

# **A FIRST STEP IN EVALUATING THE ROLE OF DIFFUSION IN EOR IN TIGHT SHALE FORMATIONS**

Son T. Dang<sup>(1)</sup>, Carl H. Sondergeld<sup>(1)</sup>, Chandra S. Rai<sup>(1)</sup>, Ali O. Tinni<sup>(1)</sup>, Nicholas Drenzek<sup>(2)</sup>

(1) Mewbourne School of Petroleum and Geological Engineering  
University of Oklahoma

(2) Baker Hughes, a GE Company

## **ABSTRACT**

Miscible Gas Injection has been proven to be amongst the few successful Enhanced Oil Recovery (EOR) techniques, which can be applied in unconventional reservoirs. Recent reports from Oil & Gas companies suggested this process can enhance 30% up to 70% of current recovery. An effective and economical project depends on the understanding of gas transportation during both injection and flow-back. Previous modelling and theoretical investigations have shown that diffusion could be one of dominant transport mechanisms in low permeability shales (microporous media). Despite the importance of diffusion as a transport mechanism in shales, direct measurements of diffusion coefficients in shales are not currently available. The main reason for the lack of currently available techniques due to the fact of pore volume in shale is generally small. This work summarizes a novel approach to measure of the diffusion coefficient of injected gases' components into shale samples. The effective diffusion between methane versus nitrogen were simultaneously measured with Infrared Spectroscopy (IR) methods. IR captured the change in methane/nitrogen concentration at the outlet of the sample as function of time. The difference of effective diffusions without and with microporous media, provide sample tortuosity. In the end, a simulation model was established based on the experimental setup to back-calculate diffusion rate.

## **INTRODUCTION**

Hill and Lacy, 1934[1]; Bertram and Lacy, 1935[2]; Reamer et al., 1956[3] have shown that the rate of dissolution of methane in a body of hydrocarbon liquid is controlled primarily by the rate of diffusion of the dissolved gas from the gas-liquid interface into the body of the liquid phase. On the other hand, the tortuous features of porous media also govern how fast gas injected into matrix. Therefore, it is critical to understand the diffusion processes in any gas injection process in oil reservoirs.

Effective diffusion measurements in both dry and saturated porous media has been well established, although the availability of measurement data is limited (Chen, 1973[4]; Pandey et al., 1974[5]). Many different methods utilizing secondary parameters, including pressure decay (Chen et al., 2018[6]) or resistivity (Garrouch et al., 2001[7]) to capture diffusional characteristics. However, the most direct technique to measure diffusion rate is Wicke and Kallenbach, 1941[8] method, in which nitrogen is injected across one face of cylindrical porous media, and methane is injected across the other. Equation (1) developed by Evans et al., 1961[9] to back calculate diffusion rate by monitoring change in fluid composition on both side of the porous media.

$$D_e = \frac{N_n \alpha R T L}{P A \ln\left(\frac{1 - \alpha Y_{nf}}{1 - \alpha Y_{ni}}\right)} \quad (1)$$

$$\alpha = 1 - \frac{N_m}{N_n}$$

, in which  $D_e$  as effective diffusion coefficient;  $N_n$  and  $N_m$  are respectively molar diffusion rate of nitrogen and methane, mole/s;  $T$  is absolute temperature, °K;  $L$  is sample length, cm;  $R$  is gas constant;  $P$  is pore pressure, cm Hg;  $A$  is area of cross section, cm<sup>2</sup>;  $Y_{nf}$  and  $Y_{ni}$  are respectively nitrogen mole fraction at final and initial points.

Most of diffusion rates were computed or measured from previous methods for conventional rocks reasonably agree. However, for unconventional tight rock like shales, there are drawbacks from each of those methods mainly due to the small storage and transmissibility factor. One common method is the monitoring of pressure decay while injecting gases to saturated sample; one of assumptions to validate this method is the instant pressure transit from the sample borders to the sample center. This is very weak assumption for tight rocks. Wicke and Kallenbach method theoretically can be applied for tight rock; however, the practical difficulty of this technique lies on how fluid composition should be examined without flow interference. Small transmissibility characteristics of shales make conventional fluid sampling impossible. Moreover, the time-discrete fluid sampling make it challenging to capture breakthrough time.

In this work, we develop a new experimental approach, and introduce a new experimental set up to measure diffusion in tight rock like shales.

## EXPERIMENTAL APPROACH AND METHOD

Previous diffusion measurement data on sandstones Chen et al., 1977[10] suggested diffusion factor (DF), the ratio of the diffusion coefficient across the porous media to the

diffusion coefficient across open space, is a reverse function of samples tortuosity. The ultimate objective of the study is estimate effective diffusion coefficient of methane through liquid saturated tight rock samples. We propose the experimental approach, in which effective diffusion coefficient of methane through liquid saturated porous matrix can be estimated from bulk methane-liquid diffusion coefficient and diffusion factor of porous media.

Many previous studies have been done on bulk methane-liquid diffusion. Riazi et al., 1996[11] developed a method for determining diffusion coefficients of gases in liquids at constant volume and temperature using a PVT cell. Jamialahmadi et al., 2006[12] proposed an interesting approach using oil swelling factor as a function of time to estimate methane diffusion rate into different alkanes at high pressure and temperature.

The focus of the study is to measure diffusion factor of porous media. By modifying Wicke and Kallenbach method, we introduce novel approach to continuously monitor change in fluid composition on one face of cylindrical sample.

Infrared Spectroscopy (IR) has been applied extensively to characterize materials in different forms, including solid, liquid, and gas phases. In oil and gas industry, this spectral analysis had been employed to measure mineralogy (Ballard, 2007[13]) and reservoir fluid composition (Livanos et al., 2016[14]). Typically, all of these measurement was prepared under ambient or low range of pressure condition. For our objective, high pressure IR cells with transparent IR windows (Zinc Selenium for maximum 2500 psi and Sapphire for maximum 5000 psi) was installed in line with rock sample holder to capture flow-through fluid signal. Thermo-Scientific Nicolet 6700® FT-IR spectrometer (wavelength number ranges  $600 - 4000 \text{ cm}^{-1}$ ) was used to continuously measure and analyze fluid signal. The schematic experimental set up is presented in Figure 1.

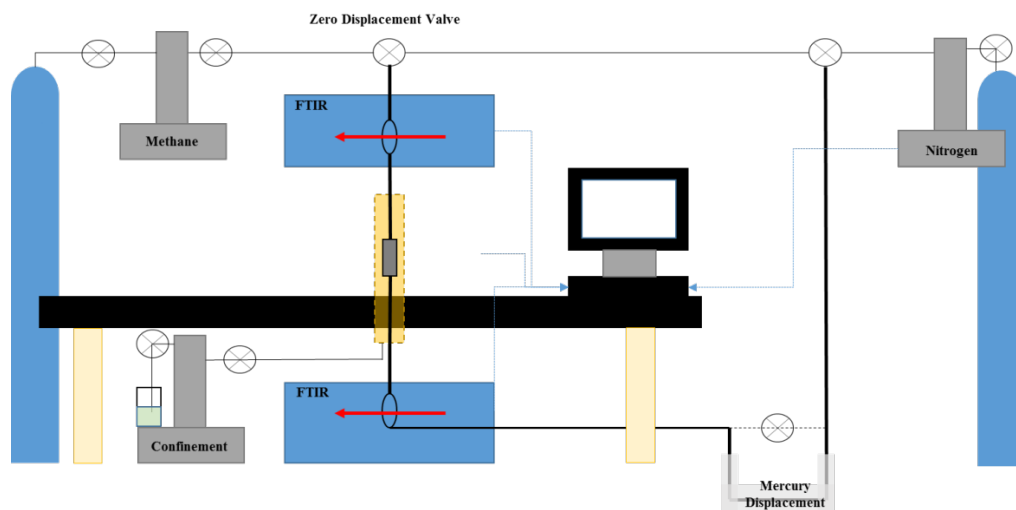


Figure 1. Experimental apparatus, in which porous media was filled with nitrogen for 24 hours, then methane was diffused through the porous media when the zero displacement valve was opened. Mercury

displacement pump was used to keep the system under constant pore pressure throughout the diffusion process.

During experiments, methane was diffused through rock sample saturated with nitrogen, constant pressure was maintained from both ends using mercury displacement pump. Rock sample was confined with effective pressure of 3000 psi.

## FOURIER TRANSFORM – INFRARED SPECTROSCOPY (FT-IR) CALIBRATION

Throughout the diffusion process, the dynamic change of fluid composition is due to the exchange of methane and nitrogen molecules. Single light beam shot across transparent IR windows; the spectrometer captures IR absorbance intensity, which is due to the vibration of gas molecules between IR windows. As a symmetric diatomic molecule, nitrogen does not yield IR absorbance. On the other hand, methane absorbance spectrum can easily be captured with the main absorbance range of 2800-3100  $\text{cm}^{-1}$  (Figure 2. Nistchem Webbook[15])

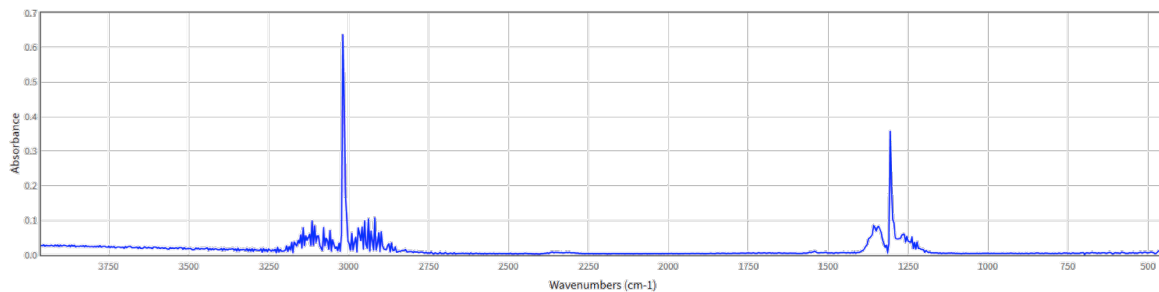


Figure 2. Mid-range FTIR absorbance spectrum of methane. The main absorbance range is from 2800-3100  $\text{cm}^{-1}$ .

Beer-Lambert law (Equation 2) proposes the linear relationship between IR absorbance intensity and gas concentration.  $C_o$ , defined as IR absorptivity coefficient of a particular gas, is a function of pressure and temperature. In this study, every experiment was executed at room temperature. Therefore, for a single diffusion test at a certain pressure, methane concentration calibration need to be provided.

$$A = l \sum_{i=1}^N \epsilon_i c_i \quad (2)$$

, in which  $A$  is absorbance,  $l$  is the path length of the beam of light through IR transparent windows,  $\epsilon_i$  is the absorptivity of each gas component at a particular pressure-temperature condition, and  $c_i$  is the concentration of each gas component within the gaseous phase.

Rubotherm Flexidose® Gas mixer was used to generate three mixtures of methane – nitrogen with different concentrations. These three gas mixtures were used to estimate IR absorptivity coefficient at different pressures. Figure 3 presents the relationship between IR absorbance intensity versus pressure (pressure ranges from 100-500 psi) for different

gas mixtures. Figure 4 present the relationship between IR absorbance intensity versus methane molar concentration at 500 psi. The slope of linear correlation provide methane absorptivity coefficient at 500 psi. Repeating the same procedure, we obtain methane absorptivity coefficients at 200 psi and 300 psi. These coefficients later were used to convert continuous IR absorbance spectra to continuous methane concentration profile during diffusion tests.

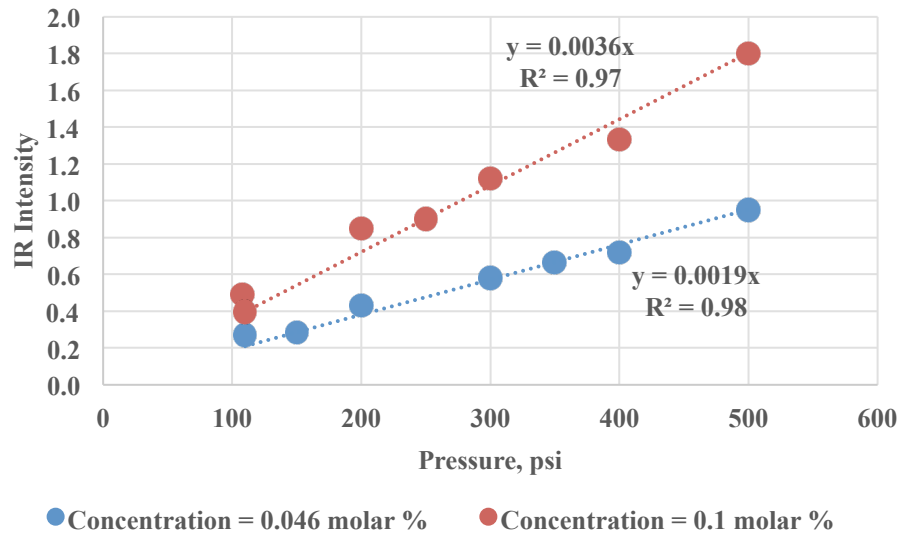


Figure 3. IR absorbance intensity of two methane-nitrogen mixtures at different pressures

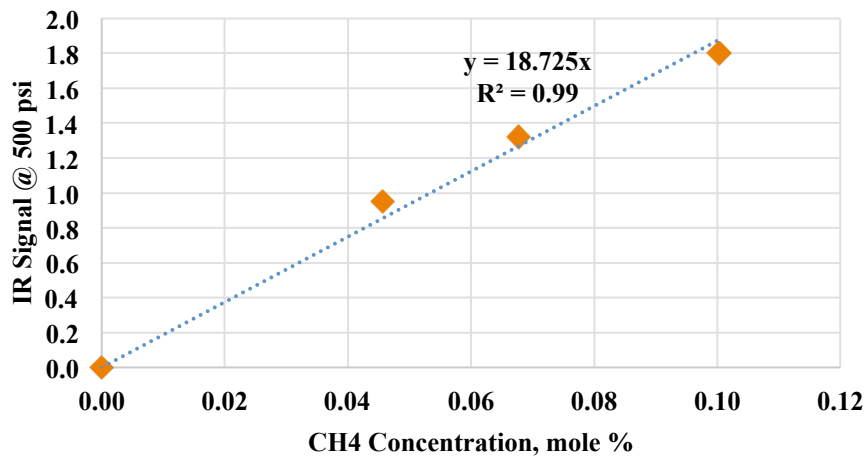


Figure 4. IR absorbance intensity of different methane-nitrogen mixtures at 500 psi, room temperature. The slope of linear correlation is considered as methane absorptivity, specifically at 500 psi.

## EXPERIMENTAL RESULTS AND DISCUSSION

A horizontal 1" core plug was selected for this study; the sample has total Helium crushed porosity of 3% was dried at 100°C under vacuum condition for 72 hours before each measurement. Different diffusion measurements were conducted at different pore

pressures, and at the same effective pressure with the same core plug. Figure 5 present methane concentration profiles versus square root of time in minutes for methane-nitrogen diffusion through a shale sample and open space at a constant pressure of 500 psi. For bulk methane-nitrogen diffusion process, the breakthrough time is about 450 mins; whereas for the diffusion within a shale sample, the breakthrough time is about 3600 mins. The maximum molar concentration of methane at the end of each experiment (6400 minutes) is about 10%. With these small concentration, conventional fluid sampling would not be able to provide robust concentration profile for diffusion rate calculation. However, IR spectrometer under stable background condition and filter denoising algorithm can detect methane signal down to the concentration of several ppm (Zhu et al., 2012[16].) Using Equation 1, effective diffusion coefficients through open space and the shale sample are estimated as  $3.25 \times 10^{-8}$  and  $0.4 \times 10^{-8}$  m<sup>2</sup>/s, respectively. Applying these coefficients with second Fick's law assuming 1-D model, we generated methane concentration profiles, which are agree reasonably with experimental data (Figure 6.) The slight difference between fitted data and measured data can be due to the fact this is a 3-D diffusion process in reality. However, the assumption of 1-D diffusion problem is not a bad assumption, due to the fact horizontal permeability is much larger than vertical permeability in shale. Diffusion factor is about 0.125 for diffusion process at 500 psi. Diffusion factor data are presented in Figure 7, as a function of pressure. Calculated diffusion factors at different pressure point are the same with 90% confidence. This confirms diffusion factor represents tortuous characteristic of porous media.

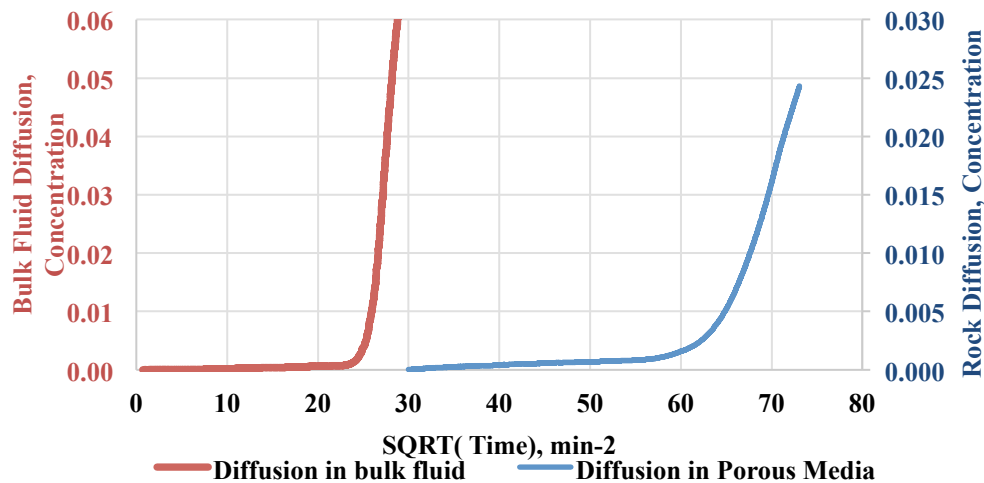


Figure 5. Methane concentration versus square root of diffusion time. The red curve is methane-nitrogen diffusion through open space. The blue curve is methane-nitrogen diffusion through a rock sample

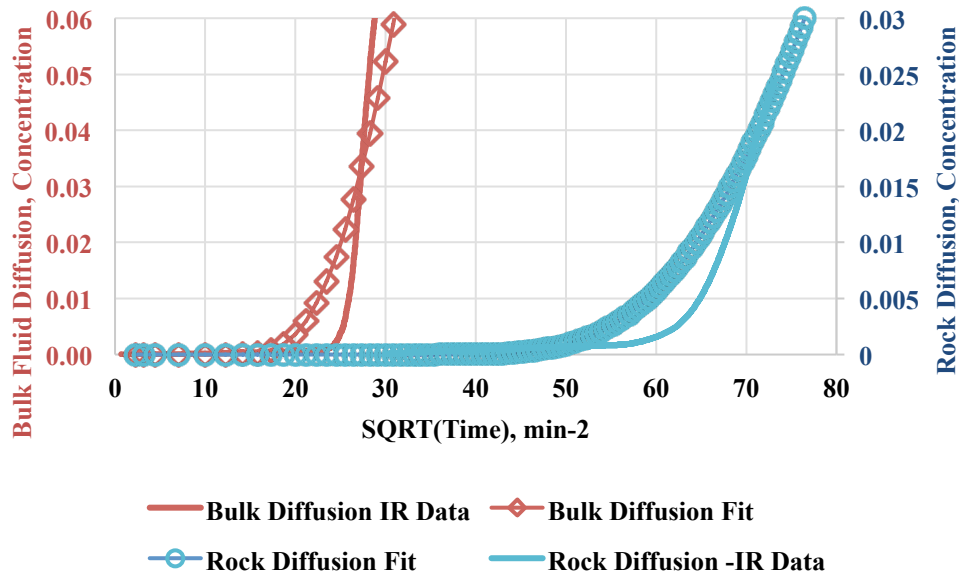


Figure 6. Methane-nitrogen diffusion through open space (red) and a rock sample (blue). Solid lines are experimental data, while open circles are fit data using second Fick’s law with effective diffusion coefficients are  $3.25 \cdot 10^{-8}$  and  $0.4 \cdot 10^{-8}$  m<sup>2</sup>/s, respectively for bulk fluid diffusion and porous media diffusion.

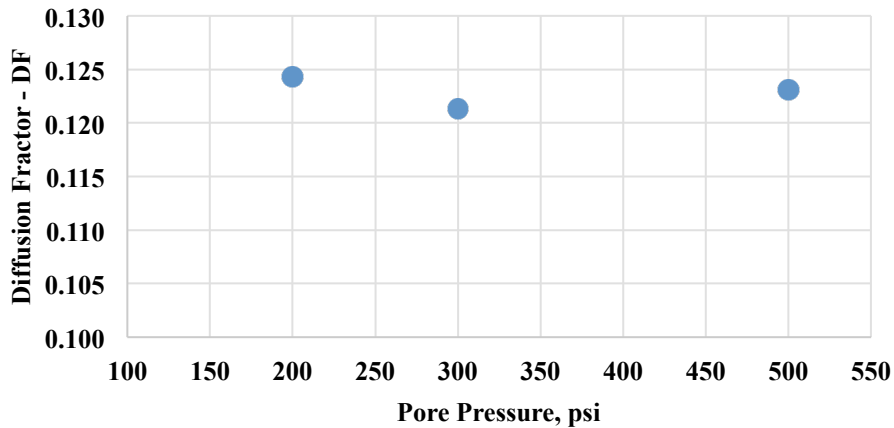


Figure 7. Diffusion factor, or the ratio of effective diffusion coefficient through porous media to diffusion coefficient through open space, is constant within pore pressure range 100-500 psi.

Tortuosity for the shale sample is estimated as the reverse of diffusion factor; this shale sample has porosity of 3%. The result was plotted in combined literature data, show the negative exponential correlation between tortuosity and porosity (Figure 8.) Note the data include measured tortuosity values for sand pack, unconsolidated sands, and tight sands.

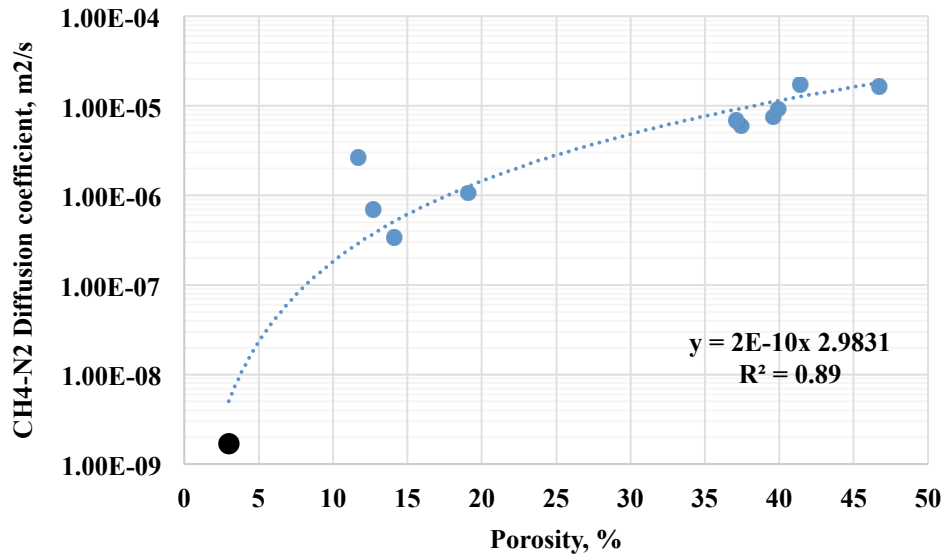


Figure 8-A. Effective methane-nitrogen diffusion coefficient from the tight rock sample used in this study (with porosity of 3%) was plot against literature data (Chen et al., 1977)

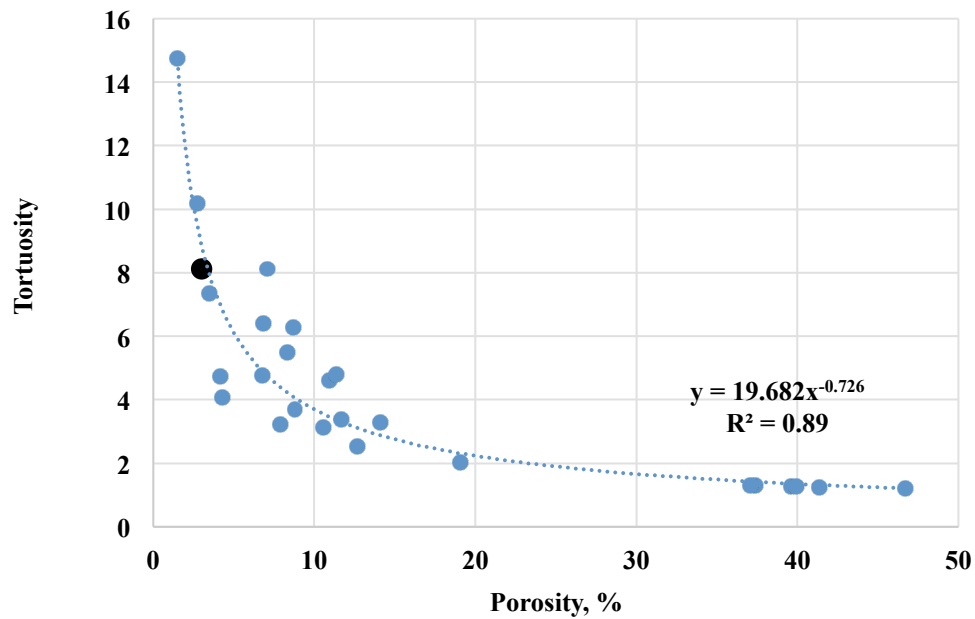


Figure 8-B. Dimensionless tortuosity, or the reverse of diffusion factor –DF, from the tight rock sample used in this study (with porosity of 3%) was plot against literature data (Chen et al., 1977.)

During huff-n-puff in shales, soaking time optimization is critical in both technical sense and practical sense. The common exercises reported by several companies, which gained



initial successes in Eagle Ford shale, is that they had tried to soak the formation for 1 to 2 months. Assuming most of shale formations with porosity less than 5-7%, shale tortuosity factor is above 5, and methane-oil diffusion ranges  $1-2 \times 10^{-8} \text{ m}^2/\text{s}$ , this means injected gas does not move into the formation for than 1-2 ft after that typical soaking time. Most of injected gas-reservoir fluid interaction would happen near fracture/cracks surfaces.

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## REFERENCES

1. Hill, E.S., and Lacy, W.N., 1934. Rate of solution of methane in quiescent liquid hydrocarbons. *Ind. Eng. Chem.* 26, 1324–1327.
2. Bertram, E.A., and Lacy, W.N., 1935. Rates of solution of gases in oils. *Ind. Eng. Chem.* 28, 316–318.
3. Reamer, H.H., Opfell, J.B., and Sage, B.H., 1956. Diffusion coefficients in hydrocarbon systems: methane–decane–methane in liquid phase. *Ind. Eng. Chem.* 48, 275–282.
4. Chen, L.L.Y., 1973. Binary Gas Diffusion of methane-nitrogen through porous media. Ph.D. Thesis, Univ. Mich.
5. Pandey, G.H., Katz, D.L., and Tek, M.R., 1974. Diffusion of fluids through porous media with implications in petroleum geology. *American Association of Petroleum Geologists Bulletin*, 58, No. 2, 291
6. Chen, M., Kang, Y., Zhang, T., You, L., Li, X., Chen, Z., Wu, K., and Yang, B., 2018. Methane diffusion in shales with multiple pore sizes at supercritical conditions. *Chemical Engineering Journal*, No. 334, 1455-1465
7. Garrouch, A.A., Liaqat, A., and Fuad, Q., 2001. Using diffusion and electrical measurement to assess tortuosity of porous media. *Ind. Eng. Chem. Res.*, No. 40, 4363-4369
8. Wicke, E., and Kallenbach R., 1941. Die Oberflächendiffusion von Kohlendioxyd in aktiven kohlen. *Kolloid Zeitschrift*, 97, 135.
9. Evans R.B., Watson G.M., and Mason E.A., 1961. Gaseous diffusion in porous media at uniform pressure, *J. Chem. Phys.*, 35, No. 6, 2076
10. Chen, L.L.Y., Katz, D.L., and Tek, M. R., 1977. Binary gas diffusion of methane-nitrogen through porous media. *AIChE Journal*, Vol. 23, No. 3, 336
11. Riazi, M.R., 1996. A new method for experimental measurement of diffusion coefficients in reservoir fluids. *J. Pet. Sci. Eng.* 14, 235–250
12. Jamialahmadi, M., Emadi, M., and Muller-Steinhagen, H., 2006. Diffusion coefficients of methane in liquid hydrocarbons at high pressure and temperature. *Journal of Petroleum Science and Engineering*, No. 53, 47-60

13. Ballard, B.D., 2007. Quantitative Mineralogy of Reservoir Rocks Using Fourier Transform Infrared Spectroscopy. Society of Petroleum Engineers. doi:10.2118/113023-STU
14. Livanos, G., Zervakis, M., Pasadakis, N., Karelioti, M., and Giakos, G., 2016. Deconvolution of petroleum mixture using mid-FTIR analysis and non-negative matrix factorization. *Measurement Science and Technology*, No. 27
15. NistchemWebbook, <https://webbook.nist.gov/cgi/cbook.cgi?ID=C74828&Units=SI&Type=IR-SPEC&Index=0#IR-SPEC>
16. Zhu, Z., Xu, Y., and Jiang, B., 2012. A one ppm NDIR methane gas sensor with single frequency filter denoising algorithm. *Sensor*, 12, 12729-12740