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:

$$\text{MgO}(c) + \text{CO}_2(g) \rightarrow \text{MgCO}_3(c).$$  \hspace{1cm} (1)

According to the current waste inventory estimates, the amount of MgO sufficient to remove all CO$_2$ is estimated to be $4 \times 10^8$ 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:

$$y_{\text{max}} = \frac{2.4M_N\text{O}_3 + 3M_\text{SO}_4}{4.8} + 0.5\left[\frac{M'_c - 6M_N\text{O}_3}{4.8} - \frac{6M_\text{SO}_4}{3}\right]$$ \hspace{1cm} (2)

$$G = \min\left\{\frac{3M_\text{SO}_4}{3}, M'_c\right\}$$ \hspace{1cm} (3)
\[ y_{\text{min}} = y_{\text{max}} - \frac{G}{M_{\text{cel}}} \]  

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

References


Appendix

A.1. How much MgO will be needed?

From Wang & Brush (1996, p. 15), the maximum quantity of CO₂ potentially to be produced in the repository is: $7.4 \times 10^8$ moles $C \times (0.04 + 0.01 + 0.05 \times 0.95)$ moles CO₂/mole $C = 4 \times 10^8$ moles of CO₂. According Reaction (1), the amount of MgO sufficient to consume all CO₂ will be $4 \times 10^8$ moles. With the molar volume of 11.2 cm$^3$/mole for MgO (Lide, 1995), the amount of MgO needed in volume will be $4.5 \times 10^3$ m$^3$, about 4% of total waste volume (DOE/CAO, 1996).

A.2. Fugacity of CO₂ buffered by Reaction (1)

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

$$\ln f_{CO₂} = \frac{\Delta G}{2.303RT}$$

where $\Delta G$ 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), $\Delta G$ is estimated to be $-15.32$ kcal/mol. $f_{CO₂}$ is thus estimated to be $10^{-11.22}$ atm.

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