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Ianovski, Dmitri

Department of Advanced Energy Engineering Science, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Munakata, Kenzo

Department of Advanced Energy Engineering Science, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Koga, Akinori

Department of Advanced Energy Engineering Science, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Narisato, Yasunobu

Department of Advanced Energy Engineering Science, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

他

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Recovery of Carbon Dioxide in Nuclear Fuel Reprocessing Cycle

Dmitri IANOVSKI^{*1,†}, Kenzo MUNAKATA^{*1}, Akinori KOGA^{*1},
Yasunobu NARISATO^{*1}, Hirofumi OKABE^{*1} and Masabumi NISHIKAWA^{*1}

[†]E-mail of corresponding author: dvi@nucl.kyushu-u.ac.jp

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Reprocessing of spent nuclear fuel produces off-gas that contains various radioactive components. Carbon-14 with a long half-life, which is mainly released in form of carbon dioxide, will continue to accumulate in environment. The adsorption process could be used for recovery of CO₂ from off-gas. In this work, the adsorption of CO₂ on synthetic zeolites and natural mordenite was studied in low partial pressure range. Moreover, effect of water vapor on co-adsorption of CO₂ was investigated. Adsorption capacity of MS4A for CO₂ was found to be almost unaffected by presence of water vapor in contrast to other adsorbents used in this work. This is a great merit and MS4A could be promising candidate for separative recovery of carbon dioxide in nuclear fuel reprocessing cycle.

Key words: Adsorption, Carbon Dioxide, Water Vapor, Molecular Sieves, Reprocessing Cycle.

1 Introduction

Reprocessing of spent nuclear fuel, for example PUREX process, produces nuclear off-gas that contains various radioactive components in different forms, such as tritium in form of ³H₂ or tritiated water vapor, ¹⁴C as carbon dioxide, ⁸⁵Kr and ¹³³Xe as chemically inert gases, ¹²⁹I as I₂ or CH₃I and so forth. Except for ¹²⁹I and particulates, these gases are being released to the environment. Radioactive ¹⁴C has a long half-life (5730 years) and thus will continue to accumulate in the environment. Therefore, an effective recovery system of carbon dioxide needs to be developed. The adsorption process¹⁾ could be one of the best candidates for effective removal of this gas. The partial pressure of carbon dioxide in the nuclear off gases is about several tens Pa, which is lower, then the regular partial pressure in the case of combustion gases. Thus, authors more thoroughly investigate the adsorption of carbon dioxide on synthetic zeolites and natural mordenites at low partial pressure range. The nuclear off-gas contains various gaseous components other than carbon dioxide. These components such as nitrogen, NO_x and water vapor may influence on the adsorption behavior of carbon dioxide. In the present work, influence of water vapor on the co-adsorption of carbon dioxide was also investigated.

2 Experimental

Figure 1 shows a schematic diagram of the experimental apparatus. The experiments were

conducted by the breakthrough method. The reactor (adsorption bed) made of Pyrex glass was placed in a constant temperature bath. Measurements were conducted in the temperature range of 195-403 K. The temperature of the bath was controlled with water, water and ice mixture (273 K), dry ice and ethanol mixture (195 K). Helium was used as the

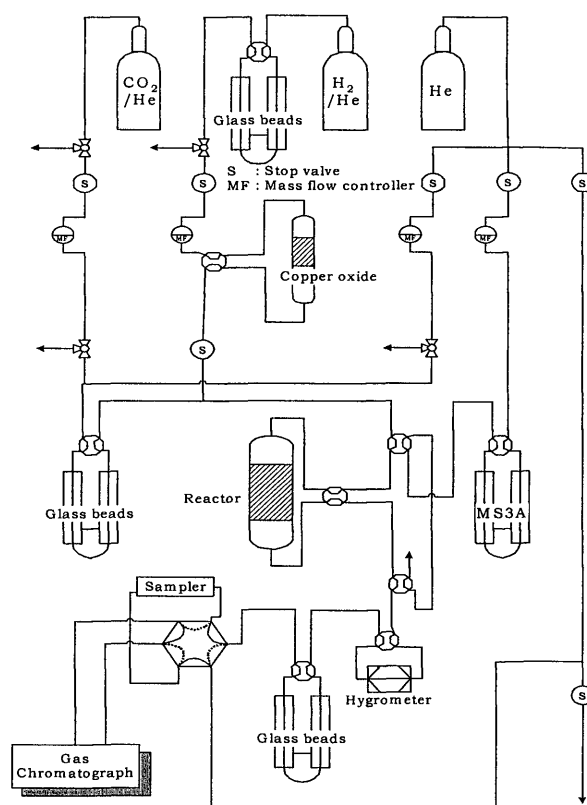


Fig.1 Experimental apparatus.

*1 Department of Advanced Energy Engineering Science,
Kyushu University

Table 1 Experimental conditions for MS4A

Adsorbates	CO ₂ , H ₂ O
Carrier gas	He
Tube inside diameter	0.6-1.65 cm
Partial pressure	33 -4943 Pa
Flow rate	198 – 1923 cm ³ /min
Temperature:	195K - 403K
Amount	0.12 – 10.0 g
Particle size (average)	2.0 mm
Void fraction	0.586
Bed density	0.58 g/cm ³
Apparent density	1.41 g/cm ³

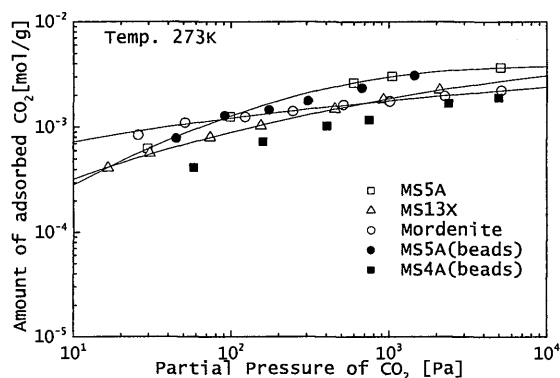
carrier gas²⁾ since it does not inhibit the adsorption of the molecules of interest. The gas flow rate was controlled with a mass flow controller fabricated by KOFLOC, Inc. Experimental conditions are summarized in Table 1. Water vapor was generated by passing H₂/He gases through a cuprum monoxide bed at 623 K. The gas composition of the inlet and outlet streams of the adsorption bed was analyzed with a gas chromatograph (Shimazu-GC8A) employing the Unibeads-C column packing. Water vapor concentration was measured with a hygrometer.

The adsorbents were dried and regenerated in the pure helium atmosphere. The drying and regeneration temperatures of the adsorbents were 523 K for the molecular sieves 4A, 5A and 13X, and 623 K for the natural mordenite. The pressures of the gases flowing over the adsorbents were 100 kPa for the adsorption experiments. The adsorption amounts of carbon dioxide and water vapor were computed by integrating breakthrough and desorption curves.

3 Results and discussion

3.1 Adsorption of carbon dioxide on various adsorbents

The amounts of carbon dioxide adsorbed on various adsorbents at 273 K as function of the partial pressure are shown in Figure 2. The adsorbents used in experiments were MS5A, MS4A and MS13X

**Fig.2** Screening test of adsorbents for recovery of CO₂

(obtained from Kishida Kagaku), and natural mordenite mined at Itado, Akita prefecture (obtained from Canto mineral). In the practical partial pressure range of carbon dioxide in nuclear off-gas that is about 30Pa, all of adsorbents have same order of magnitude adsorption capacity for carbon dioxide. Natural mordenite and molecular sieve 5A adsorbents have largest adsorption capacity for carbon dioxide. While molecular sieve 4A have smallest adsorption capacity in the case of pure carbon dioxide adsorption, the result of the adsorption experiments on the adsorption of Kr, isotope of which is one of the radioactive gases contained in the nuclear off-gas, reveals that almost no krypton is adsorbed on the MS4A adsorbent³⁾. This is probably due to the sieving effect, as the window size of the MS4A adsorbent is 0.4 nm that is smaller than the kinetic diameter of Kr. The other noble gas Xenon, constituent of the nuclear off-gas has a larger kinetic diameter than that of Kr. Therefore, for the purpose of separative recovery of radioactive gases, the use of MS4A adsorbent in radioactive carbon dioxide recovering process could be the best choice. Therefore in present work adsorption properties of molecular sieve 4A were thoroughly studied.

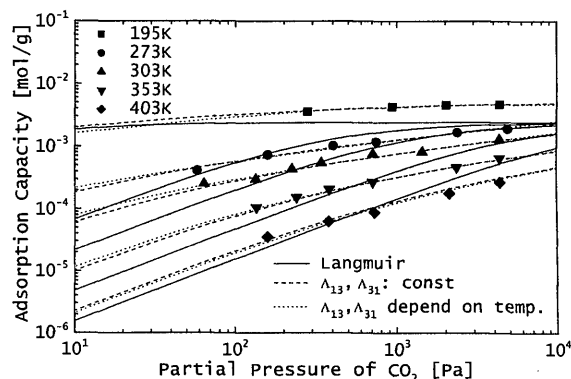
The experimental data along with calculated adsorption isotherms for the molecular sieve 4A in temperature range 195 K - 403 K are shown in Figure 3. The amount of CO₂ adsorbed on the MS4A adsorbent greatly increases with decreasing temperature. The Langmuir equation was first applied to correlate the asymptotic isotherm. The Langmuir equation is expressed as

$$p_i = \frac{q_i^{s,\infty} \theta}{b_i (1 - \theta)} \quad (1)$$

$$\theta = q_i^s / q_i^{s,\infty} \quad (2)$$

$$b_i = b_{0,i} \times \exp(-q_{st,i}^\theta / RT) \quad (3)$$

where $b_{0,i}$ [mol/g·Pa] is the temperature independent constant of the i -th component, q_i^s and $q_i^{s,\infty}$ [mol/g] are the number/maximum number of moles of i in surface phase, p_i is the partial pressure of i -th component in vapor phase, $q_{st,i}^\theta$ [J/mol] is the

**Fig.3** Adsorption isotherms of CO₂ on MS4A

isosteric heat of adsorption of i -th component and θ - fractional coverage. Solid lines in Figure 3 show the results of correlation with the Langmuir equation. The parameters in Equations (1), (2) and (3) were determined by the least-square analysis (Levenberg-Maquardt method). As shown by the solid lines Figure 3, the isotherms were not well correlated. These results indicate that the simple Langmuir equation does not give proper correlation. It is well known that the Langmuir equation starts to fail as the adsorption approaches saturation⁴⁾. The Langmuir model was derived in assumption that an adsorption phase obeys the two-dimensional van der Waals equation of state. Since this model might be too simplified to yield an accurate correlation, the authors examined other adsorption isotherm equations and found that the vacancy solution model gave the best correlation. In the vacancy solution model^{5,6)}, a concept of vacancy is introduced to the adsorbed phase and the interactions between adsorbates are taken into account. The equation of state for the adsorbed phase is derived based on the thermodynamic consideration. The non-ideality of the adsorbed solution is accounted for in terms of activity coefficients. This model can be easily applied to multi-component systems as well. According to the vacancy solution model, the isotherm for single component adsorption is given by

$$p_i = \frac{q_i^{s,\infty}}{b_i} \frac{\theta}{1-\theta} \left[\Lambda_{i3} \frac{1-(1-\Lambda_{3i})\theta}{\Lambda_{i3} + (1-\Lambda_{i3})\theta} \right] \times \exp \left[-\frac{\Lambda_{3i}(1-\Lambda_{3i})\theta}{1-(1-\Lambda_{3i})\theta} - \frac{(1-\Lambda_{i3})\theta}{\Lambda_{i3} + (1-\Lambda_{i3})\theta} \right] \quad (4)$$

where Λ_{i3} and Λ_{3i} are the constants in the Wilson equation for the activity coefficient. If the activity coefficients Λ_{i3} and Λ_{3i} are unity (which corresponds to ideal solutions), the vacancy solution model is equal to the Langmuir model. Moreover, the authors tried to introduce the temperature effect into the Wilson parameters to obtain a more accurate adsorption isotherm data correlation in the low partial pressure range. In order to introduce the effect of temperature into the parameters, the authors assumed that the general form of the Wilson parameters used for the liquid-vapor phase equilibrium is applicable. The following equations were used to express the temperature dependence of the Wilson parameters

$$\Lambda_{i3} = \frac{V_3^L}{V_i^L} \times \exp \left(\frac{-(\lambda_{i3} - \lambda_{ii})}{RT} \right) \quad (5)$$

$$\Lambda_{3i} = \frac{V_i^L}{V_3^L} \times \exp \left(\frac{-(\lambda_{3i} - \lambda_{33})}{RT} \right) \quad (6)$$

where, λ_{ij} [J/mol] is the interaction energy between i vacancy and j molecule, and V_i^L [m³/mol] is the molar liquid volume.

As shown in Figure 3, the correlation of the adsorption isotherm on the molecular sieve 4A was

improved when the above expressions were used for the Wilson parameters. The adsorption equilibria calculated with these parameters well reproduce the experimental adsorption data. The parameters determined by the least squares analysis are given in Table 2.

Table 2 Parameters determined by least-square analysis

Parameter	CO ₂	H ₂ O
$q_i^{s,\infty}$ [mol/g]	4.775×10^{-3}	1.169×10^{-2}
$b_{0,i}$ [mol/(g·Pa)]	8.736×10^{-13}	2.083×10^{-13}
$q_{st,i}^0$ [J/mol]	-4.154×10^4	-6.684×10^4
V_i^L / V_3^L [-]	3.237	0.294
$(\lambda_{i3} - \lambda_{ii})$ [J/mol]	-1599	4424
$(\lambda_{3i} - \lambda_{33})$ [J/mol]	-1356	-8095
$(\lambda_{12} - \lambda_{11})$ [J/mol]	-17802	
$(\lambda_{21} - \lambda_{22})$ [J/mol]	4737	
V_2^L / V_1^L [-]	17	

3.2 Influence of coexistent water vapor on adsorption of carbon dioxide

The next important step is to study the adsorption properties of molecular sieve 4A in the presence of water vapor. In the previous study on the natural mordenite adsorbent which has the largest adsorption capacity for CO₂ in the lower partial pressure range (as shown in Fig.2) conducted by Fukumatsu et al.⁷⁾, it was found that the amount of CO₂ adsorbed on the natural mordenite adsorbent is substantially decreased by coexistent water vapor of even as low as several tens Pa. Thus, severe hindrance effects also could take place in the adsorption of CO₂ on the MS4A adsorbent. To investigate the effect of coexistent water vapor on the adsorption of CO₂ on the MS4A adsorbent, the adsorption of water vapor was first examined. The experiments were also carried out by the breakthrough method with the hygrometer. Figure 4 show the adsorption isotherms of water vapor on the MS4A adsorbent. As expected, the amount of water vapor adsorbed on the MS4A adsorbent is much larger than that of CO₂, which is suggestive of the occurrence of hindrance effects by coexistent water vapor. The isotherms shown in Fig. 4 were also

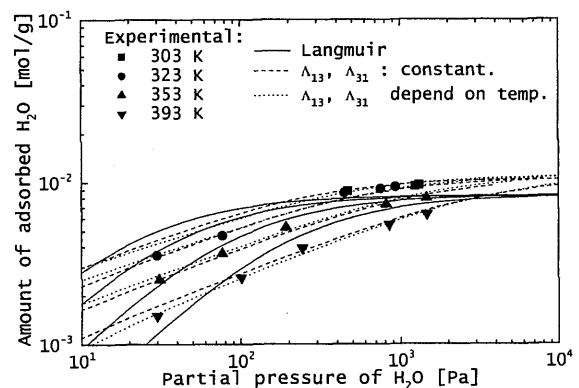


Fig.4 Adsorption isotherms of H₂O on MS4A

correlated with several adsorption models. As shown by solid lines in Fig.4, the simple Langmuir model as is in the case of adsorption of CO₂ does not work well. The vacancy solution model was found to give proper correlation for the adsorption isotherms of water vapor on the MS4A adsorbent (see broken and dotted lines in Fig.4). The dotted lines indicate that the incorporation of the effect of temperature into the Wilson parameter improves the accuracy of correlation of the isotherms. The determined parameters are summarized in Table 2.

Next, adsorption experiments of the binary system of CO₂ and water vapor were conducted. The breakthrough curves of carbon dioxide and water vapor at different temperatures are shown in Figures 5 (a) and (b). In these experiments, the He gas mixed with CO₂ and water vapor was introduced into the adsorption bed. The obtained breakthrough curves are typical for binary system with different adsorption affinities. Carbon dioxide has lower affinity to the molecular sieve 4A compared with water vapor, and thus carbon dioxide broke through earlier. Then water vapor, having higher affinity to the adsorbent, drove out adsorbed carbon dioxide with advance in its adsorption and the outlet concentration of carbon dioxide became more than the inlet concentration. Figures 6 (a) and (b) show the effect of coexistent water on the amount of CO₂ adsorbed on the MS4A adsorbent. As seen from this figures, the inhibition effect on the adsorption of CO₂ is very small. Our previous study⁷⁾ indicates that the adsorption of CO₂ on the natural mordenite adsorbent is substantially inhibited by coexistent water vapor. Coexistent water vapor even of several tens Pa decreases the amount of CO₂ adsorbed on the natural mordenite by two orders of magnitude. However, for the MS4A adsorbent, such a great inhibition effect does not take place. This peculiar characteristic is a great merit for the process design in terms of the control of water vapor concentration.

The adsorption equilibrium for carbon dioxide

and water vapor on the molecular sieve 4A was investigated. The vacancy solution model, which can be extended to multi-component adsorption system, was used to predict the binary adsorption equilibrium. In accordance with the model, isotherms for the binary component system can be written as follows:

$$p_i = \gamma_i^s x_i q_m^s \frac{q_i^{s,\infty} \Lambda_{i3}}{q_m^{s,\infty} b_i} \exp(\Lambda_{31} - 1) \exp\left(\frac{\pi \bar{a}_i}{RT}\right) \quad (7)$$

$$-\frac{\pi \bar{a}_i}{RT} = \left[1 + \frac{q_m^{s,\infty} - q_i^{s,\infty}}{q_m^s}\right] \ln(\gamma_i^s x_3^s) \quad (8)$$

$$\ln \gamma_i^s = 1 - \ln(x_i^s + x_j^s \Lambda_{ij} + x_3^s \Lambda_{i3}) - \left(\frac{x_i^s}{x_i^s + x_j^s \Lambda_{ij} + x_3^s \Lambda_{i3}} + \frac{x_i^s \Lambda_{ji}}{x_i^s \Lambda_{ij} + x_j^s + x_3^s \Lambda_{i3}} + \frac{x_3^s \Lambda_{3i}}{x_i^s \Lambda_{3i} + x_j^s \Lambda_{3j} + x_3^s} \right) \quad (9)$$

$$\ln \gamma_3^s = 1 - \ln(x_1^s \Lambda_{31} + x_2^s \Lambda_{32} + x_3^s) - \left(\frac{x_1^s \Lambda_{13}}{x_1^s + x_2^s \Lambda_{12} + x_3^s \Lambda_{13}} + \frac{x_2^s \Lambda_{23}}{x_1^s \Lambda_{21} + x_2^s + x_3^s \Lambda_{23}} + \frac{x_3^s}{x_1^s \Lambda_{31} + x_2^s \Lambda_{32} + x_3^s} \right) \quad (10)$$

$$x_i = \frac{q_i^s}{q_m^s} \quad (11)$$

$$x_i^s = \frac{x_i q_m^s}{q_m^{s,\infty}} \quad (12)$$

$$x_3^s = 1 - \frac{q_m^s}{q_m^{s,\infty}} \quad (13)$$

$$q_m^{s,\infty} = x_1 q_1^{s,\infty} + x_2 q_2^{s,\infty} \quad (14)$$

$$q_m^s = q_1^s + q_2^s \quad (15)$$

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \times \exp\left(-(\lambda_{ij} - \lambda_{ii})/RT\right) \quad (16)$$

where \bar{a}_i is partial molar surface area [m²/mol].

The parameters determined in the study of single

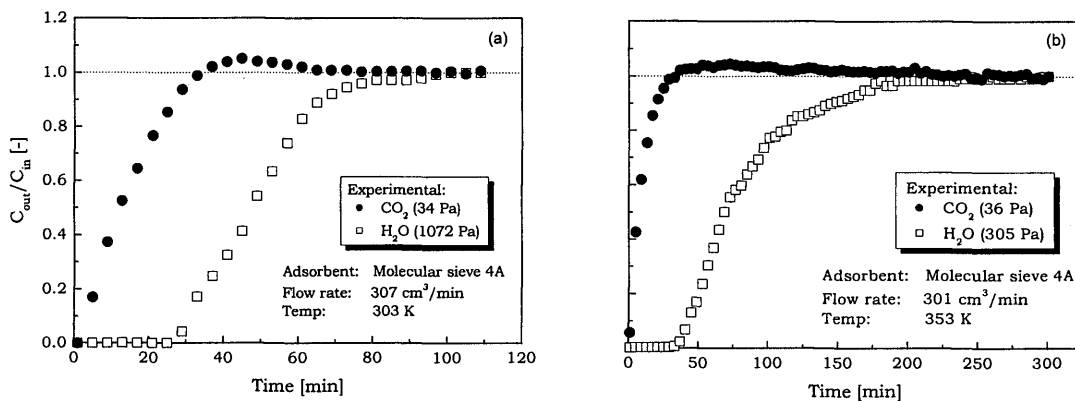


Fig.5(a,b) Breakthrough curves of CO₂ and H₂O on MS4A

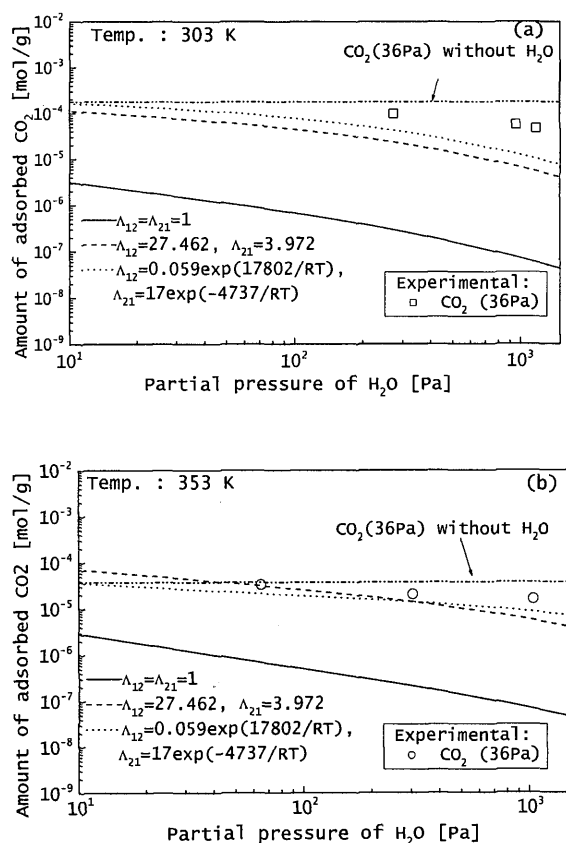


Fig.6 Effect of coexistent water on adsorption of CO₂ on MS4A

component adsorption can be used for calculation of the binary adsorption equilibrium by the vacancy solution model. The new parameters, which correspond to the cross coefficients of the Wilson parameters for the binary system can be determined from the fitting to experimental data. If the interaction between different adsorbates is small, the parameters become unity. As a first step, the binary adsorption equilibrium was calculated with this assumption. The solid lines in Figures 6 (a) and (b) represent results calculated by neglecting the interaction between different adsorbates. It could be seen that isotherms calculated with this assumption could not reproduce the experimental results; the calculated isotherms are much smaller than the experimental adsorption amount of carbon dioxide.

This is probably because the adsorbate-adsorbate interaction is not small for the binary carbon dioxide and water adsorption system. Thus, the binary adsorption equilibrium was calculated with assumption that the interaction affects the binary adsorption system. The adsorption equilibria were calculated with the optimized parameters that account for interaction between adsorbates. This approximation had better reproduce the experimental data as it shown by broken lines in Figures 6 (a) and (b). The results of calculation were considerably

improved, while the calculation still underestimates the amounts of adsorbed CO₂ when the partial pressure of water vapor is high and overestimates them when the partial pressure of water vapor is small. On the next step, in order to improve correlation with experimental data the authors introduced temperature dependence in to the cross coefficients of Wilson parameters for binary system. The parameters determined by least square analysis were $(V_2^L/V_1^L)=17$, $(\lambda_{12}-\lambda_{11})=-17802$ [J/mol], $(\lambda_{21}-\lambda_{22})=4737$ [J/mol]. These adsorption isotherms are shown by dotted lines in Figures 6 (a) and (b). As can be seen, the correlation of the experimental data was further improved. However, discrepancy between the experimental data and the calculation result remained. As shown above, incorporation of the adsorbate-adsorbate interaction into the vacancy solution model does not appear to be so successful. Therefore, the authors think that CO₂ and water vapor are adsorbed on different adsorption sites of the MS4A adsorbent, which probably results in such a small inhibition effect by coexistent water vapor. Thus, other adsorption models are necessary for the correlation of the experimental results for the binary CO₂-H₂O system on MS4A.

4 Conclusion

The adsorption equilibrium of carbon dioxide on the molecular sieve 4A adsorbent was studied for a wide range of temperatures from 195 K to 403 K. The adsorption isotherms of CO₂ were successfully correlated with vacancy solution model. Influence of water vapor on co-adsorption of carbon dioxide was investigated as well. It was found that coexistent water vapor does not give big inhibition effect on adsorption of carbon dioxide for the MS4A adsorbent. This is a great merit and molecular sieve 4A could be considered as promising adsorbent for separative recovery of carbon dioxide in nuclear fuel reprocessing cycle.

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