High pressure methane adsorption analyses for coal samples of the Matanuska Valley coal-bed methane AK 94-CBM-1 hole as follows:

Seam No. 1, Seam No. 6, Seam No. 9, and Seam No. 13.



Received 2 January 1998.

Total of 24 pages in report.

High Pressure Methane Adsorption Analyses

For Samples:

Seam 1 Canister 1,2

Seam 6, Canister 11-14

Seam 9 Canister 20

Seam 13 Canister 34,35,37

For Dan Seamount, UNOCAL PETROLEUM LTD.

Results of Adsorption Analyses

The adsorption analyses of the four provided samples are attached in both PSI and MPa units. No difficulties were encountered in any of the analyses although equilibrium times were long which undoubtedly reflected the high equilibrium moisture content of the samples. The dry ash free basis was determined utilizing the ash content we determined from the samples used in the analyses (rather then the ash content provided by Unocal).

The enclosed DOS formatted 3.5 inch disk includes the reports for each sample for your convience. The reports are in EXCEL v.7 format.

Please refer to Appendix 1 for an overview of the analyses technique.

If you have questions regarding your isotherms do not hesitate to contact me.

Table 1. Summary of EQ moisture and Langmuir volumes of the analyzed samples.

SAMPLE	EQ MOISTURE	ASH DRY BASIS	LANG. VOL cc/g
Seam 1 Canister 1,2	10,66	12.86%	11.0
Seam 6, Canister 11-14	8.42	23.26%	14.9
Seam 9 Canister 20	7.71%	15.04%	15.6
Seam 13 Canister	9.48	4.04%	13.8
34,35,37			

Sample I.D.:

Seam 1 Cannister Moisture Content (EQ) %:

1 & 2

10.66

Isotherm Temperature :

30°C

Ash Content, (dry basis), %:

12.86

Helium Density g/cc

1.424

PRESSURE (PSI)	ADSORBED METHANE (ft3/ton)	P/V
132	32.1	· 4.12
312	62.1	5.02
482	84.5	5.71
623	100.2	6.22
770	112.6	6.83
913	125.6	7.26
1049	135.8	7.73
1162	143.8	8.09
1295	152.5	8.49

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

132	42.0	3.15
31/2	81.2	3.84
482	110.5	4.36
623	131.0	4.76
770	147.2	5.23
913	164.3	5.56
1049	177.5	5.91
1162	188.0	6.18
1295	199.4	6.49

Saturated Monolayer Volume (ft³/ton @ STP, daf):

354

Correlation Coefficient:

0.9843

Langmuir Pressure (PSI):

^{*} Std error of Langmuir volume = +/- 2%

Sample I.D. :

Seam 1 Cannister Moisture Content (EQ) %:

10.66

1 & 2

Isotherm Temperature :

30°C

Ash Content, (dry basis), %

12.86

Helium Density g/cc

1.424

PRESSURE (MPa)	ADSORBED	P/V	
	METHANE (cc/g)		
0.913	1.00	0.915	
2.152	1.93	1.115	
3.324	2.62	1.267	
4.296	3.11	1.381	
5.306	3.50	1.517	
6.293	3.90	1.613	
7,232	4.22	1.715	
8.015	4.46	1.795	
8.927	4.74	1.885	

DATA CORRECTED FOR ASH AND MOISTURE CONTENT		
0.913	1.30	0.700
2.152	2.52	0.853
3.324	3.43	0.969
4.296	4.07	1,056
5.306	4.57	1.160
6.293	5.10	1.234
7.232	5.51	1.312
8.015	5.84	1.373
8.927	6.19	1.441

Saturated Monolayer Volume (cc/g @ STP, daf):

11.0

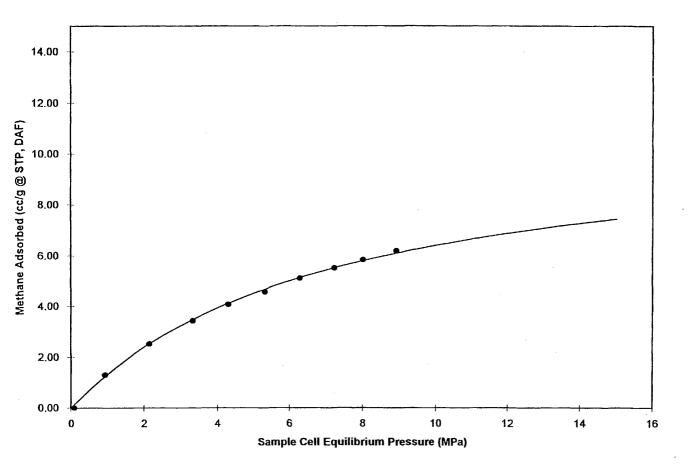
Correlation Coefficient:

0.9843

Langmuir Pressure (MPa):

^{*} Std error of Langrnuir volume = +/- 2%

Seam 1, Cannister 1 and 2



Sample I.D. :

Seam 6, Cann. 11- Moisture Content (EQ) %:

8.42

14

Isotherm Temperature :

30°C

Ash Content, (dry basis), %

23.26

Helium Density g/cc

1.503

PRESSURE (MPa)	ADSORBED	P/V
	METHANE (cc/g)	
0.876	1.08	0.812
2.044	2.04	1,004
3.242	2.76	1.173
4.240	3,35	1,265
5.211	3.81	1,366
6.179	4.22	1.463
7.127	4.66	1.530
7.858	4.94	1.592
8.576	5.24	1.636
9.216	5.62	1.641

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

0.876	1.58	0.555
2.044	2.98	0.686
3.242	4.05	0.801
4.240	4.91	0.864
5.211	5.58	0.933
6.179	6.18	1.000
7.127	6.82	1.045
7.858	7.23	1.087
8.576	7.67	1.118
9.216	8.22	1.121

Saturated Monolayer Volume (cc/g @ STP, daf):

14.9

Correlation Coefficient:

0.9707

Langmuir Pressure (MPa):

^{*} Std error of Langmuir volume = +/- 2%

Sample I.D.:

Seam 6, Cann. 11- Moisture Content (EQ) %:

14

8,42

Isotherm Temperature:

30°C

Ash Content, (dry basis), %:

23.26

Helium Density g/cc

1.503

PRESSURE (PSI)	ADSORBED METHANE (ft3/ton)	P/V
127	34.7	3.66
296	65.6	4.52
470	89.0	5,28
615	107.9	5.70
756	122.8	6.15
896	136.0	6.59
1034	150.0	6.89
1140	159.0	7.17
1244	168.8	7.37
1337	180.8	7.39

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

127	50.9	2.50
296	95.9	3.09
470	130,3	3.61
615	158.0	3.89
756	179.8	4,20 4,50
896	199.0	
1034	219.6	4.71
1140	232.7	4.90
1244	247.0	5,04
1337	264.7	5,05

Saturated Monolayer Volume (ft³/ton @ STP, daf):

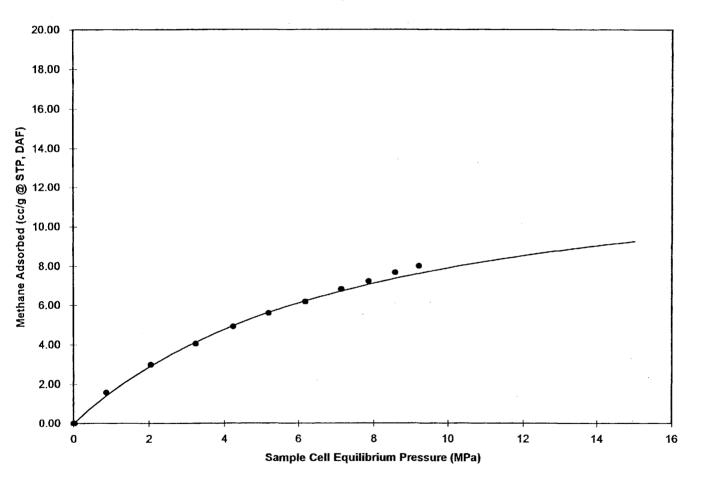
Correlation Coefficient:

479 0.9707

Langmuir Pressure (PSI):

^{*} Std error of Langmuir volume = +/- 2%

Seam 6, Cannisters 11-14



Sample I.D.:

Seam 9, Cann. 20- Moisture Content (EQ) %:

7.71

22

Isotherm Temperature :

30*C

Ash Content, (dry basis), %

15.04

Helium Density g/cc

1.399

PRESSURE (MPa)	ADSORBED	P/V
	METHANE (cc/g)	
0:698	1.25	0.556
1.847	2.48	0.745
3.140	3.50	0.897
3.559	3.79	0.938
4.560	4.42	1.031
5.241	4.89	1,072
6.324	5.62	1,126
7.240	6.19	1.170
8.084	6.74	1.199

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

0.698	1.62	0.429
1.847	3.21	0.576
3.140	4.53	0.693
3.559	4.91	0.725
4.560	5.72	0.797
5.241	6.33	0.828
6.324	7.27	0.870
7.240	. 8.01	0.904
8.084	8.73	0.926

Saturated Monolayer Volume (cc/g @ STP, daf):

15.6

Correlation Coefficient:

0.9341

Langmuir Pressure (MPa):

^{*} Std error of Langmuir volume = +/- 2%

Sample I.D.:

Seam 9, Cann. 20- Moisture Content (EQ) %:

22 30°C

Isotherm Temperature :

Ash Content, (dry basis), %:

7.71 15.04

Helium Density g/cc

1.399

PRESSURE (PSI)	ADSORBED METHANE	P/V
	(ft3/ton)	
101	40.4	2.50
268	79.8	3,36
455	112.7	4.04
516	122.2	4.23
661	142.4	4.65
760	157.5	4.83
917	180.9	5.07
1050	199.3	5.27
1172	217.1	5.40

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

101	52.3	1.93
268	103.3	2.59
455	145.9	3.12
516	158.2	3.26
661	184.3	3.59
760	203.8	3.73
917	234.1	3.92
1050	258.0	4.07
1172	281.0	4.17

Saturated Monolayer Volume (ft³/ton @ STP, daf):

501

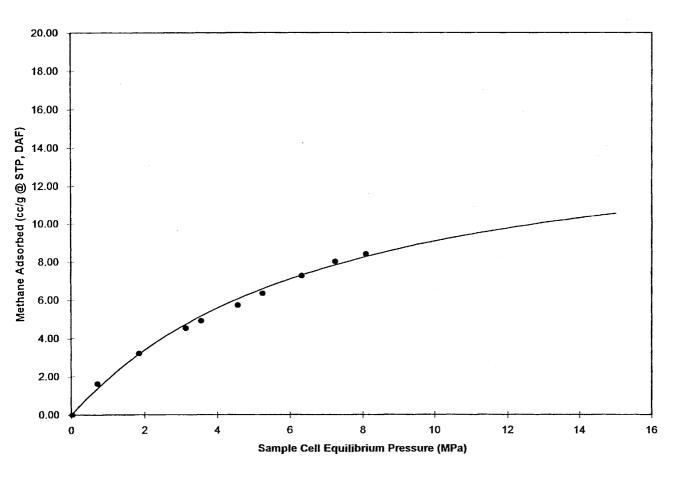
Correlation Coefficient:

0.9341

Langmuir Pressure (PSI):

^{*} Std error of Langmuir volume = +/- 2%

Seam 9, Cannisters 20-22



Sample I.D.:

Seam 13, Cann. Moisture Content (EQ) %:

9.48

34,35,37

Isotherm Temperature :

30°C

Ash Content, (dry basis), %

4.04

Helium Density g/cc

1.370

PRESSURE (MPa)	ADSORBED	P/V
	METHANE (cc/g)	
0.848	1.29	0.657
2.065	2.58	0.799
3,240	3,49	0.929
4.292	4.13	1.040
5.296	4.65	1.140
6,264	5.36	1.168
7.194	5.90	1,219
8.107	6.23	1.302
8.738	6.53	1.338

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

0.848	1.49	0.568
2.065	2.99	0,691
3.240	4.03	0.803
4.292	4.77	0.899
5.296	5.37	0.986
6.264	6.20	1.010
7.194	6.82	1.054
8.107	7.20	1.126
8.738	7.55	1.157

Saturated Monolayer Volume (cc/g @ STP, daf):

13.8

Correlation Coefficient:

0.9762

Langmuir Pressure (MPa):

^{*} Std error of Langmuir volume = +/- 2%

Sample I.D.:

Seam 13, Cann.

Moisture Content (EQ) %:

9.48

34,35,37

Isotherm Temperature :

30°C

Ash Content, (dry basis), %:

4.04

Helium Density g/cc

1.370

PRESSURE (PSI)	ADSORBED METHANE (ft3/ton)	P/V
123	41.6	2.96
300	83,2	3.60
470	112.3	4.18
622	132.9	4.68
768	149.6	5,13
909	172.7	5.26
1043	190.0	5.49
1176	200.6	5.86
1267	210.4	6.03

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

123	48.0	2.56
300	96.2	3.11
470	129.9	3.62
622	153.6	4.05
768	173.0	4.44
909	199.7	4.55
1043	219.7	4.75
1176	231.9	5.07
1267	243.2	5.21

Saturated Monolayer Volume (ft³/ton @ STP, daf):

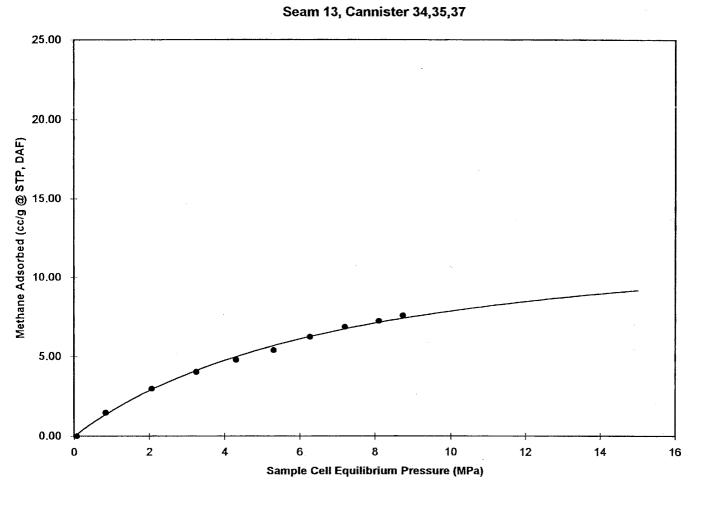
445

Correlation Coefficient:

0.9762

Langmuir Pressure (PSI):

^{*} Std error of Langmuir volume = +/- 2%



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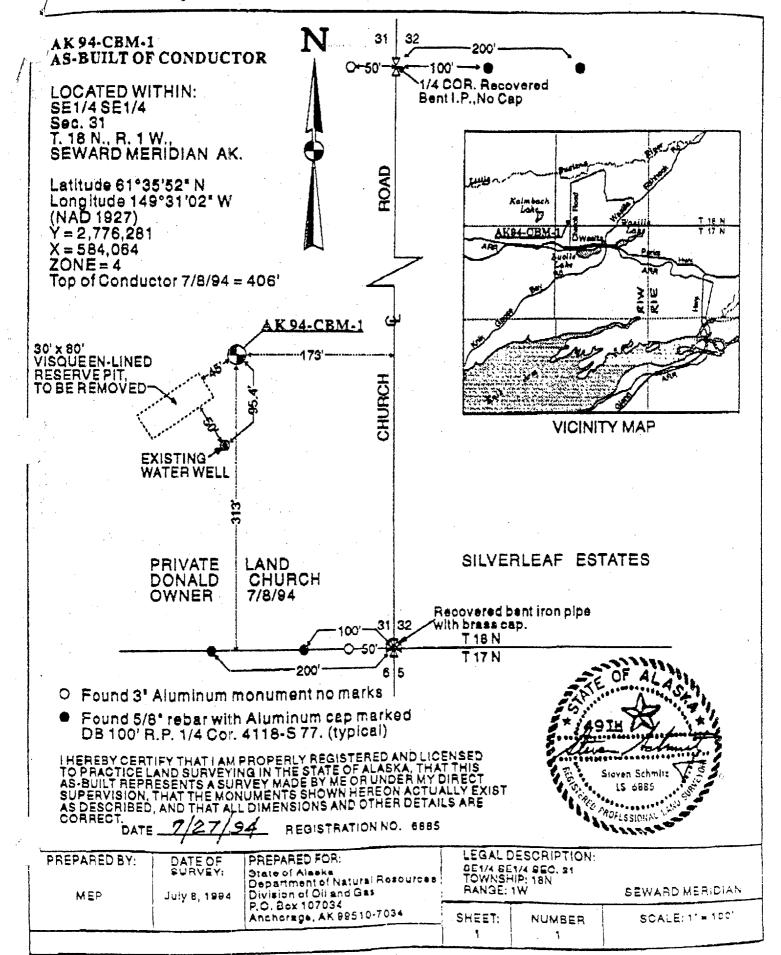
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Submit in duplicate



Well AK-94-CBM #1 COAL METHANE ADSORPTION ISOTHERM Sec 31 T18N-R1W

Sample I.D.:

Seam 1 Cannister 1 & 2

Moisture Content (EQ) %:

10.66

Isotherm Temperature 30°C

Ash Content, (dry basis), %:

12.86

Depth 522' to 524'

Helium Density g/cc

1.424064

Gas Yield 63 scf/ton

PRESSURE (PSI)

ADSORBED METHANE (ft3/ton)

P/V

132.4028729	32.12770473	4.121143
312.0592965	62.10643714	5.024589
482.1754564	84.50242913	5.706054
623.0181866	100.1707536	6.219562
769.5389164	112.5997857	6.834284
912.7438045	125.6378853	7.264877
1048.858256	135.7711957	7.72519
1162.494647	143.7589019	8.086419
1294.723873	152.5172002	8.489035

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

132.4028729	42.00798213	3,15185
312.0592965	81.2061155	3.842805
482.1754564	110.4895778	4.36399
623.0181866	130.9764038	4.756721
769.5389164	147.2277533	5.22686
912.7438045	164.2754776	5.556178
1048.858256	177.525099	5.908225
1162.494647	187.9692755	6.184493
1294.723873	199.4210253	6.492414

Saturated Monolayer Volume (ft3/ton @ STP, daf): 353.6433 Correlation Coefficient: 0.984256

Langmuir Pressure (PSI):

^{*} Std error of Langmuir volume = +/- 2%

Well AK-94-CBM #1 COAL METHANE ADSORPTION ISOTHERM Sec 31 T18N-R1W

Sample I.D.:

Seam 6, Cann. 11-14

Moisture Content (EQ) %:

8.42

Isotherm Temperature 30°C

PRESSURE (PSI)

Ash Content, (dry basis), %:

23.26

Depth 893' to 897'

Helium Density g/cc

1.503062

Gas Yield 177 scf/ton

ADSORBED METHANE (ft3/ton)

P/V

127.0870967	34.74673771	3.657526
296.4365408	65.55224685	4.522142
470.2341406	89.02788105	5,281875
614.8963432	107.9321596	5,697063
755.7365649	122.8141193	6.153499
896.2449136	135.9606702	6.591942
1033.662084	150.0053803	6,890833
1139.675904	158.9678649	7.169222
1243.778986	168.7611434	7.370055
1336.683134	180.8281534	7.392008

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

127.0870967	50.85880813	2.498822
296.4365408	95.94883906	3.089527
470.2341406	130.3101303	3.608577
614.8963432	157.9803273	3.892234
755.7365649	179.7630552	4.204071
896.2449136	199.0056647	4.503615
1033.662084	219.5629102	4.707817
1139.675904	232.6813011	4.898012
1243.778986	247.0157251	5.035222
1336.683134	264.6782104	5.05022

Saturated Monolayer Volume (ft3/ton @ STP, daf): 452.5862 Correlation Coefficient: 0.989984 Langmuir Pressure (PSI): 1129,701

^{*} Std error of Langmuir volume = +/- 2%

Well AK-94-CBM #1 COAL METHANE ADSORPTION ISOTHERM Sec 31 T18N-R1W

Sample I.D.:

Seam 9, Cann. 20-22

Moisture Content (EQ) %:

7.71

Isotherm Temperature:

30ºC

Ash Content, (dry basis), %:

15.04

Depth 1064' to 1068'

Helium Density g/cc

1.398678

Gas Yield 163 scf/ton

PRESSURE (PSI)

ADSORBED METHANE (ft3/ton)

P/V

2.504335 3.357149 4.040025 4.225113 4.645233 4.827644 5.070976 5.26886 5.40073

101.1978395	40.40906229	
267.8608054	79.78816926	
455.3822906	112.717681 7	
516.2608189	122.1886497	
661.3188627	142.3650711	
760.1130141	157.450101	
917.2264845	180.8776874	
1050.060418	199.2955444	
1172.496535	217.0996544	

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

101.1978395	52.30946574	1.934599
267.8608054	103.285656	2.593398
455.3822906	145.9128566	3.12092
516.2608189	158.1730093	3.2639
661.3188627	184.2913542	3.588442
760.1130141	203.8189009	3.729355
917.2264845	234.1458737	3.917329
1050.060418	257.9877598	4.070195
1172.496535	281.0351514	4.172064

Saturated Monolayer Volume (ft3/ton @ STP, daf): 501.0922 Correlation Coefficient: 0.934066 Langmuir Pressure (PSI): 1036.264

^{*} Std error of Langmuir volume = +/- 2%

Well AK-94-CBM #1 COAL METHANE ADSORPTION ISOTHERM Sec 31 T18N-R1W

Sample I.D.:

Seam 13, Cann. 34,35,37

Moisture Content (EQ) %:

9.48

Isotherm Temperature:

30ºC

Ash Content, (dry basis), %:

Helium Density g/cc

4.04

Depth 1235' to 1240'

1.36991

Gas Yield 245 scf/ton

PRESSURE (PSI)

ADSORBED METHANE (ft3/ton)

P/V

122.9881164	41.55059346
299.5163541	83.23413779
469.8892224	112.3307074
622.4803223	132.8733176
768.1625492	149.6419705
908.526128	172.6891883
1043.419418	190.0310849
1175.890463	200.5791101
1267.383353	210.350899

3.59848 4.183088 4.684765 5.133336 5.261048 5.490783 5.862477

6.025091

2.959961

DATA CORRECTED FOR ASH AND MOISTURE CONTENT

531		245
122.9881164	48.04647717	2.559774
299.5163541	96.24669032	3.111965
469.8892224	129.8921223	3.617534
622.4803223	153.646297	4.051385
768.1625492	173.0365061	4.439309
908.526128	199.6868505	4.549754
1043.419418	219.7399224	4.748429
1175.890463	231.9369914	5.06987
1267.383353	243.2364697	5.210499
3000	445	

Saturated Monolayer Volume (ft3/ton @ STP, daf):

Correlation Coefficient: 444.9592 Langmuir Pressure (PSI): 0.976173

^{*} Std error of Langmuir volume = +/- 2%

APPENDIX 1

Your Isotherms

To help you interpret you data I have prepared a few short paragraphs to tell you how your data was obtained. If you have any questions please do not hesitate to contact us.

Obtaining and interpreting isotherm data and Langmuir Isotherms

Your high-pressure methane, carbon dioxide or mixed gas adsorption analyses were performed using a high-pressure volumetric adsorption technique similar to that described by Mavor et al. (1990). Your isotherms were measured on a custom made apparatus modeled after an apparatus designed and built at CSIRO Lucus Heights, Australia. The apparatus is based on Boyles Law. Simply, a known volume of gas within in a reference cell is used to dose a sample cell containing your sample. The amount of gas adsorbed, using the real gas law, in the sample cell is then determined based on change in pressure in the sample cell. Normally 100 g of sample is utilized in such analyses. Tests show that reproducible results can be obtained on samples as small as 25 g but the larger samples yield better quality data. Our instrument has four sample cells.

The pressures in the reference and four samples cells are measured using pressure transducers that are interfaced to a computer equipped with specialized boards and software for this purpose. The computer monitors the transducers and determines when equilibrium is reached as well as controls valves and switches for dosing and purging the references and sample cells. Following dosing of the sample cell with a known volume of gas, the pressure in the sample cell is monitored. As gas is adsorbed by the sample the pressure drops until equilibrium is reached; that is no more gas can be adsorbed by the samples at that particular specified pressure. Critical to obtaining quality isotherms is deciding when the equilibrium is reached. In our instrument we set a stringent testequilibrium is reached only when the pressure in the cell does not change over a designated period of time. When equilibrium is reached the sample is dosed at the next highest pressure. We normally collect 12 separate pressure points selected such that the best Langmuir regression can be obtained. We can of course collect data at points selected by the client before hand. The temperate of the references and sample cells is maintained at the exact temperate requested by the client. The temperate is maintained within a tolerance less than 1/10 of one degree centigrade.

For a routine adsorption analyses about five to six days are required once equilibrium moisture has been determined.

How we assure the quality of the isotherms- potential sources of error and recognition of problems

With an apparatus such as ours the only potential error is a change in the characteristics of the pressure transducers, a leak in the system or non-isothermal conditions.

Our pressure transducers were selected for optimum performance within the range of pressures that isotherms are collected. They are not only factory guaranteed we cross-calibrate our transducers periodically to test for drift. The accuracy of our transducers is better than 0.001 MPa.

Prior to running your experiment the reference and sample cells and plumbing are pressure tested for leaks using helium. We do our leak tests at 7 MPa. Because the He molecule is smaller than either methane or carbon dioxide (the gases we normally do adsorption work with) using He assures us of a leak free system. If a leak were to develop during analyses (one never has) it would be readily apparent because the cells would never come to equilibrium at a given pressure (the leak would appear as an infinitely adsorbing material).

Non-isothermal conditions are not a potential problem utilizing our instrument unless a prolonged power failure occurs. Our bath temperature is maintained by a submerged electric heater and a circulating power. The heater is controlled by a temperature controller to a tolerance less than 1/10 of a degree centigrade.

We periodically run a standard sample in our apparatus to confirm that all is well.

Understanding Your Isotherms

The classic theory used to describe the Type I isotherm for microporous materials with small external surface area is based on the Langmuir equation (1916). The Type I isotherm displays a steep increase in adsorption at low relative pressures due to enhanced adsorption caused by the overlapping adsorption potentials between walls of pores whose diameters are commensurate in size with the adsorbate molecule. The Type I isotherm then flattens out into a plateau region at higher relative pressure, which is believed to be due to the completion of a monolayer of adsorbed gas. The micropore volume is then thought to be filled by only a few molecular layers of adsorbate, and further uptake is limited by the dimensions of the micropores.

The Langmuir model assumes that a state of dynamic equilibrium is established between the adsorbate vapor and the adsorbent surface and that adsorption is restricted to a single monolayer (Gregg and Sing, 1982). The adsorbent surface is thought to be composed of a regular array of energetically homogeneous adsorption sites upon which an adsorbed monolayer is assumed to form. The rate of condensation is assumed to be equal to the rate of evaporation from the adsorbed monolayer at a given relative pressure and

constant temperature. The Langmuir equation was developed with these assumptions and takes the following form:

$$\frac{\mathbf{P}}{\mathbf{V}} = \frac{1}{\mathbf{B}\mathbf{V_m}} + \frac{\mathbf{P}}{\mathbf{V_m}}$$

where P is the equilibrium pressure, V is the volume of gas adsorbed at equilibrium, V_m is the volume of adsorbate occupying a monolayer, and B is an empirical constant. A plot of P/V Vs relative pressure should yield a straight line whose slope will yield V_m from which the surface area may be obtained. As shown on your figures a best fit Langmuir isotherm and the data points have been plotted for each sample.

The Langmuir Isotherm can be written:

$$V(P) = \frac{V_{LP}}{P_{L+P}}$$

P = gas pressure

V(P) = predicated amount of gas adsorbed at P

 V_L = Langmuir volume parameter

 $P_L = Langmuir pressure parameter$

The difference between the measured amount of gas adsorbed (V(P)) and that predicted using the Langmuir Equation (Vi(P)) is a measure of error and is given as:

$$Err(P) = Vi(P) - V(P)$$

This error may be positive or negative. The square of the error is always positive and is a measure of the how well the calculated isotherm matches the data. This error can be calculate for each point and summed giving a measure of the overall error:

$$SSE = \sum_{i=1}^{N} Er r_{i}^{2}$$

N= number of measured points.

We express the goodness of fit of the isotherm by calculation the correlation coefficient between the measured points and the calculate points. Our results generally yield correlation's that are better than $r^2 = 0.99$. and standard errors of Lanmuir volumes of \pm 2%. The errors for your samples can be found on the bottom of the data sheets that are included with each sample.

In examining your data you should note that adsorption values are provided for the raw data and corrected for ash content. The ash content will also be corrected for equilibrium moisture content.

When does adsorption not fit a Langmuir Equation?

The Langmuir equation has been found to provide an excellent fit for almost all samples under most reservoir conditions. The Langmuir equation is based on the assumption of monolayer filling of pores. Under conditions of low temperature and very high pressures however multilayer pore filling takes place which results in a deflection (step) in the isotherm which marks the onset of multilayer pore filling. This 'step' occurs at pressures and temperatures that are not realistic in terms of natural reservoirs however since we routinely run our isotherms to pressures in excess of 12 MPa and many clients request low temperatures, the step may be present in your isotherm. If we encounter multilayer pore filling in your samples the regression will have been performed with out including the 'step'; although the data points are included in the plot and data set.

References

Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids. Journal of the American Chemical Society, 38: 2221-2295.

Mavor, M.J., Owen, L.B., and Pratt, T.J., 1990. Measurement and evaluation of isotherm data; Proceedings of 65th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, SPE 20728: 157-170.