

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

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9. Remarks

This calculation uses the Precipitates/Salts model developed in the In-Drift Precipitates/Salts Analysis AMR (ANL-EBS-MD-000045 Rev. 00) to estimate pH, chloride concentration, and ionic strength due to evaporative processes using the abstracted THC incoming water composition developed in Abstraction of Drift Scale Coupled Processes (ANL-NBS-HS-000029 Rev. 00).

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CONTENTS

	Page
FIGURES	3
TABLES	3
ACRONYMS AND ABBREVIATIONS	4
1. PURPOSE	5
2. METHOD	5
3. ASSUMPTIONS	6
3.1 RELATIVE HUMIDITY VERSUS TIME	6
3.2 INCOMING NITRATE CONCENTRATION	6
3.3 SOLUBLE SULFATE	6
4. USE OF COMPUTER SOFTWARE AND MODELS	7
4.1 MODELS	7
4.2 SOFTWARE	7
4.3 SOFTWARE ROUTINES	8
5. CALCULATION	8
5.1 INPUT DATA AND PARAMETER VALUES	8
5.1.1 Thermodynamic Constants and Salt Properties	8
5.1.2 Input Parameters	8
5.2 CALCULATIONS	10
5.2.1 Relative Humidity and Temperature History	10
5.2.2 Precipitates/Salts Model	10
6. RESULTS	11
6.1 RELATIVE HUMIDITY AND TEMPERATURE HISTORY	11
6.2 PRECIPITATES/SALTS MODEL RESULTS	12
6.2.1 High Relative Humidity Model Results	12
6.2.2 Low Relative Humidity Model Results	15
6.2.3 Precipitates/Salts Model Lookup Tables	16
6.2.4 Limitations	17
7. REFERENCES	21
8. ATTACHMENTS	23

FIGURES

	Page
Figure 1. Predictions of Bin-Weighted Mean Relative Humidity and Temperature for the Invert Over Time.....	12
Figure 2. Steady State pH, Cl Concentration, and I vs. $(1 - R^{eq})$ for Period 2.....	13
Figure 3. Steady State pH, Cl Concentration, and I vs. $(1 - R^{eq})$ for Period 3.....	13
Figure 4. Steady State pH vs. $(1 - R^{eq})$ at Different Temperatures for Period 4.....	14
Figure 5. Steady State Cl Concentration vs. $(1 - R^{eq})$ at Different Temperatures for Period 4.....	14
Figure 6. Steady State I vs. $(1 - R^{eq})$ at Different Temperatures for Period 4.....	15
Figure 7. Cl and I vs. RH for RH Less than 85 Percent.....	16

TABLES

	Page
Table 1. Incoming Seepage Composition Abstracted from THC Results	9
Table 2. Lookup Table for Period 2.....	18
Table 3. Lookup Table for Period 3.....	19
Table 4. Lookup Table for Period 4.....	20

ACRONYMS AND ABBREVIATIONS

ACC	accession number
AMR	Analysis/Model Report
C_i	concentration of component i in the incoming seepage
CRWMS M&O	Civilian Radioactive Waste Management Services Management and Operations
DIRS	Data Input Reference System
DOE	Department of Energy
DTN	Data Tracking Number
f_{CO_2}	carbon dioxide fugacity
HRH	high relative humidity
I	ionic strength
KTI	key technical issues
LRH	low relative humidity
NFE	Near Field Environment
NRC	Nuclear Regulatory Commission
PAO	Performance Assessment Operations
Q^e	evaporation rate
Q^s	incoming seepage rate
R^{ev}	relative evaporation rate
Rev.	Revision
RH	relative humidity
T	temperature
t_i	time i
TBV	to be verified
THC	thermohydrological-chemical
TIC	Technical Information Center number
$w_{b,i}$	bin weight of subset b of bins at time i
Y_i	overall bin-weighted mean RH or T at time i
$y_{b,i}$	mean RH or T for subset b of bins at time i

1. PURPOSE

The purpose of this calculation is to assist Performance Assessment Operations (PAO) and the Engineered Barrier Performance Department in modeling the geochemical environment within a repository drift, thus allowing PAO to provide a more detailed and complete in-drift geochemical model abstraction and to answer the key technical issues (KTI) raised in the NRC Issue Resolution Status Report (IRSR) for the Evolution of the Near Field Environment (NFE) Revision 2 (NRC 1999). This calculation is associated to the activity directed by written development plan, *Provide Sub-Models for the Physical and Chemical Environmental Abstraction Model for TSPA-LA* (CRWMS M&O 1999a) and is developed using procedure AP-3.12Q, *Calculations*, Rev. 0, ICN 1.

The specific objective and scope of this calculation are to document the Precipitates/Salts model calculations performed for the thermohydrological-chemical (THC) abstraction. The Precipitates/Salts model was developed in *Precipitates/Salts Analysis AMR* (CRWMS M&O 2000) according to procedure AP-3.10Q, *Analyses and Models*, Rev. 2, ICN 0. It is used to estimate the pH, chloride concentration, and ionic strength of water on the drip shield or other location within the drift during the post-closure period resulting from evaporative processes.

The major inputs for the current calculation differ from those for the calculations performed in the Precipitates/Salts AMR (CRWMS M&O 2000) in the following ways:

- Instead of average J-13 well water, the incoming seepage is represented by the THC abstractions for three periods from 50 to 100,000 years.
- Instead of a variable fugacity of carbon dioxide, the fugacity is fixed at the THC abstraction values in each period.
- Instead of a variable temperature for each incoming seepage composition, the temperature is fixed at abstracted values, except for the final period, in which the temperature is varied between 25°C, 50°C, and 75°C.
- A new history of mean relative humidity (*RH*) is used to calculate results when relative humidity is below 85 percent.

2. METHOD

The Precipitates/Salts model developed in *Precipitates/Salts Analysis AMR* (CRWMS M&O 2000) was used to perform the calculations in this document. The model incorporates two submodels, the High Relative Humidity (HRH) model and the Low Relative Humidity (LRH) model. These models, listed and summarized in Section 4, are explained in detail in *Precipitates/Salts Analysis AMR* (CRWMS M&O 2000), as are the methods of calculation. Any deviations from these methods are explained in detail in Sections 3 and 5. Control of electronic management of data, as required by AP-SV.1Q, *Control of the Electronic Management of Data*, was accomplished in accordance with the controls specified the development plan.

3. ASSUMPTIONS

The assumptions are nearly identical to those described in Section 5 of *Precipitates/Salts Analysis AMR* (CRWMS M&O 2000). The only differences are described in the following subsections.

3.1 RELATIVE HUMIDITY VERSUS TIME

The LRH salts model requires an estimate of *RH* over time at the location where the salts model is applied. The location within the drift environment where *RH* is the lowest and temperature is highest over time is the within the invert. It is assumed in this calculation that the predicted mean *RH* history within the invert is a reasonable approximation for the LRH model simulations (Assumption 3.1).

Uncertainty in the relative humidity predictions will not affect the pH, Cl concentration, and ionic strength predicted by the LRH salts model. The model only requires an estimate of the timing of these relative humidity values as a seed to generate the results which are independent of time. Thus, the timing of these relative humidity values is irrelevant in the final results. This assumption is considered reasonable for the bounding calculations performed and is therefore not TBV. This assumption replaces Assumption 5.2.4.1 stated in the *Precipitates/Salts AMR* (CRWMS M&O 2000) and is used in Sections 6.1 and 6.2.2.

3.2 INCOMING NITRATE CONCENTRATION

The incoming seepage data provided by the THC abstraction (Table 1) do not include values for nitrate. Nitrate concentrations are necessary for the LRH model. It is assumed that the concentration ratio of nitrate to chloride in the THC-abstracted incoming seepage water is equivalent to that in average J-13 well water (Assumption 3.2). The basis for this assumption is the generally unreactive behavior of both chloride and nitrate. This assumption is reasonable and will not considerably affect the results of the model. Therefore, this assumption, which is used in Sections 6.2.1 and 6.2.2, is not TBV.

3.3 SOLUBLE SULFATE

In the *Precipitates/Salts AMR* (CRWMS M&O 2000), the carbonate concentration determined as input to the LRH salts model was assumed to be the "soluble" carbonate determined by the HRH model (Assumption 5.5.7, CRWMS M&O 2000). The "soluble" carbonate was determined from the HRH model by evaporating water to 85 percent relative humidity (i.e., a water activity of 0.85). The carbonate that was in solution at that point was considered "soluble" because it excluded the carbonate that had precipitated. Beyond this point, the remaining "soluble" carbonate could only form soluble K or Na salts in significant quantities. There was no need to make a similar determination for sulfate because no sulfate had precipitated at that point or sulfate precipitation was negligible.

In the current calculation, sulfate precipitates considerably in HRH model results. Thus, both the incoming carbonate and sulfate concentrations used in the LRH model are assumed to be the "soluble" carbonate and sulfate concentrations determined by the HRH model at a water activity

of 0.85 (Assumption 3.3). This reasonable assumption is consistent with the basis of Assumption 5.5.7 of CRWMS M&O (2000) and is used for all LRH calculations (Section 6.2.2). It does not affect the uncertainty in the model and is therefore not designated TBV.

4. USE OF COMPUTER SOFTWARE AND MODELS

4.1 MODELS

The Precipitates/Salts model developed in *Precipitates/Salts Analysis AMR* (CRWMS M&O 2000) was used to perform the calculations in this document. The model incorporates two submodels, the Low Relative Humidity (LRH) model and the High Relative Humidity (HRH) model, also developed in CRWMS M&O (2000). These two sub-models are designed to provide a piece-wise continuous Precipitates/Salts model for relative humidity values from 0 to 100 percent.

The LRH model is used when the relative humidity is low (below about 85 percent), and the HRH model is used at higher relative humidity (above about 85 percent). The LRH model consists of a set of algebraic calculations performed within a MathSoft Mathcad version 7 file. The HRH model is simulated using the geochemical code EQ3/6 version 7.2b. These models are validated in CRWMS M&O (2000).

Use of the Precipitates/Salts model in this calculation is justified because the model was specifically designed to perform these calculations (CRWMS M&O 2000).

4.2 SOFTWARE

The HRH model calculations were performed using the code EQ3/6 v7.2b (CRWMS M&O 1999b) [CSCI: URCL-MA-110662 V7.2b, Wolery 1992a and 1992b, Wolery and Daveler 1992] with the solid-centered flow-through addendum [CSCI: URCL-MA-110662 V7.2b, MI: 30084-M04-001 (Addendum Only), CRWMS M&O 1998]. This software code was obtained from Configuration Management and installed on an IBM-compatible computer. It is appropriate for the application and was used only within the range of validation in accordance with AP-SLIQ *Software Management* and the Precipitates/Salts AMR (CRWMS M&O 2000). The Precipitates/Salts AMR restricts the use of this code to a water activity of about 0.85 and higher.

MathSoft Mathcad 7 Professional, a commercially-available software package for technical calculations, was used to execute the LRH model. This software performed and displayed the routine algebraic calculations developed in Section 6.4.1 of the Precipitates/Salts AMR (CRWMS M&O 2000). These equations and all calculations, shown in their entirety in Attachments II, III, and IV, have been hand-checked using a calculator to verify the software provided correct results. This software was appropriate for the application and used within the range of model validation established in the Precipitates/Salts AMR (CRWMS M&O 2000).

Microsoft Excel97, a commercially-available spreadsheet software package, was used to perform simple averaging and interpolation calculations and to chart data. Validation of the spreadsheet calculations was done by comparing input and output data in charts imbedded in the worksheets

(DTN: MO0002SPABIN46.008). Visual inspection of these charts confirms that the spreadsheet application provided correct results.

4.3 SOFTWARE ROUTINES

No software routines were used.

5. CALCULATION

Section 5.1 presents the data and parameter values used as input to the calculation, and Section 5.2 describes the calculations performed.

5.1 INPUT DATA AND PARAMETER VALUES

The calculation requires the following types of input: 1) relevant thermodynamic properties of potentially important ground-water constituents, and 2) values for model input parameters.

5.1.1 Thermodynamic Constants and Salt Properties

The thermodynamic data used in the calculations are developed and documented in the Precipitates/Salts AMR (CRWMS M&O 2000). The HRH model uses the developed PT4 database (DTN: MO9912SPAPT4PD.001) which is currently to be verified (TBV). The LRH model references the salt properties displayed in Tables 1 and 2 of CRWMS M&O (2000).

5.1.2 Input Parameters

The Precipitates/Salts model input parameters are:

- Concentration or activity of each modeled component i in the incoming seepage (C_i')
- Temperature (T)
- Relative humidity (RH)
- Fugacity of carbon dioxide (f_{CO_2})
- Seepage rate (Q^s)
- Relative evaporation rate (R^{ev})

The relative evaporation rate (or flux) (R^{ev}) refers to the steady state evaporation flux (Q^e) divided by (or relative to) the incoming seepage rate (or flux) (Q^s):

$$R^{ev} = \frac{Q^e}{Q^s} \quad (\text{Eq. 1})$$

The model is designed for a range of R^{ev} from 0 to 1. The values used in this analysis are: 0, 0.1, 0.5, 0.9, 0.99, and 0.999. These values are used to generate lookup tables that are intended to cover the range of values anticipated.

Precipitates/Salts Model Results for THC Abstraction

The modeled incoming seepage includes the following components: Na, K, Ca, Mg, Cl, F, CO₃, SO₄, NO₃, SiO₂, Fe(III), Al, H, and H₂O.

Table 1. Incoming Seepage Composition Abstracted from THC Results

Parameter	Units	Boiling Period 2	Transitional Cool-Down Period 3 (molal)	Extended Cool-Down Period 4 (molal)
Time Period	years	50-1,000	1,000-2,000	2,000-100,000
Temperature	°C	96	90	50
log CO ₂ (g)	vol. frac.	-6.5	-3.0	-2.0
Ca	molal	6.4e-04	1.0e-03	1.8e-03
Mg	molal	3.2e-07	1.6e-06	7.8e-06
Na	molal	1.4e-03	2.6e-03	2.6e-03
K	molal	8.5e-05	3.1e-04	1.0e-04
SiO ₂	molal	1.5e-03	2.1e-03	1.2e-03
NO ₃	molal	nr ^a	nr	nr
CO ₃	molal	1.9e-04	3.0e-04	2.1e-03
Cl	molal	1.8e-03	3.2e-03	3.3e-03
F	molal	2.5e-05	4.5e-05	4.5e-05
SO ₄	molal	6.6e-04	1.2e-03	1.2e-03
Fe	molal	7.8e-10	4.1e-10	2.4e-11
Al	molal	2.7e-07	6.8e-08	2.0e-09
pH	pH units	8.1 ^b	7.8 ^b	7.3 ^b

DTN: MO9912SPAPAI29.002

^a not reported

^b pH units

In this analysis, representative waters from three periods of time were used as incoming seepage. The specific compositions originate from the THC results. The abstracted representative incoming water compositions, temperatures, and CO₂ (g) volume fractions in the air for these periods are displayed in Table 1. These data are currently TBV.

As explained in Section 3.2, the ratio of nitrate to chloride in average J-13 well water is needed to estimate the concentration of nitrate in the THC-abstracted incoming seepage water. The nitrate:chloride ratio in the J-13 well water is 0.70:1 (DTN: LL980711104242.054).

In the calculation, *T* was varied between three values (75°C, 50°C, and 25°C) for Period 4 to develop a response surface intended to cover the range of values anticipated in this period. *RH* and *T* as a function of time were developed as described in Section 5.2.1 from recent calculations for the invert. The acquired data used to develop the *T* and *RH* histories came from the following files in DTN: SN0001T0872799.006:

- RIP_RHinvavg_hlw_d0010500_bin0-3_mean
- RIP_RHinvavg_hlw_d0010500_bin3-10_mean
- RIP_RHinvavg_hlw_d0010500_bin10-20_mean

- RIP_RHinvavg_hlw_d0010500_bin20-60_mean
- RIP_RHinvavg_hlw_d0010500_bin60_mean
- RIP_Tinvavg_hlw_d0010500_bin0-3_mean
- RIP_Tinvavg_hlw_d0010500_bin3-10_mean
- RIP_Tinvavg_hlw_d0010500_bin10-20_mean
- RIP_Tinvavg_hlw_d0010500_bin20-60_mean
- RIP_Tinvavg_hlw_d0010500_bin60_mean

These data are currently TBV.

5.2 CALCULATIONS

Before the Precipitates/Salts model calculation could be performed, the relative humidity as a function of time had to be determined. This initial calculation is developed in Section 5.2.1. The Precipitates/Salts model calculations are addressed in Section 5.2.2.

5.2.1 Relative Humidity and Temperature History

From the files listed in Section 5.1.2 (DTN: SN0001T0872799.006), mean, bin-averaged values for *RH* and *T* for the invert were determined for the LRH model. These overall means were calculated by taking the bin-weighted averages of *RH* and *T* for numerous values of time from 0 to 100,000 years. The actual times that were used to determine the bin-weighted averages were selected such that the resolution of *RH* and *T* as a function of time was captured.

Bin-weighted averages were calculated using the following equation:

$$Y_i = \sum_b y_{b,i} w_{b,i} \quad (\text{Eq. 2})$$

where Y_i is the overall bin-weighted mean *RH* or *T* at time i , $y_{b,i}$ is the mean *RH* or *T* for subset b of bins at time i , $w_{b,i}$ is the bin weight of subset b of bins at time i . The summation of the bin weights for the bin subsets at time i equals one (i.e., $\sum_b w_{b,i} = 1$).

Many of the *RH* and *T* values in the files are not for common times. As a result, interpolations had to be made for bin subsets before bin-weighted averages could be calculated. For the interpolations a linear relationship between *RH* and the logarithm of time ($\log t$) and between *T* and $\log t$ were imposed such that:

$$y_{b,i} = \frac{\log t_{i+1} - \log t_{i-1}}{y_{b,i+1} - y_{b,i-1}} (\log t_i - \log t_{i-1}) + y_{b,i-1} \quad (\text{Eq. 3})$$

where $i+1$ and $i-1$ are the nearest values in the acquired data file to time t_i .

5.2.2 Precipitates/Salts Model

The HRH model calculations were performed using the solid-centered flow-through mode of EQ3/6 version 7.2b according to the procedures described in Section 6.4.2.2 of the

Precipitates/Salts AMR (CRWMS M&O 2000). The only difference in the calculations were due to the different input values.

The LRH model calculations were performed according to Section 6.4.1 of the Precipitates/Salts AMR (CRWMS M&O 2000). These calculations were performed using the Mathcad 7 files displayed in Appendices II, III, and IV of this report.

For the LRH model there were three parameter values that were changed other than the adjustments to the incoming seepage composition explained in Sections 3.2 and 3.3. Two were the times at which the *RH* is determined to reach 50 percent and 85 percent. They were set at 450 years and 1300 years based on the results of the calculation described in Section 5.2.1 (The results displayed in Figure 1.). The other change was the effective solubility of the non-nitrate salts. This value was adjusted to 2.9 or 3.0 molal to provide a smooth transition between the LRH and HRH model results. The values used to provide a smooth transition for J-13 seepage water ranged from 3.6 to 4.1 molal (CRWMS M&O 2000).

It is restated here that the ionic strength (*I*) parameter of the Precipitates/Salts model is not the true ionic strength. Instead, it is an approximation based on the following equation:

$$I = C_{Na} + C_K + 4(C_{Ca} + C_{Mg}) \quad (\text{Eq. 4})$$

where C_i is the molality of component *i*. For an explanation, refer to Section 6.3.2 of the Precipitates/Salts AMR (CRWMS M&O 2000).

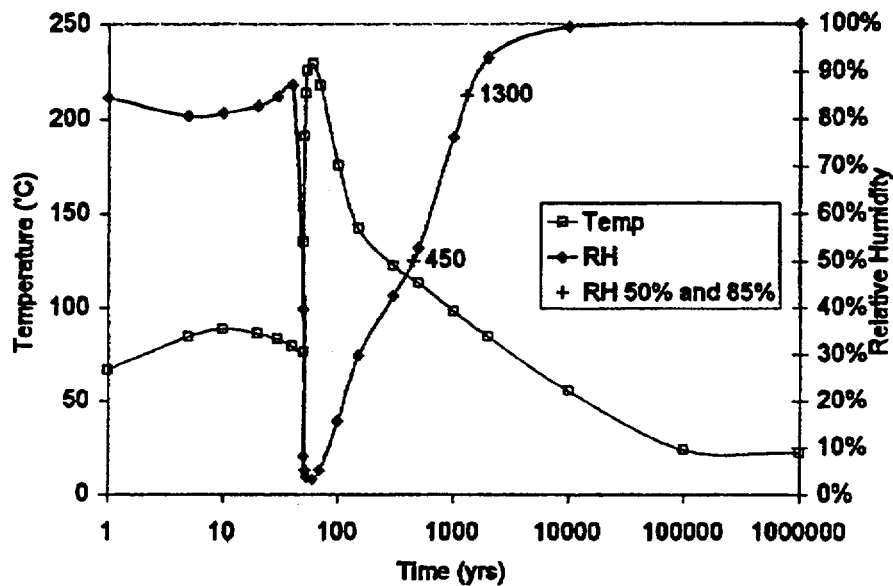
6. RESULTS

Section 6.1 presents the results of the relative humidity and temperature predictions over time. Section 6.2 presents the results of the Precipitates/Salts model using THC inputs.

6.1 RELATIVE HUMIDITY AND TEMPERATURE HISTORY

The results of the averaging and interpolation of relative humidity and temperature over time are displayed in Figure 1. These results represent the approximated average predicted values and trends for *RH* and *T* for the invert and in the drift in general (Assumption 3.1). For the purposes of the LRH model, *RH* reaches 50 and 85 percent at 450 and 1300 years, respectively.

These calculations are based on *RH* and *T* predictions that are currently unqualified and TBV (DTN: SN0001T0872799.006). The data developed in this calculation (DTN: MO0002SPABIN46.008) are therefore TBV. However, because these results are used only as a reference in the LRH model calculations to support Assumption 3.1, they do not affect the qualification or TBV status of the LRH model calculations. LRH model output is independent of time and is not a function the exact timing of *RH* and *T* values.



DTN: MO0002SPABIN46.008

Figure 1. Predictions of Bin-Weighted Mean Relative Humidity and Temperature for the Invert Over Time

6.2 PRECIPITATES/SALTS MODEL RESULTS

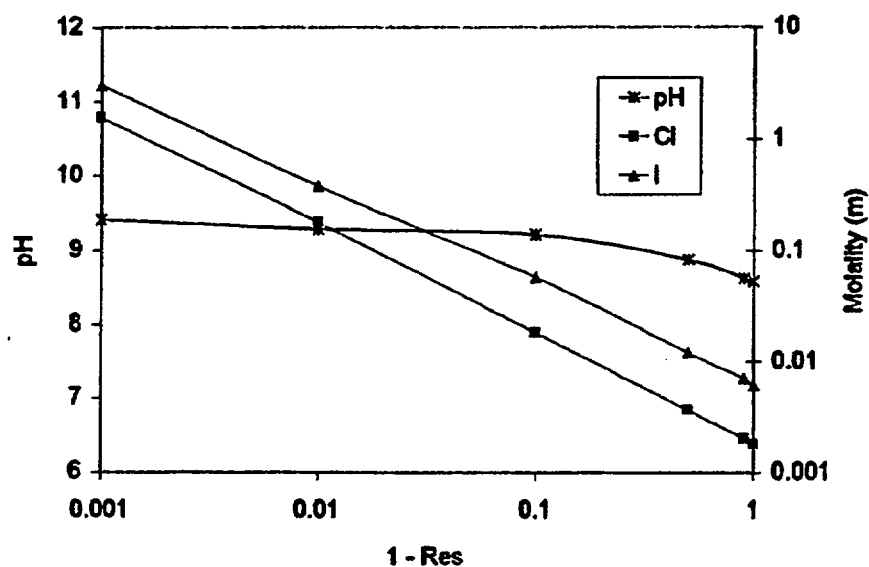
The Precipitates/Salts model output consists of calculations for pH, chloride concentration, and ionic strength (in molality) for the input parameter values described in Section 5.1. The results of the HRH and LRH models are presented in Sections 6.2.1 and 6.2.2, respectively. A complete set of these outputs is summarized in Section 6.2.3 in a set of lookup tables that can be used to interpolate model results for input conditions within the ranges modeled. Finally, the limitations of these calculations are addressed in Section 6.2.4.

6.2.1 High Relative Humidity Model Results

Figure 2 and Figure 3 display the HRH model results for Period 2. These plots show that while Cl and I are highly sensitive to relative evaporation rate, pH remains around 9 in Period 2 and around 8 in Period 3.

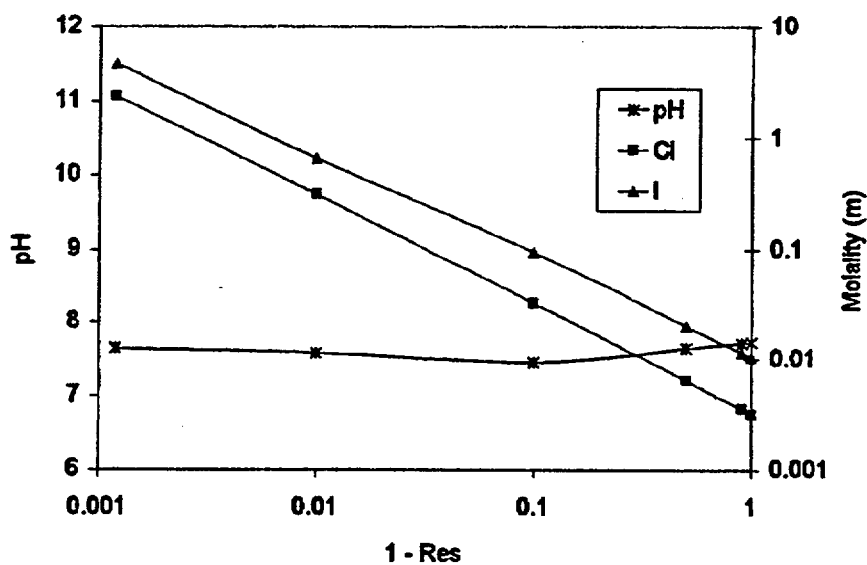
Figure 4, Figure 5, and Figure 6 show the pH, Cl, and I results, respectively, for Period 4 at three different temperatures. These data indicate that the results are not highly sensitive to temperature. Cl and I maintain their strong dependence on relative evaporation rate, and the pH drops to around 7.

Precipitates/Salts Model Results for THC Abstraction



DTN: MO0001MWDEQ345.007

Figure 2. Steady State pH, Cl Concentration, and I vs. $(1 - R^{ss})$ for Period 2



DTN: MO0001MWDEQ345.007

Figure 3. Steady State pH, Cl Concentration, and I vs. $(1 - R^{ss})$ for Period 3

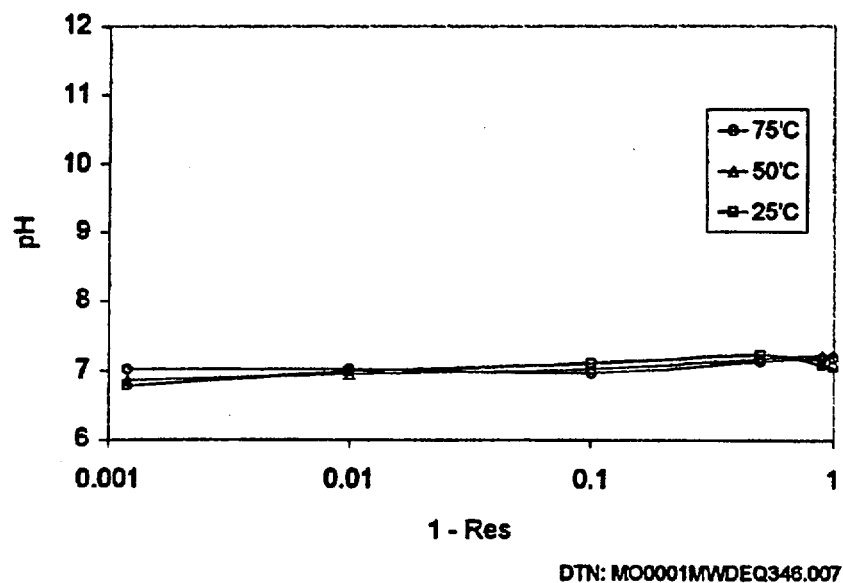


Figure 4. Steady State pH vs. $(1 - R^{ss})$ at Different Temperatures for Period 4

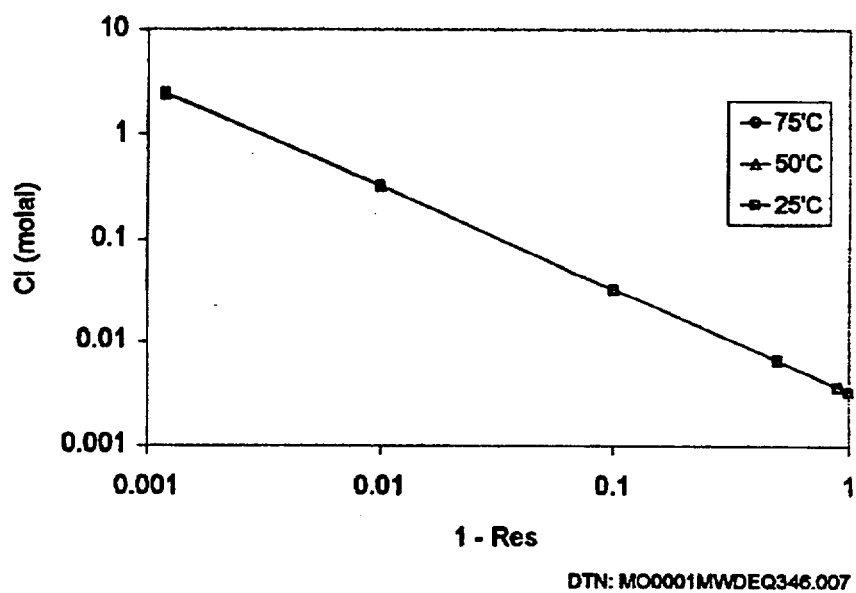


Figure 5. Steady State Cl Concentration vs. $(1 - R^{ss})$ at Different Temperatures for Period 4

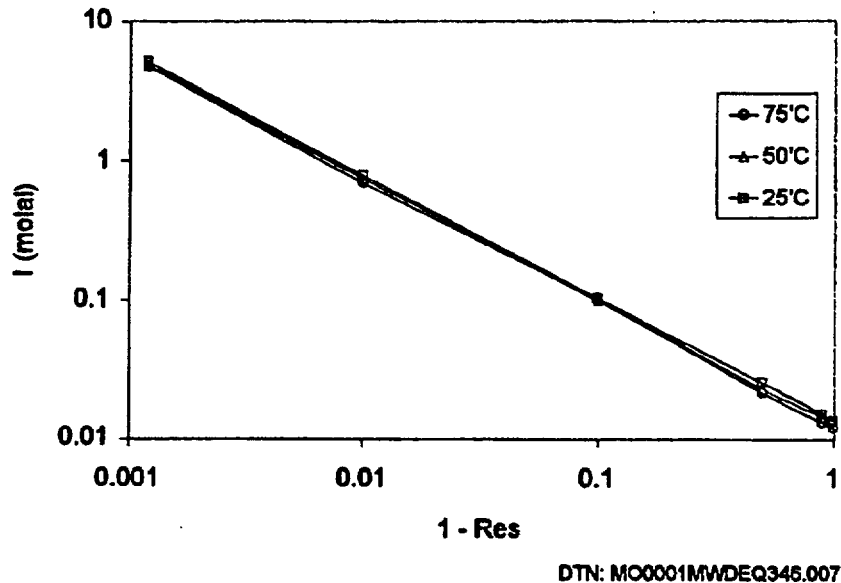
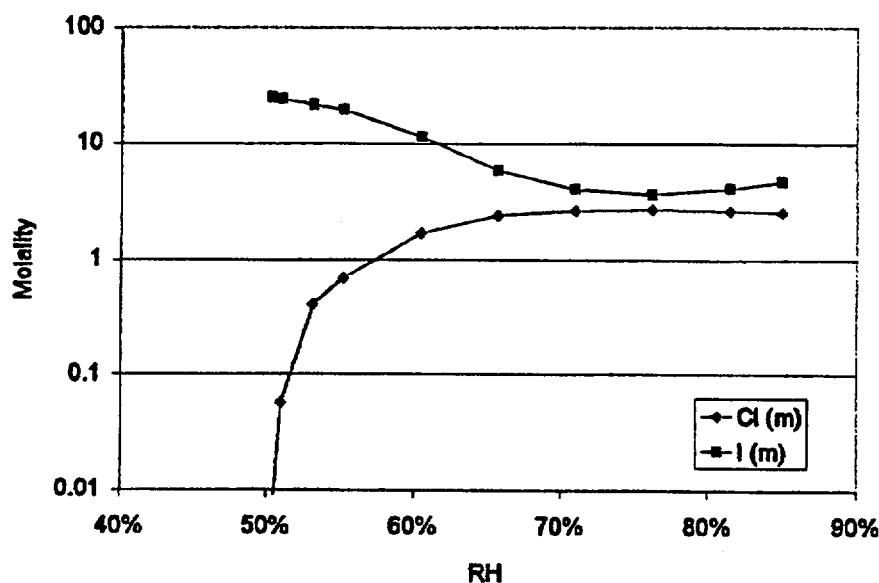


Figure 6. Steady State I vs. $(1-R^{ss})$ at Different Temperatures for Period 4

6.2.2 Low Relative Humidity Model Results

The results of the LRH model for Cl and I are displayed in Figure 7. These results are approximately the same for each period. In general, the Cl concentration is much higher and I is slightly lower than the results for average J-13 well water seepage (CRWMS M&O 2000).

As explained in the Precipitates/Salts AMR (CRWMS M&O 2000), the LRH model is insensitive to the value of the incoming seepage flux and the cumulative masses and volumes of salts and brine. Complete Mathcad calculations and files are presented in Attachments II, III, and IV.



DTN: MO0002SPALRH46.009

Figure 7. Cl and I vs. RH for RH Less than 85 Percent

6.2.3 Precipitates/Salts Model Lookup Tables

The outputs required from the Precipitates/Salts model are the values for pH, Cl concentration, and ionic strength for a given set of inputs intended to encompass the likely scenarios that could occur. These outputs are summarized in a set of lookup tables presented in Table 2 through Table 4. The important independent variables are the incoming seepage composition (C_i^s), relative humidity (RH), temperature (T), relative evaporation rate (R^s), and the fugacity of carbon dioxide (f_{CO_2}). These lookup tables include outputs from the LRH salts model (RH < or = 85 percent) and the HRH salts model (RH > 85 percent).

As explained in the Precipitates/Salts AMR (CRWMS M&O 2000), the LRH salts model incorporates a functional relationship between RH and time. For the lookup tables, time is avoided as an independent input variable by imposing a linear relationship between RH and time. Increasing RH linearly with time from 50 to 85 percent provides the abstraction used to generate the lookup values for RH less than or equal to 85 percent.

The ionic strength values presented in the lookup tables are an approximation of the true ionic strength, as described in Section 5.2.2. An additional approximation is required for lookup table pH values when the RH is less than or equal to 85 percent. Because pH cannot be calculated using the LRH salts model, it is approximated by using the HRH model to perform a simple evaporation of the incoming seepage water to a water activity of 0.85. These values for pH are included in the lookup tables for cases in which RH is less than or equal to 85 percent.

Finally, for the case in which the relative evaporation rate (R'') is one or greater, the ionic strength and Cl concentrations are set at the values obtained by the LRH model at 85 percent relative humidity for the given carbon dioxide fugacities and temperatures. This is done to approximate a reasonable transition between the LRH and HRH model results.

Compared to the Precipitates/Salts model results for J-13 water at similar carbon dioxide fugacities (CRWMS M&O 2000), Cl is consistently an order of magnitude higher in the abstracted THC cases due to the higher initial Cl concentrations (Table 1). pH is generally lower in the THC cases by approximately two pH units for similar carbon dioxide fugacities, likely due to the higher calcium to carbonate ratios in the THC seepage water (Table 1). Ionic strength values for the THC cases stay approximately in the same range as the J-13 calculations.

6.2.4 Limitations

This document may be affected by technical product input information that requires confirmation. Any changes to the document or its conclusions that may occur as a result of completing the confirmation activities will be reflected in subsequent revisions. The status of the input information quality may be confirmed by review of the Document Input Reference System database.

The Precipitate/Salts model calculations documented in this report (DTNs: MO0001MWDEQ346.007, MO0002SPALRH46.009, and MO0002SPALOO46.010) are unqualified and TBV because two of the inputs are unqualified and TBV (DTNs: MO9912SPAPAI29.002 and MO9912SPAPT4PD.001). Once these input data are confirmed, the resulting calculations can be used without TBV tracking controls. The uncertainty and limitations of these calculations are summarized in the conclusions of the Precipitates/Salts AMR (CRWMS M&O 2000).

Precipitates/Salts Model Results for THC Abstraction

Table 2. Lookup Table for Period 2

Input Parameters			Precipitates/Salts Model Output		
RH (%)	T (°C)	R ^{ss}	pH	Cl (molal)	I (molal)
< 50.3%	na ^a	na	dry	dry	dry
50.3%	96	na	9.40	3.71E-03	2.47E+01
51.0%	96	na	9.40	5.68E-02	2.42E+01
53.1%	96	na	9.40	4.09E-01	2.15E+01
55.2%	96	na	9.40	6.85E-01	1.93E+01
60.5%	96	na	9.40	1.68E+00	1.15E+01
65.7%	96	na	9.40	2.40E+00	5.89E+00
71.0%	96	na	9.40	2.63E+00	4.04E+00
76.2%	96	na	9.40	2.68E+00	3.63E+00
81.5%	96	na	9.40	2.63E+00	4.09E+00
85.0%	96	na	9.40	2.55E+00	4.69E+00
> 85%	96	0	8.58	1.80E-03	6.00E-03
> 85%	96	0.1	8.62	2.00E-03	7.00E-03
> 85%	96	0.5	8.87	3.59E-03	1.20E-02
> 85%	96	0.9	9.21	1.80E-02	5.70E-02
> 85%	96	0.99	9.28	1.77E-01	3.78E-01
> 85%	96	0.999	9.41	1.55E+00	3.04E+00
> 85%	96	> 0.999	9.40	2.44E+00	4.94E+00

DTN: MO0002SPAL0046.010

^a not applicable

Precipitates/Salts Model Results for THC Abstraction

Table 3. Lookup Table for Period 3

Input Parameters			Precipitates/Salts Model Output		
RH (%)	T (°C)	R ^{ss}	pH	Cl (molal)	I (molal)
< 50.3%	na ^a	na	dry	dry	dry
50.3%	90	na	7.64	3.73E-03	2.44E+01
51.0%	90	na	7.64	5.70E-02	2.40E+01
53.1%	90	na	7.64	4.06E-01	2.11E+01
55.2%	90	na	7.64	6.77E-01	1.89E+01
60.5%	90	na	7.64	1.63E+00	1.10E+01
65.7%	90	na	7.64	2.28E+00	5.65E+00
71.0%	90	na	7.64	2.49E+00	3.91E+00
76.2%	90	na	7.64	2.53E+00	3.54E+00
81.5%	90	na	7.64	2.48E+00	3.96E+00
85.0%	90	na	7.64	2.41E+00	4.53E+00
> 85%	90	0	7.72	3.19E-03	1.03E-02
> 85%	90	0.1	7.71	3.56E-03	1.14E-02
> 85%	90	0.5	7.64	6.40E-03	1.98E-02
> 85%	90	0.9	7.45	3.20E-02	9.48E-02
> 85%	90	0.99	7.58	3.15E-01	6.60E-01
> 85%	90	0.9988	7.64	2.36E+00	4.69E+00
> 85%	90	> 0.9988	7.64	2.41E+00	4.53E+00

DTN: MO0002SPALOO46.010

^a not applicable

Precipitates/Salts Model Results for THC Abstraction

Table 4. Lookup Table for Period 4

Input Parameters			Precipitates/Salts Model Output		
RH (%)	T (°C)	R ^{ss}	pH	Cl (molal)	I (molal)
< 50.3%	na ^a	na	dry	dry	dry
50.3%	75	na	7.02	3.85E-03	2.43E+01
51.0%	75	na	7.02	5.88E-02	2.39E+01
53.1%	75	na	7.02	4.17E-01	2.09E+01
55.2%	75	na	7.02	6.93E-01	1.86E+01
60.5%	75	na	7.02	1.64E+00	1.08E+01
65.7%	75	na	7.02	2.28E+00	5.56E+00
71.0%	75	na	7.02	2.49E+00	3.87E+00
76.2%	75	na	7.02	2.53E+00	3.51E+00
81.5%	75	na	7.02	2.48E+00	3.92E+00
85.0%	75	na	7.02	2.42E+00	4.47E+00
> 85%	75	0	7.19	3.30E-03	1.21E-02
> 85%	75	0.1	7.18	3.67E-03	1.32E-02
> 85%	75	0.5	7.14	6.60E-03	2.16E-02
> 85%	75	0.9	6.97	3.30E-02	9.85E-02
> 85%	75	0.99	7.02	3.24E-01	6.91E-01
> 85%	75	0.9988	7.02	2.41E+00	4.75E+00
> 85%	75	> 0.9988	7.02	2.41E+00	4.47E+00
> 85%	50	0	7.22	3.30E-03	1.36E-02
> 85%	50	0.1	7.22	3.67E-03	1.47E-02
> 85%	50	0.5	7.18	6.60E-03	2.31E-02
> 85%	50	0.9	7.03	3.29E-02	9.96E-02
> 85%	50	0.99	6.95	3.25E-01	7.45E-01
> 85%	50	0.9988	6.86	2.41E+00	4.87E+00
> 85%	50	> 0.9988	7.02	2.41E+00	4.47E+00
> 85%	25	0	7.05	3.30E-03	1.36E-02
> 85%	25	0.1	7.09	3.67E-03	1.51E-02
> 85%	25	0.5	7.23	6.60E-03	2.66E-02
> 85%	25	0.9	7.11	3.29E-02	1.02E-01
> 85%	25	0.99	6.89	3.25E-01	7.80E-01
> 85%	25	0.9988	6.78	2.46E+00	5.10E+00
> 85%	25	> 0.9988	7.02	2.41E+00	4.47E+00

DTN: MO0002SPALOO46.010

^a not applicable

7. REFERENCES

- AP-3.10Q, Rev. 2, ICN 0. *Analyses and Models*. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.20000217.0246.
- AP-3.12Q, Rev. 0, ICN 1. *Calculations*. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.20000512.0065.
- AP-SI.1Q, Rev. 2, ICN 4. *Software Management*. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management. ACC: MOL.20000223.0508.
- AP-SV.1Q, Rev. 0. *Control of the Electronic Management of Data*. Washington, D.C.: U.S. Department of Energy, Office of Civilian Radioactive Waste Management.
- CRWMS M&O 1998. *Software Qualification Report (SQR) Addendum to Existing LLNL Document UCRL-MA-110662 PT IV: Implementation of a Solid-Centered Flow-Through Mode for EQ6 Version 7.2B*. CSCI: UCRL-MA-110662 V 7.2b. SCR: LSCR198. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990920.0169.
- CRWMS M&O 1999a. *Provide Sub-Models for the Physical and Chemical Environmental Abstraction Model for TSPA-LA*. TDP-WIS-MD-000006 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990902.0450.
- CRWMS M&O 1999b. *Software Code: EQ3/6, Version 7.2bLV*. V7.2bLV. 10075-7.2bLV-00.
- CRWMS M&O 2000. *Precipitates Salts Analysis AMR*. Input Transmittal 00097.T. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000309.0497.
- LL980711104242.054. Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations. Submittal date: 08/05/1998.
- MO9912SPAPAI29.002. PA Initial Abstraction of THC Model Chemical Boundary Conditions. Submittal date: 01/11/2000. Submit to RPC URN-0282
- MO9912SPAPT4PD.001. PT4 Pitzer Database for EQ3/6. Submittal date: 12/06/1999.
- NRC (U.S. Nuclear Regulatory Commission) 1999. *Issue Resolution Status Report Key Technical Issue: Evolution of the Near-Field Environment*. Rev. 2. Washington, D.C.: U.S. Nuclear Regulatory Commission. ACC: MOL.19990810.0640.
- SN0001T0872799.006. In-Drift Thermodynamic Environment and Percolation Flux. Submittal date: 01/27/2000.
- Wolery, T.J. 1992a. *EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems. Package Overview and Installation Guide (Version 7.0)*. UCRL-MA-110662 PT I. Livermore, California: Lawrence Livermore National Laboratory. TIC: 205087.

Wolery, T.J. 1992b. *EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations. Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)*. UCRL-MA-110662 PT III. Livermore, California: Lawrence Livermore National Laboratory. TIC: 205154.

Wolery, T.J. and Daveler, S.A. 1992. *Theoretical Manual, User's Guide, and Related Documentation, Version 7.0. Volume IV of EQ6, A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems*. UCRL-MA-110662. Draft 1.1. Livermore, California: Lawrence Livermore National Laboratory. TIC: 238011.

8. ATTACHMENTS

Attachment	Title
I	Document Input Reference Sheet (DIRS)
II	Low Relative Humidity (LRH) Salts Model THC Period 2 Abstraction (Calculations using Mathcad 7)
III	Low Relative Humidity (LRH) Salts Model THC Period 3 Abstraction (Calculations using Mathcad 7)
IV	Low Relative Humidity (LRH) Salts Model THC Period 4 Abstraction (Calculations using Mathcad 7)

Precipitates/Salts Model Results for THC Abstraction

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT DOCUMENT INPUT REFERENCE SHEET									
1. Document Identifier No./Rev.: CAL-EBS-PA-000008 Rev. 00 (as of 31-may-2000 09:51:04)			Change: N/A		Title: PRECIPITATES/SALTS MODEL RESULTS FOR THC ABSTRACTION				
Input Document			4. Input Status	5. Section Used in	6. Input Description	7. TBV/T BD Priority	8. TBV Due To		
2a.	2. Technical Product Input Source Title and Identifier(s) with Version	3. Section					Unqual	From Uncontrolled Source	Un- Confirm ed
1	CRWMS M&O 1998. <i>Software Qualification Report (SQR) Addendum to Existing LLNL Document UCRL-MA-110662 PT IV: Implementation of a Solid-Centered Flow-Through Mode for EQ6 Version 7.2B.</i> CSCI: UCRL-MA-110662 V 7.2b. SCR: LSCR198. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990920.0169.	Entire	N/A - Reference Only	4.2	Reference to EQ3/6 software	N/A	N/A	N/A	N/A
2	CRWMS M&O 1999a. <i>Provide Sub-Models for the Physical and Chemical Environmental Abstraction Model for TSPA-LA.</i> TDP-WIS-MD-000006 REV 00. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.19990902.0450.	Entire	N/A - Reference Only	1	Reference to work direction for this calculation	N/A	N/A	N/A	N/A
3	CRWMS M&O. 1999b. <i>Software Code: EQ3/6, Version 7.2bLV.</i> V7.2bLV. 10075-7.2bLV-00.	Entire	N/A - Qualified/Confirmed/Controlled	4.2	EQ3/6 software package for geochemical modeling	N/A	N/A	N/A	N/A
4	CRWMS M&O 2000. <i>Precipitates Salts Analysis AMR.</i> Input Transmittal 00097.T. Las Vegas, Nevada: CRWMS M&O. ACC: MOL.20000309.0497.	Entire	N/A - Technical Product Output	Entire	Precipitates/Salts model used for THC abstraction	N/A	N/A	N/A	N/A
5	LL980711104242.054. Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations. Submittal date: 08/05/1998.	Entire	N/A - Qualified Verification Level 2	5.1.2	Average J-13 well water composition	N/A	N/A	N/A	N/A
6	MO9912SPAPAI29.002. PA Initial Abstraction of THC Model Chemical Boundary Conditions. Submittal date: 01/11/2000. Submit to RPC URN-0282	Entire	TBV-4577	5.1.2, 6.2.4	THC abstractions for seepage and gas composition and temperature in the drift	2	X	N/A	N/A

Precipitates/Salts Model Results for THC Abstraction

7	MO9912SPAPT4PD.001. PT4 Pitzer Database for EQ3/6. Submittal date: 12/06/1999.	Entire	IBV-3922	5.1.1, 6.2.4	DEVELOPED PITZER DATABASE FOR EQ3/6	2	X	N/A	N/A
8	NRC (U.S. Nuclear Regulatory Commission) 1999. <i>Issue Resolution Status Report Key Technical Issue: Evolution of the Near-Field Environment</i> . Rev. 2. Washington, D.C.: U.S. Nuclear Regulatory Commission. ACC: MOL.19990810.0640.	Entire	N/A - Reference Only	1	NRC criteria for license application review	N/A	N/A	N/A	N/A
9	SN0001T0872799.006. In-Drift Thermodynamic Environment and Percolation Flux. Submittal date: 01/27/2000.	Files RIP_RHI nvavg_hl w_d0010 500_bin* _mean and RIP_Tin vavg_hl w_d0010 500_bin* _mean	IBV-4564	5.1.2, 5.2.1, 6.1	BIN AVERAGED CSNF AND HLW UPPER DRIFT WALL TEMPERATURES FOR MEAN FLUX CASE FROM MSTHM	2	X	N/A	N/A
10	Wolery, T.J. 1992a. <i>EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems. Package Overview and Installation Guide (Version 7.0)</i> . UCRL-MA-110662 PT I. Livermore, California: Lawrence Livermore National Laboratory. TIC: 205087.	Entire	N/A - Reference Only	4.2	EQ3/6 software package and overview	N/A	N/A	N/A	N/A
11	Wolery, T.J. 1992b. <i>EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations. Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)</i> . UCRL-MA-110662 PT III Livermore, California: Lawrence Livermore National Laboratory. TIC: 205154.	Entire	N/A - Reference Only	4.2	Reference manual for EQ3NR	N/A	N/A	N/A	N/A
12	Wolery, T.J. and Daveler, S.A. 1992. <i>Theoretical Manual, User's Guide, and Related Documentation, Version 7.0. Volume IV of EQ6, A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems</i> . UCRL-MA-110662. Draft 1.1. Livermore, California: Lawrence Livermore National Laboratory. TIC: 238011.	Entire	N/A - Reference Only	4.2	Reference manual for EQ6 version 7	N/A	N/A	N/A	N/A

Low Relative Humidity (LRH) Salts Model
THC Period 2 Abstraction

Conceptual Model. Water seeps into "reactor" (i.e., drip shield or backfill) at a constant rate during the period. In the reactor, seepage water vaporizes and salts accumulate. Salts begin to dissolve when the relative humidity rises above 50%. This model (LRH) approximates the buildup and dissolution of soluble salts in the Na-K-N-S-Cl-C system. All fluid (brine) generated during each time interval flows out of reactor at the end of each time interval; however, mixing is allowed between half time intervals. The end point is designed to be equivalent to the evaporative evolution of seepage water to a stoichiometric ionic strength of 10 molal, as calculated using the EQ3/6 Pitzer model. The LRH salts model is a simplified approximation of salt accumulation and eventual dissolution caused by increasing relative humidity. It maintains mass and charge balance and estimates brine generation as a function of effective solubilities. Its purpose is to provide bounding and scoping calculations for an evaporite system that has not been deeply studied.

Seepage - Constant rate and constant composition are assumed.

Seepage Name:

s := "THC Period 2"

CO₂ (g) Fugacity:

fco₂ := 1·10^{-6.5}

	Seepage Comp. (molal)	Valency	Seepage Rate
NO ₃	Cs ₁ := 0.0013·mol·kg ⁻¹	z ₁ := 1	Qs := 1· $\frac{\text{kg}}{\text{yr}}$
Cl	Cs ₂ := 0.0018·mol·kg ⁻¹	z ₂ := 1	
Soluble SO ₄	Cs ₃ := 0.00018·mol·kg ⁻¹	z ₃ := 2	
Soluble CO ₃	Cs ₄ := 5.1·10 ⁻⁸ ·mol·kg ⁻¹	z ₄ := 1.33	
K	Cs ₆ := 0.000085·mol·kg ⁻¹	z ₆ := 1	
Na	Cs ₇ := 0.0034·mol·kg ⁻¹	z ₇ := 1	

Because nitrate is not included in the THC results, Cs₁ is adjusted to achieve a Cl:NO₃ ratio equivalent to the ratio in average J-13 well water.

Cs₃ and Cs₄ are adjusted to achieve Na:SO₄ and Na:CO₃ ratios equivalent to the 0.85-water-activity solution calculated from the EQ3/6 Pitzer model. *Soluble* implies the fraction that precipitates with Na or K.

Charge Balance Error

$$E = \frac{\sum_{i=1}^7 Cs_i \cdot z_i - \sum_{i=1}^4 Cs_i \cdot z_i}{\sum_{i=1}^7 Cs_i \cdot z_i}$$

$$E = 3.59 \cdot 10^{-3}$$

$$E = 0.36 \cdot \%$$

This charge balance error is approximately maintained for the entire calculation.

Dry Period. Salts accumulate. No stable brine is generated. Period ends when relative humidity (RH) rises to level where nitrate salts are no longer stable.

Time Nitrate Salts Become Unstable: t50 := 450·yr (time when RH exceeds ~50%)

i := 1..7

Total Accumulation in Dry Period

Molecular Weight

NO ₃	Mst _{1,0} := Cs ₁ ·Qs·t50	Mst _{1,0} = 0.585·mol	W ₁ := 62·gm·mol ⁻¹
Cl		Mst _{2,0} = 0.81·mol	W ₂ := 35.5·gm·mol ⁻¹
SO ₄		Mst _{3,0} = 0.081·mol	W ₃ := 96·gm·mol ⁻¹
Soluble CO ₃		Mst _{4,0} = 2.3·10 ⁻⁵ ·mol	W ₄ := 60·gm·mol ⁻¹
K		Mst _{6,0} = 0.038·mol	W ₆ := 39·gm·mol ⁻¹
Na		Mst _{7,0} = 1.53·mol	W ₇ := 23·gm·mol ⁻¹

Precipitates/Salts Model Results for THC Abstraction

Wet Period. Nitrate salts are unstable. Water vapor condenses to form nitrate brine. Soluble salts begin to dissolve as RH increases and completely dissolve by the end of the period.

Time Discretization in Wet Period

End of Wet Period at 85% RH	$t_{85} := 1300 \cdot \text{yr}$	At RH 85%, soluble salts are dissolved and the activity of water is approximately 0.85.
Time Increments in Wet Period	$j := 0 \dots 100$	Specific Times of Increments
Constant Time Increment	$\text{delt} := t_1 - t_0$	$t_j = t_{50} + (t_{85} - t_{50}) \cdot \frac{j}{100}$
Salt Solubilities	Effective Solubility at 100°C (molal)	
NO3	$S_1 := 24.5 \cdot \text{mol} \cdot \text{kg}^{-1}$	(pure phase solubility at 100°C for KNO_3)
Other Salts	$k := 2 \dots 4$ $S_k := 3.0 \cdot \text{mol} \cdot \text{kg}^{-1}$	(assumed "effective" solubility to match EQ6 model results - "effective" due to mixture of salts)
Mass of Total Condensed Water at Start of Period 2	$\text{mw}_1 := \frac{\text{Mst}_{1,0}}{S_1}$	$\text{mw}_1 = 0.024 \cdot \text{kg}$ (assumes accumulated nitrate salts dissolve to solubility)

Fraction of Soluble Salts Dissolved. While NO3 salts are assumed to dissolve completely at the beginning of the wet period, the other salts are assumed to dissolve increasingly as relative humidity increases over time.

Percentages of Salts Dissolved in Wet Period

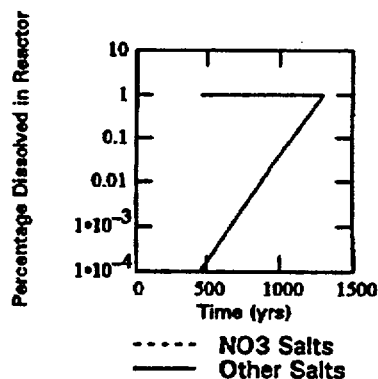
System	Assumptions	Percentage of Salts Dissolved at Start of Wet Period	Percentage Salts Dissolved at End of Wet Period
K-Na-NO3	NO3 salts are 100% dissolved at all times in Wet Period.	$f_{1,1} := 100\%$ $k := 1 \dots 2$	$f_{1,2} := 100\%$

K-Na-Cl-SO4-CO3

$j := 1 \dots 100$

$$ff_j := 10^{\frac{4 \cdot (t_j - t_{85})}{t_{85} - t_{50}}}$$

Percentage dissolved within reactor assumed to increase exponentially from 0% to 100% within Wet Period.



Percentages of Salts Dissolved

$i := 1 \dots 6$

NO3

Other Anions

K

$k := 2 \dots 4$

Initial Percentage Dissolved Within Reactor

$f_{1,0} := 0$

$f_{k,0} := 0$

$f_{6,0} := 0$

Percentage Dissolved Within Reactor

$f_{1,j} := f_{1,1}$

$f_{k,j} := ff_j$

$f_{6,j} := f_{1,1}$

(Na percentage calculated by charge balance later.)

Calculations

Incoming Seepage

Moles Added to Reactor in Incoming Seepage During Time Increment
Cumulative Moles in Incoming Seepage

$$i := 1..7 \quad j := 1..100$$

$$Ms_i := Cs_i \cdot Qs \cdot \text{delt}$$

$$Mst_{i,j} := Mst_{i,j-1} + Ms_i$$

Reactor Calculations

Moles in Reactor at Each Half delt Increment

$$i := 1..6 \quad k := 1..200$$

$$= (\text{previous moles}) + (\text{seepage moles}) - (\text{runoff moles})$$

$$Mrh_{i,0} := Mst_{i,0} (\text{initial moles})$$

$$Mrh_{i,k} := Mrh_{i,k-1} + \frac{1}{2} \cdot Ms_i - \frac{1}{2} \cdot Mrh_{i,k-1} \cdot f_{i, \text{floor}(\frac{k-1}{2})}$$

$$j := 0..100$$

Moles in Reactor at Time t_j

$$Mr_{i,j} := Mrh_{i,j/2}$$

Moles (Mass) of Dissolved Ions Generated at Time t_j

$$Md_{i,j} := Mr_{i,j} \cdot f_{i,j}$$

Dissolved Mass:

$$md_{i,j} := Md_{i,j} \cdot W_i$$

Mass of Water in Brine Generated at Time t_j (calculated from anions)

$$mw_j := \sum_{i=1}^4 \frac{Md_{i,j}}{S_i}$$

Dissolved Concentration at Time t_j

$$C_{i,j} := \frac{Md_{i,j}}{mw_j}$$

Na Moles in Reactor (calculated by charge balance, includes charge imbalance error term)

$$Mr_{7,j} := \sum_{i=1}^4 Mr_{i,j} \cdot z_i - Mr_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot Mr_{i,j} \cdot z_i \cdot (1 + E)$$

Na Dissolved Concentration (calculated by charge balance, includes charge imbalance error term)

$$C_{7,j} := \sum_{i=1}^4 C_{i,j} \cdot z_i - C_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot C_{i,j} \cdot z_i \cdot (1 + E)$$

Dissolved Moles (Mass) of Na in Reactor (calculated by charge balance, includes charge imbalance error term)

$$Md_{7,j} := \sum_{i=1}^4 Md_{i,j} \cdot z_i - Md_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot Md_{i,j} \cdot z_i \cdot (1 + E)$$

Percentage Na Dissolved in Reactor

$$f_{7,j} := \frac{C_{7,j} \cdot mw_j}{Mr_{7,j}}$$

Dissolved Mass:

$$md_{7,j} := Md_{7,j} \cdot W_7$$

Cumulative Water Runoff

$$j := 1..100$$

$$mwt_0 := 0 \cdot \text{kg}$$

$$mwt_j := mwt_{j-1} + mw_j$$

Cumulative Mass of Total Dissolved Solids Generated at Time t_j

$$mdt_0 := 0 \cdot \text{kg}$$

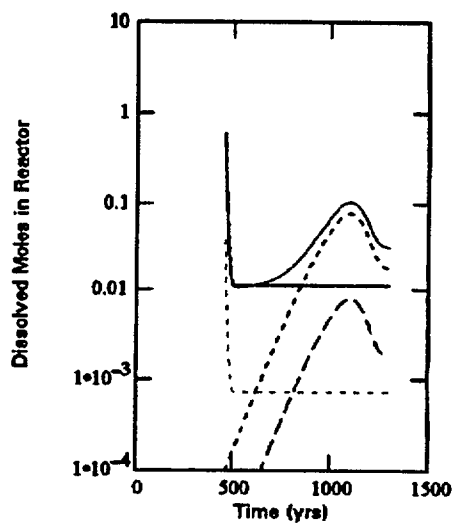
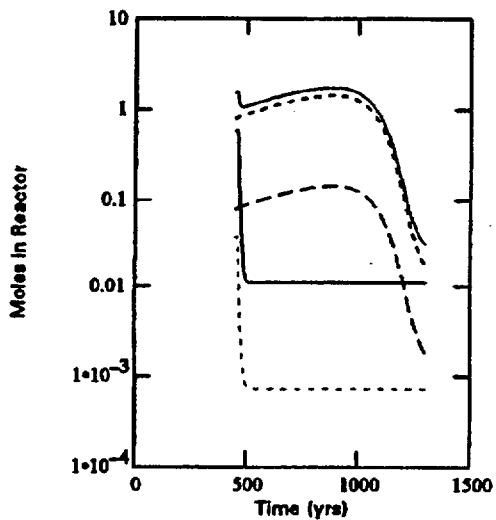
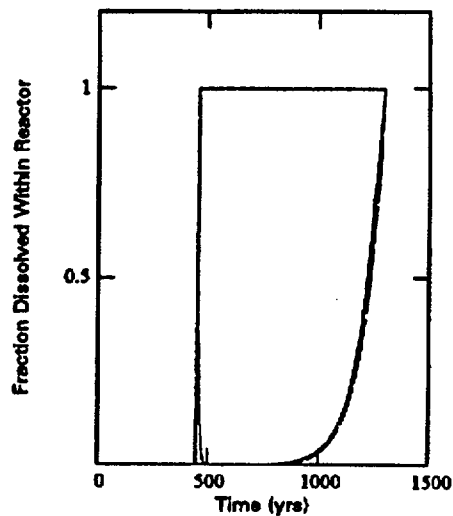
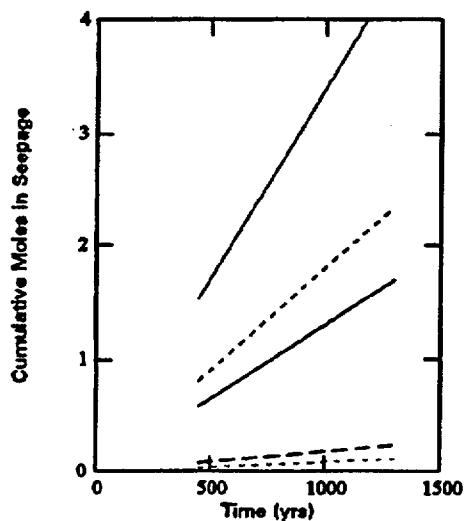
$$mdt_j := mdt_{j-1} + \sum_{i=1}^4 md_{i,j} + \sum_{i=6}^7 md_{i,j}$$

Precipitates/Salts Model Results for THC Abstraction

Results

$i = 1.7$

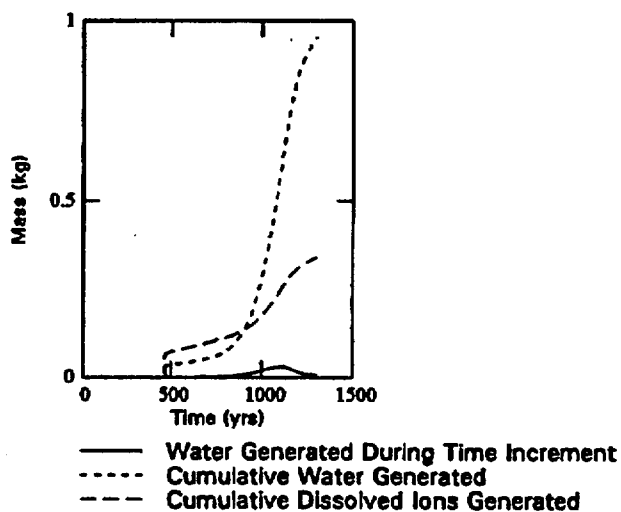
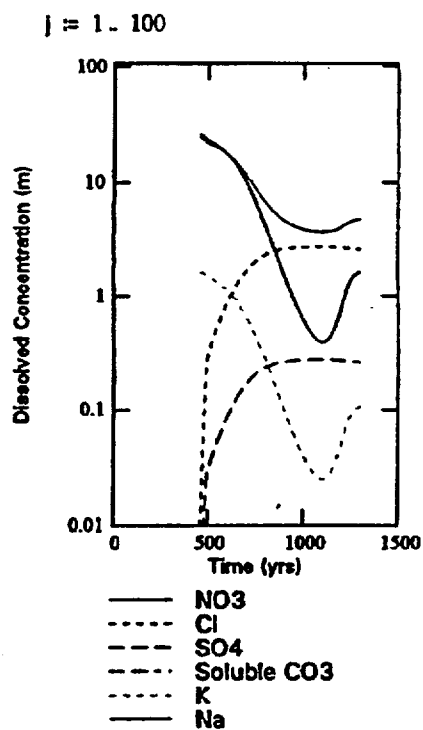
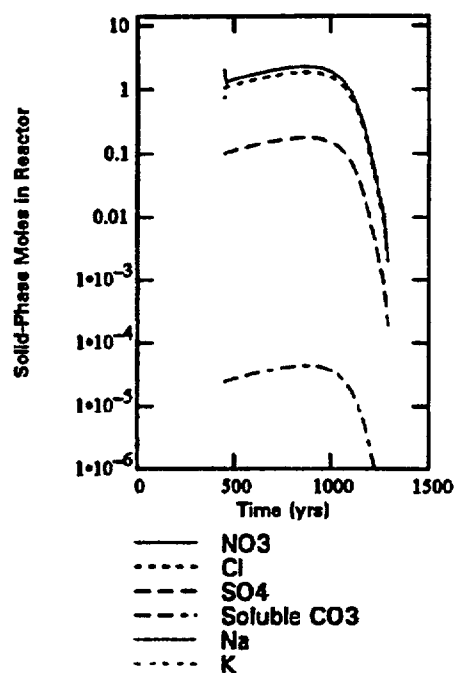
$j = 0.100$



**Solid-Phase (Undissolved)
Moles in Reactor over Time**

$$Mu_{i,j} := Mr_{i,j} - Md_{i,j}$$

Note: M_p for NO_3 and K is zero when RH exceeds 50%.



Summary and Cross-Check

	Concentrations at End of Wet Period	Concentrations Calculated by EQ3/6 Model at RH 85%	Total Moles in Reactor at End of Wet Period
NO3	$C_{1,100} = 1.6 \cdot \text{mol} \cdot \text{kg}^{-1}$	$1.76 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{1,100} = 0.011 \cdot \text{mol}$
Cl	$C_{2,100} = 2.549 \cdot \text{mol} \cdot \text{kg}^{-1}$	$2.44 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{2,100} = 0.018 \cdot \text{mol}$
SO4	$C_{3,100} = 0.255 \cdot \text{mol} \cdot \text{kg}^{-1}$	$0.25 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{3,100} = 1.761 \cdot 10^{-3} \cdot \text{mol}$
Soluble CO3	$C_{4,100} = 7.223 \cdot 10^{-5} \cdot \text{mol} \cdot \text{kg}^{-1}$	$9.1 \cdot 10^{-5} \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{4,100} = 4.989 \cdot 10^{-7} \cdot \text{mol}$
K	$C_{6,100} = 0.105 \cdot \text{mol} \cdot \text{kg}^{-1}$	$0.115 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{6,100} = 7.225 \cdot 10^{-4} \cdot \text{mol}$
Na	$C_{7,100} = 4.588 \cdot \text{mol} \cdot \text{kg}^{-1}$	$4.56 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{7,100} = 0.032 \cdot \text{mol}$

Cumulative Mass of Dissolved Solids
in Incoming Seepage at End of Wet Period

$$\sum_{i=1}^4 Mst_{i,100} \cdot W_i + \sum_{i=6}^7 Mst_{i,100} \cdot W_i = 0.316 \cdot \text{kg}$$

Cumulative Mass of Dissolved Solids
Generated at End of Wet Period

$$mdt_{100} = 0.337 \cdot \text{kg}$$

Cumulative Mass of Water in
Generated Brine at End of Wet Period

$$mwt_{100} = 0.954 \cdot \text{kg}$$

Cumulative Mass of Brine
Generated at End of Wet Period

$$mwt_{100} + mdt_{100} = 1.291 \cdot \text{kg}$$

Charge Balance Error
Maintained Over Time $j := 1, 10, 100$

$$E_j := \frac{\sum_{i=6}^7 C_{i,j} \cdot z_i - \sum_{i=1}^4 C_{i,j} \cdot z_i}{\sum_{i=1}^7 C_{i,j} \cdot z_i}$$

E_j
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$
$3.59 \cdot 10^{-3}$

Output Files:

C:\Vrh_t.xls

 $\frac{t}{\text{yr}}$

C:\Vrh_c.xls

 $C \cdot \frac{\text{kg}}{\text{mol}}$

C:\Vrh_mwt.xls

 $\frac{mwt}{\text{kg}}$

C:\Vrh_mw.xls

 $\frac{mw}{\text{kg}}$

C:\Vrh_mdt.xls

 $\frac{mdt}{\text{kg}}$

C:\Vrh_Mst.xls

 $\frac{Mst}{\text{mol}}$

C:\Vrh_f.xls

 f

C:\Vrh_Mr.xls

 $\frac{Mr}{\text{mol}}$

C:\Vrh_Md.xls

 $\frac{Md}{\text{mol}}$

C:\Vrh_Mu.xls

 $\frac{Mu}{\text{mol}}$

Precipitates/Salts Model Results for THC Abstraction

Response Surface Calculations

$$j := 0..100$$

Relative humidity as a
function of time
(approximation)

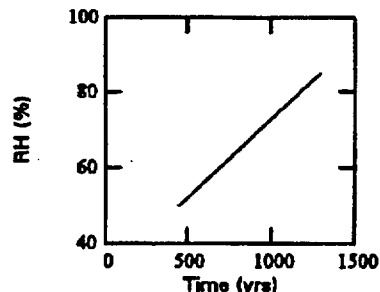
$$RH_j = 0.5 + \left(\frac{t_j - t50}{t85 - t50} \right) \cdot 0.35$$

Evaluation points:

$$j_1 = 1 \quad j_2 = 3 \quad j_3 = 9 \quad j_4 = 15 \quad j_5 = 30$$

$$j_6 = 45 \quad j_7 = 60 \quad j_8 = 75 \quad j_9 = 90 \quad j_{10} = 100$$

$$k := 1..10$$



Lookup Table for Given Seepage Composition

s = "THC Period 2"

Input Parameter

Output Parameters

$$\log(fco_2) = -6.5$$

Relative
Humidity

Cl Concentration

Na + K Concentration

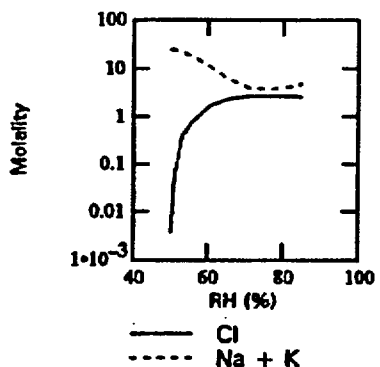
j_k	RH_{j_k}
1	0.503
3	0.510
9	0.531
15	0.552
30	0.605
45	0.657
60	0.710
75	0.762
90	0.815
100	0.850

$C_{2,k}$

$3.7145 \cdot 10^{-3} \cdot \text{kg}^{-1} \cdot \text{mol}$
$0.0568 \cdot \text{kg}^{-1} \cdot \text{mol}$
$0.4085 \cdot \text{kg}^{-1} \cdot \text{mol}$
$0.6852 \cdot \text{kg}^{-1} \cdot \text{mol}$
$1.6835 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.3969 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.6330 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.6843 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.6261 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.5491 \cdot \text{kg}^{-1} \cdot \text{mol}$

$C_{6,k} + C_{7,k}$

$24.65 \cdot \text{kg}^{-1} \cdot \text{mol}$
$24.23 \cdot \text{kg}^{-1} \cdot \text{mol}$
$21.47 \cdot \text{kg}^{-1} \cdot \text{mol}$
$19.31 \cdot \text{kg}^{-1} \cdot \text{mol}$
$11.48 \cdot \text{kg}^{-1} \cdot \text{mol}$
$5.89 \cdot \text{kg}^{-1} \cdot \text{mol}$
$4.04 \cdot \text{kg}^{-1} \cdot \text{mol}$
$3.63 \cdot \text{kg}^{-1} \cdot \text{mol}$
$4.09 \cdot \text{kg}^{-1} \cdot \text{mol}$
$4.69 \cdot \text{kg}^{-1} \cdot \text{mol}$



Low Relative Humidity (LRH) Salts Model
THC Period 3 Abstraction

Conceptual Model. Water seeps into "reactor" (i.e., drip shield or backfill) at a constant rate during the period. In the reactor, seepage water vaporizes and salts accumulate. Salts begin to dissolve when the relative humidity rises above 50%. This model (LRH) approximates the buildup and dissolution of soluble salts in the Na-K-N-S-Cl-C system. All fluid (brine) generated during each time interval flows out of reactor at the end of each time interval; however, mixing is allowed between half time intervals. The end point is designed to be equivalent to the evaporative evolution of seepage water to a stoichiometric ionic strength of 10 molal, as calculated using the EQ3/6 Pitzer model. The LRH salts model is a simplified approximation of salt accumulation and eventual dissolution caused by increasing relative humidity. It maintains mass and charge balance and estimates brine generation as a function of effective solubilities. Its purpose is to provide bounding and scoping calculations for an evaporite system that has not been deeply studied.

Seepage - Constant rate and constant composition are assumed.

Seepage Name:

s := "THC Period 3"

CO₂ (g) Fugacity:

f_{CO2} := 1·10⁻³

	Seepage Comp. (molal)	Valency	Seepage Rate	CO ₂ (g) Fugacity:
NO ₃	Cs ₁ := 0.0023·mol·kg ⁻¹	z ₁ := 1	Qs := 1· $\frac{\text{kg}}{\text{yr}}$	fco ₂ := 1·10 ⁻³
Cl	Cs ₂ := 0.0032·mol·kg ⁻¹	z ₂ := 1		
Soluble SO ₄	Cs ₃ := 0.00041·mol·kg ⁻¹	z ₃ := 2	<p>Because nitrate is not included in the THC results, Cs₁ is adjusted to achieve a Cl:NO₃ ratio equivalent to the ratio in average J-13 well water.</p> <p>Cs₃ and Cs₄ are adjusted to achieve Na:SO₄ and Na:CO₃ ratios equivalent to the 0.85-water-activity solution calculated from the EQ3/6 Pitzer model. Soluble implies the fraction that precipitates with Na or K.</p>	
Soluble CO ₃	Cs ₄ := 8.3·10 ⁻⁷ ·mol·kg ⁻¹	z ₄ := 1.33		
K	Cs ₆ := 0.00031·mol·kg ⁻¹	z ₆ := 1		
Na	Cs ₇ := 0.0060·mol·kg ⁻¹	z ₇ := 1		
<p>Charge Balance Error</p> <p>Approximation</p>				

Charge Balance Error Approximation

$$E := \frac{\sum_{i=1}^7 Cs_i \cdot z_i - \sum_{i=1}^4 Cs_i \cdot z_i}{\sum_{i=1}^7 Cs_i \cdot z_i}$$

E = -8.791·10⁻⁴ This charge balance error approximation is approximately maintained for the entire calculation.
 E = -0.09 %

Dry Period. Salts accumulate. No stable brine is generated. Period ends when relative humidity (RH) rises to level where nitrate salts are no longer stable.

Time Nitrate Salts Become Unstable: t₅₀ := 450·yr (time when RH exceeds ~50%)

i := 1..7	Total Accumulation in Dry Period		Molecular Weight
NO ₃	Mst _{i,0} := Cs _i ·Qs·t ₅₀	Mst _{1,0} = 1.035·mol	W ₁ := 62·gm·mol ⁻¹
Cl		Mst _{2,0} = 1.44·mol	W ₂ := 35.5·gm·mol ⁻¹
SO ₄		Mst _{3,0} = 0.184·mol	W ₃ := 96·gm·mol ⁻¹
Soluble CO ₃		Mst _{4,0} = 3.7·10 ⁻⁴ ·mol	W ₄ := 60·gm·mol ⁻¹
K		Mst _{6,0} = 0.139·mol	W ₆ := 39·gm·mol ⁻¹
Na		Mst _{7,0} = 2.7·mol	W ₇ := 23·gm·mol ⁻¹

Precipitates/Salts Model Results for THC Abstraction

Wet Period. Nitrate salts are unstable. Water vapor condenses to form nitrate brine. Soluble salts begin to dissolve as RH increases and completely dissolve by the end of the period.

Time Discretization in Wet Period

End of Wet Period at 85% RH	$t_{85} := 1300 \cdot \text{yr}$	At RH 85%, soluble salts are dissolved and the activity of water is approximately 0.85.
Time Increments in Wet Period	$j := 0..100$	Specific Times of Increments
Constant Time Increment	$\text{delt} := t_1 - t_0$	$t_j := t_{50} + (t_{85} - t_{50}) \cdot \frac{j}{100}$
Salt Solubilities	Effective Solubility at 100°C (molal)	$\text{delt} = 8.5 \cdot \text{yr}$
NO3	$S_1 := 24.5 \cdot \text{mol} \cdot \text{kg}^{-1}$	(pure phase solubility at 100°C for KNO_3)
Other Salts	$k := 2..4 \quad S_k := 2.9 \cdot \text{mol} \cdot \text{kg}^{-1}$	(assumed "effective" solubility to match EQ6 model results - "effective" due to mixture of salts)
Mass of Total Condensed Water at Start of Period 2	$\text{mw}_1 := \frac{\text{Mst}_{1,0}}{S_1}$	$\text{mw}_1 = 0.042 \cdot \text{kg}$
		(assumes accumulated nitrate salts dissolve to solubility)

Fraction of Soluble Salts Dissolved. While NO3 salts are assumed to dissolve completely at the beginning of the wet period, the other salts are assumed to dissolve increasingly as relative humidity increases over time.

Percentages of Salts Dissolved in Wet Period

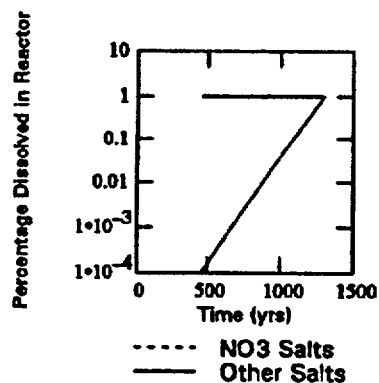
System	Assumptions	Percentage of Salts Dissolved at Start of Wet Period	Percentage Salts Dissolved at End of Wet Period
K-Na-NO3	NO3 salts are 100% dissolved at all times in Wet Period.	$f_{1,1} := 100\%$	$f_{1,2} := 100\%$
		$k := 1..2$	

K-Na-Cl-SO4-CO3

$j := 1..100$

$$f_{f,j} := 10^{\frac{4 \cdot (t_j - t_{85})}{t_{85} - t_{50}}}$$

Percentage dissolved within reactor assumed to increase exponentially from 0% to 100% within Wet Period.



Percentages of Salts Dissolved

$i := 1..6$

NO3

Other Anions

K

$k := 2..4$

Initial Percentage Dissolved Within Reactor

$f_{1,0} := 0$

$f_{k,0} := 0$

$f_{6,0} := 0$

Percentage Dissolved Within Reactor

$f_{1,j} := f_{1,1}$

$f_{k,j} := f_{f,j}$

$f_{6,j} := f_{1,1}$

(Na percentage calculated by charge balance later.)

Calculations

Incoming Seepage

Moles Added to Reactor in
Incoming Seepage During Time
Increment
Cumulative Moles in
Incoming Seepage

$$i := 1..7$$

$$j := 1..100$$

$$Ms_i := Cs_i \cdot Qs \cdot \text{delt}$$

$$Mst_{i,j} := Mst_{i,j-1} + Ms_i$$

Reactor Calculations

Moles in Reactor at Each Half
delt Increment

$$l := 1..6$$

$$k := 1..200$$

$$= (\text{previous moles}) + (\text{seepage moles}) - (\text{runoff moles})$$

$$Mrh_{i,0} := Mst_{i,0} (\text{initial moles})$$

$$Mrh_{i,k} := Mrh_{i,k-1} + \frac{1}{2} \cdot Ms_i - \frac{1}{2} \cdot Mrh_{i,k-1} \cdot f_{i, \text{floor}(\frac{k-1}{2})}$$

$$j := 0..100$$

Moles in Reactor at Time t_j

$$Mr_{i,j} := Mrh_{i,j/2}$$

Moles (Mass) of Dissolved Ions
Generated at Time t_j

$$Md_{i,j} := Mr_{i,j} \cdot f_{i,j}$$

Dissolved Mass:

$$md_{i,j} := Md_{i,j} \cdot W_i$$

Mass of Water in Brine
Generated at Time t_j (calculated
from anions)

$$mw_j := \sum_{i=1}^4 \frac{Md_{i,j}}{S_i}$$

Dissolved Concentration at Time t_j

$$C_{i,j} := \frac{Md_{i,j}}{mw_j}$$

Na Moles in Reactor (calculated
by charge balance, includes
charge imbalance error term)

$$Mr_{7,j} := \sum_{i=1}^4 Mr_{i,j} \cdot z_i - Mr_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot Mr_{i,j} \cdot z_i \cdot (1 + E)$$

Na Dissolved Concentration
(calculated by charge balance,
includes charge imbalance
error term)

$$C_{7,j} := \sum_{i=1}^4 C_{i,j} \cdot z_i - C_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot C_{i,j} \cdot z_i \cdot (1 + E)$$

Dissolved Moles (Mass) of Na
in Reactor (calculated by
charge balance, includes
charge imbalance error term)

$$Md_{7,j} := \sum_{i=1}^4 Md_{i,j} \cdot z_i - Md_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot Md_{i,j} \cdot z_i \cdot (1 + E)$$

Percentage Na Dissolved
in Reactor

$$f_{7,j} := \frac{C_{7,j} \cdot mw_j}{Mr_{7,j}}$$

Dissolved Mass:

$$md_{7,j} := Md_{7,j} \cdot W_7$$

Cumulative
Water Runoff

$$j := 1..100$$

$$mwt_0 := 0 \cdot \text{kg}$$

$$mwt_j := mwt_{j-1} + mw_j$$

Cumulative Mass of
Total Dissolved
Solids Generated at
Time t_j

$$mdt_0 := 0 \cdot \text{kg}$$

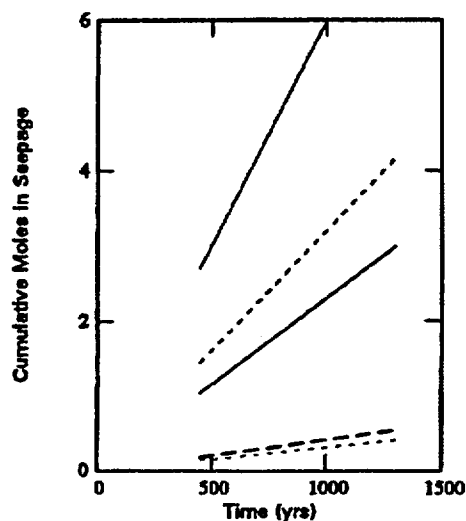
$$mdt_j := mdt_{j-1} + \sum_{i=1}^4 md_{i,j} + \sum_{i=6}^7 md_{i,j}$$

Precipitates/Salts Model Results for THC Abstraction

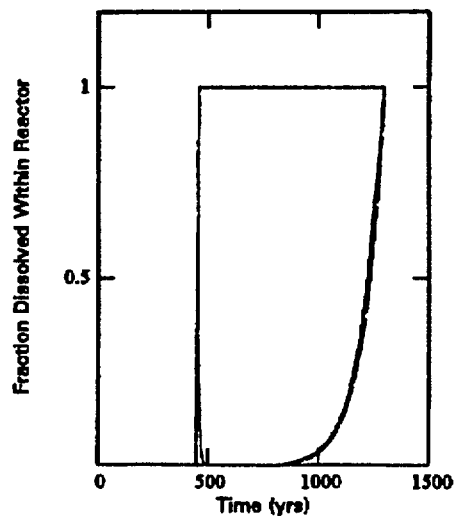
Results

I = 1.7

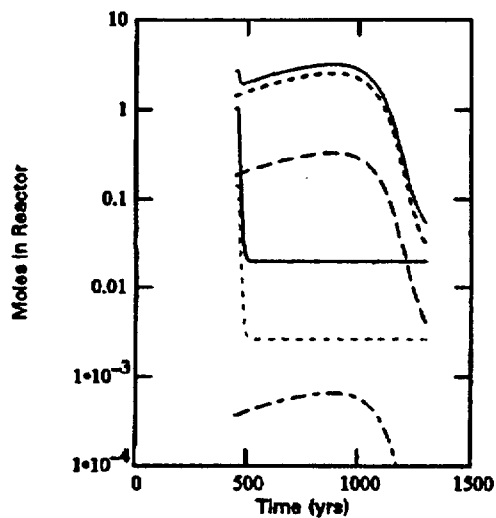
J = 0.100



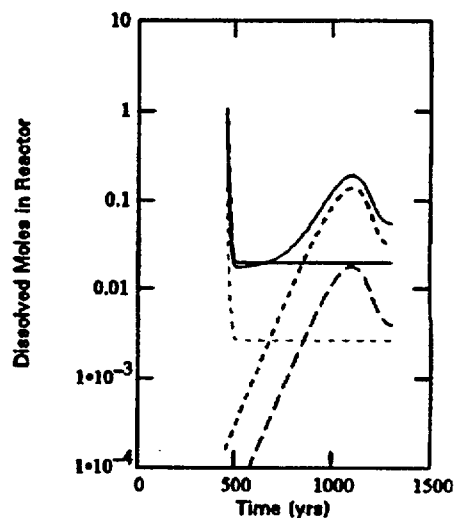
— NO3
 - - - Cl
 . . . SO4
 - . - Soluble CO3
 - - - Na
 - - - K



— NO3
 - - - Cl
 . . . SO4
 - . - Soluble CO3
 - - - Na
 - - - K



— NO3
 - - - Cl
 . . . SO4
 - . - Soluble CO3
 - - - Na
 - - - K



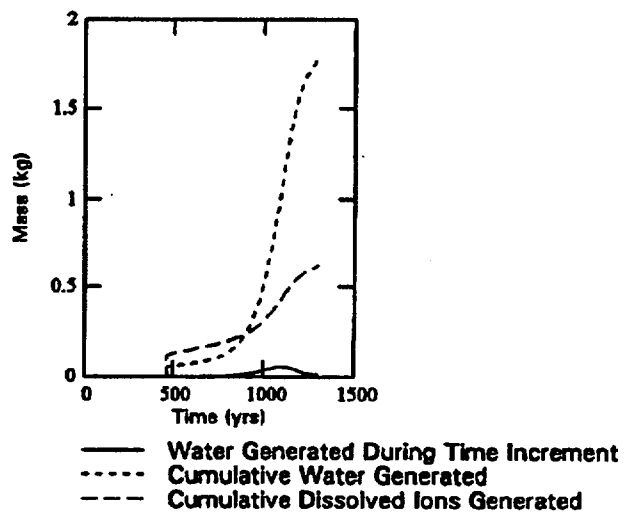
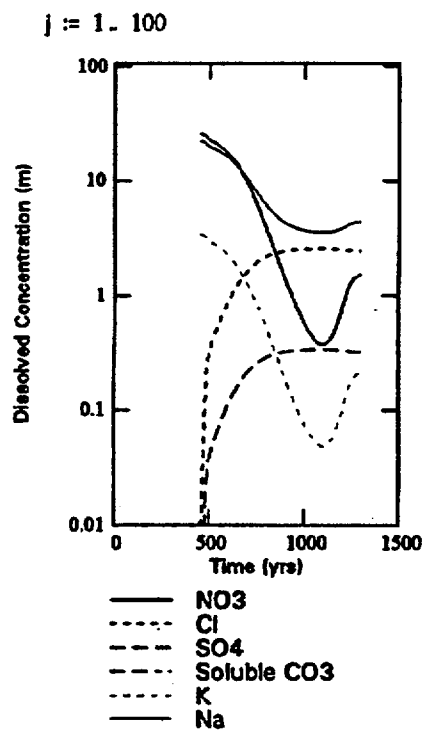
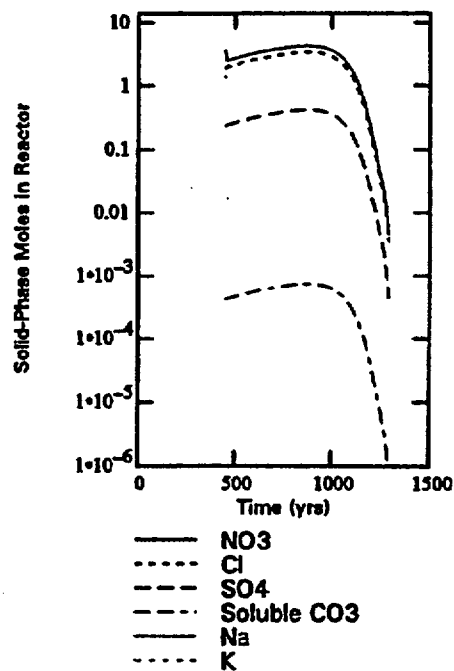
— NO3
 - - - Cl
 . . . SO4
 - . - Soluble CO3
 - - - Na
 - - - K

Precipitates/Salts Model Results for THC Abstraction

Solid-Phase (Undissolved)
Moles in Reactor over Time

$$Mu_{i,j} := Mr_{i,j} - Md_{i,j}$$

Note: Mp for NO3 and K is zero
when RH exceeds 50%.



Precipitates/Salts Model Results for THC Abstraction

Summary and Cross-Check

	Concentrations at End of Wet Period	Concentrations Calculated by EQ3/6 Model at RH 85%	Total Moles in Reactor at End of Wet Period
NO3 ⁻	$C_{1,100} = 1.507 \cdot \text{mol} \cdot \text{kg}^{-1}$	$1.68 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{1,100} = 0.02 \cdot \text{mol}$
Cl	$C_{2,100} = 2.412 \cdot \text{mol} \cdot \text{kg}^{-1}$	$2.34 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{2,100} = 0.031 \cdot \text{mol}$
SO4	$C_{3,100} = 0.309 \cdot \text{mol} \cdot \text{kg}^{-1}$	$0.30 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{3,100} = 4.01 \cdot 10^{-3} \cdot \text{mol}$
Soluble CO3	$C_{4,100} = 6.256 \cdot 10^{-4} \cdot \text{mol} \cdot \text{kg}^{-1}$	$6.0 \cdot 10^{-4} \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{4,100} = 8.119 \cdot 10^{-6} \cdot \text{mol}$
K	$C_{6,100} = 0.203 \cdot \text{mol} \cdot \text{kg}^{-1}$	$0.226 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{6,100} = 2.635 \cdot 10^{-3} \cdot \text{mol}$
Na	$C_{7,100} = 4.326 \cdot \text{mol} \cdot \text{kg}^{-1}$	$4.36 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{7,100} = 0.056 \cdot \text{mol}$

Cumulative Mass of Dissolved Solids
in Incoming Seepage at End of Wet Period

$$\sum_{i=1}^4 Mst_{i,100} \cdot W_i + \sum_{i=6}^7 Mst_{i,100} \cdot W_i = 0.579 \cdot \text{kg}$$

Cumulative Mass of Dissolved Solids
Generated at End of Wet Period

$$mdt_{100} = 0.616 \cdot \text{kg}$$

Cumulative Mass of Water in
Generated Brine at End of Wet Period

$$mwt_{100} = 1.790 \cdot \text{kg}$$

Cumulative Mass of Brine
Generated at End of Wet Period

$$mwt_{100} + mdt_{100} = 2.407 \cdot \text{kg}$$











Charge Balance Error
Maintained Over Time

$j := 1, 10, \dots, 100$

$$E_j = \frac{\sum_{i=6}^7 C_{i,j} \cdot z_i - \sum_{i=1}^4 C_{i,j} \cdot z_i}{\sum_{i=1}^7 C_{i,j} \cdot z_i}$$

E_j
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$
$-8.791 \cdot 10^{-4}$

Output Files:

				
C:\Vrh_t.xls	C:\Vrh_c.xls	C:\Vrh_mwt.xls	C:\Vrh_mw.xls	C:\Vrh_mdt.xls
$\frac{t}{\text{yr}}$	$C \cdot \frac{\text{kg}}{\text{mol}}$	$\frac{mwt}{\text{kg}}$	$\frac{mw}{\text{kg}}$	$\frac{mdt}{\text{kg}}$
				
C:\Vrh_Mst.xls	C:\Vrh_f.xls	C:\Vrh_Mr.xls	C:\Vrh_Md.xls	C:\Vrh_Mu.xls
$\frac{Mst}{\text{mol}}$	f	$\frac{Mr}{\text{mol}}$	$\frac{Md}{\text{mol}}$	$\frac{Mu}{\text{mol}}$

Precipitates/Salts Model Results for THC Abstraction

Response Surface Calculations

$$j := 0..100$$

Relative humidity as a
function of time
(approximation)

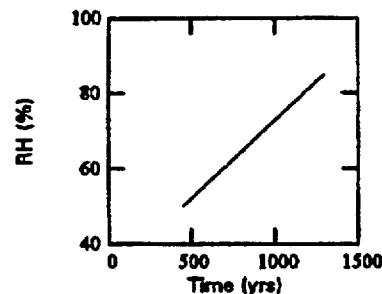
$$RH_j = 0.5 + \left(\frac{t_j - t50}{t85 - t50} \right) \cdot 0.35$$

Evaluation points:

$$j_1 = 1 \quad j_2 = 3 \quad j_3 = 9 \quad j_4 = 15 \quad j_5 = 30$$

$$j_6 = 45 \quad j_7 = 60 \quad j_8 = 75 \quad j_9 = 90 \quad j_{10} = 100$$

$$k := 1..10$$



Lookup Table for Given Seepage Composition

s = "THC Period 3"

Input Parameter

Output Parameters

$$\log(fco_2) = -3$$

Relative
Humidity

Cl Concentration

Na + K Concentration

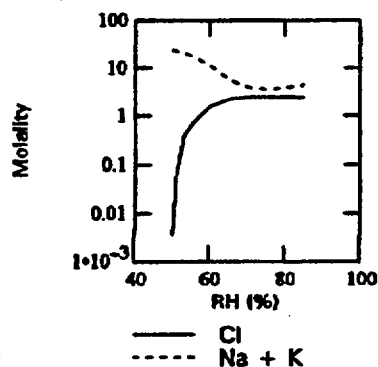
j_k	RH_k
1	0.503
3	0.510
9	0.531
15	0.552
30	0.605
45	0.657
60	0.710
75	0.762
90	0.815
100	0.850

$C_{2,k}$

$3.7321 \cdot 10^{-3} \cdot \text{kg}^{-1} \cdot \text{mol}$
$0.0570 \cdot \text{kg}^{-1} \cdot \text{mol}$
$0.4064 \cdot \text{kg}^{-1} \cdot \text{mol}$
$0.6772 \cdot \text{kg}^{-1} \cdot \text{mol}$
$1.6251 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.2759 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.4866 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.5321 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.4804 \cdot \text{kg}^{-1} \cdot \text{mol}$
$2.4120 \cdot \text{kg}^{-1} \cdot \text{mol}$

$C_{6,k} + C_{7,k}$

$24.43 \cdot \text{kg}^{-1} \cdot \text{mol}$
$23.99 \cdot \text{kg}^{-1} \cdot \text{mol}$
$21.10 \cdot \text{kg}^{-1} \cdot \text{mol}$
$18.86 \cdot \text{kg}^{-1} \cdot \text{mol}$
$11.03 \cdot \text{kg}^{-1} \cdot \text{mol}$
$5.65 \cdot \text{kg}^{-1} \cdot \text{mol}$
$3.91 \cdot \text{kg}^{-1} \cdot \text{mol}$
$3.54 \cdot \text{kg}^{-1} \cdot \text{mol}$
$3.96 \cdot \text{kg}^{-1} \cdot \text{mol}$
$4.53 \cdot \text{kg}^{-1} \cdot \text{mol}$



Low Relative Humidity (LRH) Salts Model THC Period 4 Abstraction

Conceptual Model. Water seeps into "reactor" (i.e. drip shield or backfill) at a constant rate during the period. In the reactor, seepage water vaporizes and salts accumulate. Salts begin to dissolve when the relative humidity rises above 50%. This model (LRH) approximates the buildup and dissolution of soluble salts in the Na-K-N-S-Cl-C system. All fluid (brine) generated during each time interval flows out of reactor at the end of each time interval; however, mixing is allowed between half time intervals. The end point is designed to be equivalent to the evaporative evolution of seepage water to a stoichiometric ionic strength of 10 molal, as calculated using the EQ3/6 Pitzer model. The LRH salts model is a simplified approximation of salt accumulation and eventual dissolution caused by increasing relative humidity. It maintains mass and charge balance and estimates brine generation as a function of effective solubilities. Its purpose is to provide bounding and scoping calculations for an evaporite system that has not been deeply studied.

Seepage - Constant rate and constant composition are assumed.

Seepage Name:

s := "THC Period 4 (75°C)"

	Seepage Comp. (molal)	Valency	Seepage Rate	CO ₂ (g) Fugacity:
NO ₃	Cs ₁ := 0.0023 · mol · kg ⁻¹	z ₁ = 1	Qs := 1 · $\frac{\text{kg}}{\text{yr}}$	fco ₂ = 1 · 10 ⁻²
Cl	Cs ₂ := 0.0033 · mol · kg ⁻¹	z ₂ = 1		
Soluble SO ₄	Cs ₃ := 0.00042 · mol · kg ⁻¹	z ₃ = 2	Because nitrate is not included in the THC results, Cs ₁ is adjusted to achieve a Cl:NO ₃ ratio equivalent to the ratio in average J-13 well water. Cs ₃ and Cs ₄ are adjusted to achieve Na:SO ₄ and Na:CO ₃ ratios equivalent to the 0.85-water-activity solution calculated from the EQ3/6 Pitzer model. Soluble implies the fraction that precipitates with Na or K.	
Soluble CO ₃	Cs ₄ := 2.7 · 10 ⁻⁶ · mol · kg ⁻¹	z ₄ = 1.33		
K	Cs ₅ := 0.0001 · mol · kg ⁻¹	z ₅ = 1		
Na	Cs ₆ := 0.0063 · mol · kg ⁻¹	z ₆ = 1		
	Cs ₇ := 0.0063 · mol · kg ⁻¹	z ₇ = 1		

Charge Balance Error
Approximation

$$E = \frac{\sum_{i=1}^7 Cs_i \cdot z_i - \sum_{i=1}^4 Cs_i \cdot z_i}{\sum_{i=1}^7 Cs_i \cdot z_i}$$

E = -3.394 · 10⁻³ This charge balance error approximation is
E = -0.34 · % approximately maintained for the entire calculation.

Dry Period. Salts accumulate. No stable brine is generated. Period ends when relative humidity (RH) rises to level where nitrate salts are no longer stable.

Time Nitrate Salts Become Unstable: t50 := 450 · yr (time when RH exceeds ~50%)

i := 1 - 7	Total Accumulation in Dry Period	Molecular Weight
NO ₃	Mst _{1,0} := Cs ₁ · Qs · t50 Mst _{1,0} = 1.035 · mol	W ₁ := 62 · gm · mol ⁻¹
Cl	Mst _{2,0} = 1.485 · mol	W ₂ := 35.5 · gm · mol ⁻¹
SO ₄	Mst _{3,0} = 0.189 · mol	W ₃ := 96 · gm · mol ⁻¹
Soluble CO ₃	Mst _{4,0} = 1.2 · 10 ⁻³ · mol	W ₄ := 60 · gm · mol ⁻¹
K	Mst _{5,0} = 0.045 · mol	W ₅ := 39 · gm · mol ⁻¹
Na	Mst _{6,0} = 2.835 · mol	W ₆ := 23 · gm · mol ⁻¹

Wet Period. Nitrate salts are unstable. Water vapor condenses to form nitrate brine. Soluble salts begin to dissolve as RH increases and completely dissolve by the end of the period.

Time Discretization in Wet Period

End of Wet Period at 85% RH	$t_{85} := 1300 \cdot \text{yr}$	At RH 85%, soluble salts are dissolved and the activity of water is approximately 0.85.	
Time Increments in Wet Period	$j := 0..100$	Specific Times of Increments	$t_j := t_{50} + (t_{85} - t_{50}) \cdot \frac{j}{100}$
Constant Time Increment	$\text{delt} := t_1 - t_0$		$\text{delt} = 8.5 \cdot \text{yr}$
Salt Solubilities	Effective Solubility at 100°C (mola)		
NO3	$S_1 := 24.5 \cdot \text{mol} \cdot \text{kg}^{-1}$	(pure phase solubility at 100°C for KNO ₃)	
Other Salts	$k := 2..4 \quad S_k := 2.9 \cdot \text{mol} \cdot \text{kg}^{-1}$	(assumed "effective" solubility to match EQ6 model results - "effective" due to mixture of salts)	
Mass of Total Condensed Water at Start of Period 2	$mw_1 := \frac{Mst_{1,0}}{S_1}$	$mw_1 = 0.042 \cdot \text{kg}$	(assumes accumulated nitrate salts dissolve to solubility)

Fraction of Soluble Salts Dissolved. While NO₃ salts are assumed to dissolve completely at the beginning of the wet period, the other salts are assumed to dissolve increasingly as relative humidity increases over time.

Percentages of Salts Dissolved in Wet Period

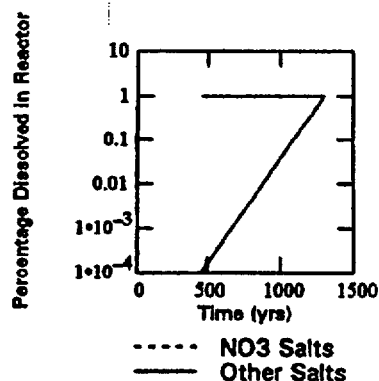
System	Assumptions	Percentage of Salts Dissolved at Start of Wet Period	Percentage Salts Dissolved at End of Wet Period
K-Na-NO3	NO3 salts are 100% dissolved at all times in Wet Period.	$f_{1,1} := 100\%$ $k := 1..2$	$f_{1,2} := 100\%$

K-Na-Cl-SO₄-CO₃

$j := 1..100$

$$ff_j := 10^{\frac{4 \cdot (t_j - t_{85})}{t_{85} - t_{50}}}$$

Percentage dissolved within reactor assumed to increase exponentially from 0% to 100% within Wet Period.



Percentages of Salts Dissolved

$i := 1..6$

NO3

Other Anions

K

$k := 2..4$

Initial Percentage Dissolved Within Reactor
 $f_{1,0} := 0$

$f_{k,0} := 0$

$f_{6,0} := 0$

Percentage Dissolved Within Reactor

$f_{1,j} := f_{1,1}$

$f_{k,j} := ff_j$

$f_{6,j} := f_{1,1}$

(Na percentage calculated by charge balance later.)

Calculations

Incoming Seepage

$$i := 1..7$$

$$j := 1..100$$

Moles Added to Reactor in Incoming Seepage During Time Increment
Cumulative Moles in Incoming Seepage

$$Ms_i := Cs_i \cdot Qs \cdot \text{delt}$$

$$Mst_{i,j} := Mst_{i,j-1} + Ms_i$$

Reactor Calculations

$$i := 1..6$$

$$k := 1..200$$

Moles in Reactor at Each Half delt Increment

$$= (\text{previous moles}) + (\text{seepage moles}) - (\text{runoff moles})$$

$$Mrh_{i,0} := Mst_{i,0} (\text{Initial moles})$$

$$Mrh_{i,k} := Mrh_{i,k-1} + \frac{1}{2} \cdot Ms_i - \frac{1}{2} \cdot Mrh_{i,k-1} \cdot f_{i, \text{floor}(\frac{k-1}{2})}$$

$$j := 0..100$$

Moles in Reactor at Time t_j

$$Mr_{i,j} := Mrh_{i,j/2}$$

Moles (Mass) of Dissolved Ions Generated at Time t_j

$$Md_{i,j} := Mr_{i,j} \cdot f_{i,j}$$

Dissolved Mass:

$$md_{i,j} := Md_{i,j} \cdot W_i$$

Mass of Water in Brine Generated at Time t_j (calculated from anions)

$$mw_j := \sum_{i=1}^4 \frac{Md_{i,j}}{S_i}$$

Dissolved Concentration at Time t_j

$$C_{i,j} := \frac{Md_{i,j}}{mw_j}$$

Na Moles in Reactor (calculated by charge balance, includes charge imbalance error term)

$$Mr_{7,j} := \sum_{i=1}^4 Mr_{i,j} \cdot z_i - Mr_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot Mr_{i,j} \cdot z_i \cdot (1 + E)$$

Na Dissolved Concentration (calculated by charge balance, includes charge imbalance error term)

$$C_{7,j} := \sum_{i=1}^4 C_{i,j} \cdot z_i - C_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot C_{i,j} \cdot z_i \cdot (1 + E)$$

Dissolved Moles (Mass) of Na in Reactor (calculated by charge balance, includes charge imbalance error term)

$$Md_{7,j} := \sum_{i=1}^4 Md_{i,j} \cdot z_i - Md_{6,j} \cdot z_6 + E \cdot \sum_{i=1}^4 2 \cdot Md_{i,j} \cdot z_i \cdot (1 + E)$$

Percentage Na Dissolved in Reactor

$$f_{7,j} := \frac{C_{7,j} \cdot mw_j}{Mr_{7,j}}$$

Dissolved Mass:

$$md_{7,j} := Md_{7,j} \cdot W_7$$

Cumulative Water Runoff

$$j := 1..100$$

$$mwt_0 := 0 \cdot \text{kg}$$

$$mwt_j := mwt_{j-1} + mw_j$$

Cumulative Mass of Total Dissolved Solids Generated at Time t_j

$$mdt_0 := 0 \cdot \text{kg}$$

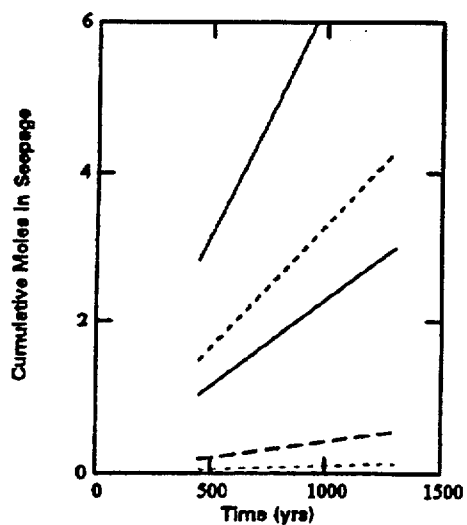
$$mdt_j := mdt_{j-1} + \sum_{i=1}^4 md_{i,j} + \sum_{i=6}^7 md_{i,j}$$

Precipitates/Salts Model Results for THC Abstraction

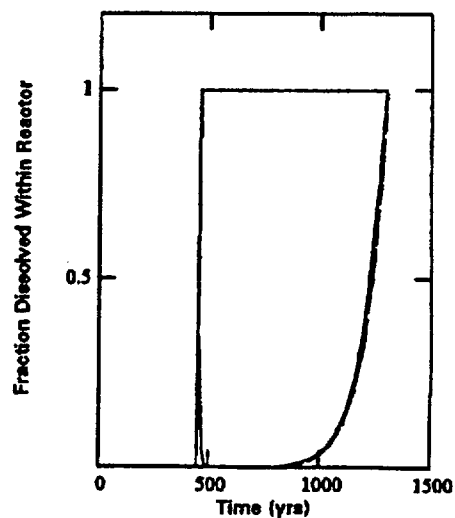
Results

i := 1..7

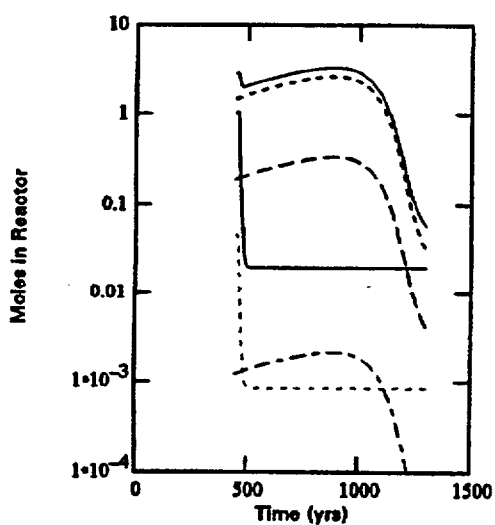
j := 0..100



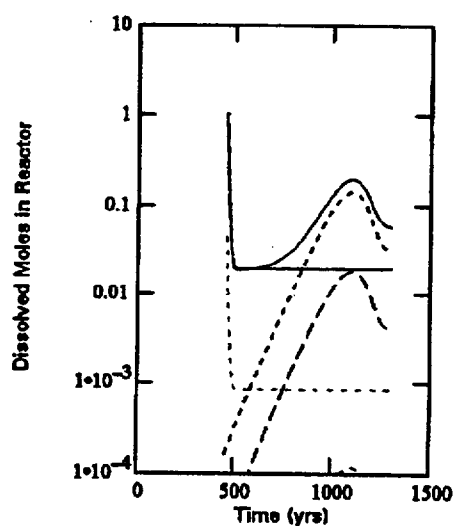
— NO3
 - - - Cl
 . . . SO4
 - . - Soluble CO3
 - - - Na
 - - - K



— NO3
 - - - Cl
 . . . SO4
 - . - Soluble CO3
 - - - Na
 - - - K



— NO3
 - - - Cl
 . . . SO4
 - . - Soluble CO3
 - - - Na
 - - - K

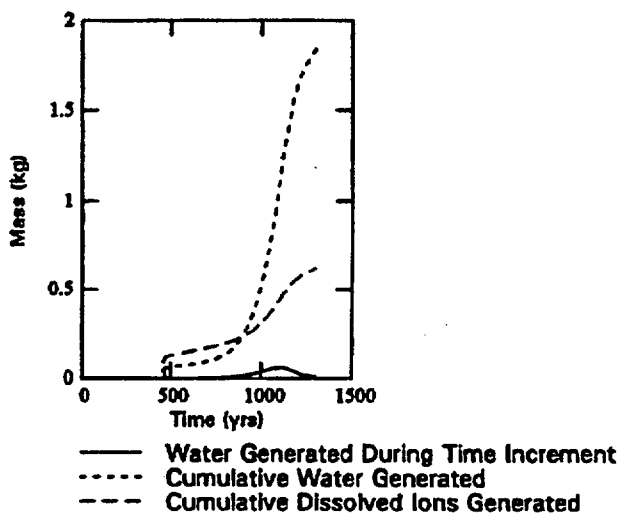
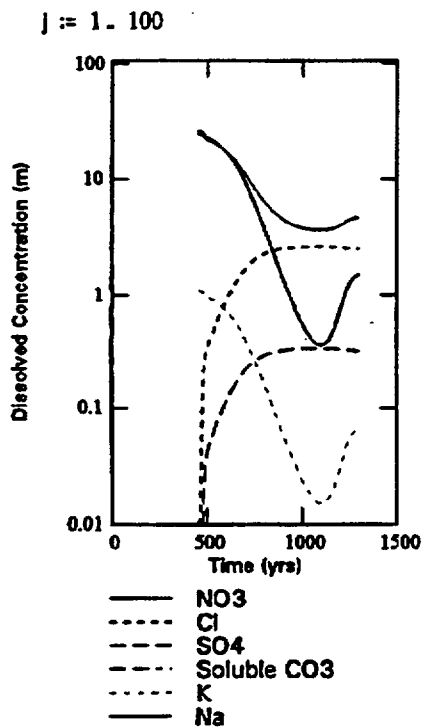
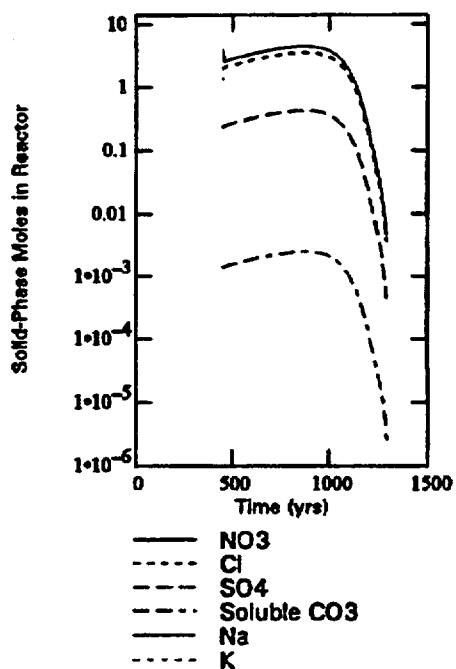


— NO3
 - - - Cl
 . . . SO4
 - . - Soluble CO3
 - - - Na
 - - - K

**Solid-Phase (Undissolved)
Moles in Reactor over Time**

$$Mu_{i,j} := Mr_{i,j} - Md_{i,j}$$

Note: Mp for NO3 and K is zero
when RH exceeds 50%.



Summary and Cross-Check

	Concentrations at End of Wet Period	Concentrations Calculated by EQ3/6 Model at RH 85%	Total Moles in Reactor at End of Wet Period
NO3	$C_{1,100} = 1.464 \cdot \text{mol} \cdot \text{kg}^{-1}$	$1.60 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{1,100} = 0.02 \cdot \text{mol}$
Cl	$C_{2,100} = 2.417 \cdot \text{mol} \cdot \text{kg}^{-1}$	$2.30 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{2,100} = 0.032 \cdot \text{mol}$
SO4	$C_{3,100} = 0.308 \cdot \text{mol} \cdot \text{kg}^{-1}$	$0.29 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{3,100} = 4.108 \cdot 10^{-3} \cdot \text{mol}$
Soluble CO3	$C_{4,100} = 1.978 \cdot 10^{-3} \cdot \text{mol} \cdot \text{kg}^{-1}$	$1.9 \cdot 10^{-3} \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{4,100} = 2.641 \cdot 10^{-5} \cdot \text{mol}$
K	$C_{6,100} = 0.064 \cdot \text{mol} \cdot \text{kg}^{-1}$	$0.070 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{6,100} = 8.5 \cdot 10^{-4} \cdot \text{mol}$
Na	$C_{7,100} = 4.405 \cdot \text{mol} \cdot \text{kg}^{-1}$	$4.38 \cdot \text{mol} \cdot \text{kg}^{-1}$	$Mr_{7,100} = 0.059 \cdot \text{mol}$

Cumulative Mass of Dissolved Solids
in Incoming Seepage at End of Wet Period

$$\sum_{i=1}^4 Mst_{i,100} \cdot W_i + \sum_{i=6}^7 Mst_{i,100} \cdot W_i = 0.584 \cdot \text{kg}$$

Cumulative Mass of Dissolved Solids
Generated at End of Wet Period

$$mdt_{100} = 0.62 \cdot \text{kg}$$

Cumulative Mass of Water in
Generated Brine at End of Wet Period

$$mwt_{100} = 1.842 \cdot \text{kg}$$

Cumulative Mass of Brine
Generated at End of Wet Period











$$mwt_{100} + mdt_{100} = 2.462 \cdot \text{kg}$$

Charge Balance Error
Maintained Over Time $j := 1, 10, 100$

$$E_j := \frac{\sum_{i=6}^7 C_{i,j} \cdot z_i - \sum_{i=1}^4 C_{i,j} \cdot z_i}{\sum_{i=1}^7 C_{i,j} \cdot z_i}$$

E_j
$-3.394 \cdot 10^{-3}$
$-3.394 \cdot 10^{-3}$
$-3.394 \cdot 10^{-3}$
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$-3.394 \cdot 10^{-3}$

Output Files:

 C:\Vrh_f.xls	 C:\Vrh_c.xls	 C:\Vrh_mw.xls	 C:\Vrh_mv.xls	 C:\Vrh_mdt.xls
$\frac{t}{\text{yr}}$	$C \cdot \frac{\text{kg}}{\text{mol}}$	$\frac{mwt}{\text{kg}}$	$\frac{mw}{\text{kg}}$	$\frac{mdt}{\text{kg}}$
 C:\Vrh_Mst.xls	 C:\Vrh_f.xls	 C:\Vrh_Mr.xls	 C:\Vrh_Md.xls	 C:\Vrh_Mu.xls
$\frac{Mst}{\text{mol}}$	f	$\frac{Mr}{\text{mol}}$	$\frac{Md}{\text{mol}}$	$\frac{Mu}{\text{mol}}$

Response Surface Calculations

$j = 0 - 100$

Relative humidity as a function of time (approximation)

$$RH_j = 0.5 + \left(\frac{t_j - 150}{185 - 150} \right) \cdot 0.35$$

Evaluation points:

$$\begin{matrix} i_1 = 1 & i_2 = 3 & i_3 = 9 & i_4 = 15 & i_5 = 30 \\ i_6 = 45 & i_7 = 60 & i_8 = 75 & i_9 = 90 & i_{10} = 100 \end{matrix}$$

$k = 1 - 10$

Lookup Table for Given Seepage Composition

$s = \text{"THC Period 4 (75C)"} \quad \text{Input Parameter}$

Output Parameters

Relative Humidity $\log(fco_2) = -2$

RH_k	1	3	9	15	30	45	60	75	90	100
	0.503	0.510	0.531	0.552	0.605	0.657	0.710	0.762	0.815	0.850

C_2, k	3.8486 · 10 ⁻³ · kg ⁻¹ · mol	0.0588 · kg ⁻¹ · mol	0.4171 · kg ⁻¹ · mol	0.6927 · kg ⁻¹ · mol	1.6437 · kg ⁻¹ · mol	2.2844 · kg ⁻¹ · mol	2.4896 · kg ⁻¹ · mol	2.5339 · kg ⁻¹ · mol	2.4837 · kg ⁻¹ · mol	2.4171 · kg ⁻¹ · mol
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Na + K Concentration

$C_6, k + C_7, k$	24.30 · kg ⁻¹ · mol	23.85 · kg ⁻¹ · mol	20.91 · kg ⁻¹ · mol	18.64 · kg ⁻¹ · mol	10.62 · kg ⁻¹ · mol	5.56 · kg ⁻¹ · mol	3.87 · kg ⁻¹ · mol	3.51 · kg ⁻¹ · mol	3.92 · kg ⁻¹ · mol	4.47 · kg ⁻¹ · mol
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