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subject: Methanogenesis and Carbon Dioxide Generation at the Waste Isolation Pilot Plant (WIPP)

INTRODUCTION

Microbial gas generation will have a significant impact on the near field chemistry of the Waste Isolation Pilot Plant (US DOE, 1996, appendix SOTERM). To mitigate the effect of microbially-generated carbon dioxide on actinide solubility, the Department of Energy (DOE) decided to emplace 77,640 metric tons (equivalent to 2×10^9 moles) of MgO as a backfill into the WIPP (Bynum et al., 1998). This total amount of MgO was estimated based on the following assumptions (Peterson, 1996):

(1) Organic materials (cellulosics, plastics, and rubber) will be completely degraded over 10,000 years,
(2) one mole carbon (C) in organic materials will be converted to one mole of carbon dioxide (CO_2),
and
(4) there will be sufficient space for the emplacement of MgO.

The first two assumptions are overly conservative. This memorandum intends to demonstrate that the conservatism associated with the second assumption conflicts with current data showing that methanogenesis will be a dominant biodegradation pathway in the WIPP repository. Therefore, at most one half of organic carbon can possibly be converted to CO_2.

METHANOGENESIS IN WIPP

Cellulosics, plastics, and rubbers have been identified as major organic materials to be emplaced in the WIPP repository (DOE/CAO, 1996) and could be degraded by microbes in 10,000 years (Brush, 1995). Depending on the availability of electron acceptors (e.g., NO_3^-, and SO_4^{2-}), microorganisms will degrade organic materials by the following reaction pathways (Brush, 1995):

$$C_6H_{10}O_5 + 4.8\ H^+ + 4.8\ NO_3^- \rightarrow 7.4\ H_2O + 6\ CO_2 + 2.4\ N_2 \quad (1)$$

$$C_6H_{10}O_5 + 6\ H^+ + 3\ SO_4^{2-} \rightarrow 5\ H_2O + 6\ CO_2 + 3\ H_2S \quad (2)$$

$$C_6H_{10}O_5 + H_2O \rightarrow 3\ CH_4 + 3\ CO_2. \quad (3)$$

The reaction pathways of aerobic respiration, Mn(IV) and Fe(III) dissimilatory reduction are ignored here, because the quantities of O_2, Mn(IV) and Fe(III) initially present in the

repository will be negligible relative to the other electron acceptors. The above reactions generally proceed sequentially from Reaction (1) to (3) according to a decreasing order of energy yields of the reactions (e.g., Berner, 1980; Criddle et al., 1991; Chapelle, 1993; Wang and Cappellen, 1996; Hunter et al., 1998). It is important to notice that methanogenesis produces only half mole of carbon dioxide from one mole of organic carbon.

Aside from theoretical consideration of the energetic perspective, the biodegradation sequence summarized above is widely observed in the nature (e.g., Berner, 1980; Griddle et al., 1991; Chapelle, 1993). The occurrence of methanogenesis following denitrification and sulfate reduction is commonly observed in marine sediments, especially in coastal sediments, which receive a high input of organic matters (e.g., Schlesinger, 1997, p.284). Methanogenesis can be a dominant biodegradation process in many terrestrial geochemical systems such as freshwater wetlands and lakes, where the supply of sulfate is usually limited (e.g., Schlesinger, 1997, p.237). Methanogenesis is observed to occur in either pristine or contaminated groundwater systems (e.g., Chapelle, 1993). Methane generation in landfills is a typical example (Baedecker and Back, 1979). In all these systems, the occurrence of methanogenesis follows, with no exception, the biodegradation sequence summarized by Reaction (1) to (3). Therefore, it follows that methanogenesis is likely to occur in the WIPP repository after all nitrate and sulfate are consumed. It is worth noting that Nirex has included methanogenesis in the performance assessment for low-level waste disposal (Nirex, 1997).

In the previous gas generation experiments, which were used to derive gas generation parameters for the WIPP Compliance Certification Application (CCA) (Wang and Brush, 1996), cellulose samples were incubated for 1228 days with microorganisms collected from WIPP-relevant environments (Francis et al., 1997). At the time of the CCA calculations no methane production was detected in any of those samples. There are two possible explanations for the absence of methane production. The first possibility is that microbial degradation in the samples had not reached the methanogenesis stage, due to a relatively short incubation time and also because of high nitrate or sulfate concentration in the brine. If this is the case, methane would be produced after the samples are incubated for a long enough time and all nitrate and sulfate in the samples are consumed. The second possibility is the lack of active methanogenic microbes in the samples. If this were the case, no methane would be produced even if the samples were incubated for a very long time. To test these possibilities, A. J. Francis and J. Gillow at Brookhaven National Laboratory (BNL) have conducted more headspace gas measurements on samples that have been preserved from the previous WIPP gas generation program (See WIPP Test Plan TP99-01). The objective of these measurements was to check if methane had been produced in those samples after extended incubation (~ 7.5 years). Methane was analyzed in selected brine-inundated samples and the results are summarized in Table 1 (Francis and Gillow, 2000).

Methane was produced in most anaerobic samples except those with excess nitrate. Nitrous oxide was detected in the headspace of samples containing excess nitrate. The lack of methane production in samples amended with nitrate-compounds indicates the inhibitory effect of nitrate on methanogenic bacterial activity. In fact, most of the methane detected was in samples that were not amended with any nitrate-containing compounds (NH_4NO_3, KNO_3) at all (unamended and unamend/inoculated samples). This supports the hypothesis of biogenic origin of methane in these samples. Of the initially aerobic samples, only two treatments contained methane (unamended and unamended/inoculated (without bentonite)). In all of the other initially aerobic treatments, the combination of oxygen, nitrate-compounds,

and other alternate electron acceptors (Fe^{3+} provided by bentonite) may have an inhibitory effect on methanogenesis.

Table 3. Methane analysis of inundated cellulose samples. All samples have been corrected for the gas produced in control treatments (without cellulose). nd = not detected.

Sample	1228 Days (nmol g^{-1} cellulose)	2718 Days (nmol g^{-1} cellulose)
Anaerobic		
Unamended	nd	3.92 ± 0.27
Unamended/Inoculated	nd	4.03 ± 1.38
Amended/Inoculated	nd	0.85 ± 0.7
Amended/Inoc. + Exc. Nitrate	nd	nd
Anaerobic + Bentonite		
Unamended	nd	3.84 ± 0.40
Unamended/Inoculated	nd	3.52 ± 0.20
Amended/Inoculated	nd	1.12 ± 0.03
Amended/Inoc. + Exc. Nitrate*	nd	nd
Initially Aerobic		
Unamended	nd	1.25 ± 0.29
Unamended/Inoculated	nd	1.10 ± 0.13

Although the quantities of methane detected are small, the new measurements have demonstrated that the absence of methane production in the previous measurements was due to the inhibitory effect of nitrate or sulfate and the insufficient incubation time period. Based on the experimental data and the observations on natural systems, it can be concluded that methanogenesis will take place in the WIPP repository after microorganisms consume all

nitrate and sulfate. In the next section, based on waste inventory estimates, it is further demonstrated that methanogenesis can eventually become a dominant reaction pathway in the WIPP repository.

AMOUNT OF CARBON DIOXIDE TO BE GENERATED IN WIPP

Inventories of organic materials and electron acceptors (NO_3^- and SO_4^{2-}):

Based on the Transuranic Baseline Inventory Report (DOE/CAO, 1996), the total equivalent cellulosics to be emplaced in the WIPP is estimated to be 2.656×10^7 kg, equivalent to 9.84×10^8 moles of C (Peterson, 1996). The total amounts of nitrate and sulfate in the waste are estimated to be 1.6×10^6 kg and 6.3×10^5 kg, respectively, and equivalently 2.6×10^7 moles of NO_3^- and 6.6×10^6 moles of SO_4^{2-} (DOE, 1996, p. B6-1; Wang and Brush, 1996, p.14). A certain amount of sulfate can be brought into the repository by brine inflow; however, this amount of sulfate is estimated to be less than 4×10^6 moles (Wang and Brush, 1996). Therefore, the total amount of sulfate to be present in the repository is estimated to be 1×10^7 moles.

Fraction of methanogenesis:

As mentioned above, the biodegradation of organic materials in the WIPP will proceed sequentially from Reaction (1) to (3). The fractions of individual degradation pathways can be calculated as follows:

Molar fraction of organic carbon degraded via denitrification
= 1.25 x moles of nitrate/moles of organic carbon
$= 1.25 \times 2.6 \times 10^7 / 9.84 \times 10^8 = 3.3\%$
Molar fraction of organic carbon degraded via sulfate reduction
= 2 x moles of sulfate/moles of organic carbon
$= 2 \times 1 \times 10^7 / 9.84 \times 10^8 = 2\%$
Molar fraction of organic carbon degraded via methanogenesis
= 1 – molar fractions of both denitrification and sulfate reduction
$= 1 - 3.3\% - 2\% = \sim 95\%$.

Therefore, based on the currently inventory estimates, methanogenesis will account for 95% of overall organic carbon degradation.

Total possible quantity of CO_2 to be generated:

Using the fractions of biodegradation pathways calculated above, it can be estimated that one mole of organic C will be converted to $(1 - 95\%) + 95\% \times 0.5 = 0.525$ mole of CO_2. Accordingly, the total possible quantity of CO_2 to be generated in the repository is estimated to be $0.525 \times 9.84 \times 10^8 = 5.17 \times 10^8$ moles, which is about 47.5% less than that estimated for the CCA (Peterson, 1996).

Given the fact that metal corrosion in the repository will generate a significant quantity of H_2, another methanogenesis pathway may also exist, in which methanogenic microbes use both CO_2 and H_2 as substrates to produce methane: $CO_2 + 4H_2 = CH_4 + H_2O$ (Brush, 1995,

p.E-16). As a result, the conversion ratio of organic carbon to CO_2 can be even smaller. Because of lack of experimental data, the second methanogenesis pathway is ignored here.

CONCLUSION

Methanogenesis will be a dominant biodegradation pathway in the WIPP repository and account for 95% of overall organic carbon degradation. Based on the current waste inventory, it is estimated that one mole of organic C will be converted to 0.525 mole of CO_2. Accordingly, the total quantity of CO_2 potentially to be generated in the repository is calculated to be 5.17×10^8 moles, which is about 47.5% less than that estimated for the CCA (Peterson, 1996).

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