IMPLEMENTATION OF A PITZER ACTIVITY MODEL INTO TOUGHREACT FOR MODELING CONCENTRATED SOLUTIONS

Guoxiang Zhang, Nicolas Spycher, Eric Sonnenthal, and Carl Steefel

Lawrence Berkeley National Laboratory, Berkeley, University of California
1 Cyclotron Road, MS 90-1116
Berkeley, California, 94720, USA
e-mail: gxzhang@lbl.gov

ABSTRACT

TOUGHREACT (Xu et al., 2006) is a general-purpose reactive geochemical transport numerical simulator. It deals with multiphase flow, solute transport and geochemical reactions including aqueous complexation, mineral dissolution/ precipitation and cation exchange. Making use of an extended Debye-Hückel ion activity model, this simulator can handle solutions concentrated to slightly above ~1 molal with caution, and only for NaCl-dominant waters at ionic strengths up to ~4 molal. However, brines produced under natural and artificial conditions are often more concentrated. To handle such brines, a Pitzer activity model was implemented in TOUGHREACT, based on the standard Harvie-Moller-Weare (HMW) formulation that accounts for all binary and ternary combinations of interaction terms. The vapor-pressure-lowering effect caused by the low water activity in brines was also accounted for by this code. The extended version was verified and tested using published results from laboratory experiments and benchmarked against other computer codes. This new version of TOUGHREACT is being applied to the investigation of boiling and evaporation within and around the proposed high-level nuclear waste emplacement tunnels at Yucca Mountain, Nevada. An example application is presented. Processes considered in the example include evaporation of porewater to near dryness, formation of highly concentrated brines, precipitation of deliquescent salts, and generation of acid gases.

1. INTRODUCTION

Concentrated aqueous solutions are in general defined as aqueous solutions with ionic strength higher than 1 molal. Such solutions may be produced in many natural and artificial processes, and exist in many natural and contaminated environments. Scientists need to deal with these solutions when solving environmental problems related to water evaporation/boiling, seawater intrusion (Harvie and Weare, 1980; Harvie et al., 1984; Krumgalz, 2001), leakage of toxic solutions and electrolytic fluids from storage tanks (Lichtner, 2001; Lichtner at al., 2004; Steefel et al., 2003; Zhang et al., 2005), and acid mine drainage (Blowes et al., 1991). Concentrated aqueous solutions are significantly different from dilute solutions in flow, transport, and geochemical processes, because of their nonidealities, (e.g., large density, viscosity, and complicated thermodynamic activities). Thus, numerical modeling of these solutions remains a challenge, since most geochemical reactive transport models are based on dilute aqueous solutions, which are not applicable to concentrated aqueous solutions (Pitzer, 1991; Oldenburg and Pruess, 1995; Zhang et al., 2005).

TOUGHREACT (Xu, et al., 2006) was developed by introducing geochemical transport to the framework of a multiphase flow code, TOUGH2 (Pruess et al., 1999). It can simulate nonisothermal multiphase groundwater flow, diffusive and advective transport of gases (including vapor) and solutes, geochemical equilibrium and kinetics, including aqueous speciation, and mineral dissolution and precipitation. This code can handle dilute solutions (ionic strength up to 1 molal) and concentrated NaCl dominant solutions (up to ~ 4 molal) by using an extended Debye-Hückel ionic activity model (HKF model, Helgeson et al., 1981). TOUGHREACT has been used to perform many numerical simulations of reactive geochemical transport processes, at various scales and a wide range of geochemical conditions for studies of geothermal energy (Xu et al., 2004), CO_2 sequestration (Xu et al., 2005), high-level nuclear waste disposal (Spycher et al., 2003 and Sonnenthal et al., 2005) and groundwater contamination. However, models of some saline geothermal systems, injection of CO_2 into deep brines, contamination involving concentrated solutions, and geochemical processes in high-level nuclear waste repositories often involve concentrated aqueous solutions with ionic strengths much higher than 1 molal. Most of these processes take place in complex flow and transport systems, such as nonisothermal multiphase flow, double porosity and dual permeability media, and complicated geochemical systems. The sophisticated capabilities of TOUGHREACT could satisfy the requirements of these applications if a suitable ionic activity model were employed. The incorporation of such an ionic activity model into TOUGHREACT is the objective of the present study.

Pitzer's ion-interaction theory (Pitzer, 1973) is often used to study ionic activity in concentrated aqueous solutions. Harvie and Weare (1980) and Harvie et al. (1984) developed an ion-interaction equilibrium model (HMW model) for seawater systems (Na-K-Mg-Ca-Cl-SO_4-H_2O) based on the Pitzer's ion-interaction theoretical model. The HMW model was implemented in several computer codes: PHRQPITZ (Plummer et al., 1988), EQ3/6 (Wolery and Daveler, 1992; Wolery and Jarek, 2003), GMIN (Felmy, 1995), UNSATCHEM-2D (Simunek and Suarez, 1994), and BIO-CORE$^{2D©}$ (Zhang, 2001 and Zhang et al., 2005).

In this paper, we present the implementation and verification of the Pitzer ion-interaction model in TOUGHREACT, and an application showing the capacity to handle high concentrations at varying temperatures, while accounting for vapor-pressure-lowering effects due to high salinity.

2. FORMULATIONS OF PITZER'S IONIC ACTIVITY MODEL

The Pitzer model evaluates the ionic activities of a solution as a function of solution ionic strength (long-distance interaction), interaction terms (short-distance interaction), temperature, and pressure. This model consists of several virial equations, sometimes called specific interaction equations, Pitzer equations, or phenomenological equations. These equations can adequately express the thermodynamic properties of the concentrated solution over a wide range of concentrations and temperatures (Clegg and Whitfield, 1991). The Pitzer model, based on a virial expansion (Pitzer, 1973; 1991), is reduced to a modified form of the Debye-Hückel formula at low ionic strength (Pitzer, 1991). This virial expansion involves summations over all possible binary and ternary short-range interaction terms, as well as mixing terms. A generally accepted form of the Pitzer model was formulated in Harvie et al. (1984) and called the HMW model. This model has been implemented in TOUGREACT. In the HMW model, water activity is formulated as:

$$\ln(a_{H_2o}) = -\frac{m_w}{1000}(\sum_{i=1}^{N} m_i)\phi \tag{1}$$

where a_{H_2o} is water activity, m_i is molality of species i, m_w is molecular weight of water, N is the number of species in the system, and ϕ is the osmotic coefficient, defined as:

$$\begin{aligned}\sum_{i=1}^{N} m_i(\phi-1) &= 2(-\frac{A^{\Phi} I^{\frac{3}{2}}}{1+1.2\sqrt{I}}) \\ &+ \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a (B_{ca}^{\Phi} + ZC_{ca}) \\ &+ \sum_{c}\sum_{c'=c+1} m_c m_{c'} (\Phi_{cc'}^{\phi} + \sum_{a=1} m_a \psi_{cc'a}) \\ &+ \sum_{a}\sum_{a'=a+1} m_a m_{a'} (\Phi_{aa'}^{\phi} + \sum_{c=1} m_c \psi_{aa'c}) \\ &+ \sum_{n=1}^{N_n}\sum_{c=1}^{N_c} m_n m_c \lambda_{nc} + \sum_{n=1}^{N_n}\sum_{a=1}^{N_a} m_n m_a \lambda_{na} \\ &+ \sum_{n=1}^{N_n}\sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_n m_c m_a \zeta_{nca}\end{aligned} \tag{2}$$

where I is the ionic strength, defined as $I = \frac{1}{2}\sum_{k=1}^{N} z_k^2 m_k$, and z_k is the electrical charge of species k. The subscripts M, C, and c denote cations and X, A, and a denote anions.

The activity coefficients of cations (γ_M), anions (γ_X), and neutral species (γ_N) are respectively calculated as:

$$\begin{aligned}\ln\gamma_M &= Z_M^2 F + \sum_{a=1}^{N_a} m_a (2B_{Ma} + ZC_{Ma}) \\ &+ \sum_{c=1} m_c (2\Phi_{Mc} + \sum_{a=1} m_a \psi_{Mca}) \\ &+ \sum_{a}\sum_{a'=a+1} m_a m_{a'} \Psi_{aa'M} \\ &+ |Z_M| \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a C_{ca} \\ &+ 2\sum_{n=1}^{N_n} m_n \lambda_{nM}\end{aligned} \tag{3}$$

$$\begin{aligned}\ln\gamma_X &= Z_X^2 F + \sum_{c=1}^{N_c} m_c (2B_{cX} + ZC_{cX}) \\ &+ \sum_{a=1} m_a (2\Phi_{Xa} + \sum_{c=1} m_c \psi_{Xac}) \\ &+ \sum_{c}\sum_{c'=c+1} m_c m_{c'} \Psi_{cc'X} \\ &+ |Z_x| \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a C_{ca} \\ &+ 2\sum_{n=1}^{N_n} m_n \lambda_{nX}\end{aligned} \tag{4}$$

$$\ln\gamma_N = \sum_{a=1}^{N_a} m_a(2\lambda_{na}) + \sum_{c=1}^{N_c} m_c(2\lambda_{nc}) + \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a \zeta_{Nca} \quad (5)$$

where F is given by:

$$F = -A^{\Phi}\left(\frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2}ln(1+1.2\sqrt{I})\right) + \sum_{c=1}\sum_{c'=c+1} m_c m_{c'} \Phi'_{cc'} + \sum_{a=1}\sum_{a'=a+1} m_a m_{a'} \Phi'_{aa'} + \sum_{c=1}^{N_c}\sum_{a=1}^{N_a} m_c m_a B'_{ca} \quad (6)$$

C_{MX} is derived from C^{Φ}_{MX} as:

$$C_{MX} = \frac{C^{\Phi}_{MX}}{2\sqrt{|z_M z_X|}} \quad (7)$$

and Z is calculated as:

$$Z = \sum_{k=1}^{N} |z_k| m_k \quad (8)$$

All Pitzer virial coefficients, B^{Φ}_{MX}, B_{MX}, B'_{MX}, α_{MX}, C_{MX}, λ_{NC} and λ_{NA} in Equation (2) through (7) are defined as follows:

B^{Φ}_{MX} is used to calculate the osmotic coefficient and water activity according to the equation:

$$B^{\Phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} e^{-\alpha_{MX}\sqrt{I}} + \beta^{(2)}_{MX} e^{-\alpha'_{MX}\sqrt{I}} \quad (9)$$

where $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $\beta^{(2)}_{MX}$, and α_{MX} are temperature-dependent ion-interaction parameters.

B_{MX} is used to calculate the activity coefficient of charged species (ions). This coefficient is calculated as:

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g(\alpha_{MX}\sqrt{I}) + \beta^{(2)}_{MX} g(\alpha'_{MX}\sqrt{I}) \quad (10)$$

with function $g(x)$ defined as:

$$g(x) = 2(1-(1+x)e^{-x})/x^2 \quad (11)$$

with x denoting $\alpha_{MX}\sqrt{I}$ or $\alpha'_{MX}\sqrt{I}$, respectively.

B'_{MX} is used to calculate the modified Debye-Hückel term, and formulated as:

$$B'_{MX} = \frac{\partial B_{MX}}{\partial I} = \beta^{(1)}_{MX}\frac{g'(\alpha_{MX}\sqrt{I})}{I} + \beta^{(2)}_{MX}\frac{g'(\alpha'_{MX}\sqrt{I})}{I} \quad (12)$$

with function $g'(x)$ defined as:

$$g'(x) = -2(1-(1+x+\frac{x^2}{2})e^{-x})/x^2 \quad (13)$$

with x denoting $\alpha_{MX}\sqrt{I}$ or $\alpha'_{MX}\sqrt{I}$, respectively.

For any salt containing a monovalent ion, α_{MX} = 2 and α'_{MX} = 12; for 2-2 electrolytes, α_{MX} = 1.4 and α'_{MX}=12; for 3-2, 4-2, and higher valence electrolytes, α_{MX} = 2.0 and α'_{MX} = 50.

Note that Φ^{ϕ}_{cc}, Φ^{ϕ}_{aa}, Φ_{cc}, Φ_{aa}, Φ'_{cc}, Φ'_{aa} are interaction parameters for like-sign ionic pairs (mixing terms). They are temperature- and ionic strength-dependent:

$$\Phi^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I) \quad (14)$$

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \quad (15)$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I) \quad (16)$$

${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ are functions of the ionic charges between the pair and solution ionic strength. These functions are defined in Pitzer (1991) and can be normally ignored in moderately concentrated solutions of ionic strength less than 10 molal (for all like-sign pairs, ${}^{E}\theta_{ij}(I) = 0$ and ${}^{E}\theta'_{ij}(I) = 0$). Also, θ_{ij} are temperature dependent fitting parameters, with ${}^{E}\theta_{ij}(I)$ and ${}^{E}\theta'_{ij}(I)$ calculated according to Pitzer (1991).

Ψ_{cca} and Ψ_{caa} are the temperature dependent interaction coefficients of ternary terms.

ζ_{nca} is the temperature dependent interaction coefficient of neutral-cation-anion terms. Normally, this term is ignored (for all neutral-cation-anion triplets, $\zeta = 0$).

3. DATABASES FOR THE TEMPERATURE-DEPENDENT ION-INTERACTION PARAMETERS

The extended TOUGHREACT can directly use the EQ3/6-formatted database, data0.ypf (Wolery et al., 2004) for both Pitzer ion-interaction parameters and thermodynamic equilibrium constants. These parameters are temperature-dependent. The previous TOUGHREACT-formatted thermodynamic database is also required to provide mineral molal volumes and gas molecular diameter, in case these data are not available in data0.ypf.

The interpolation and extrapolation equations for various thermodynamic properties of aqueous solutions, for binary and ternary systems and for multip-component mixtures within the Pitzer formulation, have been reported in many papers (Harvie et al., 1984; Pabalan and Pitzer, 1989; Harvie et al., 1987; Moller, 1988; Greenberg and Moller, 1989; Monnin, 1989 and 1994; Pitzer, 1991; Weber et al., 1999). These authors utilized a variety of activity data, enthalpy data, and heat capacities to construct comprehensive equations over the temperature range of 0 to 250°C. For example, Pabalan and Pitzer (1989) fitted their experimental results with equations using more than twenty adjustable parameters. Moller (1988) and Greenberg and Moller (1989) used an equation with ten adjustable parameters to describe the temperature-dependent parameters. In the present paper, we use the following algebraic equation from Wolery et al. (2004):

$$P(T) = a_1 + a_2(\frac{1}{T} - \frac{1}{T_0}) + a_3 \ln(\frac{T}{T_0}) + +a_4(T - T_0) \quad (17)$$

where $P(T)$ represents Pitzer parameters $\beta^{(o)}$, $\beta^{(1)}$, $\beta^{(2)}$, α, Φ, Ψ, and C^{Φ}_{MX} at temperature T (absolute temperature); T_0 is the reference temperature (298.15 K used in the database). These data are generally good up to at least 90°C, and were derived specially for the Yucca Mountain project. More details on the database can be found in Wolery et al. (2004) and Alai et al. (2005).

The dependency of the Pitzer parameters on pressure is not considered in the present model, because it is much less significant than the effect of temperature within the possible temperature range.

In addition to the EQ3/6-formatted Pitzer database, the code can also use the regular TOUGHREACT-formatted thermodynamic database, and an unformatted database for Pitzer ion-interaction parameters from Zhang et al. (2005). These unformatted databases are easy to extend and modify, and could be useful for users who develop their own parameters. Users can read the parameters from either database by simply assigning different option parameters in the input file.

Because the effect of ion pairing and aqueous complexation (forming secondary aqueous species) is generally taken into account by the ion-interaction parameters, much care must be taken to avoid "double counting" by including, in simulation, secondary species that were not specially accounted for, when fitting experimental data, for calibrating the ion-interaction parameters used in the simulation.

4. TESTS

The code was verified using a variety of published experimental data and benchmarked with EQ3/6 (Wolery and Jarek, 2003). Following are two selected test cases that show how the code reproduces the experimental ionic activities and captures the water vapor-pressure-lowering of the saline solutions resulting from the high salinity.

The first test involves the calculation of the mean activity coefficients of NaCl, and the osmotic coefficient of NaCl solutions up to 6 molal, at 0 °C, 25 °C, 50 °C, 80 °C, 100°C, and 110°C, respectively. The results are compared with data measured by Colin et al. (1985) (Figure 1). This test validates the calculated temperature dependence of activity coefficients. Note that comparisons of mean activity coefficients, rather than mean activities, are appropriate here because no Na or Cl secondary species are explicitly included in the simulation.

The mean activity coefficient of NaCl is defined as:

$$ln(\gamma_{NaCl}) = \frac{ln(\gamma_{Cl}) + ln(\gamma_{Na})}{2} \quad (18)$$

and the osmotic coefficient is calculated, according to Equation (1), as:

$$\phi = -\frac{ln(a_w) * 1000}{W_w \sum_i m_i} \quad (19)$$

Another test case involved the calculation of the mean activity of $CaCl_2$, osmotic coefficient, water activity, and water vapor pressure of $CaCl_2$ solutions at ionic strength up to 27 molal (9 molal of $CaCl_2$). The calculated osmotic coefficient (at 60°C) and mean activity of $CaCl_2$ were compared with data from Ananthaswamy and Atkinson (1985). Results show reasonably good agreement (Figure 2). These tests provided confidence in the Pitzer parameters selected for this study (Wolery at al., 2004, as published by Alai et al., 2005).

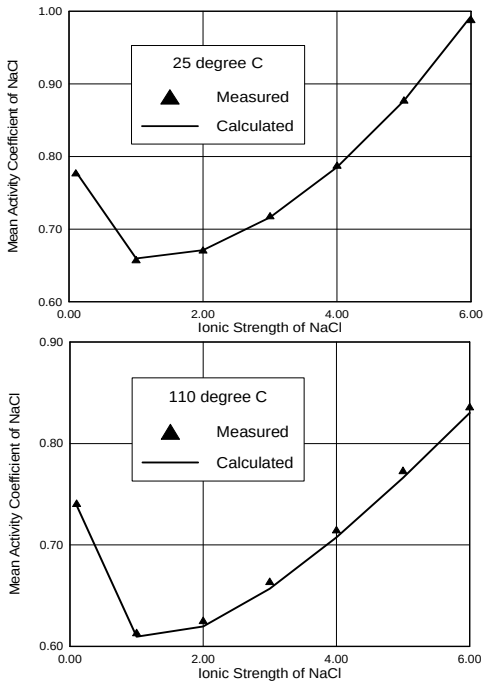

Figure 1. Examples of TOUGHREACT-calculated (solid lines) and measured (symbols) mean activity coefficients for NaCl solutions at 25°C and 110°C. Measured data are from Colin et al (1985).

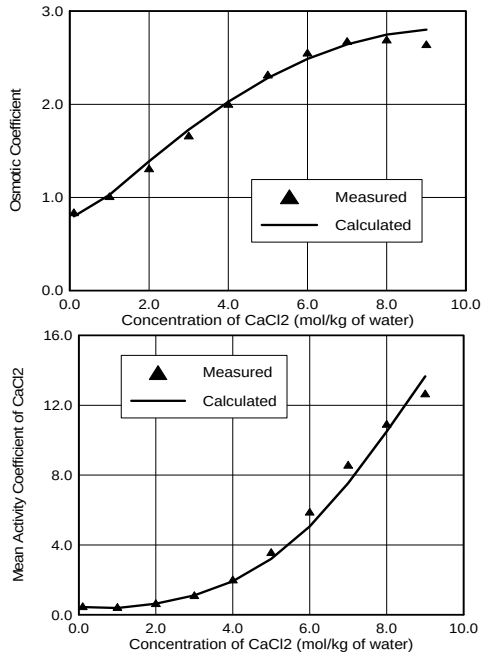

Figure 2. Comparison of calculated and measured (Ananthaswamy and Atkinson, 1985) osmotic coefficient of $CaCl_2$ solutions, and mean activity coefficient of $CaCl_2$ at 60°C and concentrations up to 9 molal of $CaCl_2$ salt.

Vapor-pressure-lowering caused by dissolved salts was implemented directly through the water activity computed with the Pitzer ion-interaction model. For equilibrium between water and H_2O vapor (i.e., for the reaction $H_2O_{(l)} \Leftrightarrow H_2O_{(g)}$), equating the chemical potentials of both phases yields

$$\mu^0_v - \mu^0_w = RT \ln(f_v / f^0_v) - RT \ln(f_w / f^0_w) = RT \ln(f_v / a_w) = -RT \ln(K) \quad (20)$$

where subscripts w and v stand for liquid water and H_2O gas, respectively, μ^0 stands for the reference chemical potential, f is fugacity, a is activity (defined as f/f^0, with f^0 being the fugacity in the reference state), K is the thermodynamic equilibrium constant, R is the gas constant, and T is temperature. The reference (standard) state of H_2O gas is taken as unit fugacity or the pure gas at 1 bar pressure and all temperatures, whereas that of liquid water is taken as unit activity of pure water at all temperatures and pressures. In our case, at low pressure (atmospheric), fugacity is approximated by pressure, and f_v and thus K in Equation (20) are respectively approximated by the actual vapor pressure, P_v, and the vapor pressure of pure water, P^0_{sat}, such that $P_v / a_w \cong P^0_{sat}$ (thus, for the pure system, $a_w = 1$ and $P_v = P^0_{sat}$). Accordingly, the vapor pressure of the solution is computed as:

$$P_v = a_w P^0_{sat} \quad (21)$$

Equation (21) is used in the coupling of chemistry and flow calculations, such that the effect of salts on vapor pressure is taken into account in the multiphase flow computations. From Equation (21), it is also apparent that if relative humidity, R_h, is defined as the ratio of the actual vapor pressure over that of pure water, then

$$R_h = a_w \quad (22)$$

The implementation of Equations (21) and (22) was verified by taking the vapor pressure of pure water from the NIST steam tables (Wagner and Pruβ, 2002), and then calculating the vapor pressure of the solution using these equations and the water activity calculated by the Pizer ion-interaction model. Simulated vapor pressure and relative humidity values for solutions up to 9 molal $CaCl_2$ agree well with the values calculated from the steam tables (Figure 3).

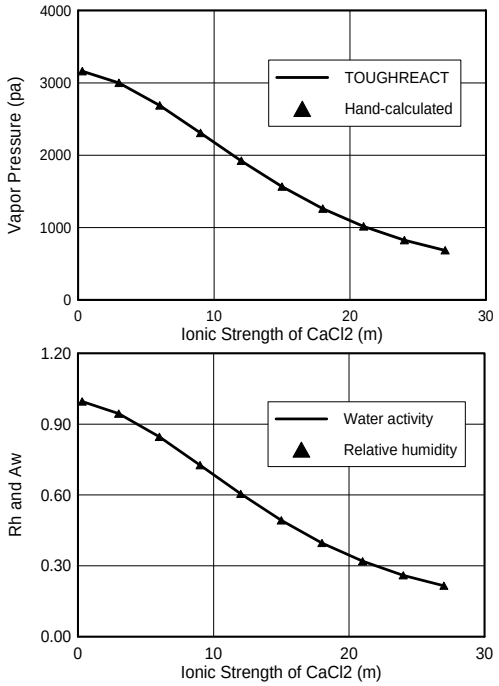

Figure 3. Comparison between hand-calculated and simulated vapor pressures and relative humidities of $CaCl_2$ solutions up to 9 molal of $CaCl_2$ salt at 25 °C, 1 bar

5. SIMULATION OF EVAPORATIVE CONCENTRATION OF YUCCA MOUNTAIN TUFF UNSATURATED ZONE POREWATER TO NEAR DRYNESS

The proposed U.S. high-level nuclear waste repository at Yucca Mountain, Nevada, is located in unsaturated volcanic tuffs. We conducted a dynamic model, representing water evaporation/boiling in the hot, open repository tunnels (Figure 4), to evaluate the trends of salt precipitation and brine composition. Figures 5–8 show the simulated trends of concentrations and precipitation of solid phases when a porewater (Table 1) is evaporated at 95°C in an open system, allowing the vapor and gas that are generated to dissipate into the tunnel atmosphere. The simulation is carried out until near dryness, to illustrate the code capability. In the real system, however, evaporation would stop at the prevailing relative humidity in the tunnel.

As shown in the figures, the porewater is concentrated to a factor ~2 x 10^6 at 95°C, at which, the predicted water activity of the remaining brine is essentially zero. Predicted major solid phase precipitates (volume fraction >1%) are halite (NaCl), calcite ($CaCO_3$), anhydrite ($CaSO_4$), amorphous silica (SiO_2), sepiolite ($Mg_4Si_6O_{15}(OH)_2{:}6H_2O$), sylvite (KCl), and $CaCl_2$. The remaining brine is mildly acidic (pH~5). Acid gas fugacity reaches 10^{-5} bar (HCl), 10^{-6} bar (HF) and 10^{-8} bar (NO_3).

Table 1. Chemical composition of one type of Yucca Mountain tuff unsaturated zone porewater

Components	Molality
Ca^{+2}	0.23×10^{-2}
Mg^{+2}	0.38×10^{-3}
Na^{+}	0.26×10^{-2}
Cl^{-}	0.33×10^{-2}
$SiO_{2(aq)}$	0.11×10^{-2}
HCO_3^{-}	0.30×10^{-2}
SO_4^{-2}	0.12×10^{-2}
K^{+}	0.20×10^{-3}
AlO_2^{-}	0.62×10^{-9}
F^{-}	0.45×10^{-4}
$HFeO_2$	0.12×10^{-11}
NO_3^{-}	0.10×10^{-3}

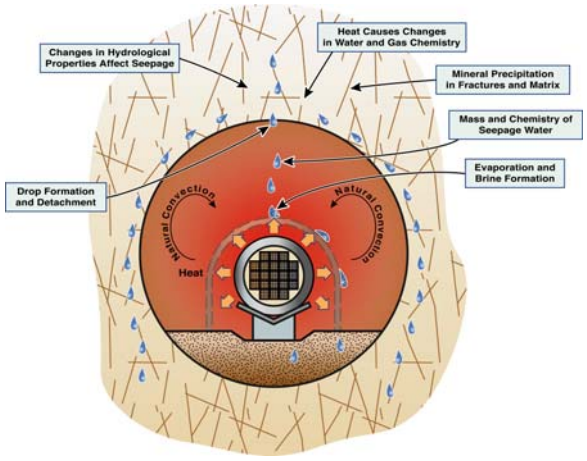

Figure 4. Schematic illustration of geochemical processes taking place when seepage water dripping onto a waste package is evaporated.

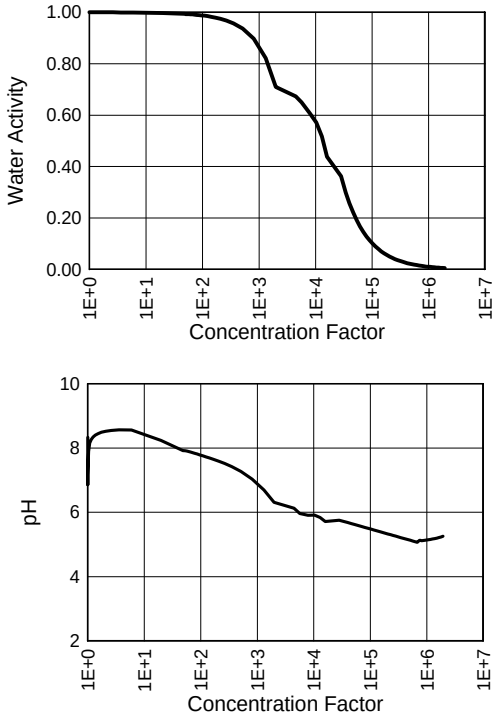

Figure 5. Evolution of water activity and brine pH. Water is evaporated to near dryness, concentrated about 2,000,000 times, water activity is close to zero, and the pH reaches about 5.

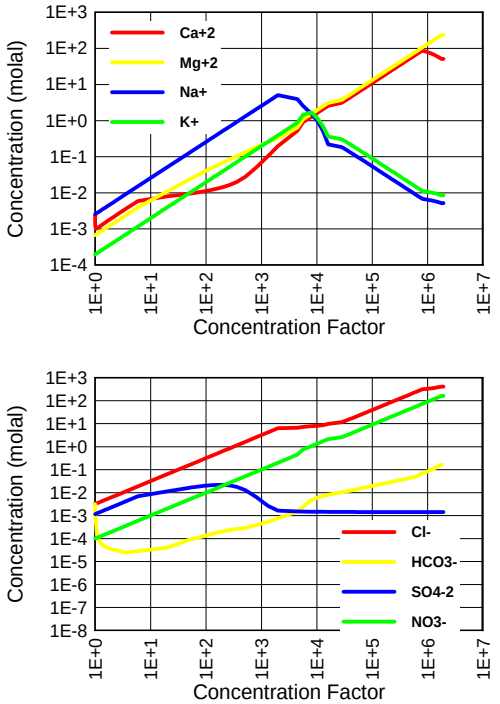

Figure 6. Evolution of aqueous species, concentrations in the brine. Concentrations increase owing to evaporation, and decrease or are stabilized by the precipitation of salts.

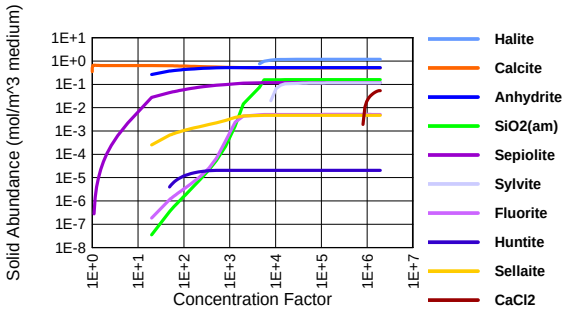

Figure 7. Evolution of precipitated solids, Halite dominates the salts assemblage.

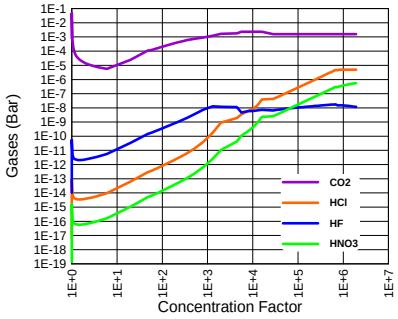

Figure 8. Evolution of gas fugacities. Acid gas fugacity increases as the solution is concentrated, with HF constrained by the precipitation of fluorite early on, and HCl constrained by the precipitation of $CaCl_2$ salt.

6. CONCLUSIONS

(1) TOUGHREACT, an existing geochemical reactive transport numerical simulator, was extended by adding a Pitzer ion-interaction model, HMW formulation, for modeling high-concentration solutions at varying temperatures, and evaporation to near-dry conditions. The incorporated HMW model accounts for binary interactions (cation-anion, cation-cation, anion-anion, cation-neutral, and anion-neutral), and ternary interactions (cation-cation-anion, cation-anion-anion and cation-anion-neutral).

(2) As a user option, the extended version of TOUGHREACT can use the original TOUGHREACT-formatted thermodynamic database or the EQ3/6-format database for equilibrium constants. The code uses the EQ3/6-formatted database for ion-interaction parameters; in addition, it also uses a free format database for ion-interaction parameters. Users can easily develop their own interaction parameters.

(3) The extended version of the TOUGHREACT code has been verified and validated with

experimental data. It captures the measured NaCl mean activity coefficient of NaCl solutions at various ionic strengths. The extended code was also verified through calculations of the $CaCl_2$ mean activity coefficient, osmotic coefficient, water vapor pressure, and water activity of $CaCl_2$ solutions with ionic strength up to 27 molal, and with consideration of vapor-pressure-lowering effect. The results are in good agreement with measurements.

(4) The extended version of TOUGHREACT code was used to dynamically model the evaporative drying, to a concentration factor ~ 2 x 10^6 at 95ºC of one type of Yucca Mountain tuff porewater, and predicted major solid-phase precipitates as well as the composition of the remaining brine.

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