

**APPENDIX I
GEOCHEMICAL SIMULATIONS OF ENGINEERED
ALTERNATIVES WITH SALADO BRINE**

M

THIS PAGE INTENTIONALLY LEFT BLANK

M

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
6

GEOCHEMICAL SIMULATIONS OF ENGINEERED
ALTERNATIVES WITH SALADO BRINE

7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
6

1.0 INTRODUCTION

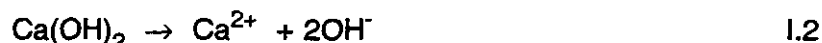
8 One pathway considered for the release of radionuclides to the accessible environment is the
9 dissolution of radionuclides in brine that may come in contact with the waste, followed by
10 transport of the contaminated brine to the accessible environment. Brine can be transported via
11 fractures caused by excessive pressurization of the repository by gas generation, or by pathways
12 created by human intrusions. A key factor controlling the release of radionuclides by these
13 mechanisms is the solubility of the radionuclides in brine. Solubility is defined, in this case, as
14 the maximum mass of a given actinide element that can dissolve in a unit volume of brine of a
15 specified composition. The solubilities of the actinide elements of concern are complex functions
16 of several parameters, however, they all show similar behavior with respect to pH. Solubility
17 decreases as the pH rises above neutrality, often reaching a solubility minimum in the range of
18 8.5 to 10.

19
20 The ability of brine to transport radionuclides could be greatly reduced if the pH of any brine that
21 accumulates in the repository is raised from the ambient value of around 6.1 to a value that is
22 closer to the solubility minimum range. Engineered alternatives (EA) that buffer the pH to a more
23 favorable range (by the addition of lime [calcium oxide, or CaO] or portland-type cement, which
24 contains a large percentage of hydrated lime [portlandite, or Ca(OH)₂], to either the drum contents
25 or backfill) will show improved performance because of lower actinide solubilities.

6
27 An increase in pH by the addition of lime can be thought of as a two-step reaction in which
28 calcium oxide forms portlandite by the reaction:



31
32 followed by portlandite dissociation by the reaction:



35
36 to yield calcium ions (Ca²⁺) and hydroxide ions (OH⁻). The additional hydroxide ions increases
37 the pH of the Salado brine which has a desirable effect of lowering actinide solubilities.

38
39 The addition of lime to pure water at and above the saturation point will raise the pH to an
40 equilibrium value of ~11.8. A significant difference between pure water and Salado brine
41 however, is the very high magnesium concentration which buffers the pH at values significantly
42 below 11.8.

43
44 Computer simulations were performed to predict the effects of the addition of lime to Salado brine
45 to determine the equilibrium pH value and buffer capacity. These simulations were performed
46 using the EQ3NR and EQ6 geochemical speciation-solubility-reaction path models (Wolery, 1992a
47 and Wolery, 1992b). The following sections describe some background information on the
48 EQ3NR/EQ6 geochemical model, the modeling approach used for the simulations, and the results
49 and conclusions of the geochemical simulations.



1
2
3
4

2.0 BACKGROUND

5 The computer code EQ3NR/EQ6 is an industry-standard chemical reaction model that performs
6 solubility, speciation, and reaction-path calculations. The initial version of the EQ3NR/EQ6 code
7 was developed in 1979 at Lawrence Livermore National Laboratory for predicting the behavior of
8 metals, radionuclides, and other contaminants in the natural environment. The code has been
9 actively maintained and improved over the last fourteen years with funding from a wide variety
10 of sources. The current version of the code accesses a database containing the thermodynamic
11 properties of 78 elements, 862 aqueous species, 886 minerals, and 76 gases; and is valid over
12 a temperature range of 0° to 300°C.
13

14 The database also contains references for all of the values to provide traceability, and can be
15 modified or expanded by the user. EQ3NR/EQ6 has been validated using standard geochemistry
16 problems such as the speciation of sea water, basalt/sea water interactions, and numerous
17 comparisons with experimentally determined mineral solubilities. Successful benchmark
18 comparisons with the results of similar codes have also been performed. The code allows the
19 use of the Pitzer approach as an option for the calculation of activity coefficients. This approach
20 allows accurate modeling of high ionic strength solutions such as Salado brines using a
21 specifically designed thermodynamic data base (Harvie, Moller, and Weare data base).
22

23 The main advantage of EQ3NR/EQ6 over other chemical reaction codes is the ability to perform
24 reaction path simulations. When operated in this mode, an assemblage of reactants (liquids,
25 solids, or gases) are introduced to an aqueous solution in a series of small steps. An unlimited
26 number of reactants can be added in parallel, each at its own rate. At each step, the
27 composition of the fluid is recalculated and the data base of solid minerals is scanned to
28 determine if any minerals are oversaturated. If oversaturation of a particular mineral occurs, then
29 it is allowed to precipitate so that it is maintained in equilibrium with the fluid. The code then
30 loops back to add another small mass of reactants, recalculate fluid composition, and solve for
31 saturation. This process is repeated (typically hundreds to thousands of times) until the either
32 the system reaches equilibrium with the reactants or the originally specified mass of reactants are
33 exhausted. The output of the code includes tables that chart the composition, pH, and redox
34 state of the fluid; the mass of each reactant consumed, and the mass of each mineral that has
35 precipitated, all as functions of reaction progress.
36
37

38
39
40

3.0 MODELING APPROACH

41 For this application, the composition of an average Salado brine is first defined. This composition
42 is based on data presented in the *1992-1993 Brine Sampling and Analysis Program report* (Deal
43 et al., 1995). Lime is then added in a series of small increments to the brine to determine the
44 effects on pH as a function of the amount of lime added. These simulations are appropriate for
45 EAs that include lime as a backfill additive, or include a portland-based grout backfill. These
46 grouts contain lime as a principal component. The simulations were performed using the Pitzer
47 approach as an option for the calculation of activity coefficients, and accessed the Harvie-Moller-
48 Weare data base which yields accurate results for high ionic strength solutions such as brines.
49



1 Results of these simulations directly provide the changes in solution composition and pH as a
2 function of the mass of lime added to a unit mass of brine. Results also provide the mass of lime
3 consumed and the mass of new minerals precipitated during the process.
4

6 4.0 RESULTS

8
9 Figure I-1 summarizes the results of the simulation of lime addition to Salado brine. The addition
10 of a very small amount of lime to the brine raises the pH from the ambient value of 6.1 to a value
11 of ~8 corresponding to the solubility of magnesium-oxychloride [$Mg_2Cl(OH)_3 \cdot 4H_2O$]. At this
12 point, the further addition of lime results in precipitation of Mg-oxychloride and brucite [$Mg(OH)_2$]
13 with little change in pH. After the addition of 1.1 moles of lime to the original kilogram of brine,
14 almost all of the original Mg present in the brine will have precipitated. At this point, further
15 addition of lime will raise the pH to values above 11, corresponding to the portlandite [$Ca(OH)_2$]
16 pH buffer. The presence of the original Mg concentration of 22,700 mg/l (0.93 moles/liter) thus
17 serves as an effective pH buffer, maintaining the pH between 8.0 and 9.0 in response to the
18 addition of anywhere between 0.05 to 1.1 moles of lime per kg of brine.
19

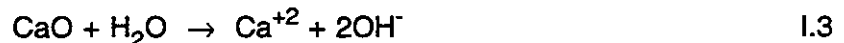
20 The results suggest that the addition of 0.5 moles of lime per kilogram of Salado brine anticipated
21 to flow into the room will poise the system in the middle of the pH-buffer zone at a pH of about
22 8.2.
23

24 Effects of Boron on pH buffer

25
26 Boron is present in the brine at an average concentration of 0.13 moles/l (Deal et al., 1995).
27 Boron can act under some conditions as a pH buffer. The results shown in Figure I-1 do not
28 consider the effects of boron in the simulation because boron is not present in the Harvie-Moller-
29 Weare database.
30

31 To investigate the role of boron on the effects of lime addition, the simulation was rerun with the
32 extended Debye-Hückel activity coefficient option. This option produces less accurate results
33 than the Pitzer option when simulating brine interactions, but it accesses a different
34 thermodynamic database that does contain boron species.
35

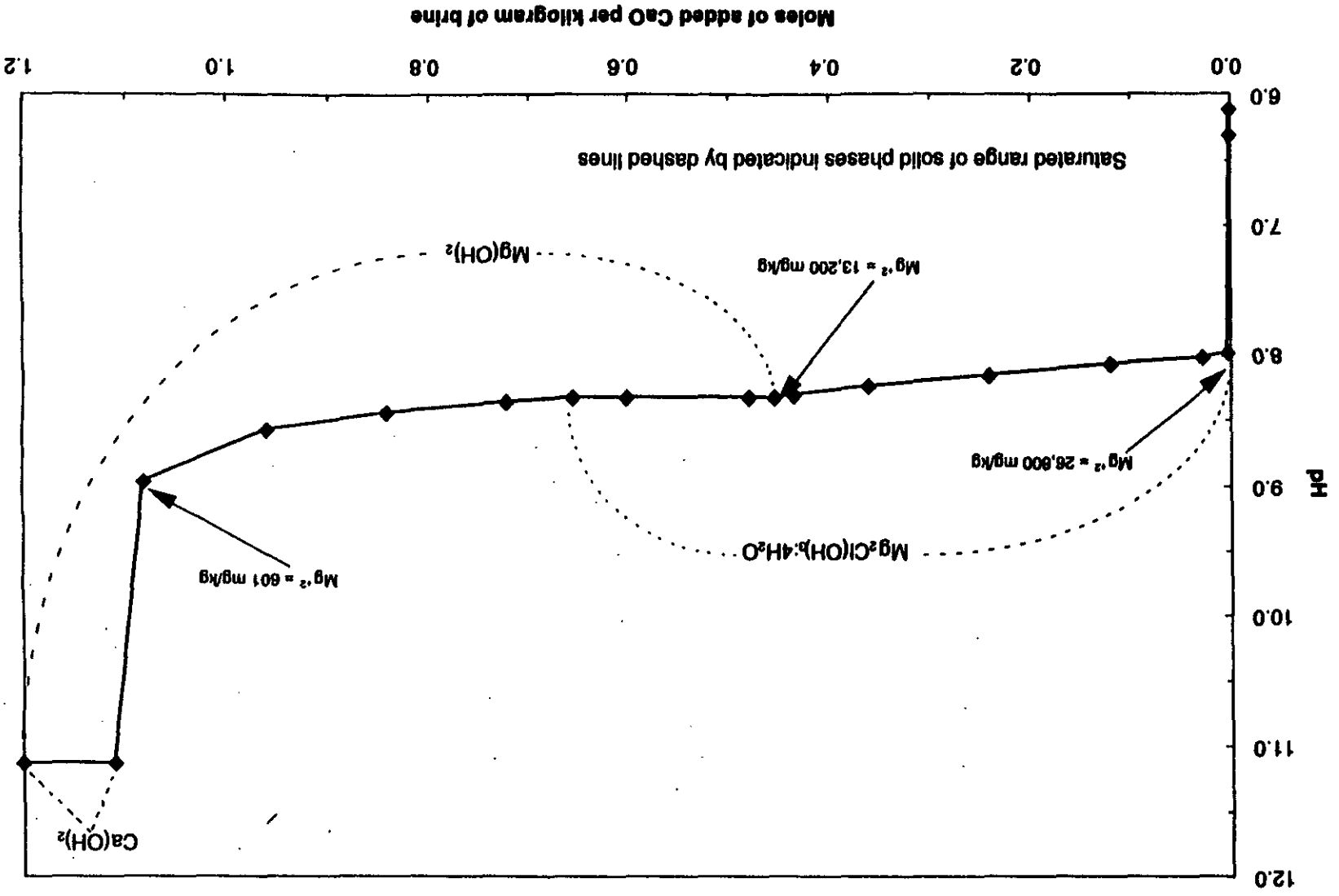
36 Results from this simulation indicate brucite will buffer the brine pH between 8.5 and 9 until
37 magnesium ion is depleted. Boron speciation is initially dominated by $B(OH)_3^0$ at near neutral
38 pH, but the speciation changes to $CaB(OH)_4^+$, $NaB(OH)_4^0$, and to $MgB(OH)_4^+$ (aqueous species
39 of Boron) as pH and calcium (Ca) ion concentration increases. Assuming an average boron
40 concentration in Salado brine of 0.13 mole/L, the addition of 0.13 mole/L of hydroxide ion is
41 necessary to convert all $B(OH)_3^0$ to metal- $B(OH)_4$ species. The addition of 0.13 mole/L of
42 hydroxide ion is equivalent to the addition of 0.07 moles of lime, since two moles of hydroxide
43 ions are liberated for each mole of lime that goes into solution by the reaction:
44



46
47 Thus, conversion of all $B(OH)_3^0$ to metal- $B(OH)_4$ species requires the addition of 0.07 moles of
48 lime. This is a small amount of lime compared to the 0.5 moles/L necessary to reach the midpoint
49 of the Mg-oxychloride/brucite pH buffer. Additionally, at the pH-buffer value of about 8.5, only 65



Figure I-1
EQ6 Modeling Results Showing pH as a function of Moles of CaO Added per Kilogram of WPP Brine



1 percent of the $B(OH)_3^0$ would be converted to metal- $B(OH)_4$ species. Therefore, it appears that
2 the presence of boron in the brine does not require any significant increase in the amount of lime
3 that must be added to the brine to reach the midpoint of the Mg-oxychloride/brucite pH buffer.
4

5.0 CONCLUSIONS

5
6
7
8
9 The pH of the brine can be controlled by adding 0.5 moles of lime per kilogram of Salado brine
10 expected to flow into the disposal rooms. The addition of this amount of lime would raise the pH
11 to ~8.2 and fix the system in the middle of the Mg-oxychloride/brucite pH buffer zone. The
12 anticipated volume of brine inflow does not need to be accurately known because the addition
13 of anywhere between 0.05 to 1.1 moles of lime per kg of brine will maintain the pH between 8
14 and 9.
15



THIS PAGE INTENTIONALLY LEFT BLANK

M