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Prediction for CH_4 adsorption isotherm based on DA model

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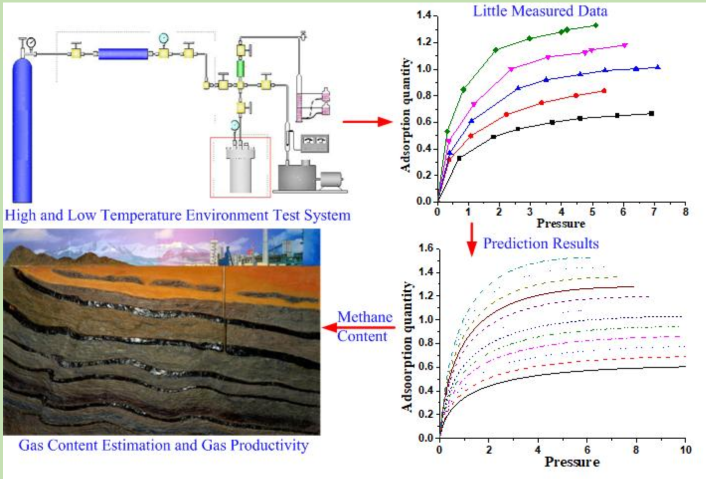

Abstract: Methane adsorption characteristics in coal play an important role in the gas content estimation and gas productivity prediction in coal-bed, one group of methane adsorption data in coal under a certain temperature is only applicable to the adsorption isotherm in this temperature which can't predict methane adsorption capacity under other temperature and pressure conditions. In the practical work, both the coalbed methane resources exploration and the prevention and control of gas disaster in coal mine need to know methane adsorption characteristics in coal seam at certain temperatures and depth. Because there are differences of methane adsorption isotherms at different temperatures, so many adsorption isotherms need to test at each temperature, which will cause high cost and long time. So according to the metamorphic grade of coal, gas-fat coal, cooking coal, meager coal and anthracite coal were chosen as test coal samples, methane isothermal adsorption tests at 243.15, 263.15, 283.15, 303.15 and 323.15 K were carried out with high and low temperature environment test system for gas adsorption and desorption. Based on Dubinbin–Astakhov (DA) equation and polanyi adsorption potential theory, the relationships of saturated adsorption quantity and characteristic adsorption energy with temperature can be gotten by fitting the measured data, and then the gas adsorption isotherm of coal at other temperature were predicted. The results showed that the gas adsorption capacity of coal with different metamorphic degree increased with the temperature decreasing, and there had good linear relationships between the gas saturated adsorption capacity and the characteristic adsorption energy of different metamorphic coals, which correlation coefficients reached above 0.98. At the same temperature, as the coal metamorphism degree increases, the methane adsorption amount increases under the same adsorption equilibrium pressure. Under different temperatures the predicted adsorption isotherms of coal based on the DA model with different metamorphic degrees agreed well with the experimental results. The relative error was no more than 5%. With little measured data of isothermal adsorption tests, DA model can accurately predict the adsorption abilities of coal at different temperatures and pressures, which will greatly reduce the workload and provide an important basis to study the coal reservoir adsorption properties.

Key words: DA model; isothermal adsorption curve; high/low temperature environment; theoretical prediction

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基于 DA 模型的煤表面甲烷吸附线预测

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摘　要： 采用高低温甲烷吸附解吸测试系统，在 243.15, 263.15, 283.15, 303.15 和 323.15 K 下用不同变质程度的煤(气肥煤、焦煤、贫煤和无烟煤等)对甲烷进行等温吸附，基于微孔填充 Dubinbin–Astakhov(DA)模型对其它环境温度下煤的 CH_4 吸附等温线进行预测. 结果表明，不同变质程度的煤对甲烷的吸附量均随温度降低而增大，且饱和吸附量和特征吸附能与温度具有良好的线性关系. 模型预测的等温吸附曲线与实验结果吻合较好，相对误差不超过 5%.

关键词： DA 模型；等温吸附线；高低温环境；理论预测

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1　前　言

不同温度下煤的吸附等温线是研究煤层吸附性能的重要依据[1]，煤层气资源勘探开发和煤矿瓦斯灾害防治需利用已知深度煤层在一定温度下的甲烷吸附特性预测不同深度，不同温度和压力下煤层的甲烷吸附量[2]. 通常通过不同温度下煤的甲烷等温吸附实验获取吸附特征常数，工作量大，成本高，时间长，所需的深部煤样难以取得[3]. 在某些温度下测得的甲烷吸附等温式不能预测其它温度和压力下煤的甲烷吸附量[4,5].

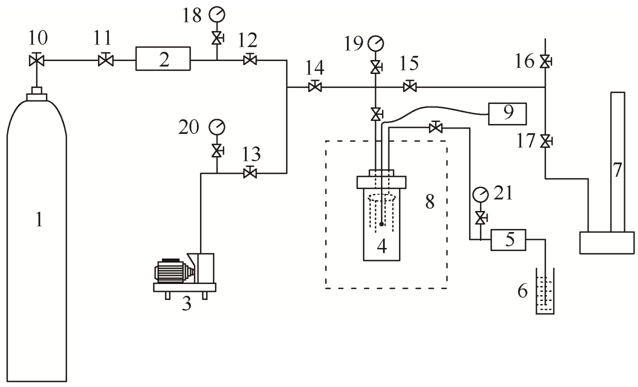
研究者基于 Polanyi 吸附势理论或 Clapeyron–Clausius 方程求解等量吸附热，对多孔介质的吸附等温线进行预测，取得了良好效果，方法是测定各温度范围内的多条吸附等温线，将等温线拟合为温度的函数，以较少的吸附等温线数据预测其它温度范围内的等温线[5]. 文献[6,7]对活性炭和石墨的气体吸附等温线进行了预测；郭为等[8]利用等量吸附热曲线预测了不同温度下页岩的等温吸附和解吸曲线；文献[3,4,9–11]基于 Clausius–Clapeyron 方程，针对煤–甲烷固气吸附体系，以某几个温度下甲烷的吸附数据预测其它温度下的甲烷等温吸附曲线，取得良好效果.

本工作基于 Dubinbin–Astakhov(DA)模型，选取气肥煤、焦煤、贫煤和无烟煤，在 323.15, 303.15, 283.15, 263.15 和 243.15 K 下进行 CH_4 等温吸附，对煤吸附 CH_4 等温线进行预测，验证了 DA 模型的准确性.

2　实　验

2.1 实验装置

高低温甲烷吸附解吸装置如图 1 所示，主要包括高低温变频控制单元、真空脱气单元、吸附平衡单元和数据实时采集系统. 温度由高低温变频实验箱控制，温度范围–50~100℃，温度偏差≤±1℃，温度波动±0.5℃.



1. Methane tank　2. Reference cell　3. Vacuum pump
4. Sample canister　5. Advection pump　6. Measuring cylinder
7. Desorption apparatus　8. Temperature control system
9. Temperature collector　10~17. Valve　18~21. Pressure gauge

图 1　高/低温吸附装置示意图

Fig.1　Diagram of high/low temperature adsorption device

2.2 实验煤样

选取 4 种不同变质程度的煤样，分别为潘北气肥煤(Gas-fat Coal, GFC)、吕梁焦煤(Coking Coal, CC)、新元贫煤(Meagre Coal, MC)和焦作九里山无烟煤(Anthracite Coal, AC). 在工作面取新鲜煤样密封保存，在室内将煤样破碎、粉碎和筛分，制成符合 GB/T19560-2004 要求粒度 0.180~0.250 mm(60~80 目)的空气干燥基煤样.

2.3 实验方法

按照《煤的高压等温吸附实验方法》(GB/T19560-2008)对不同温度下的煤样进行甲烷吸附性能测试，主要步骤如下：取筛选好的干燥煤样放入罐中，用真空泵抽真空至真空度低于 10 Pa，将煤样罐置于高低温变频控制箱中，设定实验温度，在不同充气压力下进行煤的甲烷吸附量测试.

3　煤的甲烷吸附测试结果及分析

在 243.15, 263.15, 283.15, 303.15 和 323.15 K 温度下不同变质程度煤的 CH_4 等温吸附曲线如图 2 所示. 由图可知，相同吸附平衡压力下，随温度降低，CH_4 吸附量增大. 这是因为降低温度减弱了甲烷分子的能量，更易被吸附，被吸附的甲烷分子难以获得足够的能量克服物理吸附力返回气相中. 相同温度下不同变质程度煤的甲烷吸附等温线趋势一致，随变质程度增加，相同吸附平衡压力下甲烷吸附量增大，这是因为煤是具有高交联三维空间的非晶质高分子聚合物，核心结构由许多结构相似但组成不相同的芳香核组成，随煤变质程度增加，芳香核层片形状变大、间距减小、定向排列有序，导致缩合度显著增加，而吸附能力受控于芳香核缩合程度，因此随变质程度增加煤的吸附能力逐渐加大[12].

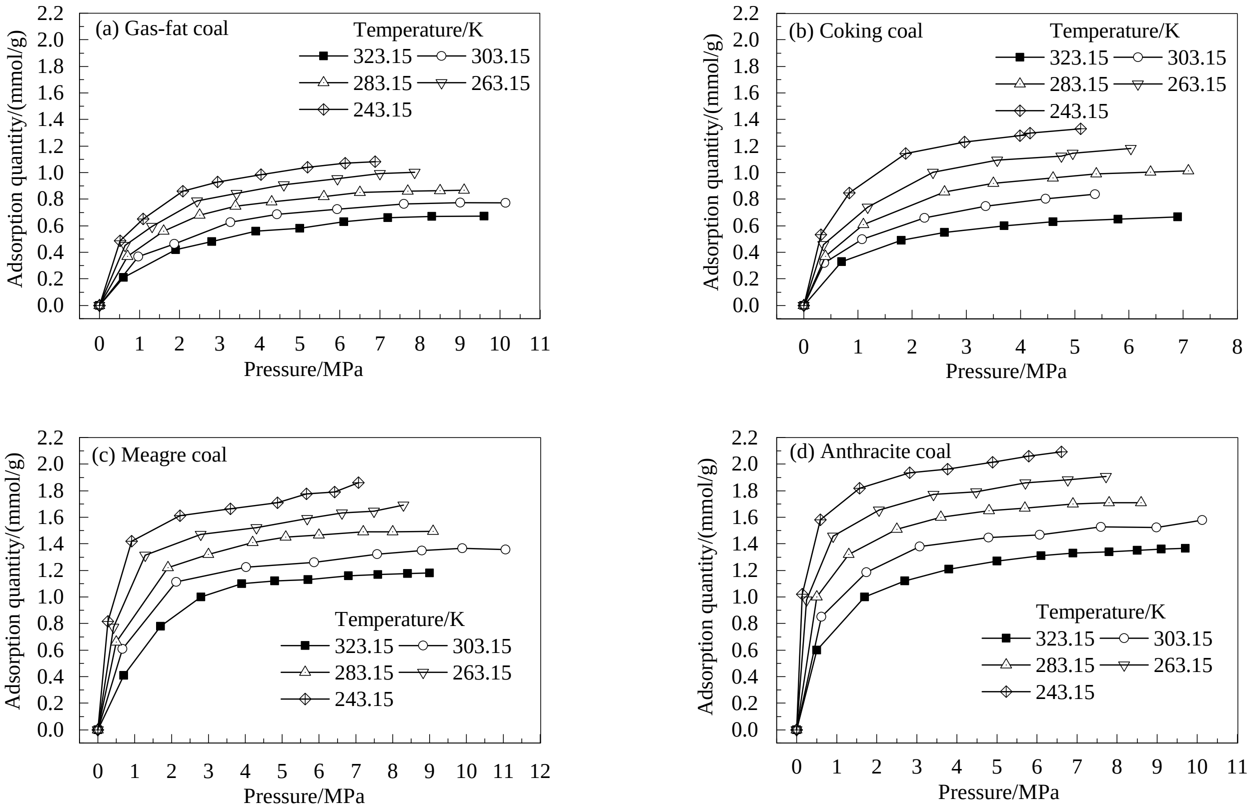


图 2　不同温度下煤的甲烷吸附性能

Fig.2　Methane adsorption isotherm on coal at different temperatures

4　DA 模型的吸附等温线函数

4.1 DA 模型

采用 DA 方程[13]描述甲烷在煤表面的等温吸附：

$$\theta(p) = \exp[-(\varepsilon / E_0)^{\gamma}], \tag{1}$$

其中，p 为气体压力(MPa)，吸附饱和度 $\theta=Q/Q_s$，Q 为压力 p 时的吸附量(mmol/g)，Q_s 为饱和吸附量(mmol/g)，ε 为吸附能(J/mol)，E_0 为特征吸附能(J/mol)，γ 为与吸附表面特性有关的经验参量，通常 $1 \leqslant \gamma \leqslant 2$[14].

根据 Polanyi 的吸附势理论，

$$\varepsilon = RT\ln(p_s / p), \tag{2}$$

其中，R 为气体常数[J/(mol·K)]，T 为温度(K)，p_s 为饱和压力(MPa). 在超临界条件下，p_s 为虚拟值，用式(3)[15]求得：

$$p_s = p_c(T/T_c)^2, \tag{3}$$

其中，甲烷临界压力 p_c=4.539 MPa，甲烷临界温度 T_c=190.7 K.

式(1)变形得：

$$\ln Q = \ln Q_s - [RT\ln(p_s / p)]^{\gamma} E_0^{-\gamma}. \tag{4}$$

4.2 DA 方程参数的确定

根据图 2 数据，以 $\ln Q$ 对 $[\ln(p_s/p)]^{\gamma}$ 作图，为使式(4)更好地满足线性结果，对 γ 取值后进行试算，最终确定 γ=1.9. $\ln Q$ 对 $[\ln(p_s/p)]^{1.9}$ 作图如图 4 所示，其线性拟合参数如表 1 所示，相关系数均达到 0.98 以上.

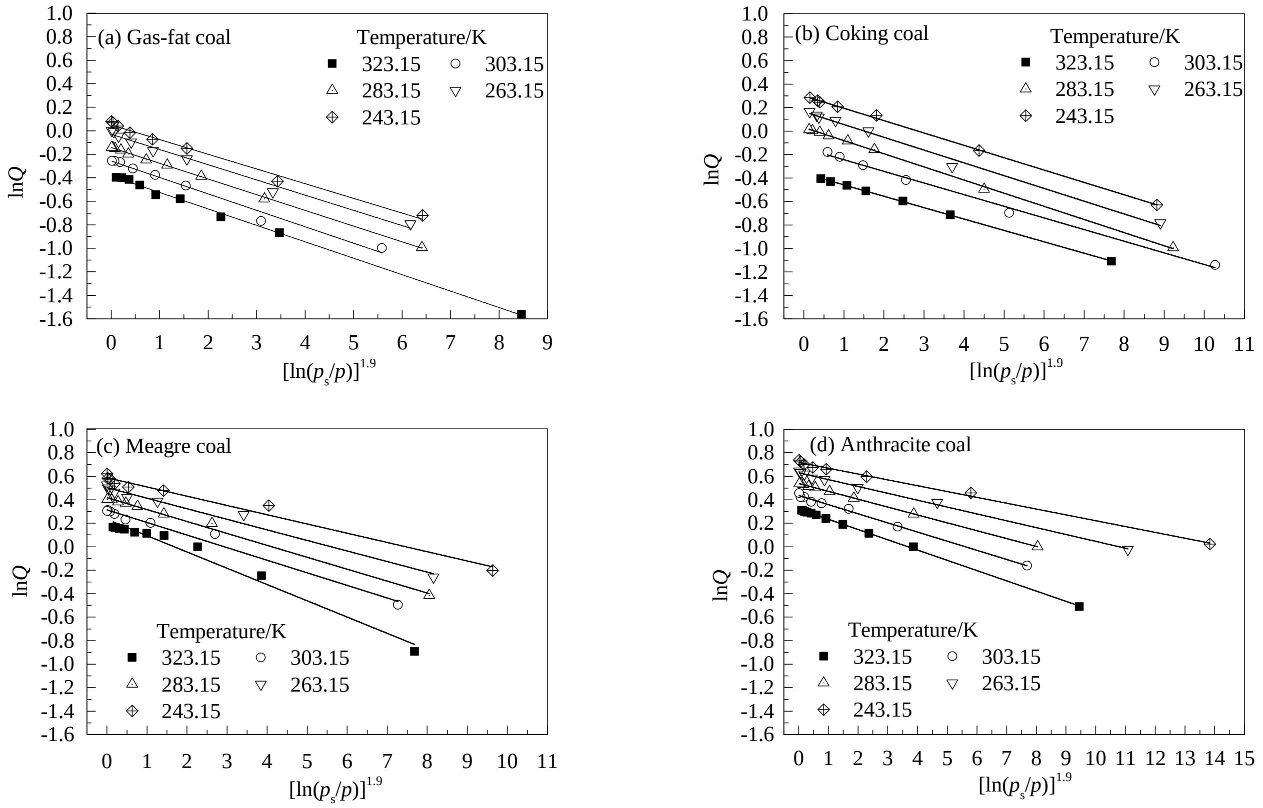


图 4　甲烷在煤表面吸附等温线 DA 模型拟合结果

Fig.4　Simulation results of methane adsorption isotherm on coal by DA equation

表 1 吸附等温线的 DA 模型线性拟合参数

Table 1　Fitting parameters of linearized DA equation

Coal	Temperature/K	$\ln Q_S$	$[RT/E_0]^{1.9}$	R^2
Gas-fat	323.15	−0.38514	0.13976	0.9971
	303.15	−0.25753	0.13970	0.9822
	283.15	−0.14290	0.13356	0.9991
	263.15	−0.03008	0.12934	0.9842
	243.15	0.05013	0.12500	0.9881
Coking	323.15	−0.36128	0.09696	0.9997
	303.15	−0.14462	0.09919	0.9937
	283.15	0.03086	0.11196	0.9991
	263.15	0.16459	0.10882	0.9910
	243.15	0.31468	0.12015	0.9985
Meagre	323.15	0.23242	0.13860	0.9740
	303.15	0.31351	0.10716	0.9796
	283.15	0.41765	0.10153	0.9937
	263.15	0.50321	0.08994	0.9767
	243.15	0.58780	0.07881	0.9734
Anthracite	323.15	0.32114	0.08741	0.9994
	303.15	0.43613	0.07783	0.9948
	283.15	0.53867	0.06706	0.9999
	263.15	0.63000	0.05845	0.9956
	243.15	0.71817	0.04968	0.9942

由式(4)可得到不同变质程度的煤在不同温度下吸附甲烷的 DA 方程的斜率和截距，即表 1 中的 $\ln Q_S$ 和 $[RT/E_0]^{1.9}$，由此可得到饱和吸附量 Q_S 和特征吸附能 E_0 与温度的关系如图 5 所示. 从图可看出，DA 模型得到的不同变质程度煤的甲烷饱和吸附量和特征吸附能均与温度线性相关，拟合参数如表 2 和 3 所示，相关系数达到 0.98 以上.

表 2 饱和吸附量拟合参数

Table 2　Fitting parameters of saturated adsorption

Coal	A	B	R^2
Gas-fat	1.40138	−0.00549	0.9920
Coking	2.35259	−0.00831	0.9877
Meagre	1.68574	−0.0045	0.9981
Anthracite	1.92748	−0.00494	0.9958

表 3 特征吸附能拟合参数

Table 3　Fitting parameters of adsorption energy

Coal	C	D	R^2
Gas-fat	1.48913	0.01870	0.9956
Coking	−2.93763	0.03745	0.9968
Meagre	6.94095	0.00319	0.9816
Anthracite	10.2195	−0.00171	0.9831

5　煤的甲烷等温吸附曲线预测

根据甲烷饱和吸附量 Q_S 和特征吸附能 E_0 与温度的函数关系，由式(4)可求得不同温度和吸附平衡压力下煤对甲烷的吸附量. 以 323.15, 313.15, 183.15, 263 和 243 K 等温吸附线为基准，预测 293.15 和 253.15 K 下气肥煤、焦煤、贫煤和无烟煤的等温吸附曲线，并与实验数据对比，结果如图 6 所示.

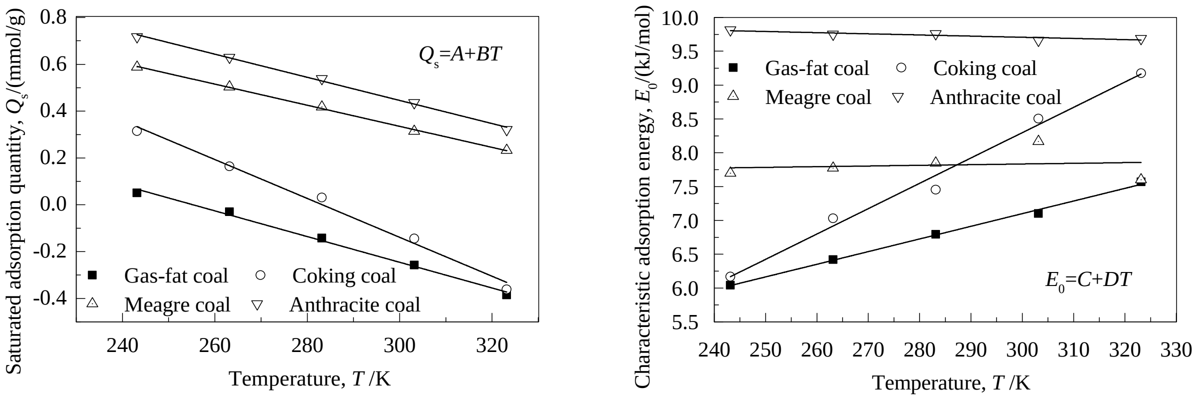


图5　甲烷饱和吸附量和特征吸附能与温度的关系

Fig.5　Relationship of methane saturated adsorption and characteristic adsorption energy with temperature

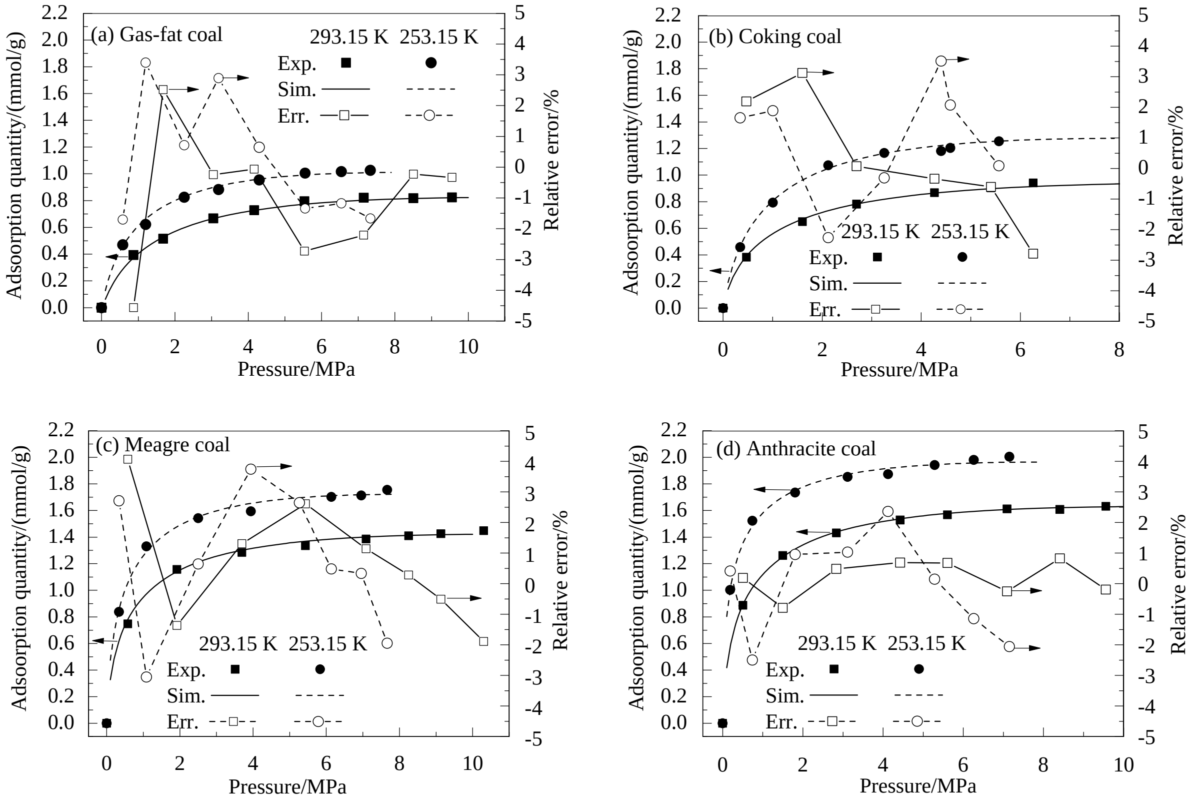


图6　293.15 和 253.15 K 下等温吸附曲线预测值与实测值对比

Fig.6　Comparison of prediction and experimental values of isothermal adsorption curves at 293.15 and 253.15 K

由图6可知，理论预测值与实验值吻合较好，相对误差均不超过5%，用该方法预测其它温度下煤的甲烷等温吸附曲线可行. 采用上述方法，在高低温环境中(333.15, 323.15, 313.15, 303.15, 283.15, 273.15, 263.15, 243.15, 233.15 和 223.15 K)对煤表面的甲烷吸附等温线进行预测，部分结果如图7所示，不同变质程度煤的甲烷吸附等温线预测的甲烷吸附量均随温度降低而增大.

6　结　论

在高低温甲烷吸附解吸装置中研究了气肥煤、焦煤、贫煤和无烟煤在不同温度下对甲烷的等温吸附，基于DA模型预测了煤的甲烷吸附等温线，得到如下结论：

(1) 对相同变质程度的煤，相同吸附平衡压力下，随温度降低，甲烷吸附量增大；相同温度下，随煤变质程度增加，相同吸附平衡压力下甲烷吸附量增大.

(2) 不同变质程度煤的甲烷饱和吸附量和特征吸附能均与温度线性相关，相关系数大于0.98.

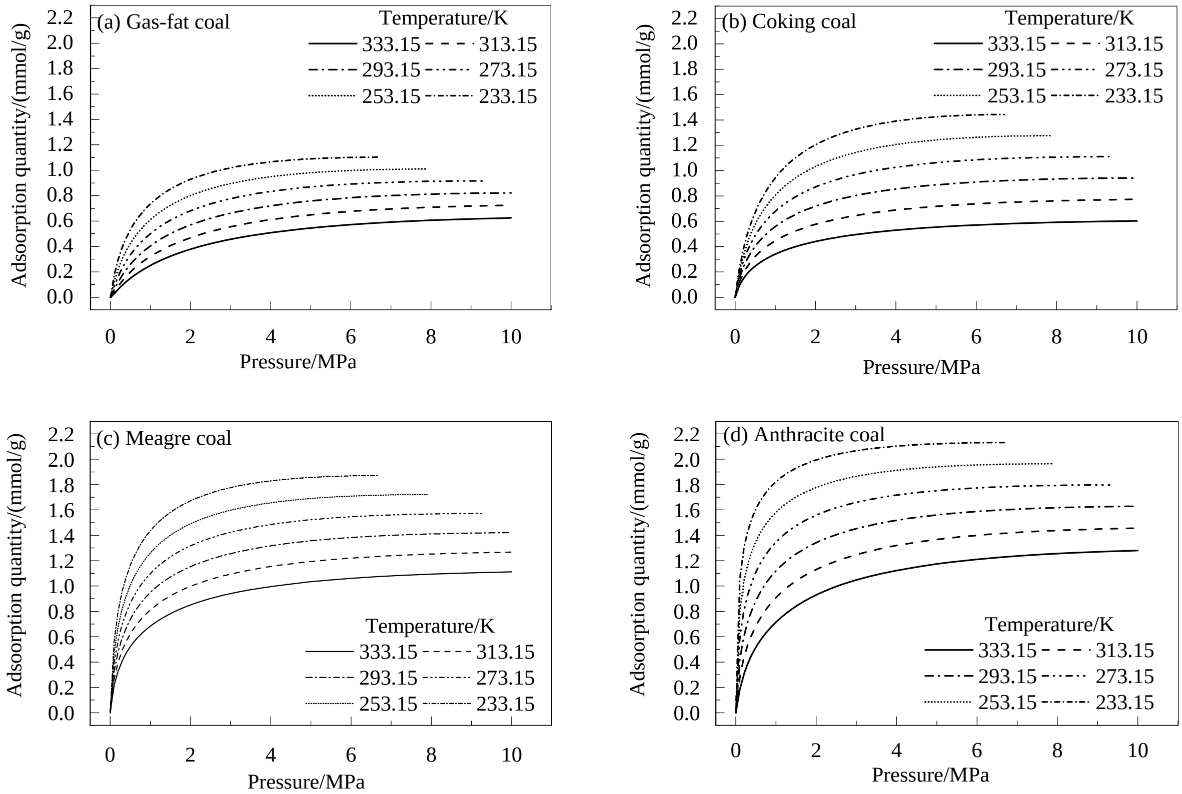


图 7　高低温下预测的煤表面甲烷吸附等温线

Fig.7　Isothermal adsorption curves prediction under low/high temperature

(3) 采用 DA 模型预测的气肥煤、焦煤、贫煤和无烟煤的等温吸附曲线与实验结果吻合较好，相对误差均不超过 5%.

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