

EXPERIMENTAL STUDY ON HALITE PRECIPITATION DURING CO₂ SEQUESTRATION

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ABSTRACT

Among different options proposed for CO₂ storage and sequestration, saline formations seem promising due to their wide availability and potentially large storage capability. As supercritical (SC) CO₂ is injected into the formation, a variety of coupled processes happen. Halite precipitation requires particular interest due to its potentially significant impact on permeability impairment, and thus reduction of injectivity in the near well bore region.

SC CO₂ core flood experiments were performed on 25% NaCl brine saturated Berea cores of 1.5 inch diameter and 1 foot length. SC CO₂ was injected continuously until no further water was produced. Gas effective permeability measured at the remaining water saturation (S_{wf}) was found to be roughly half of the expected value at similar S_{wf} for a Berea core without CO₂ exposure. With the aid of environmental scanning electron microscopy and elemental analysis, salt crystals as well as grains coated with salt material were observed on different faces of the core. The experiment was the direct demonstration of halite precipitation under the reservoir condition. Quantifying the permeability reduction aids the injectivity evaluation for CO₂ sequestration.

INTRODUCTION

Carbon dioxide (CO₂) is emitted into the atmosphere through the burning of coal and fossil fuels, and is considered as a main cause of global warming. Carbon capture and storage (CCS) is seen as one of the most technologically advanced options for dealing with anthropogenic CO₂ emissions. Among different methods proposed for CCS, injection into saline formations is promising because of their wide availability and large storage capacity. However, some formations are highly saline. This has raised issues about the possible effects of halite precipitation behind the flood front during the injection of supercritical (SC) CO₂. Deposition of halite scale has been shown to be a widespread problem in the oil industry. This phenomenon has been observed in gas storage wells in the Netherlands and Germany [1]. Halite scale in gas reservoir has been attributed to evaporation [1].

Various modelling studies have highlighted potential issue of well injectivity loss and permeability impairment caused by halite precipitation during the injection of SC CO₂ into highly saline formations [2, 3]. Based on modelling results, a series of core flood experiments were designed for the CO₂SINK pilot CCS project in Germany. This paper presents the result from one core flood experiment and discusses the possible impact on injectivity evaluation.

EXPERIMENT

Setup

The experimental setup is shown in Fig. 1. The center part was a core holder suitable for large size core sample with about 3.8 cm (1.5 inch) diameter and up to 30 cm (12 inch) length. The core holder as well as inlet and outlet pressure transducers were enclosed in an oven for better temperature control and stabilization. The oven is not shown in the figure. The saturation pump was used to saturate the core with brine and to measure its brine permeability. Two injection pumps were filled with liquid CO₂ at room temperature by a booster pump and used for continuous CO₂ injection. Produced fluids were captured by two traps, where the liquid trap was used to capture the displaced brine, and the vapour trap detained the water vapour produced with the gas phase due to evaporation.

One of the challenges in CO₂ related core experiments is that CO₂ has a relatively large permeation rate through rubber sleeves typically used in core analysis, which will cause rubber to swell and CO₂ to bypass the core. In this experiment, four different layers of protection were used to prevent the CO₂ leakage. From inside out, those layers were Teflon tape, aluminium foil, Teflon heat shrink tube, and finally a Viton sleeve. This assembly effectively prevented the CO₂ leakage.

Properties of Berea Core and CO₂

In support of the field trial, Berea sandstone with similar porosity and permeability was used to mimic reservoir rock. Experimental parameters including injection rate, pressures, confining stress, and temperature, etc. were also chosen based on the field data. In this experiment, the Berea core had the length of $L = 28.1$ cm (~ 1 ft) and the diameter of $D = 3.76$ cm (~ 1.5 inch). Its porosity was 18% by Boyle's law, and thus the pore volume (PV) was 57.1 cc.

Under room temperature and atmospheric condition, CO₂ is normally in gas phase. The critical point of CO₂ is at 73.8 bar (1071 psi) and 31.1°C. CO₂ used in this experiment was dry with water content less than 2 ppm. Before filled into pumps, CO₂ was compressed by a booster pump to liquid at pressure around 82.7 bar (1200 psi) and room temperature 19°C. The density and viscosity of CO₂ were 0.831 g/cc and 0.077 cP, respectively. As the temperature was increased to 50 °C, CO₂ was in the supercritical region. The pressure was set by back pressure regulator as 82 bar (1190 psi). The density of CO₂ was 0.233 g/cc, and the viscosity was 0.021 cP.

Experimental Procedure

The experiment included four different stages: initial core permeability calibration, SC CO₂ injection, gas permeability measurement post CO₂ flood, and microscopic analysis. First, the core was sleeved as described above, weighed, and then loaded into the core holder. Gas (CO₂) permeability was measured by the steady state method at room temperature (19 °C) as 118 mD. This result was later used to evaluate the permeability impairment after the SC CO₂ injection. The core was then saturated with brine of 25% sodium chloride (NaCl), and the steady state brine permeability was measured as 79 mD.

After the permeability measurement, temperature in the oven was elevated to 50 °C and stabilized over night. Thereafter, dry SC CO₂ was injected into the Berea core at a rate about 9.5 cc/min at 50 °C, which was scaled from the rate of 1 kg/s in the CO₂SINK pilot. The injection pressure was 82 bar (1190 psi). The effective confining stress (ie. confining stress minus injection pressure) was 64 bar (940 psi). Produced fluid including both liquid and water vapour was monitored and measured by two traps. SC CO₂ was injected into the core continuously for about 331 PV until no more liquid brine was produced and the weight change of the liquid trap became constant.

When the SC CO₂ injection stopped, the oven temperature was decreased back to room temperature of 19 °C. Steady state CO₂ gas permeability was measured again on the Berea core at this remaining brine saturation condition. To avoid additional vaporization of water during this final permeability measurement, CO₂ gas was first bubbling through water in a sparging cell to get humidified and then injected into the core.

The core assembly was then unloaded and weighed to determine the final water saturation, or the remaining water saturation S_{wf} , by mass balance. The core was kept sleeved until it was ready for the analysis by environmental scanning electron microscopy (ESEM). ESEM images were taken on different faces on the core after the flood, as well as on another dry clean Berea core that had not been exposed to CO₂. Elemental composition on each face was determined by scanning electron microscopy (SEM) energy – dispersive spectroscopy (EDS).

RESULTS AND DISCUSSION

The production and pressure drop across the core as functions of pore volume (PV) of SC CO₂ injected are plotted in Fig. 2. From the figure, SC CO₂ broke through soon after the injection commenced. The pressure drop decreased after the breakthrough due to the fact that the viscosity of SC CO₂ was lower than that of brine. The pressure drop kept on decreasing until after about 280 PV of SC CO₂ injection, where it was stabilized around 0.3 bar (4 psi). On the other hand, most of mobile water was displaced and produced during the first 30 PV of injection. As the injection continued, the production slowed down. The brine production finally stopped after about 280 PV of SC CO₂ was injected. The small amount of vapor production after that was caused by the evaporation of remaining water.

Weight difference of the core assembly including core and sleeve before and after the SC CO₂ flood was 28.11 g. Given the brine density of 1.189 g/cc and core's PV of 57 cc, the remaining water saturation was calculated as $S_{wf} = 41\%$. Due to the fact that the core after CO₂ exposure was weighted with precipitated salt and remaining brine, the above calculated S_{wf} may be slightly higher than the actual case. On the other hand, the total produced water from Fig. 2 was about 52.7 g or 44.7 cc. The measured water production included not only the mobile water in the core, but also the water in tubing and dead volume of pressure transducers. The volume of tubing was measured separately to be 8.6 cc. The amount of water displaced from the dead volume of pressure transducers was estimated to be around 0 to 4 cc.

Therefore, the remaining water saturation from production was calculated to be in the range of 36% to 43%. The result agreed reasonably with that from the mass balance calculation. The relatively large remaining water saturation even after 331 PV of SC CO₂ injection was mainly due to poor displacement efficiency. Because of the large viscosity contrast between CO₂ (0.021 cP) and brine (1.9 cP), it was an unstable situation for SC CO₂ to displace brine in the core, which resulted in early CO₂ breakthrough and large amount of brine left in the core.

During SC CO₂ injection, behind the flood front, halite may precipitate as a result of evaporation. The precipitated salt may be displaced out of core by the flood. In the experiment, salt crystals were observed tumbling through the transparent tubing. The precipitate halite may also stay in the core, plugging pore throats and causing the permeability impairment. Several permeability measurements were performed to study this effect as mentioned in the experimental procedure. Results from those permeability measurements are summarized in Table 1. It is observed from the table that the effective gas permeability of the core at S_{wf} after the flood was roughly 30 % of the initial gas permeability of the dry core.

From the absolute permeability ($k_l = 79$ mD), and gas effective permeability at S_{wf} ($k_{eg} = 31$ mD), CO₂ gas relative permeability at S_{wf} can be calculated as $k_{rg} = 0.394$, which is plotted in Fig. 3. Also shown in Fig. 3 is the gas (N₂) relative permeability on a Berea core plug with similar properties but without SC CO₂ exposure. It is shown from the plot that k_{rg} after the SC CO₂ flood was roughly half of that without SC CO₂ exposure at S_{wf} . Where to make a direct comparison, (CO₂) gas relative permeability measurements on the same Berea sample before flood is required and currently ongoing.

To observe the precipitated halite crystals directly, ESEM images were taken over four regions on each of five different faces on the core along the flow direction as shown in Fig. 4. As a comparison, ESEM images were also taken on a dry clean Berea core without CO₂ exposure. The image together with the compositional analysis result over one region is shown in Fig. 5. It is noted from the figure that the clean Berea core was rich in Si, O, and Al, and no NaCl was observed. On the other hand, halite crystals were observed through out the flow direction from images taken on the core after SC CO₂ flood. Figures 6 – 8 are a few of those images. Fig. 6 includes the image over region 1 on face 2 of the core and the tabulated results of compositional analysis on chosen grains. Grain 1 was Silica with edges coated by halite, where grain 2 and 3 were totally coated by halite. The image in Fig. 7, which was taken over region 4 on face 2, shows the case where the precipitated halite crystals blocked the pore throat. A variety of morphologies were observed for precipitated halite crystals as well.

Among them, Hopper crystals as shown in Fig. 8 were particularly noted. Hopper crystals, i.e. hollow stepped crystals, indicated fast crystallization caused by a rapid increase in super saturation. This resulted in the fully developed edges of crystals and hollow interior [4]. Presence of Hopper crystals suggested that halite precipitation occurred rapidly upon SC CO₂ was injected into the core.

CONCLUSION

In conclusion, during CO₂ injection into a saline formation, focusing only on storage capacity, or the degree to which the pore volume is reduced by halite precipitation, is insufficient, since a little precipitation in a pore-throat could have a significant effect on permeability, which is another important aspect. Moreover, the impact of halite precipitation on permeability is modeled in TOUGH2, the industry CCS simulator, but the model needs calibration/validation for each field. In this work, a core flood experiment showed that supercritical CO₂ injection in a brine saturated core sample caused halite precipitation and reduced gas phase relative permeability by approximately half at the remaining water saturation. The precipitation was the result of water dissolving into the SC CO₂. With the aid of ESEM, halite crystals were observed throughout the flow direction of the core in different morphologies. In particular, the presence of Hopper crystals suggested that halite precipitated rapidly upon SC CO₂ was injected into the core.

While the halite precipitation is an important issue in injectivity evaluation, it is affected by many factors. More research work is currently ongoing on relations between halite precipitation rate and brine salinity, SC CO₂ injection rate, and initial water saturation.

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Table1: Summary of Permeability Measurement on the Berea Core

Permeability Measurements on Berea Core	K (mD)
CO ₂ gas permeability on dry clean core	118
Brine permeability on fully saturated core	79
SC CO ₂ Permeability on the core flood at S_{wf}	29
CO ₂ gas permeability on the core post flood at S_{wf}	31

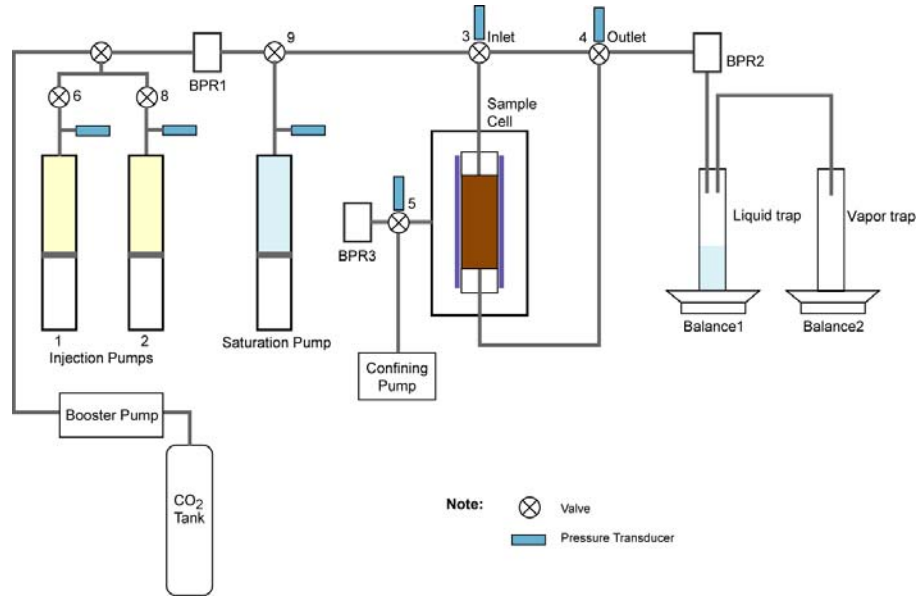


Figure 1: Setup for SC CO₂ core flood experiment.

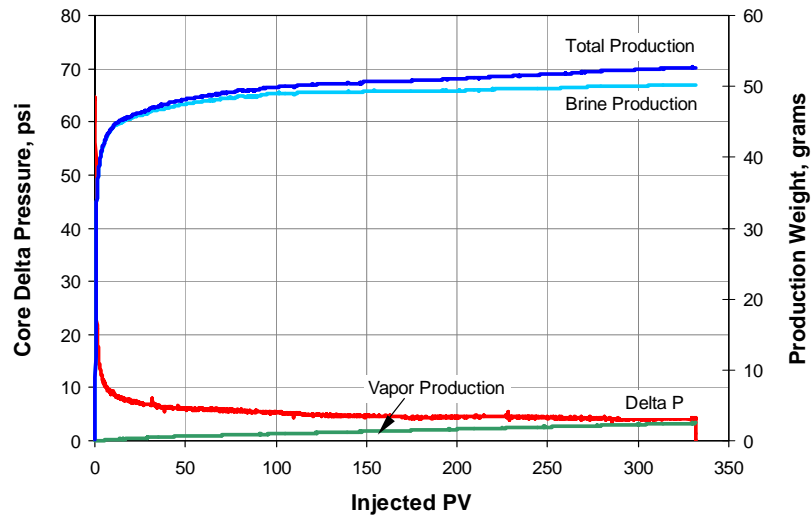


Figure 2: Pressure drop across the core and production as functions of injected SC CO₂ in PV.

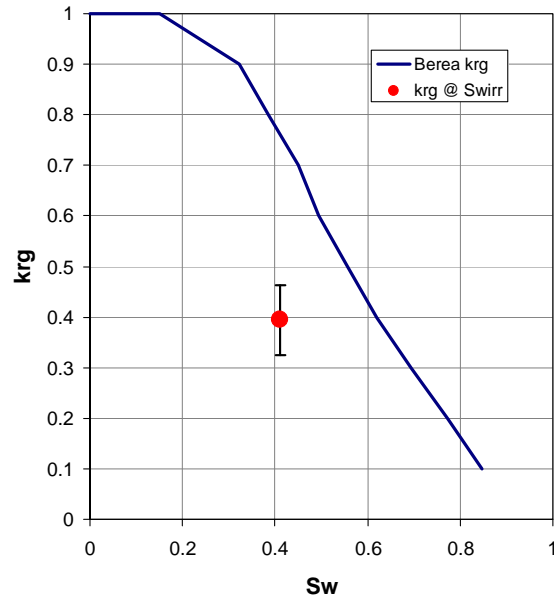


Figure 3: Gas (CO₂) relative permeability of the Berea core after SC CO₂ flood at S_{wf}, as compared to that of a Berea core without CO₂ exposure.

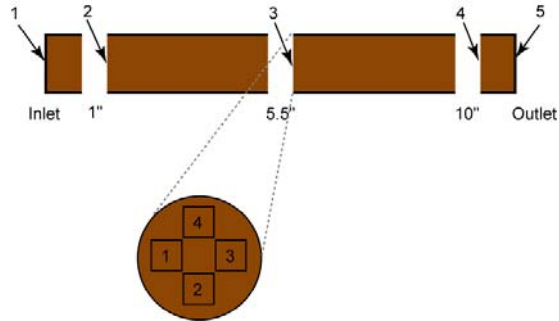
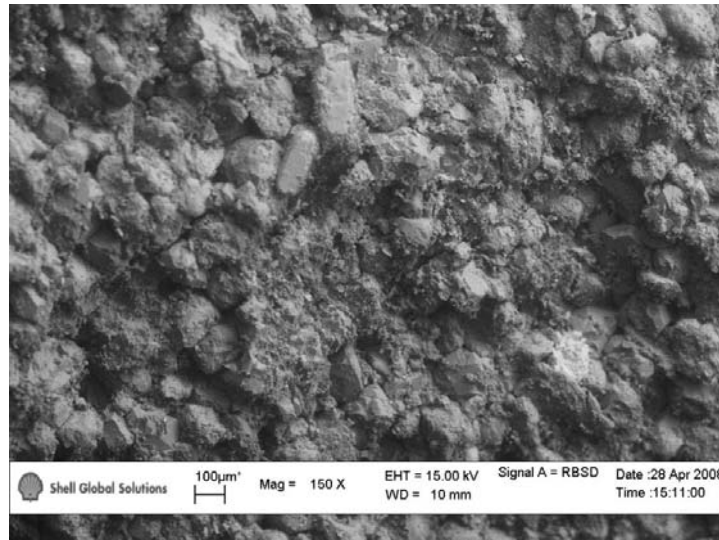


Figure 4: Schematic cross sections of the core faces used for ESEM and SEM analysis. At each face, 4 different regions were scanned.

(a)



(b)

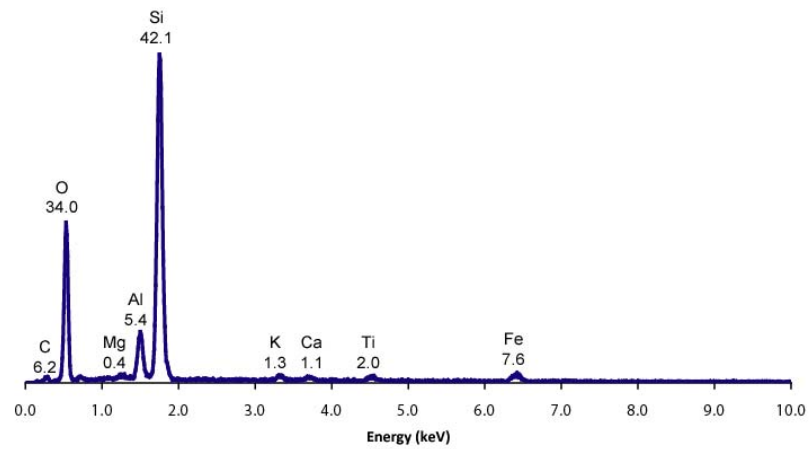
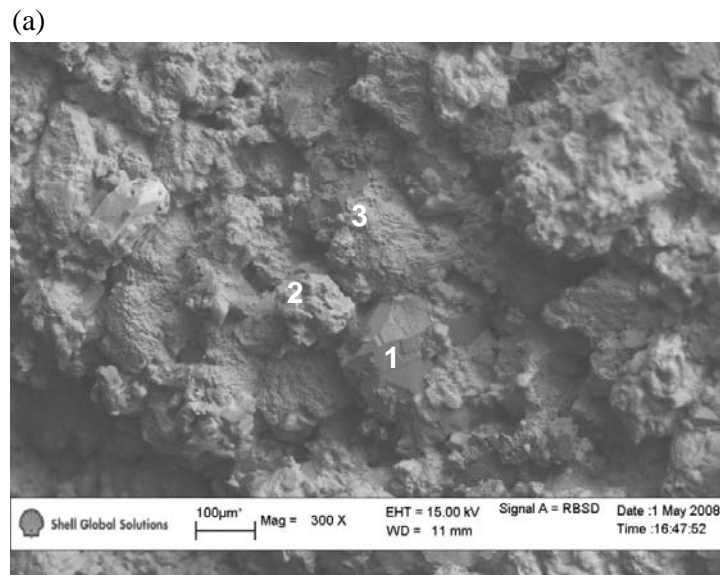


Figure 5: ESEM image (a) and elemental analysis spectrum (b) over region 1 on one face of a dry clean Berea core. In (b), the vertical axis is the relative intensity and the value on top of each peak is the weight percentage of that element.



(b)

Grain	Wt %						Total
	C	O	Na	Al	Si	Cl	
1	1.8	25.9	4.8	0.6	57.9	9.0	100
2	2.6	1.6	36.7	0.2	1.0	57.9	100
3	2.5	1.5	37.1	0.2	1.1	57.7	100

Figure 6: ESEM image (a) and elemental analysis data table (b) over region 1 on face 2 of the SC CO₂ flooded core. See text for explanation.

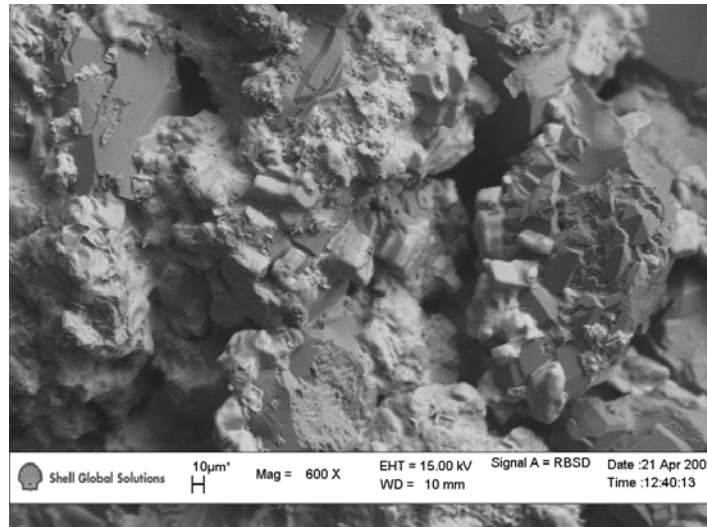


Figure 7: ESEM image over region 4 on face 2 of SC CO₂ flooded core. The pore throat was blocked by precipitated halite crystals.

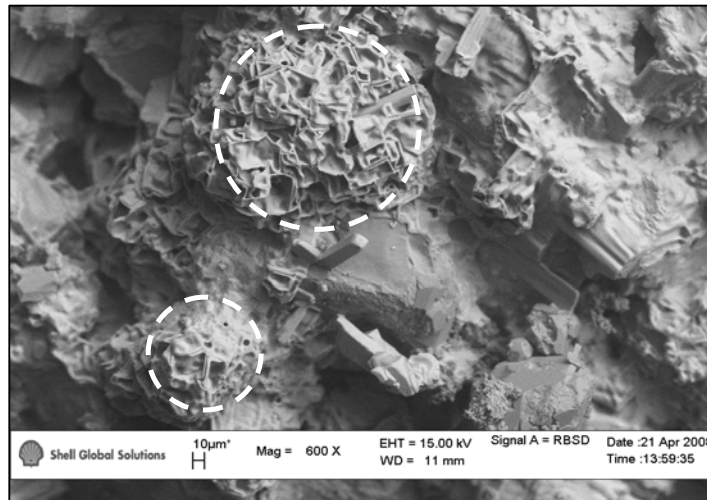


Figure 8: ESEM image over region 2 on face 3 of SC CO₂ flooded core. Hopper crystals are highlighted by write dash circles.