

WPO 32286

# Sandia National Laboratories

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subject: Modify the Stoichiometric Factor  $\gamma$  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  $\gamma$  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<sub>2</sub> 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<sub>2</sub> and buffer pH. The consumption of CO<sub>2</sub> by MgO in the repository can be described by the overall reaction:



According to the current waste inventory estimates, the amount of MgO sufficient to remove all CO<sub>2</sub> is estimated to be 4x10<sup>8</sup> moles or 4.5x10<sup>3</sup> m<sup>3</sup>, 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<sub>2</sub> around 10<sup>-11</sup> atm. Therefore, as long as sufficient MgO is added, the contribution of CO<sub>2</sub> 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  $\gamma$  in the Average-Stoichiometry model.

The following modification is proposed: CO<sub>2</sub> 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:

$$y_{\max} = \frac{2.4M_{\text{NO}_3} + \frac{3M_{\text{SO}_4}}{3} + 0.5 * \left( M'_{\text{cel}} - \frac{6M_{\text{NO}_3}}{4.8} - \frac{6M_{\text{SO}_4}}{3} \right)}{M'_{\text{cel}}} \quad (2)$$

$$G = \min \left\{ \frac{3M_{\text{SO}_4}}{3}, M'_{\text{Fe}} \right\} \quad (3)$$

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

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

### References

- DOE/CAO (1996) *Transuranic Waste Baseline Inventory Report*. (Rev. 2)
- Drever J. I. (1982) *The Geochemistry of Natural Waters*. Prentice-Hall.
- Lide D. R. (1995) *Handbook of Chemistry and Physics*. CRC.
- Wang Y. & Brush L. H. (1996) Estimates of gas-generation parameters for the long-term WIPP performance assessment. Sandia National Lab., Albuquerque, NM. (memo to M. Tierney, 1/26/1996)

## Appendix

### A.1. How much MgO will be needed?

From Wang & Brush (1996, p. 15), the maximum quantity of CO<sub>2</sub> potentially to be produced in the repository is:  $7.4 \times 10^8$  moles C \* (0.04 + 0.01 + 0.05\*0.95) moles CO<sub>2</sub>/mole C =  $4 \times 10^8$  moles of CO<sub>2</sub>. According Reaction (1), the amount of MgO sufficient to consume all CO<sub>2</sub> will be  $4 \times 10^8$  moles. With the molar volume of 11.2 cm<sup>3</sup>/mole for MgO (Lide, 1995), the amount of MgO needed in volume will be  $4.5 \times 10^3$  m<sup>3</sup>, about 4% of total waste volume (DOE/CAO, 1996).

### A.2. Fugacity of CO<sub>2</sub> buffered by Reaction (1)

The fugacity of CO<sub>2</sub>,  $f_{CO_2}$ , controlled by Reaction (1) can be calculated by

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

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.  $f_{CO_2}$  is thus estimated to be  $10^{-11.22}$  atm.

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