Numerical investigation of the partitioning phenomenon of carbon dioxide and multiple impurities in deep saline aquifers[1]

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Highlights

- The partitioning behaviours of impure CO_2 in geological formations are investigated.
- The effects of N_2, CH_4 or the mixture of N_2 and CH_4 are generally similar.
- Less soluble N_2 and CH_4 enhance gas breakthroughs and the partitioning.
- More soluble species such as H_2S dissolves preferentially in the formation brine.

Abstract

The partitioning behaviours of CO_2 with three kinds of common impurities, i.e., N_2, CH_4 and H_2S, in the formation brine are investigated by numerical simulations. The results indicate that the effects of N_2, CH_4 or the mixture of N_2 and CH_4 at the same concentrations are generally similar. The leading gas front is usually made up of less soluble impurities, such as N_2, CH_4 or the mixture of N_2 and CH_4, while more soluble species such as H_2S has dissolved preferentially in the formation brine. The separations between different gas species increase as the gas displacement front migrates forwards and contacts more of the aqueous phase. Compared with the partitioning results of the 98% CO_2 and 2% H_2S mixture, the 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. The early breakthrough of the gas phase is mainly because that the addition of N_2 and/or CH_4 lowers the viscosity of the gas phase, resulting in a higher gas velocity than that of the CO_2-H_2S mixture. Meanwhile, the mobility ratio is higher and the gas mixture contacts the formation brine over a larger area, giving rise to more efficient stripping of the more soluble gas species like H_2S and thus larger separations. In the meantime, with the same total concentrations of impurities (12%), when 2% H_2S is contained in the CO_2 streams, gas phase flows slower and thus the breakthrough time is later. Furthermore, the effects on the partitioning phenomenon are weaker with decreasing concentrations of N_2 and/or CH_4 (from 10% to 2%) with fixed concentrations of other impurity like H_2S (2%). The migration distances and the separations between different gas species change linearly with time on the whole, as confirmed by a simulation in a longer model.

Keywords: Partitioning phenomenon; Multiple impurities; Carbon capture and storage; Numerical simulation.

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[1] This paper was presented at the 7th International Conference on Applied Energy (ICAE2015), March 28-31, 2015, Abu Dhabi, UAE (Original paper title: "An investigation of chromatographic partitioning of CO_2 and multiple impurities in geological CO_2 sequestration" and Paper No.: **356**).

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1. Introduction

Since the beginning of the first industrial revolution, there are marked increases in the atmospheric concentrations of greenhouse gases, such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). These increases are believed to be the main cause of the global warming [1]. CO_2 is the most important greenhouse gas and its emissions generated from fossil fuels and industrial processes account for approximately 78% of the increase in total greenhouse gas emissions from 1970 to 2010 [2]. Carbon capture and storage (CCS) is one of the most promising carbon abatement options [1-4]. As a matter of fact, geological storage of CO_2 streams in deep saline aquifers as well as oil and gas reservoirs is the only method that can be applied on a commercial scale [5]. CCS involves the technologies to capture CO_2 produced in power plants and other industrial processes, transport it to suitable geological storage sites, and store it for long-term isolation from the atmosphere [6]. The capture process is the most expensive part of the CCS chain and the purity requirements of the captured CO_2 stream play an important role in actual capture costs [7-9]. Some on-going and/or planned CCS operations are considering impure CO_2 storage mainly due to economic reasons. However, impurities contained in the CO_2 streams are indicated to have adverse effects on both the transport process and storage process.

The presence of impurities in the injected CO_2 stream may have an influence on CO_2 storage effectiveness and security in geological formations in a variety of ways [7]. Many investigations have put emphasis on the geochemical effects of the impurities contained in the CO_2 streams, including the brine acidification effects by co-injected SO_2, NO_2, or H_2S and the corresponding effects on the porosity and permeability of reservoir and caprock, e.g. [10-15], and the hydrocarbon oxidation by the O_2 impurity, e.g. [16-17]. However, it has been suggested that except for the cases of SO_x and NO_x, the chemical effects of co-injected impurities would be minor [18]. Even for the strong reactive SO_2 impurity, it was suggested that the lower pH caused by SO_2 would be buffered by mineral dissolution during the timescale of acidification [19-21]. More importantly, concentrations of the reactive impurities like SO_x and NO_x in the captured CO_2 streams are usually much lower than those of the non-condensable or inert impurities such as N_2, CH_4 and Ar which do not have any or noticeable geochemical effects in the subsurface. Apart from the possible geochemical effects of certain reactive impurities, the physical properties of impurities could significantly affect the permanence and security of the subsurface sequestration of the impure CO_2 streams, especially in the short to medium term. The impurities would lead to changes in physical properties of the CO_2 streams, such as density and viscosity, thereby changing buoyancy, interfacial tension as well as other properties, which would affect the migration and dissolution of the CO_2 plume [18, 22-24]. It should also be noted that most existing studies give priority to the investigations of the impact of one specific co-injected impurity, such as SO_2, H_2S, N_2, O_2 or CH_4, etc., while only a few experimental and numerical investigations have examined the effects of impurities in ternary mixtures, e.g. [15, 25-27]. Since practical CO_2 streams injected typically contain several kinds of non-CO_2 species, it is necessary to investigate the effects of multiple contaminants on the geological storage.

In the past few years, some researchers have focused on the partitioning phenomena of

impure CO_2 storage. The studies were motivated by a report from a gas plant operator in southern Alberta, Canada: after injecting the mixture of 98% CO_2 and 2% H_2S into a depleted gas reservoir, pure CO_2 was observed to break through at the producing wells while the breakthrough of the CO_2-H_2S mixture was some time later [28, 29]. Both experimental and numerical studies have been performed to study the partitioning behaviour of CO_2 and H_2S in geological formations [28-31]. The laboratory experiments suggested that the solubility of the contained impurity compared to that of CO_2 played the most important role in the partitioning results of CO_2 and impurity [28, 29]. Numerical results implied that various flow parameters, such as relative permeability, dispersion, injected gas composition and flow direction, had influences on the breakthrough time of the gas phase and the separations between the breakthroughs of CO_2 and the co-injected impurity [29-31]. Numerical studies have also been carried out to investigate the migration behaviour of CO_2-N_2 mixture in the aquifer storage. The results revealed that CO_2 was stripped off at the leading displacement front because of the preferential solubility of CO_2 compared to N_2 [32, 33]. Recently, results from a pilot-scale experiment demonstrated that after the co-injection of CO_2 and air (N_2 and O_2 mixture), N_2 and O_2 migrated faster than CO_2 in the reservoir and the migration front of the gas phase was made up by N_2 and O_2 [34].

The investigations of the partitioning phenomenon are useful for understanding the migration behaviour (such as flow, dissolution as well as trapping mechanism) of the injected CO_2 mixture in geological formations. More importantly, the chromatographic partitioning process plays an important role in the design of monitoring procedures and the development of emergency plans in case of leakages. For instance, in the case of injected CO_2 and H_2S mixture in geological formations, if pure CO_2 front is detected at the monitoring wells, then it is likely that potential hazardous gas phase containing H_2S would show up after some time lag. Similarly, in the case of co-injected CO_2 and N_2, detection of N_2 front may serve as a signal of potential CO_2 leakage. However, previous studies mainly focused on the partitioning of CO_2 with one specific impurity and to the best of our knowledge, there is only one pilot-scale experiment concerning the partitioning of CO_2 with two kinds of impurities (N_2 and O_2) [34]. In the case of CO_2 storage with multiple impurities, the composition of the leading plume determines what kind of impurities is to be monitored for CO_2 leakage. This work is a first-step investigation on the partitioning phenomena of CO_2 with two or three kinds of non-CO_2 species. Three types of most common impurities, i.e., N_2, H_2S and CH_4, were chosen in the present study. Among the three kinds of potential geological formations, including deep saline formations, oil and gas reservoirs and unminable coal beds, deep saline formations were chosen for their largest storage capacity and wide distribution around the world [6].

2. Physical model

The CO_2 stream is generally injected at depths below 800 m, where the mixture is in a supercritical state (for simplicity, the "supercritical" is referred to as "gas" below) with ambient pressure and temperature higher than 7.38 MPa and 304.13 K, respectively. In the present study, the main fluid properties and model parameters (Table 1) are the same as in the simulations of Bachu et al. [30]. The simulations of the partitioning behaviour of CO_2 with two or three kinds of impurities are carried out in the tube model filled with quartz representative

of the Keg River Formation as that in the experiments of Bachu and Bennion [28]. One-dimensional horizontal radial model is employed and the 24.384-m-long model is divided into 500 equal grid blocks. The compositional reservoir simulator, CMG-GEM [35] is adopted to carry out the simulations. The good match between the numerical results of Bachu et al. [30] and the experimental results of Bachu and Bennion [28] confirms that the CMG-GEM software and the relevant model are capable of capturing the main features of the partitioning process. A horizontal injection well at one boundary is used to represent the displacement rate. At the other boundary, a production well is placed to mimic a constant pressure boundary condition. The dissolution of the gas components in the formation brine is calculated using the general Henry's law [36]:

$$x_i = \frac{f_i}{H_i} \tag{1}$$

where, x_i is the mole fraction of component i in the aqueous phase; f_i is the fugacity of component i in the gas phase, which is calculated using the Peng-Robinson equation of state [37]; The Henry's law constant of each component (H_i) is calculated by Harvey's correlation [38], which takes into account the effects of pressure, temperature and salinity. The correlation by Kestin et al. [39] is adopted to calculate the aqueous phase viscosity while the viscosity of the gas phase is calculated using the Pedersen model [40], which takes into consideration the effects of pressure, temperature and fluid composition. The brine and gas densities are calculated by the Rowe and Chou correlation [41] and the Peng-Robinson EOS respectively. The relative permeability curves for both the gas and aqueous phases are characterized by the Corey correlation [42]. It is worth mentioning here that our simulations employ a different correlation to calculate the Henry's law constants from that in the simulations of Bachu et al. [30]. Moreover, the present study adopts relations of temperature and pressure to calculate the gas viscosity, the brine viscosity as well as the gas and brine density while the corresponding properties in the simulations of Bachu et al. were regarded as constants.

Table 1. Fluid properties and model parameters.

Ten different cases are performed in this study and listed in Table 2. First, the case of 98% CO_2 + 2% H_2S (Case 1) is replicated as the baseline case (or "Case-Base"). Then the migration behaviours of the CO_2 plume containing two kinds of impurities are investigated. With the same CO_2 mole fraction (88%), four different impurity combinations are simulated (Cases 2-5): 2% H_2S + 10% N_2, 2% H_2S + 10% CH_4, 6% N_2 + 6% CH_4, and 8% N_2 + 4% CH_4. After that, two cases of CO_2 with all three kinds of non-CO_2 species, 88% CO_2 + 2% H_2S + 5% N_2 + 5% CH_4 and 88% CO_2 + 2% H_2S + 8% N_2 + 2% CH_4, are studied (Cases 6 and 7). Two more cases of CO_2-H_2S-N_2 mixtures with 5% and 2% N_2 respectively (93% and 96% CO_2 respectively) are then performed to investigate the effects of impurity concentrations on the partitioning phenomenon (Cases 8 and 9). Finally, since the model length seems small compared to real storage size, the effects of longer model length (243.84 m), ten times of the present model

length, are investigated with the 88% CO_2 + 2% H_2S + 10% N_2 mixture (Case 10). Because the estimated upper limit of N_2 concentration in the captured CO_2 streams is up to 10% [43], the mole fraction of N_2 in the injected gas mixture is set to be not more than this level. Despite the fact that the possible concentration range of CH_4 is generally much lower than that of N_2 [43], the maximum CH_4 concentration is also chosen to be 10% so that the effects of N_2 and CH_4 can be compared and analysed at the same concentration. However, the mole fraction of CH_4 in all cases is not more than that of N_2. Except for Cases 8 and 9, the mole fraction of CO_2 is chosen to be the same (88%) in the ternary and quaternary mixtures to investigate the effects of different combinations and compositions of impurities on the partitioning phenomenon. The H_2S mole fraction is 2% in all the ternary or quaternary mixtures that contain it to compare the results with the results of 98% CO_2 and 2% H_2S mixture and highlight the effects of the inclusion of other impurities on the partitioning process.

Table 2. List of cases studied.

The present simulations serve as a first step investigation of the partitioning behaviour of CO_2 and multiple impurities since practical CO_2 streams may contain other kinds of non-CO_2 species apart from the chosen three kinds of impurities. To focus on the effects of the impurities as well as to reduce computational time, some assumptions have been used in the physical model and simulations performed. Firstly, all possible thermal effects are neglected and isothermal conditions are adopted in the model. Secondly, at the chosen pressure and temperature, water mole fraction in the gas phase would be less than 2-3% [44]. In the present study, water vaporization and the relevant side effects such as salt precipitation and reductions in porosity and permeability are not taken into account. Thirdly, capillary effects are negligible because of the high permeability and porosity adopted in the study. Fourthly, the molecular diffusion is not taken into consideration. The results from the simulations are presented and discussed subsequently.

3. Results

3.1 Case-Base

Fig. 1 shows the gas saturation at five selected times as well as the evolution of the effluent gas phase compositions at the outlet for the 98% CO_2 and 2% H_2S mixture. Cumulative pore volume of production is a constant function of time. As seen in Fig. 1a, the breakthrough time of the gas phase is about 1.3 days, which is consistent with previous experimental results [28] and the numerical results [30]. The migration distances of the gas phase in the present study are somewhat different from the results of Bachu et al. [30] due to several different correlations employed. Nevertheless, the present model could capture the main features of the partitioning behaviour of the CO_2 mixture, including the breakthrough time of the gas phase and the delayed breakthrough of H_2S at the outlet (Fig. 1b). The separation between the breakthroughs of CO_2 and H_2S is in rather good agreement with

previous studies [28-31], especially with the experiment results [28].

Fig. 1. Partitioning results for Case-Base: (a) gas saturation at various times and (b) evolution of the effluent gas compositions at the outlet.

3.2 Partitioning with two impurities

Fig. 2 shows the gas position as well as the two phase compositions (mole fractions) at 0.5 day for the CO_2 streams containing 2% H_2S and 10% N_2 (Case 2), and 2% H_2S and 10% CH_4 (Case 3), respectively. It can be seen that the gas front has reached about 12 m at this time for both cases. The gas saturation at the inlet is smaller than one, which is mainly because that the irreducible water saturation is set to be 0.1 in this study (Table 1). According to the variation of the compositions, gas phase can be divided into three parts. In the first part, from 0 to about 8.8 m, gas phase is made up of CO_2, H_2S and N_2 or CH_4, with basically the same concentrations as in the feed gas. Although H_2S mole fraction is only 2% in the injected CO_2 streams, the equilibrium concentration of H_2S in the aqueous phase is much higher than that of N_2 or CH_4 due to its much higher solubility in the formation brine. In the second part (about 8.8-11.3 m), gas phase consists of CO_2 and N_2 or CH_4. This is mainly because that the more soluble H_2S has dissolved preferentially in the formation brine and has been stripped away from the CO_2 streams. In this range, CO_2 concentrations in the gas phase as well as in the aqueous phase increase slightly in response to the disappearance of H_2S. The concentrations of N_2 or CH_4 also increase slightly, but not very noticeable. In the third part, i.e., the very leading edge of the gas displacement front, gas phase is composed by pure N_2 or pure CH_4, while the more soluble CO_2 compared to them has been stripped off.

Fig. 2. Position of the gas front and the two phase compositions at 0.5 day. (a) and (b) are for Case 2 while (c) and (d) are for Case 3.

Fig. 3 shows the gas position as well as the two phase compositions at 1.0 day for Cases 2 and 3. Compared with Fig. 2, it is obvious that the separations between different gas species increase as the gas displacement front migrates forwards and contacts more of the aqueous phase. The migration distances of the gas phase as well as the separations between different gas species increase roughly linearly with time. Generally, except for some minor differences, for instance, CH_4 concentration in the aqueous phase is higher than that of N_2 because of the higher solubility of CH_4 than N_2, the results of Cases 2 and 3 are similar to each other.

Fig. 3. Position of the gas front and the two phase compositions at 1.0 day. (a) and (b) are for Case 2 while (c) and (d) are for Case 3.

The mobility of a fluid phase (λ_α) is represented by the ratio of the relative permeability to

phase viscosity [45, 46],

$$\lambda_\alpha = \frac{k_{r\alpha}}{\mu_\alpha} \qquad (2)$$

where, $k_{r\alpha}$ is the relative permeability of phase α, μ is viscosity. Mobility signifies the flowing capacity of the fluid in the reservoir, which increases with increasing mobility. According to Darcy's law [45], fluid phase velocity is proportional to phase mobility. The mobility ratio (M) is generally defined as the mobility of the displacing phase (gas in the gas/aqueous case) divided by that of the displaced phase, which is the formation brine in this study [45-48],

$$M = \frac{k_{rg}}{\mu_g} \bigg/ \frac{k_{rb}}{\mu_b} = \frac{k_{rg}\mu_b}{k_{rb}\mu_g} \qquad (3)$$

where, the subscript g stands for gas phase and b for formation brine. For certain displacing and displaced fluids, the mobility ratio has an influence on the degree of flow instability in the displacing process [47]. If $M > 1$, it indicates that the flowing capacity of the displacing phase is stronger than that of the displaced phase. In this case, the mobility ratio is regarded as "unfavourable", which means unstable displacements of the aqueous phase by the gas phase and poor sweep efficiency. The displacing phase may pass through the displaced phase in the form of "fingers" or even break through (viscous fingering), which means a larger two-phase region. Meanwhile, in a favourable mobility ratio ($M < 1$) situation, the fingering phenomenon is weakened and the displacements are in piston-like movements, which means that the leading displacing front is stable while the two-phase region is smaller.

Fig. 4 shows the variations of the gas phase velocity and the mobility ratio with distances at 0.5 day and 1.0 day for Cases 1-3. It can be seen that the trends of both the gas velocity and the mobility ratio are in accordance with that of the corresponding gas saturation (Figs. 2 and 3), decreasing with increasing distances. Compared to the baseline case of 98% CO_2 and 2% H_2S, the inclusion of 10% N_2 or 10% CH_4 increases the velocity of the gas phase as well as the mobility ratio at the leading gas displacement front. At the very leading edge of the displacing front, where the gas phase is made up of pure N_2 or pure CH_4, both the velocity of the gas phase and the mobility ratio remain constant values. Furthermore, the mobility ratios are smaller than unity at the leading gas displacement front, which indicates that the displacements at the leading gas front are rather stable. Except that the constant values at the leading gas displacement front are different mainly due to different viscosities of N_2 and CH_4, the gas phase velocity and mobility ratio of the 10% N_2 and 10% CH_4 cases are very similar to each other.

Fig. 4. The variations of (a) gas phase velocity and (b) mobility ratio with distances.

Fig. 5 shows the time evolution of the effluent gas phase compositions at the outlet of the tube model, which denotes the potential sequences of the gas species to break through if leakage occurs at 24.384 m. Compared with the baseline case of 98% CO_2 and 2% H_2S, the

inclusion of the 10% N_2 or 10% CH_4 impurity (Case 2 or 3) leads to an earlier gas breakthrough. The breakthrough time of the gas phase in Cases 2 and 3 is almost the same, about 1.0 day, while the gas breakthrough time in Case-Base is about 1.2 days. Furthermore, the breakthrough time of CO_2 in Cases 2 and 3 (about 1.11 days and 1.12 days respectively) is earlier than that (1.20 days) in Case-Base. On the contrary, the breakthrough time of H_2S in Cases 2 and 3 (about 1.45 days and 1.425 days respectively) is slightly later than that (about 1.41 days) in Case-Base. It implies that there is a longer delay between the breakthrough times of CO_2 and H_2S because of the inclusion of the 10% N_2 or CH_4.

Fig. 5. Time evolution of the effluent gas compositions at the outlet for (a) Cases 1 and 2 and
(b) Cases 1 and 3.

Figs. 6 and 7 show the gas position as well as the two phase compositions for the two cases of CO_2-N_2-CH_4 mixture (Cases 4 and 5) at 0.5 day and 1.0 day, respectively. Compared with Cases 2 and 3, it can be seen that the migration distances of the gas phase are a little longer in these two cases that do not contain the 2% H_2S. For instance, the migration distance of the gas front is about 12.3 m in Cases 4 and 5 at 0.5 day while it is about 12.0 m in Cases 2 and 3. At 1.0 day, the gas saturation at the outlet in Cases 4 and 5 is greater than zero. Accordingly, the mole fractions of N_2 and CH_4 in the gas phase and the aqueous phase do not turn into 0 at this point. It indicates that the breakthrough time of the gas phase is earlier than 1.0 day, particularly, earlier than the breakthrough times of the above cases that include 2% H_2S impurity (approximately 1.0 day in Cases 2 and 3).

Fig. 8 compares the variations of the gas phase velocity and the mobility ratio among Cases 2, 4 and 5. Different compositions of N_2 and CH_4 (6% N_2 and 6% CH_4 vs 8% N_2 and 4% CH_4) do not seem to cause noticeable change in the velocity of the gas phase and mobility ratio. The time evolution of the effluent gas phase compositions at the outlet as shown in Fig. 9 confirms that the breakthrough times of the gas phase for the two cases of CO_2-N_2-CH_4 mixture are actually before 1.0 day and that N_2 and CH_4 break through at the same time at the outlet in Cases 4 and 5.

According to the variations of the compositions, gas phase in Cases 4 and 5 can be divided into two parts. In the first part, gas phase is made up of CO_2, N_2 and CH_4, with basically the same concentrations as in the feed gas. In the second part, i.e., the leading edge of the gas displacement front, gas phase is made up of the N_2 and CH_4 mixture. The co-existence of N_2 and CH_4 at the leading gas front is mainly because that the solubilities of these two species are comparable and neither of them has been stripped off at the leading gas front. However, since N_2 is less soluble than CH_4 in the aqueous phase, N_2 concentration increases while CH_4 concentration decreases at the very leading front of gas displacement, even when the concentrations of N_2 and CH_4 are the same in the feed gas (Case 4: 6% N_2 and 6% CH_4). Generally, except that the two phase concentrations of N_2 and CH_4 are different, the results of these two cases of CO_2-N_2-CH_4 mixture, including the migration distances of the gas phase and the separations between different gas species, are similar to each other.

Fig. 6. Position of the gas front and the two phase compositions at 0.5 day. (a) and (b) are for
    Case 4 while (c) and (d) are for Case 5.

Fig. 7. Position of the gas front and the two phase compositions at 1.0 day. (a) and (b) are for
    Case 4 while (c) and (d) are for Case 5.

Fig. 8. The variations of (a) gas phase velocity and (b) mobility ratio with distances.

Fig. 9. Time evolution of the effluent gas compositions at the outlet for (a) Cases 1 and 4 and
    (b) Cases 1 and 5.

3.3 Partitioning with three impurities

Figs. 10 and 11 show the gas position as well as the two phase compositions for the two cases of CO_2-H_2S-N_2-CH_4 mixture (Cases 6 and 7) at 0.5 day and 1.0 day, respectively. With the same total concentrations (10%), different compositions of the N_2 and CH_4 mixture (5% N_2 and 5% CH_4 vs 8% N_2 and 2% CH_4) barely have an effect on the partitioning results with other species. As shown in Fig. 12a, the gas phase velocity and the mobility ratio hardly change in response to different N_2 and CH_4 compositions in Cases 6 and 7. Generally, Cases 4-7 share similar patterns and the leading edge of the gas displacement front is made up of the N_2 and CH_4 mixture. However, the inclusion of 2% H_2S and the corresponding decreasing concentrations of N_2 and/or CH_4 in Cases 6 and 7 lead to slightly lower gas phase velocity (Fig. 12a) and thus shorter migration distances of the gas phase, compared to Cases 4 and 5. At 1.0 day, the migration distance of the gas plume is about 24 m in Cases 6 and 7 while gas phase has broken through at the outlet of the 24.384-m-long tube in Cases 4 and 5 (Figs. 7 and 9).

In the meantime, comparing Cases 6 and 7 with Cases 2 and 3, it can be seen that except for the co-existence of N_2 and CH_4 in Cases 6 and 7, the general characteristics of these four cases are basically the same, including the migration distances of the gas phase, the migration distances of H_2S and CO_2, as well as the separations between different gas species. Fig. 12b compares the mobility ratios of the four cases. It is obvious that the mobility ratios of Cases 2, 3, 6 and 7 are similar with each other, except the constant values at the very leading front of gas displacement, which is due to different gas compositions and concentrations. Consequently, the breakthrough times of the gas phase, and the time intervals between the breakthroughs of different gas species are also very similar (Figs. 5 and 13).

Fig. 10. Position of the gas front and the two phase compositions at 0.5 day. (a) and (b) are
    Case 7 while (c) and (d) are for Case 8.

Fig. 11. Position of the gas front and the two phase compositions at 1.0 day. (a) and (b) are

Case 6 while (c) and (d) are for Case 7.

Fig. 12. The variations of (a) gas phase velocity and (b) mobility ratio with distances.

Fig. 13. Time evolution of the effluent gas compositions at the outlet for (a) Cases 1 and 6 and (b) Cases 1 and 7.

3.4 The effects of different concentrations of impurity

The effects of different concentrations of H_2S on the partitioning phenomenon have been investigated by other researchers [28-31]. From the above-mentioned results, it can be seen that the effects of N_2, CH_4 or the mixture N_2 and CH_4 at the same concentrations on the partitioning phenomenon are similar. Thus, the effects of different concentrations of N_2 and/or CH_4 impurity are represented by the effects of different N_2 concentrations in this study. Fig. 14 shows the gas position as well as the gas phase compositions at 0.5 day and 1.0 day for cases containing 5% N_2 and 2% N_2 (Cases 8 and 9), respectively. Compared with the 10% N_2 case (Fig. 2a and 3a), it can be seen that the migration distance of the gas phase decreases with decreasing N_2 concentrations in the injected CO_2 mixtures. The leading edge of the gas phase reached about 23.82 m for the case with 10% N_2 (Case 1) at 1.0 day, while the figures for the 5% N_2 and 2% N_2 cases are 22.36 m and 21.14 m respectively. This is because the gas phase velocity decreases with decreasing N_2 concentrations, as shown in Fig. 15a.

Comparing Figs. 2a, 3a and 14, it can be seen that the migration distance of CO_2 increases with decreasing N_2 concentrations. For instance, CO_2 has arrived at about 22.17 m in the 10% N_2 case at 1.0 day, while it only migrates 21.62 m and 21.09 m for the 5% N_2 and 2% N_2 case. Meanwhile, the migration distance of H_2S increases slightly with decreasing N_2 concentrations. As a result, the separation between H_2S and CO_2 decreases with decreasing N_2 concentrations. Furthermore, the range of the leading displacement front consisting of pure N_2, that is, the separation between CO_2 and N_2 also decreases with decreasing N_2 concentrations.

Fig. 14. Position of the gas front and the gas phase compositions for (a) Case 8 at 0.5 day, (b) Case 9 at 0.5 day, (c) Case 8 at 1.0 day and (d) Case 9 at 1.0 day.

Fig. 15. The variations of (a) gas phase velocity and (b) mobility ratio with distances.

Fig. 16 shows the time evolution of the effluent gas phase compositions at the outlet for Cases 8 and 9, respectively. The breakthrough time of the gas phase increases with decreasing N_2 concentrations in the CO_2-H_2S-N_2 mixture, from about 1.0 day in the 10% N_2 case to about 1.15 days in the 2% N_2 case. These profiles also demonstrate that there are decreasing separations between more soluble species and less soluble species with decreasing N_2

concentrations.

Fig. 16. Time evolution of the effluent gas compositions at the outlet for (a) Cases 1 and 8 and
        (b) Cases 1 and 9.

3.5 Longer model length

The model length of the preceding simulations is 24.384 m, which is very small compared to the migration distance in actual storage reservoirs, especially in long-term storage. Furthermore, the boundary conditions of the small-size model may have an impact on the simulation results. To evaluate the effects of the limited size of the model, a model with longer length of 243.84 m is chosen to simulate the case of 88% CO_2 + 2% H_2S + 10% N_2 (same composition as in Case 2). Except for the length of the model and the simulation time, all the other parameters are the same as in the 24.384-m-long model. Fig. 17 shows the position of the gas front and the two phase compositions for the CO_2-N_2-H_2S mixture at 5 days and 10 days, respectively. Fig. 18 shows the time evolution of the effluent gas compositions at the outlet. Generally, these profiles share the same trends as the corresponding profiles in previous small-size model. The migration distances of the gas phase and the separations between different gas species are almost ten times of those in Figs. 2 and 3. The breakthrough time of the gas phase and the time intervals between the breakthroughs of different gas species are also approximately tenfold of those in Case 2. The results of the longer model confirm that the migration distances of the gas phase and separations between different gas species increase roughly linearly with time.

Fig. 17. Position of the gas front and two phase compositions for 88% CO_2 + 2% H_2S + 10% N_2. (a) and (b) are at 5 days while (c) and (d) are at 10 days.

Fig. 18. Time evolution of the effluent gas compositions at the outlet of the 243.84 m-model for 88% CO_2 + 2% H_2S + 10% N_2.

4. Discussions

After injected in geological formations for storage, CO_2 and the co-injected impurities are likely to partition at the leading gas displacement front that advances through the aqueous phase. More soluble gas species would dissolve preferentially in the formation brine and be stripped off at the leading gas front. As for the three common impurities chosen in the present study, H_2S is more soluble than CO_2, while the solubility of N_2 and CH_4 is comparable and lower than that of CO_2. The leading gas front is made up of less soluble N_2, CH_4 or the mixture of N_2 and CH_4. It implies that when the injected CO_2 streams contain N_2 and/or CH_4, N_2 and/or CH_4 would break through ahead of CO_2.

The dominant factor in the mobility ratio correlation is the viscosity ratio between the aqueous and the gas phase. Since the viscosity of both N_2 and CH_4 is smaller than that of CO_2, the inclusion of N_2 and/or CH_4 leads to lower gas phase viscosity and thus higher mobility ratio (for example, Fig. 4b), resulting in more unstable displacements of the aqueous phase by the gas phase and longer two-phase regions. Since the dissolution of gas species takes place in a longer two-phase region, gas species with higher solubility such as H_2S compared to N_2 and/or CH_4 are stripped off more effectively at the leading edge of the gas displacement front, leading to larger separations between the more soluble components and the less soluble components. Accordingly, the time lags between the breakthroughs of different species are larger (e.g. Case 2 or 3 vs Case 1). The CO_2 plumes containing N_2 and/or CH_4 also flow faster and reach the outlet earlier, i.e., the breakthrough time is earlier than that for those do not contain N_2 and/or CH_4 (e.g. Fig. 5). On the contrary, the viscosity of H_2S is larger than that of CO_2. As a result, the inclusion of H_2S impurity leads to lower mobility ratio and lower gas phase velocity. For the injected gas mixtures containing the same total impurity concentration (12%), the combinations of N_2 and CH_4 impurities without H_2S lead to the fastest flowing and thus the earliest breakthrough of the gas phase. With decreasing N_2 or CH_4 concentrations, however, both the mobility ratio and the gas phase velocity are lower, leading to weaker partitioning processes (Cases 8 and 9).

The simulation results of the CO_2 streams containing the same total concentrations of N_2, CH_4 or even N_2 and CH_4 mixture are similar to each other, including the migration distances of the gas phase, the separations of the migration distances between different gas species, the breakthrough times of the gas phase, and the time intervals between the breakthrough times of different gas species (Cases 2, 3, 6 and 7). Different compositions of the N_2 and CH_4 mixture (for instance, Case 4: 6% N_2 + 6% CH_4 vs Case 5: 8% N_2 + 4% CH_4) are not likely to change the main features of the partitioning process. It seems that the effects of the N_2 and CH_4 mixture on the partitioning phenomenon can be represented by that of pure N_2 or pure CH_4 at the same concentrations. However, it should be noted that since N_2 is less soluble than CH_4 in the formation brine, N_2 concentration is higher than CH_4 concentration in the effluent gas phase, even when their concentrations are the same in the feed gas (Cases 4 and 6).

The results of the present study may be applied to the monitoring of CO_2 movement in the subsurface and near-surface leakage. In this sense, the co-injected impurities serve as tracers. Actually, tracer methods have already been used to monitor the migration and distribution of the injected CO_2 plume and track potential CO_2 leakage. For example, noble gases such as He, Ne and Ar, e.g. [49-51] and perfluorocarbon tracers [52-54] have been used as to identify CO_2 migration or to monitor leakage. The tracers were normally in very small amounts and were injected or added intentionally for short-periods monitoring while sufficient amount of these artificial tracers for large-scale projects might be cost-prohibitive [54]. Stable carbon isotopes have been regarded as suitable tracers to assess CO_2 migration and detect potential leakage, especially at large injection sites, e.g. [55-57]. However, this method requires the injected CO_2 to be isotopically distinct from background sources of CO_2 to be effective [57]. The work presented here addresses the issue of co-injected impurities. The results indicate that if leakage occurs after CO_2 streams containing N_2 and/or CH_4 are injected, N_2 and/or CH_4 would show up in the surface prior CO_2 leakage. The detection of these species can be served as a warning of CO_2 leakage that would occur after a certain time. Furthermore, it can be expected that if

leakage occurs after longer migration of the CO_2 plume in long-term storage, there will be larger time intervals between the breakthroughs of different gas species. Some saline aquifers may have pre-existing CH_4, which would have an adverse effect on its use of tracers. Since N_2 is absent in most reservoirs and less soluble than CH_4, it seems that N_2 is a better choice as a than CH_4.

5. Conclusions and future work

To realize large-scale implementation of CO_2 geological storage, it is necessary to determine the types and concentrations of impurities allowed in the CO_2 stream from both economic and regulatory perspectives. A series of numerical simulations are carried out to investigate the partitioning phenomena of CO_2 with two or three kinds of most common impurities, H_2S, N_2 and CH_4. Generally, the results of CO_2 streams containing N_2, CH_4 as well as the mixture of N_2 and CH_4 at the same concentrations are similar to each other. The gas phase flows faster and the breakthrough time of the gas phase is earlier when N_2 and/or CH_4 impurities are co-injected with CO_2, especially when the concentrations of these impurities are higher. On the contrary, the inclusion of the H_2S impurity is likely to lead to slower migration of the gas phase and delayed breakthrough time of the gas phase.

Although the model size used in the present study is small, test on a larger size model implies that the broad behaviours identified from the small size simulations are valid and may be used to predict the long-distance migration and partitioning phenomenon of the gas plume in long-term storage. The investigations of the partitioning phenomenon are helpful for understanding the migration process of the CO_2 plume with multiple impurities. The simulation results obtained in this study may provide references for devising monitoring procedures of possible leakage and developing emergency strategies. For instance, the concentrations of N_2 and/or CH_4 should be monitored in addition to the monitoring of CO_2 concentrations. The detection of sharply increasing levels of N_2, CH_4 or the mixture of N_2 and CH_4 can be seen as a warning of CO_2 leakage.

In this study, molecular diffusion has been neglected while it may play a part in the 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 dimensionality 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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