Numerical Simulation of Water Rock Interaction and Fluid Flow

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CAGS WORKSHOP II'2010

China Australia Geological Storage of CO_2
中澳二氧化碳地质封存

Outline

1. Introduction
2. Geochemical Modelling
3. Full Physics Compositional Simulation
4. Case Study
5. Summary

1 Introduction

Trapping Mechanisms for CO_2 Storage Process in Saline Aquifer

- **Hydrodynamic and structural trapping**

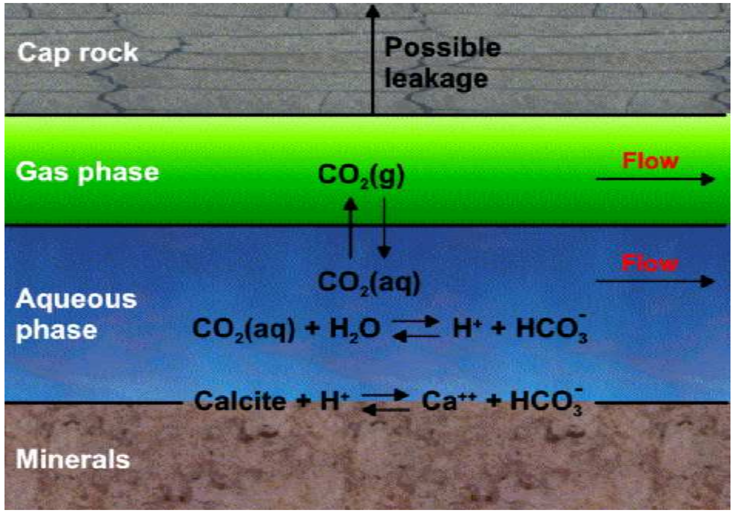
- **Solubility trapping**
  - Storing CO_2 as a soluble component in brine

- **Residual gas trapping**
  - Trapping as immobile residual gas (Sgrm)

- **Mineralization trapping**
  - Water-rock interaction
  - Long-term storage of green house gas

Full-Physics Compositional Simulation

- ➢Convective and dispersive flow
- ➢Relative permeability hysteresis
- ➢Gas solubility in aqueous phase
- ➢Aqueous chemical equilibrium reactions
- ➢Mineral dissolution and precipitation kinetics
- ➢Vaporization of H_2O
- ➢Predictions of brine density and viscosity
- ➢Leakage through cap rock and thermal capability



CMG Training, 2008

What reactions could be critical?

- As injected CO_2 dissolves in formation water, it produces a weak acid (carbonic acid) which can chemically react with minerals in the host reservoir rock. Some of these reactions can result in the precipitation of new minerals and solid compounds in the formation pore space, effectively trapping the injected CO_2 (IPCC, 2005, Chevron Australia, 2005).

- In most geological strata, the formation of calcium, magnesium, and iron carbonates is expected to be the primary mineral trapping process (White et al. 2001, 2002, 2004, 2005).

2 Geochemical Modelling

- **Static equilibrium model**
    - Solution of coupled non-linear equations

- **Closed system kinetic model**
    - Solution of coupled non-linear ordinary differential equations

- **Flowing system**
    - Solution of coupled non-linear partial differential equations

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Static Equilibrium Model

- **Input:**
  - ✓Water Analysis
  - ✓Thermodynamic Database
  - ✓Temperature
  - ✓Pressure

- **Output:**
  - ✓Saturation Index and Aqueous Speciation
  - ✓Charge Balance
  - ✓Modification to Downhole Conditions
  - ✓Geothermometers

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Fundamental Concepts (1)

- **Charge Balance:**

$$\frac{\sum(\text{molality}\times\text{charge})_{\text{Cations}}-\sum(\text{molality}\times\text{charge})_{\text{Anions}}}{\sum(\text{molality}\times\text{charge})_{\text{Cations}}+\sum(\text{molality}\times\text{charge})_{\text{Anions}}}\times 100$$

---More than +/-5% indicates problems with major components in aqueous phase.

- **CO_2 Pressure** in equilibrium with the fluid:

$$CO_2(\text{gas}) + H_2O \leftrightarrow HCO_3^{-} + H^{+}$$

---Atmospheric log PCO_2=-3.5
If fluid $PCO_2 >$ atmospheric, degassing occurs
If fluid $PCO_2 <$ atmospheric, adsorption from atmosphere occurs

Fundamental Concepts (2)

- **Law of Mass Action**:

  Any reaction at EQUILIBRIUM, the activity product is a constant (***Keq***) at a given temperature and pressure. For example,

$$CaCO_3(s) + 2H^+(aq) \leftrightarrow Ca^{++}(aq) + H_2CO_3(aq)$$

$$Q = \frac{a_{Ca^{++}(aq)} \cdot a_{H_2CO_3(aq)}}{a_{CaCO_3(s)} \cdot a_{H^+}{}^2}$$

- ***Activity = Concentration × Activity Coefficient***

  The activity of a pure solid (e.g. **$CaCO_3$(s)**) is generally 1.0

Chemical Equilibrium Between Aqueous Species

➢ Fast reversible aqueous reactions are modeled with chemical equilibrium reactions

  ✓Instantaneous and no rate associated with them.

➢ Typical reaction:

$$CO_2(aq) + H_2O = H^+ + HCO_3^-$$

➢ The concentrations of the species in solution are determined from chemical equilibrium constants

$$K_{eq}(T) = \frac{a_{H^+} \cdot a_{HCO_3^-}}{a_{CO_2(aq)} \cdot a_{H_2O}}$$

‘*a*’ is the activity which is also a measure of concentration.

Aqueous Species

- Activities of aqueous species:

$$a_{H_2O} \approx 1$$

$$a_i = \gamma_i \cdot m_i$$

$$\gamma_i = \text{activity coefficient of species i}$$

$$m_i = \text{molality of species i (moles i / kgH}_2\text{O)}$$

- Activity coefficient models
  - Ideal solution: $\gamma_i = 1$
  - Debye-Hückel model
  - B-dot model

B-dot Model

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + \dot{a}_i B \sqrt{I}} + \dot{B} I$$

$$I = \frac{1}{2} \sum_{k=1}^{n_{aq}} m_k z_k^2$$

I = ionic strength

$\mathrm{m_k}$ = molality of component k

$\mathrm{z_k}$ = charge of component k

$\dot{a}_i$ = ion size parameter of component i

A, B, $\dot{\mathrm{B}}$ = temperature - dependent parameters

pH Value

- Definition: $-\log_{10}(a_{\mathrm{H}^+})$

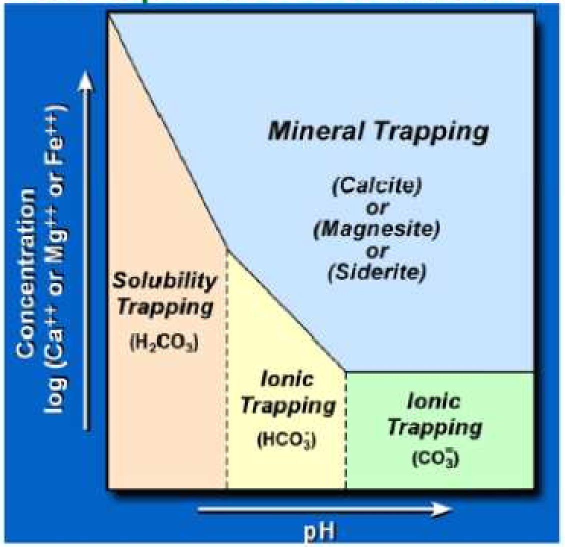
  a_{H^+} is the activity of the hydrogen ion in the solution.

The pH is of critical importance in determining the behaviour of many ions and solids in solutions.
e.g.,

$$\mathrm{CaCO_3(s)} + 2\mathrm{H}^+ \leftrightarrow \mathrm{Ca}^{++} + \mathrm{HCO_3}^-$$

$$\mathrm{CO_2(aq)} + \mathrm{H_2O} \leftrightarrow \mathrm{HCO_3}^- + \mathrm{H}^+$$

Aqueous Species Dominance Diagram



After Gunter et al., 2004

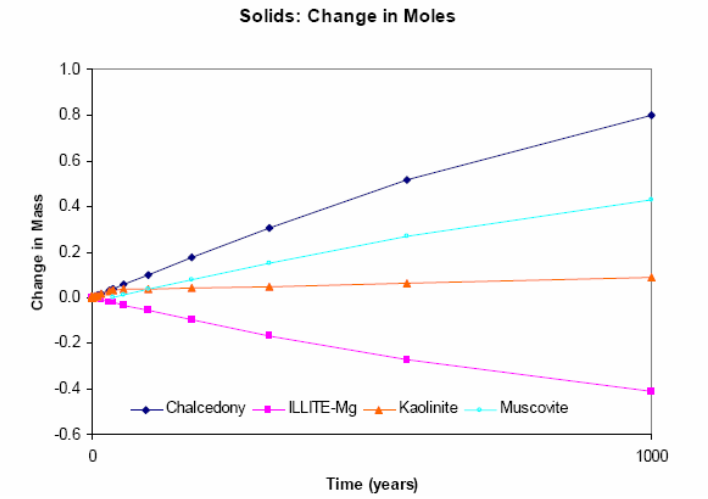
Closed System Kinetic Model

➢ **Input:**

- ✓Static equilibrium modelling results
- ✓Mineral Characteristics
- ✓Kinetic Database
- ✓Time

➢ **Output:**

- ✓Saturation Index with Time
- ✓Mineral Mass Changes
- ✓Gas Uptake
- ✓Solution Composition with Time



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Unstable Minerals under Acidic Environment

(Examples)

- Geochemical modelling considers all kinds of chemical reactions

- Carbonate mineral:
  - ---Calcium, magnesium, and iron carbonates

- Feldspar:
  - ---Potassium-feldspar to Anorthite, etc.

- Clay minerals:
  - ---Kaolinite, Illite, Smectite, etc.

- Volcanic clastics (?)

- Others (?)

Simple Example of Water-Rock Interaction

$$\mathrm{CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-}$$

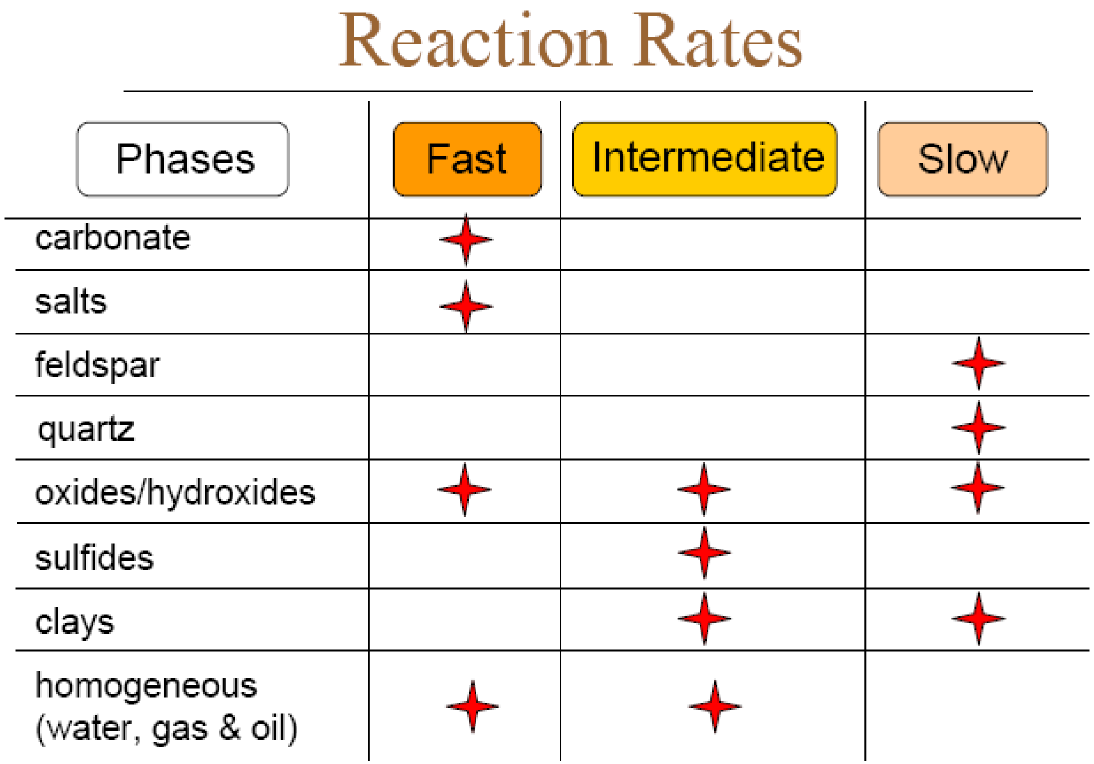
$$\mathrm{CaAl_2Si_2O_8 + 2H^+ + H_2O \leftrightarrow Ca^{2+} + AlSi_2O_5(OH)_4}$$

$$\mathrm{Ca^{2+} + HCO_3^- \leftrightarrow CaCO_3 + H^+}$$

$$\mathrm{CaAl_2Si_2O_8 + CO_2(aq) + H_2O = Al_2Si_2O_5(OH)_4 + CaCO_3}$$

Anorthite Kaolinite Calcite

Reaction Rate



Reaction Rates

Phases	Fast	Intermediate	Slow
carbonate	✦		
salts	✦		
feldspar			✦
quartz			✦
oxides/hydroxides	✦	✦	✦
sulfides		✦	
clays		✦	✦
homogeneous (water, gas & oil)	✦	✦	

Stephen Talman, 2010

$$k = k_0 \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

k : reaction rate at temperature T

k_0 : reaction rate at temperature T_0

E_a : activation energy

R : gas constant

3 Full Physics Compositional Simulation

➢**Input:**

✓Important chemical reactions based on the kinetic modelling
✓Reservoir Characteristics (eg. Relperm, porosity, saturation, etc.)
✓PVT
✓Injection/Production History

➢**Output:**

✓Fluid Composition
✓Mineralogical Changes
✓Flow Paths
✓Phase Redistribution

Mineral Dissolution & Precipitation

$$\mathrm{Calcite(solid)} + \mathrm{H}^+ = \mathrm{Ca}^{++} + \mathrm{HCO}_3^-$$

$$\frac{\mathrm{V}}{\Delta \mathrm{t}}(N_i^{n+1} - N_i^n) = r_i$$

$$r_i = V \cdot A \cdot k \cdot \left(1 - \frac{Q}{K_{eq}}\right)$$

$$Q = \frac{a_{Ca^{++}} \cdot a_{HCO_3^-}}{a_{H^+}}$$

$\mathrm{V} =$ bulk volume (m^3)

$\mathrm{A} =$ reactive surface area ($\mathrm{m}^2/\mathrm{m}^3$)

$\mathrm{k} =$ rate constant ($\mathrm{mol/m}^2\ \mathrm{s}$)

$\mathrm{K}_{eq} =$ chemical equilibrium constant

$\mathrm{Q/K}_{eq} =$ saturation index

$\mathrm{Q/K}_{eq} > 1 \rightarrow$ mineral precipitation

$\mathrm{Q/K}_{eq} < 1 \rightarrow$ mineral dissolution

Material Balance Equation for CO_2

$$\begin{aligned}
&\Delta T_g \, y_{CO_2,g} \, \Delta \Phi_g \; + \\
&\Delta T_w \left(y_{CO_2,aq} + y_{HCO_3^-,aq} + y_{CO_3^{--},aq} \right) \Delta \Phi_w \\
&+ r_x + q_{CO_2(g)} + q_{CO_2(aq)} + q_{HCO_3^-} + q_{CO_3^{--}} \\
&- \frac{V}{\Delta t} \Big[\left(N_{CO_2} + N_{HCO_3^-} + N_{CO_3^{--}} \right)^{n+1} - \\
&\qquad \left(N_{CO_2} + N_{HCO_3^-} + N_{CO_3^{--}} \right)^{n} \Big] = 0
\end{aligned}$$

$$N_{CO_2} = N_{CO_2(g)} + N_{CO_2(aq)}$$

T_{ij} - molar transmissibility of component i in phase j

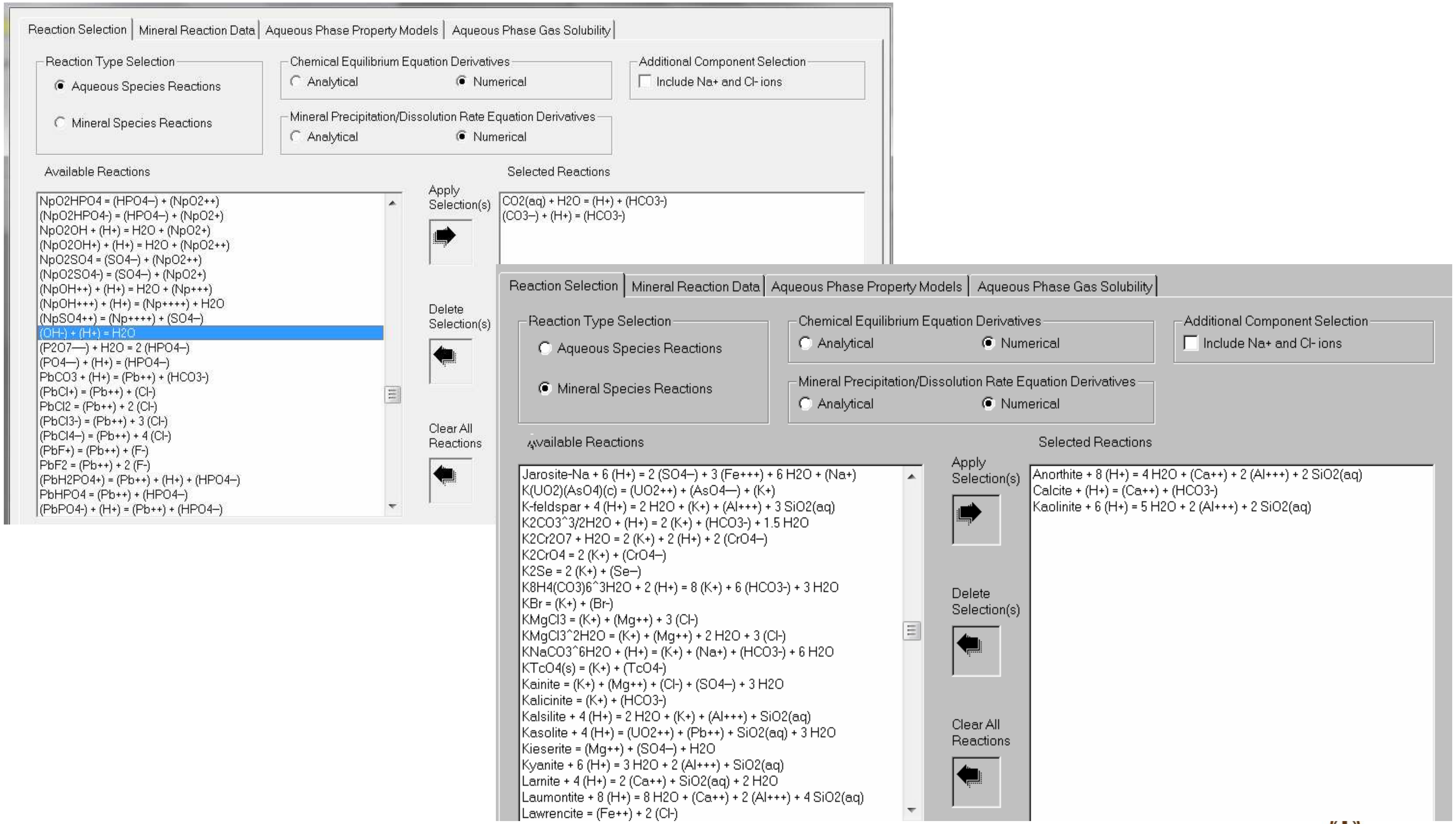
y_{ij} - molar fraction of component i in phase j

V - gridblock bulk volume (m3)

q_i - molar injection rate of component i (mol/day)

N_i - moles of component i per gridblock volume

Geochemical Reaction Selection in the Numerical Simulator



Reaction Type Selection
● Aqueous Species Reactions
○ Mineral Species Reactions

Chemical Equilibrium Equation Derivatives
○ Analytical ● Numerical

Mineral Precipitation/Dissolution Rate Equation Derivatives
○ Analytical ● Numerical

Additional Component Selection
☐ Include Na+ and Cl- ions

Available Reactions

```
NpO2HPO4 = (HPO4--) + (NpO2++)
(NpO2HPO4-) = (HPO4--) + (NpO2+)
NpO2OH + (H+) = H2O + (NpO2+)
(NpO2OH+) + (H+) = H2O + (NpO2++)
NpO2SO4 = (SO4--) + (NpO2++)
(NpO2SO4-) = (SO4--) + (NpO2+)
(NpOH++) + (H+) = H2O + (Np+++)
(NpOH+++) + (H+) = (Np++++) + H2O
(NpSO4++) = (Np++++) + (SO4--)
(OH-) + (H+) = H2O
(P2O7----) + H2O = 2 (HPO4--)
(PO4---) + (H+) = (HPO4--)
PbCO3 + (H+) = (Pb++) + (HCO3-)
(PbCl+) = (Pb++) + (Cl-)
PbCl2 = (Pb++) + 2 (Cl-)
(PbCl3-) = (Pb++) + 3 (Cl-)
(PbCl4--) = (Pb++) + 4 (Cl-)
(PbF+) = (Pb++) + (F-)
PbF2 = (Pb++) + 2 (F-)
(PbH2PO4+) = (Pb++) + (H+) + (HPO4--)
PbHPO4 = (Pb++) + (HPO4--)
(PbPO4-) + (H+) = (Pb++) + (HPO4--)
```

Selected Reactions

```
CO2(aq) + H2O = (H+) + (HCO3-)
(CO3--) + (H+) = (HCO3-)
```

Reaction Type Selection
○ Aqueous Species Reactions
● Mineral Species Reactions

Chemical Equilibrium Equation Derivatives
○ Analytical ● Numerical

Mineral Precipitation/Dissolution Rate Equation Derivatives
○ Analytical ● Numerical

Additional Component Selection
☐ Include Na+ and Cl- ions

Available Reactions

```
Jarosite-Na + 6 (H+) = 2 (SO4--) + 3 (Fe+++) + 6 H2O + (Na+)
K(UO2)(AsO4)(c) = (UO2++) + (AsO4---) + (K+)
K-feldspar + 4 (H+) = 2 H2O + (K+) + (Al+++) + 3 SiO2(aq)
K2CO3^3/2H2O + (H+) = 2 (K+) + (HCO3-) + 1.5 H2O
K2Cr2O7 + H2O = 2 (K+) + 2 (H+) + 2 (CrO4--)
K2CrO4 = 2 (K+) + (CrO4--)
K2Se = 2 (K+) + (Se--)
K8H4(CO3)6^3H2O + 2 (H+) = 8 (K+) + 6 (HCO3-) + 3 H2O
KBr = (K+) + (Br-)
KMgCl3 = (K+) + (Mg++) + 3 (Cl-)
KMgCl3^2H2O = (K+) + (Mg++) + 2 H2O + 3 (Cl-)
KNaCO3^6H2O + (H+) = (K+) + (Na+) + (HCO3-) + 6 H2O
KTcO4(s) = (K+) + (TcO4-)
Kainite = (K+) + (Mg++) + (Cl-) + (SO4--) + 3 H2O
Kalicinite = (K+) + (HCO3-)
Kalsilite + 4 (H+) = 2 H2O + (K+) + (Al+++) + SiO2(aq)
Kasolite + 4 (H+) = (UO2++) + (Pb++) + SiO2(aq) + 3 H2O
Kieserite = (Mg++) + (SO4--) + H2O
Kyanite + 6 (H+) = 3 H2O + 2 (Al+++) + SiO2(aq)
Larnite + 4 (H+) = 2 (Ca++) + SiO2(aq) + 2 H2O
Laumontite + 8 (H+) = 8 H2O + (Ca++) + 2 (Al+++) + 4 SiO2(aq)
Lawrencite = (Fe++) + 2 (Cl-)
```

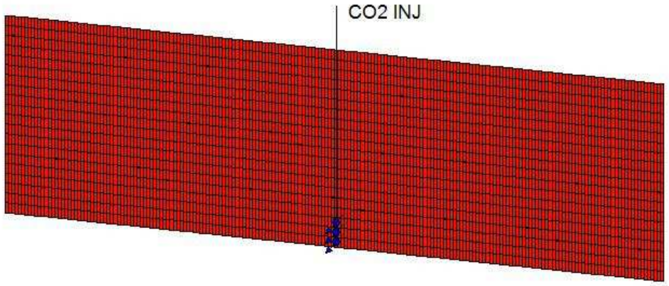
Selected Reactions

```
Anorthite + 8 (H+) = 4 H2O + (Ca++) + 2 (Al+++) + 2 SiO2(aq)
Calcite + (H+) = (Ca++) + (HCO3-)
Kaolinite + 6 (H+) = 5 H2O + 2 (Al+++) + 2 SiO2(aq)
```

4 Case Study: Case 1

➢CO_2 Injection at the Middle of Reservoir:

- ➢Grid Dimension: 5m×10m×5m
- ➢Grid Number: 200×1×20
- ➢Dip angle of grid system: 2.0 degree
- ➢Porosity: 0.18
- ➢Permeability: 100md, Kv/Kh=1
- ➢Sgrm = 0.2
- ➢Injection Well: (101, 1, 1)
- ➢Perforation Interval: (101, 1, 18) to (101,1, 20)
- ➢Injection Rate: 1×10^4 m^3/day (STG surface gas rate)
- ➢Injection Period: 2000-1-1 to 2003-1-1
- ➢Simulation Period: 2000-1-1 to 2200-1-1
- ➢Volume Fraction: Anorthite (1%), Calcite (1%) & Kaolinite (2%)



Aqueous & Mineral Reactions

Aqueous species reaction:

$$H_2O \leftrightarrow H^+ + OH^-$$

$$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{--}$$

Mineral species reaction:

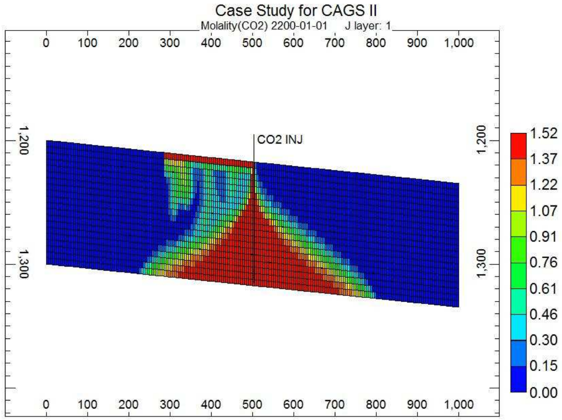
$$\text{Calcite} + H^+ \leftrightarrow Ca^{++} + HCO_3^-$$

$$\text{Anorthite} + 8H^+ \leftrightarrow Ca^{++} + 2Al^{+++} + 2SiO_2(aq) + 4H_2O$$

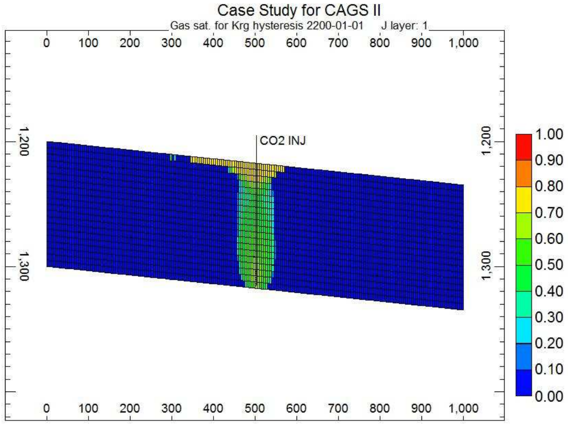
$$\text{Kaolinite} + 6H^+ \leftrightarrow 5H_2O + 2SiO_2(aq) + 2Al^{+++}$$

From CMG Training

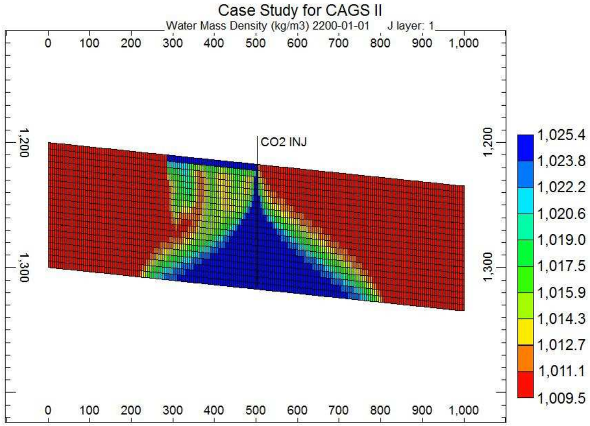
Simulation Results (200yrs) (1)



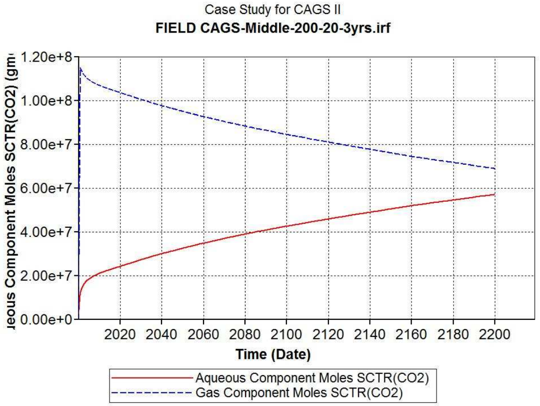
CO_2 Molality



Gas sat. for Krg hysteresis

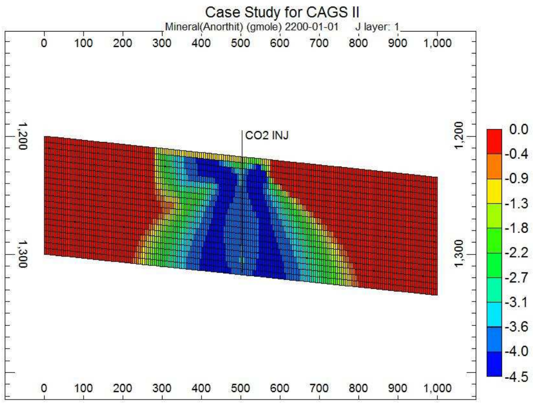


Water Mass Density

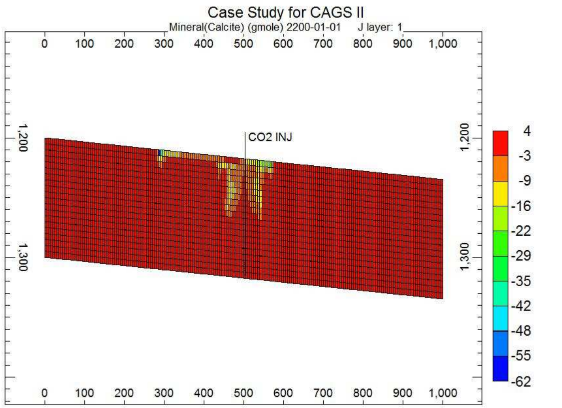


Moles of Aqueous and Gas CO_2

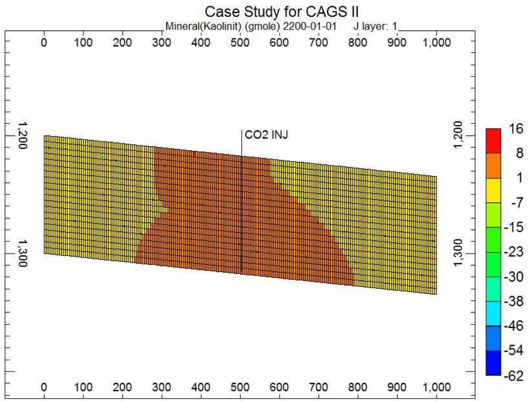
Simulation Results (200yrs) (2)



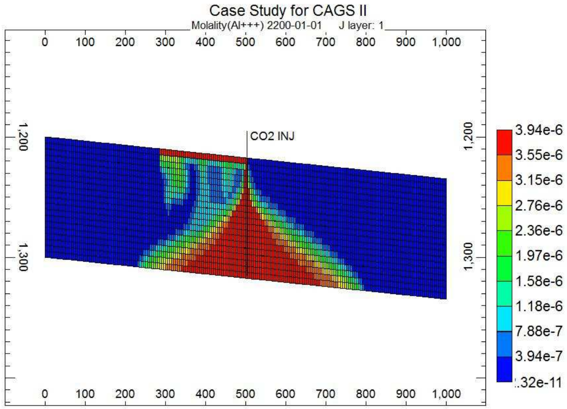
Molality of Anorthite



Molality of Calcite

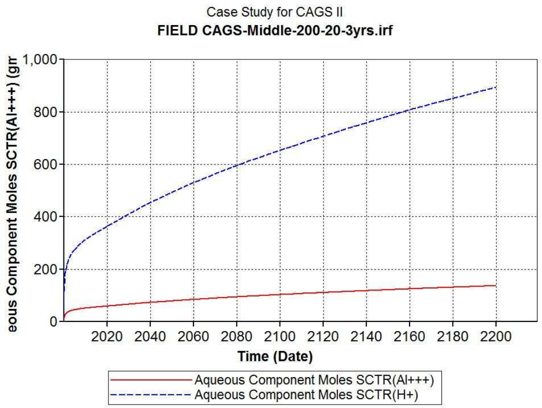


Molality of Kaolinite

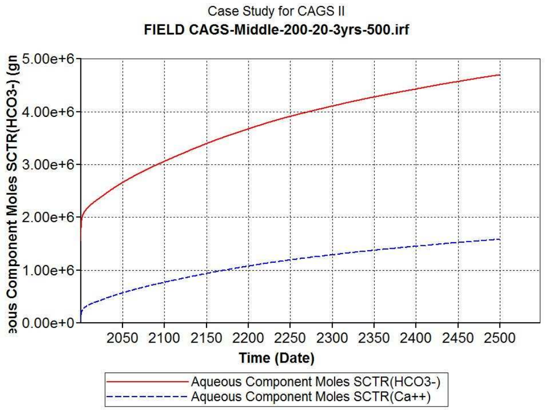


Molality of Al+++

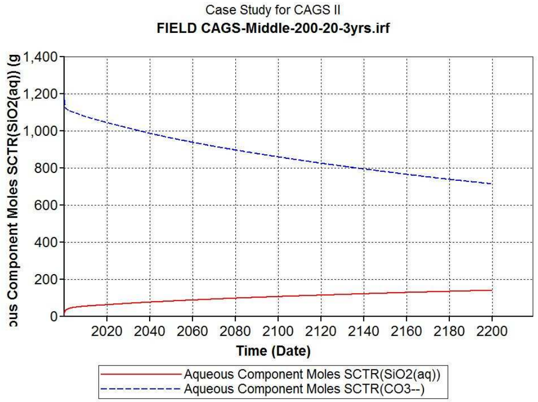
Simulation Results (200yrs) (3)



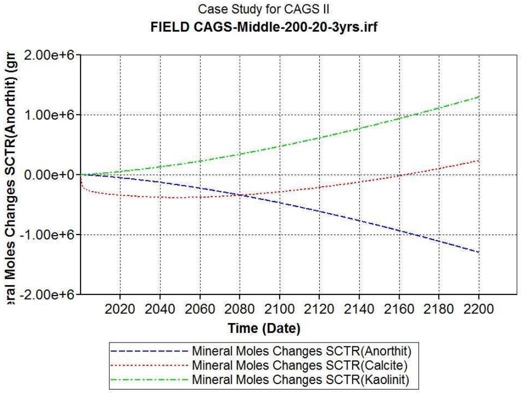
Moles of Al^{+++} & H^{+}



Moles of Ca^{++} & HCO_3^-



Moles of SiO_2 & CO_3^{--}



Moles of Minerals

Simulation Results of Case I (200yrs)

- **Total Cum Inj**, mol = 1.28126E+08

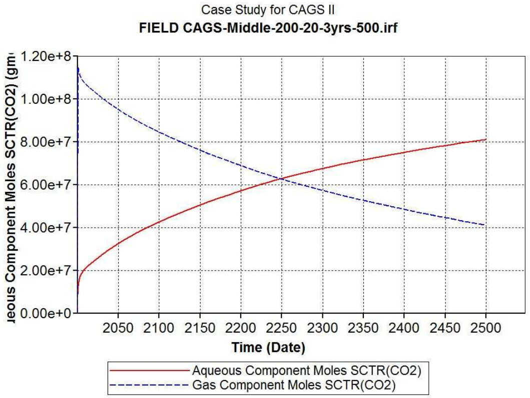
- **3 years later:**

CO_2 Storage Amounts in Reservoir	Moles	kg
Supercritical Phase	= 1.11307E+08	4.89863E+06
Trapped due to Hysteresis	= 2.42978E+07	1.06934E+06
Dissolved in Water	= 1.68263E+07	7.40524E+05
Present in Aqueous Ions	= 2.06357E+06	9.08176E+04
Present in Mineral Precipitate	= -2.50461E+05	-1.10228E+04

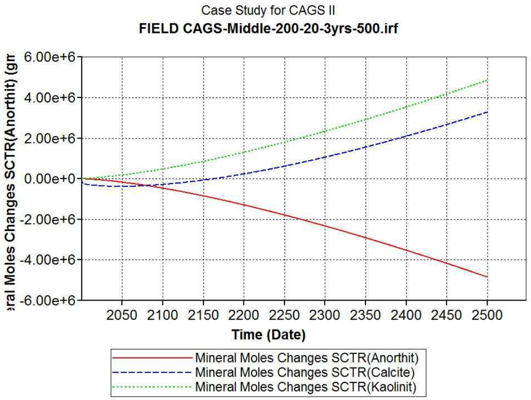
- **200years later:**

CO2 Storage Amounts in Reservoir	Moles	kg
Supercritical Phase	= 6.89380E+07	3.03396E+06
Trapped due to Hysteresis	= 4.11539E+07	1.81118E+06
Dissolved in Water	= 5.71292E+07	2.51426E+06
Present in Aqueous Ions	= 3.67423E+06	1.61703E+05
Present in Mineral Precipitate	= 2.35526E+05	1.03655E+04

Long-Term Storage



Moles of CO_2

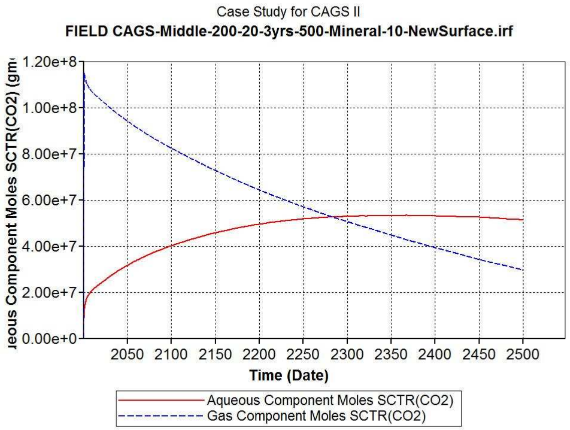


Moles of minerals

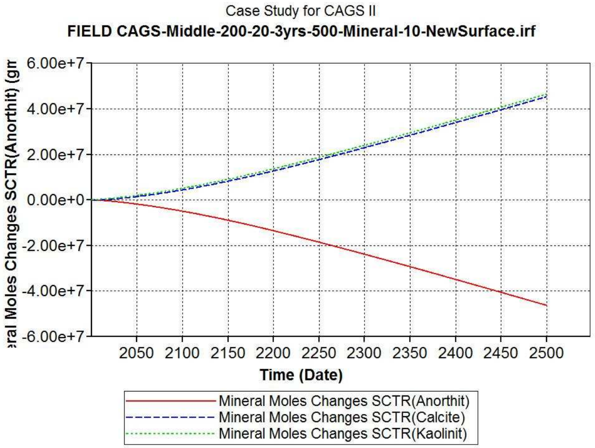
Influence of Mineral Content

(Case 2)

- Volume Fraction: Anorthite (10%), Calcite (10%) & Kaolinite (2%)
- Other conditions same as in Case 1

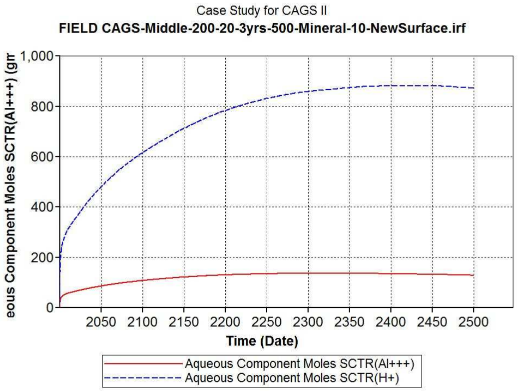


Moles of CO_2

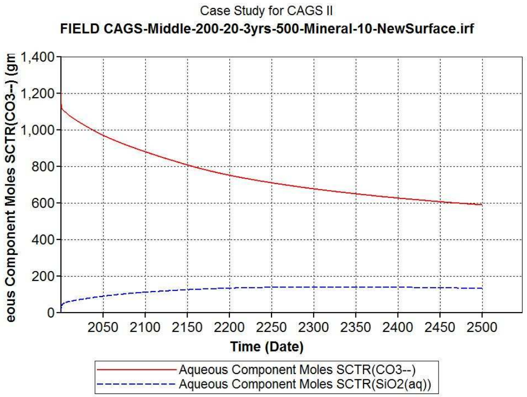


Moles of minerals

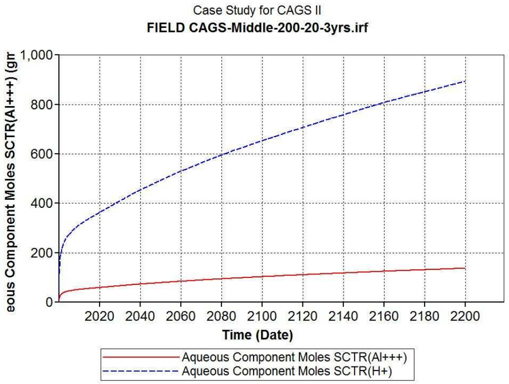
Influence of Mineral Content



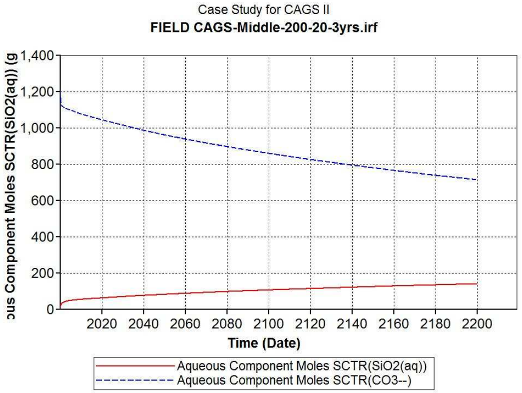
Moles of Al+++ & H+ (Case 2)



Moles of CO3-- & SiO2 (Case 2)



Moles of Al+++ & H+ (Case 1)



Moles of CO3-- & SiO2 (Case 1)

5 Summary

- Analyses on the chemical properties of aqueous phase and initial mineral components are critical before numerical simulation process.

- Geochemical modelling (static equilibrium model and closed system kinetic model) provides understandings of geochemical evolution after CO_2 injection through modelling saturation index, solution composition and mineral mass with time. Hence the important chemical reactions will be advised for the full-physics compositional simulator.

- Based on the combinations of fluid flow dynamics and the selection of important geochemical reactions, the coupled simulation is able to provide information on CO_2 plume movement, effective storage capacity together with changes of minerals of rock, chemical properties (ions) of brine water and petrophysical properties.

- Mineral precipitation will be significant for safe long-term storage of CO_2 in saline aquifer.

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