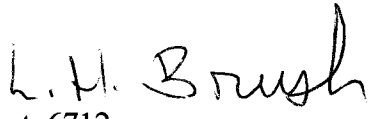


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Sandia National Laboratories  
Waste Isolation Pilot Plant

## Improvements in Our Understanding of How MgO Will Control pH in WIPP Disposal Rooms

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Work Carried Out to Support the CRA-2009

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Page 1 of 9

# Information Only



## 1 INTRODUCTION

This write-up is a response to a request from Los Alamos National Laboratory – Carlsbad Operations (LANL - CO) for information for the CRA-2009, Appendix SOTERM. LANL – CO made this request at a chemistry-and-geochemistry technical exchange meeting that included the U.S. Department of Energy’s Carlsbad Field Office, LANL - CO, and Sandia National Laboratories’ Carlsbad Programs Group (SNL/CPG). This meeting took place on February 20, 2008.

This write-up is an excerpt from a draft report on the status of the WIPP engineered barrier that is being prepared to support the CRA-2009. This excerpt has been reviewed and approved according to the applicable quality assurance procedures of the SNL/CPG, and is in the SNL/CPG WIPP Records Center.

This write-up will also appear in the status report on the WIPP engineered barrier once this report has been completed, reviewed, and approved. Currently, it is included in Section 6, Effects of MgO on the WIPP Disposal System; Subsection 6.1, Effects of MgO on Brine Composition,  $f_{CO_2}$ , pH, and An Solubilities; Subsection 6.1.1, Changes since the CRA-2004. However, these section and subsection numbers and their titles could change as this report is completed, reviewed, and approved.



## 2 IMPROVEMENTS IN OUR UNDERSTANDING OF HOW MgO WILL CONTROL pH IN WIPP DISPOSAL ROOMS

Our understanding of the mechanism by which MgO will control the pH of WIPP brines has evolved since the CRA-2004. The U.S. DOE (2004, Appendix BARRIERS, Subsection BARRIERS- 2.3.2.3) stated that: “The brucite dissolution reaction,



will buffer pH in the WIPP ...” Note that U.S DOE (2004, Appendix BARRIERS, Subsection BARRIERS-2.3.2.3) referred to Reaction 11 as “Reaction 3.”

Brush and Xiong (2003, Table 6) predicted that, in vectors with microbial activity, the pH of GWB and ERDA-6 would be 8.69 and 9.02, respectively, after these brines equilibrate with brucite,  $\text{Mg}_2\text{Cl(OH)}_3 \cdot 4\text{H}_2\text{O}$  (in the case of GWB), hydromagnesite (5424), halite, anhydrite, glauberite (ERDA-6), whewellite, and the An-bearing solids  $\text{Am(OH)}_3$ ; hydrous, amorphous  $\text{ThO}_2$ ; and  $\text{KNpO}_2\text{CO}_3$ .

At the time of the CRA-2004, we expected that: (1) if acidification (addition of  $\text{H}^+$ ) of WIPP brines occurs, dissolution of brucite (and  $\text{Mg}_2\text{Cl(OH)}_3 \cdot 4\text{H}_2\text{O}$  in GWB) would release  $\text{OH}^-$ , which would react with  $\text{H}^+$  to make  $\text{H}_2\text{O}$ ; and (2) if basification (addition of  $\text{OH}^-$ ) occurs, precipitation of brucite (and  $\text{Mg}_2\text{Cl(OH)}_3 \cdot 4\text{H}_2\text{O}$  from GWB) would remove  $\text{OH}^-$ .

The reason why we expected that the brucite dissolution-precipitation reaction would buffer the pH is that the ratio of the product of the activity (the concentration times the activity coefficient) of each product of Reaction 11 ( $\text{Mg}^{2+}$  and  $\text{OH}^-$ ) divided by the activity of the reactant (brucite) is a constant:

$$K_{sp} = ([\text{Mg}^{2+}] \times [\text{OH}^-]^2) \div [\text{Mg(OH)}_2]. \quad (2)$$

In Equation 12, the equilibrium constant  $K_{sp}$  is referred to as the “solubility product” because it is the equilibrium constant for a dissolution-precipitation reaction, and the brackets denote the activities of the species enclosed in brackets.

The activity of a pure solid such as brucite is usually taken to be unity. Although Fe(II) might substitute for the Mg in brucite to some extent, the activity of brucite is assumed to be 1 to simplify this discussion. Equation 12 then becomes:

$$K_{sp} = [\text{Mg}^{2+}] \times [\text{OH}^-]^2 = 10^{-10.8842} \quad (3)$$

The value of  $K_{sp}$  in Equation 13 is the value in the EQ3/6 and FMT databases, and is from Harvie et al. (1984).

Therefore, dissolution or precipitation of brucite (and  $\text{Mg}_2\text{Cl(OH)}_3 \cdot 4\text{H}_2\text{O}$  from GWB) would occur in response to acidification or basification, respectively, to maintain the product of

the activities of  $Mg^{2+}$  and  $OH^-$  at a constant value equal to  $K_{sp}$ . Reaction 11 would be an effective buffer reaction as long as sufficient brucite were present to dissolve in response to acidification, and as long as sufficient  $Mg^{2+}$  were present to precipitate  $OH^-$  in the event of basification. The  $Mg^{2+}$  could come from the brine or dissolution of a Mg-bearing mineral that yields  $Mg^{2+}$  in stoichiometric excess of any  $OH^-$  or other highly basic anion (e.g.,  $CO_3^{2-}$ ) produced. Thus, hydromagnesite (5424) ( $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ) or magnesite ( $MgCO_3$ ) would not contribute any  $Mg^{2+}$  useful for pH buffering because the dissolution of these solids would not yield  $Mg^{2+}$  in stoichiometric excess of  $OH^-$  and/or  $CO_3^{2-}$ . Various hydrates of otherwise pure  $MgCl_2$  and  $MgSO_4$ , on the other hand, could contribute substantial useful  $Mg^{2+}$ , but these phases are not present in the repository or the Salado. Dissolution of polyhalite ( $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$ , which is present in the disturbed rock zone (DRZ), could produce useful  $Mg^{2+}$  due to its  $MgSO_4$  content, but it is uncertain to what extent brine would react with minerals in the DRZ. Hence, the amount of Mg in the near-field chemical system that is useful for buffering pH against basification is limited, and high pH is obtainable under those circumstances in which  $OH^-$  production is sufficient to overwhelm this Mg.

Since the CRA-2004, however, Brush et al. (2006) identified a mechanism that could increase the pH of WIPP brines under some circumstances. Based on calculations carried out using EQ3/6 (Daveler and Wolery, 1992; Wolery, 1992a; 1992b; Wolery and Daveler, 1992), Brush et al. (2006) predicted that, if microbial sulfate ( $SO_4^{2-}$ ) reduction continues after the consumption of all of the  $SO_4^{2-}$  in the waste by dissolving the minerals anhydrite ( $CaSO_4$ ) and gypsum ( $CaSO_4 \cdot 2H_2O$ ) from the disturbed rock zone (DRZ) surrounding the repository, the pH would remain at a value of about 9. If, however,  $SO_4^{2-}$  reduction proceeds using the mineral polyhalite ( $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$ ) or its alteration product syngenite ( $K_2Ca(SO_4)_2 \cdot H_2O$ ), the pH could increase to values in the range of 9.5 to 11.3, due to production of  $OH^-$  in sufficient quantities to overwhelm the available useful Mg (even though polyhalite would add some useful Mg).

Therefore, the buffer capacity of Reaction 11 with respect to basification is limited by the availability of sufficient useful Mg, which consists of dissolved  $Mg^{2+}$  and some Mg present in DRZ minerals. However, there is more than enough brucite available to prevent acidification because the DOE is emplacing more MgO than necessary to consume all of the  $CO_2$  that would be produced by microbial activity should all of the CPR materials in the repository be consumed (Section 7).

Thus, we now view the brucite dissolution-precipitation reaction as a reaction that will control the pH in the WIPP by effectively preventing the acidification of brines, not as a buffer that would necessarily prevent both acidification and basification in all possible scenarios.

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