Recent Advances in the Analytical Methods Used for Shale Gas Reservoir Gas-in-Place Assessment*

By

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Search and Discovery Article #40317 (2008)
Posted October 30, 2008

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Abstract

Shale gas reservoirs are a commingling between conventional (compressed) and unconventional (adsorbed;, i.e., CBM) gas reservoirs. Therefore, shale gas-in-place (GIP) evaluations require the use of analytical methods originally developed for each specific reservoir system. Unfortunately, many analytical techniques used to determine GIP and permeability for conventional and CBM reservoirs do not translate well when evaluating shale due to its complex lithology. Presented are the results of a rigorous study, conducted in an effort to improve existing shale analytical protocol to more accurately define the critical parameters necessary for shale GIP assessment.

The petrographic impact on the adsorbed phase gas storage capacity in shale was investigated to determine what, if any, gas adsorption vectors beyond available TOC exist. Research was also conducted to define the influence of liquid phase hydrocarbons on the adsorbed phase gas storage capacity (dissolution) in shale. The results provide insight into the mechanisms responsible for some of the unexplained phenomena observed when adsorption isotherm analysis is conducted on shale samples.

Improved sample handling methods were developed to maintain in-situ moisture conditions during processing and laboratory testing. Techniques were developed to allow the delineation of water saturations into its pore, irreducible, and bound water components. Procedures were developed to improve shale permeability and porosity measurements, using competent core under in-situ stress conditions. Furthermore, grain density measurements (required for porosity determinations) were conducted using select inert gas species with molecular diameters similar to methane to contrast and compare the results determined using the standard gas, helium, which can potentially overestimate available porosity.

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April 23, 2008

AAPG 2008 Annual Convention & Exhibition

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Outline

- Gas-In-Place (GIP) Determination In Shale Gas Reservoirs
  - Shale Characteristics
  - Standard GIP protocols
- Some Investigated Variables and Their Implications on Current Interpretation and Evaluation Methods
  - Mineral adsorption vectors
  - Moisture effects on shale gas storage capacity
  - Effects of sample handling and analytical protocol on water saturations
- Conclusions

"Unconventional" Natural Gas Reservoirs

Geologically complex and low permeability (<0.1 md normally) gas reservoirs that require special (non-standard) evaluation and technology.

Reservoir Spectrum

"Tight Sand" ← Fractured "Shale" → Coal
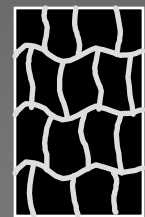
0 ← 25 ← 50 ← 75 → 100
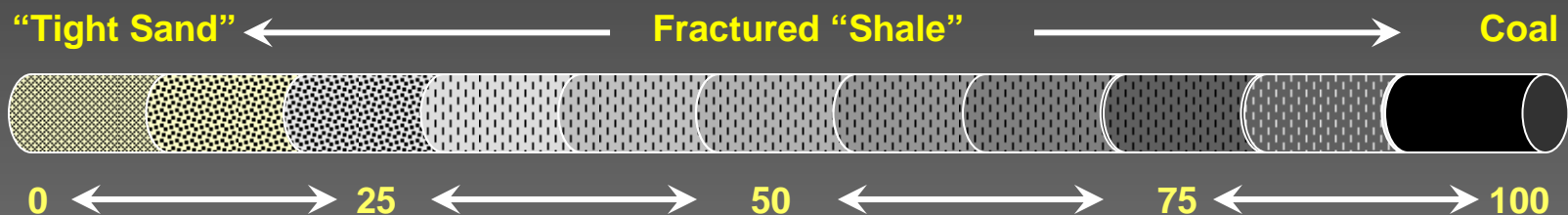
Organic Content, wt. %

Gas Filled Porosity
(Compression)

Water Filled Porosity

Gas Filled Micropores
(Adsorption)

"Estimated" Gas-In-Place Volume

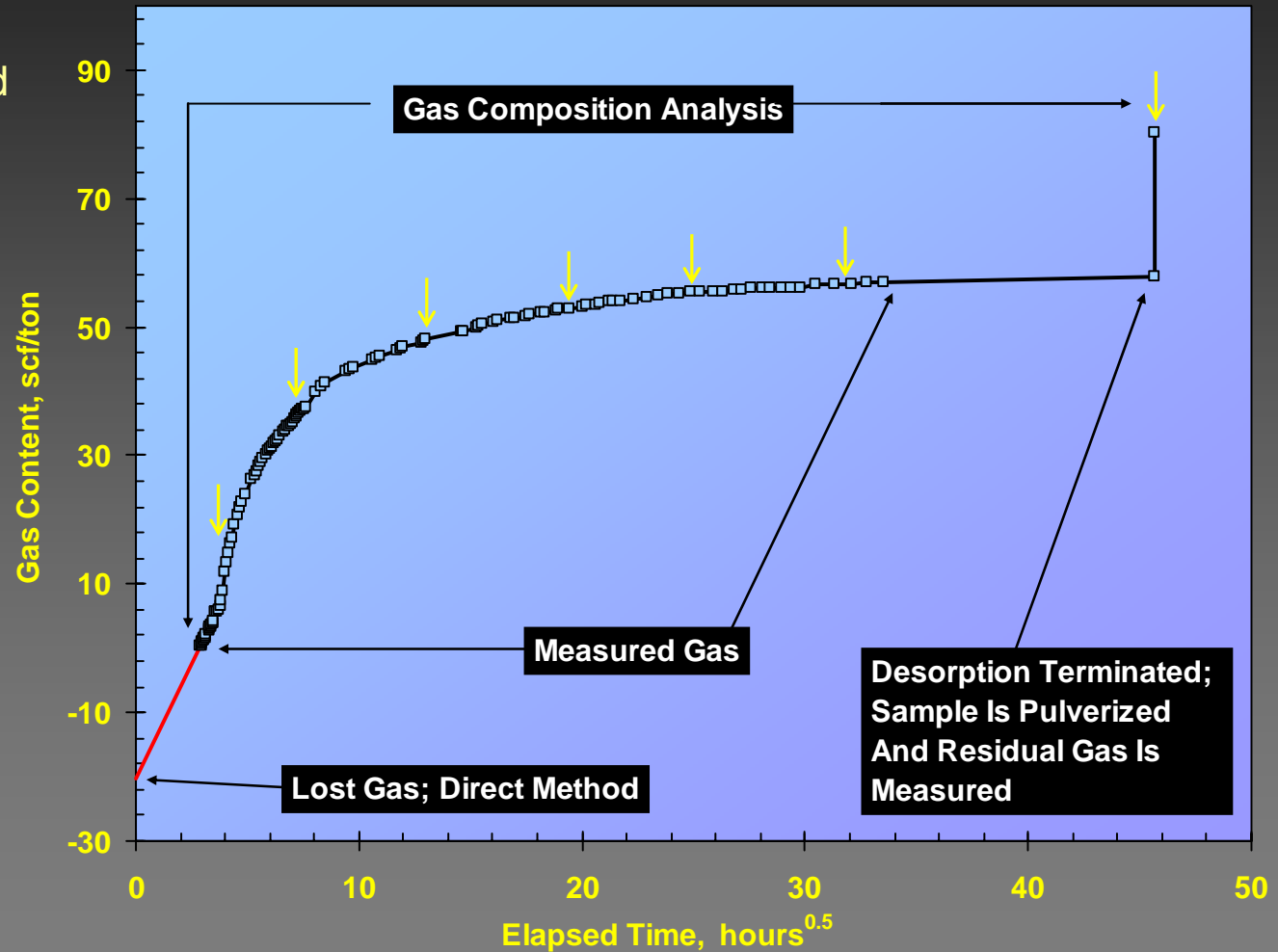$$GIP = 1359.7\ A \times h \times \rho \times G_{ct}$$

- *Drainage Area (A)*
- *Reservoir Thickness (h)*
- *Bulk Density (ρ)*
- *Total Gas Content (G_{ct})*
  - *Indirect Method Assumes Total Gas Storage Capacity = G_{ct}*

Unconventional Reservoir Gas Content

• Present day in-situ GIP is a function of the geological factors which the reservoir has been subjected to since deposition (reservoir "burping", uplift, faulting, hydraulic stripping). Thus, accurate gas content data often cannot be calculated from knowledge of physical rock properties alone but instead must be directly measured from freshly cut rock samples

• Indirect GIP determination (i.e. gas storage capacity = gas content) can still provide valuable information on resource potential and economic viability but has the potential to high grade the results

Total Gas Content/Composition Analysis

- Provides a direct empirical measurement of all free, absorbed, and adsorbed gas

- Evolved gas can be assessed for composition and fractionation with time

- Gas composition provides further information for appropriate adsorption isotherm analytes

- Rates of gas evolution from the core matrix provide an indication of relative diffusivity

Gas Content, scf/ton (y-axis): 90, 70, 50, 30, 10, -10, -30

Elapsed Time, hours$^{0.5}$ (x-axis): 0, 10, 20, 30, 40, 50

Gas Composition Analysis

Measured Gas

Lost Gas; Direct Method

Desorption Terminated; Sample Is Pulverized And Residual Gas Is Measured
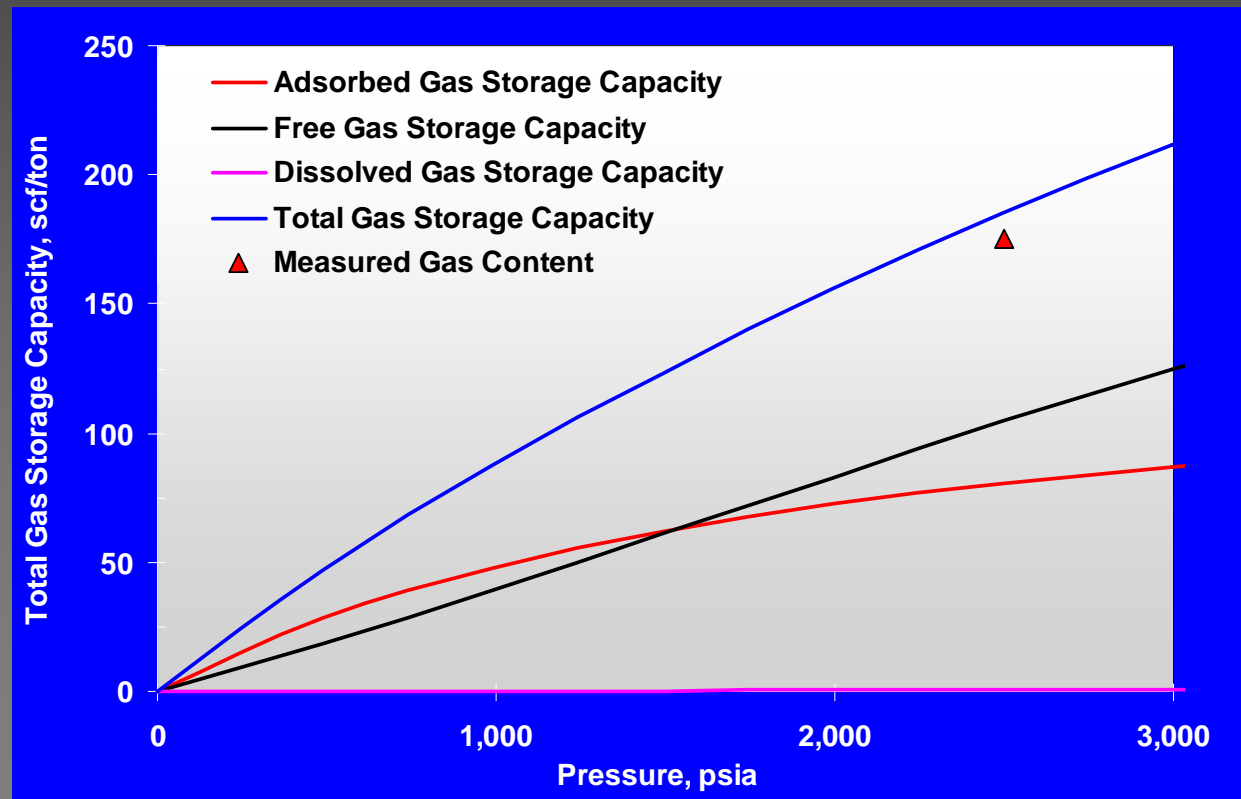
Shale Total Gas Storage Content & Capacity

- Three Existing Mechanisms For Storage
  - Adsorbed Gas Within Existing Kerogen *(and other constituents)*
  - Free (Compressed) Gas In Available Porosity
  - Dissolved Gas Within Existing Mobile Hydrocarbons or Brine
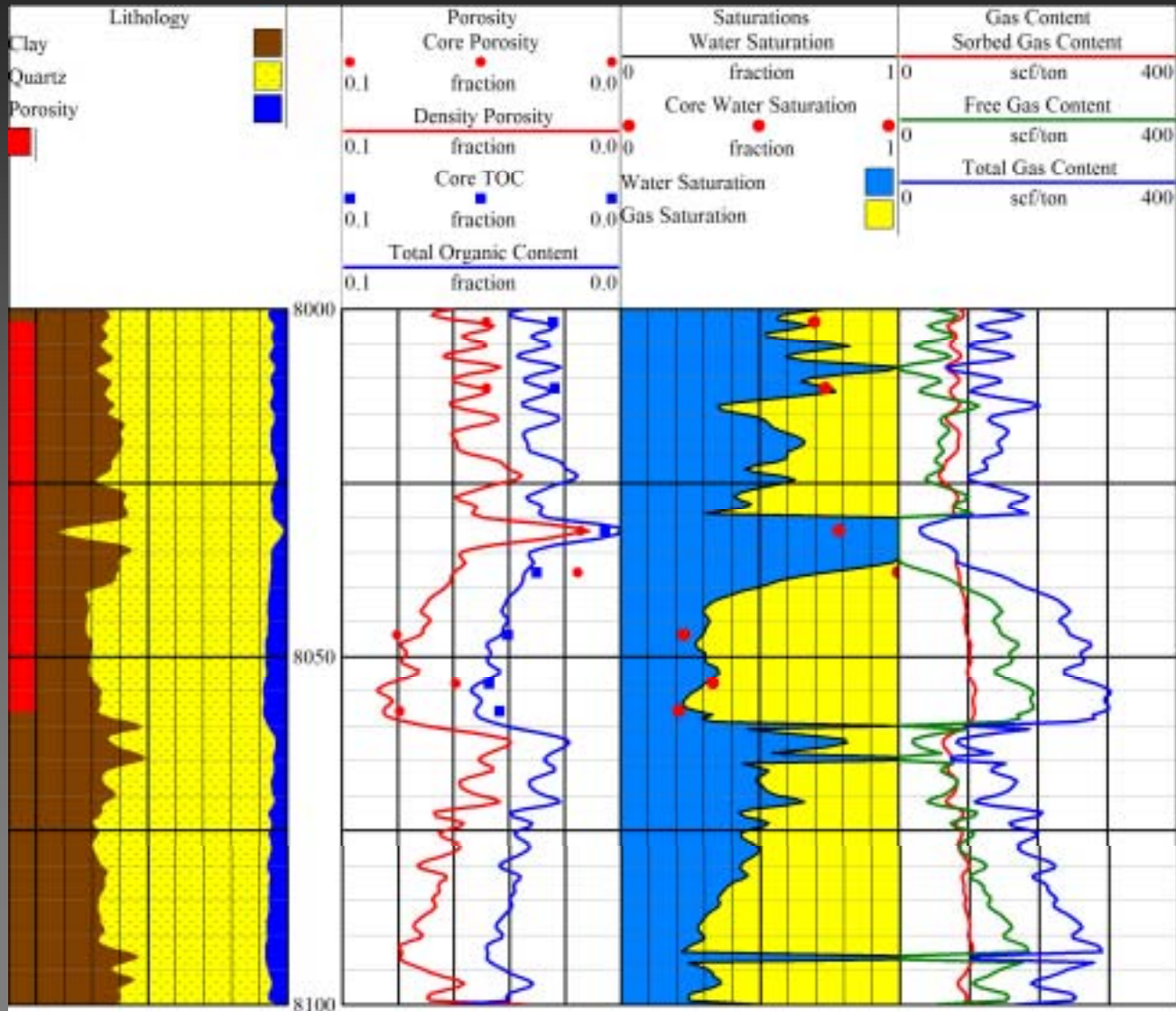
$$G_{ct} = G_{cs} + G_{cf} + G_{cd}$$

$$G_{cs} = G_{sL} \frac{p}{p + p_L}$$

$$G_{cf} = 32.0368 \frac{\phi(1 - S_w)}{\rho B_g}$$

$$G_{cd} = \frac{32.0368}{5.6146} \frac{\phi S_w}{\rho B_w} R_{sw}$$

Shale Core Bulk Properties and GIP to Geophysical Log Calibration

Adsorbed Gas Storage Capacity

- What is adsorption?
  - A physical phenomena common to microporous materials, such as kerogen, where gas and solids share a weak attraction (van Der Waal's force) in response to high surface area to pore volume ratio (10^8 ft^2 per ft^3).

- Significance
  - A primary storage mechanism in many unconventional reservoirs
  - Necessary for indirect gas content estimates, GIP estimates and core-geophysical log calibration
  - Provides information needed to delineate between the adsorbed and free gas content

Correlations Between Adsorbed Phase Gas Storage Capacity and Empirically Measured Gas Content
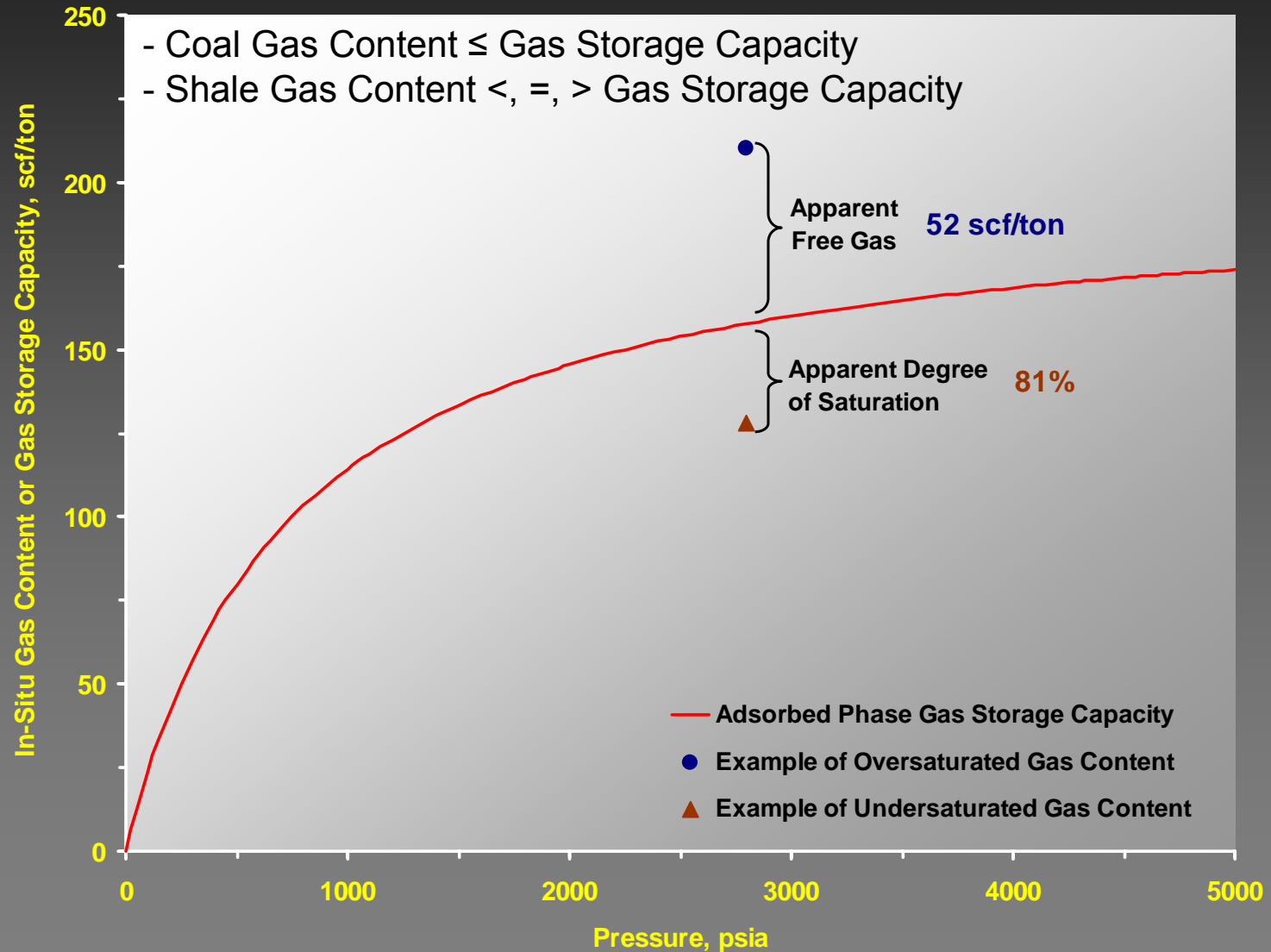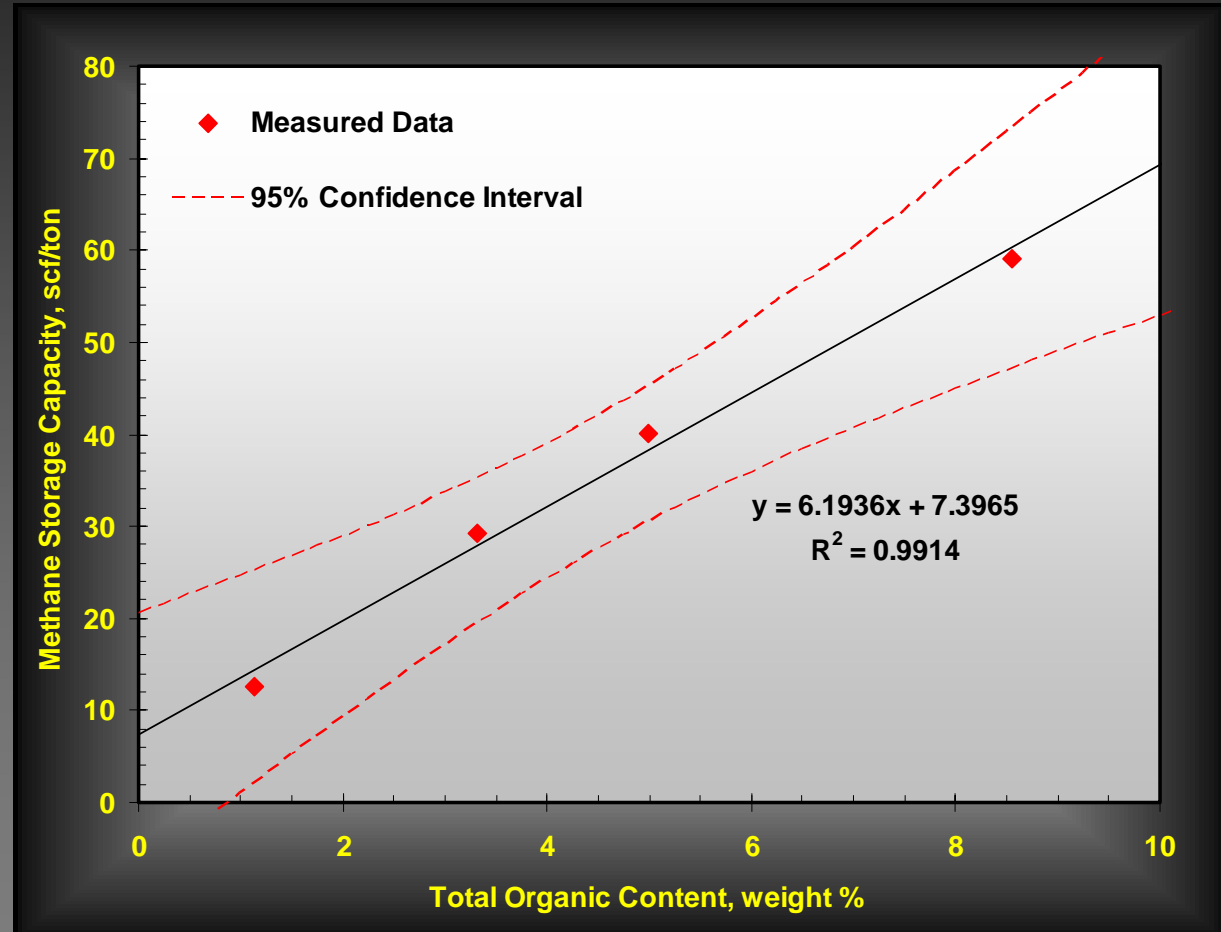
Adsorbed Gas Storage Capacity vs. TOC Shale Reservoirs

The organic material is the primary sorbent within the shale matrix

Often the erroneous assumption is made that at zero TOC there should be zero gas storage capacity

Good Relationship

Chart: Methane Storage Capacity, scf/ton vs. Total Organic Content, weight %

- ◆ Measured Data
- − − − 95% Confidence Interval

$y = 6.1936x + 7.3965$
$R^2 = 0.9914$

Illite Sample Bulk Rock Properties

Based on preliminary observations Illite was chosen as a promising mineral for a case study of potential secondary adsorption vectors within shales

Clays, wt. %				Quartz	Carbonates & Other Minerals
Chlorite	Kaolinite	Illite	Mixed Layers of Illite/Smectite	wt. %	wt. %
4	1	46	16	27	6

| TOC	As-Received Moisture Content	Density
wt. %	wt. %	g/cc
0.1	1.81	2.74

Illite Isotherm Sample Preparation

- As-Received: Large slate rock pieces, dull green/grey
- Bulk sample was crushed, sieved, and riffled to obtain representative splits between -16 and -20 mesh
- One split was run as-received
- One was oven dried at 110°C for three hours
- One was moisture equilibrated using a modified ASTM method D 1412
  - Wetted the sample with a 3% KCL solution until substantial excess moisture was apparent (muddy).
  - Sealed sample under helium and let age for 24 hours
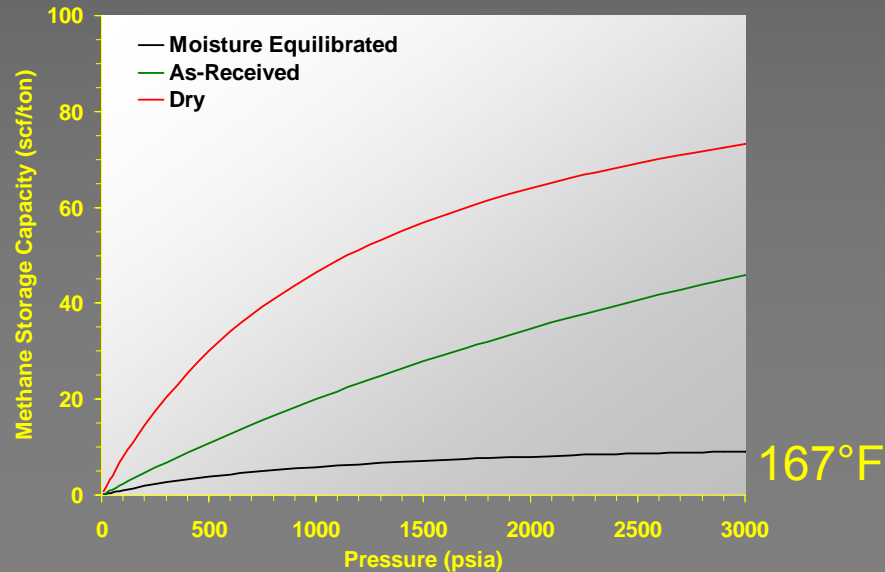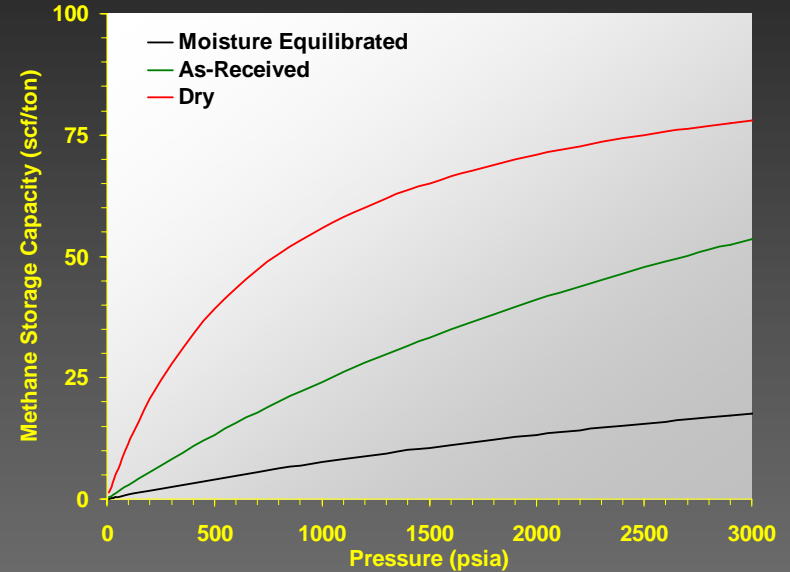 - Placed in vacuum oven for 48 hours at 86°F to equilibrate

Methane Isotherm Analysis on Illite

The adsorbed phase storage capacity of Illite was determined over
a range of temperatures and moisture contents
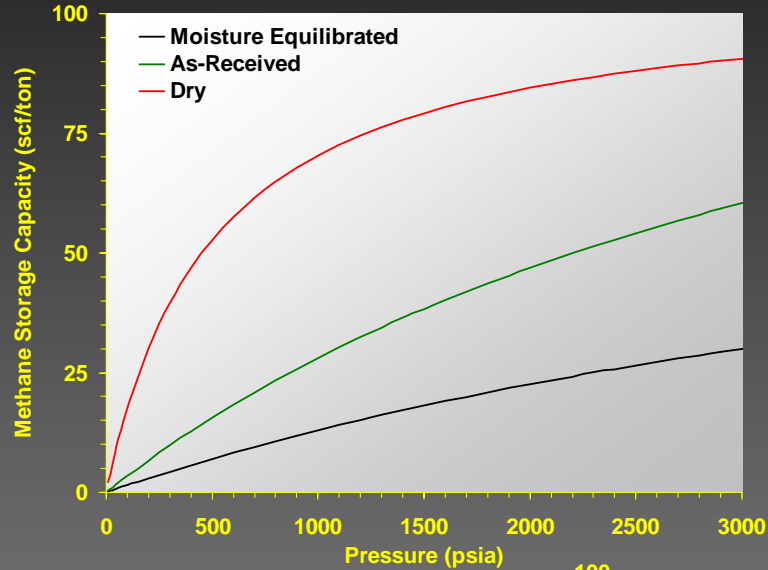
Illite Methane Isotherm Results

Illite Sample ≈ 67 wt.% Illite & 33 wt.% Quartz
Arbitrary Reservoir Pressure of 2,500 psia

Methane Isotherms Conducted At 77°F (25°C)	
Illite Sample	Methane Gas Storage Capacity, scf/ton
Moisture Equilibrated (2.33 wt. % Moisture)	26.52
As-Received (1.81 wt. % Moisture)	54.13
Dry (0.77 wt. % Moisture)	88.03

Methane Isotherms Conducted At 122°F (50°C)	
Illite Sample	Methane Gas Storage Capacity, scf/ton
Moisture Equilibrated (2.33 wt. % Moisture)	15.53
As-Received (1.81 wt. % Moisture)	47.77
Dry (0.77 wt. % Moisture)	75.01

Methane Isotherms Conducted At 167°F (75°C)	
Illite Sample	Methane Gas Storage Capacity, scf/ton
Moisture Equilibrated (2.33 wt. % Moisture)	8.61
As-Received (1.81 wt. % Moisture)	40.66
Dry (0.77 wt. % Moisture)	69.23

Mineral Density Data

Component	In-Situ Density	Dry Density	Apparent Water Content	Apparent Water Content
	g/cc	g/cc	vol fraction	wt fraction
Quartz	2.65	2.65		
K-Feldspar	2.55	2.55		
Plagioclase	2.62	2.62		
Calcite	2.71	2.71		
Dolomite	2.87	2.87		
Siderite	3.94	3.94		
Pyrite	5.06	5.06		
Montmorillonite	2.12	2.53	0.2680	0.1264
Illite	2.53	2.65	0.0727	0.0287
Kaolinite	2.42	2.44	0.0139	0.0057
Chlorite	2.77	2.79	0.0112	0.0040

Edmondson, SPWLA 1979

- Moisture equilibrated sample at 2.33 wt.% water
- Pure Illite contains ~ 2.87 wt.% water
- Sample mass – "quartz" fraction ≈ 3.32 wt% water in Illite

Implications of Illite Isotherms Results

- **Other minerals and components of shale contribute to adsorbed gas capacity**

- Leads one to ask: What other minerals or structural elements might be contributing to adsorption storage potential?

- Moisture content / water saturations have an impact on adsorption potential of inorganic constituents in shale

- **Sample handling and preservation is critical**

# Shale Samples Bulk Rock Properties

These shale samples were prepared for methane adsorption isotherm analysis using the same methods applied to the Illite samples

Kerogen Type	TOC, wt. %	Calculated Ro %	Moisture Content, wt.%		
			Moisture Equilibrated	As-Received	Dry
I	14.22	0.58	2.48	1.56	0.065
II	7.73	0.80	3.24	1.01	0.000
III	3.54	1.28	2.61	0.79	0.064
IV	5.39	1.98	0.78	0.39	0.013

Kerogen Type	Clays, wt. %				Quartz	Carbonates & Other Minerals
	Chlorite	Kaolinite	Illite	Mixed Layers of Illite/Smectite	wt. %	wt. %
I	9	2	16	7	40	26
II	13	3	15	10	42	19
III	0	0	34	0	42	26
IV	10	28	13	2	31	7

Shale Methane Isotherm Results – 1

Type I Kerogen, 14.22% TOC
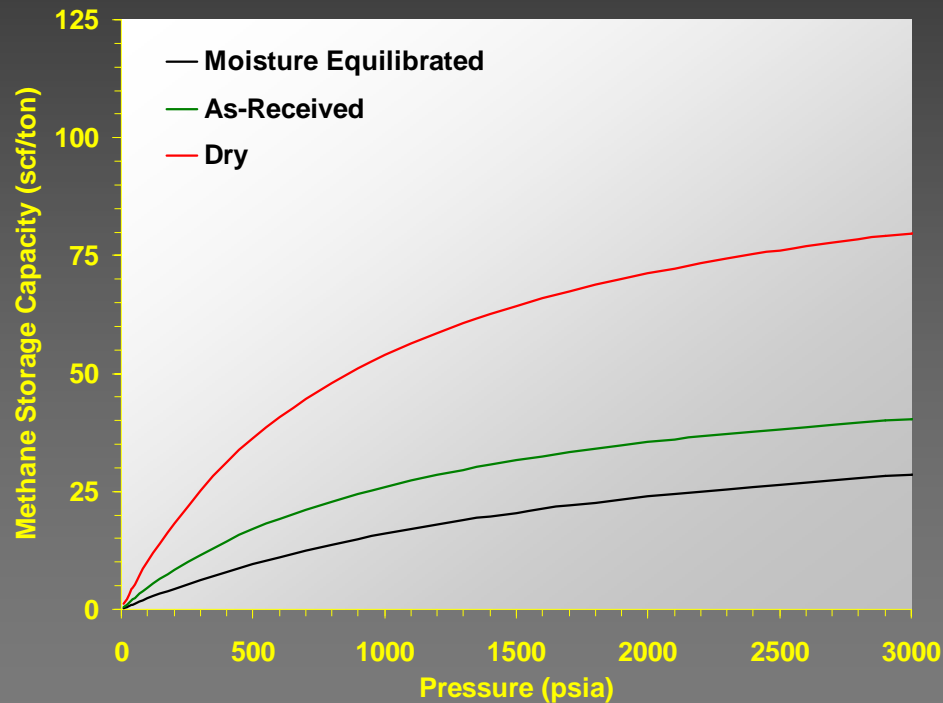Reservoir Temperature of 75°F
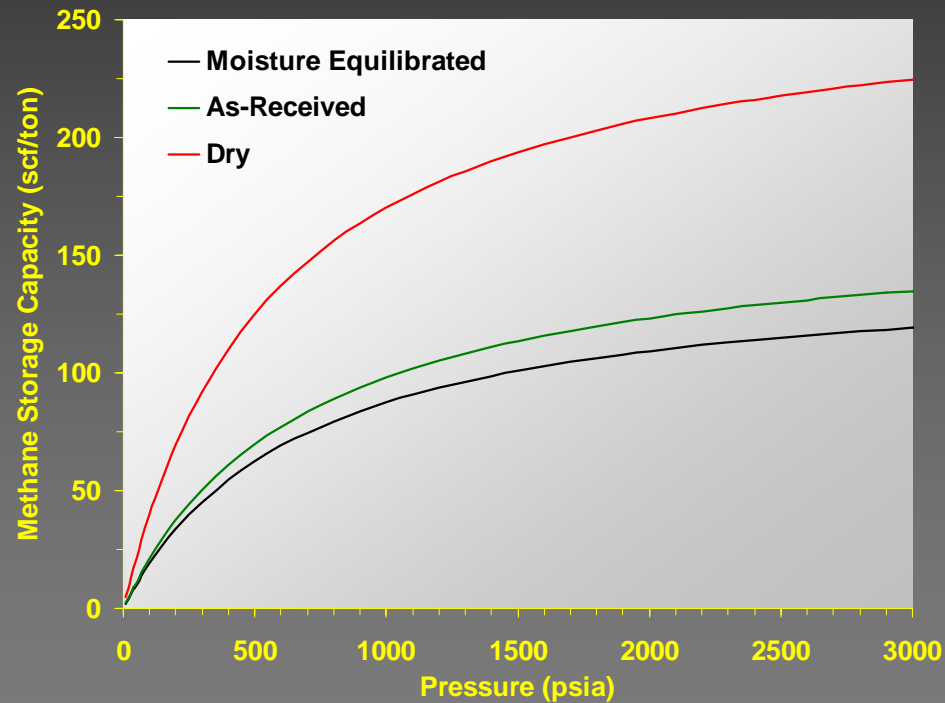
Type II Kerogen, 7.73% TOC
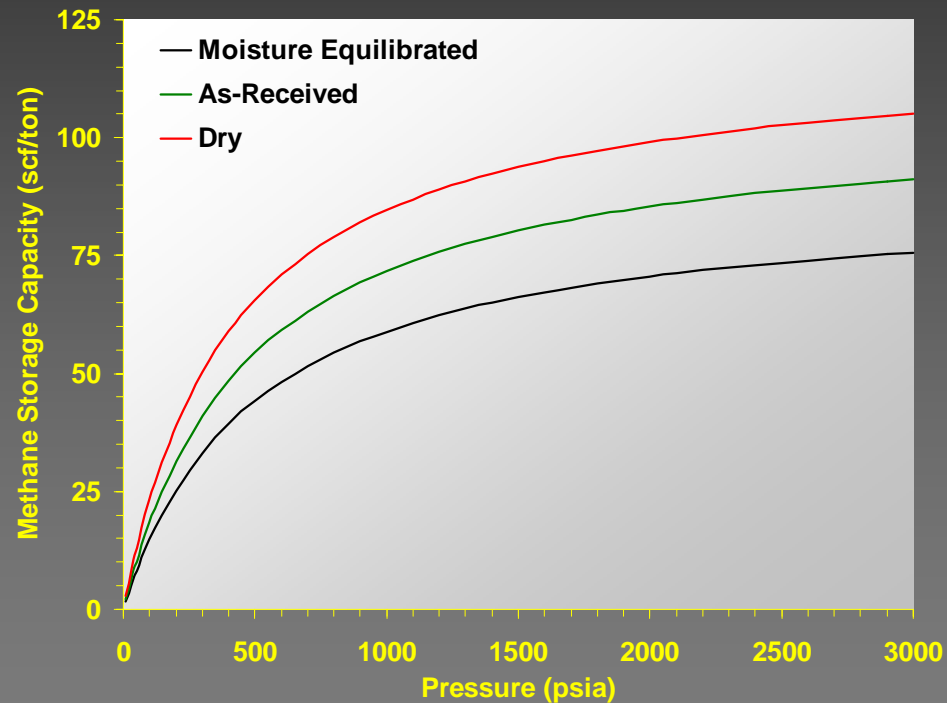Reservoir Temperature of 140°F
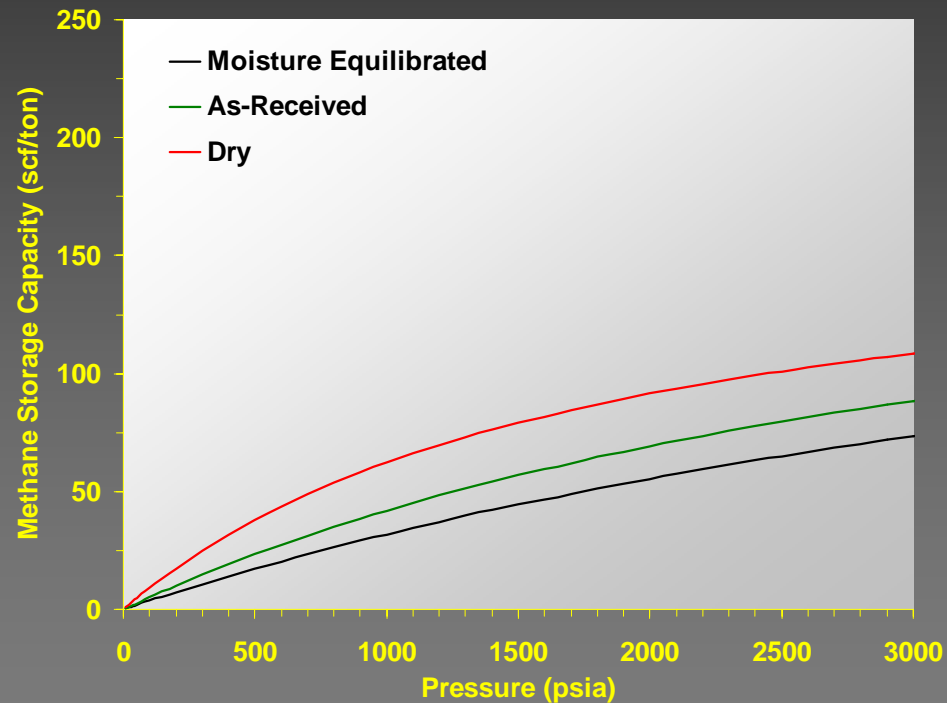
Shale Methane Isotherm Results – 2

Type III Kerogen, 3.54% TOC
Reservoir Temperature of 140°F

Type IV Kerogen, 4.39% TOC
Reservoir Temperature of 90°F

Shale Methane Isotherm Summary

Reservoir Temperature = 75°F, Arbitrary Reservoir Pressure = 2,500 psia	
Type I Kerogen, 14.22% TOC	Methane Gas Storage Capacity, scf/ton
Moisture Equilibrated (2.48 wt. % Moisture)	115.06
As-Received (1.56 wt. % Moisture)	129.91
Dry (0.065 wt. % Moisture)	217.65

Reservoir Temperature = 140°F, Arbitrary Reservoir Pressure = 2,500 psia	
Type II Kerogen, 7.73% TOC	Methane Gas Storage Capacity, scf/ton
Moisture Equilibrated (3.24 wt. % Moisture)	64.99
As-Received (1.01 wt. % Moisture)	79.57
Dry (0.00 wt. % Moisture)	100.92

Reservoir Temperature = 140°F, Arbitrary Reservoir Pressure = 2,500 psia	
Type III Kerogen, 3.54% TOC	Methane Gas Storage Capacity, scf/ton
Moisture Equilibrated (2.61 wt. % Moisture)	26.50
As-Received (0.79 wt. % Moisture)	38.23
Dry (0.064 wt. % Moisture)	76.09

Reservoir Temperature = 90°F, Arbitrary Reservoir Pressure = 2,500 psia	
Type IV Kerogen, 5.39% TOC	Methane Gas Storage Capacity, scf/ton
Moisture Equilibrated (.78 wt. % Moisture)	73.52
As-Received (0.39 wt. % Moisture)	88.76
Dry (0..013 wt. % Moisture)	102.58

Implications of Shale Isotherms at Various Moisture Contents

- The of porosity (meso-micro) within shale is either predominately located in the organic matter fraction and/or the water saturation within the inorganic fraction also has an impact on adsorption potential, indicating adsorbed gas storage mechanisms in shales are not well understood (ex: Type I kerogen, R_o = 0.58, 100% TOC basis adsorbed storage = 913 scf/ton)

- **Sample handling and preservation is critical**

Free Gas Storage Capacity

$$G_{cf} = 32.0368 \frac{\phi\left(1 - S_w\right)}{\rho B_g}$$

- Significance
  - Shale and Tight Gas reservoirs often contain substantial amounts of free gas stored by compression within available porosity.
  - Necessary for indirect gas content estimates, GIP estimates and core-geophysical log calibration
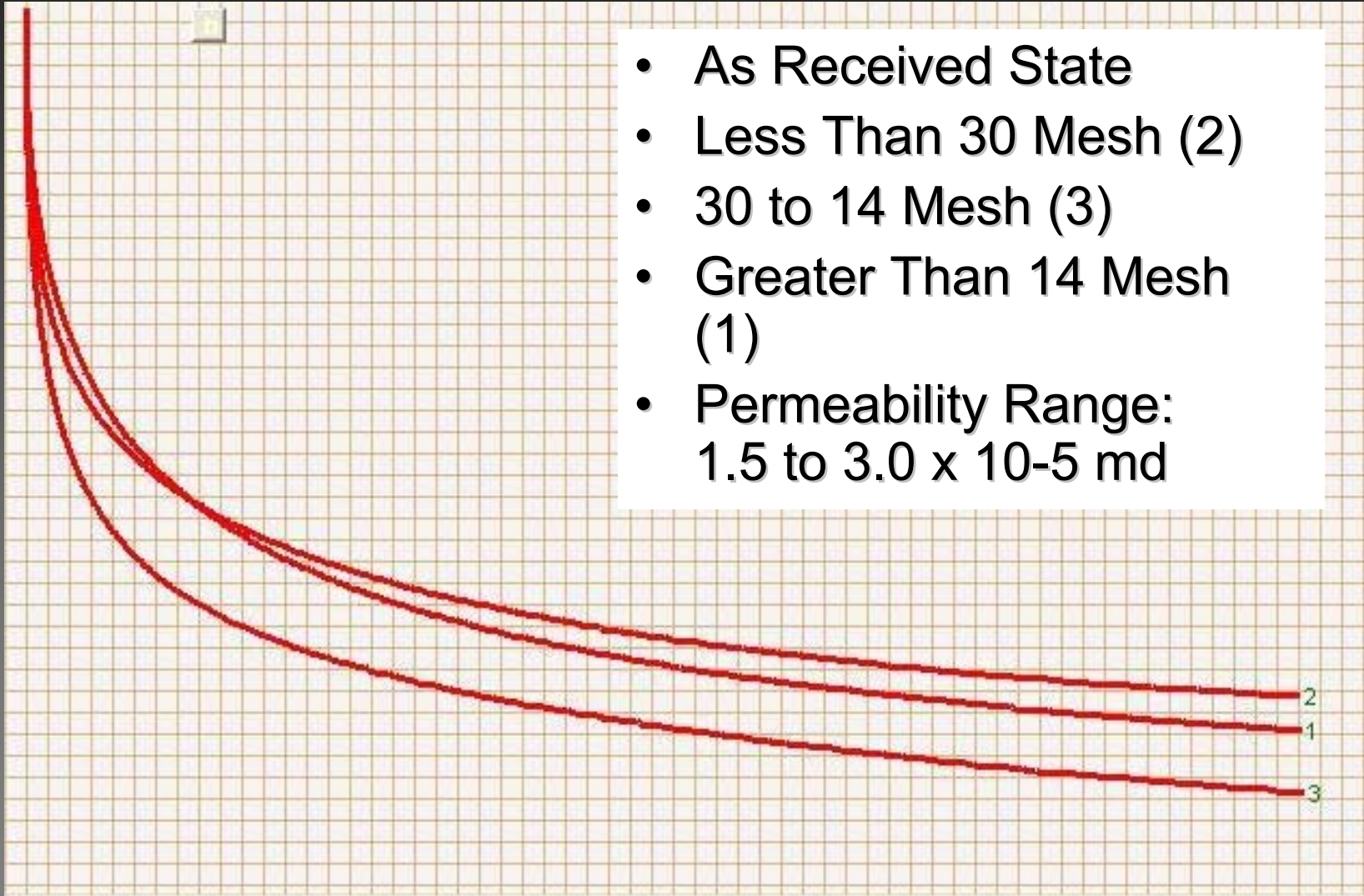 - Provides information needed to delineate between the adsorbed and free gas content

Shale Free Gas Volume Determination

To quantify the potential free gas storage capacity requires additional specialized Dean Stark analysis on crushed rock (Luffel, SPE 21297, 1992).
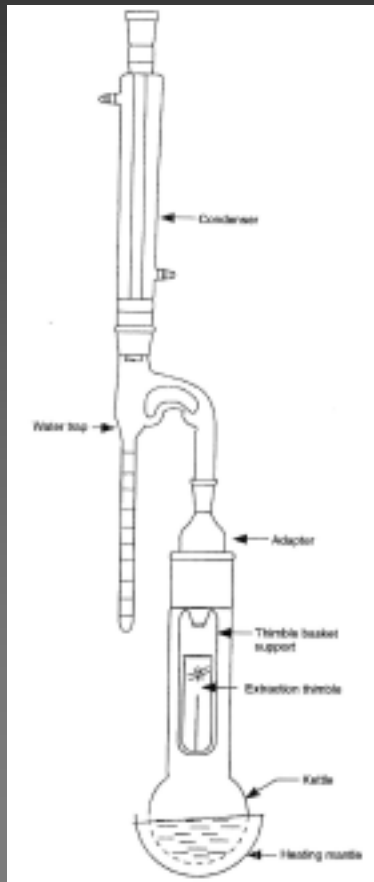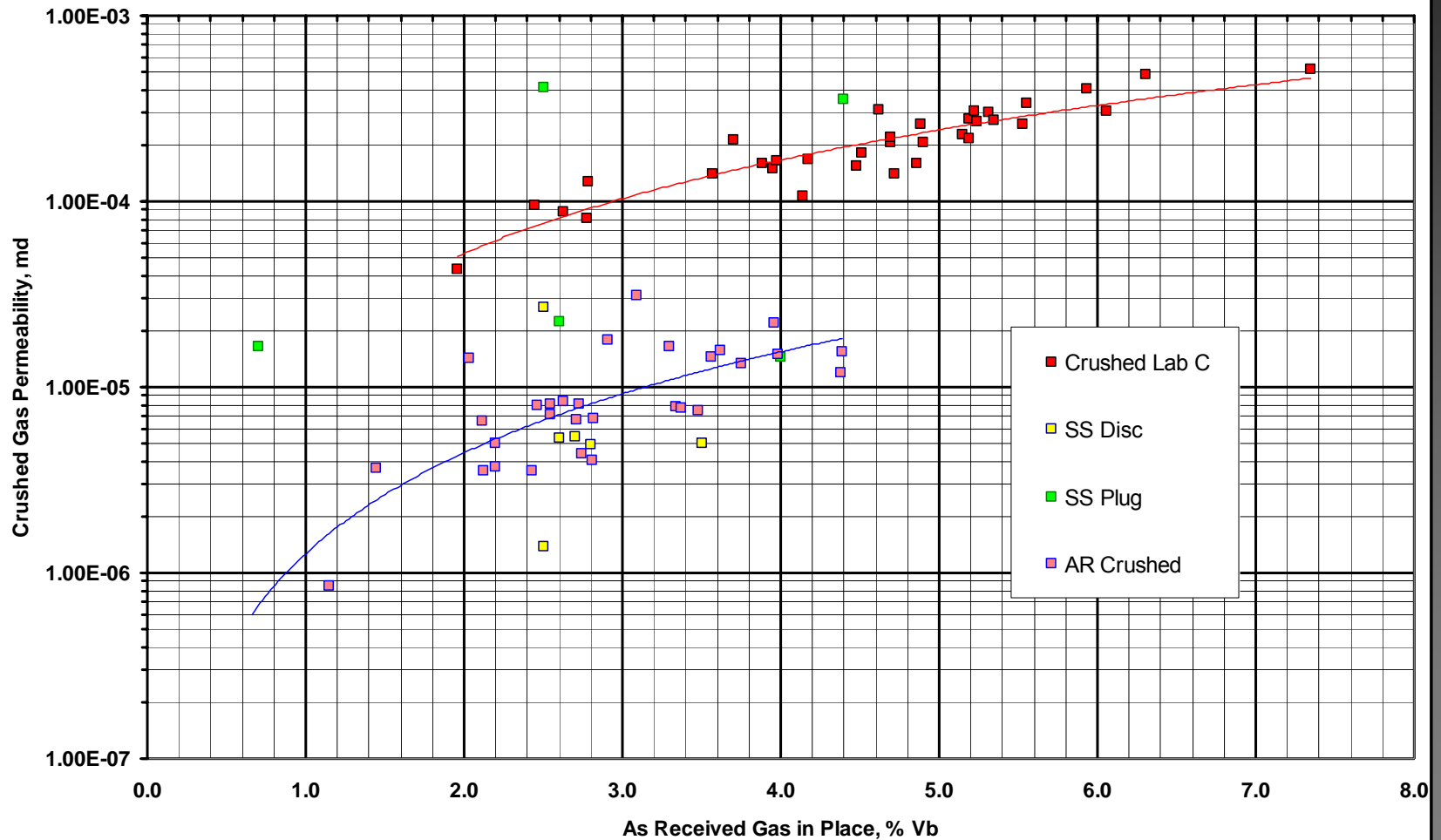

Parameter	Units	A	B	C
Porosity	%	**5.39**	**4.70**	**6.27**
Water saturation	%	**53.4**	**18.0**	**39.5**
Bulk density	g/cm^3	**2.533**	**2.674**	**2.447**
Grain Density	g/cm^3	**2.644**	**2.796**	**2.580**
Mobil Oil Saturation	%	*3.3*	*2.6*	*8.4*
Gas filled porosity	%	*2.33*	*3.73*	*3.27*
Matrix Permeability	*md*	*1.21 (10^{-6})*	*1.65 (10^{-8})*	*2.06 (10^{-7})*

As Received Pressure Decay Gas Permeability vs. Crushed Shale Fraction Size

- As Received State
- Less Than 30 Mesh (2)
- 30 to 14 Mesh (3)
- Greater Than 14 Mesh (1)
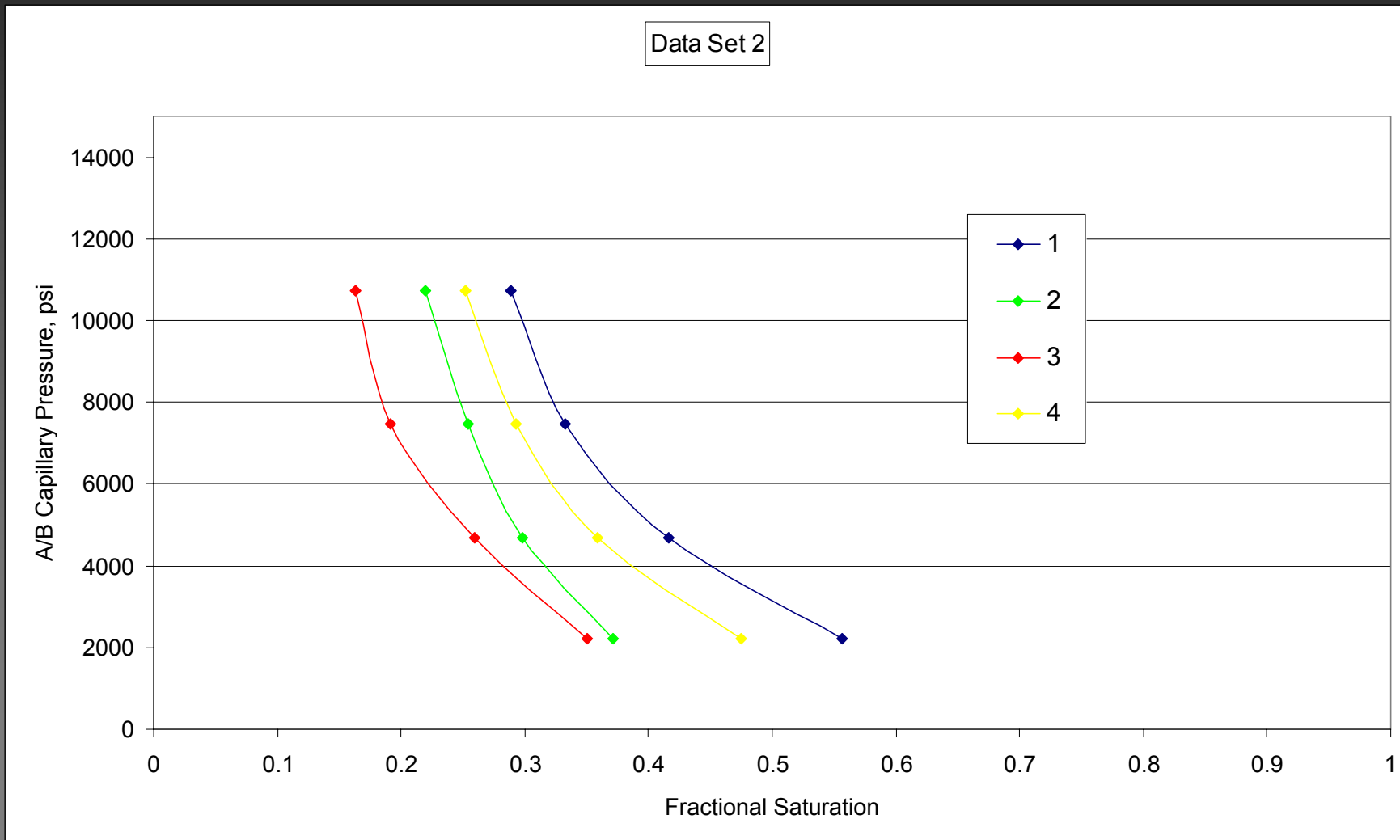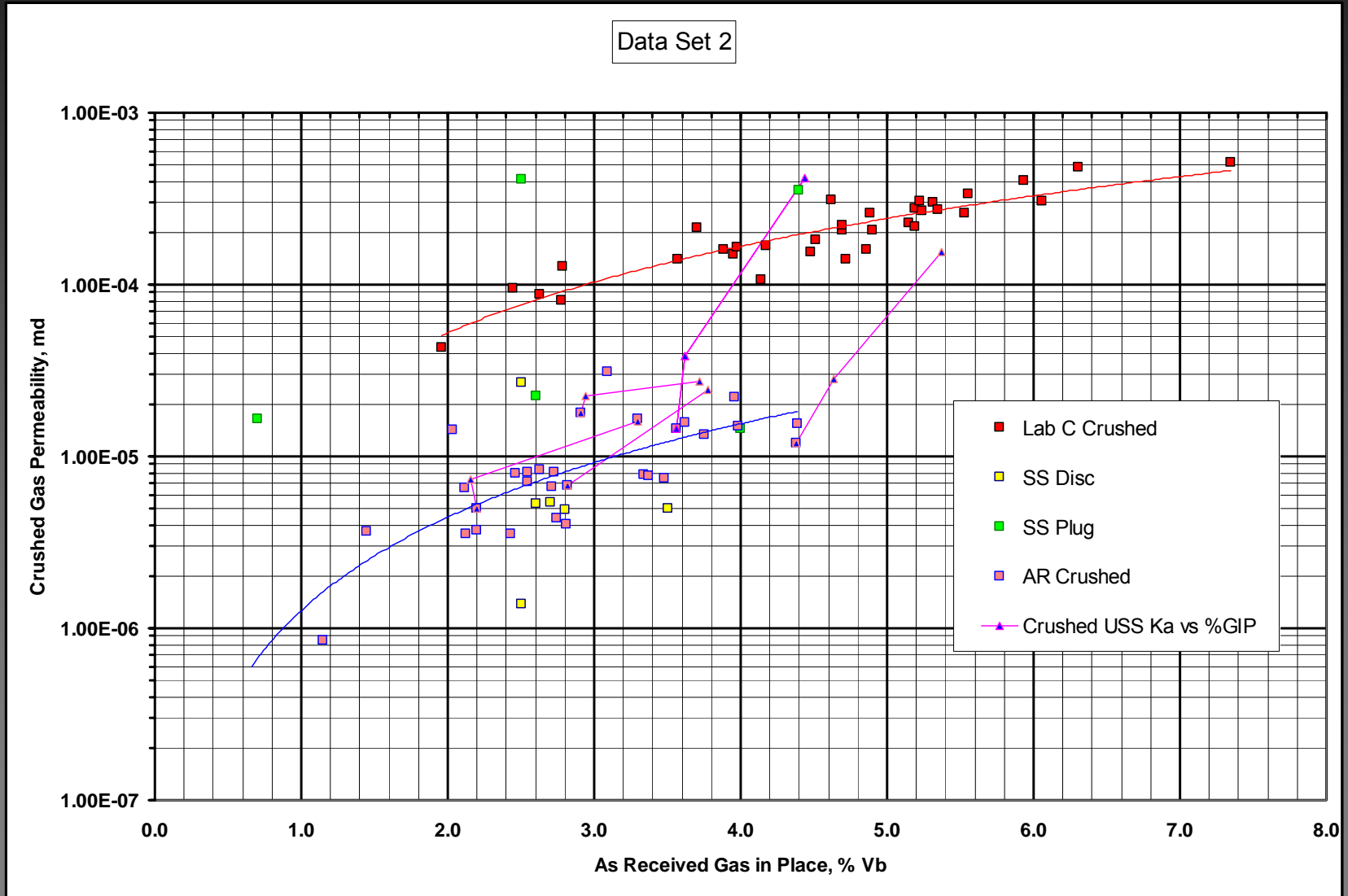- Permeability Range: 1.5 to 3.0 x 10-5 md

PERMEABILITY vs. AR GAS IN PLACE

As Received Crushed Shale Vapor Desorption

Vapor Desorption Effects on K_g and S_{wi}

Implications of Vapor Desorption on S_{wi}, Free Gas Volumes, and Matrix Permeability

- Shale moisture content is very sensitive to environmental conditions and is susceptible to imbibition or desiccation during sample handling and processing

- Performing pressure decay permeability measurements on sample splits with a broad range of particle sizes is less detrimental to the results than spending the additional time to screen for a more discrete particle size interval.

- Erroneous S_{wi} measurements can substantially impact estimated shale free gas volumes

- Sample preservation and handling are critical

Conclusions

- The adsorbed gas storage mechanisms in shale reservoirs are very complex and potentially a function of absolute matrix properties rather than the organic fraction alone

- Proper sample preservation and strict handling protocols are critical to obtain data that accurately represents in-situ reservoir properties

- Rigorous efforts should be made to determine if indeed the mere act of core acquisition is in itself altering the in-situ reservoir properties. As a proactive measure, SOP's should include removal of the core rind before any analyses

Thanks for Your Participation!

For additional information, please contact:

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