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2-D Numerical Modeling of CO$_2$ Storage in the Devonian H$_2$S Containing Nisku Aquifer in the Wabamun Lake Area (Alberta, Canada)

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Abstract

The Devonian Nisku aquifer has been identified as a suitable CO$_2$ storage site in the Alberta Basin, but this aquifer contains significant amounts of H$_2$S. Numerical simulations were performed to investigate the impact of dissolved H$_2$S in the brine on the behavior of the injected CO$_2$. No major differences in geochemical reactions were observed between model runs with and without H$_2$S. Extensive dolomite dissolution was observed in both model runs, which caused a minor increase in porosity and permeability of the aquifer. The majority of the injected CO$_2$ was trapped in the Middle Nisku as a free supercritical phase and the rest was dissolved in the brine.

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Keyword: TOUGHREACT; reactive transport modeling; CO$_2$ storage; H$_2$S; Nisku;

1. Introduction

The Western Canadian Sedimentary Basin (WCSB) has been studied to evaluate the capacity for CO$_2$ storage and to assess the fate of injected CO$_2$ in its formations [1], [2], [3]. The capacity of the Alberta Basin for CO$_2$ storage was estimated at approximately 8.3 Gt of CO$_2$ [4]. The Wabamun Area CO$_2$ Sequestration project (WASP) examined the feasibility of storing 20 Mton CO$_2$/year over 50 years in a Devonian saline aquifer in central Alberta, Canada [5]. The Devonian Nisku aquifer was selected as the primary target for potential CO$_2$ sequestration. H$_2$S is a common constituent in Devonian oil and gas plays in the Alberta Basin [6]. H$_2$S in the Devonian rocks is largely the product of thermochemical reduction of...
sulphate derived from the dissolution of Devonian anhydrite [7]. Much of the Devonian section has been buried during the Laramide orogeny to depths greater than 4 km. These depths are sufficient for thermochemical sulphate reduction to occur [7]. Figure 1 shows the H$_2$S gas distribution determined from drill stem tests from the Devonian rocks of the Alberta Basin. H$_2$S concentrations range up to 0.8 mole fraction with the highest H$_2$S concentrations in the deepest western portions of the basin.

Figure 1. Distribution map of the H$_2$S (mole frac.) in the Devonian rocks of the Alberta Basin [7].

Previously, 1-D and 2-D modelling studies of the fate of the injected CO$_2$ into the Nisku aquifer were performed [8], [9]. Shevalier et al. [8] investigated differences in simple 1D radial modeling with and without H$_2$S and indicated that there was no difference between the two models. Dalkhaa et al. [9] extended the work of Shevalier et al. [8] by developing a 2-D radial model for CO$_2$ injection into the Devonian Nisku aquifer without considering H$_2$S contents. The objective of this study was to investigate the influence of H$_2$S (aq) on the behaviour of the injected supercritical CO$_2$ using a 2-D radial reactive transport model.

2. Model geometry
The same 2-D radially symmetric TOUGHREACT model described by Dalkhaa et al. [9] was used to assess the impact of the H$_2$S content on the fate of the injected CO$_2$ in the Devonian Nisku saline aquifer. Three different zones of the Nisku aquifer (the Upper, Middle and Lower Nisku) were introduced into the 2-D model. These different flow regimes in the Nisku formation were identified by petro-physical analyses during the WASP project [5]. The overlying (Calmar shale) caprock and underlying (Ireton shale) formation were also considered in the model. The model is 90 m thick and 20,000 m wide in radial distance. Figure 2 shows the vertical cross section of the model geometry.

3. Storage site characteristics

3.1 Mineralogy and Hydrogeological parameter
The hydrogeological parameters and the detailed mineralogical data for the Calmar, Upper, Middle and Lower Nisku and Ireton were given in Tables 1 and 3 of Dalkhaa et al. [9]. The Nisku Formation is a carbonate formation, composed of usually >80% dolomite with some variability among Upper, Middle and Lower Nisku zones. The Calmar caprock is predominantly composed of shales. The bottom rock, Ireton is composed of calcareous shales and argillaceous limestone. The Middle Nisku with a thickness of 20 m has the highest porosity of 20.9% and a permeability of 91 md. The porosity in the other parts of the Nisku and Calmar and Ireton Formations is usually <5.0%. The Calmar caprock is impermeable with a permeability of 2.9x10$^{-6}$ md. The Van Genuchten [10] model was used to calculate the capillary and
relative permeability curves with the residual CO₂ and water values of the Nisku Formation obtained from the work by Bennion and Bachu [11].

### 3.2 Water Chemistry

Table 1 shows the chemical composition of a sample obtained from a water producing well in the Nisku Formation. The Nisku Formation contains a Na-Cl brine with total dissolved solids of more than 195,000 mg/L. The brine is “sour”, containing a considerable amount of dissolved H₂S gas.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (mol/kg)</th>
<th>Species</th>
<th>Concentration (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.10</td>
<td>SiO₂(aq)</td>
<td>4.56*10⁻⁴</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.41</td>
<td>HCO₃⁻</td>
<td>2.01*10⁻²</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>9.33*10⁻²</td>
<td>Cl⁻</td>
<td>3.44</td>
</tr>
<tr>
<td>Na⁺</td>
<td>2.56</td>
<td>AlO₂⁻</td>
<td>1.6*10⁻⁷</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.1</td>
<td>O₂(aq)</td>
<td>4.88*10⁻³⁰</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>1.08*10⁻²</td>
<td>H₂S(aq)</td>
<td>6.03*10⁻²</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>9.35*10⁻⁶</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The measured concentration of dissolved H₂S in the produced brine at the wellhead varied from 0.52*10⁻² to 0.02 mol/kg. These values are not identical to the H₂S content at the reservoir condition since H₂S exsolves from the brine due to the pressure drop in the tubing during the fluid production from the reservoir to the wellhead. Based on a gas/water ratio of 4:1 and the produced gas containing ~36% H₂S [8], the concentration of H₂S(aq) was calculated to be 6.03 x 10⁻² mol/kg under reservoir conditions (Table 1). According to a calculation after the Duan et al. [12], the Nisku brine is under-saturated with respect to H₂S gas as its solubility is ~2.00 mol/kg at the reservoir condition with a temperature of 70 C and pressure of 17.5MPa and salinity of 195,000 mg/L.

### 4. Numerical Simulation

All numerical simulations were carried out using the code TOUGHREACT [13]. The Fluid property module, ECO2N was used [14]. The thermodynamic database of the code was modified by including H₂S(aq) species in the primary component species by using the KSWITCH program, a source code that was distributed together with the TOUGHREACT code. The program KSWITCH reads TOUGHREACT thermodynamic database entries and creates another identical set of entries with one of the components species “switched” with a derived species. In our work, the SO₄²⁻ species was switched with H₂S(aq) species. The parameters for the kinetics of dissolution and precipitation for the minerals used in the models were taken from the work by Palandri and Kharaka [15]. Thermodynamic equilibrium of the formation water with the mineralogy of the each formation was assumed as the initial condition. Thus, before commencement of CO₂ injection, batch modelling was performed for a time period of 10 years to equilibrate the formation water (Table 1) with the primary minerals present in each formation. This resulted in the initial formation water chemical properties for the Calmar, Upper, Middle and Lower Nisku and Ireton Formations prior to CO₂ injection. The obtained initial pH value of the Ireton Formation for the models with and without H₂S were quite different as pyrite was precipitated in the H₂S model to reach equilibrium. Simulations were performed for a 50 year-CO₂ injection period and a 1000 year-post injection period to investigate the fate of the injected CO₂ in the Nisku Formation with and without H₂S. CO₂ was injected at the bottom 10 m of the Middle Nisku at a rate of 0.5 Mt/year for 50 years.

### 5. Results and Discussion
The simulation results are presented in 2-D plots as a function of depth and radial distance of 5000 m at discrete time intervals of 1 and 50 years of CO₂ injection simulation and 500 and 1000 years of post-injection simulation.

5.1 Dissolved H₂S Concentration and abundance of pyrite

Figure 3 shows the spatial distribution of H₂S(aq) concentrations and abundance of pyrite over the simulation periods in the H₂S model. The initial H₂S(aq) concentrations in the brine of the Calmar and three different zones of the Nisku aquifer were around 0.06 mol/kg, whereas H₂S contents in the brine of the Ireton shale were 0.02 mol/kg. The H₂S content remained essentially unchanged over the simulation periods of injection and post-injection. However, it was observed that the H₂S(aq) concentration decreased to zero around the injection point after 50 years of injection due to a complete brine displacement by the supercritical injected CO₂, forming a dehydrated zone. The dehydrated zone disappeared as the supercritical CO₂ migrated up by buoyancy force and the brine came back by capillary forces over the simulation time after CO₂ injection ceased. After 50 years of injection and during the post-injection period, H₂S concentration in the brine of the Ireton and at the interface of the Ireton and Lower Nisku decreased to zero from the initial value of 0.02 mol/kg. The decrease was likely due to precipitation of pyrite in that region. Maximum increase in the volume fraction of the pyrite in the model was 4.0*10⁻⁵.

![Figure 3. Spatial distribution of H₂S(aq) concentrations (mol/kg) in the brine and abundance (change in volume fraction) over the simulation time.](image-url)

5.2 CO₂ plume
Figure 4 shows the spatial distribution of the injected supercritical CO$_2$ plume during the injection and post-injection periods for the two model runs with and without H$_2$S. The distribution of the CO$_2$ plume was essentially identical in both model runs. The injected supercritical CO$_2$ not only spread radially around the injector but also had a tendency to migrate upwards due to buoyancy-driven force until reaching the Calmar caprock, as it was less dense than the brine. CO$_2$ migrated towards the Calmar caprock and started forming a CO$_2$ plume beneath this caprock after 1 year of injection. The top of the CO$_2$ plume reached a radial distance of approximately 3 km after 50 years of injection, and 4 km after 1000 years of post-injection, respectively. Due to buoyancy, the injected supercritical CO$_2$ migrated up into the bottom two layers of the Calmar shale. It was also observed that CO$_2$ had migrated down into the Ireton shale during the injection phase, but after 500 years of post-injection almost no supercritical CO$_2$ remained in the Ireton Formation indicating that the CO$_2$ had dissolved in the brine.

5.3 Mass fraction of the dissolved CO$_2$, X$_{CO2}$

The amount of injected supercritical CO$_2$ that dissolves in the brine depends on the reservoir condition and the salinity of the brine. At the reservoir condition of 70°C and a pressure of 17.5 MPa and brine salinity of 195,000 mg/L, the maximum dissolved mass fraction of the CO$_2$ was 0.03 in each formation. The spatial distribution of the X$_{CO2}$ was identical in the models with and without H$_2$S (not plotted).

![Figure 4. Spatial distribution of the saturation of supercritical CO$_2$ (frac.) over the simulation time](image)

5.4 pH of the brine
The pH of formation water is controlled by water-rock-interactions. The initial pH value for the Calmar, the Nisku and Ireton Formations was 6.0, 6.4 and 6.4 respectively before CO₂ injection in the no H₂S model. When dissolved H₂S content was considered in the H₂S model, the initial pH value for the Calmar, the Nisku and Ireton Formation was estimated to be 5.3, 6.0 and 8.3 respectively. This indicated that H₂S(aq) content decreased the initial pH value for the Calmar and Nisku Formation. For the Ireton shale, however, the initial pH value was 8.3 in the H₂S model, which was likely due to pyrite precipitation consuming H₂S(aq). As CO₂ injection started, the brine became acidic as a result of CO₂ dissolution. The brine pH decreased to values as low as 5.0 in the CO₂ affected part in both models (Figure 5). Over the simulation time in both models, the pH was increasing in the Calmar and Ireton Formations, probably due to dissolution of some aluminosilicate minerals such as albite (not plotted).

Figure 5. Spatial distribution of the brine pH over simulation time

5.5 Evolution of main minerals and effect on formation porosity and permeability
More than 80 % of the Nisku aquifer (89% of the Upper Nisku, 81% of Middle Nisku and 91 % of Lower Nisku) is composed of dolomite. The acidic brine with a pH value of ~5.0 as a result of dissolution of the supercritical injected CO₂, facilitated dolomite dissolution in the formation (Figure 6). The maximum change in the volume fraction of the dolomite after 1000 years was ~ -0.004 in both models, corresponding to ~0.3% decrease in the dolomite abundance in the Nisku Formation. Mg²⁺ concentrations in the brine increased as dolomite dissolved (not plotted). The second major mineral reaction was calcite precipitation as a result of mineral disequilibria in the formation (not plotted). The change in the volume fraction of calcite was ~0.002 after 1000 years, resulting in a 0.2% increase in the calcite abundance. Extensive dissolution of dolomite in the aquifer caused an increase in porosity of ~ 0.2 % and thus an increase (3md) in permeability of the Nisku aquifer (not plotted) in both models with and without H₂S. This small increase in the permeability may affect the fluid flow.

5.6 Sequestration of CO₂ Injected
A total of 25 Mt of supercritical CO\textsubscript{2} was injected over 50 years. Figure 7 shows the amount of CO\textsubscript{2} sequestered via hydrodynamic and solubility trapping mechanisms after 1000 years of post injection for both models. It was observed that the majority of the injected CO\textsubscript{2} was trapped in the Upper and Middle Nisku. In the Middle Nisku, 65\% of the injected CO\textsubscript{2} was trapped as a supercritical free phase. 10\% of the injected CO\textsubscript{2} was dissolved in the brine of the Middle Nisku. The extent of CO\textsubscript{2} retained via solubility trapping in the Middle Nisku increased over the simulation period as the CO\textsubscript{2} saturated brine mixed with unsaturated brine. The remaining ∼25 \% of the injected CO\textsubscript{2} was trapped as a free phase in the Upper Nisku. Negligible amounts of the CO\textsubscript{2} were trapped in the Calmar and Lower Nisku via hydrodynamic and solubility trapping and in the Ireton Formations via mineral trapping due to its high content of weatherable silicate minerals.

Figure 6. Spatial distribution of dolomite abundance (change in volume fraction) over the simulation time

![Graph](image)

Figure 7. Sequestered CO\textsubscript{2} via different mechanisms during CO\textsubscript{2} injection into the Devonian Nisku aquifer.

6. Conclusions
In Alberta, Canada, the Devonian Nisku saline aquifer in the Wabamun Lake Area has been considered for potential CO₂ storage. The Devonian Nisku aquifer contains considerable dissolved H₂S. This simulation study indicates that the dissolved H₂S does not have any significant impact on the fate of the injected CO₂. The H₂S(aq) content slightly decreased the initial pH of the formation water as it has acidic characteristics. Small amounts of pyrite precipitated in the Ireton shale over the simulation period. 65% of the injected CO₂ was trapped in the Middle Nisku as a supercritical free phase. 10% of the injected CO₂ was dissolved in the brine of the Middle Nisku. The remaining ~25% was trapped as a free phase in the Upper Nisku. Mineral trapping of injected CO₂ in the Nisku aquifer was not observed, because dissolution of dolomite exceeded precipitation of calcite. The overlying Calmar formation was a good sealing cap rock for the injected CO₂ in the Nisku aquifer. The results from this 2-D modelling study suggest that the Nisku aquifer is a suitable formation for CO₂ storage in terms of geochemistry, storage capacity and caprock integrity. This information will be highly beneficial for potential future CO₂ injection projects targeting the saline aquifer of the Nisku Formation in Western Canada.

7. References
8 Shevalier, M., Nightingale, M., Mayer, B., and Hutcheon, I. Toughreact modeling of the fate of CO₂ injected into a H₂S containing saline aquifer: example of the Wabamun Area Sequestration project (WASP), Energy Procedia, 2011, 4, 4403-4410.