

EXPERIMENTAL INVESTIGATION OF COOLING EFFECTS RESULTING FROM INJECTING HIGH PRESSURE LIQUID OR SUPERCRITICAL CO₂ INTO A LOW PRESSURE GAS RESERVOIR

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ABSTRACT

Depleted natural gas reservoirs are being seriously considered as potential sinks for geologic carbon sequestration. Several factors make depleted gas reservoirs attractive candidates for long term CO₂ storage. Most natural gas reservoirs have demonstrated sealing capacity, as evidenced by long term containment of hydrocarbons. As a result of prior development and production activity related to hydrocarbon recovery, these fields are relatively well characterized and understood. Existing infrastructure of wells and pipelines provides additional advantage.

The lack of industry experience in injecting large quantities of CO₂ into heavily depleted gas reservoirs, however, contributes uncertainty regarding the viability of the concept. During CO₂ injection into a low pressure natural gas reservoir, pressure decreases with distance from an injection well as gas expands into the reservoir. The Joule-Thomson effect is the adiabatic cooling or heating that accompanies the expansion of a real gas. If Joule-Thomson cooling during this expansion is significant, injectivity could be affected by formation of hydrates or freezing of connate water.

The focus of this study was to evaluate phase behavior and potential impact of Joule-Thomson cooling effects during injection of liquid or supercritical CO₂ into pressure depleted systems. The intent was to mechanistically model conditions considered in the design of CO₂ injection operations in a pressure-depleted offshore gas reservoir. Tests were performed in an oven using a 50 ft.-long insulated tube packed with 156 mD sand. The sand was initially saturated with 80% methane and 20% brine. Sensors measured temperature and pressure along the length of the sand-packed tube. Each experiment began by abruptly opening a valve to flood the sand-packed tube with room-temperature CO₂ from a 3,500 psig constant-pressure source. At the downstream end of the tube, pressure was maintained at the starting pore pressure magnitude (200, 300, or 500 psig).

The following conceptual model is offered from experience gained in this effort. Initially, when injecting cold, high pressure CO₂ into a hot low pressure environment, heat transfer from the surrounding reservoir environment will mask or counter Joule-Thomson gas expansion cooling effects. The most significant early-time cool down effect may be the result of injecting a cold fluid into a hot reservoir. As the near-well region cools and the

cool zone extends deeper into the reservoir, injected CO₂ may remain in the liquid phase for greater and greater distances into the reservoir. The worst-case scenario will occur if, when, and where CO₂ changes from liquid to vapor. This will occur with pressure and temperature below the critical point (1070 psia and 87.7 °F). A pronounced cooling effect accompanies the phase change from liquid to vapor. When and where this occurs, if the rock is still partially saturated with brine, the potential will exist for forming ice or hydrates that may significantly decrease CO₂ injectivity. Simulation modeling efforts are ongoing to translate results into more meaningful reservoir-scale conclusions.

INTRODUCTION

For storage or sequestration, the possibility of injecting high-pressure CO₂ into a large pressure-depleted gas reservoir may seem attractive because such a reservoir could store significant volumes of CO₂. However, expansion of high-pressure CO₂ into a low-pressure reservoir may cause cooling owing to the Joule-Thomson effect, which in turn might promote ice or hydrate formation and adversely affect CO₂ injectivity.

An application of current interest involves collecting and transporting significant daily volumes of CO₂ for storage in depleted gas reservoirs. A candidate reservoir is an offshore field with 200 to 500 psig pore pressure, 198 °F temperature, 200 mD sandstone rock with 20% brine and 80% methane fluid saturations. At bottom-hole conditions, estimates are that the CO₂ would enter the reservoir from the well bore at 3,500 to 5,000 psig pressure and 60 to 110 °F temperature. When CO₂ injection begins, at some distance from the well bore, the CO₂ will transition to gas. As a result of significant reduction in pressure, Joule-Thomson cooling is anticipated. The magnitude of cooling and whether it will take place before or after brine is dehydrated from the near-well bore region is unknown. A worst-case scenario would be the formation of hydrate or ice that would impair CO₂ injectivity.

The intent of this project was to investigate what happens soon after opening a valve to flood 3500 psig CO₂ at room temperature into sand saturated with methane and brine at 200 to 500 psig and 198 °F. A hypothesis was that Joule Thomson cooling might immediately form hydrate or ice within the porous media, severely reducing CO₂ injectivity.

Joule-Thomson Effect

The Joule-Thomson phenomenon is named after James Joule and William Thomson (1st Baron Kelvin). They identified the effect in the mid-1800's from experiments in which the change in temperature of gas was noted as it expanded through porous media. For any given pressure, a real gas has a Joule-Thomson inversion temperature. For the given pressure, if the real gas is expanded from an initial temperature that is greater than the inversion temperature, the gas cools during expansion. Beginning with temperature less than the inversion temperature, gas warms upon expansion.

One can estimate adiabatic cooling that might occur during expansion of a real gas by: **(1)** plotting enthalpy versus pressure and temperature for the gas, **(2)** identifying enthalpy at

initial pressure and temperature, and (3) inferring temperature upon expansion to lower pressure along a path of constant enthalpy. This is illustrated by the plot of Figure 1. The figure was constructed using data from Lemmon et al (2005). From starting conditions of 3,500 psia and temperature of 198 °F, final temperature upon constant enthalpy expansion to 200 psia is – 20 °F. Note that regions of significant change in enthalpy with pressure on Figure 1 correspond to CO₂ liquid-to-vapor phase transitions.

In the example of Figure 1, constant enthalpy expansion assumes steady-state conditions and that there is no transfer of external heat into the system. In practice, heat transfer will occur -- when hot and cold bodies are placed together, the hot ones get cooler, and the cold ones get warmer. Thus, we might expect transfer of heat from the reservoir environment to the CO₂, with extent of transfer changing with time.

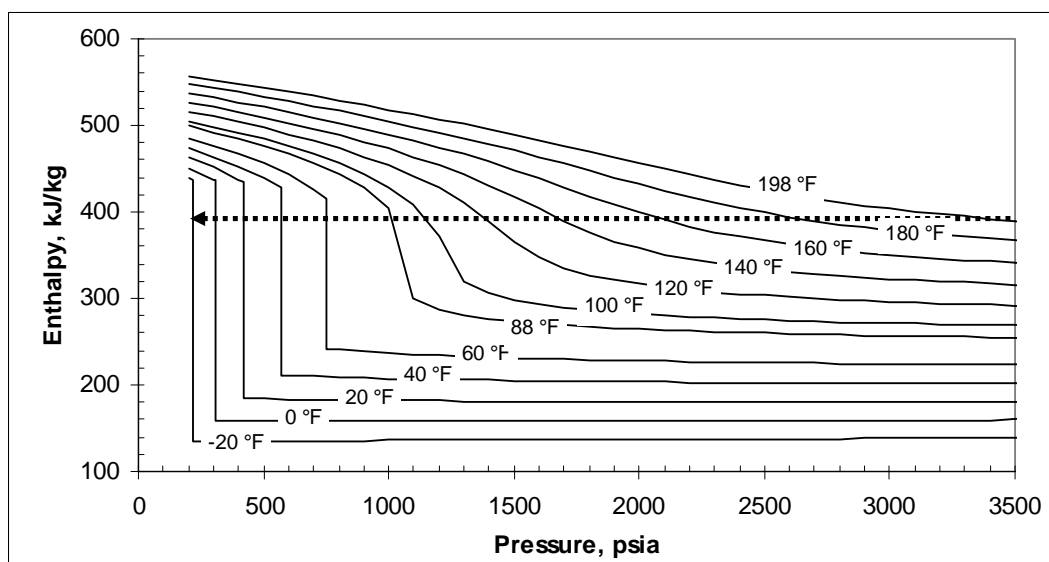


Figure 1. CO₂ enthalpy versus pressure and temperature.

EXPERIMENTAL

Test Designs and Preparations

Laboratory tests were designed to examine what happens immediately after opening a valve to flood 3500 psig room temperature CO₂ into low-pressure reservoir-like material. CO₂ properties (density, viscosity, and enthalpy) were obtained from Lemmon et al (2005). Preliminary calculations estimated pressure profiles and positions where CO₂ phase change would likely occur in different-sized samples. This evaluation revealed that a long sample would be best suited for causing interesting effects to occur at reasonable distance from the outlet end of the sample. It was decided to conduct tests using a “slim tube” – a sand-packed ¼ inch outside diameter stainless steel tube jacketed with insulating material. To provide a reasonable model, sand permeability in the 100 to 200 mD range was desired. Two sands were blended to achieve permeability in this range. The sand was packed into

insulated ¼-inch outside diameter stainless steel tubing. The tubing was bent into a coil so that it could be placed within an oven. Pressure transducers and thermocouples were affixed according to the spacing of Table 1. For the entire length of the tube, average permeability of the sand to gas was 156 mD.

Pressure/Temperature station	Distance from outlet
2.	1524.0 cm (52.6 ft)
3.	1000.0 cm (35.4 ft)
4.	762.0 cm (27.7 ft)
5.	304.8 cm (12.6 ft)
6.	243.8 cm (9.8 ft)
7.	121.9 cm (5.1 ft)
8.	30.5 cm (1.3 ft)
9.	15.2 cm (0.7 ft)
10.	10.2 cm (0.5 ft)

A valve was placed at the upstream end of the tube to initially separate injection fluids from fluids within the sand. Pressure relief devices were placed downstream of the inlet and upstream of the outlet to provide pressure relief and safe venting of fluids in case of over-pressurization. A backpressure regulator was placed at the downstream end.

For the first test, the sand-packed tube was vacuum saturated with brine. Pore volume was determined. The sand was flooded with methane at room temperature and with 200 psig backpressure. At several times during the flood, gas permeability was calculated from flow rate and pressure profile data while average saturation was calculated from measurements of produced brine volume. Gas relative permeability versus normalized gas saturation data were fitted with a Corey equation. Gas permeability corresponding to $S_w=0.2$ was calculated from the Corey fit to the data. The gas flood continued as temperature was increased to 198 °F. At 198 °F, brine saturation decreased through displacement of either brine or water vapor. Methane injection was stopped when permeability equaled that predicted from the Corey equation for $S_w = 0.20$. Thereafter, sufficient time was allowed for methane to drain through the backpressure regulator in achieving uniform pore pressure.

Similar procedures were used to re-initialize saturation before subsequent tests. Backpressure was set to the desired test pressure. The sand was flooded with brine at room temperature, and then flooded with methane at 198 °F, until average permeability of equaled the target permeability with $S_w = 0.2$. For room temperature floods, the sand was cooled to room temperature. Additional methane was injected when necessary to increase average pore pressure to the desired pressure condition before proceeding with the CO₂ flood.

As a guide toward understanding what to expect from CO₂ floods, calculations were performed to predict steady-state CO₂ pressure and volumetric flow rate profiles for conditions of 3500 psig inlet pressure, room temperature and 198 °F CO₂ temperature, and outlet or backpressure conditions of 200 and 500 psig. Anticipated trends are shown in Figures 2 and 3. From phase behavior, we observed the following:

- At 71 °F, liquid to vapor transition is expected at 850 psig. With 200 psig backpressure, transition is expected at a distance 249 cm from the outlet. With 500 psig backpressure, transition is expected at a distance 199 cm from the outlet.
- At 198 °F, supercritical to vapor transition is expected at 1055 psig. With 200 psig backpressure, transition is expected at a distance of about 171 cm from the outlet. With 500 psig backpressure, transition is expected at a distance of about 142 cm from the outlet.

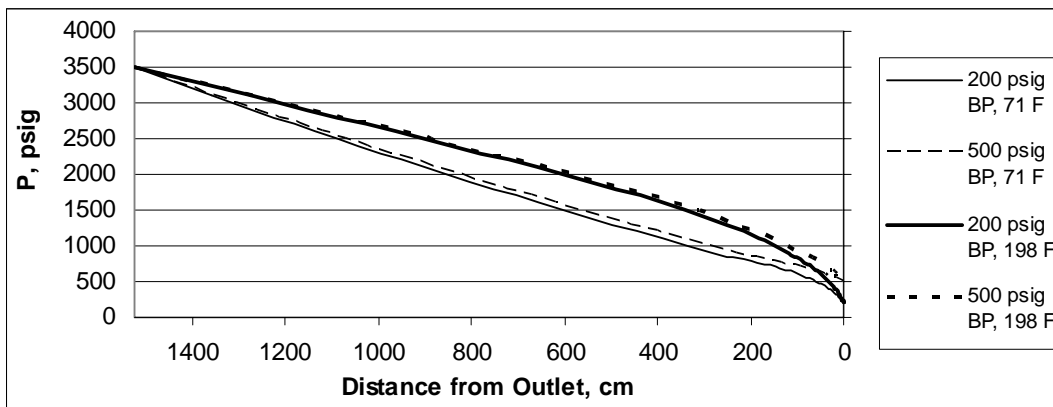


Figure 2. Anticipated pressure profiles.

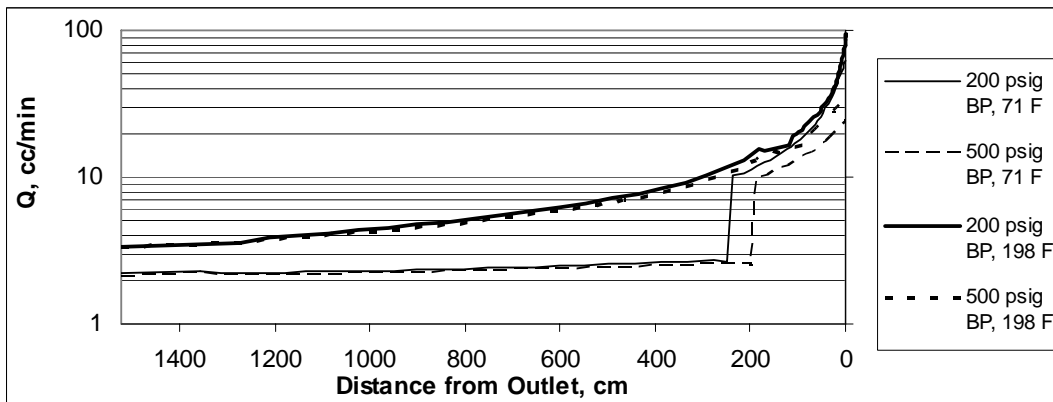


Figure 3. Anticipated flow rate profiles.

CO₂ Floods

Each test began by abruptly opening the upstream valve to flood the sand-packed tube with CO₂ from a 3,500 psig constant pressure source. Three scenarios were tested:

- **Scenario A** — room temperature 3500 psig CO₂ injection into porous media of low pressure and 198 °F temperature
- **Scenario B** — room temperature 3500 psig CO₂ injection into porous media of low pressure and 198 °F temperature followed by continuous injection while cooling to room temperature
- **Scenario C** — room temperature 3500 psig CO₂ injection into low-pressure room temperature porous media

At most, 3.5 pore volumes of CO₂ were injected through the sand during a given test. This was essentially a pump capacity limitation. We used a Quizix C-6000-10K pump in constant pressure delivery mode for CO₂ injection. Although each of the two pump cylinders could hold 275 cm³ of CO₂, when filling the pump with CO₂, it was necessary to use one of the cylinders to compress and transfer CO₂ to the second cylinder (because the CO₂ bottles used to fill the pump were only of 870 psig initial pressure). By this technique, the volume of CO₂ at 3,500 psig that could be loaded into the pump was approximately 310 cm³.

RESULTS

Except for cases in which ice or hydrate formed, pressure and rate profiles were similar to predictions of Figures 2 and 3. In each case, nothing catastrophic happened immediately upon opening the upstream valve to slam the upstream sand face with 3,500 psig CO₂. Although the leading edge of the CO₂ front initially underwent severe reduction in pressure from 3,500 psig to the initial average pore pressure within the sand (200, 300, or 500 psig), pressure rebounded very quickly as the flood front progressed into the sand, until a pseudo steady-state pressure profile developed.

Figures 4 and 5 show pressure and temperature histories from one of the **Scenario A** tests illustrating this effect. Only data for the first 100 minutes of flow are shown because thereafter pressures and temperatures remained stable. Consider the position 1000 cm from the outlet in Figures 4 and 5. Beginning with 200 psig pressure, by the third minute of the test, pressure had increased by 2000 psig, and rather than having experienced a cooling effect, temperature increased by several degrees at this location.

Methane at the leading edge of the flood front was abruptly compressed because the permeability of the sand moderated the rate at which methane was able to be displaced ahead of the flood front. So it appears that at the inlet sand face, the cooling effect from CO₂ expansion was also countered by a warming effect from methane compression. Some tests showed an immediate slight increase in temperature at the upstream sand face immediately after beginning the CO₂ flood, presumably because of the nearly instantaneous compression and pressurization of methane in that region. Temperature profiles from the **Scenario C** test of Figure 8 also show that the inlet temperature increased as a result of high pressure CO₂ injection.

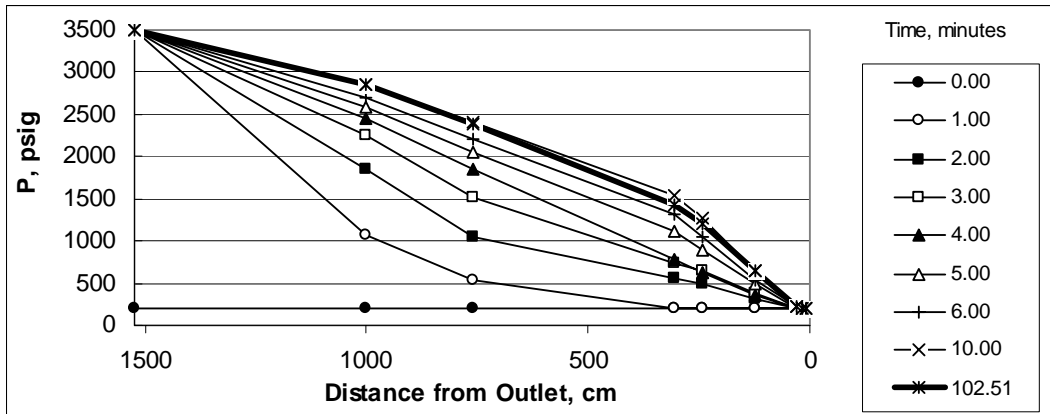


Figure 4. Pressure profiles during a **Scenario A** test.

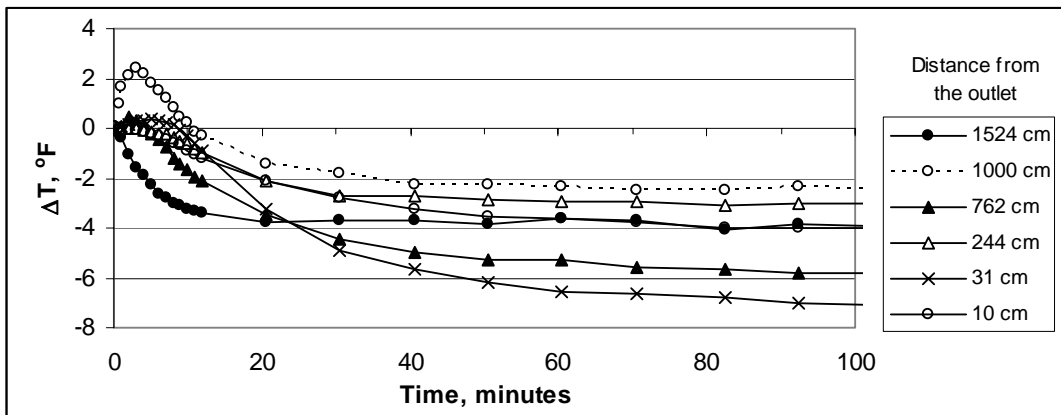


Figure 5. Temperature histories during a **Scenario A** test.

Key results from the three test scenarios are:

- Scenario A** — Appreciable cooling effects were not observed. Although the tubing was insulated, apparently the insulation was not sufficient to prevent heat transfer to the sand from the 198 °F environment within the oven. It appears that heat transfer from the external environment (oven) masked the Joule-Thomson cooling effect. For this reason, data from these tests should be considered qualitative rather than quantitative and should not be used to estimate Joule-Thomson coefficients or cooling rates. Temperature profiles of the sand reduced by less than 10 °F with approximately 3.5 pore volumes of CO₂ injection. We speculate that the cooling effect observed was mostly related to injecting cool fluid (liquid CO₂) into a hot system. For example, one could interpret that the temperature histories of Figure 5 show that the injected fluid receives heat from the external environment as it flows through the tube, moderating temperature change at the downstream end of the tube. From Figure 1, one would expect Joule-Thomson effects to be more pronounced with the lower pressures.

- Scenario B** — During cool-down portions of these tests, as temperature and pressure dropped below the critical point, significant cooling was observed when and where CO₂ changed from liquid to vapor. Temperatures as low as 30 °F were measured close to where the phase change occurred. Flow impairment was not observed, although temperature and pressure conditions appear to be favorable for causing hydrates. Why ice or hydrate did not form is unknown, but possibilities include: (a) an absence of brine due to previous flooding, (b) an increase in local brine salinity as a result of having vaporized some of the water from the brine, or (c) the displacement of methane, meaning that lower temperatures would be needed for CO₂ hydrate to form than those at which hydrate would form when methane is present. Trends of Figure 6 from Wegener (2007) show that hydrate of water and methane or methane and carbon dioxide can form at higher temperatures compared to hydrate consisting of only water and carbon dioxide. Salinity is shown to suppress the temperature at which hydrate forms.

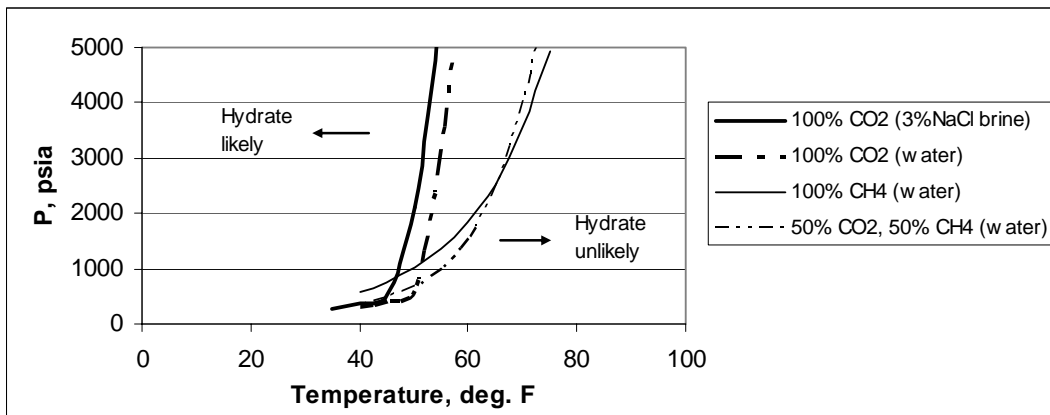


Figure 6. Static pressure and temperature conditions conducive to forming hydrates.

- Scenario C** — These tests were a dramatic demonstration of Joule-Thomson cooling and flow impairment because of ice or hydrate blockage. Almost immediately after a pseudo-steady state pressure profile developed, near the location where CO₂ changed from liquid to vapor, significant temperature reduction and flow impairment occurred. For example, results from a **Scenario C** test are provided in Figures 7 and 8. Ten minutes into the test, a pseudo-steady-state pressure profile had developed. Within minutes, blockage that impaired flow formed at about 122 cm from the outlet as shown by the nearly step-change in pressure across the plug and reduced temperature in that vicinity. Note that temperature measurements were only available at thermocouple locations. The exact temperature where the plug occurred is unknown. Mass flow rate was reduced by 98%. Even with 98% reduction in mass flow rate, there was enough CO₂ flow through the ice or hydrate plug to sustain the blockage. The blockage was removed by heating the system. In some tests, temperatures as low as 30 °F were noted near the place where CO₂ changed from liquid to vapor. Because the blockage formed

after less than a pore volume of CO₂ injection, it could have been a hydrate of methane, CO₂, and brine.

An important point to keep in mind is that, when a flowing gas expands, Joule-Thomson cooling may significantly decrease local temperature. This concept should be taken into account when making predictions from static test data such as that of Figure 6. Figure 6 predicts that methane or CO₂ hydrates are unlikely at 71 °F with pressures from 3,500 psig to 200 psig. Yet each **Scenario C** test, conducted at 71 °F with *flowing* pressures from 3,500 psig to 200 psig, showed dramatic cooling and ice or hydrate blockage effects because of significant Joule-Thomson cooling.

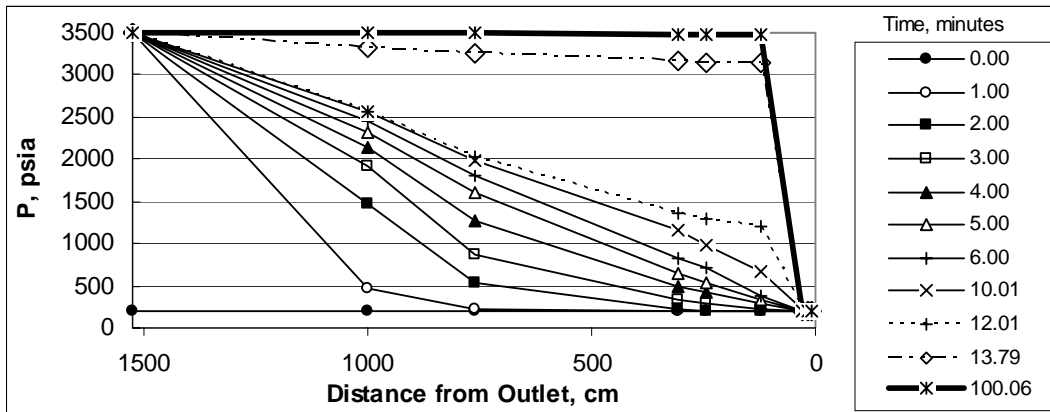


Figure 7. Pressure profile during a **Scenario C** test.

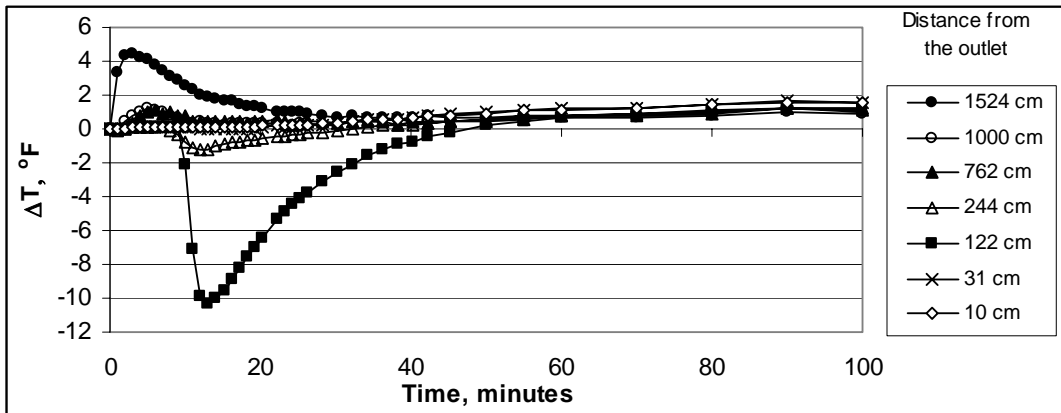


Figure 8. Temperature profile during a **Scenario C** test.

DISCUSSION

The most noteworthy cooling effect observed in this experimental program was observed with CO₂ phase transition from liquid to vapor. The worst case scenario for formation of hydrate or ice is when the porous media remains partially saturated with brine at the place

where liquid CO₂ changes to vapor. Blockage from ice or hydrates, once formed, seem to be self-replenishing. Continuous flow with large pressure drop across the ice or hydrate plug contributed to a very significant and localized Joule-Thomson cooling effect. As a result, the blockage did not “go away” over a period of several days until the sand was heated.

Because of heat transfer from the external environment, our lab tests probably do not reveal the true extent of Joule-Thomson cooling. It seems unlikely that Joule-Thomson cooling will initially cause loss in reservoir injectivity, but rather, problems may occur later — after injection of significant volumes of cold fluid have locally cooled the near-wellbore region. The main contribution of this investigation may be a confirmation that if one can understand and model thermodynamics for the reservoir storage scenario, one will be able to predict whether injection will be successful or problematic.

Thermodynamics of the reservoir injection scenario are complex. Near well bore compression of CH₄ may cause temperature to initially increase at the sand face. Because of this compression-heating effect, one would want to be particularly careful to keep air out of the well prior to the onset of CO₂ injection to avoid a potential auto-ignition event.

Initial warm-up of CO₂ by the reservoir environment will cause a phase change from liquid to supercritical. Methane will be displaced by or mixed with CO₂ at the leading edge of the CO₂ front. At some distance from the injection well, while local reservoir temperature is greater than the critical temperature, CO₂ will undergo a phase change from supercritical to vapor. As copious volumes of cold CO₂ are injected, a cool zone will develop around injection wells. With cool down, injection fluid may remain liquid at increasing distances from an injection well. Eventually, the cool zone may extend sufficiently far into the reservoir that the CO₂ transitions from liquid to vapor, causing significant localized cooling. If brine is also present, it is possible that hydrate will form.

Understanding how and when these processes will occur is probably best modeled with a flow simulator that includes all thermodynamics effects. Oldenburg (2006) used the program TOUGH2 (see <http://esd.lbl.gov/TOUGH2/>) with a module called EOS7C to simulate Joule-Thomson cooling due to CO₂ injection into natural gas reservoirs. Oldenburg's simulations are for scenarios different than those studied in this project. For his first constant high-pressure injection case, he simulates injection of CO₂ of initial pressure of approximately 1160 psia and temperature of 167 °F into a reservoir of 770 psia approximate pressure and 165 °F initial temperature. He concludes that strong Joule-Thomson cooling effects cause a temperature drop of 68 deg F for this case. He goes on to speculate that if CO₂ was injected at lower temperature, 77 °F instead of 165 °F, the temperature drop could be larger than 68 °F and “could lead to freezing conditions in the reservoir resulting potentially in CO₂-hydrate formation and freezing of residual water.”

After beginning CO₂ injection, it is probably a good idea to avoid practices that would cause CO₂ to backflow into the injection well. The near-well region could already be at

reduced temperature from prior cold CO₂ injection. Backflow expansion of CO₂ into the cool near-well region could yield very low temperatures because of the Joule-Thomson effect. Low temperatures could promote hydrate formation. This type of backflow expansion of CO₂ may have taken place in a CO₂ storage project conducted in the Pearl Queen Field of New Mexico (Pawar et al, 2004). After injecting 2100 tons of CO₂ over a 2-month period into the Stevason Federal #4 well, and after a 2-month soak period in which bottom hole pressure reduced from 2800 psig to 1600 psig as CO₂ “soaked” into the reservoir, CO₂ was vented from the injection well. Over a nine-day period, CO₂ production gradually decreased by 90 to 98%. Down hole pressure in the well decreased from 1,600 psig to 300 psig. A temperature probe in the well indicated temperature reduction from 95 °F to 75 °F, before rebounding to 90 °F. Even after putting a pump on the well, the authors were unable to substantially increase CO₂ production or recovery. Seismic measurements detected an “anomaly” near the injection well. Grigg et al (2004) describe “Because the cooling effect starts at very low flow rates when the pore pressure is close to the critical pressure of CO₂, attention should be paid to avoid flowing CO₂ in this pressure/temperature region. Once the cooling effect starts, it will build on itself by increasing the pressure gradient and developing multiphase flow, and could eventually contribute to killing the well. This could be a mechanism that contributes to injectivity and productivity losses in many CO₂ flooding wells.” As an example, the authors describe what happened with backflow of CO₂ from the Stevason Federal #4 well.

Results from this investigation show that the magnitude and location of Joule-Thomson cooling depend on the injection pressure and pressure gradient within the system. Considering that the pressure gradient from a CO₂ injection well within a reservoir can be significantly different than the linear flow scenario investigated in the laboratory; no final conclusion regarding CO₂ injectivity impairment in a pressure-depleted reservoir can be drawn until results are translated into reservoir-scale conditions. Even in the case that pressure and temperature conditions during initial injection may not cause loss in reservoir injectivity, problems may still occur later after injection of significant volumes of cold CO₂ which could significantly cool down the near well-bore region.

Reservoir simulation has resulted into a very challenging task due to the lack of adequate numerical models that can handle both the thermodynamic nature of the problem and the characteristic phase behavior of CO₂ under the pressure and temperature conditions considered in this study. Simulation modeling efforts are ongoing to gain a better understanding of reservoir-scale implications.

CONCLUSIONS

The following conclusions are drawn from this work:

- Initially, when injecting cold, high pressure CO₂ into a hot low pressure environment, heat transfer from the surrounding reservoir environment will mask or counter Joule-Thomson gas expansion cooling effects. The most significant early-time cool down effect may be the result of injecting a cold fluid into a hot reservoir.

- As the near-well region cools and the cool zone extends deeper into the reservoir, injected CO₂ may remain in the liquid phase for greater and greater distances into the reservoir. The worst-case scenario will occur if, when, and where CO₂ changes from liquid to vapor. This will occur with pressure and temperature below the critical point (1055 psig and 87.7 °F). A pronounced cooling effect accompanies the phase change from liquid to vapor. When and where this occurs, if the rock is still partially saturated with brine, the potential will exist for forming ice or hydrates that may significantly decrease CO₂ injectivity.
- Once formed, hydrates may be self-regenerating unless the environment is allowed to warm-up again without flowing additional CO₂.
- When assessing risk of forming hydrates for a process involving a real (non-ideal) gas, one needs to consider not only the initial temperature of the environment but also the degree to which the flowing CO₂ may influence local temperatures.
- The main contribution of this investigation may be a confirmation that if one can understand and model thermodynamics for the reservoir storage scenario, one will be able to predict whether injection will be successful or problematic.

ACKNOWLEDGEMENTS

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