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RADIOLYTIC GAS GENERATION FROM CEMENT-BASED WASTE HOSTS FOR DOE LOW-LEVEL RADIOACTIVE WASTES

L. R. Dole and H. A. Friedman
Oak Ridge National Laboratory*
Oak Ridge, Tennessee

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RADIOLYTIC GAS GENERATION FROM CEMENT-BASED WASTE HOSTS FOR DOE LOW-LEVEL RADIOACTIVE WASTES

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Oak Ridge National Laboratory
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ABSTRACT: Using cement-based immobilization binders with simulated radioactive waste containing sulfate, nitrate, nitrite, phosphate, and fluoride anions, the gamma- and alpha-radiolytic gas generation factors (G_t, molecules/100 eV) and gas compositions were measured on specimens of cured grouts. These tests studied the effects of (1) waste composition, (2) the sample surface-to-volume ratio, (3) the waste slurry particle size, and (4) the water content of the waste host formula. The radiolysis test vessels were designed to minimize the "dead" volume and to simulate the configuration of waste packages.

A 2.8 M nitrate current acid-waste (CAW) in a cement-based grout had an alpha-G_t of 0.42 molec/100 eV, and the radiolytic gas was composed of H_2 and O_2 in a 2:1 ratio, with a trace of N_2O. A grouted double-shell slurry (DSS) with both nitrate (2.0 M) and nitrite (1.6 M) anions had G_t values of 0.12 and 0.018 molec/100 eV for alpha and gamma radiation, respectively. The gas composition in the latter case consisted of N_2O, N_2, and a trace of CH_4, with no O_2 generation.

Within the variation of these experiments exhibiting problems with leaking seals, no significant difference in alpha-radiolysis rates

could be measured between sludges of different age, samples of different sizes (10 and 200 cm^3), or samples with different dose rates (0.5–0.8 Mrad/h). The DSS waste with the higher nitrate and nitrite levels showed a lower radiolysis rate for the first 250 h (G_t = 0.05 molec/100 eV). After 250 h, the next 100 h showed an alpha-G_t = 0.15 molec/100 ev until the experiments were concluded at 350 h. Although these experiments were not conclusive, one can speculate that the 1.6 M nitrite solution suppressed the generation of alpha-radiolysis products for the first 250 h at a dose rate of 0.5 Mrad/h. If the actual waste form will receive less than 0.6 Mrad/h, the nitrite will result in the lower alpha-radiolysis rate for the first 40 years of package life.

KEY WORDS: radiation effects, cement-based grout, immobilization, low-level radioactive wastes, liquid wastes, slurry wastes, nitrates, nitrites, sulfates, radiolysis, gas composition, gas generation rates, alpha radiation, gamma radiation, porewater

Introduction

Cement-based grouts are used to treat and immobilize a wide spectrum of low-level radioactive waste (LLRW) solutions and slurries [1] that are produced in the specialty-metals production and fabrication plants of the U.S. Department of Energy (DOE). These wastes contain mixtures of nuclides, which emit both gamma and alpha radiation, whose adsorption results in different local radiolytic ion-pair concentrations in the hydrosilicates and the porewater of these waste hosts. In the course of Oak Ridge National Laboratory's (ORNL) process and waste-form development programs, we have studied the radiolytic decomposition of the bound and unbound waters in the hydrosilicate phases and in the pores of cementitious waste hosts [2].

This paper summarizes the work reported in ORNL/TM-9412, which addressed the gas generation rates of radioactive aqueous solutions and slurries that are immobilized in cement-based grouts. The concerns regarding the radiolytic gas evolution from radioactive waste hosts are twofold [3]: (1) the total gas buildup in the sealed waste container and/or overpack may result in pressures that cause premature failure of these packages as barriers to nuclide migration, and (2) the composition of the radiolytic gases in the free space of the container, the annulus of the overpack, or the storage chamber may become explosive. Therefore, the safety issues raised by the radiolysis of the porewater in cement-based grouts are important aspects in the application of hydraulic binders to radioactive waste management.

The cement-based and other hydraulic binders [4] commonly used for the immobilization of low- and middle-level radioactive wastes [5] for both commercial [6] and defense wastes require water in their curing reactions. Generally, these products contain an excess of unreacted water in a closed-pore system. Usually, the excess water is necessary in the production of a fluid grout that can be readily mixed and easily poured. The radiolysis of this unbound water contributes most to the gas generation from within these solidified radioactive waste hosts [7].

Experimental Procedure

Specimens

Compositions of the major salts in the two waste streams that were studied, current acid-waste (CAW) and double-shell slurry (DSS), are presented in Table 1. Two tailored grouts were formulated, as shown in Table 2, for these two simulated radioactive waste streams to (1) maximize the waste loading, (2) eliminate free-drainable water, (3) establish acceptable leach rates for specific nuclides and hazardous inorganics, and (4) remain pumpable for up to one-half mile at a rate of 50 gpm in a 3-in. internal diameter pipe.

A double series of five CAW and one DSS grout specimens was made to study the effects of (1) waste composition and age, (2) the sample surface-to-volume ratio, (3) the waste slurry precipitant particle size, (4) the water content of the waste-host formula, and (5) differences in the alpha- and gamma-radiation linear energy transfer coefficient. Table 3 presents the experimental matrix.

All specimens were cured for 28 d before the radiolysis gases were collected. In the case of the aged precipitants, the neutralized simulated waste was heated to a temperature of 90 to 96°C for 72 h in order to allow the primary precipitation particles to flocculate and form larger agglomerates than occur with a normal acid addition of ^{244}Cm followed by the immediate fixation in the grout matrix. To establish the role of the porewater in the production of radiolytic gases, the dewatered specimens were dried for 7 d at 140°C before the radiolysis gases were monitored. At this temperature, most of the hydrosilicates formed during curing reactions still hold their bound water.

TABLE 1 — *The major salt compositions of the simulated current acid-waste (CAW) and double-shell slurry (DSS) radioactive waste streams.*

Compound	Concentrations (mol/L) CAW (acid)	DSS (slurry)
H_2SO_4	0.27	
HNO_3	0.26	
HF	0.15	
$C(NO_3)_3$	0.0013	
$Al(NO_3)_3$	0.72	
$Fe(NO_3)_3$	0.13	
$NaNO_3$	0.16	2.0
$NaNO_2$		1.6
$NaAlO_2$		1.1
NaOH	1.95	2.6
Na_2SO_4		0.02
Na_3PO_4		0.04
Na_2CrO_4		0.04
NaCl		0.08
NaF		0.02
TOC[a]		4.8 g/L
Total NO_3	2.8	2.0
Total NO_2	...	1.6

[a]TOC = Total organic carbon.

TABLE 2 — *Tailored grout formulas for the simulated current acid-waste (CAW) and double-shell slurry (DSS) radioactive waste streams.*

Grout Component	CAW (acid) (wt %)	DSS (slurry) (wt %)
Cement (ASTM Type I-II LA[a])	15.0	16.2
ASTM Class F Fly Ash	15.0	16.2
Indian Red Pottery	3.5	3.24
Attapulgite (Attagel 150)		6.44
Waste Stream Solids	20.0	14.04
Super Plasticizer (Plastiment)	0.2	
Water	46.3	42.88
Water:Cement ratio	3.1	2.6
Density, g/cm^3	1.61 ±.02	1.7

[a]LA = low alumina.

TABLE 3 — *Specimen test matrix for the alpha- and gamma-radiolysis measurements of the grout porewater and simulated current acid-waste (CAW) and double-shell slurry (DSS) radioactive waste streams.*

Grout Specimen and Treatment	Volume (cm^3)	^{244}Cm (mg)	Dose Rate (Mrad/h)
1. CAW normal acid spike	10	8.3	0.52
2. CAW normal acid spike	200	263.0	0.81
3. CAW aged precipitant	10	8.3	0.52
4. CAW aged precipitant	200	264.5	0.809
5. CAW dried after cure	10	8.2	0.51
6. DSS normal acid spike	10	9.6	0.57
7. DSS normal acid spike[a]	200[a]	0.0[a]	0.80[a]

[a]Gamma source ^{60}Co.

Equipment

The radiolysis test vessels in Figs. 1 and 2 were designed to minimize the "dead" volume and to simulate the configuration of waste packages. The actual dead volume of each specimen holder was measured by the expansion of a known volume of gas into the fully assembled holder and miniature pressure transducers. The void volume measurements include the vacant pore volume as well as the container and sensor "dead" volumes. For the alpha-radiolysis tests, the measured dead volumes of the 10-cm^3 holders averaged 4.5 ±0.4 cm^3, and the 200-cm^3 holders averaged 51.0 ±0.7 cm^3. Because the lines were lengthened for the

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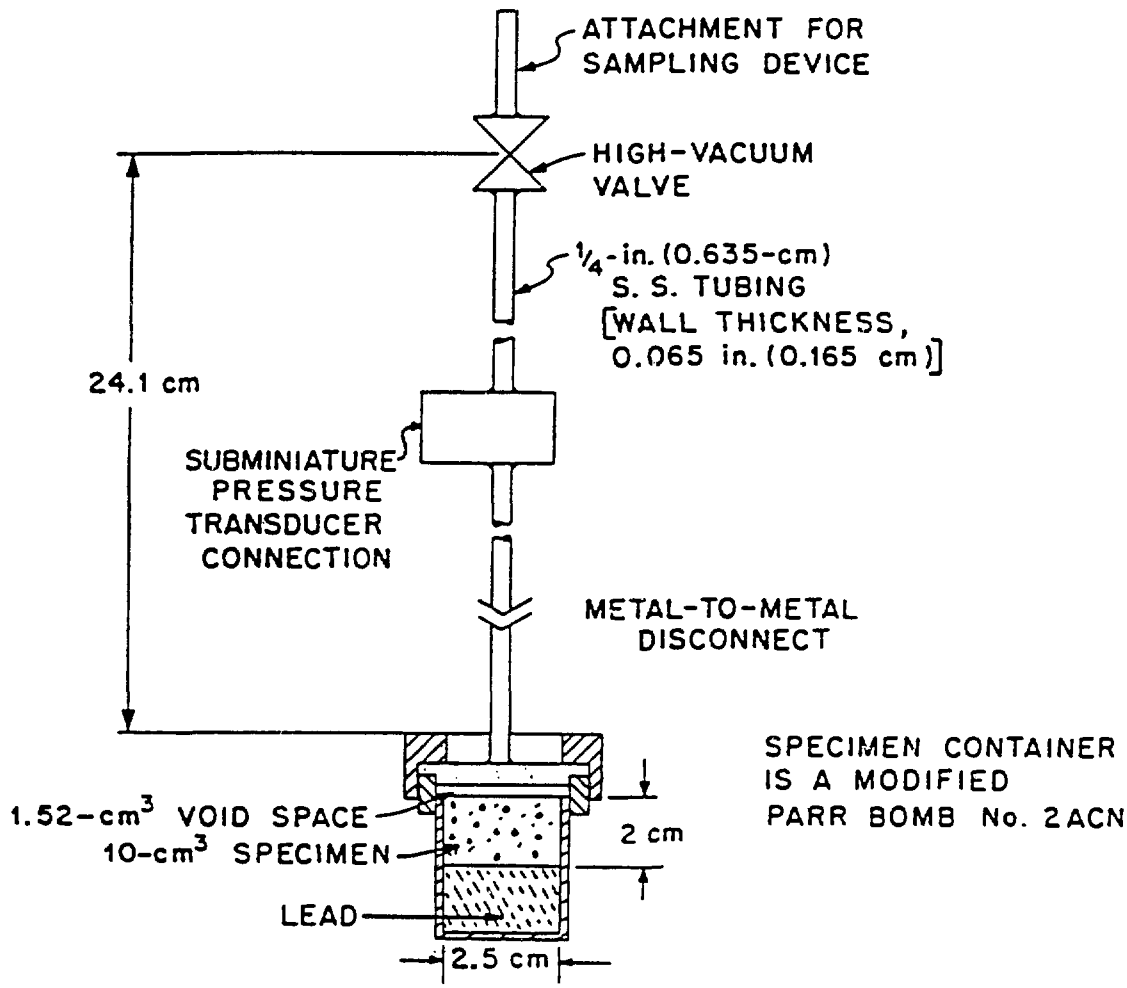

FIG. 1 — *Alpha- and gamma-radiolysis specimen holder and pressure-measuring equipment for the 10-cm^3 specimens of cured grouts with simulated current acid-waste (CAW) and double-shell slurry (DSS) radioactive waste streams.*

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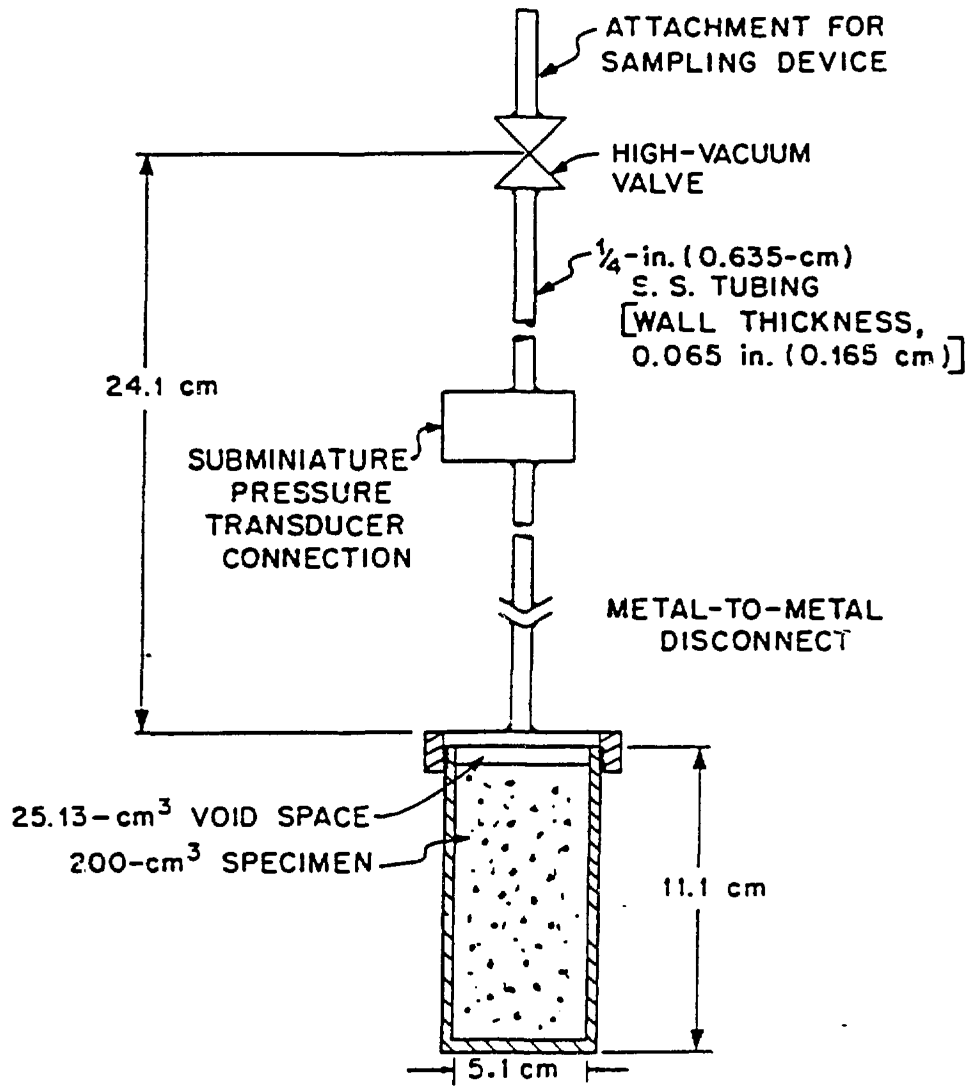

FIG. 2 — *Alpha- and gamma-radiolysis specimen holder and pressure-measuring equipment for the 200-cm³ specimens of cured grouts with simulated current acid waste (CAW) and double-shell slurry (DSS) radioactive waste streams.*

gamma-radiolysis experiment in order to keep the transducers out of the intense ^{60}Co field (0.8 Mrad/h), the dead volumes of these holders were 68 cm^3.

The pressure range of these miniature transducers was -5 to 200 psig, and they were read at two sensitivity ranges of about 1 mV per 1 psig and 25 mV per 1 psig. Air was present in the containers at the start of the experiments, and no attempt was made to flush them in order to prevent drying of the specimens.

The gas tightness of these holders was unreliable, and the seals were broken as the pressure in them increased. There were many restarts of the gas collection phase of the experiments because of gasket failures in these modified Parr Bombs (No. 2ACN). While the slopes of the pressure increases nearly match before and after tightening of these threaded caps, these failures contributed to the scatter of the rated data and obscured the interpretation of the gas composition data which were measured with a mass spectrometer.

Results and Discussion

Alpha and Gamma Radiolysis

Table 4 summarizes the results of measuring the buildup of pressure in the calibrated "dead" volumes of the specimen holders and calculating the total number of molecules evolved from the radiolytic breakdown of the porewater in the cement-based grouts. The analyses of the composition of these gases are presented in Table 5.

The 2.8 M nitrate CAW cement-based grout had an alpha-G_t of 0.42 molec/100 eV, and the radiolytic gas was composed of H_2 and O_2 in a 2:1 ratio, with a trace of N_2O. The DSS grouted waste solution with

TABLE 4 — *Summary of total alpha- and gamma-radiolytic gas evolution coefficients (G_t, molec/100 eV) for specimens of cured grouts with simulated current acid-waste (CAW) and double-shell slurry (DSS) radioactive waste streams.*

Grout Specimen and Treatment	Volume (cm^3)	G_t (molec/100 eV)
1. CAW normal acid spike	10	0.32-0.43
2. CAW normal acid spike	200	0.43
3. CAW aged precipitant	10	0.36-0.55
4. CAW aged precipitant	200	0.41
5. CAW dried after cure	10	0.-0.
6. DSS normal acid spike	10	0.04-0.05 (<280 h) 0.10-0.15 (>280 h)
7. DSS normal acid spike [a]	200[a]	0.018[a]

[a]Gamma source ^{60}Co (0.8 Mrad/h).

TABLE 5 — *Compositions of alpha- and gamma-radiolysis gases*[a] *and residual air*[b] *from grouts with simulated current acid-waste (CAW) and double-shell slurry (DSS) radioactive waste streams.*

Grout and Treatment	Specimen Volume (cm^3)	Gas Composition (vol %)					
		Ar	N_2	O_2	H_2	N_2O	CH_4
1. CAW normal acid spike	10	.06	5.8	30.5	63.1	0.52	<.01
2. CAW normal acid spike	10	.03	3.1	30.7	65.6	0.53	<.01
3. CAW normal acid spike	200	<.01	0.4	34.3	64.8	0.44	<.01
4. CAW aged precipitant	10	.06	5.1	30.4	64.2	0.3	<.01
5. CAW aged precipitant	10	.07	6.4	33.9	59.0	0.33	<.01
6. CAW aged precipitant	200	.01	0.7	31.4	67.6	0.18	<.01
7. DSS normal acid spike	10	.47	22.7	34.8	38.3	3.7	0.01
8. DSS normal acid spike	10	.26	29.9	0.7	61.1	8.1	0.01
9. DSS normal acid spike[a]	200	.76	68.1	7.7	5.7	14.8	0.04
10. DSS normal acid spike[a]	200	.70	62.4	6.5	7.2	19.5	0.05
11. DSS normal acid spike[a]	200	.74	65.6	7.9	7.2	18.3	0.04

[a] Gamma source ^{60}Co (0.8 Mrad/h).
[b] Air (Ar = 0.934%, N_2 = 78.083%, and O_2 = 20.946%).

both nitrate (2.0 M) and nitrite (1.6 M) anions had G_t values of 0.12 and 0.018 molec/100 eV for alpha and gamma radiation, respectively. These gas compositions consisted of N_2O, N_2, and a trace of CH_4 from the organic carbon component of the DSS. Also, the O_2 generation was supressed.

Within the variation of these experiments exhibiting problems with leaking seals, no significant difference in alpha-radiolysis rates could be measured between sludges of different age, samples of different sizes (10 and 200 cc), or samples with different dose rates (0.5-0.8 Mrad/h). The double-shell slurry waste with nitrite showed a lower radiolysis rate for the first 250 h (G_t = 0.05 molec/100 eV). After 250 h, the next 100 h showed an alpha-G_t = 0.15 molec/100 eV, until the experiments were concluded at 350 h. Although these experiments were not conclusive, one can speculate that the 1.6 M nitrite solution suppressed [8] the generation of alpha-radiolysis products for the first 250 h at a dose rate of 0.5 Mrad/h. If the actual waste form will receive less than 0.6 Mrad/h, the nitrite will result in the lower alpha-radiolysis rates for the first 40 years of package life.

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FIGURE LIST

TABLE LIST