Second Annual Conference on Carbon Sequestration May 5-8, 2003

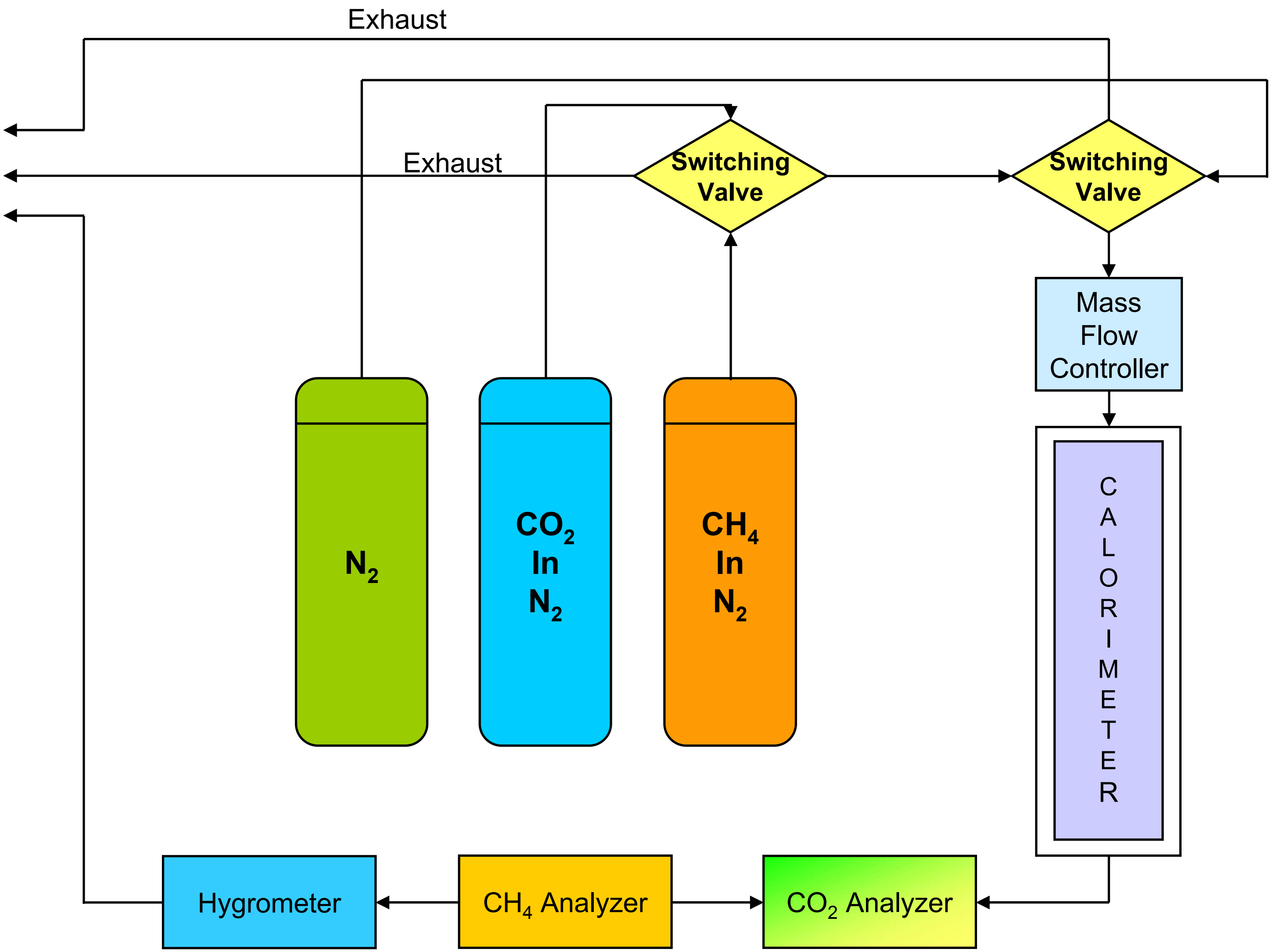
Concurrent Flow Calorimetric, Dew-Point Hygrometric, and Non-dispersive Infrared Analyses of the Production of Methane and/or Sequestration of CO_2 by Coal Under Dynamic (Flow-through) Conditions

Kenneth L. Jones
U.S. Department of Energy
National Energy Technology Laboratory
P.O. Box 10940
Pittsburgh, PA 15236-0940

Description of Coals Studied
("Argonne premium" coals)

Coal Seam	Coal Rank	Analysis	As-received	Dry, mineral matter free
Upper Freeport	medium volatile bituminous	% H_2O	1.13	-
		% Ash	13.03	-
		% volatile matter	27.14	-
		% C	-	88.08
		% H	-	4.84
		% O	-	4.72
Illinois No. 6	high volatile bituminous	% H_2O	7.97	-
		% Ash	14.25	-
		% volatile matter	36.86	-
		% C	-	80.73
		% H	-	5.20
		% O	-	10.11
Wyodak Anderson	subbituminous	% H_2O	28.09	-
		% Ash	6.31	-
		% volatile matter	31.17	-
		% C	-	76.04
		% H	-	5.42
		% O	-	16.90

Process Flow Diagram/Apparatus



Experimental Approach

Study A (comparison of coals)

- Coal sample temperature: 31.1°C
- Inlet gas pressure: 40 PSI
- Volumetric flow rate: 450-500 SCCM

Step	Gas(es) in Contact with Coal	Major Events[a]
Baseline[b]	air	thermal equilibration
1[c]	5 vol. % CO_2 in N_2	• CO_2 sorption/sequestration on *moist* coal • dehydration of *most* of 1 or more coal sites
2[c]	pure N_2	• CO_2 desorption from nearly-dry coal • N_2 sorption • continuation of dehydration
3[c]	5 vol. % CH_4 in N_2	• CH_4 sorption on nearly-dry coal • displacement of pre-sorbed N_2 • continuation of dehydration
4[c]	5 vol. % CO_2 in N_2	• CO_2 sorption/sequestration on nearly-dry coal • CH_4 desorption/production • continuation of dehydration
5[c]	pure N_2	• desorption of *physisorbed* CO_2 (*chemisorbed* CO_2 remains on coal) • N_2 sorption • "Completion" of dehydration

[a]Each step also involves the reduction or increase of viscous friction created by the flow of gas(es) between the coal particles.
[b]Stagnant conditions
[c]Gas(es) flowing ("dynamic" conditions)

Experimental Approach

Study B (variation of gases used to dehydrate Wyodak subbituminous coal)

- Coal sample temperature: 31.1°C
- Inlet gas pressure: 40 PSI
- Volumetric flow rate: 450-500 SCCM

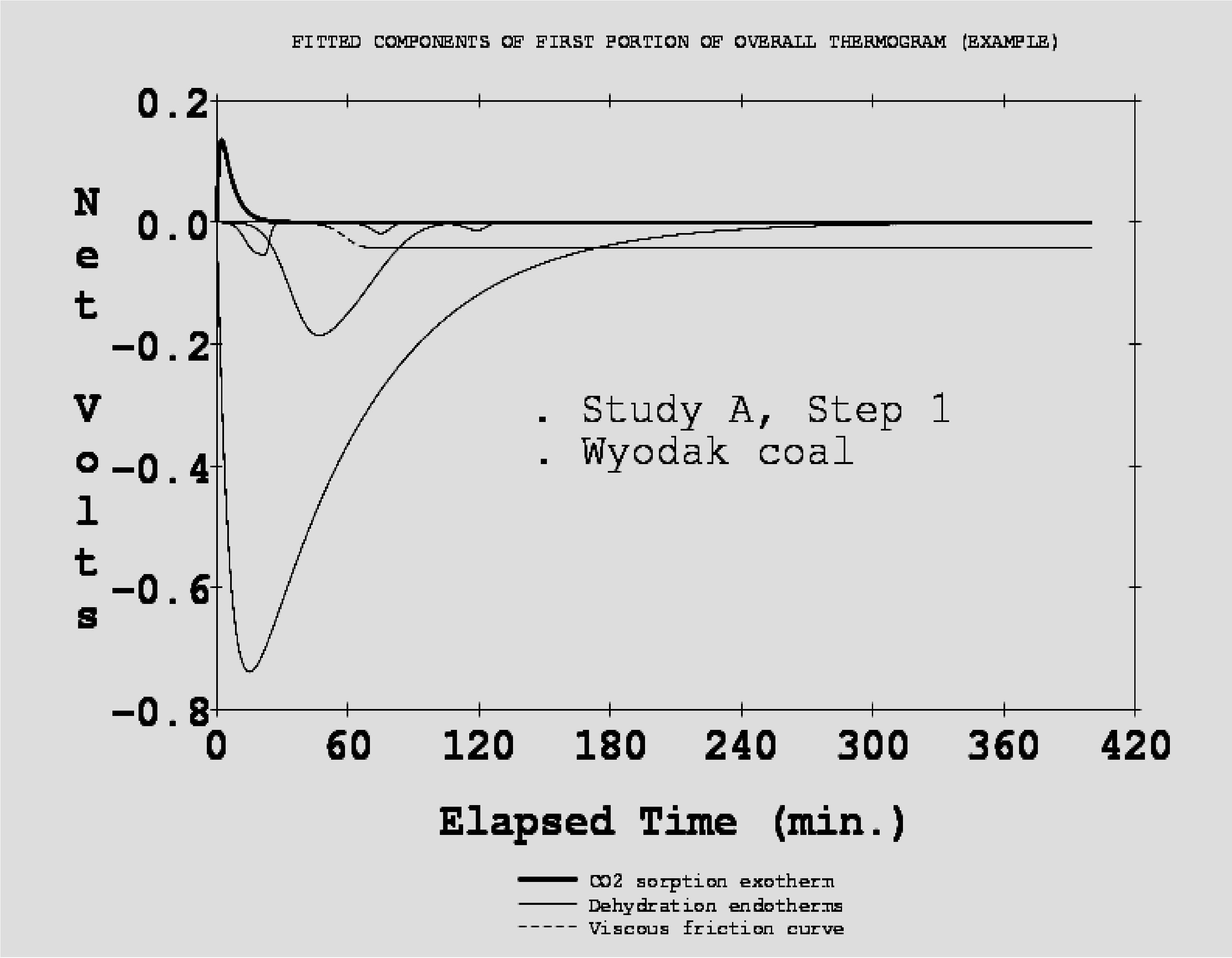
Step	Gas(es) in Contact with Coal	Major Events[a]
Baseline[b]	air	thermal equilibration
1[c]	5 vol. % CO_2 in N_2 *or* 5 vols. % CH_4 in N_2 *or* pure N_2	• sorption of CO_2 or CH_4 or N_2 on *moist* coal • dehydration of *most* of 1 or more coal sites
2[c]	pure N_2	• desorption of CO_2 or CH_4 from nearly-dry coal • N_2 sorption • continuation of dehydration
3[c]	5 vol. % CH_4 in N_2	• CH_4 sorption on nearly-dry coal • displacement of pre-sorbed N_2 • continuation of dehydration
4[c]	5 vol. % CO_2 in N_2	• CO_2 sorption/sequestration on *nearly-dry* coal • CH_4 desorption/production • continuation of dehydration
5[c]	pure N_2	• desorption of *physisorbed* CO_2 (*chemisorbed* CO_2 remains on coal) • N_2 sorption • "Completion" of dehydration

[a]Each step also involves the reduction or increase of viscous friction created by the flow of gas(es) between the coal particles.

[b]Stagnant conditions

[c]Gas(es) flowing ("dynamic" conditions)

Mathematical Signal Resolution



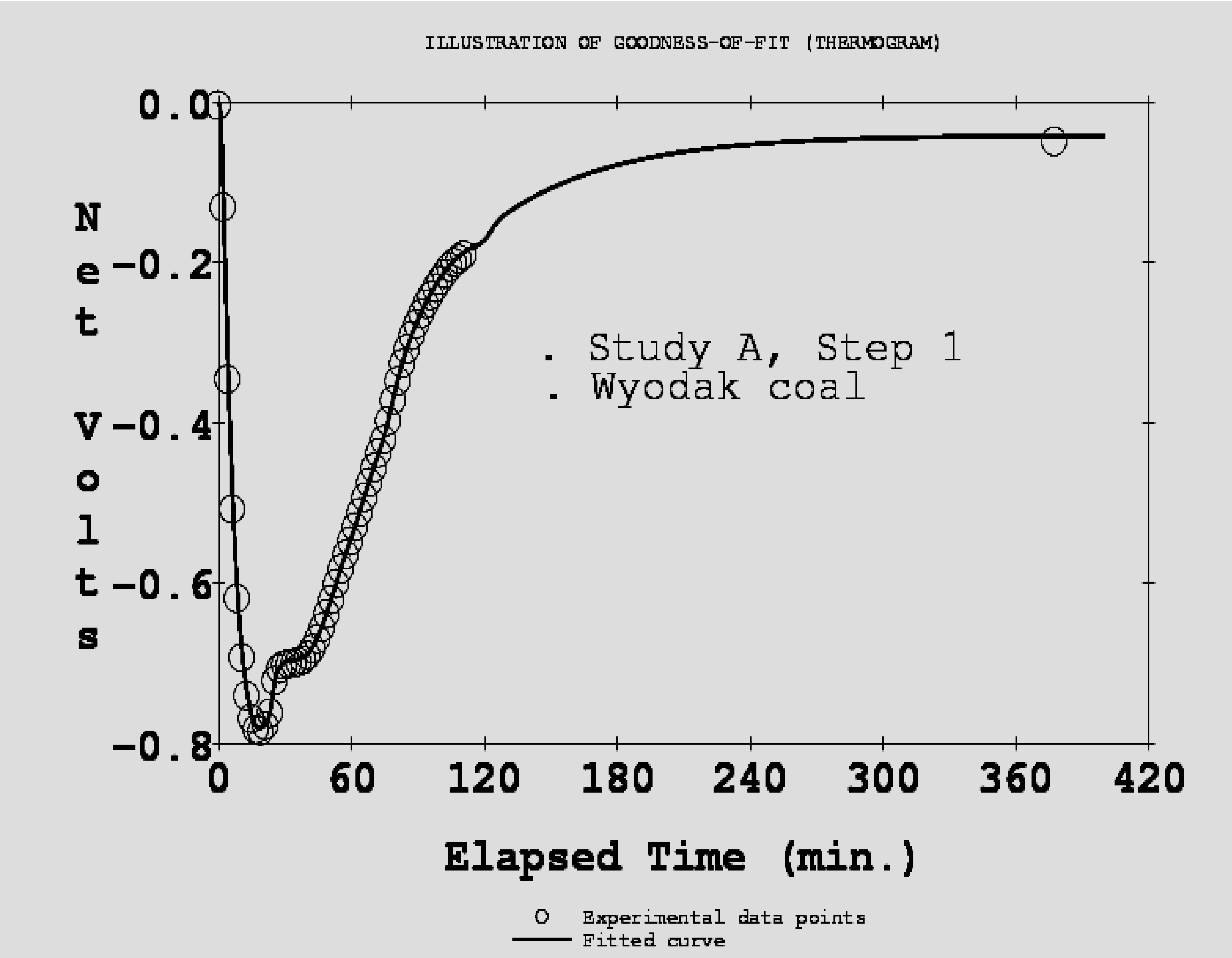
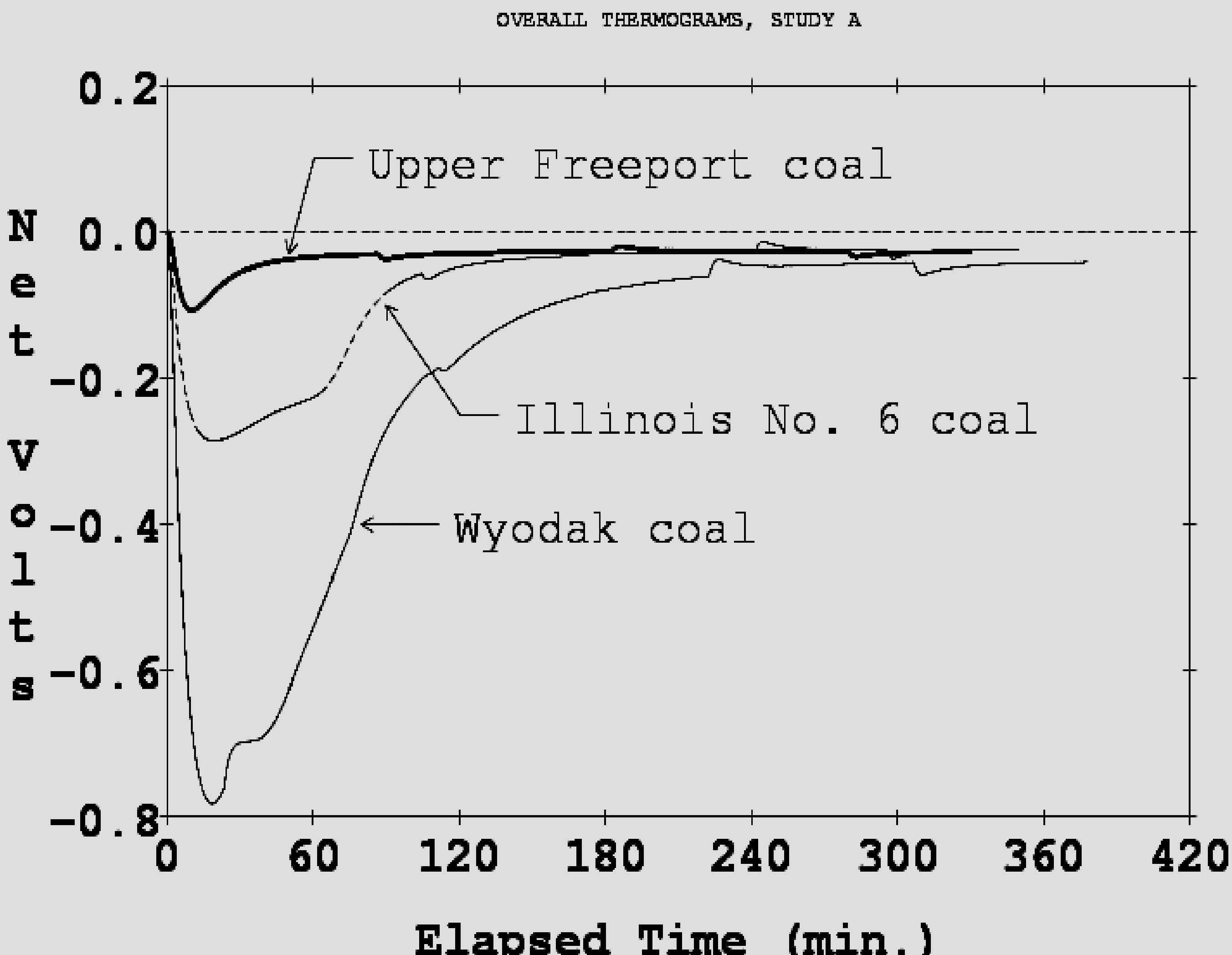
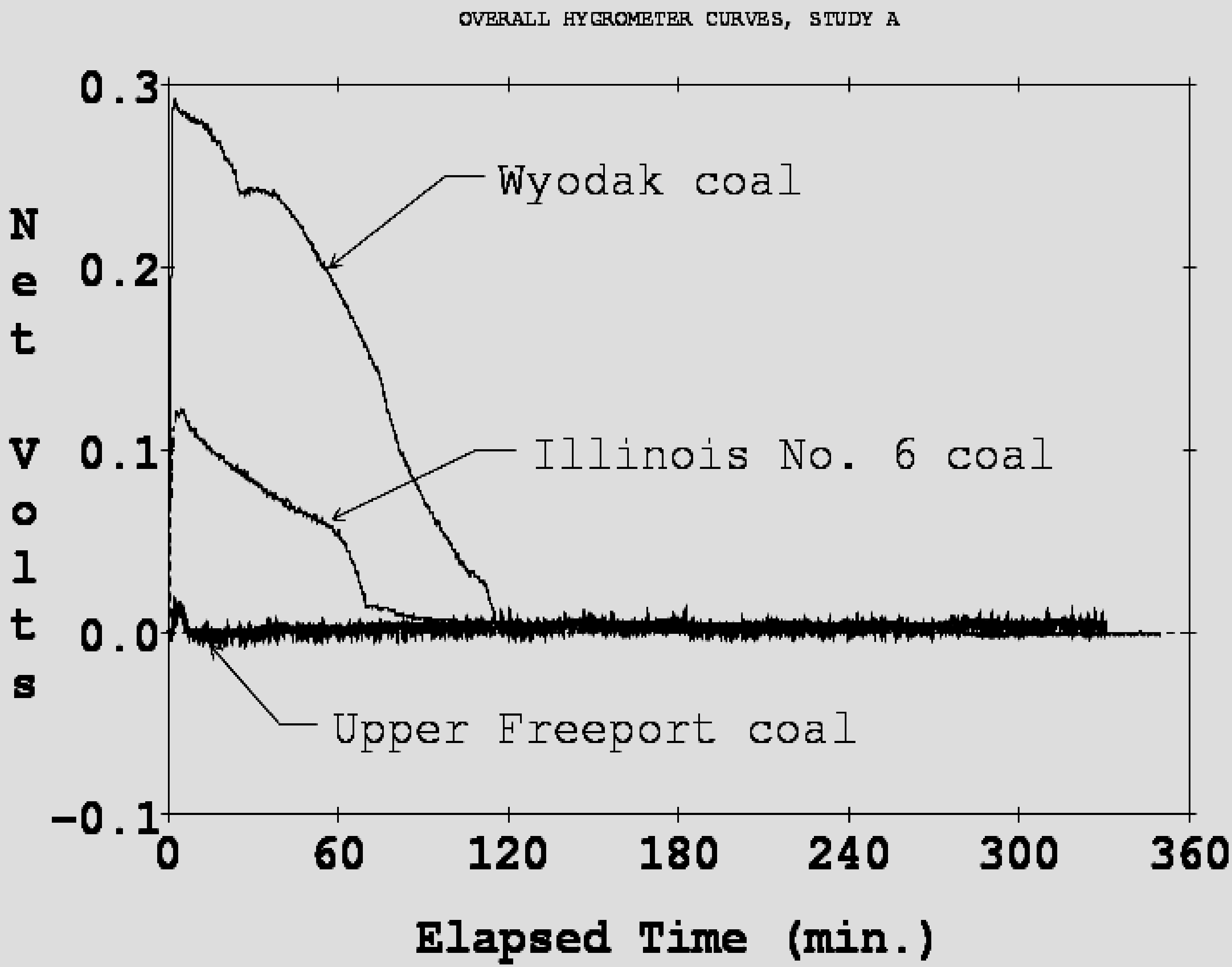


ILLUSTRATION OF GOODNESS-OF-FIT (THERMOGRAM)
Net Volts
0.00
-0.2
-0.4
-0.6
-0.8
0
60
120
180
240
300
360
420
Elapsed Time (min.)
. Study A, Step 1
. Wyodak coal
O Experimental data points
Fitted curve

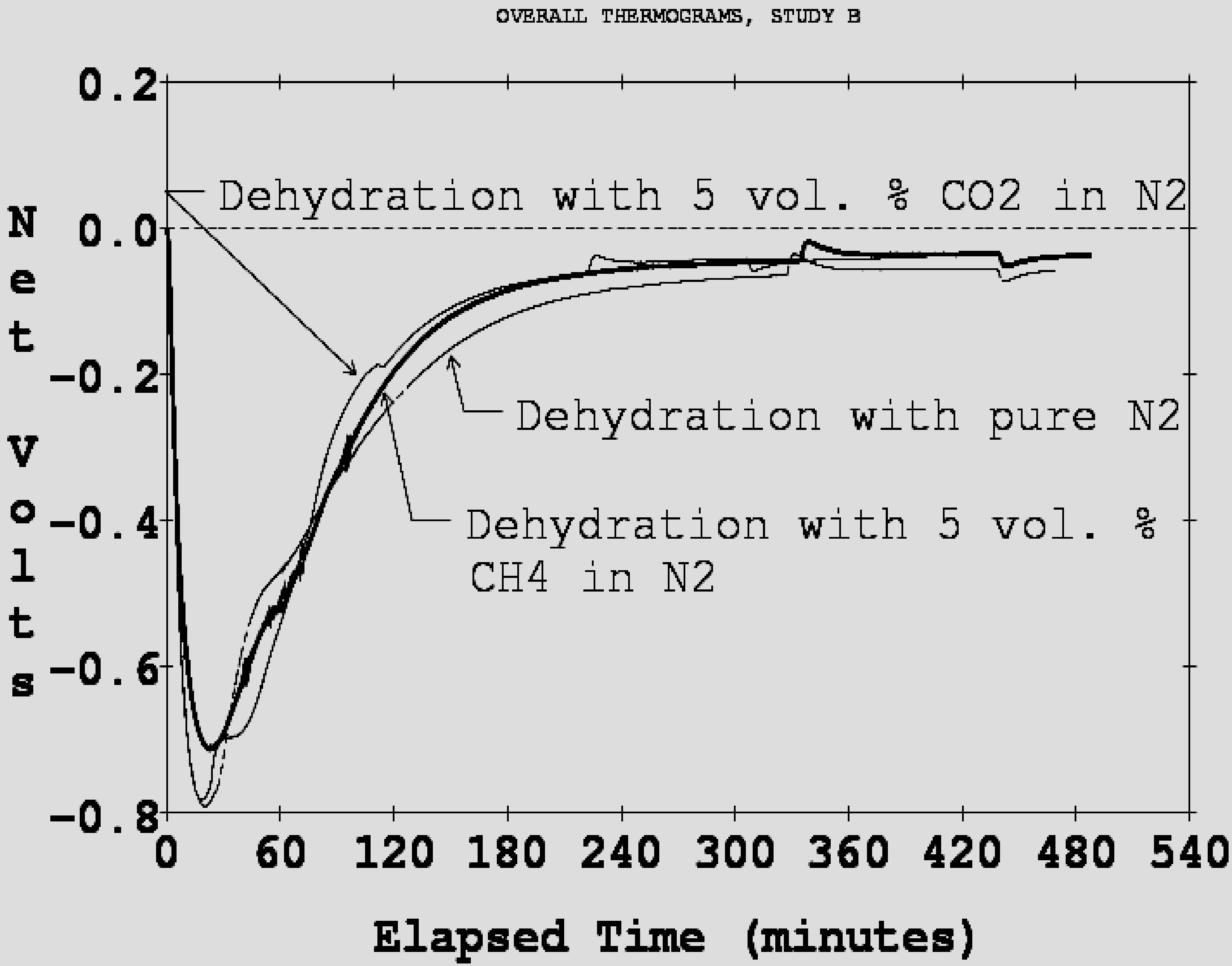
Results



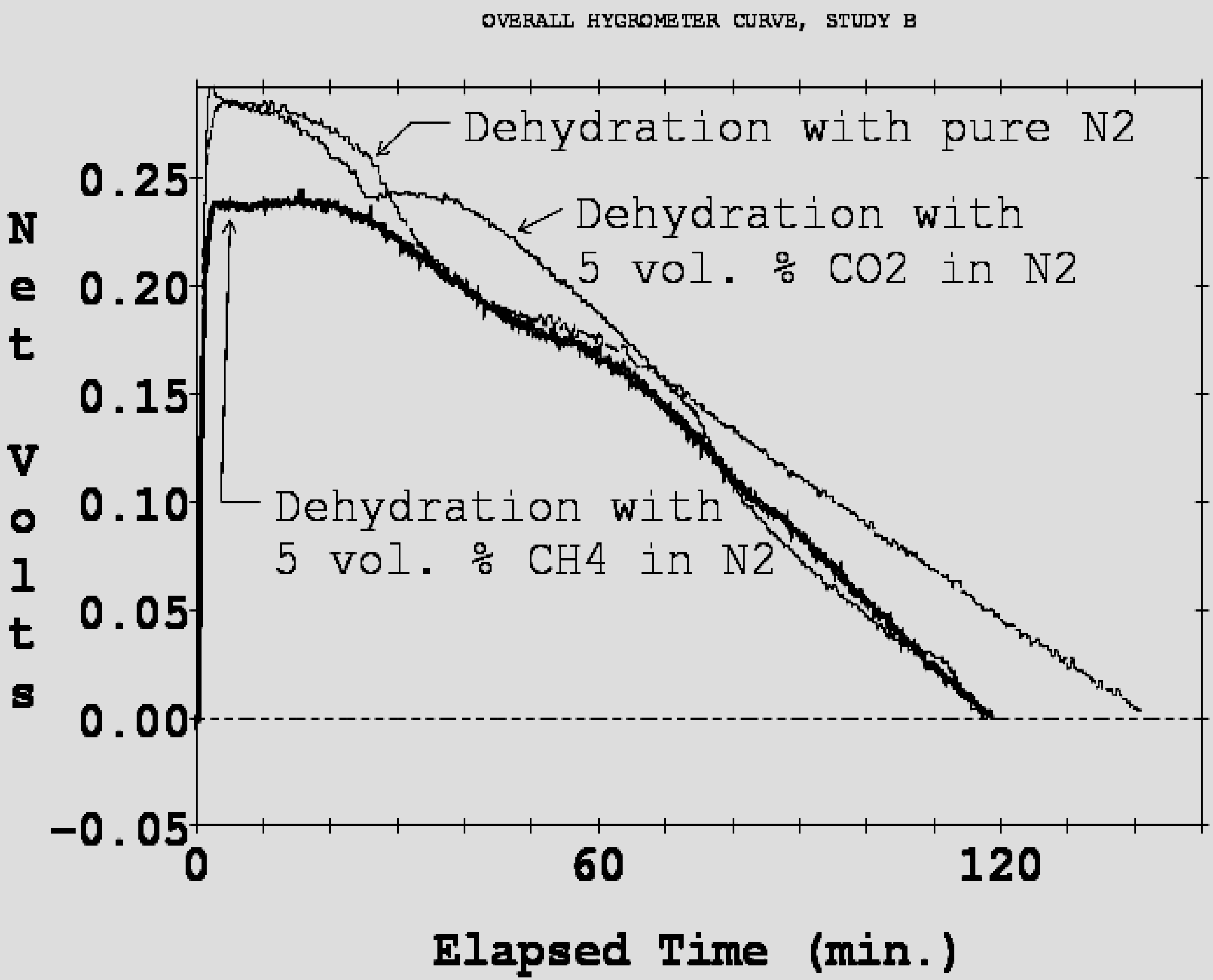
In all cases, the coal was dehydrated with 5 vol. % CO2 in N2.



In all cases, the coal was dehydrated with 5 vol. % CO_2 in N_2.



In all cases, the coal was Wyodak subbituminous coal.



In all cases, the coal was Wyodak subbituminous coal.

Calorimetric Data from Study A for Upper Freeport Bituminous Coal

		ΔH	
Step	Sorbate	sorption	desorption
1	CO_2 H_2O	-5.68 kJ/kg coal -	- +36.7 kJ/kg coal
2	CO_2 CO_2 N_2	- - -1.88×10^{-2} kJ/kg coal	+0.511 kJ/kg coal +3.13 mJ/m^2 coal* -
3	CH_4 N_2	-9.28×10^{-2} kJ/kg coal -	- $+2.05 \times 10^{-2}$ kJ/kg coal
4	CO_2 CO_2 CH_4	-0.809 kJ/kg coal -4.96 mJ/m^2 coal* -	- - $+4.78 \times 10^{-2}$ kJ/kg coal
5	CO_2 CO_2 N_2	- - -3.42×10^{-2} kJ/kg coal	+1.03 kJ/kg coal +6.32 mJ/m^2 coal* -

*Based on a specific CO_2 surface area of 163 m^2/g for dry Upper Freeport coal (data source: Ekrem Ozdemir, doctoral research, University of Pittsburgh, 2003).

NETL

Calorimetric Data from Study A for Illinois No. 6 Bituminous Coal

		ΔH	
Step	Sorbate	sorption	desorption
1	CO_2 H_2O H_2O	-5.38 kJ/kg coal - -	- +201 kJ/kg coal +40.1 kJ/mole H_2O[a]
2	CO_2 CO_2 N_2	- - -0.111 kJ/kg coal	+1.02 kJ/kg coal +7.73 mJ/m^2 coal[b] -
3	CH_4 N_2	-0.122 kJ/kg coal -	- +1.86x10^{-2} kJ/kg coal
4	CO_2 CO_2 CH_4	-1.30 kJ/kg coal -9.85 mJ/m^2 coal[b] -	- - +4.97x10^{-2} kJ/kg coal
5	CO_2 CO_2 N_2	- - -8.66x10^{-2} kJ/kg coal	+1.43 kJ/kg coal +10.8 mJ/m^2 coal[b] -

[a]Closely approximates the heat of vaporization of H_2O at 30°C (+43.7 kJ/mole H_2O).

[b]Based on a specific CO_2 surface area of 132 m^2/g for dry Illinois No. 6 coal (data source: Argonne premium coal handbook).

Calorimetric Data from Study A for Wyodak Bituminous Coal

		ΔH	
Step	Sorbate	sorption	desorption
1	CO_2 H_2O H_2O	-11.8 kJ/kg coal - -	- +667 kJ/kg coal +44.5 kJ/mole H_2O[a]
2	CO_2 CO_2 N_2	- - -0.111 kJ/kg coal	+0.995 kJ/kg coal +4.81 mJ/m^2 coal[b] -
3	CH_4 N_2	-0.121 kJ/kg coal -	- (negligible)
4	CO_2 CO_2 CH_4	-2.55 kJ/kg coal -12.35 mJ/m^2 coal[b] -	- - +0.106 kJ/kg coal
5	CO_2 CO_2 N_2	- - -0.129 kJ/kg coal	+2.87 kJ/kg coal +13.9 mJ/m^2 coal[b] -

[a]Closely approximates the heat of vaporization of H_2O at 30°C (+43.7 kJ/mole H_2O).
[b]Based on a specific CO_2 surface area of 207 m^2/g for dry Wyodak coal (data source: Ekrem Ozdemir, doctoral research, University of Pittsburgh, 2003).

Calorimetric Data from Study B with 5% Vol.% of CH_4 in N_2 as the Dehydrating Gas

		ΔH	
Step	Sorbate	sorption	desorption
1	CH_4 H_2O H_2O	-1.28 kJ/kg coal - -	- +662 kJ/kg coal +46.8 kJ/mole H_2O[a]
2	CH_4 N_2	- (negligible)	$+2.60 \times 10^{-2}$ kJ/kg coal -
3	CH_4 N_2	-6.49×10^{-2} kJ/kg coal -	- (negligible)
4	CO_2 CO_2 CH_4	-2.84 kJ/kg coal -13.7 mJ/m^2 coal[b] -	- - +0.133 kJ/kg coal
5	CO_2 CO_2 N_2	- - -0.143 kJ/kg coal	+2.27 kJ/kg coal +11.0 mJ/m^2 coal[b] -

[a]Closely approximates the heat of vaporization of H_2O at 30°C (+43.7 kJ/mole H_2O).
[b]Based on a specific CO_2 surface area of 207 m^2/g for dry Wyodak coal (data source: Ekrem Ozdemir, doctoral research, University of Pittsburgh, 2003).

NETL

Calorimetric Data from Study B with Pure N_2 as the Dehydrating Gas

		ΔH	
Step	Sorbate	sorption	desorption
1	N_2 H_2O H_2O	-4.28 kJ/kg coal - -	- +625 kJ/kg coal +43.8 kJ/mole H_2O[a]
2	-	-	-
3	CH_4 N_2	-9.67x10^{-2} kJ/kg coal -	- (negligible)
4	CO_2 CO_2 CH_4	-3.63 kJ/kg coal -17.5 mJ/m^2 coal[b] -	- - +0.240 kJ/kg coal
5	CO_2 CO_2 N_2	- - -0.133 kJ/kg coal	+3.23 kJ/kg coal +15.60 mJ/m^2 coal[b] -

[a]Closely approximates the heat of vaporization of H_2O at 30°C (+43.7 kJ/mole H_2O).

[b]Based on a specific CO_2 surface area of 207 m^2/g for dry Wyodak coal (data source: Ekrem Ozdemir, doctoral research, University of Pittsburgh, 2003).

NETL

Conclusions

- **CO_2 sorbs irreversibly on *moist* bituminous and subbituminous coals, but is not retained by the dry coals.**
- **The sorption of CO_2 on moist bituminous and subbituminous coals is considerably more energetic than that on the dry coals.**
- **During the sequestration of low concentrations of CO_2 by moist coals, most of the change in heat energy is attributable to coal dehydration, the amount of such energy correlating highly with the as-received moisture level.**
- **The molar heat of dehydration of both bituminous and subbituminous coals closely approximates the molar heat of vaporization of water.**
- **The heats of dehydration of (equivalent masses of) subbituminous coal by 5 vol. % CH_4 in N_2, 5 vol. % CO_2 in N_2, and pure N_2 are similar.**
- **The sorption/sequestration of CO_2 by dry subbituminous coal is accompanied by higher levels of CH_4 desorption/production than the sorption/sequestration of CO_2 by dry bituminous coal. (I.e., methane is less strongly retained by dry subbituminous coal than by dry bituminous coal.)**

Future Work

- Quantify the amounts of CO_2 and CH_4 sorbed or desorbed during the experiments by analyzing data produced by the non-dispersive infrared analyzers.
  NOTE: New data analysis methods/concepts that insure good reproducibility are needed in this area.

- Examine the temperature dependence of CBM production and/or coal seam CO_2 sequestration.