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An investigation of chromatographic partitioning of CO_2 and multiple impurities in geological CO_2 sequestration

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Abstract

Different solubilities of CO_2 and impurities contained in the injected streams would result in partitioning of the components at the leading gas front advancing through the aqueous phase. In this study, the chromatographic partitioning phenomena of CO_2 with multiple impurities are investigated by numerical simulations. Three most common impurities, i.e., N_2, H_2S and CH_4, are selected and studied. Compared with the partitioning phenomenon of CO_2 and H_2S, our simulation results indicate that, the inclusion of less soluble N_2 and/or CH_4 results in an earlier gas breakthrough and a longer delay between the breakthrough times of CO_2 and H_2S. This is mainly because that the addition of N_2 and/or CH_4 lowers the viscosity of the gas phase, resulting in much higher gas mobility than that of the CO_2-H_2S mixture. Thus, gas mixture contacts with brine over a larger area, giving rise to more efficient stripping of H_2S.

Keywords: Chromatographic partitioning; Multiple impurities; Carbon capture and storage; Numerical simulation.

1. Introduction

Carbon capture and storage (CCS) has been recognized as one of the most promising options to reduce the emissions of CO_2 into the atmosphere [1-3]. Capture and compression of CO_2 from industrial waste streams are very expensive, accounting for about 75% of the total CCS costs [4, 5]. Co-injection of CO_2 with certain amount of impurities, such as N_2, H_2S, SO_2 and CH_4, may be economically advantageous. It is important to evaluate the effects of impurities on pipeline transport and geological storage to realize economic optimization. Chromatographic partitioning of CO_2 and associated non-CO_2 species occurred in geological storage is an interesting phenomenon that has been investigated in recent years. The investigations were initiated by the observation that the breakthrough of pure CO_2 at the producing wells

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was prior to the breakthrough of H_2S, after an acid gas mixture containing 98% CO_2 and 2% H_2S was injected [6, 7]. Laboratory experiments confirmed the hypothesis that H_2S would be stripped off at the leading edge of the advancing gas displacement front due to the preferential solubility of H_2S compared to that of CO_2, resulting in the delayed breakthrough [6, 7]. Numerical simulations were carried out to investigate the effects of various parameters, including permeability, dispersion, gas mobility as well as flow direction, on the chromatographic partitioning of H_2S with CO_2 [7-9]. Similar studies have been performed to investigate the migration of CO_2-N_2 mixture injected in deep saline formations [10, 11]. The simulation results revealed that CO_2 was stripped off at the leading edge of the displacement front that advanced through the aqueous phase owing to the higher solubility of CO_2 over N_2.

The investigations of chromatographic partitioning are of great importance to the monitoring of impure CO_2 storage in geological formations. For instance, detection of pure CO_2 front may signal the arriving of potential hazardous gas phase containing more soluble impurities like H_2S while detection of less soluble impurities like N_2 may be the signal that CO_2 front is approaching. However, CO_2 streams captured from industrial sources generally contain more than one kind of impurities while almost all the previous studies have focused on the partitioning of CO_2 with one specific impurity. The chromatographic partitioning of CO_2 with multiple impurities should be investigated to obtain a better and more practical understanding of impure carbon geological sequestration. In this study, preliminary numerical simulations of the partitioning of CO_2 with three types of most common impurities, i.e., N_2, H_2S and CH_4, are performed.

2. Physical model

In the reservoir, fluids mainly flow in the horizontal direction. Furthermore, in order to compare and verify our results with that of the laboratory experiments [6], one-dimensional horizontal tube model with the length of 24.384 m is set up in the present study. Properties of the aquifer and fluids as well as the model parameters are listed in Table 1. Numerical simulations are performed using the compositional reservoir simulator, CMG-GEM^{TM} [12]. The solubility of each gas component in the aqueous phase is modelled employing the general Henry's Law [13]. The fugacity of each component in the gaseous phase is calculated using the Peng-Robinson equation of state. The Henry's constants are calculated by Harvey's correlation [14], which is a function of temperature, pressure and salinity. For the calculation of the aqueous phase density and viscosity, Rowe and Chou correlation [15] and the correlation by Kestin et al. [16] are adopted, respectively. The viscosity of the gas mixture is calculated using the Pedersen model [17], which takes into consideration fluid composition, temperature and pressure. The Corey correlation [18] is employed to characterize the relative permeability curves for both gas and brine. The relative permeability parameters are the same as the values that were used by Bachu et al. [8].

Table 1. Fluid properties and model parameters.

Temperature (K)	334
Brine salinity (mg/L)	118950
Pressure (kPa)	13500
Permeability (mD)	5915
Porosity	0.37
Tube length (m)	24.384
Tube inner diameter (m)	7.75×10^{-3}
Displacement rate (cm^3/h)	7.5

To verify our simulation results with previous laboratory results, chromatographic partitioning of 98% CO_2 and 2% H_2S gas mixture is simulated. As listed in Table 2, chromatographic partitioning of CO_2 with two kinds of impurities is then investigated and analyzed. The upper limit of N_2 mole fraction in the gas mixture is chosen to be 10% because the possible concentration of N_2 is up to that level [19].The possible concentration range of CH_4 in the captured CO_2 streams is generally 0.7-4 mol% [19]. However, in order to compare and analyze the effects of N_2 and CH_4 at equal concentration, the upper limit of CH_4 is also chosen to be 10%. Finally, the migration of the CO_2 plume containing these three kinds of non-CO_2 species is simulated.

Table 2. List of cases studied.

Case	Component composition
Case-Base	98% CO_2 + 2% H_2S
Case-N_2=10%	88% CO_2 + 2% H_2S + 10% N_2
Case-CH_4=10%	88% CO_2 + 2% H_2S + 10% CH_4
Case-CH_4=6%	88% CO_2 + 6% N_2 + 6% CH_4
Case-CH_4+N_2=10%	88% CO_2 + 2% H_2S + 5% N_2 + 5% CH_4

This physical model is mainly based on the following assumptions. First, isothermal conditions are used, which means that all possible thermal effects are neglected. Second, water vaporization is not considered. Third, with high permeability and porosity adopted in the model, the capillary effects are negligible. Fourth, the molecular diffusion is not taken into account in this study.

3. Results and discussion

For the chromatographic partitioning phenomenon, gas breakthrough time and the time lag between the breakthroughs of different components are two important indicators. Fig. 1 shows the time (as expressed by cumulative pore volume of production) evolution of the mole fractions of different gases in the effluent gas phase for CO_2 streams containing two kinds of impurities, in comparison with the base case. Using the present model and the associated assumptions, a good match is obtained between the results of our base case and that of the laboratory experiments [6]. This indicates that the present model is accurate for the simulation of the physical problem and the assumptions and simplifications are reasonable. Gas front consisting of pure CO_2 breaks through at approximately 0.5 pore volume of brine production and the breakthrough of H_2S occurs after some delay. The breakthrough time of H_2S is a little later than observed in the experiment, which may be the result of equations of state adopted in the simulations, or the neglect of the sand pack heterogeneity and/or the molecular diffusion.

Compared with the base case, the inclusion of less soluble N_2 and/or CH_4 leads to an earlier gas breakthrough (Fig. 1). As observed in Fig. 1a and b, pure N_2 or CH_4 is the first to break through at the outlet. When CO_2 begins to break through, N_2 or CH_4 concentration in the effluent gas phase would drop to the concentration in the feed gas. Compared to the base case, the breakthrough time of CO_2 is earlier when the gas mixture contains 10% N_2 or CH_4 while the breakthrough time of H_2S is a little later, that is, there is a longer delay between CO_2 and H_2S breakthrough times. This is mainly due to the fact that N_2 or CH_4 lowers the viscosity of the gas mixture while the same gas relative permeability is used for all the cases, resulting in higher gas mobility. Thus, the two-phase region is longer and H_2S is stripped off more effectively from the leading gas front. In the case of the CO_2-N_2-CH_4 mixture, the advancing leading gas

front is made up of less soluble N_2 and CH_4 (Fig. 1c). Because CH_4 is a little more soluble than N_2, the mole fraction of N_2 in the initial effluent gas phase is higher than that of CH_4. Since the viscosity of CH_4 is slightly lower than that of N_2, CH_4 transports faster than N_2 in the gas phase, giving rise to a decrease of N_2 concentration and an increase of CH_4 concentration in the effluent gas phase. When CO_2 starts to break through, both N_2 and CH_4 mole fractions decrease to the initial concentrations in the feed gas.
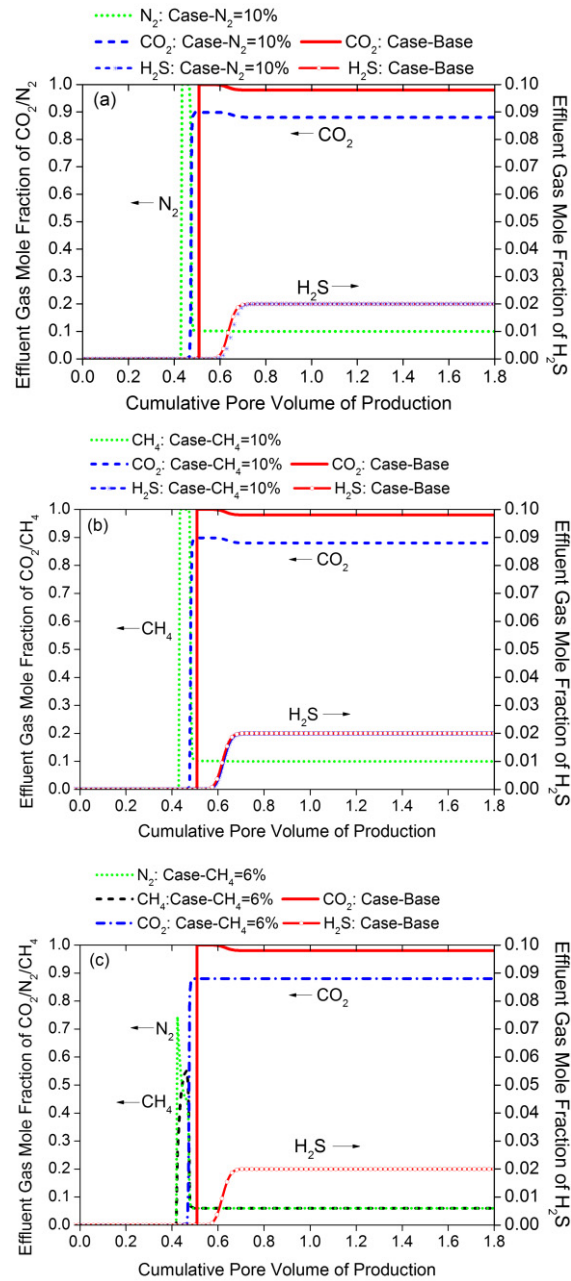

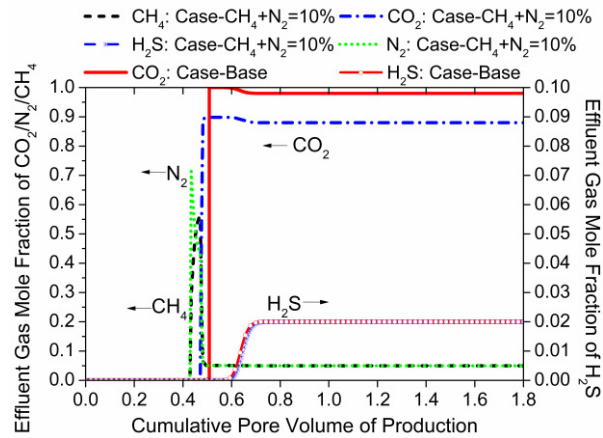Fig. 1. Time evolution of effluent gas compositions for (a) Case-N_2=10%; (b) Case-CH_4=10%; (c) Case-CH_4=6%.

Fig. 2. Time evolution of effluent gas compositions for CO_2 stream containing 5% N_2, 5% CH_4 and 2% H_2S.

The migration of CO_2 plume with 5% N_2, 5% CH_4 and 2% H_2S (Fig. 2) shares a similar pattern with that of the gas mixture containing 88% CO_2, 6% CH_4 and 6% N_2 (Fig. 1c). The main differences are a little later gas breakthrough and a slightly smaller time lag between N_2/CH_4 and CO_2 breakthrough times. This is mainly attributed to the higher viscosity of H_2S, which results in a lower gas mobility. The gas mixture spreads over a smaller contact area with the aqueous phase, leading to less efficient stripping of CO_2. The differences are not very significant because of the low H_2S concentration in the present case. It can be expected that the differences will increase with increasing H_2S concentration in the feed gas.

4. Conclusion

Understanding the migration processes of CO_2 plume containing multiple impurities is very important to geological storage security. It is necessary for devising monitoring procedures of possible leakage and developing emergency strategies. In this study, chromatographic partitioning of CO_2 and multiple impurities is investigated by numerical simulations. Three kinds of most common impurities, i.e., N_2, H_2S and CH_4 are chosen. When CO_2 streams contain less soluble impurities than CO_2, e.g. N_2 and/or CH_4 in our case, gas breaks through earlier than in the case of CO_2 and H_2S mixture. The time lag between the breakthroughs of CO_2 and the more soluble H_2S is also larger. The reason is mainly that N_2 and/or CH_4 lower the viscosity of the gas phase, leading to higher gas mobility and a more diffuse gas front. Thus, gas contacts with brine in a larger area, resulting in more efficient stripping of more soluble components. The simulation results also indicate that, when CO_2 streams containing less soluble impurities, such as N_2 or CH_4, are sequestered in geological formations, detection of these impurities may signal the arriving of CO_2 front or CO_2 and H_2S gas mixture.

In this preliminary study, molecular diffusion has been neglected while it may play a part in the chromatographic partitioning phenomena. In the future, the migration of injected CO_2 with multiple impurities taking into account molecular diffusion, reservoir heterogeneity as well as the effects of impurity concentrations will be investigated. Some potential storage sites may contain pre-existing impurities such as H_2S and/or CH_4, whose effects on the partitioning phenomena will also be considered.

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Biography

Xi Jiang holds Chair in Energy Use and Transport at Lancaster University. His research has been focused on high-fidelity numerical simulation and modelling of fluid flow, turbulence, heat and mass transfer, combustion and aeroacoustics. His on-going research activities mainly include the applications of modelling and simulation to three areas: (1) cleaner energy utilisation, (2) flow in porous media and geological carbon storage, and (3) battery thermal management and thermal management in electronic systems.