2.0 Microbial Degradation

Results from the Gas Generation Experiments at Argonne National Laboratory - West[1]

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Abstract
Fourteen test containers were placed under long-term test to measure the rates at which gases are produced in transuranic (TRU) waste containers should the WIPP repository become inundated with brine. Approximately 3/4 of the depth was loosely filled with various actual TRU waste material. A synthetic brine, having the same chemical composition as that in the WIPP vicinity and inoculated with microbes typical of those found at WIPP, was added to all of the test containers, completely covering the waste. The test containers were sealed, purged and pressurized with nitrogen gas to approximately 2150 psia, placed in an argon-filled glovebox, and maintained at 30° C. Gas samples were periodically extracted and analyzed to measure the generation of gases from metal corrosion, microbial action, and radiolysis. Gas generation was found to depend on the waste composition. The maximum hydrogen generation was found to be over 2-1/2 % by volume after four years. Only small quantities of other gases such as carbon dioxide, methane, or hydrogen sulfide were generated. The maximum steel corrosion rate was calculated to be over 2.3 microns penetration per year. Conversion of carbon to carbon dioxide was calculated to be up to 2.3E-6 g-mol/yr/g-carbon.

Progress Report
The Gas-Generation Experiments (GGE) were designed to assist Sandia National Laboratory in estimating the rates at which gases are produced in transuranic (TRU) waste containers should the WIPP repository become inundated with brine. The GGE were very carefully structured and controlled experiments. Fourteen specially manufactured, corrosion-resistant test containers having a nominal volume of about 7 liters each were placed under test. In twelve of these containers approximately 3/4 of the 16-in depth was loosely filled with various actual TRU waste material. The remaining two test containers had no wastes and served as experiment controls. A synthetic brine (Brine-A) having the same chemical composition as that in the WIPP vicinity was added to all of the test containers, completely covering the waste and filling approximately 90% of the test containers' volumes. To include metabolic gas generation, the brine was inoculated

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1 This work is covered by BOE #1.3.05.04.02 and WBS #1.3.5.4.2. A more recent description of this work appears in Sandia National Laboratories WIPP/NTP Work Scope for FY01, December 14, 2000.

with microbes typical of those found at WIPP. These test containers were then sealed, purged, and backfilled with nitrogen gas and pressurized to approximately 2150 psia, the lithostatic pressure level expected to eventually occur at WIPP.

All of the test containers were fitted with highly sensitive and stable temperature and pressure instrumentation, along with suitable systems for periodically extracting very small samples of the vessel headspace gas for chemical analysis. The test containers were placed in an inert-gas (argon)-filled glovebox having a sophisticated gas-purification system to restrict the level of oxygen. Each test container was fitted with electric heater belts and had its own proportional, integral, and derivative electronic controller that controlled the temperature of each test container individually to nominally 30° C, the temperature expected in the repository. A data-acquisition system acquired temperature and pressure measurements every hour. Regular calibrations were made to the instruments. Chemical analyses of the gas samples were made over the ensuing four-year testing period to deduce the rates at which gases were being produced and the identification of the gases. Pressure measurements were recorded as a backup indication of gross gas generation. To date, temperature and pressure data have been collected and archived for over five years, totaling in excess of 30,000 data points per container. The results reported here represent approximately four years of testing, through July 2000.

Analyses of the July 2000 samples by the ANL Analytic Laboratory provide a good indication of the quantity and species of gases generated over the four-year operation. Table 1 lists the types of waste materials within each of the test containers and shows the composition of headspace gases after four years of testing. Previous headspace gas sampling showed that the levels of gases listed in Table 1 were continuously accumulating. Several of the test containers showed significantly elevated levels of generated gases, virtually all of which was hydrogen. Test Container No. 166 measured 25448 ppm by volume, i.e., over 2-1/2 % hydrogen. Two other test containers measured over 1% hydrogen, and another was at nearly 1%. It should be noted that the initial headspace gas composition was nominally 99 % nitrogen, 1 % helium, 0.1 % argon, and traces of other gases, principally carbon dioxide. Only small quantities of other gases such as carbon dioxide, methane, or hydrogen sulfide were generated. The total quantities of generated gases measured by the sample analyses agree reasonably well with total pressure trends that were measured over the four-year-long test period.

Table 2 provides a detailed breakdown of the hydrogen and carbon-dioxide generated. This table shows the relevant measure of the quantities of TRU materials in each of the waste-bearing test containers and the intermediate deductions for the corrosion rates for the carbon steel constituents and the rate of carbon dioxide generation as a function of the carbon content. The maximum steel corrosion rate was found to be over 2.3 microns penetration per year. The highest conversion of carbon to carbon dioxide was determined to be approximately 2.3E-6 g-mol/yr/g carbon.

This work was performed under Argonne National Laboratory-West TD Waste Programs Test and Quality Assurance Project Plan for WIPP Gas Generation Experiments, ANL-W Doc No: A005-0014-AQ, Rev. 01.

Gas-Generation Experiment Program
Table 1.
Analyses of Headspace-Gas Samples Drawn July 2000

Container Number	Waste Type [2]	Analysis (ppm by volume) and Uncertainties [1]							
		Ar [3] ±20%	CO_2 ±10%	CO ±10%	He [4] ±15%	H_2 ±10%	H_2S --	CH_4 ±10%	O_2 --
151	Stl, Pb-R	1546	<d [5]	<d	12370	5094	<d	<d	<d
152	No Waste	1714	<d	<d	12145	<d	<d	<d	<d
153	No Waste	2872	<d	<d	12050	<d	<d	<d	<d
160	Stl, Sldg, Pb-R, R, P, C	1296	246	<d	12260	9310	<d	<d	<d
161	Stl, Sldg, Pb-R, R, P, C	1231	193	<d	12290	10155	<d	<d	<d
162	Stl, Sldg, Pb-R, R, P, C	4760	178	<d	12290	1939	<d	<d	<d
163	Sldg, Pb-R, C	1454	506	<d	12180	768	<d	<d	<d
164	Sldg, Pb-R, C	1586	698	<d	12060	938	<d	<d	<d
165	Sldg, R, P	1195	555	<d	12140	1362	<d	<d	<d
166	Stl, Sldg	1857	73	<d	11891	25448	<d	<d	<d
167	Stl, R, P, C	1715	134	169	12071	11708	<d	79	<d
168	C	1740	186	<d	11900	<d	<d	<d	<d
169	C	1687	179	<d	12071	<d	<d	<d	<d
170	Pb-R, R, P	1826	<d	59	12360	1280	<d	<d	<d
Detection Limits (d)		--	50	50	--	50	500	50	50

Notes:
(1) Uncertainties are 2-sigma values.
(2) Stl = Steel; Sldg = Sludge; R = Rubber; Pb-R = Leaded Rubber; P = Plastic; C = Cellulose.
(3) Ar is a residual following N_2/He purging of the test container in the Ar-filled glovebox.
(4) Approximately 1% He was added to the N_2 fill gas for leak-detection use after initial pressurization.
(5) d = detection limit

Table 2

Estimation of GGE Carbon-Steel Corrosion, & CO_2 Generation Rates from Carbon

***Usage:** make entries only to shaded cells; others are computed.*

Steel Corrosion Conversion Constant	g-mol H_2/m^2/micron	0.141
Molar volume at STP	l/g-mol	22.420
Sample Volume	ml	3.05

		Test Container Number												
		VSL-151	VSL-160	VSL-161	VSL-162	VSL-163	VSL-164	VSL-165	VSL-166	VSL-167	VSL-168	VSL-169	VSL-170	Hand-Check Case
Waste Quantities														
Steel Surface Area Exposed	in^2	133.19	143.61	140.18	144.11	0.00	0.00	0.00	139.90	140.33	0.00	0.00	0.00	120.00
Sludge Mass	g		269.10	273.68	267.56	271.62	269.87	285.10	275.63					200.00
Leaded Rubber Mass	g	129.28	124.72	125.96	123.36	125.52	127.41						123.03	100.00
Rubber (Neoprene) Mass	g		44.83	43.64	45.00			43.77		42.52			43.48	50.00
Plastic Mass	g		91.84	86.38	86.90			88.47		88.43			88.80	80.00
Cellulose Mass	g		344.24	344.35	343.85	345.22	343.72			345.56	345.90	341.83		300.00
Conditions at End of Interval														
Date of Measurement		25-Jul-00	25-Jul-00	24-Jul-00	24-Jul-00	20-Jul-00	19-Jul-00	20-Jul-00	14-Jul-00	14-Jul-00	13-Jul-00	12-Jul-00	25-Jul-00	15-Jul-00
H_2 Concentration Measured	ppm (vol)	5094	9310	10155	1939	768	938	1362	25448	11708	<50	<50	1280	25000
CO_2 Concentration Measured	ppm (vol)	<50	246	193	178	506	698	555	73	134	186	179	<50	500
Pressure (initial)	psia	2163.8	2118.5	2089.3	2074.0	2147.9	2158.3	2128.9	2187.4	2162.9	2099.9	2165.3	2140.6	2179.2
Pressure (final)	psia	2154.3	2112.1	2081.9	2066.5	2140.4	2150.6	2120.0	2177.0	2155.0	2092.2	2156.9	2131.3	2170.0
	std-atm	146.59	143.72	141.66	140.62	145.65	146.34	144.26	148.14	146.64	142.37	146.77	145.03	147.66
TC RTD Reading when Sampled	C	30.4	29.2	29.1	29.2	29.0	30.0	29.8	29.8	29.6	29.6	29.5	29.6	0.0
Glovebox RTD Reading when Sampled	C	27.4	27.4	27.4	27.4	27.2	27.4	27.4	27.6	27.6	27.4	27.3	27.4	0.0
HS Temperature Estimate for Sample	C	29.65	28.75	28.68	28.75	28.55	29.35	29.20	29.25	29.10	29.05	28.95	29.05	0.00
Vapor Pressure of Brine (H_20)	psia	0.6037	0.5731	0.5708	0.5731	0.5665	0.5933	0.5882	0.5899	0.5847	0.5830	0.5796	0.5830	0.0000
Compressibility Factor (initial)	--	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0000
Compressibility Factor (final)	--	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0000
HS Volume at Measurement Conditions	ml	691.4	1006.3	857.8	840.1	870.2	851.6	726.3	638.3	831.8	828.5	782.9	698.8	719.4
H_2 vol at Prevailing Press & Temp	ml	3.522	9.368	8.711	1.629	0.668	0.799	0.989	16.243	9.738	<d	<d	0.894	17.985
H_2 vol adjusted to STP	l	0.466	1.218	1.117	0.207	0.088	0.106	0.129	2.173	1.291	<d	<d	0.117	2.656
CO_2 vol at Prevailing Press & Temp	ml	<d	0.248	0.166	0.150	0.440	0.594	0.403	0.047	0.111	0.154	0.140	<d	0.360
CO_2 vol adjusted to STP	l	<d	0.032	0.021	0.019	0.058	0.079	0.053	0.006	0.015	0.020	0.019	<d	0.053
Conditions at the Start of Interval														
Date of Measurement		12-May-97	31-Mar-97	1-Apr-97	8-Apr-97	9-May-97	8-May-97	8-May-97	13-May-97	14-May-97	29-May-97	8-Apr-97	12-May-97	15-Jul-96
H_2 Concentration Measured	ppm (vol)	1940	1580	1730	503	124	161	278	776	4040	<50	<50	277	0
CO_2 Concentration Measured	ppm (vol)	<50	206	120	125	365	483	386	77	97	141	118	<50	200
Pressure (initial)	psia	2171.2	2128.0	2098.5	2097.9	2172.3	2172.0	2147.4	2151.6	2169.0	2147.9	2188.4	2159.4	2179.2
Pressure (final)	psia	2161.8	2121.6	2091.3	2090.5	2164.9	2164.1	2138.4	2142.5	2161.2	2140.1	2180.0	2150.0	2170.0
	std-atm	147.10	144.37	142.30	142.25	147.31	147.26	145.51	145.79	147.06	145.62	148.34	146.30	147.66
TC RTD Reading when Sampled	C	30.6	30.9	30.8	30.7	30.4	30.6	30.6	30.5	30.6	30.8	30.7	30.5	0.0
Glovebox RTD Reading when Sampled	C	28.0	27.3	28.3	28.4	28.2	27.8	27.3	28.3	28.1	28.3	27.9	27.6	0.0
HS Temperature Estimate for Sample	C	29.95	30.00	30.18	30.11	29.85	29.89	29.78	29.95	29.98	30.18	30.00	29.78	0.00
Vapor Pressure of Brine (H_20)	psia	0.6140	0.6158	0.6223	0.6197	0.6106	0.6120	0.6082	0.6140	0.6151	0.6223	0.6158	0.6082	0.0000
Compressibility Factor (initial)	--	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0000
Compressibility Factor (final)	--	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0200	1.0000
HS Volume at Measurement Conditions	ml	701.2	1010.8	885.6	861.4	892.0	835.3	724.5	717.9	844.8	836.6	791.3	697.4	719.4
H_2 vol at Prevailing Press & Temp	ml	1.360	1.597	1.532	0.433	0.111	0.134	0.201	0.557	3.413	<d	<d	0.193	0.000
H_2 vol adjusted to STP	l	0.180	0.208	0.196	0.056	0.015	0.018	0.026	0.073	0.452	<d	<d	0.025	0.000
CO_2 vol at Prevailing Press & Temp	ml	<d	0.208	0.106	0.108	0.326	0.403	0.280	0.055	0.082	0.118	0.093	<d	0.144
CO_2 vol adjusted to STP	l	<d	0.027	0.014	0.014	0.043	0.054	0.037	0.007	0.011	0.015	0.012	<d	0.021

Specific Gas-Generation & Rates		VSL-151	VSL-160	VSL-161	VSL-162	VSL-163	VSL-164	VSL-165	VSL-166	VSL-167	VSL-168	VSL-169	VSL-170	Hand-Check Case
Carbon Mass in Leaded Rubber[(2)]	g	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon Mass in Rubber (Neoprene)[(3)]	g	0.00	24.43	23.78	24.53	0.00	0.00	23.85	0.00	23.17	0.00	0.00	23.70	27.25
Carbon Mass in Plastic[(4)]	g	0.00	78.71	74.03	74.47	0.00	0.00	75.82	0.00	75.78	0.00	0.00	76.10	68.56
Carbon Mass in Cellulose[(5)]	g	0.00	152.84	152.89	152.67	153.28	152.61	0.00	0.00	153.43	153.58	151.77	0.00	133.20
Total Carbon Content	g	0.00	255.98	250.70	251.67	153.28	152.61	99.67	0.00	252.39	153.58	151.77	99.80	229.01
Time Interval Between Measurements	days	1170	1212	1210	1203	1168	1168	1169	1158	1157	1141	1191	1170	1461
	months	38.4	39.7	39.7	39.4	38.3	38.3	38.3	38.0	37.9	37.4	39.0	38.4	47.9
	years	3.21	3.32	3.32	3.30	3.20	3.20	3.20	3.17	3.17	3.13	3.26	3.21	4.00
Net H_2 Generated During Interval	g-mol	0.013	0.045	0.041	0.007	0.003	0.004	0.005	0.094	0.037	<d	<d	0.004	0.118
Net H_2 per Unit Surface Area of Steel	g-mol/m^2	0.148	0.486	0.454	0.073	N/A	N/A	N/A	1.038	0.413	<d	<d	N/A	1.530
Rate of H_2 Generation per Area	g-mol/yr/m^2	0.046	0.146	0.137	0.022	N/A	N/A	N/A	0.327	0.130	<d	<d	N/A	0.382
Steel Corrosion Penetration Rate	micron/yr	0.328	1.039	0.971	0.157	N/A	N/A	N/A	2.320	0.924	<d	<d	N/A	2.711
Net CO_2 Generated During Interval	g-mol	<d	2.276E-04	3.393E-04	2.333E-04	6.612E-04	1.115E-03	7.067E-04	-4.584E-05	1.744E-04	1.945E-04	2.729E-04	<d	1.421E-03
Net CO_2 Generated per Mass of Carbon	g-mol/g-carbon	<d	8.893E-07	1.353E-06	9.270E-07	4.313E-06	7.306E-06	7.090E-06	N/A	6.911E-07	1.266E-06	1.798E-06	<d	6.207E-06
Rate of CO_2 Generation per Mass of Carbon	g-mol/yr/g-carbon	<d	2.678E-07	4.083E-07	2.813E-07	1.348E-06	2.283E-06	2.214E-06	N/A	2.180E-07	4.051E-07	5.510E-07	<d	1.551E-06
Radioactive Materials Content														
Pu-238	mg	9.4463E-03	1.4382E-02	1.2501E-02	1.7512E-02	1.0994E-02	1.1251E-02	1.1509E-02	3.7567E-03	6.5153E-02	2.5985E-04	3.3542E-04	1.8127E-02	
Pu-239	mg	8.8692E+01	1.3503E+02	1.1737E+02	1.6442E+02	1.0322E+02	1.0563E+02	1.0806E+02	3.5272E+01	6.1172E+02	2.4397E+00	3.1492E+00	1.7019E+02	
Pu-240	mg	5.4316E+00	8.2696E+00	7.1880E+00	1.0069E+01	6.3216E+00	6.4691E+00	6.6175E+00	2.1601E+00	3.7463E+01	1.4941E-01	1.9287E-01	1.0423E+01	
Pu-241	mg	3.2118E-01	4.8898E-01	4.2503E-01	5.9541E-01	3.7380E-01	3.8252E-01	3.9130E-01	1.2773E-01	2.2152E+00	8.8349E-03	1.1404E-02	6.1631E-01	
Pu-242	mg	1.8893E-02	2.8764E-02	2.5002E-02	3.5024E-02	2.1988E-02	2.2501E-02	2.3017E-02	7.5134E-03	1.3031E-01	5.1970E-04	6.7084E-04	3.6253E-02	
Am-241	mg	1.5796E+02	2.1175E+03	1.6236E+03	1.3201E+03	2.0487E+03	1.7253E+03	1.3639E+03	2.2102E+03	1.0012E+03	4.5754E+00	7.5200E+00	2.6732E+02	

Notes

(1) "<d" denotes less than detection limits

Carbon Mass Fractions of Waste Materials

(2) Leaded Rubber - negligible	0
(3) Neoprene $[C_4H_5Cl]_n$	0.545
(4) Polyethylene $[CH_2\text{-}CH_2]_n$	0.857
(5) Cellulose $[C_6H_{10}O_5]_n$	0.444