GHGT-10

Effects of Impurities on CO$_2$ Transport, Injection and Storage

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Abstract

Effects of impurities in CO$_2$ streams on geological storage of CO$_2$ have been investigated. A number of key issues have been addressed, and several significant findings have been made. Highlighted among the findings are: (1) non-condensable impurites such as N$_2$, O$_2$ and Ar greatly reduce CO$_2$ storage capacity of geological formations, and there is a maximum reduction of the storage capacity at a certain pressure under a given temperature. By contrast, impurities which are more condensable than CO$_2$, such as SO$_2$, can increase the storage capacity, and there is a maximum increase at a certain pressure under a given temperature; (2) change of density caused by non-condensable gas impurities results in lower injectivity of impure CO$_2$ into geological formations. However, above a threshold pressure range the injectivity could reach the level of pure CO$_2$ due to lowered viscosity; (3) non-condensable impurities increase the buoyancy of the CO$_2$ plume. This would negatively affect the efficiency of solubility trapping and residual trapping of CO$_2$. (4) the effect of SO$_2$ on reduction of rock porosity and hence CO$_2$ injectivity would be much smaller than previously thought. A simple formula has been developed to enable quick determination of the effect.

Keywords: CO$_2$, impurities, storage capacity, injectivity

Effects of Impurities on Phase Behaviour of CO$_2$

CO$_2$ capture and storage (CCS) has been identified as a key potential technology in mitigating CO$_2$ emissions. The capture process represents the major cost component of CCS. CO$_2$ may be captured by different technologies, and various gaseous impurities exist in the CO$_2$ stream, such as N$_2$, O$_2$, SO$_2$ and H$_2$S. Separation of the impurities would drastically increase the cost of capture and it would be more cost effective to co-inject the impurities with CO$_2$ for underground storage. Moreover, some technologies aim at co-capture and co-storage of multiple air pollutants together with CO$_2$.

Unfortunately, impurities in the CO$_2$ stream can have negative effects on transport, injection and storage of CO$_2$. For instance, non-condensable impurities such as N$_2$, O$_2$ and Ar would increase the saturation pressure of liquid CO$_2$ and decrease the critical temperature. As a result, lower temperature and additional overpressure is required to avoid two-phase flow in CO$_2$ pipeline transport. Non-condensable impurities would also increase the pressure for injection

and reduce the capacity of the storage sites by decreasing the density of the CO_2 stream. Moreover, acid impurities like SO_x and NO_x can react with formation and cap rocks and affect the injectivity and storage integrity. In addition, the fate of hazardous impurities is of special concern in the event of CO_2 leakage, as they may be released to the environment.

Natural Resources Canada (NRCan) has been leading Canada's federal CCS programs. Along with a range of R&D projects for capturing CO_2 from coal-fired power plants and other sources, NRCan is also involved in and collaborating in research endeavours for CO_2 storage, including CO_2 injection, monitoring, measurement and verification, storage integrity assessment, and capacity estimation. The effects of impurities on transport, injection and storage of captured CO_2 are of vital importance to successful implementation of the CCS research strategies. In this context NRCan has undertaken a study supported by IEA GHG on the effects of the impurities, focusing on storage of CO_2 in saline formations – a promising target for underground CO_2 storage. As the literature on a number of critical impurity effects is scarce, such as the effects on storage capacity, storage integrity and injectivity, we have carried out extensive evaluations of our own. Part of the findings are presented here.

Effects of Impurities on Phase Behaviour of CO_2

Figure 1 shows phase envelopes calculated using the Peng-Robinson equation of state for the following cases:

1) CO_2 stream from oxyfuel combustion in a fluidized bed pilot plant combustor in CanmetENERGY, containing 5.2 vol % O_2, 221 ppm CO, 1431 ppm SO_2 and 243 ppm NO [1];
2) CO_2 stream from a zero-emissions process proposed by CanmetENERGY, containing 1.05% CO, 1.7% SO_2, 0.32% H_2 and 690 ppm H_2S [2];
3) CO_2 stream from Cansolv® absorption system containing 2.9% SO_2, studied in a previous IEA GHG report [3];
4) Expected CO_2 stream from a pre-combustion removal plant, whose composition information is provided by IEA GHG, including 1 vol % H_2, 0.9 vol % N_2, 300 ppm Ar, 100 ppm H_2S + COS and other impurities in ppm level;
5) Expected CO_2 stream from an oxyfuel combustion plant, whose composition information is also provided by IEA GHG, including 5.8 vol % N_2, 4.7 vol % O_2, 4.47 vol% Ar, 100 ppm NO_x, 50 ppm SO_2, 20 ppm SO_2 and 50 ppm CO.
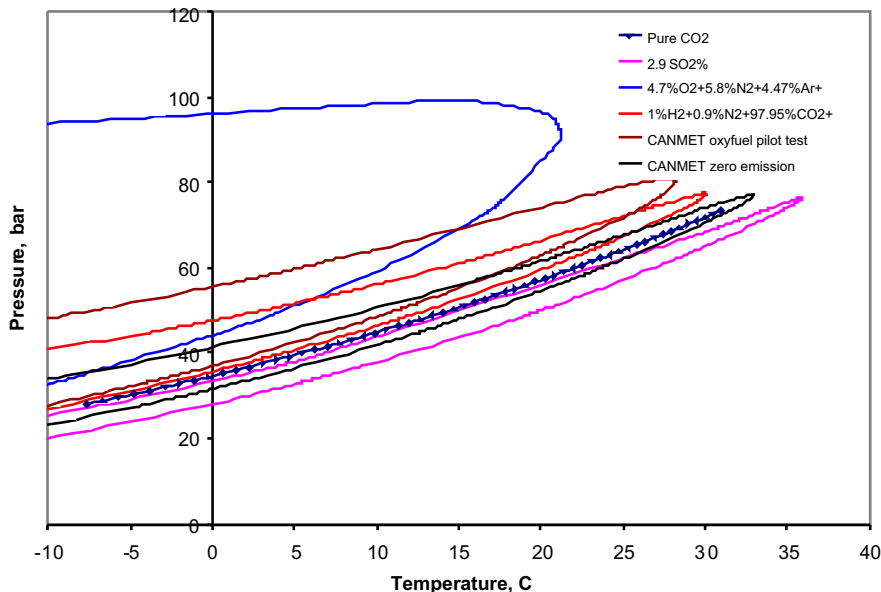

Figure 1 Calculated phase evelopess for CO_2 and CO_2 mixtures.

From the results it can be seen that the critical temperature and pressure of the mixtures are quite different from that of pure CO_2. N_2, O_2, Ar and H_2 show the greatest effect of increasing the saturation pressure of the liquid and decreasing the critical temperature. One extreme case is the mixture from oxyfuel combustion containing 5.8% N_2, 4.7% O_2, 4.47% Ar and other impurities at ppm level. The critical temperature decreases by about 10°C in comparison with that of pure CO_2, and the liquefaction pressure increases by over 50 bar. On the other hand, SO_2 results in a decrease in the saturation pressure and an increase of the critical temperature, as is expected from the high critical temperature of pure SO_2 (157.6°C). It can also be seen that low-concentration impurities, such as CO and NO_x would not significantly affect the phase behaviour of CO_2.

Effects of Impurities on Storage Capacity

Impurities will affect the volumetric properties of injected CO_2. Figure 2 shows calculated density of supercritical CO_2 with non-condensable impurities for a number of cases at 330 K, which is in the typical temperature range for CO_2 storage evaluations in western Canada. It can be seen that non-condensable impurities such as O_2, Ar, N_2 and H_2 significantly reduce the density of the supercritical CO_2 stream. The reduced density is largely related to increased volume, except for H_2, where the effect of smaller molecular weight is also significant. All these impurity components in CO_2 would cause a volume increase greater than their molar or volume fractions at standard temperature and pressure (STP) For example, 5% vol (STP) N_2 will result in a volume increase greater than 5 percent in the temperature range not high above the critical temperature of CO_2. This can be understood from the fact that non-condensable impurities are less dense than CO_2 and hence take greater volumes. If they have the same molar volume as CO_2 there would be no volume increase, provided the interactions between unlike molecules are negligible.
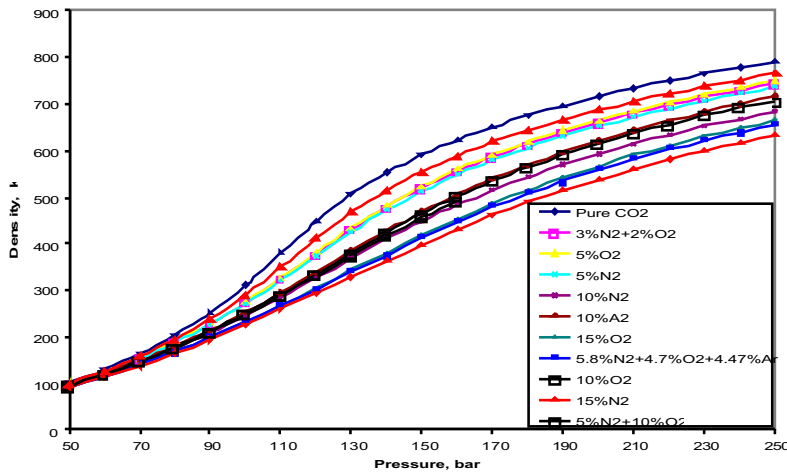

Figure 2   Calculated density for CO_2 and CO_2 mixtures as a function of pressure at 330 K.

The decrease of CO_2 storage capacity due to the contained impurities is thus not only caused by the lower volume fraction of CO_2, but also by the additional volume of less dense impurities. To produce a simple relation regarding the effect of the impurities on the storage capacity for CO_2 for given storage volume, we propose the following expression for the storage capacity (expressed in mass) as a function of density of the CO_2 stream:

$$\frac{M}{M_0} = \frac{\bar{\rho}}{\rho_0 \left(1 + \sum_i m_i / m_{CO2}\right)} \tag{1}$$

where M and M_0 denote the mass of CO_2 in the mixture and in the pure stream, respectively, which occupy the same volume. $\bar{\rho}$ and ρ_0 are the density of the mixture and the pure stream, and m_i/m_{CO_2} is the ratio of the mass of impurity i to the mass of CO_2 in the mixture. The ratio M/M_0 on the left hand side of this relation, which can also be viewed as the ratio of the mass of CO_2 per unit volume in the mixture to that in the pure state, represents a normalized storage capacity for CO_2 in its supercritical phase, *i.e.*, the capacity for structural trapping of CO_2. In the case of pure CO_2 (zero impurity effect) the ratio equals unity. The right hand side is a function of temperature, pressure and mixture composition and can be calculated from equations of state. Accordingly, the normalized storage capacity can be determined for given temperature and pressure conditions. Calculated results for a number of mixtures are shown in Figure 3.

The existence of the minimum has been verified through both theoretical analysis and experimental data (details will be shown in a new IEA GHG report).

For impurities which have higher critical temperature than that of CO_2, no storage capacity minimum would occur in the corresponding CO_2 mixture. Rather, a maximum can appear based on an analysis similar to that for the non-condensable impurities. This has been verified with calculated results for the CO_2 mixture with 2.9 vol % SO_2 (the Cansolv® absorption system case presented in the previous IEA GHG report [3]). The result shows a maximum at about 110 bar, where the storage capacity is increased by over 5% (figure not shown). It is interesting to see that in the maximum region, SO_2 can create space for CO_2. This can be rationalized from the consideration that SO_2 decreases average distance between the molecules of the mixture – an opposite effect of that of the non-condensable gases.
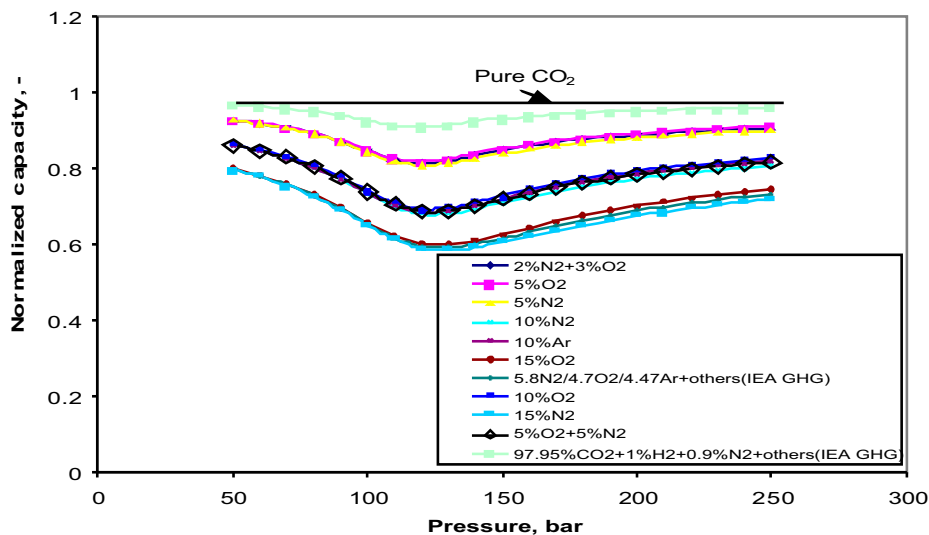

Figure 3 Normalized CO_2 storage capacity at 330 K in terms of Equation 1.

Impact of the Minimum CO_2 Storage Capacity

The minimum caused by non-condensable impurities is of particular concern, because these impurities are typical for CO_2 streams from oxyfuel combustion. Besides, the pressure for this minimum falls in the pressure range for CO_2 storage. Calculated pressure dependence of the normalized CO_2 storage capacity for several temperatures show that with temperature increasing, the minimum shifts to higher pressure and the magnitude of the minimum decreases (Figure 4). In subsurface formations, the pressure and temperature are interrelated as both of them increase with the depth from the surface. At certain depths, the minimums which correspond to the largest decreases of storage capacities may occur due to pressure and temperature conditions. By assuming a hydrostatic pressure gradient of 10 MPa/km, and geothermal gradients from 20 to 33 °C/km for the subsurface and a ground temperature of 15°C, the impact of the minimum on the CO_2 storage capacity for the high-impurity stream are illustrated in Table 1. As can be understood, the storage capacity can decrease to as low as 54.3% at 320 K (47°C) and 56.4% at

330 K (57°C) in the case of 33°C/km geothermal gradient. At higher temperature, 350 K (77°C), the decrease in the storage capacity is smaller and at still higher temperatures the decrease would be smaller still.

As structural trapping is deemed the most important trapping mechanism for CO_2 storage at least in the injection phase of a CCS operation, the pressure effect should be taken into account in estimation of capacity for underground formations. Moreover, in storage operations, the minimum would cause reduced storage efficiency. At a given depth, increasing the storage pressure well beyond the level for the minimum would increase storage efficiency. This may be attained for closed formations within the allowable overpressure range. For open formations where overpressure may not be attainable, one possibility to increase the storage efficiency is to increase the depth of injection and storage. With increasing depth the temperature and pressure will increase so that the capacity decrease can be alleviated.

The above discussion should also be applicable to residual trapping of CO_2, where CO_2 is trapped in rock pores as an immobile phase. Here the changes of interfacial tensions of the CO_2/water/pore wall system due to the impurities are neglected. The decrease of the trapping capacity due to the impurities can be greater than their molar fractions or STP volume fractions. Moreover, at lower temperatures a minimum may occur at a certain pressure, causing a greater drop in the storage capacity. Furthermore, injection at deeper levels can increase the storage efficiency of impure CO_2 streams.
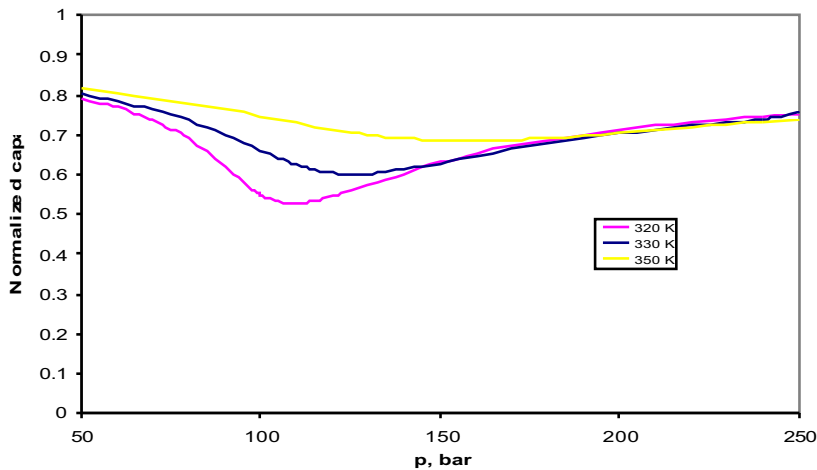

Figure 4   Normalized CO_2 storage capacity for the high-impurity oxyfuel combustion stream (5.8 vol % N_2, 4.7 vol % O_2, 4.47 vol % Ar and other impurities at ppm level) at different temperatures.

Table 1 Normalized CO_2 storage capacity for the high impurity CO_2 stream at several subsurface temperatures

T gradient	20°C/km		25°C/km		33°C/km	
T (K)	p (bar)	Capacity (-)	p (bar)	Capacity (-)	p (bar)	Capacity (-)
320	160	0.653	130	0.574	100	0.543
330	210	0.723	170	0.672	130	0.564
350	310	0.755	250	0.734	190	0.698

Permeation Flux

The presence of impurities would also affect CO_2 injection. Here we discuss their physical effects (no chemical reactions involved) first. For the single phase flow of injected CO_2, the effects may be analyzed in terms of an expression based on Darcy's Law, for the permeation flux of injected CO_2:

$$\dot{M} = \frac{-\rho k}{\mu} \nabla p \tag{2}$$

where $\dot{M}$ is the mass flow per unit area, ρ is the density of injected stream, k is rock permeability, ∇ is the gradient operator, p is the pressure, and μ is the viscosity of the fluid. As the impurities lower the density of the CO_2 stream, the mass flux will decrease for the same pressure drop. However, the impurities also affect the viscosity of the injected fluid. When the viscosity of the impure CO_2 stream is lower than the viscosity of pure CO_2, the CO_2 flux increases, hence the decrease in density may be compensated by a corresponding decrease in viscosity. The density and viscosity are functions of temperature and pressure. The permeability and pressure gradient vary case by case. However, for an estimation of the impurity effects under the same permeability and pressure drop conditions, one may use the following relation which is a consequence of Equation 2.15

$$\frac{\dot{M}_{CO2}}{\dot{M}_0} = \frac{\rho(\mu_0/\mu)}{\rho_0(1 + \sum_i m_i/m_0)} \tag{3}$$

This expression represents a normalized permeation flux, and should be able to provide a measure of the relative injectivity of the impure CO_2 stream. As non-condensable impurities reduce the density of the CO_2 stream, and thus reduce the permeation flux. However, the impurities would also reduce the viscosity of the stream, and thus compensate the effect of reduced density. Calculated result for the high impurity CO_2 stream (with about 15% $N_2/O_2/Ar$ and other minor-quantity impurities) shows that the permeation flux is lower than that of pure CO_2 by more than 15 percent at lower pressures, but reaches the same level as pure CO_2 above a transition pressure (Figure not shown).

Buoyancy and Rising Velocity

The light-impurity species will result in greater buoyancy for the CO_2 plume, due to the lower density. When a mass of the plume in a unit volume is in contact with the formation water, the buoyant force can be expressed as

$$F = (\rho_{H2O} - \rho_m)g \tag{4}$$

where ρ_{H2O} and ρ_m are the density of the water and the plume, respectively. The effect of impurities on this force with reference to pure CO_2 may be given as

$$\frac{F}{F_0} = \frac{\rho_{H2O} - \rho_m}{\rho_{H2O} - \rho_{CO2}} \tag{5}$$

where F and F_0 are the buoyancy force for the CO_2 mixture and pure CO_2, respectively. The greater the difference between the densities of the mixture and CO_2, the greater the change in the buoyancy would be. Calculated result shows that with about 15 vol% non-condensable impurities (the high-impurity stream from oxyfuel combustion) the buoyancy of the CO_2 plume can increase by over 50%. This would significantly increase the rising velocity of the plume. The velocity of the impure CO_2 stream (v) can be related to that of the pure CO_2 stream (v_0) by

$$\frac{v}{v_0} = \frac{F/(\rho\mu)}{F_0/(\rho_0\mu_0)} \tag{6}$$

According to calculations, the velocity of the high-impurity plume can reach nearly three times that of the pure CO_2 plume. The high rising velocity would reduce the time for CO_2 contact with water and formation of dissolved species. It would also reduce the formation of a residual phase, because it reduces the lateral spreading of the plume, leaving a smaller area for trapping CO_2 in the pores of rocks. When the plume reaches the caprock it will spread laterally, but the contact with water is only at the interface. Besides, near the caprock the pressure is lower than in the deeper region, and hence the efficiency of CO_2 dissolution and trapping in the pores as a residual phase would be lower. As a result, the potential for leakage increases if pathways are available.

Impact of Reactive Impurities on Injectivity of CO_2

The most common reactive impurities are H_2S, SO_2, NO_x and CO. CO is highly reductive and will be oxidized to CO_2 by oxygen or mineral oxides. There have been several studies on co-injection of H_2S and/or SO_2 with CO_2 [4-8]. The general view is that H_2S is not an issue, and it has been co-injected with CO_2 for 20 years in Canada in acid gas disposal. However, SO_2 is believed to alter the geochemistry, causing increased dissolution and precipitation. SO_2 can greatly lower the pH of the formation water and hence enhance the dissolution of rock minerals. When the species become oversaturated precipitation of sulphates would occur. Reduction of pore volume and hence the injectivity of CO_2 is a concern. The effect of the impurities is difficult to quantify. Numerical simulation studies performed so far have either assumed that SO_2 is injected as an aqueous solution or the injection zone is never dry. This situation would be different from the injection operations where SO_2 migrates with CO_2 in an immiscible plume which results in a desiccation or dry-out zone [9-11]. The important point is that SO_2 is far less reactive when it is dry. Further, continuous dissolution of minerals as in the "wet cases" would not occur in the dry-out zone. The contact of SO_2 with water only occurs on the front of the plume and the two-phase flow zone, and the time would be limited. Therefore, build-up and precipitation of minerals in the downstream which were dissolved in the upstream and carried by water flow would be much less, compared with the "wet cases". In the following we give an analysis for the impact of SO_2 on the injectivity of CO_2.

SO_2 will be highly reactive if it is dissolved and oxidized to form sulphuric acid. In CO_2 streams from oxyfuel combustion and post-combustion capture plants O_2 and NO_x will also be present. NO_x is known to catalyze SO_2 oxidation and hence formation of sulphuric acid according to the lead chamber process. The rate of the oxidation depends on various factors such as concentrations of reactants and products, pressure and temperature. However, the maximum effect of NO_x is to oxidize all SO_2. Therefore, we assume that all SO_2 can be converted to sulphuric acid and the concentration of SO_4^{2-} ions is equal to that of dissolved SO_2, when NO_x and O_2 are present in sufficient amounts.

Clearly, the rate of sulphate precipitation will not exceed the rate of SO_2 supply. As a limiting case, we consider that all SO_2 passing the reaction zone, *i.e.*, from the front of the two-phase zone to the front of the dry-out zone, is converted to sulphate precipitate. Taking the dissolution of calcite and precipitation of anhydrite as an example, 2.9 vol % SO_2 (the stream considered in the previous IEA GHG report PH4/32 [3]) at 330 K under 200 bar would result in a pore volume decrease 0.44%. This is much less significant compared with the "wet cases".

Other Effects of Impurities

Other effects of impurities, such as the effects on cap rock integrity, corrosion of injection well materials, and cost of CO_2 storage, have also been evaluated. The fate of hazardous impurities, such as SO_x, NO_x, CO and Hg, has also been assessed. The results will be included in the new IEA GHG report.

Conclusions

Impurities have important impacts on CO_2 storage capacity, storage integrity, injectivity, etc. However, previously existing knowledge could not provide solutions to the problems that will be inevitably encountered. The results obtained from the present work are expected to have significant applications or implications to all CO_2 storage operations.

Acknowledgement

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