

GHGT-10

Geochemical effects of impurities in CO₂ on a sandstone reservoir

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Elsevier use only: Received date here; revised date here; accepted date here

Abstract

In most cases, CO₂ captured from power plants or large industrial sources contains impurities. As purification of the stream is energy and cost intensive it is necessary to allow a certain level of impurities. The effects of impurities on (short- and long-term) geological storage are, however, uncertain. In this work, geochemical modelling with *PHREEQC* is performed to describe such effects on a sandstone reservoir (depleted gas field). The impact of two possible CO₂ streams, originating from pre-combustion and oxyfuel capture technology is investigated. The streams contain O₂, H₂, CO, H₂S, SO₂, and/or NO as potential chemically reactive components. H₂S, SO₂ and NO are computed to oxidize, thereby forming sulfuric or nitric acid, and decrease the pH of the formation water. A low pH of the brine may be the result of extensive dissolution and dissociation, and therefore accumulation in the brine phase, especially close to the injection well. The impact of impurities on fast reacting minerals (short-term effects) is predicted to be relatively insignificant, due to the low amount of brine generally present in a gas field. On the long-term (equilibrium stage), impurities cause a slightly different mineralogy compared to pure CO₂ injection. For the latter case a final increase in porosity of 3.5% is predicted whilst impurities (especially oxygen) could mitigate the porosity increase to zero due to the precipitation of minerals with higher molar volumes, like alunite and nontronite. Overall, the impurities do not seem to have a significant impact on the reservoir, even if accumulation in the brine takes place. The possible limiting effect of diffusion of impurities within the supercritical CO₂ towards the brine has not been taken into account, even though the effect could be relevant. It could delay the effect of the impurities due to retarded dissolution. Further research should focus on this issue. Also the spatial effects and effects on different reservoir types, cap rock and well cement need to be investigated.

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Keywords: CO₂ storage; impurities; geochemical modelling; sandstone reservoir, mineral assemblage

1. Introduction

The costs of separation and compression of CO₂ from point sources, such as power plants, cover the largest part of the total costs of CCS [1-2]. Unfortunately, CO₂ captured from a point source is almost never a pure stream. Depending on the type of capture technology (pre-combustion, oxy-fuel, or post-combustion) the captured CO₂ stream contains a certain amount of impurities. It requires additional money and energy to increase the purity of the stream and decrease the number or level of impurities. Permitting a less pure CO₂ stream for injection would lower the costs on the capture side. Requirements on the purity of the CO₂

stream for transport by pipeline have received some attention (e.g. [3]). The effects of impurities on (long term) storage are still unclear.

In this paper, a preliminary assessment of the effects of impurities in the CO₂ stream on storage is presented, based on geochemical modelling and comparison of the results to existing literature. The work focuses on the interaction between the supercritical (sc) CO₂ stream with impurities, the formation water and the host rock.

2. Materials and methods

Two possible CO₂ streams from pre-combustion and oxyfuel (semi-purified) capture technology are chosen to investigate the effects of impurities on storage (Table 1). In the pre-combustion stream some hydrocarbons are present which are assumed to be chemically inert. N₂ and Ar are also assumed to be chemically inert.

Table 1 CO₂ streams with impurities from a pre-combustion and an oxyfuel capture technology.

	pre-combustion (mole %)	Semi-purified oxyfuel (mole %)
CO ₂	99.64	98.0
N ₂	0.077	0.7
O ₂	0.0045	0.7
H ₂	0.14	-
CO	0.03	0.005
H ₂ S	0.00014	-
SO ₂	-	0.007
NO	-	0.01
Ar	-	0.6

Three different scenarios are investigated. The first is a base case scenario, for which the impact of pure CO₂ injection is computed. The second and third scenarios are based on the pre-combustion and oxyfuel streams, respectively.

The mineralogical composition from a potential Dutch CO₂ storage field (depleted gas field) is used [4] and listed in Table 2. The reservoir has a porosity of 20% and a water saturation of 15%. The final pressure after CO₂ injection is set at 175 bar. Taking into account the partial pressure of the remaining gas in place (31bar), partial pressures were calculated for the different gas phases, proportional to their mole fractions. The temperature is 72°C and the brine mass fraction is 0.07. Geochemical modelling is carried out with *PHREEQC* (version 2) and the LLNL-database. *PHREEQC* computes the chemical equilibria of aqueous solutions interacting with minerals and gases [5]. Batch-reaction calculations have been performed, allowing the simulation of the conditions at a specific location within the reservoir. Kinetics are taken into account on a qualitative base; calcite dissolution and precipitation of minerals with rates higher than 0.1 mol m⁻² s⁻¹ are considered in order to investigate short-term effects (in the order of years). Minerals with lower precipitation/dissolution rates are only taken into account in the long-term equilibrium calculations. In the modelling assessment, partial pressures of the different gases are kept constant. A surplus amount of CO₂ is used to maintain a constant partial pressure. For impurities such an approach can result in

unrealistically high concentrations due to the high solubility of several impurities in the brine. The kinetics of impurity dissolution and the dependence on diffusion within the scCO₂ are, however, still unclear [6]. If diffusion of impurities in scCO₂ to and subsequent dissolution in the brine is slow relative to the injection rate, a minimum concentration of the impurities in brine can be calculated based on the assumption of equal distribution of the CO₂ and impurities over the storage reservoir. Accumulation of impurities in the brine would take place near the well in case the impurities quickly diffuse towards and dissolve in the brine during the injection period. For both the pre-combustion stream and the oxyfuel stream a ‘complete distribution’ and an ‘accumulation’ scenario (ten times the minimum concentration, calculated for the ‘complete distribution’ scenario) has been modelled.

Table 2 Wt% of the rock minerals and corresponding number of moles which are in accordance with a porosity of 20% and water saturation of 15%.

	Reservoir composition (wt%)	Reservoir composition (moles)
Quartz	83.0	144.4
Muscovite	1.0	0.3
Glauconite	1.0	0.2
Kaolinite	4.0	1.6
K-Feldspar	2.0	0.3
Calcite	0.5	0.5
Halite	0.2	0.4
Pyrite	0.2	0.2
Illite	8.1	2.2
Dawsonite		0.1727
Dolomite-ord		0.0089

2.1. Model workflow

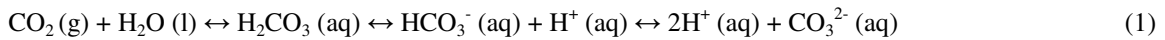
The following workflow is applied for each scenario using *PHREEQC*:

- 1) Computation of the formation water composition in equilibrium with the reservoir mineralogy;
- 2) Equilibration of computed formation water with the injected gases to investigate pH effects on the brine;
- 3) The computed formation water (step 1) is equilibrated with the gases and the minerals in the reservoir which are known to dissolve (calcite in this reservoir) and precipitate (e.g. anhydrite) quickly, to study short-term porosity effects;
- 4) The computed formation water (step 1) is equilibrated with the gases and the full mineral assemblage of the reservoir (final formation water).

3. Results

3.1. Base case scenario; pure CO₂

Initially, injected CO₂ will partially dissolve in the formation water. As a result, the pH of the calculated formation water (step 2) decreases from 6.1 (after step 1) to 4.6 due to formation of carbonic acid and further dissociation by the following equations:



The pH decrease results in an insignificant amount of calcite dissolution on the short-term while mineral precipitation does not occur. The main long-term changes in mineralogy are disappearance of illite, kaolinite, calcite and K-feldspar and the formation of muscovite, diaspore, and the carbon containing minerals dolomite and siderite (Figure 1). The final pH of the pore water is 4.5. The porosity increases slightly by 0.7 percentage point (pp) to 20.7%.

3.2. Scenario 2; pre-combustion CO₂ stream

The modelling results show that the reactions between the impurities and the ions in the formation water are highly dependent on the presence and availability of O₂. The following two sub-scenarios have been investigated:

- 2-1) Equal distribution of impurities (minimum concentration)
- 2-2) Accumulation of impurities and surplus O₂

In the presence of O₂, CO and H₂ react to CO₂ and water respectively which are already present in the reservoir in large amounts. Remaining O₂ is used in the model for the conversion of H₂S to SO₄²⁻, thereby decreasing the pH:



Without residual O₂, H₂S remains in the gaseous phase. The pH is 4.6 in scenario 2-1 (low H₂S concentration and lack of sufficient O₂) and 4.5 in scenario 2-2.

Like in the base case scenario calcite partially dissolves on the short-term without any mineral precipitation but the effect on porosity is again insignificant in each sub-scenario.

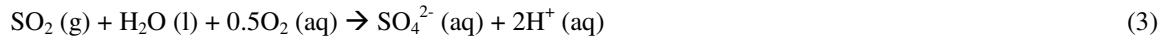
The final mineral assemblages of the three sub-scenarios as computed by the model are very similar to the base case scenario (Figure 1). Only the assemblage of scenario 2-3 is slightly different. Siderite has not formed, pyrite is converted to alunite and a significant amount of nontronite (1.6 wt%) has formed at the expense of siderite, muscovite, diaspore and magnesite, caused by the surplus amount of oxygen present. The porosity increase is negligible due to the relatively high molar volume of alunite, while the increase is 0.6 pp in the other sub-scenario. The final pH of the formation water is 4.5 in each case.

3.3. Scenario 3; semi-purified oxyfuel stream

The following sub-scenarios have been investigated:

- 3-1) Equal distribution of impurities (minimum concentration)
- 3-2) Accumulation of impurities (ten times the minimum concentration)

Like for scenario 2, H₂ and CO will form additional water and CO₂. SO₂ is computed to completely dissolve and dissociate into SO₄²⁻, thereby lowering the pH:



NO is computed to react to NO₃⁻, according to the following reaction:



The more SO₂ and NO present in the system, the lower the pH becomes. This results in a pH of 1.8 in sub-scenario 3-2, compared to 4.5 in 3-1. The very low pH in 3-2 results in slightly higher calcite dissolution on the short-term, but porosity increase is still negligible. In both scenarios the pH of the formation water will increase due to the short-term calcite dissolution to a value of approximately 4.8.

Like for the pre-combustion scenarios, the final computed mineral assemblage is very similar to the assemblage of the base case scenario. In scenario 3-2, however, slightly more alunite has precipitated (0.5 wt%) than in 3-1, mainly at the expense of muscovite. Porosity increase is 0.6 pp and 0.4 pp in sub-scenarios 3-1 and 3-2 respectively, and the final pH of the formation water is 4.5 in both sub-scenarios.

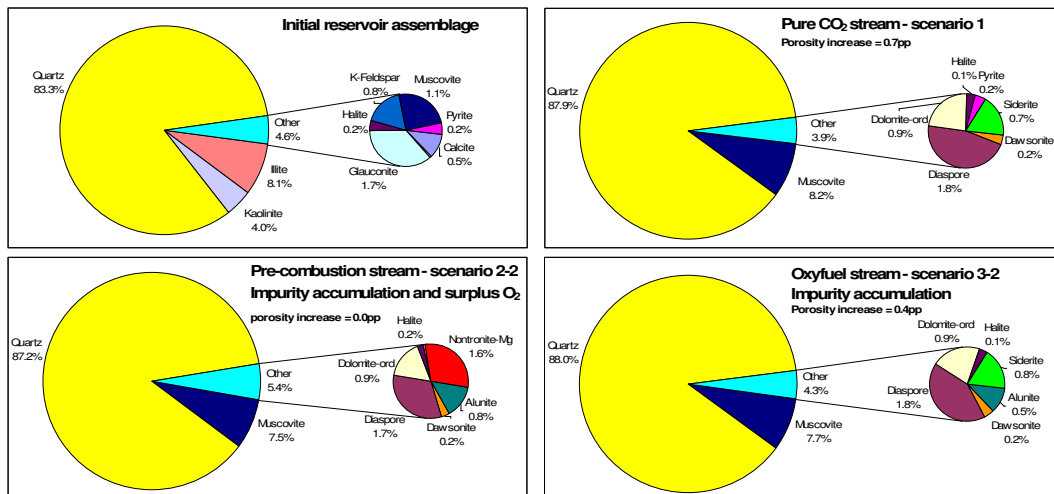


Figure 1 Initial reservoir assemblage and final reservoir assemblages (wt%) of the baseline scenario (scenario 1) and scenarios 2-2 and 3-2.

4. Discussion

The results show that, besides CO₂, impurities can decrease the pH of the brine by the formation of sulfuric and nitric acid, which are both stronger acids than carbonic acid. In a gas field, injected gas is not in contact with a saturated brine phase like in an aquifer, but with connate water, present as thin films surrounding mineral grains. Due to the low amount of brine in contact with the minerals (water saturation of 15% for the reservoir used in this study), the effect on calcite dissolution is small, even if pH reaches values as low as 1.8 (scenario 3-2). The pH is buffered by a low amount of calcite dissolution into the brine.

Most research on the effects of impurities focuses on H_2S and SO_2 present in the CO_2 [6-8], injected into aquifers. Oxidation of SO_2 is predicted, even without much O_2 present, with pyrite and water providing the oxidizing conditions [7] and pH decreasing to values close to 1. This observation is in agreement with our results. Complete dissolution of calcite and short-term anhydrite (CaSO_4) precipitation near the injection zone predicted by [7-8] was not observed in our work. This is probably due to the simulation of a brine saturated area in their work, compared to a low amount of brine present in the reservoir in our calculations. Long-term sulfur immobilization through alunite precipitation was also shown [6-7] and our study additionally predicts that this depends on the availability of oxygen. Sufficient oxygen availability is also important for conversion of H_2S to sulfuric acid. Without oxygen available (in the oxygen deficient scenario), this conversion is not observed, which is in agreement with other studies [7-8].

Since SO_2 , H_2S and NO can extensively partition in the brine phase, thereby significantly decreasing pH, accumulation of these impurities near the injection well could severely acidify the brine. Recent work on co-injection of SO_2 into an aquifer [6] shows that dissolution of SO_2 in (stagnant) brine is probably limited by slow diffusion of SO_2 in the scCO_2 . Diffusion limitation could be relevant in the water saturated area ($S_w = 1$) of an aquifer, where also diffusion of aqueous SO_2 and its dissociation products plays a role [6]. In the area of the CO_2 plume where connate water is still present, which can be compared to a depleted gas field filled with CO_2 , diffusion limited dissolution and dissociation of SO_2 (and other impurities) might be less relevant due to the lower scale at which the diffusion occurs. Spatial and quantitative kinetic effects have not been taken into account in our work and would retardate the impact on pH and other geochemical reactions. The significance of this the retardation on the pH of connate water requires further research.

5. Conclusions

Geochemical modelling of CO_2 and impurities injection into a sandstone reservoir shows that:

1. The model predicts that, in addition to CO_2 , H_2S , NO and SO_2 can lower the pH of the pore water on the short-term. If accumulation near the injection well results in very high concentrations in the brine, the pH decrease can cause enhanced short-term dissolution of calcite, but without significant effects on the porosity due to the low amount of brine present in a gas field.
2. Impurities do not result in significant differences in long-term mineral changes compared to the base case scenario, except when surplus amounts of oxygen are present. Oxygen present in the CO_2 could result in the formation of nontronite and alunite, at the expense of siderite and pyrite. Due to the low reaction rate of these minerals, the effects would only occur in the long-term. Instead of a slight increase in porosity in the absence of oxygen which occurs in the other scenarios, the porosity change is negligible.
3. The effects caused by H_2S , SO_2 , NO and O_2 would only be significant in case of accumulation of these impurities near the injection well. Whether accumulation could occur depends on the kinetics of aqueous species, on gas flow and on diffusion within the scCO_2 plume and the brine.
4. Further research should focus on the kinetics of diffusion and chemical reactions to see whether impurities can accumulate near the injection well, affect the pH of the connate water in gas fields, and subsequently affect reservoir, caprock and well cement.

6. References

- [1] McKinsey&Company. Carbon Capture and Storage: Assessing the Economics. McKinsey Climate Change Initiative;2008
- [2] Damen KJ. Reforming fossil fuel use; the merits, costs and risks of carbon dioxide capture and storage. PhD thesis isbn 978-90-8672-020-0;2007
- [3] Visser E de, Hendriks C, Barrio M, Mølnvik MJ, Koeijer G de, Liljemark S and Gallo Y le. Dynamis CO₂ quality recommendations. Int Jour of GHG Cont 2008;2:p478-484
- [4] Tambach TJ, Benedictus T, van Bergen F, Vandeweyer VP and van der Meer LGH. A geochemical study of CO₂ injection into depleted gas fields in the Netherlands. Proceedings, TOUGH Symposium 2009. Berkeley, California
- [5] Parkhurst DL and Appelo CAJ. User's guide to PHREEQC (version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 1999;99-4259. Denver, Colorado
- [6] Ellis BR, Crandell LE and Peters CA. Limitations for brine acidification due to SO₂ co-injection in geologic carbon sequestration. Int Jour of GHG Cont 2010;4:575-582
- [7] Xu T, Apps JA Pruess K and Yamamoto H. Numerical modelling of injection and mineral trapping of CO₂ with H₂S and SO₂ in a sandstone formation. Chem Geol 2007;242:319-346
- [8] Knauss KG, Johnson JW and Steefel CI. Evaluation of the impact of CO₂, co-contaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO₂. Chem geol 2005;217:339-350

