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Sandia National Laboratories
Operated for the U.S. Department of Energy by
Sandia Corporation
Phone: (505) 284-5360
Fax: (505) 844-2348
Internet: djclayt@sandia.gov

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To: Records Center

From: Daniel J. Clayton DJC (For)

Technical Review: Todd Zeitler

QA Review: Shelly Nielson

Management Review: Sean Dunagan

Subject: Justification of Chemistry Parameters for Use in BRAGFLO for AP-164, Rev 1.

1.0 Introduction

Analysis Plan for the 2014 WIPP Compliance Recertification Application Performance Assessment, AP-164 (Camphouse, 2013) describes an analysis that will include refinements to performance assessment (PA) models. The code BRAGFLO Version 6.02 has been developed for use in this analysis, and this version of BRAGFLO requires several parameters that were not used by previous versions of the code. The purpose of this document is to justify the values of the parameters that will be used by the code for the AP-164 analysis. Furthermore, several parameters will be updated based on new information.

Due to limitations of the parameter database, if parameter descriptions are changed, the history of values is lost. This necessitated the change in the order of species in Table 2, since MgCO3 was previously designated as species 9 and therefore, hydromagnesite should then be added as species 10. This revision of this memo is a result of that change.

2.0 Stoichiometric Coefficients

In BRAGFLO the stoichiometric coefficients for the chemical reactions have been reorganized into a single matrix S(I,J) (Camphouse 2012);. This matrix is organized as follows: I represents the reaction and J represents the individual species. Table 1 lists the reactions of interest, and Table 2 lists the species. A positive value of S(I,J) represents production, and a negative value represents consumption. All reactions described in the following sections are more fully discussed in Camphouse (2012).

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Table 1. Stoichiometric Matrix S(I,J) Row Number I and Corresponding Reaction (Table 1 in Camphouse (2012).

Index (I)	Reaction
1	Anoxic corrosion of iron
2	Microbial gas generation
3	Iron hydroxide sulfidation
4	Metallic iron sulfidation
5	MgO hydration
6	Magnesium hydroxide (brucite) carbonation
7	MgO carbonation
8	Hydromagnesite conversion

Table 2. Stoichiometric Matrix S(I,J) Column Number J and Corresponding Compound (Table 2 in Camphouse (2012).

Index (J)	Compound
1	H_2
2	H_2O
3	Fe
4	Cellulosics
5	$Fe(OH)_2$
6	FeS
7	MgO
8	$Mg(OH)_2$
9	$MgCO_3$
10	Hydromagnesite

2.1 *Anoxic Corrosion of Iron: I=1*

For the AP-164 calculations, BRAGFLO will model the anoxic iron corrosion reaction with the following equation:

$$Fe(s) + 2\ H_2O(l) \rightarrow H_2(g) + Fe(OH)_2(s) \qquad (1)$$

Since the iron corrosion rate is calculated per mole of iron in BRAGFLO, equation (1) should be normalized per mole of iron, which it is. Consequently,

1) S(1,1) = 1;
2) S(1,2) = -2;
3) S(1,3) = -1;
4) S(1,5) = 1;
5) S(1,J) = 0, J=4,6,7,8,9,10.

These values are the same as were used for the 2009 Compliance Recertification Application PA Baseline Calculation (PABC-2009), except for the creation of S(1,10) as the hydromagnesite coefficient with a zero value.

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2.2 *Microbial Gas Generation: I=2*

Cellulose, plastic, and rubber (CPR) materials are consumed by the denitrification and by sulfate reduction reactions in the following equations:

$$C_6H_{10}O_5(s) + 4.8\ H^+ + 4.8\ NO_3^- \rightarrow 7.4\ H_2O(l) + 6\ CO_2(g) + 2.4\ N_2(g) \quad (2)$$

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

BRAGFLO uses the average stoichiometry model (Wang and Brush, 1996; Nemer and Zelinski, 2005). In the average stoichiometry model, equations (2)-(3) are replaced with the following equation:

$$[C_6H_{10}O_5]/6 + \text{microbes} \rightarrow y\ H_2 + z\ H_2O + \text{unknowns}. \quad (4)$$

where y is the amount of gas produced per mole of organic carbon and z is the amount of water produced per mole of organic carbon and both depend on the amount of nitrate and sulfate available, as equations (2) and (3) produce different amounts of gas and water. It is assumed that all CO_2 is sequestered by MgO.

Since the CPR degradation rate is calculated per mole of organic carbon in BRAGFLO, equation (4) should be normalized per mole of organic carbon, which it is. Furthermore, for the AP-164 calculations, the moles of gas (assumed to be hydrogen in BRAGFLO) and water produced in reaction 4 are calculated in the ALGEBRA1 pre-processing step of the BRAGFLO calculations with the ALGEBRACDB code and are described below. A value of 0 is assigned to S(2,1) and S(2,2) as a placeholder. Thus,

1) S(2,4) = -1.
2) S(2,J) = 0, J=1,2,3,5,6,7,8,9,10.

These values are the same as were used for the PABC-2009, except for the creation of S(2,10) as the hydromagnesite coefficient with a zero value.

For the calculation of y and z, the first step is to determine the maximum amount of CPR that could be potentially consumed in the 10,000 year simulation (MAX_C). This is dependent on the total amount of CPR assumed for the particular vector, as well as the CPR degradation rate. Multiplying the sampled inundated CPR degradation rate for the vector, which has the units of mol/kg/s, by the number of seconds in 10,000 years and the total amount of CPR in the vector, (in kg,) gives the total moles of CPR that could be consumed during the 10,000 year simulation. This value is then compared to the total moles of CPR considered in the vector, and the smaller of the two is then used as MAX_C.

The next step in calculating y and z is to determine the fraction of the CPR that could be potentially consumed using the nitrate in the repository (F_NO3) versus using the sulfate in the repository (F_SO4). Multiplying the number of moles of nitrate in the waste by the ratio of moles of nitrate to organic carbon in equation (2), 6/4.8, and dividing by MAX_C, gives F_NO3. If F_NO3 is greater than one, then F_NO3 should be set equal to one. F_SO4 is calculated by subtracting F_NO3 from one, which gives the remaining fraction of the CPR that could be potentially consumed using the sulfate in the repository.

The y and z are calculated by using F_NO3 and F_SO4 and the moles of gas and water generated from the respective degradation equations. The y is calculated by summing the product of

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F_NO3 and the ratio of moles of gas produced (not including CO_2) to moles of organic carbon in equation (2), 2.4/6, and the product of F_SO4 and the ratio of moles of gas produced (not including CO_2) to moles of organic carbon in equation (3), 3/6. The *z* is calculated by summing the product of F_NO3 and the ratio of moles of water produced to moles of organic carbon in equation (2), 7.4/6, and the product of F_SO4 and the ratio of moles of water produced to moles of organic carbon in equation (3), 5/6.

2.3 *Iron Hydroxide Sulfidation: I=3*

For the AP-164 calculations, BRAGFLO will model iron hydroxide sulfidation with the following reaction:

$$Fe(OH)_2(s) + H_2S(g) \rightarrow FeS(s) + 2\ H_2O(l). \quad (5)$$

Since the iron hydroxide sulfidation rate is calculated per mole of H_2S produced from CPR degradation in BRAGFLO, equation (5) should be normalized per mole of H_2S, which it is. Consequently,

1) S(3,1) = -1, since BRAGFLO assumes all gas (H_2S in Eq. 5) is hydrogen;
2) S(3,2) = 2;
3) S(3,5) = -1;
4) S(3,6) = 1;
5) S(3,J) = 0, J=3,4,7,8,9,10.

These values are the same as were used for the PABC-2009, except for the creation of S(3,10) as the hydromagnesite coefficient with a zero value.

2.4 *Metallic Iron Sulfidation: I=4*

For the AP-164 calculations, BRAGFLO will model metallic iron sulfidation with the following reaction:

$$Fe(s) + H_2S(g) \rightarrow FeS(s) + H_2(g). \quad (6)$$

Since the metallic iron sulfidation rate is calculated per mole of H_2S produced from CPR degradation in BRAGFLO, equation (6) should be normalized per mole of H_2S, which it is. As this reaction converts the gas species from H_2S to H_2 with no change in the moles of gas, the stoichiometric coefficient representing the moles of gas produced S(4,1) should be zero. Consequently,

1) S(4,3) = -1;
2) S(4,6) = 1;
3) S(4,J) = 0, J=1,2,4,5,7,8,9,10.

These values are the same as were used for the PABC-2009, except for the creation of S(4,10) as the hydromagnesite coefficient with a zero value.

2.5 *MgO Hydration: I=5*

For the AP-164 calculations, BRAGFLO will model MgO hydration with the following reaction:

$$MgO(s) + H_2O(g,aq) \rightarrow Mg(OH)_2(s). \quad (7)$$

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Since the MgO hydration rate is calculated per mole of MgO in BRAGFLO, equation (7) should be normalized per mole of MgO, which it is. Consequently,

1) S(5,2) = -1;
2) S(5,7) = -1;
3) S(5,8) = 1;
4) S(5,J) = 0, J=1,3,4,5,6,9,10.

These values are the same as were used for the PABC-2009, except for the creation of S(5,10) as the hydromagnesite coefficient with a zero value.

2.6 *Magnesium Hydroxide (Brucite) Carbonation: I=6*

For the AP-164 calculations, BRAGFLO will model brucite carbonation with the following reaction:

$$5\ Mg(OH)_2(s) + 4\ CO_2(g,aq) \rightarrow Mg_5(CO_3)_4(OH)_2{:}4H_2O(s). \quad (8)$$

Since the brucite carbonation rate is calculated per mole of CO_2 produced from CPR degradation in BRAGFLO, equation (8) should be normalized per mole of CO_2. Normalizing equation (8) per mole of CO_2 gives:

$$1.25\ Mg(OH)_2(s) + CO_2(g,aq) \rightarrow 0.25\ Mg_5(CO_3)_4(OH)_2{:}4H_2O(s). \quad (9)$$

Consequently,

1) S(6,8) = -1.25;
2) S(6,10) = 0.25;
3) S(6,J) = 0, J=1,2,3,4,5,6,7,10.

These values are the same as were used for the PABC-2009, except for a change in the value of S(6,2) to zero, the change in the value of S(6,8) to -1.25, the change in the value of S(6,9) to zero and the creation of S(6,10) as the hydromagnesite coefficient with a value 0.25.

2.7 *MgO Carbonation: I=7*

In the event that CO_2 production is occurring, but brucite is not available in BRAGFLO simulations, MgO will be converted directly to magnesite. This direct conversion is included to account for humid conditions at very low saturation levels. For the AP-164 calculations, BRAGFLO will model MgO carbonation with the following reaction:

$$MgO(s) + CO_2\ (g,aq) \rightarrow MgCO_3(s) \quad (10)$$

Since the MgO carbonation rate is calculated per mole of CO_2 produced from CPR degradation in BRAGFLO, equation (10) should be normalized per mole of CO_2, which it is. Consequently,

1) S(7,7) = -1;
2) S(7,9) = 1;
3) S(7,J) = 0, J=1,2,3,4,5,6,8,9.

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These values are the same as were used for the PABC-2009, except for the creation of S(7,10) as the hydromagnesite coefficient with a zero value.

2.8 *Hydromagnesite Conversion: I=8*

For the AP-164 calculations, BRAGFLO will model hydromagnesite conversion with the following reaction:

$$Mg_5(CO_3)_4(OH)_2{:}4H_2O(s) \rightarrow 4\ MgCO_3(s) + Mg(OH)_2(s) + 4\ H_2O(l) \qquad (11)$$

Since the hydromagnesite conversion rate is calculated per mole of hydromagnesite in BRAGFLO, equation (11) should be normalized per mole of hydromagnesite, which it is. Consequently,

1) S(8,2) = 4;
2) S(8,8) = 1;
3) S(8,9) = 4;
4) S(8,10) = -1;
5) S(8,J) = 0, J=1,3,4,5,6,7.

Since this reaction is new for the CRA-2014, the PAPDB does not contain parameters that represent these stoichiometric coefficients, so these parameters must be created for the AP-164 BRAGFLO calculations.

2.9 *Parameter Definition*

In order to use the aforementioned stoichiometric coefficients in the AP-164 calculations, parameters must be defined and entered into the PA parameter database (PAPDB). This section lists the MATERIAL:PROPERTY names and values that will be assigned to each stoichiometric coefficient that are modified or created for the CRA-2014.

The material REFCON will be assigned to all stoichiometric coefficient parameters. The property STCO_*IJ* will be used to denote the coefficient that is in the I^{th} row and J^{th} column (denoted S(I,J) in Sections 2.1-2.7) of the BRAGFLO stoichiometric coefficient matrix. For convenience, representation of the 10^{th} column will be shown a 0 in the property name instead of 10. For example, S(1,1) was determined to have a value of 1 in Section 2.1, so the parameter REFCON:STCO_11 will be assigned a value of 1. S(3,10) was determined to have a value of 0 in Section 2.3, so the parameter REFCON:STCO_30 will be assigned a value of 0.

Table 3 lists the property names, descriptions and values of the new stoichiometric coefficient parameters that will be created for AP-164. The stoichiometric coefficient parameters with only a value change are shown in Table 4.

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Table 3. Stoichiometric Coefficient Parameters New for AP-164. All properties are constant, dimensionless, and assigned to the REFCON material.

PROPERTY	Description	Value
STCO_10	Fe Corrosion: Hydromagnesite Stoichiometric Coefficient	0
STCO_20	Microbial Gas Generation: Hydromagnesite Stoichiometric Coefficient	0
STCO_30	FeOH2 Sulfidation: Hydromagnesite Stoichiometric Coefficient	0
STCO_40	Metallic Fe Sulfidation: Hydromagnesite Stoichiometric Coefficient	0
STCO_50	MgO Hydration: Hydromagnesite Stoichiometric Coefficient	0
STCO_60	MgOH2 Carbonation: Hydromagnesite Stoichiometric Coefficient	0.25
STCO_70	MgO Carbonation: Hydromagnesite Stoichiometric Coefficient	0
STCO_81	Hydromagnesite Conversion: H2 Stoichiometric Coefficient	0
STCO_82	Hydromagnesite Conversion: H2O Stoichiometric Coefficient	4
STCO_83	Hydromagnesite Conversion: Fe Stoichiometric Coefficient	0
STCO_84	Hydromagnesite Conversion: Cellulosics Stoichiometric Coefficient	0
STCO_85	Hydromagnesite Conversion: FeOH2 Stoichiometric Coefficient	0
STCO_86	Hydromagnesite Conversion: FeS Stoichiometric Coefficient	0
STCO_87	Hydromagnesite Conversion: MgO Stoichiometric Coefficient	0
STCO_88	Hydromagnesite Conversion: MgOH2 Stoichiometric Coefficient	1
STCO_89	Hydromagnesite Conversion: MgCO3 Stoichiometric Coefficient	4
STCO_80	Hydromagnesite Conversion: Hydromagnesite Stoichiometric Coefficient	-1

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Table 4. Stoichiometric Coefficient Parameters with a Modified Value for AP-164. All properties are constant, dimensionless, and assigned to the REFCON material.

PROPERTY	Description	Value
STCO_62	MgOH2 Carbonation: H2O Stoichiometric Coefficient	0
STCO_68	MgOH2 Carbonation: MgOH2 Stoichiometric Coefficient	-1.25
STCO_69	MgOH2 Carbonation: MgCO3 Stoichiometric Coefficient	0

3.0 Hydromagnesite Properties

The addition of the hydromagnesite conversion reaction to BRAGFLO requires that the molecular weight and density of hydromagnesite be input to the code. The PAPDB does not contain parameters that represent this molecular weight and density, so these parameters must be created for the AP-164 BRAGFLO calculations. Table 5 lists names and values of the molecular weight and density parameters that will be created. All parameters will be modeled with constant values, and the material REFCON will be assigned to the molecular weight and density parameters.

Table 5. Molecular Weight Parameters. All properties are constant and assigned to the REFCON material.

Parameter	Description	Value (unit)	Source
REFCON: DN_HYDRO	Density of Hydromagnesite	2300 (kg/m^3)	Lide (2006) p.4-73
REFCON: MW_HYDRO	Molecular Weight of Hydromagnesite	467.636×10^{-3} (kg/mol)	Lide (2006) p.4-73

4.0 Hydromagnesite Conversion Rate

To model the conversion of hydromagnesite to magnesite in the BRAGFLO calculations, the rate of this reaction is needed. There is uncertainty regarding the hydromagnesite to magnesite conversion rate. This uncertainty was characterized by U.S. Environmental Protection Agency (1998) in Section 3.0 as reacting on the order of "hundreds to thousands of years". The range of 100 to 10,000 years captures this uncertainty. Using this range of times of reaction, the reaction rate, in the appropriate units needed for BRAGFLO, mol/(kg*s), can be determined. To calculate the reaction rate, take the inverse of the reaction time (in seconds) and divide by the molecular weight of hydromagnesite (see Section 3.0). This generates a maximum rate, using the minimum reaction time (100 years), of 6.8e-10 mol/(kg*s) (1/(100*3.1557e7)/467.636e-3) and a minimum rate, using the maximum reaction time (10,000 years), of 6.8e-12 mol/(kg*s) (1/(10,000*3.1557e7)/467.636e-3). Since we only have a maximum and minimum value for this

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parameter, a uniform distribution will be used (Tierney 1996). Table 6 lists the distribution and values for this new parameter that will be input into the PAPDB.

Table 6. Hydromagnesite Conversion Rate Parameter.

Parameter	Units	Description	Distribution Type	Distribution Parameters	Default Value
WAS_AREA: HYMAGCON	mol/(kg*s)	Rate of conversion of hydromagnesite to magnesite	Uniform	Max = 6.8e-10 Min = 6.8e-12 Mean = 3.4e-10 S.D. = 1.9e-10	3.4e-10

5.0 MgO Hydration Rates

The MgO hydration rates for each brine type can be updated using the information shown in Nowak and Clayton (2007). This analysis determined the MgO hydration rates and associated uncertainties for each brine type using linear regression to calculate the slope of the line that represents each data set. The student-t distribution should be used for these parameters to represent the uncertainty on the slope, but currently the student-t distribution in LHS is configured to use a list of data values, and hence is not suitable. A normal distribution, with the standard error adjusted to give equivalent minimum and maximum values on the 98% confidence interval, is similar to the student-t distribution and will be used instead. To adjust the minimum and maximum values, the standard error is multiplied by the ratio of the t-value for the number of degrees of freedom for the data set and the Z-value (t-value at infinite degrees of freedom). The number of degrees of freedom for each data set is the number of data points in the data set minus two (one for the slope and one for the intercept). The Z-value using the 0.02 2-tailed values is 2.326. The t-values for each brine type, along with the original and adjusted standard error is shown in Table 7. Since WIPP PA employs a truncated normal distribution, the maximum and minimum are calculated by multiplying the adjusted standard error by 2.32 and adding to (for the maximum) or subtracting from (for the minimum) the mean value. The 2.32 is used to calculate the 0.01 and 0.99 quantiles (Tierney 1996). Table 8 lists the updated MgO hydration rates that will be input into the PAPDB.

Table 7. Standard Error Adjustment Factors.

Brine	Standard Error	Number of Data Points	Degrees of Freedom	t-Value (0.02 2-tailed)	Adjusted Standard Error
ERDA-6	1.8e-9	26	24	2.492	1.9e-9
GWB	3.4e-9	12	10	2.764	4.0e-9
Humid	7.1e-10	14	12	2.681	8.2e-10

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Table 8. MgO Hydration Rate Parameters.

Parameter	Units	Description	Distribution Type	Distribution Parameters	Default Value
WAS_AREA: BRUCITEC	mol/kg/s	MgO inundated hydration rate in ERDA-6 brine	Normal	Mean = 5.2e-8 S.E. = 1.9e-9 Max = 5.64e-8 Min = 4.76e-8	5.2e-8
WAS_AREA: BRUCITES	mol/kg/s	MgO inundated hydration rate in GWB brine	Normal	Mean = 5.2e-8 S.E. = 4.0e-9 Max = 6.13e-8 Min = 4.27e-8	5.2e-8
WAS_AREA: BRUCITEH	mol/kg/s	MgO humid hydration rate	Normal	Mean = 2.0e-8 S.E. = 8.2e-10 Max = 2.19e-8 Min = 1.81e-8	2.0e-8

6.0 References

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