

Sorption hysteresis and its influence on Gas Drainage of High CO₂ coal seams

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1. Sorption isotherm and sorption hysteresis on coal

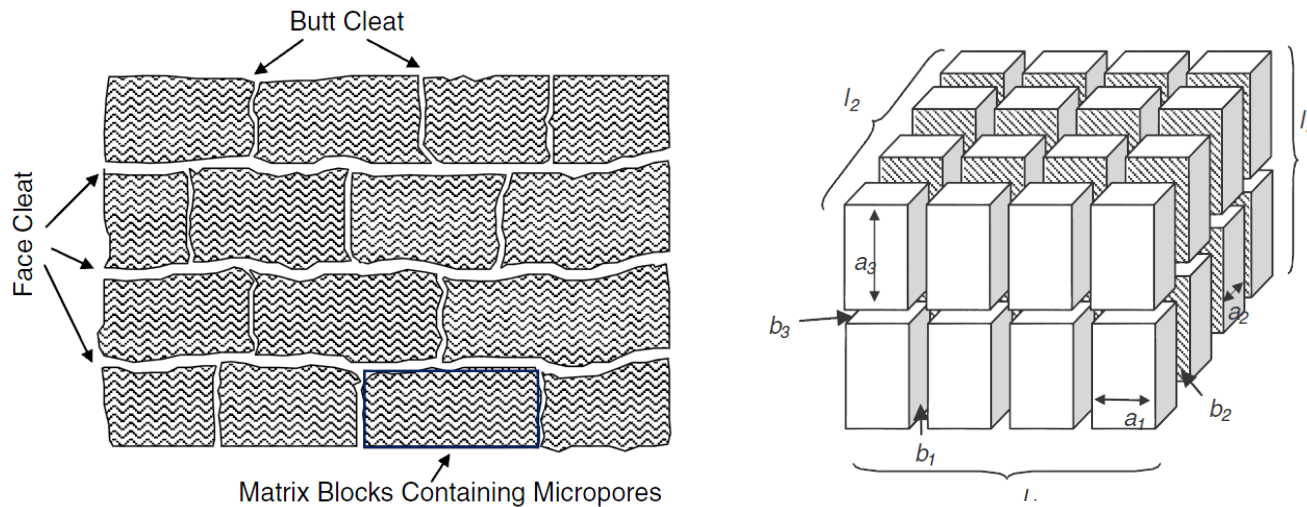
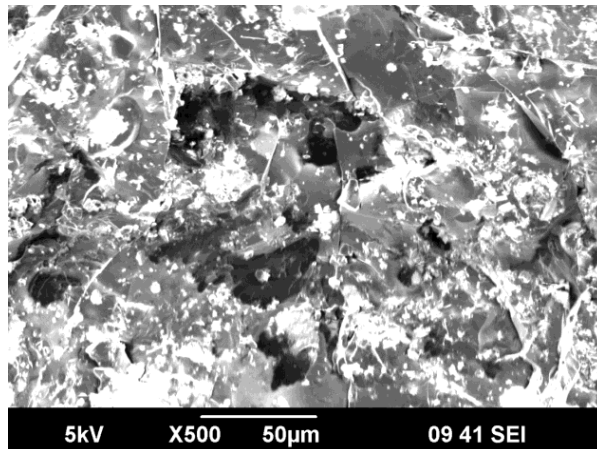


Fig.1 Schematic of coal matrix and coal cleat system



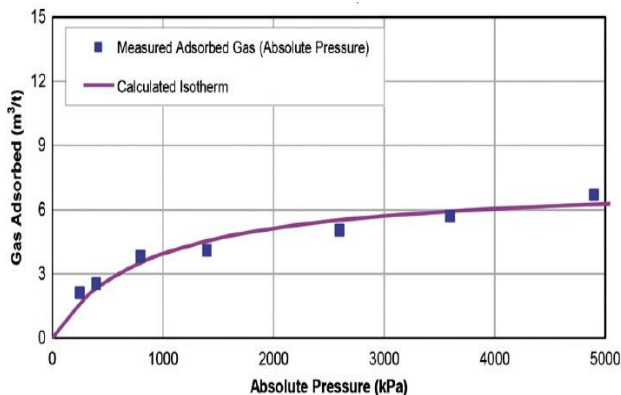
Although macro-, meso-, and micropores are present in the coal matrix, it is thought that the micropores are where most gas adsorption occurs.

Fig.2 SEM images of the coal porous structure

Determination of the gas content of a specific coal seam

Direct method: desorption test

Indirect method:
adsorption isotherm test



The gas holding capacity of a sample of coal at any particular pressure at a stable temperature

Gas emission volume with respect to gas pressure change

$$\varepsilon = \alpha V_a$$

Gas permeability change due to sorption-induced swelling which is in proportion to gas content

- What is sorption hysteresis?

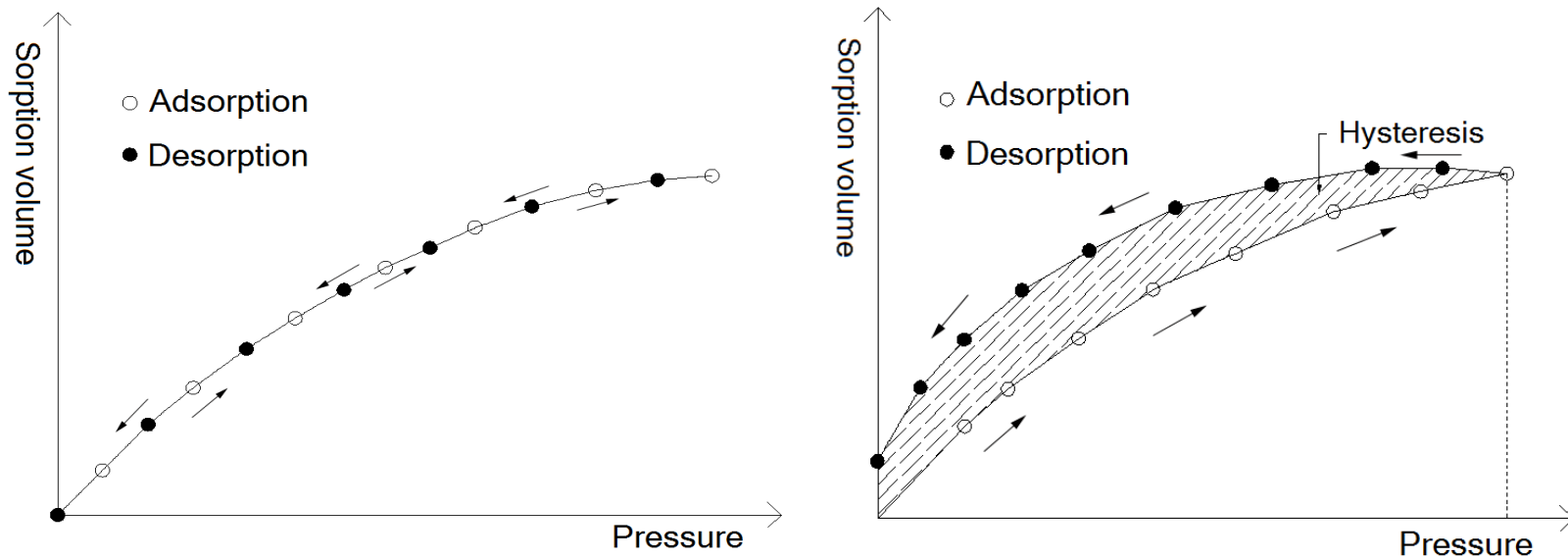
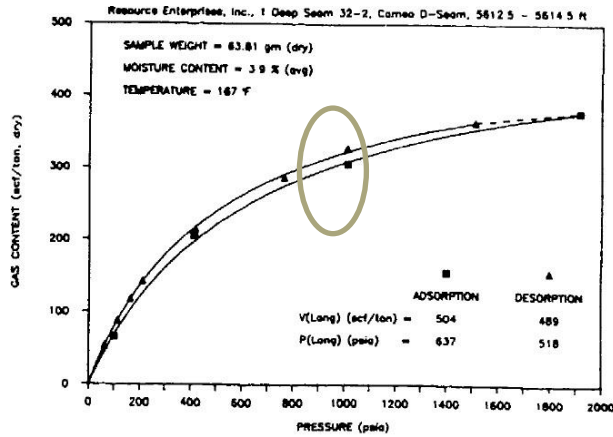


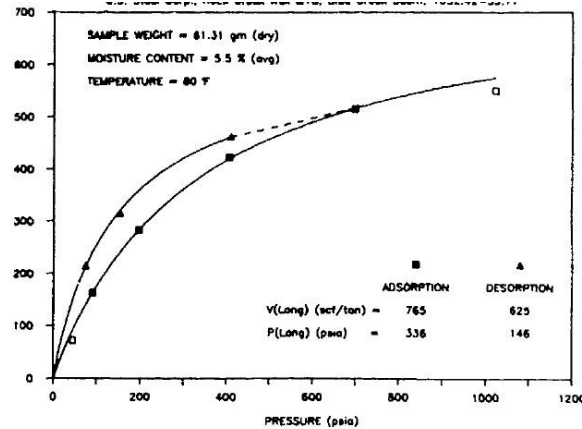
Fig.3 Schematic diagrams of two cases: (left) Fully reversible sorption; (right) Sorption with positive hysteresis

2. Methane and CO₂ sorption hysteresis: Previous studies

Bell and Rakop, 1986

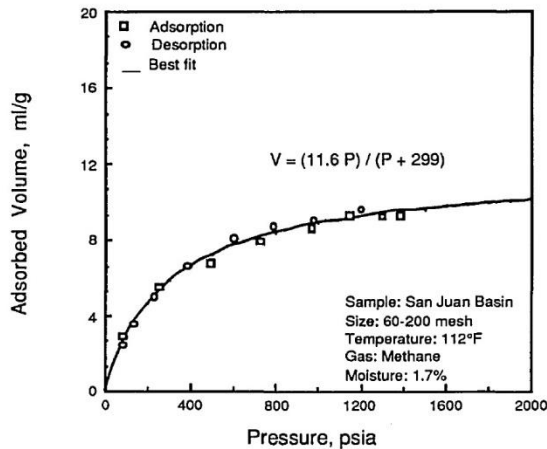


methane

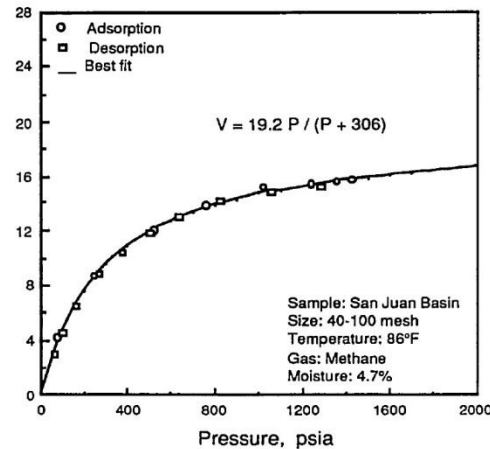


Pariti, 1992

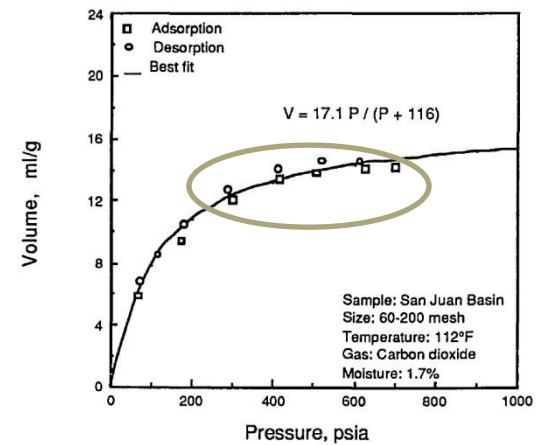
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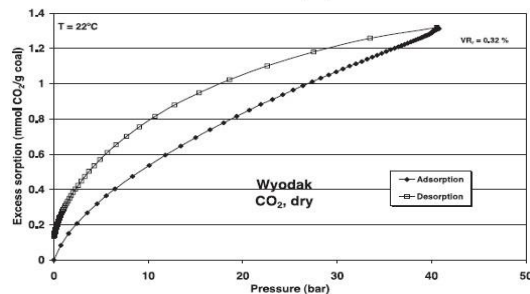
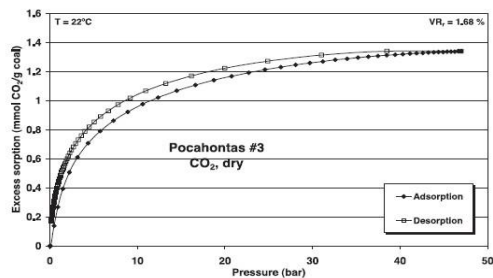
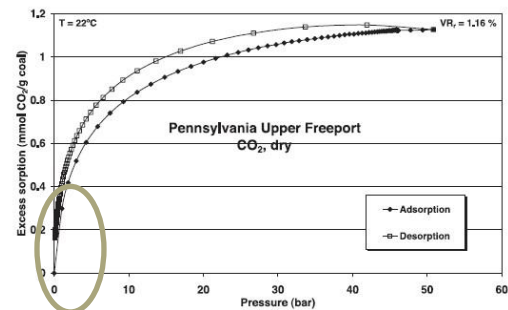
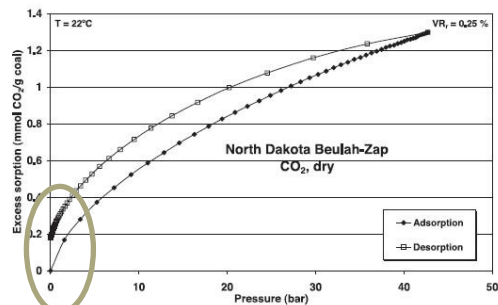
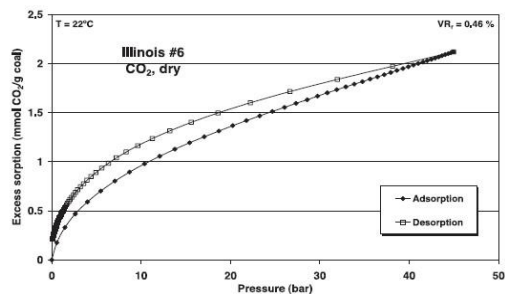
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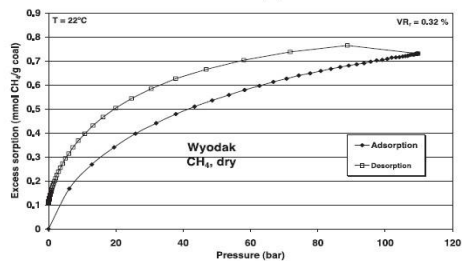
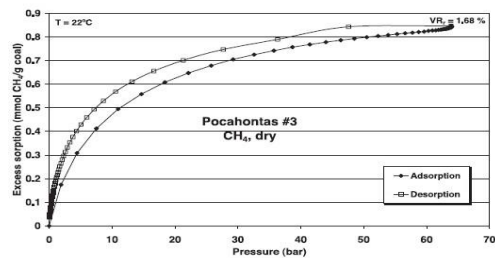
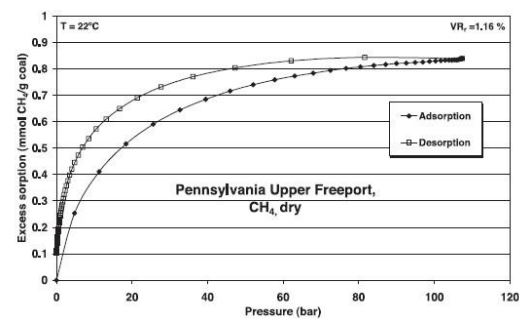
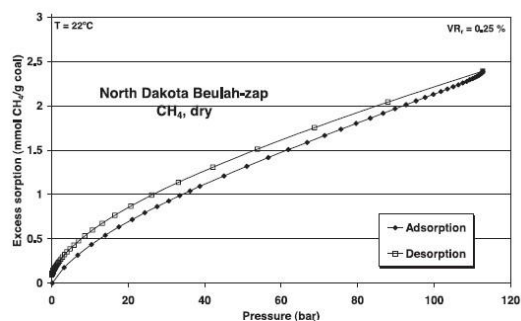
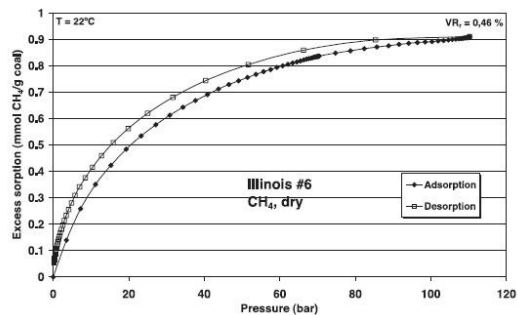
CO₂

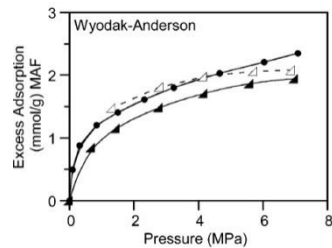
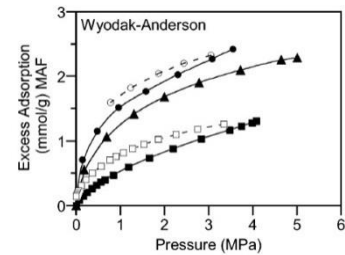
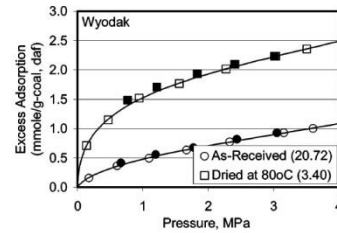
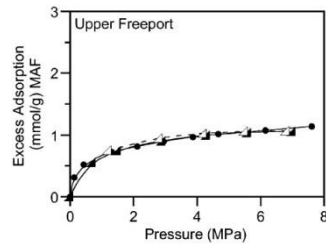
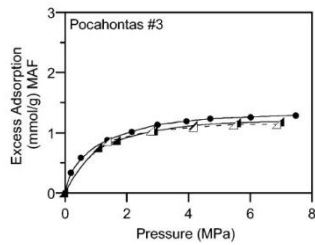
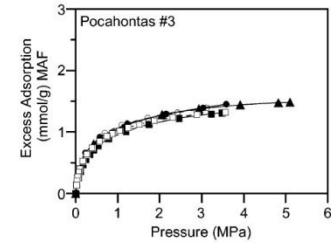
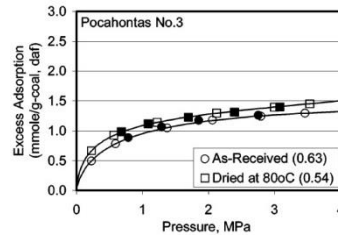
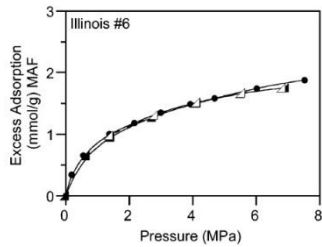
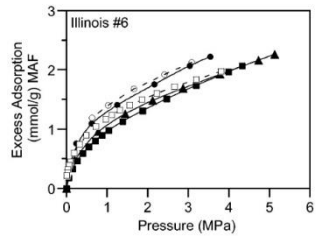
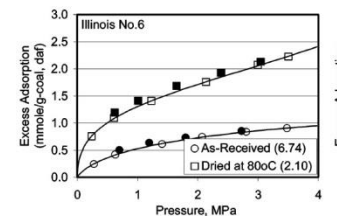
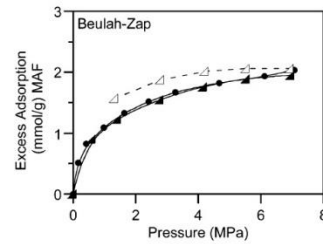
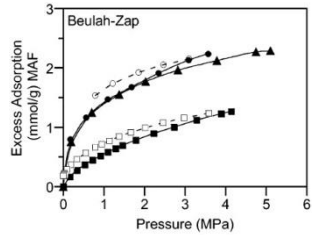
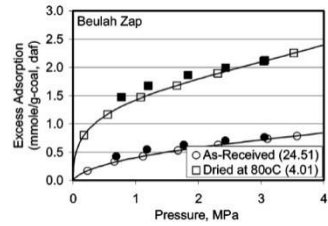


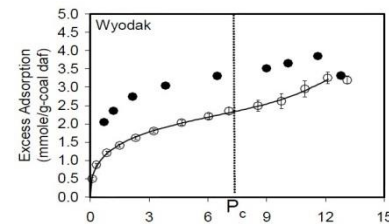
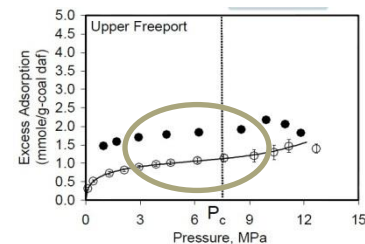
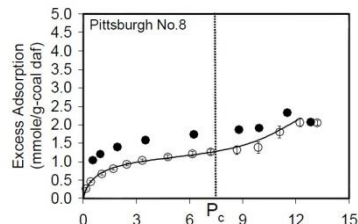
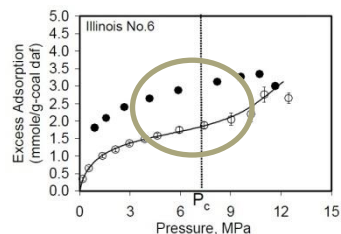
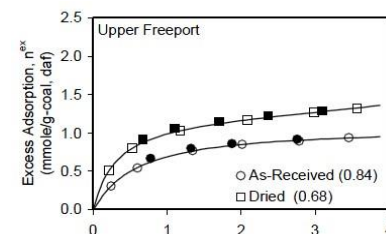
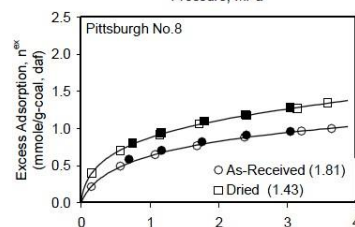
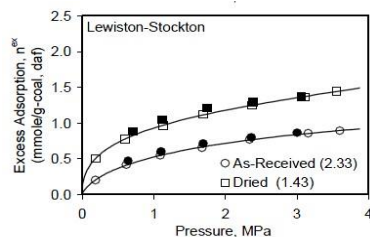
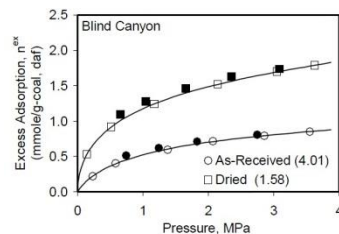
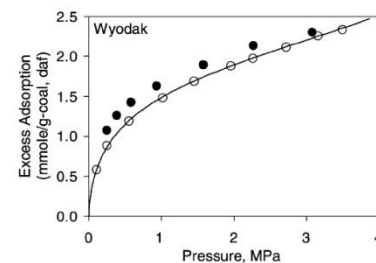
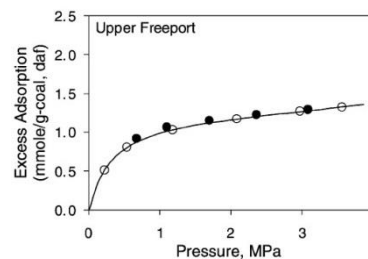
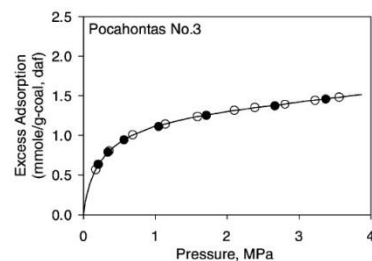
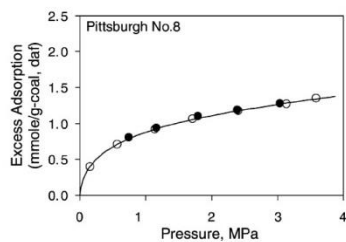
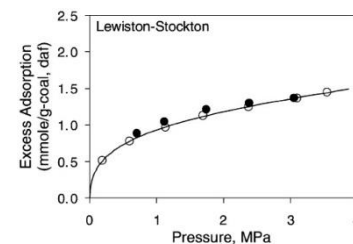
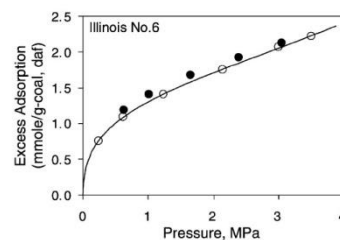
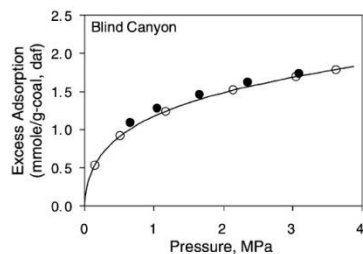
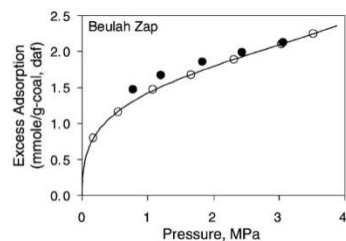
Busch et al., 2003 CO_2



methane

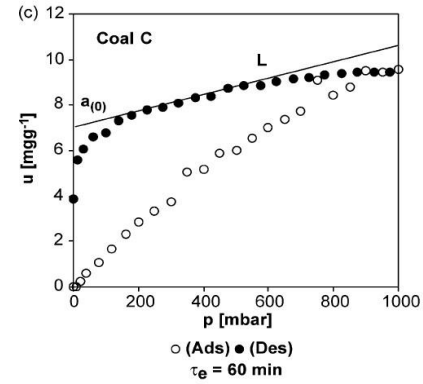
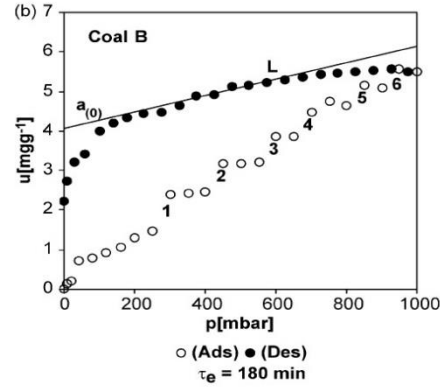
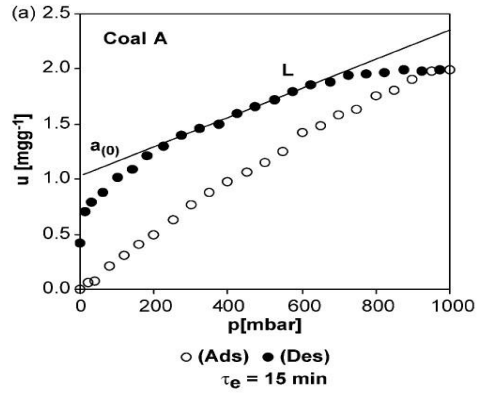






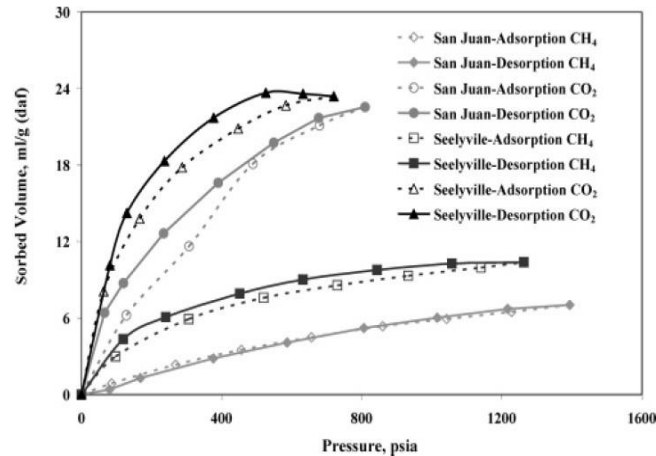
Weishauptova' et al., 2004

methane



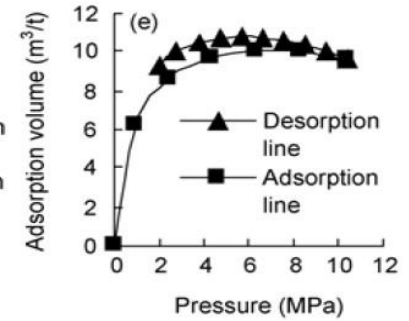
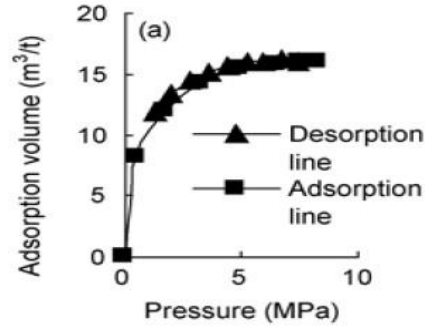
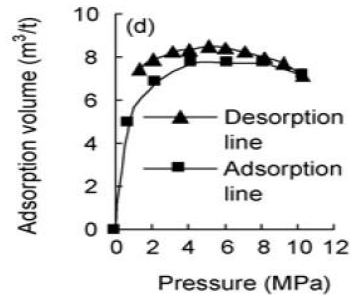
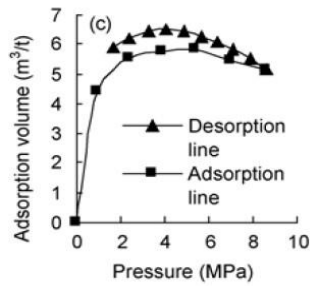
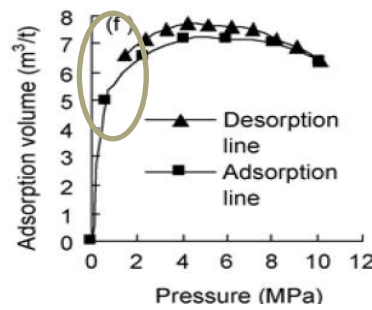
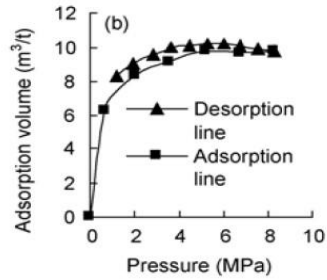
Harpalani et al., 2006

Methane and CO₂



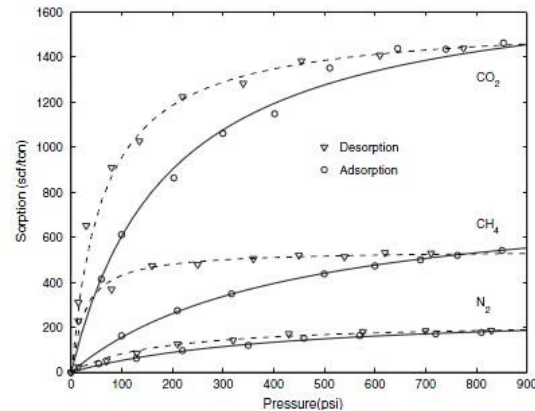
Ju et al., 2008

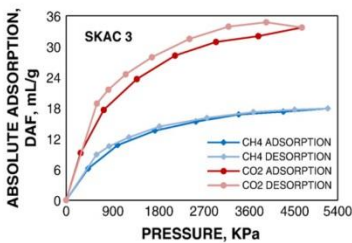
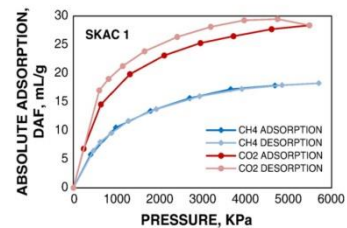
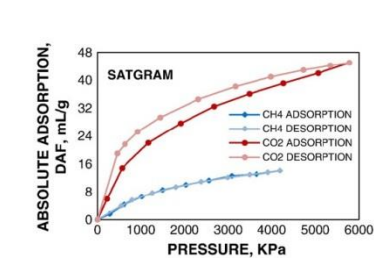
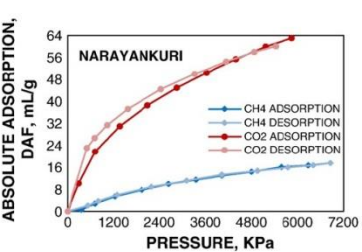
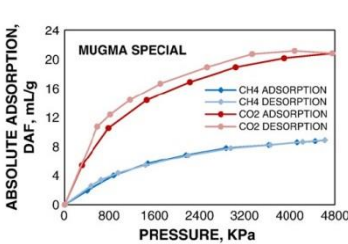
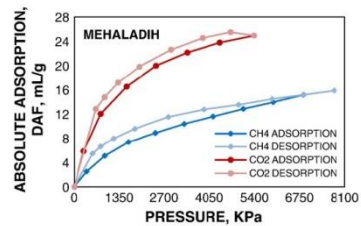
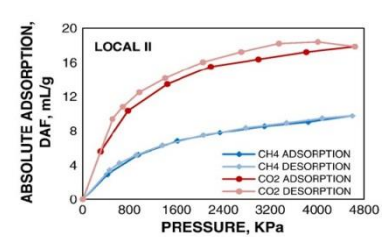
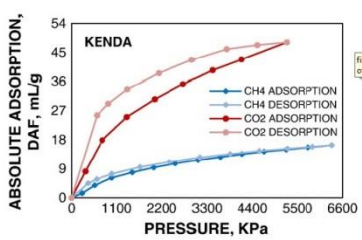
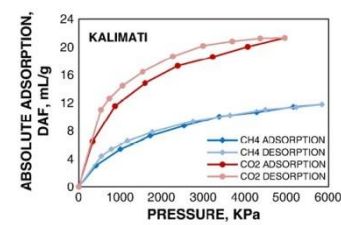
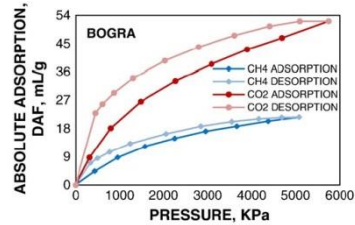
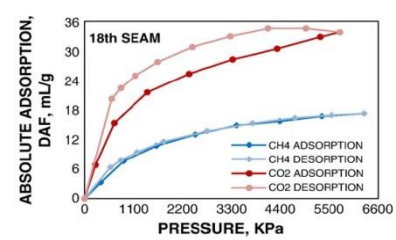
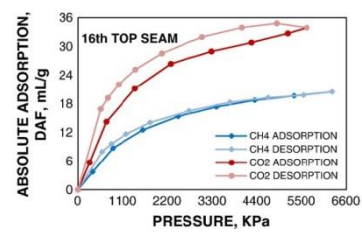
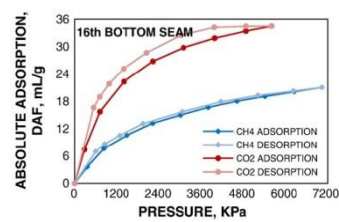
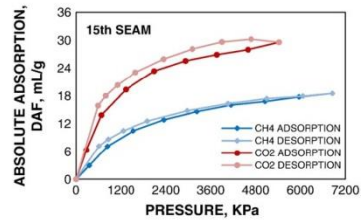
methane



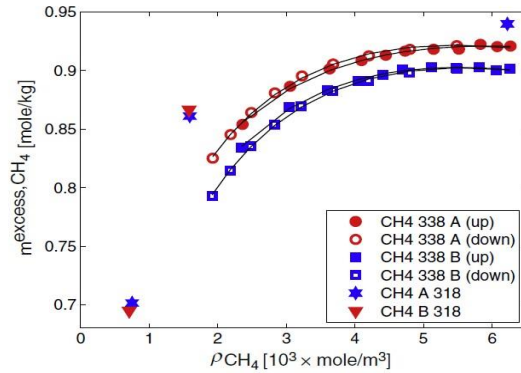
Jessen et al., 2008

Methane and CO_2

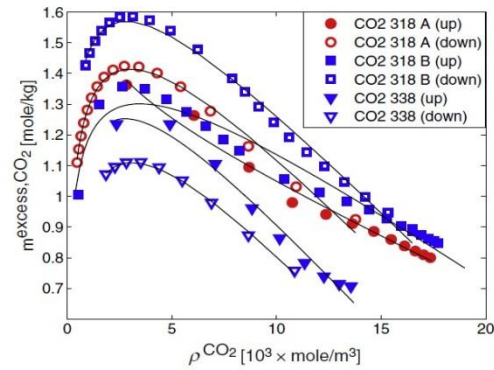




methane

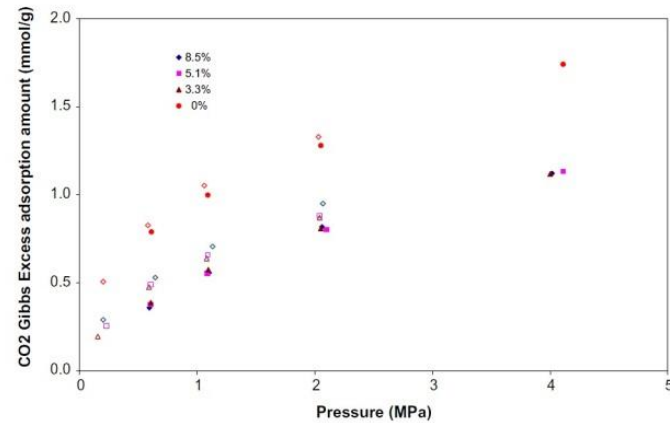
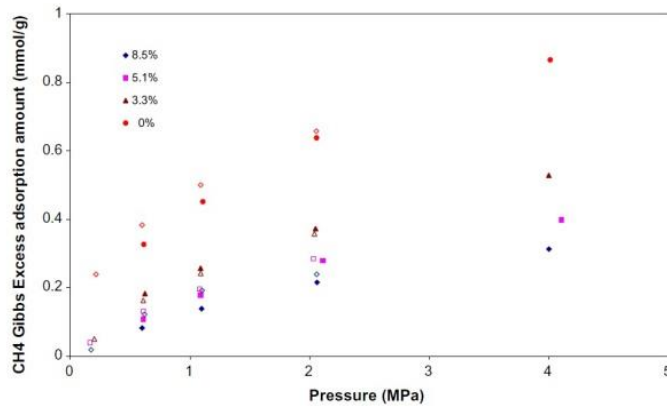


CO₂



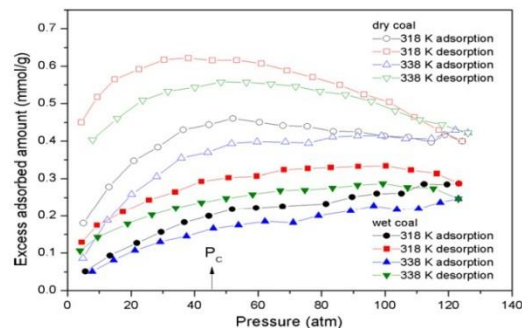
Pan et al., 2010

methane

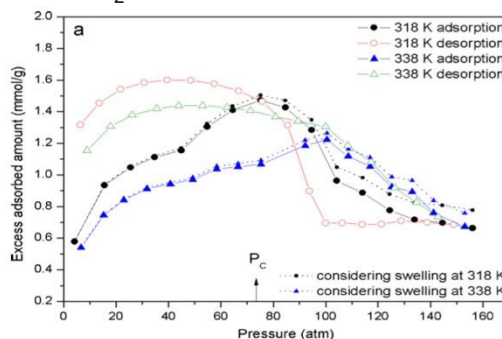


Kim et al., 2011

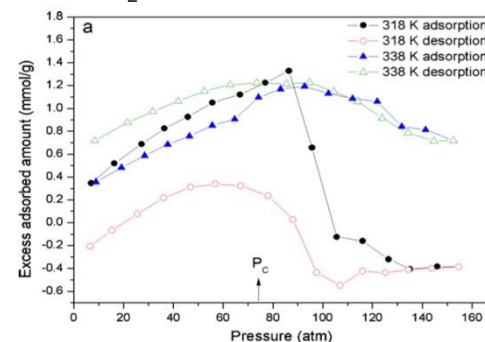
methane



CO₂



CO₂



Pillalamarry, et al., 2011

methane

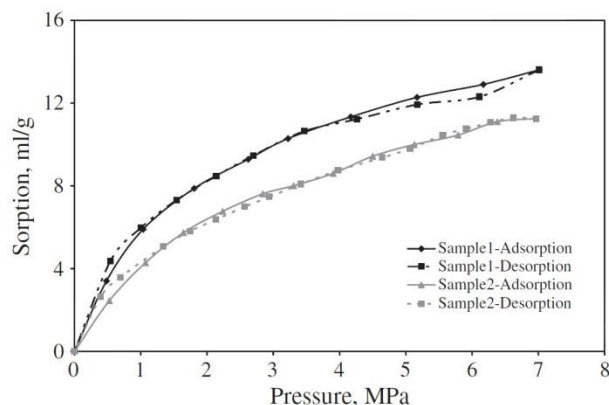


Fig. 3. Experimental absolute ad/de-sorption isotherms for methane.

Zhou et al., 2013

Methane and CO₂

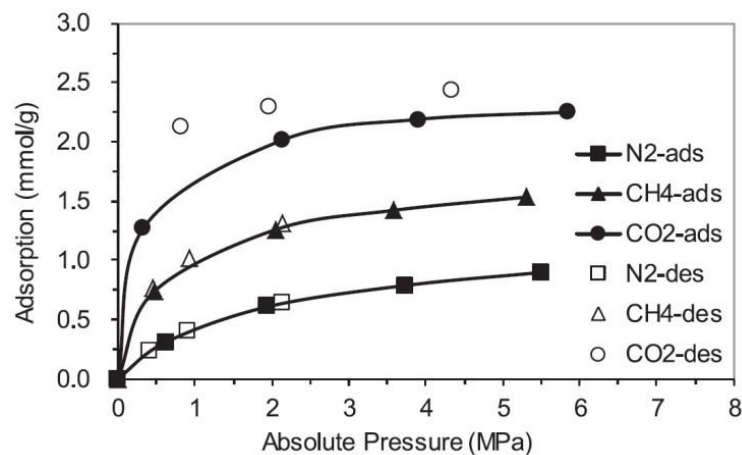


Table 1 Summary of sorption hysteresis experiments reported by various authors

Reference	Gas	Sample location	Experimental method	Sample size	Moisture or dry method	Temperature	Maximum pressure, Mpa	Description of sorption hysteresis by author
Bell and Rakop, 1986	Methane	Black Warrior Basin and Piceance Basin, USA	Volumetric	<0.149mm	5.5%	26°C	5MPa	Adsorption/desorption hysteresis is encountered for methane/coal systems at high pressure and simulated <i>in situ</i> temperature.
					3.9%	86°C	13MPa	
Pariti, 1992	Methane	San Juan Basin	Volumetric	0.149~0.42m m	4.7%	30°C	10MPa	It is also apparent that there is no hysteresis between the adsorption and desorption results.
				0.074~0.25m m	1.7%	44°C		
	CO ₂			0.074~0.25m m	1.7%	44°C	5MPa	
Busch et al., 2003	Methane	Argonne coals, USA	Volumetric	<0.149mm	Evacuated for at least 36h at 80°C	22°C	11MPa	The isotherms show different degrees of hysteresis.
	CO ₂						5MPa	The degrees of hysteresis for CO ₂ tended to decrease with increasing rank.
Goodman et al., 2004	CO ₂	Argonne coals, USA	Manometric and volumetric	<0.149mm	Evacuated continuously or intermittently for 36 h at 80°C	22°C	5MPa	Some hysteresis was noted by both laboratories for all coal samples.
						55°C	7MPa	The desorption data collected by laboratory D showed that the hysteresis was larger for the low-rank coal samples than for the high-rank coal samples.
Ozdemir et al., 2003, 2004	CO ₂	Argonne coals, USA	Volumetric	<0.149mm	Under vacuum in-situ at 80°C for 36 hours before the measurements	22°C	4MPa	The hysteresis was small or negligible for high rank coals but discernable for low rank coals.
Ozdemir, 2004	CO ₂	Argonne coals, USA	Manometric	<0.149mm	Under vacuum in-situ at 80°C for 36 hours before the measurements	55°C	15MPa	There was significant hysteresis between the excess adsorption and desorption isotherms for all ranks of coal.
					As-received			

Table 1 continued

<u>Ozdemir, 2004; Ozdemir and Schroeder, 2009</u>	CO ₂	Argonne coals, USA	<u>Manometric</u>	<0.149mm	As-received coal	22°C	4MPa	This hysteresis was absent or negligible for as-received coals.
<u>Weishauptová et al., 2004</u>	Methane	Upper Silesian coal basin and North Bohemian basin, Czech Republic	Gravimetric	<0.2mm	Outgassed at 100°C until constant weight was achieved at 10-6 Pa	25°C	0.1MPa	Desorption branch reflects release of a smaller gas amount compared to the total amount <u>sorbed</u> .
<u>Jessen et al., 2008</u>	Methane	Powder River Basin, USA	Gravimetric	0.25mm (mean size)	Preserved in desiccators under vacuum	22°C	6MPa	There is significant hysteresis between adsorption and desorption curves.
	CO ₂							CO ₂ adsorption/desorption curves versus pressure also display significant hysteresis and follow a Langmuir-type relationship.
<u>Harpalani et al., 2006</u>	Methane	San Juan Basin, USA	Volumetric	0.149~0.42mm	Moisture equilibrated by keeping them in an environmental chamber at the experimental temperature and ~95% humidity level	45°C	10MPa	No hysteresis
		Illinois Basin, USA				23.5°C	10MPa	Methane and CO ₂ desorption isotherms lie above the adsorption isotherms.
	CO ₂	San Juan Basin, USA				45°C	6MPa	
		Illinois Basin, USA				23.5°C	6MPa	
<u>Ju et al., 2008</u>	Methane	<u>Huaibei and Huainan</u> coalfields, China	Volumetric	N.A.	As-received coal	30°C	10MPa	The methane isotherms showed different degrees of hysteresis.
Pan et al., 2010	Methane	Sydney Basin, Australia	Volumetric	Coal core, 25.4 mm in diameter and 82.6 mm in length	Four moisture degree, dry sample was obtained by dried in the oven at 50°C for two weeks	26°C	4MPa	A small amount of hysteresis observed between adsorption and desorption quantities for all the isotherms
	CO ₂							
He et al., 2010	CO ₂	<u>Kyungdong coal</u> , Korea	Volumetric	N.A.	Dried overnight in a vacuum oven at 105°C.	45°C	15MPa	The crossover between adsorption and desorption isotherms in dry coal was observed near the critical region.
					3.64%			The excess amount of adsorbed CO ₂ on wet coal was lower during desorption than during adsorption.

Table 1 continued

<u>Battistutta et al., 2010</u>	Methane	<u>Selar Cornish, South Wales Coalfield, UK</u>	<u>Manometric</u>	1.5~2.0mm	Dried in oven for 24 h at 105°C under vacuum conditions	45°C	16MPa	The excess isotherm of CH ₄ shows no hysteresis.
	CO ₂					65°C		The excess isotherm of CO ₂ shows hysteresis.
						45°C		
						65°C		
Dutta et al., 2010	Methane	<u>Gondwana coals, India</u>	<u>Manometric</u>	0.1~0.149mm	Dried by keeping them in a vacuum-oven chamber maintained at 105 °C for 48 h	30°C	7.8MPa	Significant hysteresis was observed between the ad/desorption isotherms for CO ₂
	CO ₂						5.8MPa	
<u>Pillalamarry et al., 2011</u>	Methane	Illinois basin, USA	Volumetric	0.149~0.425 mm	Moisture equilibrium at 22.8°C and humid conditions (99%)	22.8°C	9MPa	The isotherm shows that desorption hysteresis is insignificant.
Kim et al., 2011	Methane	<u>Kyungdong coal, Korea</u>	Volumetric	0.15~0.5mm	Dried for more than 12h in a vacuum oven at 105°C.	45°C	13MPa	All the CH ₄ desorption isotherms showed a weak positive hysteresis.
					3.64%	65°C		
					Dry			
					3.66%			
	CO ₂				Dry	45°C	15MPa	CO ₂ desorption isotherms had different shapes, depending on temperature.
					3.64%	65°C		
					Dry			
Zhou et al., 2013	Methane	<u>South Qinshui Basin, China</u>	Volumetric	0.25~0.5mm	Dried at 60 °C for two hours	25°C	6MPa	No significant hysteresis is observed for pure CH ₄ .
	CO ₂							CO ₂ adsorption/desorption isotherms show a hysteresis.

Questions?

- Is this phenomenon important?
- This phenomenon actually exists or it is only occasional?
- How to study this phenomenon?

Our answers

- CBM recovery/gas drainage of high CO₂ coal seams is process of desorption rather than adsorption, and for CO₂ sequestration, the sequestered CO₂ may desorb due to the reduction of gas pressure, hence understanding the difference between adsorption and desorption has significant values.
- Both methane and CO₂ sorption hysteresis on coal have been observed by various researchers, it is a factual phenomenon rather than an experimental error.
- We need to evaluate the degree of hysteresis quantitatively, and then try to figure out the likely control factors and the possible mechanism.

3. Improved evaluation method and corresponding calculation results

Table 2 Hysteresis indices (HI) from literature

Index based on	Equation	Notation	Reference
Freundlich exponent	$S = K_{ad} \times C^{1/n_{ad}} \quad (1)$ $S = K_{de} \times C^{1/n_{de}} \quad (2)$ $HI = \frac{n_{de}}{n_{ad}} \quad (3)$	S: equilibrium concentration in solid phase; C: equilibrium concentration in sorbent; K: Freundlich sorption factor; n: Freundlich exponent; subscript ad and de: adsorption and desorption, respectively	Baskaran and Kennedy, 1999; Ding and Rice, 2011; Ding et al., 2002; Hong et al., 2009; O'Connor et al., 1980
Equilibrium concentration in solid phase	$HI = \frac{\text{Max}(S_{de} - S_{ad})}{S_{ad}} \quad (4)$ $HI = \left. \frac{S_{de} - S_{ad}}{S_{ad}} \right _{T,C} \quad (5)$	S: equilibrium concentration in solid phase; T: temperature; C: equilibrium concentration in sorbent; subscript ad and de: adsorption and desorption, respectively	Bhandari and Xu, 2001; Ma et al., 1993; Ran et al., 2004
Slope	$HI = \frac{f'_{ad}(C) - f'_{de}(C)}{f'_{ad}(C)} \quad (6)$	$f'_{ad}(C)$, $f'_{de}(C)$: first derivatives of the functions describing the adsorption and desorption isotherms, respectively	Braida et al., 2003; Wu and Sun, 2010
Area	$HI = 100 \left(\frac{A_{de} - A_{ad}}{A_{ad}} \right) \quad (7)$	A_{ad} , A_{de} : areas under the adsorption and desorption isotherms, respectively. Integration from $C = 0$ (lower limit) to C_{max} (maximum sorption point, upper limit)	Zhu and Selim, 2000

These indices are unsatisfactory for our case because:

- (i) the index based on the Freundlich exponent relies on a specific isotherm model (the Freundlich equation) which is not commonly used for fitting gas sorption isotherms on coal;
- (ii) indices based on slope and equilibrium concentration in the solid phase describe the hysteresis degree at different single points rather than the whole isotherm, thus small experimental errors can seriously affect the result.

Improved method and index for quantitative evaluation of the degree of gas sorption hysteresis on coal

Step 1 representation of isotherms

{

Langmuir model:

$V = V_0 \frac{P}{P_L + P}$

D-R model:

$V = V_{\text{micro}} \exp \left\{ -D \left[\ln \left(\frac{P_0}{P} \right) \right]^2 \right\}$

Dual sorption model:

$V = kP + V'_0 \frac{P}{P'_L + P}$

Choose the best

polynomial for fitting supercritical CO₂ sorption data

Step 2 improved hysteresis index

$$IHI = \frac{A_{hy}}{A_{hf}} = \frac{A_{de} - A_{ad}}{A_{sf} - A_{ad}} \times 100\%$$

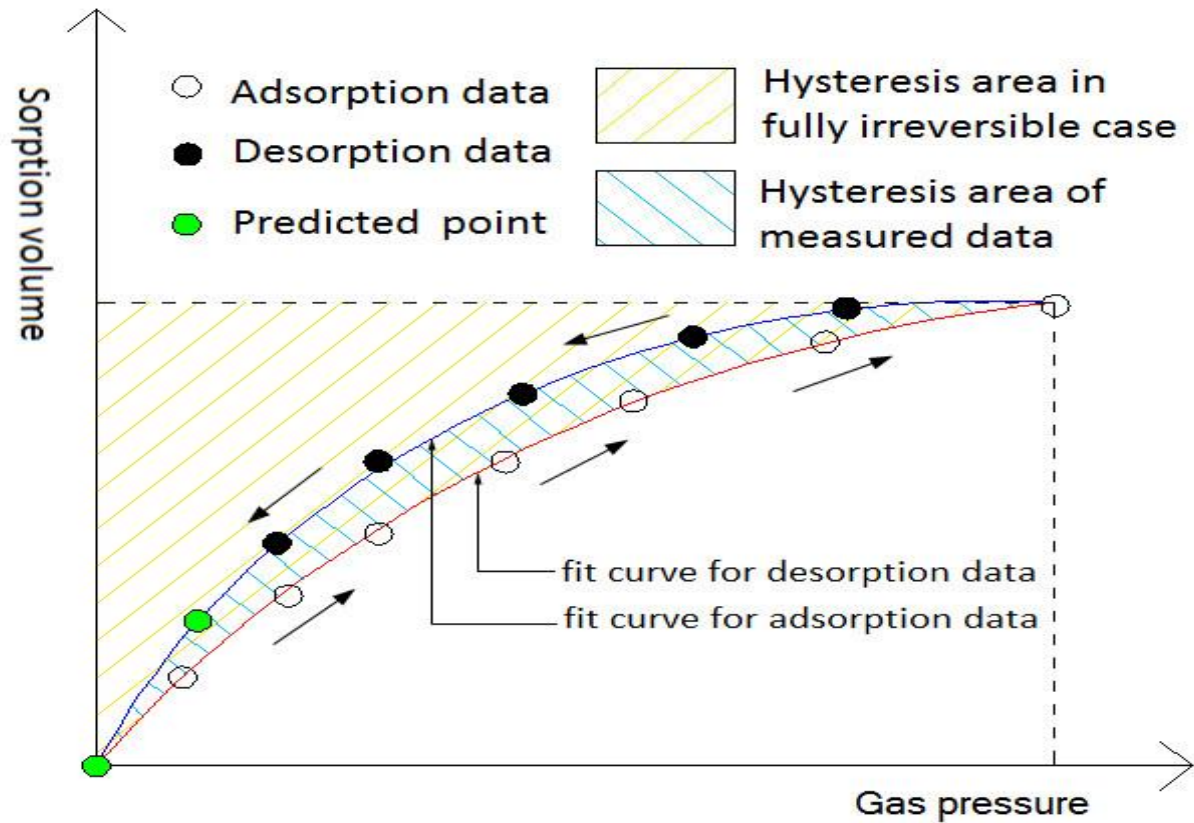


Fig. 4 Schematic diagram of the improved hysteresis index (IHI)

Table 3 Correlation coefficients for fitting methane sorption data from different models, and calculated values of IHI . Yellow and blue grids represent best and second-best fitting model for each group of data, respectively.

Reference	Coal sample	Correlation coefficient (R^2) for fitting adsorption data			Correlation coefficient (R^2) for fitting desorption data			IHI
		Langmuir model	D-R model	Dual sorption model	Langmuir model	D-R model	Dual sorption model	
Bell and Rakop, 1986	Black Warrior Basin coal	0.9992825	0.9994169	0.9992942	0.9994843	0.9995637	0.9995347	9.95%
	Piceance Basin coal	0.9999207	0.9998934	0.9999207	0.9998764	0.9999649	0.9998830	25.43%
Pariti, 1992	San Juan Basin coal (1.7% moisture)	0.9951880	0.9980468	0.9977292	0.9972380	0.9984688	0.9972380	11.86%
	San Juan Basin coal (4.7% moisture)	0.9988407	0.9992241	0.9988510	0.9991955	0.9996743	0.9991955	-6.12%
Busch et al., 2003	Illinois coal	0.9994225	0.9996396	0.9994225	0.9884889	0.9961358	0.9921035	19.64%
	North Dakota Beulah-zap coal	0.9945955	0.9991362	0.9997868	0.9764177	0.9977096	0.9969999	13.22%
	Pennsylvania Upper Freeport coal	0.9988319	0.9997455	0.9989737	0.9516169	0.9859466	0.9660021	48.95%
	Pocahontas #3 coal	0.9986088	0.9998445	0.9996275	0.9857268	0.99749148	0.9920858	28.37%
	Wyodak coal	0.9971293	0.9999231	0.9995161	0.9380059	0.97847944	0.9551240	51.36%
Weishauptová et al., 2004	Upper Silesian basin coal A	0.9989218	0.9989093	0.9989218	0.8688033	0.95541102	0.9387783	53.79%
	Upper Silesian basin coal B	0.9895822	0.9897988	0.9895834	0.5747015	0.75643435	0.7243758	73.87%
	North Bohemian basin coal C	0.9939468	0.99405421	0.9939468	0.5040014	0.68924697	0.6734168	70.24%
Jessen et al., 2008	Powder River Basin coal	0.9996846	0.9998916	0.9999242	0.9902672	0.9966341	0.9935634	66.50%
Harpalani et al., 2006	San Juan Basin coal	0.9996547	0.9997854	0.9997072	0.9960243	0.9993913	0.9960243	-1.47%
	Illinois Basin coal	0.9987698	0.9997582	0.9998384	0.9978770	0.9989467	0.9982269	22.94%
Ju et al., 2008	cataclastic structure coal	0.9975012	0.9986353	0.9978368	0.9932479	0.9894474	0.9932479	53.19%

	mylonitic structure coal	0.9849529	0.9942747	0.9849529	0.9666232	0.9959481	0.9666232	37.13%
	primary coal	0.9887407	0.9983269	0.9955545	0.9993884	0.9997233	0.9993884	3.04%
	scaled structure coal	0.9953085	0.9990081	0.9953085	0.9858433	0.9996664	0.9858433	40.71%
	schistose structure coal	0.9791317	0.9982993	0.9791317	0.9870999	0.9987935	0.9870999	71.95%
	schistose-wrinkle structure coal	0.9905285	0.9972139	0.9905285	0.9773478	0.9961128	0.97734782	84.10%
Pan et al., 2010	Sydney Basin coal (0% moisture)	0.9979128	0.9998662	0.9997013	0.9836752	0.9999951	0.9991319	10.55%
	Sydney Basin coal (3.3% moisture)	0.9980413	0.9999981	0.9999570	0.9982539	0.9999891	0.9999982	-7.38%
	Sydney Basin coal (5.1% moisture)	0.9999784	0.9999997	0.9999784	0.9997381	0.9999588	0.9998624	7.75%
	Sydney Basin coal (8.5% moisture)	0.9997936	0.9998852	0.9997936	0.9904860	0.9944729	0.9904860	22.13%
Battistutta et al., 2010	Selar Cornish coal A	0.9941061	0.9996935	0.9941061	0.9839309	0.9995640	0.9839309	0.04%
	Selar Cornish coal B	0.9880978	0.9996225	0.9880978	0.9736294	0.9991828	0.9736294	-7.16%
Dutta et al., 2010	15th seam coal	0.9990553	0.9992667	0.9990553	0.9984547	0.9998697	0.9994829	13.94%
	16th bottom seam coal	0.9982619	0.9992390	0.9994268	0.9968555	0.9996135	0.9990782	9.56%
	16th top seam coal	0.9990577	0.9997290	0.9990577	0.9993606	0.9998379	0.9996625	8.82%
	18th seam coal	0.9985628	0.9989037	0.9985628	0.9985182	0.9997757	0.9993309	5.84%
	Borga coal	0.9990569	0.9992806	0.9992452	0.9932879	0.9987047	0.9971754	26.87%
	Kalimati coal	0.9990964	0.9996440	0.9994478	0.9981974	0.9999151	0.9996454	9.07%
	Kenda coal	0.9979326	0.9985959	0.9986506	0.9950941	0.9998326	0.9995224	11.65%
	Local II coal	0.9984666	0.9983479	0.9986599	0.9985085	0.9998440	0.9998577	4.45%
	Mehaladih coal	0.9935468	0.9990192	0.9995767	0.9921561	0.9997062	0.9993326	22.72%
	Mugma Special coal	0.9976692	0.9996949	0.9976692	0.9994180	0.9994730	0.9994330	-0.77%
Pillalamarri et al., 2011	Naravankuri coal	0.9960930	0.9989232	0.9960930	0.9983178	0.9993073	0.9983178	2.28%
	Sataram coal	0.9981581	0.9990098	0.9981581	0.9989785	0.9994329	0.9994920	-0.51%
	SKAC 1 coal	0.9992494	0.9994701	0.9992494	0.9995432	0.9996963	0.9995432	-1.80%
	SKAC 2 coal	0.9996743	0.9997848	0.9996743	0.9994188	0.9996664	0.9994262	11.17%
	Illinois basin coal (sample 1)	0.9982973	0.9997390	0.9998224	0.9924199	0.9977853	0.9975515	-0.95%
	Illinois basin coal (sample 2)	0.9972784	0.9988115	0.9990980	0.9884587	0.9991271	0.9984508	2.37%
	Kyungdong coal (3.66% moisture, 65°C)	0.9925883	0.9930618	0.9935709	0.9729398	0.9801337	0.9730292	94.82%
	Kyungdong coal (3.64% moisture, 45°C)	0.9915300	0.9919361	0.9926605	0.9713228	0.8897028	0.9713228	93.81%
	Kyungdong coal (dry, 65°C)	0.9866048	0.9956886	0.9866048	0.8834720	0.9791517	0.8834720	212.27%
	Kyungdong coal (dry, 45°C)	0.9416289	0.9869085	0.9416289	0.7802417	0.9585394	0.7802417	312.78%
Zhou et al., 2013	South Qinshui Basin coal	0.9986270	0.9998802	0.9999951	0.9986850	0.9999851	0.9996967	12.40%

Table 4 Correlation coefficients for fitting subcritical CO₂ sorption data from different models and calculated values. Yellow and blue grids represent best and second-best fitting model for each group of data, respectively.

Reference	Coal sample	Correlation coefficient (R ²) for fitting adsorption data			Correlation coefficient (R ²) for fitting desorption data			IHI
		Langmuir model	D-R model	Dual sorption model	Langmuir model	D-R model	Dual sorption model	
Pariti, 1992	San Juan Basin coal	0.9979057	0.9985769	0.9979057	0.9947013	0.9971629	0.9947013	21.64%
	Illinois coal	0.9855028	0.9993652	0.9997122	0.9444343	0.9920313	0.9849749	20.20%
	North Dakota Beulah-Zap coal	0.9946735	0.9999597	0.9995629	0.9390034	0.9823262	0.9726423	25.17%
Busch et al., 2003	Pennsylvania Upper Freeport coal	0.9940157	0.9997229	0.9978185	0.9541614	0.9834409	0.9645166	36.24%
	Pocahontas #3 coal	0.9974784	0.9990490	0.9992214	0.9751047	0.9904941	0.9842831	29.92%
	Wyodak coal	0.9948058	0.9998650	0.9997931	0.9536866	0.9899930	0.9764757	34.66%
	Beulah-Zap coal (Lab A, dry)	0.9686096	0.9990192	0.9994673	0.9961147	0.9993364	0.9996365	14.39%
	Beulah-Zap coal (Lab A, as-received)	0.9926671	0.9995811	0.9999172	0.9992707	0.9925298	0.9997384	25.44%
	Beulah-Zap coal (Lab D)	0.9776558	0.9991859	0.9963545	0.9988129	0.9996767	0.9988129	42.59%
	Illinois coal (Lab A, dry)	0.9789694	0.9986804	0.9999012	0.9939254	0.9997687	0.9988117	10.20%
	Illinois coal (Lab A, as-received)	0.9967963	0.9995792	0.9994196	0.9992027	0.9998133	0.9998024	15.14%
	Illinois coal (Lab D)	0.9970102	0.9997163	0.9991254	0.9996743	0.9999193	0.9998624	1.38%
Goodman et al., 2004	Pocahontas coal (Lab A, dry)	0.9935470	0.9999310	0.9996938	0.9981286	0.9998430	0.9999520	-4.03%
	Pocahontas coal (Lab A, as-received)	0.9979803	0.9995218	0.9992204	0.9997440	0.9999974	0.9997440	3.43%
	Pocahontas coal (Lab D)	0.9992137	0.9994495	0.9992137	0.9994471	0.9998306	0.9994471	-0.82%
	Upper Freeport coal (Lab D)	0.9992060	0.9402503	0.9992615	0.9985362	0.9992660	0.9985362	24.38%
	Wyodak-Anderson coal (Lab A, dry)	0.9796354	0.9997138	0.9989695	0.9966573	0.9999104	0.9999781	6.91%
	Wyodak-Anderson coal (Lab A, as-received)	0.9924771	0.9996424	0.9996569	0.9952400	0.9996096	0.9997163	6.38%
	Wyodak-Anderson coal (Lab D)	0.9962730	0.9994181	0.9985469	0.9997868	0.9998820	0.9997868	56.83%
Ozdemir et al., 2004	Wyodak coal	0.9782431	0.9994476	0.9995107	0.9861645	0.9994615	0.9982541	23.50%
	Blind Canyon coal (dry)	0.9881057	0.9999791	0.9990814	0.9981424	0.9998218	0.9996339	11.33%
	Blind Canyon coal (as-received)	0.9972499	0.9995727	0.9993998	0.9991895	0.9999488	0.9998569	14.53%
	Lewiston-Stockton coal (dry)	0.9807058	0.9997018	0.9991380	0.9989966	0.9995509	0.9996984	12.03%
	Lewiston-Stockton coal (as-received)	0.9930101	0.9993377	0.9991266	0.9988432	0.9994375	0.9992583	12.75%
Ozdemir, 2004	Pittsburgh No. 8 coal (dry)	0.9875163	0.9995803	0.9992345	0.9987172	0.9999202	0.9999009	4.38%
	Pittsburgh No. 8 coal (as-received)	0.9961080	0.9993267	0.9997816	0.9991289	0.9998446	0.9996704	12.71%
	Upper-Freeport coal (dry)	0.9976124	0.9993807	0.9998579	0.9993396	0.9997707	0.9998718	10.34%
	Upper-Freeport coal (as-received)	0.9997844	0.9996081	0.9997917	0.9999863	0.9999857	0.9999872	15.46%

Jessup et al., 2008	Powder River Basin coal	0.9948253	0.9953996	0.9948693	0.9886831	0.9871863	0.9890767	40.53%
Harpalani et al., 2006	San Juan Basin coal	0.9956931	0.9956717	0.9956931	0.9947478	0.9985911	0.9974614	19.17%
	Illinois Basin coal	0.9988085	0.9996440	0.9992337	0.9957490	0.9982918	0.9957490	24.93%
Pan et al., 2010	Sydney Basin coal (0% moisture)	0.9902710	0.9995882	0.9999911	0.9814990	0.9997993	0.9996175	9.76%
	Sydney Basin coal (3.3% moisture)	0.9989085	0.9998833	0.9999532	0.9963470	0.9998182	0.9995330	13.98%
	Sydney Basin coal (5.1% moisture)	0.9986160	0.9999739	0.9999997	0.9974692	0.9999209	0.9997791	18.72%
	Sydney Basin coal (8.5% moisture)	0.9999311	0.9999997	0.9999998	0.9947549	0.9977301	0.9959319	24.77%
	15th seam coal	0.9983891	0.9982977	0.9983891	0.9976411	0.9983732	0.9976445	29.64%
	16th bottom seam coal	0.9995844	0.9995302	0.9995846	0.9977901	0.9985246	0.9977901	27.13%
	16th top seam coal	0.9975642	0.9979480	0.9975642	0.9973871	0.9981439	0.9973871	34.61%
	18th seam coal	0.9956517	0.9971159	0.9987192	0.9962633	0.9973761	0.9962633	48.09%
	Borga coal	0.9932879	0.9997154	0.9971754	0.9916183	0.9991989	0.9978878	36.60%
	Kallam coal	0.9978416	0.9995634	0.9997906	0.9984443	0.9991935	0.9985316	27.50%
Dutta et al., 2010	Kenda coal	0.9961990	0.9982011	0.9988595	0.9969746	0.9994949	0.9988707	37.93%
	Local II coal	0.9997196	0.9995751	0.9997196	0.9967815	0.9975918	0.9967815	24.75%
	Mehaladi coal	0.9984239	0.9998834	0.9996456	0.9975966	0.9982349	0.9976509	22.63%
	Muzma Special coal	0.9997049	0.9997690	0.9997289	0.9976680	0.9981676	0.9976680	22.08%
	Naravankur coal	0.9952526	0.9994407	0.9997720	0.9879882	0.9996774	0.9995231	11.46%
	Satgram coal	0.9953229	0.9988790	0.9996061	0.9913123	0.9998239	0.9990362	26.38%
	SKAC 1 coal	0.9994798	0.9999555	0.9998323	0.9961317	0.9972363	0.9961317	34.84%
	SKAC 2 coal	0.9995953	0.9996366	0.9995953	0.9964362	0.9972029	0.9964362	26.05%
Zhou et al., 2013	South Qinshui Basin coal	0.9989295	0.9999893	0.9998440	0.9955221	0.9971307	0.9955221	93.54%

Table 5 Correlation coefficient and the order of polynomial for fitting supercritical CO₂ sorption data by using polynomial, and calculated values of IHI.

Reference	Coal sample	Adsorption		Desorption		IHI
		Order of polynomial	Correlation coefficient (R ²)	Order of polynomial	Correlation coefficient (R ²)	
Ozdemir, 2004	Illinois coal	6	0.9949772	4	0.9938965	96.23%
	Pittsburgh No.8 coal	6	0.9952342	8	0.9912296	60.18%
	Upper Freeport coal	8	0.9930832	7	0.9907476	117.08%
	Wyodak coal	6	0.9918789	5	0.9940749	93.88%
Battistutta et al., 2010	Selar Cornish coal A (45°C)	4	0.9905556	5	0.9909451	21.01%
	Selar Cornish coal B (45°C)	6	0.9905738	4	0.9979742	57.59%
	Selar Cornish coal (65°C)	4	0.9961618	3	0.9994271	-27.20%
Kim et al., 2011	Kyungdong coal (dry, 45°C)	6	0.9905737	9	0.9817374	26.33%
	Kyungdong coal (dry, 65°C)	5	0.9908901	5	0.9974277	95.51%
	Kyungdong coal (3.64% moisture, 45°C)	9	0.9764189	9	0.9849827	117.35%
	Kyungdong coal (3.66% moisture, 65°C)	7	0.9901256	5	0.9968484	51.90%

In comparison:

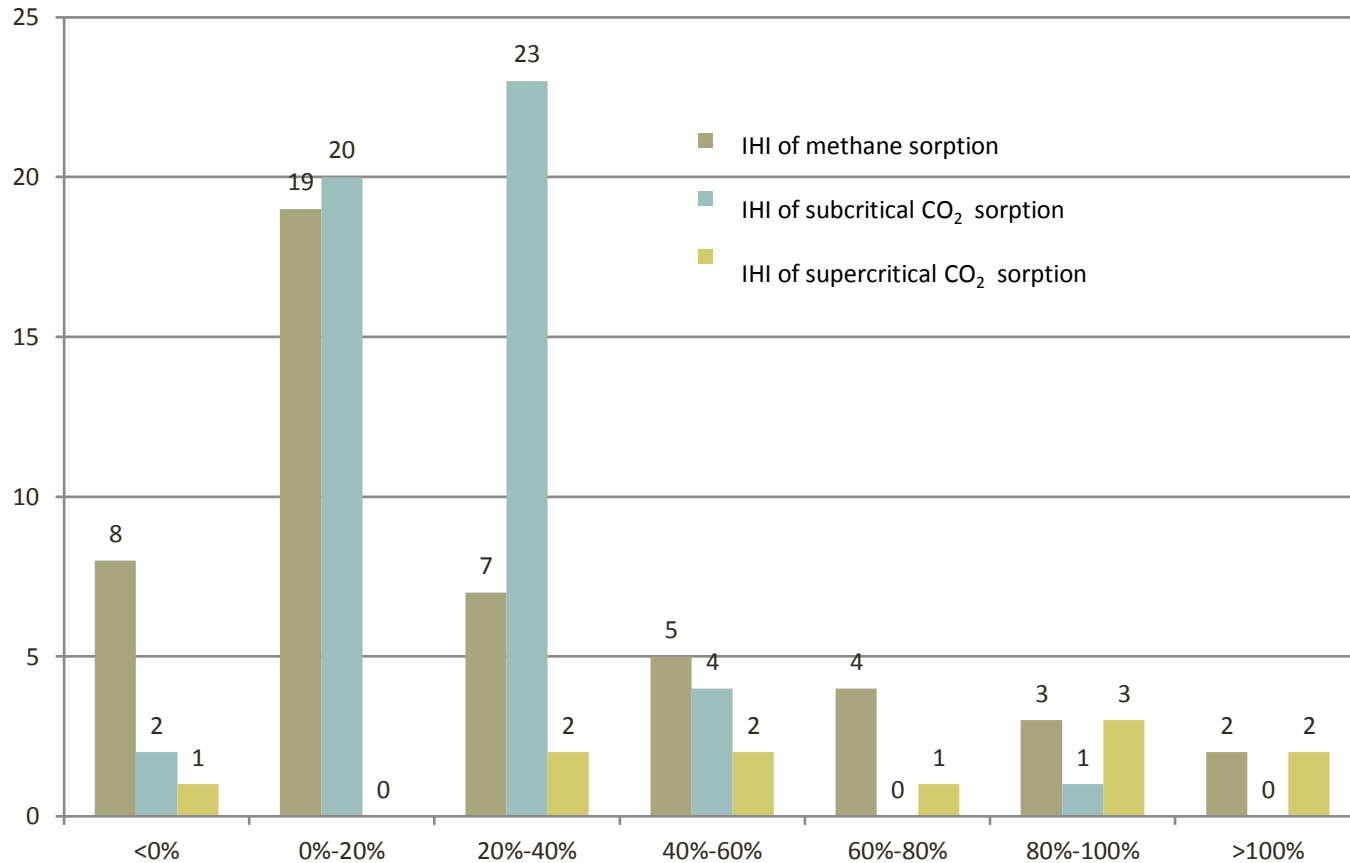
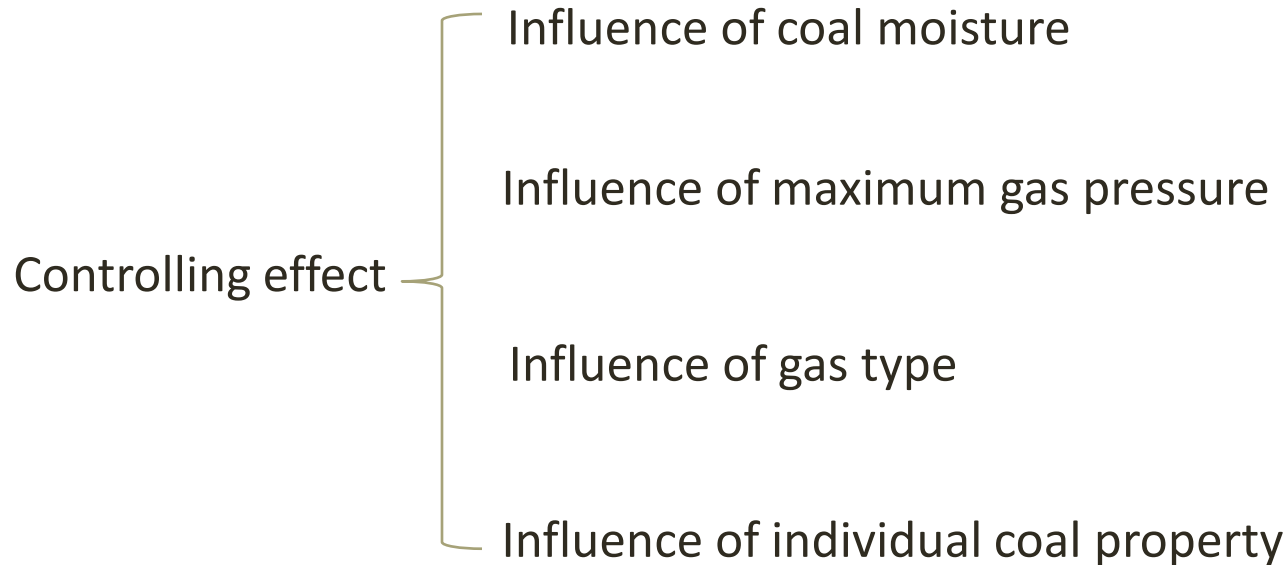


Fig. 5 Comparison of the numbers of methane, subcritical CO₂ and supercritical CO₂ IHI in different scales

4. Controlling factors and possible explanation of sorption hysteresis on coal



Note:

Different groups are chosen for minimising the influence of other factors when investigating the individual influence of each factor on hysteresis.

If the correlation between a factor and the IHI are strong disregarding the discrepancies of other factors, the relationship between this factor and the degree of hysteresis can be seen to correlate.

The influence of moisture on hysteresis

$$IC = \frac{IHI_{\text{wet}} - IHI_{\text{dry}}}{IHI_{\text{wet}}} \times 100\%$$

Conclusion: the hysteresis degree decreases after drying the coal sample, however there is no distinct tendency between the influence coefficient and the moisture of the wet coal sample.

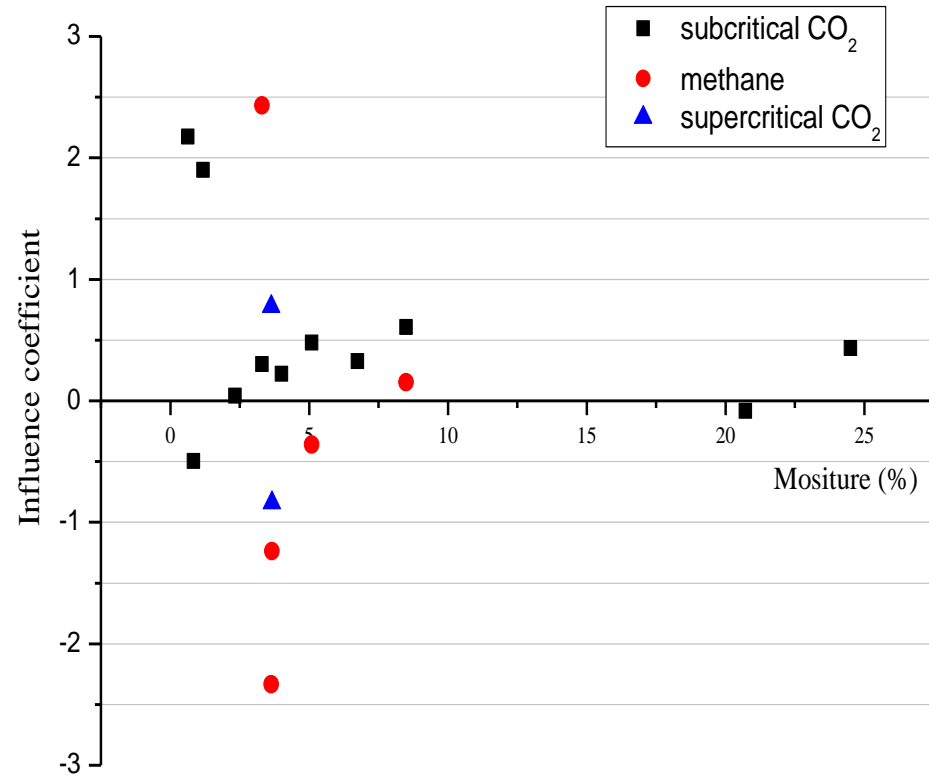


Fig. 6 Influence coefficient versus the moisture of wet sample, red, black and blue points represent methane, subcritical and supercritical CO₂ sorption, respectively.

The influence of maximum CO₂ pressure on hysteresis

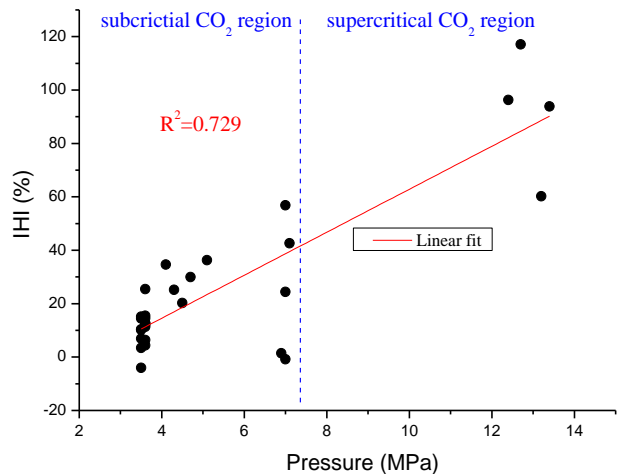


Fig. 7 IHI of experiments conducted on different Argonne coals versus the maximum gas pressure

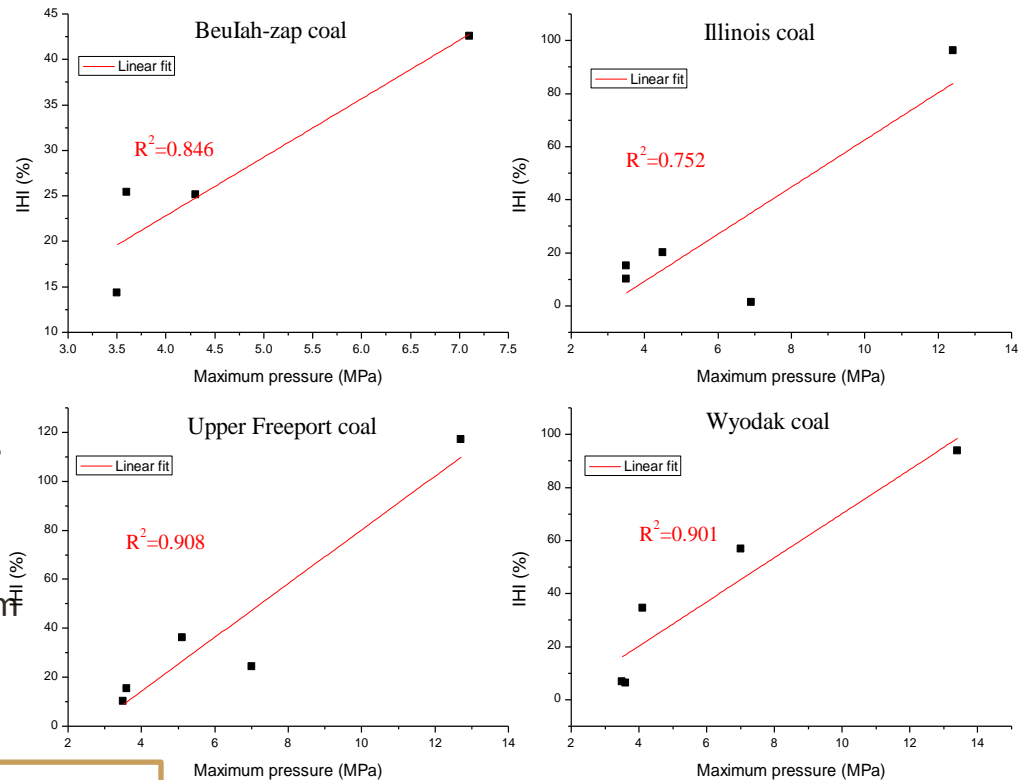
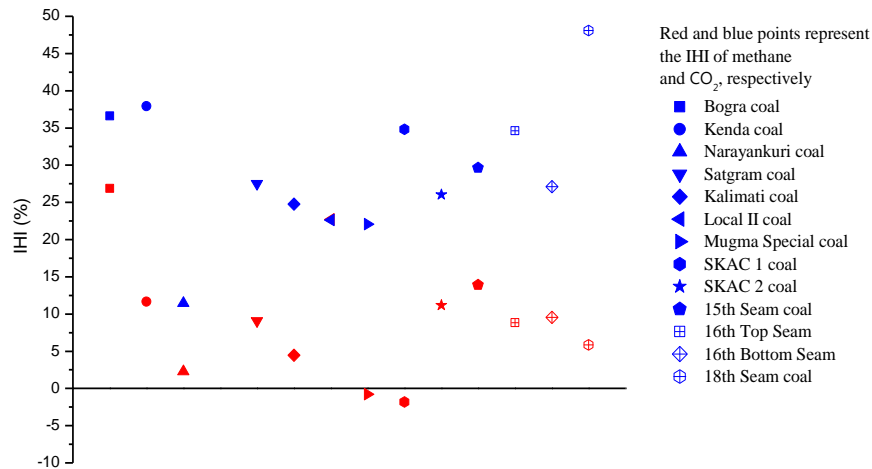


Fig. 8 IHI of experiments conducted on individual coal sample versus the maximum gas pressure

Conclusion: the maximum pressure of CO₂ has a strong controlling effect on the degree of hysteresis.

However, no systematic relationship between the maximum pressure of methane and the corresponding degree of hysteresis can be established when the influence of other factors cannot be ruled out.

The influence of gas type on hysteresis



Conclusion: the CO₂ hysteresis is stronger than methane hysteresis, however the hysteresis phenomenon is also present in methane sorption.

Fig. 9 Comparison of IHI between methane and CO₂ sorption

The influence of coal properties on hysteresis

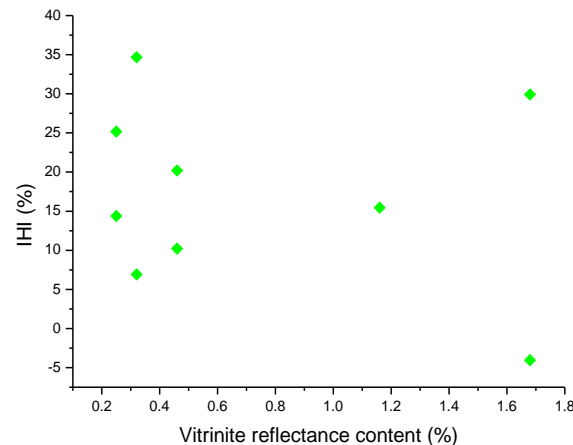


Fig. 10 IHI of Argonne coals from dried samples and same temperature (22°C) versus vitrinite reflectance content

IHI versus different coal properties

▲ CO₂
● methane

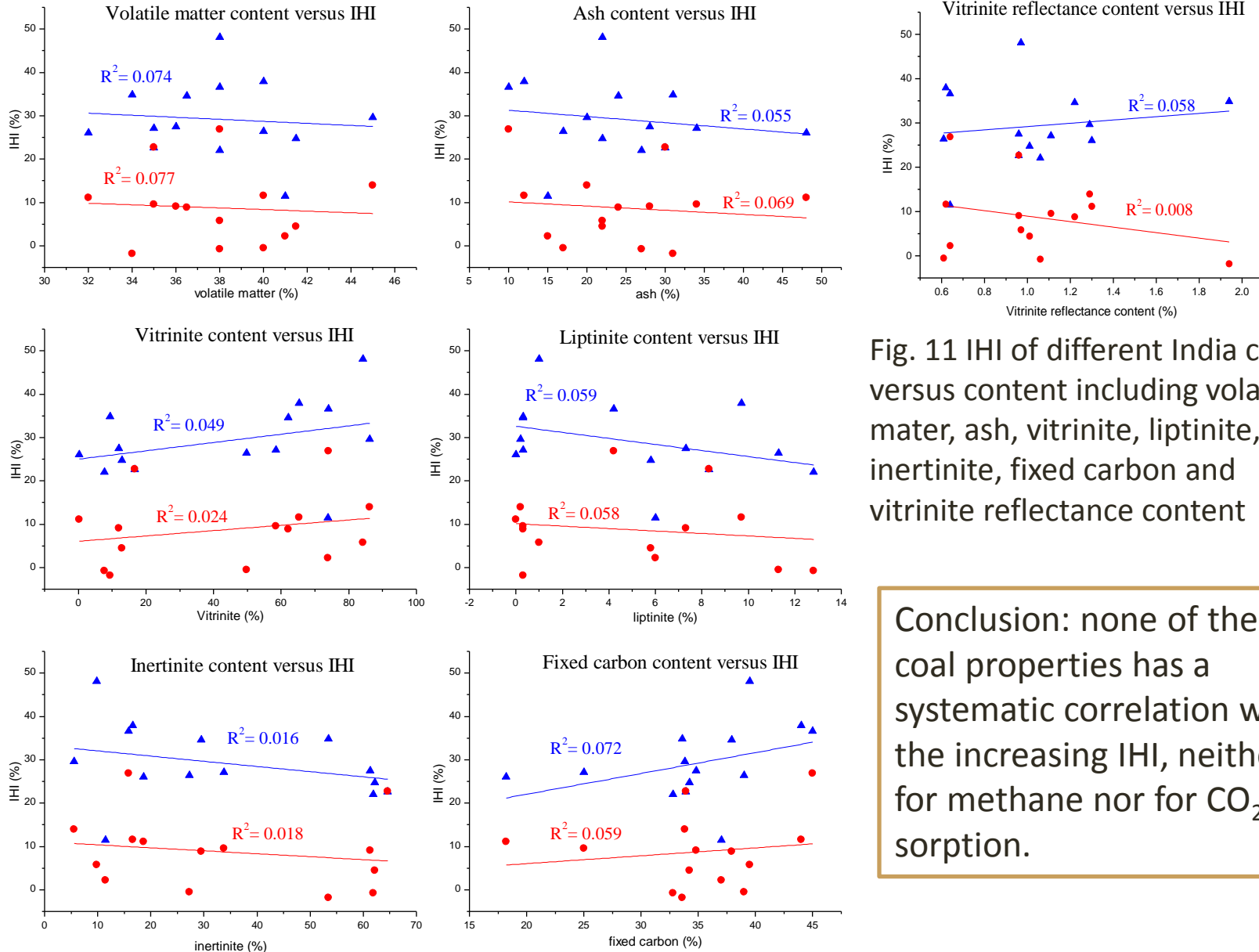


Fig. 11 IHI of different India coals versus content including volatile mater, ash, vitrinite, liptinite, inertinite, fixed carbon and vitrinite reflectance content

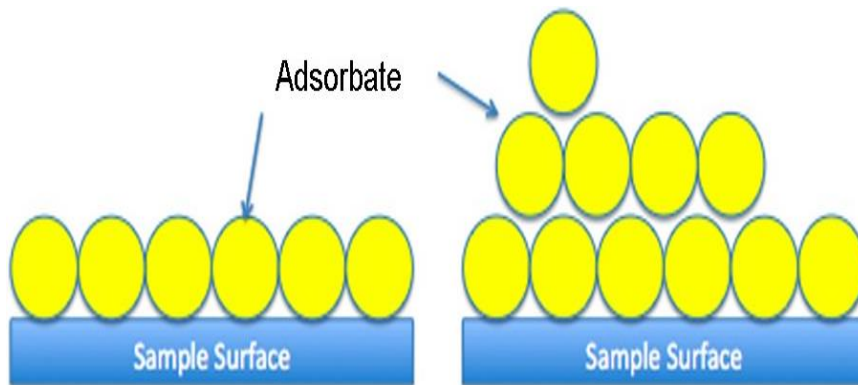
Conclusion: none of the coal properties has a systematic correlation with the increasing IHI, neither for methane nor for CO₂ sorption.

Interpretation of methane and CO₂ sorption hysteresis

Physical sorption or chemisorption?

The direct interaction between CO₂ and two Argonne coals at pressures up to 8.0 MPa was investigated by Goodman et al. (2005a, b), attenuated total reflectance-Fourier transformation infrared (ATR-FTIR) spectroscopy was used, and the spectral data indicated that only one type of site was available for sorption. No evidence could be found for specific interactions between CO₂ and oxygen functional groups in the coals.

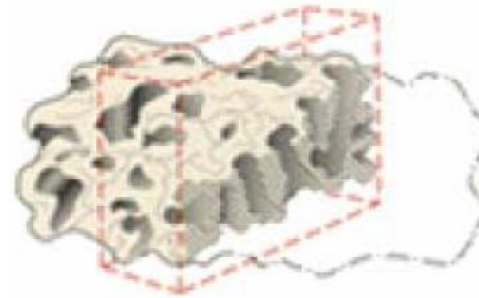
Which kind of physical sorption may relate to sorption hysteresis?



monolayer
adsorption



multilayer
adsorption

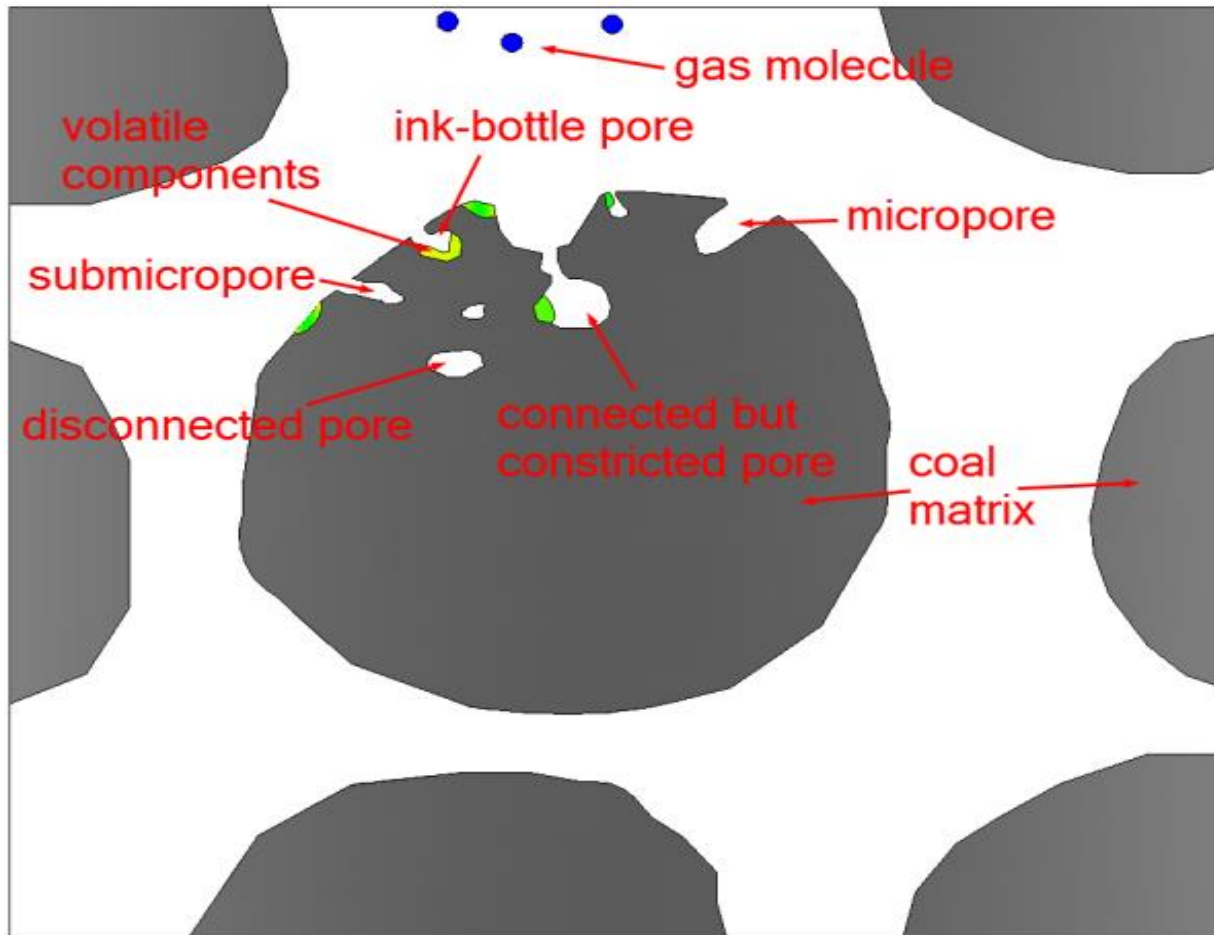


pore filling
adsorption

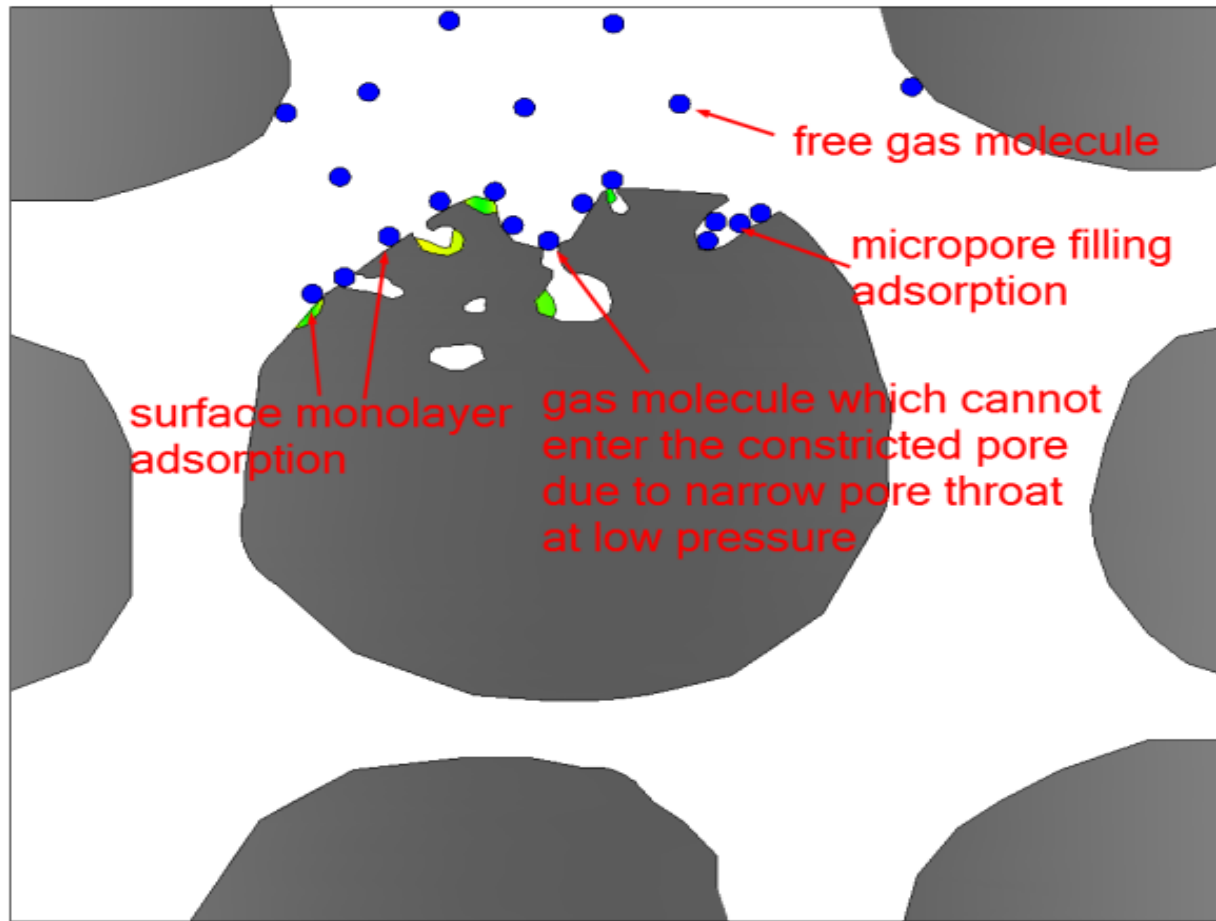


coal swelling and sorption hysteresis?

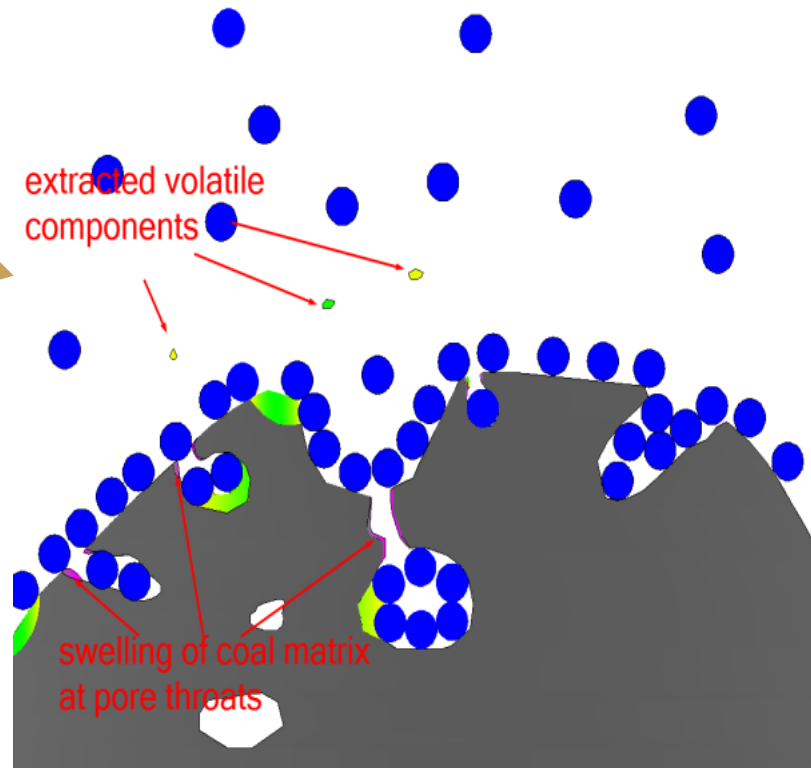
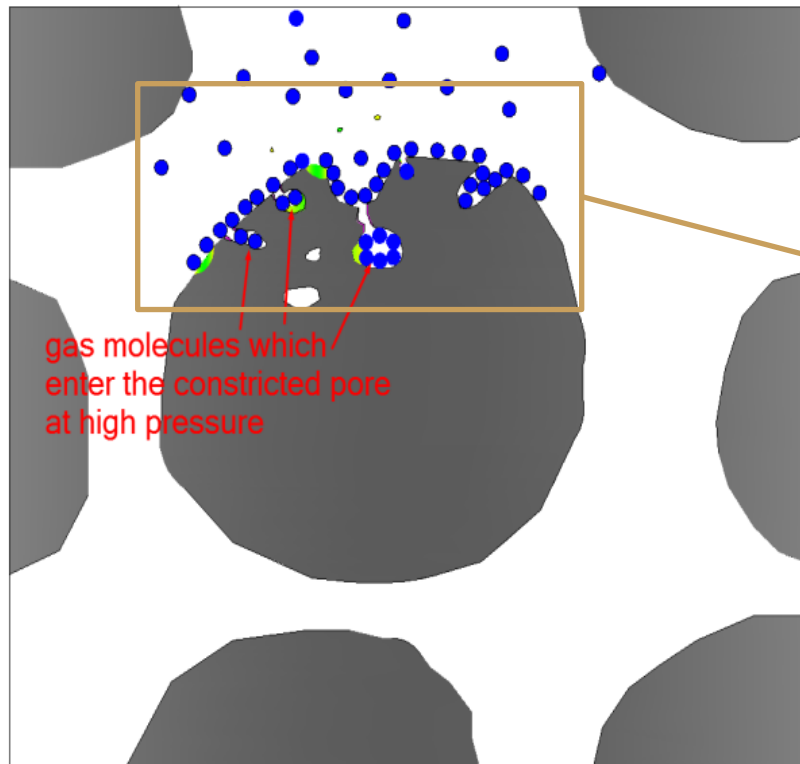
- It is believed that the filling of submicropores and the penetration into the organic mass of coal by gas molecules are the reasons for coal swelling (e.g., Milewska-Duda et al., 2000), which may causes the deformation of the pore and pore throats.
- The change of pore throats induces the different energies required for entering and escaping from the constricted pores, and thus accounts for the sorption hysteresis.



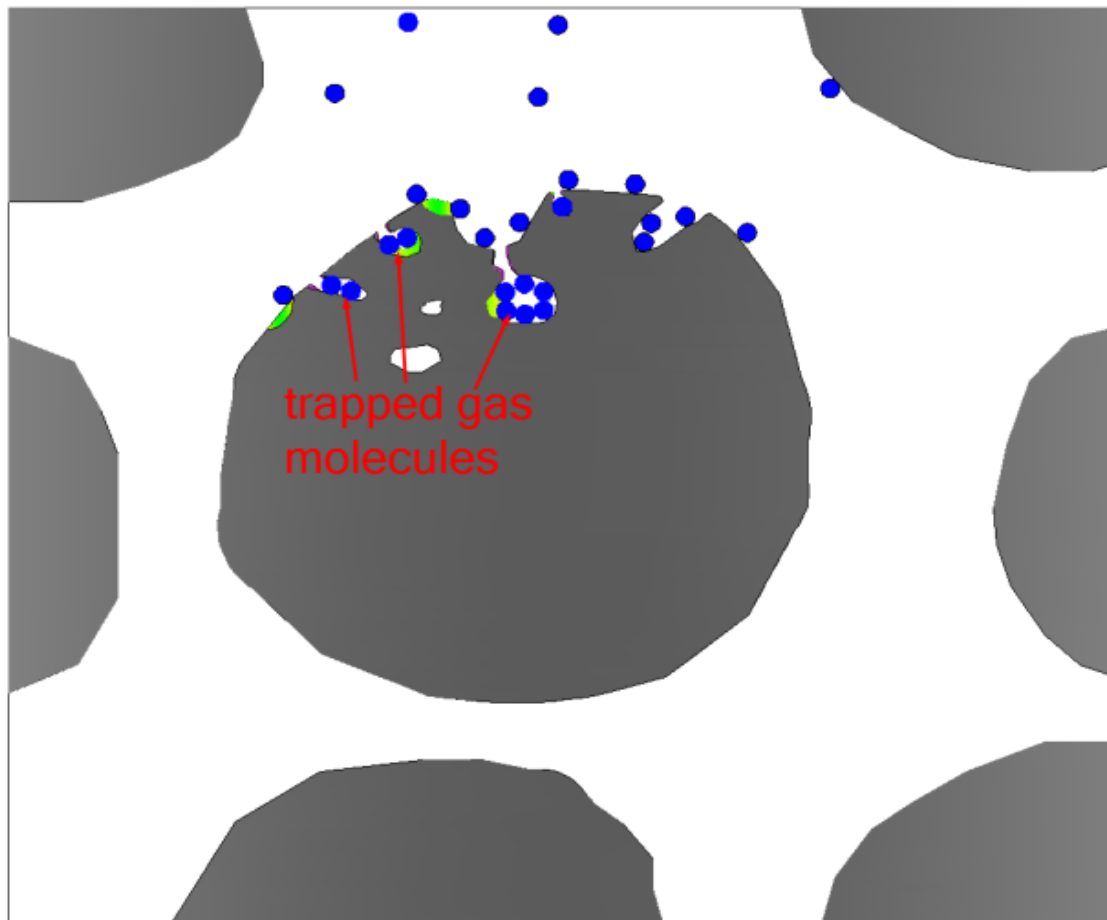
a) coal matrix system with different pore shapes



b) gas sorption at low pressure in the adsorption process



c) gas sorption at high pressure in the adsorption process



d) gas sorption at low pressure in the desorption process

A possible explanation for sorption hysteresis on coal

- Coal contains constricted pores with narrow pore throats, which are smaller than the kinetic diameters of methane and CO₂.
- The gas molecules can enter the constricted pores with increasing gas pressure, but this leads to swelling of the coal matrix which further narrows the pore throats.
- During depressurization, the gas molecules which have entered can escape from the constricted pores through the further narrowed pore throats, but this requires more energy than that which enables them to enter the pores. In other words, during the desorption process, fewer gas molecules can escape from the constricted pores of coal than the sorption volume in the adsorption process at the same gas pressure. This is the origin of methane and CO₂ sorption hysteresis.

Note: not only the in-bottle type pore, but also other pore structures with narrow pore throats, such as submicropores, macromolecular and molecular fractions, contribute to the sorption hysteresis, because all the pore configurations have identical properties in term of kinetic restriction for gas molecules.

Controlling factors

maximum pressure of CO_2

More gas molecules can enter the constricted pores with narrow pore throat during pressurization

gas type

Compared to methane (0.38nm), CO_2 molecules have a smaller kinetic diameter (0.33nm) and a larger quadrupole moment, and this results in higher interaction energy with the coal matrix, thus more CO_2 molecules can enter the constricted pores at the same gas pressure.

moisture

the pore which is occupied by easy-to-escape water molecules will be re-available due to the loss of water, and the gas molecules can be adsorbed in the re-available pores during desorption

independent

individual
coal
properties

The development of micropores and submicropores of coal is both type- and rank-dependent, since these constricted pores are not detectable by conventional methods, the relationship between the constricted pores and the coal property is still mysterious till now.

5. Influence of sorption hysteresis on gas drainage of high CO₂ coal seams

- **Hard-to-drain areas** are found in the Bulli coal seam of Sydney Basin, Sydney Basin such as Tahmoor, Metropolitan, Appin and West Cliff mines. **Extended drainage time (not compatible with mine development) is required** for reducing the gas content in coals to the threshold value by using traditional borehole-drainage method, even with additional boreholes.
- Previous studies show a common characteristic of these regions is the higher concentration of CO₂, hence they are named as '**High CO₂ coal seam**'.

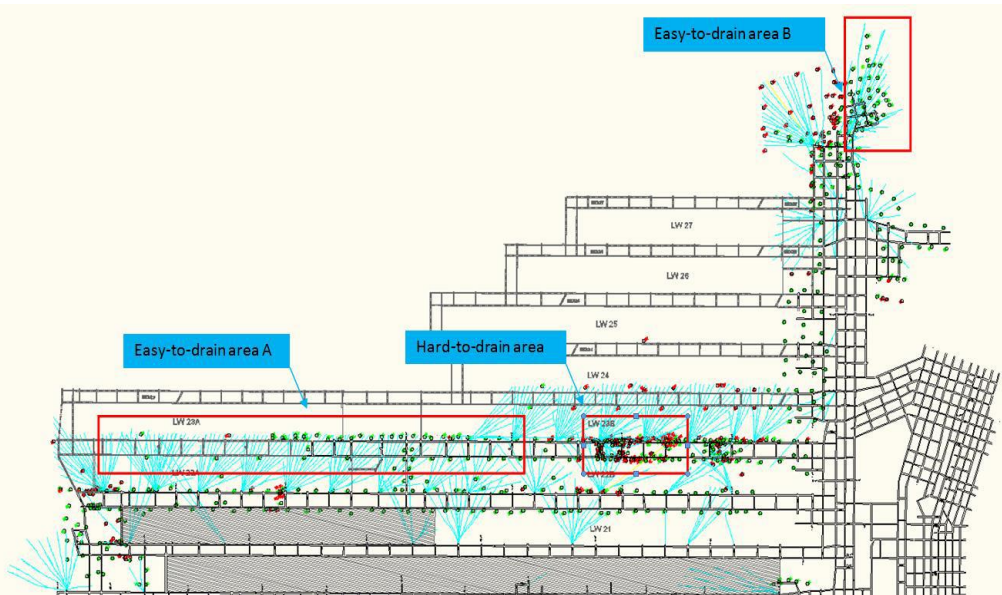
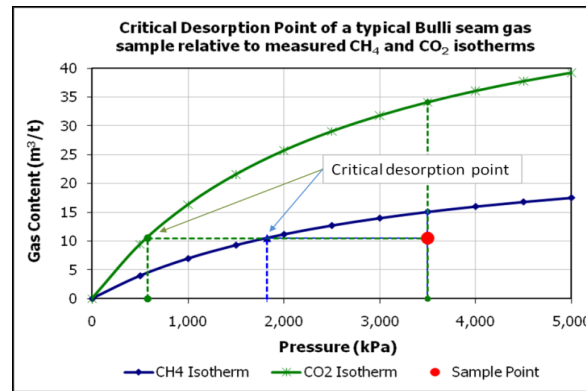


Fig. 12 hard-to-drain and easy-to-drain areas of Metropolitan mine

Why is the high CO₂ coal seam hard-to-drain?

Difference of
adsorption capacity

a larger volume of CO₂ need to
desorb than methane

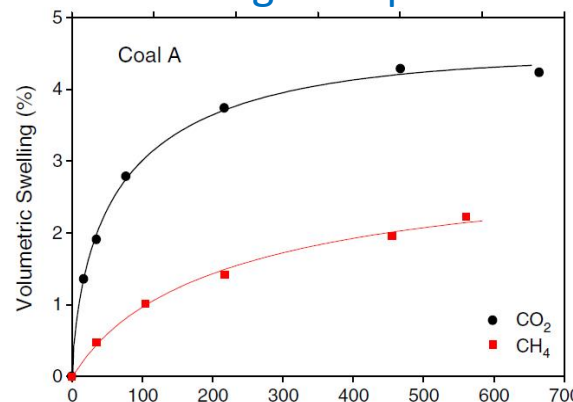


Critical
desorption point
of a typical Bulli
seam gas sample
relative to
measured
methane and CO₂
isotherms
(Black, 2011)

Difference of gas
permeability

the larger sorption-induced-swelling of CO₂

What's the influence of
sorption hysteresis?



coal swelling induced by
CO₂ and methane
sorption with respect to
gas pressure

Sorption test



crusher machine

Sample preparation



different sizes of sieve

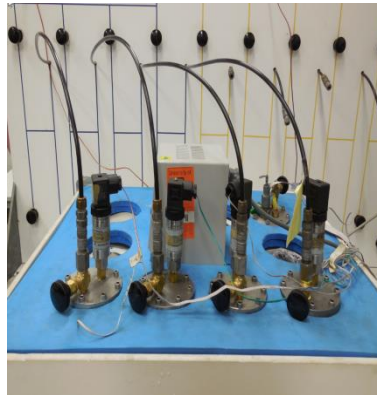


automatic shaking rig

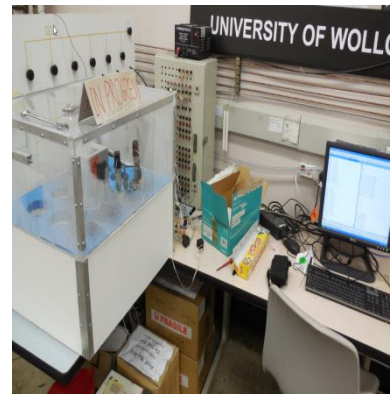
Sorption test apparatus



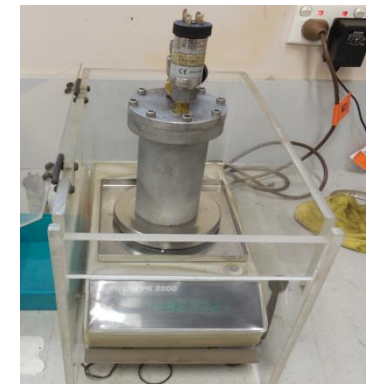
gas supply



sorption bomb



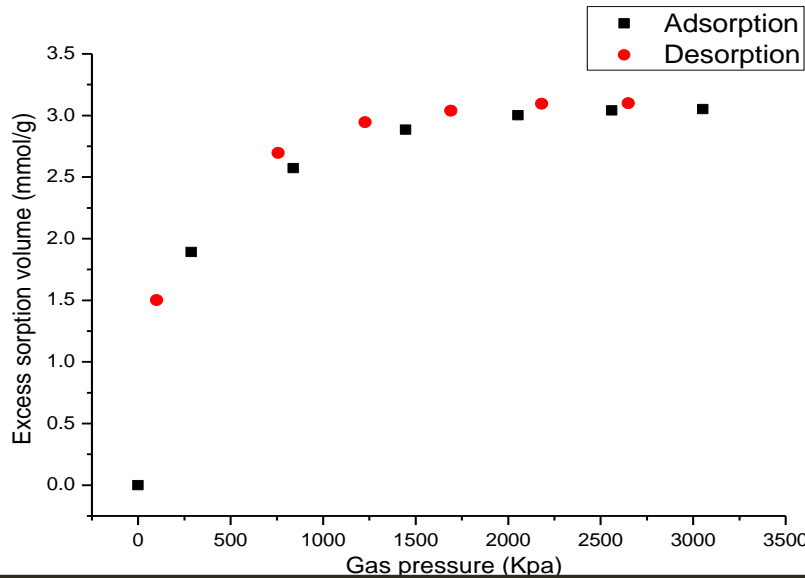
whole system



high accurate
balance

Aim: study the influence of gas type, sample size, experimental temperature, maximum pressure on the degree of hysteresis.





Sample from: Tahmoor Mine
 Temperature: 308K
 Sample Size: 1.13-2.36mm
 Gas: CO₂(99.999%)

Desorbed CO₂ volume without considering hysteresis: V1
 Desorbed CO₂ volume with considering hysteresis: V2

Gas pressure dropping from 3MPa to 1MPa:

V1=8.1m³/t V2=4.3m³/t

Gas pressure dropping from 3MPa to 0.5MPa:

V1=17.2m³/t V2=10.4m³/t

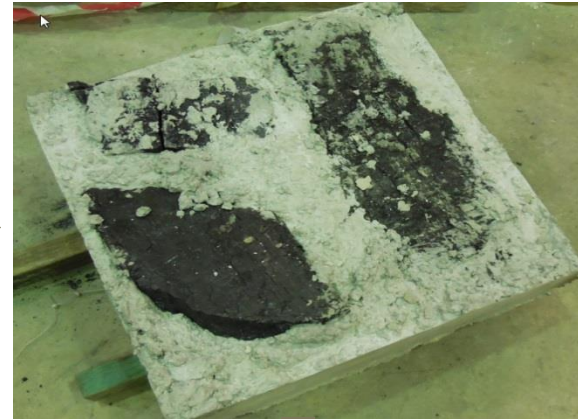
Gas pressure dropping from 3MPa to 0.2MPa:

V1=33.3m³/t V2=23.3m³/t

Recommendation:
 Desorption isotherm
 should be tested in
 laboratory, and used for
 predicting gas emission
 and drainability.

Permeability test

Sample preparation



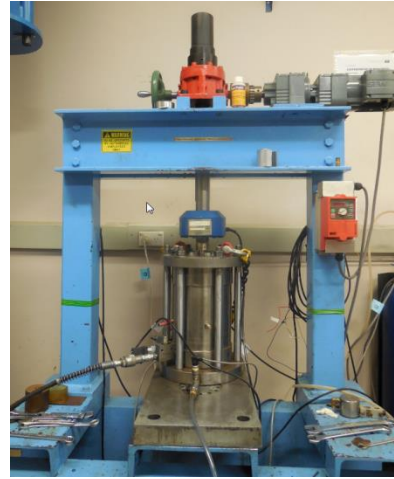
High pressure permeability test apparatus with three kinds of gas



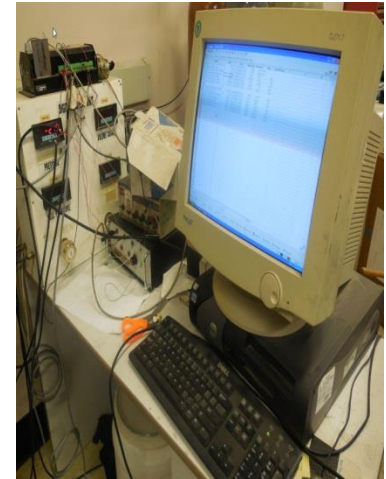
gas cylinders



oil pump



pressure cell



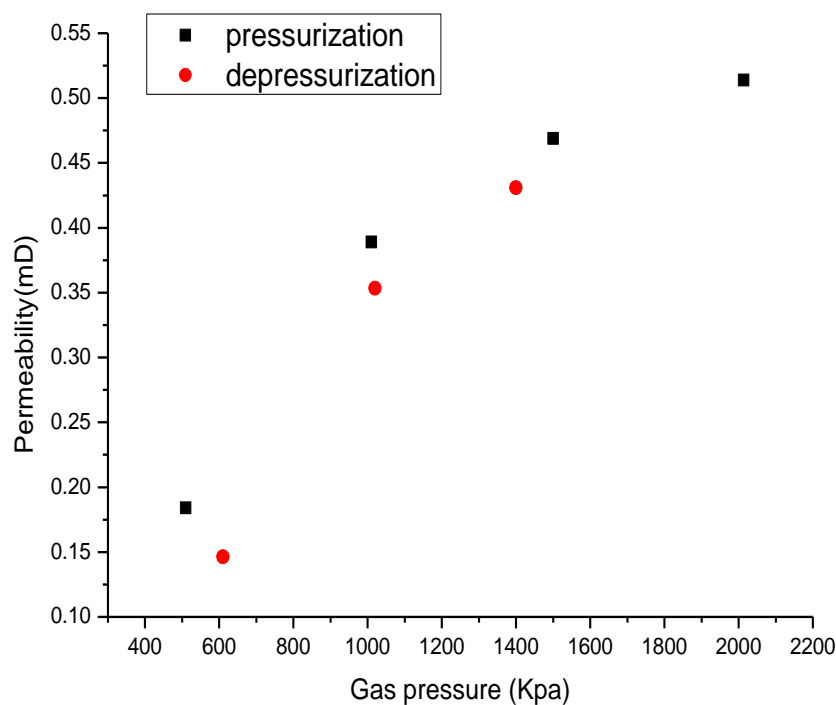
data acquisition

Aim: determine the relationship between sorption swelling, effective stress, direction of coal, and the permeability hysteresis with respect to sorption hysteresis.

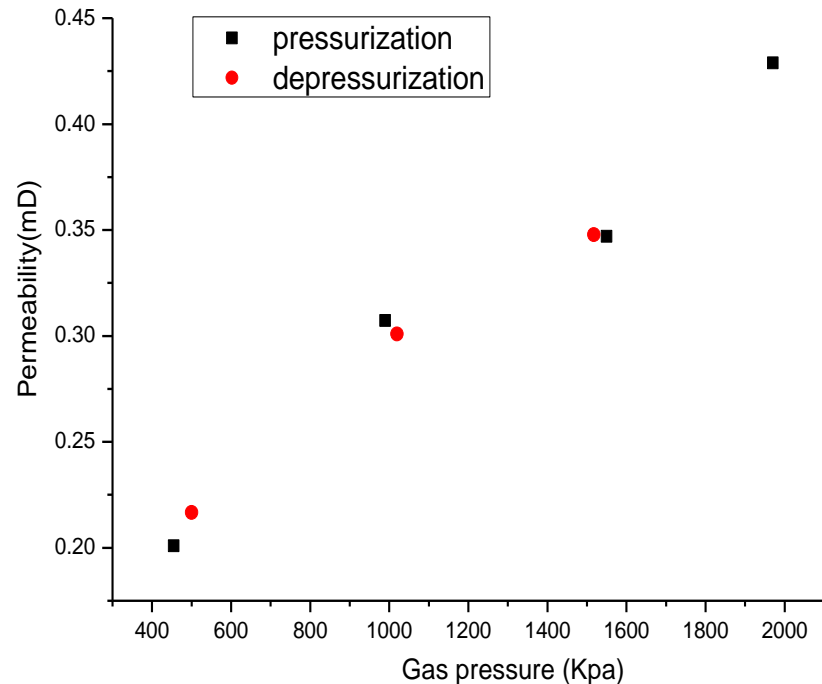
Sample from: Tahmoor Mine Temperature: 293K

Confining stress: 3Mpa Loading stress: 2Mpa

Equilibrium is considered to be reached
until the flux is stable for at least two hours



Permeability with CO₂



Permeability with Nitrogen

Recommendation:

Permeability test should be tested during depressurization!

6. Conclusion and future work

- Methane and CO₂ sorption hysteresis is **detrimental to CBM recovery and gas drainage of high CO₂ coal seam**. Strong hysteresis means a large proportion of gas cannot desorb until the gas pressure drops to a very low level.
- The **minable methane reserves may be less than expected** due to the existence of un-desorbed methane.
- Hysteretic methane and CO₂ will induce extra coal swelling. This will **decrease the permeability** of the gas in coal, and then **reduce the production of CBM and gas drainage efficiency of high CO₂ coal seam**.
- Both adsorption and desorption isotherms on coal should be measured in **sorption tests**, especially when the result is used for estimating the gas emission volume of coal seams.
- **Permeability test** used for predicting gas drainage should be conducted during depressurization .

6. Conclusion and future work

Nitrogen flush technology is suggested to be used for enhancing the drainage efficiency of high CO₂ coal seam since:

- 1) The injected N₂ can maintain or enhance the gas pressure in coal cleat system, hence reduce the effective stress then increase the gas permeability.
- 2) The sorption capacity of N₂ is much less than that of coal seam gas (methane and CO₂), thus the N₂ flush can reduce the gas content in coal sharply even if only part of coal seam gas is replaced by N₂.
- 3) matrix swelling is proportional to the volume of sorbed gas, the coal swelling induced by N₂ sorption is much less than by coal seam gas sorption and will not be detrimental to the gas permeability even if the injection pressure of N₂ is relatively high.
- ACARP proposal submitted for funding (2014)

Acknowledgements:

- ❖ Supports from Tahmoor Colliery and Metropolitan Colliery
- ❖ Scholarships from China Scholarship Council and University of Wollongong
- ❖ Technical staff at UOW

Questions and Discussion

Ian Gray, Sigra – Many of these pathways have been trodden before in much detail. The fact that you are measuring permeability on core samples is nonsense. You should be looking at mass measurements of permeability in-situ because of the importance of cleating. Do not consider core pressure measurements as being of any value whatsoever in the gas drainage process. I know that sounds negative, but it is from practical experience. I built the core pressure gear in the early 1990's and have been through the learning curve.

Ting Ren – We never intended to use the laboratory testing to infer bulk permeability. We know that in-situ permeability is very different. But the laboratory test will at least give some indication that some coals have different permeability. The testing in the laboratory will give an indication of how permeable a coal sample is. If we can get more data, perhaps on drillability or how easily the seam can be drained it will be useful. If you do the laboratory permeability test and the isotherms through the de-stressing process, you might get a more realistic indication rather than estimates of permeability. Using the conventional isotherms and gas content, the gas drainage volumes might be slightly overestimated. From a practical point of view, the estimates might be too optimistic and you might be facing a potential outburst.