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Phase Transitions in Porous Media

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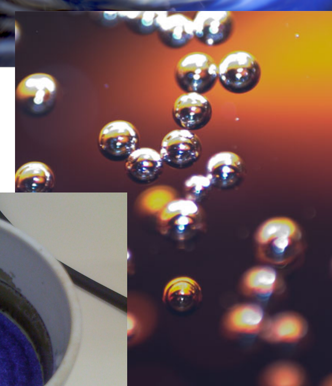
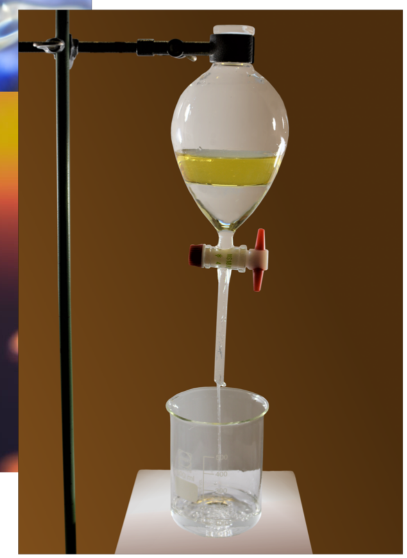
Components

- Water
- Carbon Dioxide
- Methane
- Salt
- C7
- Nitrogen
- Oil

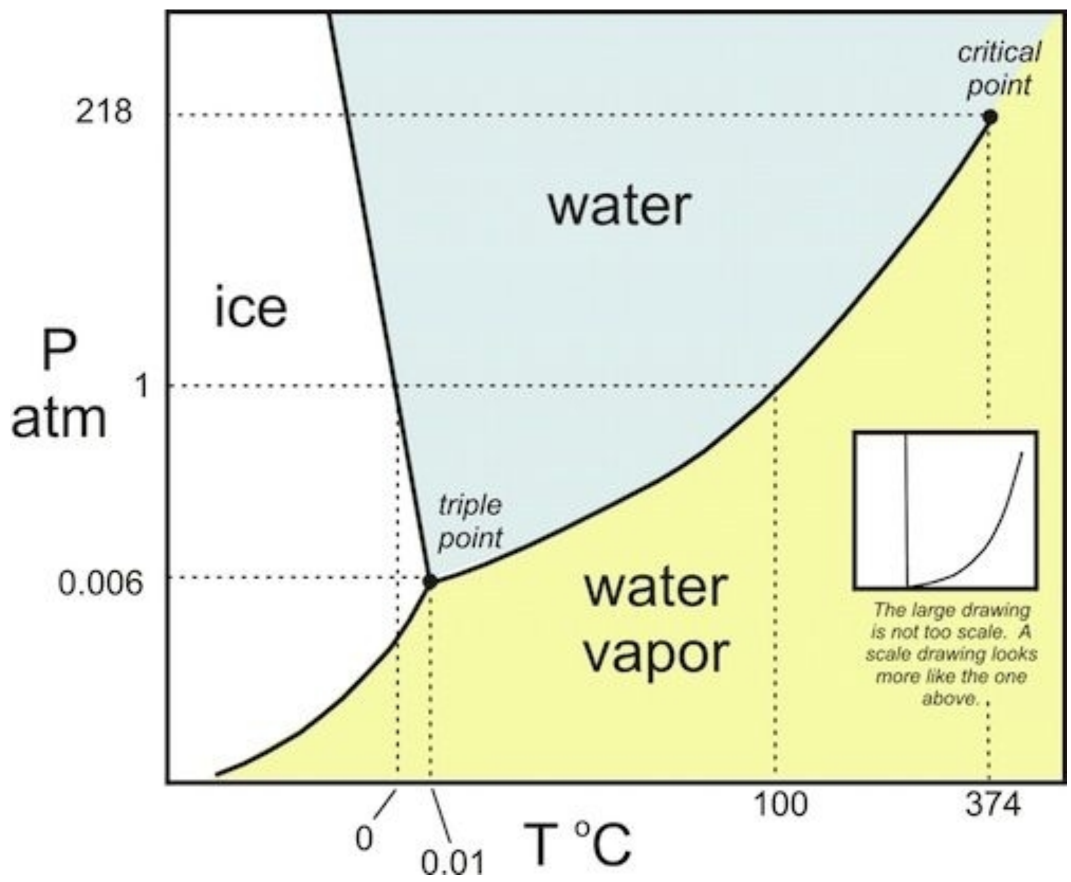
Phases

- Aqueous
- Gas
- Non-aqueous Liquid
- Hydrate
- Ice
- Precipitated Salt
- Minerals

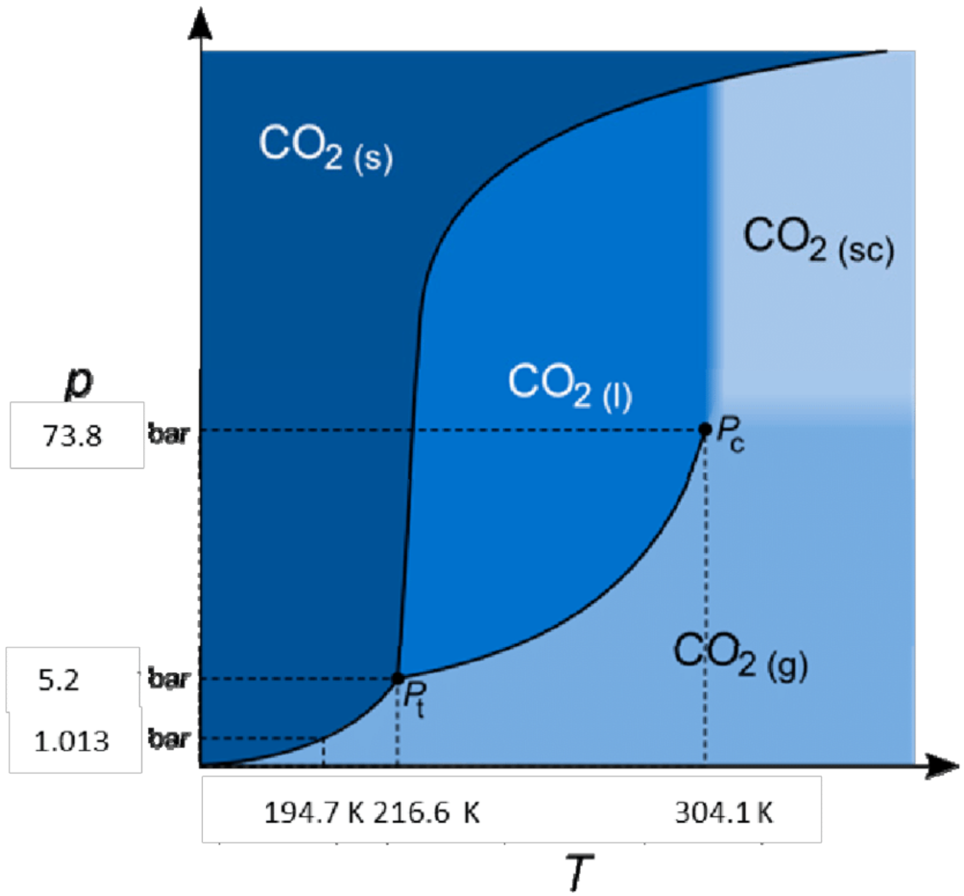





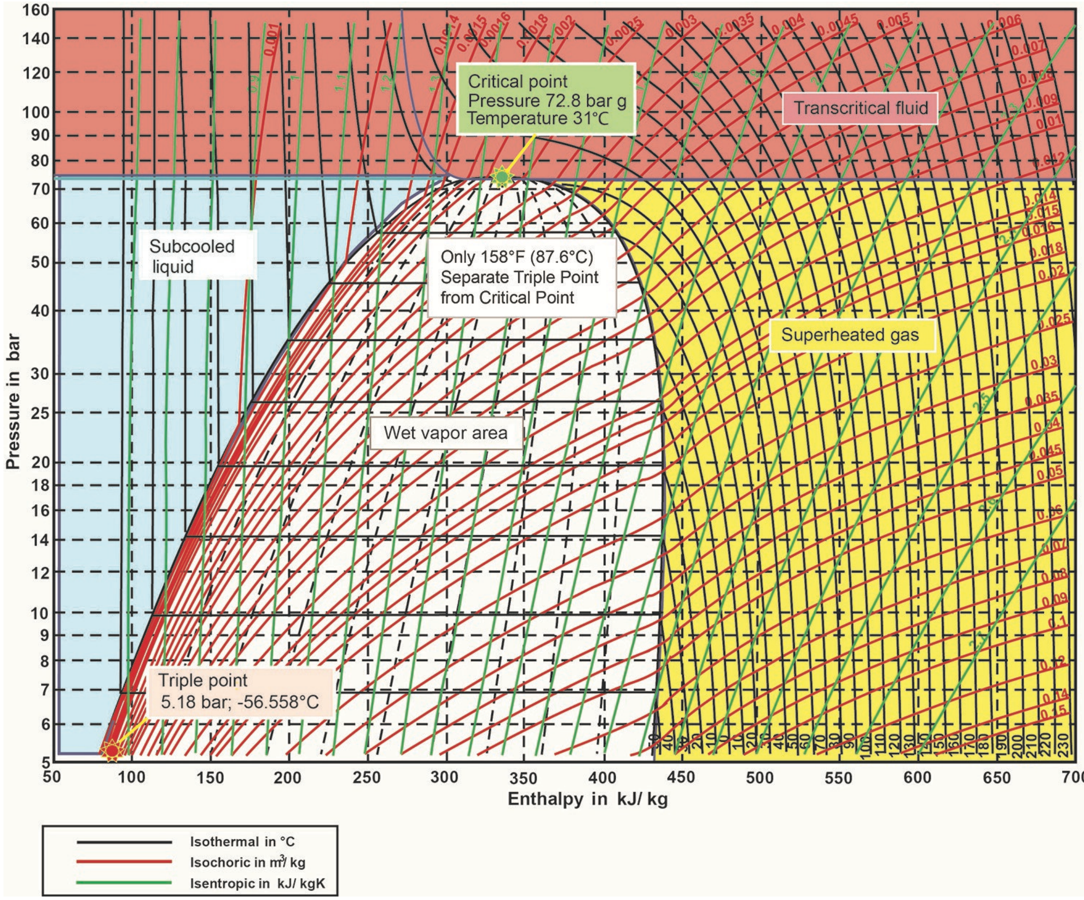
Pressure-Temperature Phase Diagram for Water



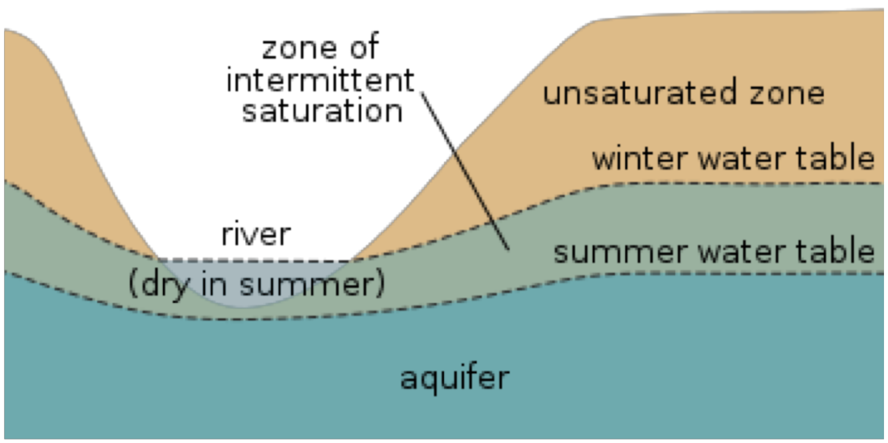
Pressure-Temperature Phase Diagram for CO_2

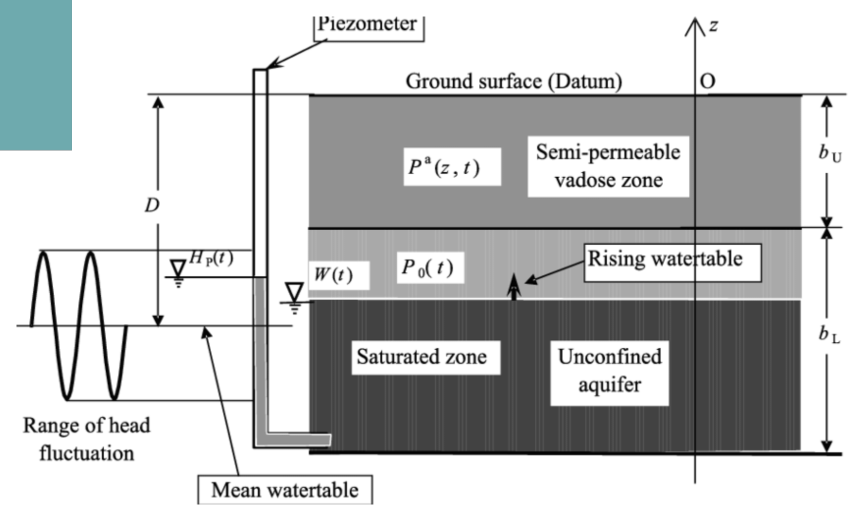


Pressure-Enthalpy Phase Diagram for CO_2



Phase Transitions: Fluctuating Water Table Examples





Modeling Scheme for Saturated to Unsaturated Phase Transitions

Fixed Variables

- Temperature (Isothermal)
- Gas Pressure (Passive Gas)

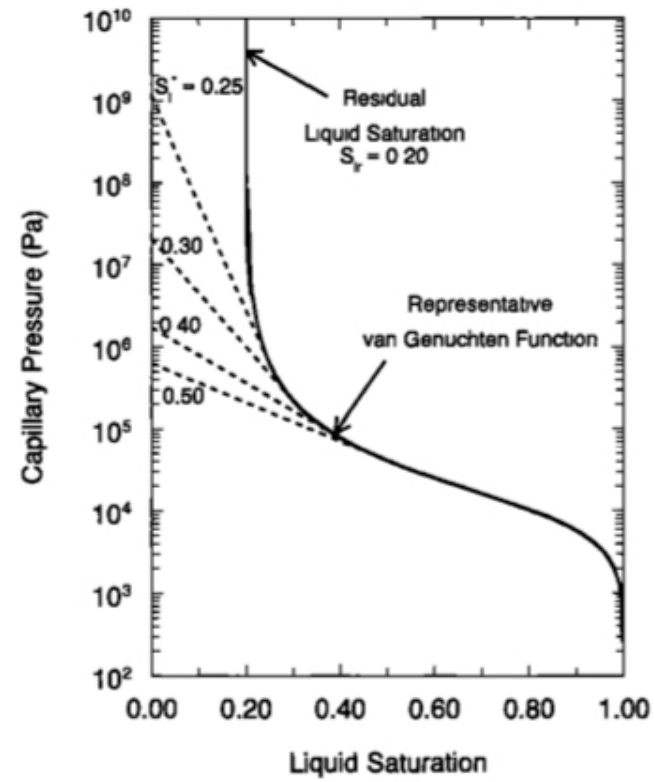
Primary Variable Options

- Aqueous Saturation
- Aqueous Pressure

Simple Relaxation Scheme

```
DPL – Update to Aqueous Pressure
PG(2,N) – Gas Pressure
PL(2,N) – Aqueous Pressure
PAE – Air Entry Pressure

IF( PG(2,N)-PL(2,N)-PAE.GT.ZERO .AND.
PG(2,N)-PL(2,N)-PAE-DPL.LT.ZERO ) DPL = 6.D-1*DPL
PL(2,N) = PL(2,N) + DPL
```



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Subsurface Transport Over Multiple Phases

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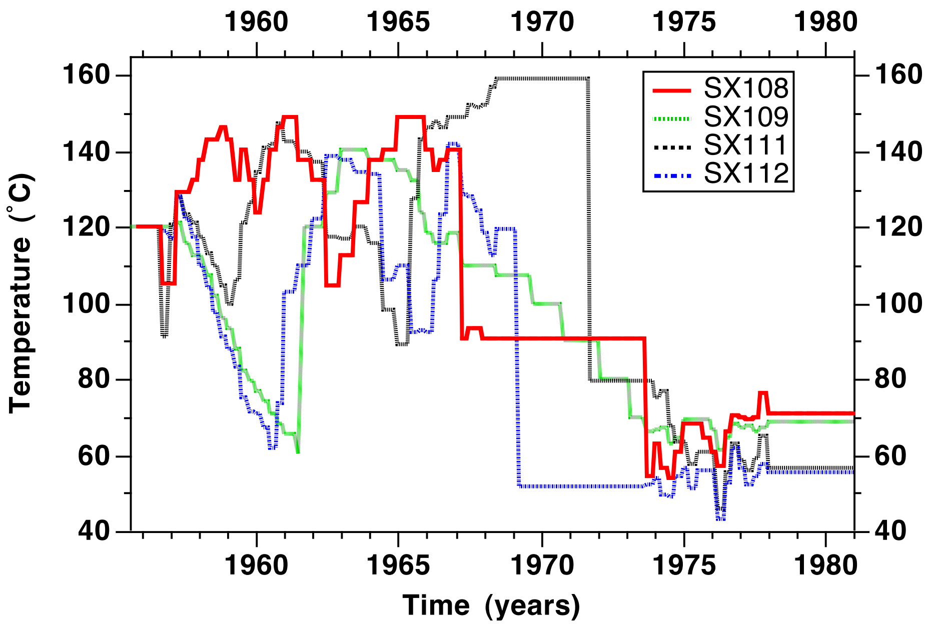
Low-Pressure Air-Water Systems: Example of Coupled Thermal and Hydraulic Environments



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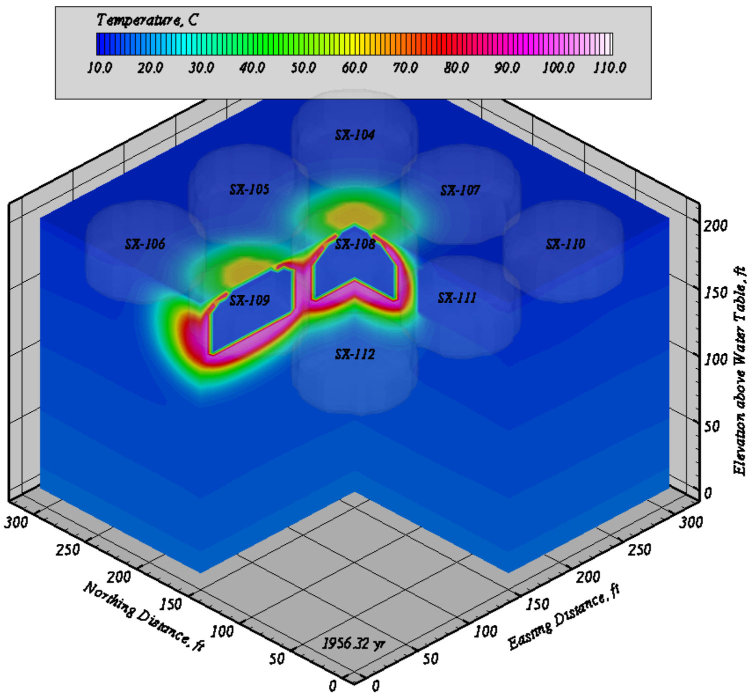

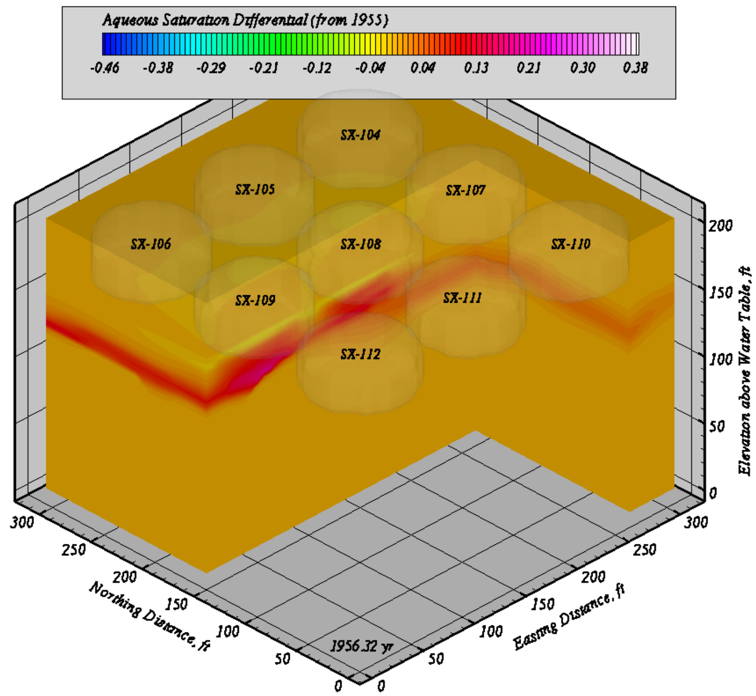

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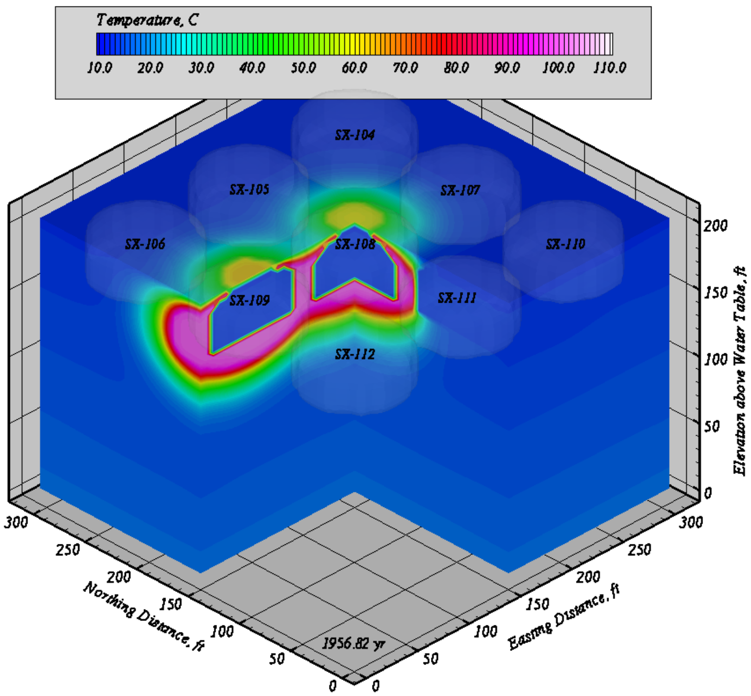

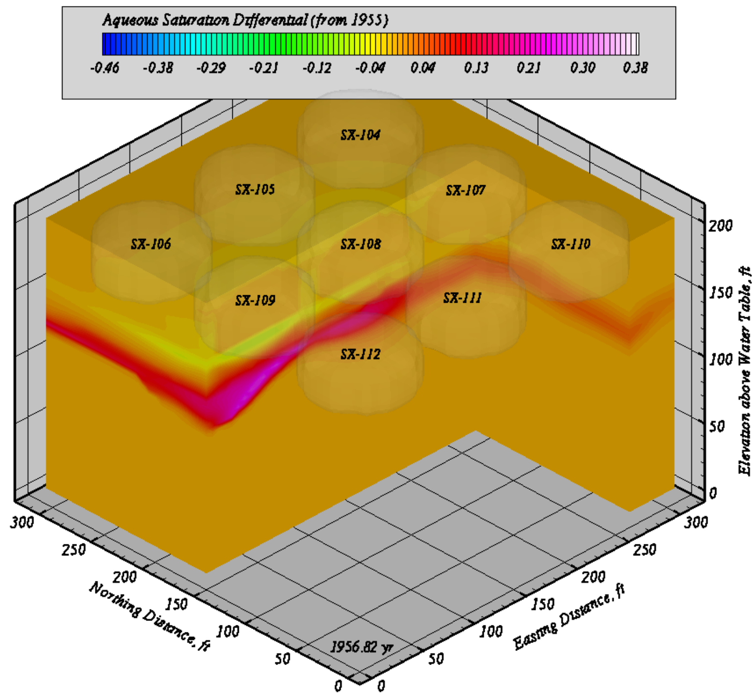

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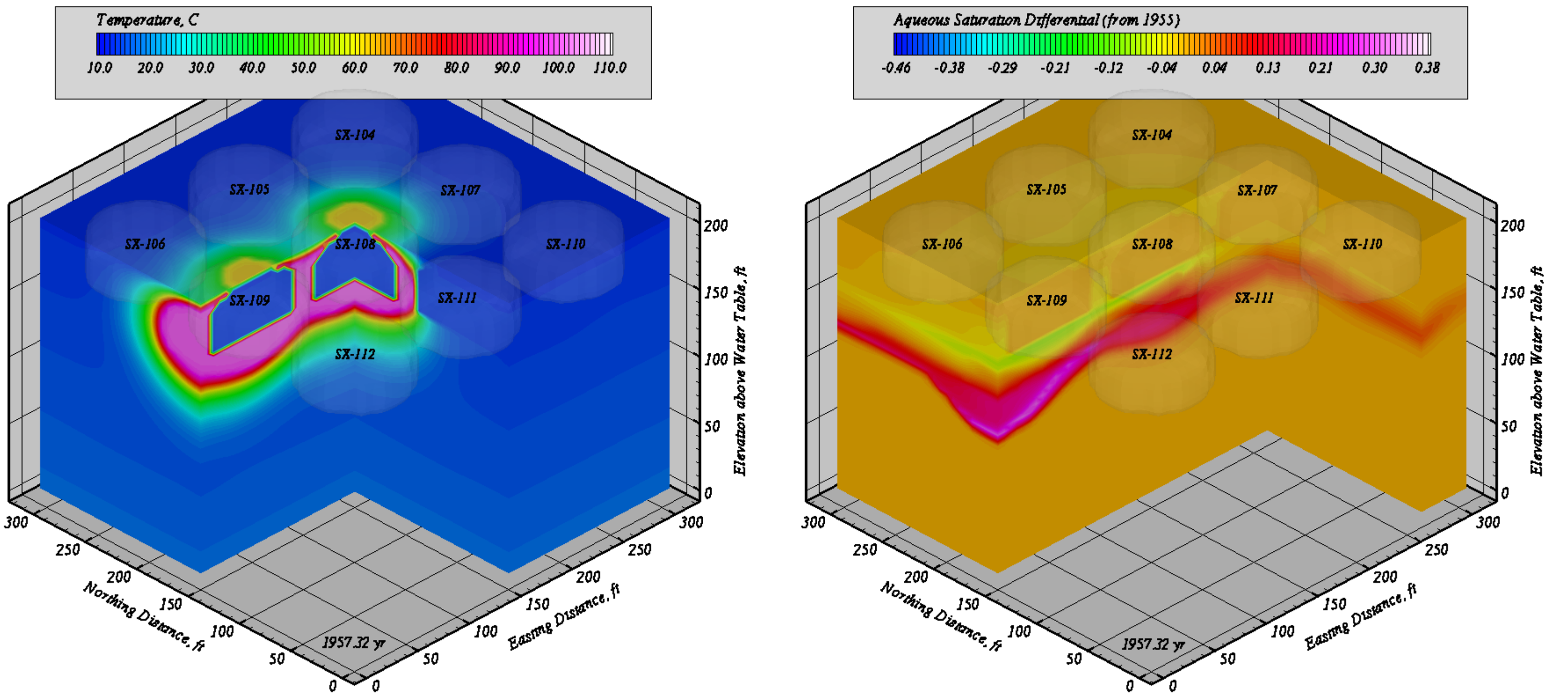

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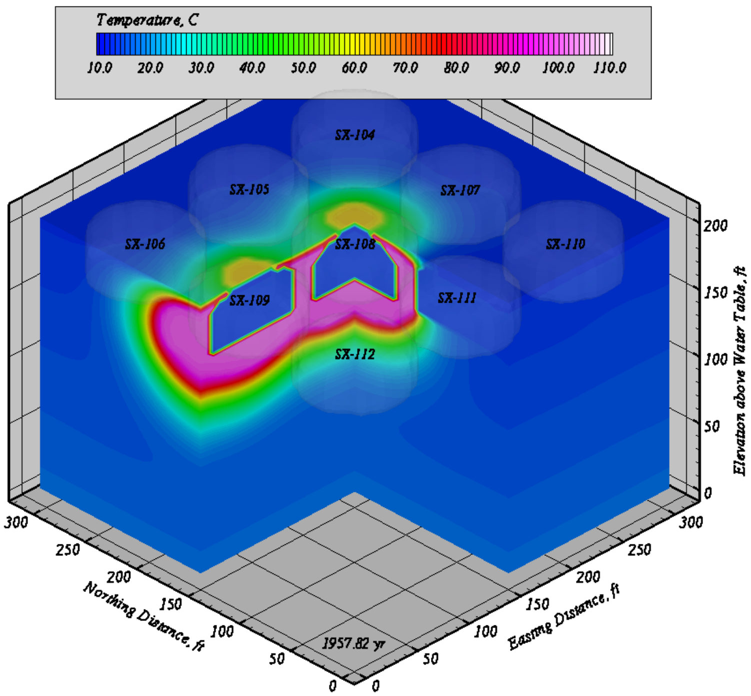

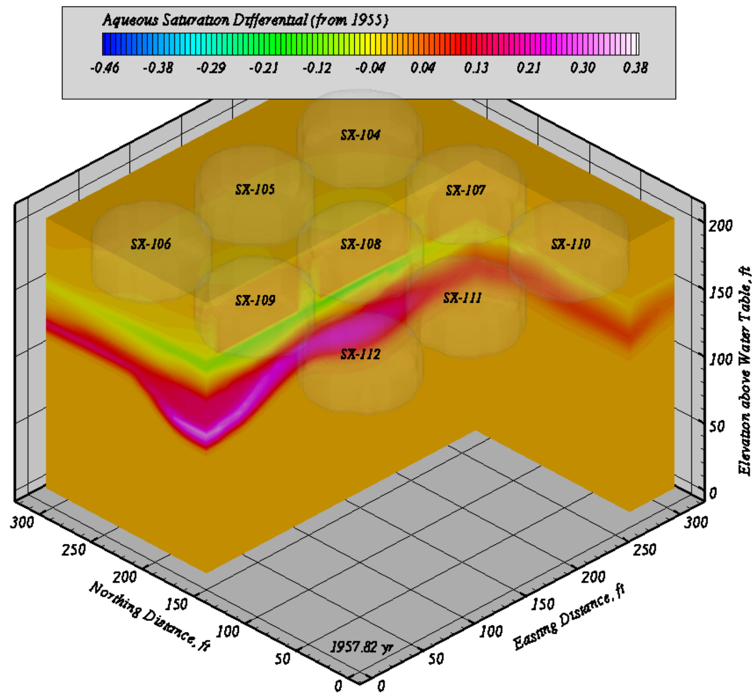

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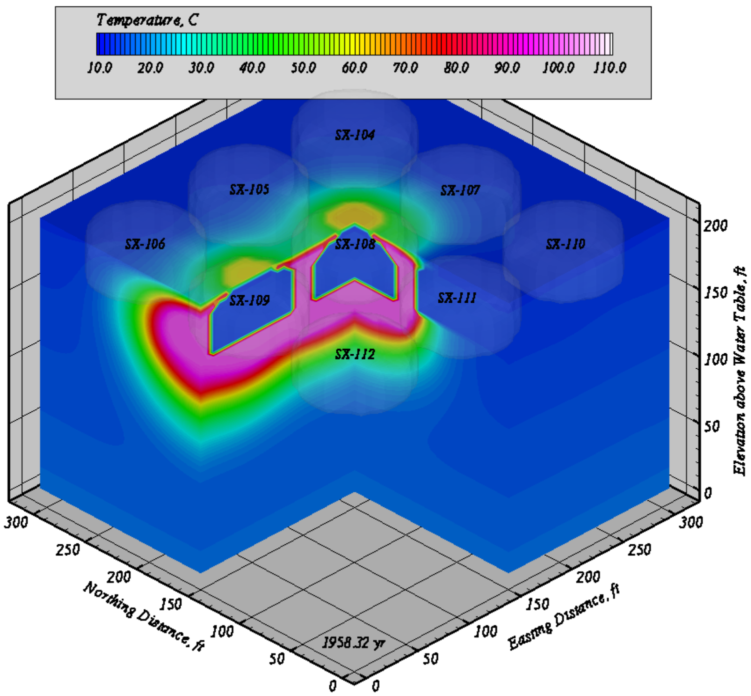

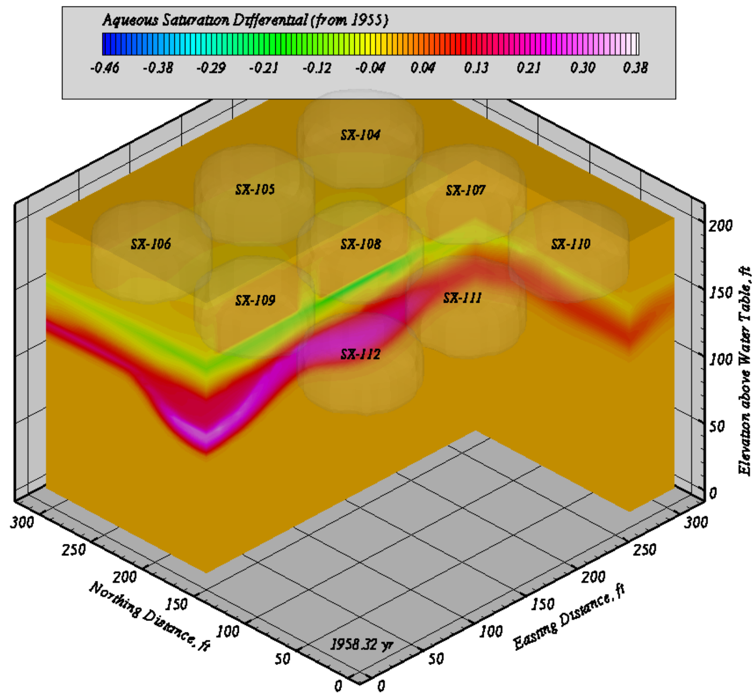

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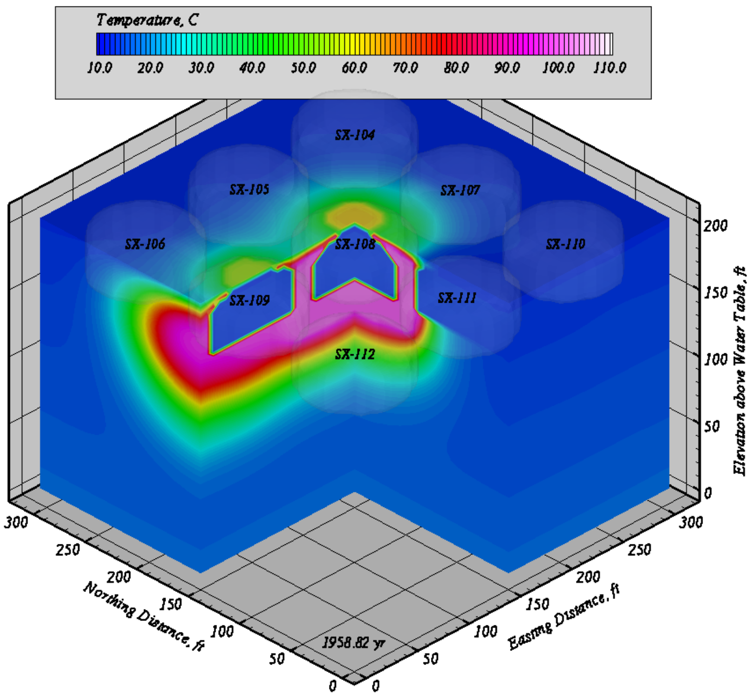

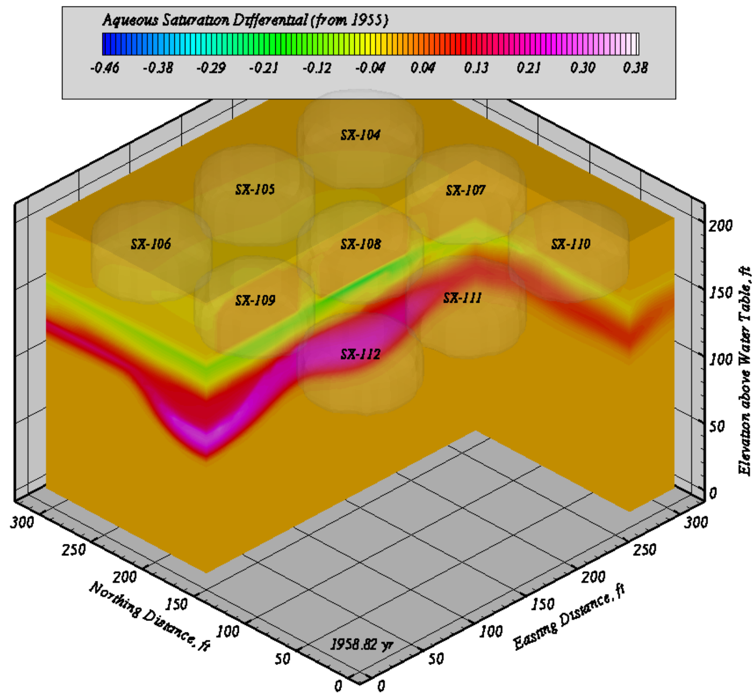

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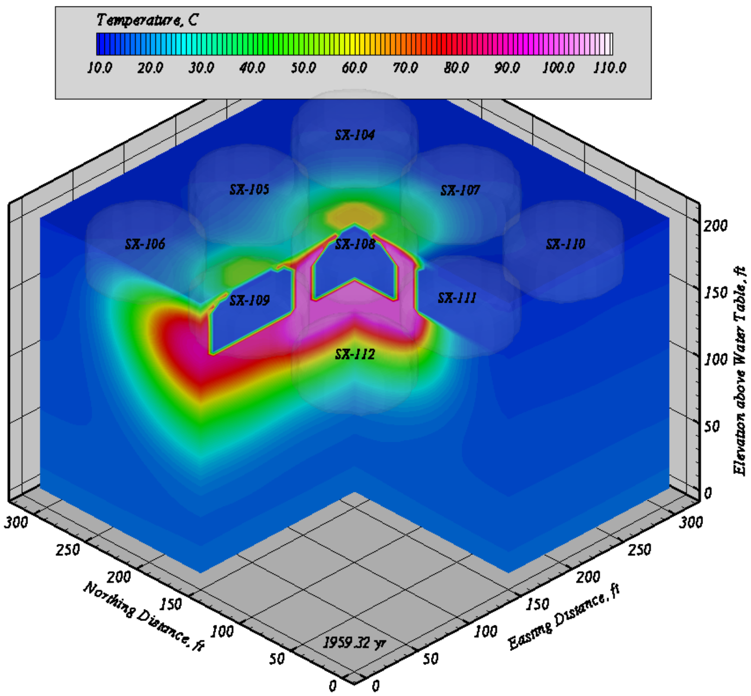

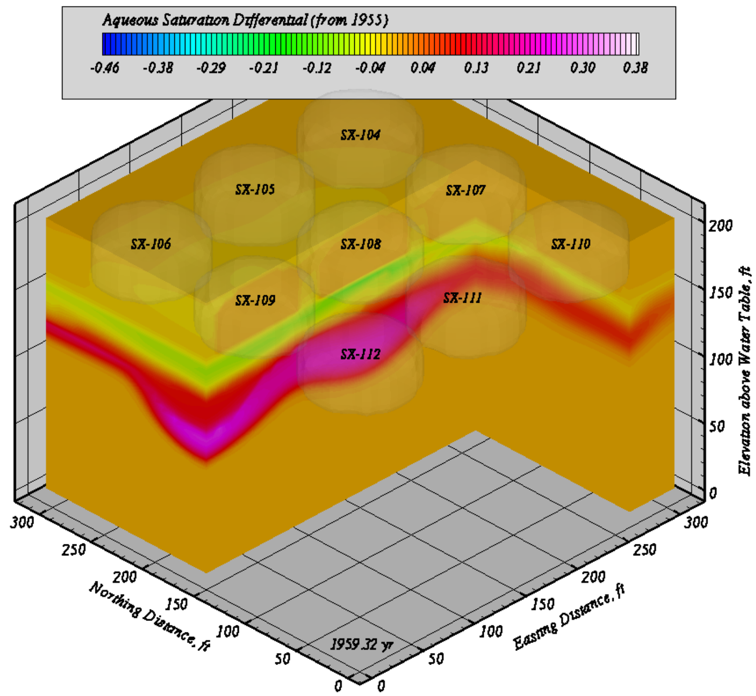

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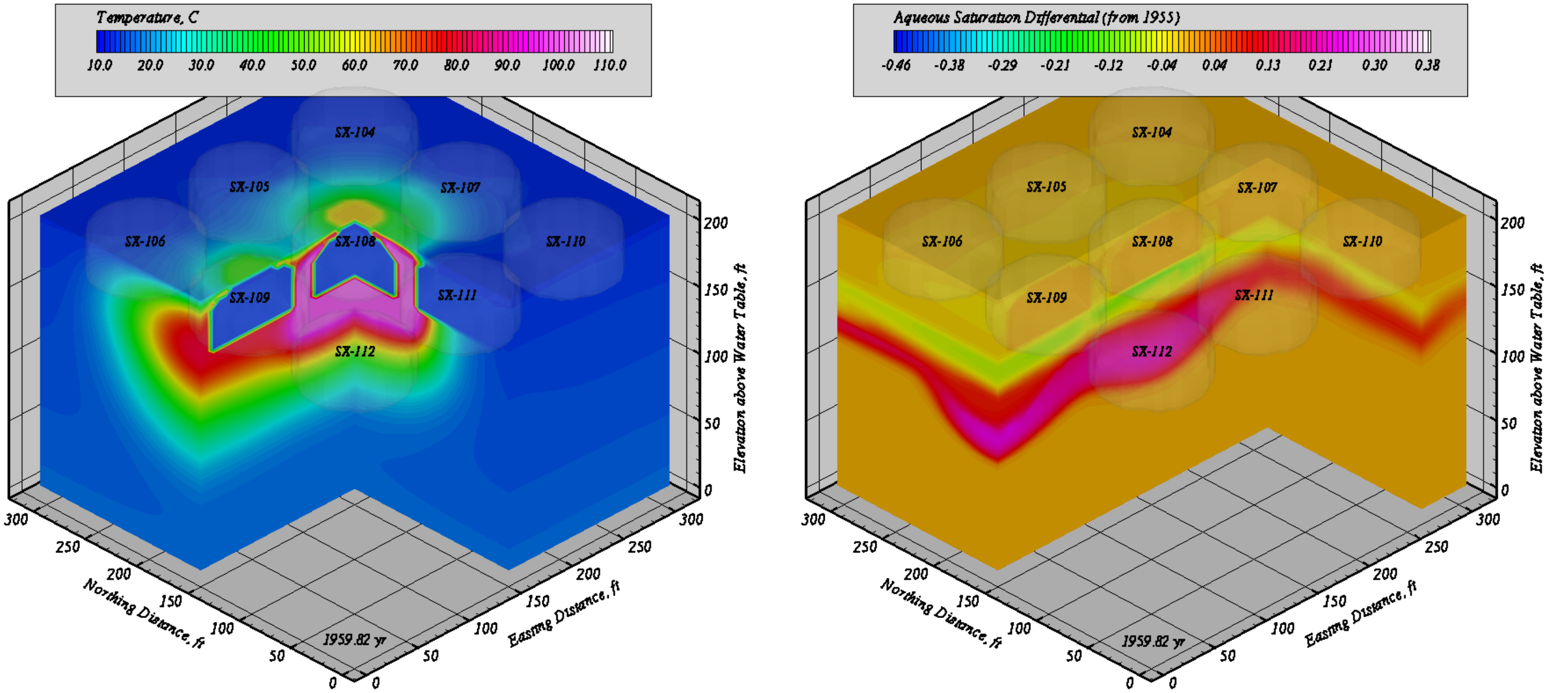

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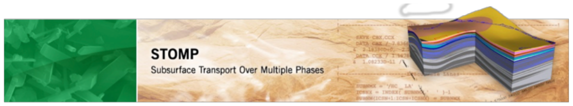

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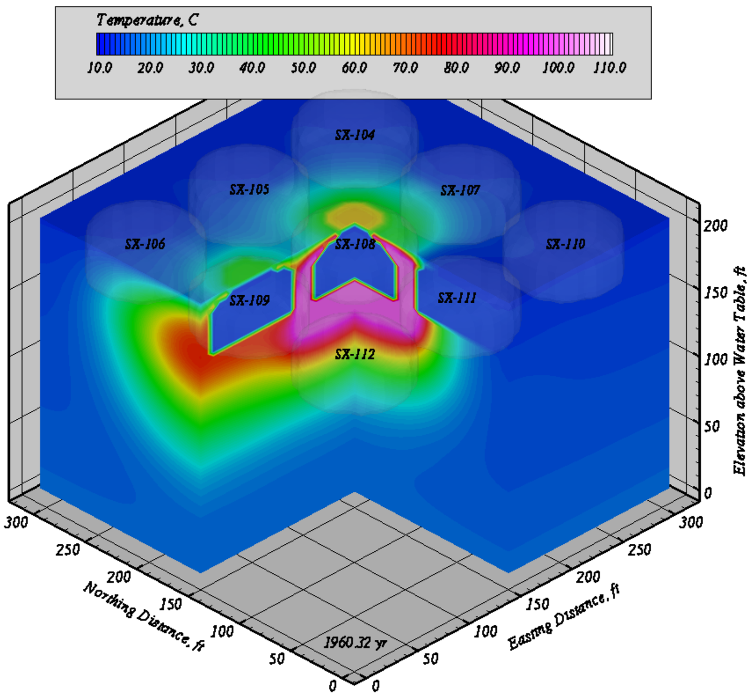

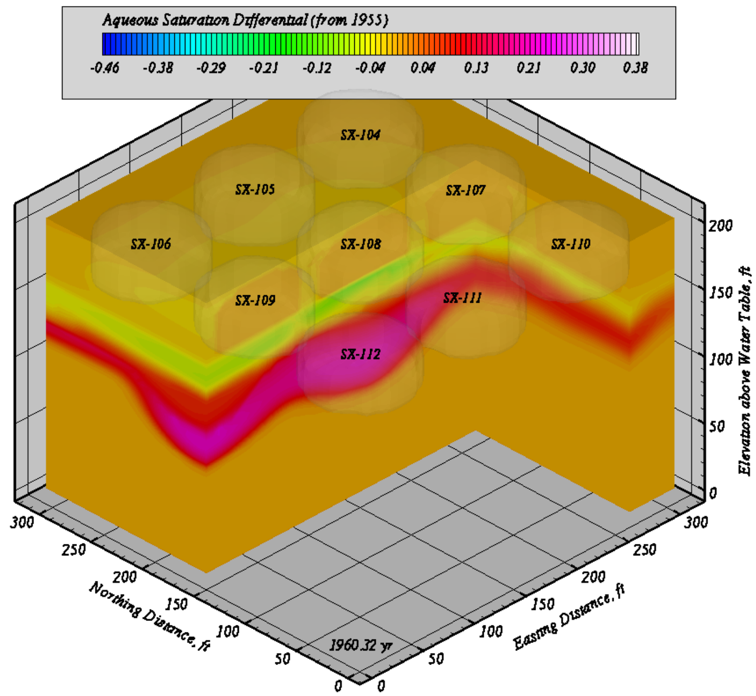

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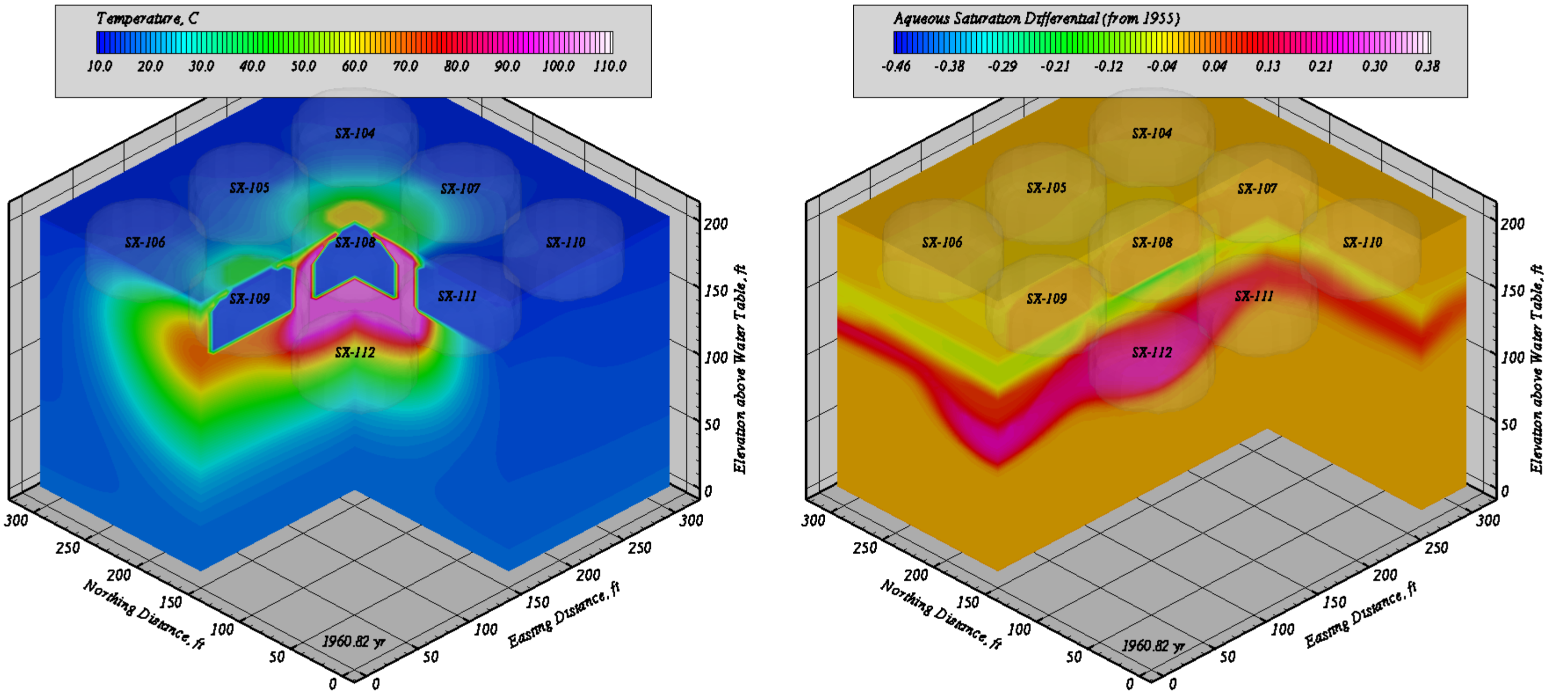

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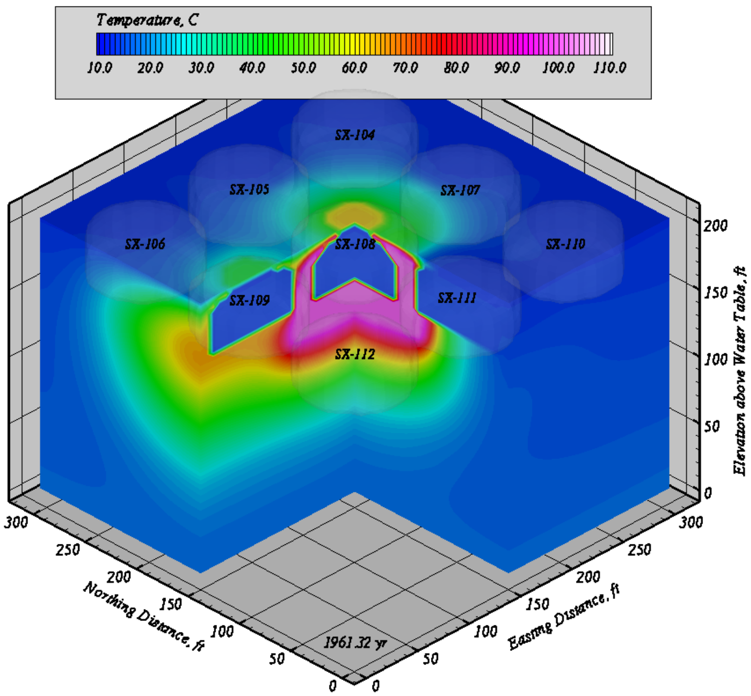

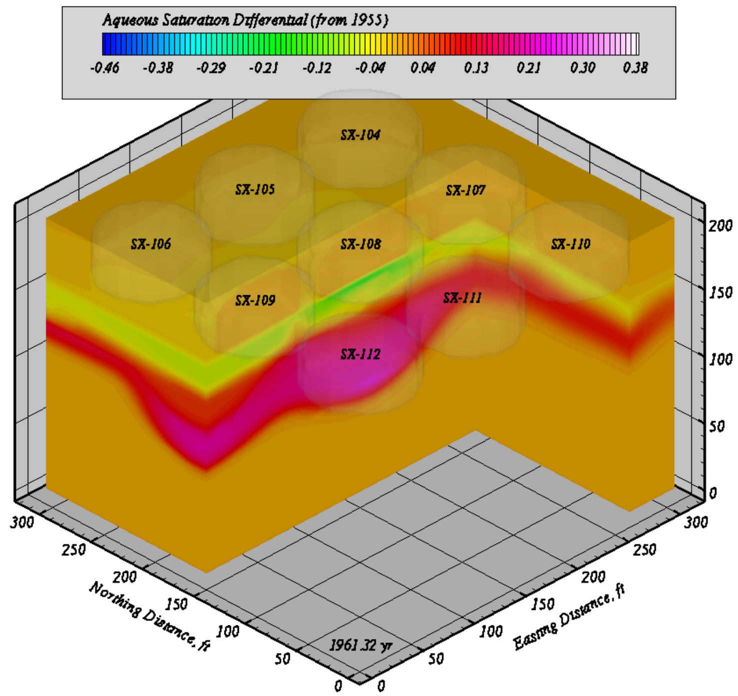

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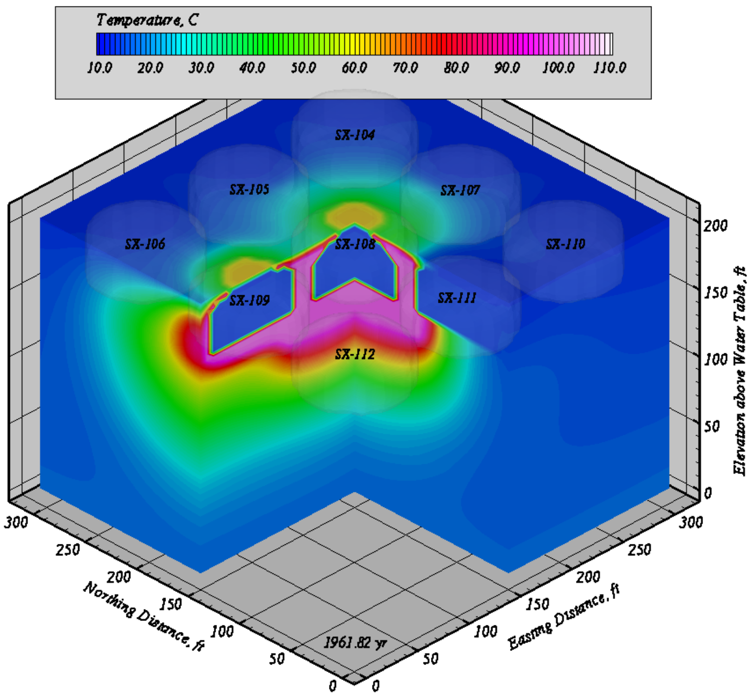

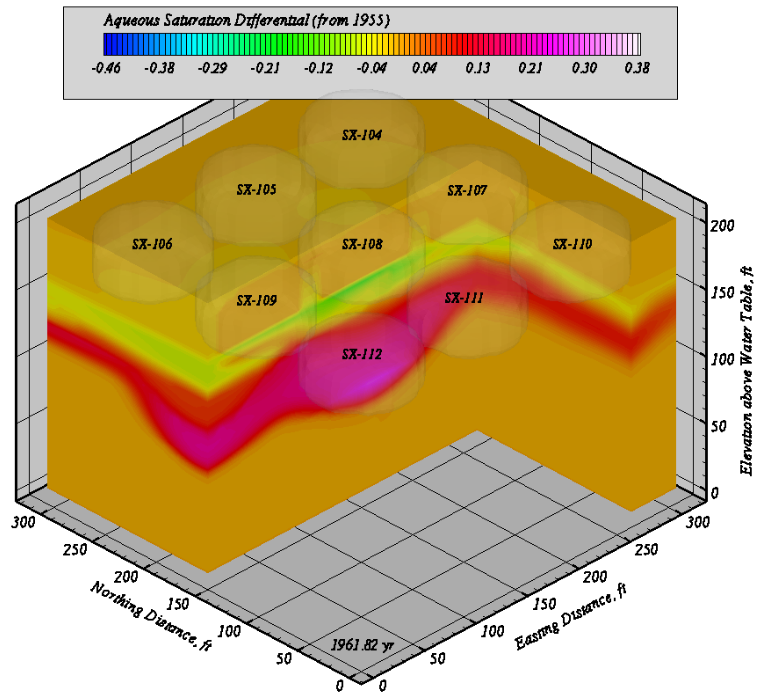

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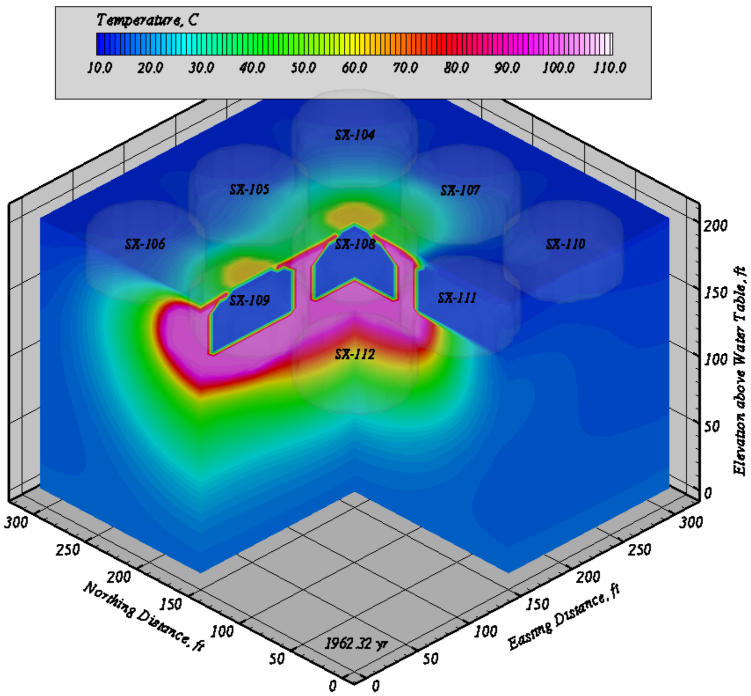

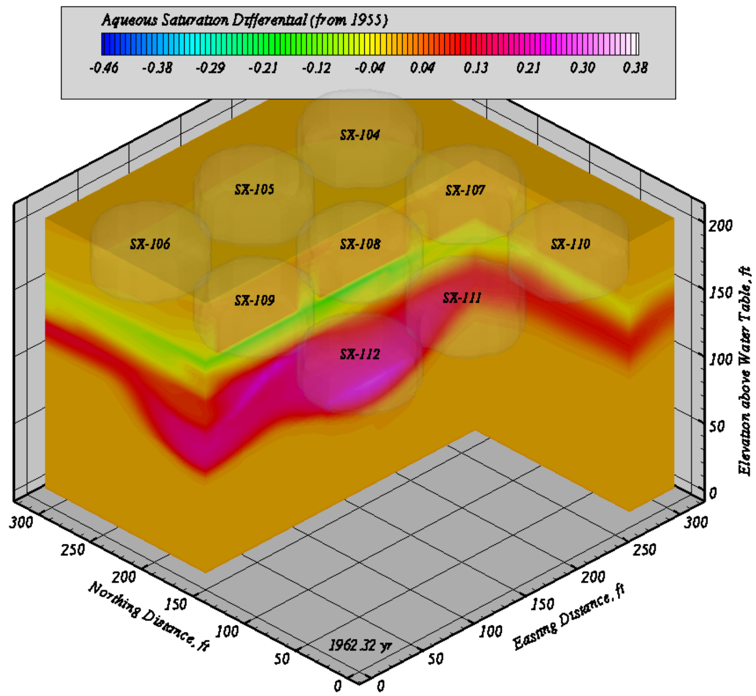

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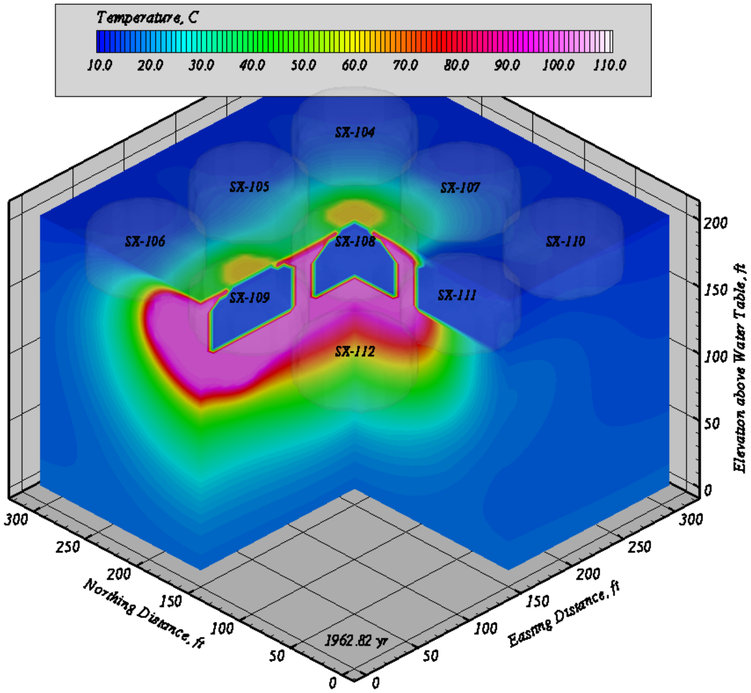

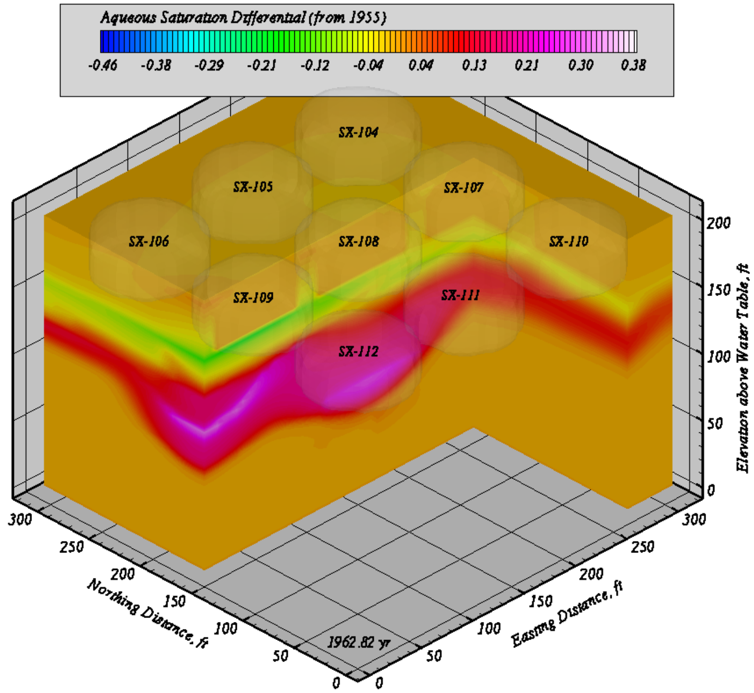

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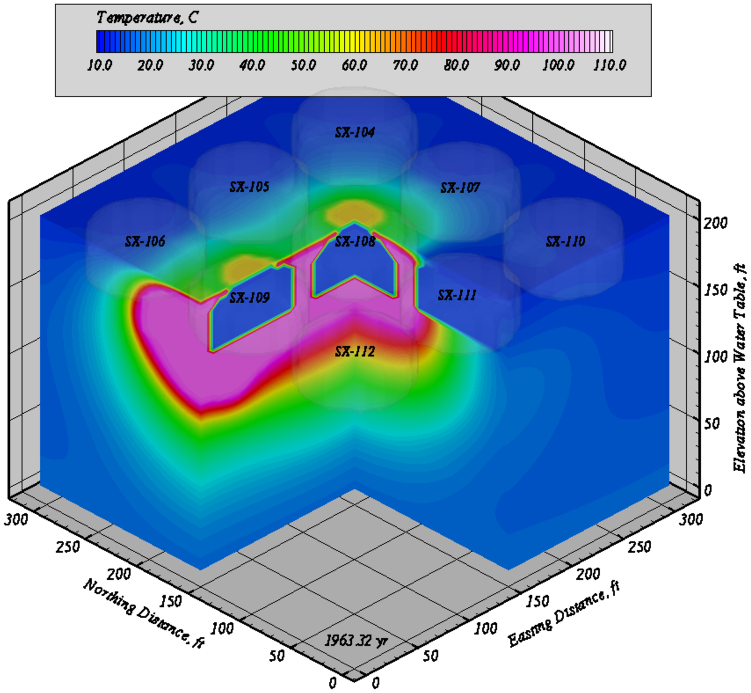

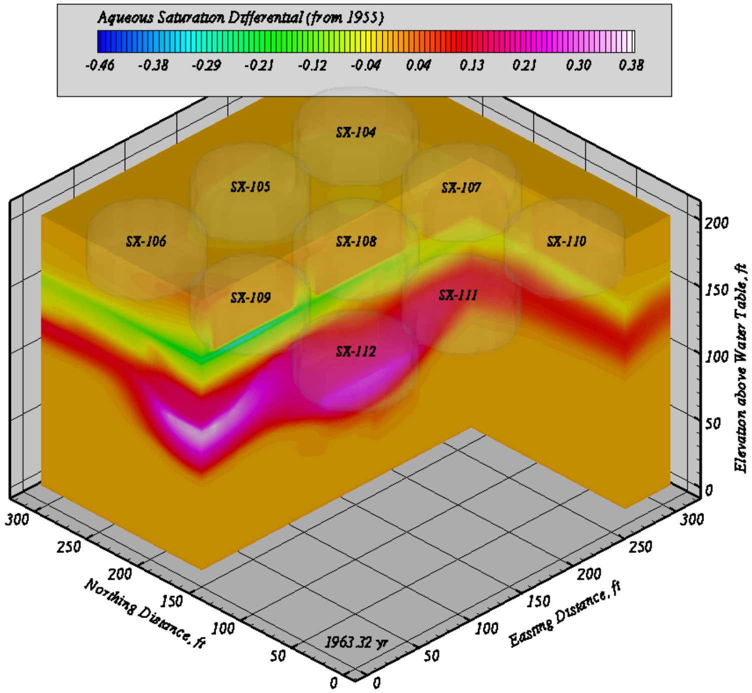

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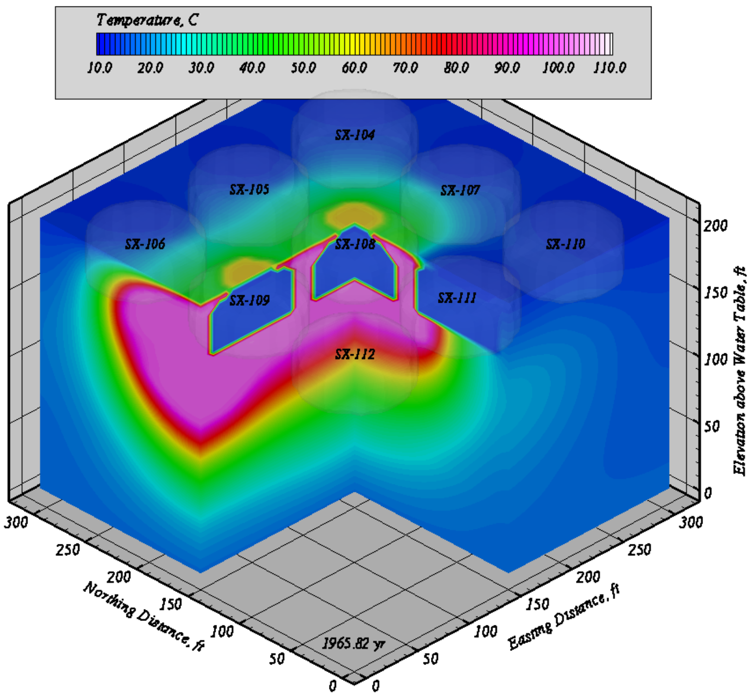

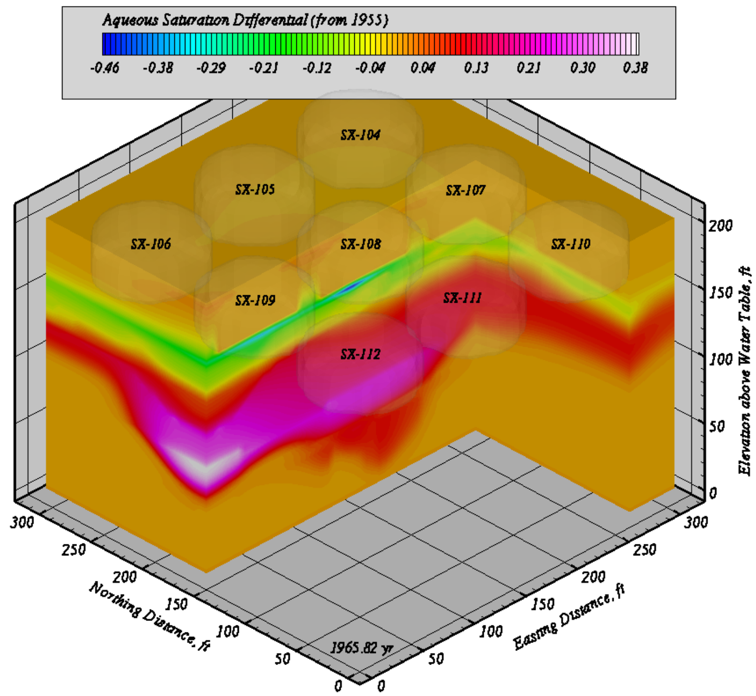

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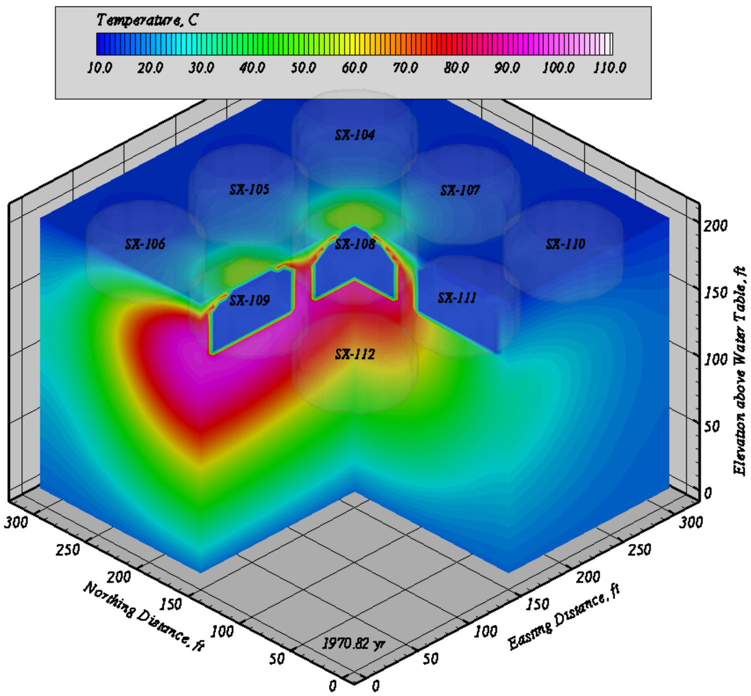

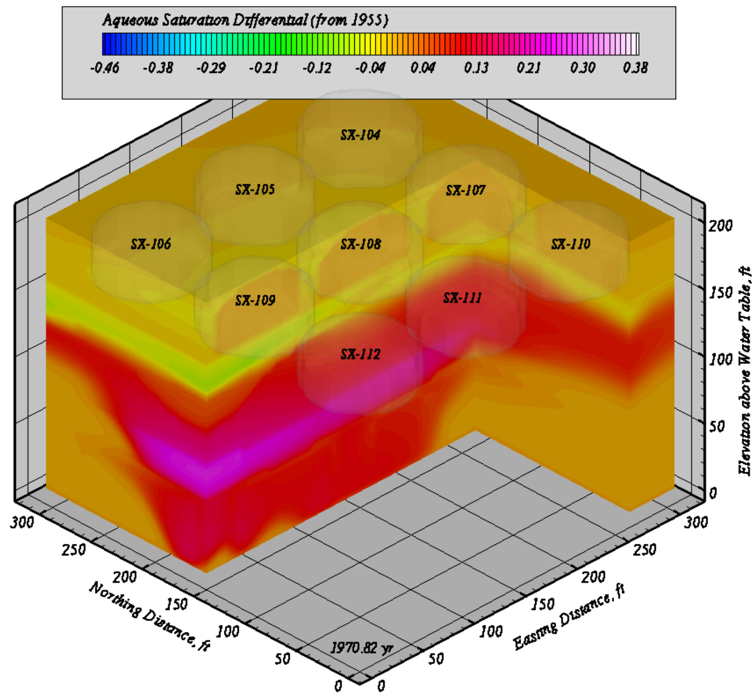

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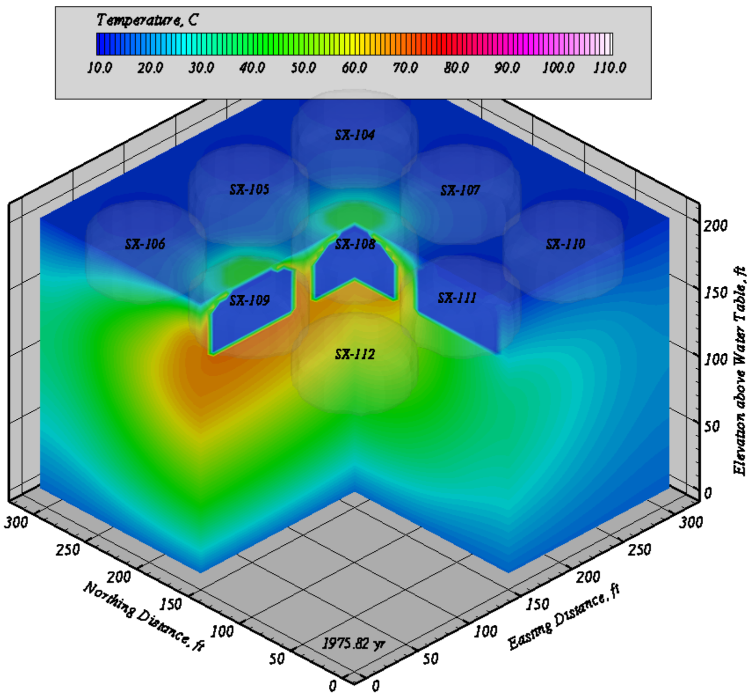

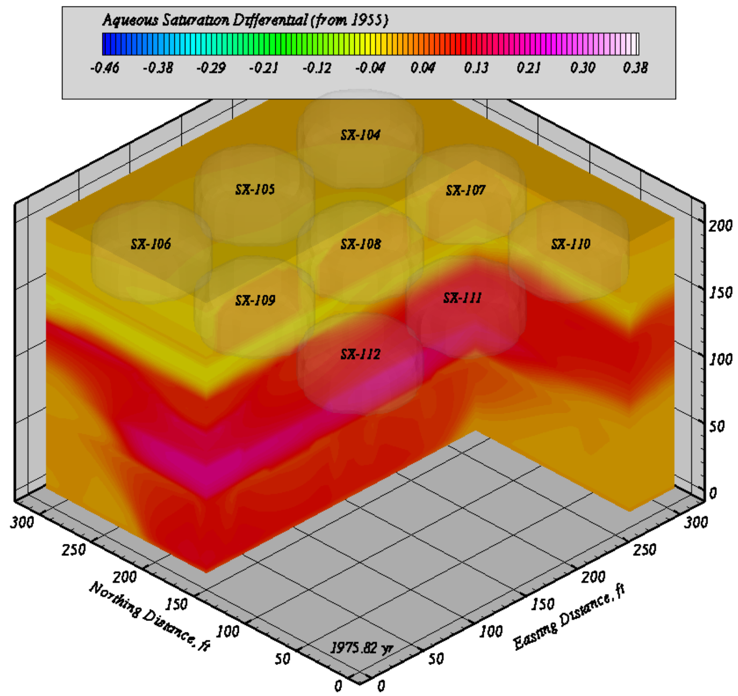

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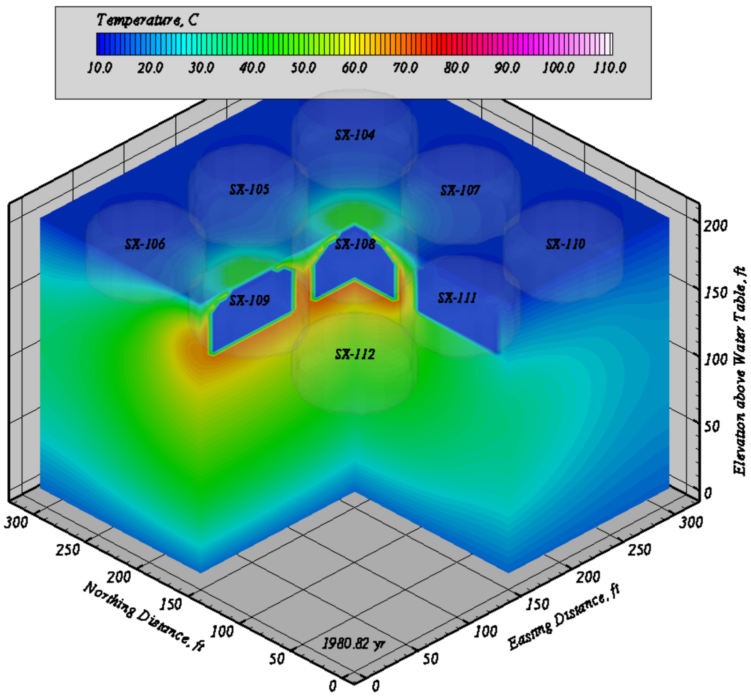

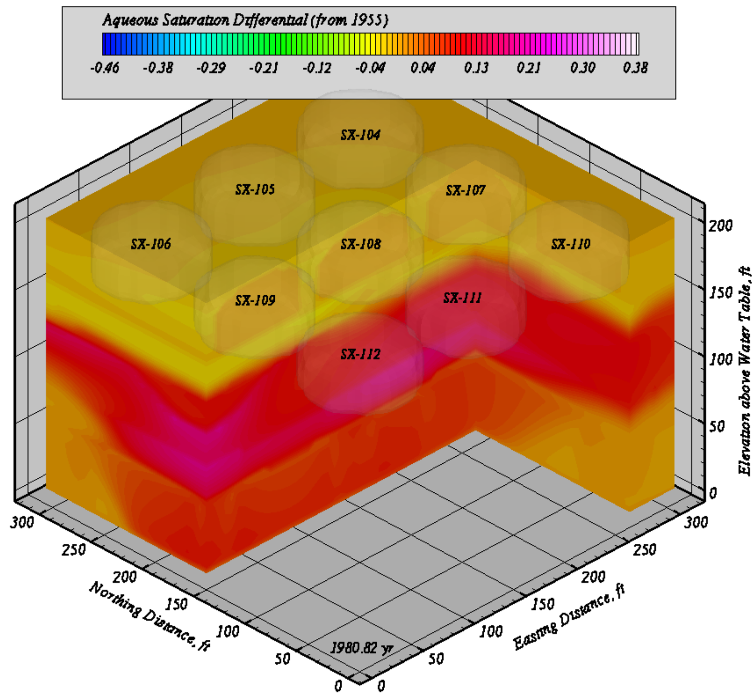

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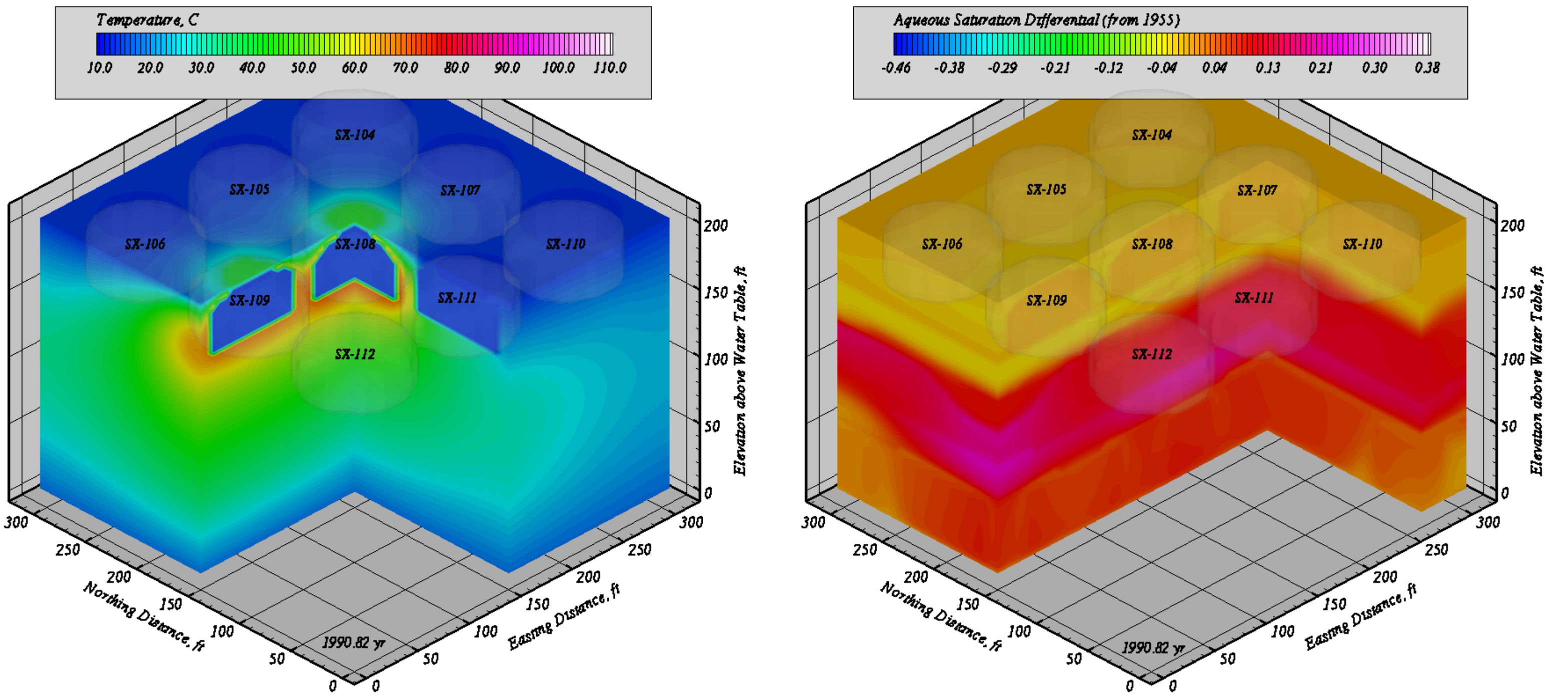

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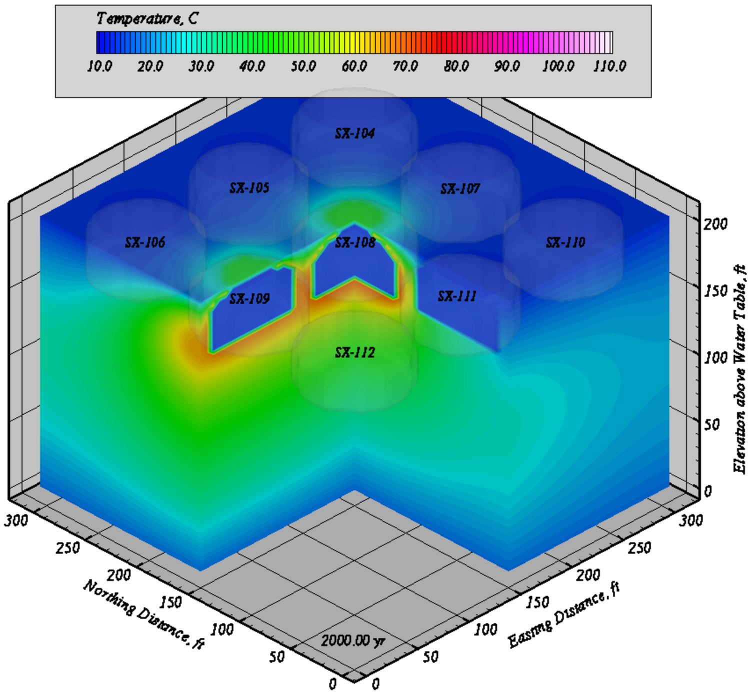

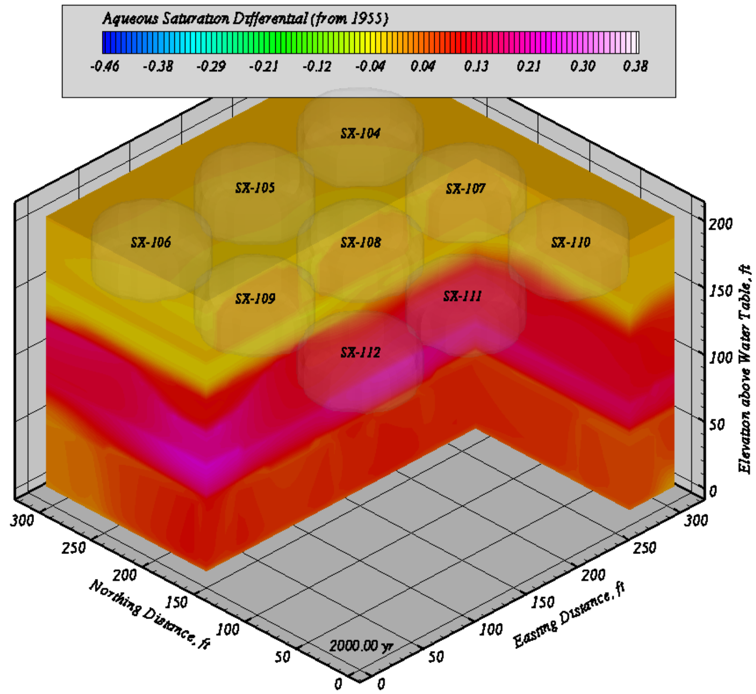

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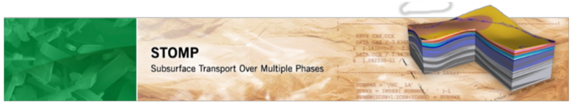
Low-Pressure Air-Water Systems: Phase Conditions and Transitions



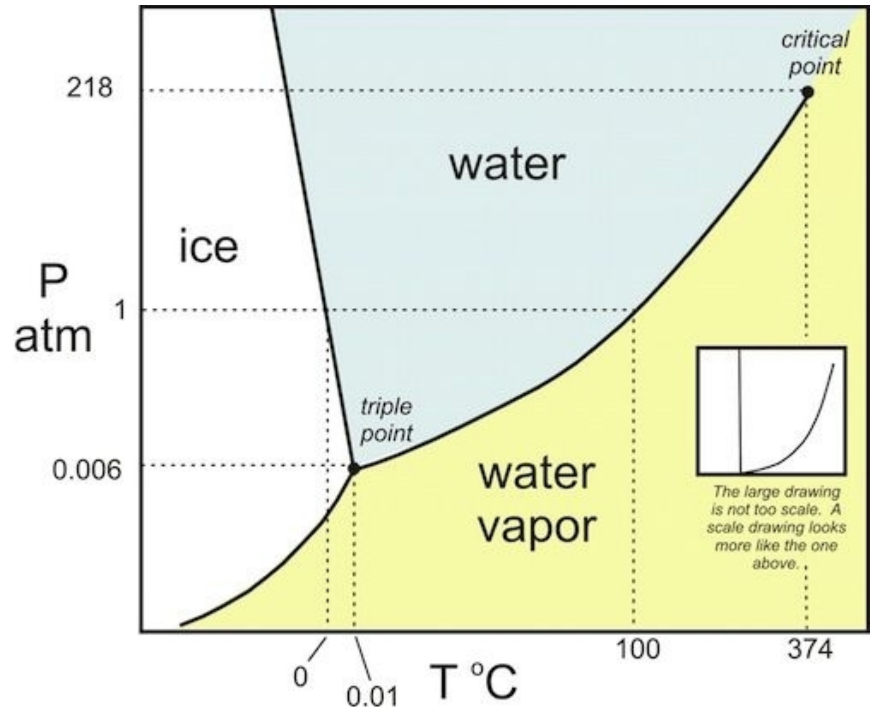
Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Aqueous Air Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Salt Mass

Low-Pressure Water Systems: Phase Conditions and Transitions

Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Beta Factor
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - Salt Mass – Salt Mass



Low-Pressure Air-Water Systems: Phase Conditions and Transitions

Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Aqueous Air Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Salt Mass

```
PGA - air partial pressure
PGW – water partial pressure
PG – gas pressure
PL – aqueous pressure
SG – gas saturation
SL – aqueous saturation

PGA = FUNC( XMLA )
PGW = FUNC( T,PCAP )
PG = PGW + PGA
PCAP = PG – PL
SL = FUNC( PCAP )
SG = 1.D+0 – SL
IF( SG > 1.D-3 ) NPHAZ = 2
```

Low-Pressure Air-Water Systems: Phase Conditions and Transitions

Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Aqueous Air Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Salt Mass

```
PG – gas pressure
PL – aqueous pressure
ASL – apparent aqueous sat.
SGT – trapped gas sat.

PCAP = PG – PL
ASL = FUNC( PCAP )
IF( ASL == 0 && SGT == 0 )
NPHAZ = 1
```

Low-Pressure Air-Water Systems: Phase Conditions and Transitions

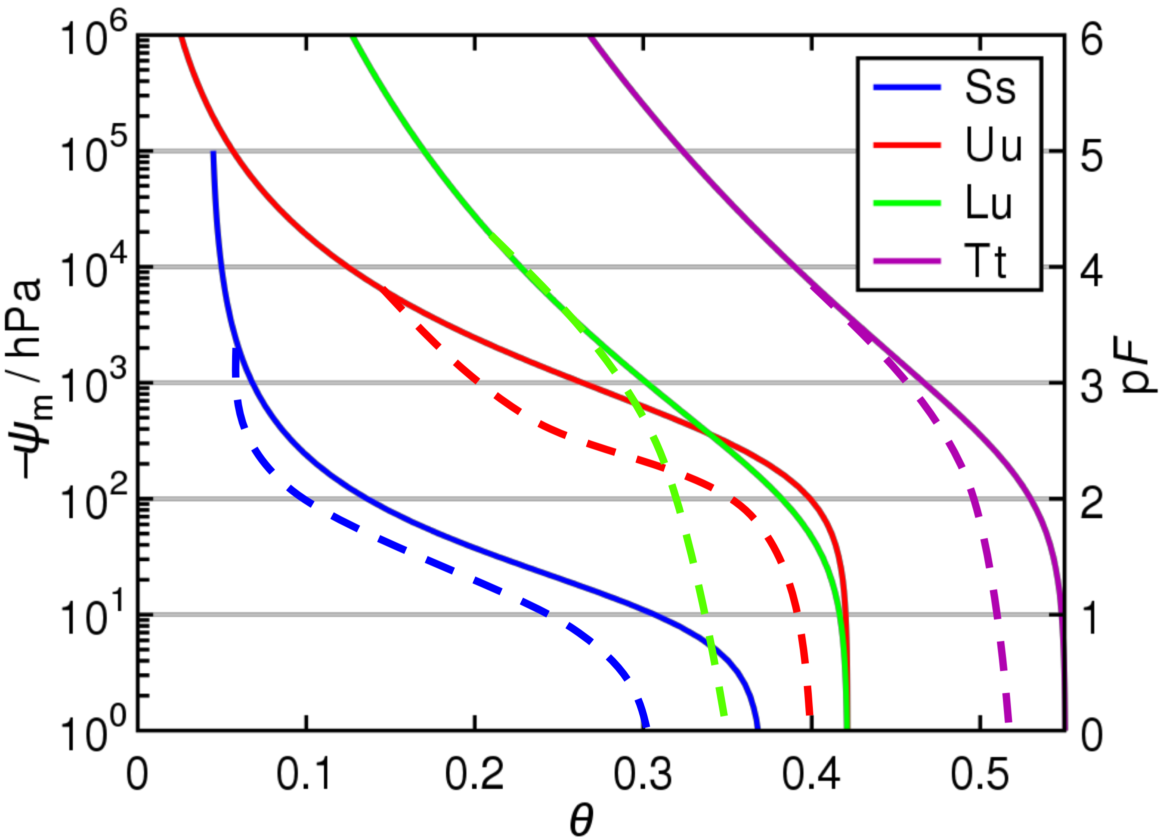
Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Aqueous Air Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Salt Mass

```
PG – gas pressure
PL – aqueous pressure
ASL – apparent aqueous sat.
SGT – trapped gas sat.

PCAP = PG – PL
ASL = FUNC( PCAP )
IF( ASL == 0 && SGT > 0 )
NPHAZ = 3
```

Low-Pressure Air-Water Systems: Phase Conditions and Transitions



Ss – sand

Uu – silt or clay loam

LU – loam-silt or clay

Tt – clay or peat

Low-Pressure Air-Water Systems: Phase Conditions and Transitions

Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Aqueous Air Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - Air Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - Air Mass – Gas Pressure
   - Salt Mass – Salt Mass

```
PG – gas pressure
PL – aqueous pressure
ASL – apparent aqueous sat.
SL – aqueous saturation
SGT – trapped gas sat.

PCAP = PG – PL
ASL = FUNC( PCAP )
SL = ASL - SGT
IF( SL == 0 ) NPHAZ = 4
```

Guidance on Primary Variables

- Direct Solution Path Between Primary and Secondary Variables
- Equation Residual is Sensitive to Primary Variable
- Think Creatively … y_ℓ^s - brine mass fraction of total salt

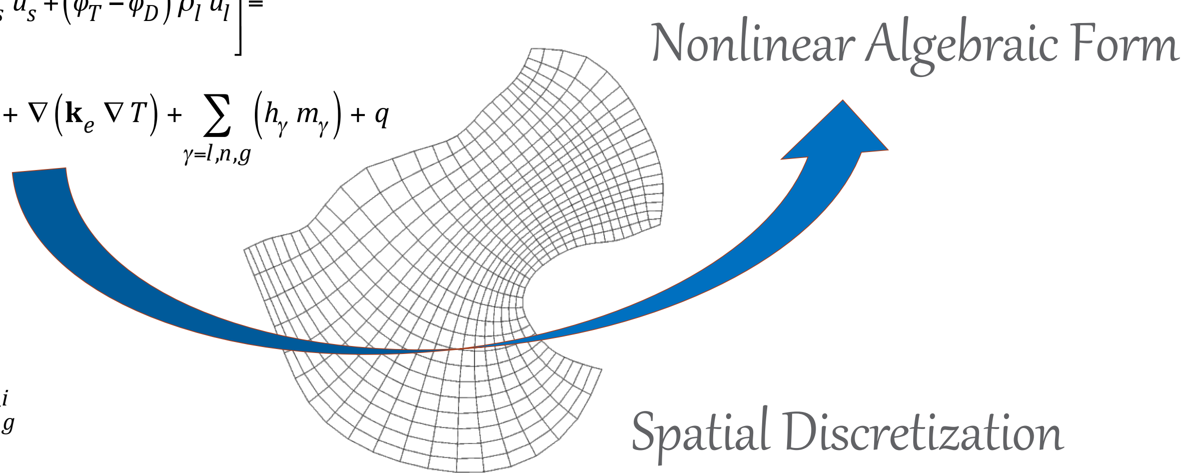
Differential Form

$$\frac{\partial}{\partial t}\left[\sum_{\gamma=l,n,g,h,i,p}\left(\phi_D\,\rho_\gamma\,s_\gamma\,u_\gamma\right)+\left(1-\phi_T\right)\rho_s\,u_s+\left(\phi_T-\phi_D\right)\rho_l\,u_l\right]=$$

$$-\sum_{\gamma=l,n,g}\nabla\left(\rho_\gamma\,h_\gamma\,\mathbf{V}_\gamma\right)-\sum_{i=w,a,o}\nabla\left(h_g^i\,\mathbf{J}_g^i\right)+\nabla\left(\mathbf{k}_e\,\nabla T\right)+\sum_{\gamma=l,n,g}\left(h_\gamma\,m_\gamma\right)+q$$

$$\mathbf{V}_\gamma=-\frac{k_{r\gamma}\,\mathbf{k}}{\mu_\gamma}\left(\nabla P_\gamma+\rho_\gamma\,g\,\mathbf{z}_g\right)$$

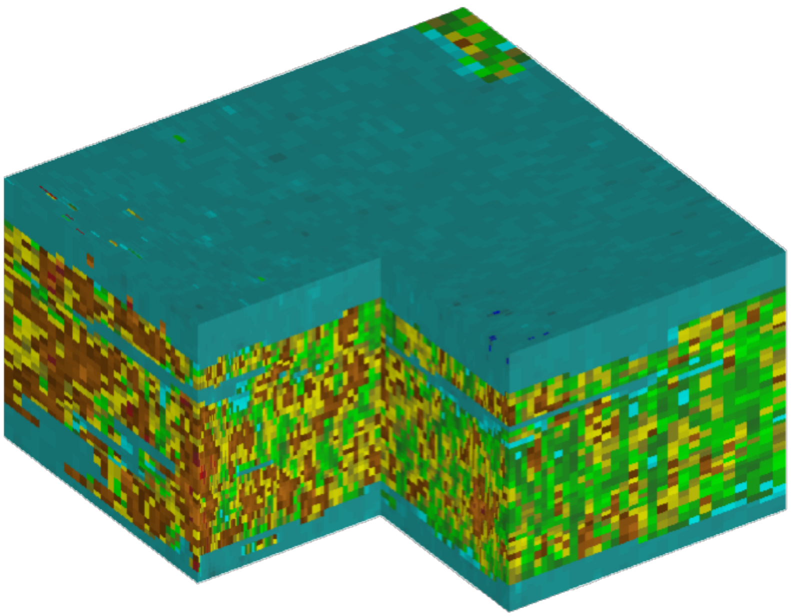
$$\mathbf{J}_g^i=-\phi_D\,\rho_g\,s_g\,\frac{M^i}{M_g}\left(\tau_g\,D_g^i+\mathbf{D}_{h_g}\right)\nabla\chi_g^i$$

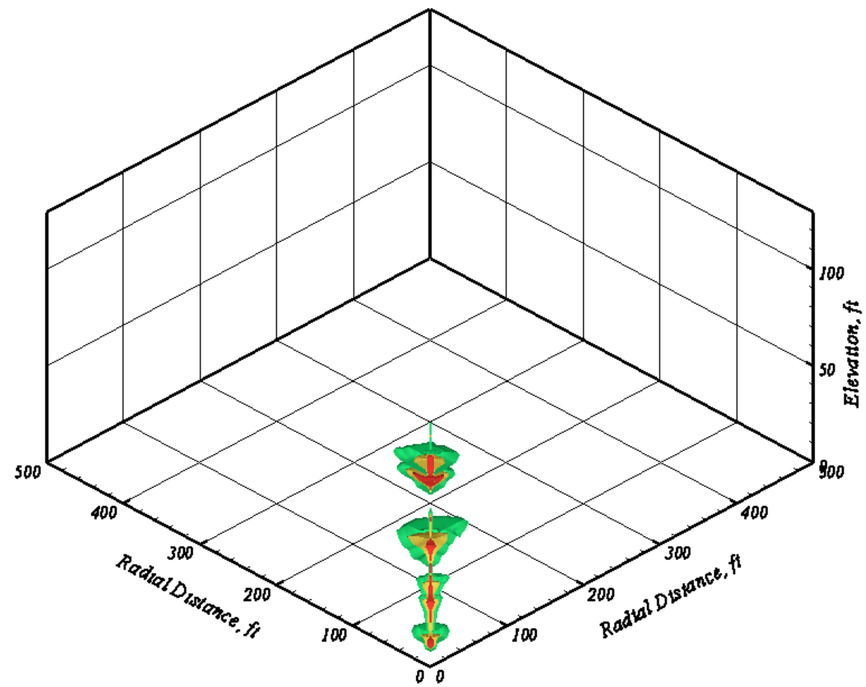


High-Pressure CO_2-Brine Systems

STOMP
Subsurface Transport Over Multiple Phases

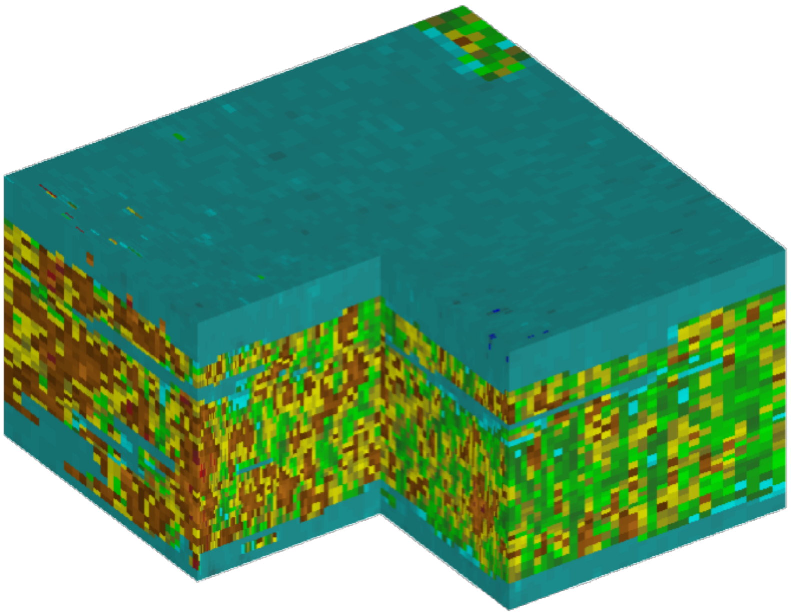
High-Pressure CO_2-Brine Systems: Example of Injection into Heterogeneous Domain

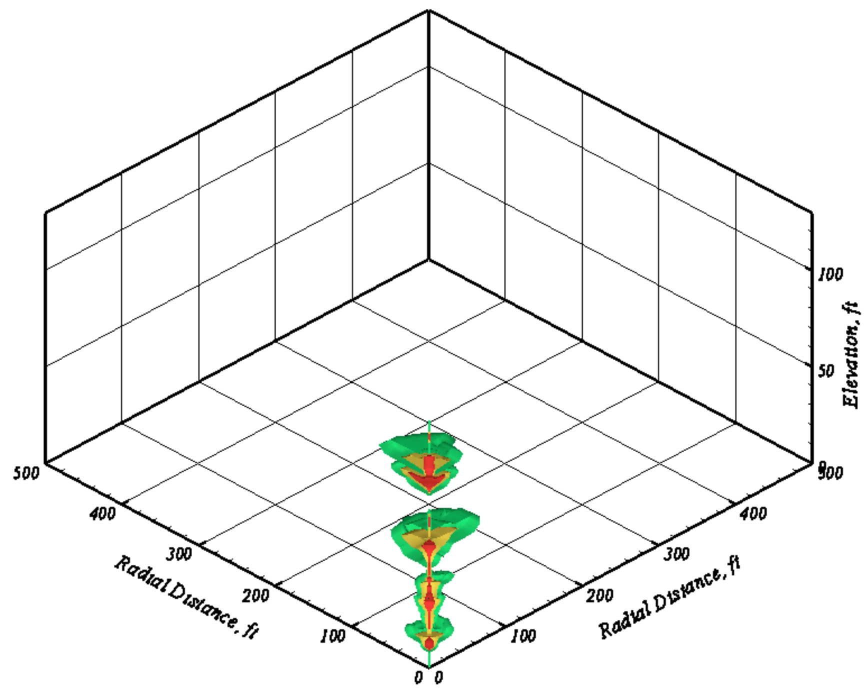




High-Pressure CO_2-Brine Systems: Example of Injection into Heterogeneous Domain

STOMP
Subsurface Transport Over Multiple Phases





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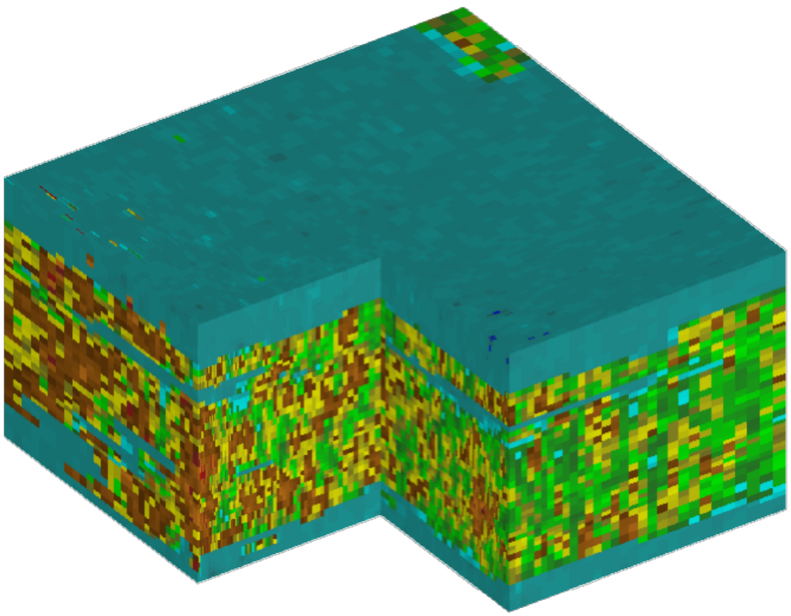
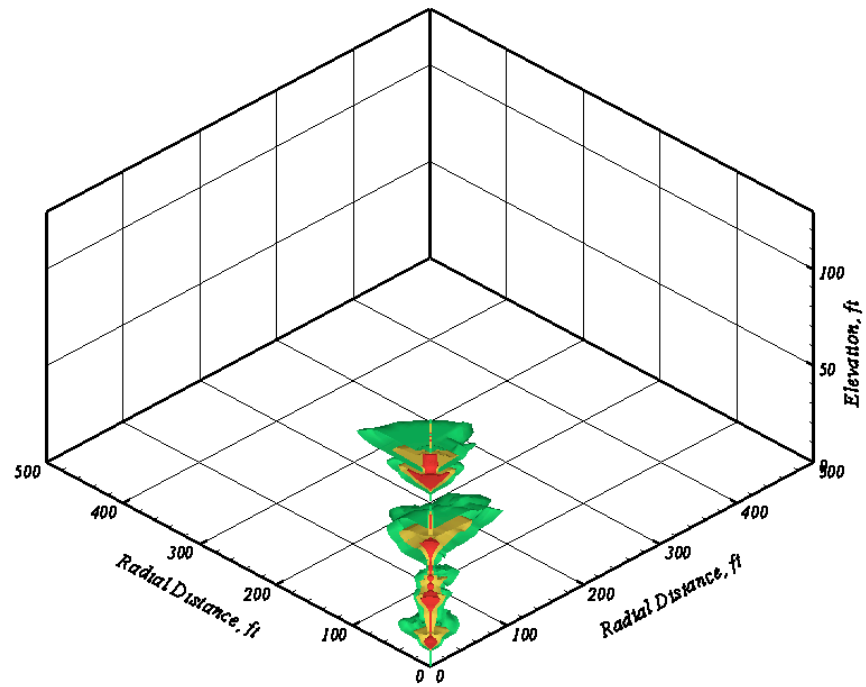
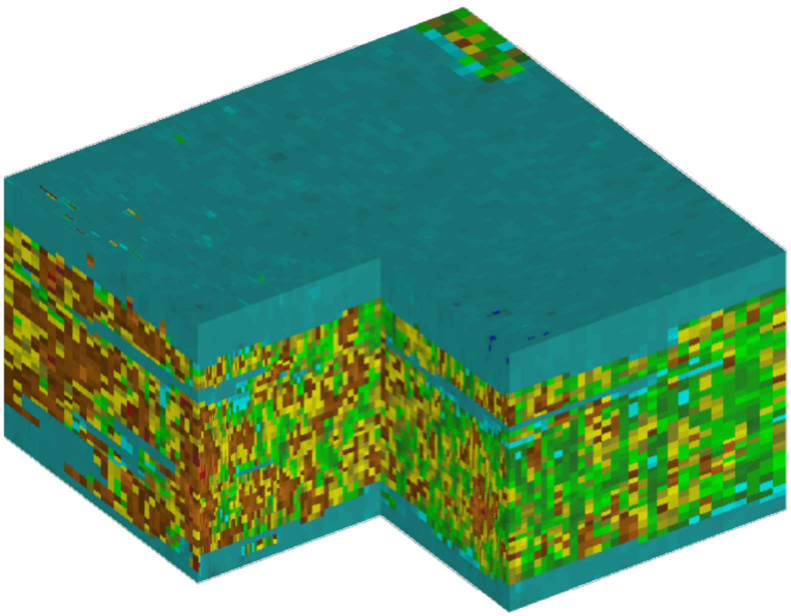
High-Pressure CO_2-Brine Systems: Example of Injection into Heterogeneous Domain

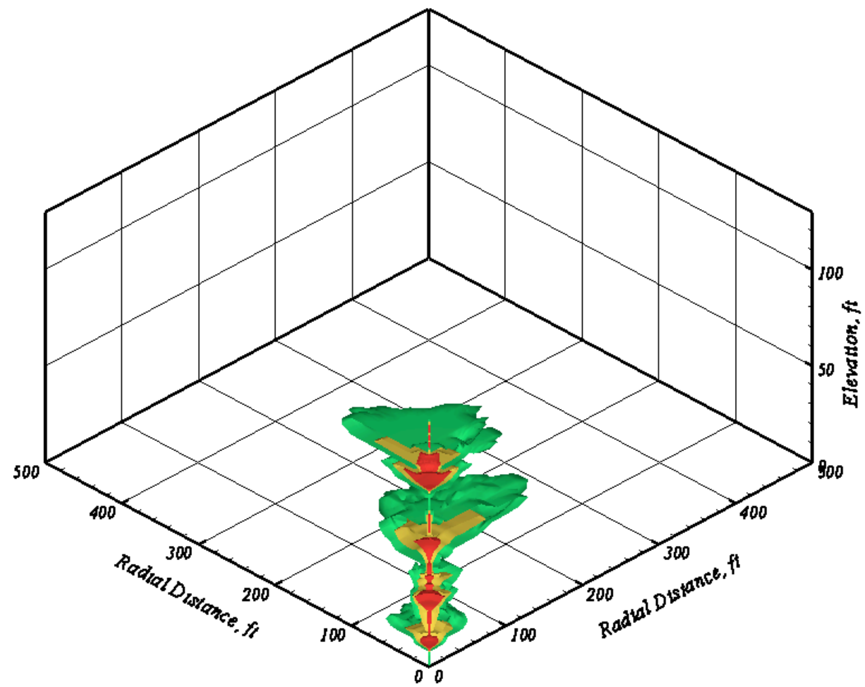




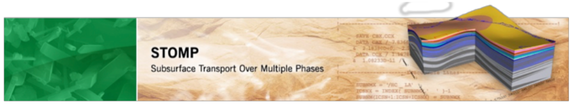
High-Pressure CO_2-Brine Systems: Example of Injection into Heterogeneous Domain

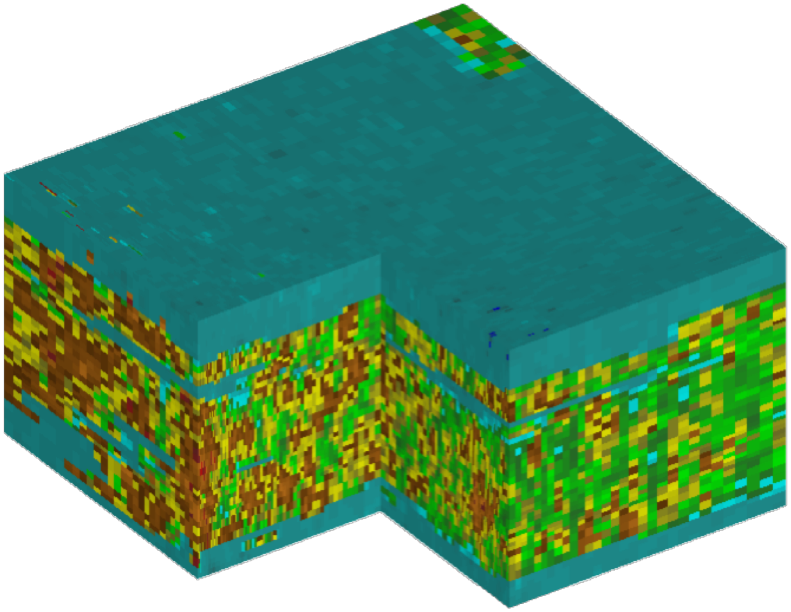
STOMP
Subsurface Transport Over Multiple Phases

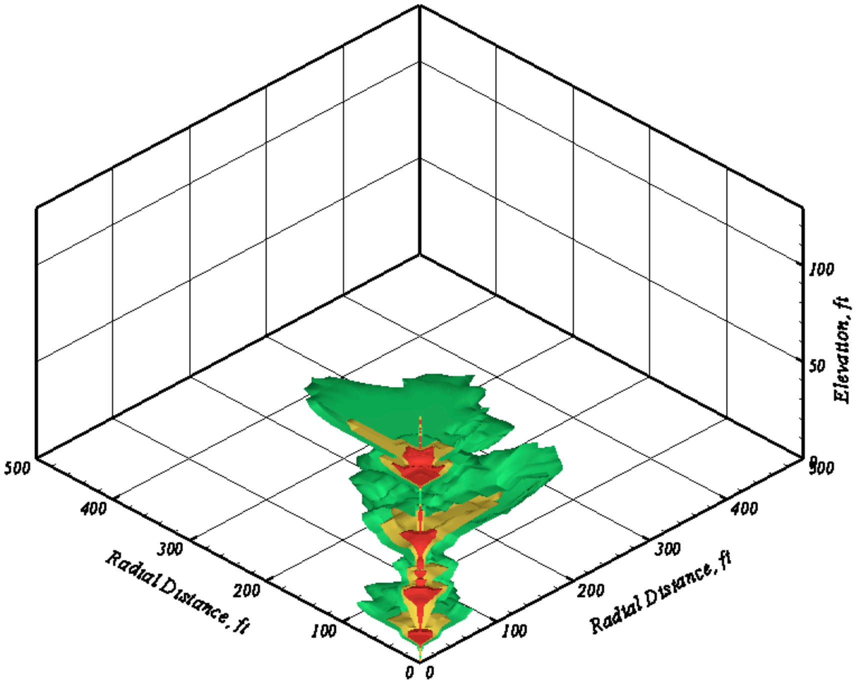




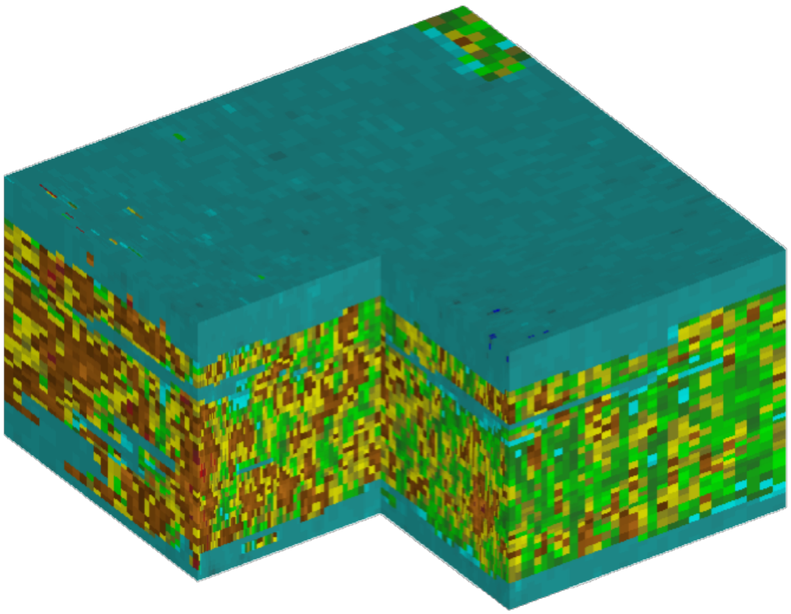
High-Pressure CO_2-Brine Systems: Example of Injection into Heterogeneous Domain

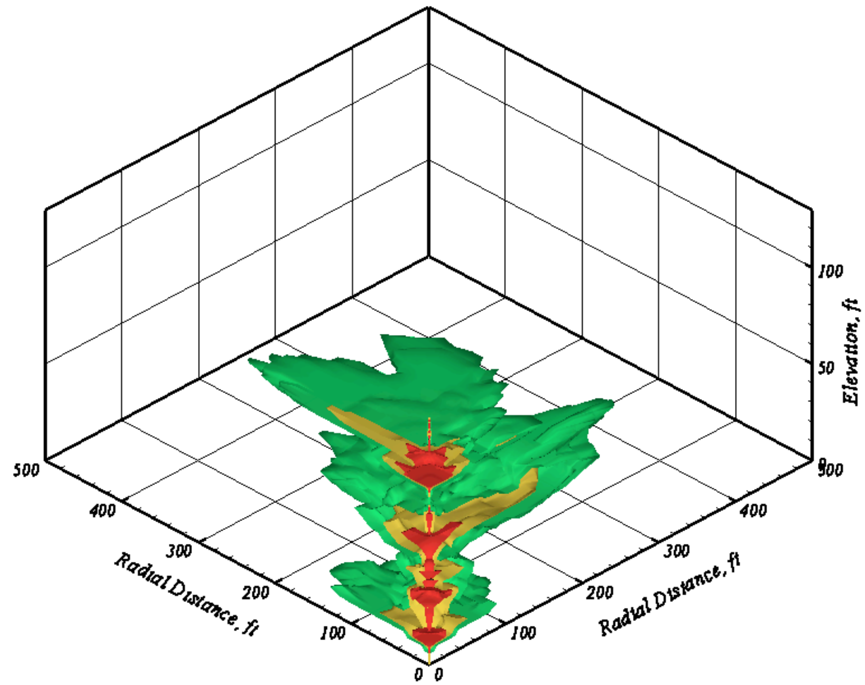




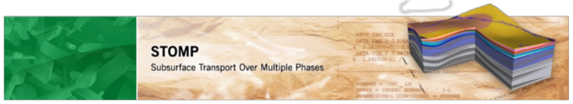


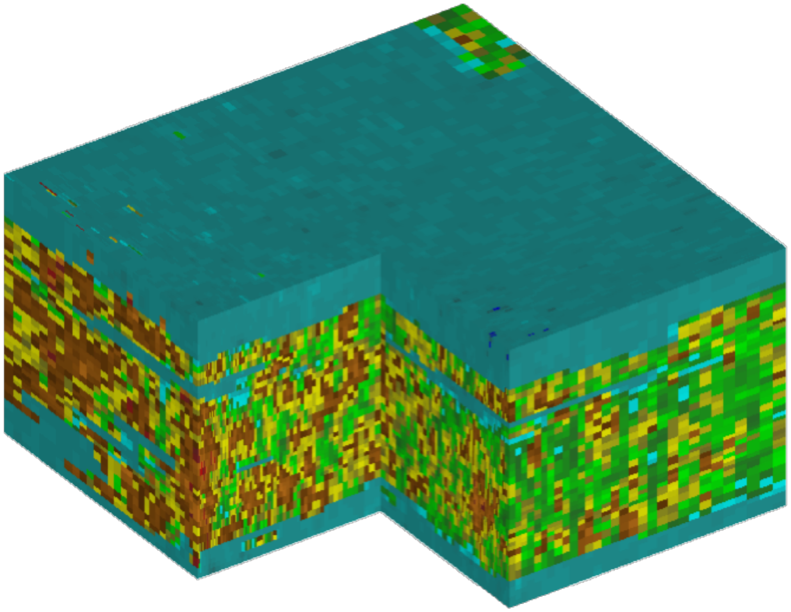
High-Pressure CO_2-Brine Systems: Example of Injection into Heterogeneous Domain

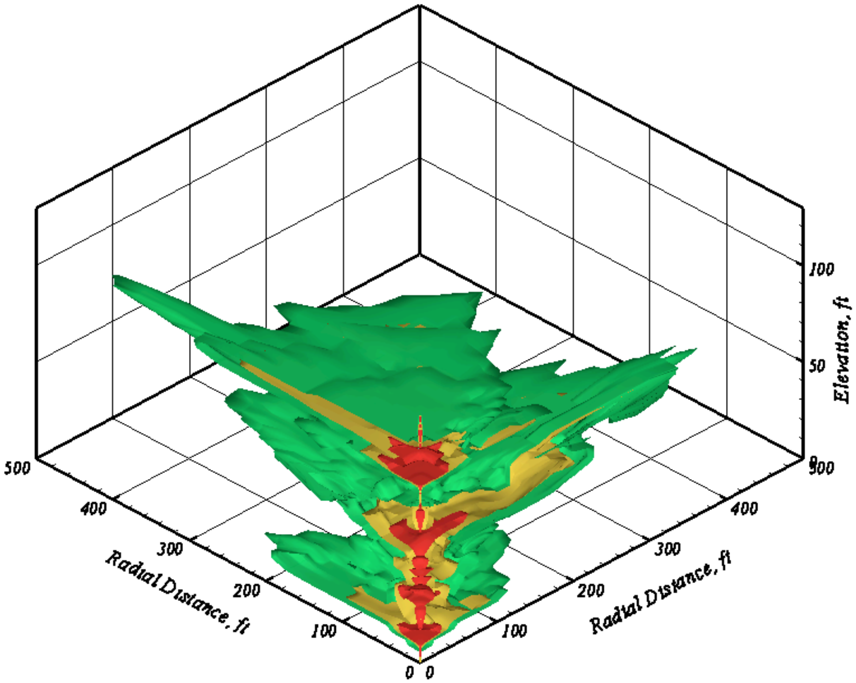




High-Pressure CO_2-Brine Systems: Example of Injection into Heterogeneous Domain







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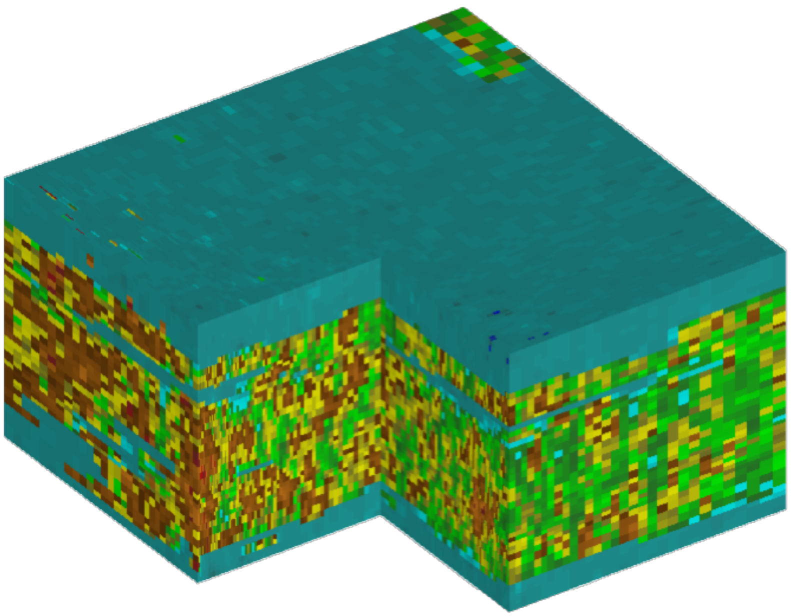
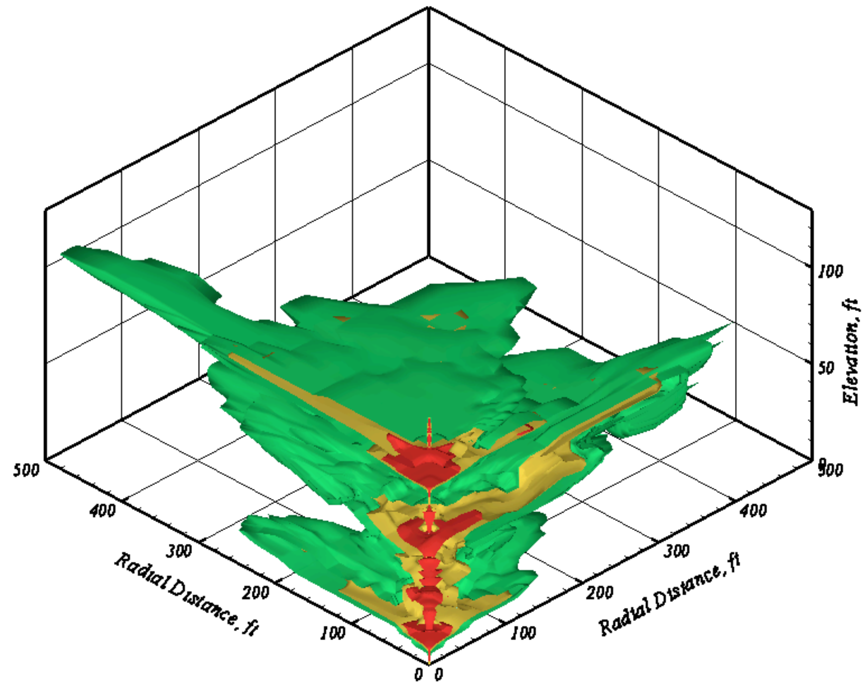
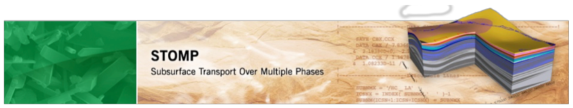
High-Pressure CO_2-Brine Systems: Example of Injection into Heterogeneous Domain



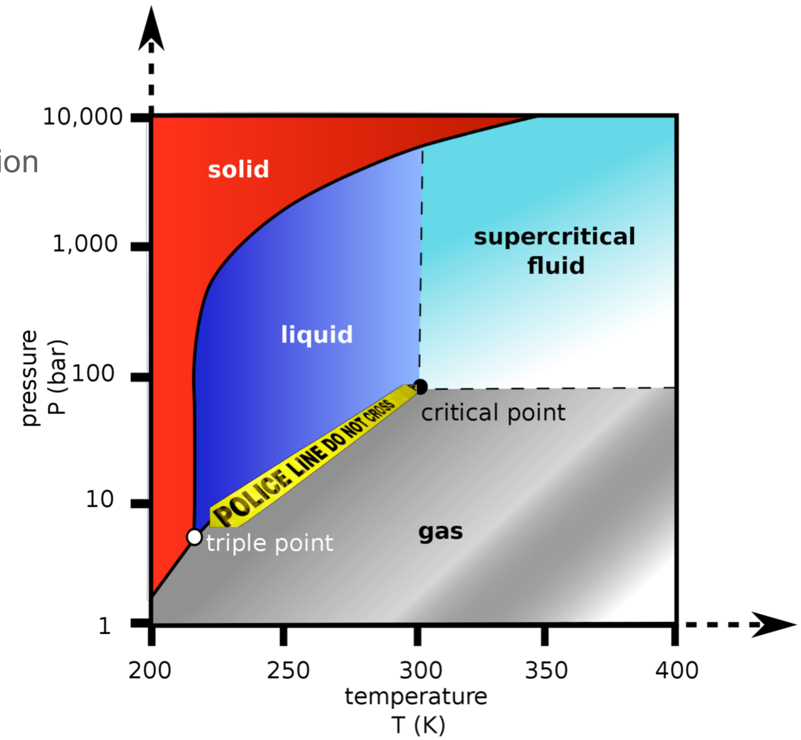


High-Pressure CO_2-Brine Systems: Phase Conditions



Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Aqueous CO_2 Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Salt Mass



High-Pressure CO_2-Brine Systems: Phase Conditions and Transitions

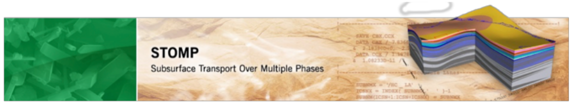
Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Aqueous CO_2 Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Salt Mass

```
PGA – CO2 partial pressure
PGW – water partial pressure
PG – gas pressure
PL – aqueous pressure
SG – gas saturation
SL – aqueous saturation

PGA = FUNC( XMLA )
PGW = FUNC( T,PCAP )
PG = PGW + PGA
PCAP = PG – PL
SL = FUNC( PCAP )
SG = 1.D+0 – SL
IF( SG > 1.D-3 ) NPHAZ = 2
```

High-Pressure CO_2-Brine Systems: Phase Conditions and Transitions



Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Aqueous CO2 Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Salt Mass

```
PG – gas pressure
PL – aqueous pressure
ASL – apparent aqueous sat.
SGT – trapped gas sat.

PCAP = PG – PL
ASL = FUNC( PCAP )
IF( ASL == 0 && SGT == 0 )
NPHAZ = 1
```

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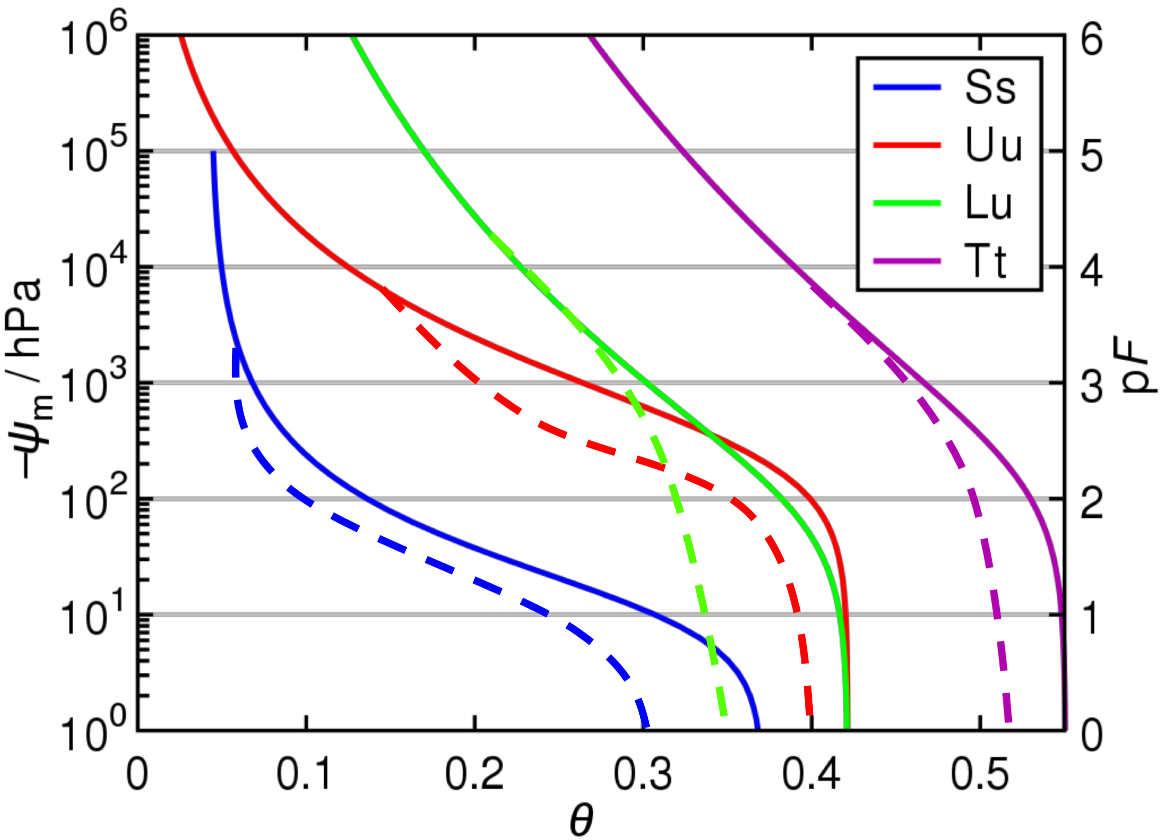
High-Pressure CO_2-Brine Systems: Phase Conditions and Transitions

Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Aqueous CO2 Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Salt Mass

```
PG – gas pressure
PL – aqueous pressure
ASL – apparent aqueous sat.
SGT – trapped gas sat.

PCAP = PG – PL
ASL = FUNC( PCAP )
IF( ASL == 0 && SGT > 0 )
NPHAZ = 3
```

Low-Pressure Air-Water Systems: Phase Conditions and Transitions



Ss – sand

Uu – silt or clay loam

LU – loam-silt or clay

Tt – clay or peat

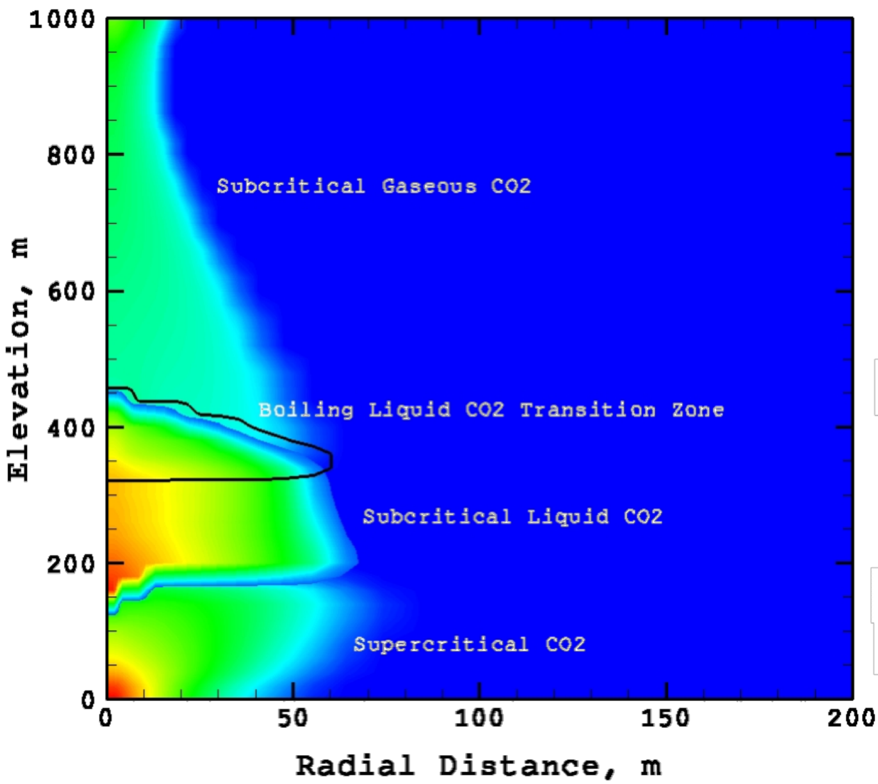
High-Pressure CO_2-Brine Systems: Phase Conditions and Transitions

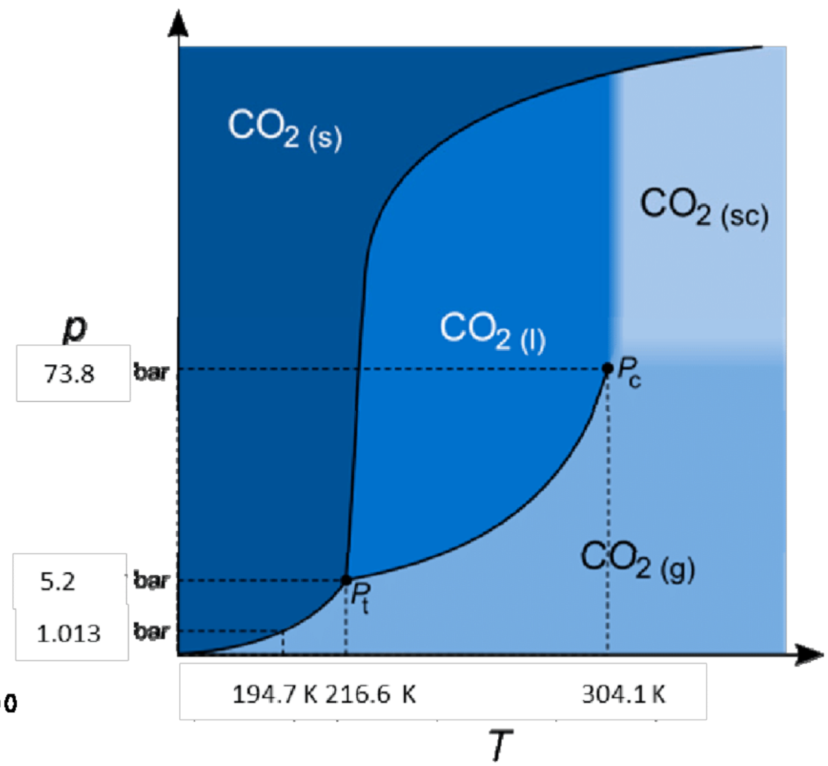
Phase Conditions

1. Saturated without Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Aqueous CO_2 Mole Fraction
   - Salt Mass – Total Brine Mass Fraction
2. Partially Saturated
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Total Brine Mass Fraction
3. Saturated with Trapped Gas
   - Energy – Temperature
   - Water Mass – Aqueous Pressure
   - CO_2 Mass – Trapped Gas Saturation
   - Salt Mass – Total Brine Mass Fraction
4. Fully Unsaturated
   - Energy – Temperature
   - Water Mass – Water Vapor Partial Pressure
   - CO_2 Mass – Gas Pressure
   - Salt Mass – Salt Mass

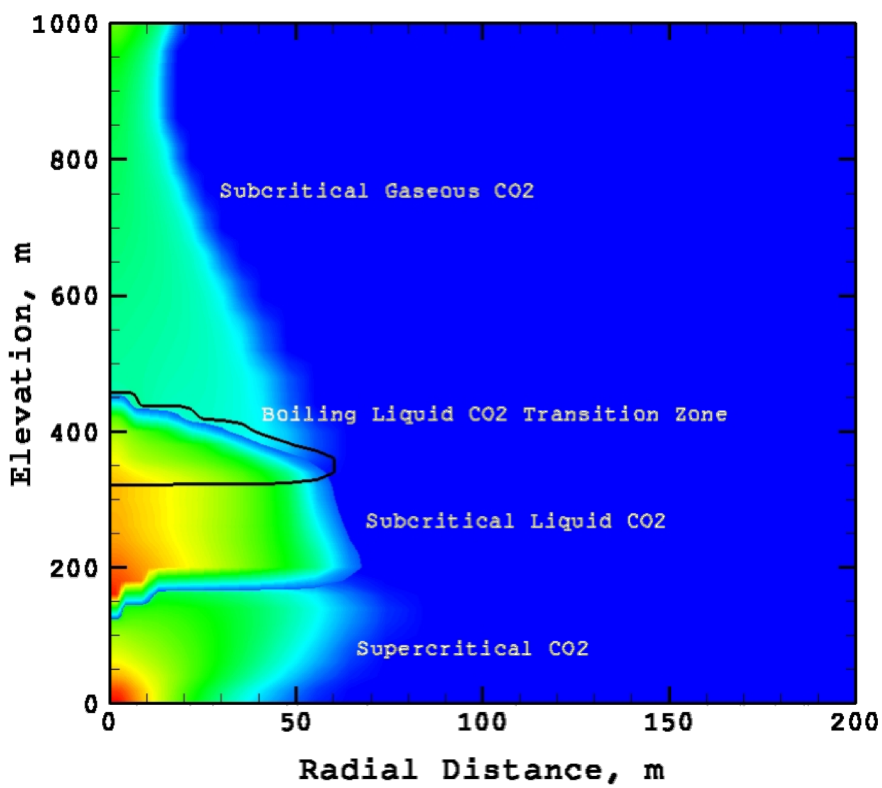
```
PG – gas pressure
PL – aqueous pressure
ASL – apparent aqueous sat.
SL – aqueous saturation
SGT – trapped gas sat.

PCAP = PG – PL
ASL = FUNC( PCAP )
SL = ASL - SGT
IF( SL == 0 ) NPHAZ = 4
```

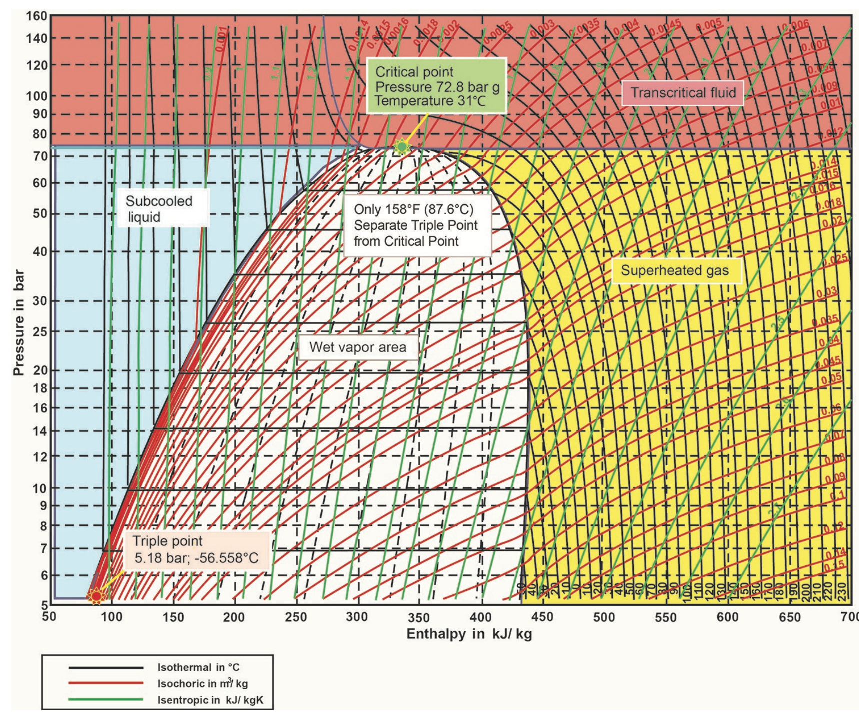
Leakage of CO_2 from Deep Reservoirs to the Ground Surface



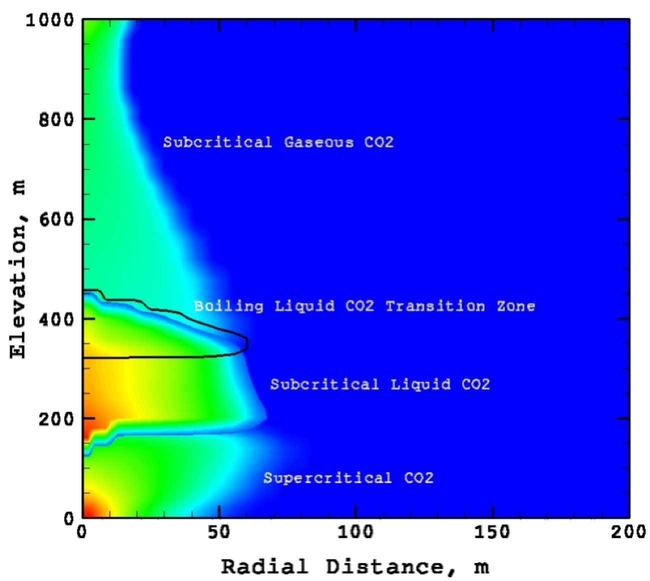


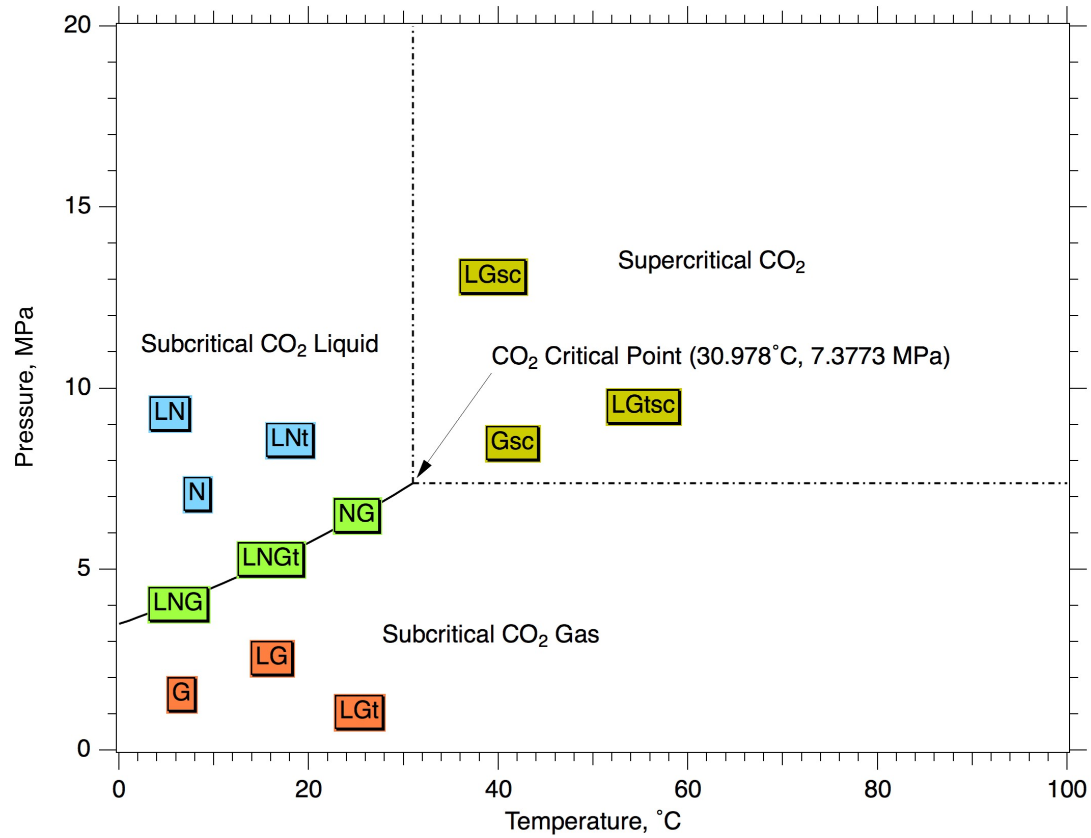
Leakage of CO_2 from Deep Reservoirs to the Ground Surface





Three-Phase System for CO_2 Migration through the Subsurface: Phase Condition Mapping

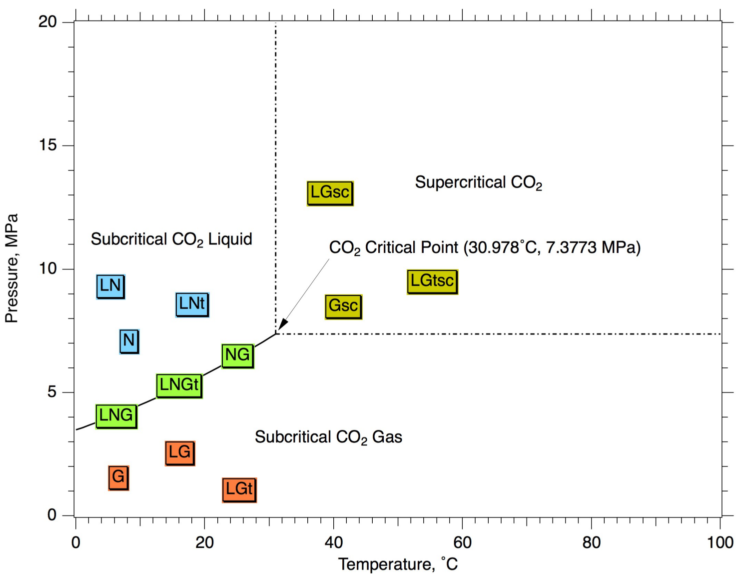




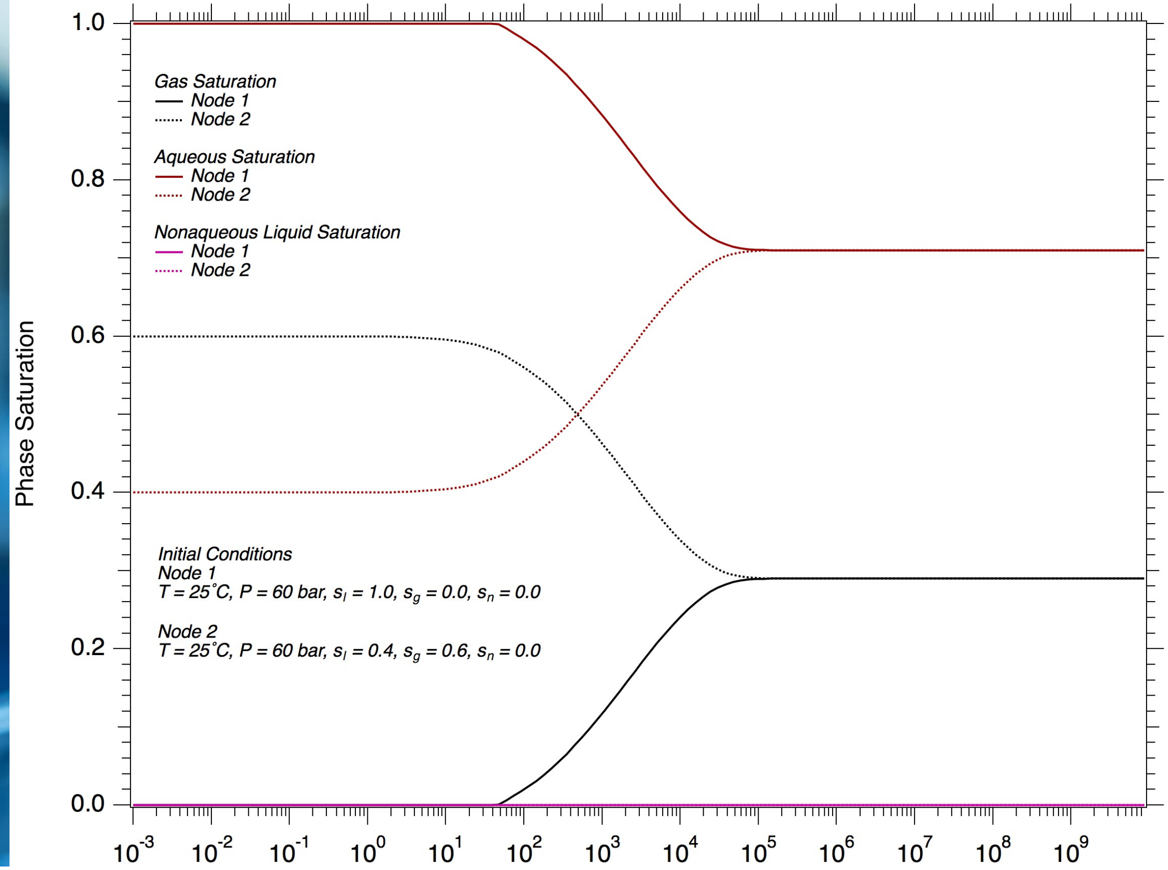
Three-Phase System for CO_2 Migration through the Subsurface: Phase Conditions and Primary Variables

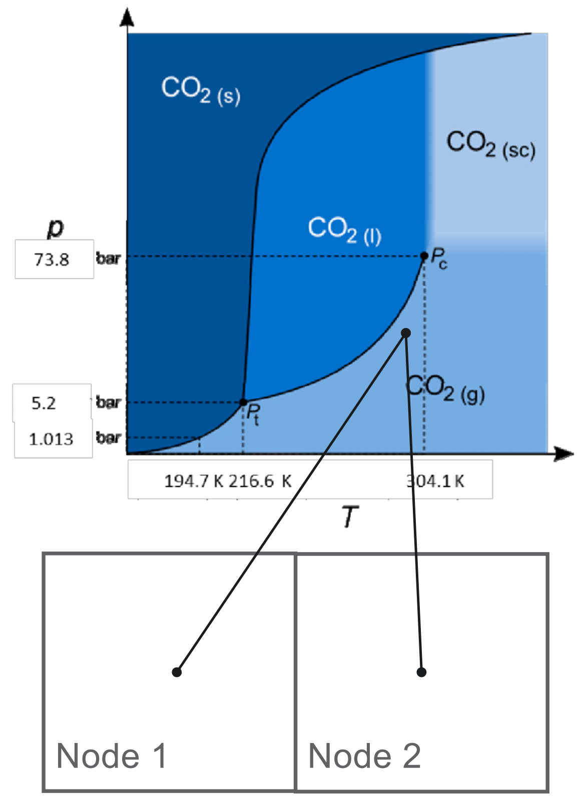
Table 1. STOMP-SEQ primary variable switching scheme.

Phase Condition	Energy Equation	Water Mass Equation	CO_2 Mass Equation	Salt Mass Equation
L	T	P_ℓ	ω_ℓ^C	y_ℓ^S
G	T	P_v^W	P_g	T_m^S
Gsc	T	P_v^W	P_g	T_m^S
N	T	P_v^W	P_n	T_m^S
LG	T	P_ℓ	P_g	y_ℓ^S
LGt	T	P_ℓ	s_{gt}	y_ℓ^S
LGsc	T	P_ℓ	P_g	y_ℓ^S
LGtsc	T	P_ℓ	s_{gt}	y_ℓ^S
LN	T	P_ℓ	P_n	y_ℓ^S
LNt	T	P_ℓ	s_{nt}	y_ℓ^S
NG	T	P_v^W	β	T_m^S
LNG	T	P_ℓ	β	y_ℓ^S
LNGt	T	$s_{gt} + s_{nt}$	β	y_ℓ^S



Code Validation via False Transients to Equilibrium Conditions





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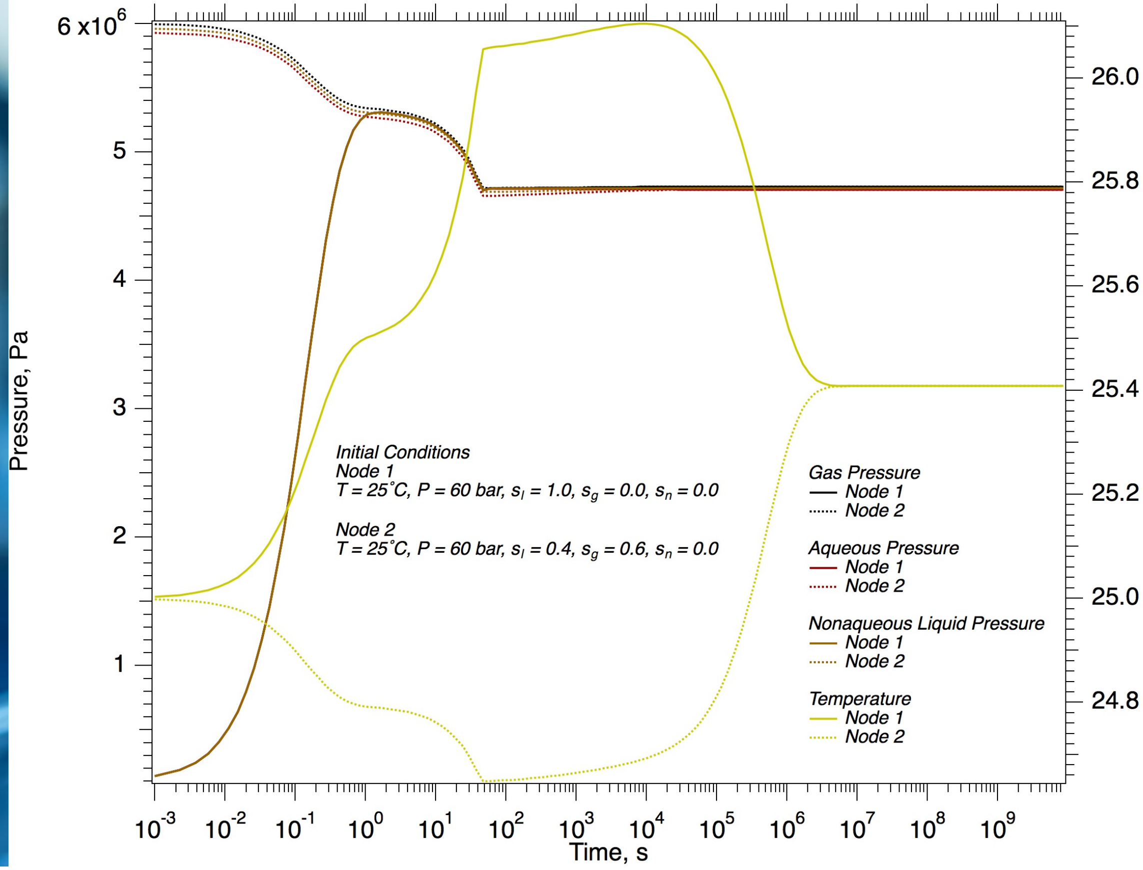

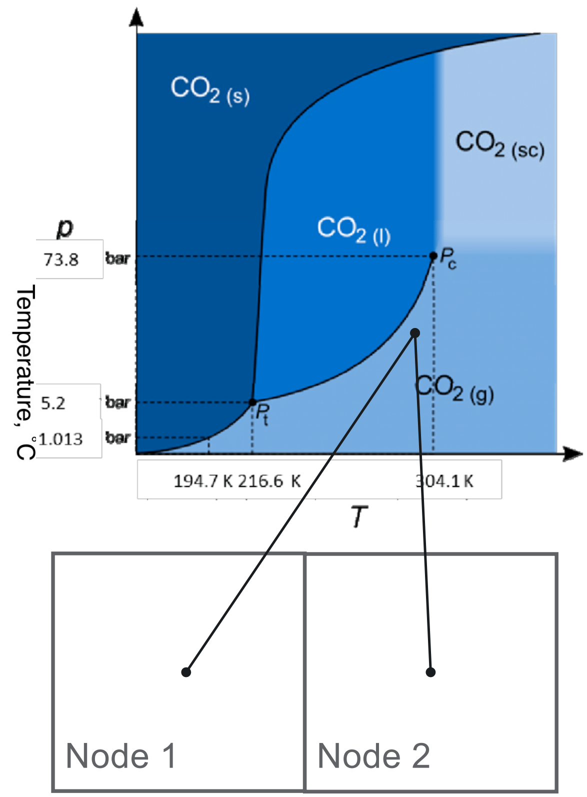

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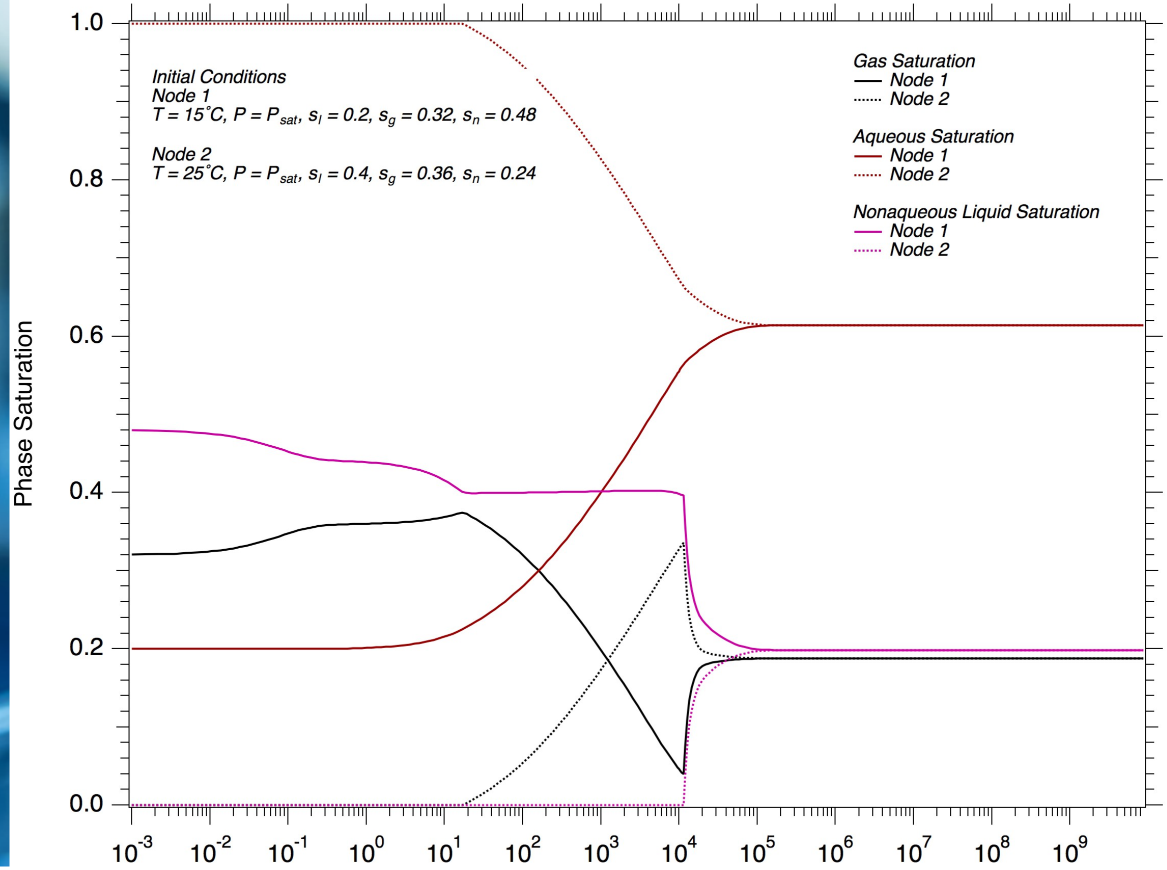

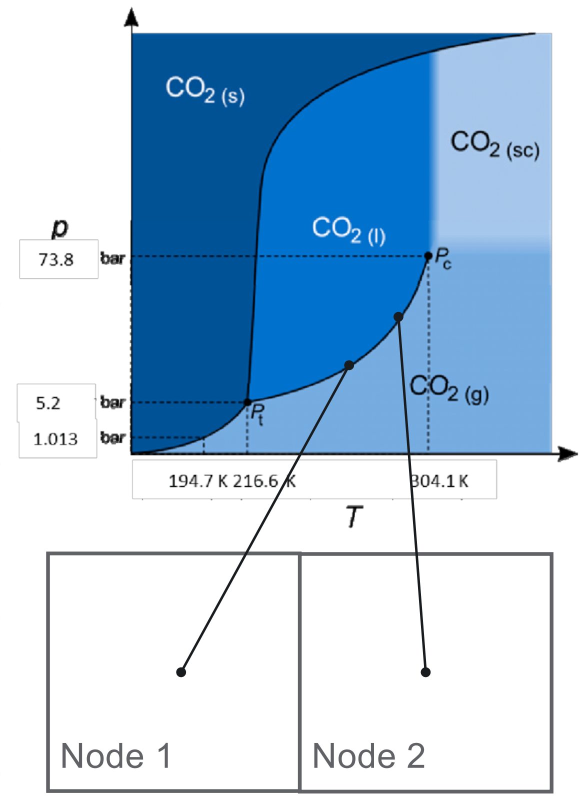

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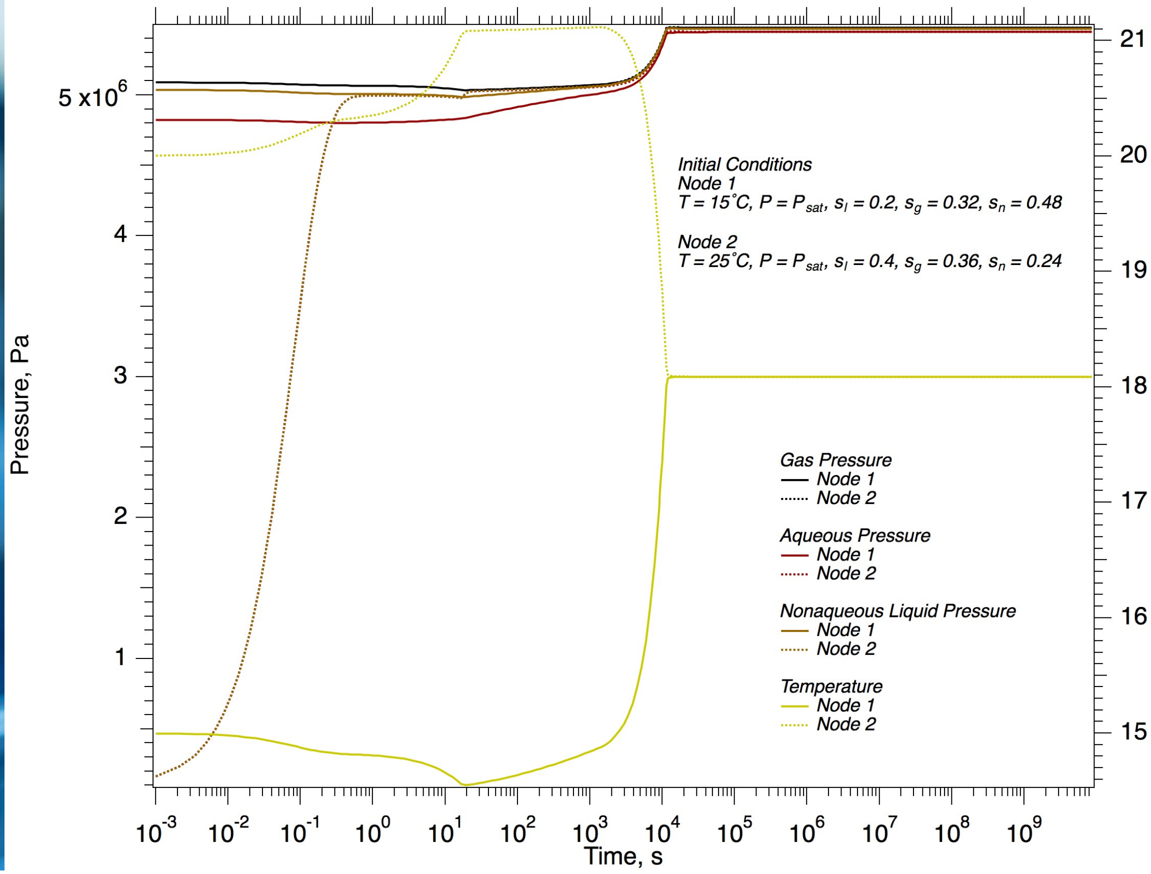

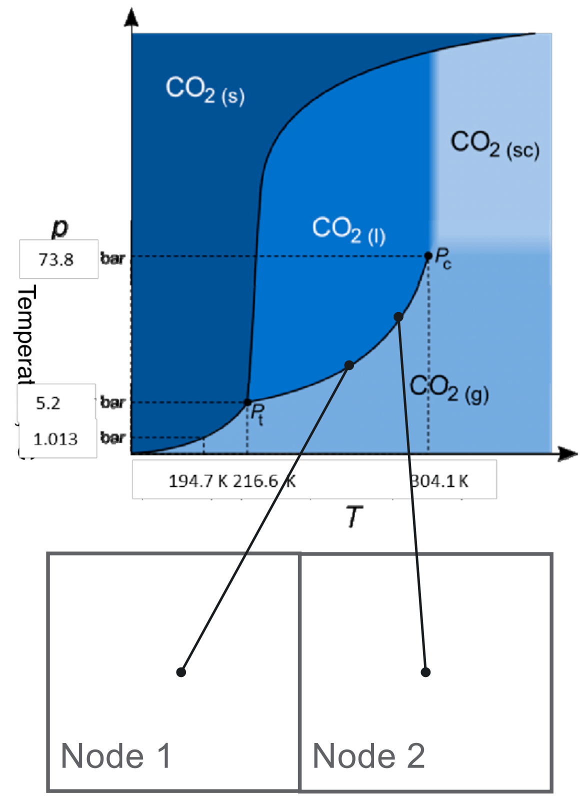

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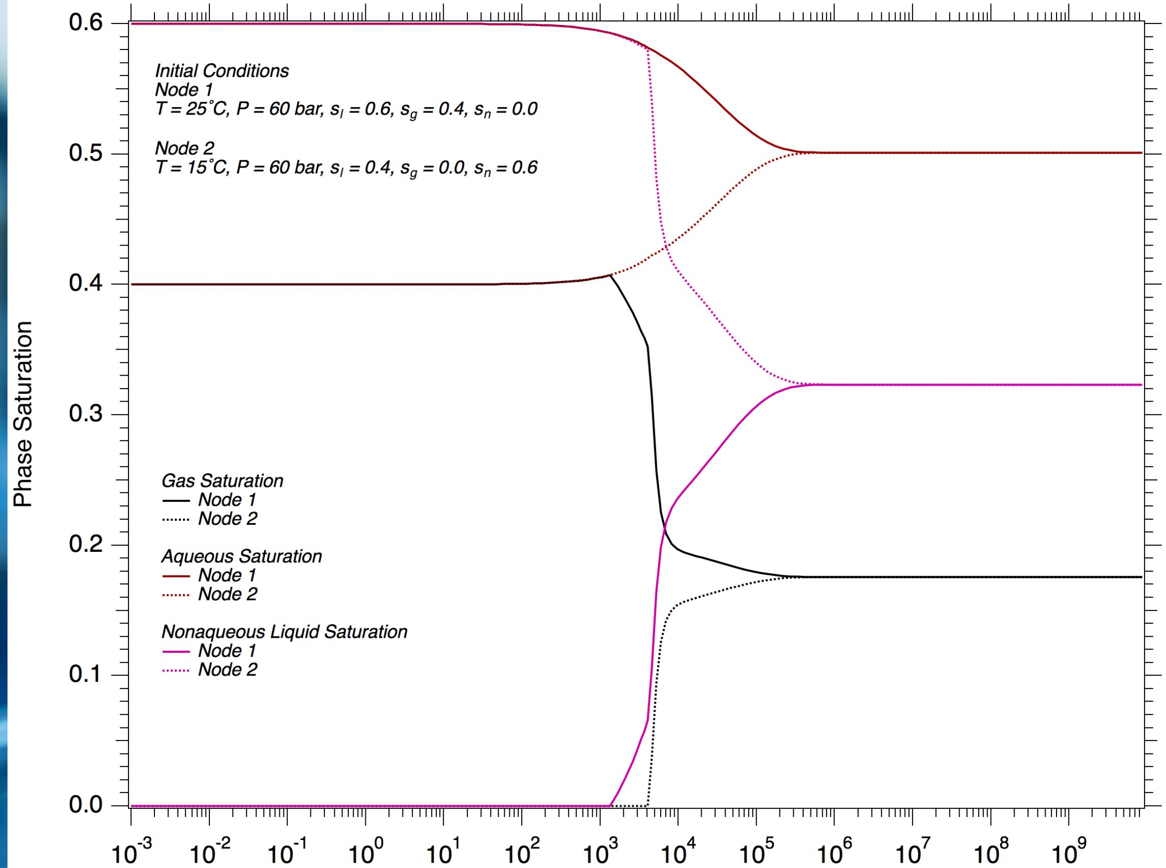

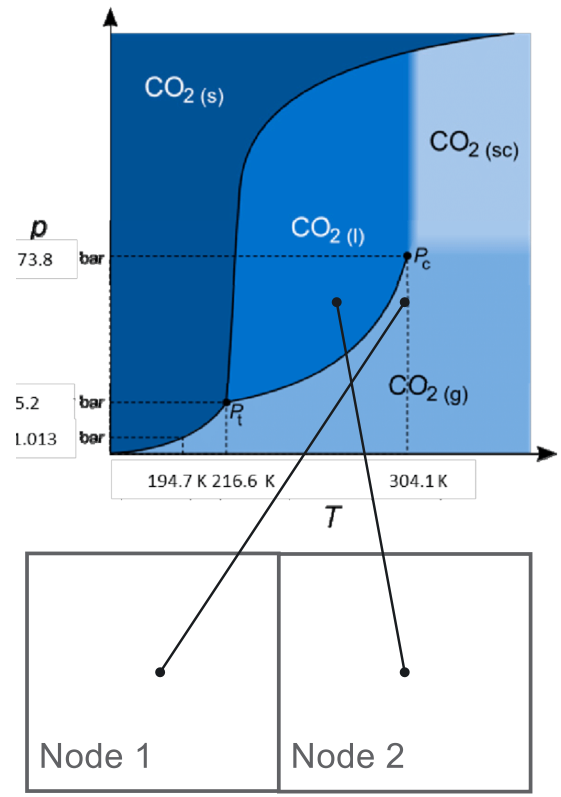

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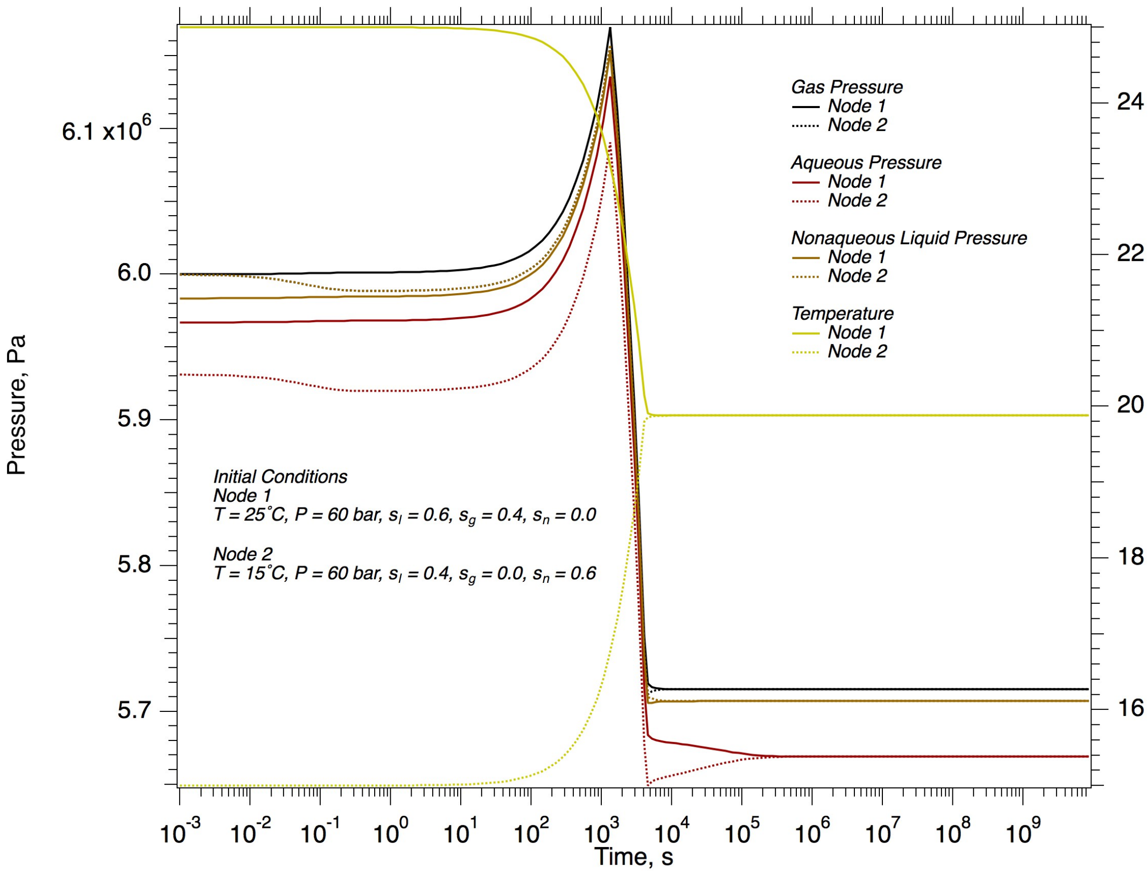
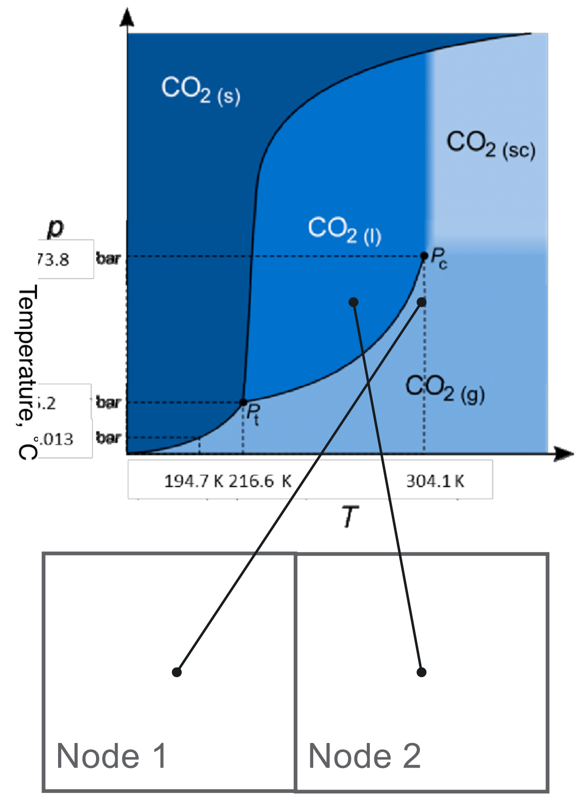


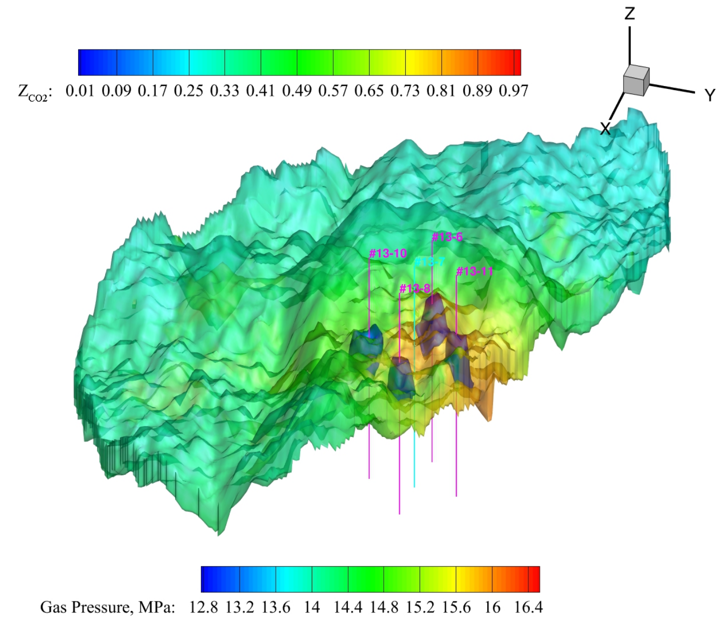


Three-Phase System for Enhanced Oil Recovery: Basics

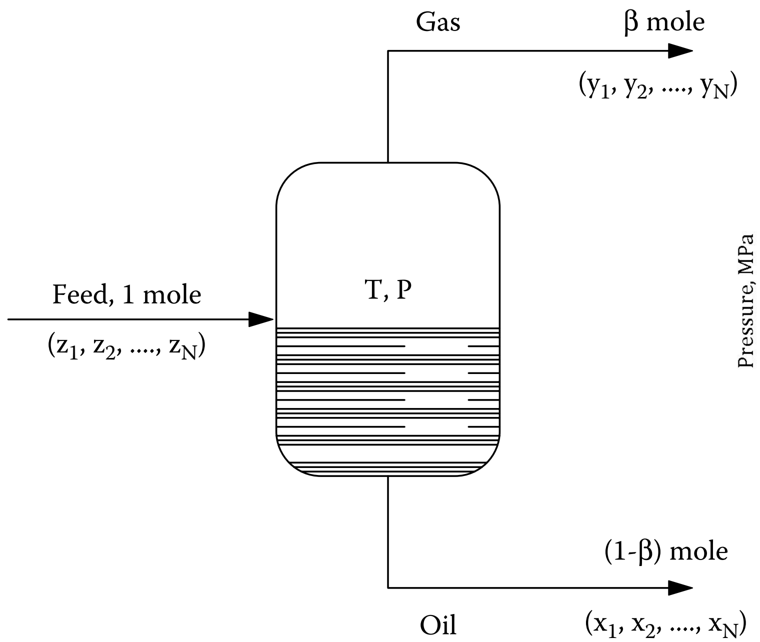
- Mobile phases
  - Aqueous (water, CO_2, salt)
  - Nonaqueous liquid (CO_2, CH_4, n-petroleum components)
  - Gas (CO_2, CH_4, n-petroleum components)

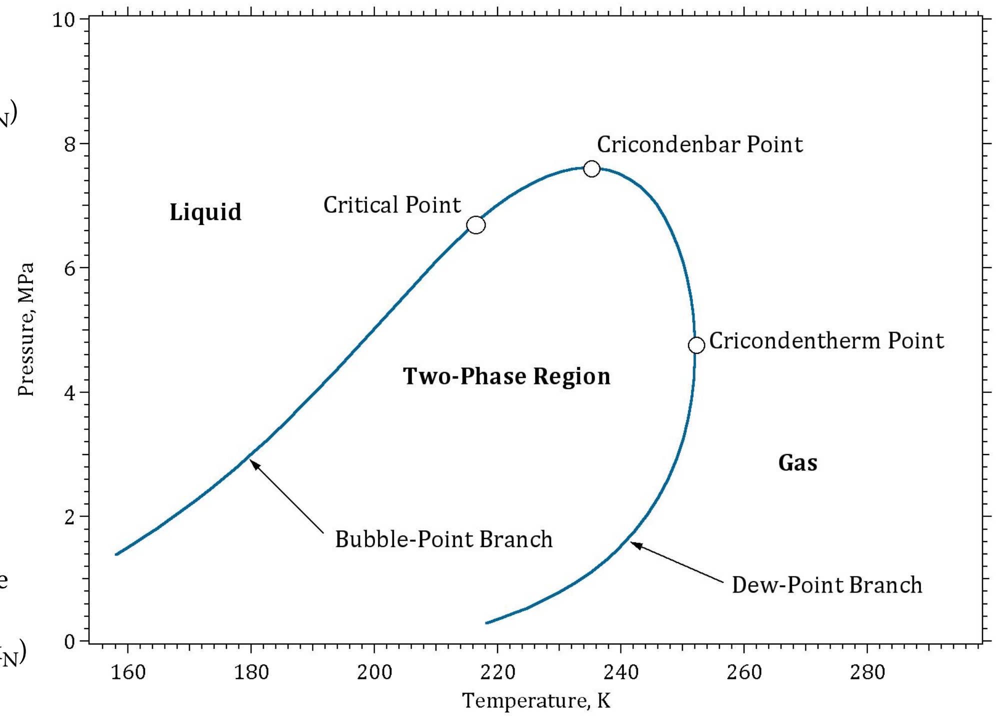
- Phase equilibria from cubic equation of state
  - Peng-Robinson
  - Soave-Redlich-Kwong

- Phase properties
  - Cubic equation of state
  - Corresponding state method
  - Empirical correlations



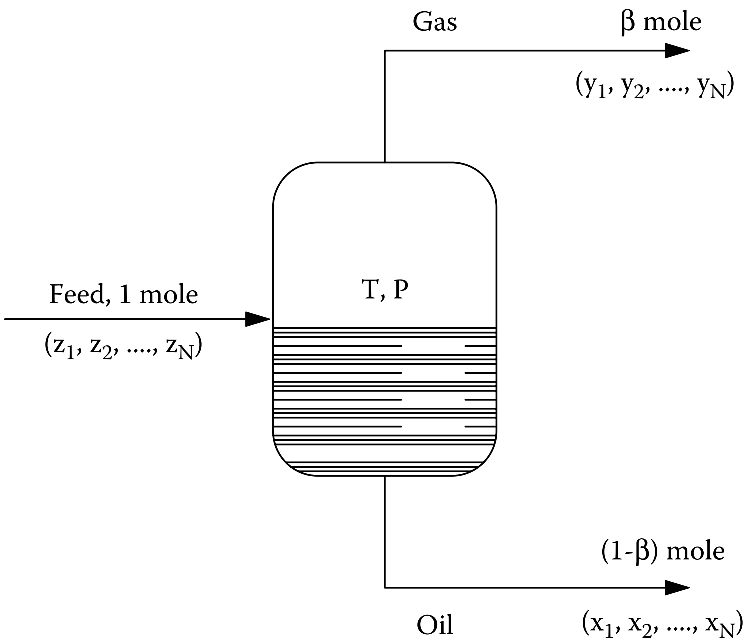
Three-Phase System for Enhanced Oil Recovery: Phase Equilibria

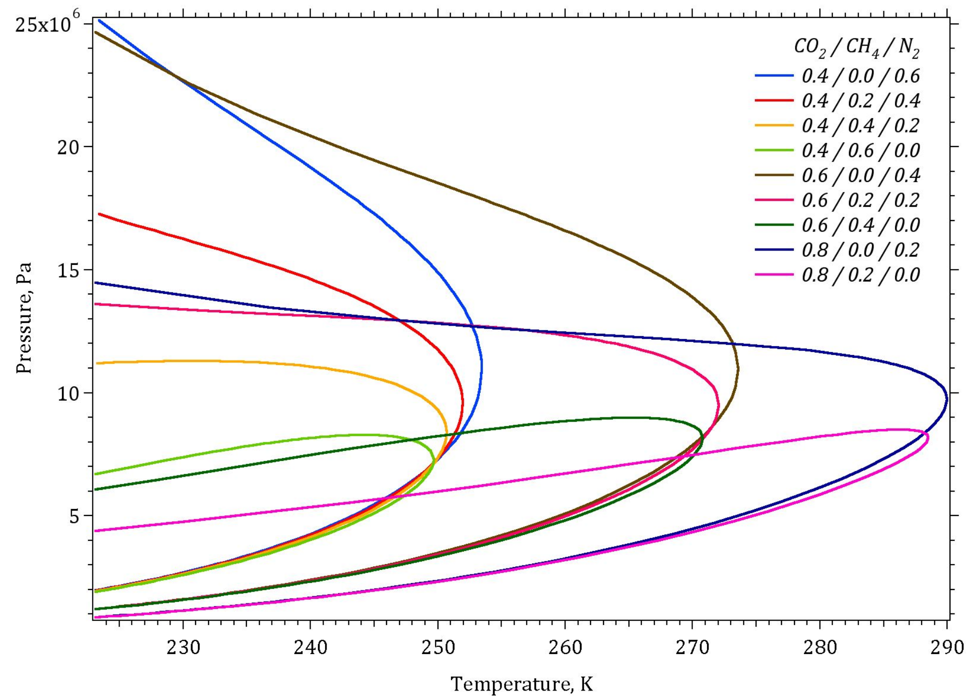




Source: Pedersen, K. S., and P. L. Christensen. 2007. *Phase Behavior of Petroleum Reservoir Fluids*. CRC Taylor & Francis, New York.

Three-Phase System for Enhanced Oil Recovery: Phase Equilibria





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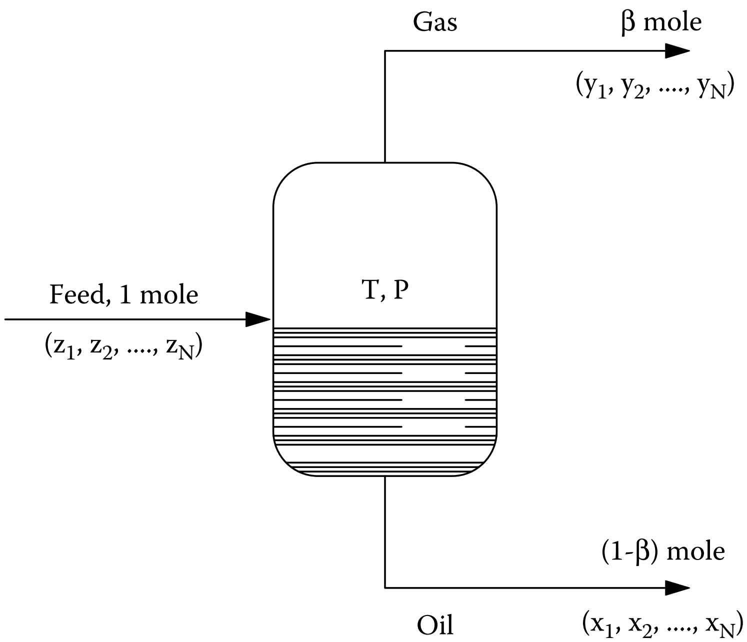
Three-Phase System for Enhanced Oil Recovery: Michelsen Reference



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Phase equilibrium calculations. What is easy and what is difficult?

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Abstract

Calculation of phase equilibrium for a mixture of given composition requires specification of two process variables, typically chosen among the following: Temperature, pressure, vapour fraction, enthalpy, entropy or volume. The difficulties associated with solving the equilibrium equations are strongly related to the chosen selection of these process variables. The aim of the present paper is to outline the characteristics associated with the different types of specification in order to provide guidelines for efficient and robust solution algorithms.

Three-Phase System for Enhanced Oil Recovery: Phase Conditions and Primary Variables

- State #1 (aqueous saturated)

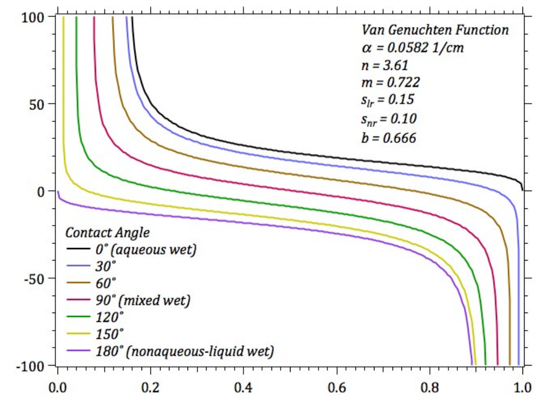
$$T,\ P_l,\ \omega_l^{CO_2},\ m^{CH_4},\ m^i,\ \omega_l^{salt}\ \ for\ \ i = 3,n$$

- State #2 (aqueous + nonaqueous)

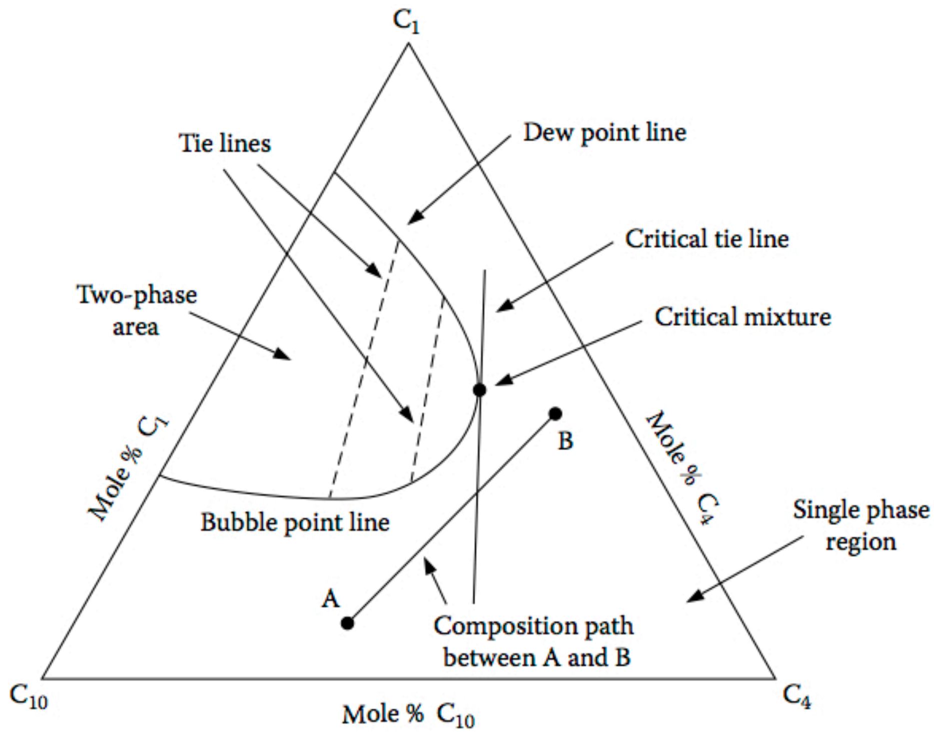
$$T,\ P_l,\ P_{ng},\ \chi_t^{CO_2},\ \chi_t^{CH_4},\ \chi_t^i,\ \omega_l^{salt}\ \ for\ \ i = 3,n-1$$

- State #3 (nonaqueous saturated)

$$T,\ m^{water},\ P_{ng},\ \chi_t^{CO_2},\ \chi_t^{CH_4},\ \chi_t^i,\ m^{salt}\ \ for\ \ i = 3,n-1$$



Three-Phase System for Enhanced Oil Recovery – First Contact



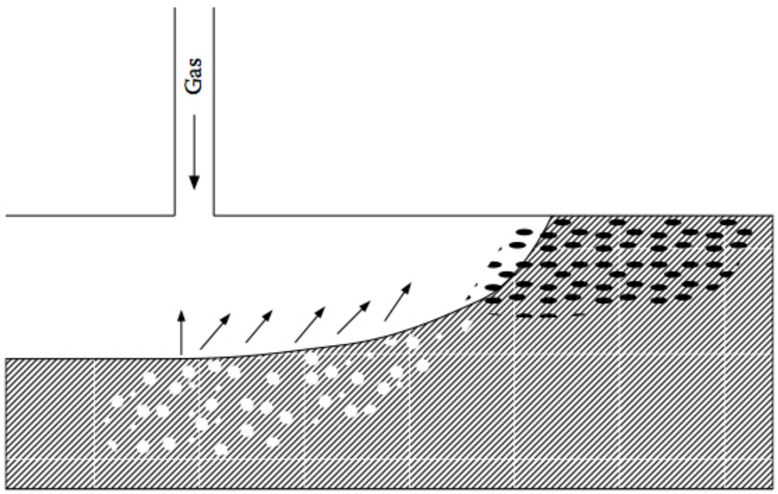
Source: Pedersen, K. S., and P. L. Christensen. 2007. *Phase Behavior of Petroleum Reservoir Fluids*. CRC Taylor & Francis, New York.

A – Composition of Oil

B – Composition of Gas

Fixed temperature & pressure

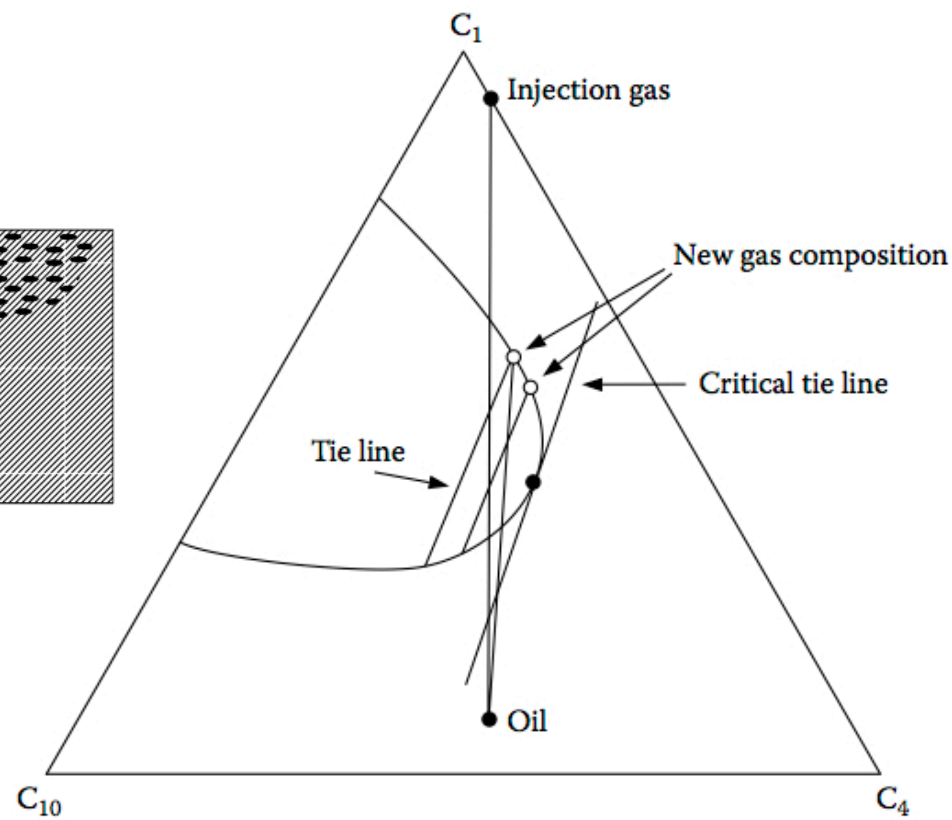
Three-Phase System for Enhanced Oil Recovery – Vaporization Drive



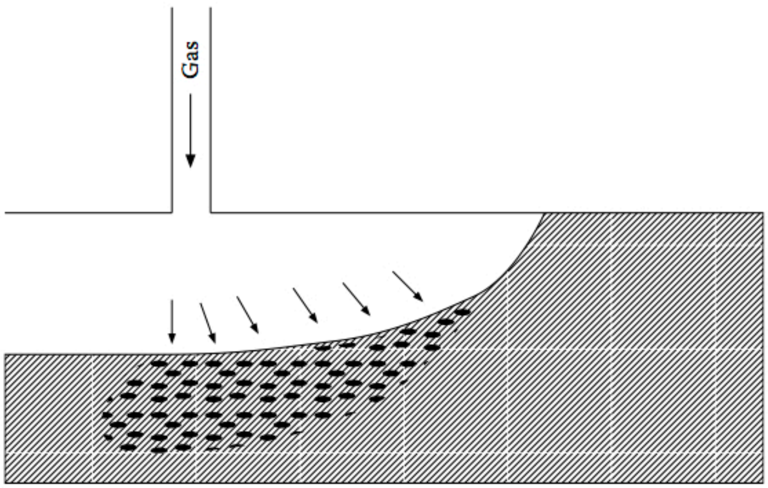
A – Composition of Oil

B – Composition of Gas

Fixed temperature & pressure



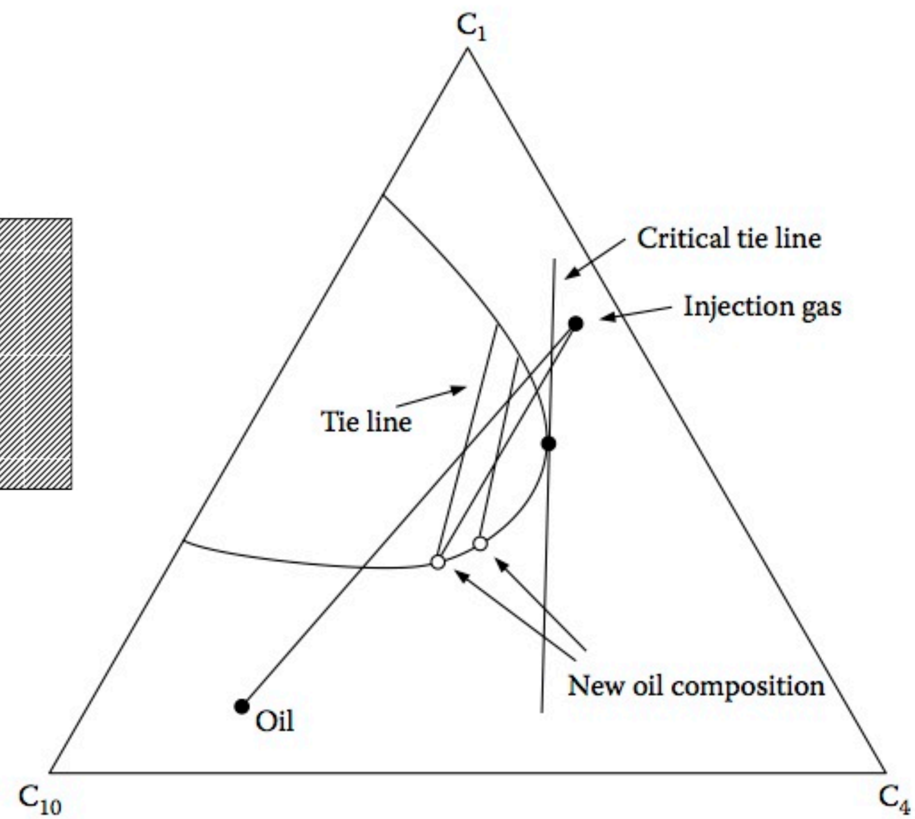
Three-Phase System for Enhanced Oil Recovery – Condensing Drive



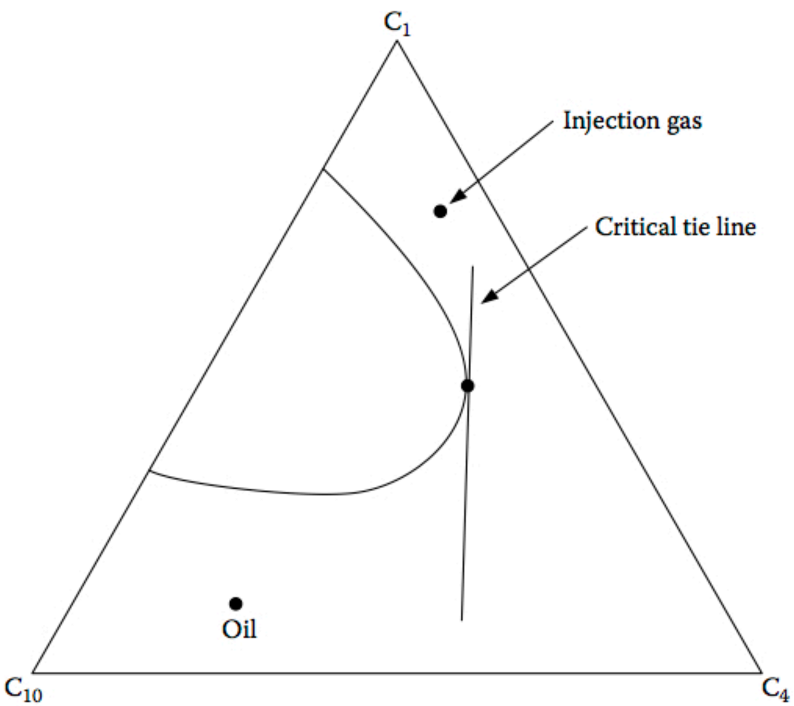
A – Composition of Oil

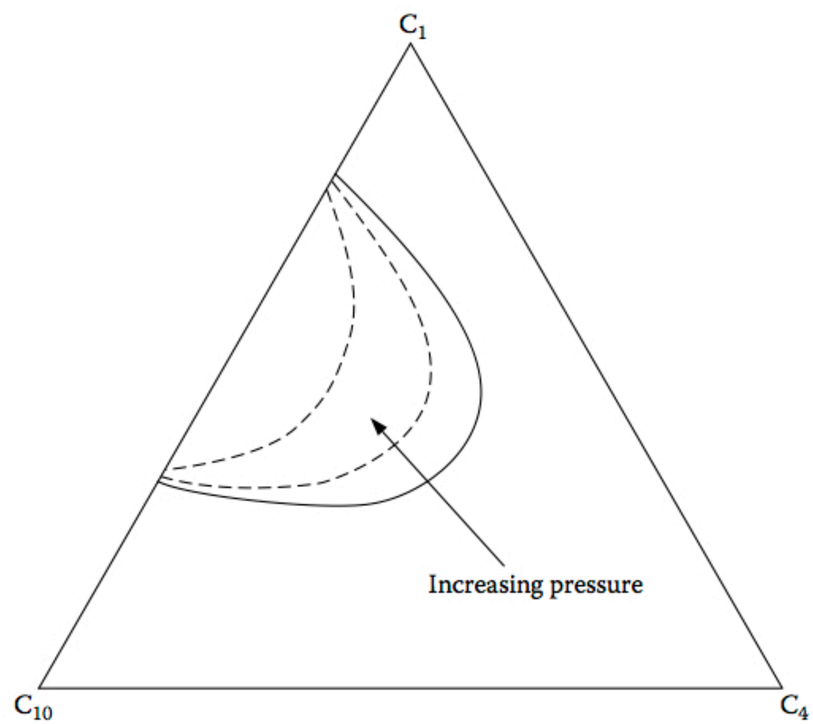
B – Composition of Gas

Fixed temperature & pressure

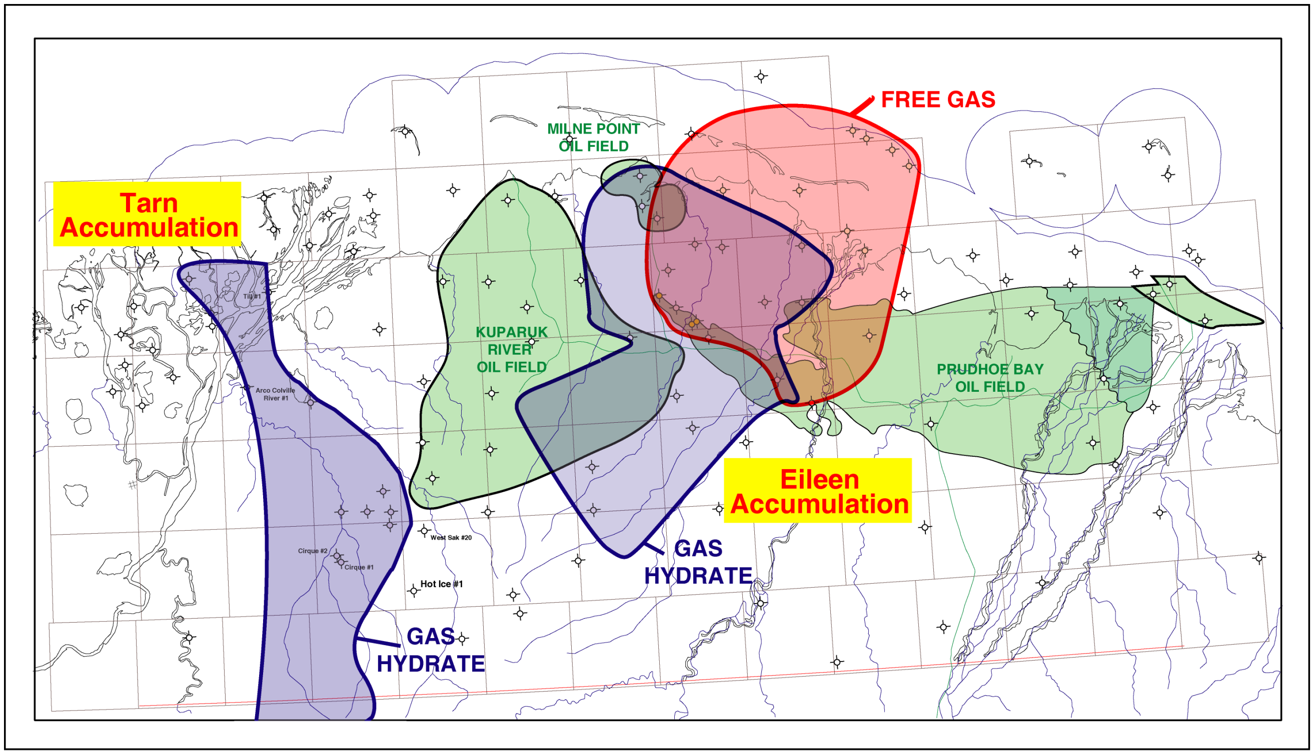


Three-Phase System for Enhanced Oil Recovery – Miscibility & Pressure





Gas Hydrate Systems



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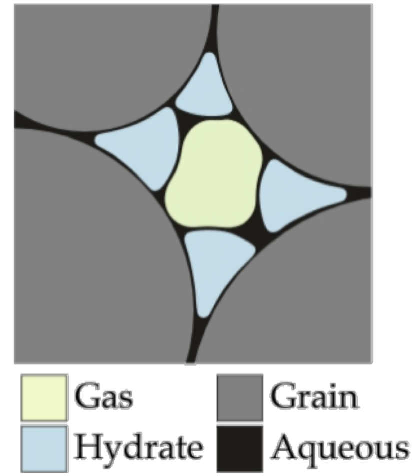
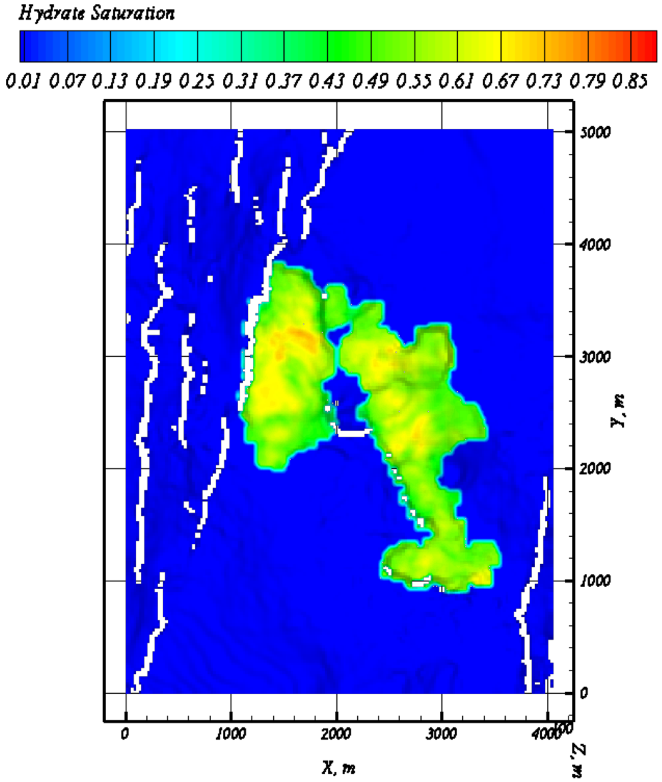
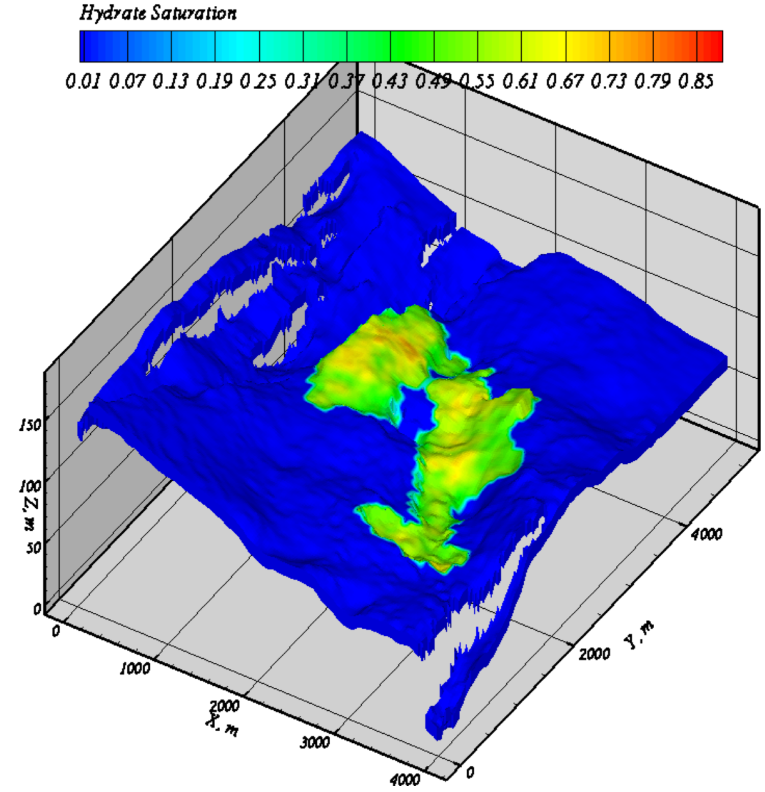
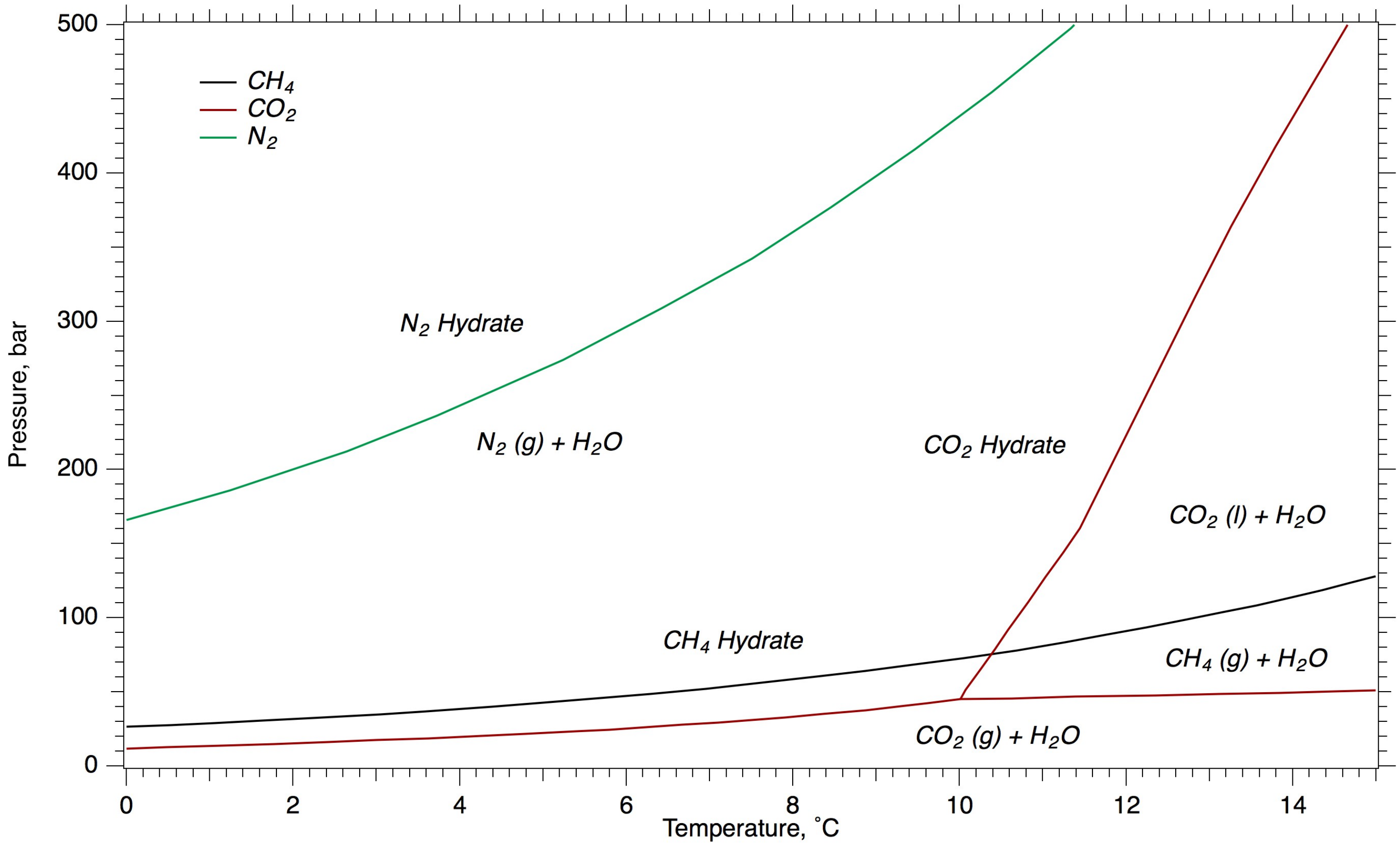


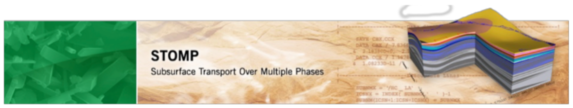
Gas Hydrate Systems: Hydrate Distributions on the Alaska Northslope



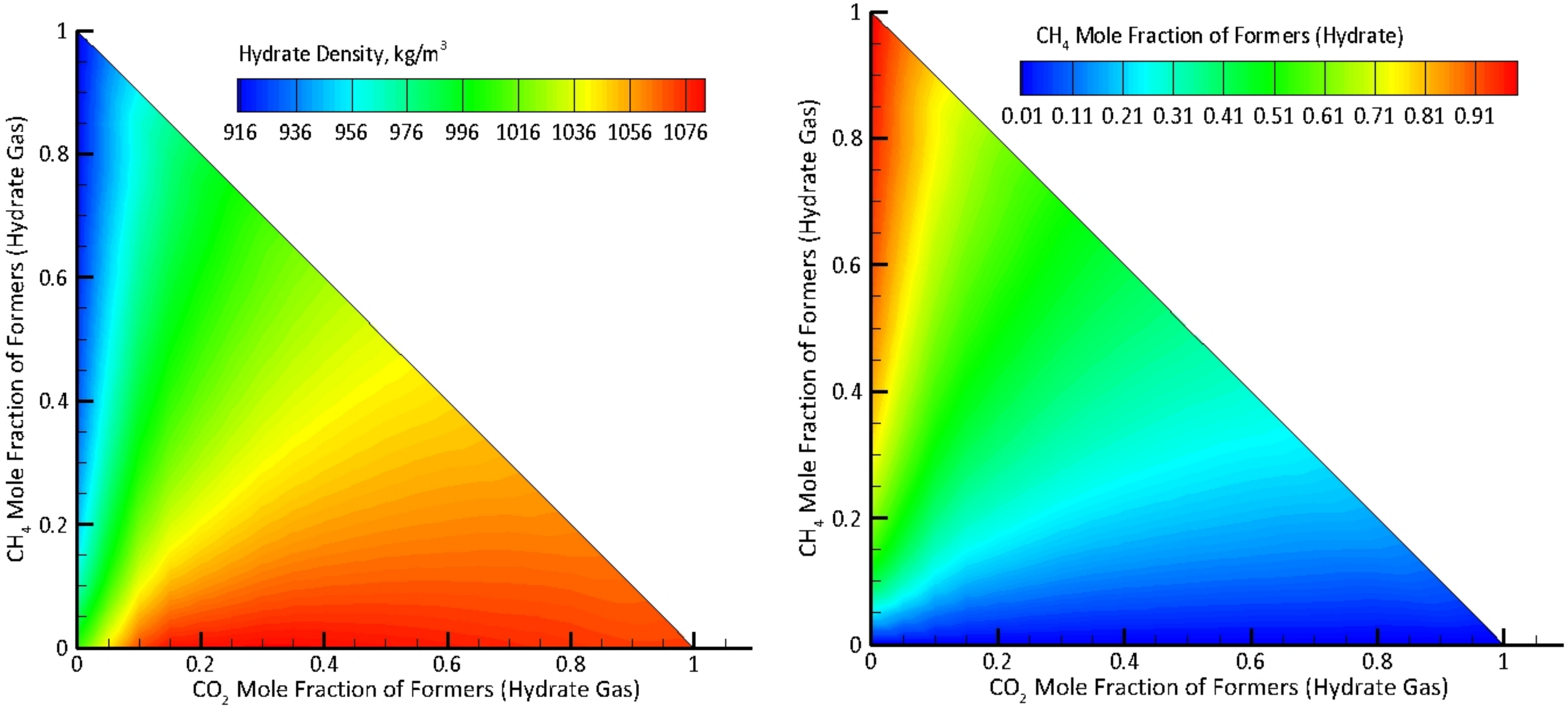


Gas Hydrate Systems – Hydrate Phase Equilibria





Gas Hydrate Systems – Ternary Hydrate Properties from Tables



Gas Hydrate Systems – Phase Conditions and Primary Variables

Phase Condition #10 Series	$s_h = 0.0, s_n + s_g = 0.0, s_\ell + s_i = 1.0$	
Energy	T	Temperature
Water Mass	P	Pressure
Mobile CO_2 Mass	$P_v^{CO_2}$	CO_2 Vapor Pressure
Mobile CH_4 Mass	$P_v^{CH_4}$	CH_4 Vapor Pressure
Mobile N_2 Mass	$P_v^{N_2}$	N_2 Vapor Pressure
Hydrate CO_2 Mass	$M_h^{CO_2}$	Hydrate CO_2 Mass
Hydrate CH_4 Mass	$M_h^{CH_4}$	Hydrate CO_2 Mass
Hydrate N_2 Mass	$M_h^{N_2}$	Hydrate CO_2 Mass
Salt	y_ℓ^s	Brine Mass Fraction of Total Salt

Gas Hydrate Systems – Phase Conditions and Primary Variables

Phase Condition #20 Series	$s_h = 0.0, s_n + s_g > 0.0, s_\ell + s_i < 1.0$	
Energy	T	Temperature
Water Mass	$s_\ell + s_i$	Aqueous + Ice Saturation
Mobile CO_2 Mass	$z_m^{CO_2}$ or P	CO_2 Mole Fraction or Pressure
Mobile CH_4 Mass	$z_m^{CH_4}$ or P	CH_4 Mole Fraction or Pressure
Mobile N_2 Mass	$z_m^{N_2}$ or P	N_2 Mole Fraction or Pressure
Hydrate CO_2 Mass	$M_h^{CO_2}$	Hydrate CO_2 Mass
Hydrate CH_4 Mass	$M_h^{CH_4}$	Hydrate CO_2 Mass
Hydrate N_2 Mass	$M_h^{N_2}$	Hydrate CO_2 Mass
Salt	y_ℓ^S	Brine Mass Fraction of Total Salt

Gas Hydrate Systems – Phase Conditions and Primary Variables

Phase Condition #30 Series	$s_h > 0.0, s_n + s_g > 0.0, s_\ell + s_i < 1.0$	
Energy	T	Temperature
Water Mass	$s_\ell + s_i$	Aqueous + Ice Saturation
Mobile CO_2 Mass	$z_m^{CO_2}$ or P	CO_2 Mole Fraction or Pressure
Mobile CH_4 Mass	$z_m^{CH_4}$ or P	CH_4 Mole Fraction or Pressure
Mobile N_2 Mass	$z_m^{N_2}$ or P	N_2 Mole Fraction or Pressure
Hydrate CO_2 Mass	$\psi_h^{CO_2}$ or s_h	CO_2 Mole Fraction of Former
Hydrate CH_4 Mass	$\psi_h^{CH_4}$ or s_h	CH_4 Mole Fraction of Former
Hydrate N_2 Mass	$\psi_h^{N_2}$ or s_h	N_2 Mole Fraction of Former
Salt	y_ℓ^s	Brine Mass Fraction of Total Salt

Gas Hydrate Systems – Phase Conditions and Primary Variables

Phase Condition #40 Series	$s_h > 0.0, s_n + s_g = 0.0, s_\ell + s_i < 1.0$	
Energy	T	Temperature
Water Mass	P	Pressure
Mobile CO_2 Mass	$P_v^{CO_2}$	CO_2 Vapor Pressure
Mobile CH_4 Mass	$P_v^{CH_4}$	CH_4 Vapor Pressure
Mobile N_2 Mass	$P_v^{N_2}$	N_2 Vapor Pressure
Hydrate CO_2 Mass	$\psi_h^{CO_2}$ or s_h	CO_2 Mole Fraction of Former
Hydrate CH_4 Mass	$\psi_h^{CH_4}$ or s_h	CH_4 Mole Fraction of Former
Hydrate N_2 Mass	$\psi_h^{N_2}$ or s_h	N_2 Mole Fraction of Former
Salt	y_ℓ^s	Brine Mass Fraction of Total Salt

Gas Hydrate Systems – Phase Transitions

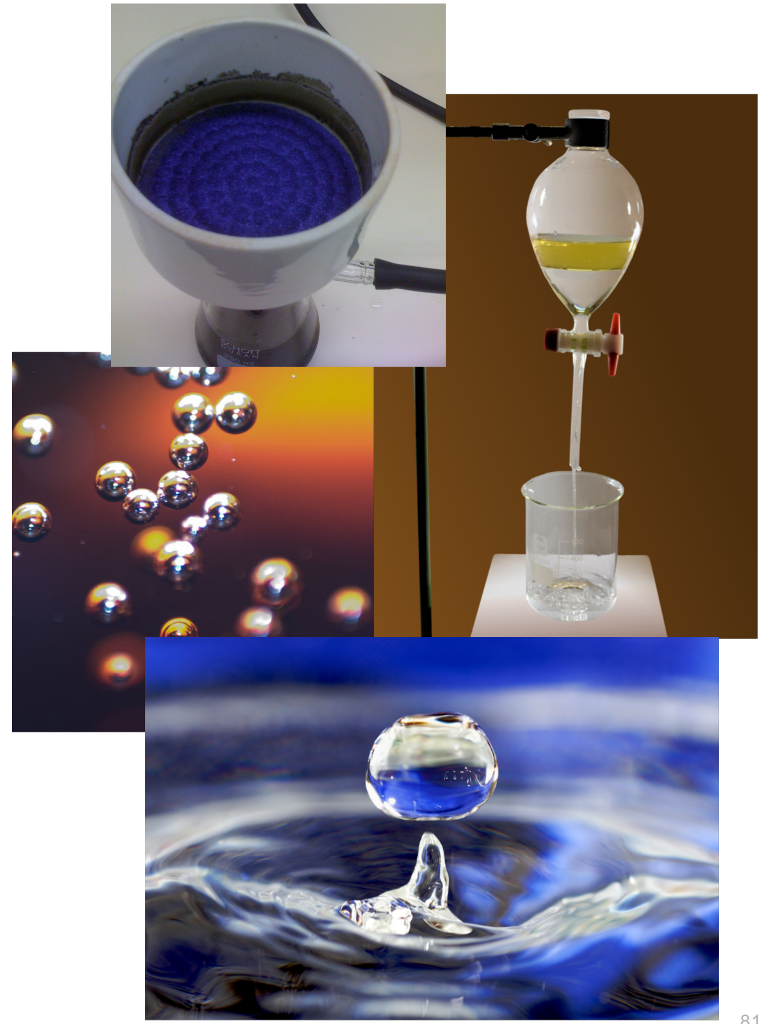
Phase Condition #10 Series $s_h = 0.0, s_n + s_g = 0.0, s_\ell + s_i = 1.0$

- Assume a hydrate phase exists (common approach!)
- Compute a hydrate equilibrium pressure $P_h^{eq} = func[T, \psi_h^{CO_2}, \psi_h^{CH_4}, \psi_h^{N_2}]$
- Compute the vapor pressure of formers $P_v = P_v^{CO_2} + P_v^{CH_4} + P_v^{N_2}$
- Compute the total gas pressure $P_g = P_v^{CO_2} + P_v^{CH_4} + P_v^{N_2} + P_v^{H_2O}$
- $if \left(P_v > P_h^{eq}\right)\ then$ hydrate forms
- $if \left(P_g > P_\ell + P_{entry}\right)\ then$ hydrate forms

Phase Condition #30 Series $s_h > 0.0, s_n + s_g > 0.0, s_\ell + s_i < 1.0$

Takeaways / Conclusions

- Primary variable switching is an effective scheme for modeling phase transitions
- Select primary variables that yield direct calculations of all secondary variables
- Phase equilibria calculations are harder than they appear
- Discontinuities slow convergence
- Be creative in defining primary variables and phase conditions



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Thank you