

Fast and Economic Gas Isotherm Measurements Using Small Shale Samples*

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Abstract

Automated field desorption experiments and laboratory adsorption isotherms, performed with various gases and shale samples, are used to compare and validate the total gas content of the shale, to define the free and adsorbed gas proportions, to verify the USBM lost gas calculation, sample crushing size and sample preparation and handling techniques. Normal and abnormal desorption curves are examined. Full diameter and sidewall desorption data is compared.

High pressure mercury injection - pore size distribution experiments are performed on solid and crushed small shale samples to illustrate the reservoir quality and the crushed rock analysis concept. The diffusion parameter ratio (plug to crushed sample) is used to describe the shale pore network interconnectivity. Crushed and powdered adsorption isotherms are generated and used to show the crushing size importance in determining the total gas content. Over crushing the shale can seriously overestimate the adsorption isotherms by generating new surface while destroying pore volume.

Shale evaluation procedures consist of automated desorption isotherms, microfracture evaluation, tight rock analysis, diffusion parameter measurements, geochemical (TOC and Rock Evaluation, Ro), sorption isotherms, x-ray diffraction, SEM, capillary suction time for fluid optimization, mercury injection capillary pressure and pore size distribution, acoustic velocity measurements and dynamic rock mechanics are all performed on a small plug sample in a timely and economic manner.

Acknowledgments

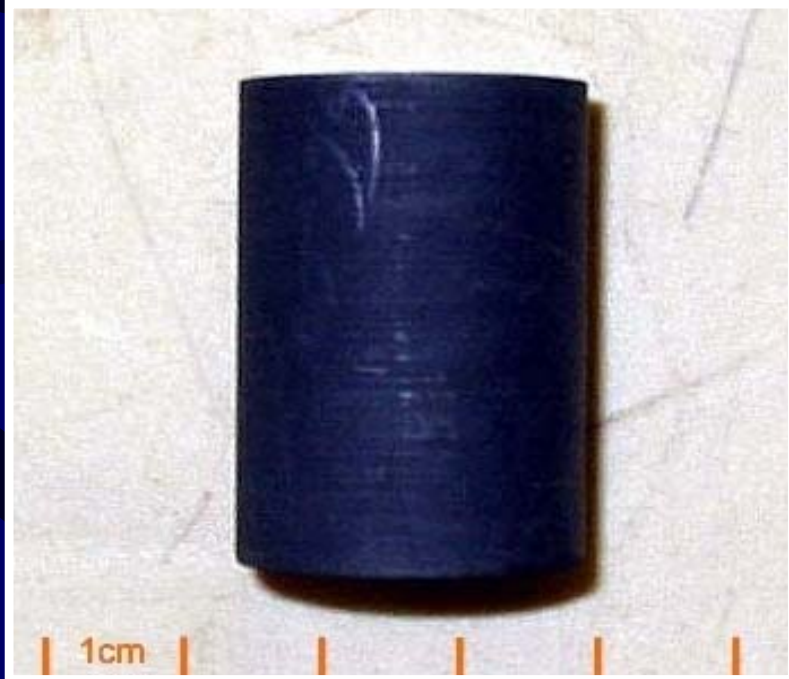
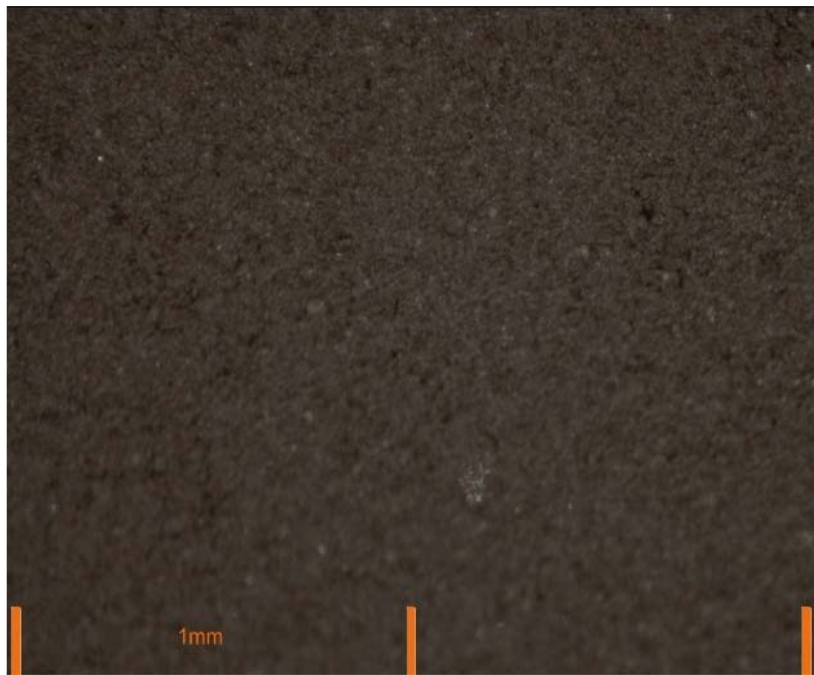
Personal conversations with Dr. Dan Suciu, consultant, Mr. Alton Brown, consultant, and Dr. Martin Thomas, Quantachrome Corporation.

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Fast and Economic Gas Isotherm Measurements using Small Shale Samples

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Shale is Source, Seal and Lately ... Reservoir Rock

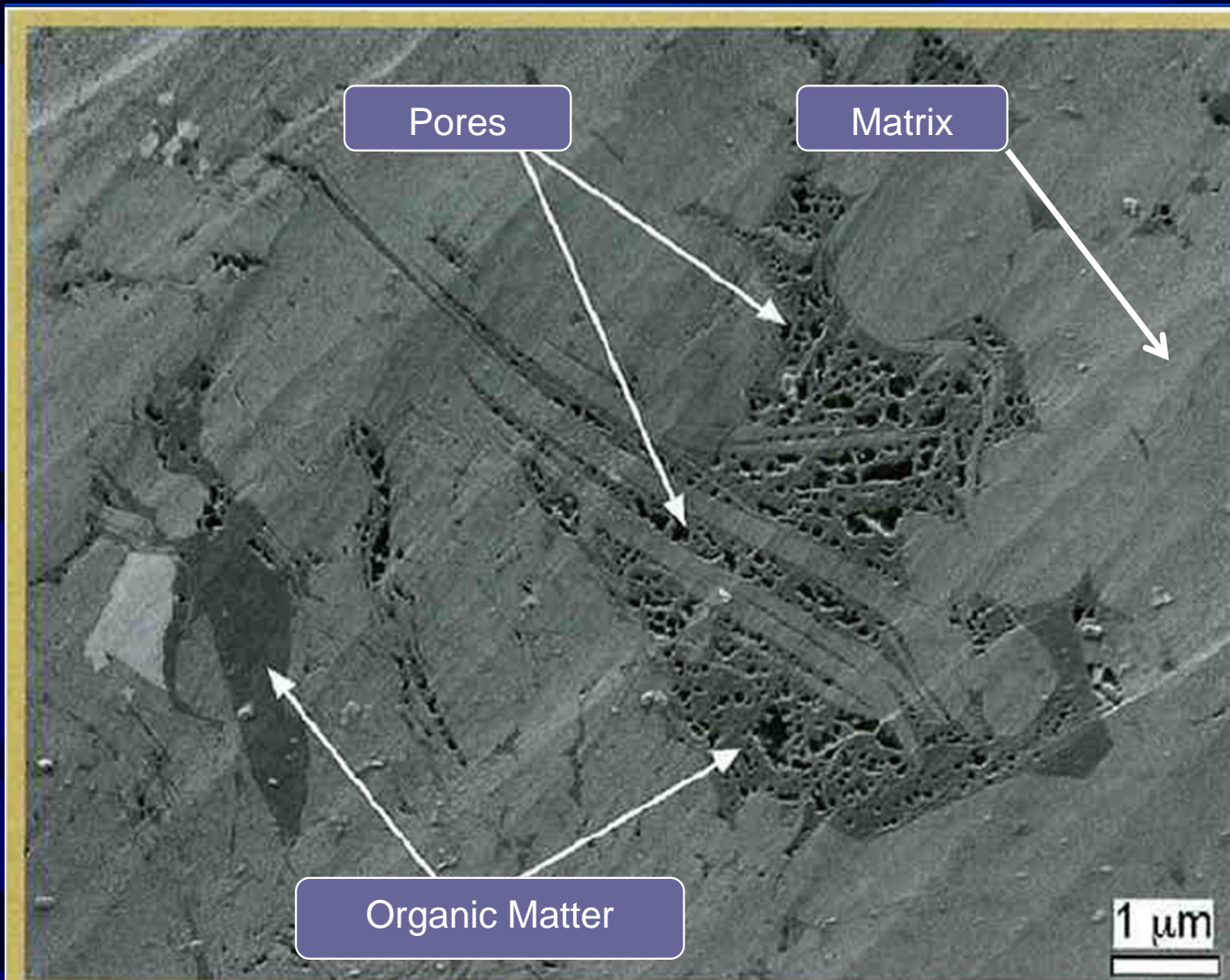


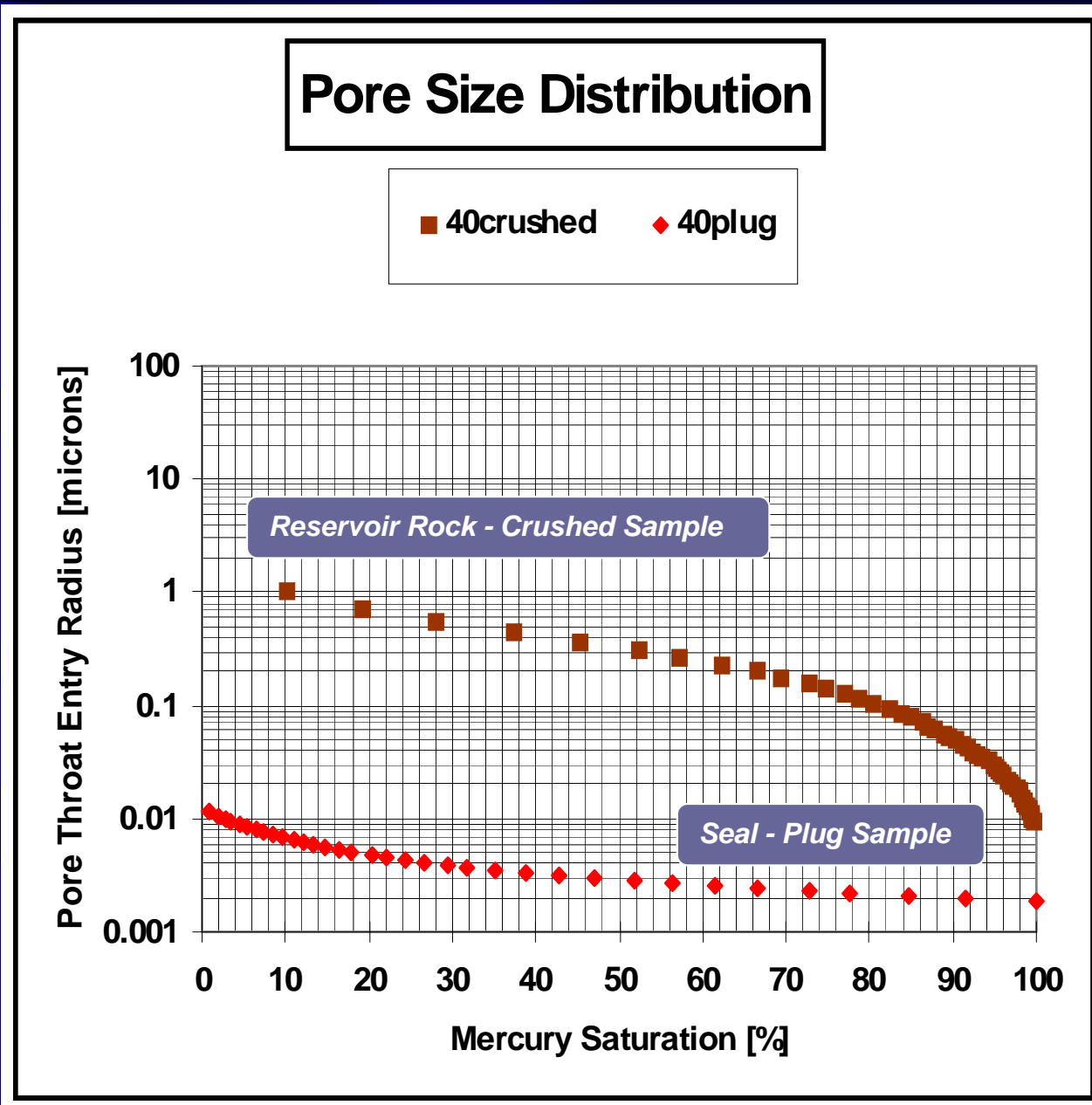
Figure 3. Field emission scanning electron photomicrograph of nanoscale pore architecture in the Barnett Formation. Image provided by R. Reed.

“More mature samples show well-developed nanopores concentrated in micron-scale carbonaceous grains. Large numbers of subelliptical to rectangular nanopores are present, and porosities within individual grains of as much as 20% have been observed. Shallowly buried, lower thermal maturity samples, in contrast, show few or no pores within carbonaceous grains.

These observations are consistent with decomposition of organic matter during hydrocarbon maturation being responsible for the intragranular nanopores found in carbonaceous grains of higher maturity samples. As organic matter (kerogen) is converted to hydrocarbons, nanopores are created to contain the liquids and gases. With continued thermal maturation, pores grow and may form into networks. The specific thermal maturity level at which nanopore development begins has not been determined. However, current observations support nanopore formation being tied to the onset of conversion of kerogen to hydrocarbons.”

Shale as a Seal and as a Reservoir Rock

The Crushed Rock Analysis Concept



A sidewall sample was divided in 2 parts. One part was crushed to approx 45 mesh. High pressure mercury injection test (60,000 psia) was performed on each part (plug and crushed). The plug sample pore size distribution looks like a “seal” while the crushed sample looks more like a “reservoir rock”.

The pore sizes measured on the crushed sample are similar to the ones showed in the SEM picture.

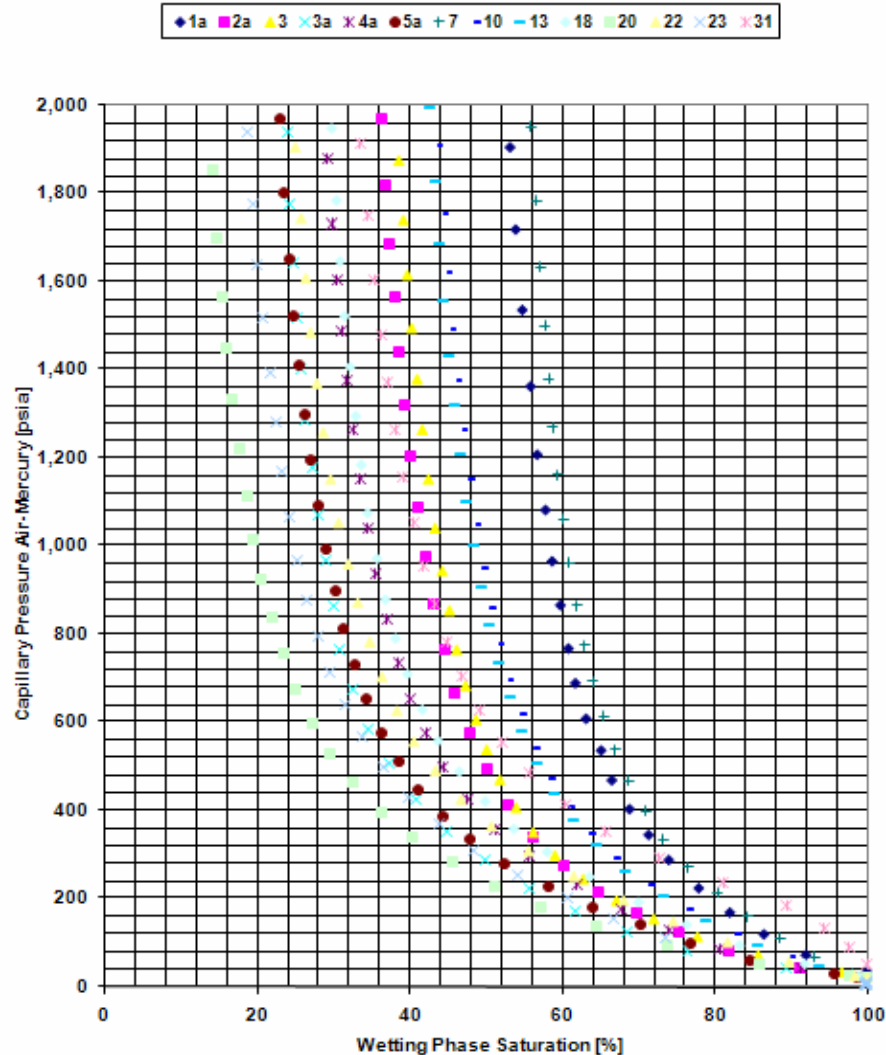
The kerogen to hydrocarbon conversion pores form a local network (LAN). However these pores are not very well connected in a wide area network (WAN).

These pores observed in the crushed sample are large enough for a mD range permeability. However, the measured shale matrix permeability is often nano to micro Darcy range, therefore the connectivity is limited at best.

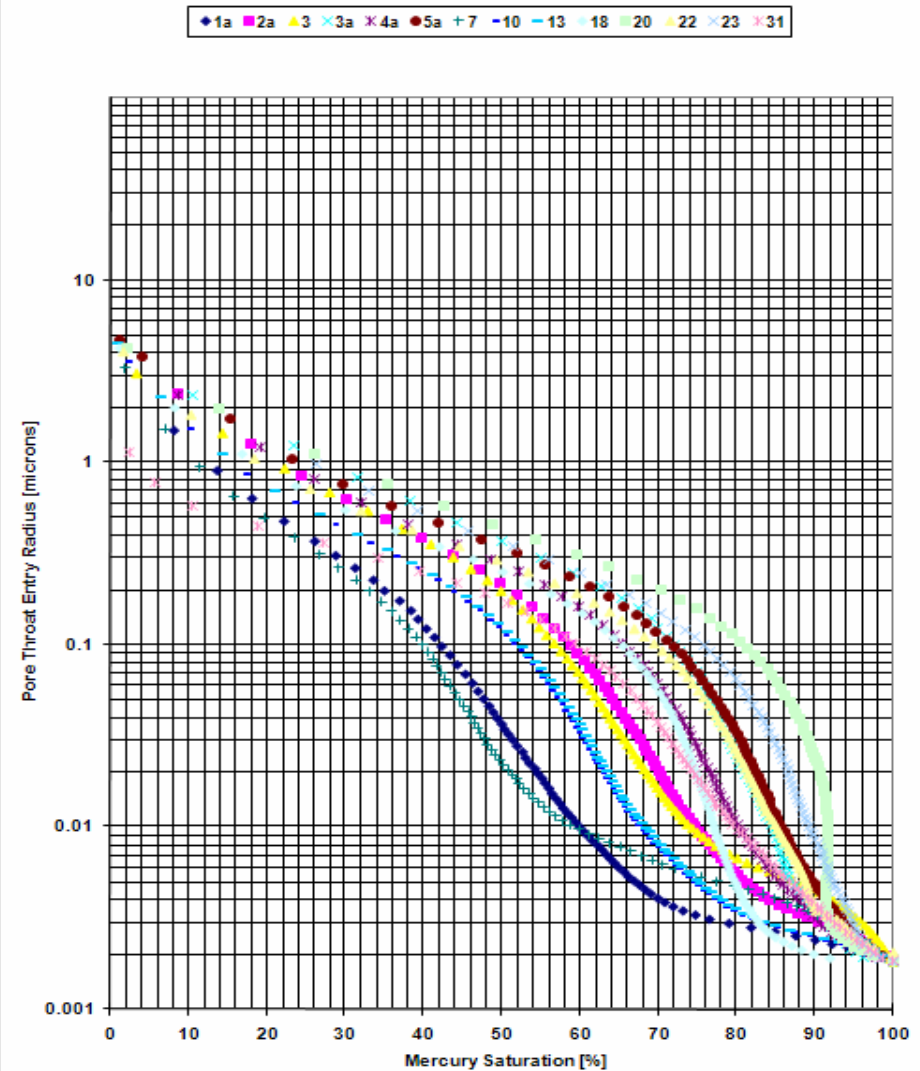
The pore network connectivity can be described using the **Diffusion Parameter Ratio** for the plug and crushed sample.

Capillary Pressure and Pore Size Distribution Crushed Barnett Shale

Air-Mercury Capillary Pressure



Pore Size Distribution



The shale gas reservoir has two components:

Free Gas (Conventional) – is the gas stored by compression and solution in the larger pores.

Adsorbed Gas (Unconventional) – is the gas stored by molecular attraction to the surface of the organic material present in the shale.

The surface area of the organic shale is very large and known to attract natural gas.

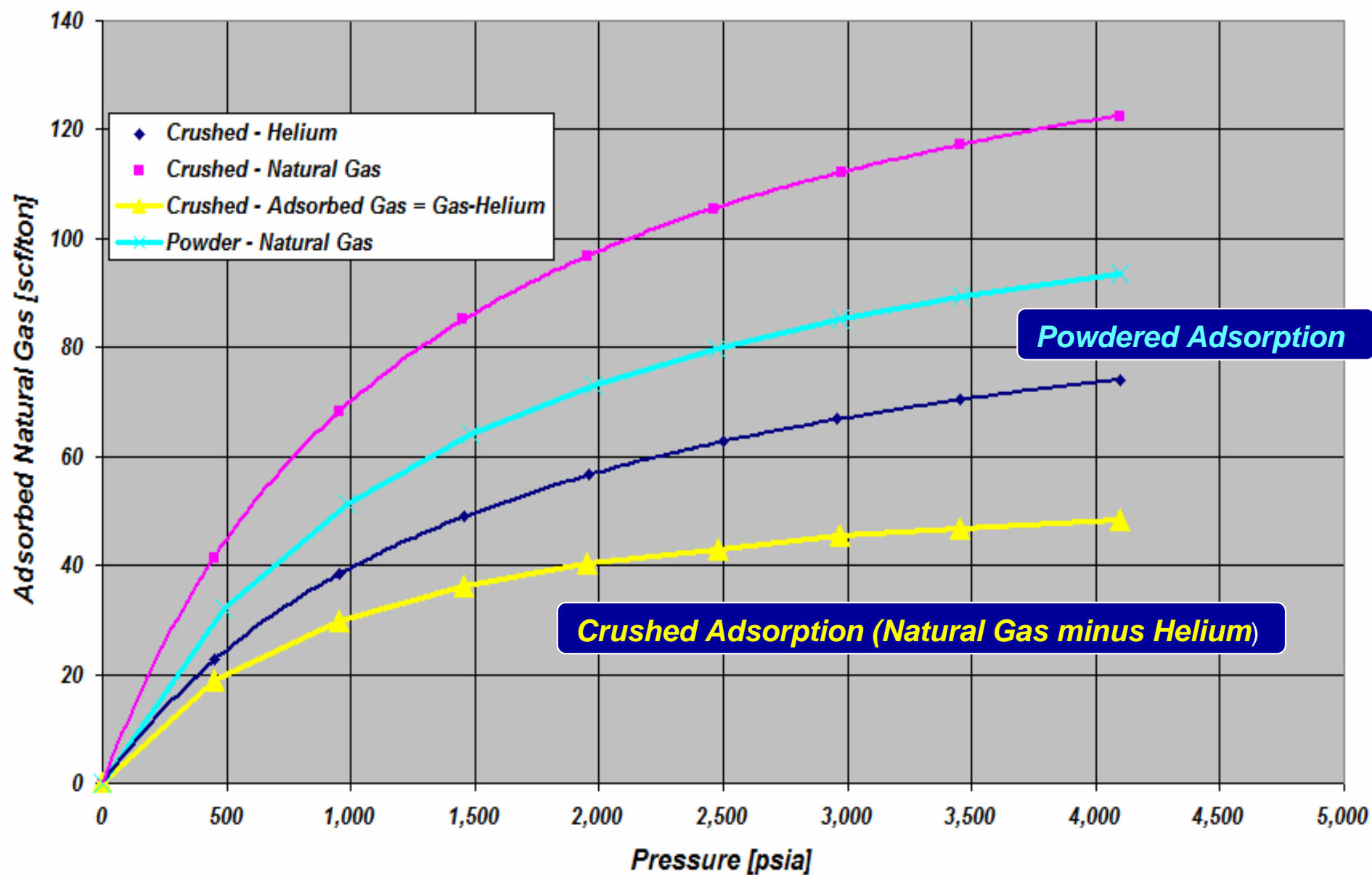
Capillary Condensation can occur in micro pores due to the molecular vapor-solid attraction in a multilayer adsorption environment. The interesting aspect of capillary condensation is that this vapor condensation occurs well below the saturation vapor pressure. Abnormally high gas condensate densities are observed at low pressures due to strong molecular attraction (much like a compressed liquefied gas). This can explain relatively large gas reserves found in some shale reservoirs.

Shale Analysis Problems

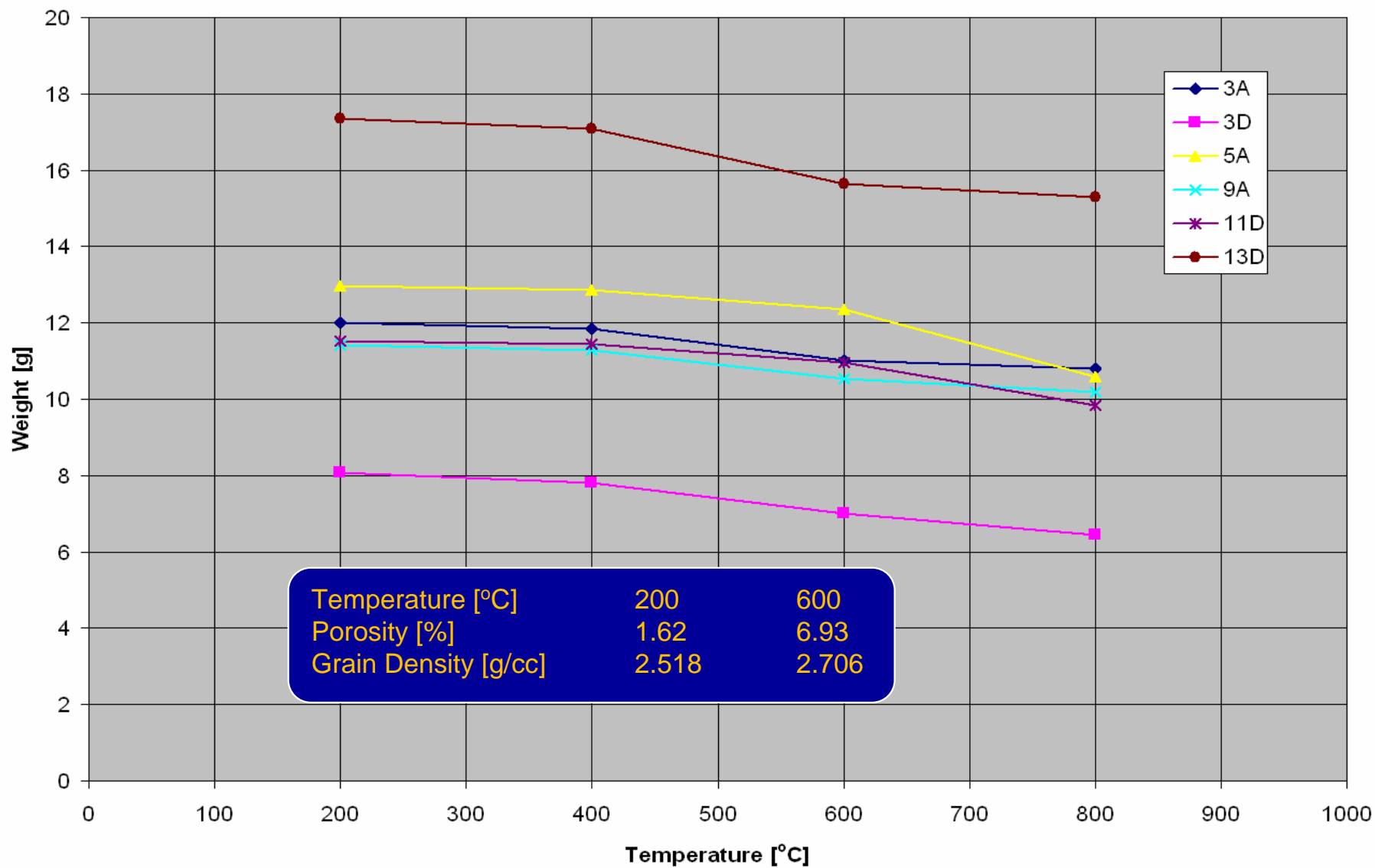
1. **Sample Crushing and/or Grinding.** Provides measuring access to the local pore systems, however the adsorption surface area is increased and exposed to oxygen.
2. **Baking the Kerogen and Liquid Hydrocarbons.** The higher the extraction temperature in the laboratory the higher the measured total porosity.
3. **Large lost gas calculations** when the sample retrieval time is long (conventional cores).
4. **Unusual measured gas curves** showing gas generation (bacterial, capillary evaporation in dual pore size, catalytic generation ...)

A good correlation of the desorption and adsorption isotherms can address these problems

Crushed and Powdered Shale Adsorption



Sample Weight vs Extraction Temperature



Gas Estimate Using Adsorption Data Conventional Core with Long USBM Time

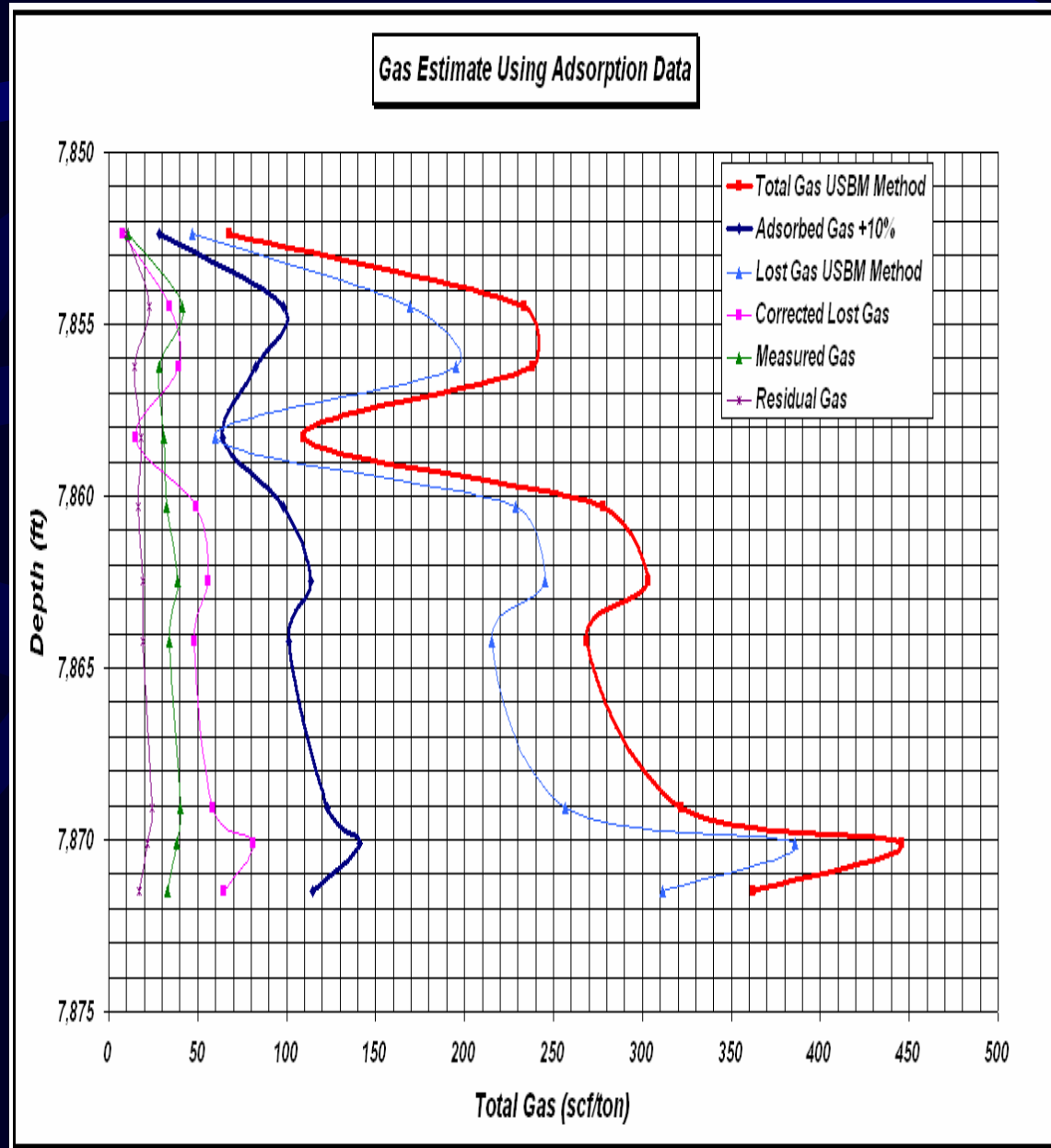
Quick-Desorption™ and Shale Evaluation

Company: SCAL, Inc.

Desorption Temperature: 200 °F

County: Midland County, Texas

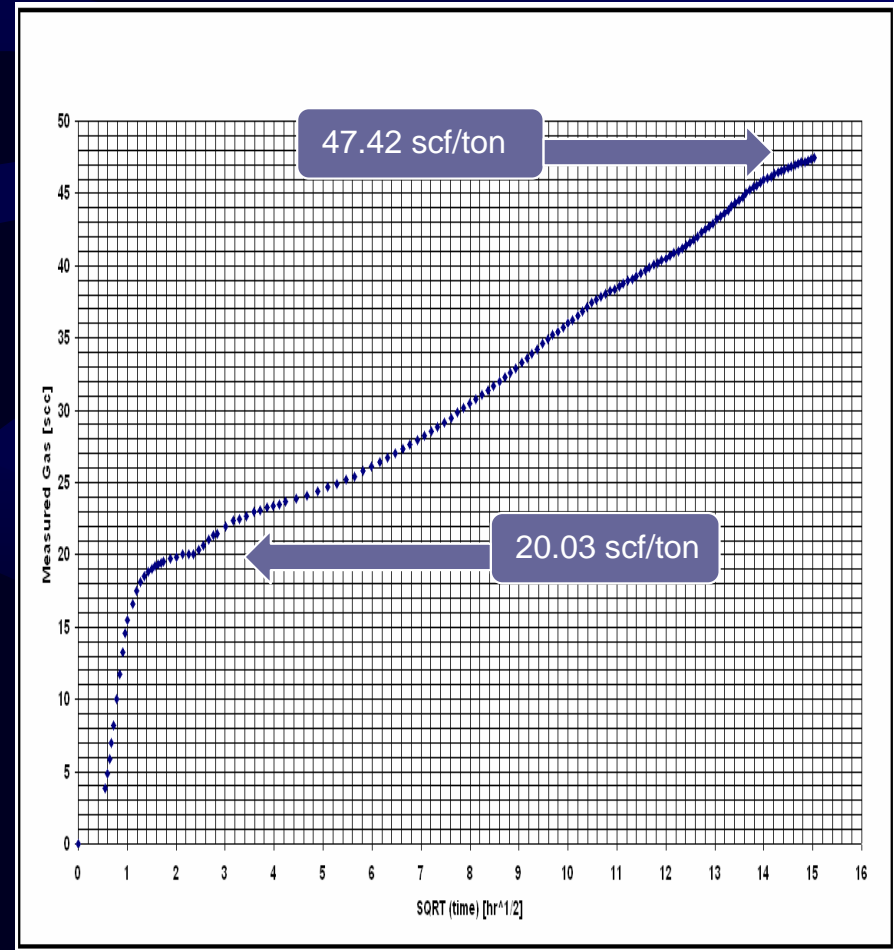
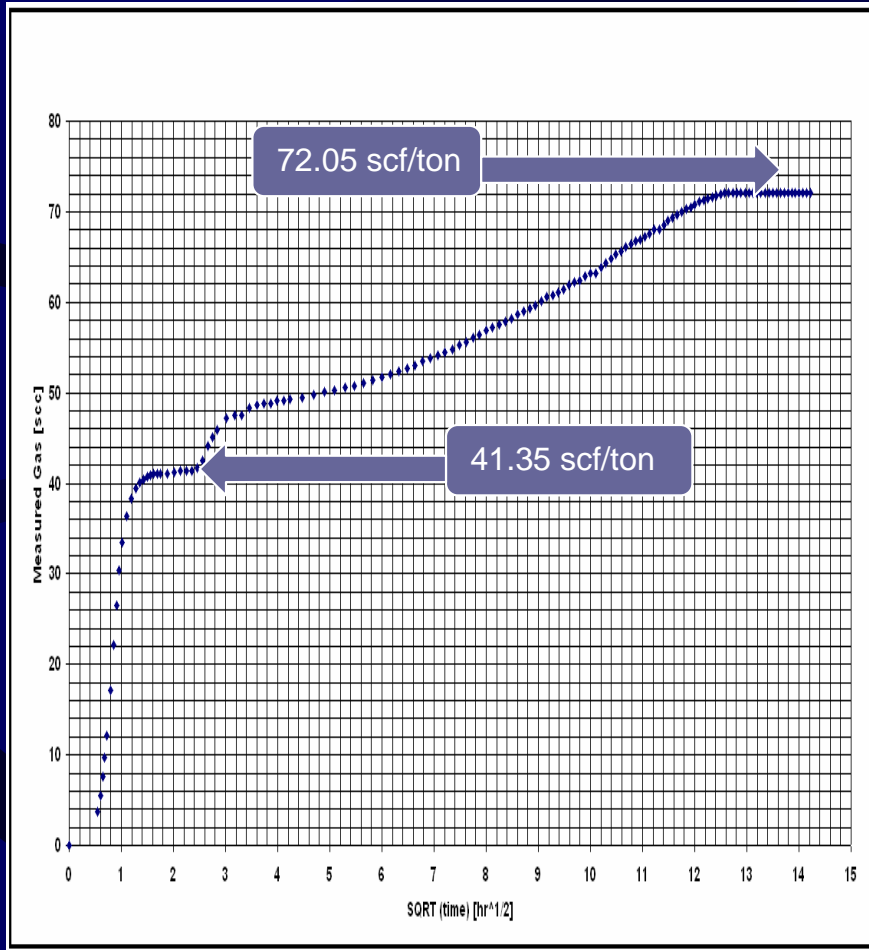
Sample		Quick-Desorption			Adsorption Data			
		As received						
No.	Depth ft	Measured Gas scf/ton*	Lost Gas scf/ton*	Residual Gas scf/ton*	TOTAL Gas scf/ton*	ADS Gas scf/ton*	ADS Gas + 10% scf/ton*	Corrected Lost Gas scf/ton*
1	7,852.35	10.8	47.1	9.8	67.7	25.6	28.2	7.5
2	7,854.50	41.1	169.5	22.7	233.3	89.2	98.1	34.2
3	7,856.25	28.6	195.0	14.6	238.2	75.1	82.7	39.5
4	7,858.30	31.1	60.2	18.2	109.5	58.3	64.1	14.8
5	7,860.30	32.6	228.8	16.7	278.1	89.3	98.2	48.9
6	7,862.45	38.7	245.3	18.9	303.0	103.4	113.7	56.0
7	7,864.25	33.9	215.6	19.3	268.8	92.0	101.2	48.0
8	7,869.05	40.3	256.9	24.4	321.6	111.9	123.1	58.3
9	7,870.10	38.2	385.6	21.8	445.6	128.1	140.9	81.0
10	7,871.50	33.3	311.6	16.9	361.8	104.3	114.8	64.5
Average		32.9	211.6	18.3	262.8	87.7	96.5	45.3



Unusual Measured Gas Curves

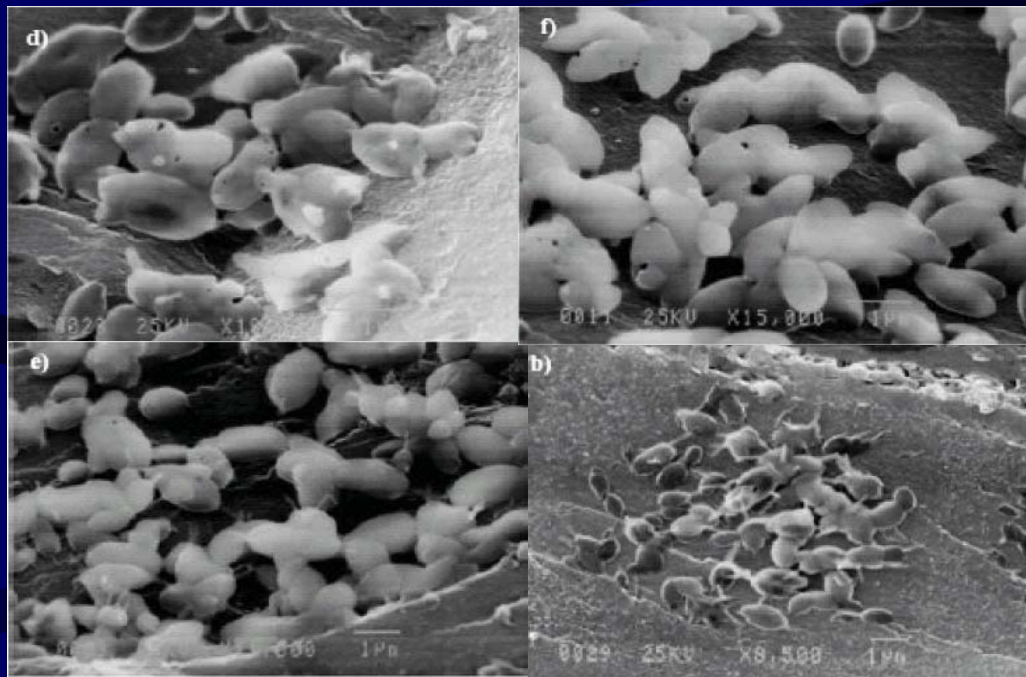
Gas Generation (catalytic, bacterial, capillary evaporation in dual pore size distribution)

Reservoir Pressure 3,900 psia, Temperature 200 °F



A fast desorption also prevents the errors associated with hydrogen generation by anaerobic bacterial growth.

Bacterial hydrogen generation starts several days into the test. The bacterial hydrogen can be a significant portion of the total gas (up to 82 mole %).



“The time range for the first occurrence of H₂ identified in this study is the variable and found to occur at any time between 5 days and 100 days from the start of the desorption experiments. Trace amounts of H₂ may have been generated earlier than 5 days. However, no GC analysis was performed for periods less than 5 days, making this impossible to confirm.”

Sample No.	Total Desorbed H ₂ Volume (cm ³)	Total Desorbed CH ₄ Volume (cm ³)	Experiment Duration	Mole% of H ₂ to Total Gas Desorbed	Corrected Gas Content (Scf/ton)	Air-dry Sample Weight (gm)
1	2,079.8	2,753.8	71.0	43%	47.4	1,861
2	4,430.4	950.4	70.6	82%	14.2	2,145
3	1,041.9	1,373.1	242.5	43%	50.3	--
4	14.8	7,885.2	172.9	0.2%	1,153.0	--
5	1,789.4	5,553.6	254.2	24%	116.2	--
6	1,887.2	2,635.9	71.1	42%	50.5	1,670
7	117.6	5,337.1	172.7	2.2%	79.6	2,145
8	165.7	542.3	245.3	23.4%	12.7	--
9	1,537.5	2,816.5	250.1	35.3%	91.1	--
10	1,280.6	2,563.4	337.9	33.3%	64.9	1,264.3
11	0.01	2,799.0	337.9	0.01%	61.0	1,468.1
12	963.9	5,733.1	337.3	14.4%	88.8	2,067.2
13	464.2	864.8	236.6	35%	36.5	1,165.8
14	1,713.8	1,949.2	236.4	47%	36.9	1,689.3
15	142.1	6,240.4	260.5	1.9%	92.9	--
16	7.9	9,089.2	260.4	0.1%	132.5	--
17	55.2	3,000.5	258.4	1.8%	54.3	1,768
18	692.8	2,832.0	253.5	19.7%	42.7	2,121
19	141.9	3,945.1	272.7	3.5%	82.0	--
20	1,030.4	2,285.6	272.1	31.1%	67.9	--

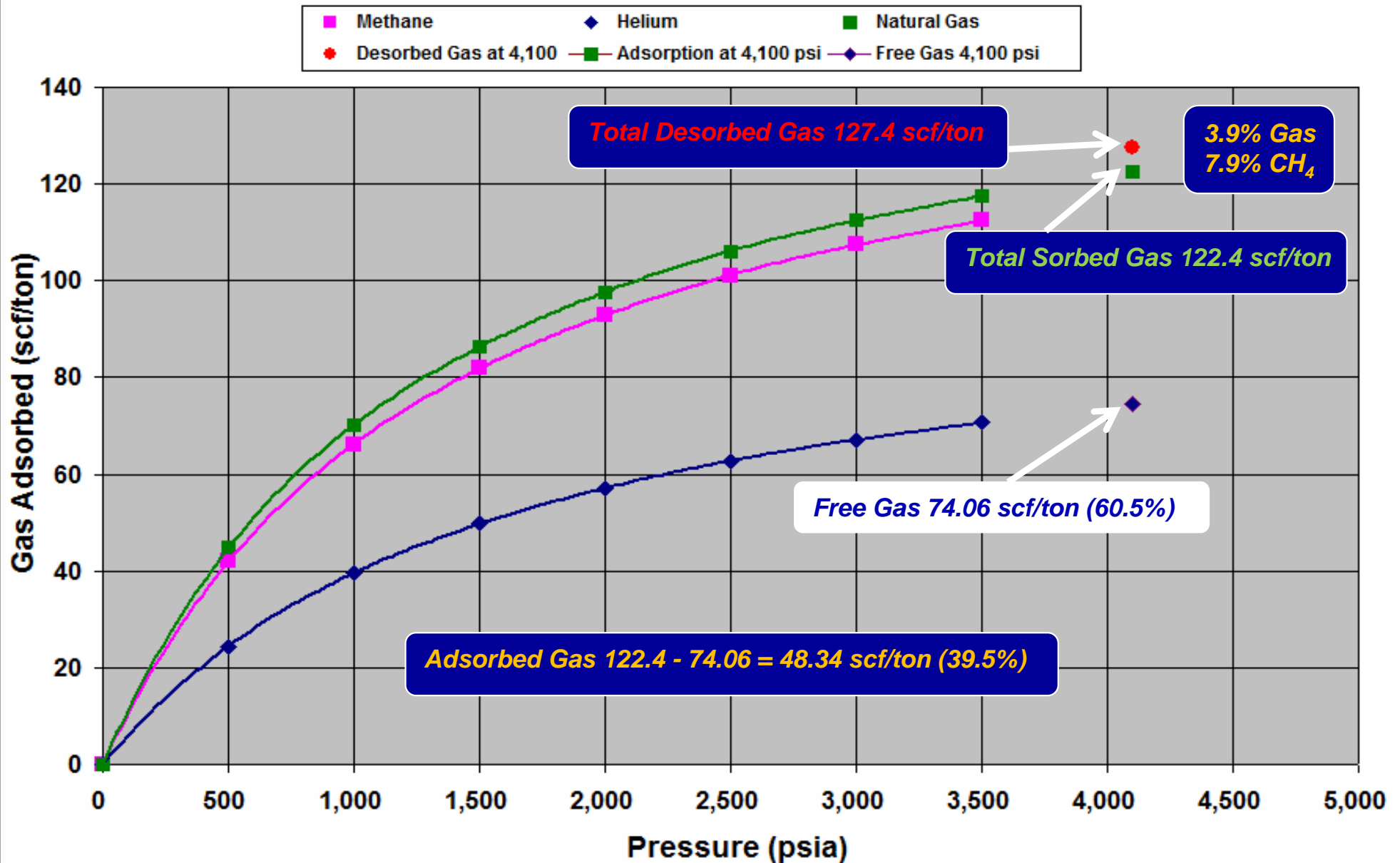


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Chart and pictures from “Mechanism of Hydrogen Generation in Coalbed Methane Desorption Canisters: Causes and Remedies” by Basim Faraj and Anna Hatch, with contributions from Derek Krivak and Paul Smolarchuk, and all of GTI E&P Services Canada.

Desorption-Adsorption Correlation Reservoir Pressure 4,100 psia, Temperature 175 °F



Shale Gas Reserves

1. Calculate Total Gas (not a function of porosity):

$$G = 1359.7 A h \rho_c G_c$$

G = Gas-in-Place, scf

A = Reservoir Area, acres

h = Thickness, feet

ρ_c = Average In-Situ Shale Density, g/cm³

G_c = Average In-Situ Gas Content, scf/ton

2. Determine the free (conventional) gas. The total and free gas proportions are determined by measuring sorption isotherms with natural gas and helium on preserved sidewall samples.

3. Calculate the porosity responsible for holding the conventional gas (compressed and solution) and compare to the laboratory porosity. Adjust the laboratory procedures (extraction temperature) to match the calculated porosity for a given area.

The Quick-Desorption™ System



SCAL, Inc.

SPECIAL CORE ANALYSIS LABORATORIES, INC.

Quick-Desorption™ Portable Laboratory



The equipment is installed in an SUV and consists of 2 accurate mechanical convection laboratory ovens (0.3 °C uniformity), stainless steel canisters and a very accurate gas measuring system operating isothermal at reservoir temperature. The measuring system includes an industrial computer interfaced with a laptop computer. The equipment is powered by digital inverter-generators and in-line digital UPS systems. A backup generator is also included in the system.



SCAL, Inc.

SPECIAL CORE ANALYSIS LABORATORIES, INC.

Desorption Canisters



The sidewall cores are cut top to bottom to minimize the lost gas. After retrieval the samples are sealed in canisters at the well site. We collect desorption data at reservoir temperature as we drive back to our laboratory facility where the testing is continued.



SCAL, Inc.

SPECIAL CORE ANALYSIS LABORATORIES, INC.

Full Diameter Quick-Desorption™



Using a portable diamond drill, 1 inch diameter plugs are drilled vertically into the center of the full diameter sample at the well site. These smaller samples are loaded into our standard desorption canister.



SCAL, Inc.

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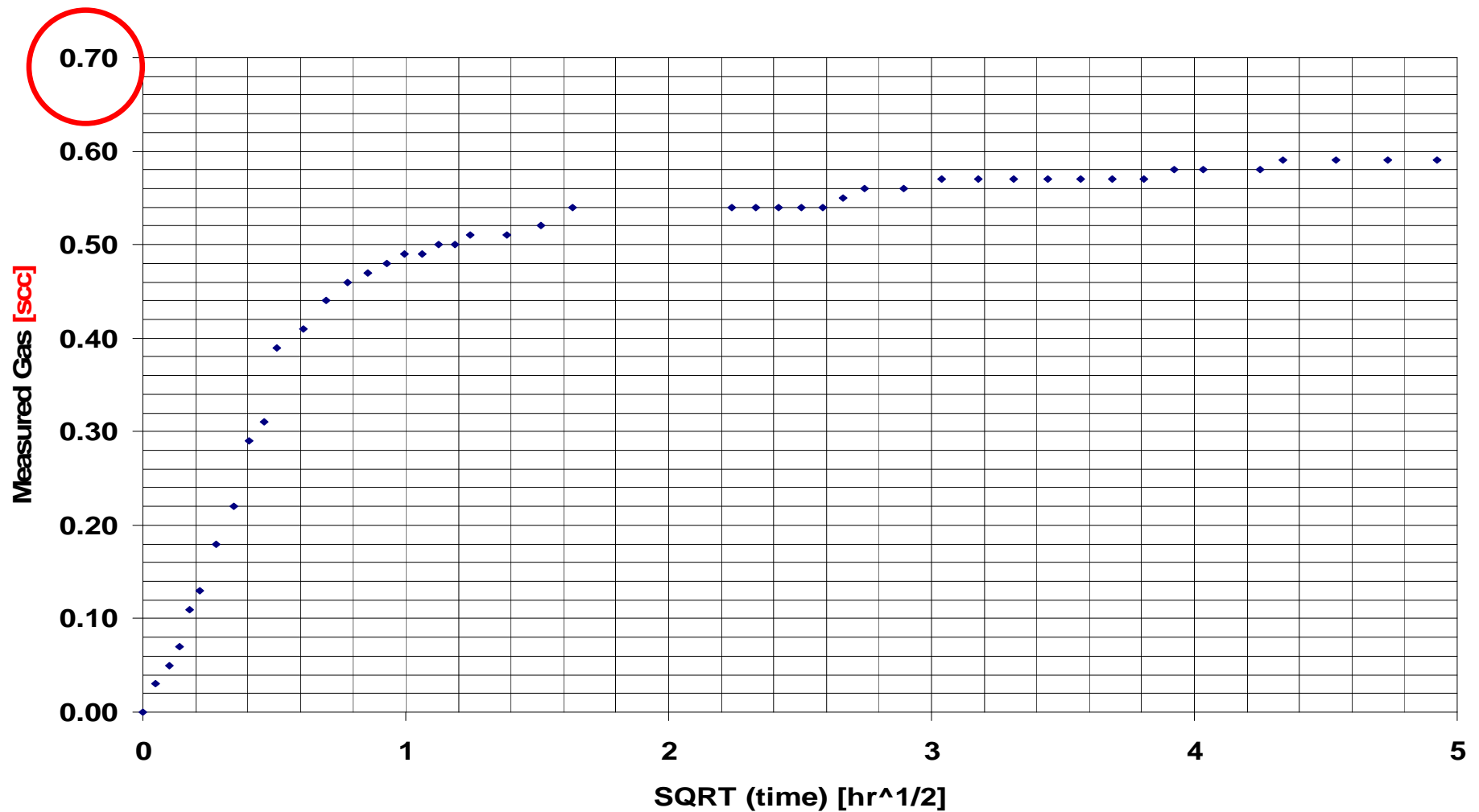
Quick-Desorption™ Equipment and Software



SCAL, Inc.
SPECIAL CORE ANALYSIS LABORATORIES, INC.

Quick-Desorption™ Resolution

Measured Gas



The equipment can measure small shale fragments (incomplete sidewall recovery).

Quick-Desorption™ Test

Company : SCAL, Inc. Sample : 1
 Well Name : Test #1 Depth : 9,500.0 ft
 File No. : 8000

Standard pressure: 14.7 psia Fluid : drilling mud
 Standard temperature: 60 °F

Date 1/22/2008
 Start tripping out: 3:08 Trip time : 2:02 hr:min
 At surface : 5:10 At the surface : 0:37 hr:min
 In the canister : 5:47 USBM time : 1:38 hr:min

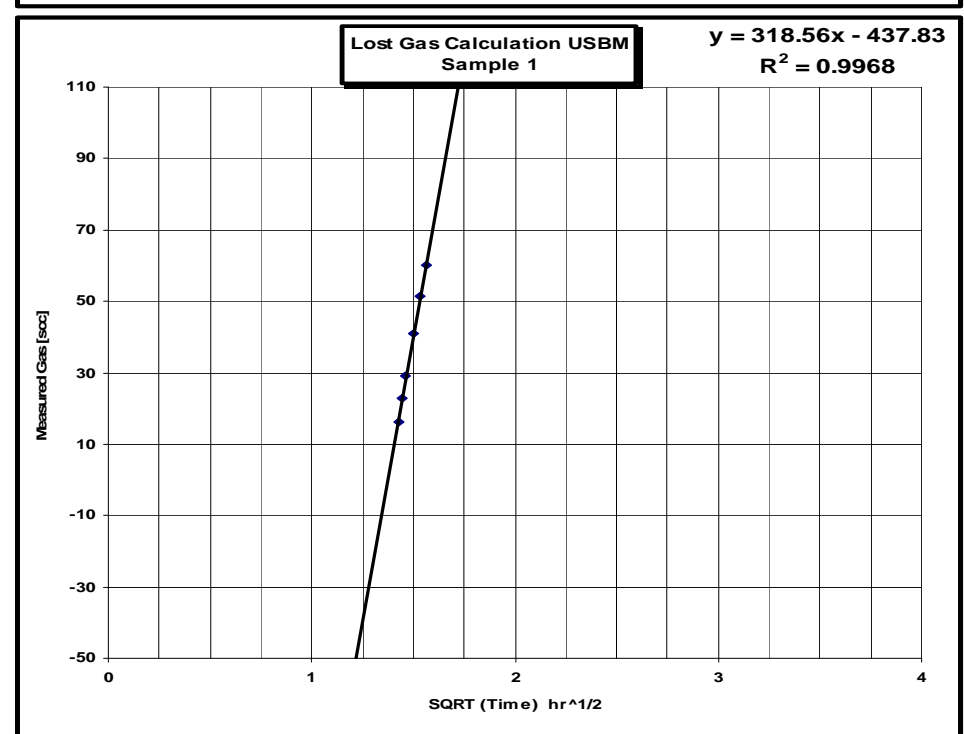
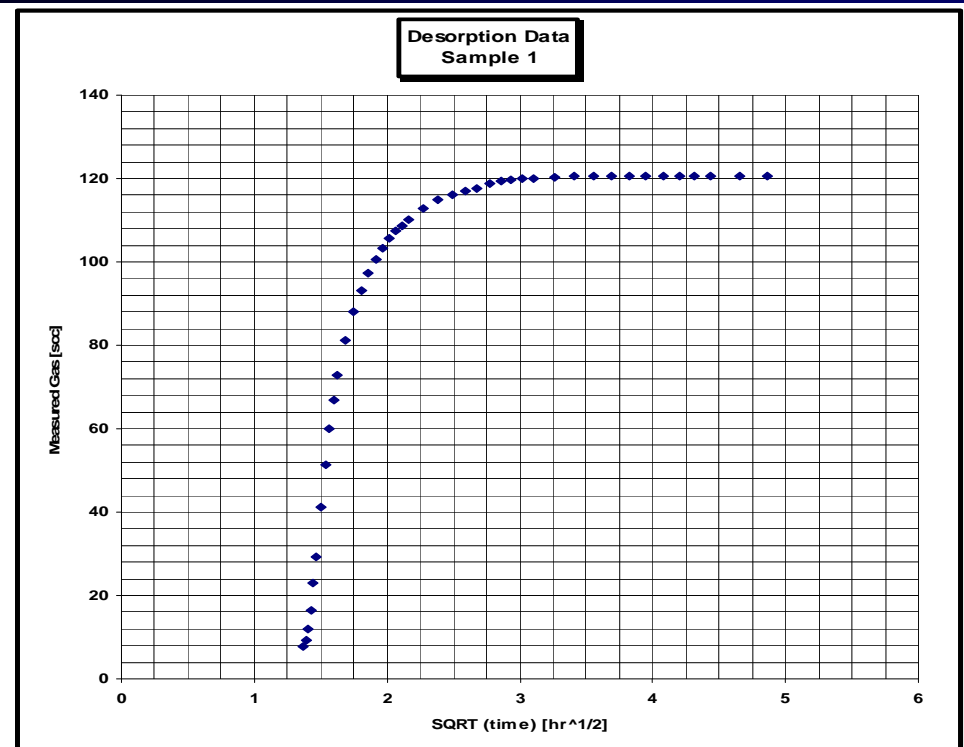
Measured Gas (M) 2.40 scc/g 76.7 scf/ton*
 Lost Gas (L) 8.70 scc/g 278.7 scf/ton*
 Residual Gas (R) 0.89 scc/g 28.6 scf/ton*

Total Gas Content (M+L) 11.99 scc/g 384.1 scf/ton*

Measured Gas 120.53 scc Weight : 50.322 g
 Lost Gas Intercept 437.83 scc Desorption temperature: 180 °F

No. SQRT(TotalTime) hr^{1/2} Gas scc Regression Data for Lost Gas Calculation USBM:

1	1.37	7.64		
2	1.39	9.16		
3	1.41	12.01		
4	1.43	16.38	1.43	16.38
5	1.45	22.94	1.45	22.94
6	1.46	29.26	1.46	29.26
7	1.50	41.15	1.50	41.15
8	1.53	51.46	1.53	51.46
9	1.57	59.98	1.57	59.98
10	1.60	66.98		
11	1.63	72.71		
12	1.69	81.24		
13	1.75	87.94		
14	1.81	93.27		
15	1.86	97.33		
16	1.92	100.64		
17	1.97	103.40		
18	2.02	105.63		
19	2.07	107.40		
20	2.12	108.69		
21	2.16	110.02		
22	2.28	112.88		
23	2.38	114.96		
24	2.49	116.00		
25	2.59	117.09		
26	2.68	117.72		
27	2.77	118.70		
28	2.86	119.26		
29	2.93	119.56		
30	3.02	119.93		



Micro fracture Porosity and Permeability

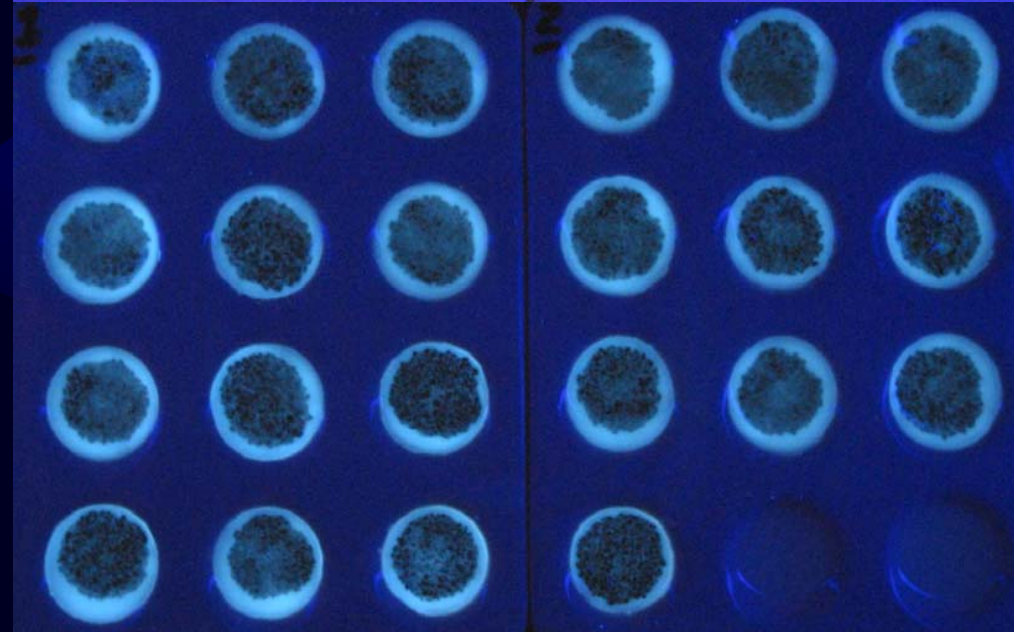
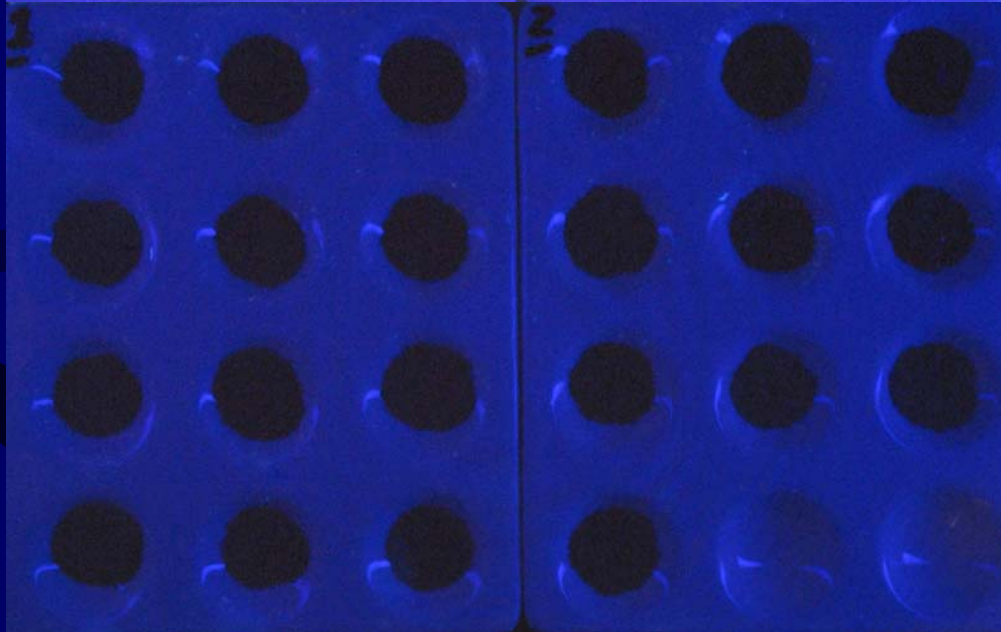
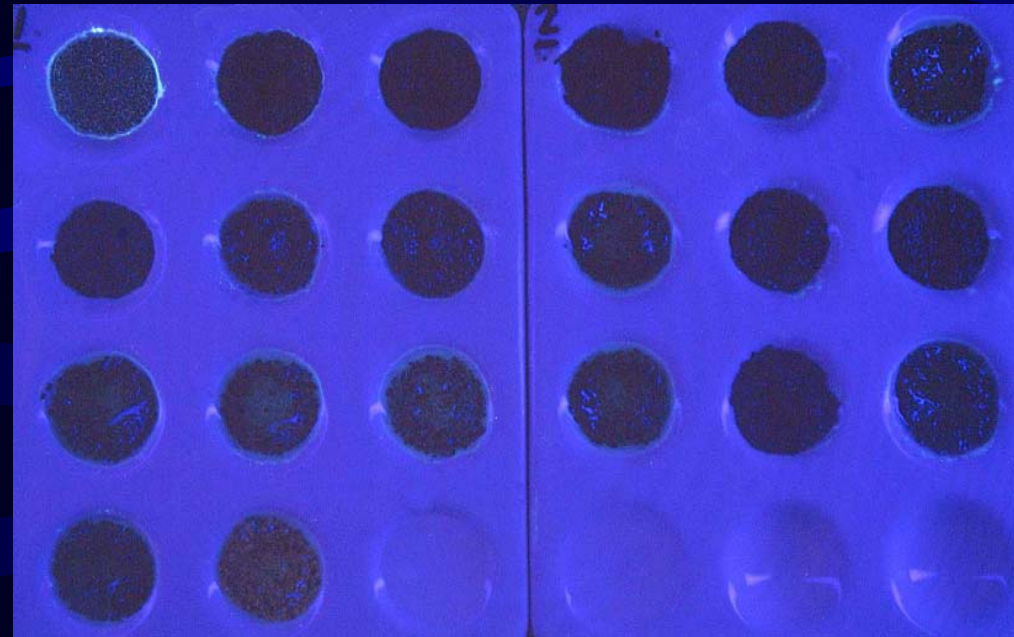
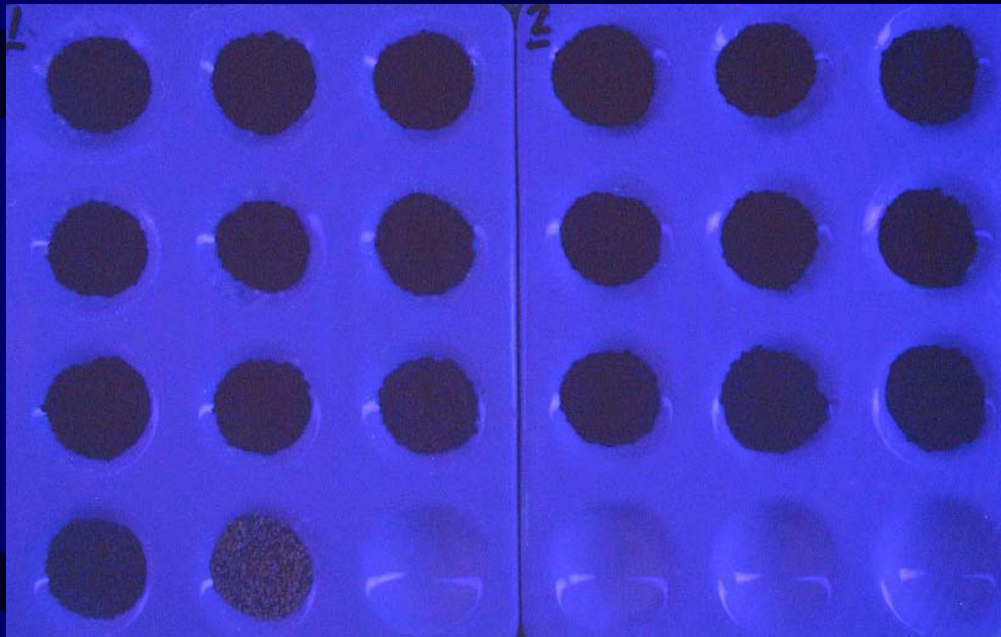
The plug or sidewall porosity and permeability are measured at confining stress “as received” with the reservoir fluids intact. An automated porosimeter and permeameter expands helium into the gas filled microfractures of the sample. The micro fracture porosity and permeability are measured.



Crushed Rock Analysis and Diffusion Parameters

- Properties measured before extraction (as received):
 - » Matrix Permeability
 - » Gas-Filled Porosity
 - » Shale Density
 - » TOC and Rock Evaluation
- Properties measured after Dean-Stark extraction:
 - » Oil and Water Saturations
 - » Total Porosity
 - » Grain Density
- The diffusion parameter is determined from the slope of the desorption curve for the plug sample and also for the crushed sample. The diffusion parameter ratio is an indication of pore network interconnectivity.
 - » D/r^2 = Diffusion Parameter [1/sec]
 - » D = Diffusion Coefficient [cm^2/sec]
 - » r = Sphere Radius [cm]

Fluorescence



Before the addition of a cutting solvent

After the addition of a cutting solvent, with empty wells for comparison

Quick-Desorption™ and Shale Evaluation

Quick-Desorption™ and Shale Evaluation

Company: SCAL, Inc.

County: Midland

Desorption Temperature: 200 °F

Well: Test 1

State: Texas

Confining Pressure: 1,500 psi

Sample		Quick-Desorption					Plug (microfracture) Data			Crushed Sample Data		Dean-Stark Data			Diffusion Parameter		
		As received										Extracted and dried			As received		
No.	Depth ft	Measured Gas scf/ton*	Lost Gas scf/ton*	Residual Gas scf/ton*	TOTAL Gas scf/ton*	Matrix Perm nD	Plug Perm mD	Plug Porosity %	Bulk Density g/cc	Gas Filled Porosity %	Total Porosity %	Saturations Water %	Oil %	Grain Density g/cc	Plug D/r ² 1/sec	Crushed D/r ² 1/sec	Ratio
1	9,210.0	29.1	23.7	22.4	75.1	604.4	0.0901	0.28	2.655	2.20	3.78	32.1	0.8	2.605	2.12E-05	3.17E-04	0.07
2	9,270.0	60.4	47.3	50.9	158.6	1363.0	tbfa	2.84	2.590	3.60	4.92	31.0	1.3	2.470	1.87E-05	1.69E-04	0.11
3	9,304.0	29.6	22.2	16.6	68.4	584.6	0.0234	0.55	2.538	1.09	4.10	35.2	1.2	2.532	1.74E-05	1.80E-04	0.10
4	9,415.0	39.3	27.4	31.8	98.6	793.7	0.0234	1.43	2.495	1.88	4.48	29.6	1.1	2.571	1.39E-05	1.75E-04	0.08
5	9,445.0	34.0	26.8	25.7	86.5	990.5	0.0310	0.33	2.547	1.67	4.10	33.8	1.5	2.627	1.77E-05	2.27E-04	0.08
6	9,456.0	34.9	31.9	39.1	105.9	842.5	0.0233	2.19	2.649	2.92	3.47	33.4	1.8	2.648	2.28E-05	2.32E-04	0.10
7	9,510.0	47.4	28.0	50.2	125.6	1129.8	0.0251	1.58	2.474	2.41	5.72	26.6	1.4	2.512	9.55E-06	2.11E-04	0.05
8	9,539.0	124.8	63.0	79.5	267.2	386.6	tbfa	2.64	2.791	2.93	5.09	25.8	1.3	2.318	6.66E-06	1.97E-04	0.03
9	9,550.0	30.4	19.0	19.6	68.9	262.4	0.0002	0.29	2.544	1.91	5.68	35.9	1.0	2.632	1.02E-05	2.08E-04	0.05
10	9,562.0	37.8	24.4	16.7	78.8	483.8	0.0002	1.03	2.497	2.32	4.66	30.0	1.6	2.632	1.02E-05	2.17E-04	0.05
11	9,580.0	40.9	28.3	30.9	100.0	506.2	0.0541	0.51	2.540	1.62	4.55	27.6	1.4	2.618	1.19E-05	1.46E-04	0.08
12	9,599.0	38.7	23.0	27.8	89.5	617.3	0.0002	0.82	2.598	1.51	3.03	32.1	1.5	2.613	8.16E-06	1.45E-04	0.06
13	9,613.0	26.2	17.7	12.3	56.1	831.6	0.0002	1.64	2.576	3.49	5.36	29.7	0.7	2.646	1.04E-05	2.48E-04	0.04
14	9,643.0	32.8	23.1	13.3	69.2	159.9	0.0002	0.44	2.532	2.02	4.43	29.9	0.8	2.643	1.15E-05	1.23E-04	0.09
15	9,666.0	34.0	21.2	30.0	85.2	523.1	0.0004	0.01	2.550	1.60	3.53	36.5	0.6	2.615	6.91E-05	1.55E-04	0.45
16	9,692.0	31.8	21.6	16.7	70.1	331.4	0.0003	0.01	2.500	1.05	4.45	31.5	0.9	2.638	1.02E-05	1.52E-04	0.07
17	9,718.0	29.2	24.6	15.6	69.4	418.7	0.0307	0.30	2.572	1.81	5.31	30.0	0.9	2.666	1.55E-05	1.22E-04	0.13
18	9,732.0	32.8	23.5	16.7	73.0	653.7	0.0001	0.58	2.595	1.31	3.97	31.8	1.0	2.640	1.10E-05	1.52E-04	0.07
19	9,740.0	30.3	22.1	15.9	68.3	282.5	0.0001	0.20	2.507	2.76	3.81	30.2	1.2	2.671	1.12E-05	1.00E-04	0.11
20	9,752.0	20.4	17.8	13.0	51.2	301.0	0.0013	0.17	2.744	2.00	1.63	27.3	0.8	2.772	1.57E-05	1.05E-04	0.15
21	9,766.0	33.5	26.6	19.9	79.9	674.0	0.0006	0.32	2.607	1.81	4.19	24.1	1.1	2.714	1.29E-05	1.39E-04	0.09
22	9,778.0	31.8	26.4	13.9	72.1	391.7	0.0006	0.11	2.524	1.74	3.67	26.0	1.3	2.655	1.38E-05	1.80E-04	0.08
Average		38.6	26.8	26.3	91.7	596.9	0.0153	0.83	2.574	2.08	4.27	30.5	1.1	2.611	1.59E-05	1.77E-04	0.10

Notations:

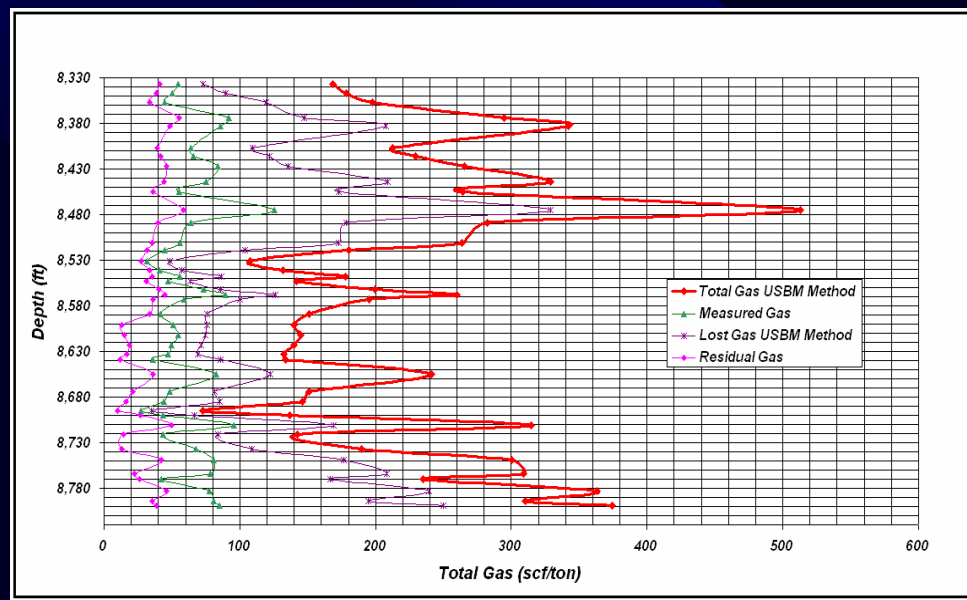
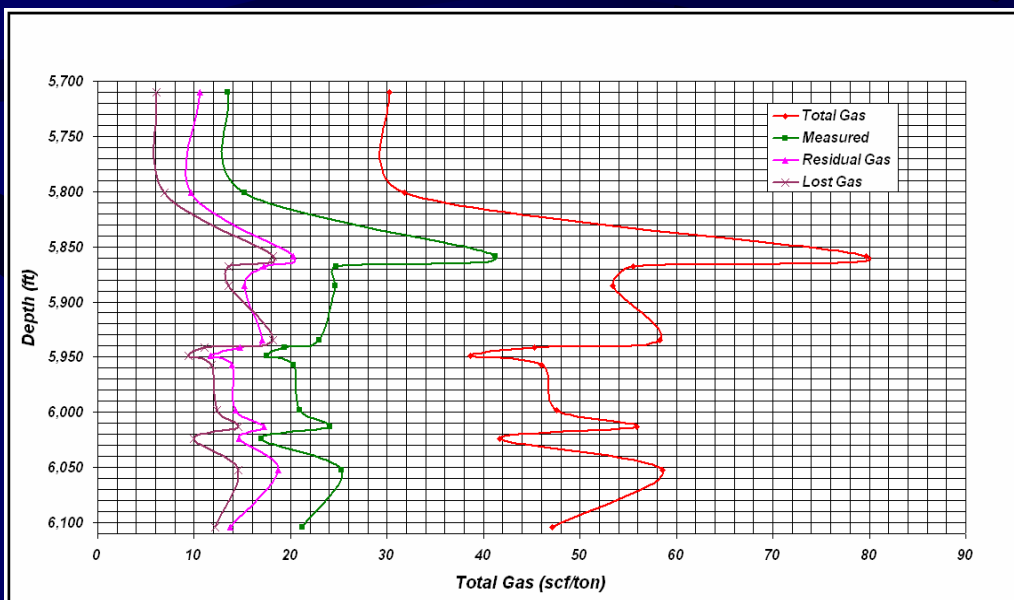
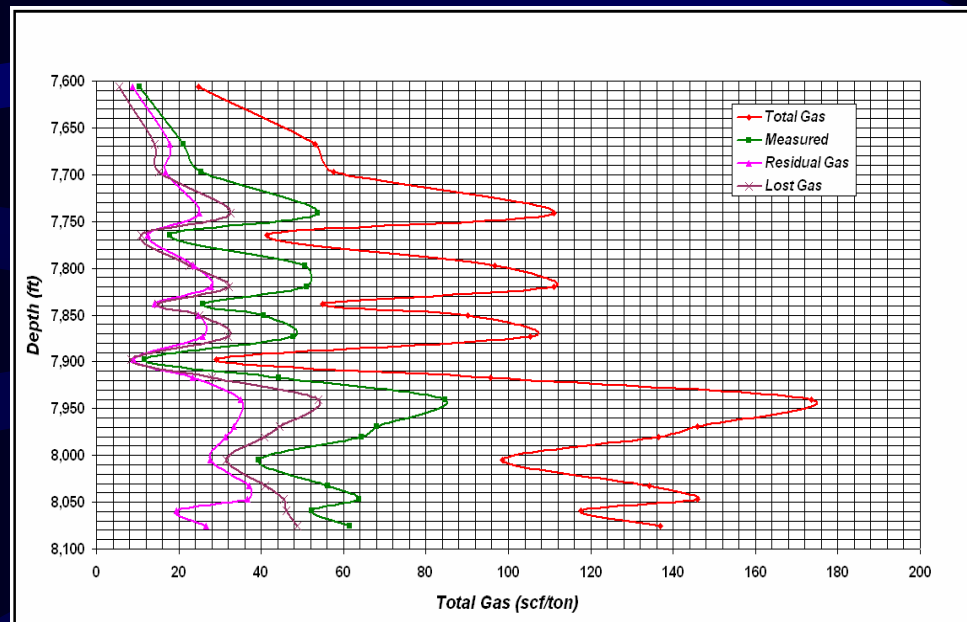
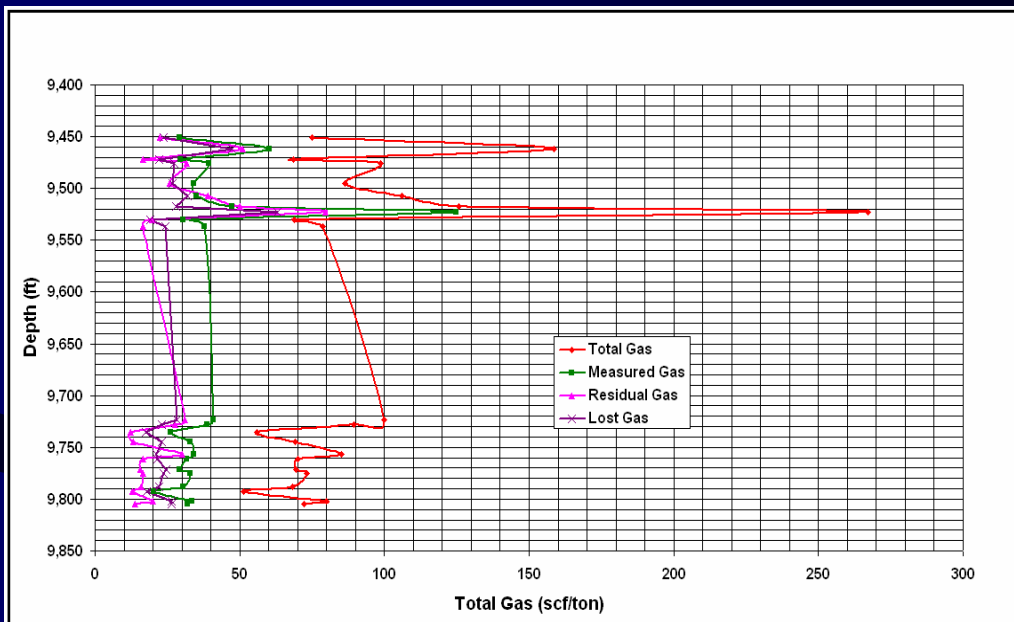
- D Diffusion coefficient [cm²/sec]
- r Sphere Radius [cm]
- D/r² Diffusion parameter [1/sec]
- ton* US Short ton equal to 2,000 lbs



SCAL, Inc.

SPECIAL CORE ANALYSIS LABORATORIES, INC.

Quick-Desorption™ Gas Composite Plots



Shale Evaluation using Desorption Isotherms

- 1 Measured gas.** A fully automated laboratory is present on location when the rotary sidewall samples are taken. The cores are cut from top to bottom and retrieved from the coring tool ASAP to minimize the lost gas. The wire line trip out time is recorded and used in the USBM lost gas calculation. Vertical plug samples can be cut, in the center of a conventional core, at the well site and used for Quick-Desorption and Shale Evaluation. The portable laboratory returns to our laboratory facility while collecting desorption data at constant reservoir temperature. The desorption is conducted until the gas production ends.
- 2 Lost gas and matrix permeability.** The linear portion of the desorption curve is used to determine lost gas and the diffusion parameter for the plug samples.
- 3 Bulk density, micro fracture porosity and permeability at confining stress.** Bulk density and micro fracture permeability and porosity measurements are performed at reservoir confining stress on the wet shale sample (if a straight cylinder can be shaped from the recovered core material). If the sample quality is poor, only the bulk density is measured.
- 4 Residual gas.** The shale is grinded to about 45 mesh using special mills. Another desorption is performed at reservoir temperature on the granular sample to measure the residual gas and the diffusion parameter.
- 5 Total gas.** Total gas is calculated by adding measured, lost and residual gas.
- 6 Geochemistry.** A small portion of the sample is collected to perform TOC and Rock-Evaluation. The plug end trims are also available for further geochemistry and/or petrography analysis (TS, XRD, SEM).
- 7 Gas filled porosity.** The gas filled porosity is measured on the crushed sidewall sample by gas expansion into the “as received” shale.
- 8 Water and oil saturations, total porosity, and grain density.** The samples are extracted to measure the water and oil saturations. The total porosity and the grain density are also measured.

Sorption Isotherms – Reservoir Performance

Sorption isotherms can be measured on sidewall samples using a new 8 cell design. Various gases can be used. The Langmuir gas storage for a particular pressure can be calculated:

$$G_s = VL \times P / (P + PL)$$

Where:

G_s = Gas storage capacity (scf/ton)

VL = The Langmuir Volume (scf/ton) is the maximum amount of gas that can be adsorbed at infinite pressure

P = Absolute pressure (psia)

PL = The Langmuir pressure (psia) affects the curvature of the isotherm and corresponds to the pressure at which half of the VL is adsorbed.

Sorption Isotherm Methane 191 °F

Company : Good Oil Company

Well Name : Well #1

County : This County

State : New Mexico

Sample : 1
Depth : 12,000 ft

Porosity : 0.4 %
Grain Density : 2.541 g/cc
Confining Pressure : 3,600 psi

Temperature : 191 °F
Atmospheric Pressure : 13.1 psi

Sample Weight : 13.00 g

Test Results:

Step No.	Pressure psia	Adsorption scc/g	Adsorption scf/ton	Langmuir Gas Storage* scf/ton
1	512.7	0.6	21.4	20.8
2	1007.4	0.97	34.1	35.5
3	1503.1	1.3	46	46.8
4	2001.1	1.54	54.3	55.8
5	2493.4	1.81	64	63
6	2989.4	2.06	72.8	69.1
7	3475.2	2.14	75.5	74.1
8	3968.4	2.12	74.9	78.4

* Langmuir Regression and Coefficients :

PL : 2,781.50 psia
VL : 133.33 scf/ton

$$G_s = VL \times P / (P + PL)$$

Where:

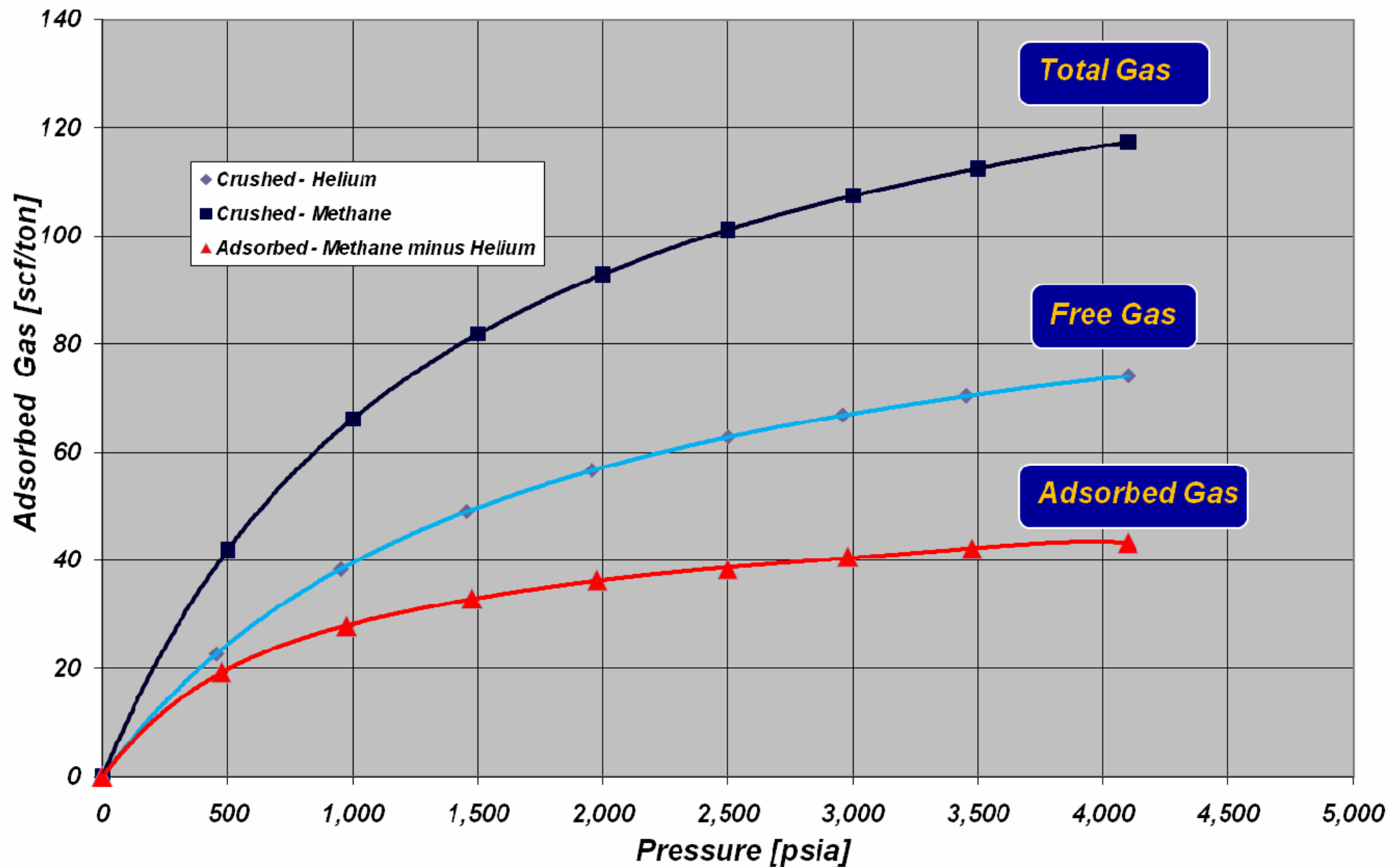
G_s Gas storage capacity (scf/ton)

VL The Langmuir volume (scf/ton) is the maximum amount of gas that can be adsorbed at infinite pressure.

P Absolute pressure (psia)

PL The Langmuir pressure (psia) affects the curvature of the isotherm and corresponds to the pressure at which half of the VL is adsorbed.

Free and Adsorbed Gas



Shale Evaluation using Sorption Isotherms

Only one sidewall sample is required for this new test procedure.

1. **Rotary sidewall samples are preserved** at the well site and shipped to our laboratory in Midland, Texas; therefore there are not any field expenses associated with this procedure. The preservation consists of surface mud cleaned with a wet towel, then the samples are wrapped in saran wrap and aluminum foil. A few drops of water are added to each glass jar before the samples are sealed to prevent evaporation during transportation.
2. **The samples are trimmed and photographed** in UV and white light.
3. **Micro fracture analysis.** The as-received samples are loaded at reservoir stress and the porosity and permeability of the gas filled micro fractures are measured. **The bulk density and matrix permeability are also measured.**
4. **Residual gas measurement.** The sidewall samples are ground to an approximate 45 mesh. A complete desorption isotherm is performed at reservoir temperature to determine the residual gas and the diffusion parameter.
5. **The gas filled porosity** is measured by helium expansion into the as-received samples.
6. **Sorption isotherms** at reservoir temperature with methane are measured on each sample. These isotherms are normally close to the desorption isotherms (not measured in the field).
7. **Cut fluorescence.** A small fraction of the ground sample is photographed in UV without and with a cut solvent to document the cut fluorescence.
8. **Geochemistry.** A small portion of the sample is collected to perform TOC and Rock-Evaluation. The plug end trims are also available for further geochemistry and/or petrography analysis (TS, XRD, SEM).
9. **Water and oil saturations, total porosity, and grain density.** The samples are extracted to measure the water and oil saturations. The total porosity and the grain density are also measured.

Fluid Optimization: XRD and Capillary Suction Time

X-Ray Diffraction Mineral Data

Company : SCAL, Inc.
Well : Test #1
Location : Midland County, Texas

Sample Number	Depth	Air Perm	KK Perm	Por	Grain Density	Qtz	Plag	K Feld	Cal	Dol	Ank	Sid	Anhy	Gyp	NaCl	Pyr	Total Bulk	Illite + Mica	EML i/s	Sme	Kao	Chl	Total Clay
	ft	mD	mD	%	g/cc												%						%
1	6073.5	0.01	0.01	3.12	2.50	50	6		1	2		1				4	64	20	6		3	7	36
2	6435.5	tbfa	tbfa	2.83	2.53	35	5	2	1	2		1				3	49	30	11		+	10	51
3	6,855.8	0.03	0.02	2.01	2.55	34	5			3						4	46	30	14			10	54
4	6,875.5	tbfa	tbfa	3.95	2.46	34	5			3		1				7	50	25	15			10	50
5	7,042.5	0.01	0.01	2.23	2.72	25	4			16						3	48	30	15			7	52
6	7,438.0	0.01	0.0056	3.48	2.64	22	4		9	14						5	54	30	16				46
7	7,462.0	0.01	0.0025	8.11	2.39	51	5		19	3		1				5	84	10	6				16
8	7491.5	0.01	0.0034	2.24	2.41	38	5		20	4						8	75	15	10				25
9	7,524.0	0.01	0.0072	4.47	2.23	18	2		78	2							100						0
10	7,550.0	0	0.0002	3.56	2.53	37	3		40	2						3	85	10	5				15
11	7,578.5	0.01	0.0044	2.81	2.56	39	3		8	2		1				8	61	25	14				39
12	7,623.0	0.01	0.0029	3.26	2.49	39	4		8	4		1				7	63	20	17				37
13	7,656.0	0	0.0019	1.8	2.43	42	4		4	2						11	63	20	17				37
14	7,694.0	0.4	0.3253	3.32	2.46	46	5		2	3						7	63	20	17				37

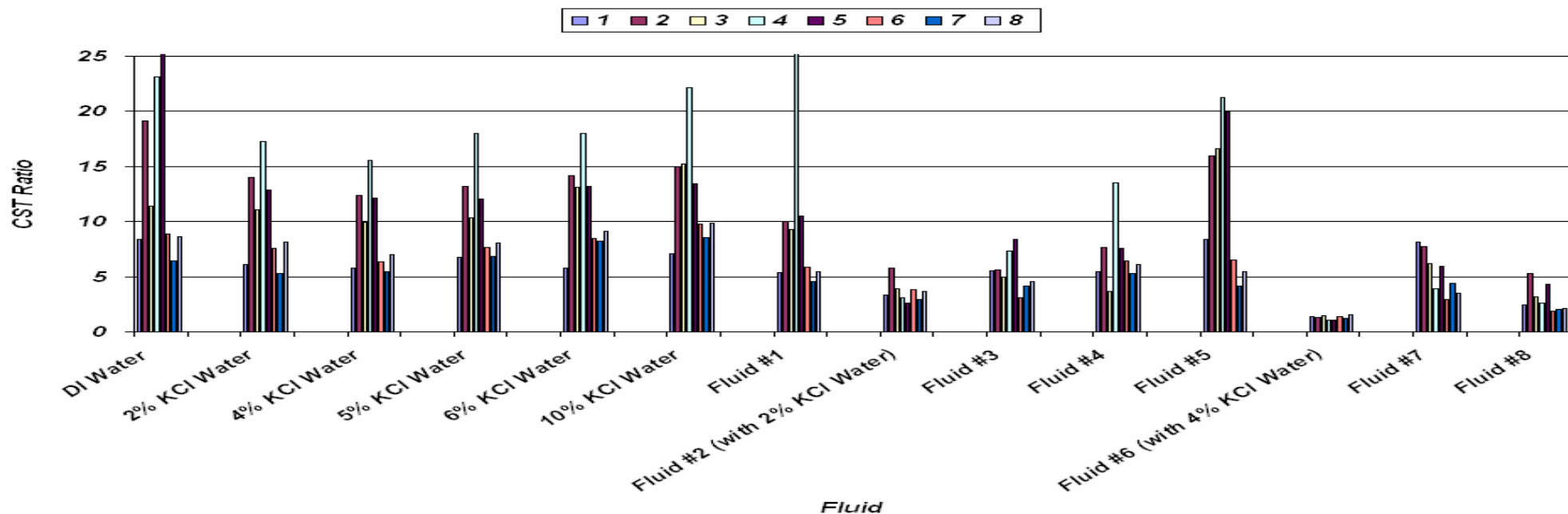
Qtz Quartz SiO₂
Cal Calcite Ca CO₃
Sid Siderite Fe CO₃
Pyr Pyrite Fe S₂
Gyp Gypsum CaSO₄.2H₂O
Ank Ankerite

KFeld Potassium Feldspar KAISi₃O₈
Dol Dolomite CaMg(CO₃)₂
Bar Barite BaSO₄
Plag (Ca, Na)Al(1-2)Si(3-2)O₈
Anhy Anhydrite CaSO₄

Clay Minerals = Aluminosilicates
Kao Kaolinite
Chl Chlorite
Sme Smectite
EML Expandable Mixed Layer (Illite/Smectite)

"+" Denotes a trace percentage

Capillary Suction Time Ratio



Dynamic Rock Mechanics

Acoustic Velocities Measurements

Company: Good Oil Company

Well Name: Good Well #2

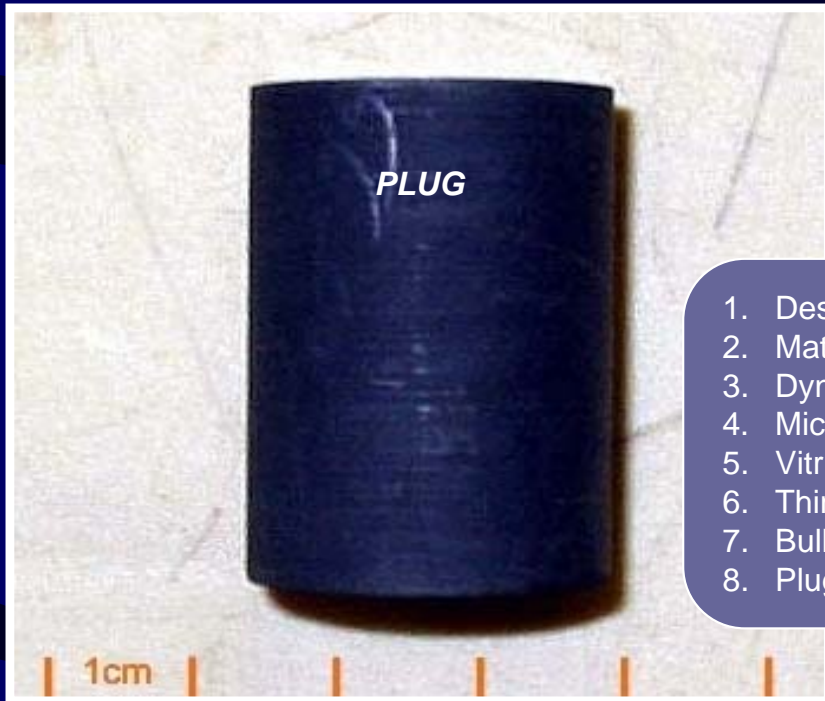
County: Some County, Oklahoma

Brine Density: 1.03 g/cc

Temperature: 23 °C

Sample	Depth	Porosity %	Matrix Permeability nD	Grain Density g/cc	Dry Bulk Density g/cc	Wet Bulk Density dg/cc	Confining Pressure psi	Pore Pressure psi	Compresional Velocity ft/sec	Shear Velocity ft/sec	Dynamic Bulk Moduli psi	Dynamic Shear Moduli psi	Young's psi	Poisson Ratio -
1	10,950.0	0.13	73.8	2.52	2.514	2.515	10,000	4,700	16,967	10,409	4,858,581	3,670,824	8,796,996	0.198
2	10,960.0	0.33	62.0	2.29	2.281	2.285	10,000	4,700	14,358	8,965	3,046,125	2,473,666	5,840,132	0.180
3	10,970.0	0.51	97.2	2.39	2.377	2.382	10,000	4,700	14,758	9,277	3,307,017	2,761,236	6,480,147	0.173
4	10,980.0	0.41	113.1	2.41	2.399	2.403	10,000	4,700	14,639	9,422	3,105,248	2,874,052	6,589,265	0.146
5	10,990.0	0.24	70.2	2.36	2.352	2.355	10,000	4,700	15,286	9,730	3,407,480	3,002,770	6,962,983	0.159
6	11,000.0	0.57	107.5	2.45	2.432	2.438	10,000	4,700	15,227	9,639	3,545,909	3,050,792	7,112,565	0.166
7	11,100.0	0.25	135.3	2.44	2.430	2.432	10,000	4,700	15,821	10,115	3,731,575	3,352,466	7,739,625	0.154

Sample Fractions and Associated Testing

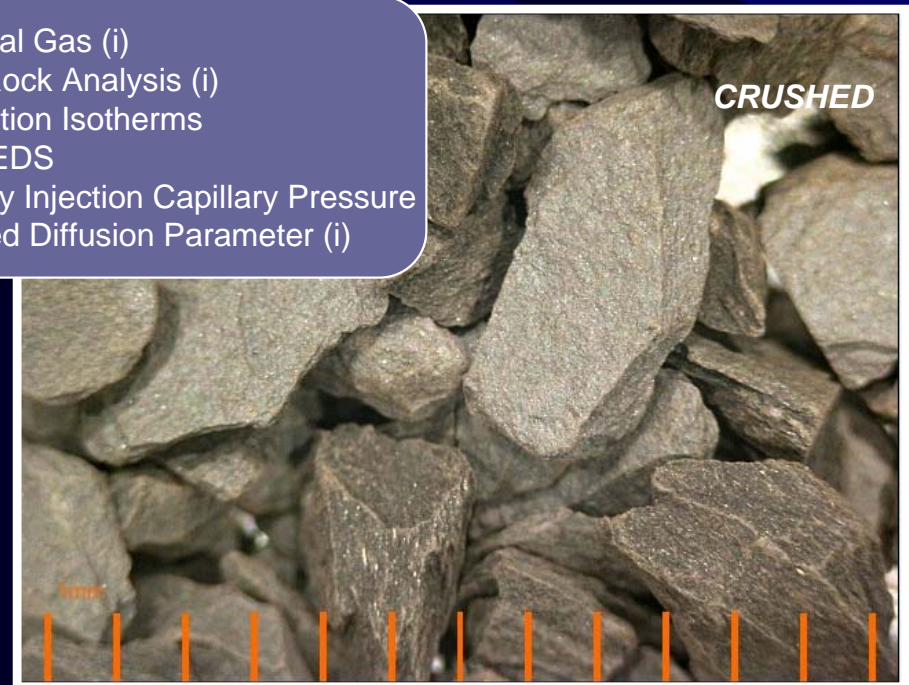


1. Desorption Isotherms (i)
2. Matrix Permeability (i)
3. Dynamic Rock Mechanics
4. Micro fracture Porosity and Permeability (i)
5. Vitrinite Reflectance
6. Thin Section Preparation
7. Bulk Density (i)
8. Plug Diffusion Parameter (i)



1. TOC and Rock Evaluation (i)
2. XRD
3. Capillary Suction Time
4. Acid Solubility

1. Residual Gas (i)
2. Tight Rock Analysis (i)
3. Adsorption Isotherms
4. SEM -EDS
5. Mercury Injection Capillary Pressure
6. Crushed Diffusion Parameter (i)



Conclusions:

- The desorption – adsorption correlation is very important to assure accurate shale gas content . Is the best check available for the lost gas calculations, sample grinding size and saturation preservation. It can also validate a total gas measurement curve with gas generation (if the generated gas is bacterial the adsorption isotherm will be closer to the first plateau).
- The averaging technique currently used, where a number of sidewall samples from various depths are sealed inside the same desorption canister, can turn an excellent prospect into a mediocre one. Small canisters and high resolution equipment are necessary to measure the gas content of individual shale sidewall samples.
- The technology can accurately find the “sweet gas zone” before horizontal drilling begins.
- This technique is time and cost effective and provides major savings when compared with the cost of a full diameter core project.

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- Personal conversations with Dr. Dan Suciu consultant, Mr. Alton Brown consultant and Dr. Martin Thomas of Quantachrome Corporation.