A Study on the Removal Efficiency of a TEDA Impregnated Charcoal Bed for Methyl Iodide under Humid Conditions

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습윤 조건하에서 TEDA함침 탄소층에 의한 Methyl Iodide 제거효율에 관한 연구

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Abstract

The adsorption model to predict the time dependent removal efficiency of methyl iodide by triethylenediamine (TEDA) impregnated charcoal bed under humid condition is proposed. Under humid conditions, the reduction of equilibrium adsorption capacity and effective pore diffusivity is considered. The predicted values are compared with the experimental results.

요 약

습윤 조건하에서 triethylenediamine (TEDA) 함침활성탄소층의 시간에 따른 methyl iodide제거 효율을 예측하기 위한 흡착모델이 제안되었다. 습윤 조건하에서 평형 흡착용량과 유효 가공 확산 계수의 감소가 고려되었다. 예측된 값은 실험결과과 비교되었다.

Nomenclatnre

C : gas phase concentration, (g mole/cm^3)

C : intraparticle concentration in pore fluid, (g mole/cm^3)

C_0 : gas phase concentration at bed inlet, (g mole/cm^3)

C_l : concentration of methyl iodide in aqueous solution, (g mole/cm^3)

F : volumetric flow rate, (cm^3/sec)

K : Langmuir constant

K' : Freundlich constant

K_f : external mass transfer coefficient, (cm/sec)

N_{pore} : number of pore diffusion mass transfer unit, ($\equiv 15 D_{pore} \cdot (1 - \varepsilon_B) V / r_p^2 \cdot F$

P : total pressure, (atm)

P_s : saturation pressure, (atm)

q : adsorbent phase concentration, (g mole/g)

$\bar{q}$: intraparticle concentration on the pore surface, (g mole/g)

q^* : adsorbent phase equilibrium concentration, (g mole/g)

q_i^* : equilibrium adsorption capacity by liquid phase adsorption at the composition of capillary condensed phase, (g mole/g)

R : constant separation factor, $\left(=\dfrac{1}{1+KC^0}\right)$

R_C : gas constant

S_D : surface area of dry pore, (m²/g)

S_C : surface area of condensed pore, (m²/g)

S_T : total surface area of charcoal, (m²/g)

T : throughput parameter, $\left(=\dfrac{t-[V\varepsilon_B/F]}{AV/F}\right)$

T_a : absolute tempeatrure, (°K)

t : time, (sec)

V_C : volume of condensed pore

V_L : molar volume of condensed liquid, (cm³/g mole)

X : dimensionless fluid phase concentration, $(=C/C_0)$

X_m : volume fraction of methyl iodide in condensed free liquid

Greek Letter

α : contact angle

ε_B : void fraction of adsorption bed

A : distribution coefficient, $(=q^*\rho_B/C_0)$

ρ_B : bulk density of adsorption bed, (g/cm³)

ρ_m : density of methyl iodide, (g/cm³)

ρ_p : density of adsorbent particle, (g/cm³)

σ : surface tension of condensed liquid, (dyne/cm)

1. Introduction

After a postulated LOCA in light water reac tors, it is very important to control the release of radioactive organic iodide (mainly methyl iodide) to atmosphere for the safety of nuclear

power plant[1~4].

In the previous paper[5], the adsorption model to pereict the performance of TEDA impregnated charcoal bed that is one of the most effective means for the removal of methyl iodide, under dry condition was proposed. The removal efficiency of methyl iodide by impregnated charcoal bed, however, is strongly influenced by the presence of water vapor in air stream, and decreased with increasing relative humidity. In very high humid condition, the performance falls off abruptly. Since, following a LOCA, the relative humidity of air stream in a containment becomes very high, it is necessary to predict the useful time of charcoal bed undr humid conditions. This paper intends to analyze quantitatively the influence of the relative humidity on the efficiency of a charcoal bed.

2. Theoretical Consideration

The theoretical model to describe the performance of TEDA impregnated charcoal bed is proposed as follows. The following assumptions have been made for the modelling.

a) The cylindrical adsorption bed of depth Z and D_C is packed with the spherical charcoal of radius r_p.

b) The air mixture containing a single absorbable component flows through the bed at a constant superficial velocity U under the isothermal and isobaric condition.

c) Axial diffusion in the fixed adsorption bed is negligible with respect to bulk flow.

d) Concentration gradient in the radial direction in the gas phase, is negligible.

The governing equation for modellin are as follows.

Gas phase mass balance in the bed

$$U\frac{\partial c}{\partial z}+\varepsilon_B\frac{\partial c}{\partial t}+\rho_B\frac{\partial q}{\partial t}=0 \qquad (1)$$

boundary conditions,

$q=0$, $c=\bar{c}=0$, at $t=0$, $z\geq0$

$c = c_0$, at $z = 0$, $t \geq 0$

Mass balance in a charcoal

$$D_{pore}\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) = \varepsilon_p\frac{\partial C}{\partial t} + \rho_p\frac{\partial \bar{q}}{\partial t}$$

(2)

External mass transfer, or boundary condition for charcoal pellets.

$$K_f(C - \bar{C}) = D_{pore}\left(\frac{\partial C}{\partial r}\right)_{r=r_*}$$

(3)

In the previous paper[5], the adsorption of methyl iodide by TEDA impregnated charcoal under dry condition showed constant pattern condition and was explained well by pore diffusion controlling mechanism. Therefore, the solution of Eq. (1), (2), and (3) gives,[6~9]

$$N_{pore}(T-1) = \frac{1}{\phi_{pore}}\left\{-2\sqrt{(1-R)X}\right.$$

$$-\frac{R}{1-R}\ln\left[\frac{1+\sqrt{1-(1-R)X}}{1-\sqrt{1-(1-R)X}}\right]$$

$$+\frac{\sqrt{R}}{1-R}\ln\left[\frac{\sqrt{1-(1-R)X}+\sqrt{R}}{\sqrt{1-(1-R)X}-\sqrt{R}}\right]\right\}$$

$$+C_1,$$

(4)

where

$$\phi_{pore} = \frac{1.0}{R^{2.0}+1.83(1-R)^{0.92}}$$

$$C_1 = 2.44 - 2.15R$$

If water vapors exist in air stream when air containing methyl iodide passes through a charcoal bed, the capillary condensation of water vapors into the pores of charcoal takes place and the removal efficiency is decreased. Therefore, we consider the reduction of adsorption capacity of methyl iodide due to the capillary condensation of water vapors.

When water vapors exist in air, the pore size that capillary condensation occurs depends on the relative humidity. At a given relative humidity, the capillary condensation takes place in micropores and does not take place in macropores.[10,11] To estimate the adsorption capacity, the following assumptions have been made.

a) Only vapor phase adsorption of methyl iodide takes place, and adsorbed amount of

water vapor is neglected in the dry pore where capillary condensation does not take place, because the hydrophilic areas are much larger than the hydrophilic areas on the pore wall of charcoal.

b) In the capillary condensed pore, there takes place the dissolution of methyl iodide from the gas phase and successive liquid phase adsorption on the wall of capillary condensed pore.

c) By the adsorption of methyl iodide, the contact angle of water in adsorption step gives the same value as that in the desorption step.

d) The methyl iodide concentration in air stream is so low that the value of contact angle is the same as that of single adsorption isotherm of water vapor.

Based on these assumptions, the equilibrium methyl iodide adsorption capacity (q_{total}^*) is the sum of the amount adsorbed in the dry pore (q_1^*), the amount adsorbed on the wall of condensed pore by liquid phase adsorption (q_2^*), and the amount dissolved in the condensed pore (q_3^*), that is

$$q^*_{total} = q^*_1 + q^*_2 + q^*_3,$$

(5)

where

$$q^*_1 = q^* S_D/S_T$$

(6)

$$q^*_2 = q^*_l S_C/S_T$$

(7)

$$q^*_3 = \rho_m X_m (V_C - q^*_2/\rho_m),$$

(8)

The liquid phase equilibrium adsorption in Eq. (7) is obtained from the liquid phase adsorption in the aqueous solution of which concentration is in equilibrium with the gas phase concentration of methyl iodide.

R.A. Hasty[12] obtained the partition coefficient (β) between the vapor phase and the liquid phase of methyl iodide in the range of concentration of p.p.m.. These data can be correlated as follows, in the range of concentration of 6.4×10^{-3} to 1.28×10^{-7}M and of temperature of 4.8 to 68.5°C:

$$\log_{10}(\beta) = -4.82 + \frac{1597}{T_a}$$

(9)

The capillary condensation of water vapor into the pores of charcoal can be expressed by well known Kelvin equation. If the charcoal pores are cylindrical, the maximum radius (r_k) of pores that the capillary condensation occurs is given by the following equation:

$$r_k = -2\sigma V_L \cos\alpha/(R_c T_o \ln P/P_s) \qquad (10)$$

and the value of $\cos\alpha$ is 0.62 for the water vapor[10,13].

The distribution of pore volume and surface area of impregnated charcoal with respect to the pore radius is determined from the desorption isotherm of nitrogen measured at liquid nitrogen temperature.

3. Experiments

3.1. Materials and Reagents

The activated charcoals used in this experiment are coconut based granular type,and both of methyl iodide ($CH_3^{127}I$) and triethylenediamine (TEDA) are research grades. These charcoals were dried at 200°C under the vacuum condition of 10^{-3}mmHg for 4 hours and impregnated with TEDA in aqueous solution. The properties of impregnated charcoal are listed in Table 1.

3.2. Removal of Methyl Iodide By impregnated Charcoal

The schematic diagram of experimental apparatus is shown in Fig. 1.

Air from the gas cylinder was dehumidified in the dryer. A part of air stream was introduced to the humidifier and saturated, and then returned to the main stream to obtain the req-

Table 1. Typical Properties of Impregnated Charcoal

bulk density (g/cm^3)	0.542
mesh (Taylor)	10/12
surface area (m^2/g)	873.4
impregnation	6wt% TEDA

1. Air Cylinder 2. Dryer 3. Rota Meter 4. Humidifier 5. Methyl iodide Saturator 6. Activated charcoal bed 7. Gas chromatograph 8. Hygrometer 9. Back-up bed
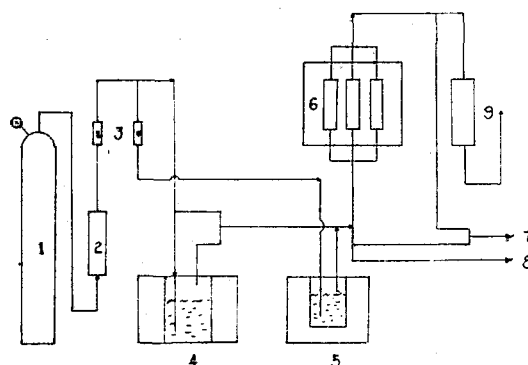
Fig. 1. Schematic Diagram of Experimental Apparatus

uired relative humidity of air stream. Also a small part of air stream was diverted to the methyl iodide saturator, and then return to main stream to control the concentration of methyl iodide.

Then air stream conditioned at the required concentration of methyl iodide and relative humidity was introduced into charcoal bed. At each experimental condition, for the conditioning of adsorption bed, the methyl iodide free air with the same relative humidity as the experimental condition was passed through the bed for 30 minutes, before the adsorption of methyl iodide. Inlet methyl iodide concentration of 1.10×10^{-7}g mole/cm^3 and a air flow rate of 20cm/sec in superficial velocity were employed. The depth and inside diameter of charcoal bed used are 5cm and 1.622cm respectively.

To estimate the influence of relative humidity on the removal of methyl iodide, the variation of the removal efficiency of methyl iodide to the change of relative humidity (0~70%) were measured.

The charcoal bed and humidifier were maintained at 50°C, and the rest parts of experimental apparatus were maintained at 55°C to prevent the condensation of water vapor except

for the methyl iodide saturator. The temperatures are measured by the thermocouple and digital thermometers.

The concentrations of methyl iodide and relative humidities of inlet and outlet air stream were analysed with a thermal conductivity detector of a gas chromatograph (Hewlett Pack ard 5840A with G/K terminal) and hygrometer (Hygrotest Testo 6400) respectively. The sampling of air was done by the autosampler of gas chromatograph. The accuracy of humidity is±2%, RH.

3.3. Measurement of Liquid Phase Adsorption

After impregnated charcoals were mixed with the aqueous solution of methyl iodide in a flask, the flask was shaken in the temperature controlled water bath maintained at 50°C for 24 hours.

The adsorbed amount of methyl iodide was determined by the measurement of methyl iodide concentration of the aqueous solution before and after the adsorption. The thermal conductivity detector of gas chromatograph was used to analyze the methyl iodide concentration of aqueous solution.

3.4. Measurement of Nitrogen Isotherm of Impegnated Charcoal

To determine the pore size distribution and the total surface area, the adsorption and desorption isotherm of nitrogen of impregnated charcoal was measured at liquid nitrogen temperature (77.15°K) by Accusorb 2100E Physical Adsorption Analyzer (Micrometric U.S.A.).

4. Results and Disccussion

The gas phase adsorption isotherm of methyl iodide by the TEDA impregnated charcoal is shown in Fig. 2 and can be expressed well by the Langmuir equation as follows under exper-
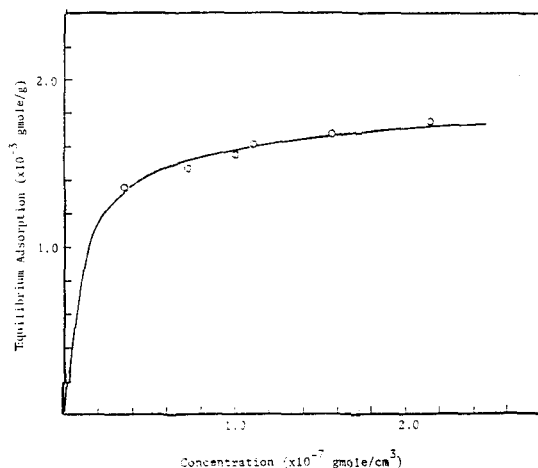

Fig. 2. Gas Phase Methyl Iodide Adsorption Isotherm at 50°C under Dry Condition

imental conditions.

$$q^*(g \ mole/g) = \frac{1.743 \times 10^5 C}{1 + 1.000 \times 10^8 C}$$

The distributions of pore surface area and pore volume of TEDA impregnated charcoal with respect to the pore radius are obtained from the desorption side of nitrogen isotherm and the results are shown in Fig. 3.

The liquid pahse adsorption isotherm of methyl iodide was measured in aqueous solution and can be expressed by Freundlich equation in the range of methyl iodide concentration of 10^{-4} to $10^{-2}g \ mole/l$ (Fig. 4):

$$q_l^* = K'C_l{}^n = 0.486_l{}^{0.763},$$

where q_l^*: g mole/g·charcoal

C_l: g mole/l.

Among the total pore volume and surface area of impregnated charcoal, the cumulative volume and corresponding surface area of pores that capillary condensation takes place at given relative humidity can be determined from the Kelvin equation Eq. (10) and Fig. 3.

The q^*_1, q^*_2, and q_3^* are determined by Eq. (6), (7), (8), and the gas liquid equilibrium correlation. The variation of q^*_{total} due to the change of relative humidity are shown in Fig.5.
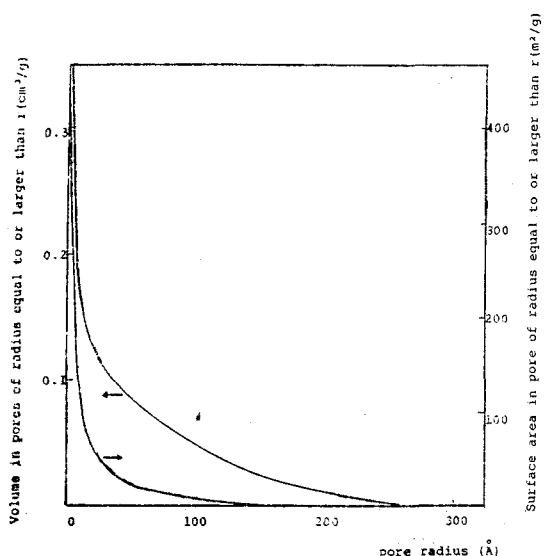
The breakthrough curves of impregnated

Fig. 3. Cumulative Pore Volume and Surface Area Curves of Impregnated Charcoal
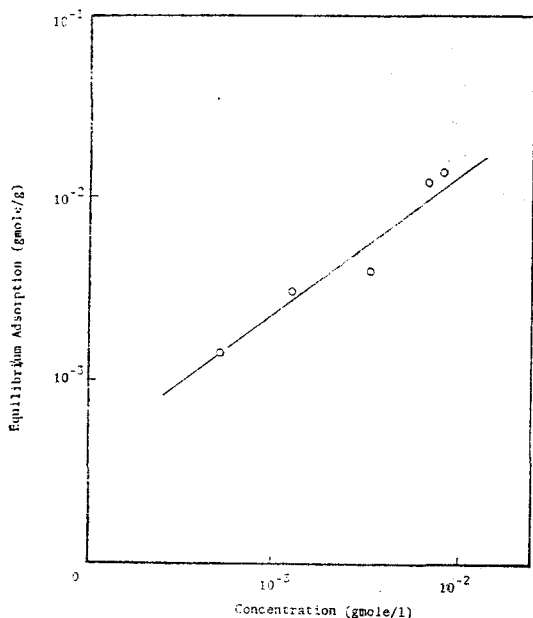

Fig. 4. Methyl Iodide Adsorption Isotherm in Aqueous Solution

charcoal bed, however,are variep with not only the equilibrium adsorption capacity of charcoal but also mass transfer rate from gas phase into the charcoal pores.

It was shown that the mass transfer controlling step under dry condition is the pore diff-

usion,[5] and it is also applied to the humid condition. But the methyl iodide transfer under dry condition takes place by gas phase diffusion, on the contrary methyl iodide transfer under humid condition is composed of the gas phase diffusion in dry pores and the liquid phase diffusion in condensed pores. Mass transfer rate in liquid phase is lower than that in gas phase and the gas-liquid film resistance exist when methyl iodide molecules are dissolved into condensed phase.
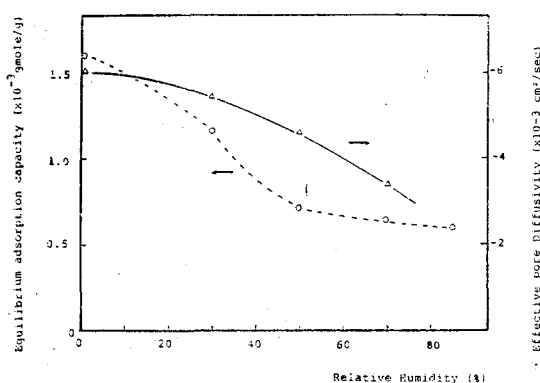
Therefore, the effective pore diffusivity, D_{pore},

Fig. 5. Variation of Equilibrium Adsorption Capacity and Effective Pore Diffusivity of Methyl Iodide According to the Change of Relative Humidity
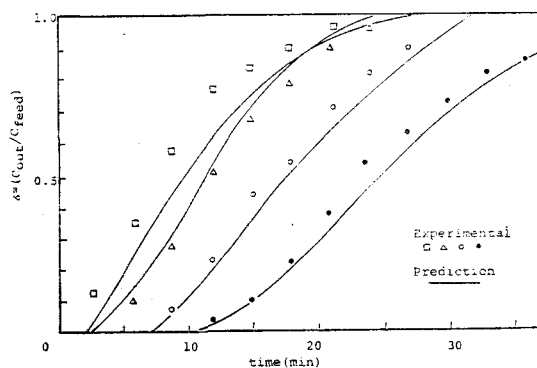

Fig. 6. Effect of Relative Humidity on the Breakthrough Curves for the Adsorption of Methyl iodide at 50°C (bed depth: 5cm, superficial velocity; 20cm/sec, feed concentration: 1.10×10^{-7} g mole/cm³, relative humidity, •; 0%, ∘; 30%, △; 50% □; 70 %).

representing the overall mass transfer rate under humid condition is smaller than that in dry condition. D_{pore} under humid condition was determined by fitting Eq. (4) and the equilibrium adsorption capacity as shown in Fig. 5 to the experimental breakthrough curve obtained at various relative humidity.

The obtained value of D_{pore} is also shown in Fig. 5. From this figure, it is known that the decrease of effective pore diffusivity is more important than the reduction of equilibrium capacity to explain the poor removal efficiency of methyl iodide under high humid condition.

The calculated breakthrough curves and experimental data are shown in Fig. 6. The summary of comparison between the calculated values and experimental data is shown in Fig. 7. As shown in this figure, experimental data are distributed in the error range of 20% of the calculated values except for some data. Both agree well with each other when relative humidity is 30% or 50%, however, actual equilibrium adsorption capacity is smaller as comp ared with the calculated value at 70% relative humidity. This appears to be caused by the fo-

llowing facts. For the theoretical modelling to estimate the equilibrium adsorption capacity of methyl iodide under humid condition, it is assumed that the physical adsorption of water vapors does not occur in dry pore which capillary condensation of water vapors does not take place. In practice, however, the physical adsorption occurs to some degree in dry pore at high relative humidity. Accordingly, the dry surface area of pores is reduced and it leads the subsequent reduction of equilibrium adsorption capacity. Also the rise of bed temperature due to the adsorption heat of water vapor under high humid conditions seems to the deviation of experimental data from those calculated by isothermal model.

5. Conclusion

The adsorption model to analyze quantitatively the influence of relative humidity on the removal efficiency of methyl iodide by TEDA impregnated charcoal bed under humid condition is proposed.

The reduction of removal efficiency under humid condition should be considered in view of the reduction of equilibrium adsorption capacity and the decrease of effective pore diffusivity.

The proposed model predicts the removal efficiency of charcoal bed reasonably provided that the relative humidity is not very high.

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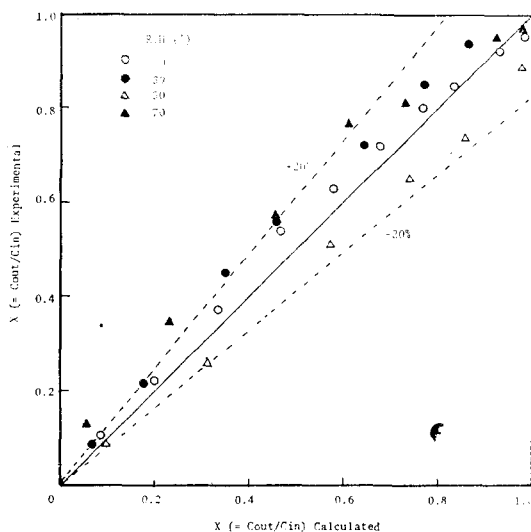4. F.G. May and H.J. Palson, *AAEC/E 322*, Rese-

Fig. 7. Comparison between the Calculated and Experimental Results for x (=Cout/Cin) under Humid Condition

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