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Risk associated with H₂S evolution in sour aquifers during CO₂ injection

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Abstract

Many aquifers suitable for CO₂ sequestration contain measurable concentration of dissolved non-hydrocarbon species. In this paper, the compositional modelling of the CO₂ injection into aquifers that contain dissolved hydrogen sulfide, described here as sour aquifers, is studied. According to the results of this study, when CO₂ is injected into such aquifers, exsolution of dissolved components will occur and gaseous H₂S will accumulate at the leading edge of the CO₂ plume. At any time after the start of CO₂ injection, the region swept by the plume consists of two sub-regions. An inner radial sub-region extending from the injection well is characterized by the absence of H₂S in both the aqueous (brine) and gaseous (supercritical CO₂) phases. The dissolved H₂S in this first sub-region is almost completely removed from the brine and released to the migrating gas phase. The second sub-region extends from the outer edge of the first sub-region to the leading edge of the gas plume. In this outer sub-region, the mole fraction of H₂S in the CO₂ plume gradually increases toward a constant value at the edge (which is defined by the CO₂-H₂O-H₂S phase equilibrium conditions at specific temperature, pressure, and salinity of the brine) and thereafter only the size of this sub-region progressively increases.

For dissolved H₂S concentrations typically found in the Western Canada Sedimentary Basin, mole fraction of gaseous H₂S in the leading edge of the gas plume can be higher than 50%. This may have important implications for assessing the risk of CO₂ injection into sour aquifers. Leakage into abandoned wells, for example, might plausibly occur when the gas phase first reaches the wellbore, so initial leakage may contain substantial amounts of H₂S even though the average H₂S fraction in the stored CO₂ is quite small. H₂S is highly toxic, with acute short term toxicity at 100 to 1000 times larger than that of CO₂. This suggests that one need to account for this phenomenon when establishing risk assessment, monitoring and management strategies at planned CO₂ geo-storage sites.

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Keywords: Sour Aquifer, CO₂ sequestration, H₂S Exsolution, Numerical simulation

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1. Introduction

The occurrence of the non-hydrocarbon gases (CO_2 , H_2S , He and etc.) is quite common in aquifers of Alberta Basin which is a part of the Western Canada Sedimentary Basin [1]. The Rocky Mountains and the Appalachians in North America, where the injection of large quantities of CO_2 is most likely to be implemented in Canada and the United States [2], are among these formations. The existence of such dissolved components may occur in other aquifers worldwide. More importantly, many aquifers suitable for CO_2 sequestration contain measurable concentrations of H_2S [1]. These aquifers are described here as sour aquifers. The Nisku aquifer located in Wabamun Lake Area, Alberta, Canada [3] which is designated for injection of very large volumes of CO_2 (≈ 1 Gt) contains variable mole fraction of dissolved H_2S [1]. The Nisku aquifer properties have been used in presented results.

Although several studies have assessed the implication of impurities in the injection stream [4-7], minor attention has been paid to explore the consequences of injecting CO_2 into formations that contain pre-existing impurities in the in-situ brine. In this study a compositional simulator, CMG-GEM, is used to perform numerical simulations of CO_2 injection into sour aquifers.

The organization of this paper is as follows. Section 2 covers the properties of the fluid as well as the reservoir model used in the simulations. In section 3 some preliminary simulation results for the base case scenario will be presented. In the next section, the sensitivity analysis of the important parameters is described followed by summary and conclusions.

2. Simulation Model

2.1. Fluid Representation of CO_2 -Brine and CO_2 - H_2S -Brine Systems

The solubility of gaseous components in the aqueous phase in CMG-GEM is modelled by employing Henry's law. The fugacity of components is calculated using the Peng-Robinson Equation-of-State. GEM version 2008.12 uses accurate models for the Henry's constants of CO_2 and H_2S taking into account pressure, temperature and salinity (salting-out coefficient) by Harvey semi-empirical correlation [8]. At initial condition of the Nisku formation (Pressure = 16 MPa, Temperature = 60 °C, and salinity = 190,000 mg/liter), the CMG calculates the concentration of dissolved H_2S equal to 0.023 by mole fraction in the aqueous phase which aligns with the value reported in the literature [9]. For calculating the viscosity and density of the aqueous phase, Kestin's [10] and Rowe's [11] correlation were used respectively.

2.2. Description of the Simulation Model

Since the focus of this study was to investigate the fate of existing H_2S in the Nisku formation during CO_2 injection, the simulation was limited to a single well located at the center of a cylindrical domain with a production well at the boundary to mimic a constant pressure boundary condition. Simulations were performed in a one-dimensional radial ($r \times z$) model with radius of 500 m and net aquifer thickness of 5.0 m. The absolute permeability and porosity of the model were considered equal to 2000 mD and 0.3, respectively to allow proper propagation of CO_2 plume after few days. With respect to initial concentration of dissolved H_2S , two cases were considered. In the first case the initial mole fraction of dissolved H_2S was taken as 0.02; in the second case as 0.005.

Limited information about the relative permeability curves encouraged us to use the Corey correlation with exponents of 2.0 and 1.5 for the gas and water relative permeability curves. The residual brine saturation was set equal to 0.1 and two different end points relative permeability values for the gas phase of 0.4 and 1.0 were considered for the base case and one for sensitivity analysis respectively. Pure CO_2 at supercritical conditions was injected for 200 days at a rate equal to 5000 sm^3/day .

The preliminary simulation results indicated that injection of pure CO_2 into an aquifer that initially contains dissolved H_2S causes the exsolution and release of H_2S into the expanding CO_2 plume.

Moreover, the expanding CO₂ plume delivers all of the exsolved H₂S progressively towards the leading edge of the plume. Figure 1 shows the gas saturation variation within the aquifer after 200 days.

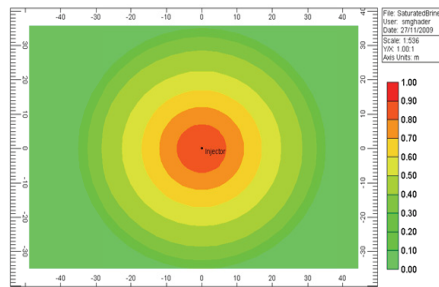


Figure 1: Variation of gas saturation around the injection well at the top of the aquifer after 200 days.

As shown in Figure 2, the mole fraction of CO₂ within this plume changes from 1.0 at the point of injection and gradually decreases toward zero close to the outer boundary of the plume.

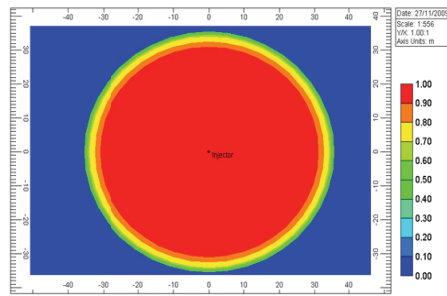


Figure 2: Variation of CO₂ mole fraction ($y_{CO_2}^V$) in the gas phase at the top of the aquifer after 200 days. Note that the mole fraction of H₂S ($y_{H_2S}^V$) at any location is equal to $1.0 - y_{CO_2}^V$.

Figure 3 illustrates the variation in the composition of the plume in a side view after 200 days.

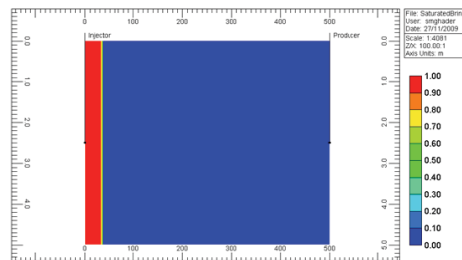


Figure 3: Side view of the variation of CO₂ mole fraction in the gas after 200 days. This figure also shows the position of the production well.

3. Base Case Simulation Results and Observations

For the base case scenario, pure CO_2 is injected at a rate of $5000 \text{ m}^3/\text{day}$ for 200 days into a vertical well located at the center of the domain. As previously described, when the injected CO_2 comes into contact with brine, H_2S progressively exsolves out of the aqueous phase into the gas phase of the advancing CO_2 plume. The CO_2 plume pushes the mobile portion of the brine as well as the exsolved H_2S toward the outer boundary of the domain while CO_2 continuously dissolves into the residual brine.

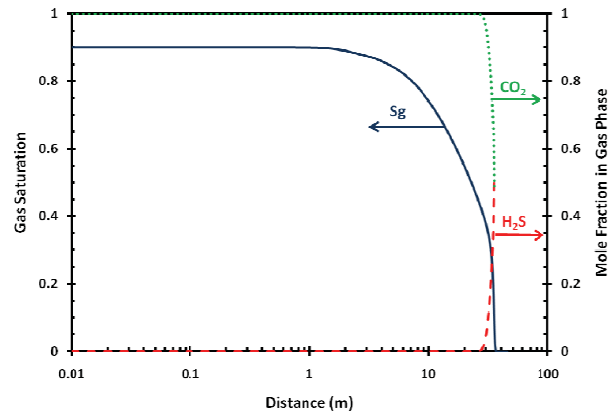


Figure 4: Distribution of different phases and components beneath the caprock after 200 days; Midnight blue solid curve: Variation of gas saturation vs. distance around the injection well, residual brine saturation is equal to 0.1; Green dotted curve: Variation of CO_2 mole fraction in the gas phase; Red dashed curve: Variation of H_2S mole fraction in the gas phase.

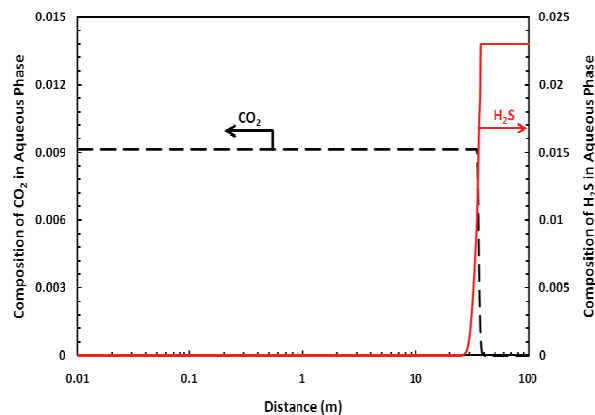


Figure 5: Composition of the aqueous phase in the region swept by the plume after 200 days. Note that the position at which the CO_2 mole fraction reaches zero corresponds to the outer edge of the plume, after which the brine saturation is equal to one.

Therefore, at any time after the start of CO₂ injection, the region swept by the plume consists of two sub-regions. An inner radial sub-region extending from the injection well is characterized by the absence of H₂S in both aqueous phase and gaseous phase. In fact, the dissolved H₂S in this inner sub-region is nearly completely removed from the brine via the vaporizing gas process. The second sub-region extends from the outer edge of the inner sub-region to the leading edge of the plume. In this outer sub-region, the mole fraction of H₂S in the CO₂ plume gradually increases toward the leading edge. Figure 4 shows that for the base case scenario and after 200 days of injection, the plume radius will approximately reach 35.5 meters of which 27 meters belong to first sub-region and the remaining 8.5 meters is considered to be in the second sub-region.

Figure 5 clearly shows that the CO₂ has been dissolved into the immobile portion of the brine while H₂S has been exsolved and released into the gas phase.

4. Sensitivity Analysis

In this section the sensitivity of the results (specifically the evolution of H₂S at the leading edge of the plume) to different flow conditions were investigated. For simplicity, the results after 200 days of injection are presented. The most important parameters which affect the problem are gas solubility, gas mobility, and initial H₂S concentration in the brine. The results are illustrated in Figure 6.

4.1. Effect of Gas Solubility

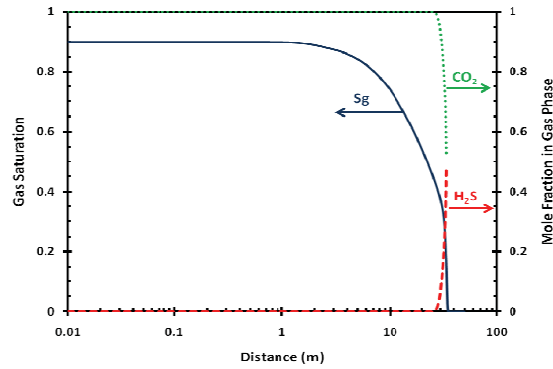
The effect of solubility was examined by considering pure water. It was assumed that the initial mole fraction of dissolved H₂S was the same as in the base case. Higher solubility of the non-hydrocarbon components in the pure water relative to the brine case causes the ultimate radius of the CO₂ plume to shrink, from 35.5 to 34.5 meters in the base case, indicating less H₂S was released from the (sour) pure water case (see Figure 6-a).

4.2. Effect of Gas Mobility

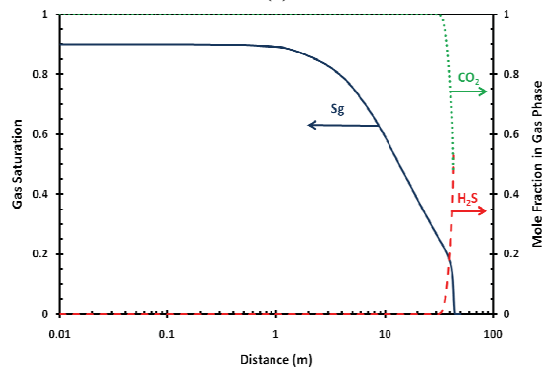
The effect of gas mobility was examined by increasing the end point of gas relative permeability from 0.4 to 1.0. In the case of higher gas mobility, the gas spreads over a larger contact area with the aqueous phase (larger radius of plume which in here equals to 42 meters), thereby stripping H₂S more effectively away from the brine in contact with the advancing gas front (See Figure 6-b).

4.3. Effect of Initial Concentration of Dissolved H₂S in Brine

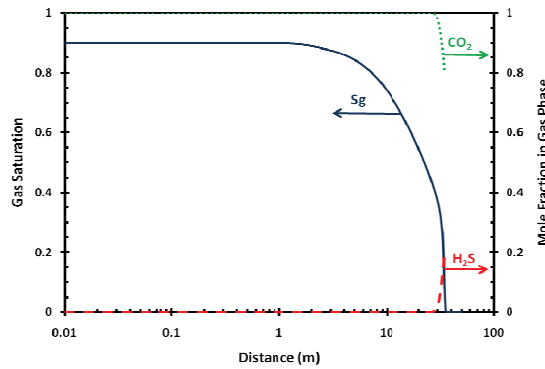
Simulations were run for another case where the initial mole fraction of the dissolved H₂S in brine was decreased four times. Hence, in this case the initial mole fraction of H₂S in the brine was equal to 0.005. The simulation results in Figures 6-c reveal that although the cumulative mass of released H₂S is reduced by decreasing the initial mole fraction of the dissolved H₂S in brine, the mole fraction of released H₂S in the gas phase is still high. These results also illustrate the fact that the initial concentration of H₂S in brine is not a serious barrier for the evolution of H₂S during CO₂ sequestration.



(a)



(b)



(c)

Figure 6: Effect of different parameters on the distribution of different phases and components beneath the caprock after 200 days; (a) increased gas solubility (b) increased gas mobility (c) four times decrease in the initial mole fraction of dissolved H₂S in the brine.

5. Summary and Conclusions

Compositional model simulations were performed to characterize the exsolution of H₂S during carbon dioxide sequestration into aquifers containing pre-existing dissolved H₂S. Simulation results confirm the formation of two distinguishable sub-regions in the volume swept by the gas plume. The first of these two sub-regions occupies the interior cylindrical region centered at the injection point and characterized by the absence of H₂S in both aqueous and gaseous phases. However, the mole fraction of H₂S in the second sub-region gradually increases and finally stabilizes at a constant value which is determined by the reservoir conditions including pressure, temperature, and salinity.

Sensitivity analysis was carried out to investigate the effects of flow conditions and fluid characteristics on the sizes of these sub-regions and particularly the alteration of the H₂S mole fraction profile in the second sub-region. The study was limited to the main parameters such as gas mobility, gas solubility, and initial mole fraction of dissolved H₂S impurity.

The results of this study are vital in establishing monitoring strategies at CO₂ storage sites, and in evaluating the risks associated with the possible leakage of evolved H₂S during CO₂ and acid gas injection into sour aquifers.

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