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Subject: MgO Engineered Barrier System at WIPP Buffering Cement in the Waste Repository

The U.S. environmental Protection Agency (EPA) submitted "Completeness Questions" to the U.S. Department of Energy (DOE) as part of the 2019 Compliance Recertification Application (CRA-2019) through performance assessment, including the question regarding "*Effects of Cements on Brine Chemistry*" (EPA, 2020). The DOE examined the effects of cement in depth and responded to this question (DOE, 2021a and 2021b). Domski (Domski, 2025) documented a similar analysis for the 12-panel repository using the minimum brine volume, a thermodynamic database, DATA0.FM6 (Domski, 2023), the iron and lead reactants, the suppression of solid phases (calcite, $Am(OH)_3(s)$, and Phase 5), an updated repository area and inventory in the 2026 Compliance Recertification Application for the Interim State repository (CRA-2026 IS).

Portland cement is comprised of 60 – 67% by weight CaO, which is conservatively assumed to be present as the mineral portlandite [$Ca(OH)_2(s)$]. The MgO WIPP engineered barrier, via the chemical conditions conceptual model, specifies that 50% of the MgO is present as the carbonated phase hydromagnesite [$Mg_5(CO_3)_4(OH)_2.4H_2O$]. The reaction of portlandite with hydromagnesite is a pH neutralizing reaction where the hydroxide ion (OH^-) released by portlandite dissolution is converted to water via hydromagnesite dissolution. The reaction is provided below:

$$4\,\mathrm{Ca(OH)_2} + Mg_5(CO_3)_4(OH)_2 * 4\,H_2O + 10\,H^+ \rightleftharpoons 4\,CaCO_3 + 5\,Mg^{2+} + 14\,H_2O \quad (1)$$

The Ca^{2+} ion from the dissolution of portlandite ($Ca(OH)_2(s)$) and the CO_3^{2-} ion from the dissolution of hydromagnesite form a calcium carbonate phase, aragonite ($CaCO_3(s)$) was assumed by Domski (2025), while the hydroxide from the portlandite combines with H^+ ion to form water. The reaction neutralizes four moles of portlandite with four moles of CO_3^{2-} in one mole of hydromagnesite (Domski, 2025).

To determine if the MgO engineered barrier system at WIPP is sufficient to buffer any pH effects of cement in the waste inventory, the ratio of total moles of carbonate to total moles of portlandite,

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$Ratio_{CO3:Port}$, is estimated in the repository. The ratio between carbonate (CO_3^{2-}) and portlandite is defined based on methods (Domski, 2025) for calculating total moles of hydromagnesite and $Ca(OH)_2(s)$:

$$Ratio_{CO3:Port} = 0.0402 \frac{K_{cell}+K_{plas}f_{plasfac}+K_{rubb}}{f_{mw_cell}K_{cement}} \quad (2)$$

A constant value of 0.0402 Kg/mole is determined by five parameter values (= 1.2 × 0.1 × 4 × 0.056077 / 0.67):

(1) MgO excess factor of 1.2;
(2) Distribution probability of 0.1 that the MgO can be present as hydromagnesite;
(3) Mole ratio of CO_3^{2-} in hydromagnesite of 4;
(4) Molar weight of CaO of 0.056077 Kg/mole; and
(5) Assumed mass ratio of 0.67 that CaO can be present in cement.

The variables K_{cell}, K_{plas}, K_{rubb}, and K_{cement} represent total masses (in Kg) of cellulose, plastic, rubber, and cement in the PAIR repository inventory data. The variables $f_{plasfac}$ and f_{mw_cell} are the WIPP PA parameter values of REFCON:PLASFAC (1.7 Kg equivalent cellulose/Kg plastic) and REFCON:MW_CELL (0.027023 Kg/mole carbon).

If $Ratio_{CO3:Port} < 1$, then the capacity of the MgO buffer could be exceeded by cement, thereby affecting the pH and actinide solubility. If $Ratio_{CO3:Port} > 1$, then the MgO buffer will not be exceeded by cement and neutralizes potential pH increase by OH- increase from portlandite dissolution. Therefore, there should be no effect of inventory cement on the system pH.

With the CRA-2026 IS PAIR values (Tables 5-5, 5-6, and 5-7 of Van Soest, 2025b) of cellulose, plastic, rubber, and cement as input, Equation (2) estimates $Ratio_{CO3:Port}$ at 5.4. For comparison with other previous analyses, Table 1 lists input values of cellulose, plastic, rubber, and cement, and calculated $Ratio_{CO3:Port}$ values in the CRA-2019, Replacement Panels Planned Change Request (RPPCR), 2026 Compliance Recertification Application for the Final State repository (CRA-2026 FS), and CRA-2026 IS analyses.

Table 1. Properties determined based on computation steps for the mole ratio of CPR/Cement (= moles of CO_3^{2-} / moles of $Ca(OH)_2(s)$) and the PAIR data for the CRA-2019 (Van Soest, 2018), RPPCR (Van Soest, 2022), CRA-2026 FS (Van Soest, 2025a), and CRA-2026 IS (Van Soest, 2025b) analyses.

Analysis	CRA-2019	RPPCR	CRA-2026 FS	CRA-2026 IS
Total Cellulose (kg)	5.97E+06	7.18E+06	1.10E+07	9.71E+06
Total Plastic (kg)	1.06E+07	1.29E+07	1.41E+07	1.18E+07
Total Rubber (kg)	1.22E+06	1.33E+06	1.30E+06	1.14E+06
Total Cement (kg)	8.88E+06	8.75E+06	8.61E+06	8.55E+06
Ratio of CO_3^{2-} to $Ca(OH)_2(s)$	4.2	5.2	6.3	5.4

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The $Ratio_{CO3:Port}$ values in four recent analyses (Table 1) indicate that the MgO buffer sufficiently neutralize the pH increase by portlandite dissolution. The MgO buffer interaction with portlandite (Equation 1) also demonstrates the liberation of 14 moles of water per one mole of hydromagnesite consumed from 4 moles of portlandite dissolution. The thermodynamic model simulations for the cement cases by the EQ6 and the WIPP thermodynamic database, DATA0.FM6, also showed the negligible increase in pH and the small changes in the actinide solubilities by the increased value of water activity (Domski, 2025). These changes had a negligible effect on the dissolved actinide concentrations.

An Excel spreadsheet (*Ratio_calculation_in_analyses.xlsx*) was developed to calculate the ratio of total moles of carbonate to total moles of portlandite that is included in the CVS repository at /CVSLIB/WIPP EXTERNAL/MgOCRA26.

References

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