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^{14}CO and ^{12}CO Separation on Na-X Using Pressure Swing Adsorption at Low Temperatures

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Abstract. Economical ^{14}CO separation is very important to provide the means of removal and fixation of the radio-acitve carbon (carbon-14) in atomic power industry.

^{13}C has been separated from ^{13}C/^{12}C CO or ^{13}C/^{12}C CH_4 by cryogenic process conventionally. However, since the separation factor is not so large, the separation cost is very expensive and thus the industrial application of ^{13}C is very limited. Meanwhile, there is no report on the separation of ^{14}C from ^{14}C/^{12}C until now. The authors found that there was a great difference on the adsorption equilibrium coefficient between ^{14}CO and ^{12}CO when they are adsorbed on low SiO_2/Al_2O_3 ratio Na-X type zeolite (Na-X) at low temperatures.

Keywords: Na-X type zeolite, ^{14}CO selectivity, low temperature, equilibrium adsorbent, pressure swing adsorption

1. Introduction

The earliest nuclear reactors, graphite reactors, have come to be disposed in Japan. The amount of waste graphite, which is contaminated by ^{14}C, reaches to a few thousands of tons. The most feasible waste treatment system is considered to store the waste under ground. In this case a very large storage facility is required. Another promising alternative for the highly efficient treatment of waste graphite, by which ^{14}C is separated from gasified graphite and enriched to about 100 times, is proposed.

It is shown theoretically that ^{14}C can be separated from either ^{14}C/^{12}C CO or ^{14}C/^{12}C CH_4 by cryogenic processes. However, the separation cost will be very expensive because the separation factor is not so large (less than 1.01) for both of the systems. Thus the application of this method to the disposal of graphite reactors is not expected.

It has been well known that CO is strongly adsorbed on Na-X type zeolite (Izumi et al., 1991). The authors confirmed that Na-X type zeolite (Na-X) showed the

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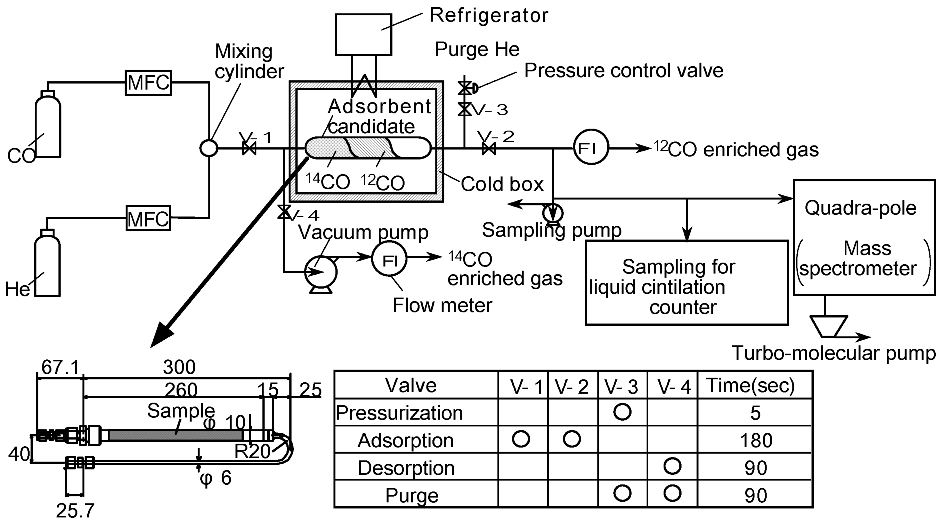

Valve	V- 1	V- 2	V- 3	V- 4	Time(sec)
Pressurization			○		5
Adsorption	○	○			180
Desorption				○	90
Purge			○	○	90

Figure 1. Small column apparatus for ^{14}CO/^{12}CO separation evaluation using PSA.

selectivity of ^{13}CO in the binary system of ^{13}CO and ^{12}CO (Izumi et al., 2002). In this study, we examine the ^{14}CO selective adsorption on Na-X.

2. Experimental

2.1. Apparatus

A gas mixture of CO(^{14}C/^{12}C $= 1/1{,}000{,}000$, ^{13}C/^{12}C $= 0.011$) and helium as a carrier gas was introduced into a small column of zeolite pellets for a scheduled time and desorbed by evacuation of the column.

A small column adsorption technique was used to obtain adsorption equilibrium and rate characteristics of a multi-component system of ^{12}CO, ^{13}CO, ^{14}CO. Figure 1 shows a schematic illustration of the small column apparatus. Between 10 and 15 grams of zeolite samples pellets (Na-X, SiO2/Al2O3 ratio = 2.3, zeolite/binder = 8/2(w/w)) prepared for a screening test, which were in extruded cylindrical form of 1.6 mm in diameter, were loaded into the column. Samples were first heated to 400 K in an atmospheric condition for 2 hrs to remove surface water and then the temperature was raised to 723 K so that the adsorbents were regenerated and became thoroughly free of preadsorbed water vapor. The column was then placed in a refrigerator at a constant temperature of 213 K.

Inlet flow rate and pressure were controlled by a mass flow controller. Another mass flow meter was put on the outlet of the column to detect the change of flow rate A quadra pole mass spectrometer was equipped at the exit of the column to determine the ^{12}CO, ^{13}CO and helium concentrations in the exit gas. After being oxidized by Na_2CO_3 in the presence of catalytic material (Fe), ^{14}C radioactivity was measured by scintillation counter to determine ^{14}C concentration and ^{14}C/CO ratio in the effluent.

Evacuation of the column was made by a vacuum pump with V-3 opened and V-1 and V-2 closed. When the column pressure reached the desorption pressure, V-4 opened and helium was supplied for the counter current purge. The amount of gas desorbed by evacuation was measured by a rotary flowmeter connected to the outlet of the vacuum pump. ^{12}CO, ^{13}CO, ^{14}CO and helium concentrations at the desorption stage were not measured and these values were determined with the mass balance between the inlet and outlet at the adsorption stage.

2.2. Procedure

Adsorption pressure was adjusted by means of a pressure gauge installed on the inlet gas line. The programmed sequence of the adsorption experiment was as follows: (1) Valve V-1 was opened, the inlet gas of CO concentration C_{0i} ($I = 1$; ^{12}CO, $I = 2$; ^{13}CO, $I = 3$; ^{14}CO, $I = 4$; He) was introduced into the column, and the column pressure reached the adsorption pressure Pa. This took about five seconds. Valve V-2 was then opened and adsorption in the column from

Table 1. Measurement conditions of ^{14}CO/ ^{12}CO separation using a small column apparatus.

Adsorbent	See Table 2
Adsorbent shape and weight	1/16″, 2 grams
Inlet gas rate	600 mlN/minute
Inlet gas composition	^{14}CO 0.988Bq/ml, CO 10 vol%, He 90 vol% (^{14}C/ ^{12}C ratio; Natural abundance 0.011)
Adsorption temperature	213–298 K
Adsorption pressure	120 kPa
Desorption pressure	1 kPa
Adsorption time	180 seconds

Table 2. Adsorbent specification.

Sample no.	Adsorbent	SiO_2 /Al_2O_3 (−)	Shape (mmφ)	Weight (g)
1	Na-X type zeolite	2.3	1.6	12

the inlet gas took place (adsorption step). During this period, the flow rate and concentration of CO, $G_{1\mathrm{i}}$ and $C_{1\mathrm{i}}$, were measured. (2) Valves V-1 and V-2 were closed and V-3 was opened and evacuation of the column was performed (desorption step). At the end of the desorption step, the pressure was below 13 Pa after a duration of 600 seconds. (3) As V-4 was also opened under evacuation, helium was supplied as a counter current purge to remove CO thoroughly (counter current purge step). (4) As V-3 was closed and V-4 was still opened, the column pressure was repressurized to the adsorption pressure with helium. The measurement conditions are summarized in Table 1 and an adsorbent specification is shown in Table 2. Adsorption temperature was the parameter examined in this study, and a sequence controller was programmed for each set of conditions so that steps (1), (2), (3) and (4) were repeated for more than four hours. The total amount of desorbed gas G_2 was determined from the gas collected at the exit of the rotary flowmeter.

2.3. *Calculation of Amount Adsorbed*

The amount of ^{12}CO, ^{13}CO and ^{14}CO adsorbed during the pressurization and adsorption periods was calculated using the following equation.

$$q_{COi2} = \{G_2 \cdot C_{COi2} - Gdead, COi\}/w \qquad (1)$$

where q_{COi} denotes the adsorbed amount of ^{12}CO, ^{13}CO and ^{14}CO on unit mass of zeolite and *Gdead,COi* represents the amount of ^{12}CO, ^{13}CO and ^{14}CO in the dead volume of the apparatus. W denotes the amount of adsorbents packed in the column, *Gdead,COi* is estimated from the dead volumes at the inlet part of the apparatus V_f, in the column V_m, and at the exit part of the apparatus V_r.

The temperatures of these parts are, respectively, T_f, T_m, and T_r. ^{12}CO, ^{13}CO and ^{14}CO concentration are C_{0i} at the inlet, C_{1i} at the exit and is thus assumed as $C_{mi} = (C_{Oi} + C_{1i})/2$ in the column. The following equations were then used for calculation of *Gdead,COi* and *Gdead,He*.

$$Gdead,\ COi = Pa\left(V_f \cdot \frac{273}{T_f} \cdot C_{0i} + V_m \cdot \frac{273}{T_m} \cdot C_{mi} + V_r \cdot \frac{273}{T_r} \cdot C_{1Ei}\right) \qquad (2)$$

Regarding the average concentration in the column, C_{mi}, the approximation assumed here should not introduce appreciable error since the exit concentration at the end of adsorption step, C_{1i}, is close to the concentration at the inlet, C_{Oi}.

3. Results and Discussion

3.1. *The Results of Screening Test*

Table 3 shows an example of mass balance of ^{14}CO/^{13}CO/^{12}CO separation, using a small column under the pressure swing adsorption. The adsorption pressure, the inlet oxygen concentrations, and the flow rates for all the runs were; $Pa = 120$ KPa, $Pd = 1$ Kpa, $C_{O1} = 0.1$, $C_{O2} = 0.0011$ $C_{O3} = 0.9$, and $G_1 = 600$ ml/min. The adsorption temperature was 213–273 K. The adsorption period was 180 seconds.

Shown in Table 3, when the inlet gas rate(mlN/batch) was adjusted to the effluent ratio of 12.8% for ^{12}CO, that of ^{13}CO was 10.1% and that of ^{14}CO was 9.92%. th the Eqs. (1) and (2), the separation factor of ^{13}CO/^{12}CO was1.03 and that of ^{14}CO/^{12}CO was 1.11.

The adsorbed amount of ^{12}CO, ^{13}CO and ^{14}CO, measured, were 20.2 mlN/g, 0.23 mlN/g and 226 Bq/g.

Table 3. ^{14}CO/^{13}CO/^{12}CO separation using a small column.

Conc.		1) Inlet	2) Outlet	3) Desorption	4) Vf	5) Vm	6) Vr	7) Δ amount
(vol%)	^{12}CO	9.87E+00	1.26E+00	5.20E+01	9.87E+00	5.57E+00	1.26E+00	
(vol%)	^{13}CO	1.09E–01	1.09E–02	5.92E–01	1.09E–01	5.98E–02	1.09E–02	
(Bq/mlN)	^{14}CO	9.88E–01	9.80E–02	5.80E+00	9.88E–01	5.43E–01	9.80E–02	
(vol%)	TCO	1.00E+01	1.30E+00	5.28E+01	1.00E+01	5.65E+00	1.30E+00	
Flow rate								
(mlN/batch)	^{12}CO	231.449	27.100	205.791	1.868	0.664	0.565	202.693
(mlN/batch)	^{13}CO	2.546	0.235	2.344	0.021	0.007	0.005	2.311
(Bq/batch)	^{14}CO	2.32E+03	2.10E+02	2.30E+03	1.87E+01	6.48E+00	4.39E+00	2268.009
(mlN/batch)	TCO	234.427	27.894	209.158	1.892	0.674	0.582	206.010
	Total	2344.266	2145.706	396.132	18.920	11.930	44.750	
Effuluent ratio		^{12}CO	1.28E−01		Separation factor		C13/C12	1.037
		^{13}CO	1.01E−01				C14/C12	1.118
		^{14}CO	9.92E−02					

Experimental conditions; Adsorption pressure: 120 kPa, Desorption pressure: 1 kPa, Adsorption temperature: 243 k, Counter current purge ratio: 190%, Adsorbnet: Na-X(SiO_2/Al_2O_3 2.3, 1.6 mmpellet).

3.2. ^{14}CO Selectivity of Na-X

As the strong ^{13}CO selectivity of Na-X was suggested at the screening test, ^{13}CO and ^{12}CO adsorption behavior of Na-X was evaluated. The adsorption equilibrium constants of ^{13}CO and ^{12}CO ($\beta 13$, $\beta 12$) on Na-X at temperatures of 213–273 K is shown in Fig. 2(a).

As the lower the temperatures, the greater the adsorption equilibrium constants of ^{14}CO,^{13}CO and ^{12}CO ($\beta 14$, $\beta 13$, $\beta 12$). $\beta 14$ and $\beta 13$ were greater than $\beta 12$ at all temperature regions. Here, the separation factors $\alpha 13$ and $\alpha 14$ in the binary system of ^{13}CO-^{12}CO and ^{14}CO-^{12}CO are defined with equations Eqs. (3) and (3′).

$$\alpha 13 = \beta 13/\beta 12 \qquad (3)$$

$$\alpha 14 = \beta 14/\beta 12 \qquad (3')$$

The temperature dependencies of the ^{14}CO and ^{13}CO separation factor of Na-X are shown in Fig. 2(b). When the temperature was decreased, the maximum separation factor of ^{14}CO was indicated at 243 K and that of ^{13}CO reached 1.1 at 213 K.

As the separation factor of $^{13}CH_4/^{12}CH_4$ with the cryogenics is 1.003 and that of ^{13}CO/^{12}CO is 1.007, the value with the gas phase adsorption on Na-X is extremely high. Shown in Fig. 3 this phenomenon can be assumed that the interaction energy (mainly vibration energy) between ^{14}CO, ^{13}CO and Na at SIII site,

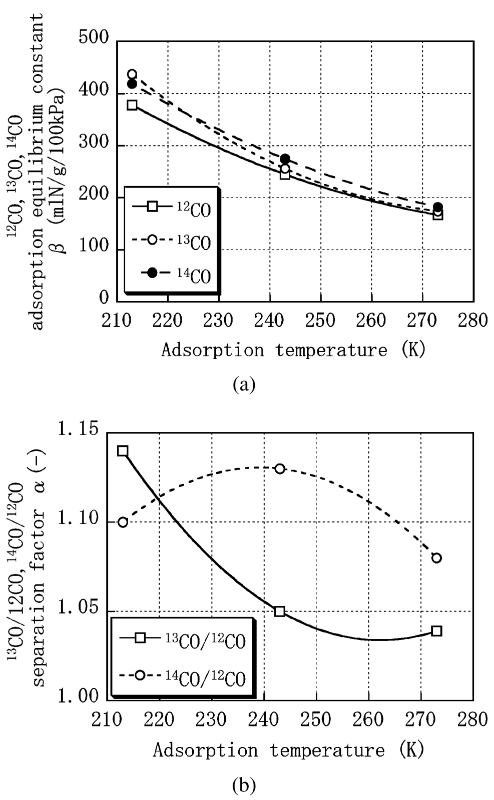

Figure 2. (a) Temperature dependency of ^{12}CO and ^{14}CO equilibrium constants of Na-X. (b) Temperature dependency of ^{14}CO/^{12}CO separation factor.

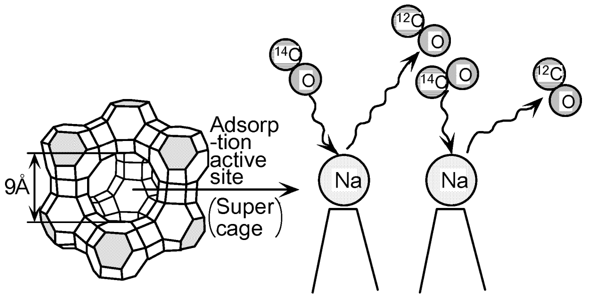

Figure 3. $^{14}CO/^{12}CO$ separation mechanism.

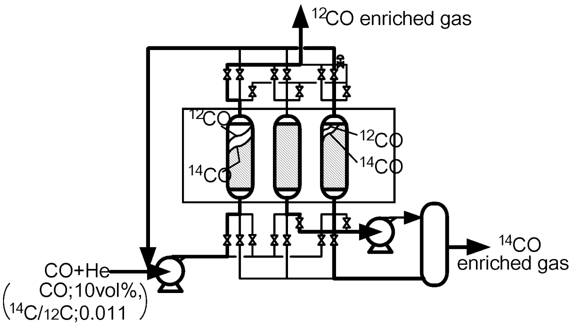

Figure 4. PSA-$^{14}CO/^{12}CO$ separation unit (single stage).

which forms the adsorption active site, is greater than that between ^{12}CO and Na at SIII site and the statistical residence time of ^{14}CO and ^{13}CO at Na at SIII site are longer than that of ^{12}CO (Izumi et al., 2003).

3.3. $^{14}CO/^{12}CO$ Separation Performance Using PSA

The authors are studying the enrichment system of a desorbed gas, using a parallel flow purge (When the adsorption is completed, the desorbed gas is supplied as a parallel flow to the tower to substitute ^{12}CO with ^{14}CO) for a three-tower VPSA unit (Fig. 4).

The authors assumed the enrichment performance of this VPSA unit, using the PSA simulation relating to the parallel purge ratio R. The parallel purge ratio R is defined with equation Eq. (4).

$$R = Gp\,/\,Gd \tag{4}$$

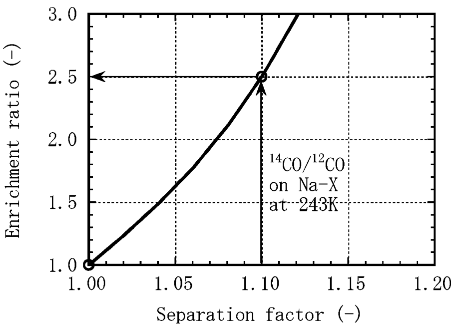

Figure 5. Separation factor and enrichment ratio.

Gp: Gas rate of parallel purge, Gd, Gas rate of desorption.

The relationship between the separation factor and the enrichment ratio is shown in Fig. 5. As the ^{13}CO separation factor of Na-X at 213 K is 1.1, it is expected that the enrichment ratio with a single stage of this VPSA is 2.5.

4. Summary

The isotope separation using the gas phase adsorption is quite new trial. With the small column test of ^{14}CO adsorption on zeolite samples in the multi isotope system of ^{14}CO-^{13}CO-^{12}CO system, it was found that Na-X(SiO_2/Al_2O_3 ratio 2.0) adsorbed ^{14}CO selectively at low temperatures and its ^{14}CO separation factor reaches 1.1 at 243 K. Comparing with the cryogenic separation, this separation factor is extremely high.

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