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Reservoir fluid monitoring in carbon dioxide sequestration at Cranfield

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Abstract

Carbon dioxide (CO₂) injection into the lower Tuscaloosa formation at Cranfield started in December 2009 and has been maintained at over one million tonnes per year. Two observation wells F2 and F3 are approximately two degrees down-dip of the injection well F1 at a distance of 68 m and 112 m, respectively. The top of the formation varies from 10,428' (3178.45 m) at the injector F1 to 10,434' (3180.28 m) at observation well F3. All wells are perforated below 10,450' (3185.16) to the bottom of the lower Tuscaloosa formation.

Temperature, pressure and density (*T*, *P*, and ρ respectively) of the fluid in F2 and F3 were measured several months after displacement of brine from the wells by the lighter phase flowing past the perforations at the bottom of the wells. The static temperature profiles in wells F2 and F3 are identical, and thus are an excellent proxy for the geothermal gradient at the site. Using a suitable equation of state, and the measured *T*, *P* and ρ , fluid compositional profiles in F2 and F3 were inferred, assuming a binary mixture.

The measured density profile in F1, confirmed by pressure derivative with respect to depth, was inconsistent with that of pure CO_2 at the measured *P* and *T*. Contamination of CO_2 with a lower density fluid was therefore hypothesized, with methane being a natural choice. With this assumption, the error between the measured and calculated densities was minimized to estimate the binary mixture composition using the GERG 2008 equation of state. The resultant amount of methane was found to be almost 8 mol%. Analysis of samples taken from surface supply pipeline of the injected gas validated this contamination estimate, which was due to the mixing of recycled CO_2 from an enhanced oil recovery (EOR) site.

The density profiles measured in observation wells F2 and F3 indicate a change in fluid composition with depth. An analysis similar to that conducted for F1 allowed us to calculate the mixture composition based on the measured density profile. The best fit curve indicates that F2 contained >18 mol% methane near the surface decreasing to significantly less than 18% at the well bottom. F3 contained approximately 8 mol% methane in the top 65% of the well with almost pure CO_2 near the bottom.

The observation that the fluid in F2 contains a higher fraction of methane than the injected stream can be explained by dissolution of CO_2 and concomitant stripping of adsorbed and dissolved methane in the reservoir between F1 and the observation wells. Consequently, a methane-enriched fluid bank precedes the CO_2 -rich hyperbolic wave. The

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compositional variation of the CO₂-rich fluid as a function of depth in the wellbore reflects the fluid compositional profile in the formation.

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1. Introduction

Subsurface gas injection is used for enhanced oil or gas recovery, and in sequestration of carbon dioxide (CO₂). In certain circumstances it may be useful to know the injected gas composition introduced via an injection well into a reservoir. In the reservoir, the injected gas contacts and displaces the reservoir fluid. This changes the previously established thermodynamic equilibrium in the reservoir. The injected gas mixes with the reservoir gas or vapor phase (henceforth referred to as gas phase) and simultaneously diffuses into the liquid phase. This drive to equilibrium may cause repartitioning of components into phases, e.g., injection of CO₂ into methane saturated brine stream leads to preferential release of methane into the gas phase and dissolution of CO₂ into the brine or the liquid phase. Subsequently, the change in liquid and/or gas composition may lead to additional mass transfer with the solid phase, e.g., addition of CO₂ in the gas and liquid phases leads to preferential release of methane surfaces. Additionally, it may lead to dissolution/precipitation reactions with reservoir minerals. Consequently, the reservoir fluid and the injected gas compositions change due to mass transfer.

Observation wells are drilled away from injection wells to provide real-time measurements of the fluid composition at bottom-hole conditions. These measurements include sampling, well-well pressure interference, electromagnetic or seismic/acoustics, and well logs. The observation wells are usually perforated to allow fluid to enter the well if sampling is desired.

In all of these wells, a production log is used to measure flow rates, pressures, temperatures, and density as a function of depth. A density sonde infers density through differential pressures under flowing and static conditions. In this paper, the data available through such a log is used to (i) verify internal data consistency and (ii) present a calculation scheme to obtain wellbore composition (as a function of depth) that is representative of gas composition in the reservoir (as a function of time).

2. Site, reservoir and tool details

The Southeast Regional Carbon Sequestration Partnership (SECARB) Phase III projects share a common goal of safely demonstrating large-scale, long-term CO_2 injection and storage in saline reservoirs that hold significant promise for future development within the SECARB region.

The site, where the SECARB Early Test was conducted, is the Cranfield Unit near Natchez, Mississippi [1]. This field has an anticlinal four-way closure at a depth of 3,000 m, and was discovered in 1943. The reservoir is in the lower Tuscaloosa formation, above a regional unconformity, in valley-fill-fluvial conglomerates and sandstones separated by alluvial and overbank within-unit seals. The reservoir comprises stacked and incised channel fills and is heterogeneous, with an average porosity of 0.25 and permeability ranging from 50 millidarcy (mD) ranging to a Darcy (D). The field was produced to sub-economic water-cut by recycled gas drive. Subsequently, gas was produced to economic limit, and all wells were plugged and abandoned in 1965. A strong aquifer drive is documented by return to hydrostatic pressure prior to resumption of production in late 2008. New injectors with modern logs and cores and a pre-injection three-dimensional (3-D) seismic survey were completed in preparation for a new CO₂-

enhanced oil recovery (EOR) flood, concurrently permitting a measurement of the pressure response of the formation to a large volume CO_2 injection.

 CO_2 is sourced from the Jackson Dome reservoir. Injection pressure is boosted to a constant 2,900 psig and the CO_2 is distributed across the field via a buried pipeline system. Injection volumes and pressure is measured several times daily at each wellhead. Injection initiation was phased across the field and in the HiVIT (a 10 km² area in the north-east quadrant of the Cranfield unit lease). In order to meet project metrics CO_2 injection was boosted in the downdip areas. Injection began in the HiVIT in a few wells in 2008, and the 1 Mt/y rate for the HiVIT was obtained in December 2009. The 1.5 Mt stored goal was reached in early 2011.

Platform Basic Measurement Sonde (PBMS) is an essential part of the modular Production Services Platform and provides traditional measurements taken in producing wells including gamma ray, casing collar location, pressure, and temperature. Crystal Quartz Gauge (CQG) is used for pressure measurements ensuring high accuracy (2 psi+0.01%), high resolution (0.01 psi), and temperature compensation, which is particularly important when logging flow profiles with high-temperature gradients. We refer the reader to the PBMS and PGMS (Platform Gradiomanometer Sonde) literature for understanding pressure, temperature, and density measurement [2]. For our purposes here, it suffices to note that the accuracy and resolution of the temperature measurement are 1 °C and 0.005 °C respectively. The accuracy of the density measurement is 0.04 g/mL with the resolution being 0.002 g/mL.

3. CO₂-CH₄-brine system

Qin et al. [3] present experimental data for the $H_2O + CO_2 + CH_4$ ternary system. They also present solubility data for the binary $H_2O + CO_2$ and the $H_2O + CH_4$ systems. A comparison with previously generated models [4, 5] shows a good fit. Table 1 is a compilation of some of these experimental results for the binary $H_2O + CH_4$ and ternary $H_2O + CO_2 + CH_4$ system. These results clearly indicate that methane solubility in water decreases in the presence of CO_2 . The column labeled 'ratio' presents the ratio of the measured value of the methane mole fraction in water after CO_2 addition to experimental value for the methane mole fraction in water in the absence of CO_2 (i.e., for the binary CH_4 – H_2O mixture). Numbers in this column vary from 0.27 to 0.37 indicating release of methane from the aqueous phase with the addition of CO_2 to the binary mixture. Multicomponent-multiphase displacement leads to a Riemann problem that predicts CH_4 leading CO_2 in the produced fluid [6].

		Binary		Ternary mixture		
T (K)	P (MPa)	x (CH ₄)	y (CH ₄)	x (CH ₄)	ratio	x (CO ₂)
375.8	49.9	0.0041	0.9948	0.00152	0.3707317	0.01971
375.8	40.2	0.0035	0.9943	0.00127	0.3628571	0.01882
375.6	30.2	0.003	0.9934	0.00104	0.3466667	0.01801
376.1	20.6	0.0023	0.9916	0.00077	0.3347826	0.01524
375.7	10.9	0.0014	0.9869	0.00038	0.2714286	0.01065
324.4	49.5	0.0039	0.9992	0.00125	0.3205128	0.02231
324.2	30.1	0.003	0.999	0.00092	0.3066667	0.01966

Table 1: Experimental solubility data for the binary $H_2O + CH_4$ and the $H_2O + CH_4 + CO_2$ systems [3].

4. Data Interpretation

Fig. 1 is a graph of pressure versus depth for an injection well F1, collinear first and second observation wells, F2 and F3. As expected, bottom-hole pressure is higher in the injection well F1, than in the observation wells. F2 and F3 are only 44 m apart and their bottom-hole pressure is close to the far-field reservoir pressure at the corresponding depth. The pressure derivative along the wellbore in F1 and F2 differ because of dissimilar fluid compositions.



Fig. 1: PBMS measured pressure profiles in injection and observation wells.

Fig. 2 is a graph of temperature versus depth for the injection well F1 and observation wells F2 and F3. The temperature in the injector well increases as a function of depth due to geothermal heating and the compressive heating. The static temperature profiles in observation wells F2 and F3 are identical and thus are reflective of the local geothermal gradient.



Fig. 2: PBMS measured temperature profiles in injection and observation wells.

4.1. Injection well F1

Fig. 3 shows a plot of the measured and calculated CO_2 density in injection well F1, as a function of depth. PGMS measured density is almost a constant with an increase in pressure offset by the decrease in temperature. As expected, the density measured has noticeable fluctuations. To ensure that the density measurement was accurate (as opposed to precise), fluid density was also computed from the differential of pressure (measured using the PBMS sonde as shown in Fig. 1) using 1/g. dp/dz where g is the acceleration due to gravity, p is the pressure and z is the depth. Although the calculated density exhibits scatter, accuracy of the PGMS density is evident. The calculated CO₂ density, calculated at each depth using the measured pressure and temperature, is higher than the measured density at all depths and the difference is fairly constant over the entire depth. The obvious conclusion from this observation is that the injected fluid is not pure CO₂ but a mixture of CO₂ and fluid(s) of lower density.



Fig. 3: PGMS measured and EoS calculated density profiles in injection well F1.

Injected CO_2 at this site is supplied by Jackson Dome, a natural source in Mississippi. Gas composition is 98.75-99.38% CO_2 , with small amounts of methane and nitrogen [7].

Since both methane and nitrogen are fluids of density lower than CO_2 at identical pressure and temperature, they could be potential contaminants in the injected CO_2 stream. To quantitatively determine composition of a binary mixture, methane and nitrogen were assumed in turn, and the mole fraction was computed using the computation scheme is shown in Fig. 4. We assume a mole fraction for the contaminant in the injected stream. Using the injection well measured temperature and pressure; we compute the density of the fluid mixture (CO_2 and contaminant) along the depth of the wellbore. We used the GERG 2008 equation of state (EoS) for this computation. The sum of the square of the difference in measured and computed densities at each depth along the wellbore is minimized to converge to a binary composition.



Fig. 4: Details of the computation scheme used to calculate the composition of the unknown gas mixture, given the density profile.

The analysis indicated a converged injected molar fluid composition of 91.66% CO₂, 8.34% methane. The amount of methane in this stream is significantly higher than in the CO₂ stream from Jackson Dome. The dichotomy was resolved when it was established that the injected fluid stream is a mixture of the gas from Jackson Dome and a recycle stream from the EOR operations at this site. Surface composition measurements of the injected fluid stream have confirmed the gas composition calculated using this analysis.

4.2. Observation well F2

Fig. 5 shows the measured and calculated density profiles in the stagnant observation well F2. PBMS and PGMS sondes were run in this well on September 7, 2010. As in the injection well F1, the measured density profile is shown as the noisy curve labeled PGMS, whose agreement is with pressure differential is also shown. Density of pure CO_2 at wellbore pressure and temperature is also plotted on this graph. It is obvious that the observation well is filled with a CO_2 fluid mixture that contains contaminants that have a lower density than CO_2 .



Fig. 5: PGMS measured and EoS calculated density profiles in observation well F2.

Using the computation scheme detailed in Fig. 4, and choosing methane as a contaminant, we converge to a fluid mixture molar composition of 81.84% CO₂, 18.16% methane. However, an examination of the calculated density for this mixture shows that it does not fit the measured density profile as well as in F1. The cross-over to a higher concentration of methane from the inferred average is at about 1219 m (4000'). Rather than carrying out a global least square error with a single density, composition was allowed to vary. The resulting density curve, also shown in Fig. 5, matches the measured density well. The corresponding fluid composition profile is shown in Fig. 6. The CO₂ mole fraction increases almost monotonically with depth, except for a couple of sharp changes close to 3048 m (10000 feet).



Fig. 6: EoS calculated gas composition in injection well F2.

Prior to CO_2 injection, observation well F2 was filled with brine to match the bottomhole pressure. Any unintended flow from the wellbore was prevented. During injection, migration of CO_2 past wells F2 and F3 results in displacement of brine (see schematic in Fig. 7), dissolution of CO_2 into the brine, and possibly concomitant stripping of methane from the mineral surface and the brine. As per the dictates of local thermodynamic equilibrium in pseudo one-dimensional flow, a methane rich finite pulse precedes CO_2 . As the CH_4 and CO_2 plume migrate to F2 and F3, bubbles of the respective gases buoyantly rise within the wellbore and displace brine until nearly the entire wellbore is ultimately filled with the CO_2 rich phase. During this phase replacement, the fluid composition in the CO_2 -rich plume changes with time due to (i) changes in injected fluid composition, and (ii) mass transfer within the reservoir.



Fig. 7: Schematic representation of the CO_2 plume migration in the lower Tuscaloosa formation. Note that the brine in the observation wells is gradually displaced with the less dense CO_2 -CH₄ gas mixture flowing past the perforations.

Wellhead pressure was also monitored for wells F1, F2 and F3. These are shown in Fig. 8. Given that the bottomhole pressure in F2 and F3 are close to *local* reservoir pressure, the difference in bottomhole and wellhead pressures are indicative of fluid column weight. A decrease in this difference is therefore indicative of a decrease in fluid density in the wellbore. As estimated from Fig. 8, the CO₂ plume arrived near F2 on December 16th, 2009 and took 5 days, 19 hours and 37 minutes to completely displace the brine from the wellbore. Due to buoyancy within the wellbore, in the absence of mixing, the earliest CO₂ to arrive at the perforations is likely to be at the top. A time sequence is therefore preserved in the vertical compositional variation in the wellbore.



Fig. 8: Surface pressure measurements in injection well F1 and observation wells F2 and F3. Note the increase in surface pressure in observation wells F2 and F3, reflecting the displacement of brine by the CO_2 -CH₄ mixture flowing past the perforations.

Using a U-tube sampling technique [8], fluid samples were withdrawn from the wellbore at bottomhole pressure conditions for compositional analysis (Fig. 9). These samples indicate an increase in CO_2 mole fraction with time. We superpose the plot of U-tube fluid composition versus time with the EoS composition versus depth, also shown in Fig. 9. The flow of CO_2 -containing fluid into the wellbore is assumed to be a constant as bottomhole pressure is relatively constant during the time it takes for the wellbore brine to be displaced. Note that the time scale starts at the time that the CO_2 -containing fluid to completely displace the brine in the wellbore. The U-tube samples show systematically higher methane content than the computed EoS values. There is also a significant amount of noise in the U-tube fluid sample composition.



Fig. 9: Comparison of the EoS calculated composition in observation well F2 to the U-tube measured composition of the gas flowing past the perforations. The U-tube measured composition indicates significant noise and consistently reports a higher level of methane in the gas stream. The solid curves with the lower compositional noise represent the Eos calculated composition of the gas in the wellbore for observation well F2, as a function of depth.

U-tube samples were withdrawn at a depth of 10,450 - 10,452 feet (3185.16 - 3185.77 m), about five feet (1.52 m) below the packer. The tubing is perforated from 10,450 - 10,484 feet (3185 - 3195.5 m), or the upper half of the injection interval. It is likely that there is a composition difference in the gases that exist within the casing interval at these depths. This could potentially explain the difference in composition between the U-tube samples and the EoS analysis.

4.3. Observation well F3

PGMS measured density for the fluid in observation well F3 is shown in Fig. x10. A density increase from the bottom to about 6000' (1828.8 m) is followed by a sharp decrease and a subsequent increase to the surface. Pure CO_2 density, at wellbore pressures and temperatures, is also shown on this graph, indicating that at depths greater than 2000 m, the fluid is almost pure CO_2 . At depths less than 6000' (1828.8 m), a significant amount of methane is likely present in the wellbore fluid.



Fig. 10: PGMS measured and EoS calculated density profiles in observation well F3. Note that the density calculated from differential of the PBMS measured pressure does not coincide with the PGMS measured density, indicating a measurement drift.

Using a computational scheme similar to that for well F2, the fluid composition as a function of depth was calculated. The fluid density for this calculated composition is plotted on this graph as 'GERG08'. The estimated fluid composition as a function of depth is shown in Fig. x11. As indicated by the density plot, at depths greater than 6500' (1981.2 m), the wellbore fluid is mostly CO_2 . There is a transition region over approximately 500' (152.4 m) where the methane mole fraction in the fluid rapidly increases with decrease in depth. From 6000' (1828.8 m) to the surface, the methane mole fraction decreases marginally.



Fig. 11: The Eos calculated composition of the gas in the wellbore for observation well F3, as a function of depth.

From the wellhead pressure data shown in Fig. 8, we know that wellbore F3 filled up with CO_2 containing fluid from December 19, 2009 over a period of six days, eight hours and 42 minutes. During this time, there were no sudden concentration changes in the injected CO_2 -rich stream. In addition, there were no rapid concentration changes observed in F2. The rapid change in density (and therefore, the composition) of the fluid around 6000' (1828.8 m) has to be related to an event specific to F3. Correspondence with GCCC revealed that the wellbore had been vented for a small time in April 2010. This caused the fluid in the wellbore to depressurize. It is likely that initially, a mixture of CO_2 -rich fluid and brine from the reservoir was drawn into the wellbore till the composite (gas and liquid) column pressure in the wellbore equalled reservoir pressure. Then, gradually the brine was expelled from the wellbore by bubbles of CO_2 -rich fluid rising up through the brine. The CO_2 -rich fluid flowing past the perforations in April 2010 was significantly different in composition from the initial plume that had been captured in F3. Therefore, this leads to the observed sharp transition in CO_2 composition and fluid density in the wellbore around 6000' (1828.8 m).

5. Results and conclusions

Pressure, temperature and density measurements were obtained in injection well F1, and observation wells F2 and F3 at the Cranfield injection site. These measurements were conducted almost nine months after CO_2 injection commenced in December 2009. The binary gas mixture composition in these wells could be inferred by forcing consistency with a mixture equation of state and indicated a substantial methane content in injection well F1.

For observation well F2, the change in gas composition with depth was correlated well to the U-tube measured gas composition for the fluid flowing past the wellbore. This indicates that this measurement and post computation scheme for gas composition analysis may be used as a downhole fluid monitoring technique. It is more robust and significantly cheaper than downhole measurement techniques.

In observation well F3, a remarkable transition in gas density was calculated at a depth of 6000' (1828.8 m). This assessment could be reconciled with a well venting event.

In conclusion, P, T and/or C coupled with a suitable EoS allow for the calculation of fluid composition in a wellbore. This represents a simple and inexpensive way to monitor downhole fluid composition as a function of time in observation wells. This analysis may also be used to investigate anomalous density, pressure or compositional profiles observed in wellbores. The purity of injected gas may also be confirmed with this analysis.

References

- [1] Hovorka, S. D., Meckel, T. A., Trevino, R. H., Lu, J., Nicot, J. P., Choi, J. -W., Freeman, D., Cook, P., Daley, T. M., Ajo-Franklin, J. B., Freifeld, B. M., Doughty, C., Carrigan, C. R., La Brecque, D., Kharaka, Y. K., Thordsen, J. J., Phelps, T. J., Yang, C., Romanak, C. D., Zhang, T., Holt, R. M., Lindler, J. S., and Butsch, R. J., 2011, Monitoring a large volume CO₂ injection: Year two results from SECARB project at Denbury's Cranfield, Mississippi, USA: *Energy Procedia*, 4, 3478–3485, doi: 10.1016/j.egypro.2011.02.274.
- [3] Qin, J., Rosenbauer, R. J. and Duan, Z. H., Experimental measurements of vapor-liquid equilibria of the H₂O + CO₂ + CH₄ ternary system, *J. Chem. Eng. Data*, 2008, **53**, 1246-1249.
- [4] Duan, Z. H.; Mao, S. D. A Thermodynamic Model for Calculating Methane Solubility, Density and Gas Phase Composition of Methane-bearing Aqueous Fluids from 273 to 523 K and from 1 to 2000 bar. *Geochim. Cosmochim. Acta* 2006, 70, 3369–3386.
- [5] Duan, Z. H.; Sun, R. An Improved Model Calculating CO₂ Solubility in Pure Water and Aqueous NaCl Solutions from 273 to 533 K and from 0 to 2000 bar. *Chem. Geol.* 2003, **193**, 257–271.
- [6] Rhee, H. K., Aris, R., and Amundson, N. R., 'On the Theory of Multicomponent Chromatography', Phil. Trans. Royal Soc. London, 1970, A267, 419-455.
- [7] Zhou, Z., Ballentine, C. J., Schoell, M., and Stevens, S. H, American Geophysical Union, Fall Meeting 2003.
- [8] Freifeld, B. M., Trautz, R. C., Yousif, K. K., Phelps, T. J., Myer, L. R., Hovorka, S. D., and Collins, D., 2005, The U-tube: A novel system for acquiring borehole fluid samples from a deep geologic CO₂ sequestration experiment: *Journal of Geophysical Research*, **110**, B10203, doi:10.1029/2005JB003735.