GCEP Final Report

“Collaborative Research on Carbon Sequestration
In Saline Aquifers in China”

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Abstract
Injection of CO2 into saline formations represents a sequestration option of large potential capacity in China. As a leading research, this work represents a unique international collaborative effort by professors and researchers from Peking University, China University of Geosciences at Wuhan, and University of Southern California to address fundamental issues associated with large-scale sequestration of CO2 in saline formations with emphasis on developing the potential for CO2 sequestration projects in China.

The collaborative research aims to address three parts: 1) a comprehensive review of sedimentary basins in China in terms of basin characteristics and its proximity to CO2 point sources; Salinity impact on solids precipitation during CO2 injection to saline aquifers in China’s Jianghan Basin; Salt precipitation and pressure buildup during CO2 injection; 2) experimental study to investigate the dynamic behavior of CO2 migration in the context of storage in saline aquifers; the impact of changes in mobility for the two-phase brine/CO2 system as a result of transitions between co- and counter-current flow settings; validation of the accuracy of numerical simulations based on co-current relative permeability functions; 3) modeling and simulation for microscopic interactions and macroscopic long-term fate of injected CO2 versus the host environment; discrete fracture modeling application in an actual CO2 sequestration site of China; enhancement of the performance of the existed reactive transport simulator, and extension of modeling Enhanced Coal Bed Methane process.
For sedimentary basin study, a regional study on potential CO2 sequestration in the Jianghan Basin was performed. The two formations, Qianjiang and Xingouzui Formation, were firstly identified and investigated with respect to the lateral extend and quality of reservoirs, the geological and hydrogeological properties of the formation including the depth, thickness, porosity, permeability and hydrochemical conditions. Preliminary analysis indicated that the two formations could be suitable candidate sites for CO2 injection.

We use numerical simulation to highlight the salinity impact affecting the dry-out and precipitation while injecting dry supercritical CO2 into Jianghan basin in central of China. The aim of this effort is on the quantitative aspects of salt precipitation in the vicinity of a CO2 injection well, as induced by formation dry-out from water dissolution into the flowing CO2 stream. The Jianghan Basin formations properties were used. In order to assess the effects, a 1D model was developed which was considered to be homogenous sandstone of about 100m thickness. Then a number of sensitivity simulations were performed to analyze the impact. The 2-D model results showed that the effects of gravity override on gas saturation distributions were strong and also reflect the effect. More details and mechanisms are needed to be explored in future’s research.

Two methods were tried to relieve salt precipitation and pressure buildup during CO2 injection. Pre-flush with fresh water before CO2 injection can obviously alleviate the pressure buildup induced by halite precipitation around the injection well. In addition, it could lower the salinity of the aquifers and increase the solubility of CO2, with the benefit of reducing the leakage risk. Pumping saline water out of the target formation while injecting CO2 could reduce the pressure buildup both in the near-well region and the formation as whole. Increase in the water production rate leads to further decrease in pressure buildup, this phenomenon was demonstrated by tripling the production where the pressure decreased about 15 bars. The introduction of two wells (left side and right side of the production well) increases the horizontal migration of the CO2 but contributes a little to the amount of CO2 dissolved.

For dynamic experimental study, we have investigated the dynamics of countercurrent flows in well-defined porous materials (glass bead packs) using an analog isoctane/brine fluid system. The experimental work utilizes dynamic resistivity measurements to monitor the evolution of an isoctane plume initially located at the bottom of the column. Time estimates for residual entrapment via scaling analysis for counter-current flow and design of segregation experiments based on an analog fluid system in glass-bead pack were studied.

We study the impact of changes in mobility for the two-phase brine/CO2 system as a result of transitions between co- and counter-current flow settings. We have included this effect in a simulator (GPRS) and studied the impact of the related mobility reduction on the saturation distribution and residual saturation of CO2 in aquifers over relevant time scales. We demonstrate that the reduction in relative permeability in the vertical direction changes the plume migration pattern and has an impact on the amount of gas that is trapped as a function of time. This is to our best knowledge the first attempt to
integrate counter-current relative permeability into the simulation of injection and subsequent migration of CO2 in aquifers.

Four-electrode resistivity measurements were used to monitor the migration of the non-wetting phase by relating the resistivity index (RI) to the brine saturation. The observations are compared with numerical calculations to demonstrate that co-current relative permeability functions, that were measured directly, are inadequate to reproduce the experimental observations.

For microscopic modeling and simulation, a coupled multiphase Lattice Boltzmann (LB) model was developed to simulate the dissolution of immiscible liquid droplets in another liquid during the rising process resulting from buoyancy. It was found that there exists a terminal rise velocity for each droplet, and there was a power law relationship between the Eötvös (Eo) number and the terminal Reynolds (Re) number. The simulation results were in agreement with the empirical correlation derived for predicting bubble rise. The Damkohler (Da) and Peclet (Pe) numbers were varied to investigate the coupling between droplet size, flow field, dissolution at the interface, and solute transport. For macroscopic modeling and simulation study, a CO2 sequestration simulation framework that can account for natural and drilling/injection induced fractures and chemical reactions was developed. This framework is capable of modeling dynamic flow in micro-scale and reservoir-scale simultaneously. Simulations have been done using Discrete Fracture Modeling (DFM). Systems with fractures in CO2 injection formation versus in cap rocks are compared. Results have shown that the existence of mudstone layers could prevent injected CO2 from leaking outside the reservoir when no fractures are present. While vertical fractures intersecting with mudstone layers will cause significant leakage increase as fractures form extremely preferential pathways for CO2 transport.

Discrete Fracture Modeling (DFM) is applied to simulate CO2 transport in a saline aquifer in China’s Urdos basin. This requires unstructured gridding of the saline formation using Delaunay triangulation and transmissibility evaluation between each pair of adjacent cells. Simulations have been done using a connection list based simulator. Several examples, including injection to a formation with or without fractures and with different hydraulic fracture length, have been simulated based on data from an actual CO2 sequestration project. Results have shown that the existence of mudstone layers could prevent injected CO2 from leaking outside the reservoir when no fractures are present. While vertical fractures intersecting with mudstone layers will cause significant leakage as the fractures forms extremely preferential pathways for CO2 transport. On the other hand, if fractures are far enough away from the CO2 plume, it could alleviate dramatic pressure buildup caused by CO2 injection in the formation and thus help expedite CO2 propagation.

We present our progress on stabilizing the geochemical simulator and the implementation of Enhanced Coal Bed Methane to a General Propose Reservoir Simulator Chemical Reaction Module. The former section of this part presents our progress on designing a general scheme to eliminate equilibrium reaction rates for GPRS chemical reaction simulator. Then we introduce the procedure of extending chemical
simulator to model CBM/ECBM process. The idea is based on the fact that gas sorption is solely a kinetic chemical reaction whose reaction rate is correlated with gas pressure or other environmental parameters. Differ from the common CBM/ECBM simulators, geochemical approach has a better handle of complex adsorption model, which leave us a wider space to enhance the current Langmuir type reaction sorption model. Cases are carried out to validate the approach.

Introduction

Injection of CO2 into saline formations represents a sequestration option of large potential capacity in China. However, no systematic investigation of this potential including specific site selection and characterization has yet been performed. In these formations, the main CO2 sequestration mechanisms are structural trapping (due to low-permeability traps), capillary trapping due to interfacial phenomena, solubility trapping (CO2 dissolution into brine), and mineral trapping (reactions with minerals to form new, permanent mineral products). Gravity segregation, viscous fingering, solubility, reaction kinetics, and possible leakage through natural/artificial pathways are some of the factors that may significantly affect the sequestration capacity as well as the long-term fate and redistribution of the injected CO2. These factors must all be included in a scientifically sound assessment of large-scale storage potentials and long-term fate of any injected CO2.

This collaborative research integrates geological modeling, reservoir simulation and laboratory experiments to identify the appropriate scientific approach for quantifying the storage capacity in these highly complex geological settings.

1. Sedimentary basin study

In Geology and hydrogeology, we aim to investigate the geology, stratigraphy and hydrogeology of the Jianghan Basin in detail to identify combinations of strata that may provide suitable reservoir and seal pairs with respect to the CO2 geo-sequestration potential and further quantify the storage capacity by integrating geological modeling, reservoir simulation and laboratory experiments. The Jianghan Basin is a representative salt-lake rift basin with the Cretaceous and Quaternary sedimentary deposits up to 10km in depth. CO2 emissions in the region directly overlying the Jianghan-Nanyang Basins contributed approximately 116 Mt CO2 per year to China’s estimated total stationary source CO2 emissions of 2970 Mt/yr. In a 300 km radius from the two basins there are sources totaling approximately 604 Mt/yr and there are four power plants and a steel mill releasing about 25 Mt of CO2 per year in the vicinity of Wuhan city. The gypsum-salt rock and mudstone are well developed in the basin, and hydrocarbon resources are in great abundance as the well-known Jianghan Oilfield is located in the central of the basin.

2. Study on Salinity impact on solids precipitation during CO2 injection to saline aquifers in China’s Jianghan Basin

The Jianghan Basin lies in the south-central part of the Hubei Province, the Jianghan Plain between Yangtzi River and Hanshui River, west to Yichang city, east to Yingcheng city, south to Huhong city, and north to the north of Jingzhou city (Fig 1). It is a salt-lake rift basin developed on the Zhongyangzi paraplatform during the Cretaceous and Tertiary covering an area of 36350 km2.
The Jianghan Basin contains Late Cretaceous to Quaternary sedimentary deposits up to 10km thick. There are two prominent sedimentary cycles including the Haiyang Formation of upper Cretaceous, the Shashi Formation of Paleocene, the Xingouzui Formation, the Jingsha Formation and the Qianjiang Formation of Eocene, the Jinghezhen Formation of Oligocene, the Guanghuasi Formation of Miocene to Pliocene as well as the Pingyuan Formation of Pleistocene to recent.

The reservoir rocks in the Jianghan Basin include sandstone, globulitic marl, fractured mudstone and basalt, sandstone reservoir as the major. Xingouzui Formation and Qianjiang Formation is the predominant petrolierous and saliniferous sandstone reservoir as shown in Fig. 1. The sediment supply is unidirectional and adequate, mainly from the Jingmen, Hanshui and Dangyang palaeodrainage pattern in the north of the basin during the Qianjiang and Xingouzui Formation deposits.

**Table I:** Reservoir and seal pairs of Xingouzui Formation in the Jianghan Basin

<table>
<thead>
<tr>
<th>Formation</th>
<th>Thickness (m)</th>
<th>Lithologic character</th>
<th>Reservoir</th>
<th>Seal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xingouzui Formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>200–600</td>
<td>Red mudstone with sandstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>5–20</td>
<td>Grey argillaceous gypsum and white gypsum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandstone I</td>
<td>50–150</td>
<td>Red-grey mudstone and sandstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandstone II</td>
<td>100–250</td>
<td>Grey mudstone with sandstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mudstone</td>
<td>100–250</td>
<td>Grey mudstone with gypsum-bearing mudstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandstone III</td>
<td>100–250</td>
<td>Red-grey mudstone and sandstone</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As described in Table I, Xingouzui Formation distributes three delta sand bodies in the Mashan, Hougang and Hanchuan area from west to east in the north of the basin and they connect together into a reservoir development zone in horizon and get thin to the south. The sand body is widely distributed with the area of 11000 km$^2$, and the thickness of the sandstone is generally 20 to 140 meters in range, with the maximum thickness up to 237 meters. Siltstone is the main rock type, with the average porosity of 17% and the average permeability of 98×10$^{-3}$µm$^2$.

The formation water in Xingouzui Formation is mainly calcium chloride and sodium sulfate type. As the burial depth deeper than 1000m, the water salinity appears little differences with the increasing depth, mainly between 100000 mg/L to 260000 mg/L.

3. Solutions to salt precipitation and pressure buildup during CO2 injection into saline aquifers in Jianghan Basin

As pressure buildup due to CO2 injection in saline aquifers, especially under the context of high salinity, can be the most limiting factors affecting the injectivity, strategies of relieving pressure are urgently needed to be considered. The aim of the present work is to investigate the solutions of reducing salt precipitation and pressure buildup during CO2 injection to saline aquifers. Two solutions are introduced. One refers to pre-flushing the saline water with the fresh water before CO2 injection; the other refers to pumping out saline formation water and injecting CO2 simultaneously to control pressure buildup.

4. Experimental study to investigate the dynamic behavior of CO2 migration in the context of storage in saline aquifers

Along our research in dynamic experiments, we focus on the dynamics of CO2 plume migration after the injection phase has ended. It is well established (e.g. Zhou et al. 2002) that the relative permeability behavior observed in co-current immiscible displacement experiments (e.g. water displacing oil) differs significantly from the relative permeability behavior observed in counter-current flow experiments such as counter-current imbibition processes of relevance to oil production from fractured reservoirs. To date, however, all published efforts towards understanding the time scales associated with immobilization of CO2 by capillary entrapment in brine formations (e.g. Kumar et al. 2005; Ide et al. 2007) have utilized existing simulation technology that does not distinguish between co-current and counter-current in the representation of relative permeability.

To improve the fundamental understanding of the time scales associated with residual entrapment of CO2 in aquifers and to strengthen the state-of-the-art simulation technology by honoring different flow regimes, we combine experimental investigations of gravity segregation processes with analytical and numerical modeling efforts. Time estimates for residual entrapment via scaling analysis for counter-current flow and design of segregation experiments based on an analog fluid system in a well-defined porous medium (glass-bead pack) were studied.

In modeling and simulation, of the collaborative research project, during the first year we investigated the motion and dissolution of rising CO2 droplet/bubble during geological carbon sequestration in saline aquifers. During carbon sequestration, the
upward motion of supercritical carbon dioxide (scCO$_2$) due to buoyancy leads to brine flowing around it, which accelerates the dissolution of scCO$_2$. In addition, the dissolved scCO$_2$ slightly increases the density of brine, which might give rise to downward density-driven flow at the large temporal and spatial scales. This process also favors the dissolution of scCO$_2$. The dissolution of scCO$_2$ in water is an important sequestration mechanism and is usually referred to as solubility trapping.

5. **Study on the impact of changes in mobility for the two-phase brine/CO$_2$ system as a result of transitions between co- and counter-current flow settings**

During as well as after injection of CO$_2$ into an aquifer, CO$_2$ migrates towards the top of the formation due to density differences between the formation brine and the injected CO$_2$. The time scales of CO$_2$ migration towards the top of an aquifer and the fraction of CO$_2$ that is trapped as residual gas depends strongly on the driving forces that are acting on the injected CO$_2$.

When CO$_2$ migrates to the top of an aquifer, brine may be displaced downwards in a counter-current flow setting particularly during the injection period. A majority of the published work on counter-current flow measurements have reported significant reductions in the associated relative permeability functions as compared to co-current measurements [1-7]. However, this phenomenon has not yet been considered in the simulation of CO$_2$ storage into saline aquifers.

6. **Dynamics of Plume Migration in Counter-Current Flows**

A reduction in the relative permeability of both phases is required to improve the agreement between experimental observations and numerical calculations. Numerical calculations based on co-current input data predicts a much faster migration of iC8 to the top of the column than what is observed in the segregation experiments. Our findings demonstrate that the prevailing flow regime affects the phase mobilities, in part because of the viscous coupling, and must therefore be considered in displacement processes where counter-current flow may occur, such as during injection/storage of CO$_2$ in saline aquifers.

7. **Modeling and simulation for microscopic interactions and macroscopic long-term fate of injected CO$_2$ versus the host environment**

For microscopic simulation, we proposed a coupled LB model that takes into account two-phase flow, dissolution at the interface, and solute transport during the rising process of immiscible liquid droplets. The two-phase LB model accounting for droplet motion is based on the code of Kang et al (2002a). The dissolution simulator accounts for the dissolution taking place at the liquid-liquid interface, based on the method of Kang et al. (2002b, 2003). The solute transport simulator describes the transport of the dissolved mass (Dawson et al., 1993) and is based on the single-phase LB model of Chen et al. (2008). The rise and dissolution of the same amount of dispersed phase were simulated, when it was in a single, two, and three droplets. By means of simultaneous numerical simulations of the multiple processes, we are able to better understand the complicated interplay and coupling between droplet number, size, rise velocity, dissolution, and solute transport. Specifically, this study aims to describe the rise of one or more scCO$_2$ droplets...
in brine, with mass transfer across the interface due to dissolution. Understanding of this coupled process is important for geological carbon sequestration.

Numerical simulation is the key approach to study the long-term fate of injected CO\textsubscript{2} and potential impact of escape of CO\textsubscript{2} due to the failure of natural barriers or migration along natural/anthropogenic escape paths such as faults or wells. As we view the static modeling of saline aquifer would be following the well-established industry standard using commercial tools such as GOCAD and Petrel, the focus of this research is put on designing the simulation framework, code development and its implementation to China’s candidate formations.

8. Study on discrete fracture modeling application in an actual CO\textsubscript{2} sequestration site of China

One of the main concerns for CO\textsubscript{2} geological storage is the potential leakage from the target saline aquifer into other places including the caprock, buffer aquifers, potable water sources, and the atmosphere. Quantification on each of the above consequences is important to risk evaluation and for decision makers to propose critical remedies in case of leakage.

Natural fractures exist commonly in most target sites for CO\textsubscript{2} storage. For example, In Algerian In Salah CCS project, fractures are present and it is found that CO\textsubscript{2} prefers to go through fractures than matrix. Natural and artificially-induced hydraulic fractures have been identified as the most important factors in risk assessment of CO\textsubscript{2} storage, and regarded as potential escape routes for CO\textsubscript{2}.

On the other hand, natural and hydraulic fractures may help injected CO\textsubscript{2} to move quicker and wider in the saline aquifer. Research has shown that fractures existed in the aquifer will facilitate the horizontal movement [8].

Discrete Fracture Modeling (DFM) begins to be used increasingly in reservoir simulation and CO\textsubscript{2} geological storage simulation as it greatly improves the fracture characterization and speeds up the simulation. In DFM, fractures are discretized as standalone grid cells using an unstructured grid. In CO\textsubscript{2} geological storage, DFM has been implemented in the Black Warrior Coal Basin where CO\textsubscript{2} sequestration and enhanced coal bed methane recovery shows high potential in coal-bearing geological strata. Leakage risks associated with hydraulic fracturing are also provided. DFM proves to be a more efficient and accurate approach than traditional methods as unstructured gridding is applied.

In this work, we use Discrete Fracture Modeling to simulate the CO\textsubscript{2} leakage along fractures and wellbores. A general and flexible control volume approach to model and two-point flux approximations are applied in the calculations. Stanford’s General Purpose Research Simulator (GPRS) is used for the simulation. A real-case from one of the ongoing CCS projects in the world is presented in this paper. The results show that mudstone would prevent CO\textsubscript{2} from leaking while fractures will cause leakage if they are close enough to the CO\textsubscript{2} plume. Hydraulic fracturing will cause CO\textsubscript{2} to move much
quicker along the formation and enhance the injectivity as it improves the permeability of the aquifer

9. *Enhancement of Geochemical Simulator and the Application in ECBM*

In this work, we first present the supplement of GPRS geochemical simulator. The key issue we focus on is to design a general scheme to eliminate fast thermodynamic equilibrium reaction rates from the species conservation equations. The Equilibrium Rate Annihilation (ERA) matrix method and Decomposing Method are introduced. An illustration of ECBM implemented GPRS chemical simulator is also presented in the later section. The validations of our model are performed by comparing the results with commercial software which is widely used in ECBM. It should be noted that the sorption model we used at present is also the Langmuir type sorption model. Reaction occurs in the aqueous phase is not included in current work. More sophisticated models are under investigation.

**Background**

1. *Geological Indicators for Storage Site Suitability*

The regional potential of CO₂ geological storage can be evaluated by five key factors such as storage capacity, injectivity potential, site details, containment and existing natural resources. Key geological indicators for storage site suitability are shown in Table II (EU Geocapacity, 2009).

2. *Study on Salinity impact on solids precipitation during CO₂ injection to saline aquifers in China’s Jianghan Basin*

Our initial numerical simulations were done with ECO₂N module from the TOUGH2 simulator. ECO₂N designed for applications to geologic sequestration of CO₂ in saline aquifers. It includes a comprehensive description of the thermodynamics and thermo-physical properties of H₂O-NaCl-CO₂ mixtures [9]. The development of ECO₂N mainly starts from EWASG fluid property module.

EWASG was designed for applications to geothermal reservoir engineering, which generally involve elevated temperatures and modest CO₂ partial pressures, typically of order 10 bar or less. In contrast, the thermodynamic regime of interest for CO₂ storage in saline formations typically involves moderate (near ambient) temperatures, and high CO₂ pressures of the order of a few hundred bars. Lower CO₂ pressures are of interest in connection with studies of CO₂ leakage from the primary storage reservoir [10].

The space discretization used for a numerical method to solve fluid flow in our simulation is the integral finite difference method [11,12]. The entire geometric information of the space discretization is provided in the form of a list of grid block volumes $V_n$, interface areas $A_{nm}$, nodal distances $D_{nm}$ and components $g_{nm}$ of gravitational acceleration along nodal lines. This discretization method can be used for irregular grids in one, two or three dimensions in heterogeneous porous medium and fracture rock systems. It’s equivalent to a conventional finite difference method when applied to regular grids dissection. For the time discretization, it is discretized as a first-order finite difference [12].
### Table II: Key geological indicators for storage site suitability

<table>
<thead>
<tr>
<th>Basic, geological related criteria</th>
<th>Influential geological and physical parameters</th>
<th>Criteria to investigate in the screening process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Positive indicators</td>
<td>Cautionary indicators</td>
</tr>
<tr>
<td>Sufficient depth of reservoir</td>
<td>Pressure and Temperature</td>
<td>Depth of crest of reservoir &gt;1000m</td>
</tr>
<tr>
<td></td>
<td>Porosity and Permeability</td>
<td>Depth of base of reservoir &lt;2500m</td>
</tr>
<tr>
<td>Petrophysical reservoir properties</td>
<td>Porosity</td>
<td>&gt;20%</td>
</tr>
<tr>
<td></td>
<td>Permeability</td>
<td>&gt;300mD</td>
</tr>
<tr>
<td>Integrity of seal</td>
<td>Lithology (Porosity, Permeability)</td>
<td>Low permeable lithologies, such as clay</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td>&gt;100m</td>
</tr>
<tr>
<td></td>
<td>Faults</td>
<td>Unfaulted</td>
</tr>
<tr>
<td></td>
<td>Heterogeneity</td>
<td>Homegenous</td>
</tr>
<tr>
<td></td>
<td>Tectonic activity</td>
<td>No tectonic activity</td>
</tr>
<tr>
<td>Storage capacity</td>
<td>Reservoir:</td>
<td>Total capacity of reservoir estimated to be much larger than the total amount produced from CO₂ source</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td>&gt;50m</td>
</tr>
<tr>
<td></td>
<td>Areal extent</td>
<td>Well defined</td>
</tr>
<tr>
<td></td>
<td>Heterogeneity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Faults</td>
<td>Unfaulted</td>
</tr>
<tr>
<td></td>
<td>Trap type</td>
<td>Well defined structure</td>
</tr>
<tr>
<td></td>
<td>Petrophysic prop</td>
<td>Values given above</td>
</tr>
</tbody>
</table>

This treatment of flux terms is known as “fully implicit”, these unknowns thermodynamic parameters are only implicitly defined in the resulting equations. Then the system of equations is solved on a grid-block basis by Newton-Raphson iteration.

The aquifer is assumed as a homogeneous, isotropic, infinite-acting one. The injection rate is constant at 50kg/s for a time period of 1000 days. Parameters and schematic map are shown below.

3. **Solutions to salt precipitation and pressure buildup during CO₂ injection into saline aquifers in Jianghan Basin**
Table III: Hydrogeological parameters used in the simulations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.16</td>
</tr>
<tr>
<td>Horizontal permeability (m²)</td>
<td>1.0×10⁻¹³</td>
</tr>
<tr>
<td>Vertical permeability (m²)</td>
<td>1.0×10⁻¹³</td>
</tr>
<tr>
<td>Pore compressibility (Pa⁻¹)</td>
<td>4.5×10⁻¹⁰</td>
</tr>
<tr>
<td>Rock grain density (kg/m³)</td>
<td>2600</td>
</tr>
<tr>
<td>Formation heat conductivity (W/m °C)</td>
<td>2.51</td>
</tr>
<tr>
<td>Rock grain specific heat (J/kg °C)</td>
<td>920</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>64</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>120</td>
</tr>
<tr>
<td>Relative permeability</td>
<td></td>
</tr>
</tbody>
</table>

Liquid: Van Genuchten function
\[ k_r = \sqrt{S^* \left[ 1 - \left( 1 - \left[ S^{-m} \right]^{-1/m} \right]^2 \right]} \]
\[ S^* = \frac{(S_i - S_w)}{(1 - S_w)} \]
\[ S_w = 0.30 \]
\[ m = 0.457 \]

Gas: Corey
\[ k_g = (1 - \hat{S})^2 (1 - \hat{S}^2) \]
\[ \hat{S} = \frac{(S_i - S_w)}{(S_i - S_w - S_w)} \]
\[ S_w = 0.05 \]

Capillary pressure
Van Genuchten function
\[ P_{cap} = -P_o \left[ S^* \left( 1 - \left[ S^{-m} \right]^{-1/m} \right)^{-m} \right] \]
\[ S^* = \frac{(S_i - S_w)}{(1 - S_w)} \]
\[ S_w = 0.00 \]
\[ m = 0.457 \]
\[ P_o = 19.61 \text{ kPa} \]
Two solutions to salt precipitation and pressure buildup were tried in the present work. For using pre-flush with water before CO2 injection, a 2D radially symmetric model was used to represent a CO2 storage site in the Qianjiang depression area (Figure 3). The storage formation into which CO2 is injected is 120 m thick and located at a depth of about 1380 m below the ground surface. The storage formation is bounded at the top by a sealing layer of 30 m, followed by a sequence of aquifers with various thicknesses and sealing layers with various thicknesses. The model domain includes four aquifers and five aquitards. The lateral extent boundary at 200 km corresponds to a footprint area of about 125,664 km². The large lateral extent was chosen in order to ensure that the boundary condition would have minimal effect on the simulation results. The sand permeability and porosity of the target formation is $9 \times 10^{-13}$ m² and 0.16, respectively. For the sealing layer, the permeability and porosity of the mudstones is $9 \times 10^{-17}$ m² and 0.10. Carbon dioxide is injected into a zone where lies in the depth of about 1512 m at the rate of 50 kg/s. The simulation time runs cover a time period of two years injection. For base case, we first inject water for 2 months, and then inject CO2 for 2 years.

For pumping out saline formation water while injecting CO2, 2D (XZ) model is used to simulate the storage process around an injection well in this work, with a permeability of $77.6 \times 10^{-15}$ m², a porosity of 15.4 % [77] and a net aquifer of 110 m with Caprock as well as Baserock of 20 m each. The aquifer temperature is 89°C corresponding to temperature in Jianghan basin at the depth of about 2200 m [78]. Relative permeability was modeled using the van Genuchten- Mualem model and the Corey’s function was used to get relative permeability for free CO2 phase. A vertical saline formation water well of 30 m thickness from the bottom of aquifer is placed at 9.5 km (left and right sides of the CO2 injection well) from the CO2 injection well (Figure 4) whereas for carbon dioxide injection well was placed in the middle of the aquifer and the injection height is similar to the saline formation water well height, 30 m for both.
Figure 3: Radial symmetric model domain with deep brine formation in Jianghan Basin.

Figure 4: Schematic diagram of placement of injection and production wells
4. Numerical Modeling for Carbon Dioxide Storage

For the study of long-term behavior on carbon dioxide sequestration, which occurs in a long geohistory time, the numerical method has certain advantages than the experimental method, but because the sequestration of carbon dioxide subsurface is a complex physics-chemical problem which includes:

i. The co-existence of supercritical carbon dioxide and subsurface flow (water, oil or else). The transport of the carbon dioxide and the interaction between the two fluids is in the scope of multiphase flow.

ii. During the transportation, chemical reaction happened between carbon dioxide and subsurface strata.

iii. Ions, the production of the chemical reaction, diffuse and advect in the multiphase flow.

iv. The special structures, for example the fractures or karsts, makes it easy for transportation of carbon dioxide. Meanwhile, the chemical reaction enlarge the fractures (sometimes plug). The leakage of carbon dioxide began while the fracture development to certain extent.

v. Multi-scale exists in the system. The exquisite description of the problem expands from porous scale to field scale.

vi. The system is thermal.

Therefore, the corresponding numerical simulators should be able to address these issues. Recent numerical modeling for CO$_2$ storage applications can be split into three categories: (i) hydrodynamic modeling simulating structural, residual gas and dissolution trapping processes, (ii) geochemical modeling simulating batch geochemical reactivity (closed system without any fluid flow) and (iii) reactive transport modeling combining the two previous types of simulations and therefore providing a complete calculation over time of the amount of CO$_2$ trapped through structural, dissolution or mineral trapping. Reactive transport modeling is the most realistic modeling technique to quantify the long-term fate of CO$_2$ as well as other aspects during geological storage, but also the most challenging to perform (Gaus et al, 2008).

Table IV: Comparison of CO2STORE, ECO2N and GPRS

<table>
<thead>
<tr>
<th></th>
<th>CO2STORE (ECLIPSE)</th>
<th>ECO2N (TOUGHREACT)</th>
<th>GPRS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compositional model</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Fully implicit solver</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Oil phase inclusion</td>
<td>×</td>
<td>×</td>
<td>✔</td>
</tr>
<tr>
<td>CO$_2$ dissolve in water phase</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>H$_2$O dissolve in gas phase</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Molecular diffusion</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>physical dispersion</td>
<td>×</td>
<td>×</td>
<td>✔</td>
</tr>
<tr>
<td>Hysteresis effect</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Non-isothermal</td>
<td>×</td>
<td>✔</td>
<td>×</td>
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<tr>
<td>Parallelize</td>
<td>✔</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>Chemical reaction</td>
<td>Bad</td>
<td>Good</td>
<td>Normal</td>
</tr>
<tr>
<td>Computational speed</td>
<td>Fast</td>
<td>Slow</td>
<td>Fastest</td>
</tr>
<tr>
<td>Expansibility</td>
<td>Bad</td>
<td>Normal</td>
<td>Good</td>
</tr>
<tr>
<td>Redevelop</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Until now, several simulators for geologic CO$_2$ sequestration are being developed by some research groups. In this part, we generally summarize three major simulators,
ECLIPSE CO2STORE module, TOUGHREACT ECO2N module, and GPRS CO2 modeling part. For comparison of the three simulators, see Table IV.

5. **Study on the impact of changes in mobility for the two-phase brine/CO2 system as a result of transitions between co- and counter-current flow settings**

We use a two-dimensional aquifer model to study the impact of transitions between co- and counter-current flow settings. The dimensions of the synthetic model are 2000 m by 300 m in the horizontal and vertical directions, respectively. A volume of CO2 accounting for 5% of the pore volume is injected at a constant rate at the bottom of the aquifer over a 2400 day period. We subsequently study the migration pattern for up to 15000 days. The top and bottom boundaries are closed and the side boundaries are open.

We study four different permeability fields, with an average permeability of 125 mD in the horizontal direction. The four permeability maps include one homogeneous field and three spatially heterogeneous maps with different correlation lengths. The four settings used in this study are shown in Fig. 5b. Four different vertical-to-horizontal permeability ratios are considered for each aquifer setting.

![Aquifer properties and permeability distributions](image)

**Figure 5:** Aquifer properties (left) and permeability distributions (right)

We include hysteresis in relative permeability of both phases as well as in capillary pressure. The scanning curves of the relative permeabilities are assumed to be reversible between drainage and imbibition processes. Killough’s hysteresis model [13] is used for both relative permeability and capillary pressure. We use Land’s model [14] with a trapping coefficient of 2 to account for residual trapping. Hysteresis in relative permeability is based on the Killough’s model via sets of bounding relative permeability...
curves; one set for co-current flow and another set for counter-current flow. The endpoint relative permeability of CO\textsubscript{2} is reduced from 0.6 in co-current flows to 0.4 in counter-current flows, a reduction of one-third that is consistent with experimental observations [2-4]. The value of residual gas saturation is assumed to be the same for both co-current and counter-current relative permeabilities during imbibition processes. There are no experimental observations available in the literature to support whether the residual saturation depends on the mode of flow or not, and we assume, for simplicity, that it is independent of flow mode. The scanning curves of the co-current and counter-current relative permeabilities of CO\textsubscript{2} start from the same saturation on the drainage curves with different values of relative permeabilities (depending on whether the flow is co-current or counter-current), and end at the same point at the residual saturation of CO\textsubscript{2} corresponding to zero relative permeability. For the wetting phase, the endpoints of the relative permeabilities of the two flow modes are the same (relative permeability of the wetting phase is one when the saturation of the wetting phase is one, and zero at the irreducible wetting phase saturation). We adjust the exponent of the Corey-type relative permeability function from 2 for co-current flow to 3 for counter-current flow.

We track the individual phase velocities throughout the numerical calculations to identify transitions between co- and counter-current flows. This is the procedure that is normally used to ensure the selection of appropriate upwind directions for fluid mobilities in the pressure equation. When a transition in flow direction is observed, we have implemented an option to transition between the input co-current and counter-current relative permeability functions. In our current implementation, we allow for an abrupt jump from e.g. the co-current relative permeability curve to the counter-current relative permeability curve at a given saturation when a change in flow direction occurs. The impact of our implementation on the numerical stability and overall performance of the numerical calculations are discussed in more detail below.

6. Dynamics of Plume Migration in Counter-Current Flows

The porous media used in this work consists of a borosilicate glass column with adjustable plungers. The glass column has an inner diameter of 50 mm and a height of 500 mm. Stainless steel frits (type 316) with an average pore size of 10 \( \mu \text{m} \) were attached to the end of each plunger. The frits were used as current electrodes and to create a uniform flow distribution of injected fluids. A hole was drilled through each plunger and an electrical wire was inserted to connect the metal frits to a power source without disturbing the flow. The glass column was further modified by drilling holes along the length to insert the potential electrodes. In each selected interval, three holes were drilled on the perimeter of the column with a spacing of 120 degrees. A total of 36 holes were drilled along the glass column to establish a total of 11 sections. The electrodes were placed in contact with the beads through the holes along the column and carefully sealed with epoxy to prevent leakage. At each level along the column, the 3 wires were connected together and used as the voltage electrodes.

To represent and study the migration of a supercritical CO\textsubscript{2} plume in a saline aquifer, we conducted a series of segregation experiments at low-pressure using the synthetic porous material and analog fluids. We used BT13 (170 Mesh) glass beads with an average particle diameter of 88 \( \mu \text{m} \) to represent the porous media while the immiscible
two-phase brine/iso-octane (iC8) fluid system was used to represent brine/supercritical CO2 at reservoir conditions. Brine was prepared from deionized water and NaCl with a concentration of 20,000 ppm resulting in a density of 1013 kg/m³ at 70°F while the non-wetting phase (iC8) has a density of 692 kg/m³ at 70°F. To visualize the propagation of iC8 in the column we used an oil soluble dye (Sudan Red 7B). The viscosity of brine and iC8 are 1.0 and 0.48 mPa.s, respectively, as reported by Cinar et al. (2006). Pendant drop measurement was performed to determine the interfacial tension of the brine/iC8 system and a value of 47.3 mN/m was observed from repeated measurements.

The porosity and permeability of the packed column were measured to 38.6% and 4.8 Darcy, respectively. At fully saturated conditions, the porosity at each section of the column was calculated from the resistance and found to be in good agreement with the overall porosity.

Relative permeability functions for primary drainage and imbibition processes were measured from steady-state flow experiments. Figure 6 reports the relative permeability measurements and a Corey-type representation for both drainage and imbibition processes.

Capillary pressure functions were adopted from Dawe et al. (1992), who measured capillary pressure for drainage and imbibition processes in glass bead packs. As their measurements were performed for different glass bead sizes and fluid systems, their capillary pressure observations were initially scaled using Leverett J-scaling (Leverett, 1941).

![Figure 6: Steady-state relative permeability functions for drainage and imbibition processes](image)

The primary drainage and imbibition capillary pressures corresponding to the glass bead used in our segregation experiments were constructed from the J-functions extracted from Dawe et al. (1992): van Genuchten (1980) capillary pressure functions were used to smooth the capillary pressure data for both drainage and imbibition processes. To match
the irreducible wetting phase saturation and maximum trapped non-wetting saturation obtained from our steady-state relative permeability experiments, we re-normalized the phase saturations. In addition, the drainage capillary pressure was measured using the porous-plate technique. The capillary pressure function was subsequently re-scaled to fit the measured values.

In order to capture the dynamic changes in the electric potential across the individual sections of the column during segregation experiments, two data acquisition modules from National Instruments (NI-DAQ) were used to provide and acquire signals. A 0.5 V AC signal with frequency of 1 kHz was generated from the analogue channel of one NI-DAQ unit. A shunt resistor with a resistance of 2 kΩ was connected in series to the top of the packed column to prevent current overflow (and accelerated corrosion). The wires from the packed column were connected to the analogue input channels of the second NI-DAQ module. Both NI-DAQ modules were connected to a PC to control the units and to collect data. The potential difference across each section of the packed column and across the shunt resistor was continuously recorded using LabView software. Figure 7 shows a schematic diagram of the dynamic segregation experiment including connections to the source and acquisition systems. Once the column was fully saturated with brine, the resistivity of each section of the packed column was determined.

A Teledyne 260D syringe pump was used to inject iC8 at the top of the column at a rate below the critical velocity as calculated from the petro-physical properties discussed earlier. The dyed iC8 was then injected into the column to create an initial non-wetting saturation distribution as uniform as possible. After the desired amount of iC8 was injected, the packed column was inverted and the segregation experiment initiated. The potential differences at each section of the packed column were continuously recorded allowing for subsequent calculation of the wetting phase saturation from the resistivity index.

Figure 7: Schematic diagram of experimental setup for segregation experiment
To repeat the segregation experiment, two pore-volumes of isopropanol were injected to remove iC8 and brine from the column. Deionized water was subsequently used to flush the column and remove the isopropanol and finally, brine was loaded from the bottom to displace the deionized water.

7. Discrete Fracture Modeling (DFM)

Reservoirs with fractures may cause leakage problems which will be detrimental to the environment and safety to human race. It is found in Algerian In Salah CCS project that CO₂ prefers to go through fractures than matrix. Research on CO₂ flow in fracture reservoirs is urgent as well as significant. In the work of Nelson et al. (2005), natural and artificially-induced hydraulic fractures have been identified as the most important factors in risk assessment of CO₂ storage, and regarded as potential escape routes for CO₂, which could damage the prospective storage ability of a specific storage site. Natural fractures could potentially allow CO₂ to quickly migrate through the cap rock to the surface, while local pressure increase caused by CO₂ injection can also lead to hydro fracturing in the vicinity of wells.

Discrete Fracture Modeling (DFM) begins to be used more and more in reservoir simulation because of isolated and disconnected fractures. In DFM, the fracture plays as a standalone grid block but a secondary factor in the matrix-fracture system, which allows us to separately deal with matrix and fracture properties and flows occurring in them. DFM can also be used in combination with dual porosity model. DFM models have proven to be useful for measuring leakage risks associated with hydraulic fracturing and coal bed methane production (Pashin, Jin, and Payton, 2004). It is for this reason that DFM is expected to become an effective modeling approach for measuring the risks associated with carbon sequestration.

8. Study on discrete fracture modeling application in an actual CO₂ sequestration site of China

The section model from an actual geologic grid based on seismic interpretation is used. The saline formations consist of six alternating high-low permeability layers. One injector is completed at the bottom high-perm layer and one observation well is completed below, above and at the middle low-perm layer to monitor the pressure and CO₂ concentration change. The system is discretized into triangles using the gridding software triangle [15]. The transmissibilities between each grid block (including fracture-fracture, matrix-matrix and fracture-matrix) are calculated following the Karimi-Fard’s approach [16]. With properties for each cell and transmissibility data between cells, the whole system is simulated using GPRS.

The generic curves use the van Genuchten functional form for aqueous relative permeability $k_w$, and the Corey functional form for gas relative permeability $k_r g$ in sandstone and mudstone [17] (Akaku, 2008; Doughty, 2004). For fractures, straight lines are used to describe the relative permeability. Relative permeability not only affects CO₂ movement in the aquifer and caprock, but also has significant effect on the initial injectivity since the near-wellbore region is initially filled with water [18]. The injectivity increases with the increase in gas saturation, and effective permeability.
Figure 8: Geological setup, well locations and porosity field

Figure 9: Geological setup, well locations and permeability field
Six cases have been studied. In case 1, we simulate the system with no natural or hydraulic fractures. In case 2, 3 and 4, we simulate the system with fractures located at
different distance to the injector. In case 5 and 6, we simulate the system with hydraulic fractures of different half length. For all cases, we inject CO$_2$ for 10 years with bottom hole pressure constraint set to be 1.5 times the initial formation pressure for each layer. This is to avoid artificial fracturing caused by injection induced over pressure. Injection is stopped at the end of 10 years and we simulate the system up to 100 years.

For all cases, we illustrate results including pressure and CO$_2$ concentration maps, injection rate/cumulative injection curves, and pressure and CO$_2$ concentration observed at the monitoring well at three different intervals.

9. **Enhancement of Geochemical Simulator and the application in the aspect of ECBM**

Chemical reaction and transport in the subsurface occurs over a wide range of space and time scales. For a given amount of mass at a fix point and time, chemical reactions determine the partition of the components among different phases. The reactions can be typically divided into two classes: equilibrium reactions whose reaction rates are fast and reversible and the kinetic reactions with finite rates. As the rates of thermodynamic equilibrium reaction are fast and hard to be detected, a direct solution for the species mass balance equation is unpractical. Some strategies have been introduced to solve this problem. Among them there are Equilibrium Rate Annihilation (ERA) matrix method and Decomposing method. Meanwhile, these methods reduce the number of mass balance equations to be solved.

Previous version of GPRS geochemical simulator uses an element-balance approach to reduce the number of equations as well as eliminate fast reactions rates. The element can be but not limited to the concept of atoms in the sense of chemistry. This approach based on a simple relation that the reaction stoichiometric matrix multiplied by the stoichiometric coefficients matrix is zero under the assumption of element balance. It can be shown as

$$E_{n \times n_s} S_{n_s \times n_r} = 0_{n \times n_r}$$  \(1\)

Where $E$ and $S$ are reaction stoichiometric matrix and component-element correlation matrix, respectively. It is straightforward to use component-element correlation matrix to derive ERA matrix. However, some researchers declare that it may lead to numerical solving problem when some member of elements is very low and the other is several orders of magnitude higher. Another ERA building strategy is adapted to the simulator which has been reported in the literature [96]. It assumes equilibrium reactions only exist in the aqueous phase. For aqueous part, the reactions and the corresponding stoichiometric matrix can be expressed as:

$$V = \begin{bmatrix} v_{1,1} & \cdots & v_{1,R_{aq}} \\ \vdots & \ddots & \vdots \\ v_{n_{aq},1} & \cdots & v_{n_{aq},R_{aq}} \end{bmatrix}_{n_{aq} \times R_{aq}}$$  \(2\)
$n_{eq}$ is the number of aqueous species and $R_{aq}$ is the number of aqueous reactions. The canonical stoichiometric matrix has the following form:

$$V_c = \begin{bmatrix} V_{p\times R_{aq}} \\ I_{R_{aq} \times R_{aq}} \end{bmatrix}_{n_{eq} \times R_{aq}}$$ (3)

$I$ is the identity matrix. The subscript $p$ denotes the number of primary species or components. To eliminate equilibrium rates in the mass balance equations, ERA matrix must be non-singular and satisfies

$$EV_c = 0$$ (4)

Then the ERA matrix can be

$$E = [I_{p \times p}, -V_{p \times R_{aq}}]$$ (5)

Dissolution–precipitation only involves one mineral species normally. Therefore the stoichiometric coefficient is all zeros except for the corresponding mineral species mass balance function. The kinetic rate term that was included in aqueous species mass balance don’t have to be eliminated. Then extended ERA matrix for the full system can be expressed as

$$\begin{array}{|c|c|}
\hline
ERA_{p \times n_{eq}} & U_{R_{p} \times R_{mix}} \\
\hline
0_{R_{mix} \times n_{eq}} & I_{R_{mix} \times R_{mix}} \\
\hline
\end{array}$$

The matrix $U$ can be any form only if it can keep the extended ERA matrix invertible. A validation is carried out by comparing our results with GEM, which also use the canonical matrix strategy. The case is a simple CO2 mineralization in aqueous. It involves four reactions listed below: three intra-aqueous chemical-equilibrium reactions and the mineral dissolution reaction. Stoichiometric matrix for aqueous part is shown in Table V. The ideal activity model is used for both simulators. Water vaporization is activated.

$$OH^- + H^+ = H_2O$$

$$CO_{2(aq)} + H2O = H^+ + HCO_3^-$$

$$H^+ + CO_3^{2-} = HCO_3^-$$

$$CaCO_{3(s)} + H^+ = Ca^{2+} + HCO_3^-$$
Table V: Stoichiometric matrix for aqueous part

<table>
<thead>
<tr>
<th>Species Reaction</th>
<th>CO2(aq)</th>
<th>H2O</th>
<th>H+</th>
<th>Ca++</th>
<th>OH-</th>
<th>HCO3-</th>
<th>CO3--</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R2</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>R3</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

The two methods mentioned above both aim to eliminate fast reactions rate in the species mass balance equations. ERA matrix is employed on the purpose. Decomposition Method is another option. The reactions can be written as a set of ODEs for each species. The main idea of the decomposition method is though gauss elimination to reduce the reactions into three subsets of equations: mass conservation equations, infinite rate equation that can be represented by equilibrium equation and finite rate of kinetic equation. The detail of the this method can be found in the paper reported by Fang, Y.(2003).

Although ERA matrix method and decomposition method are different approach, they are consistent in principle. The optimal method is chosen according to the problem and variable set.

CO2 storage in coal seam is presently also an appealing way for reducing greenhouse gas emissions as well as a significant methane enhancement by experiments and field test. Differ from the conventional gas which is trapped in the pore space, the majority of gas in the CBM reservoir is stored in the coal matrix by sorption. The sorption effect makes CBM reservoir a vast potential volume for geological sequestration. CBM water also plays an important role in CO2 flooding. In some places where the aqueous phase has high salinity contents, the solution of CO2 is significantly impacted. It requires a coupled geochemical tool to model the process. Although there are a number of geochemical simulators are available at present, most of them are used for contamination and water resource issues. A coupled CBM/ECBM geochemical tool has been undertaken by some groups. One reported study comes from the Issued by Sandia National Laboratories, which modify the exiting geochemical simulator TOUGH2 on this purpose. Unfortunately no satisfying results are derived. Another group worth to mention is the Stanford University Petroleum Research Institute (SUPRI-B). A fully implicit transport and reactive model is implemented within the General Purpose Reservoir Simulator (GPRS). The modular object–oriented design facilitates he extension of GPRS chemical simulator to model ECBM process.

The main idea we implement the CBM/ECBM model is based on the similarity between of adsorption process of surface reaction and ECBM. Adsorption is the process by which fluid constituents adhere to a solid surface (i.e., the coal, in this case). To illustrate it, a basic knowledge of CBM adsorption process is necessary. The typical adsorption model we use is Langmuir isotherm, which is also available by most commercial software. To start with, we propose a single component, two-parameter Langmuir model of the following form
\[
C(p_i) = \frac{V_L p_i}{(P_L + p_i)}
\]  \hspace{1cm} (6)

Where \( V_L \) is the maximum amount of gas that can be absorbed, and \( P_L \) is a characteristic pressure. Both \( V_L \) and \( P_L \) are determined from laboratory adsorption isotherm measurements. Under the assumption of local phase equilibrium between the entire domains, the adsorbed concentration on the surface of the coal is solely the function of pressure. Hence the pressure determines the storage capacity for coal seams. The initial concentration of methane is also calculated by means of this method.

For the prediction of mixed gas adsorption, convenient method is to extend the pure component Langmuir model to a multicomponent type. Then the adsorption capacity is function of pressure and composition. For each component in a system of \( N_g \) absorbable component, the extended Langmuir model is yield to be

\[
C_i = \frac{V_L p_i / P_L}{(1 + \sum_{j=1}^{N_g} p_j / P_j)}
\]  \hspace{1cm} (7)

Where \( p_i \) is the partial pressure for the corresponding component and can be defined as

\[
p_i = p_g \bar{y}_{ig}
\]  \hspace{1cm} (8)

Langmuir parameters for pure component isotherms are also used. Diffusion of gas between the two media (cleat and matrix) is traditionally modeled as a Fickian process which is given by

\[
F_g = \chi D_{ci} \left[ C_{si} - C(p_i) \right]
\]  \hspace{1cm} (9)

Where the diffusivity \( \chi \) can be written as

\[
\chi = V \bar{\sigma}
\]  \hspace{1cm} (10)

The parameter \( V \) and \( \sigma \) are bulk volume and shape factor respectively. \( \sigma \) is the factor account for the interface area per unit volume. Commonly, the diffusion coefficient and the shape factor are combined to be diffusion time as below, which is easier to obtain in the lab

\[
\tau = \frac{1}{D_{ci} \sigma}
\]  \hspace{1cm} (11)

Then the production rate from the adsorbed state to the cleat can be written as
\[ q_i = \frac{V}{\tau} (C_{si} - C(p_i)) \]  

(12)

For a chemical reaction simulator, the adsorption process for each component can be represented by the following expression in a system of \( N_c \) absorbable components.

\[ M_i(g) \leftrightarrow M_i(a) \]  

(13)

Where \( M_i(g) \) and \( M_i(a) \) are symbols of component \( i \) in the gas phase and in the adsorbed phase. The kinetic reaction rate \( r_i \) for unit coal volume is defined as

\[ r_i = \frac{1}{\tau} (C_{si} - C(p_i)) \]  

(14)

A complete ODE form of this solid kinetic reaction is

\[ -\frac{dC_{si}}{dt} = r_i \]  

(15)

Due to the similarity between the present problem and the reaction module already implemented in GPRS, we only need to provide the derivatives of the reaction term with respect to the unknown variables.

The implemented chemical reaction module inherits the former compositional parts. Phase behavior is represented by Peng-Robinson Equation of State (EOs) model. The following relation can be yield for each component at phase equilibrium

\[ f_{i,p1} - f_{i,p2} = 0 \]  

(16)

For a primary CBM recovery problem, the species in the system are: CH4 (g), CH4 (l), H2O (g), H2O (l), CH4(s), where the script g, l, s indicates gas, liquid and solid phase. If we choose the element based ERA, the elements are: CH4, H2O. The component-element correlation matrix and reaction coefficient are tabled as Table VI and Table VII.

**Table VI: Component-element correlation matrix**

<table>
<thead>
<tr>
<th></th>
<th>CH4</th>
<th>H2O</th>
<th>CH4s</th>
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<tbody>
<tr>
<td>CH4</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>H2O</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table VII: Reaction coefficient matrix**

<table>
<thead>
<tr>
<th></th>
<th>CH4(g)</th>
<th>H2O(g)</th>
<th>CH4(l)</th>
<th>H2O(l)</th>
<th>CH4s</th>
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</thead>
<tbody>
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<td>CH4</td>
<td>1</td>
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</tbody>
</table>

Similarly, for the ECBM process the species in the system are: CH4 (g), CH4 (l), CO2 (l), H2O (g), H2O (l), CH4(s), CO2(s). The elements are: CH4, H2O and CO2. The component-Element correlation matrix and reaction coefficient are tabled as Table VIII and Table IX.
Table VIII: Component-element correlation matrix

<table>
<thead>
<tr>
<th></th>
<th>CH4</th>
<th>H2O</th>
<th>CO2</th>
<th>CH4(s)</th>
<th>CO2(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>H2O</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

Table IX: Reaction coefficient matrix

<table>
<thead>
<tr>
<th></th>
<th>CH4(g)</th>
<th>H2O(g)</th>
<th>CO2(g)</th>
<th>CH4(l)</th>
<th>H2O(l)</th>
<th>CO2(l)</th>
<th>CH4(s)</th>
<th>CO2(s)</th>
</tr>
</thead>
<tbody>
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<td>CH4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td></td>
</tr>
</tbody>
</table>

We can find that it is convenient for the simulator in modeling multi-component competitive sorption case. Results and validation are shown in the following section.

Results

1. Jianghan Basin Evaluation

The Jianghan Basin lies in the south-central part of the Hubei Province, south China, the Jianghan Plain between Yangtzi River and Han River, west to Yichang city, east to Yingcheng city, south to Huhong city and north to the north of Jingzhou city covering an area of 36350 km². CO₂ emissions in the region directly overlying the Jianghan-Nanyang Basins contributed approximately 116 Mt CO₂ per year to China’s estimated total stationary source CO₂ emissions of 2970 Mt/yr.

Major point sources in the vicinity of Wuhan city amount to approximately 25 Mt of generation (including four power plants and a steel mill) corresponding to approximately 25 Mt of CO₂ per year.

The Jianghan Basin is a representative salt lake rift basin developed on the Zhongyangzi Paraplatform during the Cretaceous and Tertiary Period covering an area of 36350 km². The tectonic structure location is in the central part of the Zhongyangzi Depression in Yangzi Paraplatform, west to Western Hubei fold belt, east to Wuhan-Tongshan fold belt, north to Bahong fold belt and south to Jianghan fold belt (Pan and Zhu, 1988). The Early Cretaceous Basement of the basin is a double-deck structure consisting of Proterozoic metamorphic rocks in the lower part and sedimentary rocks deposited from Sinian to Mesozoic Jurassic in the in the upper part acting as the caprock of the Zhongyangzi Depression of Yangzi Paraplatform. The development process of the Jianghan Basin contains seven different phases controlled by tectonic movements which can be grouped into two tectonic cycles characterized by tension crack-rift-depression. In addition, together with the controls of the northeast and northwest basement faults, the basin forms eight- depression and four-uplift (or low uplift) tectonic pattern as shown in Table X (Li et al., 2002).

The Jianghan Basin contains Late Cretaceous to Quaternary sedimentary deposits up to 10km thick, which are grouped into two predominant sedimentary cycles. The first sedimentary cycle contains the sediments from the Upper Cretaceous to Xingouzui formation of Lower Eocene in Paleogene period. Upper Cretaceous is composed of red terrestrial clastic rocks formation with the thickness ranging from 500 to 2000m. Shashi Formation of Paleocene in Paleogene period consists of gypsum-salt and red mudstone
formation with the thickness varying from 200 to 900 meters. Xingouzui Formation of low Eocene is composed of sandstone and mudstone with interbedded gypsum salt, which is a petroliferous formation with the thickness ranging from 600 to 1900 meters. The second sedimentary cycle consists of the sedimentary deposits from Jingsha Formation of middle Eocene in Paleogene period to the Jinghezhen Formation of Oligocene. Jingsha Formation is composed of red terrestrial clastic rocks formation with the thickness ranging from 600 to 1870 meters. Qianjiang Formation is a red terrestrial clastic rocks formation with the thickness varying from 750 to 5000 meters. Jinghezhen Formation deposits the grey-green and green-grey siltstone. The gypsum salt is widely distributed

**Figure 12:** Location map of the Jianghan Basin (Li et al., 2002)

Formation is composed of red terrestrial clastic rocks formation with the thickness ranging from 600 to 1870 meters. Qianjiang Formation is a red terrestrial clastic rocks formation with the thickness varying from 750 to 5000 meters. Jinghezhen Formation deposits the grey-green and green-grey siltstone. The gypsum salt is widely distributed.
extending from the Jiangling Depression to Mianyang Depression with the area up to 9000 km² in the first sedimentary cycle. However, the salt rock deposits very well in the second sedimentary cycle, with the accumulative thickness up to 1800 meters, and is widely distributed in the Qianjiang, Xiaoban and Yunying Depression. Figure 15 and 16 give a generalised stratigraphy and distribution of Jianghan Basin.

**Table X:** The secondary tectonic units of the Jianghan basin

<table>
<thead>
<tr>
<th>Category</th>
<th>Name</th>
<th>Area(km²)</th>
<th>Sedimentary thickness (m)</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depression</td>
<td>Jiangling depression</td>
<td>7400</td>
<td>6500</td>
<td>Depression sag</td>
</tr>
<tr>
<td></td>
<td>Chentuokou depression</td>
<td>1400</td>
<td>4500</td>
<td>Single fault type depression</td>
</tr>
<tr>
<td></td>
<td>Qiangjiang depression</td>
<td>2400</td>
<td>8500</td>
<td>Double fault type depression</td>
</tr>
<tr>
<td></td>
<td>Mianyang depression</td>
<td>3400</td>
<td>4000</td>
<td>Depression sag</td>
</tr>
<tr>
<td></td>
<td>Xiaoban depression</td>
<td>500</td>
<td>6000</td>
<td>Single fault type depression</td>
</tr>
<tr>
<td></td>
<td>Zhijiang depression</td>
<td>3300</td>
<td>2000</td>
<td>Depression sag</td>
</tr>
<tr>
<td></td>
<td>Yunying depression</td>
<td>4500</td>
<td>--</td>
<td>Single fault type depression</td>
</tr>
<tr>
<td></td>
<td>Herong depression</td>
<td>1600</td>
<td>--</td>
<td>Depression sag</td>
</tr>
<tr>
<td></td>
<td>Jinneng depression</td>
<td>3200</td>
<td>--</td>
<td>Single fault type depression</td>
</tr>
<tr>
<td></td>
<td>Hanshui depression</td>
<td>3600</td>
<td>3000</td>
<td>Single fault type depression</td>
</tr>
<tr>
<td></td>
<td>Yuanan depression</td>
<td>600</td>
<td>--</td>
<td>Double fault type depression</td>
</tr>
<tr>
<td>Uplift</td>
<td>Tonghaikou uplift</td>
<td>1000</td>
<td>--</td>
<td>Uplift</td>
</tr>
<tr>
<td></td>
<td>Longsaihu lower uplift</td>
<td>2300</td>
<td>--</td>
<td>Lower uplift</td>
</tr>
<tr>
<td></td>
<td>Yuekou lower uplift</td>
<td>300</td>
<td>--</td>
<td>Lower uplift</td>
</tr>
<tr>
<td></td>
<td>Yajiao-Xingou lower uplift</td>
<td>500</td>
<td>--</td>
<td>Lower uplift</td>
</tr>
</tbody>
</table>

The sandstones of Haiyang formation of Cretaceous; the sandstones and siltstones of Jinghenthezhen Formation, Qianjiang Formation, Jingsha Formation, Xingouzui Formation and Shashi Formation of Paleogene; the sandy conglomerate of Guanghuasi Formation of Neocene; and the surfical sediments of Pingyuan Formation of Quaternary form the main aquifers in the Jianghan Basin. To be pointed out, the shallow reservoir bed is composed of the sandstones and gravel bed of the Quaternary Pingyuan Formation and the middle and upper part of the Neocene Guanghuasi Formation, which usually has a close connection with the surface water since the runoff condition of the surface is quite poor due to the low ground and accumulated rivers and lakes. However, in the north area of the Qianjiang Depression, the lower and middle Guanghuashi Formation can act as the
regional confining bed since it contains varicolored clay layer and minor calcareous mudstone with the thickness of 100m. And the logging information shows that there is a great distinction between of the freshwater and saline water between the upper and lower of the Guanghuasi Formation. The groundwater in most of the region of Guanghuasi Formation is in free water exchange zone. Below the plane of unconformity between Neocene and Paleogene, however, the groundwater is usually brackish water and saline water. The salinity both rises in vertical from above to below and in horizon from the edge to center of the depressions. Whatever in vertical or in horizon, the hydrogeology of the reservoirs both present closed to semi-closed states.

**Figure 13:** Tectonic map of the Jianghan Basin (Pan and Zhu, 1988)
The Cretaceous aquifer and the Paleogene aquifer can be divided into three formation water belt in depth, namely alternate belt, alternate and stagnant belt, and alternate and stasis belt. In the alternate belt, as the burial depth is less than 1100m, the groundwater is influenced by the surface water and mainly is sulfate-sodium type. The salinity is less than 200000 mg/L. In the alternate and stagnant belt, the groundwater is mainly sulfate-sodium type as the burial depth between 1100 to 2000m where is the mixed zone of surface and sedimentary formation water. The salinity varies from 200000 mg/L to 340000 mg/L. In the alternate and stasis belt, the burial depth is deeper than 2000m, and the water type is mainly magnesium chloride, and then sodium sulfate. The distribution of salinity of reservoir water is concentrated, varying from 100000 mg/L to 340000 mg/L. Water chemical symbol shows that the belt is nearly not influenced by the infiltration of

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**Figure 14:** Interpretation of the profile lines in Northeast and Northwest in the Jianghan Basin (Yang et al. 2009)
the surface water. Table XI provides the data on the salinity of the information water in Paleogene of the Jianghan Basin.

The reservoir rocks in the Jianghan Basin include sandstone, globulitic marl, fractured mudstone and basalt, sandstone reservoir as the major. Xingouzui Formation and Qianjiang Formation is the predominant petroliferous and saliniferous sandstone reservoir as shown in Figure 16. The sediment supply is unidirectional and adequate, mainly from the Jingmen, Hanshui and Dangyang palaeodrainage pattern in the north of the basin during the Qianjiang and Xingouzui Formation deposits.

Figure 15: Stratigraphy from Triassic to Paleocene of the Jianghan Basin (Pan and Zhu, 1988)
**Table XI**: Salinity of the formation water in Paleogene of the Jianghan Basin

<table>
<thead>
<tr>
<th>Formation Member</th>
<th>Number of samples</th>
<th>Paleosalinity %</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Lowest</td>
<td>Highest</td>
<td></td>
</tr>
<tr>
<td>Jinghengzhen Fm</td>
<td>5</td>
<td>2.00</td>
<td>3.69</td>
<td>2.4~3.5</td>
</tr>
<tr>
<td>Qianjiang Fm</td>
<td></td>
<td>28</td>
<td>5.21</td>
<td>2.6~4.5</td>
</tr>
<tr>
<td></td>
<td>Qian 1</td>
<td>24</td>
<td>9.10</td>
<td>3.3~5.5</td>
</tr>
<tr>
<td></td>
<td>Qian 2</td>
<td>58</td>
<td>8.01</td>
<td>3.0~4.7</td>
</tr>
<tr>
<td></td>
<td>Qian 3</td>
<td>32</td>
<td>7.01</td>
<td>1.8~3.6</td>
</tr>
<tr>
<td></td>
<td>Qian 4</td>
<td>32</td>
<td>3.13</td>
<td>1.4~3.1</td>
</tr>
<tr>
<td>Jingsha Fm</td>
<td>5</td>
<td>1.40</td>
<td>3.13</td>
<td>1.4~3.1</td>
</tr>
<tr>
<td>Xingouzui Fm</td>
<td>9</td>
<td>1.73</td>
<td>3.30</td>
<td>2.0~3.2</td>
</tr>
</tbody>
</table>

**Figure 16**: Generalized stratigraphy of the Jianghan Basin (Li et al., 2002)
The main cap rocks in the basin involve mudstone and gypsum-slat bed. The lower Xingouzui Formation contains two sets of the regional seals, one referring to mudstone confining bed with 20~40 meters thick lying between Sandstone II and Sandstone III, another referring to gypsum on the top of the low Xingouzui Formaiton with 5~20 meters thick. What’s more, the upper Xingouzui Formation depositing red mudstone with minor sandstone actually can act as the regional seal since its sediment thickness surpasses 200 meters, and even up to 600 meters in some area. Table XII provides a simple generalized model of the reservoir and seal pairs of Xingouzui Formation in the Jianghan Basin. Qianjiang Formation, however, contains four sets of the regional seals, namely 1~6 rhythms in the Upper Qian Four, 4~8 rhythms in the Lower Qian Three, 11~15 rhythms in the Qian Two and argillaceous gypsum bed on the top of Qian One. The rhythm gaprock is composed of the grey mudstone, salt rock and argillaceous gypsum. Table XIII gives a simple generalized model of the reservoir and seal pairs of Qianjiang Formation in Jiangling Depression of the Jianghan Basin.

**Table XII:** Reservoir and seal pairs of Xingouzui Formation in the Jianghan Basin

<table>
<thead>
<tr>
<th>Formation</th>
<th>Thickness (m)</th>
<th>Lithologic character</th>
<th>Reservoir</th>
<th>Seal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>200–600</td>
<td>Red mudstone with sandstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>5–20</td>
<td>Grey argillaceous gypsum and white gypsum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandstone I</td>
<td>50–150</td>
<td>Red-grey mudstone and sandstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandstone II</td>
<td>100–250</td>
<td>Grey mudstone with marl and sandstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mudstone</td>
<td>100–250</td>
<td>Grey mudstone with gypsum-bearing mudstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandstone III</td>
<td>100–250</td>
<td>Red-grey mudstone and sandstone</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The sandstone in Qianjiang Formation is not well deposited because of the complicated epalaeeeographic setting and palaeoclimate, poor hydrodynamic force and great density of aqueous medium in saline lake, but concentrated distributes in Qianjiang Depression, Jiangling Depression and Xiaoban Depression covering the area of the 6078 km², accounting for 16.9 percent of the basin. Moreover, the thickness of the sandstone is comparatively large, ranging from 30m to 300m, with the maximum thickness up to 649 m. The favorable facies belt lies in the north of the Qianjiang Depression with the overlay area of 1630 km². The petrophysical property of the sandstone is good. The average porosity is 19.2% and the permeability is $325.8 \times 10^{-3} \mu m^2$. Figure 17 gives the sandstone isopachs of Paleogene Qianjiang Formaion of in the Jianghan Basin.

The formation water in Qianjiang formation mainly is sulfate-sodium type. As the depth of burial lower than 1250m, water salinity increases with depth; as the burial depth deeper than 1250m, the water salinity vary from 250000 mg/L to 340000 mg/L, almost in the saturation state; when the burial depth deeper than 1650m, the chemistry of formation water appears the same features of sedimentary storage water. Table XIV shows the major species of formation groundwater in Qianjiang Formation from different regions.
<table>
<thead>
<tr>
<th>Formation</th>
<th>Thickness (m)</th>
<th>Sandstone&amp;Interlayer</th>
<th>Reservoir</th>
<th>Caprock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qian 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mud-gypsum rock</td>
<td>110~450</td>
<td>Regional Interlayer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zhouji Sandstone</td>
<td></td>
<td>Sandstone Segment 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soft-mud rock</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qian 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper Qian 2</td>
<td>110~700</td>
<td>Regional Interlayer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower Qian 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper Qian 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qian 3-1</td>
<td></td>
<td>Sandstone Segment 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Three-high resistant Fm</td>
<td>150~640</td>
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<tr>
<td>Qian 3-2</td>
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<tr>
<td>Qian 3-3</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Lower Qian 3</td>
<td></td>
<td>Regional Interlayer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4~8 rhythm</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Qian 3-4</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Upper Qian 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qian 4-1</td>
<td></td>
<td>Sandstone Segment 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2rhythm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qian 4-0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1~6 rhythm</td>
<td>100~700</td>
<td>Regional Interlayer</td>
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<tr>
<td>7~6 rhythm</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>4 rhythm</td>
<td></td>
<td>Sandstone Segment 4</td>
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<tr>
<td>Qian 4-3</td>
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</tr>
<tr>
<td>Lower Qian 4</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower Qian 4</td>
<td>173~2218</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 17: Sandstone isopachs of Qianjiang Formation in Jianghan Basin (Yang et al. 2009)

Xingouzui Formation distributes three delta sand bodies in the Mashan, Hougang and Hanchuan region from west to east in the north of the basin and they connect together into a reservoir development belt in horizon and get thin to the south. The sand body is widely distributed with the area of 11000 km$^2$, and the thickness of the sandstone is generally 20 to 140 meters in range, with the maximum thickness up to 237 meters. Siltstone is the main rock type, with the average porosity of 17% and the average permeability of $98 \times 10^{-3}$ μm$^2$. Figure 18 shows the sandstone isopachs of Lower Xingouzui Formation in the Jianghan Basin. In Jiangling Depression, the major component of the sandstone is feldspar with the quartz content of 50.7% to 66.1%. Porous cement acts as the main cementation type containing low impurity less than 5%. The formation water in Xingouzui Formation is mainly calcium chloride and sodium sulfate type. As the burial depth deeper than 1000m, the water salinity appears little differences with the increasing depth, mainly between 100000 mg/L to 260000 mg/L. Table XV shows the major species of formation groundwater in Xingouzui Formation from different regions.
### Table XIV: Major Species of formation groundwater in Qianjiang Formation from different region

<table>
<thead>
<tr>
<th>Region</th>
<th>Relative density</th>
<th>Na⁺ (mg/l)</th>
<th>Ca²⁺ (mg/l)</th>
<th>Mg²⁺ (mg/l)</th>
<th>Cl⁻ (mg/l)</th>
<th>SO₄²⁻ (mg/l)</th>
<th>HCO₃⁻ (mg/l)</th>
<th>F⁻ (mg/l)</th>
<th>Br⁻ (mg/l)</th>
<th>B (mg/l)</th>
<th>Li⁺ (mg/l)</th>
<th>K⁺ (mg/l)</th>
<th>Salinity (mg/l)</th>
<th>Others (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xijiakou</td>
<td>1.0986</td>
<td>56932</td>
<td>1566</td>
<td>491</td>
<td>88957</td>
<td>3594</td>
<td>659</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>152199</td>
<td></td>
</tr>
<tr>
<td>Yajiao</td>
<td>1.1101</td>
<td>66563</td>
<td>1608</td>
<td>444</td>
<td>102970</td>
<td>4640</td>
<td>722</td>
<td>11.6</td>
<td>392</td>
<td>53</td>
<td>56</td>
<td>481</td>
<td>177946</td>
<td></td>
</tr>
<tr>
<td>Haokou</td>
<td>1.1776</td>
<td>107385</td>
<td>661</td>
<td>104</td>
<td>162220</td>
<td>6093</td>
<td>656</td>
<td>10.4</td>
<td>461</td>
<td>161</td>
<td>57</td>
<td>2126</td>
<td>279934</td>
<td></td>
</tr>
<tr>
<td>Zhongshi</td>
<td>1.1774</td>
<td>111101</td>
<td>861</td>
<td>129</td>
<td>166853</td>
<td>8093</td>
<td>622</td>
<td>12.1</td>
<td>288</td>
<td>173</td>
<td>63</td>
<td>1647</td>
<td>289842</td>
<td></td>
</tr>
<tr>
<td>Gaochang</td>
<td>1.2054</td>
<td>123835</td>
<td>685</td>
<td>150</td>
<td>185836</td>
<td>8903</td>
<td>654</td>
<td>14.0</td>
<td>558</td>
<td>172</td>
<td>51</td>
<td>1883</td>
<td>322741</td>
<td></td>
</tr>
<tr>
<td>Guanghua</td>
<td>1.2078</td>
<td>126220</td>
<td>490</td>
<td>170</td>
<td>189423</td>
<td>8432</td>
<td>645</td>
<td>9.7</td>
<td>226</td>
<td>349</td>
<td>69</td>
<td>3898</td>
<td>329932</td>
<td></td>
</tr>
<tr>
<td>Wangchang</td>
<td>1.1812</td>
<td>111975</td>
<td>416</td>
<td>138</td>
<td>161482</td>
<td>17423</td>
<td>1048</td>
<td>6.9</td>
<td>272</td>
<td>208</td>
<td>57</td>
<td>1195</td>
<td>294221</td>
<td></td>
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<tr>
<td>Huangchang</td>
<td>1.2023</td>
<td>1.7507</td>
<td>403</td>
<td>23</td>
<td>171555</td>
<td>13565</td>
<td>830</td>
<td>10.3</td>
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<td>149</td>
<td>53</td>
<td>919</td>
<td>305282</td>
<td></td>
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<td>Zhanggang</td>
<td>1.1684</td>
<td>91592</td>
<td>277</td>
<td>53</td>
<td>125419</td>
<td>21045</td>
<td>1628</td>
<td>3.8</td>
<td>82</td>
<td></td>
<td></td>
<td></td>
<td>240100</td>
<td></td>
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<tr>
<td>Guangmingtai</td>
<td>1.1908</td>
<td>117772</td>
<td>1231</td>
<td>227</td>
<td>184800</td>
<td>3402</td>
<td>689</td>
<td>12.8</td>
<td>745</td>
<td>125</td>
<td>54</td>
<td>2425</td>
<td>311483</td>
<td></td>
</tr>
<tr>
<td>Tankou</td>
<td>1.1482</td>
<td>90825</td>
<td>515</td>
<td>163</td>
<td>136297</td>
<td>6666</td>
<td>418</td>
<td>8.2</td>
<td>196</td>
<td>136</td>
<td>61</td>
<td>673</td>
<td>235958</td>
<td>H₂S 1098</td>
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<tr>
<td>Xiongkou</td>
<td>1.2167</td>
<td>130570</td>
<td>156</td>
<td>34</td>
<td>187400</td>
<td>19040</td>
<td>987</td>
<td>11.5</td>
<td>611</td>
<td>102</td>
<td>60</td>
<td>1090</td>
<td>340062</td>
<td></td>
</tr>
</tbody>
</table>

### Table XV: Major Species of formation water in Xingouzui Formation

<table>
<thead>
<tr>
<th>Region</th>
<th>Density g/cm³</th>
<th>Salinity mg/L</th>
<th>Na⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xingou Oilfield</td>
<td>1.1134</td>
<td>166417</td>
<td>62675</td>
<td>401</td>
<td>991</td>
<td>91679</td>
<td>10500</td>
<td>168</td>
</tr>
<tr>
<td>Xingou Oilfield</td>
<td>1.1221</td>
<td>229616</td>
<td>86569</td>
<td>554</td>
<td>2426</td>
<td>137368</td>
<td>2563</td>
<td>133</td>
</tr>
<tr>
<td>Laoxin Region</td>
<td>1.0834</td>
<td>125721</td>
<td>46619</td>
<td>136</td>
<td>2304</td>
<td>75483</td>
<td>1020</td>
<td>157</td>
</tr>
<tr>
<td>Jiangling Region</td>
<td>1.1326</td>
<td>203932</td>
<td>71012</td>
<td>1240</td>
<td>6569</td>
<td>123552</td>
<td>1470</td>
<td>87</td>
</tr>
<tr>
<td>Shashi Region</td>
<td>1.1295</td>
<td>192563</td>
<td>69197</td>
<td>793</td>
<td>4759</td>
<td>116271</td>
<td>1399</td>
<td>143</td>
</tr>
</tbody>
</table>
Figure 18: Sandstone Isopachs of Lower Xingouzui Formation in Jianghan Basin

The Jianghan Basin is a representative petroliferous basin bearing salt lake sedimentary deposit with the maximum thickness up to 10 km deposited from Cretaceous to Paleogene, characterized by the development of gypsum, mudstone and salt rock. The caprock includes gypsum rock, salt rock, and mudstone, mudstone acting as the prominent caprock distributed in each formation in vertical, deposited in the river alluvial plain, river delta and lacustrine environment which is highly favourable for forming good seals. The parameters of mudstone as caprock in different depositional environments are shown in Table XVI.

Table XVI: Parameters of mudstone as caprock in different depositional environments (Yin and Li, 2005)

<table>
<thead>
<tr>
<th>Sedimentary facies</th>
<th>Porosity (%)</th>
<th>Breakthrough pressure (MPa)</th>
<th>Median Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluvial facies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interval value</td>
<td>1.31~5.41</td>
<td>0.131~10.2</td>
<td>3.98~25</td>
</tr>
<tr>
<td>Medium value</td>
<td>3.10</td>
<td>5.02</td>
<td>13.54</td>
</tr>
<tr>
<td>Delta facies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interval value</td>
<td>0.97~13.95</td>
<td>4.18~13.29</td>
<td>2.42~10.64</td>
</tr>
<tr>
<td>Medium value</td>
<td>9.39</td>
<td>8.10</td>
<td>5.46</td>
</tr>
<tr>
<td>Lacustrine facies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interval value</td>
<td>3.97~14.35</td>
<td>2.94~14.46</td>
<td>1.97~10.16</td>
</tr>
<tr>
<td>Medium value</td>
<td>8.35</td>
<td>9.40</td>
<td>5.76</td>
</tr>
</tbody>
</table>

2. Study on Salinity impact on solids precipitation during CO₂ injection to saline aquifers in China’s Jianghan Basin
We use the average value of salinity 0.2 in the base case modeling. The gas saturation, solid saturation salt mass fraction in liquid, dissolved CO₂ mass fraction, pressure, liquid and gas densities as function of the similarity variable are shown below.

Pruess and Spycher [19], have shown that the numerical results for the reference case follow a similarity solution, where the solution remains invariant when plotted versus the similarity variable $R^2/t$, where $R$ is a selected radial distance while $t$ is time. In this paper, we also use it to plot the results to check the accuracy of the numerical simulations.

![Figure 19](image)

**Figure 19:** Simulated gas saturation as a function of the similarity variable. The thick solid line represents a spatial profile at a simulation time of 8.64x10⁷ s, while the thick dashed and dashdot lines represent a time series of data for grid blocks at a radial distance of $R = 0.99$ m and 5.99 m.

There are two sharp moving fronts, that is, the gas saturation front at $\xi_f = R^2/t \approx 6.6 \times 10^{-3}$ m²/s and the dry-out front at $\xi_d = R^2/t \approx 6.9 \times 10^{-6}$ m²/s. According to the two moving fronts, the displacement process could be divided into three regions. In the region $\xi < \xi_d$, the gas saturation can reach to 0.9469 while all the liquid phase has been removed. The rest saturation is occupied by the precipitated salt. The two phase region locates at $\xi_d < \xi < \xi_f$, as an intermediate region. The supercritical carbon dioxide and the saline water coexist there. When $\xi > \xi_f$, in this region, CO₂ haven’t yet reached.

The solid saturation should be constant throughout. This remarkable feature can be proved directly from the similarity property. The simulation results show variable solid
salt saturation in the dry-out zone, which could be the result of numerical instability problems [22]. We can get the value of solid precipitation 0.05312.

NaCl mass fraction in aqueous phase is a function of the similarity variable. In this base-case, NaCl mass fraction decreases infinitesimally from the initial value of 0.2 to about 0.117 in the two-phase zone which lies between $6.9 \times 10^{-6} < R^2/t < 6.6 \times 10^{-3}$. This is due to aqueous volume increase as a result of CO2 dissolution [20]. The sharp peak in salt concentration at the inner boundary of the two phase zone occurs because conditions are approaching dry-out at this point, because of water evaporation into the CO2 stream.

Fluid pressurization is an important aspect. Especially the solid precipitation has significant impacts on it. If the solid precipitation could be avoided, the extent of fluid pressurization could also be alleviated. The pressure can be easily accumulated in region near the injection well within a short time.

![Solid saturation](image.png)

**Figure 20:** Solid saturation (fraction of pore volume containing solid precipitate) as function of the similarity variable
Figure 21: salt mass fraction in liquid as function of the similarity variable

Figure 22: Fluid pressure as function of the similarity variable (neglected permeability reduction from precipitation)
Salinity varies greatly in Jianghan Basin. Three sensitivity tests were conducted by changing the salinity from the base-case of 20wt.% to 10wt.% , 15 wt.% and 25 wt.% These salinities were selected by taking account of the variable range between the lowest range of salinity and the highest concentration of salinity. The effect of changes in salinity on solid precipitation versus the similarity variable would be discussed hereunder.

The increasing multiples of solid precipitation is slightly bigger than those of salinity. It’s also revealed that reducing salinity by a factor 2 reduces solid saturation overproportionately by a factor of 2.23 by Pruess and Muller [23]. It can be concluded that solid precipitation depends strongly on aqueous phase salinity. With the increase of salinity, the brine viscosity increases. The increase in brine viscosity means the decreasing mobility of the brine in the zone of two-phase flow reduces the displaced brine by CO₂ gas, and increases the evaporated brine. Thus for higher-salinity brine, the solid saturation of the porous medium in the completed dry-out zone has a higher ratio than that for the lower-salinity brine. However, we should note that the increasing salinity reduces the brine vapor pressure (i.e. the water dissolution in gas phase), which is not favorable to the increase in brine salinity during the displacement process.

For the several cases compared to base-case, the dry-out areas in all four cases occur at similar areas on the x-axis (ξ=R²/t) with occurring in an almost similar pattern as base-case. Solid saturation is the volume fraction of precipitated salt in the original pore space [23]. The fraction of the original pore porosity that remains after salt precipitation is
what is available for fluid flow (referred to as active flow porosity [23]. Hence greater salinity means lesser active flow porosity which in turn reduces the permeability of the medium as discussed by Verma and Pruess [24]. Greater salt precipitation may also reduce porosity and impair permeability of the reservoir in the vicinity of the wellbore which could lead to reduction in injectivity which may affect storage operations if it injection times perpetuate [22]. In addition, porosity reduction of the reservoir may affect the overall storage potential since it affects CO2 migration distance within the reservoir [25]. Increase in brine salinity leads to a decrease in CO2 solubility and higher pressures around the injection well may induce movement effects within the formation leading to increased risk of opening up of pre-existing fractures and faults causing possible CO2 leakage. Hence it should be considered for future CO2 sequestration projects in Jianghan Basin.

Figure 24: Solid saturation at different salinities as function of the similarity variable
Figure 25: Gas saturation at different salinities as function of the similarity variable

Figure 26: Salt mass fraction in liquid at different salinities as function of the similarity variable
**Figure 27:** Fluid pressure at different salinities as function of the similarity variable

**Figure 28:** Dissolved CO$_2$ mass fraction at different salinities as function of the similarity variable
We have got the values of solid saturation from the modeling results shown in figures. In addition, the theoretical precipitation of all the dissolved salt could be calculated by the formula [17]:

$$ S_{s,a} = \frac{\rho_{aq} \times X_s}{\rho_s} $$

(17)

Where $\rho_{aq}$ representing aqueous density, $X_s$ is mass fraction of dissolved salt in the aqueous phase, and $\rho_S$ is density of precipitated salt. The density of halite is only slightly dependent upon pressure, the effect of temperature is remarkable. The values could be calculated by the following equation accounting for the compression and expansion of halite [18], where the reference density at $0^\circ C$ and 0 Pa is 2165 kg/m$^3$:

$$ \rho_s(P, T) = 2165 \times \exp(-1.2 \times 10^{-4} T + 4 \times 10^{-11} P) $$

(18)

Through the calculation, $\rho_S$ equals to 2149.5 kg/m$^3$. Shown from Table XVII, though solid saturation and the theoretical precipitation of all the dissolved salt increases overproportionately to the increase of salinity, the precipitation percent does not change as the salinity increases and vary in a small range.

**Table XVII:** Theoretical precipitation of all the dissolved salt and precipitation percentage

<table>
<thead>
<tr>
<th>Salinity</th>
<th>0.1</th>
<th>0.15</th>
<th>0.2</th>
<th>0.25</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>0.02317</td>
<td>0.03672</td>
<td>0.05312</td>
<td>0.06572</td>
</tr>
<tr>
<td>$\rho_{aq}$</td>
<td>1055</td>
<td>1092</td>
<td>1131</td>
<td>1172</td>
</tr>
<tr>
<td>$S_{s,a}$</td>
<td>0.04908</td>
<td>0.07620</td>
<td>0.10523</td>
<td>0.13631</td>
</tr>
<tr>
<td>Precipitation percent</td>
<td>47.21%</td>
<td>48.19%</td>
<td>50.48%</td>
<td>48.21%</td>
</tr>
</tbody>
</table>

In order to explore salinity impact on solid precipitation within gravity effects, we carried on several simulation modeling into a 2D R-Z system with different initial salinities, 20wt.%, 10wt.%, 15 wt.% and 25 wt.%. The thick of the aquifer is assumed as 10 meters. Parameters setting are similar with those in 1-D case. The gas saturation distribution with initial salinity 0.2 is shown in Figure 29. Effects of gravity override on gas saturation distribution are strong [26]. Figure 30 and 31 are solid precipitation distributions near the well with 20wt.% and 25wt.% salinities. The distributions are similar. The average solid saturation in the dry-out regions is 0.0537 and 0.0705 respectively. With higher salinity, the value of solid precipitation can reach higher.
3. Solutions to salt precipitation and pressure buildup during CO2 injection into saline aquifers in Jianghan Basin

As discussed above, salt precipitation substantially reduces the reservoir permeability and severely causes pressure buildup around the injection well, which compromises the sustainable injection of CO2. How to relieve the salt precipitation and pressure buildup is a technological problem faced when CO2 is injected into the saline formations with high salinity. In this work, we tried to inject fresh water before injecting CO2 to dilute the saline water. For base case, we first inject water for 2 months, and then inject CO2 for 2 years. For reference case, we just inject CO2 for 2 years.
**Figure 32:** Solid saturation distribution of base case and reference case.

**Figure 33:** Permeability reduction distribution of base case and reference case.

**Figure 34:** Fluid pressure distribution of base case.
Figure 32, Figure 33 and Figure 34 present the distribution comparison of solid saturation, permeability reduction and fluid pressure of base case and reference case after 2years’ CO2 injection, respectively. There is a significant decline of salt precipitation by means of injecting fresh water to flush the saline formation before CO2 injection. The permeability of reservoir is nearly not influenced by the little salt precipitation. Therefore, there is no accumulation of fluid pressure around the injection well. For the reference case, the pressure around the injection well has reached 40Mpa.

Flushing the saline formation with the fresh water is an effective method to prevent the salt precipitation around the injection well when injection CO2 into saline aquifers with high salinity. However, the fresh water is very precious, especially in the north China where water resource is very deficient. Taking into account the hydrochemical setting of saline aquifer of Jianghan Basin, we tried another way to relieve the salt precipitation and pressure buildup.

The brine resources in Jianghan Basin are in great abundance. The concentration of potassium ion is extremely high with the average value up to 1457.5 mg/L[86] in Qianjiang Depression. The brine resources have great potential for exploitation. The state and local government is planning to develop the potassium salt in large scale. Space will be made at the time of pumping water from the aquifers. In the present work, we tried to study the feasibility of injection CO2 and pumping out saline formation water simultaneously to control pressure buildup while strong CO2. The production well should be placed in a way that they should not interact with the injected CO2 in order to avoid production of CO2. It was achieved by placing the production well at 9.5km from the CO2 injection well. It is assumed that the saline formation water can be extracted and processed at the industrial level in order to produce Commercial Salt.
Figure 35: Distribution of CO2 mobile phase for different times and for three cases of without (left plates), with (middle plates) one brine production well and with (right plates) two brine production wells.

Figure 35 shows the distribution of CO2 mobile phase saturation for different times and for three cases without (left plates), with one production well (middle plates) and with two production wells, left side and right side of the injection well (right plates), the figure demonstrates that in case one production is used the CO2 in gas phase will migrate towards the production well, on the other hand the introduction of the two wells (left side and right side of the production well) increases more or less the horizontal migration of the CO2.

Two methods were tried to relieve salt precipitation and pressure buildup during CO2 injection. The method of pre-flush with fresh water before CO2 injection can obviously alleviate the pressure buildup problem induced by halite precipitation around the injection well. In addition, this method could lower the salinity of the aquifers and increase the solubility of CO2, with the benefit of reducing the leakage risk. Pumping saline water out of the target formation while injecting CO2 simultaneously could reduce the pressure buildup both in the near-well region and the formation as whole. Increase in the saline water production rate leads to further decrease in pressure buildup, this phenomenon was demonstrated by tripling the production where the pressure decreased about 15 bars. The introduction of two wells (left side and right side of the production well) increases the horizontal migration of the CO2 but contributes a little to the amount of CO2 dissolved.
Figure 36: Baseline reservoir model with 20 years of injection, showing pressure evolution considering different parameters.

As is shown in Figure 36 the introduction of production wells decreases the maximum pressure buildup, even after the injection stops the pressure will be lower than the case of CO2 injection without production wells. When the production was tripled (for each production well) the maximum pressure decreases further and it decreased about 15 bar lower than the base case. This shows that an increase in production rate leads to further decrease in pressure buildup and furthermore an increase in production rate will increase the brine quantity to be processed at the industry level in order to produce commercial salt.

Figure 37: Comparison of CO2 dissolved fractions in different cases.
Figure 37 demonstrates that CO2 dissolution fraction depends on the salt mass fraction when the salinity became half of the base case mass fraction (14.5% instead of 29%) the dissolved CO2 fraction became higher and the same figure shows that the introduction of two injection wells (left and right sides of the injection well) contribute slightly to CO2 dissolved amount, on the other hand when one side, although the introduction of one side production well induces the CO2 mobile phase saturation to move toward the production well side but it also increases the CO2 dissolved amounts.

4. Experimental and Modeling Investigation of Post-Injection Plume Migration

Scaling analysis for crossflow mechanisms has been widely used to characterize the contribution of relevant physics including viscous, gravity and capillary forces. In this study, we have focused on the use of the Bond number, $N_B$, (e.g. Zhou et al. 1994) to characterize the magnitude of gravity and capillary forces in counter-current vertical flows. The $N_B$ scaling term is given by the ratio of gravity to capillary forces and has a general form

$$N_B = \frac{\rho g H}{\rho_c}$$  \hspace{1cm} (19)

where $\rho_c^*$ is the characteristic capillary pressure and can be expressed as

$$\rho_c^* = \int_{S_w}^{S_w - S_{w_c}} \frac{P_c(S_w)}{(1 - S_S - S_{w_c})} dS$$ \hspace{1cm} (20)

Previous studies (e.g. Zhou et al. (1994), Cinar et al. (2006)) have investigated the transition from capillary to gravity dominated flows: If $N_B \geq 5$, gravity dominates the flow whereas for $N_B \leq 0.2$, capillary forces dominate the flow. Accordingly, when $0.2 < N_B < 0.5$, a displacement is in the transition between capillary and gravity dominated flow regimes.

To correctly capture the interplay between capillary and gravity forces, a new dimensionless time has been derived for counter-current vertical flows. The scaling is based on the assumption that the displacement of CO2 plume in brine aquifers is completely immiscible with no dispersion and diffusion. The proposed dimensionless timescale is given by

$$t_d = \frac{t}{t^*} = \sqrt{\frac{k}{\mu_{w_g}} \frac{1}{\rho_c L_c} \left( \frac{\exp(-N_B)}{\cos} + \frac{1 - \exp(-N_B)}{\sqrt{\frac{k}{\mu_{w_g}}} g L_c} \right)^{-1}}$$ \hspace{1cm} (21)
This dimensionless time includes the impact of effective permeability, porosity, phase mobilities, characteristic length, interfacial tension, fluids densities and the ratio of gravity to capillary forces (NB). A full derivation of our proposed dimensionless time scale is presented in Nattwongasem and Jessen (2009).

To test the proposed dimensionless time we start by considering the idealized model system shown in Fig 38 and use the fluid properties listed in Table XVIII. The CO₂ plume initially occupies the lower 20% of the pore volume.

\[
S_{\text{w,i}} = 1.0 \\
S_{\text{CO₂,i}} = 1 - S_{\text{wc}}
\]

Figure 38: Model dimensions and initial fluid distribution

Simulations of the segregation process were performed for a) homogeneous and isotropic setting, b) homogeneous and anisotropic settings and c) heterogeneous, anisotropic settings with three different correlation lengths. In this example, the Bond number was calculated to 1.34 and hence the flow is in the capillary-gravity transition zone, shifted towards the capillary dominated regime. Figure 39 compares the simulation results in terms of the fraction of gas that is trapped as a function of the proposed dimensionless time on time scales proposed by Ma et al. (1997), Xie and Morrow (2000) and Zhou et al. (2002).

Table XVIII: Fluid properties based on the aquifer setting of Ide et al. (2007)

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>w</td>
<td>1054.8</td>
<td>kg/m³</td>
</tr>
<tr>
<td>CO₂</td>
<td>728.8</td>
<td>kg/m³</td>
</tr>
<tr>
<td>w</td>
<td>0.4921</td>
<td>mPa.s</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0612</td>
<td>mPa.s</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>N/m</td>
</tr>
</tbody>
</table>
Figure 39: Comparison of the fraction of trapped gas vs. Dimensionless time scales for homogeneous and heterogeneous anisotropic models: K1-3 represent short, medium and long correlation lengths respectively.

It is clear from Figure 39 that the proposed dimensionless time more accurately captures the dynamics of the plume migration for this set of model parameters. This observation demonstrates the importance of including the magnitude of both gravity and capillary forces and that appropriate scaling by use of the Bond Number, $N_B$, allow us to improve the accuracy of an estimate of trapped gas as well as the associated immobilization time.

Next, we consider a range or relevant aquifer settings reported in the work of Kopp et al. (2009a, 2009b). reports the fluid properties and $N_B$ for different relevant aquifers based on $H = 100m$, porosity of 0.3, and $kr$ and $Pc$ functions that are similar to the base case model discussed previously. The initial plume is assumed to occupy the 20% of the available pore volume and to be located at the bottom of the model at $t = 0$. From the scaling groups of Zhou et al. (1994), we estimate the range of $N_B$ to span the capillary/gravity transition zone and the gravity dominated flow regime (see Table XIX).

Table XIX: Fluid properties and Bond number ($N_B$) at different aquifer conditions reported by Kopp et al. (2009a, 2009b).

<table>
<thead>
<tr>
<th>Aquifer ID</th>
<th>Depth (m)</th>
<th>P (MPa)</th>
<th>T (°C)</th>
<th>$w$ (kg/m³)</th>
<th>$\rho_{CO2}$ (kg/m³)</th>
<th>$\sigma$ (Pa.s)</th>
<th>$N_B$</th>
<th>$M^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median M</td>
<td>1524</td>
<td>15.47</td>
<td>55.13</td>
<td>1025.5</td>
<td>622.8</td>
<td>0.5429</td>
<td>0.053</td>
<td>27.28</td>
</tr>
<tr>
<td>Warm W</td>
<td>1524</td>
<td>14.95</td>
<td>104.4</td>
<td>994.5</td>
<td>313.1</td>
<td>0.2977</td>
<td>0.030</td>
<td>30.84</td>
</tr>
<tr>
<td>Cold C</td>
<td>1524</td>
<td>15.51</td>
<td>37.43</td>
<td>1031.7</td>
<td>779.5</td>
<td>0.7282</td>
<td>0.067</td>
<td>27.01</td>
</tr>
<tr>
<td>Shallow S</td>
<td>386</td>
<td>4.06</td>
<td>21.58</td>
<td>1032.9</td>
<td>100.2</td>
<td>1.0200</td>
<td>0.017</td>
<td>40.32</td>
</tr>
<tr>
<td>Deep D</td>
<td>3495</td>
<td>35.31</td>
<td>115</td>
<td>995.2</td>
<td>666.1</td>
<td>0.2725</td>
<td>0.055</td>
<td>27.21</td>
</tr>
</tbody>
</table>

0 = a constant
Numerical calculations based on the above properties were performed and Figure 40 compares, the fraction of gas trapped as a function of the proposed dimensionless time for the five aquifer settings.

Figure 40: Comparison of the fraction of gas trapped for various Bond Numbers for a range of relevant aquifer settings reported by Kopp (2009a, 2009b).

From Figure 40, we observe that the propose time scale substantially collapses the relevant range of aquifer settings onto a single curve with moderate deviation of the shallow aquifer setting. Accordingly, the proposed scaling can be used to estimate the immobilization time based on $N_B$ and the characteristic mobility ratio from a given aquifer setting.

5. Study on the impact of changes in mobility for the two-phase brine/CO$_2$ system as a result of transitions between co- and counter-current flow settings

We study the CO$_2$ migration dynamics in four different permeability fields derived from Ide et al. [27]. In each case, three flow models are considered:

1. A co-current flow model using a single set of relative permeability functions.
3. A mixed-flow model allowing for transitions between co- and counter-current flows.

In the co-current flow model, the relative permeability for co-current flow is used in both horizontal and vertical directions (via a single set of bounding relative permeability functions). This model assumes that transitions from co-current to counter-current flow and vice versa do not have any impact on the phase mobilities. In the counter-current flow model, the migration of CO$_2$ in the vertical direction is forced to trace the counter-current relative permeability curves in both directions. The impact of using co-current or counter-current relative permeabilities in the horizontal direction has been studied as discussed later. Finally, in the mixed-flow model both co-current and counter-current flows are considered: That is, co-current relative permeability is used wherever the flow is co-current, and counter-current relative permeability is used wherever the flow is counter-current. In the following sections we report and compare our findings for the individual flow models and aquifer settings.
Considering a homogeneous aquifer with a constant permeability of 125 mD in the horizontal direction, four different vertical to horizontal permeability ratios of 0.1, 0.3, 0.5 and 1 are investigated. Figure 41 reports the fraction of the injected gas that is trapped by imbibition processes as a function of time for the four different vertical to horizontal permeability ratios and the three flow models.

For this aquifer setting, we observe that the integration of the counter-current relative permeability model in our displacement calculations results in an increase in the residual trapping. This is particularly evident as the vertical permeability increases. In contrast, for a vertical to horizontal permeability ratio of 0.1, we observe only a modest difference between calculations that utilize the co-current flow model and the mixed-flow model in terms of the fraction of the gas that is ultimately trapped. However, when the permeability ratio (vertical to horizontal) increases, the difference in the predicted trapping between the two flow models also increases. We observe also, as expected, that as the vertical permeability increases, the ultimate amount of gas that is trapped decreases. This is caused by a shift in the balance between capillary, viscous and gravity forces towards a more gravity dominated flow setting. In terms of the predicted residual entrapment, we observe that the use of a co-current flow model instead of a mixed-flow model may underestimate the residual trapping by more than 20% (relative).

After the injection ends, brine starts to imbibe into the plume. Therefore, a sharp increase in the trapped gas saturation is observed at this time. The rate at which the gas is trapped depends, in part, on the vertical permeability as discussed below. As the vertical permeability increases from 12.5 mD to 125 mD, the resistance to imbibition in the vertical direction is reduced (due to an increase in the vertical gas mobility) and the initial rate of residual trapping increases. Higher vertical permeability also eases the vertical migration of the injected CO₂ and the initial plume after injection is not as wide as when
the vertical permeability is low. In addition, more free gas accumulates at the top of the aquifer for higher vertical permeabilities, and the final amount of trapped gas decreases.

The trapped gas saturation approaches a plateau when brine has invaded the entire initial CO$_2$ plume. Any gas that has reached the top boundary at this point can be displaced further in the horizontal direction by capillary forces that gradually allow for brine to re-invade the top portion of the aquifer. The reinvasion of brine into the upper part of the aquifer and the associated horizontal displacement of CO$_2$ is a much slower process than the invasion of the initial plume. Therefore, in settings with a relatively high vertical permeability, an abrupt rise is observed in the fractional trapping of the injected gas, followed by a gradual increase until the final plateau is reached. This general trend is evident from where the initial rate of entrapment increases as the permeability ratio increases from 0.1 to 1.

By comparing the four panels, we observe that the initial rate of residual entrapment after injection is predicted to be higher for the co-current model than for the counter-current and mixed models. Furthermore, the difference in the initial rate of entrapment is observed to depend on the vertical permeability: The lower the vertical permeability, the larger the difference.

To explain the difference in the initial rate of entrapment, we report the fluid distributions in terms of gas saturations after injection as predicted by the co-current model and the mixed model.

**Figure 42:** CO$_2$ saturation post-injection in co-current model (left) and the mixed model (right).
The rate of entrapment is controlled by two factors: a) the magnitude and distribution of the gas saturation in the plume after injection and b) the resistance to imbibition of brine into the plume. Based on conventional initial-residual considerations, a higher initial saturation of CO$_2$ will result in a larger fraction of residual entrapment during an imbibition process. The rate of imbibition into the plume is set by gravity and capillary forces as well as the vertical permeability as discussed by Nattwongasem and Jessen [29]: The characteristic time for vertical plume migration is proportional to the inverse of the vertical permeability for gravity dominated flows.

For $k_v/k_h = 0.1$, we observe that the initial plume after injection is very similar for the two flow models in terms of extent and saturation. Accordingly, we expect the ultimate residual entrapment to be similar for the two flow models (initial-residual consideration). However, as the vertical fluid mobility is higher for the co-current model than for the mixed (and counter-current) flow model, the initial rate of entrapment will be higher for the co-current model.

As the vertical permeability is increased to $k_v/k_h = 0.3$, we observe differences in the initial plumes as predicted by the co-current and mixed-flow models. For the co-current model, the plume is now shifted upwards relative to the plume of the mixed model with lower CO2 saturations in the lower portion of the plume. Although the resistance to flow in the vertical direction is still lower in the co-current model, less CO2 will now be trapped per volume of imbibition. This results in an initial rate of entrapment that is more similar to the mixed and counter-current models.

A similar argument is valid for $k_v/k_h$ of 0.5 and 1: The rate of imbibition is higher for the co-current model (volume per time). However, the entrapment per volume is less than for the mixed model (initial-residual argument) and the effective initial rate of entrapment as predicted by co-current and mixed models becomes similar.

To further investigate the differences in the residual entrapment of CO$_2$ observed, we turn to the maps of the saturation distribution. After 200 days of injection, most of the region invaded by CO$_2$ (except at the very tip of the plume and in a small region near the injector) is experiencing counter-current flow. Regions with counter-current flow are shown in dark color. A similar pattern is observed after 500 and 1000 days of injection. During the early time, only a very small region in the bottom of the plume experiences imbibition. After 2400 days, when the injection is stopped, the majority of the CO$_2$ plume is in a counter-current flow mode. Therefore, during the injection period, the plume experiences primarily counter-current flow in its upward motion.

After the end of injection, brine starts to imbibe into the plume from the sides and bottom, and this circulation initiates co-current flow at the bottom of the plume towards its center and upwards. The same trend in development of counter-current flow during the plume migration is observed for the heterogeneous aquifer settings that are discussed in the following sections.
We have demonstrated the importance of considering counter-current relative permeability in the simulation of CO$_2$ injection into saline aquifers.

During the injection period, the leading edge of the plume is in a co-current flow mode, while the rest of the plume experiences counter-current flow (except near the injection well). When the plume reaches the top of the aquifer, nearly the entire region occupied by the plume is under counter-current flow conditions. After injection stops, a co-current flow region starts to develop from the bottom of the plume towards the top of the aquifer. This transition is caused by a circular movement of brine that is displaced from the top of the aquifer by the less dense CO$_2$-rich phase.

Figure 44 summarizes our example calculations in terms of the relative difference in fractional gas entrapment as predicted by the co-current flow model and the proposed mixed-flow model.
The relative differences in the range of 15-20% clearly demonstrate the need for including the impact of counter-current flow in the simulation of CO₂ injection into saline aquifers.

The current literature on counter-current relative permeability is largely limited to two-phase oil/water systems. To our best knowledge, no such experimental observations are available for the system of brine and CO₂. Hence, there is a need for new experimental evidence with emphasis on this important application.

Our calculated results that are based on tracking the velocities of the flowing phases show that the CO₂ plume is mainly in a counter-current flow mode during its vertical migration, and therefore, it appears that the use of counter-current relative permeability in the vertical direction is appropriate. In the horizontal direction, co-current flow is the predominant flow mode based on the boundary conditions used.

From the results presented in this study, the use of the counter-current relative permeability model may appear to be a good choice for representing the fluid mobilities during plume migration. However, this observation cannot be generalized to settings where a part of the plume is in a counter-current flow mode (rising plume) and another part is in a co-current flow mode (CO₂ migrating horizontally below the cap-rock). The use of a counter-current relative permeability model can in such settings lead to erroneous results, as the lateral movement of CO₂ at the top boundary will be underestimated. Accordingly, we recommend the use of a mixed-flow model.

An important issue is related to the transitions between the two sets of relative permeability functions when the mode of flow is changed. We have used a simple rule for transitioning between the curves that is based on the velocities of the two phases; whenever the mode of flow changes, a discontinuous change in relative permeability is introduced. The transitioning between relative permeability curves should not (and did...
not in our calculation examples) introduce any numerical instability as similar discontinuities in the coefficients of the pressure equation caused by phase transitions is routine in e.g. compositional simulation of gas injection processes. In addition, a change in flow direction can only occur when the phase potential passes through a value of zero.

The introduction of counter-current relative permeabilities (and transitions) in our flow calculations had only a minor effect on the pressure solver in terms of the number of required iterations.

It may be argued that the transition between the two sets of relative permeability functions should follow a smooth path (similar to scanning curves in e.g. capillary pressure). However, as noted above, any change in the flow direction of a given phase is caused by a variation in the driving force that must pass through zero. Therefore, any discontinuous change in the value of the phase relative permeability will not be problematic due to the vanishing driving force.

In our IMPES implementation, the flow directions/modes at each time step are recognized from the previous time step. In adaptive-implicit or fully-implicit implementations, additional caution may be warranted to ensure adequate stability/performance. We note, however, that this study is a first attempt to incorporate the use of counter-current relative permeability and to demonstrate the importance of identifying flow modes in the simulation of CO$_2$ injection into saline aquifers. Additional experimental and theoretical studies are under way to further prove the validity of the concepts and its implementation in large-scale simulation.

6. Validation of the accuracy of numerical simulations based on co-current relative permeability functions

Two gravity segregation experiments were performed with the apparatus. In the first experiment (experiment A) 90 cm$^3$ of iC8 (~0.23 PV) was injected from the top of the column and in the second experiment (experiment B) 120 cm$^3$ of iC8 (~0.31 PV) was used. Figure 45 reports the saturation distribution in the packed column as a function of time for the two segregation experiments. In experiment A, we observe that the non-wetting phase does not reach the top of the column after 24 hours. This indicates that the fluids in the column reach a gravity-capillary equilibrium before the plume reaches the top. To ensure that the plume reaches the top of the column, experiment B was performed with a larger initial volume (plume) of the non-wetting phase. From Figure 45 (right) we see that the plume in experiment B reaches the top of the column after approximately 24 hours and continues to migrate upwards at later times until the experiment was stopped after 72 hours.
Figure 45: Saturation profiles of iC\textsubscript{8} in the column at various times; left: Experiment A and right experiment B

To simulate and interpret the experimental observations, we assume a 1D fluid flow and the physical properties of brine and iC\textsubscript{8} (viscosity and density) are assumed to be constants. An IMPES formulation was used to solve the incompressible two-phase flow problem. In the numerical calculations we use a spatially refined model to reduce numerical diffusion and upscale (average) the calculation results to compare with the iC\textsubscript{8} saturations from the experiments. The permeability is assumed to be a constant (4.8 Darcy) in all cells, while the porosity in each cell of the refined model is set equal to the porosity of relevant section in the experimental setup. The initial iC\textsubscript{8} saturation in the refined calculation is created from a piece-wise linear interpretation of the initial iC\textsubscript{8} saturation in the experiment preserving the actual pore volume of the non-wetting phase.

Killough’s model (Killough, 1976) was used to represent hysteresis in the relative permeability of both phases. Residual entrapment of iC\textsubscript{8} was calculated from Land’s model (Land, 1968) with Land’s coefficient, C, obtained from the maximum residual non-wetting phase saturation observed in the steady-state relative permeability measurements. The scanning curves of the capillary pressure were obtained from Killough’s model (Killough, 1976) by interpolation between the drainage and imbibitions curves.

From the measured and estimated input parameters, the changes in the wetting phase saturation in each section of the packed column are calculated in a purely predictive mode. The numerical calculations presented in this section are hence based on the co-current measurements and assume that there is no difference between co-current and counter-current saturation functions. Figure 46 compares the saturation profiles of iC\textsubscript{8} as observed in the experiments with the calculated saturation profiles based on co-current model parameters.
Figure 46: Saturation of iC8 in the column observed in the experiments and predicted based on co-current model parameters (upper panel: Experiment A, lower panel: Experiment B)

We observe that the iC8 plume is predicted to moves much faster by the numerical calculations than what is observed in the experiments. In the numerical calculation, the iC8 is predicted to reach the top of the column after only 5 hours for experiment A and after three hours in experiment B, while this is not observed in the experiment before after one day (24 hrs for experiment B). Therefore, we conclude that the numerical calculations based on co-current saturation functions fail to replicate the observed data. This is particularly evident for experiment B, where the arrival time of the plume at the top of the column is approaching an order of magnitude in error.

To match our experimental observations, model input parameters were changed by optimization. Lelievre (1966), Bentsen & Manai (1993) and Bourbiaux & Kalaydjian
(1990) have demonstrated a reduction in the relative permeability functions for counter-current flow relative to co-current values. In the modification of the model input parameters, two approaches were used to mimic counter-current relative permeability:

1) Fix the endpoint values of the relative permeability of both phases and adjust the saturation exponents – two adjustable parameters.

2) Adjust the endpoint relative permeability for the non-wetting phase, $k_{re}$, as well as the saturation exponent for both phases – three adjustable parameters.

From the first approach we found that the exponents of the relative permeability increase if the endpoint relative permeability of iC8 is kept constant and that the increase is more significant for iC8. In the second approach, the endpoint is decreased and the exponents of the relative permeability increase. The adjusted parameters from the second approach are consistent with previous studies where the endpoint relative permeability of the non-wetting phase is reduced during counter-current flow. If the iC8 endpoint relative permeability is kept constant, the saturation exponents increase further in the parameter estimation. In the second approach, the reduction of the relative permeability of the non-wetting phase during counter-current flow may be a consequence of factors beyond viscous drag: A new fluid configuration of the residual non-wetting phase can e.g. result in additional drag. Accordingly, the main contribution to the reduction in relative permeability cannot be isolated from the presented experiments and additional work is warranted on this topic. Figure 47 compares the numerical calculations with experimental observations after adjustment of model parameters (2nd approach) while Table XX summarizes the adjustment of the parameters used in the numerical calculations. The sum of relative errors is reduced significantly relative to the initial input by any of the approaches used in matching the experimental observations.

The difference between measured and adjusted relative permeabilities clearly demonstrates that the relative permeability measured in a co-current flow regime cannot be used to accurately predict the dynamics in a counter-current flow regime.

Table XX: Comparison of observed and adjusted input parameters

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Parameters</th>
<th>$n_{sw}$</th>
<th>$n_{iC8}$</th>
<th>$k_{re,nw}$</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-current</td>
<td></td>
<td>3.8</td>
<td>1.7</td>
<td>0.15</td>
<td>25.4</td>
</tr>
<tr>
<td>Adjustment (P1)</td>
<td></td>
<td>4.4</td>
<td>2.4</td>
<td>0.15</td>
<td>11.2</td>
</tr>
<tr>
<td>Adjustment (P2)</td>
<td></td>
<td>4.3</td>
<td>2.7</td>
<td>0.15</td>
<td>11.5</td>
</tr>
<tr>
<td>Adjustment (P3)</td>
<td></td>
<td>4.4</td>
<td>2.4</td>
<td>0.11</td>
<td>10.9</td>
</tr>
</tbody>
</table>
Figure 47: Comparison of experiments and simulation (A -upper panel, B- lower panel when endpoint non-wetting phase relative permeability is allowed to change (decrease).

7. Modeling and simulation for microscopic and field scale simulation
7.1 Lattice Boltzmann simulation of the rise and dissolution of two-dimensional immiscible droplets

The methodology and main results are summarized in the publication of Chen and Zhang (2009). We developed a LB model that is able to handle an arbitrary number of fluid components and different density ratios. By simulating the rise of droplets with different sizes, we found a power law relationship between the Eo number and terminal Re number. Our simulation results can be described by Rodrigue’s empirical correlation, which was originally derived for predicting gas bubble motion. Also, by simulating the simultaneous rise of two and three identical droplets in a finite domain, we found that the average rise velocity was lower than that of a single droplet with the same size, due to the mutual resistant interactions. In addition, the trajectories of droplet except for the central
one were not straightly upward, but moved away from each other gradually, resulting from the non-zero net horizontal forces acting on the droplets.

The two-phase LB model was combined with a solute transport model, as well as a boundary condition handling dissolution at the liquid-liquid interface, in order to investigate the complicated coupling between droplet size, flow field, solute transport, and dissolution at the interface. For a given Pe, the case with a higher Da always had a faster dissolution rate compared to the case with a lower Da. This implies that the physicochemical property of the liquid-liquid interface is the fundamental factor affecting the whole dissolution process. For a given Da, the case with a higher Pe always had a faster dissolution rate compared to the case with a lower Pe. This was because with the higher Pe the advective transport relative to the droplet was able to move the dissolved mass into the bulk solution quickly, which favored the subsequent dissolution.

For a large Da and a small Pe, the process near the interface was diffusion-limited, and there was a thick layer of dissolved mass covering around the droplet. The advective flow at the top side of the droplet resulting from droplet rise was unable to clean up the solute near the interface quickly. In order to accelerate the dissolution process, it was favorable to split one single droplet into two or more small droplets, by increasing the interface area per unit mass of droplet. In contrast, for a small Da and a large Pe, the process near the interface was dissolution-limited. The dissolved mass accumulated near the interface was little, which was sensitive to the advective flow at the top side of the droplet. The advective flow relative to a big droplet was able to quickly clean the accumulated solute away from the interface, which enhanced the whole dissolution process. Thus, in this case it was favorable to keep the droplet as a single one to accelerate the dissolution process.

Based on the investigations of both Pe and Da numbers, we constructed a Da-Pe phase plane, and proposed there exists an interface that divides the plane into region 1 and 2. In region 1 it is favorable to split the single droplet into as many small ones as possible in order to accelerate dissolution, while in region 2 it is favorable to keep the droplet as a single one for the same purpose. This interface is expected to be an increasing function of the Pe number, which implies that a small Pe number and large Da number lead to a region 1 case, while a large Pe number and a small Da number lead to a region 2 case. This research has important applications in many engineered and medical processes where fast dissolution of immiscible liquid droplets is desired, such as geological carbon sequestration and drug delivery in blood vessels. Different combinations of Pe and Da numbers can be investigated by numerical simulation presented in this study, and a Da-Pe phase plane as well as the interface can be obtained. After the real Pe and Da numbers of the system are determined, we will have a clear idea whether it is favorable to break down the droplet or not in order to accelerate dissolution, by judging whether the point (Pe, Da) falls in region 1 or 2.

7.2 General Framework of Simulator for Carbon Storage

A modular simulator, which is available under various circumstances, consists of three pretreatment modules and eleven main program modules, the structural drawing as shown in Figure 48.
The three pretreatment modules are particularly used for preparing EOS parameters, fluid-solid coupling parameters and special structure change.

EOS parameter preparation module is built based on experiment data. It is used to generate EOS parameters concerning carbon dioxide and brine, and the relationship between physical property of formation and pressure and temperature. Any differences between the measured and calculated data are minimized using regression facility which adjusts various Equation of State parameters. This ‘tuned’ model is then exported in a form suitable for the simulator.

Fluid-solid coupling module is used to prepare parameters for relative permeability and capillary curves. This module is prepared for the purpose of figuring out the relationship between relative permeability, capillary pressure and rock porosity, pore-throat ratio, throat-to-pore coordination number through applying the corresponding theory and formula, together with the figure of core experiments in the lab. While observing the long-term state of carbon dioxide, we have to put into consideration the dissolution and deposition of the mineral compositions brought about by the existence of carbon dioxide. The dissolution and deposition of mineral compositions cause the change of formation porosity, which is obvious. Besides, dissolution of mineral compositions (mainly carbonatite) brings about secondary pores (also dissolved pores). Mineral deposition leads to the jamming of pore throat. In general, the geologic chemical reaction concerning carbon dioxide will change the natures of rock porosity, pore-throat ratio, throat-to-pore coordination number of formation. Yet the changes of the nature will accordingly cause deviations of residual water saturation, residual gas saturation, threshold pressure and trends of relative permeability and capillary pressure curves.

Therefore, this module ought to be prepared for the purpose of generating a set of formulas revealing the relationship between relative permeability and capillary pressure.
curves and rock porosity, pore-throat ratio, throat-to-pore coordination number, so as to update relative permeability and capillary pressure curves when necessary.

In the main program, we need a module that can be used for analyzing gridding flexibly according to specific geologic construction (such as fracture and fault). It is a plain fact that geologic chemical reaction will probably cause new fracture in the reservoir. Or it will enlarge the original fracture. But it is indicated in the core experiment that carbon dioxide will erode the core of the rocks and thereby, produce worm hole. So we had better build up our gridding model by using the method of discrete fracture. This module will be applied to other modules during the calculation process, so as to update the gridding model and make it better serve the purpose of portraying the local geologic construction. What is worth being pointed out is that we don’t need to update the whole reservoir, but only the concerned area and the gridding suggesting the changes of geological construction. That is due to the large quantity of the updating work, including updating cell list and connection list, working out the compositional distribution and physical property parameters of the new gridding according to the compositional distribution and physical property parameters based on the original gridding.

As in the regular compositional model, we need modules for flash calculation, Jacobi matrix construction, linear solver and fluid property update. We also need an explicit geological chemical reaction module whose calculation is processed by applying the composition distribution worked out by and mineral ion concentration with the method of chemical thermodynamic. It will help to figure out the direction and degree of the chemical reaction happening in each grid block. This module surely can be added to Newton iteration in an implicit way, which can make the result of chemical reaction accurate, yet increase calculation work to a great extent.

Then we need another module updating the porosity of the grid block based on the calculation result of the above module. This module should also be available in adding or deleting the special geological structure (such as caverns and fracture) in the grid blocks according to the changes of porosity. Scale changes of the special geologic structure must also be acceptable in this module. These operations ought to be based on the statistic regulation of a series of micro-block simulation.

Likewise, we can build up an independent module to update the curve of absolute permeability curves. This is not only reasonable but also advantageous for openness and maintenance of the program. Yet since the relationship between absolute permeability and porosity can be expressed with a simple log relationship, this very module can be included into another module which is applied for the purpose of updating the porosity of reservoir according to the result of the chemical reaction.

We also need a module to update relative permeability and capillary pressure curve base on chemical reaction progress. The module is base on the relationship between fluid-solid coupling parameters and porosity.
Finally, we need a module to update the special structure in certain block base on chemical reaction calculation.

7.3 CO2 Sequestration Simulation Using Discrete Fracture Modeling (DFM)

CO2 sequestration without chemical reactions is considered. The chemical reaction module is still in development.

In this part, DFM is used to characterize the reservoir geometry. We firstly discretize the reservoir into triangles and calculate the transmissibility between each grid block. The triangulation is prolonged into a one-dimension volume reservoir and simulated. In this simulation, we use GPRS as the reservoir simulator.

7.3.1 Multi fracture system

The system has a sandstone reservoir with many fractures. Sandstone porosity is 0.25. Fracture porosity is 1. Sandstone permeability is 10mD. Fracture permeability is 1000000mD. Fracture aperture is 0.1mm. Medium is firstly filled with water. CO2 is injected into the left bottom corner Injection water at bottom left corner. CO2 injection rate fixed at 0.01PVI/d.

The system has 83 fractures. The fractures are distributed randomly in the reservoir. 83 fractures are discretized into 814 fractures, as shown in Figure 49.

![Fracture System](image)

**Figure 49:** Fracture System
Figure 50: triangulation of fractured reservoir

Figure 50 represents the CO$_2$ saturation profiles after several time steps of water injection. After CO$_2$ has arrived at the fractures, it will firstly flow through fractures rather than sandstone. Finally we could find CO$_2$ is distributed all around the fractures.

7.3.2 Multi fracture system with mud layers

The system has 10 layers, including reservoir: 0-10m, 20-30m, 40-50m, 60-70m, 80-90m and mud: 10-20m, 30-40m, 50-60m, 70-80m, 90-100m. Sandstone porosity is 0.25. Mud porosity is 0.01. Fracture porosity is 1. Sandstone permeability is 0.1mD. Sandstone permeability is 0.001mD. Fracture permeability is 1000000mD. Fracture aperture is 0.1mm. Medium is firstly filled with water. CO$_2$ is injected into the left bottom corner Injection water at bottom left corner. CO$_2$ injection rate fixed at 0.01PV/16/d.
**Figure 51:** CO₂ saturation distribution
Figure 52: triangulation of fractured reservoir

Figure 53 represents the CO₂ saturation profiles after several time steps of water injection. CO₂ will preferentially pass through the fractures, then sandstone, and then mud.

0.008PVI 0.04PVI
7.3.3 Leakage along wellbore

Preexisting wells and wellbores may play major pathways through the crust as their high permeability. Current well closure and abandonment technology seems sufficient to confine CO$_2$, however, individual wells may suffer from a variety of factors that limit their integrity, including improper cementation, improper plugging, overpressure, corrosion, and other failure conditions.

In this case, we describe a wellbore leakage system. The blue line in the middle of the reservoir is a well, which has main fractures along the wellbore.

The system has 10 layers, including reservoir: 0-10m, 20-30m, 40-50m, 60-70m, 80-90m and mud: 10-20m, 30-40m, 50-60m, 70-80m, 90-100m. Sandstone porosity is 0.25. Mud porosity is 0.01. Fracture porosity is 1. Sandstone permeability is 0.1mD. Sandstone permeability is 0.001mD. Fracture permeability is 1000000mD. Wellbore fracture aperture is 0.1mm. Medium is firstly filled with water. CO$_2$ is injected into the left bottom corner Injection water at bottom left corner. CO$_2$ injection rate fixed at 0.01PVI/d.
We could clearly find that CO$_2$ will move up along the wellbore and disperse into the sandstone. While in the mud, CO$_2$ does not move that clearly. We may conclude that wellbore leakage induces main movement of CO$_2$ in the sandstone. Figure 55 represents the CO$_2$ saturation profiles after several time steps of water injection.
8. Study on discrete fracture modeling application in an actual CO2 sequestration site of China

Case 1: With no natural or hydraulic fractures

Local refinement near the injection spot is performed to better capture the flow front. CO2 concentration maps were given on top of the field permeability distribution shown in grayscale. As clearly seen, the low-perm mudstone effectively stops CO2 from moving up. The four maps at 500, 3,650, 20,000, and 36,500 days depicts how CO2 plume get propagated. The difference in CO2 concentration at 3,650 and 36,500 days is caused by segregation between injected CO2 and formation saline water.

Cases 2-4: With natural fractures

Fig. 58-60 show the system with natural fractures located at different distance to the injector. The low-perm mudstone largely stops CO2 from moving up especially when fractures are farther away (cases 3-4). In case 2, CO2 leakage through fractures reached 14% at the end of 100 years. These cases indicate that not only the existence of natural fractures but also how close they are to the injector makes it critical to quantify CO2 leakage. If fractures are far enough away from the injector, leakage through them could be limited.

Cases 5-6: With natural and hydraulic fractures

In cases 5-6, the system contains hydraulic fractures of different half length (100m and 300m). In both figures, CO2 moves quickly during injection, the CO2 plume shape is more lateral, and leakage is observed once it hits natural fractures. The longer the hydraulic fracture length is, the more horizontal the CO2 plume is formed and more CO2 is escaped through natural fractures (Fig. 62).

Comparison among Case 1, 2, 3, and 4

Fig. 63 shows the injection rates and cumulative CO2 injection of case 1, 2, 3 and 4. As clearly seen, the existence of natural fractures help improve the injectivity as the pressure buildup in the target formation is slower and bottom hole pressure constraint is later reached. As a result, twice as much CO2 can be injected when natural fractures are
present (Fig. 64). But the fact that curves for cases 2-4 are overlapping with each other indicates the injectivity is not sensitive to the fracture location.

We can see that even with fractures, as long as they are far enough away from the injector, leakage could be very low (about 1% for case 3 and 4); but a nearby fracture such as in case 2 could cause significant CO$_2$ leakage (about 14% in 100 years). Also noted is that leakage occurred after injection is stopped, which mean post-injection is also very important (Fig. 65).

Also compared are the pressure and CO$_2$ concentration observed at the monitoring well (Fig. 66-67). In Fig. 66, we see that the mud layer is effectively behaved as a “barrier” so the pressure above are much lower than that in the target layer, especially in the early time.

**Comparison among Case 2, 5, and 6**

Fig. 68 shows the injection rates and cumulative CO$_2$ injection of case 2, 5 and 6. We see that the existence of hydraulic fractures helps improve the injectivity significantly at early time. As a result, CO$_2$ is injected much quicker. But the fact that curves for cases 2-4 are on getting very close in late time (>2000 days) indicates hydraulic fracturing may expedite the injection but has limited impact on improving the overall injection in the long run (Fig. 69).

Fig. 70 shows the percentage of leaked CO$_2$ for the 3 cases. It is interesting to see that hydraulic fracture with a short half-length actually mitigate CO$_2$ leakage as it helps CO$_2$ to move horizontally other than vertically. But when fracture half-length is big, it facilitates connection to the natural fractures. As a consequence, severe leakage (about 26% in case 6) is observed through hydraulic-natural fracture network.

We also compared the pressure and CO$_2$ concentration detected at the observation well. Almost no difference in pressure curves shown in Fig. 71 is observed as long as fractures are present to relive the pressure. In Fig. 72, we see that the observation well may not able to see the CO$_2$ front as it moves dramatically towards the natural fractures.

**Table XXI:** Case description

<table>
<thead>
<tr>
<th>Cases</th>
<th>Case description</th>
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<tbody>
<tr>
<td>Case 1</td>
<td>Real case without natural fractures</td>
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<tr>
<td>Case 2</td>
<td>Real case with natural fractures</td>
</tr>
<tr>
<td>Case 3</td>
<td>Real case with hydraulic fracturing connected with natural fractures</td>
</tr>
<tr>
<td>Case 4</td>
<td>Real case with hydraulic fracturing unconnected with natural fractures</td>
</tr>
<tr>
<td>Case 5</td>
<td>100ft horizontal fracturing, leakage by monitoring well</td>
</tr>
<tr>
<td>Case 6</td>
<td>300ft horizontal fracturing, leakage by monitoring well</td>
</tr>
</tbody>
</table>
Figure 56: Triangulated mesh and local grid refinement for case 1

Figure 57: CO$_2$ concentration maps for case 1
Figure 58: Geological setup, well locations and permeability field for case 2

Figure 59: Geological setup, well locations and permeability field for case 3
Figure 60: Geological setup, well locations and permeability field for case 4

Figure 61: CO₂ concentration maps for cases 2-4
Case 5

**Figure 62**: CO$_2$ concentration maps for cases 4-5

Case 6

**Figure 63**: CO$_2$ injection rate for cases 1-4
Figure 64: Cumulative CO₂ injection for cases 1-4

Figure 65: CO₂ leakage rate for cases 1-4
Figure 66: Pressure at observation well for cases 1-4

Figure 67: CO₂ concentration at observation well for cases 1-4
Figure 68: CO₂ injection rate for cases 2, 5, 6

Figure 69: Cumulative CO₂ injection for cases 2, 5, 6
Figure 70: CO₂ leakage rate for cases 2, 5, 6

Figure 71: Pressure at observation well for cases 2, 5, 6
9. **Enhancement of Geochemical Simulator and the application of ECBM**

Two methods of building ERA matrix are optimal in current GPRS. In this case the canonical matrix method is adapted. Canonical matrix for the reaction system mentioned above is expressed as:

\[
\begin{array}{ccc}
0 & -1 & -1 \\
-1 & -1 & -1 \\
1 & 1 & 2 \\
0 & 0 & 0 \\
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{array}
\]

The corresponding ERA matrix is

\[
\begin{array}{cccc}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{array}
\begin{array}{ccc}
0 & 1 & 1 \\
1 & 1 & 1 \\
-1 & -1 & -2 \\
0 & 0 & 0 \\
\end{array}
\]

The extending ERA matrix needs a mineral part. It should be added according to the rule as former states. The validation is performed by comparing the molality of aqueous species H+ and Ca2+ after 10 days continuous injection. Results are shown in Figure 73 and 74. We can find that the GPRS can fit well with GEM.
Figure 73: H+ molality distribution
To validate the performance of the extended ECBM module, two cases are carried out. The first problem is dealing with CH4 depletion process. It is following the published work of Law et al. (2002). All the input data, such as Langmuir isotherm parameters, grid system, fracture relative permeability, well control are introduced. One difference is we assume the CBM reservoir is saturated with water initially. Eclipse300 and CMG-GEM simulator are participated in the comparison. The model we use in Eclipse300 is instant desorption single porosity model. GEM ECBM model is a dual porosity single permeability model. Both of them are pseudo compositional model and use Langmuir type sorption curve. Water component is not existed in the gas phase. Eclipse300 instant model requires a tiny desorption time, so we set 1e-3day for the input of both CMG-GEM and GPRS.

The first stage of production is water depletion. CBM reservoir pressure is decreasing as production continues. Meanwhile, gas desorption occurs due to pressure change. Peak production emerges at 10 days, and then decreases rapidly. Figure 75 shows the comparison of methane production rate for simulators. We can find that our results have good agreement with Eclipse300 and GEM. The deviation mainly comes from the initialization and model difference. Currently gas desorption hasn’t been brought into the initialization part in GPRS, and the initialized adsorbed concentration in GPRS is set as an input parameter. It should be improved in the further work.

**Figure 74:** Ca2+ molality distribution
Case 2 is a CO2 flooding process. The CBM reservoir model is the same as case 1. The desorption time for CH4 and CO2 is 1 day. A constant injection rate of 7079.2 m³/day is performed throughout the production period. The result that was shown in Figure 76 shows comparison of gas production rate for GEM and GPRS. In the former stage, the desorbed methane dominant the total gas production rate. The enhancement of methane production remains until CO2 breakthrough occurs at the producer after about 60 days. In general, the gas production rate in the former stage fit well with GEM. A better fit can be derived through lower the initial adsorbed concentration to correct the difference in initialization. However our production rate is larger than the commercial software. A clear study shows the reabsorption model that GEM uses consider gas saturation, which hasn’t been included in our model. A fine comparison is undertaken at present.

![Graph showing gas production rate for primary recovery.](image)

**Figure 75:** Gas production rate for primary recovery
Figure 76: Gas production curve for CO2 flooding

**Conclusions**

For basin evaluation, a regional study on potential CO2 sequestration in the Jianghan Basin was performed. The two formations, Qianjiang and Xingouzui Formation, were firstly identified and investigated with respect to various factors and conditions. Preliminary analysis indicated that the two formations could be suitable candidate sites for CO2 injection.

Salinity impact on solids precipitation during CO2 injection to saline aquifers in China’s Jianghan Basin is studied. For 1-D radial flow under the similarity property constraints mentioned above, the simulations have provided the following results. Three different zones: $\zeta_d = R^2/t = 6.9 \times 10^{-6} \text{ m}^2/\text{s}$ a zone where complete dry-out of aqueous phase has occurred, the liquid phase has been removed by dissolution into the flowing CO2, the gas saturation in this region is slightly less than 1. The dry out zone is followed by an intermediate zone $\zeta_d \leq R^2/t \leq \zeta_f$, finally, there is an outer region: $\zeta_f = R^2/t > 6.6 \times 10^{-3} \text{ m}^2/\text{s}$. From the obtained results it was shown that precipitation occurs only behind a sharp dry-out front. The numerical simulation results indicate that solid saturation (fraction of pore space filled by precipitate) in the dry-out region is constant. As the salinity increases, the solid precipitation increases. The increasing multiple of solid precipitation is slightly bigger than those of salinity. Two-dimensional simulations of CO2 injection results showed the following results: Effects of gravity override on gas saturation distributions
are strong and solid precipitation distributions are similar. With higher salinity, the value of solid precipitation can reach higher.

Two methods were tried to relieve salt precipitation and pressure buildup during CO2 injection. The method of pre-flush with fresh water before CO2 injection can obviously alleviate the pressure buildup problem induced by halite precipitation around the injection well. In addition, this method could lower the salinity of the aquifers and increase the solubility of CO2, with the benefit of reducing the leakage risk. Pumping saline water out of the target formation while injecting CO2 simultaneously could reduce the pressure buildup both in the near-well region and the formation as a whole. Increase in the saline water production rate leads to further decrease in pressure buildup, this phenomenon was demonstrated by tripling the production where the pressure decreased about 15 bars. The introduction of two wells (left side and right side of the production well) increases the horizontal migration of the CO2 but contributes a little to the amount of CO2 dissolved.

For dynamic experiments, the experimental work was carried out utilizing dynamic resistivity measurements to monitor the evolution of an isoctane plume initially located at the bottom of the column. Time estimates for residual entrapment via scaling analysis for counter-current flow and design of segregation experiments based on an analog fluid system in glass-bead pack were studied.

Based on study of the impact of changes in mobility for the two-phase brine/CO2 system as a result of transitions between co- and counter-current flow settings, we made the following progress: 1) Counter-current flow and associated relative permeability is found to play an important role in determining the migration dynamics of CO2 that is injected into a saline aquifer, especially when the average vertical permeability of the aquifer is high. 2) Counter-current flow can be a dominant mode of flow during the injection period and influences both the plume evolution and the rate and amount of subsequent residual entrapment. 3) Numerical calculations including transitions between co-current and counter-current relative permeability functions are found to predict a higher residual saturation of CO2 relative to calculations with a single set of co-current relative permeability functions. 4) Simulation of CO2 injection into saline aquifers based on a single set of relative permeability functions may accordingly not be sufficiently accurate for predicting plume evolution and long term fate of the injected CO2.

Direct measurement of counter-current relative permeability is not trivial. In this study, we used an alternate approach to show that relative permeabilities that are obtained in a co-current flow setting cannot be applied directly in the prediction of dynamics in counter-current flow settings. A comparison of measurements and predictions based on co-current observations show that the migration time of a non-wetting phase plume may be misrepresented by approximately an order of magnitude. Therefore, we propose that it is necessary to use a displacement dependent representation of relative permeability in the simulation of CO2 injection into saline aquifers to represent the migration of CO2 accurately.

For microscopic modeling and simulation, a coupled multiphase Lattice Boltzmann (LB) model was developed to simulate the dissolution of immiscible liquid droplets in
another liquid during the rising process resulting from buoyancy. It was found that there exists a terminal rise velocity for each droplet, and there was a power law relationship between the Eötvös (Eo) number and the terminal Reynolds (Re) number. The simulation results were in agreement with the empirical correlation derived for predicting bubble rise. The Damköhler (Da) and Peclet (Pe) numbers were varied to investigate the coupling between droplet size, flow field, dissolution at the interface, and solute transport.

For macroscopic modeling and simulation study, a CO2 sequestration simulation framework that can account for natural and drilling/injection induced fractures and chemical reactions was developed. This framework is capable of modeling dynamic flow in micro-scale and reservoir-scale simultaneously. Simulations have been done using Discrete Fracture Modeling (DFM). Systems with fractures in CO2 injection formation versus in cap rocks are compared. Results have shown that the existence of mudstone layers could prevent injected CO2 from leaking outside the reservoir when no fractures are present. While vertical fractures intersecting with mudstone layers will cause significant leakage increase as fractures form extremely preferential pathways for CO2 transport.

A discrete fracture model for CO2 sequestration was studied with considering natural and hydraulic fractures based on an actual CCS project. The following progresses are made to help evaluate the roles of fractures in CCS projects. 1) The existence of cap rock and mudstone layers was showed to prevent injected CO2 from leaking outside the saline aquifer when no fractures are present. However, fractures intersecting with mudstone layers will cause significant leakage increase as the fractures form extremely preferential pathways for CO2 transport. Cycles with sandstones and mudstones would also efficiently help store CO2. 2) Fracturing was proved to help CO2 moving horizontally. The longer the hydraulic fracture, the more CO2 will be retained in the target formation. Hydraulic fractures, if not commnicate with natural fractures, will not only help improve injectivity but also mitigate the leakage risk; But if they are close enough to natural fractures up out of the target formation, it may cause severe CO2 leakage. 3) If the location of the injector is far enough from fractures in the cap rock, the leakage risk is found very limited and injectivity is found to be significantly improved.

To enhance the stability of GPRS geochemical simulator, a general scheme is designed. Two methods are employed to eliminate fast reaction rates in the aqueous phase. Element-component correlation matrix and canonical matrix are two strategies to build ERA matrix. Decomposing method is also investigated and applied. The fully coupled fully implicit simulator offers us a sufficient tool in modeling large scale and sophisticated CO2 geological sequestration case.

The extended GPRS geochemical simulator has the ability of modeling ECBM process. Validations are performed by comparing the results with commercial software. The results show good agreements. It proves the feasibility of modeling Langmuir type reaction on the basis of GPRS platform. Reactions in the aqueous phase during ECBM can also be considered for an accurate simulation.
This work is designed to accelerate translation of data into scientific understanding, simulation of site performance, and establishment of best standards. For example, this work is highly recognized by Shenhua Group. For the first CO₂ sequestration in a saline aquifer project in China, we are working with Shenhua on building the geological model, performing long-term simulations and history match with monitored data. The ultimate goal of this research is to develop realistic simulation tools, provide specific guidance and establish standards for the design and evaluation of CO₂ sequestration in saline aquifers in China.

Publications and Patents


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24. Xuan Liu, Bin Gong, Da Huo, Numerical Simulation on CO2 Sequestration in Saline Formations with Natural or Hydraulic Fractures Using a Discrete Modeling Approach, presented at the Canadian Unconventional Resources & International Petroleum Conference held in Calgary, Alberta, Canada, 19–21 October 2010.


27. Javaheri, M., Jessen, K., CO2 Mobility and Transitions between Co-current and Counter-Current Flows, SPE 163596, to be presented at the SPE Reservoir Simulation Symposium, 18-20 February 2013, The Woodlands, Texas, USA.

28. Javaheri, M., Nattwongassem, D., Jessen, J., Counter-Current Relative Permeability and Immobilization of CO2 in Saline Aquifers, XIX International Conference on Computational


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