# Measurement of Z-Factors for Carbon Dioxide Sequestration 

Paulus Adisoemarta, Texas Tech University; Scott M. Frailey, ISGS; Akanni S. Lawal, Texas Tech University


#### Abstract

Due to concerns about global climate change, carbon dioxide gases from natural and industrial sources are more and more re-injected into depleted gas reservoirs. The PVT laboratory at Texas Tech University has undertaken a comprehensive study on compressibility factor (Z-factor) of hydrocarbon (HC) gas at various amount of $\mathrm{CO}_{2}$. For the sole purpose of the measured Z-factor data, three temperatures of $100^{\circ} \mathrm{F}, 160^{\circ} \mathrm{F}$ and $220^{\circ} \mathrm{F}$ and pressures ranges from 50 psia to 5000 psia are selected as representative of the depleted gas reservoirs (DGRs). In order to analyze the various phase behavior to be encountered in gas reservoirs (dry gas, wet gas and retrograde gas), the median gas compositions for dry, wet and retrograde gases are specified by gas type. The gas types are categorized by representative compositional analysis for the three types of gas reservoirs (dry gas, wet gas and retrograde gas). The measurements of z-factors for CO2-hydrocarbon mixtures in varying proportions and at the three specified temperatures for various pressures are performed on the median gas compositions of the type gases. The results of the Z-factor measurements of $\mathrm{CO}_{2}$-hydrocarbon mixtures are used to interpret the expected phase behavior to be encountered in the geologic storage of $\mathrm{CO}_{2}$ in gas reservoirs. Also, the Z-factor measurements of CO 2 -retrograde gas mixtures are used to quality the benefits of enhanced gas and condensate recovery in gas reservoirs.


## Introduction

Carbon dioxide $\left(\mathrm{CO}_{2}\right)$ gas has been used for enhanced oil recovery through miscible and immiscible displacement of oil at high pressures and moderate temperatures since the earlier 1970. Recently, research is being directed for the use of carbon dioxide in the oil refining through supercritical extraction of hydrocarbons. ${ }^{1}$ Current activities are to find ways for geologic storage of $\mathrm{CO}_{2}$ in oil or gas reservoirs. ${ }^{2}$ Although one laboratory measurement of $\mathrm{CO}_{2}$-hydrocarbon mixture in the limited ranges of temperatures and pressures used in this project has been reported in Venezuela (Rojas-Requena, 1992), ${ }^{3}$ this paper presents experimental measurements of $Z$-factors for $\mathrm{CO}_{2}$-hydrocarbon mixtures at three specified temperatures and pressures ranging from 50 psia to 5000 psia. The results of the experimental Z-factors are used to quantify economic benefits (such as enhanced oil recovery (EOR) and enhanced condensate vaporization) of geologic storage of $\mathrm{CO}_{2}$ in gas reservoir.

## Procedure for Z-factor Determination

The compressibility factor, or Z-factor, is determined by manipulating the Real Gas Law and assuming that reservoir gas will behaves as an ideal gas at ambient pressure and temperature (McCain, 1990, page 106).

The Real Gas Law is defined as follows:

$$
\begin{equation*}
P V=Z n R T \tag{1}
\end{equation*}
$$

For a constant composition system, the product of pressure and volume is constant, thus

$$
\begin{equation*}
\frac{P_{1} V_{1}}{P_{2} V_{2}}=\frac{Z_{1} n R T_{1}}{Z_{2} n R T_{2}} \tag{2}
\end{equation*}
$$

Where the subscripts are:

1. Condition in the cell
2. Ambient condition

Solving for the ratio of compressibility factors:

$$
\begin{equation*}
\frac{Z_{1}}{Z_{2}}=\frac{P_{1} V_{1} T_{2}}{P_{2} V_{2} T_{1}} \tag{3}
\end{equation*}
$$

At ambient pressure and temperature all gases are assumed to behave like an Ideal Gas, so that its compressibility factor is unity. Substituting $Z 2$ with 1 result in the primary formula for this study:

$$
\begin{equation*}
Z_{1}=\frac{P_{1} V_{1} T_{2}}{P_{2} V_{2} T_{1}} \tag{4}
\end{equation*}
$$

Where:
$P_{1} \quad$ cell pressure
$V_{1} \quad$ volume of gas released from the cell
$T_{1} \quad$ cell temperature
$P_{2} \quad$ ambient pressure
$V_{2}$ volume of gas at ambient pressure and temperature
$T_{2}$ ambient temperature
Pressure and temperature are in absolute units.

## Hydrocarbon Type Gas Samples

The first part of the study is identifying major components of reservoir gas and the range of compositions for each of the categories of the gas reservoirs (i.e., dry gas, wet gas, and retrograde gas).

The gas compositions are obtained from published SPE papers, Petroleum Engineering Journals, Gas Information System (GASIS) and PVT analyses. The major components of gas reservoir are identified as nitrogen, carbon dioxide, methane, ethane, propane, $n$-butane, n pentane, hexane, and heptane-plus ( $\mathrm{N}_{2}, \mathrm{CO}_{2}, \mathrm{C}_{1}, \mathrm{C}_{2}, \mathrm{C}_{3}, \mathrm{nC}_{4}, \mathrm{nC}_{5}, \mathrm{C}_{6}, \mathrm{C}_{7}{ }^{+}$). Non-hydrocarbon components are removed and the hydrocarbon components are normalized to 1.0 mole. These compositions are analyzed to find the median composition for each of the categories of gas reservoirs, and a means of identifying the Gas Type from the composition is established. Tables containing the normalized median compositions for each category of gas reservoirs are constructed. The median compositions are derived from 131 dry gas, 12 wet gas, and 11 retrograde gas samples. A sample of the normalized median composition for gas reservoir is shown in Table 1.

Table 1 - Normalized Median Composition

|  | $\mathrm{C}_{1}$ | $\mathrm{C}_{2}$ | $\mathrm{C}_{3}$ | $\mathrm{C}_{4}$ | $\mathrm{C}_{5}$ | $\mathrm{C}_{6}$ | $\mathrm{C}_{7}{ }^{+}$ | Total Mol \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Dry Gas | 96.61 | 2.67 | 0.51 | 0.21 | 0.00 | 0.00 | 0.00 | 100.00 |
|  |  |  |  |  |  |  |  |  |
| Wet Gas | 90.03 | 4.75 | 2.03 | 1.03 | 0.42 | 0.35 | 1.40 | 100.00 |
|  |  |  |  |  |  |  |  |  |
| Retrograde Gas | 73.09 | 8.57 | 4.53 | 3.40 | 1.89 | 1.64 | 6.88 | 100.00 |

Table 1 shows that dry gas reservoir is mainly $\mathrm{C}_{1}$, whereas wet and retrograde gas reservoirs have appreciable amount of heptanes-plus fractions $\left(\mathrm{C}_{7}^{+}\right)$. Anticipating sequestration of $\mathrm{CO}_{2}$ in depleted gas reservoirs (DGRs) to vary based on the phase behavior of the mixture of the $\mathrm{CO}_{2}$ and the resident hydrocarbon gases and liquids, the Z-factor measurements are based on each gas types.

The gas compositions of Table 1 are the compositions of the initial or discovery gas reservoirs. By definition there are no phase changes in the reservoir for dry and wet gases; consequently, the median dry and wet gas compositions are also the compositions of the respective gases at depleted reservoir conditions. This is not the case for retrograde gas, which undergoes a phase change at reservoir conditions. As such, the composition of the retrograde gas' liquid and vapor phases varies with pressure. Three depleted pressures of 50, 250 and 500 psia are used as a range to define the depleted gas reservoir pressure, which is also the initial sequestration pressure. These three gases are labeled as retrograde gases $A$, $B$ and $C$ for the gases at 50, 250 and 500 psia, respectively, and their respective compositions are show in Table 2.

Table 2 - Normalized Median Composition of Retrograde Gas at Depleted Pressure

|  | $\mathrm{C}_{1}$ | $\mathrm{C}_{2}$ | $\mathrm{C}_{3}$ | $\mathrm{C}_{4}$ | $\mathrm{C}_{5}$ | $\mathrm{C}_{6}$ | $\mathrm{C}_{10}$ | Total Mol \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Retrograde Gas A <br> (50 psia) | 24.77 | 5.27 | 5.41 | 7.71 | 6.67 | 7.34 | 42.82 | 100.00 |
|  |  |  |  |  |  |  |  |  |
| Retrograde Gas B <br> (250 psia) | 39.05 | 6.99 | 5.82 | 6.83 | 5.25 | 5.49 | 30.57 | 100.00 |
|  |  |  |  |  |  |  |  |  |
| Retrograde Gas C <br> (500 psia) | 50.78 | 7.92 | 5.64 | 5.75 | 4.05 | 4.07 | 21.76 | 100.00 |
|  |  |  |  |  |  |  |  |  |

To ensure the broadest applicability of the lab data to $\mathrm{CO}_{2}$ sequestration in gas reservoirs, gas compositions are required for as many sources as possible so that a representative average composition of dry, wet and retrograde gases could be established. Therefore, a specific gas reservoir could be selected or fabricated in the laboratory that is close to the median composition found from data collected for each gas type. As broadest applications into gas reservoirs are required, a specific gas reservoir study is not mandated. Consequently, the 154 gas compositions found in the literature and private sources could be categorized by gas types: dry, wet, and retrograde. Median gas types are calculated for each gas type in order to have gas compositions that are not unique to specific gas reservoir. A plot
is made that identify regions type gases (dry, wet, and retrograde gasses) based on their compositions. Several plots were made to find the combination of compositions that would provide the greatest distinction of the gas type and thus yields unique gas-type identification.

The final plot (see Figure 1) is the sum of the mole fraction of the butane, propane, pentane, hexane and heptane divided by the mole fraction methane (y-axis) versus mole fraction of ethane divided by mole fraction of methane (x-axis). Figure 1 is the basis for gas samples specification ordered for the experimental work on $\mathrm{CO}_{2}$-hydrocarbon mixtures.


Figure 1 - TTU Gas Identification Chart based on hydrocarbon composition of $\mathrm{C}_{1}-\mathrm{C}_{7+}$

## Experimental Gas Samples

To ensure repeatability of the Z-factor measurements for each gas type, pre-mixed gas with the median composition of each gas type that has been shown in Table 1 were ordered from a commercial analytical-gas vendor. Two more procedure were implemented to ensure sample consistency:

1. Single-phase sample loading from the gas bottle to the PVT cell must be performed all the time. To ensure single-phase loading each bottle has to be heated to above its cricondentherm temperature plus $15^{\circ} \mathrm{F}$.
2. To prevent sample segregation in the bottle due to molecular weight difference of each component, the bottle must be heated in a non-uniform form. The lower part of the bottle is heated at $200^{\circ} \mathrm{F}$ while the top part is heated at the cricondentherm temperature plus $15^{\circ} \mathrm{F}$. The much hotter lower part of the bottle will make the sample gas lighter than the upper part, and thus created a continuous convection upward that ensures no sample segregation occurs.

As the median retrograde gas has a cricondentherm temperature much higher than the safety limit of the sample bottle to ensure single-phase loading, the median retrograde gas sample must be loaded in two steps. The step one is to load the liquid part of the heptaneplus, in the form of liquid decane to the PVT cell. Then the second step is to load the pre-
mixed median retrograde gas but without the heptane-plus part. Then an overnight mixing was done in the cell at the target temperature of $100^{\circ} \mathrm{F}, 160^{\circ} \mathrm{F}$, and $220^{\circ} \mathrm{F}$.

## Ruska PVT Equipment

This research project uses equipment commercially available from Chandler Engineering Products (previously Ruska) Model 2370 Mercury-Free PVT Oven, and the produced gas is measured with the Model 2331 Gasometer and Model 2353 Separator. Measurement automation and remote monitoring is performed by in-house developed LabVIEW-based software running on an off-the-shelf computer in-house.

To ensure a leak-free system, a special compound that is compatible with high concentration of $\mathrm{CO}_{2}$ has been utilized. This special compound is called V1238-95, a fluorocarbon material (FKM) product of Parker Hannifin.

To prevent the premature destruction of seals in the system, due to the absorbed gas and/or $\mathrm{CO}_{2}$ that suddenly expands when the system pressure is dropped, a measure similar to deep sea divers do to prevent a syndrome called "bends" has been implemented. This method calls for a waiting period until the system stabilized, for at least 15 minutes, after a volume expansion of maximum 1.5 times the initial volume has been performed. During this waiting time all absorbed gas will have sufficient time to diffuse out from the seal material safely.

## Laboratory Measurement Results

Great effort has been spent during the measurement in the lab to minimize measurement error. These efforts comprised of repeating each measurement six times and rejecting the outlier data before the averaging, running the system against known gas to detect any system drifts between HC sample runs, and letting the system stays overnight to ensure a completely stabilized system before each sample run.

Figures 2 to 4 shows $\mathrm{CO}_{2}$ compressibility factor measured in the lab compared to published data by Sage and Lacey (1955), and Burton Corblin (1990). The plot shows a very good match between lab results and the two published data sets that confirm equipment and methodology. At pressure less than 100 psia, the measured data deviates slightly (less than $10 \%$ absolute error) compared to the two published data sets.


Figure 2 - Benchmark TTU $\mathrm{CO}_{2}$ Measurements at $100^{\circ} \mathrm{F}$ to Sage and Lacy (1955) and Burton Corblin Technical Bulletin (1990)


Figure 3 - Benchmark TTU $\mathrm{CO}_{2}$ Measurements at $160^{\circ} \mathrm{F}$ to Sage and Lacy (1955) and Burton Corblin Technical Bulletin (1990)


Figure 4 - Benchmark TTU $\mathrm{CO}_{2}$ Measurements at $220^{\circ} \mathrm{F}$ to Sage and Lacy (1955) and Burton Corblin Technical Bulletin (1990)

The smoothed compressibility factors of dry gas samples from laboratory measurement are shown in Figure 5 to 7 and Table 3 to 5 . Each table shows the actual lab result, and the smoothed data are listed next to the lab measurements. Figure 5 shows the compressibility factor of various median dry gas and carbon dioxide composition at $100^{\circ} \mathrm{F}$. Also shown on the plot is the compressibility factor of pure carbon dioxide gas. As can be observed from the plot, a consistent progression in the increasing amount of carbon dioxide gas in the median dry gas mixture is shown. The result of the compressibility factor at $160^{\circ} \mathrm{F}$ is shown in Figure 6. The plot shows a consistent trend as a function of increasing carbon dioxide content. Figure 7 shows the compressibility factor of various dry gas and carbon dioxide mixture at $220^{\circ} \mathrm{F}$. This plot shows a correct trend as a function of the amount of carbon dioxide in the mixture.


Figure 5 - Median Dry Gas and $\mathrm{CO}_{2}$ Mixture at $100^{\circ} \mathrm{F}$


Figure 6 - Median Dry Gas and $\mathrm{CO}_{2}$ Mixture at $160^{\circ} \mathrm{F}$


Figure 7 - Median Dry Gas and $\mathrm{CO}_{2}$ Mixture at $220^{\circ} \mathrm{F}$

Table 3 - Compressibility Factor of Median Dry Gas and $\mathrm{CO}_{2}$ Mixture at $100^{\circ} \mathrm{F}$

|  | $0 \%$ | $\mathrm{CO}_{2}$ | $25 \%$ | $\mathrm{CO}_{2}$ | $50 \%$ | $\mathrm{CO}_{2}$ | $75 \%$ | $\mathrm{CO}_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pressure <br> psia | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab |
| 5000 | 0.9950 | 0.9947 | 0.9040 | 0.8981 | 0.8260 | 0.8227 | 0.7000 | 0.7538 |
| 4500 | 0.9400 |  | 0.8550 |  | 0.7650 |  | 0.6500 |  |
| 4000 | 0.8900 | 0.8918 | 0.8100 | 0.8023 | 0.7150 | 0.7161 | 0.6000 | 0.6584 |
| 3500 | 0.8580 |  | 0.7750 |  | 0.6750 |  | 0.5600 |  |
| 3000 | 0.8350 | 0.8382 | 0.7550 | 0.7382 | 0.6590 | 0.6452 | 0.5250 | 0.5327 |
| 2500 | 0.8300 | 0.8253 | 0.7560 | 0.7297 | 0.6600 | 0.6278 | 0.5090 | 0.5166 |
| 2000 | 0.8360 | 0.8596 | 0.7780 | 0.8251 | 0.6850 | 0.6932 | 0.5180 | 0.5045 |
| 1500 | 0.8600 | 0.8603 | 0.8150 | 0.8486 | 0.7275 | 0.7293 | 0.5800 | 0.5866 |
| 1000 | 0.8950 | 0.9024 | 0.8630 | 0.8985 | 0.7950 | 0.8149 | 0.7050 | 0.7485 |
| 500 | 0.9450 | 0.9473 | 0.9300 | 0.9325 | 0.8950 | 0.9073 | 0.8500 | 0.8747 |
| 200 | 0.9800 | 0.9908 | 0.9720 | 0.9807 | 0.9580 | 0.9500 | 0.9350 | 0.9669 |
| 100 | 0.9910 | 1.0050 | 0.9870 | 0.9937 | 0.9780 | 0.9715 | 0.9620 | 0.9875 |
| 50 | 0.9970 | 1.0146 | 0.9940 | 0.9958 | 0.9900 | 0.9815 | 0.9750 | 1.0051 |

Table 4 - Compressibility Factor of Median Dry Gas and $\mathrm{CO}_{2}$ Mixture at $160^{\circ} \mathrm{F}$

|  | $0 \% \mathrm{CO}_{2}$ |  | $25 \% \mathrm{CO}_{2}$ |  | $50 \% \mathrm{CO}_{2}$ |  | $75 \% \mathrm{CO}_{2}$ |  |
| ---: | ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pressure <br> psia | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab |
| 5000 | 1.0300 | 0.9968 | 0.9500 | 0.9449 | 0.8600 | 0.8625 | 0.7550 | 0.7535 |
| 4500 | 0.9830 |  | 0.9175 |  | 0.8150 |  | 0.7100 |  |
| 4000 | 0.9420 | 0.9309 | 0.8900 | 0.8874 | 0.7800 | 0.7814 | 0.6700 | 0.6737 |
| 3500 | 0.9070 |  | 0.8700 |  | 0.7580 |  | 0.6420 |  |
| 3000 | 0.8912 | 0.8918 | 0.8550 | 0.8584 | 0.7450 | 0.7487 | 0.6325 | 0.6333 |
| 2500 | 0.8828 | 0.8879 | 0.8500 | 0.8532 | 0.7500 | 0.7530 | 0.6400 | 0.6320 |
| 2000 | 0.8855 | 0.8830 | 0.8550 | 0.8527 | 0.7680 | 0.7764 | 0.6700 | 0.6787 |
| 1500 | 0.9014 | 0.8379 | 0.8680 | 0.8734 | 0.8000 | 0.8093 | 0.7250 | 0.7414 |
| 1000 | 0.9275 | 0.8617 | 0.8950 | 0.8942 | 0.8500 | 0.8737 | 0.8000 | 0.8095 |
| 500 | 0.9609 | 0.9011 | 0.9450 | 0.9439 | 0.9200 | 0.9330 | 0.8900 | 0.8872 |
| 200 | 0.9900 | 0.9230 | 0.9810 | 0.9785 | 0.9670 | 0.9655 | 0.9500 | 0.9686 |
| 100 | 0.9996 | 0.9489 | 0.9945 | 1.0226 | 0.9840 | 0.9903 | 0.9700 | 0.9868 |
| 50 | 1.0050 | 0.9868 | 1.0000 | 1.0189 | 0.9930 | 0.9598 | 0.9800 | 1.0208 |

Table 5 - Compressibility Factor of Median Dry Gas and $\mathrm{CO}_{2}$ Mixture at $220^{\circ} \mathrm{F}$

|  | $0 \% \mathrm{CO}_{2}$ |  | $25 \% \mathrm{CO}_{2}$ |  | $50 \% \mathrm{CO}_{2}$ |  | $75 \% \mathrm{CO}_{2}$ |  |
| ---: | ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pressure <br> psia | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab |
| 5000 | 1.0650 | 1.0638 | 0.9675 | 0.9648 | 0.9050 | 0.9027 | 0.8500 | 0.8481 |
| 4500 | 1.0350 |  | 0.9400 |  | 0.8725 |  | 0.7950 |  |
| 4000 | 1.0050 | 1.0152 | 0.9100 | 0.9134 | 0.8450 | 0.8477 | 0.7600 | 0.7517 |
| 3500 | 0.9760 |  | 0.8930 |  | 0.8300 |  | 0.7390 |  |
| 3000 | 0.9500 | 0.9467 | 0.8825 | 0.8789 | 0.8280 | 0.8249 | 0.7340 | 0.7325 |
| 2500 | 0.9320 | 0.9288 | 0.8850 | 0.8883 | 0.8350 | 0.8308 | 0.7460 | 0.7470 |
| 2000 | 0.9280 | 0.9148 | 0.8950 | 0.8997 | 0.8500 | 0.8576 | 0.7720 | 0.7715 |
| 1500 | 0.9350 | 0.9293 | 0.9100 | 0.9224 | 0.8800 | 0.8862 | 0.8100 | 0.8008 |
| 1000 | 0.9550 | 0.9486 | 0.9400 | 0.9425 | 0.9150 | 0.9151 | 0.8600 | 0.8632 |
| 500 | 0.9840 | 0.9878 | 0.9740 | 0.9683 | 0.9550 | 0.9505 | 0.9250 | 0.9198 |
| 200 | 1.0013 | 1.0141 | 0.9950 | 0.9894 | 0.9800 | 0.9672 | 0.9640 | 0.9173 |
| 100 | 1.0075 | 0.9762 | 1.0022 | 0.9669 | 0.9900 | 0.9703 | 0.9770 | 0.8737 |
| 50 | 1.0110 | 0.9657 | 1.0070 | 0.9768 | 0.9960 | 0.9796 | 0.9840 | 0.7603 |

Because wet gas sample generate liquid in the separator at temperature lower than $145^{\circ} \mathrm{F}$, there is no plot of compressibility factor at $100^{\circ} \mathrm{F}$. The compressibility factors at $160^{\circ} \mathrm{F}$ and $220^{\circ} \mathrm{F}$ are shown in Figures 8-9.


Figure 8 - Median Wet Gas and $\mathrm{CO}_{2}$ Mixture at $160^{\circ} \mathrm{F}$


Figure 9 - Median Wet Gas and $\mathrm{CO}_{2}$ Mixture at $220^{\circ} \mathrm{F}$

Compressibility factor of various wet gas with carbon dioxide at $160^{\circ} \mathrm{F}$ shows a consistent trend as a function of the amount of carbon dioxide. At $220^{\circ} \mathrm{F}$, the compressibility factor also shows the expected trend as a function of the amount of carbon dioxide. Tables 6 and 7 shows the compressibility factor of various wet gas with carbon dioxide in numerical format

Table 6 - Compressibility Factor of Median Wet Gas and $\mathrm{CO}_{2}$ Mixture at $160^{\circ} \mathrm{F}$

|  | $0 \% \mathrm{CO}_{2}$ |  | $25 \% \mathrm{CO}_{2}$ |  | $50 \% \mathrm{CO}_{2}$ |  | $75 \% \mathrm{CO}_{2}$ |  |
| ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| Pressure <br> psia | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab |
| 5000 | 1.0050 | 1.0046 | 0.9380 | 0.9368 | 0.8210 | 0.8224 | 0.7400 | 0.8386 |
| 4500 | 0.9400 |  | 0.8950 |  | 0.7800 |  | 0.7050 |  |
| 4000 | 0.8920 | 0.8928 | 0.8510 | 0.8517 | 0.7450 | 0.7479 | 0.6700 | 0.7296 |
| 3500 | 0.8600 |  | 0.8200 |  | 0.7200 |  | 0.6400 | 0.7296 |
| 3000 | 0.8380 | 0.8557 | 0.8000 | 0.7938 | 0.7100 | 0.7108 | 0.6150 | 0.6237 |
| 2500 | 0.8290 | 0.8284 | 0.7900 | 0.7880 | 0.7180 | 0.7140 | 0.6150 | 0.6041 |
| 2000 | 0.8380 | 0.8434 | 0.8070 | 0.8023 | 0.7410 | 0.7375 | 0.6400 | 0.6514 |
| 1500 | 0.8650 | 0.8634 | 0.8400 | 0.8388 | 0.7850 | 0.7829 | 0.6980 | 0.7244 |
| 1000 | 0.9030 | 0.9050 | 0.8900 | 0.8869 | 0.8450 | 0.8504 | 0.7950 | 0.8952 |
| 500 | 0.9560 | 0.9608 | 0.9450 | 0.9536 | 0.9150 | 0.9116 | 0.8900 | 0.9439 |
| 200 | 0.9890 | 0.9849 | 0.9780 | 0.9830 | 0.9610 | 0.9692 | 0.9440 | 1.0891 |
| 100 | 0.9990 | 0.9891 | 0.9900 | 0.9919 | 0.9760 | 0.9801 | 0.9620 | 1.1870 |
| 50 | 1.0040 | 0.9896 | 0.9970 | 1.1588 | 0.9830 | 0.9772 | 0.9700 | 1.2069 |

Table 7 - Compressibility Factor of Median Wet Gas and $\mathrm{CO}_{2}$ Mixture at $220^{\circ} \mathrm{F}$

|  | $0 \% \mathrm{CO}_{2}$ |  | $25 \% \mathrm{CO}_{2}$ |  | $50 \% \mathrm{CO}_{2}$ |  | $75 \% \mathrm{CO}_{2}$ |  |
| ---: | ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Pressure <br> psia | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab |
| 5000 | 1.0350 | 1.0365 | 0.9600 | 0.9605 | 0.8840 | 0.8838 | 0.8300 | 0.9190 |
| 4500 | 0.9950 |  | 0.9250 |  | 0.8540 |  | 0.8000 |  |
| 4000 | 0.9575 | 0.9420 | 0.8950 | 0.8948 | 0.8265 | 0.8336 | 0.7750 | 0.8457 |
| 3500 | 0.9240 |  | 0.8760 |  | 0.8080 |  | 0.7550 |  |
| 3000 | 0.9030 | 0.9106 | 0.8650 | 0.8632 | 0.7990 | 0.7977 | 0.7450 | 0.8223 |
| 2500 | 0.8940 | 0.8913 | 0.8640 | 0.8616 | 0.8030 | 0.8015 | 0.7450 | 0.8194 |
| 2000 | 0.8960 | 0.8948 | 0.8725 | 0.8714 | 0.8210 | 0.8261 | 0.7600 | 0.8056 |
| 1500 | 0.9090 | 0.9208 | 0.8900 | 0.8817 | 0.8530 | 0.8438 | 0.8100 | 0.8410 |
| 1000 | 0.9320 | 0.9211 | 0.9175 | 0.9148 | 0.8975 | 0.9120 | 0.8700 | 0.9863 |
| 500 | 0.9700 | 0.9688 | 0.9560 | 0.9644 | 0.9450 | 0.9631 | 0.9300 | 1.0686 |
| 200 | 0.9970 | 0.9753 | 0.9840 | 0.9902 | 0.9770 | 0.9854 | 0.9650 | 0.9701 |
| 100 | 1.0060 | 0.9855 | 0.9950 | 0.9709 | 0.9900 | 1.0044 | 0.9800 | 0.9680 |
| 50 | 1.0100 | 0.9864 | 0.9996 | 0.9574 | 0.9950 | 0.9936 | 0.9870 | 0.9983 |

As the retrograde gas is expected to have a fraction of the volume as liquid at certain pressure and temperatures, the compressibility factor measurement was done using two different methods and the result is merged together. For pressures above the dew-point pressure, the constant composition expansion (CCE) method was utilized whereby the cell is kept closed, and system pressure is gradually increased and the respective cell volume is recorded. For pressures below the dew-point pressure the constant volume depletion (CVD) method was utilized. This method mimics the actual condition in the reservoir during depletion process as the reservoir volume stays constant and the liquid precipitation stays in the pore space of the reservoir rock.

The dew-point pressure of median retrograde gas is 3400 psia, and drops to 1300 psia after $\mathrm{CO}_{2}$ has been injected. Figures 10, 11, and 12 shows the compressibility factor of median retrograde gas and depleted retrograde gas after $\mathrm{CO}_{2}$ has been mixed at temperatures of $100^{\circ} \mathrm{F}, 160^{\circ} \mathrm{F}$, and $190^{\circ} \mathrm{F}$. Tables 8,9 , and 10 show the result in numeric format, respectively. Owing to the equipment failures as a result of premature seal degradation at high temperatures, there is no result for cell temperature of $220^{\circ} \mathrm{F}$.


Figure 10 - Retrograde and Depleted Retrograde Gas and $\mathrm{CO}_{2}$ Mixture at $100^{\circ} \mathrm{F}$


Figure 11 - Retrograde and Depleted Retrograde Gas and $\mathrm{CO}_{2}$ Mixture at $160^{\circ} \mathrm{F}$


Figure 12 - Retrograde and Depleted Retrograde Gas and $\mathrm{CO}_{2}$ Mixture at $190^{\circ} \mathrm{F}$

Table 8 - Compressibility Factor of Median Retrograde Gas and Depleted Retrograde Gas $+\mathrm{CO}_{2}$ Mixture at $100^{\circ} \mathrm{F}$

| Median Retrograde |  |  | Depleted Median Retrograde Sample |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Pressure | 50 psia |  | 250 psia |  | 500 psia |  |
| Pressure | Smoothed | Lab |  | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab |
| 5000 | 0.93 | 0.935 | 5000 | 0.65000 | 0.6540 | 0.7000 | 0.6900 | 0.7500 | 0.7600 |
| 4500 | 0.89 |  | 4500 | 0.6000 |  | 0.6400 |  | 0.6800 |  |
| 4000 | 0.855 | 0.845 | 4000 | 0.5400 | 0.5340 | 0.5700 | 0.5800 | 0.6100 | 0.6050 |
| 3500 | 0.825 |  | 3500 | 0.4800 |  | 0.5100 |  | 0.5500 |  |
| 3000 | 0.8 | 0.79 | 3000 | 0.4200 | 0.4100 | 0.4500 | 0.4400 | 0.4850 | 0.4800 |
| 2500 | 0.786 |  | 2500 | 0.3750 |  | 0.3900 |  | 0.4200 |  |
| 2000 | 0.7808 | 0.785 | 2000 | 0.3250 | 0.3300 | 0.3400 | 0.3200 | 0.3600 | 0.3500 |
| 1500 | 0.8027 |  | 1500 | 0.2850 | 0.2900 | 0.3050 | 0.3000 | 0.3250 | 0.3200 |
| 1000 | 0.8605 | 0.86 | 1250 | 0.2950 |  | 0.3300 |  | 0.3600 |  |
| 500 | 0.9283 | 0.92 | 1200 | 0.3700 |  | 0.4150 |  | 0.4350 |  |
| 250 | 0.9627 |  | 1100 | 0.4940 |  | 0.5100 |  | 0.5600 |  |
| 100 | 0.9867 | 0.98 | 1000 | 0.5900 | 0.6000 | 0.6050 | 0.5900 | 0.6300 | 0.6200 |
| 50 | 0.993 |  | 900 | 0.6500 |  | 0.6700 |  | 0.7000 |  |
|  |  |  | 800 | 0.7100 |  | 0.7250 |  | 0.7500 |  |
|  |  |  | 700 | 0.7600 |  | 0.7750 |  | 0.8000 |  |
|  |  |  | 600 | 0.8100 |  | 0.8200 |  | 0.8400 |  |
|  |  |  | 500 | 0.8500 | 0.8400 | 0.8600 | 0.8700 | 0.8800 | 0.8600 |
|  |  |  | 400 | 0.8800 |  | 0.8900 |  |  |  |
|  |  |  | 300 | 0.9100 |  | 0.9200 | 0.9100 |  |  |
|  |  |  | 200 | 0.9400 | 0.9300 |  |  |  |  |
|  |  |  | 100 | 0.9600 | 0.9500 |  |  |  |  |
|  |  |  | 50 | 0.9700 |  |  |  |  |  |

Table 9 - Compressibility Factor of Median Retrograde Gas and Depleted Retrograde Gas $+\mathrm{CO}_{2}$ Mixture at $160^{\circ} \mathrm{F}$

| Median Retrograde Gas |  |  | Pressure | Depleted Retrograde $+\mathrm{CO}_{2}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | 50 psia | 250 psia |  | 500 psia |  |
| P | Smooth | Lab |  | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab |
| 5000 | 0.96 | 0.95 |  | 5000 | 0.6572 | 0.64 | 0.6672 | 0.656 | 0.695 | 0.7 |
| 4500 | 0.92 |  | 4500 | 0.6115 |  | 0.6215 |  | 0.645 |  |
| 4000 | 0.885 | 0.88 | 4000 | 0.5667 | 0.55 | 0.5767 | 0.58 | 0.595 | 0.6 |
| 3500 | 0.855 |  | 3500 | 0.5232 |  | 0.5332 |  | 0.56 |  |
| 3000 | 0.83 | 0.84 | 3000 | 0.4872 | 0.49 | 0.505 | 0.51 | 0.54 | 0.55 |
| 2500 | 0.815 |  | 2750 | 0.4732 |  | 0.495 |  | 0.54 |  |
| 2000 | 0.8177 | 0.82 | 2500 | 0.4654 | 0.47 | 0.495 |  | 0.54 |  |
| 1500 | 0.84 |  | 2250 | 0.469 |  | 0.499 |  | 0.55 |  |
| 1000 | 0.8871 | 0.89 | 2000 | 0.495 | 0.5 | 0.525 | 0.53 | 0.58 | 0.57 |
| 500 | 0.9427 | 0.95 | 1750 | 0.5498 |  | 0.59 |  | 0.64 |  |
| 250 | 0.97 |  | 1500 | 0.62 | 0.61 | 0.66 |  | 0.71 | 0.715 |
| 100 | 0.9874 | 0.99 | 1300 | 0.685 |  | 0.725 |  | 0.765 |  |
| 50 | 0.994 |  | 1200 | 0.71 |  | 0.75 |  | 0.79 |  |
|  |  |  | 1100 | 0.737 |  | 0.775 |  | 0.81 |  |
|  |  |  | 1000 | 0.765 | 0.75 | 0.801 | 0.8 | 0.83 | 0.83 |
|  |  |  | 900 | 0.79 |  | 0.825 |  | 0.85 |  |
|  |  |  | 800 | 0.82 |  | 0.845 |  | 0.868 |  |
|  |  |  | 700 | 0.845 |  | 0.865 |  | 0.885 |  |
|  |  |  | 600 | 0.865 |  | 0.885 |  | 0.9 |  |
|  |  |  | 500 | 0.89 | 0.88 | 0.905 | 0.9 | 0.915 | 0.92 |
|  |  |  | 400 | 0.915 |  | 0.926 |  |  |  |
|  |  |  | 300 | 0.938 |  | 0.945 |  |  |  |
|  |  |  | 200 | 0.96 |  |  |  |  |  |
|  |  |  | 100 | 0.981 | 0.97 |  |  |  |  |

Table 10 - Compressibility Factor of Median Retrograde Gas and Depleted Retrograde Gas $+\mathrm{CO}_{2}$ Mixture at $190^{\circ} \mathrm{F}$

|  | Depleted Median Retrograde Sample $+\mathrm{CO}_{2}$ |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Median Retrograde |  | 50 | Psia | 250 | psia | 500 | Psia |  |
| Pressure Smoothed | Lab | Smoothed | Lab | Smoothed | Lab | Smoothed | Lab |  |
| 5000 | 0.971 | 0.97 | 0.6874 | 0.68 | 0.7184 | 0.72 | 0.748 | 0.75 |
| 4500 | 0.9335 |  | 0.6475 |  | 0.6806 |  | 0.7126 |  |
| 4000 | 0.889 | 0.89 | 0.6084 | 0.62 | 0.6439 | 0.65 | 0.6784 | 0.68 |
| 3500 | 0.8534 |  | 0.575 |  | 0.61 |  | 0.6467 |  |
| 3000 | 0.84 | 0.83 | 0.554 | 0.57 | 0.585 | 0.59 | 0.6209 | 0.63 |
| 2500 | 0.84 |  | 0.555 |  | 0.58 |  | 0.611 |  |
| 2000 | 0.85 | 0.84 | 0.6 | 0.58 | 0.63 | 0.64 | 0.66 | 0.67 |
| 1500 | 0.88 |  | 0.705 |  | 0.735 |  | 0.76 |  |
| 1000 | 0.92 | 0.92 | 0.815 | 0.8 | 0.83 | 0.82 | 0.845 | 0.85 |
| 500 | 0.96 | 0.955 | 0.91 |  | 0.92 |  | 0.9251 | 0.92 |
| 200 | 0.983 |  | 0.967 | 0.96 | 0.975 | 0.98 |  |  |
| 100 | 0.992 | 0.99 | 0.986 | 0.99 |  |  |  |  |
| 50 | 0.996 |  | 0.994 |  |  |  |  |  |

## Benefits of Geologic $\mathbf{C O}_{2}$ Storage

One side benefit of $\mathrm{CO}_{2}$ sequestration is the additional production of hydrocarbon gasses due to re-vaporization of retrograde condensate in the reservoir.

Figure 13 shows the amount of re-vaporized liquid, in percent of original condensate volume, as a function of temperature and depletion pressure. As it can be seen on the plot, the amount of condensate that is re-vaporized range from as low as 5.7 percent to as high as 35 percent. Stated in different ways, as much as one-third of the condensate liquid in a depleted reservoir can be produced as gas after $\mathrm{CO}_{2}$ is sequestered. Table 11 shows the complete result in tabular format.


Figure 13 - Revaporized Condensate as a Function of Pressure and Depletion Pressure

Table 11- Revaporized Condensate

|  | Condensate Volume at Depleted Pressure (cc) |  |  |  |  |  | Condensate Re-vaporized (\%) <br> at Depleted Pressure |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Median Retrograde |  |  | $\mathrm{CO}_{2}+\mathrm{RG}$ |  |  |  |  |  |
| Temp ( ${ }^{\circ} \mathrm{F}$ ) | 50 psia | 250 psi | 500 psia | 50 psia | 250 psia | 500 psia | 50 psia | 250 psia | 500 psia |
| 100 | 19.85 | 19.59 | 18.39 | 18.26 | 14.53 | 17.69 | 16.93 | 25.85 | 7.98 |
| 160 | 11.93 | 14.41 | 19.85 | 11.25 | 11.79 | 12.77 | 5.70 | 18.18 | 35.67 |
| 190 | No Data | 18.19 | 19.10 | No Data | 15.12 | 15.12 | No Data | 16.88 | 14.14 |

## Conclusions

This research uses laboratory measured Z-factor of $\mathrm{CO}_{2}$-hydrocarbon mixture to analyze phase behavior, enhanced gas and enhanced condensate recovery for $\mathrm{CO}_{2}$ storage in depleted gas reservoirs. The laboratory measured $\mathrm{CO}_{2}$ compressibility factor (or Z-factor) is much lower than hydrocarbon gas mixtures at the specified temperatures and pressures. Therefore, that offers the opportunity to store larger surface volumes of $\mathrm{CO}_{2}$ than hydrocarbon gases. Five times the storage is possible depending on pressure, temperature and hydrocarbon gas composition

Storage of $\mathrm{CO}_{2}$ increases if the $\mathrm{CO}_{2} / \mathrm{HC}$ gas mixture compressibility (Z-factor) is low. Furthermore, if a liquid condensate occupies the reservoir pore space and the addition of $\mathrm{CO}_{2}$ vaporizes the liquid, then additional pore space is acquired for $\mathrm{CO}_{2}$ storage.

Nomenclature

$$
\begin{array}{ll}
P_{1} & =\text { cell pressure, psia } \\
V_{1} & =\text { volume of gas released from the cell, cc } \\
T_{1} & =\text { cell temperature, }{ }^{\circ} \mathrm{R} \\
P_{2} & =\text { ambient pressure, psia } \\
V_{2} & =\text { volume of gas at ambient pressure and temperature, } \mathrm{cc} \\
T_{2} & =\text { ambient temperature, }{ }^{\circ} \mathrm{R} \\
\mathrm{n} & =\text { number of moles of the system } \\
\mathrm{Z} & =\text { compressibility factor } \\
\mathrm{DGR} & =\text { Depleted Gas Reservoir } \\
\mathrm{HC} & =\text { Hydrocarbon } \\
\mathrm{CVD} & =\text { Constant Volume Depletion } \\
\mathrm{CCE} & =\text { Constant Composition Expansion }
\end{array}
$$

Subscripts
1 = Initial condition
$2=$ Final condition

## Acknowledgments

The authors wish to express their gratitude to the U.S. Department of Energy for sponsoring this study through research grant No. DE-FC26-01NT41145 awarded to the Center for Applied Petrophysical and Reservoir Studies in the Petroleum Engineering Department of Texas Tech University.

## References

1. Williams, D. F., "Extraction with Supercritical Gases," Chem. Eng. Sci., 361981.
2. Katz, D. L. and M. Rasin Tek, "Overview of Underground Storage of Natural Gas," SPE Paper 9390 presented at the 59th Annual Fall Technical Conference and Exhibition of the Society of Petroleum Engineers of AIME, held in Dallas, Texas, Sept. 21-24, 1980.
3. Rojas, G. and Requena, O.: "A New Method to Estimate Compressibility Factors for CO2 Hydrocarbon Mixtures," paper SPE 23661 presented at the Second Latin America Petroleum Engineering Conference, Caracas, Venezuela, March 8-11, 1992.
4. PVT System Model 2370 User's Manual, Ruska Instrument Corporation, March, 1995.
5. Burton Corblin Technical Bulletin (BCTB): http://www.burtoncorblin.com/BCTB302.pdf
6. Sage, B. H. and Lacey. W. N.: "Some properties of the Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide," API Research Project 37, American Petroleum Institute, New York (1955).
7. Sobers, L., Frailey, S. M. and Lawal, A. S., "Geological Sequestration of Carbon Dioxide in Depleted Gas Reservoirs," SPE 89345 to be presented at the Fourteenth Symposium on Improved Oil Recovery, Tulsa, Oklahoma, April 17-21, 2004.
8. McCain, W.D., "Chemical Composition Determines Behavior of Reservoir Fluids." Petroleum Engineer International (October 1993) 18-25.
9. McCain, W.D., "Heavy Components Control Reservoir Fluid Behavior," SPE 28214 (1994).
10. McCain, W., D., Properties of Petroleum Fluids 2nd Edition, PennWell Publishing, 1990.
11. Sources for NIST Database reference Version 7.0: C:INIST_Technical Databases Databases Distributed Standard Reference Data Program.htm
12. Standing, M.B.: "Volumetric and Phase Behavior of Oil Field Hydrocarbon Systems," Society of Petroleum Engineers of AIME. Dallas, Texas. (1977).
