Investigation of Transuranic Waste Drums to Assess Mechanisms of Methane Generation

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BACKGROUND

Waste drums bound for disposal at the Waste Isolation Pilot Plant must meet rigorous acceptance criteria. One criterion is that levels of methane in drum headspace must not exceed 1250 ppmV—a limit imposed by the US Department of Transportation to ensure safe passage along US highways. Recently, several drums from the Idaho National Laboratory were found to have high levels of methane in the headspace. As microbial methanogenesis is exclusively an anaerobic process, the drums were treated by splaying and repackaging the contents, in an effort to aerate the waste and inactivate the microorganisms responsible. However, even after such treatment, high levels of methane were still detected in the drums' headspaces. Los Alamos National Laboratory's Repository Science & Operations Group in Carlsbad, NM, was asked to investigate the possible sources of methane generation in two drums. This investigation evaluated two possible mechanisms for methane production: microbial methanogenesis and radiolytic degradation pathways. In our investigations, we have seen a steady decrease in the rates of methane gas evolution under anoxic (Nitrogen glovebox) conditions which we have interpreted as an exhaustion of the sorbed methane. Since the time of this investigation, methane levels in the INL drums seem to be decreasing although measurable levels are still being observed.

SAMPLE HANDLING AND ANALYSES

- Waste drums breached and transferred to enclosed glove box
- Six ~10g samples obtained from each drum
- Upon receipt, 10 of 12 samples transferred to enclosed once-through air glove box; 2 of 12 transferred to anoxic box. All were analyzed for continued methane production.

Constituent	Drum 6	Drum 9
Organic sludge (kg)	120	106
Graphite (kg)	0.50	2.00
Fe-based Metal (kg)	Trace	Trace
Rubber	Trace	0
Transuranic alpha (nCi/g)	481	1085
Am-241 (mCi)	55.3	72.9
Pu-239 (mCi)	7.64	16.1
Pu-240 (mCi)	1.75	3.67

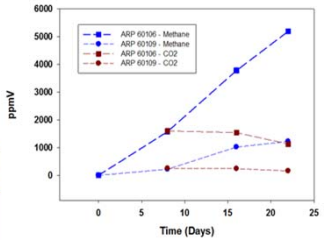
Additional analyses by ICP-MS (of dissolved waste samples):

- U-238 accounts for majority of radionuclides by mass (~175-225 µg/g in ARP60106; 150-246 µg/g in ARP60109)
- Am-241 and Pu-239 account for majority by activity (see chart) and were present in 0.044 and 0.35 µg/g (ARP60106) and 0.12 and 0.85 µg/g (ARP60109) respectively
- Trace Np-237 and Th-232
- These qualitatively agree with waste source-term data

RADIOLYTIC ANALYSES

Continued headspace analysis by GC:

- Aliquots from each waste drum analyzed over time, concomitant to DNA analyses
- Continued methane "generation" in samples from both drums under oxic and anoxic conditions



Estimated G(values) for methane generation, assuming a radiolytic process			
Sample	[1]Estimated Dose to Sample (MeV)	[2]Moles of Methane Observed	[3]Estimated G(value) for Methane Production (molec/100 eV)
ARP60106	5.32 E+11	9.26 E-06	1048
ARP60109	1.16 E+12	2.18 E-06	113

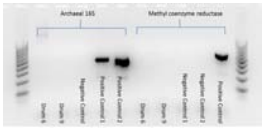
1 – dose/day from Table 4-1 x 10 g (approximate weight of sample) x 22 days
2 – moles based on final ppmV measurements at 22 days and an estimated free volume of 48 cc
3 – G-value is the molecules of methane / # of 100 eV

The unreasonably high G-values do not support radiolysis as the cause of methane generation

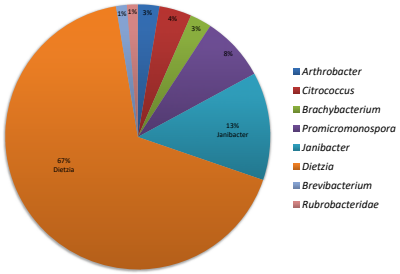
MICROBIAL ANALYSES

Cultivation-Independent Results

- DNA was extractable from one drum only (ARP60106)
- No archaeal signatures were amplifiable from the extracted DNA using standard PCR (i.e., no methanogens), see figure below



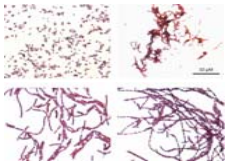
- Bacterial DNA was amplified and sequenced
- All identified organisms fall within phylum *Actinobacteria* (see figure below)



- Nested PCR shows archaeal DNA is present at extremely low proportions in both drums; preliminary metagenomic sequencing data show extremely low signatures of methanogen DNA, supporting nested PCR results
- *Actinobacteria* have been found in other radionuclide contaminated environments [refs]

Cultivation-Dependent Results

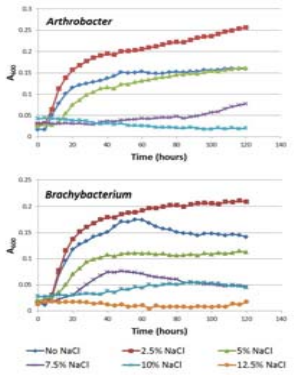
- Waste was suspended in normal saline solution and plated onto low-nutrient agars with varying salt concentrations; incubated under aerobic conditions
- Five isolates cultivated from drum ARP60106 under aerobic, low-salt conditions



2 *Actinobacteria* (also detected by DNA analysis)

3 *Firmicutes* (*Bacillus* spp.)

- Isolates are tolerant of low [NaCl] but are not expected to be active under WIPP conditions (see figure below); may play a role in within-drum waste degradation prior to emplacement and in biocolloid transport



- Fungal growth on carboxymethylcellulose agar with 10% NaCl, possible contaminant

CONCLUSIONS

The results of DNA analyses show that there were no active methanogens present in the drums at the time of sampling. The analyses do not exclude the real possibility that methanogens were present and active at some point in the past. Results of radiolytic investigations and waster analysis show that radiolytic decomposition of organic waste components cannot account for the levels of methane measured in the drum headspaces. It is hypothesized that methane produced by microorganisms, and even radiolysis, in the past was sorbed onto the porous waste matrix and had outgassed within the sealed drums prior to initial headspace analysis. Continued repackaging efforts may have exposed further waste surface area to outgassing, which could explain the continued measurement of methane after these efforts took place. In the end, for the samples where rigorous degassing was done, the methane formation observed was greatly reduced.

REFERENCES

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2. Zavilgelsky GB, Abilev SK, Sukhodolets VV, Ahmad SI. 1998. Isolation and Analysis of UV and Radio-Resistant Bacteria from Chernobyl. Journal of Photochemistry and Photobiology B: Biology 43: 152-157.