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2-D Numerical Modeling of CO_2 Storage in the Devonian H_2S 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_2S. Numerical simulations were performed to investigate the impact of dissolved H_2S 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_2S. 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_2S; 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_2S is a common constituent in Devonian oil and gas plays in the Alberta Basin [6]. H_2S in the Devonian rocks is largely the product of thermochemical reduction of

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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_2S gas distribution determined from drill stem tests from the Devonian rocks of the Alberta Basin. H_2S concentrations range up to 0.8 mole fraction with the highest H_2S concentrations in the deepest western portions of the basin.

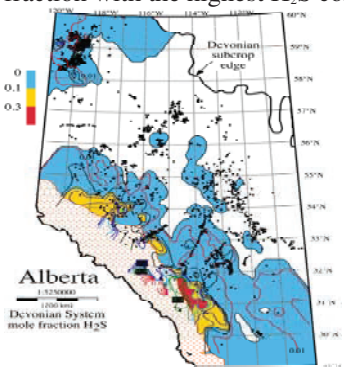

Figure 1. Distribution map of the H_2S (mole frac.) in the Devonian rocks of the Alberta Basin [7].

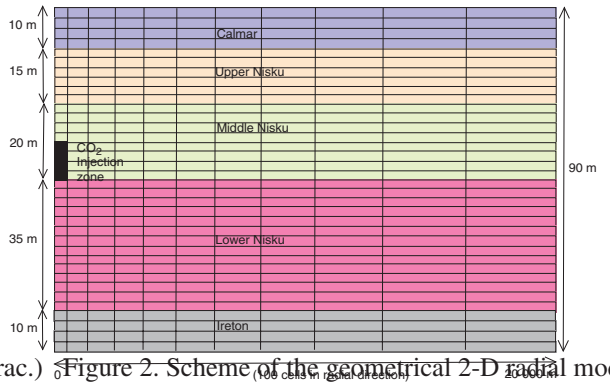

Figure 2. Scheme of the geometrical 2-D radial model

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_2S 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_2S contents. The objective of this study was to investigate the influence of H_2S (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_2S 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 2.9×10^{-6} md. The Van Genuchten [10] model was used to calculate the capillary and

relative permeability curves with the residual CO_2 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 H_2S gas.

Table 1. Water analysis of water producing well in the Nisku Formation

Species	Concentration (mol/kg)	Species	Concentration (mol/kg)
pH	6.10	SiO_2(aq)	$4.56*10^{-4}$
Ca^{2+}	0.41	HCO_3^-	$2.01\text{-}10^{-2}$
Mg^{2+}	$9.33*10^{-2}$	Cl^-	3.44
Na^+	2.56	AlO_2^-	$1.6*10^{-7}$
K^+	0.1	O_2(aq)	$4.88*10^{-70}$
Sr^{2+}	$1.08*10^{-2}$	H_2S(aq)	$6.03*10^{-2}$
Fe^{2+}	$9.35*10^{-6}$		

The measured concentration of dissolved H_2S 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 H_2S content at the reservoir condition since H_2S 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% H_2S [8], the concentration of H_2S(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 H_2S 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 H_2S(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 SO_4^{2-} species was switched with H_2S(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 CO_2 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 CO_2 injection. The obtained initial pH value of the Ireton Formation for the models with and without H_2S were quite different as pyrite was precipitated in the H_2S model to reach equilibrium. Simulations were performed for a 50 year-CO_2 injection period and a 1000 year-post injection period to investigate the fate of the injected CO_2 in the Nisku Formation with and without H_2S. CO_2 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 CO_2 injection simulation and 500 and 1000 years of post-injection simulation.

5.1 Dissolved H_2S Concentration and abundance of pyrite

Figure 3 shows the spatial distribution of H_2S(aq) concentrations and abundance of pyrite over the simulation periods in the H_2S model. The initial H_2S(aq) concentrations in the brine of the Calmar and three different zones of the Nisku aquifer were around 0.06 mol/kg, whereas H_2S contents in the brine of the Ireton shale were 0.02 mol/kg. The H_2S content remained essentially unchanged over the simulation periods of injection and post-injection. However, it was observed that the H_2S(aq) concentration decreased to zero around the injection point after 50 years of injection due to a complete brine displacement by the supercritical injected CO_2, forming a dehydrated zone. The dehydrated zone disappeared as the supercritical CO_2 migrated up by buoyancy force and the brine came back by capillary forces over the simulation time after CO_2 injection ceased. After 50 years of injection and during the post-injection period, H_2S 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 $4.0*10^{-5}$.

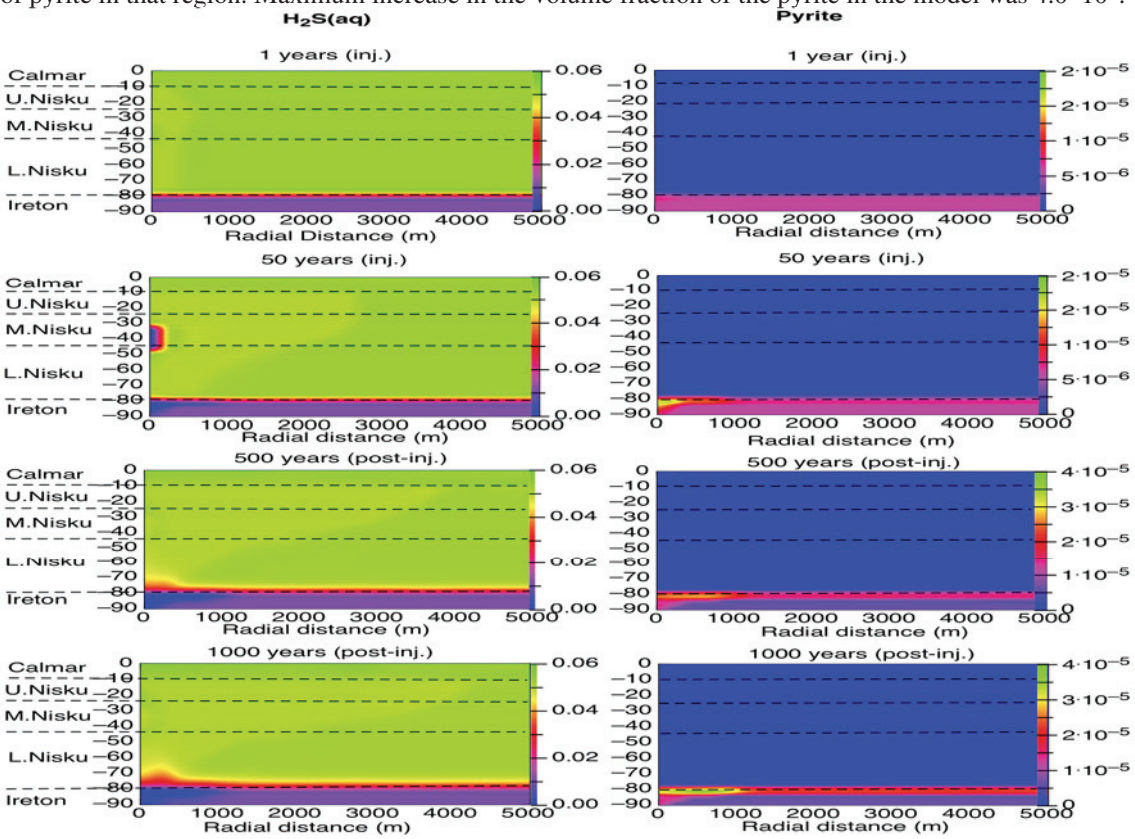

Figure 3. Spatial distribution of H_2S(aq) concentrations(mol/kg) in the brine and abundance (change in volume fraction) over the simulation time.

5.2 CO_2 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_2S. 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_2S (not plotted).

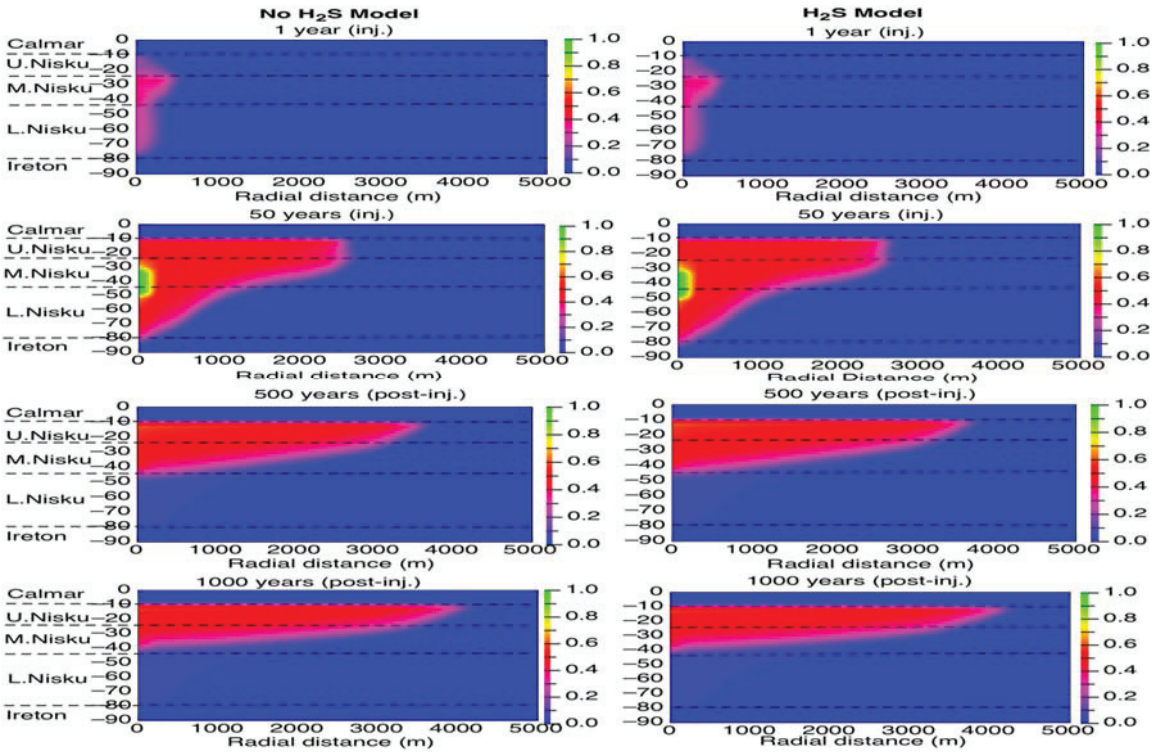

Figure 4. Spatial distribution of the saturation of supercritical CO_2 (frac.) over the simulation time

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 CO_2 injection in the no H_2S model. When dissolved H_2S content was considered in the H_2S 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 H_2S(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 H_2S model, which was likely due to pyrite precipitation consuming H_2S(aq). As CO_2 injection started, the brine became acidic as a result of CO_2 dissolution. The brine pH decreased to values as low as 5.0 in the CO_2 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).

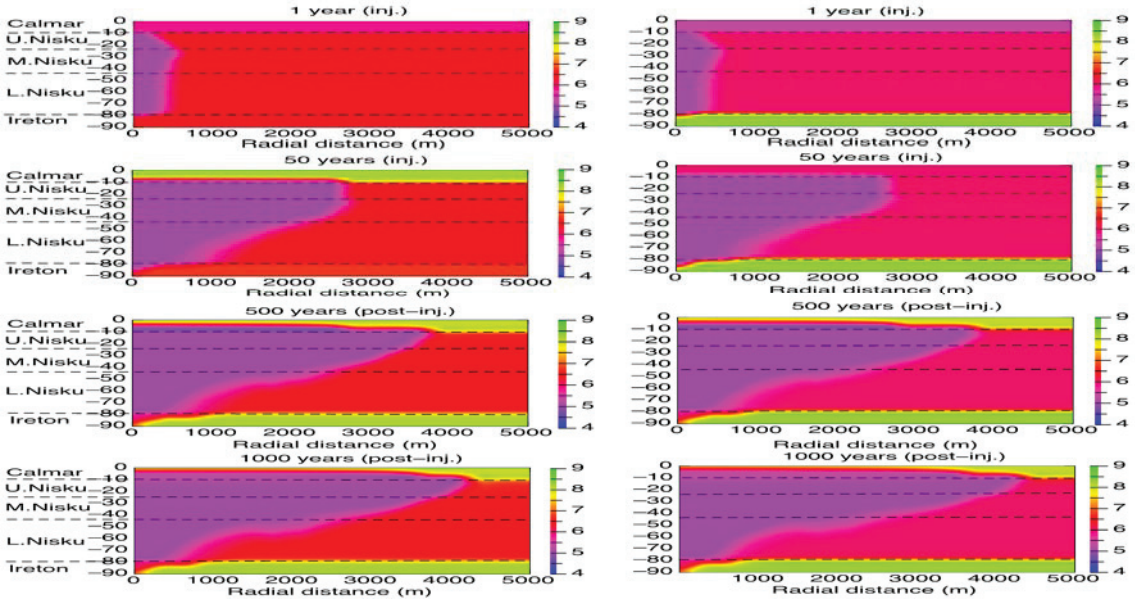

Figure 5. Spatial distribution of the brine pH over simulation time

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 CO_2, 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. Mg^{2+} 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 H_2S. This small increase in the permeability may affect the fluid flow.

5.6 Sequestration of CO_2 Injected

A total of 25 Mt of supercritical CO_2 was injected over 50 years. Figure 7 shows the amount of CO_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_2 was trapped in the Upper and Middle Nisku. In the Middle Nisku, 65% of the injected CO_2 was trapped as a supercritical free phase. 10% of the injected CO_2 was dissolved in the brine of the Middle Nisku. The extent of CO_2 retained via solubility trapping in the Middle Nisku increased over the simulation period as the CO_2 saturated brine mixed with unsaturated brine. The remaining ~25 % of the injected CO_2 was trapped as a free phase in the Upper Nisku. Negligible amounts of the CO_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.

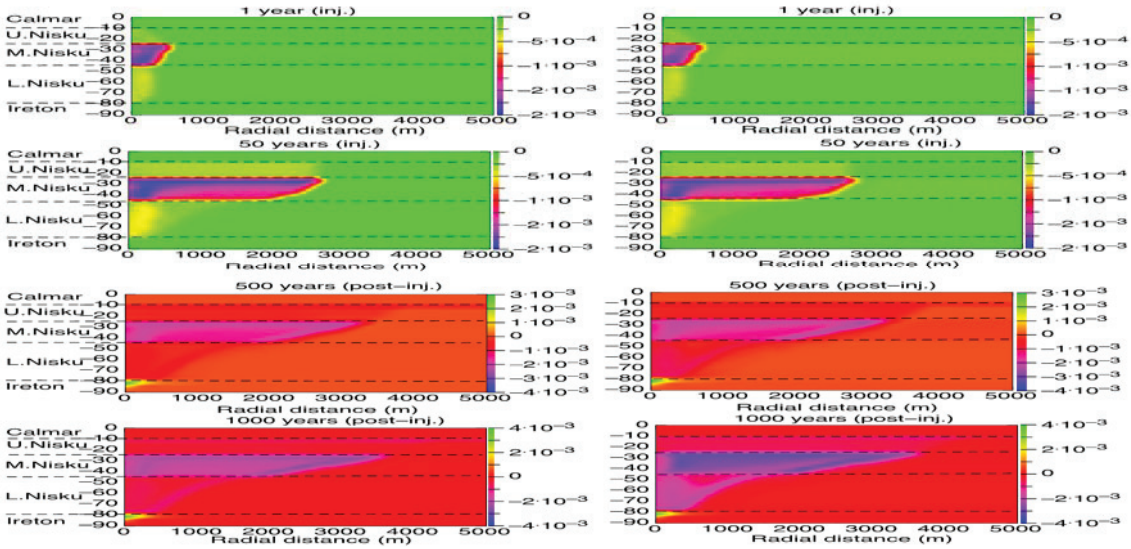

Figure 6. Spatial distribution of dolomite abundance (change in volume fraction) over the simulation time

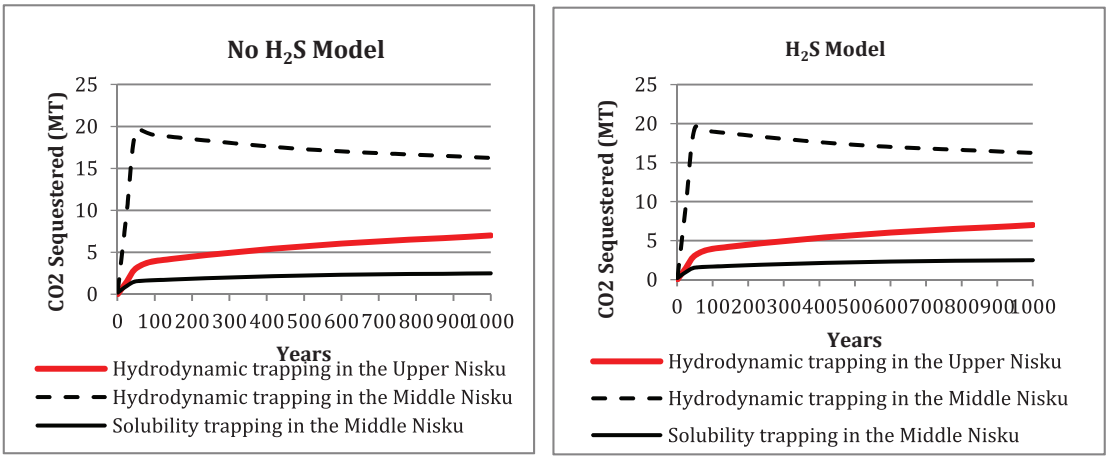

Figure 7. Sequestered CO_2 via different mechanisms during CO_2 injection into the Devonian Nisku aquifer.

6. Concludions

In Alberta, Canada, the Devonian Nisku saline aquifer in the Wabamun Lake Area has been considered for potential CO_2 storage. The Devonian Nisku aquifer contains considerable dissolved H_2S. This simulation study indicates that the dissolved H_2S does not have any significant impact on the fate of the injected CO_2. The H_2S(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 CO_2 was trapped in the Middle Nisku as a supercritical free phase. 10% of the injected CO_2 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 CO_2 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 CO_2 in the Nisku aquifer. The results from this 2-D modelling study suggest that the Nisku aquifer is a suitable formation for CO_2 storage in terms of geochemistry, storage capacity and caprock integrity. This information will be highly beneficial for potential future CO_2 injection projects targeting the saline aquifer of the Nisku Formation in Western Canada.

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