Multicomponent and multiphase CO2-brine system in microfluidic characterised “in-situ” by Raman spectroscopy

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Introduction

Today, climate changes caused by anthropogenic carbon dioxide emissions are one of the most important global issues. One of the most promising technologies that can manage the problem is carbon capture and Storage (CCS) [Friedmann, 2007]. However, there are a limited number of sites that can store enough CO_2 produced in industrial facilities. In particular, depleted oil and gas reservoirs, coal seams, and deep saline aquifers should be considered as appropriate geological locations to bury this type of greenhouse gas underground [Alkan et al., 2023].

Despite the excellent pore volume and good reservoir properties of structures in which liquid media exist, they are good candidates for CCS and there are many threats related to formation damage [Khurshid and Choe, 2013]. In most cases, salt precipitation clogs the channels and can cause a 3-15% decrease in porosity and reduce absolute permeability from 30% to 86% of the initial value, significantly decreasing the injectivity of carbon dioxide [Miri and Hellevang, 2016].

Salt deposition amid carbon dioxide storage in deep saline aquifers is a complex process. There are many aspects that affect precipitation, such as CO_2 solubility and its reactions with water, salinity, injection flow rate, capillary pressure, aqueous phase mobility, temperature, brine zone drying and rock interaction[Miri and Hellevang, 2016], [Kaszuba et al., 2003]. Mostly, halite is the main cause of clogging, and its occurrence has been extensively investigated [Smith et al., 2022]. However, precipitation of other compounds such as calcium, iron, magnesium carbonate [Orr, 2009], [Delerce et al., 2023], or even sulphates [Mohamed et al., 2011] is possible and could likely occur in some cases.

In geological conditions, brines can contain dozens of cations and ions, which could react with carbon dioxide in many configurations, but existing research is focused on simple systems that include single salt solutions (NaCl, $CaCl_2$) [Nooraiepour et al., 2021], [Bacci et al., 2011]. Therefore, a few aspects such as salinity and common ion effects or complex inorganic compounds are not counted but can be important for specific solutions. Our work sheds light on this problem. We used the microfluidic system and Raman spectroscopy to trace the carbon dioxide/brine (various salts and concentrations) interactions. The combination of these two methods allowed us to observe and collect data on both reactive CO_2 flow and precipitation products.

Materials and Methods

To obtain conditions that are as close as possible to thermodynamic properties inside deep saline aquifers, we have built a microfluidic platform; the scheme is shown in Figure 1. We have used a commercial set (from Micronit) for high-pressure applications. The supply of fluids was applied by high-pressure pumps and a backpressure outlet, to maintain a constant pressure gradient. Borosilicate microfluidics used different geometries, from linear, long channels through regular porous structures to rock-like porous structures with hydrophilic and hydrophobic coatings. Additionally, a Raman probe, with an excitation wavelength of 532 nm, was installed on moving rails precisely driven by programmed stepper motors, which allowed one to trace changes in composition through the microfluidic in any position or path. Our platform was also integrated with high-speed microscope cameras, pressure gauges, and temperature gauges. Pressure was applied from 6 MPa to 10 MPa at laboratory temperature (22°C), various salt concentrations by weight% (for NaCl 5% - 25%, K_2SO_4 1%-10%, $CaCl_2$ 1%-10% and $MgSO_4$, $MgCl_2$, $FeCl_2$, $FeCl_3$, $MnCl_2$, $Sr(NO_3)_2$ 1%-5%), 99,99% pure carbon dioxide and distilled water.

First, a set of concentrated solutions of pure salts was prepared in beakers and mixed shortly before use. Then the concentration of compounds was calculated and 30 ml of brine was loaded onto the syringe pump. Before measurements, the platform was sluiced with 20 ml of brine. After that, the pressure in the system was increased to the assumed value and the valves were closed. Then the pump with CO_2 was started, both fluids were started mixing. The Raman probe collected data from a specific point; however, if precipitation occurs, the crystals inside the microfluidic were scanned. Immediately after the procedure, the system was flushed with 100 ml of distilled water. In case of crystallite occurrence, microfluidic and streamlines were sluiced with citric acid or hydrochloric acid solution. The mixture tests lasted no more than 1 hour.

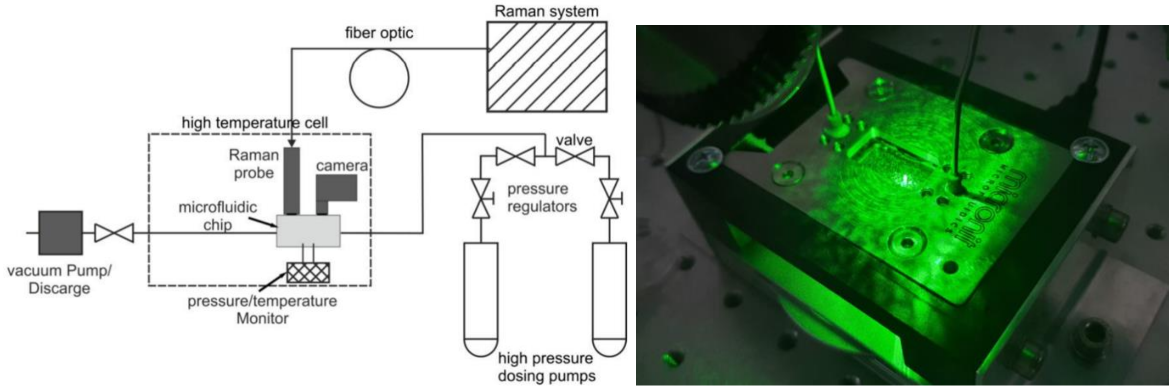

Figure 1 *A scheme of the microfluidic platform for the precipitation of salts in brines amid super critical* CO_2 *flow (left). System under Raman spectra collection (right).*

Results and Discussion

In our work, we present the usefulness of prepared to investigate salt precipitation while carbon dioxide is injected, as shown in Figure 2. Immediately after adding CO2 at high pressure (6 MPa) to the uncoated (hydrophilic) microfluidic filled brine (20% wt%), a few crystals occurred. It is worth mentioning that salt precipitation has not occurred in random places but on the grain boundaries and in bottlenecks despite inert borosilicate glass properties. Within 30 minutes, the crystals have grown and occupy a significant part of the porous space. After the test, we have noticed a decrease in permeability (at the beginning there was 2 D, due to the producer's information) to the extent that it was difficult to pump CO_2 even applying 10 MPa and the flow has never reached the initial value.

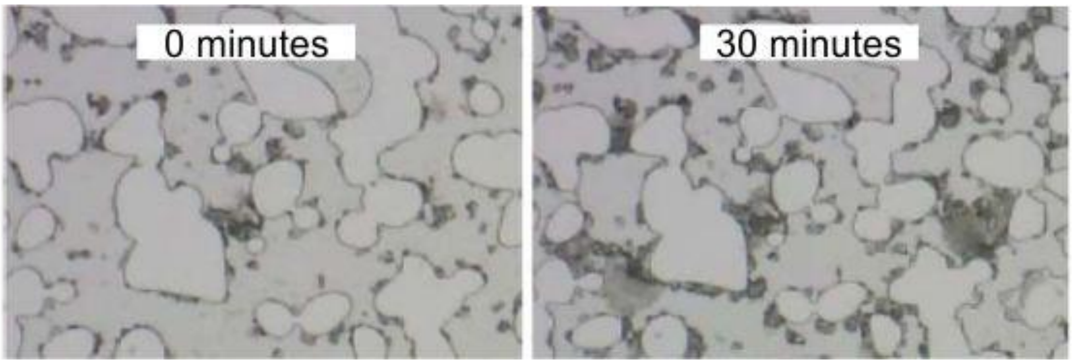

Figure 2 *Stills from the video during the carbon dioxide and brine reaction in the porous rock-like microfluidic.*

We have characterized the carbon dioxide brine system in microfluidics by Raman spectroscopy. Due to the optical transparency of the model, we have obtained spectra shown in Figure 3 and Figure 4. The former is from light-wave scattering of CO_2 [Anderson, 1977] with characteristic bands around the 1285 cm^{-1} and 1386 cm^{-1}, the latter represents a signal around 1064 cm^{-1} of precipitated crystals inside microfluidic channel occurring in

NaCl (20% by weight%) solution and indicates the existence of carbonate (natrite) [Bishop et al., 2021].

However, only the most concentrated solutions were sensitive to precipitation when mixed with carbon dioxide, especially in relatively short periods (up to an hour), although the kinetics of some reactions is slow and the process could even last a few days [Saldi et al., 2009]. However, this means that crystals should occur far from the well and that this would not affect the injectivity significantly. In the case of magnesite or dolomite in $CaCl_2$, MgSO4 and $MgCl_2$ solutions, precipitation also did not appear. It is likely that the temperature has been too low to exceed energy activation [Saldi et al., 2009].

The spectra for precipitated carbonate from sodium chloride solution are slightly shifted in comparison to the literature data, however, the fine structure of fast-reacted compounds has affection on the spectra shape [Bishop et al., 2021].

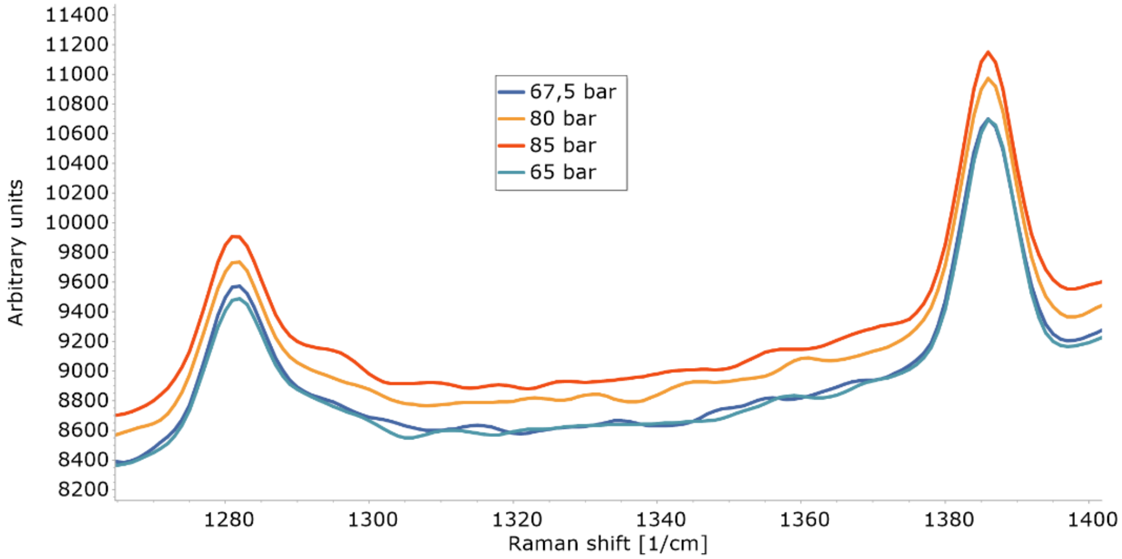

Figure 3 *Raman spectra of carbon dioxide at various pressure values (65-85bar) in microfluidic at 22 ° C.*

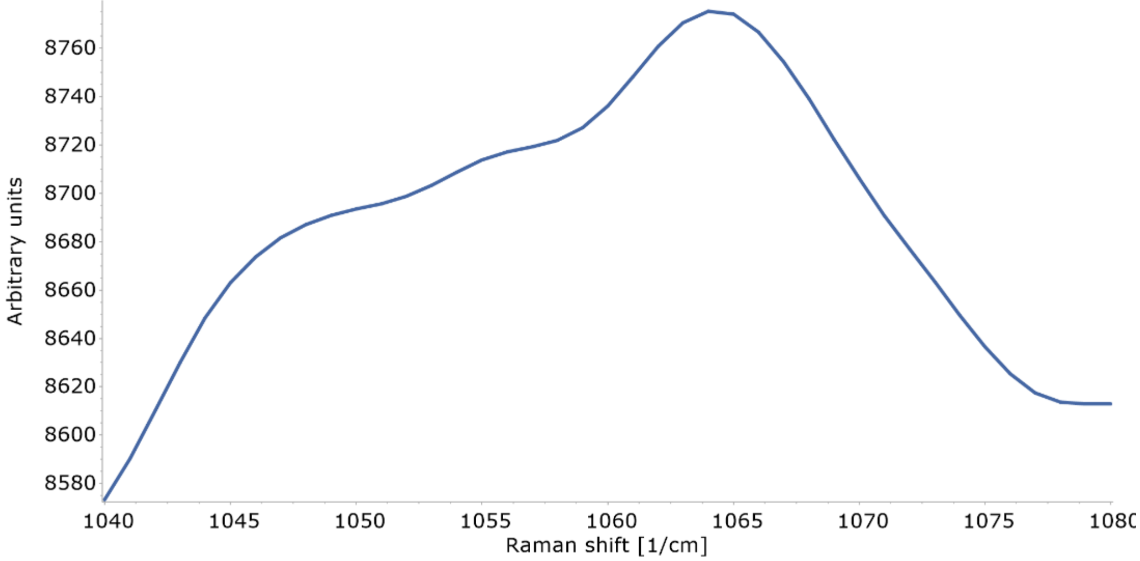

Figure 4 *Raman spectra of precipitated carbonates with a characteristic Raman shift at ~1064* cm^{-1}*.*

Conclusions

Our work showed a complex approach to salt precipitation in brine amid CO_2 injection. We proved the usefulness of our platform for investigating CCS problems related to the thermodynamics of such systems ability to identify compounds like carbon dioxide, ions, and salt deposition in different structures of microfluidic devices. The data refer to the salt precipitation problem in high salinity aquifers. Due to our results, salt sedimentation in pores could significantly reduce the injectivity of the well, especially when it would exist in the vicinity of the wellbore; simultaneously, it is a complex process with numerous variables, chemical and physical. Additionally, precipitated salts decrease the volume of the reservoir, but do not store carbon dioxide.

Acknowledgements

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