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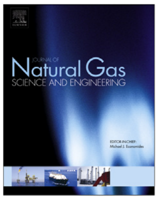

# $CO_2$ storage capacity in laboratory simulated depleted hydrocarbon reservoirs – Impact of salinity and additives

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ABSTRACT

A number of depleted hydrocarbon reservoirs in Alberta, Canada provide an opportunity for enhanced $CO_2$ storage density because the reservoir conditions favor $CO_2$ gas hydrate crystal formation. A laboratory simulation study was conducted to study this process and assess the impact of injection method, presence of additives and salinity on the $CO_2$ storage density. Results indicated constant flow rate followed by constant pressure $CO_2$ injection enhanced $CO_2$ hydrate formation compared to constant pressure gas injection. It was noted that 85 % of the original water in the reservoir formed $CO_2$ hydrate after 24 h experiments and that figure rose to 90 % after a 120 h period. Certain amount of tapioca starch and Polyvinylpyrrolidone (PVP) added to the water prevented the hydrate formation in the earlier stage (delay of the onset of hydrate nucleation but subsequently more $CO_2$ was stored as hydrate in the reservoir compared to the inhibitor-free systems. Hydrate formation in saline reservoirs was reduced compared to pure water conditions. The hydrate technology provides an improved $CO_2$ storage density.

## 1. Introduction

The injection of $CO_2$ in a chamber containing a water saturated porous medium may result in the formation of hydrate crystals when the pressure/temperature conditions are within the hydrate stable region. This phenomenon is of interest to the injection of $CO_2$ or $CO_2/N_2/O_2$ mixtures (concentrated flue gas) in depleted hydrocarbon reservoirs. Field projects in Australia and Europe demonstrated that geological storage of $CO_2$ in depleted oil and gas reservoirs is a strategy with significant potential to mitigate climate change concerns arising from the emission of $CO_2$ from the combustion of fossil fuels (Bickle, 2009; Jenkins et al., 2012; Haszeldine, 2009). The storage potential in depleted oil and gas fields worldwide is estimated to be 400 to 900 Gt of $CO_2$ (Gunter et al., 1998; Shukla et al., 2010). A porous and permeable reservoir in the Sleipner West gas field in the North Sea was employed to store $CO_2$ (Holloway, 2005). Similarly, the Otway project demonstrated the long term storage of $CO_2$ in a gas filed (Jenkins et al., 2012). It should be noted that when $CO_2$ gas is injected into a low permeability reservoir the risk of hydrate crystal formation and or freezing of residual water in the injection system due to Joule-Thomson cooling needs to be assessed (Oldenburg, 2007).

Because at storage conditions $CO_2$ may form solid gas hydrates the potential exists for exploiting this occurrence owing to the fact that hydrates contain significantly more gas at the same volume compared to the gas state. The gas hydrates have large gas storage potential. It may contain approximate 160 $m^3$ of gas in 1 $m^3$ itself at standard pressure and temperature condition (Englezos, 1993; Sloan and Koh, 2008). Storage of $CO_2$ as gas hydrates was proposed in 2004 and the possibility of this concept has been discussed (Shaw, 2004; Wright et al., 2008; Cote and Wright, 2010). Gas hydrates are crystalline compounds consisting of water and other molecules such as $CO_2$, light hydrocarbons, $H_2S$, $SO_2$ and other molecules (Davidson, 1973). Interestingly, the idea of storing natural gas as hydrate has been presented as early as in 1945 and related applications were proposed (Miller and Strong, 1945; Evrenos et al., 1971; Hatzikiriakos and Englezos, 1994).

The concept of storing $CO_2$ at hydrate formation conditions was demonstrated in the lab and it was shown that the water conversion is not complete and depends on the $CO_2$ injection mode (Sun and Englezos, 2014). This reflects the possibility for process optimization. Natural gas and oil reservoirs contain electrolytes and thus the salinity of the reservoir may be a consideration since it will affect the hydrate phase equilibrium conditions. Dissolved electrolytes were also reported to slightly reduce the water conversion

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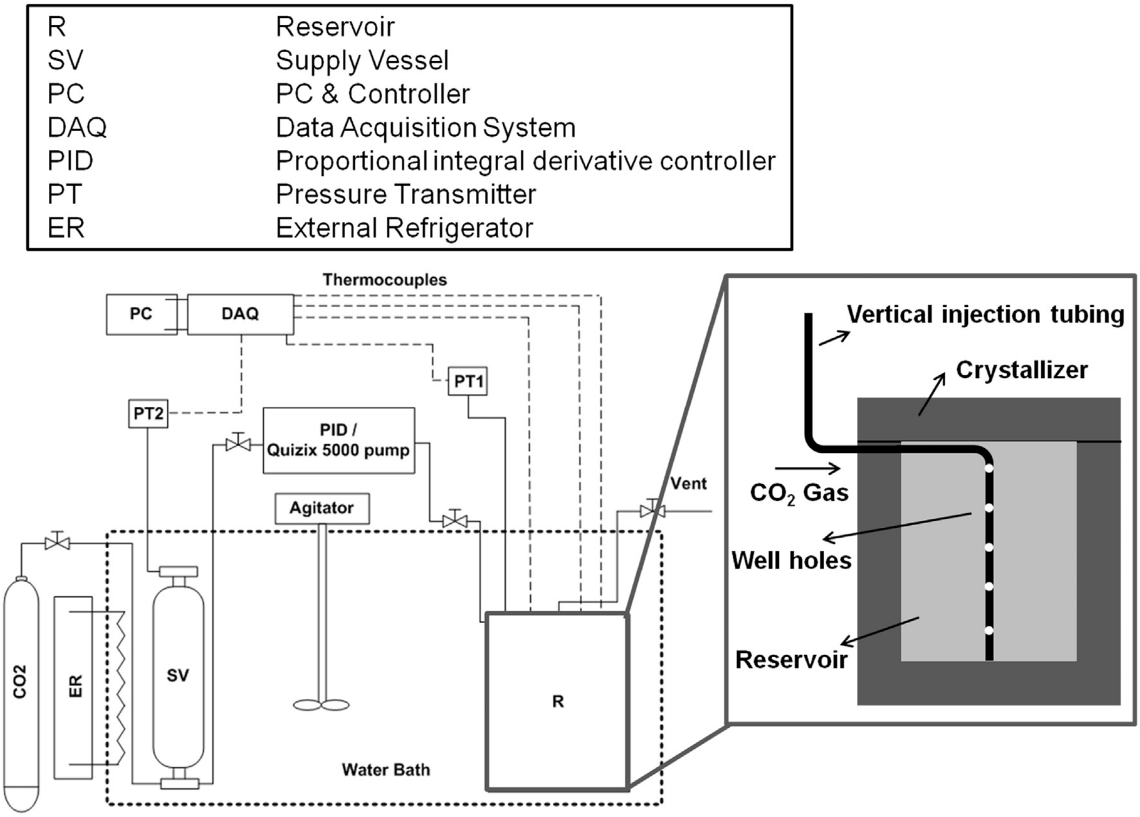

**Fig. 1.** Schematic of the apparatus for $CO_2$ gas injection into a reservoir simulating $CO_2$ injection into a depleted hydrocarbon reservoir.

to hydrate in porous media (Yang et al., 2014). Our focus is on hydrocarbon reservoirs in Alberta, Canada but the conclusions can be generalized to reservoirs elsewhere in the world. Canada Geological Survey reported up to 4 wt % salinity is existing in some of the Alberta reservoirs which have $CO_2$ storage potential as hydrate form (Cote and Wright, 2013).

While hydrate formation kinetics was found to be enhanced with decrease in the particle size fraction of porous medium (Bhattacharjee et al., 2015) in a given hydrate reservoir the porous medium is given. Polyvinylpyrrolidone (PVP) and tapioca starch are known to prolong the hydrate formation induction time and reduce the hydrate crystalline growth rate (Lee et al., 2007; Daraboina et al., 2011; Sharifi et al., 2014). A delay in hydrate nucleation may reduce the possibility of undesirable hydrate formation in the injection system but over long periods of time may lead to improved hydrate conversion (Sharifi and Englezos, 2015).

In this work a vertical injection procedure that simulates possible field application was followed. The porous medium of the laboratory reservoir was sand and it was saturated by water uniformly. The initial water saturation of the porous medium was determined. $CO_2$ gas was injected into the lab reservoir under constant pressure or constant flow rate followed by constant pressure injection method through a vertical tubing. The $CO_2$ consumption and gas storage capacity was determined at conditions that investigated the impact of salinity and the additive.

## 2. Material and methods

The $CO_2$ gas was obtained from Praxair and had 99.5 % purity. Sodium Chloride (NaCl, Fisher Scientific), Polyvinylpyrrolidone (PVP, average molecular mass of 3.5 kDa, Acros Organics) and tapioca starch (average molecular mass of 3 mDa, National Starch ULC) were used. Silica sand was obtained from Sigma–Aldrich with the average diameter of 329 μm and porosity of 0.35. The simulated reservoir (sand bed) was contained in a stainless steel high pressure chamber (crystallizer) that is described elsewhere (Linga et al., 2009; Sun and Englezos, 2014). Fig. 1 shows the apparatus of gas injection and hydrate formation. The crystallizer was immersed into a temperature controlled water bath. An external chiller (VWR Scientific) was employed to adjust the water bath to have a required temperature. Pressure transmitters (Rosemount) with a maximum uncertainty of 11.25 kPa (0.075 % of the span 0–15 000 kPa) were connected to the crystallizer and a supply vessel which was also located in the water bath. Three thermocouples (Omega) with the uncertainty of 0.1 K were located in top, middle and bottom positions of the sand bed to measure the inner temperature. A PID controller and a control valve (Fisher Bauman) were employed to regulate the pressure and ensure a constant pressure gas injection. A Quizix Q5000 precision metering pump (Chandler Engineering) was employed to deliver gas into the simulated reservoir under constant flow rate. A data acquisition system and the LabView 8.0 software (National Instrument) were used to control the PID valve and collect pressure and temperature data to a computer every 20 s.

Fig. 2 shows the vertical injection tube used for gas injection. The tube has four 1.0 mm diameter holes in each one of 5 positions located at a distance of 2.5 cm from each other. The end of the vertical tube was sealed. The vertical tube was located in the center of the sand bed to deliver $CO_2$ gas into the simulated reservoir. Gas injection under constant pressure (a), constant flow rate followed by constant pressure (b) into pure water reservoir, gas injection under constant flow rate followed by constant pressure into 1 wt % PVP (c), 3 wt % PVP (d), 0.5 wt % (e), 1 wt % (f) and 3 wt % tapioca starch (g), 2 wt % saline (h) and 4 wt % saline (i) reservoir were conducted in this work. The list of experiments is given in Table 1.

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