Sandia National Laboratories
Waste Isolation Pilot Plant

Review of the Calculations of the Quantity of MgO That Could Be Lost from the WIPP By Dissolution in Brine: Mg Solubility in Castile Brine

Work carried out under the Analysis Plan for CRA Response Activities, AP-112, Rev. 0

Author: L. H. Brush   8/26/04
                         Laurence H. Brush, 6822   Date

Technical Reviewer: (signature)   8/26/04
                         Nathalie A. Wall, 6822   Date

QA Reviewer: (signature)   8/26/04
                         Mario J. Chavez, 6820   Date

Management Reviewer: (signature)   9/1/04
                         Mark J. Rigali, 6822   Date

WIPP: 1.3.1: PA: QA-L: DTRPI: Pkg 533999

TABLE OF CONTENTS

1 INTRODUCTION

Sandia National Laboratories' Carlsbad Programs Group has carried out an internal review of the methods used to calculate MgO safety factors. This review has identified the solubility of MgO in brine that could flow up a borehole in the event of human intrusion as one of the parameters that changed significantly from the WIPP Compliance Certification Application (CCA) in 1996 to the first WIPP Compliance Recertification Application (CRA) in 2004. Therefore, I have reviewed both the original and the updated calculations of Mg solubilities. This work was carried out under the Analysis Plan for CRA Response Activities (Kirkes and Wagner, 2004).

I have concluded that the best estimate of the solubility of Mg in the Castile brine ERDA-6 is 130-145 mM, the range calculated by the geochemical speciation and solubility code Fracture-Matrix Transport (FMT) (Babb and Novak, 1997 and addenda) during the actinide-solubility calculations for the CRA performance assessment (PA) (Brush and Xiong, 2003a; 2003c; Downes, 2003).

2 DISCUSSION

Peterson (1996, p. 1) calculated "the mass of MgO backfill that could be emplaced in the total free volume of the WIPP, ... the amount of MgO required to react with all the CO_2 generated from microbial processes, ... and the amount of MgO that will be dissolved in Castile brine and a mixture of 90% Castile and 10% Salado brine."

Peterson (1996) never stated that the "MgO" dissolved in brine would be lost in the event of human intrusion. Nevertheless, it seems to have become conventional wisdom that this is what his calculations of "the amount of MgO that will be dissolved in Castile brine and a mixture of 90% Castile and 10% Salado brine" were intended for. From a geochemical point of view, the MgO dissolved in brine would not be lost *unless* it were released from the repository, either by human intrusion or by pressure-induced flow into fractures surrounding the repository.

Peterson (1996, p. 2) stated:

> "The [Mg] concentration in Castile brine was estimated from an EQ3NR calculation by Yifeng Wang. Appendix B contains the first page of the input file and the calculated concentration of Mg^{++}.

> "As shown in Appendix B, the maximum concentration of Mg^{++} was about 0.02 moles per kg of H_2O.

> "As is also shown in the input file in Appendix B, the initial Mg^{++} concentration was 0.019 moles per kg of H_2O."

Appendix B of Peterson (1996) contains an EQ3NR input file for the Castile brine ERDA-6 and a plot from an EQ6 run that simulated the reaction of ERDA-6 with periclase (pure, crystalline MgO - the main reactive constituent of the WIPP engineered barrier). The EQ6 plot shows the predicted concentrations of Mg^{2+} (the dominant dissolved Mg species under the conditions of this run) along with the predicted concentrations of $MgOH^+$ and $MgCO_3(aq)$ (the second and third most important aqueous species, respectively) as ERDA-6 reacts with periclase. However, Appendix B does not contain any EQ3NR output files, any EQ6 input or output files, or any references to such files.

Nevertheless, the EQ6 plot for ERDA-6 shows that the Mg^{2+} concentration (and hence the total dissolved Mg concentration) increased slightly from its initial concentration for values of log_{10}(mol MgO added/kg H_2O) from about −2.5 to −0.5, then decreased to values slightly lower than its initial concentration for the rest of the run. Therefore, Peterson (1996, p. 2) probably concluded that reaction of ERDA-6 with periclase would increase the Mg concentration of ERDA-6 from 19×10^{-3} m to 20×10^{-3} m based on this plot, not on the EQ3NR run. Peterson (1996, p. 2) then multiplied ((20 - 19) $\times 10^{-3}$ m Mg) × (1.216 kg brine/L) × (0.73 kg H_2O/kg brine) × 10^6 m^3 of brine × 10^3 L/m^3 to obtain 8.88×10^5 mol "MgO" dissolved in Castile brine.

Yongliang Xiong talked to Wang in May 2003 about updating Wang's EQ3/6 runs for Peterson (1996). Wang suggested it would be easier to use EQ3NR to calculate the solubility of brucite ($Mg(OH)_2$, the hydration product of periclase), in ERDA-6 than to rerun EQ6. Xiong's EQ3NR run (Snider, 2003, Appendix D) yielded a Mg solubility of 100 mm, or 88.3 mM. This implied that significantly more MgO would have to dissolve in ERDA-6 to increase its concentration from 19 mM (Popielak et al., 1983) to 88.3 mM, the solubility of brucite, than predicted by Wang in 1996. The aqueous Mg speciation predicted by Xiong's EQ3NR run was: Mg^{2+}: 90.8 mm; $MgCO_3(aq)$: 9.15 mm; $MgOH^+$: 0.493 mm (see Table 1).

Xiong's higher Mg solubility (Snider, 2003, Appendix D) apparently resulted from differences in the simulation of reactions between brines and the engineered barrier. For Peterson (1996), Wang titrated periclase into ERDA-6 and Brine A. Thereafter, however, Wang titrated brucite into these brines. In particular, Wang used EQ6 runs in which he titrated brucite into Brine A or ERDA-6 to predict the f_{CO_2} and pH used for the FMT solubility calculations for the CCA PA. FMT runs consistent with this approach have also been used for the PAVT and the CRA PA. Therefore, Xiong's EQ3NR run (Snider, 2003, Appendix D) is consistent with the methods used to calculate actinide solubilities for PA.

Xiong's EQ3NR output file (Snider, 2003, Appendix D) demonstrated that ERDA-6 was saturated or supersaturated with the following minerals in his run: aragonite ($CaCO_3$), anhydrite ($CaSO_4$), brucite ($Mg(OH)_2$), calcite ($CaCO_3$), gaylussite ($Na_2Ca(CO_3)_2 \cdot 5H_2O$), glauberite ($Na_2Ca(SO_4)_2$), gypsum ($CaSO_4 \cdot 2H_2O$), halite ($NaCl$), hydromagnesite ($Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$ and $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$), and pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$). Xiong suppressed dolomite ($CaMg(CO_3)_2$) and magnesite ($MgCO_3$); therefore, these minerals did not appear in the table of mineral saturation states. Furthermore, the pH calculated by EQ3NR was 8.9. The saturated and supersaturated minerals and the pH obtained by Xiong in May 2003 are very similar to those obtained by Brush and Xiong (2003a, 2003c) and Downes (2003) with Fracture-Matrix Transport (FMT) for ERDA-6 after equilibration with brucite, hydromagnesite, halite, anhydrite, and other minerals for the actinide-solubility calculations for the CRA PA. However, these FMT calculations predicted dissolved Mg concentrations in ERDA-6 of 145 mM for nonmicrobial PA vectors (Run 22) and 130 mM for microbial PA vectors (Run 28). These concentrations are significantly higher than those predicted by Xiong with EQ3NR (Snider, 2003, Appendix D).

These differences result from: (1) inclusion of Pitzer parameters for the organic ligands acetate, citrate, ethylenediaminetetraacetate (EDTA), and oxalate in the FMT database, but not in the EQ3/6 database; (2) inclusion of Pitzer parameters for dissolved boron (B) species and B-bearing solids in the FMT thermodynamic database, but not in the EQ3/6 database; (3) a slightly higher Gibbs free energy of formation for brucite in the FMT database than in the EQ3/6 database.

Table 1. Comparison of Mg Speciation Calculated by EQ3NR without B or Organics and by FMT with B and with and without Organics (mM). All concentrations rounded to three significant figures.

Dissolved Species	Xiong's May 2003 EQ3NR Run (mM)[B, C]	FMT Run 21[A] (non-microbial PA vectors, without organics) (mM)	FMT Run 22[A] (non-microbial PA vectors, with organics) (mM)	FMT Run 27[A] (microbial PA vectors, without organics) (mM)	FMT Run 28[A] (microbial PA vectors, with organics) (mM)
Inorganic Species:					
Mg^{2+}	79.8	109	111	94.6	97.4
$MgB(OH)_4^+$	-	11.7	11.8	10.5	10.7
$MgOH^+$	0.433	0.666	0.672	0.618	0.626
$MgCO_3(aq)$	8.04	0.0617	0.0629	0.279	0.279
Organic Species:					
$MgOx(aq)$	-	-	19.9	-	19.7
$MgAc^+$	-	-	1.42	-	1.31
$MgCit^-$	-	-	0.353	-	0.349
$MgEDTA^{2-}$	-	-	0.00358	-	0.00355
Total Dissolved Mg	88.3	121	145	106	130

A. Brush and Xiong (2003c, Table 2) provided the file names, file numbers, brine types, equilibrium mineral assemblages, and whether or not organic ligands were included in the 30 runs used to calculate actinide speciation and solubility for the CRA PA.

B. The concentrations given in the EQ3NR output file (rounded to three significant figures) were Mg^{2+}: 90.8 mm (millimolal); $MgOH^+$: 0.493 mm; $MgCO_3(aq)$: 9.15. The Mg solubility was 100 mm.

C. The concentration of $MgCO_3(aq)$ is higher than that of $MgOH^+$ because f_{CO_2} in this run was $10^{-4.03}$ atm, significantly higher than that in FMT Run 21, 22, or 28.

Inclusion of Pitzer parameters for the organic ligands acetate, citrate, EDTA, and oxalate in the FMT database is the most important reason why higher Mg solubilities were obtained with FMT. Comparisons of the solubilities predicted by FMT Run ap098_fmt_run021 and

FMT Run ap098_fmt_run022 (stored in Configuration Management System Library LIB_AP098_FMT), hereafter referred to as "Run 21" and "Run 22," respectively; and by Run 27 and Run 28 illustrate the effects of organics. The conditions for these runs were identical, except that Run 21 and Run 27 had no organics, but Run 22 and Run 28 included organics at the concentrations calculated by Brush and Xiong (2003b) for the CRA PA. The Mg solubility predicted by Run 22 is 145 mM, 19.8% higher than the solubility of 121 mM predicted in Run 21; the Mg solubility predicted by Run 28 is 130 mM, 22.6% higher than the solubility of 106 mM predicted by Run 27 (see Table 1). The Mg speciation predicted by Run 22 is: Mg^{2+}: 111 mM; Mg oxalate(aq): 19.9 mM; $MgB(OH)_4^+$: 11.8 mM; Mg acetate$^+$: 1.42 mM; $MgOH^-$: 0.672 mM; Mg citrate$^-$: 0.353 mM; $MgCO_3$(aq): 0.0629 mM; and Mg $EDTA^{2-}$: 0.00358 mM. However, the Mg oxalate(aq) concentration predicted by Run 22 (and that predicted by Run 28) is probably too high because the FMT database includes Na oxalate(solid), but not Ca oxalate(solid) (the solid expected to control the solubility of oxalate(aq) in WIPP brines). Xiong found that inclusion of the Gibbs free energy of formation for Ca oxalate(solid) from the National Bureau of Standards database would decrease the dissolved oxalate concentration by about four orders of magnitude, which would in turn decrease the Mg oxalate(aq) concentration significantly. The differences between Run 21 and Run 27 and between Run 22 and Run 28 result from the use of the brucite-calcite carbonation reaction to buffer f_{CO_2} in nonmicrobial vectors, and the brucite-hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) carbonation reaction to buffer f_{CO_2} in nonmicrobial vectors. These reactions buffered f_{CO_2} at values of $10^{-6.15}$ and $10^{-5.50}$ atm, respectively, in these runs.

Inclusion of B in the FMT database also increased the solubility of Mg somewhat. Comparison of Xiong's EQ3NR run and FMT Run 21 illustrates the effect of B. The EQ3NR and FMT thermodynamic databases used for these runs are very similar, except that the FMT database includes Pitzer parameters for B. The Mg solubility predicted by Xiong's EQ3NR run is 100 mm (88.3 mM); that predicted by FMT Run 21 is 121 mM (Table 1). The Mg speciation predicted by FMT Run 21 is: Mg^{2+}: 109 mM; $MgB(OH)_4^+$: 11.7 mM; $MgOH^-$: 0.666 mM; $MgCO_3$(aq): 0.0617 mM. Thus, $MgB(OH)_4^+$ constituted 9.67% of the dissolved Mg.

Finally, the Gibbs free energy of formation of brucite in the EQ3/6 database is -831.440 kJ/mol; the corresponding value in the FMT database is -831.396 kJ/mol. Therefore, if all other parameters in these databases were identical, FMT would predict brucite solubilities slightly higher than those predicted by EQ3/6.

This discussion demonstrates that the best estimate of the solubility of Mg in the Castile brine ERDA-6 is 130-145 mM, the range calculated by FMT during the actinide-solubility calculations for the CRA PA (Brush and Xiong, 2003a; 2003c; Downes, 2003). However, this range probably overestimates the Mg solubility somewhat because the FMT thermodynamic database used for the CRA PA did not contain the Gibbs free energy of formation of solid Ca oxalate, the solid phase expected to control the solubility of oxalate in WIPP brines. Inclusion of Ca oxalate in FMT calculations: (1) decreases the dissolved oxalate concentration relative to that in equilibrium with Na oxalate, the solid phase that controlled the solubility of oxalate in the FMT calculations for the CRA PA; and (2) decreases the total dissolved Mg concentration, because MgOx(aq) is the dissolved Mg species with the second highest concentration (see Table 1). Inclusion of Ca oxalate in the FMT database also decreases the

solubility of Np(V), because oxalate forms strong complexes with actinides in the +V oxidation state. Xiong (2004) has added Ca oxalate to QA'ed version of the FMT database, but QA'ed speciation and solubility calculations have not been carried out with this database yet. Therefore, the best estimate of the solubility of Mg in ERDA-6 will continue to be 130-145 mM until new, QA'ed FMT calculations are carried out.

3 CONCLUSIONS

I have reviewed both the original and the updated calculations of Mg solubilities ERDA-6 and have concluded that the best estimate of the solubility of Mg in this brine is 130-145 mM, the range calculated by FMT during the actinide-solubility calculations for the CRA PA (Brush and Xiong, 2003a; 2003c; Downes, 2003).

4 REFERENCES

Babb, S.C., and C.F. Novak. 1997 and addenda. "User's Manual for FMT Version 2.3: A Computer Code Employing the Pitzer Activity Coefficient Formalism for Calculating Thermodynamic Equilibrium in Geochemical Systems to High Electrolyte Concentrations." Albuquerque, NM: Sandia National Laboratories. ERMS 243037.

Brush, L.H., and Y. Xiong. 2003a. "Calculation of Actinide Solubilities for the WIPP Compliance Recertification Application, Analysis Plan AP-098, Rev. 1." April 14, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 527714.

Brush, L.H., and Y. Xiong. 2003b. "Calculation of Organic Ligand Concentrations for the WIPP Compliance Recertification Application." Analysis report, April 14, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 527567.

Brush, L.H., and Y. Xiong. 2003c. "Calculation of Actinide Solubilities for the WIPP Compliance Recertification Application." Analysis report, May 8, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 529131.

Downes, P.S. 2003. "Spreadsheet Calculations of Actinide Solubilities for the WIPP Compliance Recertification Application in Support of AP-098, 'Calculation of Actinide Solubilities for the WIPP Compliance Recertification Application, Analysis Plan AP-098, Rev. 1.'" Analysis report, July 22, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 530441.

Kirkes, G.R., and S.W. Wagner. 2004. "Analysis Plan for CRA Response Activities." AP 112, Rev. 0, April 26, 2004. Carlsbad, NM: Sandia National Laboratories. ERMS 534690.

Peterson, A.C. 1996. "Mass of MgO That Could Be Added as Backfill in the WIPP and the Mass of MgO Required to Saturate the Brine and React with the CO_2 Generated by Microbial Processes." Unpublished analysis report, March 11, 1996. Albuquerque, NM: Sandia National Laboratories. ERMS 236214.

Popielak, R.S., R.L. Beauheim, S.R. Black, W.E. Coons, C.T. Ellingson and R.L. Olsen. 1983. *Brine Reservoirs in the Castile Formation, Waste Isolation Pilot Plant Project, Southeastern New Mexico*. TME 3153. Carlsbad, NM: U.S. Department of Energy WIPP Project Office.

Snider, A.C. 2003. "Calculation of the Quantities of MgO Required for Consumption of CO_2 for the WIPP Compliance Recertification Application." Unpublished analysis report, July 3, 2003. Carlsbad, NM: Sandia National Laboratories. ERMS 530220.

Xiong, Y. 2004. "A Correction of the Molecular Weight of Oxalate in FMT_021120.CHEMDAT, and Incorporation of Calcium Oxalate Monohydrate (Whewellite) into CHEMDAT with Its Recommended Dimensionless Standard Chemical Potential (μ^0/RT) Value." Memorandum to L.H. Brush, June 8, 2004. Carlsbad, NM: Sandia National Laboratories. ERMS 535813.