Validation and Recalibration of the Solubility Models in Support of the Heater Test in Salt Formations

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Abstract

The US Department of Energy Office of Nuclear Energy is conducting a brine availability heater test to characterize the thermal, mechanical, hydrological and chemical response of salt at elevated temperatures. In the heater test, brines will be collected and analyzed for chemical compositions. In order to support the geochemical modeling of chemical evolutions of the brines during the heater test, we are recalibrating and validating the solubility models for the mineral constituents in salt formations up to 100℃, based on the solubility data in multiple component systems as well as simple systems from literature.

In this work, we systematically compare the model-predicted values based on the various solubility models related to the constituents of salt formations, with the experimental data. As halite is the dominant constituent in salt formations, we first test the halite solubility model in the Na-Mg-Cl dominated brines. We find the existing halite solubility model systematically over-predict the solubility of halite. We recalibrate the halite model, which can reproduce halite solubilities in Na-Mg-Cl dominated brines well.

As gypsum/anhydrite in salt formations controls the sulfate concentrations in associated brines, we test the gypsum solubility model in NaCl solutions up to 5.87 mol•kg^{-1} from 25°C to 50°C. The testing shows that the current gypsum solubility model reproduces the experimental data well when NaCl concentrations are less than 1 mol•kg^{-1}. However, at NaCl concentrations higher than 1, the model systematically overpredicts the solubility of gypsum.

In the Na^+—Cl^-—SO_4^{2-}—CO_3^{2-} system, the validation tests up to 100°C demonstrate that the model excellently reproduces the experimental data for the solution compositions equilibrated with one single phase such as halite (NaCl) or thenardite (Na_2SO_4), with deviations equal to, or less than, 1.5 %. The model is much less ideal in reproducing the compositions in equilibrium with the assemblages of halite + thenardite, and of halite + thermonatrite (Na_2CO_3•H_2O), with deviations up to 31 %. The high deviations from the experimental data for the multiple assemblages in this system at elevated temperatures may be attributed to the facts that the database has the Pitzer interaction parameters for Cl^-—CO_3^{2-} and SO_4^{2-}—CO_3^{2-} only at 25°C.

In the Na^+—Ca^{2+}—SO_4^{2-}—HCO_3^- system, the validation tests also demonstrate that the model reproduces the equilibrium compositions for one single phase such as gypsum better than the assemblages of more than one phase.

INTRODUCTION

The US Department of Energy Office of Nuclear Energy is conducting a brine availability heater test to further characterize the thermal, mechanical, hydrological and chemical response of salt to higher temperatures [1]. In the heater test, the brines will be collected and analyzed for chemical compositions. In order to support the geochemical modeling of chemical evolutions of the brines during the heater test, the accurate solubility models for constituent minerals in salt formations are needed. Salt formations were formed when seawater was evaporated, and are usually composed mainly of halite, and of lesser amounts of anhydrite, gypsum, polyhalite, carnallite, sylvite, tachydrite, borax, burkeite, bloedite, thernardite, and carbonates (such as calcite and magnesium carbonate) [2]. As the brines associated with salt formations are in equilibrium with the constituent minerals, the compositions of the brines are controlled by the solubility of the constituent minerals. Therefore, in order to model the chemical evolution of the brines during the heater test, the accurate knowledge of solubilities of the constituent minerals at elevated temperatures is needed.

To support the geochemical modeling of chemical evolutions of the brines based on the chemical analyses of brines samples collected, in response to heating during the heater test, we are performing validation tests and recalibration up to 100°C, for the solubility models of the constituent minerals, based on the solubility data in multiple component systems such as those described in [3] and in more recent studies [4-5].

METHOD

In this work, we use EQ3/6 Version 8.0a [6-7] for model calculations with a database called DATA0.BAT in which the targeted solubility models are incorporated.

In our model calculations, we first generate EQ3NR files based on the chemical components required for the targeted equilibrium assemblages for comparison. Then we perform EQ6 calculations for the equilibrium compositions in the targeted equilibrium assemblages.

We focus on the solubility models for halite (NaCl), gypsum ($CaSO_4 \cdot 2H_2O$) and thernardite (Na_2SO_4) in concentrated brines at elevated temperatures up to $100^\circ C$. The experimental data used for comparison are from various sources including those from [3-5, 8]. When the model is found to perform less ideally, the Pitzer parameters that strongly impact the solubility model in respective solutions are re-evaluated based on the experimental data in order to re-calibrate the model to be in better agreement with the experimental data. The temperature function of Pitzer parameters is represented by the following 298.15 K ($25^\circ C$)-centric form,

$$x(T) = a_1 + a_2(\frac{1}{T} - \frac{1}{298.15}) + a_3 \ln \frac{T}{298.15} + a_4(T - 298.15) \quad (1)$$

RESULTS

Halite Solubility in Multiple Component Brines

As halite is the dominant mineral in salt formations, its solubilities at elevated temperatures have a considerable impact on the brine compositions at elevated temperatures in equilibrium with salt formations. Therefore, we first compare the model-predicted halite solubilities in the WIPP-A brine with multiple components including Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}, from $20^\circ C$ to $100^\circ C$ with the experimental data from USGS [8]. The WIPP-A brine (Table 1) was formulated by Chou et al. [8] for the brine in the Salado Formation, and is similar to the Generic Weep Brine (GWB) in the Salado Formation formulated by Xiong and Lord [9]. However, it should be noted that the formulation of the WIPP-A brine by Chou et al. [8] is not saturated with halite, whereas the GWB formulated by Xiong and Lord [9] is saturated with halite.

Greenberg and Moller [10] and Pabalan and Pitzer [11] developed the halite solubility model to high temperature and high ionic strengths. As indicated below, the model-predicted halite solubilities in pure water and Na_2SO_4 solutions are in good agreement with the experimental values, which implies that the dissolution constants for halite in the database are accurate. In Figure 1, the halite solubilities predicted by the model of Pabalan and Pitzer [11] are compared with the experimental values in the WIPP-A brine from Chou et al. [8]. It is clear from Figure 1 that the predicted values are higher than the experimental values at temperatures $\leq 80^\circ C$.

The predicted higher solubilities for halite in the WIPP-A brine can be attributed to the interaction parameters for Mg^{2+}—Na^+ and Mg^{2+}—Na^+—Cl^-. As indicated by Table 1, the WIPP-A brine has a high concentration of Mg(II), and these interaction parameters involving Mg^{2+} in the current halite solubility model may not be adequate to accurately describe halite solubilities in Mg-Na-Cl dominated brines.

In this work, we re-parameterize the theta ($\theta_{Mg, Na}$) and psi ($\Psi_{Mg, Na, Cl}$) parameters (Table 2), based on the solubility from Chou et al. [8]. Notice that the theta parameter ($\theta_{Mg, Na}$) was only at $25^\circ C$ in the original model (Table 2). In the revised model, we generate its temperature function (Table 2). Figure 1 shows that the recalibrated model with the above revised theta and psi parameters is excellent in reproducing the experimental data.

Table 1. Compositions of the WIPP-A brine [A]

Component	Concentration, mol•kg^{-1}
Na	2.006
K	0.8500
Mg	1.595
Ca	0.01660
Cl	5.9984
SO$_4$	0.04033

[A]: Calculated from the formulation in [8], which was based on weight percentage.

Table 2. Pitzer interaction parameters impacting halite solubility model in Mg-Na-Cl dominated brines

Species, i	Species, j	Species, k	θ_{ij} [A]	Ψ_{ijk} [A]	Reference
Mg^{2+}	Na$^+$	Cl$^-$	$a_1 = 0.07$ $a_2 = 0$ $a_3 = 0$ $a_4 = 0$	$a_1 = -0.012$ $a_2 = -9.51$ $a_3 = 0$ $a_4 = 0$	[11]
Mg^{2+}	Na$^+$	Cl$^-$	$a_1 = 0.1710$ $a_2 = 21.6817$ $a_3 = 0$ $a_4 = 0$	$a_1 = -0.02755$ $a_2 = -8.1214$ $a_3 = 0$ $a_4 = 0$	Recalibrated model, this work

[A]: The temperature function of Pitzer parameters is represented by the following 298.15 K (25°C)-centric form. Please see Eq. (1) in the text.
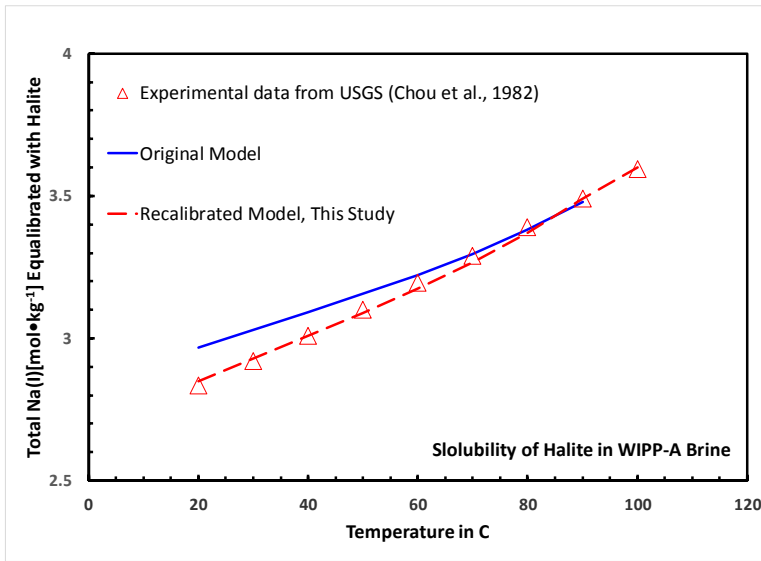
Figure 1. Comparison of experimental halite solubilities in the WIPP-A brine in the temperature range from 20°C to 100°C produced by Chou et al. [8] with the model-predicted values.

Gypsum Solubility in Concentrated Brines

In salt formations, the calcium and sulfate concentrations are mainly controlled by the solubility of gypsum/anhydrite. Therefore, the temperature dependence of the solubilities of gypsum/anhydrite affects the brine compositions. Here we compare the predicted gypsum solubility in NaCl solutions up 5.87 mol•kg^{-1} from 25°C to 50°C with the experimental data.
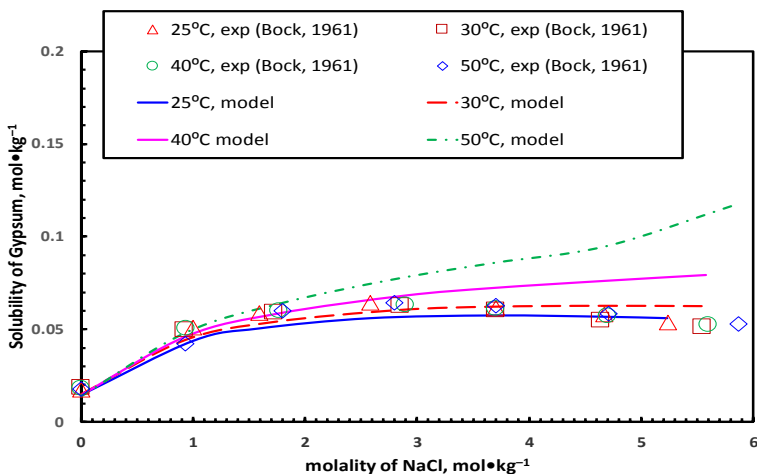
Figure 2. Comparison of experimental gypsum solubilities in NaCl solutions in the temperature range from 25 °C to 50 °C produced by Bock et al. [13] with the model-predicted values.

Greenberg and Moller [10], and Raju and Atkinson [12] developed the gypsum/anhydrite model to high temperature and high ionic strengths. In Figure 2, the gypsum solubilities predicted by using the model of Raju and Atkinson [12] are compared with the experimental values in NaCl solutions from [13]. It is clear from Figure 2 that the predicted values are systematically higher than the experimental values when NaCl concentrations are higher than 1 mol•kg^{-1} and T > 25 °C. As indicated in Figure 2 and below, the model-predicted gypsum solubilities in pure water are in good agreement with the experimental values, which implies that the dissolution constants for gypsum in the database are accurate.

In the gypsum solubility model of Raju and Atkinson [12], the solubility of gypsum in NaCl solutions is mainly described by the equilibrium constants for dissolution of gypsum at infinite dilution and the Pitzer parameters for the following interactions: Ca^{2+}—SO_4^{2-}, and Ca^{2+}—Cl^-. The above initial testing seems to indicate that the gypsum/anhydrite model of Raju and Atkinson [12] requires some slight updates with regard to temperature dependence of the solubility, as the experimental data have a very weak dependence in this temperature range.

Solubility of Halite, Thenardite, Thermonatrite, and their Assemblages in the Na-Cl-SO$_4$-CO$_3$ System

Teeple [3] provided the solubility data for halite, thernardite, thermonatrite and their assemblages to 100 °C. Greenberg and Moller [10] and Pabalan and Pitzer [11] developed the thenardite solubility model to high temperature and high ionic strengths. In Table 3, the equilibrium compositions predicted by the model of Greenberg and Moller [10] are compared with the respective experimental data in the Na-Cl-SO$_4$-CO$_3$ system from 50 °C to 100 °C. It is clear from Table 3 that the model is excellent in reproducing the saturated compositions in equilibrium with only one single phase [i.e.,

halite, NaCl, or thenardite, Na_2SO_4] at all of the temperatures considered. In other words, the model reproduces well the solubilities of various phases in water. The deviations from the experimental values are usually less than or equal to 1.5 %. This indicates that the equilibrium constants for those phases at infinite dilution are accurate. The model is reasonable in reproducing the compositions for the assemblage of halite and thenardite with deviations up to 14 % (Table 3).

The solubility model for thermonatrite was not explicitly developed. Robie and Hemingway [14] provided the equilibrium constants for the dissolution of thermonatrite at infinite dilution to 100°C. He and Morse [15] evaluated the Pitzer interaction parameters for Na^+—CO_3^{2-} to 100°C, and Pitzer [16] evaluated the Pitzer interaction parameter for Cl^-—CO_3^{2-} at 25°C. If these are combined, the solubility for the assemblage halite and thermonatrite can be predicted. However, the deviations for the assemblage of halite and thermonatrite ($Na_2CO_3 \cdot H_2O$) are high, up to 31 %. The high deviations for the assemblage of halite and thermonatrite can be attributed to the facts that the interaction parameter for Cl^-—CO_3^{2-} is only at 25°C in the database. It is inferred that the stronger interactions between Cl^- and CO_3^{2-} at elevated temperatures contribute to the high deviations from the experimental data.

Table 3. Comparison of the experimental data with the model predicted values for the Na-Cl-SO$_4$-CO$_3$ system [A]

Temperature, $^{\circ}$C	Assemblage [B]	Na^+ mol•kg^{-1}	Cl^- mol•kg^{-1}	SO_4^{2-} mol•kg^{-1}	ΣCO_3^{2-} mol•kg^{-1}	Remarks
50	HLT	6.25	6.25	N/A	N/A	Experimental
		6.26	6.26	N/A	N/A	Model
		0.28 %	0.28 %	N/A	N/A	Difference
	THNDT	6.56	N/A	3.28	N/A	Experimental
		6.58	N/A	3.29	N/A	Model
		0.27 %	N/A	0.27 %	N/A	Difference
	HLT+THNDT	6.79	5.77	0.514	N/A	Experimental
		6.85	5.92	0.462	N/A	Model
		0.75 %	2.7 %	-10 %	N/A	Difference
	HLT+THMN	8.56	4.62	N/A	1.97	Experimental
		8.01	5.07	N/A	1.46	Model
		-6.4 %	9.8 %	N/A	-26 %	Difference
75	HLT	6.47	6.47	N/A	N/A	Experimental
		6.39	6.39	N/A	N/A	Model
		-1.2 %	-1.2 %	N/A	N/A	Difference
	THNDT	6.18	N/A	3.09	N/A	Experimental
		6.09	N/A	3.04	N/A	Model

		-1.5 %	N/A	-1.5 %	N/A	Difference
	HLT+THNDT	7.03	6.07	0.479	N/A	Experimental
		6.95	6.12	0.412	N/A	Model
		-1.2 %	0.80 %	-14 %	N/A	Difference
	HLT+THMN	8.37	5.27	N/A	1.55	Experimental
		7.72	5.59	N/A	1.06	Model
		-7.7 %	6.0 %	N/A	-31 %	Difference
100	HLT [C]	6.66 [C]	6.66 [C]	N/A	N/A	Experimental
		6.63	6.63	N/A	N/A	Model
		-0.38 %	-0.38 %	N/A	N/A	Difference
	THNDT [C]	5.94 [C]	N/A	2.97 [C]	N/A	Experimental
		5.97	N/A	2.98	N/A	Model
		0.44 %	N/A	0.44 %	N/A	Difference
	HLT+THNDT	7.30	6.38	0.458	N/A	Experimental
		7.24	6.39	0.424	N/A	Model
		-0.79 %	0.12 %	-7.3 %	N/A	Difference
	HLT+THMN	8.58	5.73	N/A	1.42	Experimental
		8.31	5.89	N/A	1.20	Model
		-3.2 %	2.8 %	N/A	-16 %	Difference

[A]: Unless otherwise noted, experimental data are from [3].

[B]: Abbreviations: HLT, halite (NaCl); THNDT, thenardite (Na_2SO_4); THMN, thermonatrite ($NaCO_3 \cdot H_2O$);

[C]: Potter et al. [17]

Solubility of Gypsum, Calcite, and their Assemblages in the Na-Cl-SO_4-CO_3 System

He and Morse [15] developed the calcite solubility model to 100°C. In combination with the gypsum solubility model from Greenberg and Moller [10], the equilibrium compositions for the assemblage of calcite and gypsum are predicted at 25°C, and 50°C. The concentrations of calcium and sulfate are in reasonable agreement with the experimental data at 25°C, but are off at 50°C (Table 4). The carbonate concentrations are off at these two temperatures (Table 4). In Table 4, the experimental solubilities of gypsum in water at 25°C and 50°C are also compared with the predicted values. They agree with each other within the experimental uncertainties. In addition, calcite solubility data in a mixture of 4.95 mol•kg^{-1} NaCl and 0.0407 mol•kg^{-1} Na_2SO_4 at 100°C from [4] are also compared with the predicted values (Table 1). The predicted

carbonate concentration is in better agreement with the experimental value than the predicted calcium concentration. One possibility may be that the equilibrium might not be attained in the experiment because of the short experimental durations. We are in the process of locating more experimental data in multiple component systems to resolve the issue.

Table 4. Comparison of the experimental data with the model predicted values for the Na-Ca-Cl-SO$_4$-CO$_3$ system

Temperature, °C	Assemblage [A]	Na$^+$/Cl$^-$ mol•kg^{-1}	Ca^{2+} mol•kg^{-1}	SO$_4{}^{2-}$ mol•kg^{-1}	ΣCO$_3{}^{2-}$ mol•kg^{-1}	Remarks
25	GYP [B]	N/A	1.54E-2 [B]	1.54E-2 [B]	N/A	Experimental
		N/A	1.41E-2	1.41E-2	N/A	Model
		N/A	-8.3 %	-8.3 %	N/A	Difference
	GYP+CLCT [B]	N/A	1.62E-2 [B]	1.57E-2 [B]	4.81E-4 [B]	Experimental
		N/A	1.41E-2	1.41E-2	3.75E-4	Model
		N/A	-13%	-11 %	-22 %	Difference
50	GYP [C]	N/A	1.55E-2 [C]	1.55E-2 [C]	N/A	Experimental
		N/A	1.45E-2	1.45E-2	N/A	Model
		N/A	-6.4 %	-6.4 %	N/A	Difference
	GYP+CLCT [C]	N/A	8.29E-3 [C]	7.87E-3 [C]	4.20E-4 [C]	Experimental
		N/A	1.45E-2	1.45E-2	2.17E-4	Model
		N/A	75%	84 %	-48 %	Difference
100	CLCT [D]	5.03/4.95	7.61E-3	4.07E-2	7.61E-3	Experimental
		5.03/4.95	2.49E-3	4.07E-2	5.88E-3	Model
		N/A	-67 %	N/A	-23 %	Difference

[A]: Abbreviations: GYP, gypsum (CaSO$_4$•2H$_2$O); CLCT, calcite (CaCO$_3$)

[B]: Soliev et al. [18]

[C]: Soliev et al. [5]

[D]: Calcite solubility data in a mixture of 4.95 mol•kg^{-1} NaCl and 0.0407 mol•kg^{-1} Na$_2$SO$_4$ at 34 bars are taken from [4].

CONCLUSIONS

In this study, we initiate the validation and re-calibration of the solubility models for the constituent minerals in salt formations with the aim for support the heater test in salt formations. Our initial tests seem to indicate that the solubility models of

halite, gypsum, thenardite, thermonatrite, and calcite performs well for single phase equilibria in water. However, they perform less ideally for multiple phase equilibria or for single phase equilibria in concentrated, multiple component brines. We have re-calibrated the halite solubility model to better match the experimental data for halite in Na-Mg-Cl-dominated brines. We are systematically searching the solubility data for gypsum and anhydrite in concentrated brines at elevated temperatures, including generation of our own new data when the data gap is identified.

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