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Sandia National Laboratories

Albuquerque, New Mexico 87185-

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to: Martin S. Tierney (6741)

Yifeng Wang Larry Brush

from: Yifeng Wang & Larry Brush (Org. 6748)

subject: Estimates of Gas-Generation Parameters for The Long-Term WIPP Performance Assessment

Introduction

Steel corrosion and organic-material biodegradation have been identified as major gas-generation processes in the WIPP repository (Brush, 1995). Gas production will affect room closure and chemistry (Butcher, 1990; Brush, 1990). This memorandum provides the current estimates of gas-generation parameters for the long-term WIPP performance assessment. The parameters provided here include the rates of gas generation under inundated and humid conditions, the stoichiometric factors of gas generation reactions, and the probability of the occurrence of organic material biodegradation (Table 1). To satisfy the quality assurance (QA) requirement (QAP 9-5), we summarize all hand calculations for estimating these parameters in Appendices I and II.

Biodegradation of Organic Materials

Cellulosics, plastics, and rubbers have been identified as the major organic materials to be emplaced in the WIPP repository (DOE/CAO, 1996) and could be degraded by microbes in 10,000 years. Cellulosics has been demonstrated experimentally to be the most biodegradable among these materials (Francis et al., 1995). The occurrence of significant microbial gas generation in the repository will depend on: (1) whether microbes capable of consuming the emplaced organic materials will be present and active; (2) whether sufficient electron acceptors will be present and available; (3) whether enough nutrients will be present and available. Considering uncertainties in evaluation of these factors and also in order to bracket all possible effect of gas generation on the WIPP performance assessment, we assign a 50% probability to the occurrence of significant microbial gas generation.

• *Microbial Reactions*

Microorganism will consume cellulosics mainly via the following reaction pathways in the repository (Brush, 1995):

$$C_6H_{10}O_5 + 4.8\ H^+ + 4.8\ NO_3^- \rightarrow 7.4\ H_2O + 6\ CO_2 + 2.4\ N_2 \quad (1)$$
$$C_6H_{10}O_5 + 6\ H^+ + 3\ SO_4^{2-} \rightarrow 5\ H_2O + 6\ CO_2 + 3\ H_2S \quad (2)$$

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

We assume that Reactions 1 to 3 will proceed sequentially according to the energy yield of each reaction. Here we ignore the reaction pathways of aerobic respiration, Mn(IV) and Fe(III) dissimilatory reduction, since the quantities of O_2, Mn(IV) and Fe(III) initially present in the repository will be negligible relative to the other electron acceptors. In Reactions 1 to 3, biomass accumulation is also not taken into account. This is because significant biomass accumulation seems unlikely in the WIPP repository and the accumulated biomass, if any, will be recycled by microbes after all biodegradable cellulosics is consumed.

In addition to Reaction (3), methanogenesis may proceed via:

$$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O. \quad (4)$$

However, this reaction will be ignored in our calculations, because (1) no experimental data are available to evaluate the rate of this reaction and (2) the net effect of this reaction is to reduce the total gas generation and the amount of CO_2 in the repository and, therefore, it is conservative to ignore this reaction in respect of repository pressurization and actinide solubility.

- *Rates of Cellulosics Biodegradation*

The rate of cellulosics biodegradtion was measured by incubating representative cellulose materials (filter paper, paper towels, and tissue) in WIPP brine with microbes enriched from various WIPP environments (Francis & Gillow, 1994; Francis et al., 1995). The incubation experiments were conducted under various conditions: aerobic or anaerobic, inundated or humid, with or without bentonite, amended or unamended with nutrients or NO_3^-. Because the repository is expected to become anoxic shortly after waste emplacement and also because bentonite will not be added as a backfill according to the current waste emplacement plan, we think that the experimental data from anaerobic incubation without bentonite present are most relevant to expected WIPP conditions. Considering that the current experimental data are mostly for denitrification (Reaction 1), but not sulfate reduction (Reaction 2) and methanogenesis (Reaction 3) (Francis & Gillow, 1994; Francis et al., 1995), we assume that the ranges of the rates of cellulosics biodegradation via sulfate reduction and methanogenesis are equal to those observed for denitrification.

We use CO_2 production data to estimate the rates of cellulosics biodegradation. There are two advantages of using CO_2 production data: (1) there are experimental data available on the CO_2 dissolution in WIPP brine (Telander & Westerman, 1995) and, therefore, it is easy to correct the CO_2 production data for gas dissolution (Appendix I); (2) since cellulosics biodegradation did not reach the stage of methanogenesis in the experiments, according to

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Reactions 1 and 2, the consumption of one mole carbon of cellulosics will produce one mole of CO_2. This 1:1 relationship is independent of oxidation state of carbon in cellulosics. Therefore, it is rather straightforward to determine the amount of cellulosics biodegraded from the amount of CO_2 produced.

Experimental data show a strong dependence of CO_2 generation on the concentrations of nutrients and nitrate (Francis & Gillow, 1994; Francis et al., 1995). The maximum CO_2 generation was observed in nitrate-and-nutrient-amended samples. In those experiments, after a short lag phase, CO_2 first linearly increased with time and then approached some limiting value as its production rate diminished. If we assume that biodegradation is nitrate- or nutrient-limited, the experimental data can be explained by Michaelis-Menton kinetics (Chapelle, 1993). Michaelis-Menton kinetics, which describes the dependence of microbial reaction rate on substrate concentration, can be expressed by:

$$V = \frac{V_{max} S}{K_s + S} \tag{5}$$

where V is the microbial reaction rate; V_{max} is the maximum value of the rate; S is the concentration of the limiting substrate; K_s is a constant. Equation (5) states that the microbial reaction rate becomes independent of the substrate concentration, if the latter is high enough, i.e. $S >> K_s$ and $V = V_{max}$. In this circumstance, the reaction product will accumulate linearly with time before the substrate is sufficiently depleted. In other words, in our cases, the linear part of CO_2 vs. time curve will give the estimate of the maximum rate of cellulosics biodegradation.

From the experimental data of Francis & Gillow (1994) and Francis et al. (1995), we estimate the maximum and minimum rates of cellulosics biodegradation under inundated conditions to be 0.3 and 0.01 mole C/kg/year, respectively (Appendix I). The maximum rate is estimated from the data obtained from both NO_3^-- and nutrients-amended experiments, whereas the minimum rate is derived from the data obtained from the inoculated-only experiments without any nutrient and NO_3^- amendment. Under humid conditions, experimental data show no clear correlation between CO_2 production and nutrient concentration. The best estimate of the maximum rate of cellulosics biodegradation under humid condition is 0.04 mole C/kg/year (Appendix I). The minimum of the humid biodegradation rate is set to 0, corresponding to the cases where microbes become inactive due to nutrient and water stress.

- *Biodegradation of Plastics and Rubbers*

The rates of plastics and rubber biodegradation under expected WIPP conditions were

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measured by Francis et al.(1995). The experimental data show that plastics and rubbers are much less biodegradable than cellulosics, although the data themselves are not sufficient for us to constrain the long-term biodegradation rate for plastics and rubbers. There are two factor that may potentially increase the biodegradibility of those materials: long time scale and cometabolism. Over a time scale of 10,000 years, plastics and rubbers may change their chemical properties and therefore their biodegradibility. Cometabolism means that microbes degrade an organic compound but do not use it as a source of energy or of their constituent elements, all of which are derived from other substrates (Alexander, 1994). In the WIPP repository, plastics and rubbers, which are resistant to biodegradation, may still be cometabolized with cellulosics and other more biodegradable organic compounds. Because of these uncertainties, we recommend a 50% chance for the biodegradation of plastics and rubbers in the event of significant microbial gas generation. We further suggest lumping plastics and rubbers into cellulosics and applying the ranges of cellulosics biodegradation rate to plastics and rubbers. This treatment is conservative in respect of repository pressurization and actinide solubility. We propose to use the following equation to convert plastics and rubbers to the carbon-equivalent quantity of cellulosics (Appendix I):

$$\text{total cellulosics (kg)} = \text{actual cellulosics (kg)} + 1.7\ \text{plastics (kg)} + \text{rubbers (kg)}. \quad (6)$$

Anoxic Steel Corrosion

According to current waste inventory estimates, a large amount of steels will be emplaced in the WIPP repository (DOE/CAO, 1996). Those steels will be capable of reacting with the repository brine to form H_2 gas. Both thermodynamic calculations and experimental observations indicate that the H_2 gas can be generated to pressures exceeding the lithostatic pressure at the WIPP horizon, if enough brine enters the repository (Brush, 1990; Telander & Westerman, 1993, 1995). Since the repository will become anoxic shortly after waste emplacement and sealing, we here focus only on anoxic steel corrosion.

- *Steel Corrosion in the Absence of CO_2 and H_2S*

In this case, steel corrosion will follow the reaction (Telander & Westerman, 1993, 1995):

$$Fe + 2\ H_2O \rightarrow Fe(OH)_2 + H_2. \quad (7)$$

In the Mg-rich WIPP brines (exemplified by Brine A), a significant fraction of Fe in the corrosion product is substituted by Mg. This substitution can substantially increase the stability of the corrosion product. Experimental observations indicate that steel corrosion can still proceed even at an 127 atm H_2 pressure (Telander & Westerman, 1995). Aside from this thermodynamic stability argument, the experimental observations indicate no

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essential effect of Mg in the brine on the corrosion rate. As a matter of fact, the corrosion rates measured in Mg-rich Brine A are not significantly different from those measured in Mg-depleted Brine ERDA-6 (Telander & Westerman, 1995).

It was observed in the experiments that the steel corrosion rate decreased with time until some limiting rate was achieved (Telander & Westerman, 1995). Our long-term corrosion rate is estimated from the longest-term data available in a WIPP-relevant Brine A environment. The estimated inundated rate is 0.5 μm/year or 0.07 mole Fe /m^2/year (Appendix II). In addition, the corrosion rate is also found to increase with decreasing brine pH (Telander & Westerman, 1993, 1995). Without addition of CO_2 from microbial reactions, the pH in the repository is unlikely to go below its experimental value, which is about 10 (Telander & Westerman, 1993, 1995). Therefore, we recommend using 0.5 μm/year as the upper limit of inundated corrosion rate for the cases without microbial gas generation. On the other hand, the pH in the repository can be ~2 units higher than its experimental value due to the presence of $Ca(OH)_2$ as a cementious material in the waste, and thus, based on the scaling factor (= 0.01) given by Telander & Westerman (1995), the steel corrosion rate could be as low as 0.005 μm/year. In addition, the experimental work for Source Term Test Program (STTP) at Los Alamose National Laboratory indicates that salt crystallization on steel surface may possibly prevent the steel from corrosion. To include this possibility, we set the minimum inundated steel corrosion rate to 0.

The corrosion rate observed on specimens exposed to humid conditions is negligible, based on essentially non-existent presence of corrosion product and lack of apparent H_2 generation (Telander & Westerman, 1995). Therefore, we set the humid steel corrosion rate to 0.

- *Steel Corrosion in the Presence of CO_2 and H_2S*

In the event of significant microbial gas generation, steel corrosion can proceed via the following reactions in addition to Reaction (7) (Telander & Westerman, 1993, 1995):

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \quad (8)$$

$$Fe + H_2S \rightarrow FeS + H_2. \quad (9)$$

One possible effect of CO_2 and H_2S on steel corrosion is that they may cause passivation of the steel. Steel passivation was observed in the experiments in which large quantities of CO_2 and H_2S were added to the reaction vessels. It usually took place after tens of days and was caused by the formation of a protective layer of $FeCO_3$ or FeS on steel surfaces (Telander & Westerman, 1995). However, we think that this passivation is unlikely to occur under the repository conditions. This is because the microbial production rate of CO_2 and H_2S is too slow and it will take an exceedingly long time period (relative to the experimental time scale) for these gases in the repository to reach their concentration levels required for

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passivation under the experimental conditions. The conclusion of no steel passivation under the WIPP repository conditions is consistent with other studies (e.g., Ikeda et al., 1983; Schmitt, 1983). In fact, aside from the previously cited work of Telander & Westerman (1993), total passivation of steel by CO_2 and H_2S in low-temperature solutions has not been reported, though varying degrees of corrosion inhibition have been observed.

In the absence of passivation, the microbial generation of CO_2 and H_2S will increase steel corrosion rates in the repository either by lowering the repository pH or by initiating additional reaction pathways (Reactions 8 and 9) (Telander & Westerman, 1995). We take this effect into account by modifying the sampling range of steel corrosion rate. Obviously, Reactions 8 and 9 will be limited by microbial CO_2 and H_2S production, and therefore the upper limit of the reaction rate can be estimated from the maximum cellulosics biodegradation rate, which is 0.3 mole/kg cellulosics/year, equivalent to 6 μm/year of steel corrosion rate (Appendix II). Thus, in the event of significant microbial gas generation, the upper limit of steel corrosion rate is 6.5 μm/year, the sum of the maximum rates of Reactions 7 through 9. The corresponding lower limit will be kept the same as that estimated for the cases without CO_2 production, i.e. 0.0 μm/year. Under humid conditions, experimental results show a negligible effect of CO_2 and H_2S on steel corrosion (Telander & Westerman, 1995). We thus set the humid corrosion rate to 0.

Stoichiometric Factors in the Average-Stoichiometry Model

In the Average-Stoichiometry Model, which is currently implemented in BRAGFLO, microbial gas generation is represented by the overall reaction:

$$\frac{1}{6}C_6H_{10}O_5 \; + \; unknown \; \rightarrow \; y \; gas \; + \; unknown \qquad (10)$$

and H_2 production due to steel corrosion is described by:

$$Fe \; + \; \frac{4+2x}{3} \; H_2O \; \rightarrow \; \frac{4-x}{3} \; H_2 \; + \; x \; Fe(OH)_2 \; + \; \frac{1-x}{3} \; Fe_3O_4. \qquad (11)$$

The stoichiometric factors x and y in Reaction 10 and 11 are estimated as follows.

• *Average-Stoichiometric FactorY in Microbial Reaction*

The stoichiometric factor y depends on the extent of the progress of each individual reaction pathway (Reactions 1 through 3). It can be estimated based on the inventory estimates of the transuranic waste to be emplaced in the Waste Isolation Pilot Plant (DOE/CAO, 1996; Drez, 1996).

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First, we estimate the maximum quantities (in moles) of cellulosics and steels that will be potentially consumed in 10,000 years:

$$M'_{cel} = \min \left\{ \frac{6000 M_{cel}}{162},\ 10000 R'_C M_{cel} \right\} \tag{12}$$

$$M'_{Fe} = \min \left\{ \frac{1000 M_{Fe}}{56},\ 1410 R_{c,i} A \right\} \tag{13}$$

with

$$R'_c = \max \left\{ R_{m,i},\ R_{m,h} \right\} \tag{14}$$

A is the total surface area of steel (m^2)

where M_{cel} and M_{Fe} are the quantities (in kg) of cellulosics and steels initially present in the repository; $R_{c,i}$ is the inundated steel-corrosion rate (μm/year); $R_{m,i}$ and $R_{m,h}$ are the sampled rates of cellulosics biodegradation under inundated and humid conditions respectively (mole/kg/year). In Equation (13), we use the factor of 0.141 mole/μm/m^2 to convert steel-corrosion-rate unit from μm/year to mole/m^2/year (Telander and Westerman, 1995). Here, we assume that cellulosics biodegradation and steel corrosion both follow zero order reaction kinetics. Next, we calculate the average stoichiometric factor y by distributing M'_{cel} into individual biodegradation pathways. Consider two extreme cases, corresponding to the maximum and minimum values of y: (1) no reaction of microbially produced CO_2 and H_2S with steel and steel-corrosion products; (2) complete reaction of microbially produced CO_2 and H_2S with steel and steel-corrosion products.

If no CO_2 or H_2S is consumed by reactions with steel and steel-corrosion products, we would expect the maximum quantity of microbial gas production in the repository and therefore the maximum value for y. We assume that Reactions 1 to 3 will proceed sequentially. The maximum value of y can be estimated by averaging the gas-yields for all reaction pathways:

$$y_{\max} = \frac{\frac{8.4 M_{NO3}}{4.8} + \frac{9 M_{SO4}}{3} + \left(M'_{cel} - \frac{6 M_{NO3}}{4.8} - \frac{6 M_{SO4}}{3} \right)}{M'_{cel}} \tag{15}$$

where M_{NO3} and M_{SO4} are the quantities of NO_3^- and SO_4^{2-} (in moles) initially present in the repository.

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If CO_2 or H_2S reacts with steel and steel-corrosion products, we expect that a significant quantity or, perhaps, all of these microbially produced gases would be consumed, thus forming $FeCO_3$ and FeS. This would result in the minimum value of y. The total gas consumed by those reactions (G) is:

$$G = \min\left\{\frac{6M_{NO3}}{4.8} + \frac{9M_{SO4}}{3} + \frac{3}{6}\left(M'_{cel} - \frac{6M_{NO3}}{4.8} - \frac{6M_{SO4}}{3}\right),\ M'_{Fe}\right\} \tag{16}$$

The minimum value of y can then be estimated by:

$$y_{\min} = \frac{\frac{8.4M_{NO3}}{4.8} + \frac{9M_{SO4}}{3} + \left(M'_{cel} - \frac{6M_{NO3}}{4.8} - \frac{6M_{SO4}}{3}\right) - G}{M'_{cel}} = y_{\max} - \frac{G}{M'_{cel}} \tag{17}$$

For each BRAGFLO simulation, y will be uniformly sampled over $[y_{min}, y_{max}]$:

$$y = y_{\min} + \beta(y_{\max} - y_{\min}) \tag{18}$$

with $0 \le \beta \le 1.0$. The calculational scheme proposed here automatically correlates y with waste inventory estimates as well as with reaction rates.

The above calculational scheme does not take into account the SO_4^{2-} that will be brought into repository by brine inflow. Based the previous BRAGFLO simulations for undisturbed cases, the total volume of the brine entering the repository in 10000 years is unlikely to be larger than $2.2x10^7$ liters, the value corresponding to the case with unrealistically low gas generation and therefore the worst repository flooding. With a typical SO_4^{2-} concentration of 200 mM in WIPP brines (Brush, 1990), we estimate that the amount of SO_4^{2-} brought into the repository by brine inflow would be less than $0.4x10^7$ moles. This amount of SO_4^{2-} will increase the fraction of sulfate reduction pathway in total cellulosics biodegradation only by less than 1%. Therefore, neglecting the sulfate brought by brine inflow would introduce an error of no more than a few percents in y values.

• *Average-Stoichiometric FactorX in Steel Corrosion Reaction*

While magnetite (Fe_3O_4) has been observed to form on steel as a corrosion product in low-Mg anoxic brines at elevated temperatures (Telander & Westerman, 1995) and in oxic brine (Haberman & Frydrych, 1988), there is no evidence that it will form at WIPP repository temperatures. If Fe_3O_4 were to form, it would be expected that H_2 would be produced (on a molar basis) in excess of Fe consumed. But, the anoxic corrosion experiments did not show the production of H_2 in excess of Fe reacted. Therefore, we set the stoichiometric factor x to 1.0 in Reaction 11.

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Table 1. Gas-Generation Parameters for the Long-Term WIPP Performance Assessment

Parameter	Estimated Value
Probability of occurrence of significant microbial gas generation	50%
Probability of occurrence of plastics and rubber biodegradation in the event of significant gas generation	50%
Rate of inundated cellulosics biodegradation	0.01 - 0.3 mole C/kg/year
Rate of humid cellulosics biodegradation	0.0 - 0.04 mole C/kg/year
Rate of inundated steel corrosion for the cases without microbial gas generation	0.0 - 0.5 μm/year[1]
Rate of humid steel corrosion for the cases without microbial gas generation	0.0 μm/year
Rate of inundated steel corrosion for the cases with microbial gas generation	0.0 - 6.5 μm/year
Rate of humid steel corrosion for the cases with microbial gas generation	0.0 μm/year
Stoichiometric factor x in Reaction 11	1.0
Stoichiometric factor y in Reaction 10	calculated from Eqn. (18)
Factor β in Equation 18	0 - 1.0
NO_3^- initially present in the waste[2]	2.6×10^7 moles
SO_4^{2-} initial present in the waste[2]	6.6×10^6 moles

1. Multiplying 0.141 mole/μm/m^2 will convert the unit of steel corrosion rate from μm/year to mole/m^2/year (Telander & Westerman, 1993). 2. See Appendix I.6.

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Appendix I. Hand Calculations for Estimating Microbial Gas generation Parameters

Name of person performing the calculations: Yifeng Wang, Jan. 26, 1996 Yifeng Wang
Name of person reviewing the calculations: Larry Brush, Jan. 26, 1996 Larry Brush

I.1 Correction for CO_2 Dissolution in the Brine

Data and definition of variables:

TCO_2: Total CO_2 produced in an incubating experiment (moles)
n: Measured CO_2 in headspace (moles)
C_l: Dissolved CO_2 (moles/l)
V_l: Brine volume = 0.104 (l) (Gillow, per. comm.)
V_g: Headspace volume 0.046 (l) (Francis & Gillow, 1994)
P: Partial pressure of CO_2 (atm)
K: Partition coefficient of CO_2 between brine and gas phase = 0.01 (mole/l/atm) (Telander & Westerman, 1995)
R: Gas constant = 0.082 (l•atm/mole/K)
T: Temperature = 303.15 (K)

Assumption: Gaseous CO_2 approximately follows the idea gas law during these experiments.

Calculations:

$TCO_2 = V_l*C_l + n = K*P*V_l + n = K*V_l*n*R*T/V_g + n = (K*V_l*R*T/V_g + 1)*n =$
$(0.01*0.104*0.082*303.15/0.046 + 1)*n = 1.56*n$ (moles).

I.2 Estimate of the Maximum Inundated Cellulosics Biodegradation Rate

Data:

Source: Francis et al. 1995, p. 41, 148-149.
Experimental conditions: anaerobic inoculated, nutrients and nitrate amended

We only take the linear part of CO_2 vs. time curve:

time	CO_2
69 days	6.1 µmol/g of cel.
411 days	163 µmol/g of cel.

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Calculations:

(1) Rate = (163 - 6.1)/(411 - 69) = 0.459 micro-moles/g/day = 0.168 mole/kg/year.
(2) Correcting it for dissolved CO_2 (see I.1), we finally have:
maximum rate = 0.168*1.56 = 0.3 mole/kg/year.

I.3 Estimate of the Minimum Inundated Cellulosics Biodegradation Rate

Data:
Source: Francis et al. 1995, p. 148-149.
Experimental conditions: anaerobic, inoculated only,

time	CO_2
0 days	2.1 µmol/g of cel.
1034 days	14.0 µmol/g of cel.

Calculations:
(1) Rate = (14.0 - 2.1)/(1034 - 0) = 0.0115 µmol/g/day = 0.004 mole/kg/year.
(2) Correcting it for dissolved CO_2 (Appendix I.1), we finally have:
minimum rate = 0.004*1.56 = 0.01 mole/kg/year.

I.4 Estimate of the Maximum Humid Cellulosics Biodegradation Rate

Data:
Source: Francis et al. 1995, p. 80.
Experimental conditions: anaerobic, inoculated only;
anaerobic, inoculated and amended

time	CO_2
6 days	(7.7 + 13.3)/2 = 10.5 µmol/g of cel.
415 days	(83.1 + 28.8)/2 = 56 µmol/g of cel.

Calculations:
Maximum rate = (56 - 10.5)/(415 - 6) = 0.11µmol/g/day = 0.04 mole/kg/year.

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I.5 Convert Plastics and Rubbers to the Equivalent Quantity of Cellulosics

Data:

Source: Molecke (1979)

Celllulosics: $C_6H_{10}O_5$	M. W. = 162 g/mole
Polyethylene: $(-C_2H_4-)n$	M. W. = 28 g/mole
Polyvinychloride: $(-C_2H_3Cl-)n$	M. W. = 62 g/mole
Neoprene: $(-C_4H_5Cl-)n$	M. W. = 88 g/mole
Hypalon: $(-(C_7H_{13}Cl)_{12}-(CHSO_2Cl)_{17}-]n$	M. W. = 3488 g/mole

Assumption:

Plastics: 80% polyethylene, 20% polyvinychloride
Rubbers: 50% neoprene, 50% hypalon
Based on Molecke (1979).

Calculations:

The P kilograms of plastics and R kilograms of rubbers are equivalent to the Q kilograms of cellulosics, based on carbon equivalence:

$Q = (0.8*2*162/28/6 + 0.2*2*162/62/6)*P + (0.5*4*162/88/6 + 0.5*101*162/3488/6)*R = 1.7\ P + R$ (kilograms)

I.6 Moles of NO_3^- and SO_4^{2-} Initially Present in the Waste

NO_3^- : $1.62x10^6$ kg (Drez, 1996) = $1000/62*1.62x10^6 = 2.6x10^7$ moles
SO_4^{2-} : $6.33x10^5$ kg (Drez, 1996) = $1000/96*6.33x10^5 = 6.6x10^6$ moles

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Appendix II. Hand Calculations for Estimating Steel Corrosion Parameters

Name of person performing the calculations: Yifeng Wang, Jan. 26, 1996
Name of person reviewing the calculations: Larry Brush, Jan. 26, 1996

Yifeng Wang
Larry Brush

II.1 Estimate of the Maximum Inundated Steel Corrosion Rate for the Cases without Microbial Gas Generation

Data:

(1) Anoxic corrosion rate obtained from the 12th to 24th month experimental data = 0.71 μm/year (Telander & Westerman, 1993, p. 6-14).

(2) Scaling factor for the long-term rate = 70% (Telander & Westerman, 1995, p. 6 - 19).

Calculation:

The maximum long-term steel corrosion rate = 0.71*70% = 0.5 μm/year.

II.2 Estimate the Maximum Inundated Steel Corrosion Rate for the Cases with Microbial Gas Generation

Data:

Total transuranic waste volume: $1.4x10^5$ m^3 (DOE/CAO, 1996)
Drum volume: 0.208 m^3 (DOE/CAO, 1996)
Surface area of steel: 6 m^2/drum (Brush, 1995)
Maximum cellulosics biodegradation rate: 0.3 mole/kg/year (Appendix I.2)
Maximum inundated steel corrosion rate for the cases without microbial gas generation: 0.5 μm/year.
Total cellulosics (including plastics and rubbers): $2.0x10^7$ kg (DOE/CAO, 1996; Appendix I.5)
NO_3^- initially present in the waste: $2.6x10^7$ moles (Appendix I.6)
SO_4^{2-} initial present in the waste: $6.6x10^6$ moles (Appendix I.6)

Assumption:

Reactions 8 and 9 will be limited by microbial CO_2 and H_2S production rate.

Calculations:

(1) Number of drums = $1.4x10^5/0.208 = 6.7x10^5$ drums.

(2) Total moles of C in cellulosics = $6*2.0x10^7*1000/162 = 7.4x10^8$ moles of C.

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Molar fraction of cellulosics biodegraded via denitrification = $2.6 \times 10^7 / 7.4 \times 10^8 = 4\%$.

Molar fraction of cellulosics biodegraded via sulfate reduction = $6.6 \times 10^6 / 7.4 \times 10^8 = 1\%$.

(3) Maximum CO_2 and H_2S production rate for the whole repository = $(0.04 + 1.5*0.01 + 0.5*0.95)*0.3*2.0 \times 10^7 = 3.2 \times 10^6$ moles CO2/year.

(4) Total steel surface area = $6*6.7 \times 10^5 = 4.0 \times 10^6$ m^2.

(5) The maximum rate of steel corrosion via Reactions 8 and 9 = $3.2 \times 10^6 / 4.0 \times 10^6 =$ 0.8 mole Fe/m^2/year = 6 μm/year.

(6) The upper limit of inundated steel corrosion rate for the cases with microbial gas generation = 0.5 + 6 = 6.5 μm/year.

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