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to: Distribution

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subject: Evaluation of the Thermal Effect of Exothermal Chemical Reactions for WIPP Performance Assessment: A revised version

Temperature increases caused by exothermal chemical reactions in the repository have been evaluated in the memo by Wang (1996). This memo is the revised version of the previous memo. Two revisions have been made: (1) anoxic steel corrosion reaction is no longer an exothermal reaction; (2) waste panel number is adjusted from eight to ten. All revisions made here do not change the conclusion that the thermal effect of exothermal chemical reactions in the repository is negligible.

Assumptions:

The following exothermal chemical reactions are considered:

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (1)$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 \quad (2)$$

$$C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2 \quad (3)$$

$$Al + 3H_2O \rightarrow Al(OH)_3 + 1.5\ H_2\ . \quad (4)$$

Anoxic steel corrosion is a major chemical reaction expected to occur in the repository:

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2. \quad (5)$$

However, this reaction is considered here, because it is not an exothermal reaction. The enthalpy change of Reaction (5) is estimated to be 0.64 Kcal/mole Fe.

Considering that the vertical dimension of the repository (~ 1 m, B. M. Butcher, personal comm.) will be much less than the horizontal extension after room closure, we assume that the heat released from the reactions will be dissipated away mainly from the ceiling and ground of the repository and the heat loss from the side walls is negligible. We also assume that all reactions will take place uniformly in a reaction region of interest. We here restrict the reaction region in a single waste panel, for the following reason: Some of the above reactions may be limited by brine inflow. BRAGFLO simulations have shown that, in the human intrusion cases, the rate of brine inflow into a borehole-penetrated waste panel will be significantly higher than that into the rest of the repository. Choosing a panel rather than the whole repository as a reaction region will make heat generation rate per unit of volume higher and the heat dissipating surface area smaller in our calculations, and

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therefore it is conservative. However, this choice will not affect the calculations for the reactions that are not limited by brine inflow, as you will see below.

Theory:

Based on these assumptions, the thermal effect of an exothermal chemical reaction can be modeled by a simplified system shown in Figure 1. The temperature distribution (T) can be described by the following equations:

$$C_p \rho \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial X^2} \tag{6}$$

$$T(X,0) = T_0 \tag{7}$$

$$R\Delta H = 2Sk \left.\frac{\partial T}{\partial X}\right|_{X=0} \tag{8}$$

$$T(\infty,t) = T_0 \tag{9}$$

where C_p is the heat capacity of surrounding rocks (J/mole/K); ρ is the molar density of surrounding rocks (moles/m^3); t is time (year); X is the spatial coordinate (m); k is the thermal conductivity of surrounding rocks (J/year/m/K); T_0 is the background temperature (K); R is the reaction rate (moles/year); ΔH is the enthalpy change of the reaction (J/mole); S is the horizontal area of a waste panel (m^2).

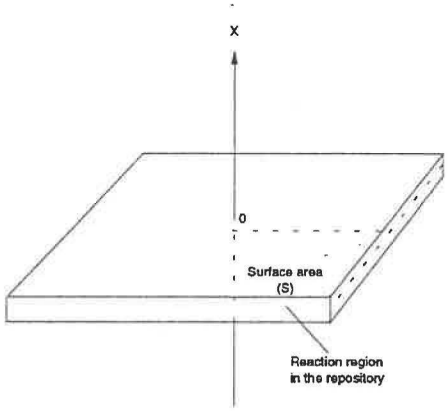


Figure 1. A modeling system for heat production and conduction.

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The above equations can be solved for T with a Laplace-transformation method:

$$T - T_0 = -\frac{R\Delta H}{2S\sqrt{C_p \rho k}}\left[2\sqrt{\frac{t}{\pi}}e^{-\frac{C_p \rho X^2}{4Kt}} - \sqrt{\frac{C_p \rho}{k}}X\,erfc\left(\frac{X}{2}\sqrt{\frac{Cp\rho}{kt}}\right)\right]. \quad (10)$$

The temperature increase in the repository (ΔT) is obtained by setting X = 0 in equation (6):

$$\Delta T = T(0,t) - T_0 = -\frac{R\Delta H}{S}\sqrt{\frac{t}{\pi C_p \rho k}}. \quad (11)$$

Equation (7) shows that the repository temperature will increase with t until $t = \frac{M}{R}$, when all the reactant is consumed. Here M is the inventory of the reactant in a waste panel (moles). Therefore, the maximum temperature increase (ΔT_{max}) in the repository due to the exothermal reaction can be calculated by

$$\Delta T_{max} = T(0,t) - T_0 = -\frac{\Delta H}{S}\sqrt{\frac{RM}{\pi C_p \rho k}}. \quad (12)$$

Equation (12) shows that, for the reactions not limited by brine inflow, reducing the reaction region size does not affect ΔT_{max}, because the parameters S, R, and M will be reduced by the same factor, which is canceled out in the equation. This is not true for the brine-limited reactions, the rates of which are no longer dependent on reactant inventory.

Assuming the physical properties of the surrounding rocks can be represented by halite, we then have:

C_p = 50 J/mole/K (Lide, 1994, p. 12-158)

$\rho = 3.7 \times 10^4$ moles/m^3 (Lide, 1994, p. 4-149)

k = 6 W/m/K = 1.9×10^8 J/year/m/K (Lide, 1994, p. 12-165)

S = 1.2×10^4 m^2 (Sandia WIPP Project, 1992, p. 3-4).

With these parameter values, we obtain from equation (12):

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$$\Delta T_{max} = 2.5x10^{-12} \Delta H \sqrt{RM} \quad . \qquad (13)$$

Results:

(1) Reaction: $MgO + H_2O \rightarrow Mg(OH)_2$

We assume that this reaction is instantaneous and thus is limited by brine inflow. Based on BRAGFLO simulations for E1 scenario (Figure 2), the conservative (maximum) estimate of the rate of brine inflow into a borehole penetrated waste panel is about 200 m^3/year, equivalent to the reaction rate of $1.1x10^7$ moles/year. With $\Delta H = -3.9x10^4$ J/mole (Drever, 1982, p. 351-356) and $M = 2x10^8$ moles, we estimate $\Delta T_{max} \approx 4.5$ K.

(2) Reaction: $Mg(OH)_2 + CO_2(g) = MgCO_3 + H_2O$

We assume that this reaction is limited by microbial CO_2 production. It is estimated that the maximum rate of CO_2 production (R) is $2.9x10^5$ moles/year and the total CO_2 that can be produced (M) is $3.6x10^7$ moles in a single waste panel (Wang & Brush, 1996; DOE/CAO, 1996). With $\Delta H = -0.8x10^5$ J/mole (Drever, 1982, p. 351-256), ΔT_{max}, is estimated to be 0.6 K.

(3) Microbial degradation: $C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2$

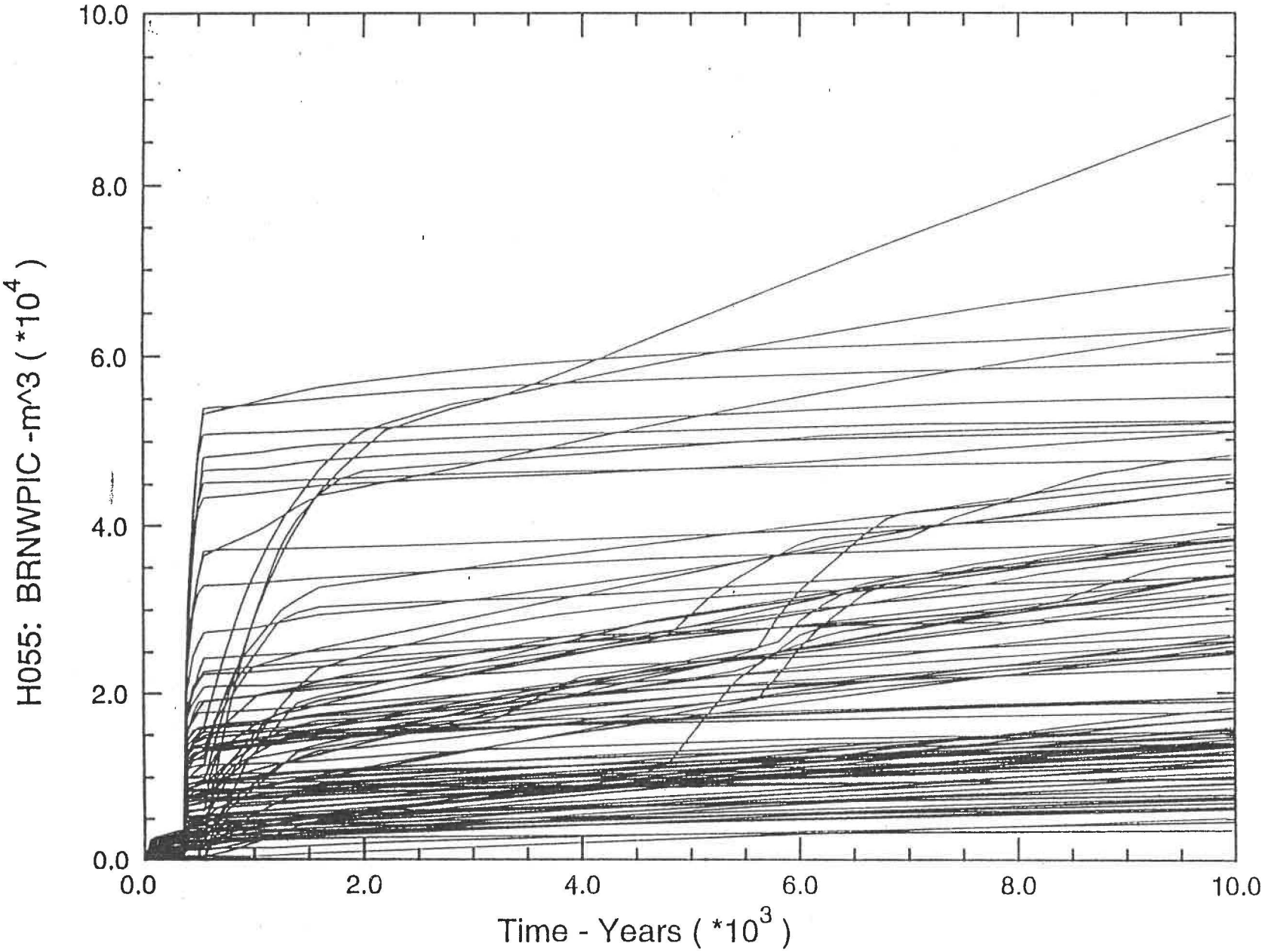
The maximum reaction rate and the inventory of $C_6H_{10}O_5$ in a single waste panel are estimated to be $1x10^5$ moles/year and $1.2x10^7$ moles (Wang & Brush, 1996; DOE/CAO, 1996). With $\Delta H = -3.1x10^5$ J/mole (Lide, 1994, p. 5-16 to 5-37), ΔT_{max}, is estimated to be 0.8 K. Because of lack of thermodynamic data for cellulose materials, we here assume that the enthalpy of $C_6H_{10}O_5$ is approximately equal to that of $C_6H_{10}O_4$.

(4) Aluminum corrosion: $Al + 3H_2O \rightarrow Al(OH)_3 + 1.5\ H_2$

The inventory of Al in a single panel is about $8x10^6$ moles (DOE/CAO, 1996). Aluminum are present as foil in the waste and its thickness is estimated to be $2.54x10^{-4}$ cm. The total surface area of Al foil is thus estimated to be ~ $2.6x10^8$ m^2. With this high surface area and the measured corrosion rate (2.9 mole H_2/m^2/year, Telander & Westerman, 1996), Al corrosion reaction is expected to be limited by brine inflow, and the maximum corrosion rate is ~ $0.4x10^7$ moles/year. With $\Delta H = -4.4x10^5$ J/mole (Drever, 1982, p. 351-356), ΔT_{max}, is estimated to be 6 K.

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Figure 2. SNL WIPP PA96: BRAGFLO SIMULATIONS (CCA R1 S2)



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The two brine-inflow-limited reactions - MgO hydration and Al corrosion - could possibly bring repository temperature up to 6 K. However, this temperature increase will not affect the overall repository performance, for two reasons: (1) The maximum temperature, if it is achieved, will be sustained only over a very short time period. For example, to achieve this temperature, Al has to be corroded completely within 2.5 years. After that, the accumulated heat will be dissipated away quickly. Thus, the maximum temperature, if it is attained, will last perhaps less than a year. (2) More importantly, because the two reactions are brine-limited, they will consume all free brine in the repository until all the reactants are completely consumed. Therefore, the maximum temperature will occur much earlier than enough free brine accumulates in the repository for the release of dissolved actinides. Based on the above calculations, the thermal effect of the other reactions, which are not limited by brine inflow and can last over a significant portion of 10000 year time period, are definitely negligible.

In conclusion, ignoring the thermal effect of chemical reactions (1 - 5) can not affect the overall repository performance assessment.

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