising the concentration of H_2 in solution and increasing its pressure in the gas phase. The presence of Cl^- also leads to the secondary products Cl_2^-, ClO^-, ClO_2^-, ClO_3^-, and ClO_4^-. The presence of organic compounds considerably complicates the picture. Methane, for example, will give rise to the methyl radical which then can react with itself and other species within the water to yield a large variety of higher-molecular-weight organic compounds.

EXPERIMENTAL

The water used in these tests was a synthetic solution made up to simulate groundwater found within Grande Ronde Basalt located within the Hanford Site. It was made up according to a recipe developed by Jones [2] and its composition is listed in Table I. Besides the components listed, Grande Ronde Basalt groundwater has been found to contain the following gases: 25 mg/L N_2, 10 mg/L Ar, and up to 700 mg/L CH_4 at 25°C. To achieve these concentrations in the irradiation tests, the solutions were sparged with argon to remove dissolved air. Then, the irradiation vessels were pressurized with 0.14 MPa N_2 and 3.30 MPa CH_4 at 25°C (the exact concentration of argon was considered unimportant because it is inert). Gas concentrations in solution changed slightly, of course, as both the temperature and pressure increased to the irradiation test conditions. Total gas pressure was recorded daily during irradiation by means of a stainless steel capillary tube that extended from the stainless steel vessel out of the irradiation facility to a pressure transducer. The ratio of liquid volume to gas plenum volume in all irradiations was about 4 to 1. Roughly 75% of the gas volume was in the high-intensity gamma radiation field with most of the remainder located outside the field in the pressure transducer.

Irradiations were conducted in a ^{60}Co facility at dose rates and total doses given in Table II. The stainless steel irradiation vessels were lined with quartz to prevent contact between the liquid and the steel. After irradiation, gas compositions were analyzed with a mass spectrometer. The solid polymeric species were analyzed using Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR), as well as for total polymer mass, molecular weight distribution, and elemental fractions of carbon, hydrogen, and oxygen.

TABLE I. Composition of synthetic Grande Ronde Basalt groundwater.

Component	Concentration mg/L
Si	35.5
Na	358
Ca	2.8
K	3.4
F	33.4
Cl	312
$SO_4^=$	173
$CO_3^=$ (as HCO_3^-)	100
pH	9.8

RESULTS

A summary of most of the post-irradiation test results are shown in Table II and Figures 1 and 2. Additional details that describe the gas and liquid phases separately follow.

TABLE II. Irradiation conditions and post-irradiation properties of samples.

Test No.	1	2	3	4	5	6
Solution[a]	BGW	DIW	BGW	BGW	BGW	BGW/Fe[b]
Irradiation Temperature (°C)	65	65	65	150	150	150
Dose Rate (MR/hr)	1.1	1.1	1.1	1.1	5.3	5.3
Total Dose (MR)	340	340	77	77	380	380
Gas Composition (vol%)						
Hydrogen	26	46	6.1	9.9	24	22
Methane	66	45	86	85	70	70
Nitrogen	5.4	5.5	5.5	5.1	4.2	4.8
Argon	2.9	3.8	2.7	0.38[c]	1.8	2.6
Mass 44	0.20	0.16	0.40	0.45	0.079	0.16
2,2-Dimethylpropane	0.054	0.14	0.034	0.52	0.30	0.62
2,2-Dimethylbutane	0.022	0.020	0.017	0.21	0.075	0.12
Solids Analysis						
Mass (g/L)	4.4	3.0	2.0	2.4	2.1	2.2
Molecular wt (no av.)	NA[d]	640	630	710	1,040	1,090
Molecular wt (wt av.)	NA	1,850	1,550	2,410	2,960	2,930
Carbon (wt%)	--[e]	84	--	--	86	86
Hydrogen (wt%)	--	13	--	--	12	12
Oxygen (wt%)	--	2.9	--	--	1.0	1.2
Solution pH	9.6	6.8	9.6	9.6	9.5	9.3

[a] BGW = basalt groundwater. DIW = deionized water. All solutions were sparged with argon and then equilibrated with 0.14 MPa N_2 and 3.30 MPa CH_4 at 25°C.

[b] This was a duplicate of Test 5 except that iron coupons with a surface area of 20 cm^2 were placed in the liquid whose volume was 60 mL.

[c] The argon concentration was low because of a leak that developed during the initial pressurization with methane.

[d] NA = Not analyzed.

[e] Results did not sum to 100% and, therefore, are not reported.

Gas Phase Results

Table II lists gas phase compositions; total gas pressure increased no more than 1% during irradiation. Oxygen is not listed as a gas component in Table II nor was it detected in any of the samples. Mass 44 is not identified in Table II. It can be partially attributed to CO_2 from carbonate in the groundwater in most cases, but it probably also has some contribution from propane and perhaps other organic compounds.

Liquid Phase Results

Figure 1 is a photograph of the liquids from Test 1 together with that from a preliminary test that had no methane. The test with methane was very milky in appearance--a result that was typical of Tests 1 to 4. Their color was slightly yellow in all cases rather than perfectly white as implied by the picture. The milky substance could be separated from the water using 0.1 μm filters, and the resulting filtrates were perfectly clear. Total carbon analysis of the filtrate in Test 1 gave an organic carbon concentration of approximately 39 mg/L and an inorganic carbon concentration of approximately 16 mg/L; the original carbon concentration (all inorganic) was 20 mg/L. These values are to be compared with solids concentrations of 4.4 g/L. Thus, it is clear that almost all of the organic carbon was retained on the filter. Inductively conducted plasma (ICP) spectroscopy and ion chromatography (IC) analysis of the filtrate showed that inorganic ions were present in about their initial concentrations. Few if any, therefore, were retained on the filter along with the organic substance.

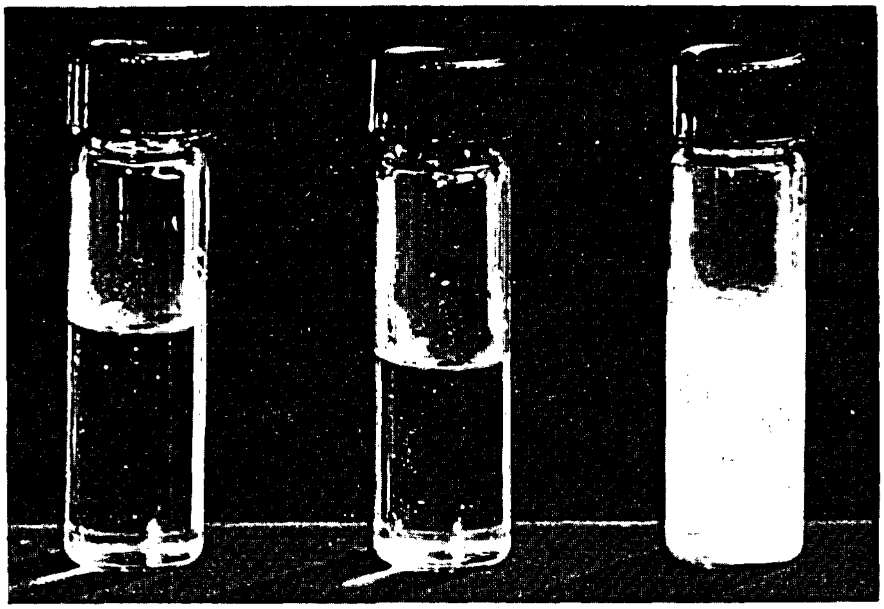

FIG. 1. Comparison of irradiated groundwater with and without methane.

The solid material in the liquid phases of Tests 5 and 6 coagulated into only a few clumps that were a brownish-yellow color. This is probably attributable to the higher dose rate used in these tests. Total carbon analyses of the liquids from Tests 5 and 6 showed that almost all the organic carbon was retained by a 1 μm filter; it was not necessary to use 0.1 μm filters as in the other tests.

Molecular weight distributions were determined by gel permeation chromatography [3]. Two types of averages are given in Table II, one based on the total number of molecules and the other based on total weight. Figure 2 shows the entire distributions based on weight. The results for Tests 5 and 6 were so close together that they are represented by one curve. Uncertainties in the absolute values of molecular weights are conservatively estimated to be in the range of 10% to 50%; smaller uncertainties apply to differences observed between samples, so the small differences shown in Figure 2 are probably real.

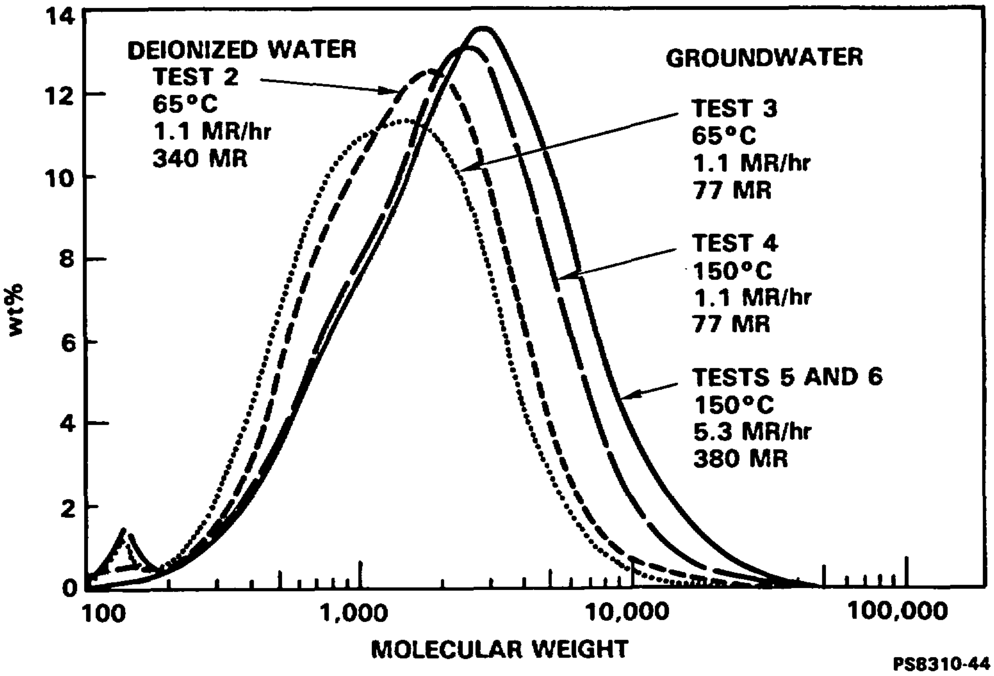

FIG. 2. Molecular weight distribution of polymers generated by gamma radiolysis of water containing methane.

Nuclear magnetic resonance analysis of solids from Test 1 showed that it was primarily a saturated hydrocarbon. None of the other samples were analyzed by NMR. The infrared spectra of the solids from Tests 1 to 4 were similar to published spectra for slightly oxidized specimens from a polyethylene/polypropylene mixture [4]. The position of the oxygen peak (5.8 μm) is indicative of a carbonyl functional group. Little difference between the spectra of the four samples was found. Results of infrared analyses have not yet been obtained for Tests 5 and 6.

DISCUSSION

All of the radiolysis tests to date have been exploratory in nature. Not enough data are yet available to definitely establish trends as a function of dose, dose rate, or temperature, although some indication of possible trends can be discerned. Hydrogen concentrations correlate best with total dose and impurities. By far the highest hydrogen concentration was found in the one test with deionized water, which had essentially no impurities. Dimethylpropane and dimethylbutane concentrations seem most dependent on irradiation temperature. The extent of polymerization of the solids, as revealed by molecular weights, is greater at the higher dose rates. This is also manifested visually, as the solids in Tests 5 and 6 were coagulated and much more highly colored. Furthermore, the solids from Tests 5 and 6 were retained by 1 μm filters whereas 0.1 μm filters were required for solids from the other tests.

Iron, which was included in Test 6 to simulate candidate canister material, had essentially no effect. Differences shown in dimethylpropane and dimethylbutane concentrations between Tests 5 and 6 are probably insignificant in view of the scatter of the data.

Rough mass balances can be calculated by comparing the mass of solids and the quantities of hydrocarbons found in the gas phase with the amount of methane consumed. Such analyses show that almost all of the methane that was consumed has gone into the polymeric solids and only a very small fraction into dimethylpropane and other low molecular weight hydrocarbons. Thus, the apparent net reaction can be represented by

$$mH_2O(\ell) + nCH_4(g) \rightarrow C_nH_{2n}O_m(s) + (n+m)H_2(g)$$

Based on total pressure measurements, m must be no more than about 1% of the value of n because the pressure increase was no more than 1%. The C, H, and O measurements suggest that m is 1% to 3% of n. Thus, based upon molecular weight values, n must be on the order of 100.

In summary, gamma radiolysis of water (including synthetic Grande Ronde Basalt groundwater) under methane at high pressure results in a milky liquid that is a suspension of fine particles of organic polymers similar to polyethylene. The amount and nature of these polymers does not vary much over the range of experimental conditions employed. It is not yet known how the radiolytic products might be affected by the presence of host rock on engineered-barrier materials (e.g., bentonite). The extent to which these polymers are able to interact with radionuclides, potentially present in solution, also must be determined. Experiments designed to answer these questions are in progress.

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