Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant

MASS Attachment 8-1

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wpo36290

Sandia National Laboratories

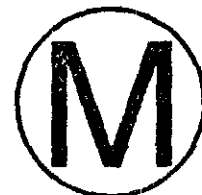Albuquerque, New Mexico 87185-1341

date: November 30, 1995

to: M. S. Y. Chu, MS 1335 (Org. 6801)

L. H. Brush   Yifeng Wg

from: L. H. Brush, MS-1341 (Org. 6748), Y. Wang, MS-1341 (Org. 6748), and
J. W. Garner, MS-1328 Org. 6749)

(M)

subject: Rationale for Discontinuing the Development of the Reaction-Path Gas-
Generation Model

We are discontinuing the development of the reaction-path gas-generation model at this time because: (1) we do not need the reaction-path model to obtain parameters for use in Brine and Gas Flow (BRAGFLO) for the 1996 performance-assessment (PA) calculation nor for use in the EQ3/6 calculations to support the Actinide Source Term Program (ASTP); (2) some of the conceptual models upon which the reaction-path model is based are no longer defensible; (3) if additional development of a gas-generation model is necessary in the future, we should use an approach different from that used by Brush et al. (1994) to develop the reaction-path model.

LACK OF NEED FOR THE REACTION-PATH MODEL

The main advantage of the reaction-path model (Brush et al., 1994) relative to the average-stoichiometry gas-generation model currently in BRAGFLO (WIPP Performance Assessment Division, 1991; Sandia WIPP Project, 1992) was that the reaction-path model includes passivation of steels and other Fe-base alloys by microbially produced CO_2 and H_2S, the most important interaction among gas-generation processes observed in laboratory studies of gas generation. Therefore, the reaction-path model predicted significant gas generation from anoxic corrosion of steels and other Fe-base alloys, or from microbial degradation of cellulosics, but not from both of these processes in the same realization. However, PA personnel have incorporated a switch in the average-stoichiometry model that essentially predicts the effects of passivation (gas production from corrosion or microbial activity, but not both). Furthermore, recent results from laboratory studies of anoxic corrosion fail to support passivation of steels by CO_2. These results imply that, although microbial activity can produce *enough* CO_2 to passivate steels and other Fe-base alloys, it probably will not produce CO_2 *fast enough* for passivation (Telander and Westerman, 1993; Francis and Gillow, 1994; Francis et al., in prep.; Telander and Westerman, in prep.). Therefore, the main advantage of the reaction-path model relative to the average-stoichiometry model no longer exists.

Moreover, we can use hand calculations instead of the reaction-path model to obtain parameters for use in BRAGFLO for the 1996 PA calculation and for the EQ3/6 calculations to support the ASTP. The average-stoichiometry model uses the overall reaction
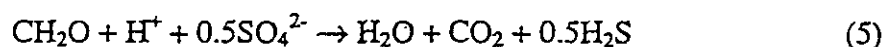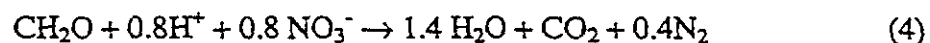
$$CH_2O + unknowns \rightarrow (y)gas + unknowns \qquad (1)$$
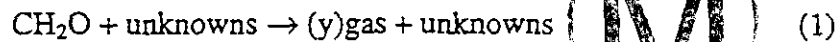
We can estimate the stoichiometric factor y independently based on estimates of the quantities of NO_3^- and SO_4^{2-} in the transuranic (TRU) waste to be emplaced in the Waste Isolation Pilot Plant (WIPP) and the experimentally determined corrosion rate for steels (R_c), and rate of microbial consumption of cellulosics (R_m) under inundated conditions. First, we use the rates R_c and R_m to estimate the maximum quantities of steels and cellulosics that will be consumed in 10,000 years:
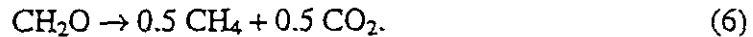
$$[Fe]_{max} = min \ \{[Fe]_i, \ [Fe]_i \bullet [1 - exp(-10000*R_c)]\}; \qquad (3)$$

$$[Cell]_{max} = min \ \{[Cell]_i, \ [Cell]_i \bullet [1 - exp(-10000*R_m)]\} \qquad (2)$$

where $[Fe]_i$ and $[Cell]_i$ are the quantities (in moles) of steels and cellulosics initially present in the repository, and the units of R_c and R_m are both $year^{-1}$. Next, we calculate the average stoichiometric factor y by distributing $[Cell]_{max}$ into individual microbial respiratory 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 steels and steel corrosion products; (2) complete reaction of CO_2 and H_2S with steels and steel-corrosion products.

If no CO_2 or H_2S are consumed by reactions with steels and steel-corrosion products, we would expect the maximum quantity of microbial gas production in WIPP disposal rooms and, therefore, the maximum value for y. Microorganisms will consume cellulosics via the following reaction pathways:

$$CH_2O + 0.8H^+ + 0.8 \ NO_3^- \rightarrow 1.4 \ H_2O + CO_2 + 0.4N_2 \qquad (4)$$

$$CH_2O + H^+ + 0.5SO_4^{2-} \rightarrow H_2O + CO_2 + 0.5H_2S \qquad (5)$$

$$CH_2O \rightarrow 0.5\ CH_4 + 0.5\ CO_2. \tag{6}$$

The maximum value of y can estimated from these reactions by:

$$y_{max} = \{\ 1.4/0.8 \bullet [NO_3^-]_i + 1.5/0.5 \bullet [SO_4^{2-}]_i$$

$$+ [Cell]_{max} - [NO_3^-]_i/0.8 - [SO_4^{2-}]_i/0.5\}/[Cell]_{max} \tag{7}$$

in which $[NO_3^-]_i$ and $[SO_4^{2-}]_i$ are the molar quantities of NO_3^- and SO_4^{2-} initially present in the repository.

If CO_2 and H_2S react with steels 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:

$$G = min\ \langle\{[NO_3^-]_i/0.8 + 1.5/0.5 \bullet [SO_4^{2-}]_i$$

$$+ 0.5 \bullet \{[Cell]_{max} - [NO_3^-]_i/0.8 - [SO_4^{2-}]_i/0.5\},\ [Fe]_{max}\rangle. \tag{8}$$

The minimum value of y can estimated from these reactions by:

$$y_{min} = \{\ 1.4/0.8 \bullet [NO_3^-]_i + 1.5/0.5 \bullet [SO_4^{2-}]_i$$

$$+ [Cell]_{max} - [NO_3^-]_i/0.8 - [SO_4^{2-}]_i/0.5 - G\}/[Cell]_{max} \tag{9}$$

For each BRAGFLO simulation, the value y should be sampled over $[y_{min},\ y_{max}]$. The calculational scheme proposed here would automatically correlate y with waste-inventory estimates as well as with reaction rates. *This scheme would allow us to estimate y independently without having to use the reaction-path model.*

The average stoichiometry model does not predict the types of gases produced by Reaction 1 (see above). However, we can use hand calculations analogous to those

described above to estimate the yield of CO_2 from Reaction 1. We can then use these predictions of the quantity of CO_2 as input to EQ3/6 to calculate total quantity of inorganic C dissolved in WIPP brines, its speciation (CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}), and the pH of these brines for the ASTP. EQ3/6 is a geochemical software package developed mainly by personnel at Lawrence Livermore National Laboratory (Daveler and Wolery, 1992; Wolery, 1992a; 1992b; Wolery and Daveler, 1992) for use by the Yucca Mountain Project.

We estimate that, *if the conceptual models upon which the reaction-path model is based were defensible (see below)*, upgrading the QA status of the reaction-path model to Level A would require about one to two man years of effort. (This effort would comprise preparing a combined Requirements Document and Verification and Validation Plan, a Validation Document, and a User's Manual for this model.) It is hard to envision how we could accomplish these tasks at a time when the WIPP Project is reducing the resources allocated to the Gas Generation Program, yet requiring that we deliver gas-generation data to PA and produce the final reports on the laboratory studies of gas generation two months earlier than originally scheduled. We believe that this effort is unnecessary in view of the fact that we can use hand calculations to obtain parameters for use in BRAGFLO for the 1996 PA calculation and for the EQ3/6 calculations to support the ASTP.

CONCEPTUAL BASIS OF THE REACTION-PATH MODEL

Some of the conceptual models upon which the reaction-path model is based are no longer defensible. Problems or potential problems revealed by reviewers and/or the laboratory studies of gas generation include: (1) the thermodynamically calculated phase boundaries in the model are based on free energies of formation for pure (Mg-free) steel-corrosion products, but at least some of these phases probably include significant quantities of Mg under expected WIPP conditions; (2) high-pressure corrosion studies (Telander and Westerman, 1993; in prep.) imply that the $Fe(OH)_2$-forming corrosion reaction does not stop at about 70 atm as predicted, probably due at least in part to substitution of Mg for Fe in this corrosion product, but perhaps also due to the fact that the crystal structure of this phase is different from that of amakinite, the only $Fe(OH)_2$ polymorph for which the free energy of formation is available; (3) some of the corrosion studies imply that the assumption of instantaneous, reversible equilibrium is invalid.

Because some of the conceptual models on which the reaction-path model is based are probably no longer defensible, significant additional work would be required before the QA status of this model could be upgraded to Level A. Additional laboratory studies would be necessary to: (1) determine the extent of Mg substitution in steel-

corrosion products, especially $Fe(OH)_2$; (2) determine the free energy of formation of $(Fe,Mg)(OH)_2$ and, perhaps, the free energies of formation of other corrosion products that contain significant Mg under expected WIPP conditions; (3) determine the H_2 partial pressure at which steels are in equilibrium with $(Fe,Mg)(OH)_2$; (4) evaluate the assumption of instantaneous, reversible equilibrium. These laboratory studies would require at least several man months and, perhaps, a few man-years of effort. Upon completion of these studies, modification of the reaction-path model to incorporate the results would probably require several man-months of work.

PROPOSED APPROACH FOR ADDITIONAL MODEL DEVELOPMENT

We believe that, to address the problems and potential problems with the conceptual models described above, it would be unwise to continue to pursue the overall approach used by Brush et al. (1994) to develop the reaction-path model. This approach consisted of using the corrosion, microbial, and radiolytic reactions observed during laboratory studies of gas generation as the basis for a simplified reaction-path model that operates independently of other reactions expected in WIPP disposal rooms. These other reactions include dissolution of gases such as CO_2 and H_2S in brines, reactions between brines and other constituents of the waste such as $Ca(OH)_2$ in cementitious materials used to solidify process sludges, mixing of brines during human intrusion, and reactions between brines and evaporite minerals in the surrounding Salado Formation. Brush et al. (1994) decided to use the reaction-path model to simulate the gas-generation reactions, especially passivation of steels and other Fe-base alloys by microbially produced CO_2 and H_2S, and to use models such as EQ3/6 to simulate other reactions expected in the repository.

The approach we favor now would be to incorporate gas-generation reactions into a global (WIPP-disposal-room-scale) model such as EQ3/6 by obtaining Pitzer ion-interaction parameters for the reactants and products of these reactions for which Pitzer parameters do not yet exist. This is, essentially, the approach being used by the ASTP to develop the actinide-source-term model. Because it would require an experimental program similar to the ASTP solubility program, we could only implement such an approach if the Environmental Protection Agency (EPA) specifies that significant additional work on gas generation is required.

Furthermore, we would still need a greatly (computationally) simplified model such as the average-stoichiometry model for use in BRAGFLO. (It would probably be infeasible to couple BRAGFLO and EQ3/6).
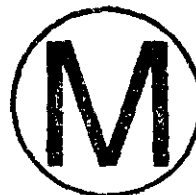
ADDITIONAL COMMENTS ON THE REACTION-PATH MODEL

We believe the reaction-path model has been a valuable research tool. It has been a significant asset for planning and interpreting the results of laboratory studies of gas generation. We believe the reaction-path model can continue to be a valuable research tool as long as we do not use any results from this model, either directly or indirectly, for PA calculations or for other compliance-related activities.

We believe the efforts spent on the reaction-path model and the Gas Generation Program, and the resources required for them, were not expended in vain. Because of these efforts, we are much better able to defend the position that gas generation will not adversely affect the performance of the WIPP with respect to EPA regulations for long-term isolation of radioactive and chemically hazardous waste.

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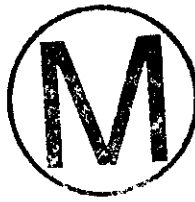# for the
Waste Isolation Pilot Plant

MASS Attachment 8-2

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Sandia National Laboratories

Albuquerque, New Mexico 87185-

date: January 26, 1996

to: Martin S. Tierney (6741)

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

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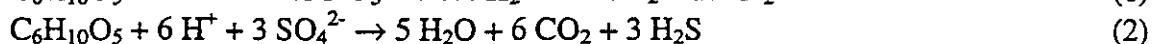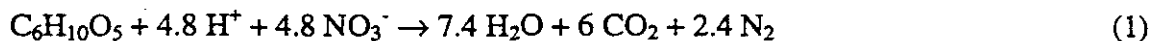
Introduction

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.
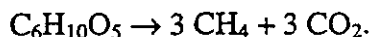
Biodegradation of Organic Materials

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):

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

$$C_6H_{10}O_5 \rightarrow 3\,CH_4 + 3\,CO_2. \tag{3}$$

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:
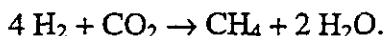
$$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O. \tag{4}$$

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

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. $S \gg K_s$ 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*
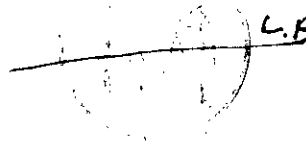
The rates of plastics and rubber biodegradation under expected WIPP conditions were

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):

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

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):

$$\text{Fe} + 2\ H_2O \rightarrow \text{Fe(OH)}_2 + H_2. \qquad (7)$$

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

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):

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \tag{8}$$
$$Fe + H_2S \rightarrow FeS + H_2. \tag{9}$$
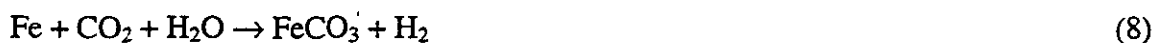
One possible effect of CO_2 and H_2S on steel corrosion is that they may cause passivation of the steel. Steel passivation was observed in the experiments in which large quantities of CO_2 and H_2S were added to the reaction vessels. It usually took place after tens of days and was caused by the formation 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

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:

$$\frac{1}{6}C_6H_{10}O_5 \ + \ unknown \ \rightarrow \ y \ gas \ + \ unknown \tag{10}$$
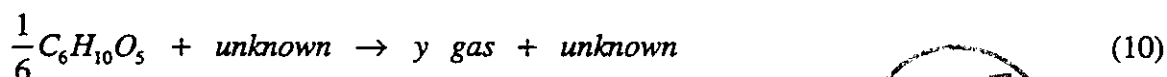
and H_2 production due to steel corrosion is described by:

$$Fe \ + \ \frac{4+2x}{3} \ H_2O \ \rightarrow \ \frac{4-x}{3} \ H_2 \ + \ x \ Fe(OH)_2 \ + \ \frac{1-x}{3} \ Fe_3O_4. \tag{11}$$
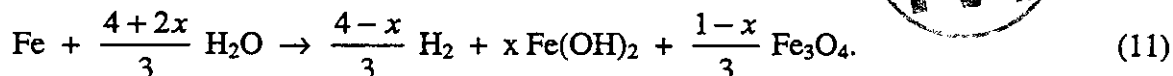
The stoichiometric factors x and y in Reaction 10 and 11 are estimated as follows.

● *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).

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:

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

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

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:

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

The minimum value of y can then be estimated by:

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

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

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

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 2.2×10^7 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 0.4×10^7 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.

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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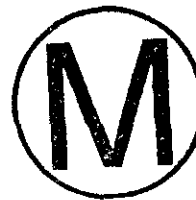
Appendix I. Hand Calculations for Estimating Microbial Gas generation Parameters

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

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.

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.

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:

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

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

NO_3^- : 1.62×10^6 kg (Drez, 1996) = $1000/62*1.62 \times 10^6 = 2.6 \times 10^7$ moles
SO_4^{2-} : 6.33×10^5 kg (Drez, 1996) = $1000/96*6.33 \times 10^5 = 6.6 \times 10^6$ moles

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

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: 1.4×10^5 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): 2.0×10^7 kg (DOE/CAO, 1996; Appendix I.5)
   NO_3^- initially present in the waste: 2.6×10^7 moles (Appendix I.6)
   SO_4^{2-} initial present in the waste: 6.6×10^6 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 = $1.4 \times 10^5/0.208 = 6.7 \times 10^5$ drums.
   (2) Total moles of C in cellulosics = $6*2.0 \times 10^7*1000/162 = 7.4 \times 10^8$ moles of C.

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 = $(0.04 + 1.5 \times 0.01 + 0.5 \times 0.95) \times 0.3 \times 2.0 \times 10^7 = 3.2 \times 10^6$ moles $CO2$/year.

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

(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.
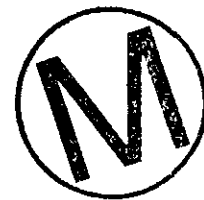
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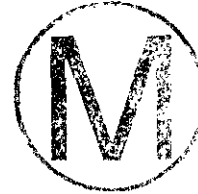
date: February 23, 1996

to: Martin S. Tierney (Org. 6741)

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

subject: Modify the Stoichiometric Factor y in BRAGFLO to Include the Effect of
MgO Added to WIPP Repository As a Backfill

This memo is supplemental to the previous one (Wang & Brush, 1996). We here request
a modification for the calculation of stoichiometric factor y in BRAGFLO, in order to take
into account the effect of MgO added to WIPP repository as a backfill. Notice that all gas-
generation-parameter values submitted in the previous memo (Wang & Brush, 1996) will
not be changed.

The accumulation of CO_2 produced by microbial reactions will decrease pH and thus
increase actinide solubility in the repository. In order to improve WIPP performance, MgO
will be added to the repository as a backfill to remove CO_2 and buffer pH. The consumption
of CO_2 by MgO in the repository can be described by the overall reaction:

$$MgO(c) + CO_2(g) \rightarrow MgCO_3(c). \tag{1}$$

According to the current waste inventory estimates, the amount of MgO sufficient to remove
all CO_2 is estimated to be 4×10^8 moles or $4.5 \times 10^3 \, m^3$, which is about 4% of total transuranic
waste volume (See Appendix). The simple thermodynamic calculation (See Appendix)
shows that Reaction (1) will buffer the fugacity of CO_2 around 10^{-11} atm. Therefore, as long
as sufficient MgO is added, the contribution of CO_2 to total gas pressure will be certainly
negligible. This effect will be taken into account in the BRAGFLO calculation simply by
modifying the stoichiometric factor y in the Average-Stoichiometry model.

The following modification is proposed: CO_2 is no longer taken into account in the
derivation of equations (15 -17) in the previous memo (Wang & Brush, 1996). Those
equations should be replaced by:

$$y_{max} = \frac{\frac{2.4 M_{NO3}}{4.8} + \frac{3 M_{SO4}}{3} + 0.5 * \left(M'_{cel} - \frac{6 M_{NO3}}{4.8} - \frac{6 M_{SO4}}{3} \right)}{M'_{cel}} \tag{2}$$

$$G = \min \left\{ \frac{3 M_{SO4}}{3}, \ M'_{Fe} \right\} \tag{3}$$

$$y_{min} = y_{max} - \frac{G}{M'_{cel}} \qquad\qquad\qquad (4)$$

All notations here are the same as those used in Wang & Brush (1996).

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Appendix

A.1. How much MgO will be needed?

From Wang & Brush (1996, p. 15), the maximum quantity of CO_2 potentially to be produced in the repository is: 7.4×10^8 moles C * (0.04 + 0.01 + 0.05*0.95) moles CO_2/mole C = 4×10^8 moles of CO_2. According Reaction (1), the amount of MgO sufficient to consume all CO_2 will be 4×10^8 moles. With the molar volume of 11.2 cm^3/mole for MgO (Lide, 1995), the amount of MgO needed in volume will be 4.5×10^3 m^3, about 4% of total waste volume (DOE/CAO, 1996).

A.2. Fugacity of CO_2 buffered by Reaction (1)

The fugacity of CO_2, f_{CO2}, controlled by Reaction (1) can be calculated by

$$\lg f_{CO_2} = \frac{\Delta G}{2.303 RT}$$

where ΔG is the free energy change of Reaction (1); R is gas constant (= 1.987 cal/mol/K); T is temperature (= 298.15 K). From the data given by Drever (1982), ΔG is estimated to be -15.32 kcal/mol. f_{CO2} is thus estimated to be $10^{-11.22}$ atm.

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MS 1341 L. H. Brush (Org. 6748)
MS 1341 Y. Wang (Org. 6748)
MS 1341 R. F. Weiner (Org. 6751)
MS 1330 SWCF (Org. 6352), WBS 1.1.09.1.1(X)

Sandia National Laboratories

date: February 29, 1996

to: Palmer Vaughn (Org. 6749)

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

subject: An Adjustment for Using Steel Corrosion Rates in BRAGFLO to Reflect
Repository Chemical Condition Changes due to Adding MgO as a Backfill

In order to control the repository chemistry, a sufficient amount of MgO will be added to the repository as a backfill. Through chemical reaction, this backfill will practically remove all CO_2 generated by microbial reactions and thus prevent any possibility of CO_2 accumulation in the repository. Therefore, the previously-suggested enhancement of steel corrosion by CO_2 (Wang & Brush, 1996) will be no longer possible. In our previous memo (Wang & Brush, 1996), two set of inundated steel corrosion rates were provided: one is 0.0 to 0.5 μm/year for the cases without CO_2 present and another is 0.0 to 6.5 μm/year for the cases with CO_2 present. *Considering the chemical condition changes due to adding MgO as a backfill, we suggest using the rate of 0 to 0.5 μm/year for __all__ BRAGFLO simulations.*

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Title 40 CFR Part 191 Compliance Certification Application for the Waste Isolation Pilot Plant

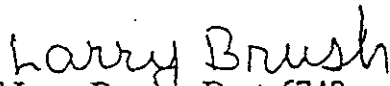# MASS Attachment 8-3

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Sandia National Laboratories

Albuquerque, New Mexico 87185-1341

date: 9/20/1995

to: D. R. Anderson

from: Yifeng Wang and Larry Brush, Dept. 6748

subject: Input Parameter Value Adjustments for the Average-Stoichiometry model

In this memo, we summarize the results of the calculation conducted for the comparison of the two existing gas generation models: Average-Stoichiometry model and Reaction-Path model. We demonstrate that the two model are in good agreement with each other in the prediction of total gas generation in the WIPP disposal rooms if more realistic input parameter values are adopted in the Average-Stoichiometry model. Our work thus places confidence in the use of the more simple Average-Stoichiometry model in the WIPP system modeling. Based on the calculation results as well as other considerations, we request two adjustments in sampling input parameter values for the Average-Stoichiometry model: (1) changing the sampling range for the stoichiometric factor of cellulosics biodegradation and (2) assigning a non-zero probability to the occurrence of the biodegradation of plastics and rubbers.
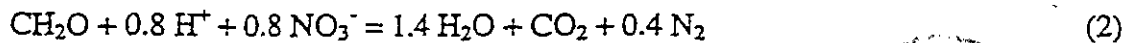
The details of the calculations can be found in the Summary Memorandum of Record (GG-2) for this FEPs activity. BRAGFLO was used with the Average-Stoichiometry model to calculate the history of gas generation in the repository and then this history was compared with that predicted by the Reaction-Path model. Using the Reaction-Path model, we have carried out 10 simulations for the cases including only steel corrosion and 10 more simulations for the cases including both microbial reaction and steel corrosion. For the steel-corrosion-only cases, the total gas generation predicted by the Average-Stoichiometry model falls in the range calculated by the Reaction-Path model. For the cases including both microbial reaction and steel corrosion, however, discrepancies are observed between the two model predictions (Table 1). But, the discrepancies can be minimized by adopting more realistic values for the stoichiometric factor of microbial reaction in the Average-Stoichiometry model. Importantly, based on the experimental data on steel passivation (Telander & Westerman, 1993), the calculation indicates that steels might become passivated shortly after the onset of microbial degradation of cellulosics, implying that microbial production of CO_2 might effectively preclude significant gas generation by steel corrosion. This, therefore, justifies the possible use of a "switch" in the Average-Stoichiometry model to mimics the effect of passivation of steels and other Fe-base alloys. This "switch" would allow only one process, either microbial reaction or steel corrosion, to occur in each calculation.

In the Average-Stoichiometry model, the biodegradation of cellulosics is represented by an overall reaction (WIPP Performance Assessment Division, 1991):

$$CH_2O + \text{unknowns} = y \text{ gas} + \text{unknowns} \qquad (1)$$

where y is the stoichiometric factor. The value of y is currently sampled over a range of 0 to 1.67. However, our results show that this sampling range is not wholly realistic and usually results in either under- or over-estimating total gas generation in the disposal rooms (Table 1). The actual value of y, we believe, is distributed over a more narrow range.

The stoichiometric factor (y) depends on the reaction pathway of cellulosics degradation and the amount of electron acceptors (such as NO_3^- and SO_4^{2-}) present in the disposal rooms. The abundance of electron acceptors determines the extent to which each individual reaction pathway can proceed. Based on the waste inventory estimates by Storz (1995), the Reaction-Path model predicts that ~10% of cellulose materials will be degraded via denitrification and sulfate reduction:

$$CH_2O + 0.8\ H^+ + 0.8\ NO_3^- = 1.4\ H_2O + CO_2 + 0.4\ N_2 \qquad (2)$$

$$CH_2O + 0.5\ SO_4^{2-} = H_2O + CO_2 + 0.5\ H_2S \qquad (3)$$

and the rest via methanogensis:

$$CH_2O = 0.5\ CH_4 + 0.5\ CO_2\ . \qquad (4)$$

In the above reactions, the gas yield per mole of carbon of cellulosics is 1.4 for denitrification, 1.5 for sulfate reduction, and 1.0 for methanogensis. Therefore, if no steel-corrosion effect is considered, the stoichiometric factor (y) should be within a range of [1.0 to 1.2]. /. 5

Now let us take a look at the effect of steel corrosion on the stoichiometric factor (y). A small amount of steel can be corroded before it becomes passivated, in the cases where significant microbial gas generation occurs. As mentioned above, methanogensis is a dominant biodegradation pathway, and thus any small amount of H_2 released from steel corrosion would be quickly consumed by the reaction:

$$CO_2 + 4\ H_2 = CH_4 + 2\ H_2O. \qquad (5)$$

Note that this reaction simply converts CO_2 to an equal amount of CH_4 and leaves the total amount of microbially-generated gas unchanged. Therefore, for a long-term prediction, release of H_2 from metal corrosion does not affect parameter y. One possible minor effect of H_2 on Reaction (1) is caused by the repression of Reaction (4) by Reaction (5), because the latter is energetically more favorable. This is equivalent to reducing the rate of cellulosic biodegradation. This effect is already taken into account by the current sampling range for microbial reaction rate in the Average-Stoichiometry model. The major effect of steel corrosion on parameter y is actually caused by the reactions between the gases generated by microbial reaction and the products of steel corrosion, e.g.:

$$Fe(OH)_2 + CO_2 = FeCO_3 \ . \tag{6}$$

All of these reactions consume microbially-generated gases (CO_2, H_2S) and thus equivalently reduce the stoichiometric factor (y) in Reaction (1). Due to steel corrosion, y can, therefore, have a value below 1.0. This effect may become significant in the cases with very high steel-corrosion rate but very low microbial reaction rate. According to the Reaction-Path-model calculation, however, it is unlikely for y to go below 0.75 (Table 1).

Table 1.   Comparison of the Reaction-Path Model with the Average-Stoichiometry Model in the Prediction of Total Gas Generation in WIPP Disposal Rooms. Listed are only the cases involving significant microbial gas generation. Recommended y values are calculated so as to bring the total amount of gas predicted by the Average-Stoichiometry model to the same levels as calculated by the Reaction-Path model.

vector #	gas predicted by average-stoich. model (10^6 mol)	gas predicted by Reaction-Path model (10^6 mol)	y value used in average-stoich. model	y value recommended
3	1040	623	1.28	0.77
5	1080	1400	0.86	1.12
6	1100	1251	1.00	1.14
7	860	859	1.11	1.10
9	1510	1094	1.61	1.17
12	961	1315	0.83	1.13
15	87	1031	0.08	0.98
17	650	1352	0.53	1.11
19	817	1505	0.61	1.12
20	306	1005	0.34	1.12

In short, by choosing the appropriate y values, the Average-Stoichiometry model is still adequate to predict the total gas generation for the cases with both microbial reaction and steel corrosion involved. From the above discussion, we recommend adjusting the sampling range for the stoichiometric factor (y) to [0.75, 1.2] in the Average-Stoichiometry model. We also recommend the following sampling scheme:

1.5 ?

y: uniform distribution over [1, 1.2]   if $g \geq 0.03$
y: uniform distribution over [0.75, 1]   if $g < 0.03$

with $g \cong R_{mic}/\max R_{mic} \cdot (1 - R_{cor}/\max R_{cor})$

where R_{mic} and R_{cor} are respectively the rates of microbial reaction and steel corrosion; max R_{mic} and max R_{cor} are respectively the maximum values of R_{mic} and R_{cor} allowed in their sampling ranges. This sampling scheme correlates the low values of y with the high rates of steel corrosion and the low rates of microbial reaction. Here we want to emphasize that the recommended sampling range could be subjected to a further adjustment as the waste inventory estimates are updated.

In addition, considering the difference between plastics (or rubbers) and cellulosics in biodegradability, we believe that it is more realistic to treat plastics and rubbers separately from cellulosics. We therefore recommend a 50% chance of plastics and rubber biodegradation in the event of significant microbial gas generation. The probability of the occurrence of significant microbial gas generation is recommended to retain the current value, i.e. 50%.

Finally, considering tight time constraints, as to the Average-Stoichiometry model, we recommend: (1) against changing kinetics of anoxic corrosion and microbial reaction from the 0th to the 1st order; (2) against inclusion of aluminum corrosion in the model; (3) retaining the assumption that microbial activity will have no significant effect on the H_2O content of WIPP disposal rooms. Leaving aluminum corrosion out of the model might be justified as follows: First, aluminum will be present only in a small amount relative to Fe alloys in the waste (U.S Department of Energy Carlsbad Area Office, 1994), and thus the effect of aluminum could be limited. Second, in the cases where significant microbial reaction occurs, as discussed above for steels, H_2 released from aluminum corrosion would be consumed quickly by reaction (5) and therefore would not have a significant effect on the long-term prediction of total gas generation. Also, note that the products of aluminum corrosion are unlikely to react with CO_2 and H_2S and thus they would not change the stoichiometric factor (y) in reaction (1).

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