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Effects of impurities on subsurface CO₂ storage in gas fields in the northeast Netherlands

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Chapter 3



Experimental and modelling study of salt precipitation during injection of CO₂ contaminated with H₂S into depleted gas fields in northeast Netherlands

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Chapter 3

3 Experimental and modelling study of salt precipitation during injection of CO₂ contaminated with H₂S into depleted gas fields in northeast Netherlands

Abstract

Depleted gas fields are amongst the most probable candidates for subsurface storage of CO₂. With proven reservoir and qualified seal these fields have retained gas over geological time scales. However, unlike methane, injection of CO₂ changes the pH of the brine due to formation of carbonic acid. Subsequent dissolution/precipitation of minerals changes the porosity/permeability of reservoir and cap-rock. Thus, for adequate, safe and effective CO₂ storage, the subsurface system needs to be fully understood. An important aspect for subsurface storage of CO₂ is purity of this gas, which influences risk and cost of the process. In order to investigate the effects of CO₂ plus impurities in a real case example, we have carried out medium-term (30 days) laboratory experiments (300 bars, 100° C) on reservoir and cap-rock core samples from gas fields in northeast Netherlands. In addition, we attempted to determine the maximum allowable concentration of one of the possible impurities in the CO₂ stream (H₂S) in these fields.

The injected gases were CO₂+100 ppm H₂S and CO₂+5000 ppm H₂S were reacting with core samples and brine (Table 2.2). Before and after the experiments the core samples were analyzed by scanning electron microscope (SEM) and X-ray diffraction (XRD) for mineralogical variations. Also the permeability of the samples was measured. Following the experiments, dissolution of feldspars, carbonates and kaolinite was observed as expected. In addition, we observed fresh precipitation of kaolinite. However, two significant results were obtained when adding H₂S in the CO₂ stream. Firstly we observed precipitation of sulfate minerals (anhydrite and pyrite). This differs from results after pure CO₂ injection where dissolution of anhydrite was dominant in the samples. Secondly, severe salt precipitation took place in the presence of H₂S. This is caused mainly by the nucleation of anhydrite and pyrite which enabled halite precipitation and to a lesser degree by the higher solubility of H₂S in water and higher water content of the gas phase in the presence of H₂S. This was confirmed by modeling using CMG-GEM (CMG, 2011) modeling software.

The precipitation of halite, anhydrite and pyrite affects the permeability of the samples in different ways. After CO₂+100 ppm H₂S injection, permeability of the reservoir samples increased by ≤3%. In caprock samples permeability increased by a 1.3. However, after addition of 5000 ppm H₂S the permeability of all samples decreased significantly. In the case of CO₂+100 ppm H₂S, halite, anhydrite and pyrite precipitation did balance mineral dissolution, causing minimal variation in the permeability of samples.

3.1 Introduction

A system of carbon capture, transport and storage is one of the feasible ways to mitigate increasing atmospheric concentration of this gas. Generally such systems consist of CO₂ capture from main stationary sources, transportation by pipelines and injection into appropriate geological formations (IPCC, 2005).

An important aspect of CO₂ transport and storage is the purity of the CO₂ product. Depending on the source, a CO₂ product stream will contain contaminants (e.g. H₂S, SO_x, NO_x and H₂O), which may cause unwanted effects during transport or storage. Technical requirements for CO₂ purity in transport and storage will impact the degree of purification and thereby the cost for CO₂ separation. Moreover, if the CO₂ originates from different sources, different types and degrees of impurities may lead to legal uncertainties. With respect to transport, CO₂ purity determines the energy requirements and infrastructure integrity. Aspects such as phase separation, hydrate formation and the presence of corrosive components are directly related to the presence of impurities. In relation to subsurface storage, CO₂ purity relates to well integrity and injectivity as well as long-term cap-rock seal integrity and risk of leakage.

It can thus be stated that the production, transport and storage of CO₂ each have their own characteristic requirements for the degree of CO₂ purity. Depending on the nature of the additional components and their levels, these requirements can be common or contradictory. Currently, a number of technologies are being developed for the capture of CO₂ from large point sources such as power plants, steel and cement factories. In general, the CO₂ product resulting from the capture unit will not be suitable to be fed directly into a transportation network. For example, pre-combustion CO₂ capture technologies can result in significant levels of sulphur components (H₂S and SO₂), CO, H₂, H₂O and N₂. For post combustion capture technologies, the CO₂ can contain SO₂, NO_x and organics resulting from the separation section (e.g. amines), H₂O and N₂. Smaller CO₂ point sources, such as natural gas pre-treatment and digester gas purification also result in CO₂ streams containing H₂S and N₂.

In the Netherlands CO₂ storage is envisaged to take place in ‘empty’ gas fields, which will become available in the next decades. In this context ‘empty’ means that through the production period the residual pressure of natural gas in the reservoir has dropped below a certain level where no economic production is feasible. In the Netherlands, most of the gas fields are located at depths between 2500 and 4000 m, where CO₂ reaches supercritical state at reservoir conditions. Three sorts of trapping can be identified to retain CO₂ in the subsurface; 1- structural trapping of the gas phase, similar to the trapping of the natural gas, 2- solubility trapping, i.e. the solubility of CO₂ in the liquid phase, 3- Mineral trapping which represents trapped CO₂ by mineral precipitation due to chemical reactions. However, more recently a distinction is made between structural trapping and residual trapping which is the immobile residual gas fraction in the pore space after injection (Audigane et al., 2007a). In the initial phase after injection, structural trapping plays an important role but with increasing time the importance of solubility and mineral

trapping increases. In addition the safety of the storage increases when moving toward mineral trapping since CO₂ is then permanently immobilized.

Various studies have been carried out to determine under these conditions the interaction of CO₂ with reservoir rock, cap-rock and well-bore cement (Bachu, 2008; Gaus, 2010; Hangx et al., 2009; Scherer and Huet, 2009; Xu et al., 2007). These effects are field specific depending on the mineralogical and brine composition of the reservoir and can vary between partial dissolution creating micro-voids to mineralisation filling up the pore space. In the following paragraph some of the relevant experimental and modeling studies from literature are reviewed.

Murphy et al. (2011, 2010) studied the formation of siderite and pyrite from hematite and ferrihydrite in the presence of CO₂ and aqueous sulfide. Palandri et al. (2005) investigated CO₂-SO₂ reactions with hematite at 300 bar and 150 °C. The result of the experiment was the formation of pyrite (after 17 hours), siderite (after 600 hours) and elemental S. In another study by Palandri and Kharaka (2005) it was mentioned that in order to trap all of the CO₂ as a mineral when using a gas mixture representative of flue gas (e.g. <1% SO₂), the targeted reservoir rock should contain other metals to make carbonate precipitation possible. In this case there is not sufficient reducing agent (e.g. H₂S and SO₂) to reduce all of the iron and no siderite is formed. Also, Lammers et al. (2011) mentioned that the relative yield of siderite compared to iron sulfide bearing minerals is a strong function of the initial sulfide concentration. Furthermore, Balashov et al. (2013) investigated the impact of geochemical kinetic parameters on CO₂ sequestration in saline aquifers. They stress the importance of different trapping mechanisms at different time scales and also the importance of kinetic rates of mineralisation for CO₂ sequestration. Xu et al. (2007) investigated the effects of CO₂, SO₂, H₂S co-injection on the storage site by using TOUGHREACT modeling software. In another study, Zirrahi et al. (2010) predicted the water content of acid gases. In this study the water content of pure CO₂ and pure H₂S at 80 bar and 30°C was 5000 and 15000 kg/MMSm³, respectively.

Against this background, our study aims to determine the effects of one of the possible impurities (H₂S) in the CO₂ stream on the storage site. More specifically, we aim to obtain boundaries for maximum allowable concentration of H₂S in the CO₂ stream in order to prevent long-term leakage as well as achieve cost effective well injectivity.

For this purpose, medium-term (30 days) laboratory tests were carried out on reservoir and cap-rock samples from the gas fields in northeast Netherlands. The samples were brought in contact with brine and gas (CO₂ + H₂S) at reservoir conditions (high pressure/temperature). These samples were analyzed both before and after the experiment by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) for the observation of alterations. In addition, permeabilities were measured for comparison. In parallel to the experiment, the injection of these gases was modeled by CMG-GEM (CMG, 2011) in order to explain some of the experimental results.

3.2 Methods and Materials

3.2.1 Sampling and experimental procedure

For our experiments we used reservoir and cap-rock core samples from 3 different fields in a depth range of 2.8-3.2 km. The porosity and permeability ranges are 1-27% and 0.006- 6000 mD respectively. The lower porosity and permeability values represent cap-rock samples. The cap-rock samples were selected from carbonate and anhydrite layers of the Zechstein seal. The experimental setup and analytical technique is similar to Section 0 and 2.2.4.

The disk shaped samples were placed in the pressure cells in contact with methane and brine with a composition obtained from gas well test data (Table 2.2). The brine to sample mass ratio was 3 in our experiments. The methane was included to simulate the presence of residual gas in the depleted gas fields. Hence, 2% methane was included in our gas mixture in all our experiments. The total reactor volume was 100 cc of which ~25 cc is consumed by brine and sample. The gas mixture was injected to a pressure of 300 bars (at a temperature of 100 °C). Under these conditions the samples and brine were reacting with the injected gases. After the end of the experiment, the samples were dried at room temperature.

Two sets of experiments were carried out: 1) CO₂ with an added impurity of 5000 ppm H₂S for duration of 30 days. 2) CO₂ with an added impurity of 100 ppm H₂S with a variable duration between 15 to 80 days.

3.3 Results and discussion

In this section we present the results regarding H₂S co injection with CO₂ and compare the results with pure CO₂ experiments. After injection, the gases are (partly) dissolved in the brine according to Reaction 3.1 and Reaction 3.2.

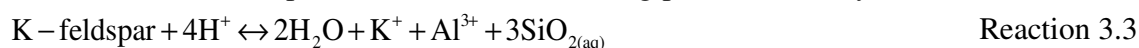


Dissolution of CO₂ and H₂S in the aqueous phase releases H⁺ ions, resulting in a decrease in pH of the formation water. However, subsequent dissolution of minerals (e.g. calcite and dolomite) consumes H⁺ ions and the pH will be buffered. In our experiments the initial pH of the brine was 6.8. After the experiments the pH was slightly reduced to 6.1 both with and without H₂S impurities. However, it should be mentioned that our pH measurements have been carried out under atmospheric conditions and it is recommended to perform pH measurement at in situ condition. Also, we calculated the in situ pH for pure CO₂ injection in the reservoir samples with the help of PHREEQC software (Parkhurst and Appelo, 1999) (version 3.1.0) and use of Pitzer based Eq 3/6 thermodynamic (Wolery, 1992) database provided by Quintessa Ltd (Benbow et al., 2008). When using a sandstone mineral composition of 87% quartz, 5% kaolinite, 2% k-feldspar, 1% illite, 2% dolomite, 1% anhydrite and 2% albite (obtained by XRD analysis) and brine, similar to those used in our experiments, the in situ pH reaches a value of 3.3.

The dissolution trend of minerals in the samples was the same after pure as well as impure CO₂ injection. However, addition of H₂S in the CO₂ stream resulted in pyrite and anhydrite precipitation, which was not the case after pure CO₂ injection. In the section below, we discuss the observed dissolution/precipitation for some of the most important minerals in the Rotliegend.

3.3.1 Potassium Feldspars

Dissolution of K-feldspar increases with decreasing pH, as shown by Reaction 3.3.



Dissolution of K-feldspar has been indeed observed in our experiments following pure and impure CO₂ injection.

3.3.2 Kaolinite

Kaolinite is one of the main clay minerals in the reservoir samples. Dissolution of kaolinite increases with decreasing pH, as observed when introducing the pure and impure CO₂ (Reaction 3.4)



As described above, kaolinite dissolution has been observed in our experiments (Figure 3.1b and Figure 3.1c). Furthermore, fresh precipitation of kaolinite was also observed (Figure 3.1e and Figure 3.1f) associated with dissolution of feldspars and use of mutual ions (Zhu, 2009) governed by the pH of the brine.

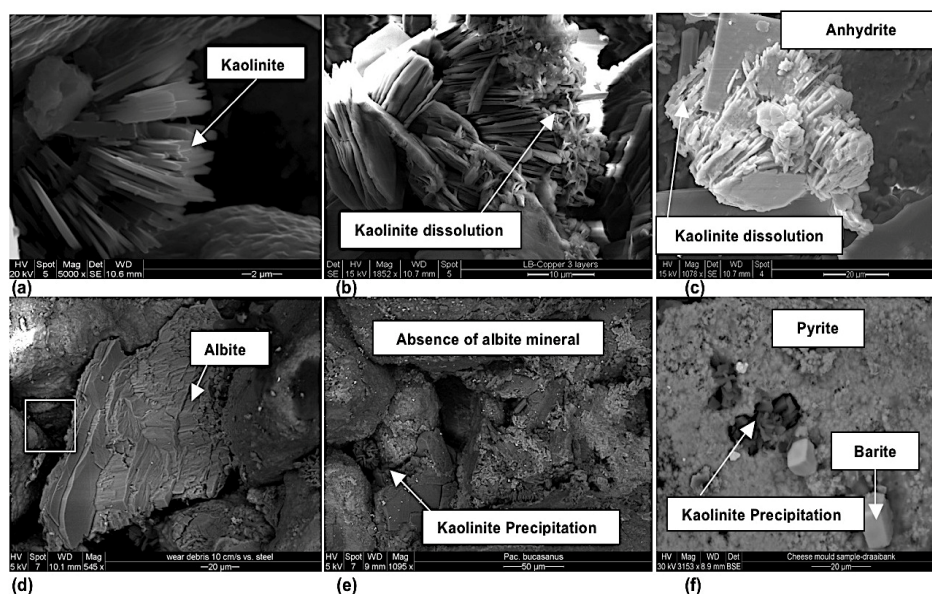


Figure 3.1 SEM image of a Rotliegend reservoir sample before the experiment (a and d), after the CO₂ experiment (b and e), after CO₂+5000 ppm H₂S (c and f). d and e images are from the same spot with different magnifications.

3.3.3 Dolomite

Dolomite is present both in reservoir and cap-rock samples. After injection of the gases in all cases dissolution of this mineral was observed due to decreasing pH, which is in line with Reaction 3.5.



In reservoir samples, dolomite is present as one of the cementing minerals (~1%). The dolomite content is higher in the caprock samples: 12% and 22% on average in samples from anhydrite and carbonate layers, respectively. Figure 3.2 shows dissolution of this mineral in reservoir samples after pure and impure CO₂ injection.

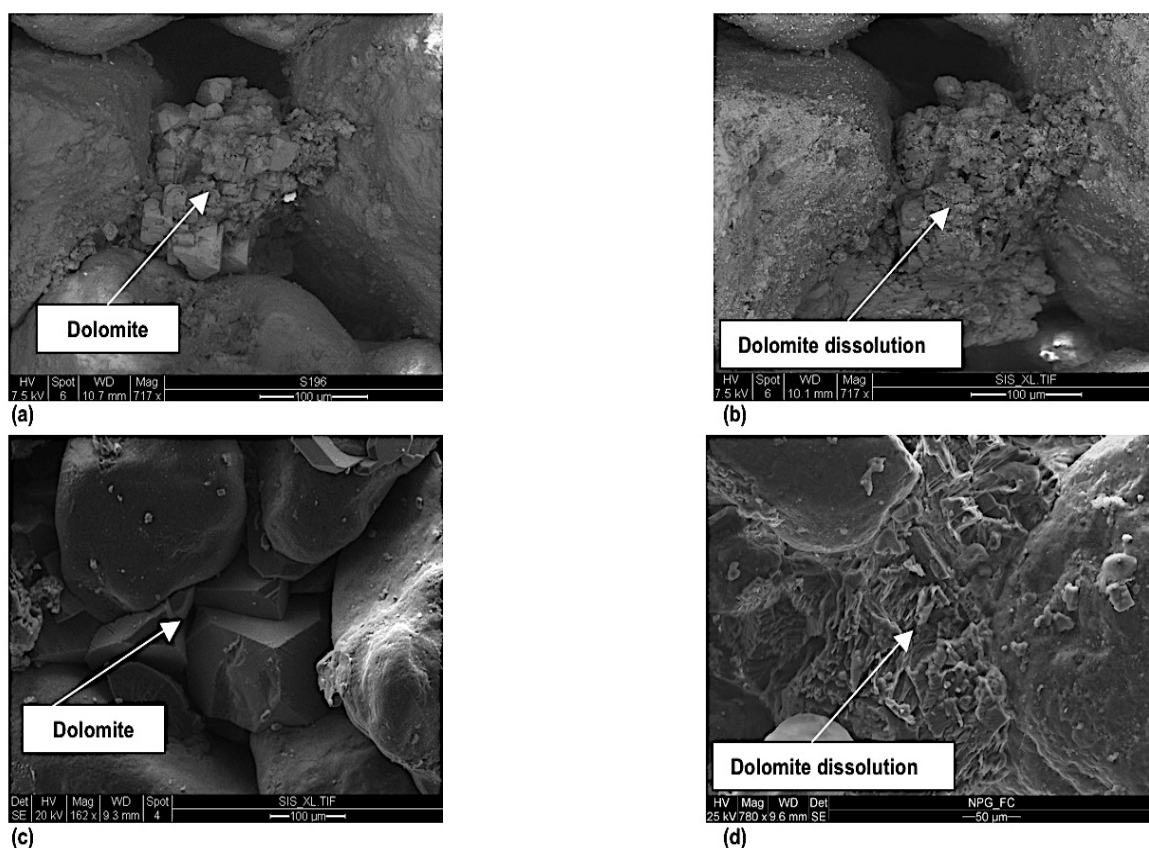


Figure 3.2 SEM image of a Rotliegend reservoir sample before the experiments (a and c). (b) after CO₂ experiment (a and b are similar magnification) and (d) after CO₂+5000 ppm H₂S experiment (Note: c and d have different magnification).

The dolomite in the Rotliegend reservoir samples contains iron which is released through dissolution, subsequently resulting in the precipitation of pyrite. This was observed after injection of CO₂ with H₂S (Figure 3.3). No pyrite precipitation was observed after pure CO₂ injection.

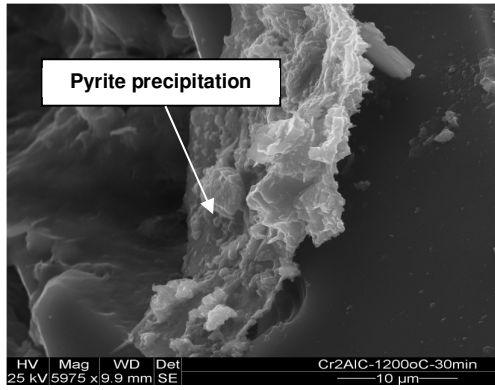


Figure 3.3 Pyrite precipitation in a Rotliegend reservoir sample after injection of CO₂+ 5000 ppm H₂S. Precipitation of this mineral did not take place following pure CO₂ injection.

3.3.4 Anhydrite

Absence and presence of H₂S in the gas mixture had different effects on anhydrite. In the case of pure CO₂ injection dissolution of anhydrite has been observed in the cap rock samples which is in line with Reaction 3.6 (Kühn et al., 2006) (Figure 3.4)



However, in the presence of H₂S, precipitation of anhydrite dominates over its dissolution due to the additional presence of sulfate ions (Figure 3.4).

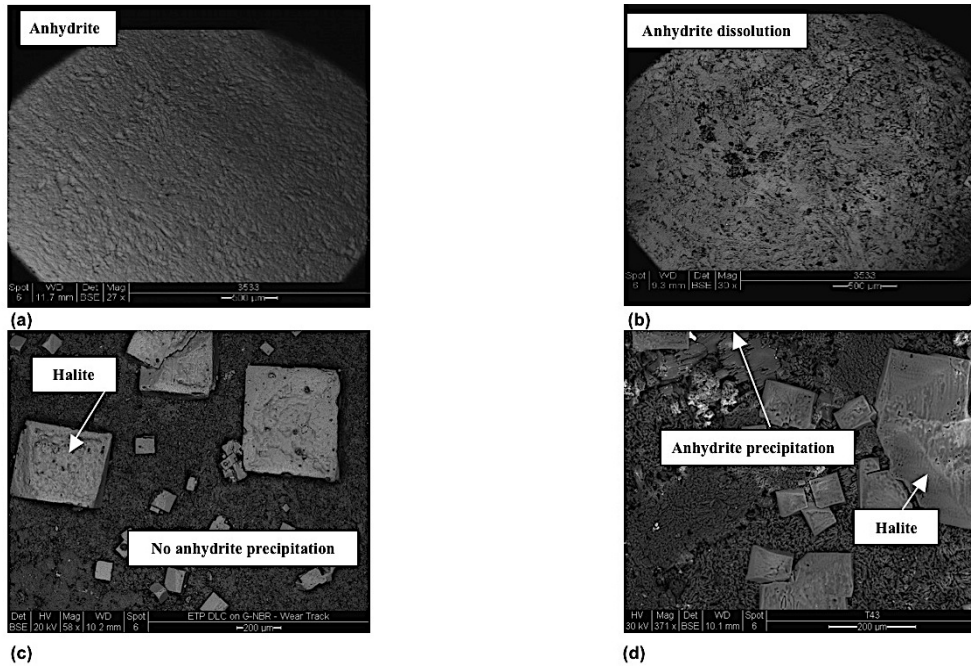


Figure 3.4 SEM images of Zechstein cap-rock sample before CO₂ injection (a) after CO₂ injection (b and c), after CO₂+ 5000 ppm H₂S injection (d). Images c and d are from samples at the same depth. In image c, no anhydrite precipitation is observed. However, in (d) anhydrite precipitation is present.

3.3.5 Permeability

Permeability is an important factor for evaluating feasible reservoir/seal pairs as potential candidates for CO₂ storage. Enhancement in initial permeability when mineral dissolution dominates over precipitation can improve well injectivity. On the other hand, decrease in permeability by dominant mineral precipitation can reduce injectivity or block the pores in the reservoir, thus reducing storage capacity. Permeability is also a controlling factor for the sealing capacity of the cap rock. In this case, permeability needs to be as low as possible to maintain seal integrity. Dissolution of cap-rock leads to increased risk of leakage from underlying reservoirs.

Salt (halite) precipitation has been observed in the pores of the samples following both pure and impure CO₂ injection albeit in different quantities. In addition, after impure injection, salt precipitation also occurred on the surface of the samples (Figure 3.5).

As described before, following pure and impure CO₂ injection the dissolution of minerals was identical but new minerals were precipitated after impure injection (anhydrite and pyrite). However, the precipitation of these minerals was of lower magnitude than the halite precipitation. Hence, we compared the magnitude of salting-out effect by looking at the permeability variation in the samples because we observed that the main difference between the samples is salt precipitation.



Figure 3.5 The surface of two reservoir samples from the same depth after the experiments. (a) is the reservoir sample after pure CO₂ injection, halite precipitation is not observed on the surface of this sample. (b) The reservoir sample after CO₂ + 5000 ppm H₂S injection, salt precipitation is observed on the surface of the sample.

Consequently, based on our experimental results we would expect to see an increase in initial permeability of the samples following pure CO₂ injection due to dominance of mineral dissolution over precipitation of kaolinite and salt. However, after CO₂ + 5000 ppm H₂S injection, a decrease in permeability of the samples is expected due to dominance of precipitation (especially salt) over dissolution of the minerals. In Table 3.1 the results of permeability measurements for different experiments are compared.

Table 3.1 Permeability measurement of the samples before and after 30 days of experiments.

Sample	Experiment	Initial permeability (mD)	Final permeability (mD)
Reservoir 1	CO ₂	149 ± 7.4	791 ± 39.5
Reservoir 2	CO ₂	216 ± 10.8	278 ± 13.9
Reservoir 3	CO ₂	1465 ± 73.2	1638 ± 81.9
Reservoir 4	CO ₂	3407 ± 170.3	4177 ± 208.8
Reservoir 5	CO ₂ + 5000 ppm H ₂ S	328 ± 16.4	112 ± 5.6
Reservoir 6	CO ₂ + 5000 ppm H ₂ S	6140 ± 307	702 ± 35.1
Reservoir 7	CO ₂ + 100 ppm H ₂ S	681 ± 34	700 ± 35
Cap-rock 1	CO ₂	0.04 ± 0.008	0.13 ± 0.02
Cap-rock 2	CO ₂	0.017 ± 0.003	0.084 ± 0.01
Cap-rock 3	CO ₂	0.006 ± 0.001	0.028 ± 0.005
Cap-rock 4	CO ₂	0.008 ± 0.001	0.080 ± 0.01
Cap-rock 5	CO ₂ + 5000 ppm H ₂ S	0.0166 ± 0.003	0.0007 ± 0.0001
Cap-rock 6	CO ₂ + 100 ppm H ₂ S	0.12 ± 0.02	0.16 ± 0.03

After CO₂ injection, the permeability of reservoir samples has increased by 10-30%, except for one sample where the permeability increased by a factor of 5. The reason for this difference is that in the latter case, the sample had the lowest initial permeability and contained the most cement minerals (feldspars and carbonates). In the cap-rock samples the permeability has increased by a factor of 3-10. This might seem severe, but it should be noted that the initial permeabilities were all in the micro-Darcy range. Furthermore seal integrity is not necessarily at risk since the effects of CO₂ injection will only occur at the interface between cap-rock and reservoir. Progression of CO₂ through fractures in cap-rock may however result in a stronger effect on the properties of the bulk cap-rock.

After CO₂+ 5000 ppm H₂S injection, a significant decrease in permeability of both reservoir and caprock samples has been observed. The reason is significant halite precipitation in the samples.

After CO₂+100 ppm H₂S injection permeability remained almost unchanged (slight increase <3%) in the reservoir sample. In the cap-rock sample permeability increased by 30% which is far less than in the case of pure CO₂ experiment. The reason for this slight increase in permeability of the samples is that salt precipitation balances the dissolution of minerals.

In addition, permeability measurements were carried out after 17 and 80 days following CO₂+100 ppm H₂S injection (Table 3.2). After 17 days, permeability of the samples had dropped. This implies that in this period the precipitation of halite overcomes dissolution of minerals and permeability decreases. However, with increasing time the mineral dissolution process takes over and permeability increases again. Mineral dissolution and precipitation are a function of kinetic rate constant and reactive surface area of minerals. A compilation of data for mineral dissolution in different conditions (neutral, acid and

basis) is provided by Palandri and Kharaka (2004). However, data for precipitation of minerals is rare. Hence, in many studies the kinetic rate data for dissolution are also used for mineral precipitation (e.g. Xu et al. (2007)). Kinetic rates for halite dissolution and precipitation are much faster than for other minerals present in the reservoir, which supports our experimental results.

Table 3.2 Permeability measurements before and after CO₂+100 ppm H₂S injection.

Sample	Experiment	Duration	Permeability before (mD)	Permeability after (mD)
Reservoir 8	CO ₂ + 100 ppm H ₂ S	17 days	419 ± 20.9	17.5 ± 0.8
Cap-rock 7	CO ₂ + 100 ppm H ₂ S	17 days	0.0058 ± 0.001	0.0014 ± 0.0002
Reservoir 7	CO ₂ + 100 ppm H ₂ S	30 days	681 ± 34	700 ± 35
Cap-rock 6	CO ₂ + 100 ppm H ₂ S	30 days	0.12 ± 0.02	0.16 ± 0.03
Reservoir 9	CO ₂ + 100 ppm H ₂ S	80 days	523 ± 26.1	574 ± 28.7
Reservoir 10	CO ₂ + 100 ppm H ₂ S	80 days	203 ± 10.1	311 ± 15.5

3.3.6 Salt precipitation

The increased precipitation of anhydrite and pyrite in the CO₂+H₂S case, compared to the CO₂ only case, assisted precipitation (nucleation) of halite. Nucleation of pyrite could be observed within the precipitated halite crystals as illustrated in Figure 3.6a. Also, SEM-EDX analysis of halite is given in Figure 3.6b.

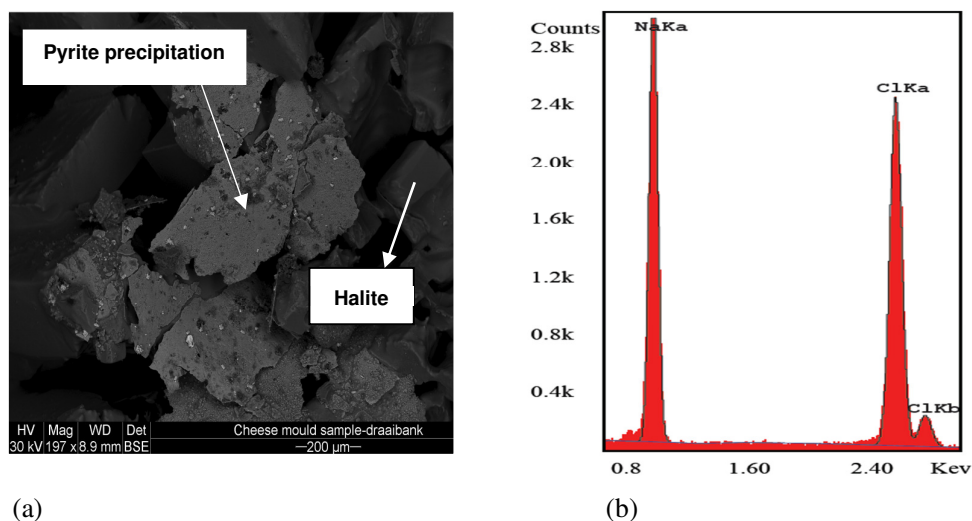


Figure 3.6 (a) Pyrite precipitation in the middle of halite (b) EDX analysis of halite.

Compared with pure CO₂, H₂S has a higher solubility in brine and H₂O has a higher solubility in the H₂S gas phase (Battistelli and Marcolini, 2009; Zirrahi et al., 2010). We have modeled this situation for our system using CMG-GEM (CMG, 2011) in order to investigate the effect of water vaporization and solubility of the gas mixture on salt precipitation. We modeled dissolution of the pure and impure CO₂ in water and compared the water content of the gas phase in different cases. For dissolution of gases in the

aqueous phase it is assumed that the gaseous and aqueous phases are in thermodynamic equilibrium by equality of fugacities of the components in both phases (Equation 3.1):

$$f_{ig} - f_{iw} = 0 \quad \text{Equation 3.1}$$

The gas is considered to be a multicomponent mixture of n_g components which is a requirement if the injected CO_2 is impure. The fugacity f_{ig} (fugacity of component i in the gas phase) is calculated from the Peng-Robinson equation of state (Peng and Robinson, 1976). The fugacity f_{iw} of a gaseous component soluble in the aqueous phase is calculated using Henry's Law (Equation 3.2) (Li and Nghiem, 1986).

$$f_{iw} = y_{iw} \cdot H_i \quad \text{Equation 3.2}$$

In this equation y_{iw} is the mole fraction of component i in the aqueous phase and H_i is Henry's constant of component i . Henry's constant is obtained by Equation 3.3.

$$\ln H_i = \ln H_i^* + \frac{\bar{v}_i (P - P^*)}{RT} \quad \text{Equation 3.3}$$

Where, H_i is Henry's constant for component i at pressure P (KPa) and temperature T ($^{\circ}\text{K}$). H_i^* is Henry's constant for component i at a reference pressure P^* and temperature T . R is the universal gas constant and $\bar{v}_i$ is the partial molar volume of component i (litre/mol).

In order to model H_2O vaporization, the thermodynamic equation of (7) is applied to the H_2O component (Equation 3.4).

$$f_{\text{H}_2\text{O,g}} - f_{\text{H}_2\text{O,w}} = 0 \quad \text{Equation 3.4}$$

The $f_{\text{H}_2\text{O,w}}$ is calculated by three steps. Firstly, the fugacity of saturated H_2O at reservoir temperature is calculated based on the work of Canjar and Manning (1967). Secondly, the saturation pressure of H_2O at reservoir temperature was calculated based on Saul and Wagner (1987) and subsequently the molar volume of H_2O was calculated based on (Rowe and Chou, 1970). Finally, the fugacity of H_2O in the aqueous solution is calculated from Equation 3.5:

$$f_{\text{H}_2\text{O,w}} = y_{\text{H}_2\text{O,w}} f_{\text{H}_2\text{O}} \quad \text{Equation 3.5}$$

For this simulation a reservoir model is designed with a length of 5 km and thickness of 100 m. Porosity and permeability of the reservoir were 20% and 3 Darcy, respectively. The initial pressure and temperature of the reservoir were 1 bar and 100°C . The salinity of brine was similar to the value used in our experiment. The gas was injected at a maximum rate of $25000 \text{ m}^3/\text{day}$ and bottom hole pressure of 290 bars for one month. Three sets of simulations have been carried out: pure CO_2 , $\text{CO}_2+5000 \text{ ppm H}_2\text{S}$ and $\text{CO}_2+100 \text{ ppm H}_2\text{S}$ injection. The purpose of these simulations is to obtain a better understanding of salt precipitation in the experiments. Figure 3.7 shows the molality of gases in brine and the water content in non-aqueous phase. As can be concluded from the figures, the solubility of H_2S in brine is higher than that of CO_2 . Hence, by addition of H_2S in the CO_2 stream the solubility of the gas mixture in brine increases. Furthermore, the presence of H_2S leads to an increase in water content of the gas phase. However, since the mole fraction of water vapor in the case where impurities were added did not

significantly increase, we conclude that the precipitation of halite in the case of impure CO₂ injection is mainly caused by the additional precipitation of pyrite and anhydrite as a basis for halite nucleation.

In summary, we want to stress that the boundary for the maximum allowable presence of impurities needs to be well known in order to avoid unwanted effects on reservoir and seal. In this research, the presence of 5000 ppm H₂S in the CO₂ stream considerably reduced the permeability of the reservoir and caprock samples due to salt precipitation. However, at 100 ppm H₂S dissolution and precipitation of minerals were in balance thus keeping the permeability reasonably constant. It should be noted that these effects are highly field specific and strongly depend on the composition of the formation water.

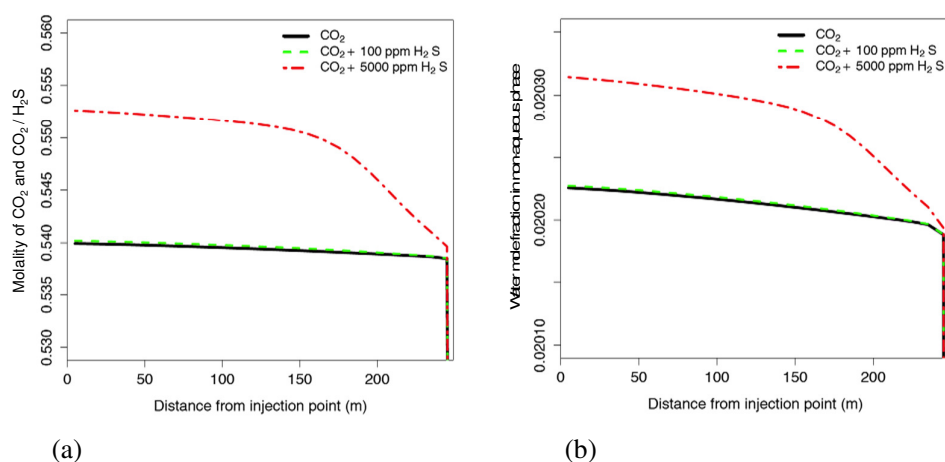


Figure 3.7 (a) Molality of different gas mixtures in brine (CO₂, CO₂+ 100 ppm H₂S and CO₂ + 5000 ppm H₂S) (b) Water mole fraction in the non- aqueous phase in case of pure and impure CO₂.

3.4 Conclusion

We have experimentally investigated the effects of H₂S as one of the possible impurities in the CO₂ stream. Part of the experiments were simulated by CMG-GEM modeling software.

The experimental setup was designed to simulate reservoir conditions (300 bars/100° C). A number of Rotliegend reservoir and Zechstein cap-rock samples were exposed to different gas mixtures (CO₂+100 ppm H₂S and CO₂+5000 ppm H₂S). The following results were obtained:

- After the experiments the pH of the brine dropped from 6.8 to 6.1 (not insitu condition).
- Dissolution of feldspars, carbonates and kaolinite was observed as expected.
- Fresh precipitation of kaolinite has been observed, linked to the dissolution of feldspars.
- Fresh precipitation of pyrite and anhydrite has been observed after impure CO₂ injection. However, when injecting pure CO₂ no pyrite precipitation was found and anhydrite dissolution was dominant.

- One of the main differences between the pure and impure CO₂ experiments was related to the precipitation of salt (halite). Following impure injection large halite crystals precipitated which was not the case after pure injection. The reason for halite nucleation and precipitation is mainly formed by the precipitation of pyrite and anhydrite which enhanced halite precipitation.
- The trend in permeability variations differed in case of pure and impure CO₂ injection. After pure CO₂ injection, the permeability of reservoir and cap rock samples increased 10-30% and by a factor of 3-10, respectively. This increase in permeability of cap rock samples looks severe but it should be noted that the initial permeabilities of the caprock samples were in the micro-darcy range. When adding 5000 ppm H₂S, a considerable decrease in permeability of the samples occurred. After adding 100 ppm H₂S the permeability of reservoir and caprock samples increased by 2.8% and 30% respectively.

In order to complete the picture of impure CO₂ injection, permeability of the samples was measured after 17 and 80 days of exposure to CO₂+100 ppm gas injection. This resulted in:

- After 17 days: the permeability of the samples decreased significantly because of the initial dominance of salt precipitation in comparison with mineral dissolution.
- After 30 days: mineral dissolution was in the same order of magnitude as salt precipitation, resulting in almost unchanged permeability of the samples.
- After 80 days: the increase in permeability was slightly higher than after the 30 days experiment (10-50 %) due to progressing mineral dissolution.