GCEP
Global Climate & Energy Project
STANFORD UNIVERSITY

Modeling CO_2 Mineralization in a General Purpose Research Simulator

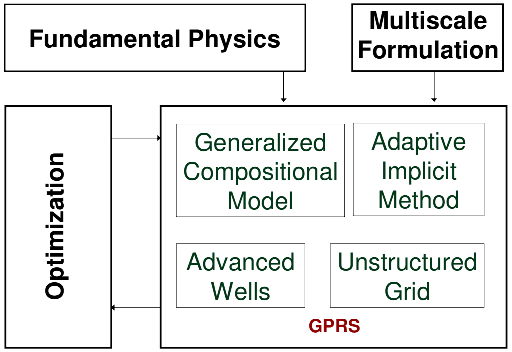
Yaqing Fan, Louis J. Durlofsky, and Hamdi Tchelepi
Department of Energy Resources Engineering, Stanford University

Background

Introduction

The design and monitoring of geological carbon storage operations require many key capabilities, including advanced techniques for computational modeling. Because an important long-term storage mechanism is the mineralization of the injected CO_2, it is essential that large-scale engineering models accurately represent the chemical interactions between liquids and minerals. The goal of this work is to develop a robust, flexible and efficient capability for such modeling and to incorporate it into Stanford's General Purpose Research Simulator.

GPRS (General Purpose Research Simulator) Framework



Fundamental Physics

Multiscale Formulation

Optimization

Generalized Compositional Model

Adaptive Implicit Method

Advanced Wells

Unstructured Grid

GPRS

Ongoing GCEP Activities

- Scaling analysis and high-accuracy simulations of miscible and immiscible CO_2 flows.
- High-order AIM (Adaptive Implicit Method) schemes.
- Algebraic finite-volume multiscale formulation.
- Propagation of gravity currents.
- Particle methods for nonlinear multiphase flow.
- Modeling CO_2 mineralization reactions.

GPRS Enhancements

Implementation

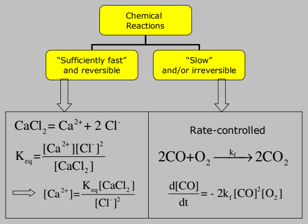
Chemical reaction modeling within the context of CO_2 sequestration has been studied by several research groups and incorporated into a number of simulators. We plan to enhance GPRS rather than use existing codes, because GPRS already has many advanced features (see figure below). By incorporating chemical reaction capabilities, GPRS will be a flexible generalized simulator for CO_2 sequestration.

Features	GEM	TOUGH	NUFT	UTCHEM	GPRS
Generalized Compositional	○	○	⊖	○	✓
Unstructured Grids	⊖	✓	⊖	⊖	✓
Chemical Reactions	○	✓	✓	✓	⊖
Adaptive Implicit	✓	⊖	⊖	⊖	✓
Thermal Options	⊖	✓	✓	✓	✓
Advanced Facilities (Wells)	⊖	⊖	⊖	⊖	✓
Optimization	○	○	○	○	✓

⊖ Not Available ○ Not Fully Flexible or Efficient ✓ Available and Flexible

Strategy

Chemical reactions involved in the process of CO_2 sequestration include both equilibrium and rate-controlled reactions. This figure shows two examples of equilibrium and rate-controlled reactions. Implementations for these two types of reactions can be very different. Our current work focuses on incorporating reactions at equilibrium.



Chemical Reactions

"Sufficiently fast" and reversible

"Slow" and/or irreversible

$$CaCl_2 = Ca^{2+} + 2\,Cl^-$$

$$K_{eq} = \frac{[Ca^{2+}][Cl^-]^2}{[CaCl_2]}$$

$$\Longrightarrow\ [Ca^{2+}] = \frac{K_{eq}[CaCl_2]}{[Cl^-]^2}$$

Rate-controlled

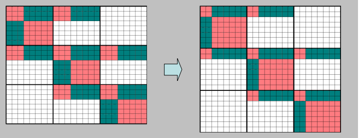
$$2CO + O_2 \xrightarrow{k_f} 2CO_2$$

$$\frac{d[CO]}{dt} = -2k_f[CO]^2[O_2]$$

Equations	Unknowns
N_e mass balance equations N_c thermodynamic equations 1 saturation constraint 2 mole fraction constraints 1 capillary pressure relation N_{neq} kinetic equations (slow)	2 pressures 2 saturations $2N_c$-N_{eq} mole fractions
sum = $N_e+N_c+4+N_{neq}$	$2N_c-N_{eq}+4 \equiv N_e+N_c+4+N_{neq}$

In order to incorporate reactions at equilibrium, the governing equations will be changed. A new method, which involves replacing component mass balance equations with element mass balance equations, will enable the new formulation to fall naturally into the existing framework.

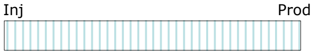
The table above shows the new break-down of equations and unknowns, using a two-phase system as example. The right figures shows the similarity between previous and new Jacobian matrix.



Results

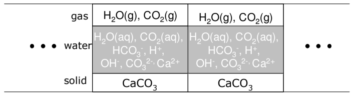
Preliminary Results

A simple case involving CO_2 injection into a carbonate reservoir is considered. The reservoir is modeled as a one-dimensional homogeneous carbonate reservoir, in which the reactive mineral is calcite ($CaCO_3$). Initially, the reservoir is saturated with 100% water. Initial equilibrium is established between water, calcite, and electrolytes in the water. A pure CO_2 stream is injected at one end of the reservoir and a producer is introduced at the other end.



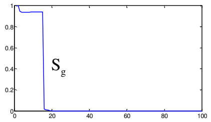
A total of four equilibrium reactions are considered. The species in these reactions are distributed in the three phases. The gas phase contains CO_2 and H_2O, the solid phase contains calcite only, and the aqueous phase contains $CO_2(aq)$, H_2O and all ions.

- $CO_2(aq) + H_2O = HCO_3^- + H^+$
- $HCO_3^- = H^+ + CO_3^{2-}$
- $H_2O = H^+ + OH^-$
- $CaCO_3 = Ca^{2+} + CO_3^{2-}$

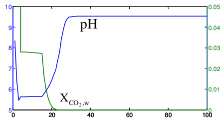


… gas	$H_2O(g)$, $CO_2(g)$	$H_2O(g)$, $CO_2(g)$	…
water	$H_2O(aq)$, $CO_2(aq)$, HCO_3^-, H^+, OH^-, CO_3^{2-}, Ca^{2+}	$H_2O(aq)$, $CO_2(aq)$, HCO_3^-, H^+, OH^-, CO_3^{2-}, Ca^{2+}	
solid	$CaCO_3$	$CaCO_3$	

Figure (a) shows the saturation of the gas after 2000 days of injection. Figure (b) shows that dissolved CO_2 reduces the pH value from approximately 9.5 to 5.5.

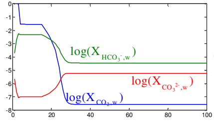


(a)

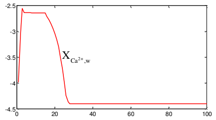


(b)

Figure (c) indicates that behind the gas front the dominant species are HCO_3^- and $CO_2(aq)$. Figure (d) shows that the mole fraction of Ca^{2+} is significantly increased by CO_2 injection, indicating more calcite is dissolved in the water.



(c)



(d)

Conclusions & Future Work

The initial design and implementation strategy have been completed. The design entails element balance equations and effectively utilizes the current GPRS framework because many of the key changes are introduced at a low level (i.e., the Jacobian matrix level) in the code. Preliminary results have been obtained for a simple case that models CO_2 injection into a carbonate reservoir with equilibrium chemistry.

The next step is to complete the implicitly coupled reactive-transport implementation. As GPRS contains a variety of numerical options for treating flow and reaction, we plan to explore the use of various combinations of options for modeling flow and reaction. We expect this to provide an efficient and flexible overall capability for the modeling of carbon dioxide injection and geologic storage.

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