The Character of the In-Drift Environment

Presented to:
Nuclear Waste Technical Review Board

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In-Drift Chemical Environment

- **Purpose**
- **Three temperature regions**
- **Evolution of the in-drift chemical environment**
- **Chemical divide theory**
- **Observed water chemistries**
- **In-drift water chemistry model and validation**
- **Investigation of deliquescence during dryout temperature region**
- **Explanation of system evolution (three regions)**
- **Conclusions**

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Purpose

- **Present the in-drift chemical environment modeling approach being developed for License Application (LA), and supporting data and measurements**

- **Describe the thermal-chemical evolution of potential incoming waters (possible seepage from the host rock)**

- **Evaluate the deliquescence of evaporative salts and dust on the waste package surface**

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Summary

- **Chemical evolution of seepage water chemistry is controlled by temperature and relative humidity, in three regions or stages of evolution (Dry-out, Transition, and Low-Temperature)**

- **Variability and uncertainty in the predicted composition of possible seepage waters is accommodated in the in-drift modeling approach**

- **Concentrated waters that could support localized corrosion have been shown to be relatively rare, and the quantities are small**

- **Deliquescence of dust or salts on barrier surfaces has been shown not to initiate localized corrosion**

- **The probable evolved seepage waters and deliquescence brines are benign. Calcium-chloride not expected**

- **The drift environment is expected to be an 'open' system**

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The Three Temperature Regions

- **Dry-out**

  – **This region is characterized by above boiling where the rock experiences dry-out and therefore "shields" the drift from significant water seepage**

  – **Deliquescent brines can occur in the absence of seepage brines**

- **Transition**

  – **A relatively brief period in time (hundreds of years) during which drift-wall temperature cools from above boiling to below boiling. The onset of seepage may occur (if local hydrologic conditions permit)**

  – **Chemical evolution of potential seepage is of interest, because evaporative concentration may produce brines**

    - **Testing is being done on evaporative concentration of ambient pore waters and waters from the Drift-Scale Test**

    - **A geochemical model has been developed to represent water compositions in the repository drifts and from testing, over a wider range of potential environmental conditions than previously possible**

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The Three Temperature Regions
(Continued)

- ## Low Temperature Region: Aqueous Brine

  - **Seepage water chemistry evolution in the drift is a function of the incoming water (amount and chemistry), temperature, and relative humidity**

  - **Water chemistry evolution is affected by committed materials in the drift**

  - **Deliquescent brines can occur in the absence of seepage brines**

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Evolution of the In-Drift Environment

Seepage

Deliquescence

In-Drift Precipitates/Salts Model

Drip Shield & WP Corrosion

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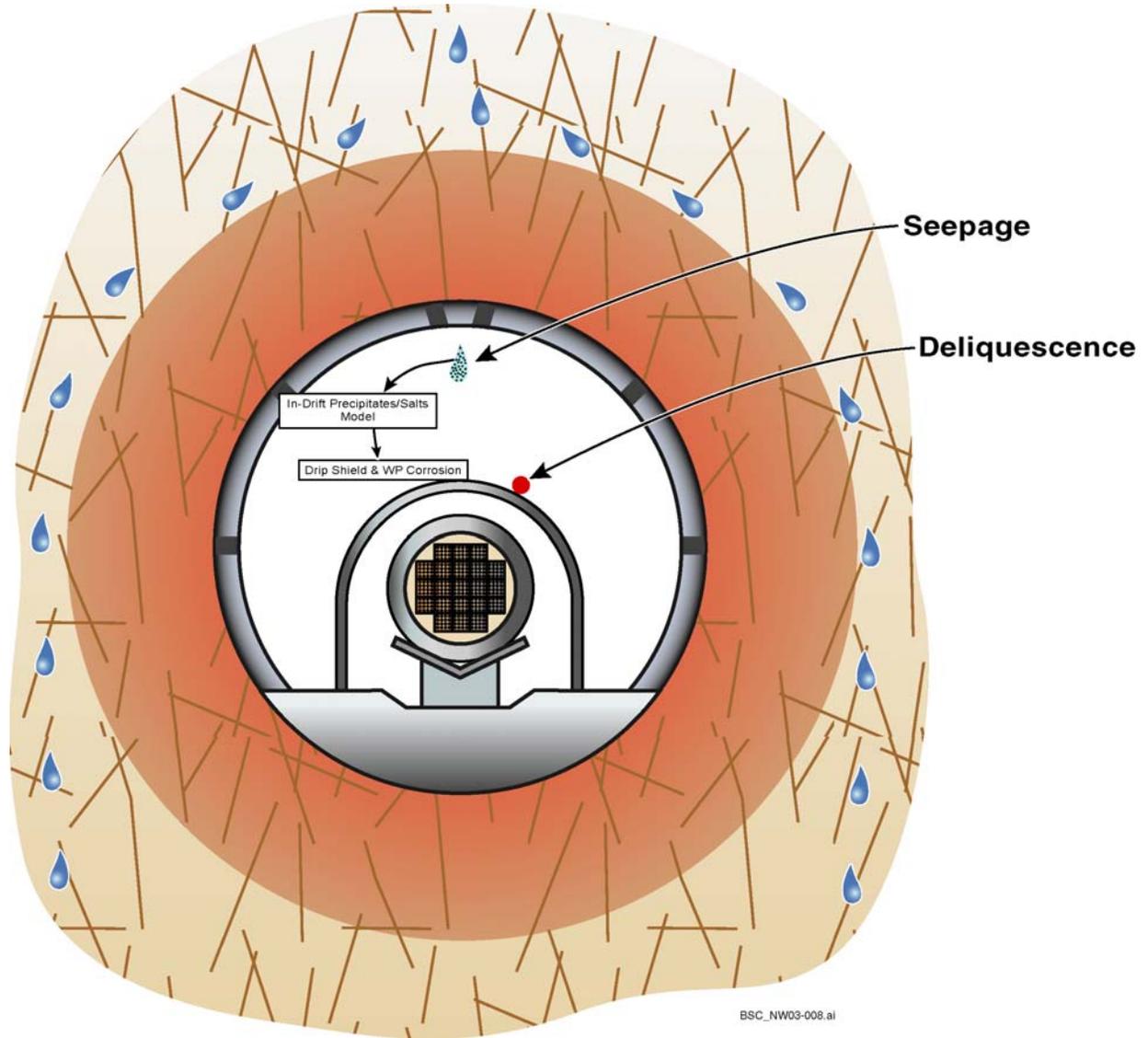
Evolution of the In-Drift Environment Available Data/Measurements

- **Exploratory Studies Facility**

    – **8 km tunnel provides access to repository host rock units**

- **Cross Drift**

    – **3 km drift provides access to rock units above and below repository horizon**

- **Alcove 5**

    – **Single-Heater Test**

    – **Drift Scale Heater Test**

        ◆ **Simulated WP Heated to 197°C**

- **Laboratory Studies**

    – **Deliquescence**

    – **Evaporation**

- Air   200°C
- Rock   195°C
- Canister   197°C
- Ambient   20 °C
- Duration   26,396 hours
- December 20, 2000

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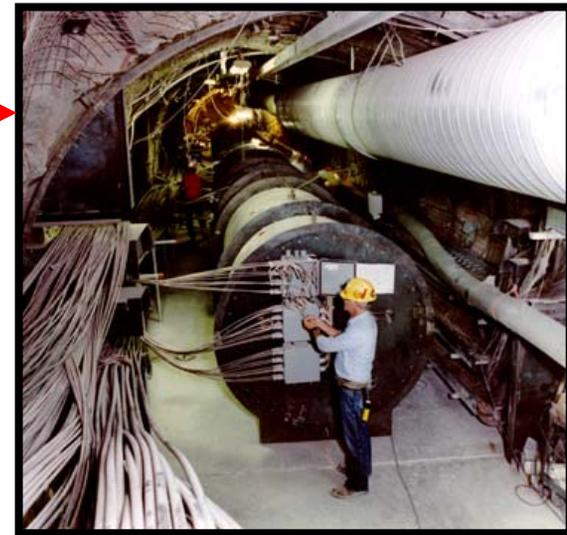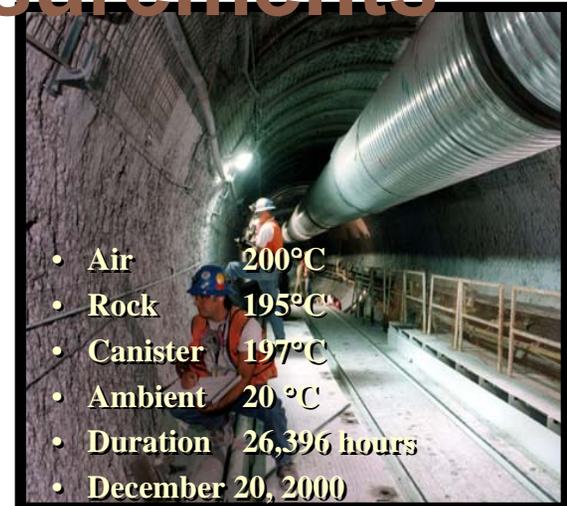
Evolution of the In-Drift Environment Model Approach

- **Modeling thermal evolution of seepage waters in the drift**

  - **Thermal-hydrological-chemical (THC) water composition time series from unsaturated zone (UZ)**

  - **Numerical modeling of chemical evolution**

  - **Validation by comparison to data/measurements**

  - **Abstraction for Total System Performance Assessment (TSPA) (binning)**

- **Experimental evaluation of deliquescence**

- **Modeling gas-phase mixing in the drifts**

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Chemical Divide Theory

Brine Evolution from Dilute Natural Waters

J.I. Drever, *The Geochemistry of Natural Waters*, Prentice-Hall, Inc., 1997.

Evaporative Concentration

$Na, Ca, Mg, HCO_3, SO_4, Cl$

$CaCO_3$ precipitates

**Carbonate species < Ca content
Carbonate removed from solution**

**Carbonate species > Ca content
Ca removed from solution**

Na, Ca, Mg, SO_4, Cl

Na, Mg, CO_3, SO_4, Cl

SO_4 content < Ca content

SO_4 content > Ca content

CO_3 species < Mg content

CO_3 species > Mg content

$CaSO_4$ precipitates

Mg silicate precipitates

SO_4 removed from solution

Ca removed from solution

CO_3 removed from solution

Mg removed from solution

Na, Ca, Mg, Cl

Na, Mg, SO_4, Cl

Na, Mg, SO_4, Cl

Na, CO_3, SO_4, Cl

Death Valley, CA	(Na)*
Bristol Dry Lake, CA	(Na, Ca)
Cadiz Lake, CA	(Na, Ca)
Carson Sink, NV	(Na)

Saline Valley, CA	(Na)*
Danby Lake, CA	(Na)
Salton Sea, CA	(Na)

Surprise Valley, CA
Mono Lake, CA
Owens Lake, CA
Soda Lake, CA
Pyramid Lake, NV
Winnemucca Lake, NV

* Dominant cations in brine

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Chemical Divide Theory
Representative Evolution of Brines During Evaporative Concentration

Ternary diagram showing the effect of calcium carbonate and calcium sulfate precipitation on water composition upon evaporation.

Ca^{2+}

$Ca > SO_4^{2-} + HCO_3^-$

$Ca < SO_4^{2-} + HCO_3^-$

$Ca < HCO_3^-$

SO_4^{2-}

HCO_3^-

Equivalent %
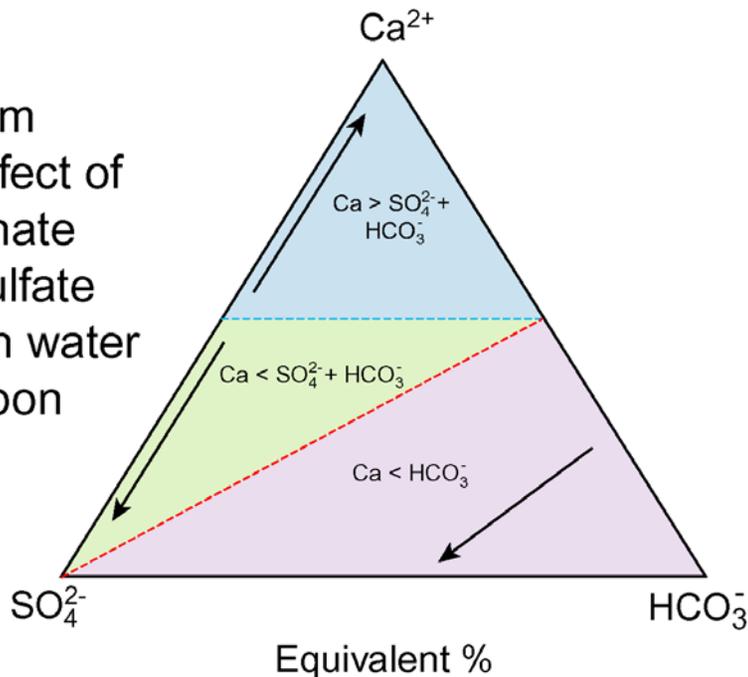
Possible Pore Water Types

- Ca-Chloride Brine ($Na-K-Ca-Mg-Cl-NO_3$)
- Sulfate Brine ($Na-K-Mg-Cl-SO_4-NO_3$)
- Na-Bicarbonate Brine ($Na-K-CO_3-Cl-SO_4-NO_3$)

Chemical Divides

$$Ca^{2+} + 2HCO_3^- = CaCO_3 \text{ (calcite)} + H_2O + CO_2$$
$$Ca^{2+} + SO_4^{2-} = CaSO_4 \cdot 2H_2O \text{ (gypsum)}$$
$$Ca^{2+} + 2F^- = CaF_2 \text{ (fluorite)}$$
$$Mg^{2+} + SiO_{2(aq)} = Mg\text{-silicates}$$

Charge Balance

$$2mCa^{2+} + 2mMg^{2+} + mNa^+ + mK^+ + mH^+ = mHCO_3^-$$
$$+ 2mCO_3^{2-} + 2mSO_4^{2-} + mCl^- + mOH^- + mNO_3^- + mF^-$$
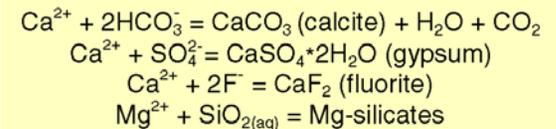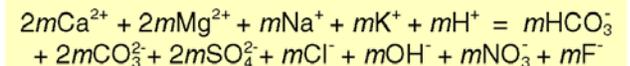
Boundaries shown on this and subsequent ternary plots represent behavior of an idealized system. (The boundaries shift with addition of more chemical components. Our geochemical model includes 50 solids and well over 100 aqueous species.)

Water Chemistries Observed at Yucca Mountain

Legend:
- ◇ Drift Scale Test BH 59-2
- ● Peterman et al. Pore Water (2002)
- ■ Yang et al. Pore Water (Paintbrush)
- ▲ Yang et al. Pore Water (Topopah)
- — — Boundary Between HCO$_3$ & SO$_4$ Brines
- — — Boundary Between SO$_4$ & CaCl$_2$ Brines

Ca^{+2}

SO$_4^{-2}$

HCO$_3^-$

Idealized Boundary Between SO$_4$ & CaCl$_2$ Regions

Represents waters that are now present.

YUCCA MOUNTAIN PROJECT
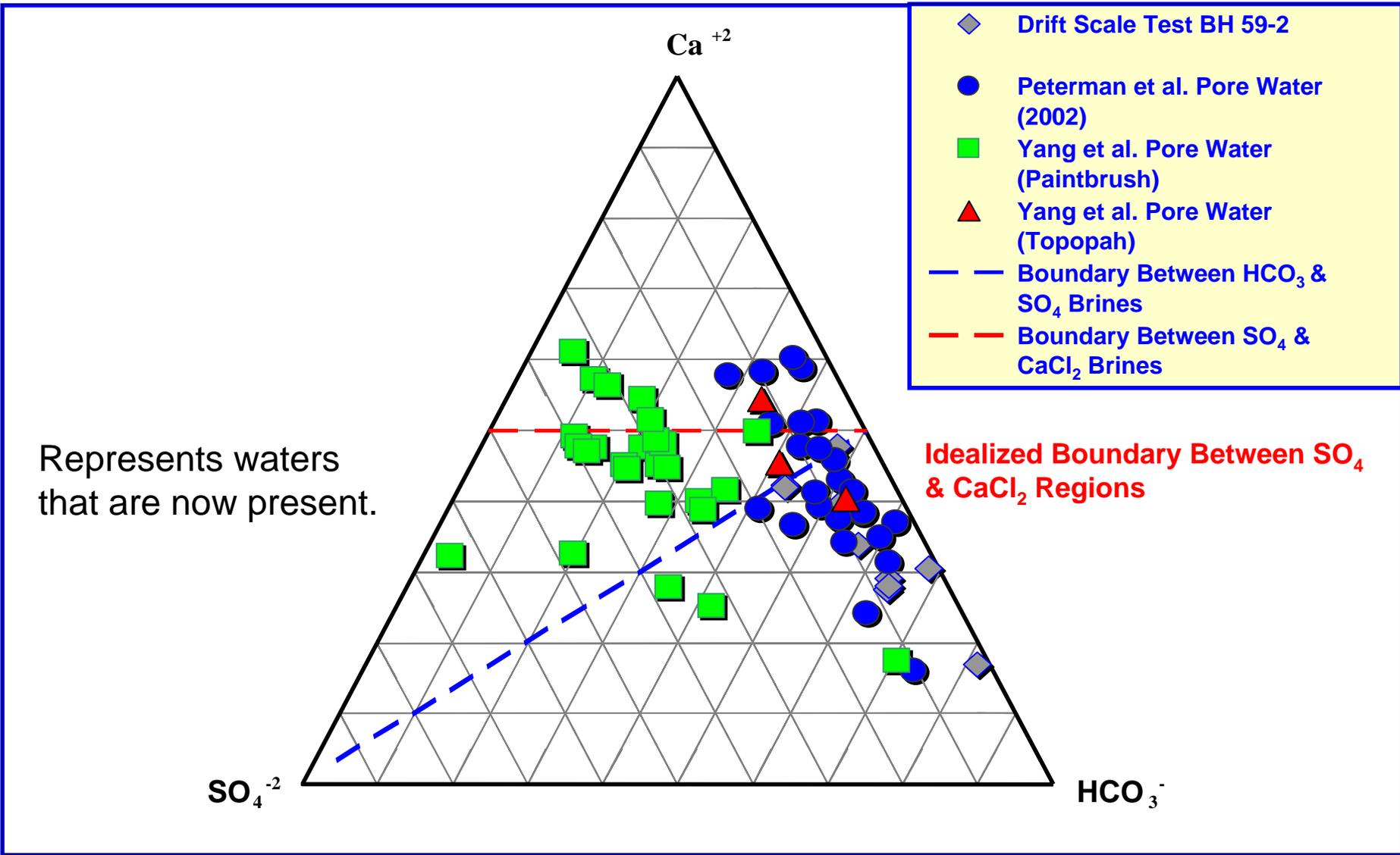
In-Drift Water Chemistry Model
Water Evolution

- **Waters observed in the UZ and field thermal tests**

- **Modeling thermal evolution of in situ waters in the host rock, using a coupled THC model**

- **Abstract the water compositions output from the THC model, representing potential seepage, into groups (bins) with common chemical characteristics**

- **Model the evaporative concentration of these waters to describe the in-drift chemical environment**

- **Identify the frequency of occurrence for chemical conditions that are important for engineered barrier performance**

Host-Rock and In-Drift Chemistry Models

Ambient Pore-Water Chemistry

THC Seepage Model TOUGHREACT

Results Selection

3 Levels P_{CO2}

3 Levels T

PC&E EQ3/6

Binning Processes

Evaporation to Dryness EQ3/6

TSPA Lookup Tables

Composition vs. RH

Materials Interactions EQ3/6
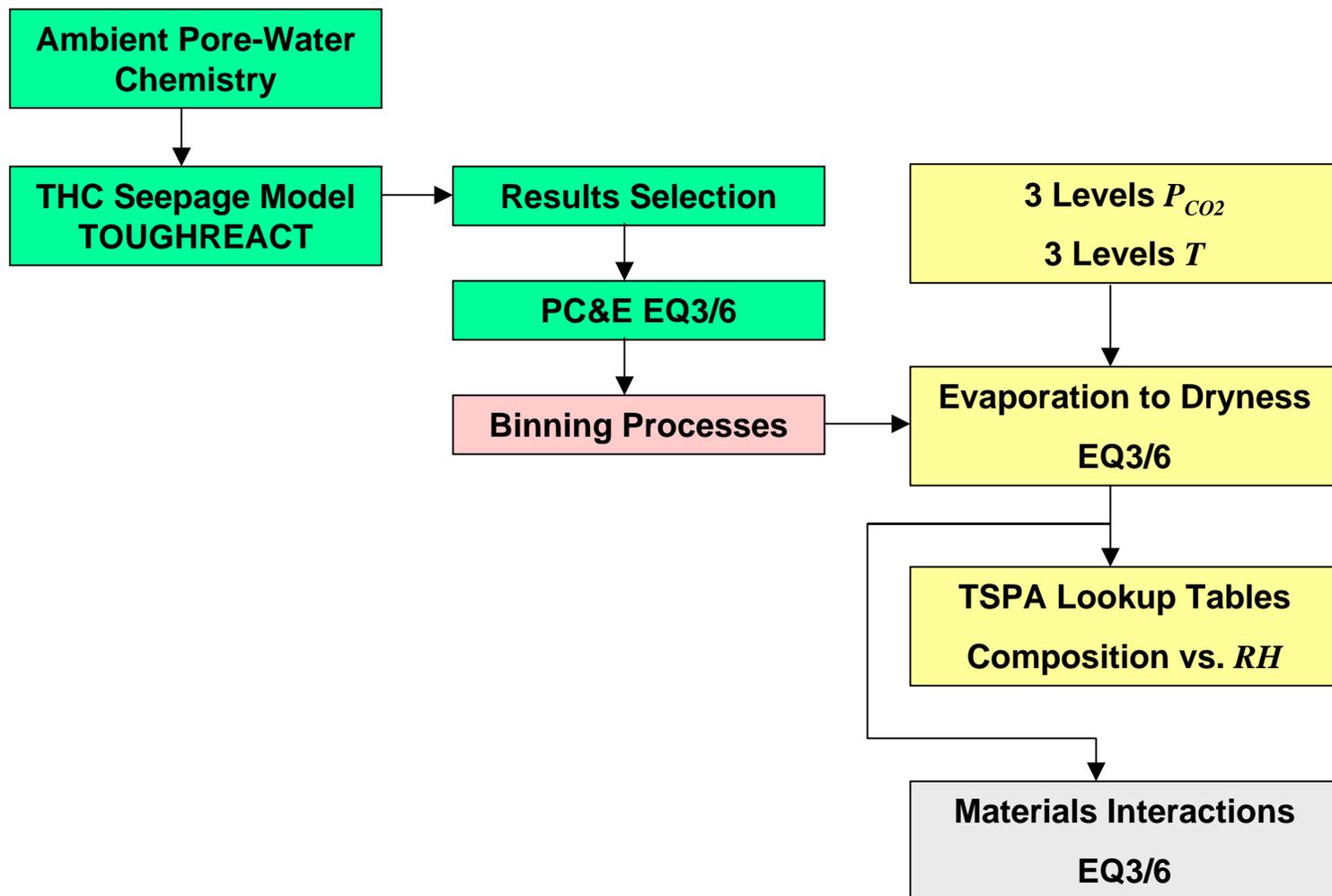
In-Drift Water Chemistry Model
Abstraction (Binning) Approach and Results

- **Reduce the number of calculated water compositions (from thousands produced by the THC model)**

- **Define 11 types of water compositions ("bins" with similar chemical characteristics) that can be evolved through many states in the abstraction model**

  - **Types of brines determined by the source location of the initial brine waters (i.e., crown and invert waters)**

- **Extract frequency of occurrence for each type of water**

- **The following two slides illustrate the binning process applied to two starting water chemistries**

Chemistry Evolution Derived from the Thermal-Hydrologic-Chemical Model (Water 0) Associated Abstraction Bins
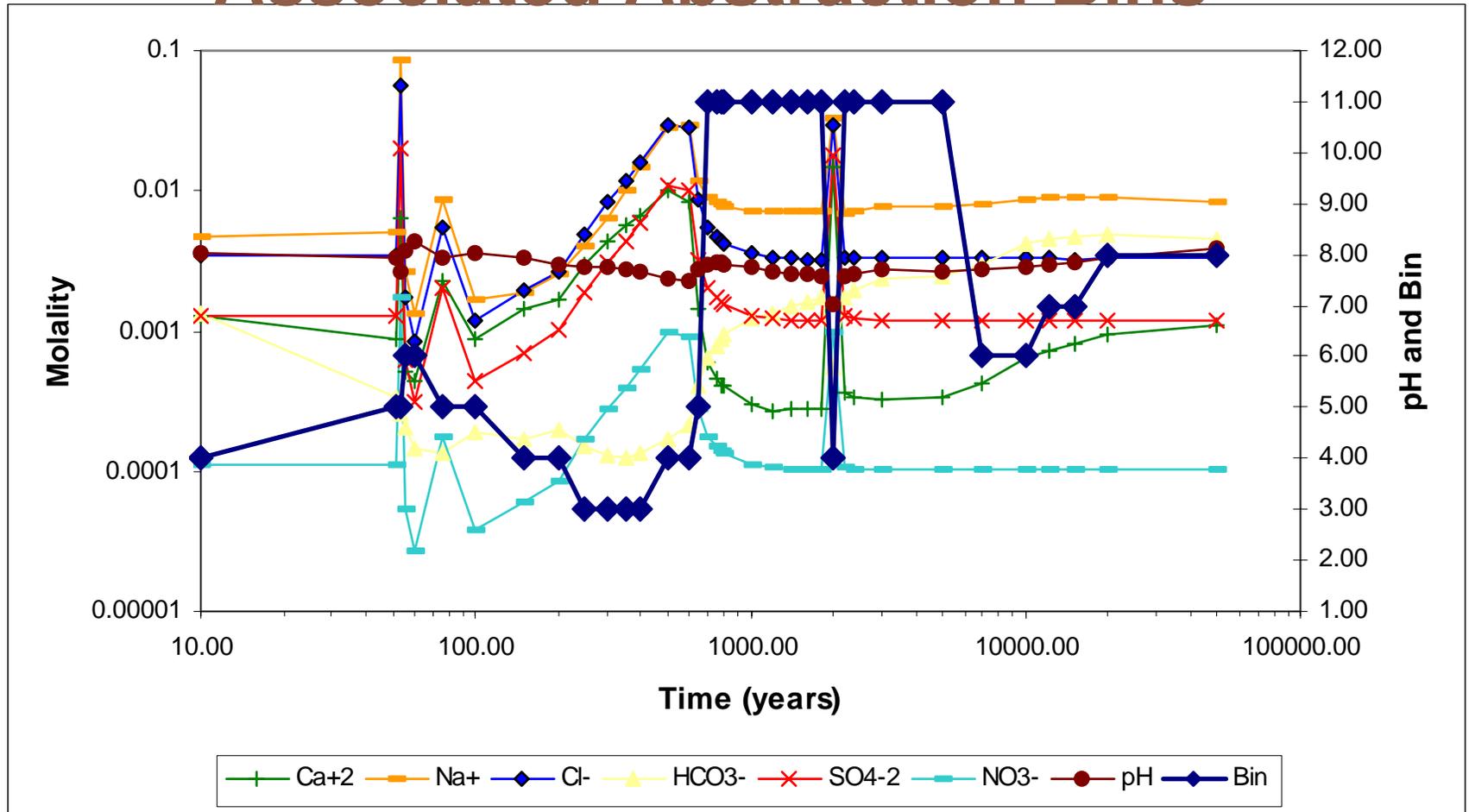
Chemistry Evolution Derived from the Thermal-Hydrologic-Chemical Model (Water 7) Associated Abstraction Bins
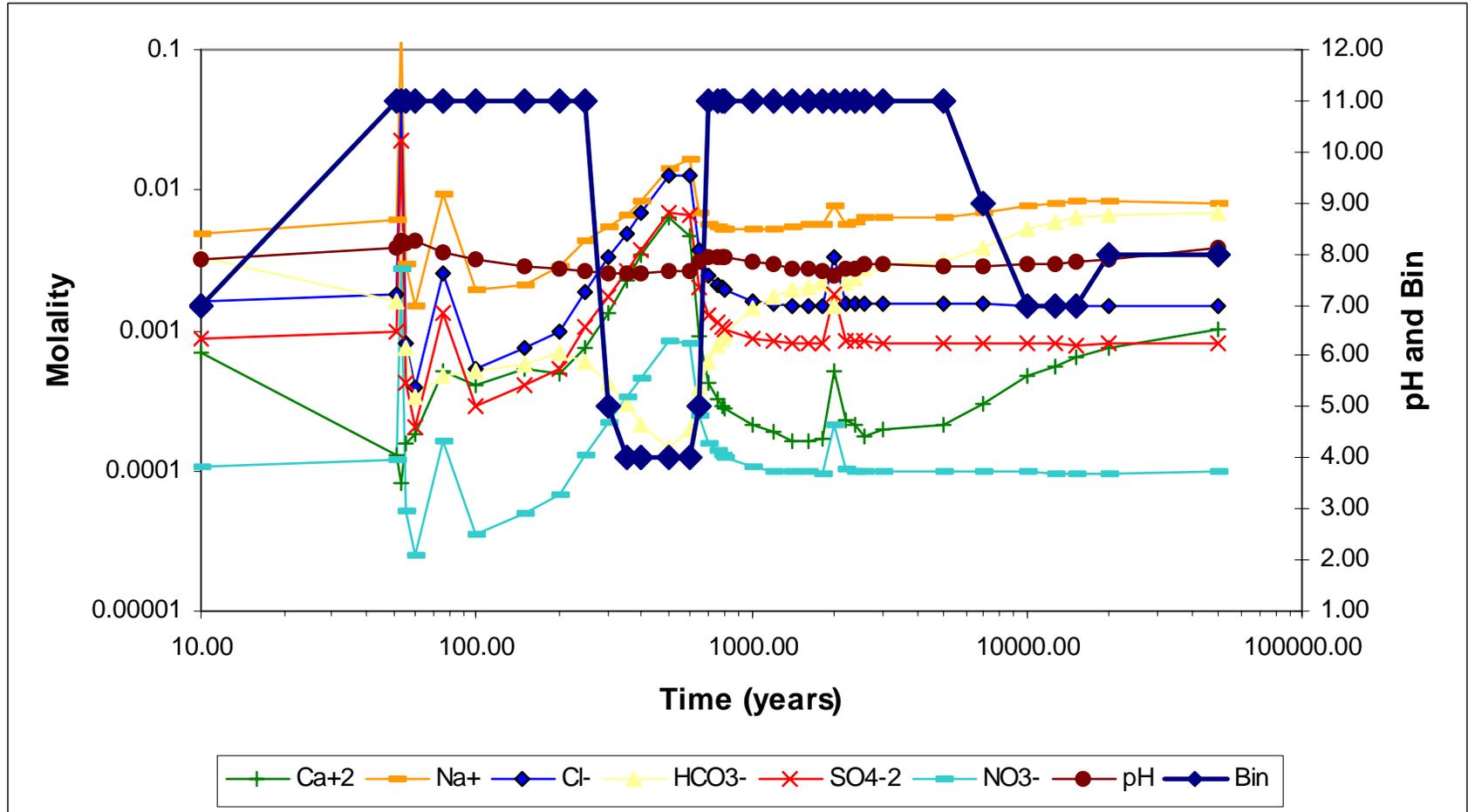
Crown Seepage Brine Evolution Path

Bin	Time-Integrated Relative Frequency for Crown Waters**	Average End Point RH	98% RH Bin	End Point Brine
1	0%	20%	Ca-Cl	Ca-Cl
2	0%	24%	Na-Cl	Ca-Cl
3	~1%	40%	Na-Cl	K-Ca-Cl-NO$_3$
4	~15%	50%	Na-Cl	Na-K-Cl-NO$_3$
5	~10%	60%	Na-Cl	Na-K-Cl
6	~1%	60%	Na-Cl	Na-K-Cl-NO$_3$
7	~1%	60%	Na-Cl	Na-K-Cl-NO$_3$
8	~1%	60%	Na-CO$_3$	Na-K-Cl
9	~20%	60%	Na-CO$_3$	Na-K-NO$_3$-Cl
10	~1%	60%	Na-CO$_3$	Na-K-CO$_3$-Cl
11	~50%	60%	Na-CO$_3$-Cl	Na-K-CO$_3$-Cl

* Highlighted Bins are the majority of waters that could potentially seep into the drift

** Crown waters are those waters in fractures above drift derived from the THC model

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Input and Output Water Compositions Host-Rock + In-Drift Water Chemistry Models

Legend:
- ● Input Pore Water Chemistries
- ● Solutions Used for Corrosion Testing
- ■ Output Binned-Water Chemistry
- ▲ Evaporative Concentrated Water Chemistry
- – – Boundary Between HCO$_3$ & SO$_4$ Brines
- – – Boundary Between SO$_4$ & CaCl$_2$ Brines

Ternary diagram axes: Ca^{+2}, SO$_4^{-2}$, HCO$_3^-$

Bin 1, Bin 2, Bin 3, Bin 4, Bin 5, Bin 6, Bin 11, Bin 7,8,9,10

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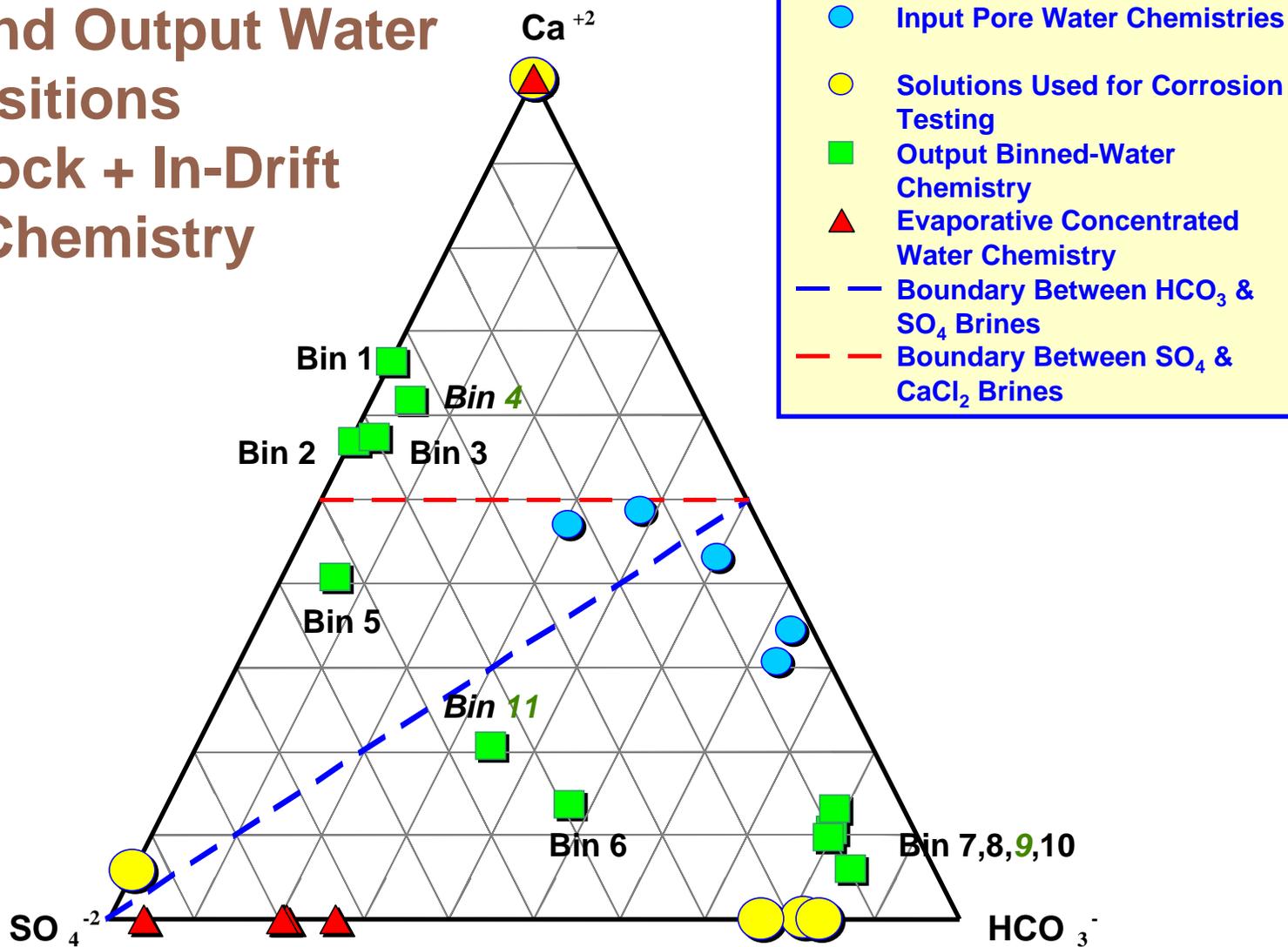
In-Drift Water Chemistry Model Model Validation Approach

- **The in-drift model developed for TSPA-LA is an enhancement of the Pitzer model used for Site Recommendation, with the capability to evaluate more concentrated solution conditions**

- **To demonstrate that the model predicts the concentrated solutions sufficiently, it has been validated against various laboratory data and published results. Examples of these follow**

Detailed model information can be found in: "In-Drift Precipitates/Salt Model," ANL-EBS-MD-000045 (to be issued this summer)

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Validation of Sierra Spring Water Evaporation to a Concentration Factor of 1000 Times

Garrels and Mackenzie in Stumm (1967)

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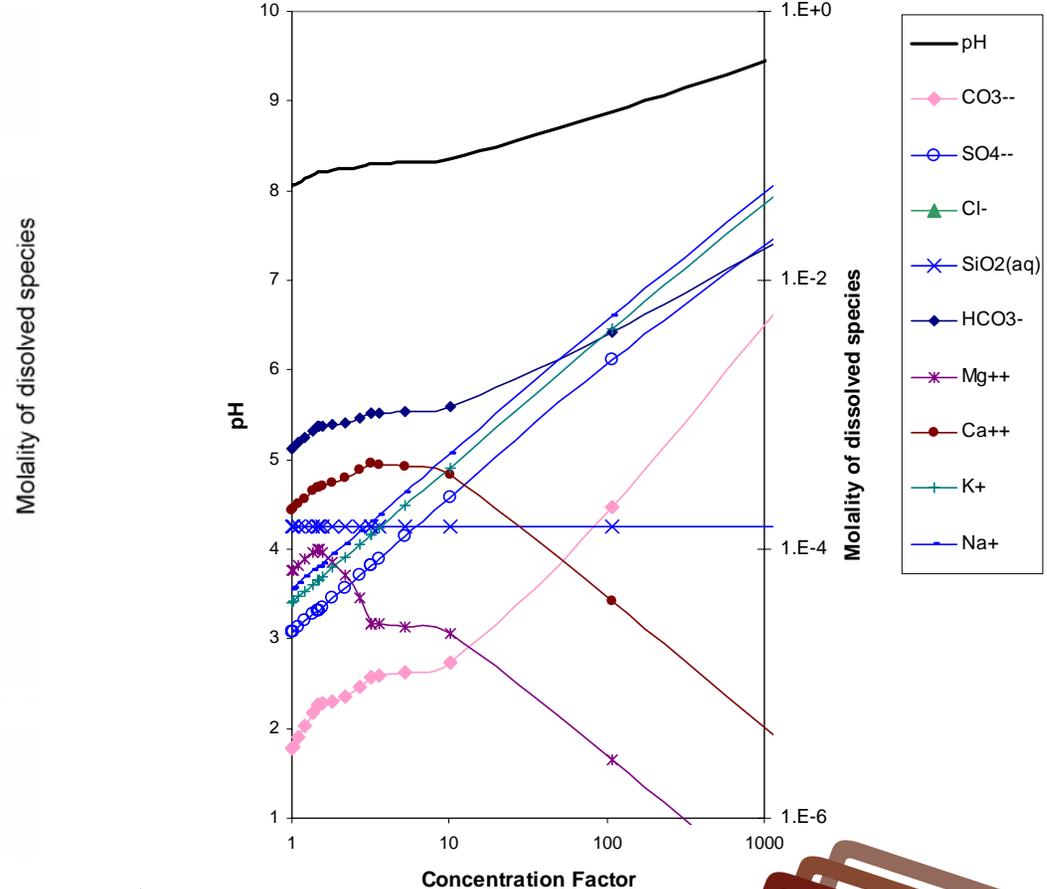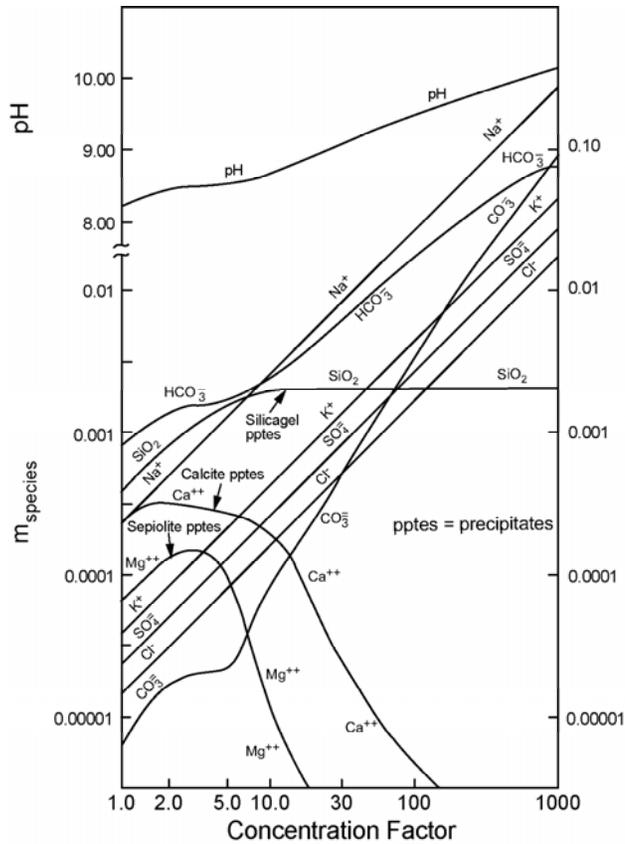
* Projected brine evolution agreement.

Predicted vs CRC* Handbook Mineral Solubility at 100°C
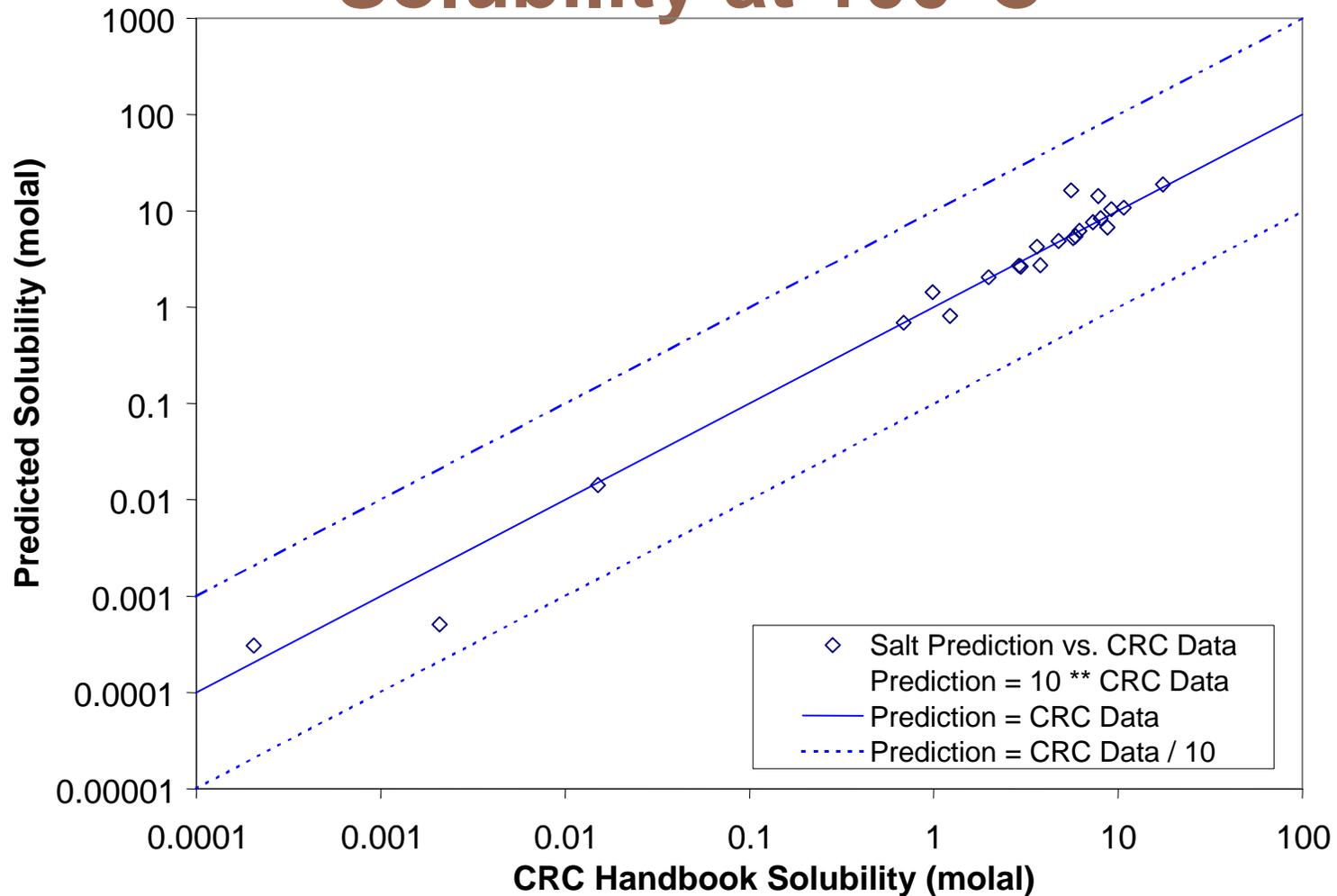
* Lide, D.R., ed. 2000. *CRC Handbook of Chemistry and Physics.*
  81st Edition. Boca Raton, Florida: CRC Press.
** Projected salt solubility agreement.

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Predicted vs. Measured Concentrations for Synthetic Topopah Spring Tuff Pore Water from Evaporation Experiments of Rosenberg et al.
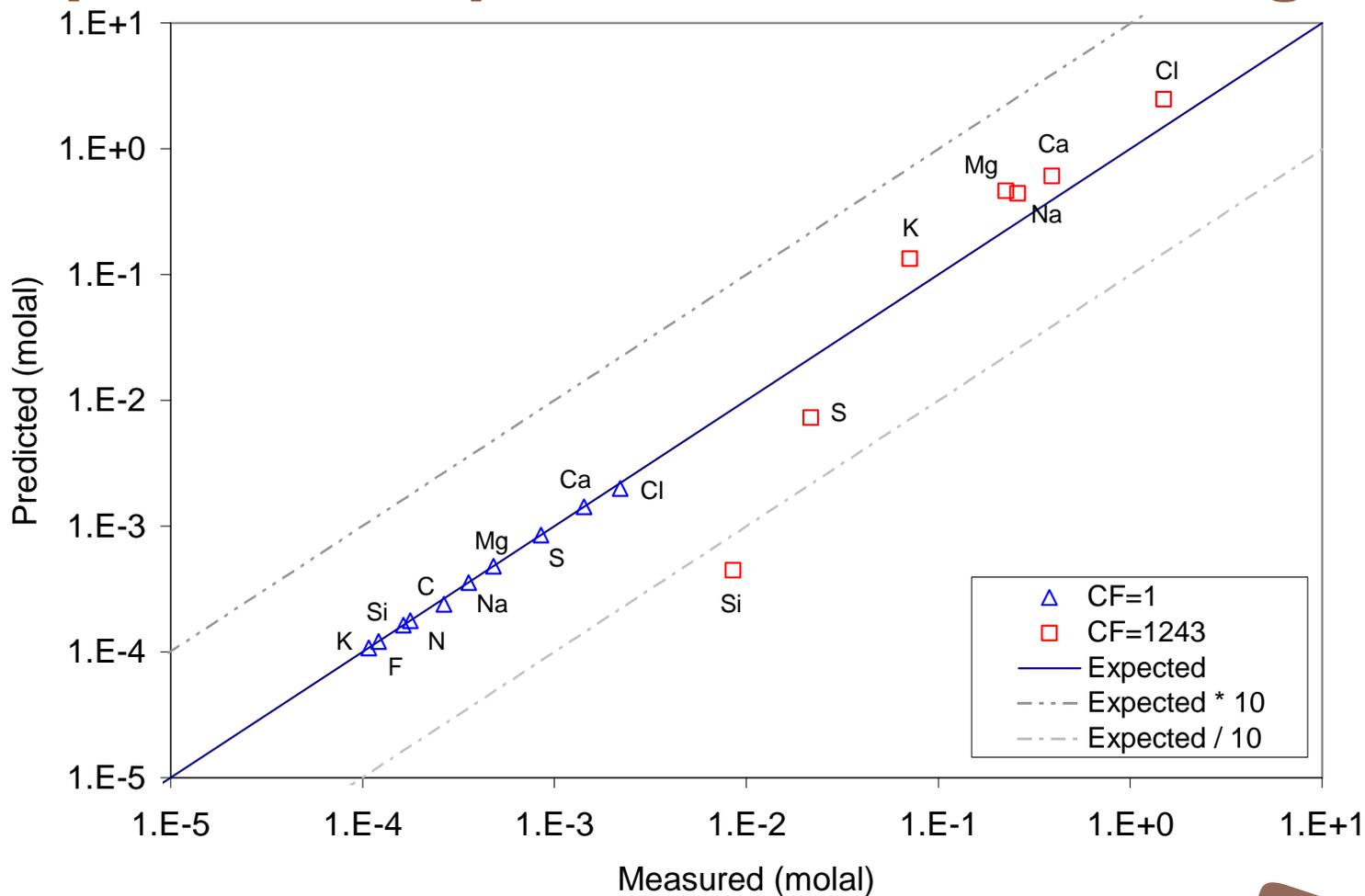
* Projected brine concentrations match experimental data.

Evaporative Concentration of Bin 4 Water Simulated with EQ3/6

Simulated Evaporation to Dryness – Deliquescence Point

YUCCA MOUNTAIN PROJECT
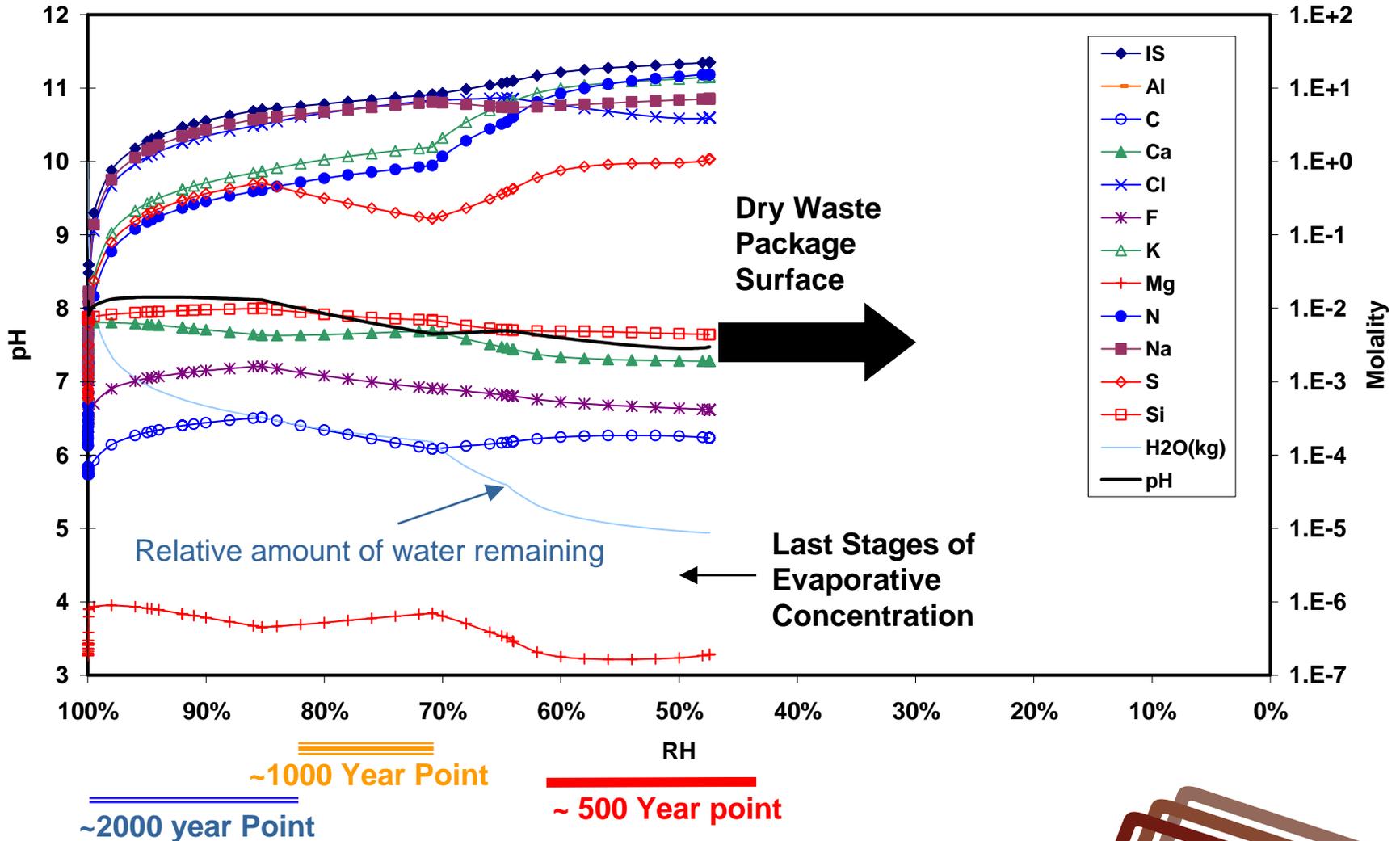
Evaporative Concentration of Bin 9 Water Simulated with EQ3/6

Simulated Evaporation to Dryness – Deliquescence Point
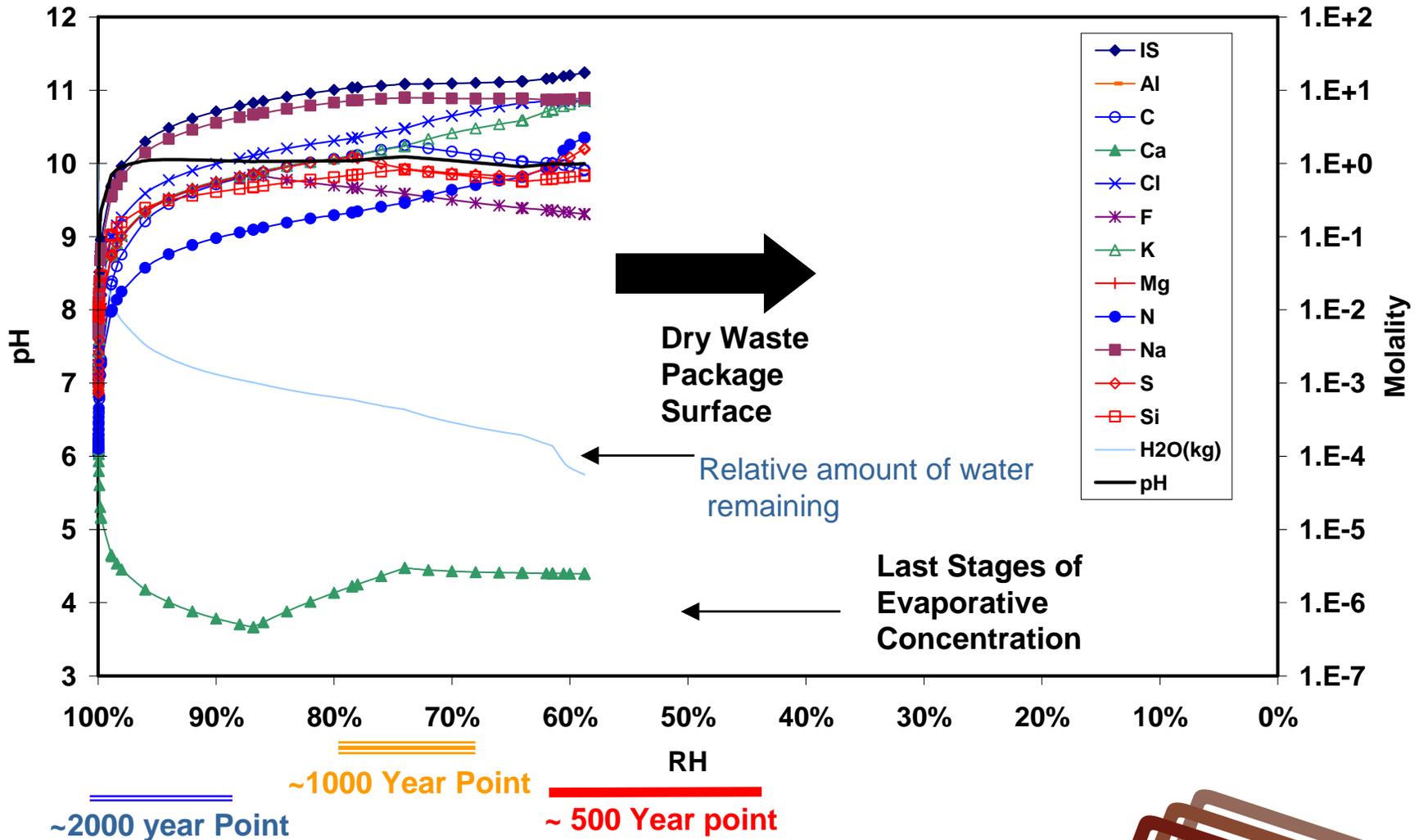
Evaporative Concentration of Bin 11 Water Simulated with EQ3/6

Simulated Evaporation to Dryness – Deliquescence Point
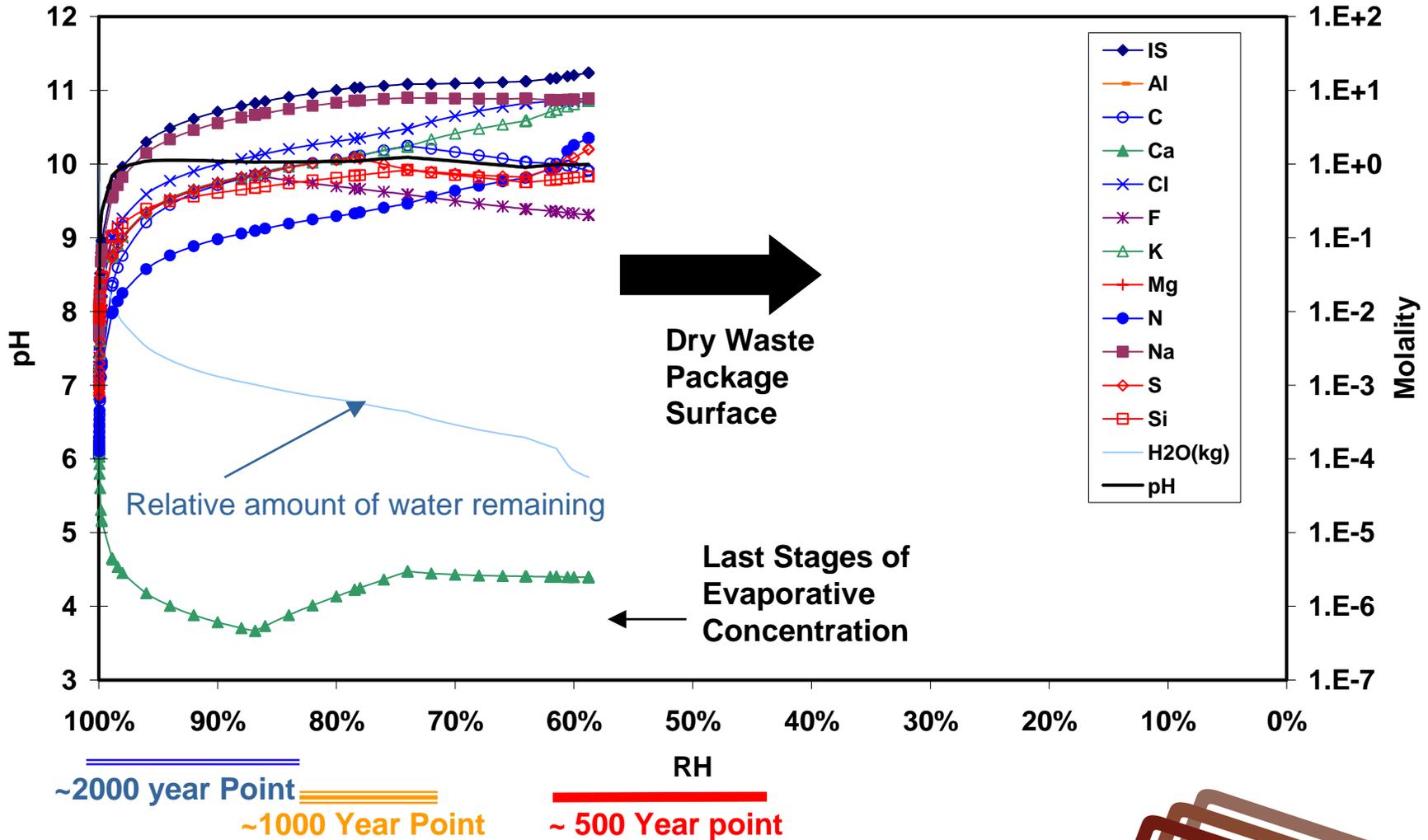
Evolution of Chloride to Nitrate Ratio for Crown Seepage Waters
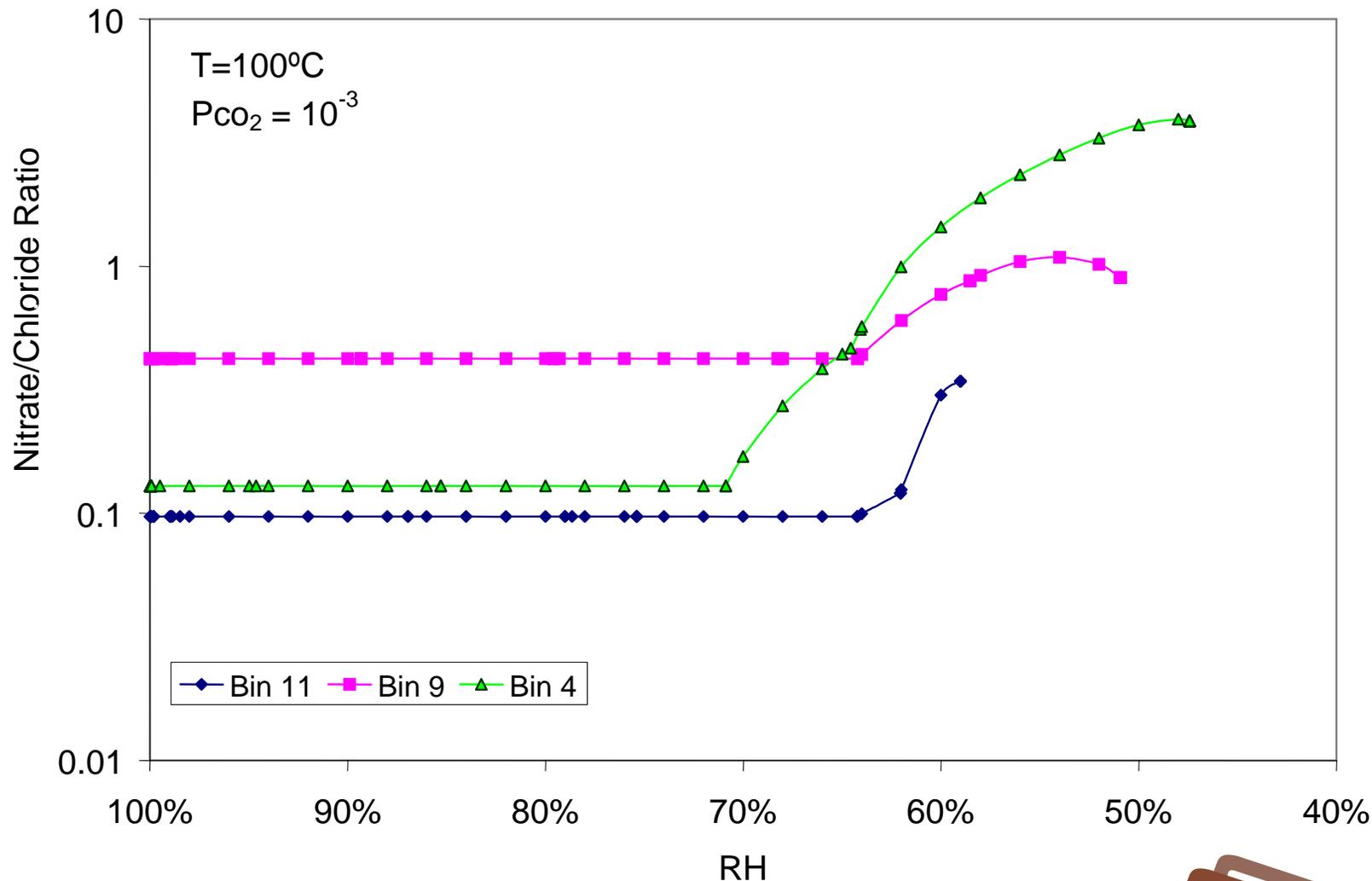
Water Chemistry Evolution of Bin 4, 9, & 11

Legend:
- Evolution of Bin 9 Brine (red square)
- Evolution of Bin 11 Brine (blue circle)
- Evolution of Bin 4 Brine (green triangle)
- Boundary Between HCO_3 & SO_4 Brines (blue dashed)
- Boundary Between SO_4 & $CaCl_2$ Brines (red dashed)

Ca^{+2}

Idealized Boundary Between SO_4 & $CaCl_2$ Regions

Curve is illustrative, due to 3-chemical ternary system

Most observed water chemistries will evolve to benign sulfate- or bicarbonate-type brines
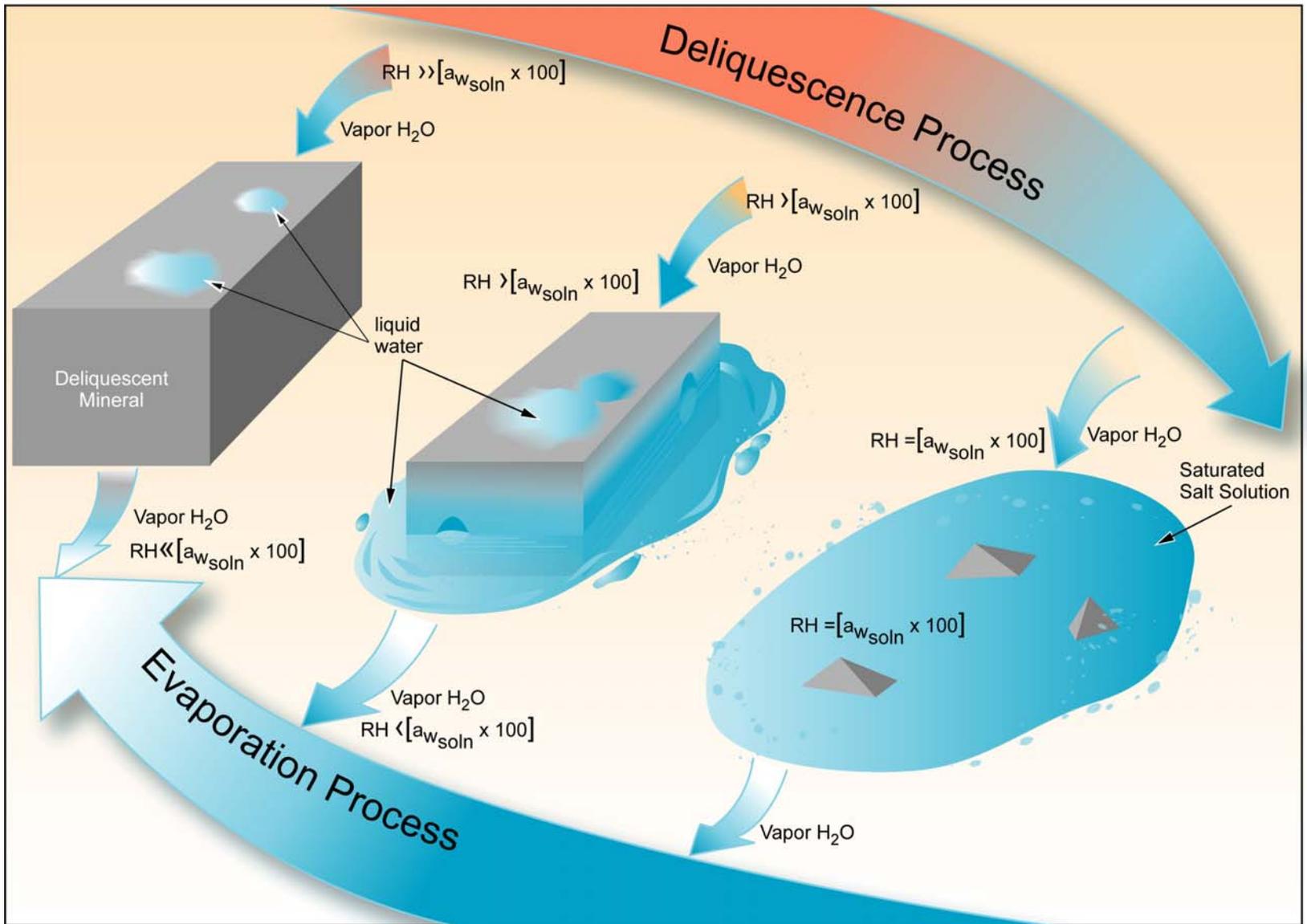
Starting Point

Starting Point

Starting Point

End Point

End Point

End Point

SO_4^{-2}

HCO_3^-
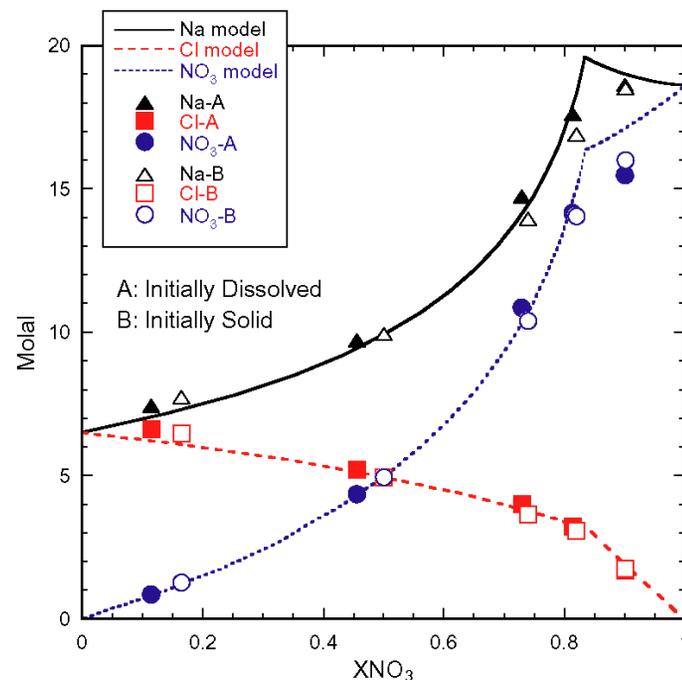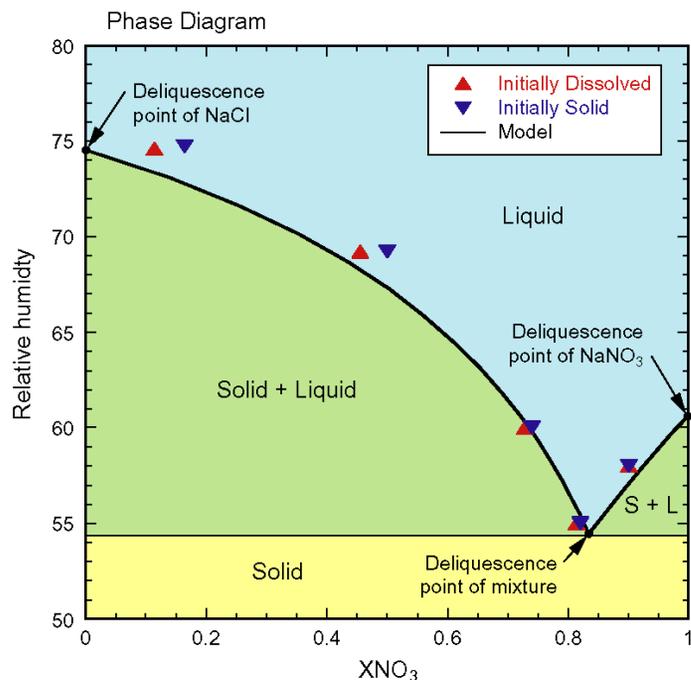
Results

The deliquescence point of salt mixtures will be lower than the deliquescence of pure salts. In a simple NaCl-NaNO$_3$ binary mixture we obtain very good agreement between our experimental results and calculations made with the Pitzer model for high ionic strength solutions. Data obtained for two-phase region; Model results from EQ 3/6 Thermodynamic Code.

Dust Deliquescence

- **In the absence of liquid water, dust deposited on the waste package surface can deliquesce**

- **Dust compositions have been measured by the U.S. Geological Survey; 55 samples were taken and evaluated**

- **The dust compositions have binned into four likely categories with respect to their deliquescence behavior**

- **Geochemical modeling of the deliquescent RH values has been performed using EQ3-6**

Dust Deliquescence Results

Legend:
- NaCl-NaNO3-KNO3
- NaCl-KNO3
- Ca(NO3)2-NaCl-NaNO3-KNO3
- K2CO3-KNO3-KCl-CO2

X-axis: Temperature °C
Y-axis: RH %
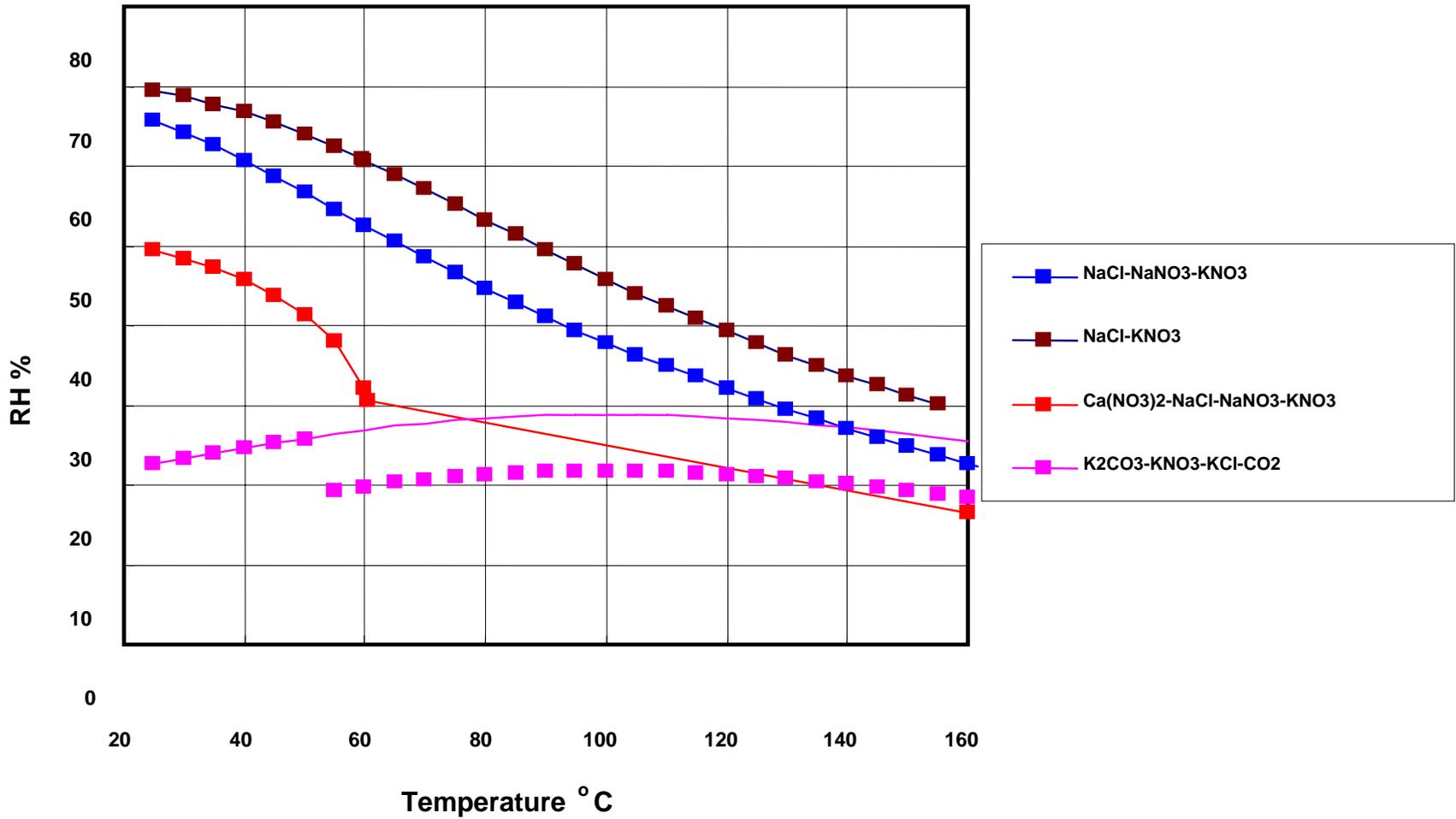
Dryout Region
Deliquescence Brines – Testing Program

- **Objective of Studies**

  - **Characterize aqueous films that may form on the waste package (WP) surface due to deliquescence**

  - **Detect and measure associated modes of corrosion**

- **Test Conditions**

  - **Fixed relative humidity (RH) and temperature (T)**

  - **Applied deposits of $CaCl_2$ and $CaNO_3$ salts**

- **Measurements**

  - **In situ measurement of weight change of samples with custom environmental thermogravimetric analyzer (thermogravimetric analysis)**

  - **Surface analysis of specimens after exposure**

Dryout Region: Deliquescence Brines Studied with Thermogravimetric Analysis
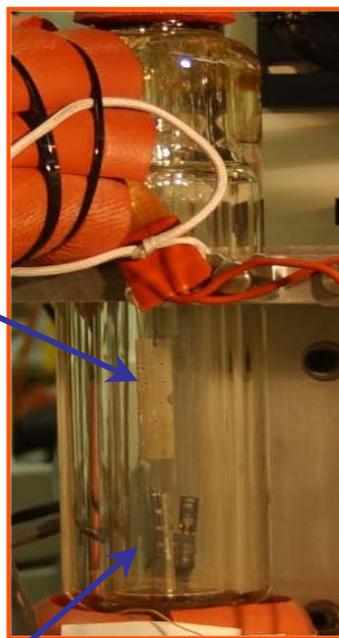
Alloy 22 or 825 Sample

Temperature and RH Sensors
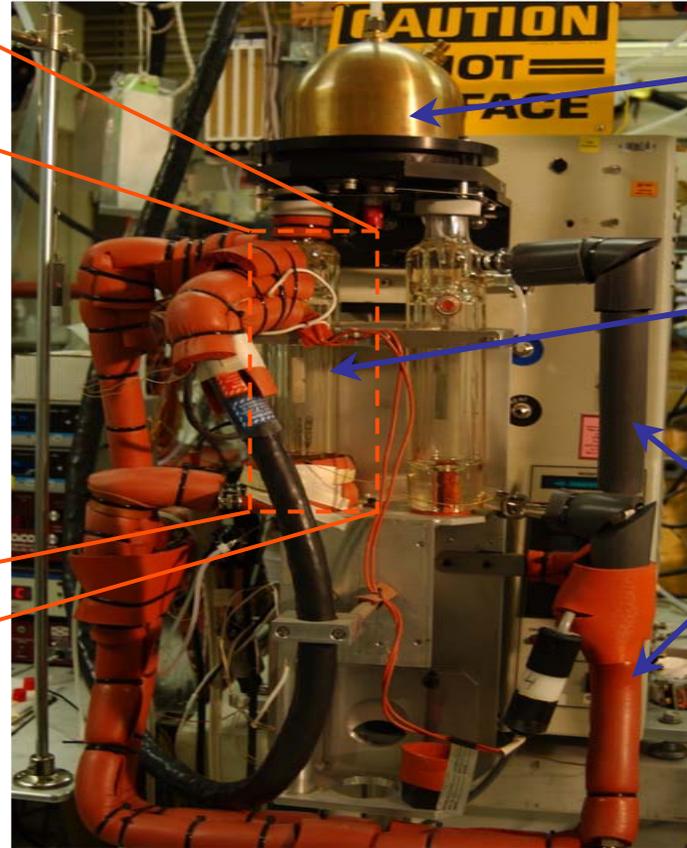
Micro Balance Housing

Sample Chamber

Heating Fluid Lines

- **Sensitive to weight changes as small as "tens of micrograms"**

- **Operation at temperatures up to 150°C**

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Dryout Region:
Deliquescence Brines – Deposit Formation
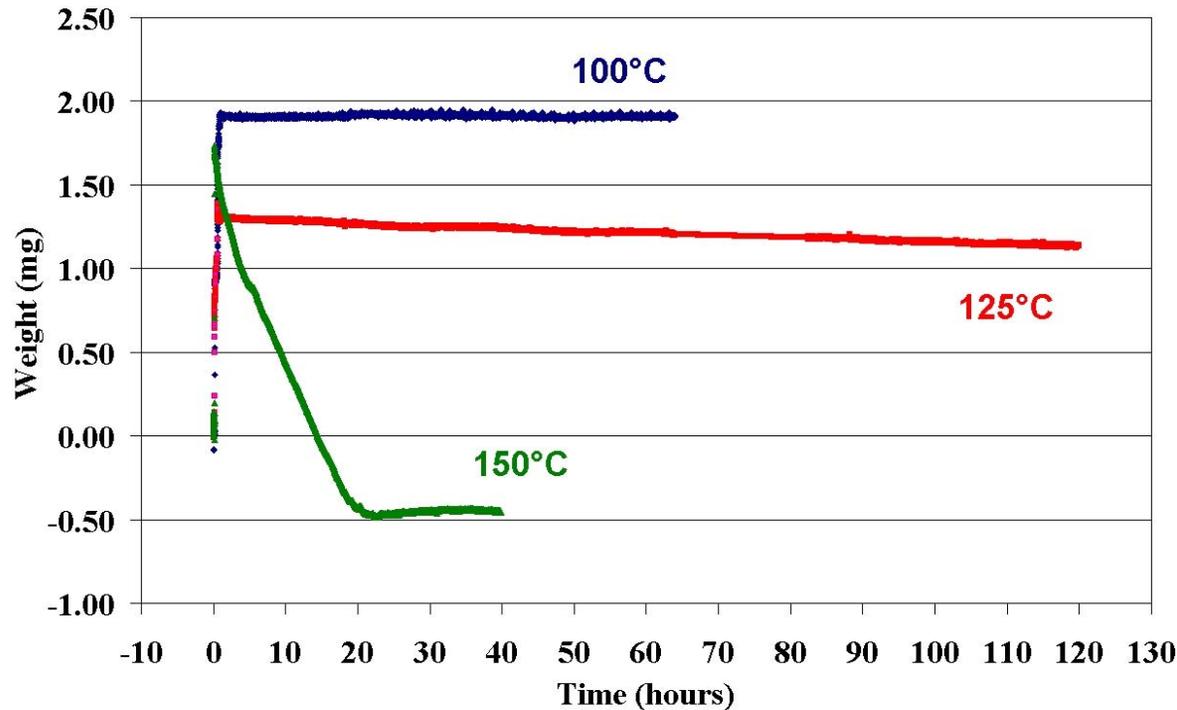
Alloy 22
22.5% RH
CaCl$_2$ initially deposited

- **100°C: CaCl$_2$ aqueous films are stable for duration for test**

- **125°C: solution evolves slowly, forming insoluble precipitates**

- **150°C: solution evolves rapidly, forming insoluble precipitates and acid gas**

- **No detectable Alloy 22 degradation (weeks)**

- **Precipitates from 150°C and 125°C tests are similar**

- **Solution properties analyzed in order to understand evolution**

Dryout Region:Deliquescence Brines – Deposit Formation
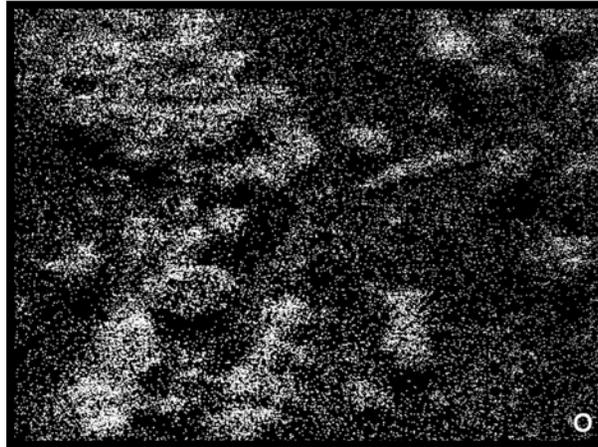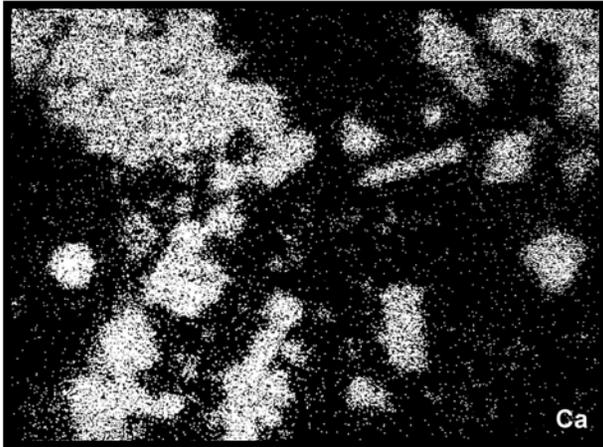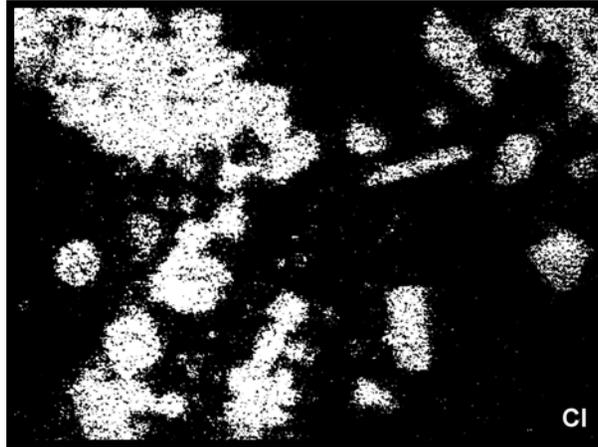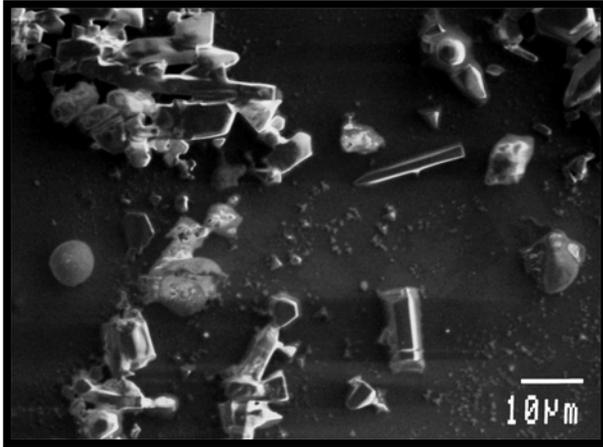
- **Electron dispersive spectroscopy (EDS) analysis indicates precipitates contain Ca, Cl, and O**

- **EDS and wet-chemical analyses indicate a loss of Cl relative to Ca (HCl volatilization)**

- **Raman spectroscopy indicates that precipitates are not $Ca(OH)_2$ or $CaCO_3$**

- **Precipitates are possibly a CaOHCl**

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Dust Leachate Brine Evolution

- **Chemical evolution on the waste package surface could be affected by condensate water mixing with dust deposits**

  - **These solutions could subsequently be evaporated into a brine**

  - **These brine compositions are a function of the starting dust composition and the degree of evaporation**

  - **The USGS has analyzed 55 potential dust leachate compositions for major cations and anions**

  - **These potential initial compositions have been numerically evaporated using EQ6**

  - **These evaporated brines have been categorized using similar chemical characteristics into six bins**

  - **The evaporated dust leachate brines are generally carbonate or nitrate-type brines**

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Dust Leachate Brine Composition Evolution

Bin	% of 55 Binning Output Runs	EndPoint RH	98% RH Brine	85% RH Brine	65% RH Brine	EndPoint Brine
1	5%	32%	Na-N	Na-N	Na-N	Ca-N
2	7%	46%	Na-K-N	Na-K-N-Cl	K-Na-N-Cl	K-N
3	16%	63%	Na-K-S-Cl-N	Na-K-S-Cl-N	K-Na-Cl-N	K-Na-Cl-N
4	7%	37%	K-Na-C	K-Na-C	K-Na-C	K-N-C
5	22%	47%	Na-N-Cl	Na-N	Na-N	K-Na-N
6	42%	61%	Na-K-S	Na-K-N-Cl	K-Na-N-Cl	K-Na-N-Cl

N = Total nitrogen in the system

C = Total inorganic Carbon in the system

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Committed Drift Materials

- The majority of the materials that are committed to the drift are metals (primarily iron, nickel, and titanium alloys)

- The major materials that could effect the chemical environment are Fe, Ni, Ti, Cr, Mo, Mn, Al, and Cu

- From the evaluations performed to date, it is not anticipated that these materials will affect the in-drift chemical environment, because the reactions form oxides and oxyhydroxides (the materials rust). The net reaction is that there will be some trace quantities of these elements in the water, but the waters are not anticipated to change ionic strength significantly

- Given that the drift environment is an open system, there will be sufficient oxygen to oxidize the committed materials

- Other trace elements that have been evaluated are fluoride and bromide. Given the chemical availability of N and Cl, these two elements do not concentrate to sufficient quantities to affect the in-drift environment

Gas Phase Migration at Yucca Mountain

- **Observations in the Cross Drift and behind closed bulkheads indicate the Topopah Spring tuff is pneumatically a well connected system**

  - Radon observations with and without ventilation

  - Barometric pressure observations

- **Pneumatic permeability tests indicate the fracture network is well connected**

- **The in situ observations are consistent with the unsaturated zone flow model**

- **Thermal testing and modeling assuming closed drift segments indicate that the gas phase can advect due to thermal gradients**

Radon and Barometric Observations
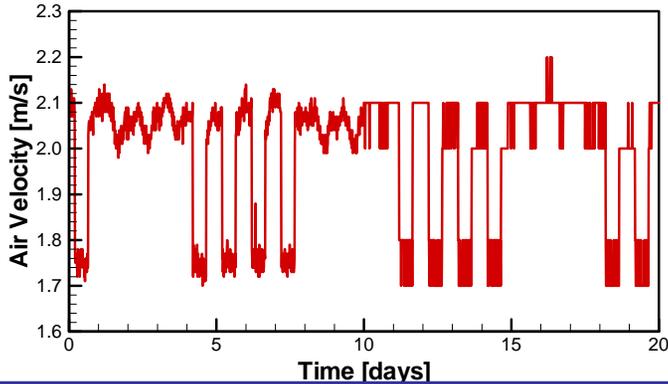
- **Air Flow in Drifts**

  - **All drilled boreholes exhibit intra-borehole gas flow**

  - **Air velocity sensors placed behind Exploratory Studies Facility (ESF) Alcove 7 bulkhead**

  - **Barometric pumping induces air flow (and radon) between rock mass and drifts**

    - **Gas flow and transport model accurately reproduces and predicts radon concentrations along ESF**
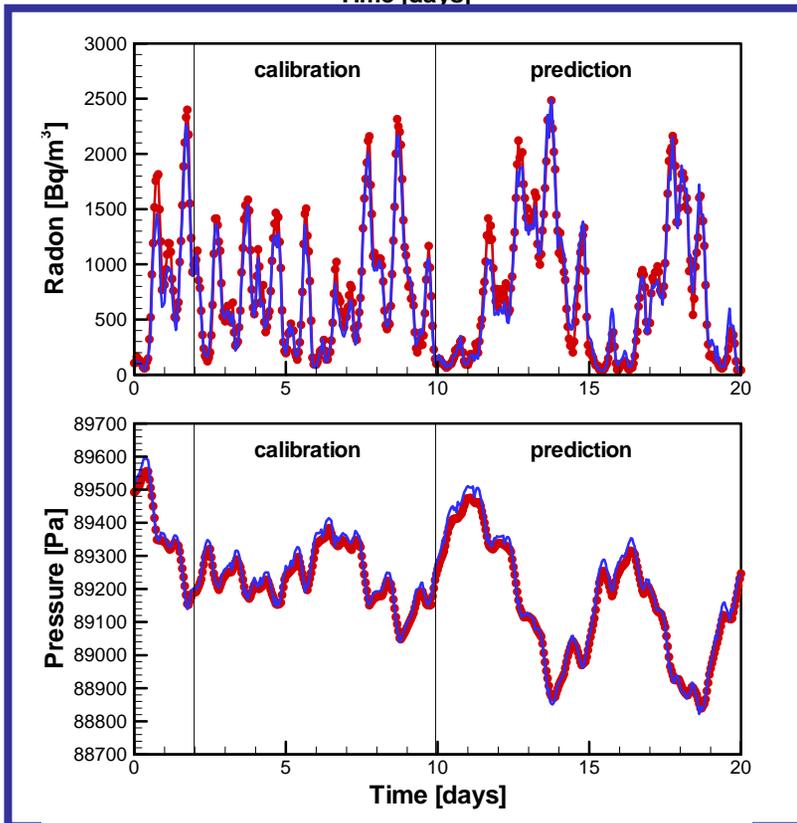
Evaluation of Mass and Heat Transfer in Drift

- **Model:**

  - **Model developed to analyze convection, conduction, and radiation - heat and mass transfer in the drift**

  - **Computational Fluid Dynamics (CFD) approach using FLUENT**

  - **3-Dimensional turbulent flow model inside of drift**

  - **14 waste package drift segment modeled over 70 meters**

  - **Conduction, natural convection, thermal radiation - heat transfer**

- **Results:**

  - **Axial transport expected to be 3-4 orders of magnitude higher than molecular diffusion**

  - **Peak velocity along drift is ~ 0.3 m/s**

  - **Significant mixing expected along drift**

- **Movie demonstrates model**

In-Drift Air Movement

Movie Clip

YUCCA MOUNTAIN PROJECT

Explanation of System Evolution (Three Regions) Dry Out Region

- **The rock above the drift will be dry (T > boiling), and there is little possibility that seepage will enter the emplacement drifts**

- **Waste package and drip shield surfaces are expected to be dry**

- **Due to the thermal environment and in-drift thermal convection processes, convection is turbulent, and an "open" environment is expected at the waste package surface**

- **Development and concentrated distillation of inorganic acids is very unlikely**

- **Deliquescence on the waste package surface is not expected to produce localized corrosion**

- **The in-drift chemical environment is expected to be benign**

Explanation of System Evolution (Three Regions) Transition Region

- **The rock above the drift cools through boiling, moisture returns, and seepage may enter the emplacement drifts if local hydrologic conditions permit (flux, fracture characteristics)**

- **Seepage diversion behavior reverts to the ambient (pre- and post-boiling) model. Seepage is likely to be much less than the percolation flux in the rock above the drifts**

- **Relative humidity increases and begins to approach 100 percent at the drift wall**

- **Thermal convection is still turbulent, and an "open" environment is expected at the waste package surface**

- **Development and concentrated distillation of inorganic acids is very unlikely**

- **Deliquescence on the waste package surface is not expected to produce localized corrosion**

- **The in-drift chemical environment is expected to be benign**

Explanation of System Evolution (Three Regions) Low-Temperature Region

- The rock temperature at the drift crown has cooled well below boiling. Moisture will have returned to the rock matrix and fractures, and seepage may enter the emplacement drifts if local hydrologic conditions permit (flux, fracture characteristics)

- Seepage diversion behavior reverts to the ambient model. Seepage is likely to be much less than the percolation flux in the rock above the drifts

- Relative humidity approaches 100 percent at the drift wall

- Thermal convection is still turbulent, and an "open" environment is expected at the waste package surface. Thus, concentrate distillation of inorganic acids remains very unlikely

- The in-drift chemical environment is expected to be benign

Backup

YUCCA MOUNTAIN PROJECT

Bin 4 Mineral Evolution T=100°C, $Pco_2 = 10^{-4}$
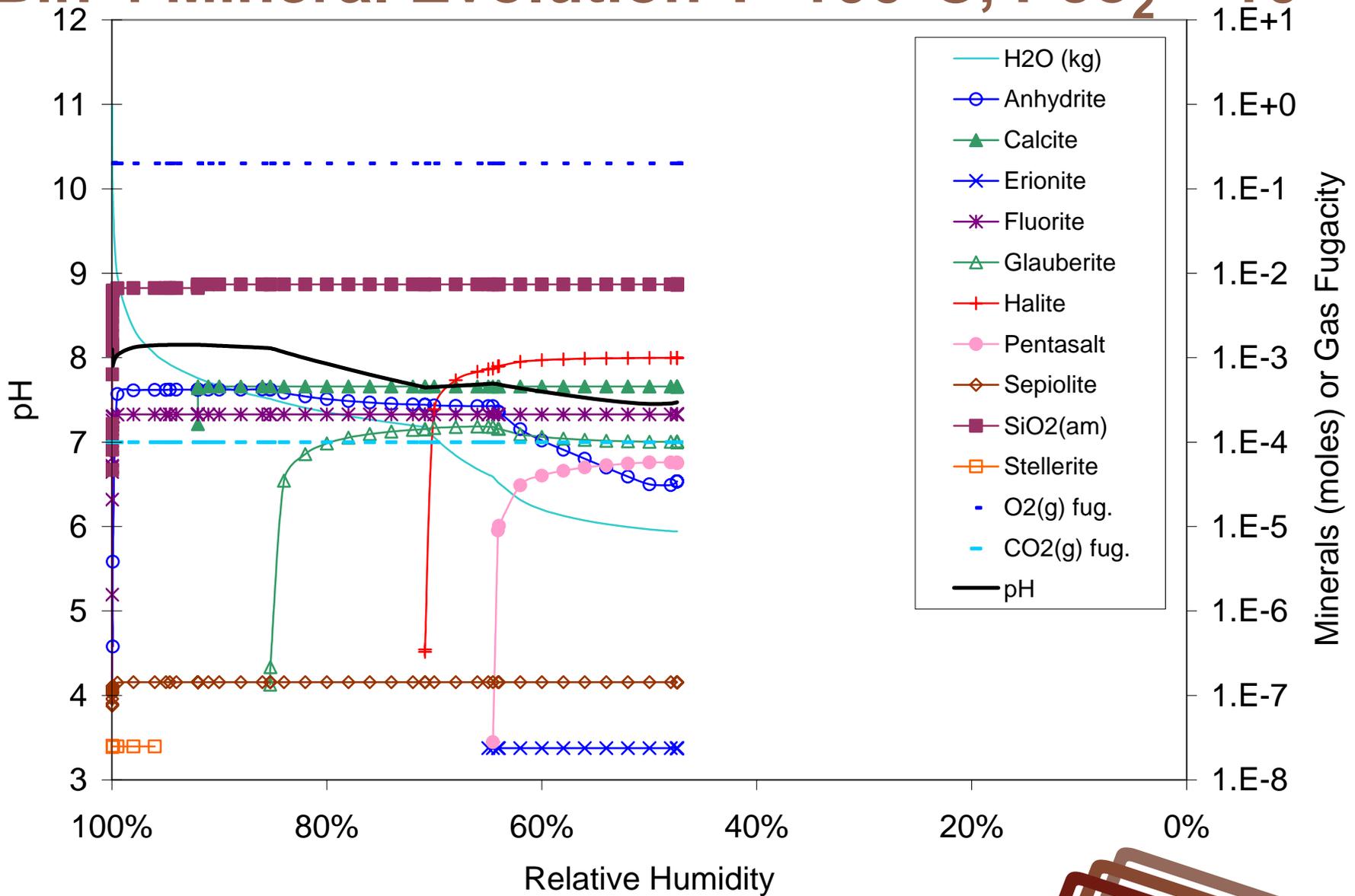
Thermal-Hydrological-Chemical Model Pco$_2$ Output Through Time for all 5 Starting Waters
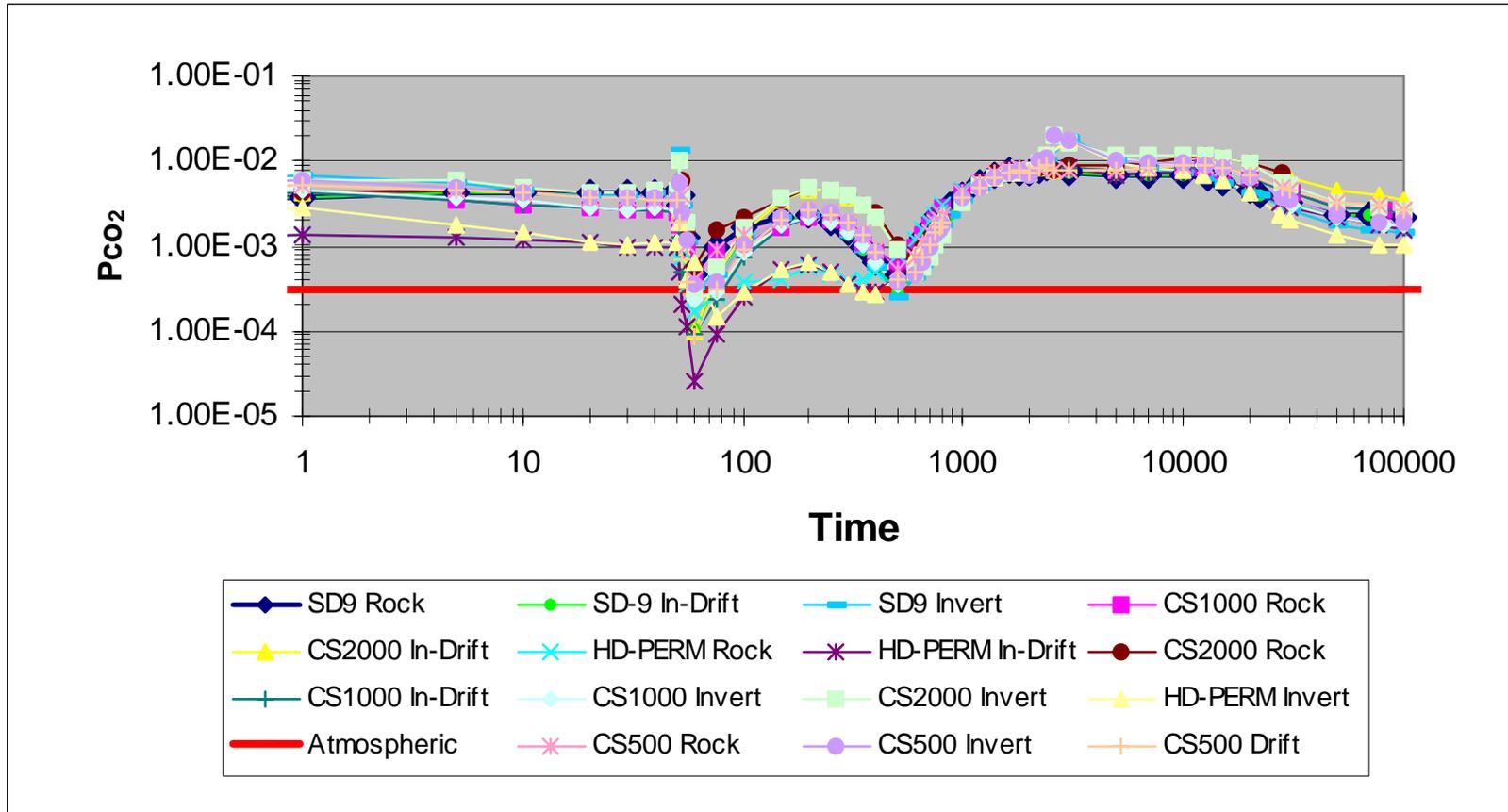
Solution Composition for a Mineral Assemblage is a Function of Temperature and Relative Humidity
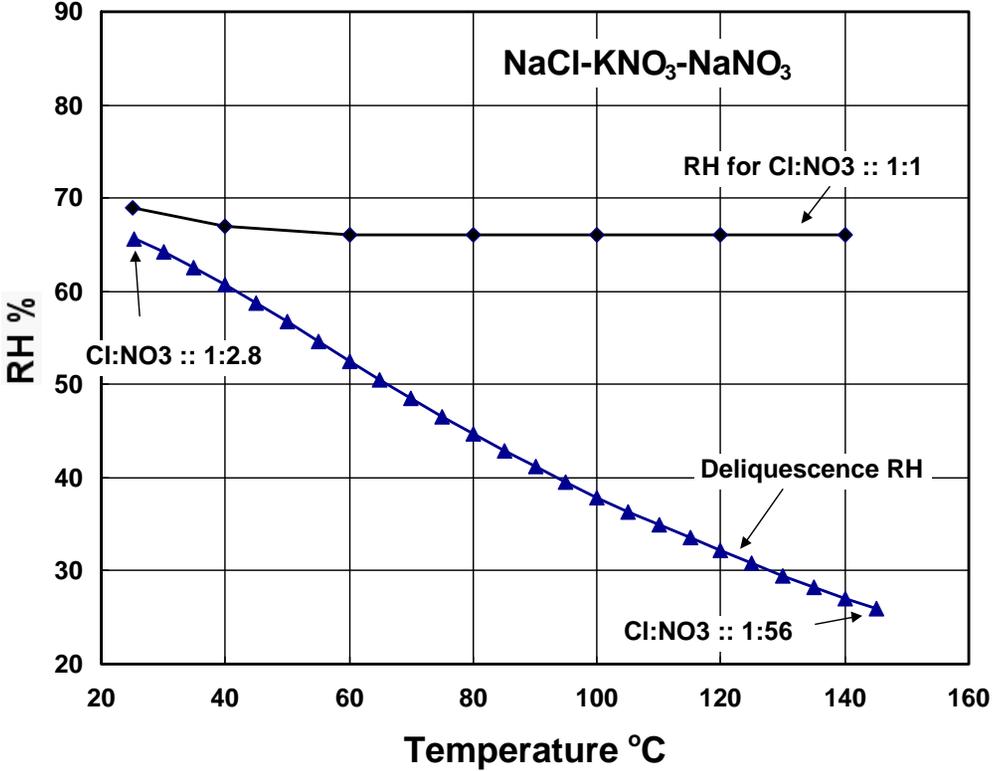
At the deliquescence point (deliquescence relative humidity) for the NaCl-NaNO$_3$-KNO$_3$ mineral assembly the nitrate content greatly exceeds the chloride content. Only at higher RHs does the chloride content become comparable.

Concentration of representative Yucca Mountain pore water
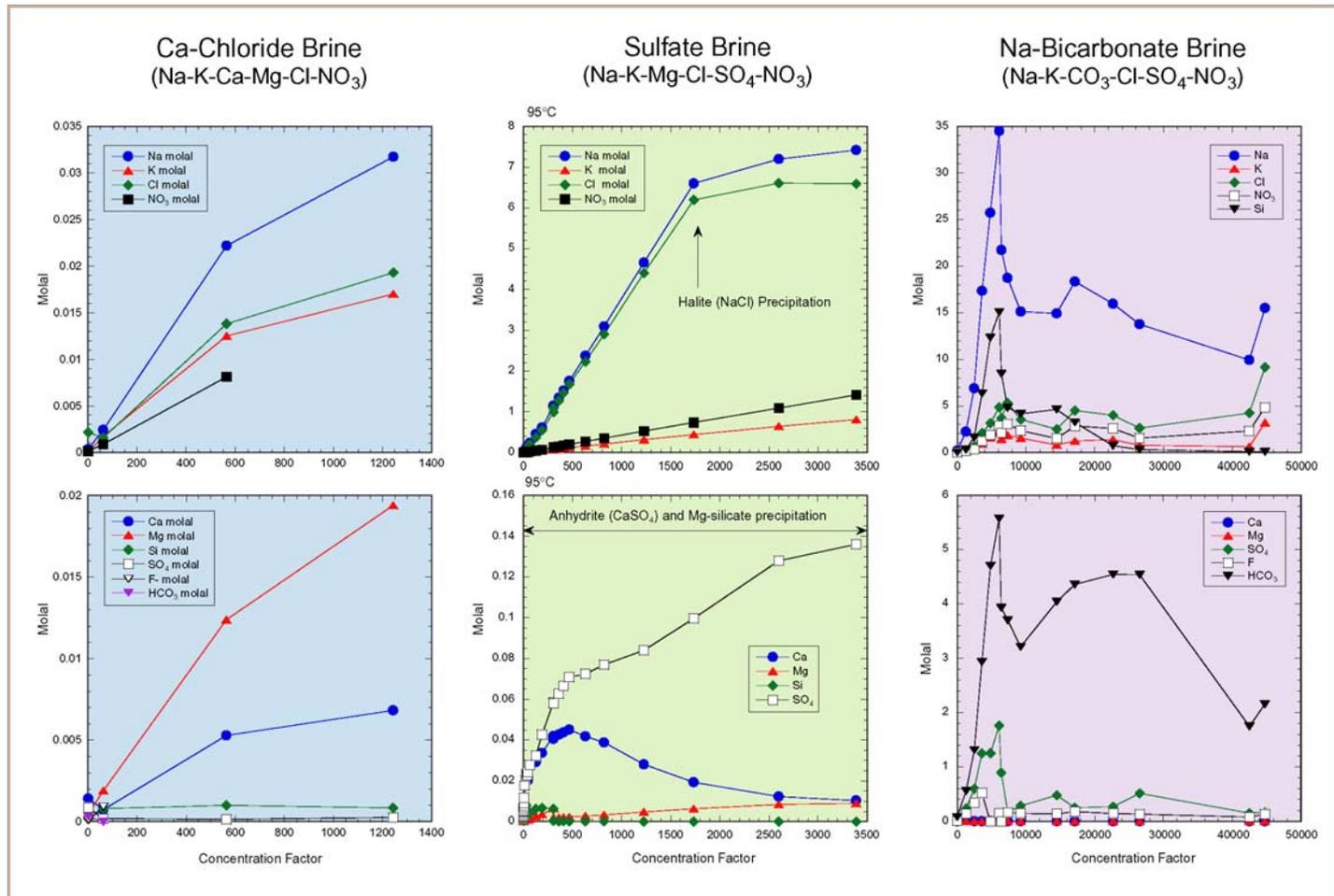
Evaporation Experiments and Corrosion Test Waters Represent Concentrated Yucca Mountain Pore Water
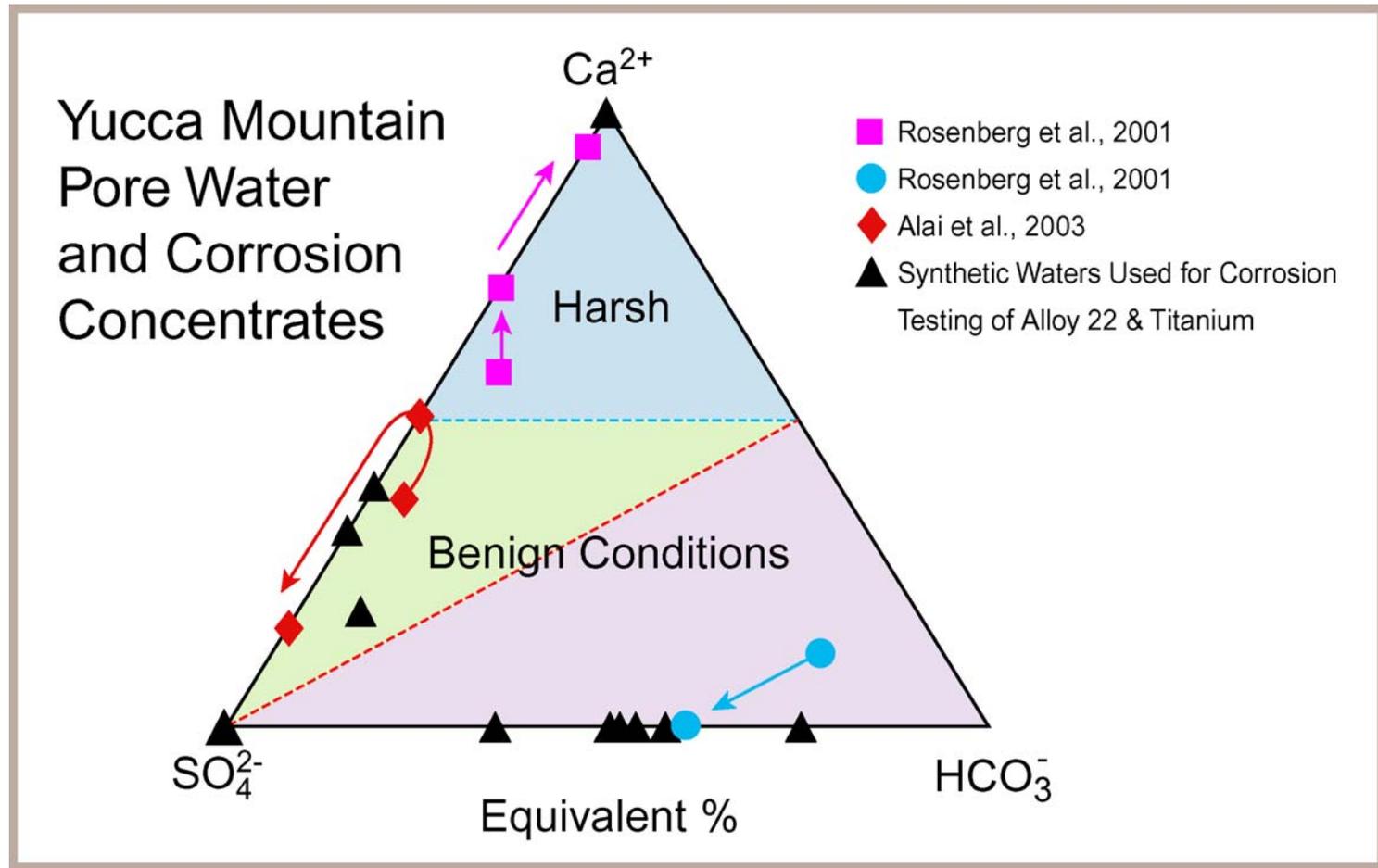
LDSRtAng.evo   Frame 45
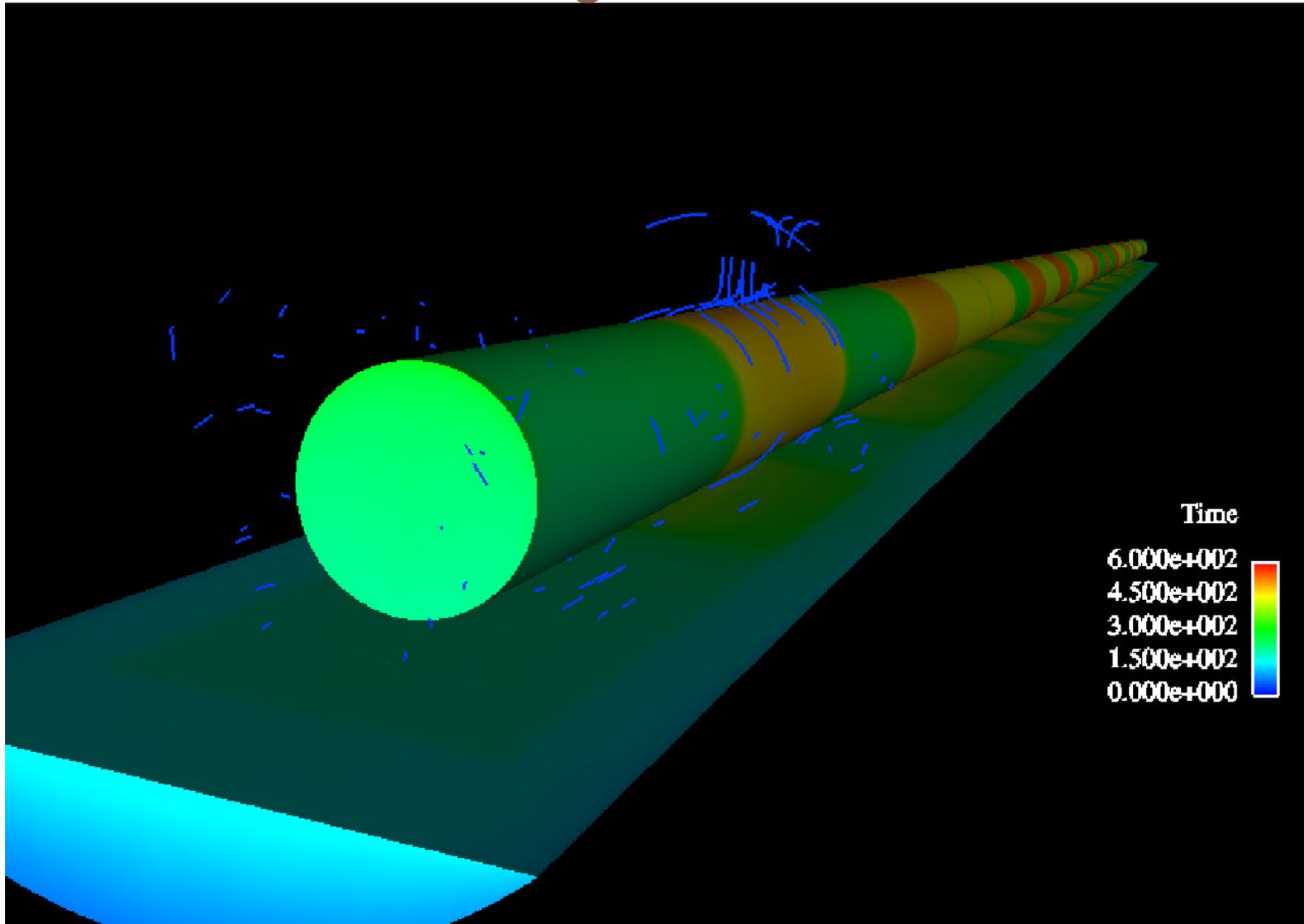
LDSRtAng.evo   Frame 100
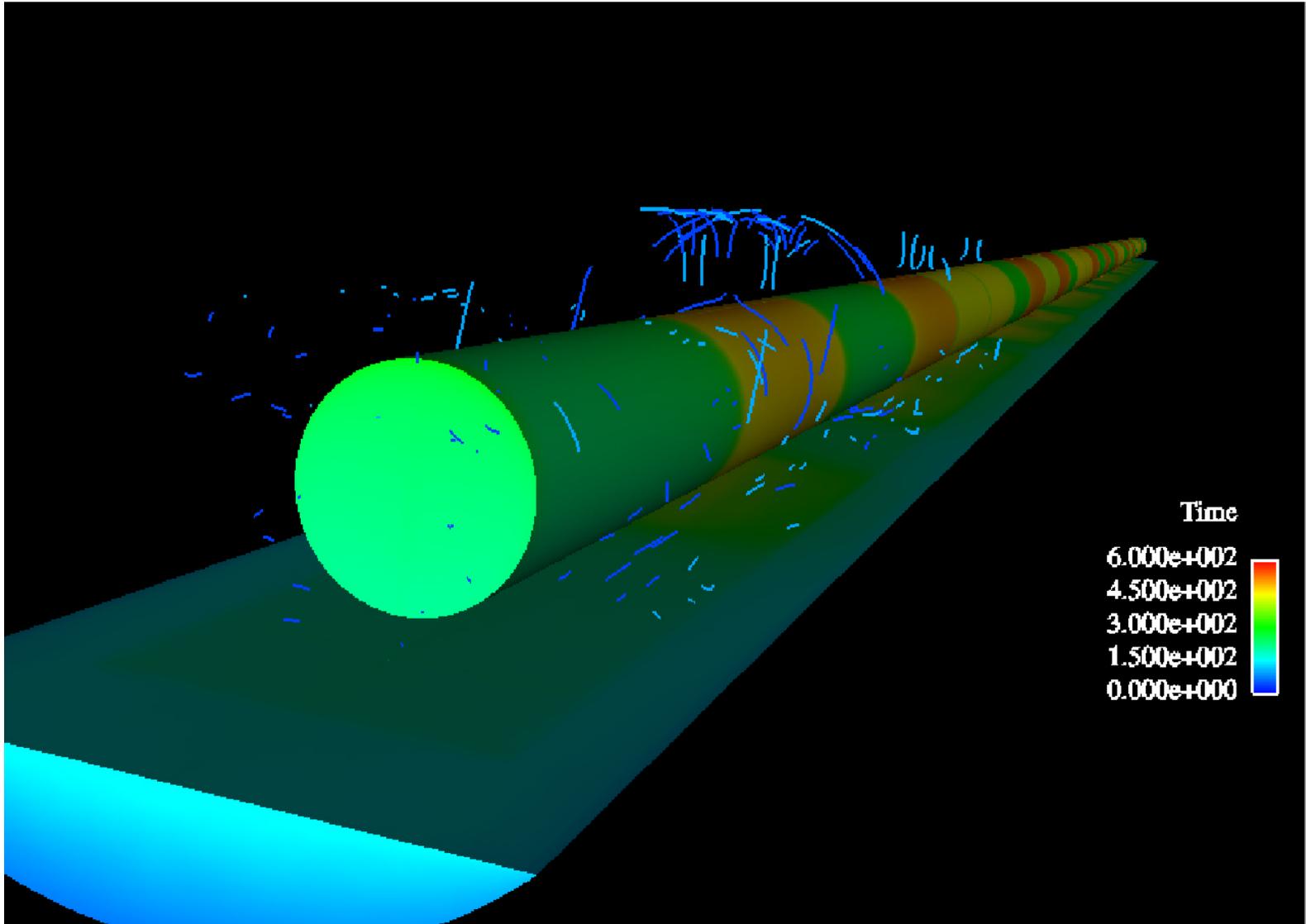
LDSRtAng.evo   Frame 220

ODSRtAng.evo   Frame 150

Time
6.000e+002
4.500e+002
3.000e+002
1.500e+002
0.000e+000

YUCCA MOUNTAIN PROJECT

ODSRtAng.evo   Frame 360