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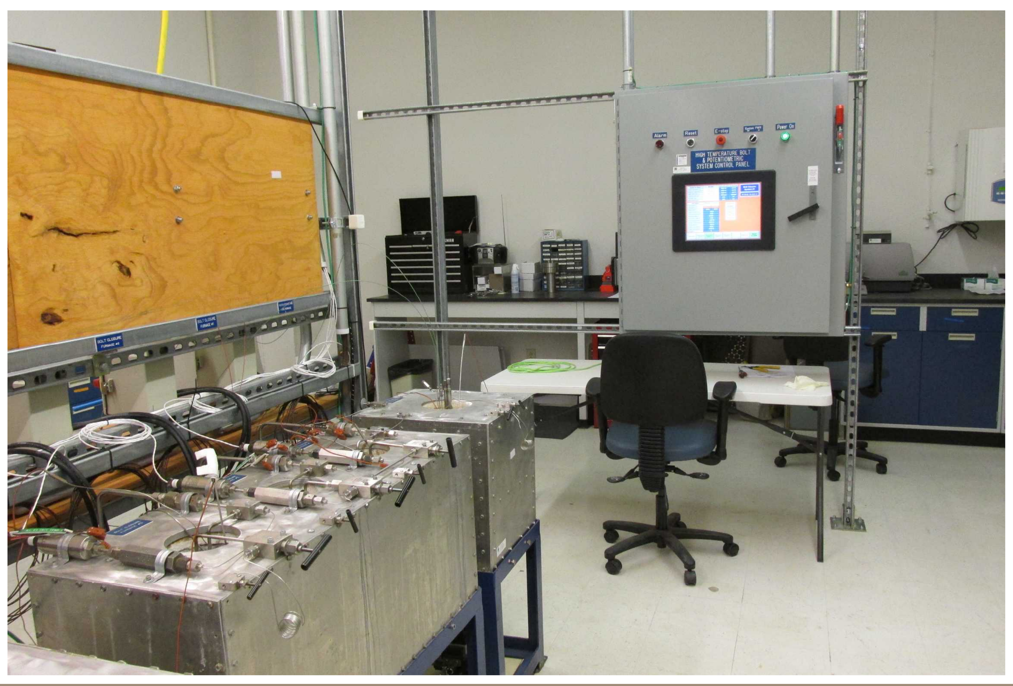

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Experimental Determination of Sorption Capacities and Kinetics of Model Materials under Shale Gas Reservoir Conditions: CO_2-CH_4 Mixtures to 125°C

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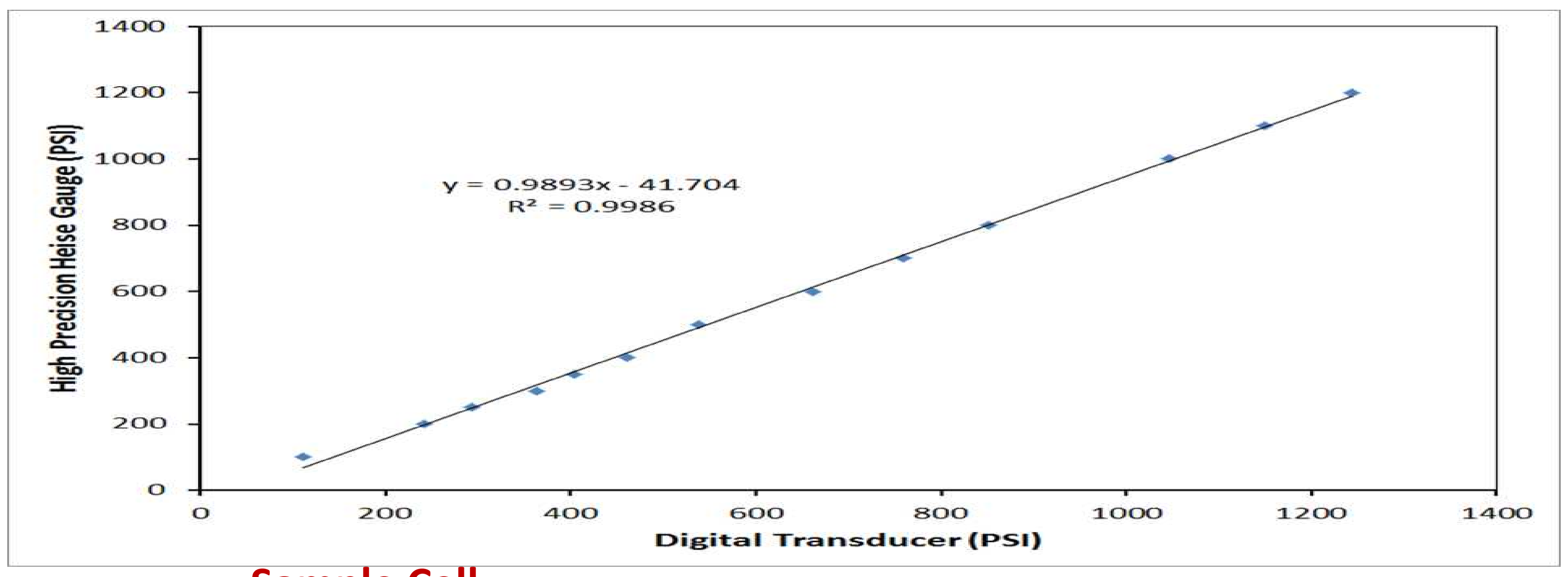
Objectives:

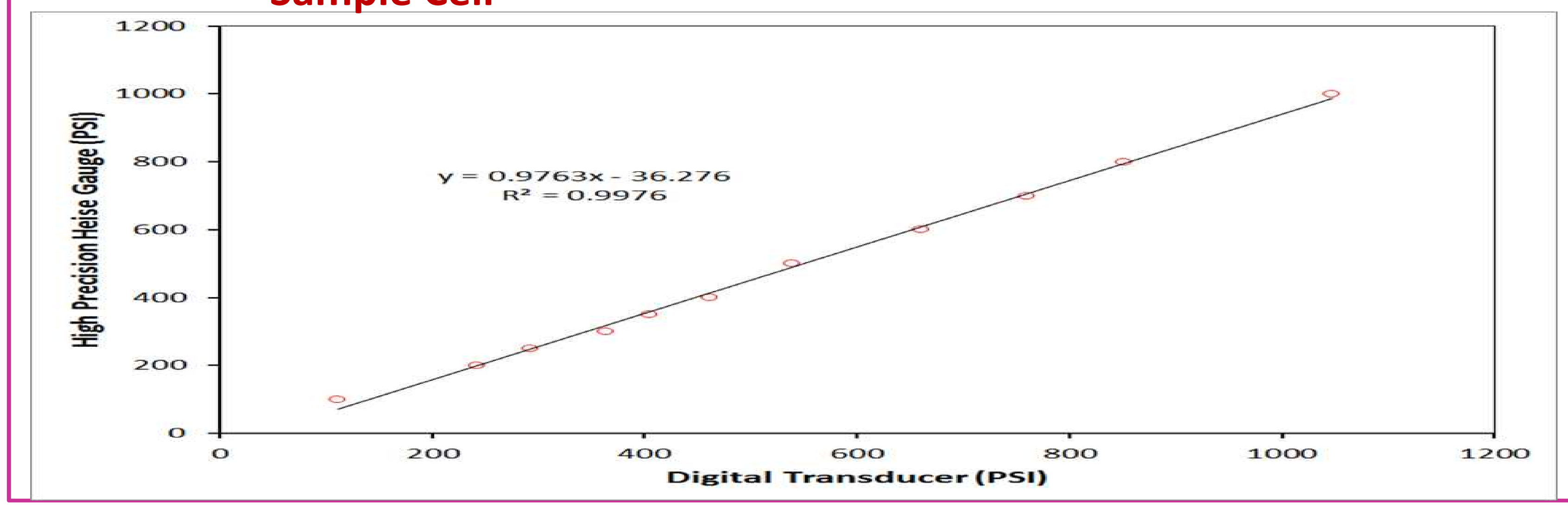
- Experimentally determine sorption capacities and kinetics of model materials.
- We have designed and constructed a unique high temperature and pressure experimental system that can measure both P-V-T-X properties and adsorption kinetics sequentially.

Instrumentation Calibration:

Reference Cell



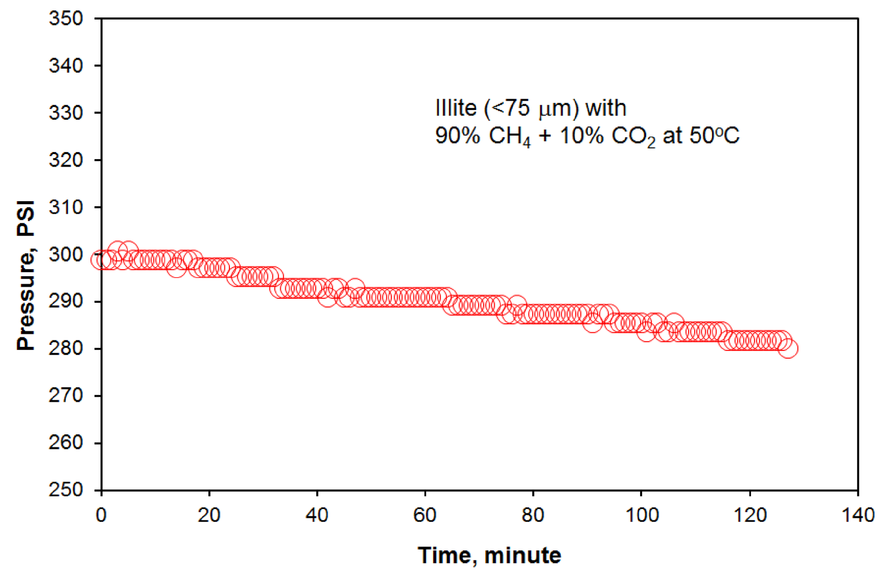
Sample Cell



High Temperature and Pressure Measurements: An Example

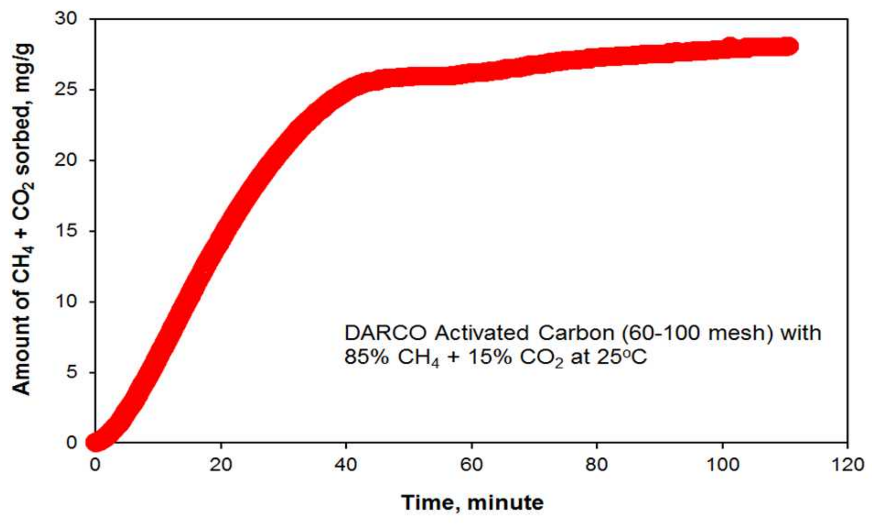
- The decrease in pressure is interpreted as absorption to the model substance.
- The amounts of absorbed gases are calculated based on the differential pressure according to the known compressibility factor of CH_4+CO_2 mixtures at the experimental temperature:

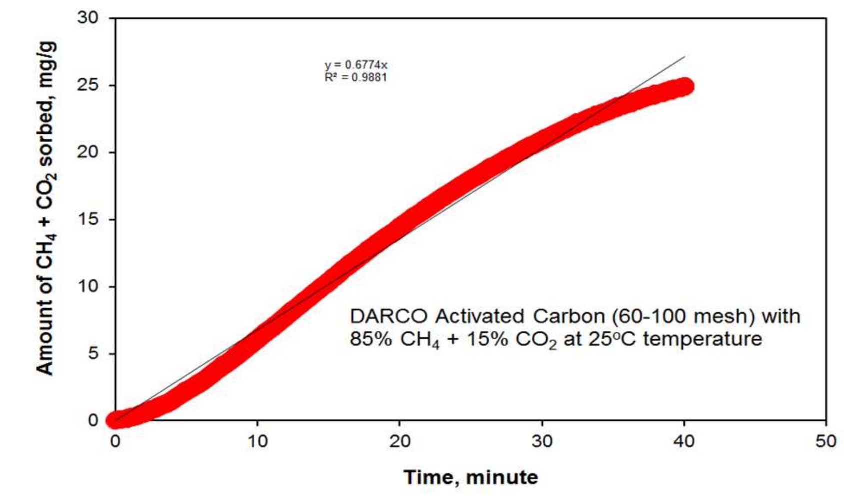
$$Z = \frac{P \times V}{n_{Total} \times R \times T}$$

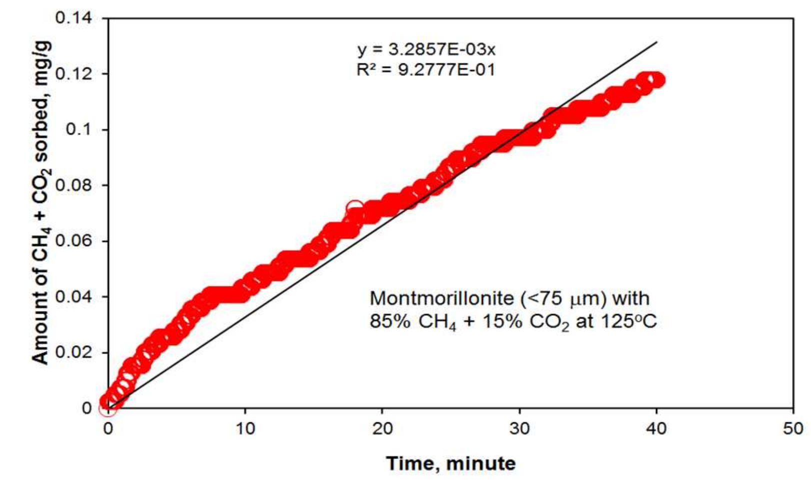


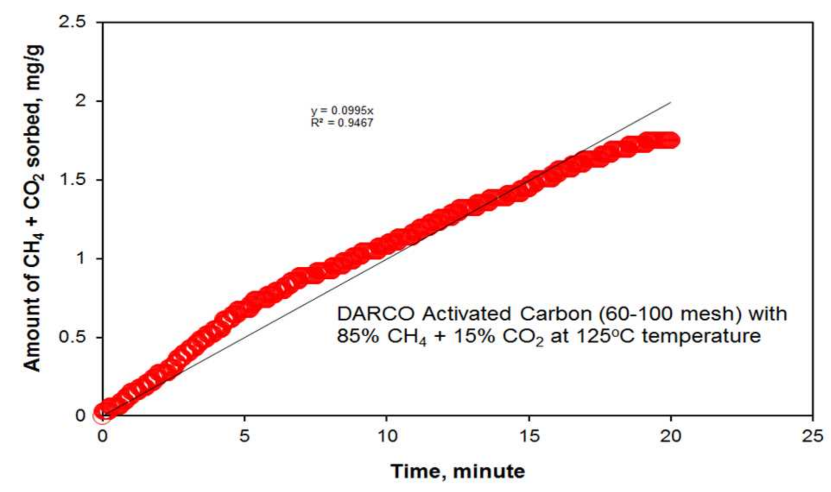
Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, PSI	Sorption Capacity (mixture) mg/g	Sorption Rate, mg/g min^{-1}
Illite, <75 µm	50	90% CH_4 + 10% CO_2	300	160	6 × 10^{-1}

Experimental Measurements with TGA at Various Temperatures and 1 bar









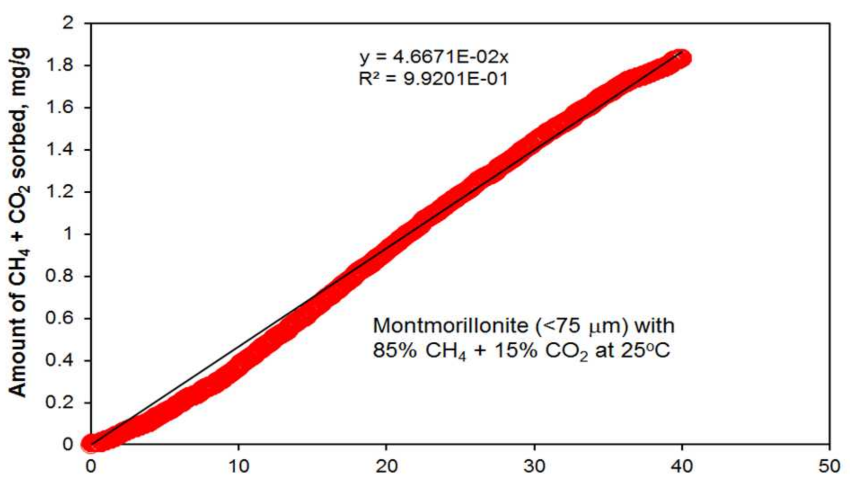


Table 1. Experimental measurements of sorption capacities and sorption rates for the model substances at 1 bar totol pressure

Model Substances	Temp, °C	Gas Mixture, volume percent	Pressure, bar	Sorption Capacity, mg/g	Sorption Rate, mg/g min^{-1}
DARCO activated carbon	25	85% CH_4 + 15% CO_2	1	28	0.68
	50	85% CH_4 + 15% CO_2	1	11	0.59
	75	85% CH_4 + 15% CO_2	1	9.0	0.31
	100	85% CH_4 + 15% CO_2	1	2.1	0.14
	125	85% CH_4 + 15% CO_2	1	1.8	0.10
Montmorillonite, <75 µm	25	85% CH_4 + 15% CO_2	1	2.8	4.7 × 10^{-2}
	50	85% CH_4 + 15% CO_2	1	0.30	9.6 × 10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.19	6.7 × 10^{-3}
	100	85% CH_4 + 15% CO_2	1	0.18	5.1 × 10^{-3}
	125	85% CH_4 + 15% CO_2	1	0.12	3.3 × 10^{-3}
Crushed Shale	25	85% CH_4 + 15% CO_2	1	0.29	3.3 × 10^{-3}
	50	85% CH_4 + 15% CO_2	1	0.21	2.7 × 10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.16	1.7 × 10^{-3}
Manos Shale Unreacted	25	85% CH_4 + 15% CO_2	1	0.34	6.1 × 10^{-3}
	50	85% CH_4 + 15% CO_2	1	0.17	9.4 × 10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.16	3.3 × 10^{-3}
	100	85% CH_4 + 15% CO_2	1	0.094	6.5 × 10^{-3}
	125	85% CH_4 + 15% CO_2	1	0.067	6.8 × 10^{-3}
Manos Shale Reacted	25	85% CH_4 + 15% CO_2	1	0.17	5.3 × 10^{-3}
	50	85% CH_4 + 15% CO_2	1	0.095	5.3 × 10^{-3}
	75	85% CH_4 + 15% CO_2	1	0.065	3.4 × 10^{-3}
	100	85% CH_4 + 15% CO_2	1	0.060	6.4 × 10^{-3}
	125	85% CH_4 + 15% CO_2	1	0.053	5.5 × 10^{-3}

Conclusions:

- We tested our instrumentation that can experimentally determine sorption capacities for any materials of interest for shale gas under the reservoir conditions.
- We have experimentally measured sorption capacities for a series of selected model materials under the reservoir conditions.
- We have found that significant amounts of CH_4 + CO_2 mixtures can be absorbed on the model materials such as illite and activated carbon.

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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