19th DOE/NRC NUCLEAR AIR CLEANING CONFERENCE

SESSION 3

ADSORPTION, ADSORBERS, IODINE RETENTION

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CHAIRMEN: J.L. Kovach
Nuclear Consulting Service
W.L. Anderson
Consultant

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REMOVAL OF RADIOACTIVE GASES BY ZEOLITE

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Abstract

Zeolite is proposed for the treatment of radioactive gases emitted from an atomic power plant. Two types of zeolites, 4A and mordenite were chosen for the adsorption study of simulated gases Ar, Kr and CH3I. A DuPont electron-microbalance was employed for the sorption rate and equilibrium measurements. Diffusion study of gas into zeolite was carried out in low pressure. Temperature ranges were 40°-70°C for zeolite 4A, 50°-70°C for mordenite. Isotherms at different temperatures were used to calculate the heat of adsorption. Fick's law decribing the mass transfer of gas into porous solid was employed to obtain the diffusivity from weight-uptake rate curves. Subsequently, the activation energy of diffusion could be evaluated. The order of effective diffusivity and activation energy of diffusion were found to be 10^{-10}-10^{-14} cm^2/sec and 5-10 Kcal/mole respectively in this study. An adsorption column model which took into consideration of the residence time and half-life of the radioactive gas was formulated and the column breakthrough curve was calculated. Consequently, the equilibrium and rate data obtained in the present study may be applied in the actual design of an adsorber for control of the radioactive gases from a nuclear power plant.

I. Introduction

Waste gases from nuclear power plant usually contain certain amount of radioactive components, such as Ar, Kr and CH_3I, etc. In the case that the level of radiation is above safety, treatment of these radioactive wastes is required before releasing them into the atmosphere. One of the applicable method is to encapsulate these radioactive components by solid adsorbents. Among all adsorbents, zeolites were found to possess the properties of high sorption capacity, special selectivity, good temperature stability and strong acid resistance. In addition, they can be easily regenerated to undertake long service cycles. Therefore, zeolites were proposed to be the potential sorbents in treating radioactive gases.

The study of adsorption and diffusion in zeolites was done by Barrer and his coworkers initially. Barrer and Ibbitson (1944) studied the sorption of various gases on chabazite and analcime. They reported that in order of increasing affinity for the zeolite lattice, one may write for a series of non-polar gas as $H_2 < He < Ar$ or $O_2 < N_2$. Barrer and Brook (1953) studied the sorption kinetics of C_3H_8, n-C_4H_{10}, CH_2Cl_2 and $(CH_3)_2NH$ in chabiazite, mordenite and levynite at room temperature, -78°C, and -185°C. They reported the diffusivities of the gases and the activation energy for diffusion increases as the chain length of the sorbate molecules increases. Iodine occlusion by chabazite was measured by Barrer and Wasilewski (1961 a,b) in the temperature range of 120°-300°C. The partial molal heat of occulsion $\Delta\bar{H}$ was determined from the adsorption isotherms. Very large value of $\Delta\bar{H}$ was reported when the amount of iodine sorbed was low. Barrer and Coughlan (1968) investigated the effects of removal of cations and anions framework charge from clinoptilolite upon the sorption characteristics of polar guest molecule CO_2 and non-polar molecule Kr. The sorbent became progressively more energetically homogeneous towards carbon dioxide as a result of the removal of the charge from the zeolite. On the other hand, all the acid-treated zeolites showed energetic homogeneity towards Kr. Barrer and Vaughan (1971) investigated the sorption and diffusion characteristics of phillipsite along with zeolite K-M and othr silicates for the trapping and storage of inert gases. After outgassing, the zeolite was exposed to high pressures of inert gas at high temperature and then quenched while still under pressure. Both sorption isotherm and diffusion coefficient were measured. Barrer and Papadopoulos (1972) obtained the equilibrium isotherms of Kr and Xe in chabazite in the temperature range of 150-450°C and at pressures up to 100 atm. Barrer and Robins (1953) studied the single gases H_2, Ne, O_2 and N_2 adsorption and diffusion in mordenite, O_2, Ar and N_2 in chabazite and binary gases H_2+N_2, H_2+Ne, N_2+O_2 sorption in mordenite, and $Ar+O_2$, $Ar+N_2$ in chabazite.

Elberly (1969) employed the chromatographic technique to study the sorption and diffusion properties of Ar, Kr in 5A and SF_6 in 13 . Sarma and Hagnes (1974) also used moment technique to investigate the Ar sorption and diffusion characteristics in 4A. Ruthven and Derrah (1972) studied the diffusion properties of Ar, Kr in 4A and Ar, Kr, Xe in 5A.

In this study, two types of zeolites, 4A and mordenite were chosen for sorption of simulated radioactive A_r, K_r and CH3I gases. A Du Pont electronmicrobalance was employed for sorption rate and equilibrium measurements. Diffusion study of gas into zeolites was carried out in low pressure (below atmospheric). Temperature ranges were 40^o-70^oC for zeolite 4A, 50^o-70^oC for mordenite. The equilibrium adsorption and diffusion data were fed into a mathematical model of adsorption column which took into consideration of the half-life and level of radiation of the gas. Consequently, the break through radiation counts can be adjusted to meet the pollution control standard by simulation of the column adsorption model.

II. Experimental Section

The adsorbent, chemicals, apparatus and procedure used in the experiment will be stated below.

1) Adsorbents and chemicals

Zeolite 4A and mordenite were purchased from Davison Chemical, W.R. Grace & Co. and Norton Co. respectively. The 4A zeolite is three-dimensional channels of approximately 0.4 μm openning and the mordenite is one-dimensional channels of 0.67x0.7 μm interconnecting with another 0.29x0.57 μm one-dimensional openning.

Research grade of Ar, K_r and CH3I gases of purity 99.9% were purchased from Matheson Chemicals.

2) Apparatus

The weighing instrument is a modified DuPont TGA with improved sealing. The set-up consists of nine parts: 1-fast response recorder , 2-microbalance, 3-gas container with heater and insulation, 4-low pressure gauge, 5-gas cylinder, 6-vacuum gauge, 7-vacuum pump, 8 and 9-variable resistors. The complete set-up is shown in Fig. 1.

3) Procedure

Before a run, the careful calibration of the micro-balance is essential. Approximately 10 mg adsorbent was placed in the sample holder. The vacuum pump was started until the system reached 0.01 mmHg then the sample was heated to 400^oC for about 10 hours, meanwhile, the system was maintained at low vacuum and degased. The dry weight of the sample was recorded. After thoroughly degased, the sample was cooled to the desired temperature and maintained at that temperature for about half of an hour. Then, the hydrocarbon gas was injected into the adsorption chamber for the sorption and diffusion study.

At a given injection pressure, the rate of adsorption is determined by the increase in weight of the sample with time. The total amount of gas adsorbed is plotted against equilibrium pressure as the adsorption isotherm. At a given low injection pressure the sorption rate curve was determined by the weight increase of the sample vs. time.

In all the runs, the amount of adsorbent was relatively small in comparison to the volume of the adsorbate. There was no appreciable change in the pressure of the gas chamber. Consequently, all the diffusion runs could be considered as under constant pressure-constant volume condition. All the diffusion runs were in the low pressure region in order to ensure the validity of the Henry's law for adsorption.

III. Correlation Equations

1) Equilibrium

Langmuir isotherm

$$\frac{S}{S_\infty} = \frac{KP}{1+KP}$$

was employed to correlate the concentration in the solid with the partial pressure in the gas phase. The S_∞ and K were obtained by least square fitting of the experimental isotherm.

2) Transient Diffusion

The rate of sorbate entering the sorbent was correlated by the second Fick's law under constant volume and constant pressure condition. The assumptions involved in the mass balance equations are

i) Solid adsorbent is spherical.

ii) Fick's law is applicable.

iii) Solid-gas film resistance can be neglected.

iv) The mobile phase and immobile phase in adsorption is related by Henry's law.

v) The effective diffusivity including pore volume and surface diffusion is constant.

vi) Adsorption equilibrium is instantaneously achieved.

The mass balance in the spherical adsorbent is

$$\varepsilon_p \frac{\partial C_r}{\partial t} + \rho_p \frac{\partial S}{\partial t} = \frac{\varepsilon_p}{r^2} \frac{\partial}{\partial r}\left(r^2 D_p \frac{\partial C_r}{\partial r}\right) \qquad (1\text{-}1)$$

the initial and boundary conditions are

$$t=0,\ C_r=0 \qquad (1\text{-}2)$$

$$r=0,\ \frac{\partial C_r}{\partial r}= 0 \qquad (1\text{-}3)$$

$$r=R,\ C_r=C_b^o \qquad (1\text{-}4)$$

and the relationship between C_r and S is

$$S=(KS_\infty RT)C_r= K'C_r \qquad (1\text{-}5)$$

The solution for the system equation (1) was obtained by Crank (11)

$$\frac{M_t}{M} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-D_e n^2 \pi^2 t/R^2}$$

where

$$D_e = \frac{\varepsilon_p D_p}{\varepsilon_p + \rho_p \bar{K}'}$$

$$M_t = C_b^o - C(t)$$

$$M_\infty = C_b^o - C_\infty$$

A least square procedure which minimized the $\Sigma[(\frac{M_t}{M_\infty})_{model} - (\frac{M_t}{M})_{experiment}]^2$ was employed in order to obtain the best De.

3) Heat of Adsorption and Activation Energy of Diffusion

The isosteric heat of adsorption can be obtained by the following equation

$$\left(\frac{\partial \ln P}{\partial T}\right)_\pi = \frac{\Delta H}{RT^2}$$

where

π = at a certain coverage or spreading pressure

Assuming the diffusivity is dependent on temperature in the Arrhenius equation, then

$$D_e = D_e^o \exp(-E_a/RT)$$

The D_e^o and E_a can be obtained from the intercept and slope of the logarithmic plot of D_e vs. 1/T respectively.

4) Radiation Breakthrough Curve

The normal practice of measuring the radiation of a radioactive substance is by γ spectroscopy. The intensity of the radiation is correspondent to the peak area of the spectrum. After corrections of the geometric configuration and the efficiency of the γ-spectroscopy, the radiation activity ϕ is related to concentration by

$$\lambda \phi = C$$

where $$\lambda = \frac{\ln 2}{t_{1/2}}$$

Consequently, the quantity $\phi = \frac{C}{\lambda}$ is used for the column break through study instead of C alone. Hence the system of equations of ϕ balance in the column was

In the zeolite particle

$$\frac{\partial \phi_r}{\partial t} = D_e \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \phi_r}{\partial r}) \tag{2-1}$$

Initial and boundary conditions are

$$t = 0, \quad \phi_r = 0 \tag{2-2}$$

$$r = 0, \quad \frac{\partial \phi_r}{\partial r} = 0 \tag{2-3}$$

$$r = R, \quad D_e \frac{\partial \phi_r}{\partial r} = k_f(\phi - \phi_s) \tag{2-4}$$

In the gas phase

$$\varepsilon_B \frac{\partial \phi}{\partial t} + \varepsilon_B U \frac{\partial \phi}{\partial z} = \varepsilon_B D_L \frac{\partial^2 \phi}{\partial z^2} - \frac{3k_f}{R} (1-\varepsilon_B)(\phi - \phi_s) \tag{3-1}$$

Initial and boundary conditions

$$t = 0, \quad \phi = 0 \tag{3-2}$$

$$z = 0, \quad U\phi = U\phi_o - D_L \frac{\partial \phi}{\partial z} \tag{3-3}$$

$$z = L, \quad \frac{\partial \phi}{\partial z} = 0 \tag{3-4}$$

Linear relationship between gas and solid phase

$$\phi_r \Big|_{r=R} = KS_\infty RT\phi = K'\phi_s \tag{4}$$

If writen in dimensionless form and simplified, the above system of equations become

$$\frac{\partial Q}{\partial \tau} = \frac{1}{X^2} \frac{\partial}{\partial X} (X^2 \frac{\partial Q}{\partial X})$$

$$\frac{\partial f}{\partial \tau} + \psi\theta \frac{\partial f}{\partial z} = \frac{\psi\theta}{Pe} \frac{\partial^2 f}{\partial z^2} - 3\psi\xi \; (f - \frac{Q|_{r=R}}{K'}) \tag{1-2}$$

Initial and boundary conditions

$$\tau = 0,\ f = Q = 0 \tag{1-3)'}$$

$$X = 0,\ \frac{\partial Q}{\partial z} = 0 \tag{1-4)'}$$

$$X = 1,\ \frac{\partial Q}{\partial X} = 0 \tag{1-5)'}$$

$$z = 0,\ 1 = f - \frac{1}{Pe}\frac{\partial f}{\partial z} \tag{1-6)'}$$

$$z = 1,\ \frac{\partial f}{\partial z} = 0 \tag{1-7)'}$$

This system of equations was solved by orthogonal collocation method using four collocation points inside the particle and eight collocation points along the column. A semi-implicit Runge-Kutta method was used to solve the resulting ordinary differential equations.

IV. Results and Discussion

The isotherms of A_r and K_r on zeolite 4A is shown in Fig. 2. in the temperature range of 40^o to 60^oC. The maximum adsorption capacities for A_r and K_r are slightly more than 3. and 1 mmoles per gram respectively. The isotherms of A_r and K_r on mordenite are shown in Fig. 3. They are of roughly the same capacity as in 4A. The adsorption capacity of CH_3I on 4A are shown in Fig 4. In the regeneration step, great difficulty was encountered, the amount of CH_3I adsorbed was extremely difficult to remove. Subsequently, new zeolite was placed in the balance for each run. The adsorption capacity is slightly under 3 mmoles per gram at 46^oC and close to 2 mmoles per gram at 72^oC. The values of heat of adsorption calculated from the equilibrium constants of the isotherms were listed in Table I.

The effective diffusivity calculated from the experimental transient curve was also listed in Table I. The order of magnitude of the effective diffusivity is in the range of $10^{-10}\sim 10^{-14}$ cm^2/sec in this study. The activation energy of diffusion is in the range of 5-10 Kcal/mole. Previous study by Walker et al. (1966) for Ar on KA and K_r on CaA zeolites was approximately 10^{-16}-10^{-18} cm^2/sec and by Ruthven and Derrah (1975) for A_r and K_r on 4A was approximately 10^{-10}-10^{-13} cm^2/sec which were extrapolated respectively to the temperature range in this study. Our results appear to be pretty close to those of Ruthven and Derrah. The order of magnitude in the zeolites can be arranged in the following sequence: $K_r/MN > CH_3I/4A > A_r/MN > A_r/4A > K_r/4A$. It is of interest to know that the pore diffusivity defined as $D_p = D_e \dfrac{\varepsilon_p + \rho_p K'}{\varepsilon_p}$ is strongly influenced by the equilibrium constant K' and does not show an exponential dependence on temperature. The values of D_p are also listed in Table I. The Arrhenius plot of effective diffusivity is illustrated in Fig. 5. The experimental data and model curves of diffusion are shown in Fig. 6 to 7 representatively. Reasonably good agreement between experiment and diffusion model has been attained.

In the simulated column breakthrough model, the required input information are the gas-sorbent equilibrium isotherm and the diffusion coefficient. Other information on the bulk phase can be estimated from the existing coorelations. The input data for the mathematical model are summarized in Table II. For simplicity, we will treated the radioactive gases one by one. The bulk phase property was considered as the property of the air because of the dilute concentration of the radioactive gases. The breakthrough radiations of Ar, K_r, and CH_3I are shown in Fig. 8 to 11. The column was assumed to have a dimension of 17.1 m height and 1.52 m diameter with a gas flow rate of 150 m^3/hr. Approximately, 5000 Kg of zeolite with particle size of 0.16 cm are packed in the column. Suppose the radioactive gas A_r of 1.903×10^{-5} μCi/ml entering the column packed with 4A zeolite, the beginning breakthrough time is about 4 min. but needs a long time to reach 80% of the initial radiation as indicated in Fig. 8. Samilarly, for A_r in mordenite, K_r in 4A and CH_3I in 4A the beginning breakthrough time are also about 4 mins, but they need even longer time to reach 60% of the initial radiation in the column outlet as indicated in Fig. 9-11. The extremely slow rising to the initial radiation may be due to the small diffusivity of the gas in zeolite and to the relatively fast gas flow rate which resulting early breakout in the column. For illustration, if no more than 10% of the initial radiation is allowed to release from the column, then 4 to 5 min. is allowed for A_r and CH_3I in 4A and several days for A_r in mordenite and K_r in 4A column.

The affinity of K_r and CH_3I toward zeolites is much higher than air. They are preferentially adsorbed and the existence of air can be considered as no interference on the adsorption of the radioactive gases. However, the affinity of A_r toward zeolite is compatible to the N_2 and O_2. Study of the mixture adsorption should be done in order to fully understand the influence of air on the sorption of A_r quantitatively. A longer column may be needed in order to accommodate the N_2 and O_2 adsorptive effects on the A_r gas.

In the mathematical model of the column breakthrough curve, Henry's law constant was used which could be unrealistically large. Hence model calculation of using Langmuir isotherm is under-way and will be reported in the future. Also experimental work of employing a small size column with temperature and flow controller should be carried out in order to obtain experimental data for justification and validation of the theoretical results.

Nomenclature

C	bulk phase concentration
C_b^o	inlet concentration
C_r	pore concentration
C_∞	bulk phase concentration for $t\rightarrow\infty$
D_e	effective diffusivity
D_e^o	pre-exponential factor in $D_e=D_e^o \exp(-E_a/RT)$
D_L	axial dispersion coefficient
D_p	pore diffusivity
E_a	diffusional activation energy
f	dimensionless bulk phase concentration, C/C_b^o
ΔH	heat of adsorption
$\Delta\bar{H}$	partial molal heat of occulsion
K	adsorption constant
K'	Henry's law adsorption equilibrium constant
k_f	mass transfer coefficient
L	adsorber length
P_e	Peclet Number , UL/D_L
Q	dimensionless pore concentration, C_r/C_b^o
R	radius of zeolite crystal
r	radius coordinate of zeolite crystal
S	solid phase adsorbate concentration
S_∞	S for $t\rightarrow\infty$
T	temperature
t	time
$t_{1/2}$	half life of radioative specie
U	superficial velocity
X	dimensionless radial coordinate, r/R
z	axial coordinate
Z	dimensionless axial coordinate, z/L

Greek symbols

ε_B	void fraction in adsorber
ε_P	particle porosity
θ	dimensioless group, $UR^2\varepsilon_B/LD_eK(1-\varepsilon_B)$
λ	radiation constant
ξ	dimensionless group, $k_f R/D_eK$
π	coverage

ρ_p	particle density
τ	dimensionless group, $D_e t/R^2$
ϕ	radiation activity
ϕ_o	ϕ at $z=0$
ϕ_r	ϕ at radius r
ϕ_s	ϕ at particle surface

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Table I Summary Results of Equilibrium and Transient Diffusion

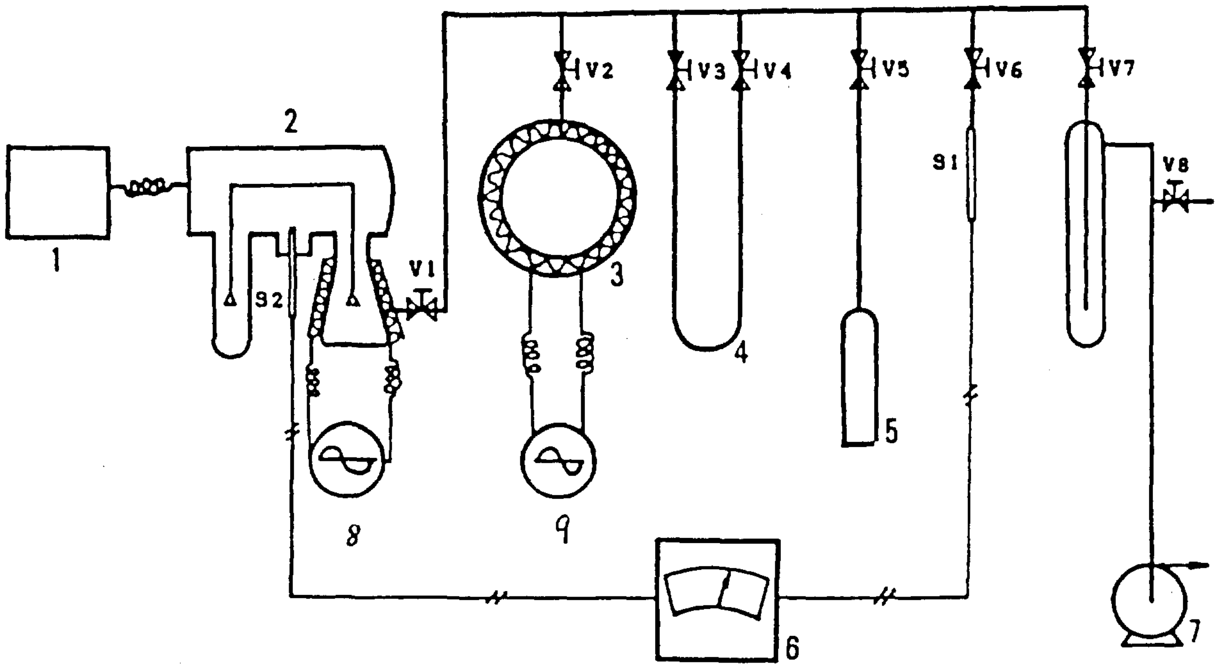
Sorbate	Sorbent	T(^{o}K)	K(l/mmHg)	$S_\infty(\frac{\text{m-mol}}{g})$	K'(cc/g)	De(cm^2/S)	D_p(cm^2/S)	H (Kca/mol)	Ea (Kcal/mol)
Ar	4A	333	41.55	3.29	2.84×10^{6}	4.07×10^{-14}	3.12×10^{-7}	16.83	7.68
Ar	4A	322	51.65	3.36	3.48×10^{6}	2.87×10^{-14}	2.70×10^{-7}		
Ar	4A	316	185.70	3.43	1.25×10^{7}	2.48×10^{-14}	8.38×10^{-7}		
Kr	4A	333	7.71	1.35	2.16×10^{5}	2.79×10^{-12}	1.63×10^{-6}	12.64	10.70
Kr	4A	323	25.90	1.44	7.52×10^{5}	1.89×10^{-12}	3.84×10^{-6}		
Kr	4A	313	26.46	1.62	8.34×10^{5}	9.92×10^{-13}	2.24×10^{-6}		
Ar	mordenite	334	24.74	3.44	1.77×10^{6}	9.14×10^{-13}	9.82×10^{-6}	15.28	5.47
Ar	mordenite	323	67.25	3.49	4.72×10^{6}	6.70×10^{-13}	1.93×10^{-5}		
Ar	mordenite	311	137.31	3.61	9.60×10^{6}	4.57×10^{-13}	2.67×10^{-5}		
Kr	mordenite	343	24.39	1.30	6.80×10^{5}	1.03×10^{-10}	4.25×10^{-4}	6.66	8.30
Kr	mordenite	323	85.96	1.36	2.89×10^{6}	5.79×10^{-11}	1.02×10^{-3}		
Kr	mordenite	303	91.03	1.50	2.58×10^{6}	2.67×10^{-11}	4.18×10^{-4}		
CH_3I	4A	345	3.55	1.97	1.50×10^{5}	2.04×10^{-12}	8.30×10^{-7}	11.37	4.13
CH_3I	4A	319	13.72	2.92	7.96×10^{5}	1.25×10^{-12}	2.69×10^{-6}		

Table II, Parameters used in model simulation*

System	De(cm^2/sec)	K(cc/cc)	k_f(cm/sec)	D_L(cm^2/sec)
A_r-4A	2.87×10^{-14}	4.42×10^{6}	4.29	0.969
K_r-4A	1.89×10^{-12}	9.55×10^{5}	3.57	0.956
A_r-MN	6.70×10^{-13}	8.02×10^{6}	4.29	0.969
K_r-MN	5.79×10^{-11}	4.91×10^{6}	3.57	0.956
CH_3I-4A	1.25×10^{-12}	1.01×10^{6}	2.81	0.942

* Common parameters:

R=0.16 cm, $\varepsilon_B=0.4$, U=11.42 cm/sec, L=17.1 m



1. Recorder
2. Electrobalance Assembly
3. Gas Reservoir
4. Manometer Assembly
5. Sorbate Gas Cylinder
6. Vacuum Gauge
7. Vacuum Pump
8&9. Resistor

Figure 1. Experimental Apparatus.

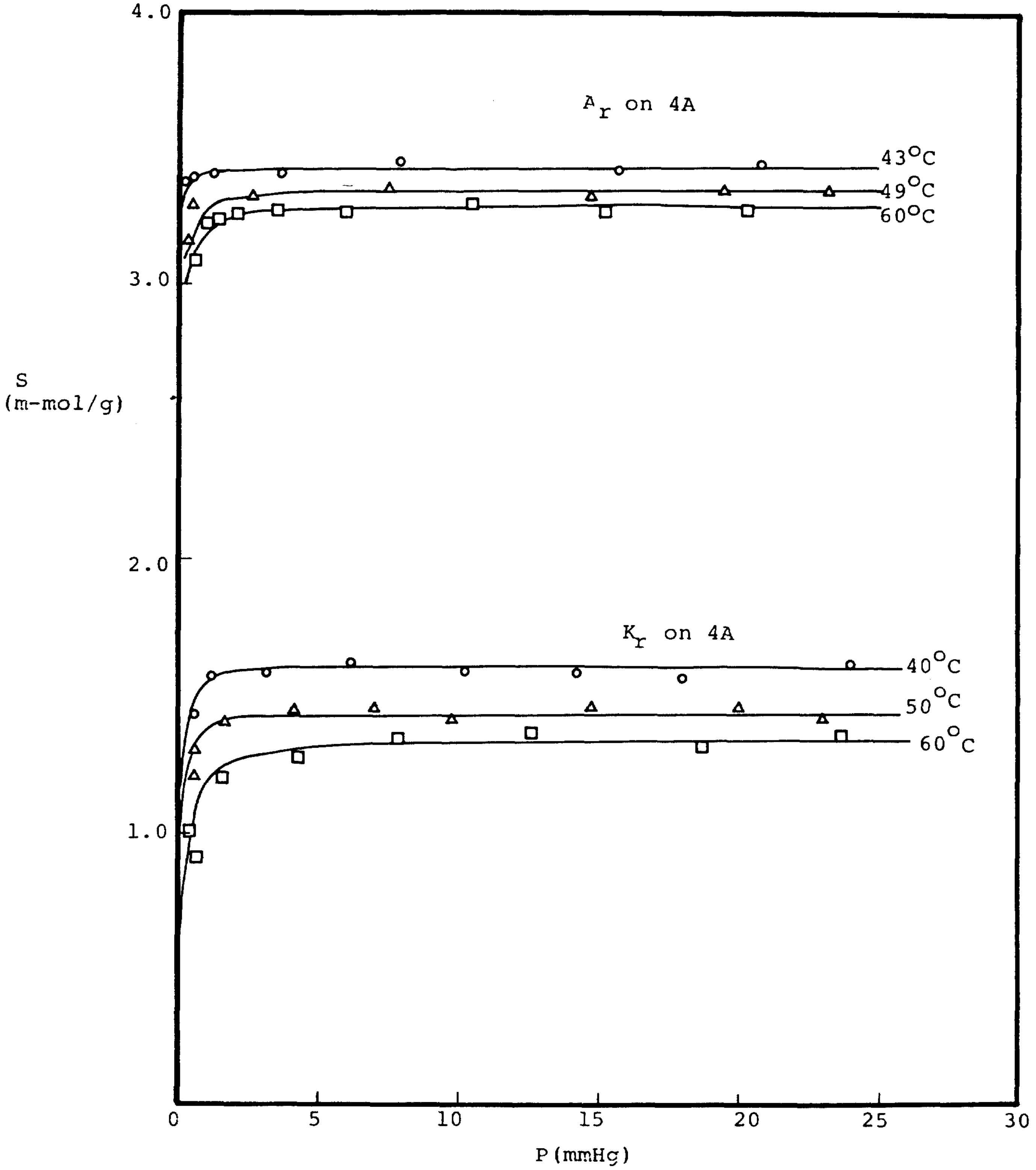


Fig. 2 Equilibrium Isotherms of A_r and K_r on 4A

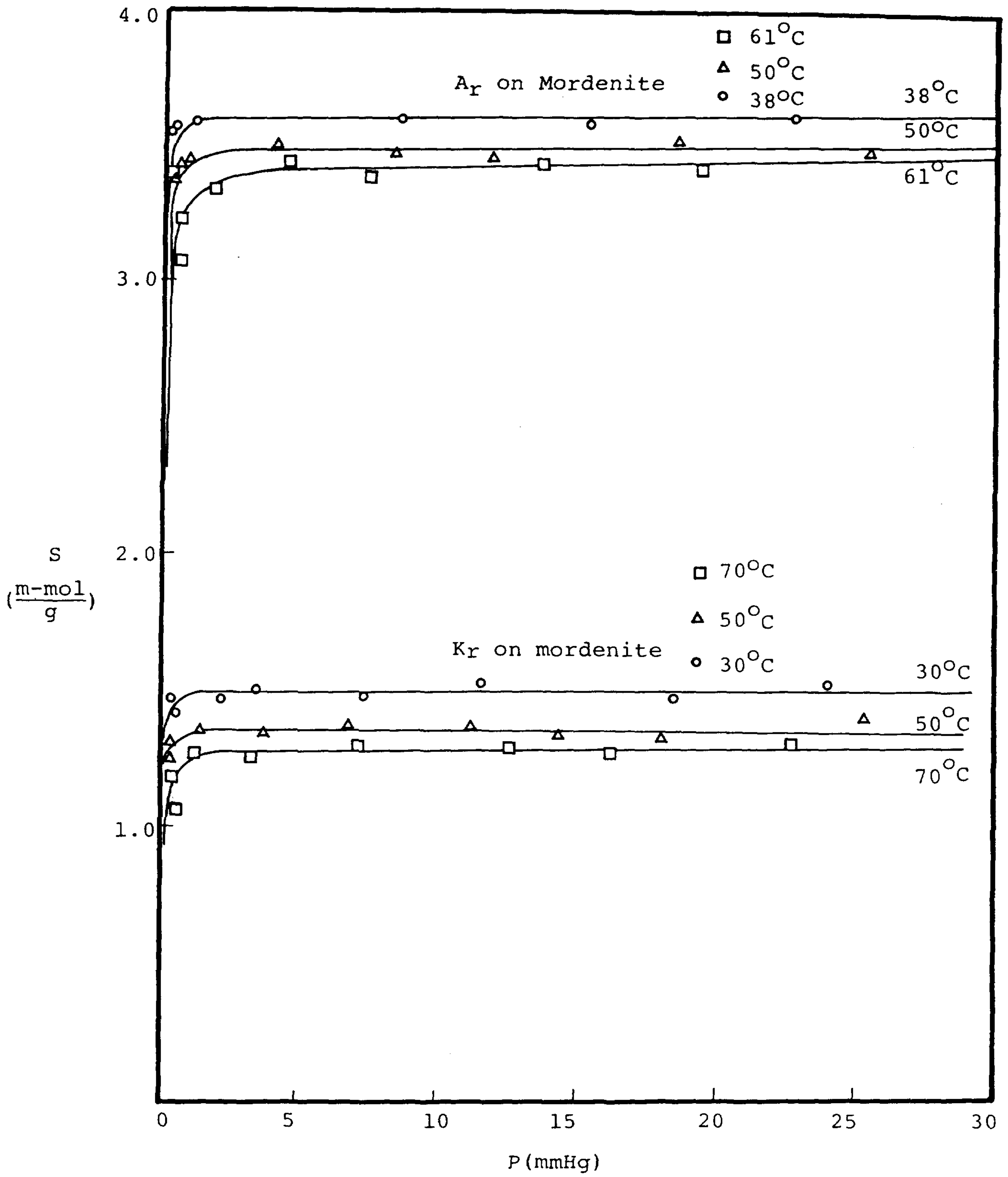


Fig. 3 Equilibrium Isotherms of Ar and Kr on Mordenite

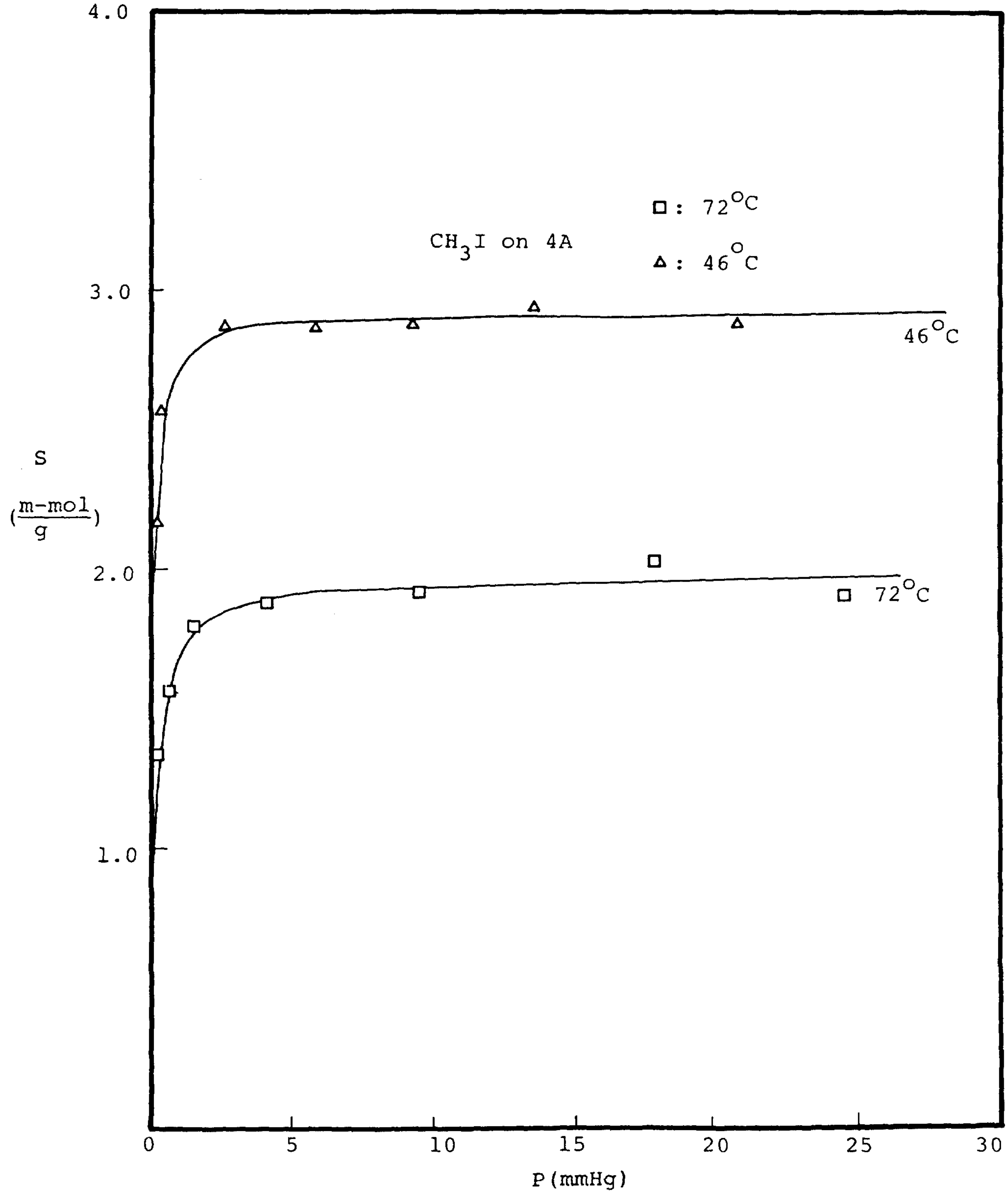


Fig. 4 Equilibrium Isotherms of CH$_3$I on 4A

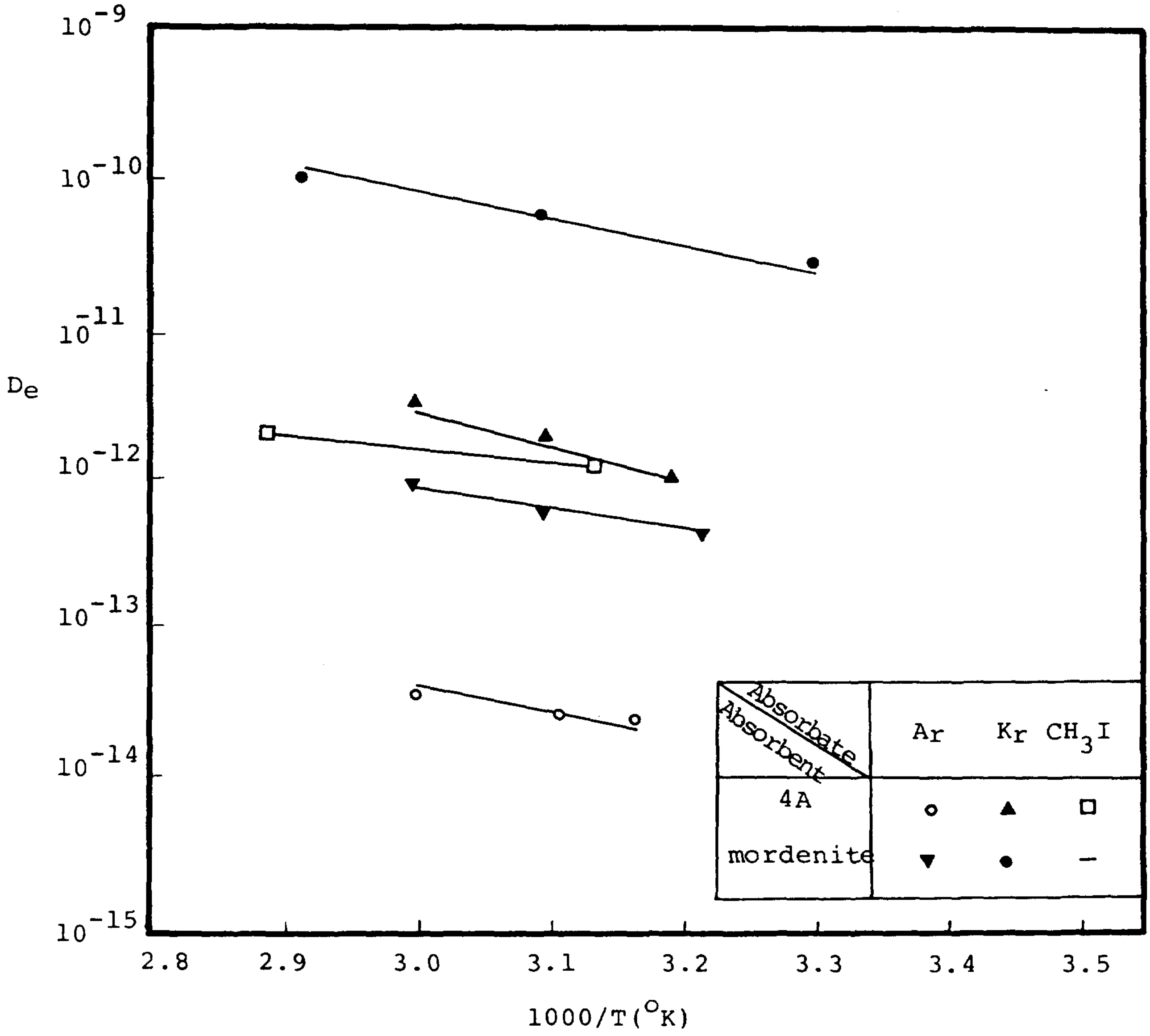


Fig. 5 Arrhenius plot of diffusivities

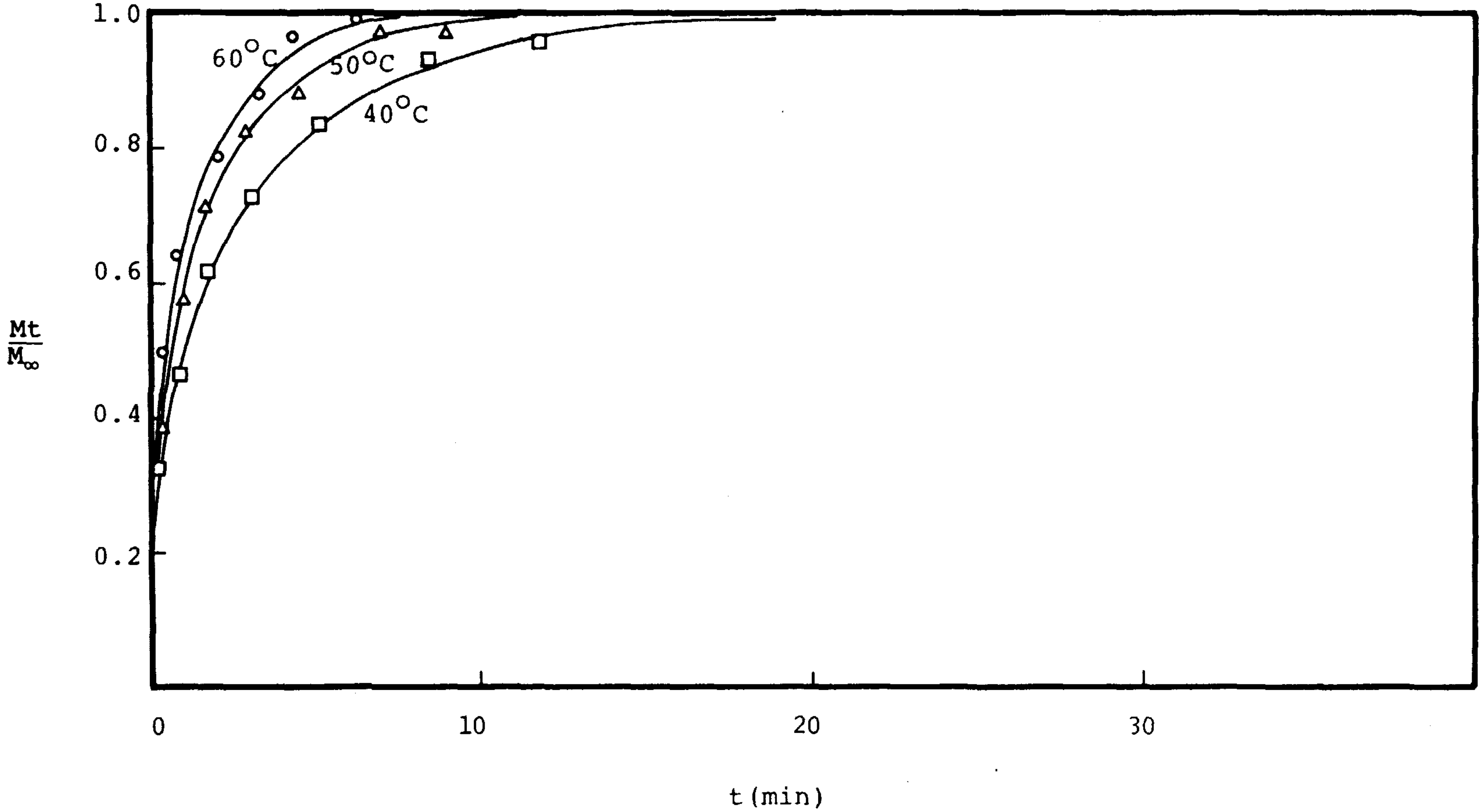


Fig. 6 Transient Diffusion of K_r in 4A Zeolite

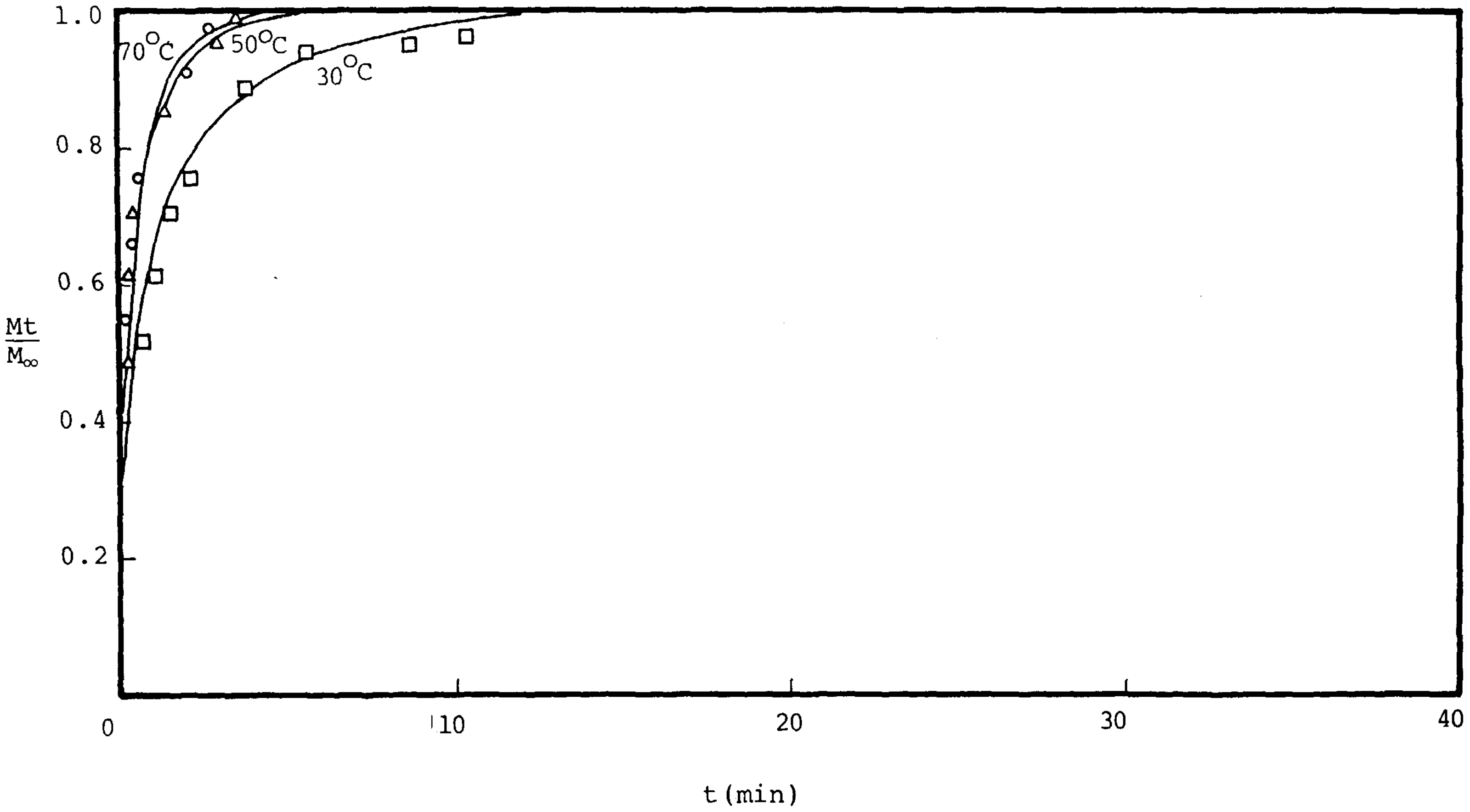


Fig. 7 Transient Diffusion of K_r in Mordenite

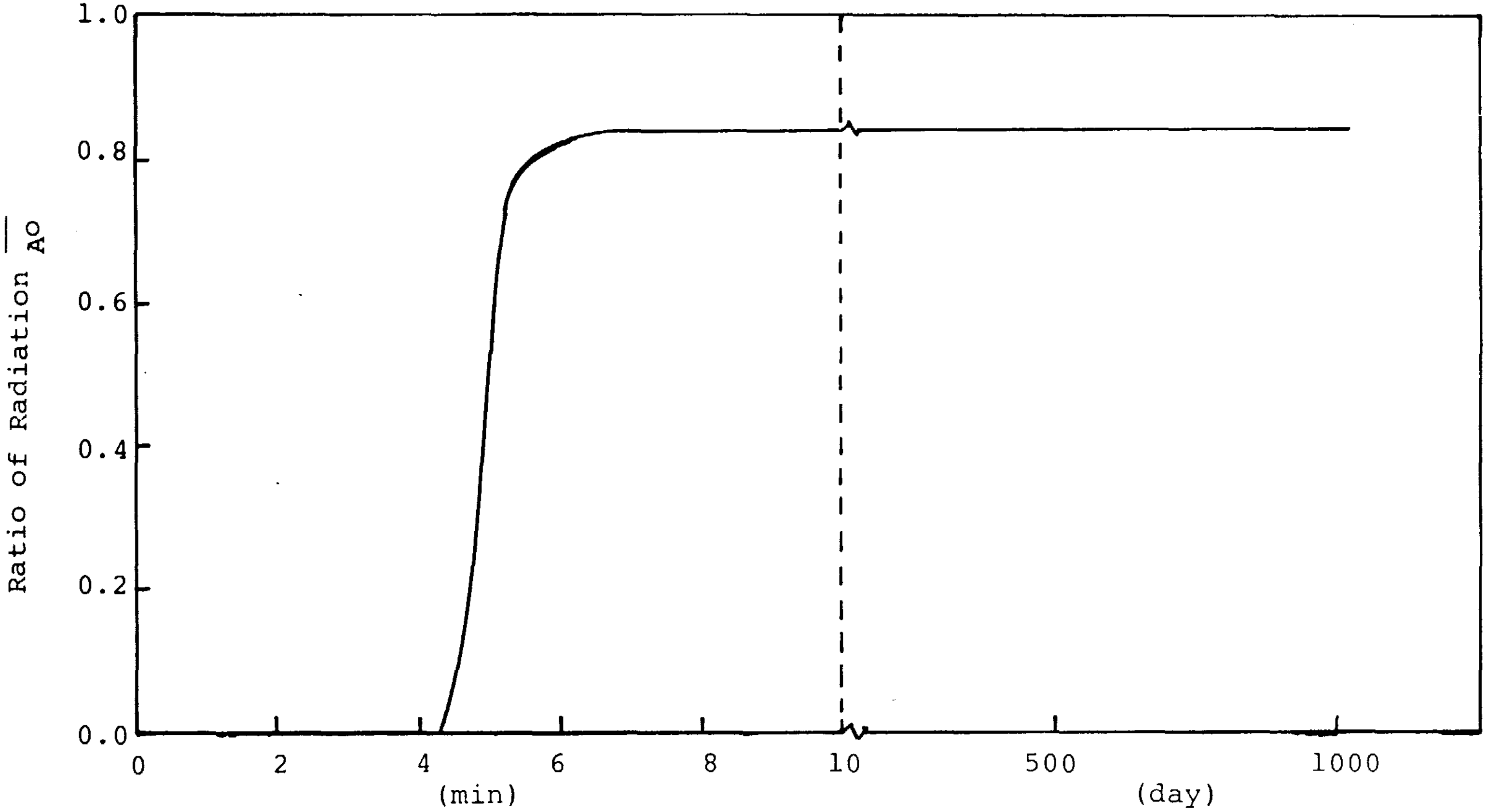


Fig. 8 Breakthrough Curve of A_r in 4A Column at 323°K

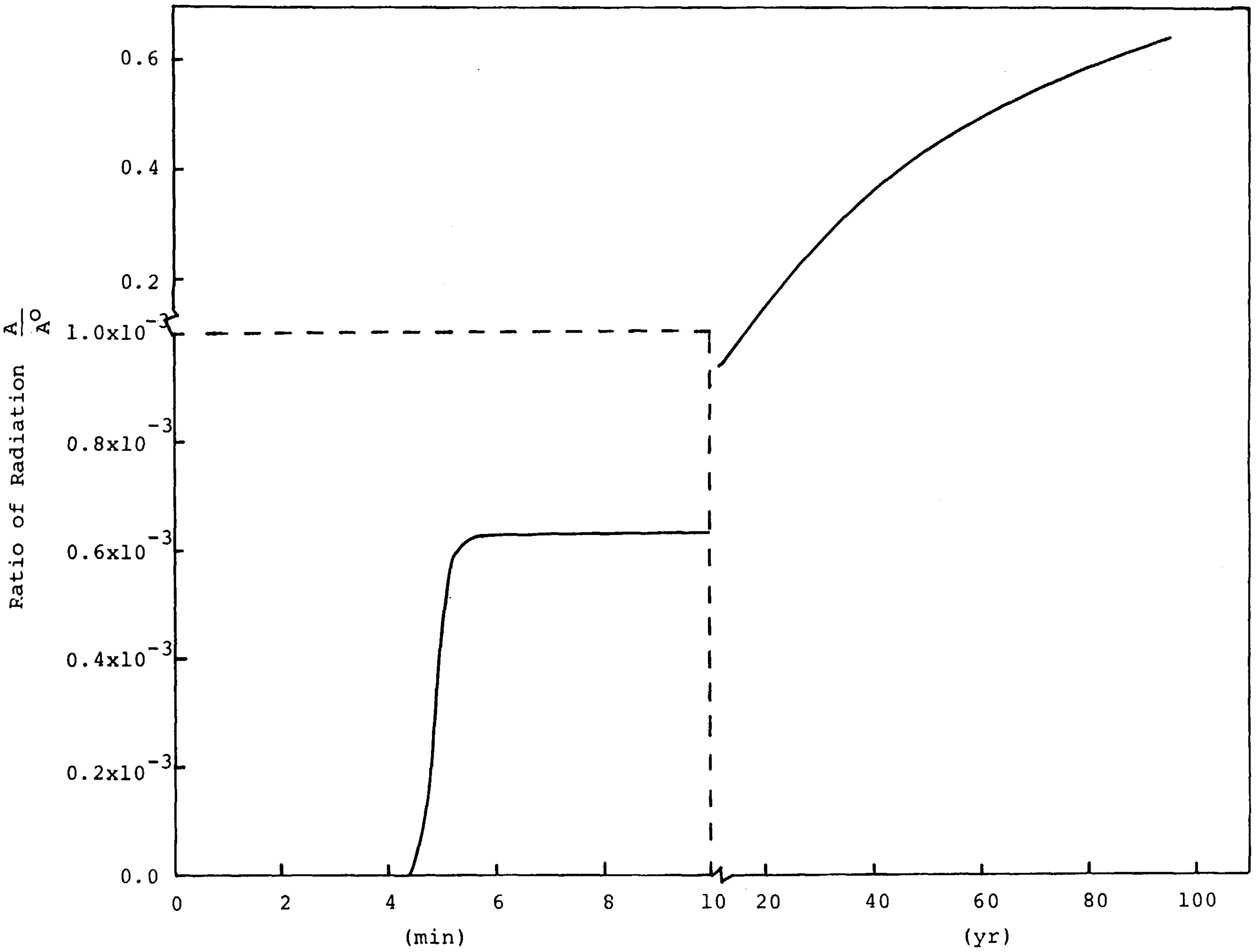


Fig. 9 Breakthrough Curve of A_r in Mordenite Column at 323^oK

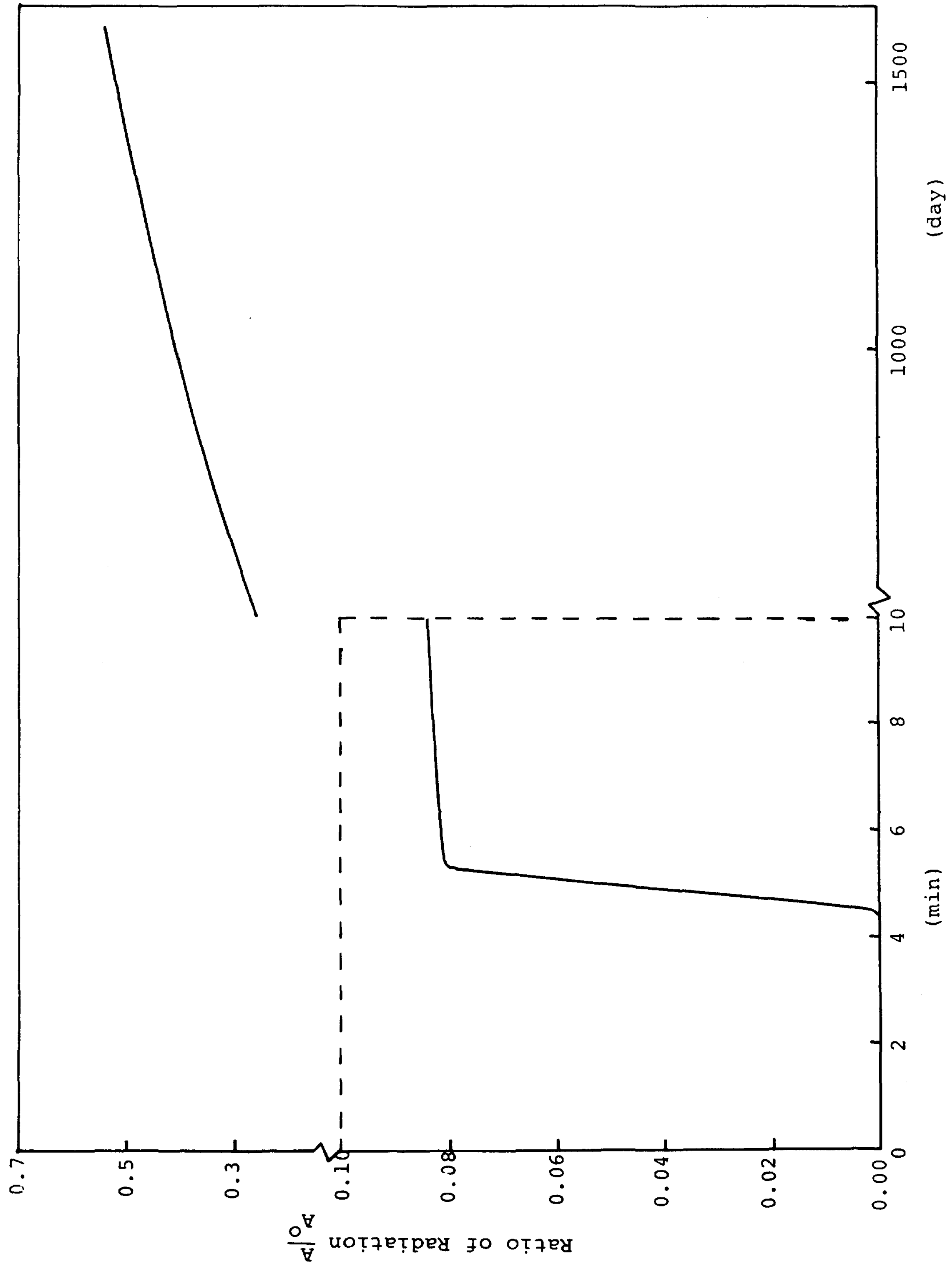


Fig. 10 Break through of Kr in 4A Column at 323°K

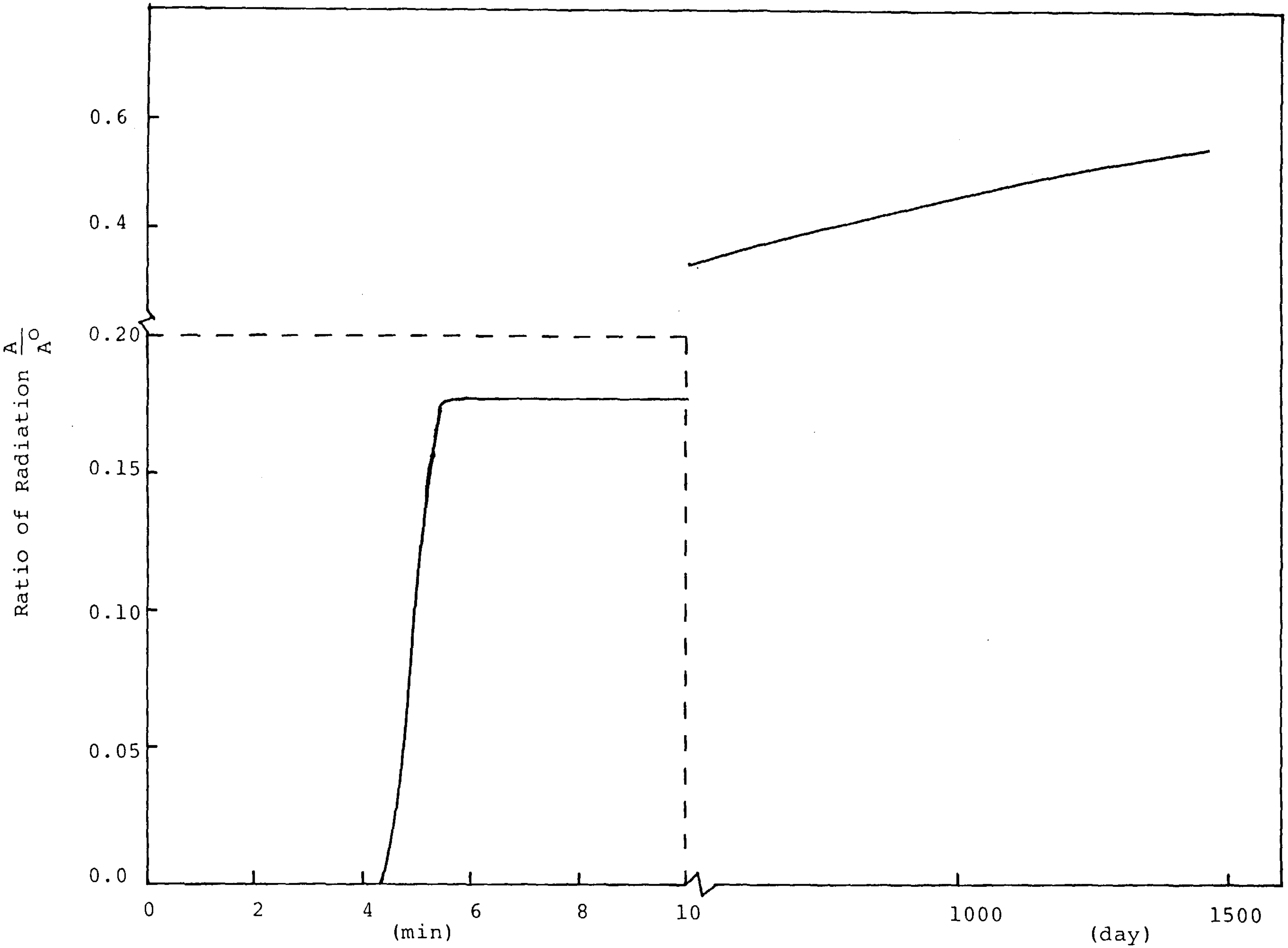


Fig. 11 Breakthrough Curve of CH_3I in 4A Column at 323°K

19th DOE/NRC NUCLEAR AIR CLEANING CONFERENCE

IN SITU MEASUREMENTS OF EFFICIENCY OF SILVER ZEOLITE FOR REMOVAL OF AIRBORNE RADIOIODINE SPECIES

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Abstract

In situ measurements of the decontamination factors (DFs) for the various species of radioiodines were performed for silver zeolite (AgX) filters used to clean up the Loss of Fluid Test (LOFT) containment air exhaust. Results indicated that the DF for elemental radioiodine was the highest, with the DFs for the particulate, hypoiodous acid (HOI), and organic (e.g. CH_3I) species being lower. Measured DFs ranged from 50 to greater than 100,000, depending on filter bank and radioiodine species.

I. Introduction

In situ measurements were made of the radioiodine in the air being exhausted from the containment building during the Fission Product 2 (FP-2) Test conducted during July 1985 at the Loss of Fluid Test (LOFT) facility located at the Idaho National Engineering Laboratory (INEL). Primary objectives of the measurements were to (1) determine the radioiodine species concentrations in the containment air, (2) observe changes with time of the radioiodine species mixture, and (3) measure the decontamination factors (DFs) realized by silver zeolite (AgX) cleanup filters for the various radioiodine species. Results of the measurements aimed at attaining the third objective are discussed in this paper.

The LOFT FP-2 Test was designed to provide data on the release and transport of radiologically significant fission products (e.g., I, Te, Cs) during accident conditions. The test simulated an accident in which a low-pressure injection system line ruptures and the emergency core cooling is delayed until severe fuel damage has occurred. Some of the radioiodines released from the fuel during the test were transported to the containment (reactor building) atmosphere. These radioiodines were subsequently passed through a silver zeolite cleanup filter and then vented to the environment. Measurements were made of the radioiodine concentrations upstream and downstream of the cleanup filter and DFs were determined for three silver zeolite filter banks.

II. Description of Experiment

A. Heating and Ventilating Systems

The LOFT containment (reactor building) has two heating and ventilating (H&V) systems that contain silver zeolite cleanup filters and which are designated as H&V 8 and H&V 9. Both H&V systems were used after the FP-2 test. H&V 9 consists of a 61-cm (24-inch) diameter line which runs from containment to a silver zeolite filter and then either back to the containment (recirculation mode) or to the environment (purge mode). A 5-cm (2-inch) diameter line runs from containment to a 25-cm (10-inch) diameter line in H&V 8. This 25-cm diameter line runs to a silver zeolite cleanup filter and then to the environment. H&V 8 contains two parallel silver zeolite filter beds (designated filters A and B for purposes of this paper), only one of which can be valved in at a time, while H&V 9 contains only one silver zeolite filter (designated filter C in this paper). H&V 8 is used to slowly vent the containment atmosphere while H&V 9 is used for high volume purge of the containment air.

Both H&V 8 and H&V 9 have sample points just upstream and just downstream of their cleanup filters. These sample points were designed for use in testing the cleanup filters. Prior to use, each sample point was shown to yield valid samples. A helium dilution technique was used in the sample point validation tests. This technique consists of injecting helium into each H&V system at a known rate upstream of the sample point and concurrently measuring the helium concentration at the sample point being validated.

B. Iodine Species Samplers

An iodine species and particulate sampler was used to collect samples for analysis.(1,2) The sampler consists of the following five media (in order encountered by flow):

1. Particulate Filter (Flanders F-700). This particulate filter is a HEPA type filter paper that has been waterproofed. It is used to retain particulate material which is pulled into the sampler.

2. Cadmium Iodide (CdI_2) on Chromosorb P (60/80 mesh supplied by Applied Science). This medium is used to adsorb elemental iodine (I_2).

3. 4-Iodophenol (IPH) on Alumina (30/60 mesh F-1 activated). This medium is used to adsorb hypoiodous acid (HOI) or, if HOI does not exist in the gaseous state, whatever iodine chemical species that deposits on the IPH but not on the CdI_2.

4. Silver Zeolite (AgX) (20/40 mesh). This medium is used to adsorb organic iodide species such as methyl iodide (CH_3I).

5. Charcoal (Barnebey-Cheney 151) or Silver Zeolite (20/40 mesh). This medium is used as a backup to adsorb any iodine species possibly escaping through the other media. For most samples, AgX was used because of its lower efficiency for adsorbing noble gases.

The media are loaded into aluminum media cups (9.5 mm high cup for the particulate filter; 35 mm high cup for the CdI_2, IPH, and AgX; and 25 mm high cup for the backup charcoal or AgX). These media cups are loaded into a cylindrical aluminum sampler body in the order given above. The sampler body is 19 cm long and 5 cm outside diameter and has an open and a closed end. The open end is threaded to accept a seal cap. Viton 'O' rings are used to insure a seal between the cups themselves and between the cups and the sampler body.

C. Experimental Setup

Figure 1 shows a schematic drawing of the experimental setup.

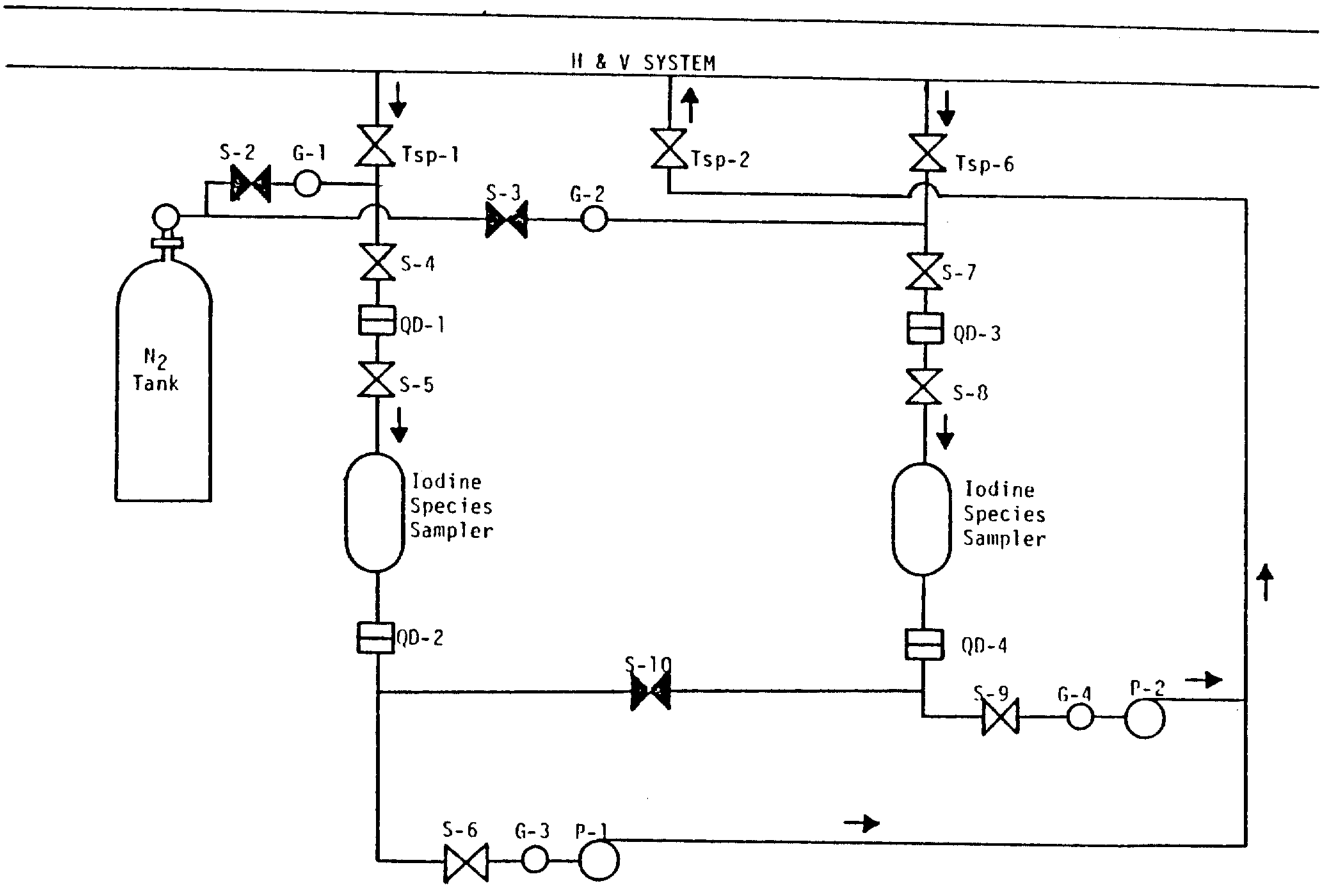

FIGURE 1
SCHEMATIC DRAWING OF SAMPLING SYSTEM

The sample upstream (downstream) of the cleanup filter was obtained from sample point TSP-1 (TSP-6). The flow went through valve S-4 (S-7), quick disconnect QD-1 (QD-3), valve S-5 (S-8), the iodine species sampler, isolating quick disconnect QD-2 (QD-4), valve S-6 (S-9), pump P-1 (P-2), and then returned to the H&V system through TSP-2. Flow rate was measured by G-3 (G-4). The N_2 tank was used to supply gas for leak testing of the system and to flush radioactive gases out of the system prior to removal of the samplers.

D. Sample Counting

After removal of an iodine species sampler from the sampling system, the sample cups were removed and placed in individual vials. These vials were then gamma counted using a hyperpure germanium detector-based spectrometer. The spectrometer was calibrated using National Bureau of Standards (NBS) traceable solutions which were loaded onto the various media.

III. Results of LOFT Measurements

One measurement of the DFs for the various radioiodine species was made on each of the three filters. Filter A was measured at 7.55 hours after the FP-2 test, Filter B at 31.3 hours after the test, and filter C at 75.8 hours after the test. Because the measurements were made at different times and the radioiodine species mixture in the LOFT containment air changed with time, each filter saw a different radioiodine species mixture at its inlet. Table 1 gives the inlet ^{131}I concentration and species mixture (i.e., fractions of the particulate, elemental, HOI, and organic species) during each measurement. The radioiodine species mixtures seen by the filters are the same as the mixtures in the LOFT containment, but the concentrations are lower than those in the containment due to addition of dilution air.

Table 1. ^{131}I Species Mixture at Filter Inlet

	^{131}I Conc.	Fractional ^{131}I Species Mixture			
Filter	(μCi/cc)	Part.	I_2	HOI	Organic
A	1.55 E-5	0.02	0.57	0.21	0.20
B	2.84 E-5	0.01	0.45	0.17	0.37
C	6.33 E-5	0.006	0.23	0.10	0.66

Tables 2, 3, and 4 give the inlet and outlet species concentrations and the resulting DFs for the radioiodines (^{131}I, ^{132}I, ^{133}I, and ^{135}I) observed in the inlets to the three AgX filters. The results for ^{132}I are not given in Table 3 because only elemental ^{132}I (the major species component) was seen in the inlet air stream. The concentrations of the other species were below detection limits. Results for ^{132}I and ^{135}I are not given in Table 4 because they were not seen in the samples due to a long delay between sampling and analysis of the samples. Results from other samples obtained of the inlet to the AgX filter several hours earlier, however, indicate that the total ^{132}I and ^{135}I concentrations were both about 2E-8 μCi/cc and that the ^{132}I was predominately elemental and the ^{135}I was predominately organic.

The results of the measurements indicate that the DF for elemental ^{131}I was the highest, with the DFs for the particulate, HOI, and organic species being lower. The ^{131}I DFs were relatively low for cleanup filters A and B (360 to 1200 for particulate, about 3000 for elemental, 46 for HOI, about 60 for organic, and 100 to 120 for the overall species mixture). The ^{131}I DFs were much higher for cleanup filter C (11,000 for particulate, 210,000 for elemental, 3800 for HOI, 1100 for organic, and 1500 for the overall species mixture). For all three cleanup filters, since each contains a HEPA filter upstream of the AgX, the particulate DF is due to the filtration of the combined components.

The results of DF measurements based on the other radioiodines (^{132}I, ^{133}I, and ^{135}I) exhibit good agreement with the results obtained using ^{131}I.

Table 2. Decontamination Factors for LOFT AgX Filter A

Nuclide	Species	Concentration (µCi/cc)		Decontamination Factor
		Inlet	Outlet	
^{131}I	Part.	3.4E-07	2.9E-10	1.2E+03
	I_2	8.8E-06	3.2E-09	2.7E+03
	HOI	3.2E-06	7.1E-08	4.6E+01
	Organic	3.1E-06	5.1E-08	6.1E+01
	Total	1.5E-05	1.3E-07	1.2E+02
^{132}I	Part.	7.1E-08	<2.0E-10	>3.5E+02
	I_2	2.5E-06	9.1E-10	2.8E+03
	HOI	7.9E-07	1.4E-08	5.6E+01
	Organic	6.4E-07	1.1E-08	5.8E+01
	Total	4.0E-06	2.6E-08	1.5E+02
^{133}I	Part.	1.1E-06	8.9E-10	1.3E+03
	I_2	3.3E-05	1.0E-08	3.2E+03
	HOI	1.1E-05	2.4E-07	4.6E+01
	Organic	1.1E-05	1.7E-07	6.2E+01
	Total	5.5E-05	4.2E-07	1.3E+02
^{135}I	Part.	6.2E-07	<9.1E-10	>6.8E+02
	I_2	1.8E-05	5.8E-09	3.1E+03
	HOI	6.0E-06	1.3E-07	4.6E+01
	Organic	5.6E-06	9.5E-08	5.9E+01
	Total	3.0E-05	2.3E-07	1.3E+02

Table 3. Decontamination Factors for LOFT AgX Filter B

Nuclide	Species	Concentration (µCi/cc)		Decontamination Factor
		Inlet	Outlet	
^{131}I	Part.	3.0E-07	8.3E-10	3.6E+02
	I_2	1.3E-05	4.3E-09	3.0E+03
	HOI	4.7E-06	1.0E-07	4.6E+01
	Organic	1.1E-05	1.7E-07	6.4E+01
	Total	2.8E-05	2.7E-07	1.0E+02
^{133}I	Part.	4.8E-07	1.4E-09	3.4E+02
	I_2	2.2E-05	6.9E-09	3.1E+03
	HOI	7.8E-06	1.7E-07	4.6E+01
	Organic	1.8E-05	2.7E-07	6.6E+01
	Total	4.8E-05	4.5E-07	1.1E+02
^{135}I	Part.	5.1E-08	<8.4E-10	>6.1E+01
	I_2	2.2E-06	<1.6E-09	>1.4E+03
	HOI	7.8E-07	1.9E-08	4.1E+01
	Organic	1.8E-06	2.9E-08	6.1E+01
	Total	4.8E-06	5.0E-08	9.5E+01

Table 4. Decontamination Factors for LOFT AgX Filter C

Nuclide	Species	Concentration (μCi/cc) Inlet	Outlet	Decontamination Factor
^{131}I	Part.	4.0E-07	3.5E-11	1.1E+04
	I_2	1.5E-05	<7.0E-11	>2.1E+05
	HOI	6.2E-06	1.6E-09	3.8E+03
	Organic	4.2E-05	3.9E-08	1.1E+03
	Total	6.3E-05	4.1E-08	1.5E+03
^{133}I	Part.	1.8E-07	<1.6E-10	>1.1E+03
	I_2	6.7E-06	<4.8E-10	>1.4E+04
	HOI	2.7E-06	7.6E-10	3.6E+03
	Organic	1.8E-05	1.7E-08	1.1E+03
	Total	2.8E-05	1.8E-08	1.5E+03

In the course of the DF analysis an anomaly was observed. The iodine species sampler contains a backup cartridge (charcoal or silver zeolite) to collect any iodine that may get through the other filter media. The amount of radioiodine on this backup cartridge is always examined to insure that the data from the various media are not compromised due to radioiodine breakthrough of these media. During examination of the data from the backup cartridge, it was noticed that the amount of radioiodine present was approximately the same for samples obtained both upstream and downstream of the cleanup filter being studied (even though the radioiodine concentration in the inlet stream was 2 to 3 orders of magnitude higher than in the outlet stream).

In addition, the ratio of the radioiodine on the backup cartridge medium to that on the medium intended for collection of organic iodine was several hundreths of a percent for samples obtained upstream of the cleanup filter but was several percent for samples obtained downstream of the cleanup filter. The above indicate that that there may be an iodine species (possibly a higher order organic than methyl iodide) that is partially adsorbed on charcoal and AgX but is not effectively removed from the gas stream. Discussions with other investigators have indicated that they have seen similar phenomena.

IV. Conclusions

In situ measurements of the DF for the LOFT H&V systems' AgX cleanup filters indicated that AgX is effective for removing radiodines from an air stream. The actual DF realized, however, depends on the condition of the filter and the radioiodine species mixture.

Measured DFs were in the range 360 to 11,000 for particulate ^{131}I, 2700 to >210,000 for elemental, 46 to 3800 for HOI, 61 to 1100 for organic, and 100 to 1500 for the overall ^{131}I species mixture. Cleanup filters A and B exhibited similar but low DFs, while cleanup filter C had much higher DFs. For all three filters, most of the efficiency for particles is probably due to the HEPA filter which is located just upstream of each AgX unit.

A comparison of the DFs measured for the LOFT AgX filters with DFs measured for charcoal filters at operating nuclear power plants indicates that the DFs for filters A and B are in the range of the values obtained for the charcoal filters.(3) The DFs measured for filter C, however, are much higher than were seen for charcoal filters at power plants. Both the LOFT AgX filters and power plant charcoal filters exhibited similar DF behavior for the various radioiodine species. The DFs for the LOFT AgX filters were highest for elemental and lowest for organic radioiodine, and the power plant charcoal filter DFs were highest for HOI and elemental and lowest for organic radioiodine.

All three of the LOFT cleanup filters exhibited lower DFs than were expected. Filter C had been tested about one month before the FP-2 experiment and had exhibited a DF of 39,000 for methyl iodide, compared to 1100 measured during the FP-2 experiment. Its DF, therefore, decreased by a factor of about 35 in only one month. Filters A and B exhibited DFs in the range 1200 to 1500 for methyl iodide about 9 months before the FP-2 experiment, but only about 60 during the FP-2 experiment. This represents a decrease of about a factor of 20 to 25 in a 9 month period. These large decreases in filter efficiency have not yet been explained.

The measurements on the LOFT AgX cleanup filters also indicated a result that has been seen at operating power plants.(3) Examination of the species mixture at the inlet of the LOFT filters indicates that (1) the radioiodine initially released from the reactor system during the FP-2 experiment was primarily elemental and (2) with time, the elemental fraction decreased while the organic fraction increased. At operating power plants, it was observed that radioiodine freshly released from the reactor coolant system had a high fraction of the more reactive species (elemental and/or HOI). In addition, the conversion with time of the more reactive species to the lesser reactive organic species was also observed.

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2. Emel, W. A. et al., "An Airborne Species Sampler and Its Application for Measuring Removal Efficiencies of Large Charcoal Adsorbers for Ventilation Exhaust Air," Proceedings of the 14th ERDA Air Cleaning Conference (1976).

3. Mandler, J. W. et al., "Measuring Gaseous Radioiodine at Power Reactors," Proceeding of the 19th DOE/NRC Nuclear Air Cleaning Conference (1986).

DISCUSSION

HULL: As I understand your presentation, it appears that Ag-Zeolite may not be the medium of choice for sampling the HOI and organic species of radioiodines under accident conditions, even though it is widely employed and even required by the NRC. Could you comment on this?

MANDLER: The DFs for HOI and organic radioiodine that we measured for the LOFT AgX filters A and B compare well with results we obtained on charcoal filters at operating power plants. You would expect these DFs to be lower than those for AgX and charcoal used for sampling - mainly because media used for sampling are fresh. I believe that AgX is indeed a good medium for sampling HOI and organic radioiodine. Recall that filter C (a filter that had been in use for at least a month prior to the LOFT test) exhibited DFs of 3,800 and 1,100 for HOI and organic radioiodine, respectively. These DFs correspond to retention efficiencies of >99.9%.

SUMMARY AND RECOMMENDATIONS OF THE NRC/INEL ACTIVATED CARBON TESTING PROGRAM*

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Abstract

The Committee on Nuclear Air and Gas Treatment (CONAGT) of the American Society of Mechanical Engineers (ASME) sponsored an interlaboratory testing program of nuclear-grade activated carbon. The results of this round-robin revealed gross differences in penetration of radio-labeled methyl iodide as measured by the various laboratories when using Method A of the ASTM D-3803-79 standard. These differences prompted the Nuclear Regulatory Commission (NRC) to establish an activated carbon testing program at the Idaho National Engineering Laboratory (INEL) to determine the causes of these discrepancies and to provide recommendations that could lead to an accurate and reliable testing procedure for assessing the capability of activated carbon to remove radioiodine from gas streams within commercial nuclear power plants.

Formal and informal interlaboratory comparisons have been carried out under the NRC/INEL Activated Carbon Testing Program to identify problems with the test method and its application and to assess the effectiveness of changes to procedures and equipment voluntarily implemented by commercial laboratories to mitigate the disparity of test results. The results of the first formal NRC/INEL Interlaboratory Comparison (IC) essentially confirmed the variability obtained in the CONAGT round-robin results despite the use of a detailed test protocol. The IC protocol required the completion of a standard report form for each test which provided information regarding critical test parameters. This data indicated that many of the participating laboratories probably had been operating outside the ASTM specifications for relative humidity (RH) and flow. Several workshops were held to discuss and attempt to rectify problems associated with activated carbon testing. Informal intercomparisons were used to guide individual laboratories in the iterative process of test system trouble-shooting and modification. In addition, this process provided information which was used to modify the testing protocol employed for the second NRC/INEL Interlaboratory Comparison (IC-2) to make it more rugged and reliable. These changes to the protocol together with the results of INEL sensitivity testing are the basis for the recommendations presented.

Introduction

The NRC/INEL Activated Testing Program has consisted of: 1) a review of the ASTM D-3803-79 Standard to determine if it adequately specifies test parameters and procedures so that consistent and accurate results should be obtained; 2) a review of the CONAGT round-robin testing in an attempt to explain the wide variation of results obtained by the laboratories; 3) visits to the commercial laboratories to review the methods and equipment used to determine if

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they adequately conformed to the ASTM D-3803 Standard; 4) fabrication of a test facility at the INEL and the performance of tests to determine the sensitivity of penetration measurements to variations of test parameters and procedures; 5) an initial workshop in Idaho on August 27-29, 1984 with representatives from manufacturers of activated carbon, testing laboratories, the NRC and EG&G Idaho to discuss activated carbon testing and the results of INEL sensitivity tests completed by that date; 6) an Interlaboratory Comparison (IC) with test laboratories performing analyses on identical samples using the procedures of ASTM D-3803 as modified by a written protocol to determine the precision with which penetration of radio-methyl iodide could be measured; 7) a second workshop held in Annapolis, Maryland on June 5 and 6, 1985 to discuss the results of the IC and pertinent INEL sensitivity test results; 8) a workshop held at the INEL on September 10-12, 1985 supervised by technical experts from the National Bureau of Standards (NBS) to calibrate and intercompare devices used to measure flow and RH at the INEL and at several commercial laboratories; 9) a program of informal one-on-one comparisons to identify remaining differences in the results obtained; and 10) a second Interlaboratory Comparison (IC-2) with laboratories required to follow the INEL Standard Test Method for Nuclear-Grade Activated Carbon, which is a substantial revision of ASTM D-3803-79, Method A.

Several important tasks were completed prior to the first NRC/INEL IC which was completed in May 1985. Details of these tasks are not included in this paper and have been reported elsewhere.(1,2) One previous task which has been critical to understanding the problems associated with carbon testing was the design, fabrication, operation and maintenance of the INEL test system. This has been an evolutionary process beginning with a system modeled after the schematic presented in the ASTM Standard and ending with the current system which is a composite of designs and instrumentation used throughout the world. This type of evolutionary system design is extremely common within the industry and is ongoing. Recent advances in off-the-shelf microprocessor controlled monitoring and control devices have contributed significantly to the ease and accuracy of parameter recording and control. The evolution of the INEL test system has been more rapid than most in the private sector because of the observations, experiences and criticisms generously contributed by the commercial carbon testing laboratories. This type of information has not previously been freely exchanged within the industry and has been extremely useful in the identification of problem areas in commercial carbon testing.

NRC/INEL Interlaboratory Comparison

The IC was conducted to determine the precision with which the penetration of radio-methyl iodide through activated carbon was being measured in different laboratories. Eight laboratories from the U.S., two laboratories from Canada, and one each from the United Kingdom, the Federal Republic of Germany, and Korea agreed to participate. The study involved measurements of penetration for a single new carbon at 30°C and 95% RH and for a single used carbon at 30°C and 70, 90, and 95% RH. The procedure used was Method A of the ASTM D-3803 Standard as modified by specific written changes. The new carbon was tested with equilibration, i.e. exposed to the specified temperature, air flow, RH, etc. for a period of 16 hours before being challenged by the methyl iodide. The used carbon was tested without equilibration. Triplicate analyses were performed at each experimental condition to distinguish between differences in results caused by interlaboratory imprecision of measurement and those caused by intralaboratory imprecision of control of the experimental conditions.

To ensure that all carbon samples tested by all laboratories were identical, a large batch of new carbon was hand screened to give a +1mm to -2mm fraction which was then homogenized by thorough blending as a single batch in a twin-shell blender. The batch was then dedusted with clean cylinder compressed air and manual mixing. A 200-ml aliquot was removed batchwise without skimming using a plastic beaker to avoid fractionation, transferred to a polyester bag, heat-sealed immediately, and labeled for distribution to the individual laboratories. The entire process was then repeated with a batch of used carbon. Samples were distributed to participating laboratories by November 23, 1984.

Of the thirteen laboratories that initially agreed to participate in the IC, ten submitted all data requested, two withdrew prior to testing, and one laboratory withdrew their results during the Second Carbon Testing Workshop in Annapolis, Maryland because of their own dissatisfaction with their results. Similarly, another laboratory withdrew their initial results because of their own dissatisfaction with the technical quality of the work. Subsequently, they submitted a second set of test results which has been included in this paper. Two fundamental conclusions were derived from the IC data obtained.

First, the precision within each laboratory was generally good to outstanding. Nine of the ten laboratories reporting triplicate runs on each of the three experimental conditions for used carbon obtained relative standard deviations of the individual measurements about their own mean of 1 to 6%. The precision for the new carbon tests was also generally good but lower than that for the used carbon because of its low values for penetration and its extreme susceptability to minor variations in relative humidity. It was clear that within each laboratory the critical experimental parameters were being controlled adequately.

Second, the precision obtained among laboratories was extremely poor. As shown by the results presented in Table 1, the new carbon results were spread uniformly from 0.23 to 8.4%. No two U.S. laboratories agreed with each other within two standard deviations of their respective means. The results from laboratory 12 are not strictly comparable with the others because of the different equilibration period used. The results for the used carbon generally fell into two distinctly different levels. One group of three laboratories obtained values of 17 to 19%, the other group of six laboratories obtained values in the range of 24 to 26%. Laboratory 8 equilibrated the samples at the 95% RH condition and these data are therefore excluded from comparisons. Although these results, 60% penetration, are not comparable to other IC data, two other laboratories informally reported results for equilibrated used carbon tests which were in close agreement, 59 and 60.2% penetration. Laboratory 10 made measurements at 22 to 23°C and are not directly comparable to the other results, although they clearly show the effect of temperature on penetration. The generally poor agreement among laboratories must be attributed to reproducible systematic differences in both test system operation and performance.

The results of sensitivity testing performed at the INEL on additional samples of the IC new carbon indicated a very strong correlation, $r^2 = 0.996$, between the final moisture content (FMC), % water, of the carbon and the log percent penetration. The log-linear regression of average penetration versus the average FMC reported for new carbon by each of the participating laboratories yielded a poor correlation, $r^2 = 0.46$. This lack of good agreement with the sensitivity data must have been due to the influence of variables other than RH

Table 1. Results of the NRC/INEL Interlaboratory Comparison (IC) of Penetration of Radio-Methyl Iodide Through Activated Carbon.

NEW CARBON AT 95% RELATIVE HUMIDITY

LABORATORY NO.	LABORATORY INITIALS	PENETRATION ± EXP. STD. DEV., %	MOISTURE CONTENT, wt. % H_2O INITIAL	MOISTURE CONTENT, wt. % H_2O FINAL	TEST BED DENSITY, g/cm^3
5	SAIC	DATA WITHDRAWN			
3	NUCON	0.233 ± 0.018 (8%)	4.0 ± 0.4 (10%)	26.8 ± 0.4 (2%)	0.492 ± 0.003 (1%)
7	MSA	0.71 ± 0.03 (4%)	3.77 ± 0.19 (5%)	27.0 ± 0.5 (2%)	0.496 ± 0.004 (1%)
9	BC	0.91 ± 0.02 (2%)	2.87 ± 0.14 (5%)	24.4 ± 0.5 (2%)	0.498 ± 0.004 (1%)
11	OH	1.06 ± 0.09 (9%)	3.04 ± 0.07 (2%)	27.0 ± 0.4 (2%)	0.4751 ± 0.0007 (1%)
8	KFK	1.8 ± 0.4 (22%)	3.80 ± 0.05 (1%)	28.5 ± 0.3 (1%)	0.469 ± 0.004 (1%)
1	EG&G	2.31 ± 0.3 (13%)	3.125 ± 0.018 (1%)	28.1 ± 0.4 (2%)	0.501 ± 0.005 (1%)
10	WNL	[a]2.88 ± 0.14 (5%)	4.9 ± 1.2 (20%)	NA	NA
13	EET	3.65 ± 0.19 (5%)	4.03 ± 0.06 (2%)	32.5 ± 0.4 (1%)	0.504 ± 0.004 (1%)
6	NCS	7.18 ± 0.10 (2%)	4.27 ± 0.06 (2%)	29.7 ± 0.5 (2%)	0.517 ± 0.008 (2%)
12	KAERI	[b]8.4 ± 2.9 (35%)	2.86 ± 0.02 (1%)	24.9 ± 1.5 (6%)	0.499 ± 0.009 (2%)

USED CARBON

LABORATORY NO.	RELATIVE HUMIDITY, %	PENETRATION ± EXP. STD. DEV., %	MOISTURE CONTENT, wt. % H_2O INITIAL	MOISTURE CONTENT, wt. % H_2O FINAL	TEST BED DENSITY, g/cm^3
3	95	18.90 ± 0.15 (1%)	20.1 ± 0.4 (2%)	29.8 ± 1.2 (4%)	0.567 ± 0.007 (1%)
	90	17.9 ± 0.7 (4%)	20.03 ± 0.15 (1%)	28.0 ± 0.3 (2%)	0.565 ± 0.004 (1%)
	70	19.0 ± 0.3 (2%)	20.3 ± 0.4 (2%)	23.6 ± 0.5 (3%)	0.572 ± 0.002 (1%)
6	95	18.6 ± 1.4 (8%)	20.5 ± 0.6 (3%)	31.4 ± 1.4 (5%)	0.599 ± 0.004 (1%)
	90	17.4 ± 0.7 (4%)	20.8 ± 0.6 (3%)	30.1 ± 0.5 (2%)	0.588 ± 0.008 (2%)
	70	19.1 ± 0.6 (3%)	21.0 ± 0.6 (3%)	26.1 ± 0.7 (3%)	0.600 ± 0.006 (1%)
13	95	18.21 ± 0.16 (1%)	20.3 ± 0.2 (1%)	33.14 ± 0.16 (5%)	0.589 ± 0.008 (2%)
	90	17.9 ± 0.5 (3%)	20.2 ± 0.3 (2%)	32.53 ± 0.06 (2%)	0.597 ± 0.006 (1%)
	70	16.6 ± 0.5 (3%)	20.5 ± 0.5 (2%)	28.6 ± 0.8 (3%)	0.590 ± 0.005 (1%)
10	[a]95	33.8 ± 1.1 (3%)	20.8 ± 0.4 (2%)	NA	NA
	[a]90	32.3 ± 0.6 (2%)	20.5 ± 0.8 (4%)	NA	NA
	[a]70	33.3 ± 0.7 (2%)	20.68 ± 0.18 (1%)	NA	NA
5	DATA WITHDRAWN				
9	95	25.1 ± 0.3 (1%)	19.4 ± 0.2 (1%)	29.4 ± 0.2 (1%)	0.574 ± 0.004 (1%)
	90	20.5 ± 0.7 (4%)	19.1 ± 0.5 (3%)	28.6 ± 0.5 (2%)	0.57 ± 0.02 (3%)
	70	22.8 ± 1.1 (5%)	19.18 ± 0.09 (1%)	24.7 ± 0.6 (2%)	0.571 ± 0.005 (1%)
1	95	25.6 ± 0.9 (4%)	20.490 ± 0.004 (1%)	32.6 ± 0.4 (1%)	0.568 ± 0.008 (2%)
	90	26.5 ± 1.7 (6%)		32.0 ± 0.5 (2%)	0.563 ± 0.014 (3%)
	70	24.5 ± 1.0 (4%)		26.5 ± 0.4 (2%)	0.573 ± 0.011 (2%)
7	95	26.4 ± 0.3 (1%)	19.82 ± 0.13 (1%)	31.5 ± 0.6 (2%)	0.561 ± 0.011 (2%)
	90	24.5 ± 0.2 (1%)	19.4 ± 0.2 (1%)	28.9 ± 0.4 (2%)	0.547 ± 0.006 (1%)
	70	24.1 ± 0.6 (3%)	19.8 ± 0.3 (2%)	21.26 ± 0.08 (1%)	0.570 ± 0.017 (3%)
8	[c]95	60.0 ± 1.7 (3%)	24.37 ± 0.18 (1%)	39.76 ± 0.08 (1%)	0.548 ± 0.002 (1%)
	90	25.4 ± 0.8 (3%)	26.2 ± 0.3 (1%)	39.8 ± 0.4 (1%)	0.557 ± 0.008 (2%)
	70	26.4 ± 0.8 (3%)	24.9 ± 0.2 (1%)	30.8 ± 1.2 (4%)	0.546 ± 0.002 (1%)
11	95	24.3 ± 0.4 (2%)	19.9 ± 0.4 (2%)	31.7 ± 1.0 (4%)	0.544 ± 0.005 (1%)
	90	25.2 ± 0.3 (1%)	19.8 ± 0.3 (2%)	30.13 ± 0.14 (1%)	0.551 ± 0.006 (1%)
	70	24.9 ± 0.5 (2%)	19.7 ± 0.7 (4%)	24.6 ± 0.8 (4%)	0.556 ± 0.003 (1%)
12	95	25.4 ± 2.0 (8%)	19.6 ± 0.3 (1%)	32.8 ± 1.2 (4%)	0.573 ± 0.003 (1%)
	90	25.3 ± 2.2 (9%)	19.32 ± 0.14 (1%)	31.6 ± 0.5 (2%)	0.566 ± 0.003 (1%)
	70	22.0 ± 3.0 (15%)	19.7 ± 0.4 (2%)	23.9 ± 0.6 (2%)	0.564 ± 0.004 (1%)

[a] Temperature Used, 22°-23°C.

[b] Equilibration Period of 1 hour.

[c] Pre-equilibrated for 16 hours.

NA - Not available.

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which determines the FMC of any particular carbon. Two variables which could easily be evaluated for their contribution to this lack of agreement were the initial moisture content (IMC) determinations made by each laboratory that were used in the calculation of their reported FMC and the initial weight of the carbon used by each laboratory. To eliminate any bias in the IC data introduced by these variables, the moisture gained by the test bed was calculated in terms of grams of water gained per initial gram of carbon. The log-linear regression of the average of this quantity versus the average percent penetration for each laboratory yielded a better correlation, $r^2 = 0.64$, than was obtained simply using the reported FMC and more closely approximates the moisture versus penetration relationship determined by INEL sensitivity testing. This improvement in correlation of moisture with penetration is primarily due to eliminating the variability in the data introduced by interlaboratory differences in the determination of the IMC. This indicates the presence of significant errors in the relatively simple determination of IMC, i.e. determining the initial and final weights of a sample of carbon dried at 150°C for a period of 16 hours. The errors are now believed to have been associated with radiative heating of the carbons and inadequate control of temperature.

Six of the U.S. laboratories which participated in the NRC/INEL IC also participated in the CONAGT round-robin. Information supplied by these laboratories indicated that the test results of each laboratory relative to all others was the same for the new carbon tested in the IC as it was for the new carbons tested in the CONAGT round-robin. In other words, when the laboratories are listed in order of penetration results for the new carbons tested in the IC and the CONAGT round-robin, the order is the same. This indicates that these laboratories have been extremely consistent in their test results and discrepancies.

The penetration results for the used carbon samples showed no effect of relative humidity by any of the reporting laboratories under the conditions prescribed, particularly without equilibration and a one-hour challenge time. However, every laboratory reported an average FMC which increased with increasing RH. To clarify this apparent lack of affect of RH on penetration, duplicate tests tests were performed at the INEL on samples of the IC used carbon using a two-hour challenge time at each prescribed RH. These results showed increasing penetration with increasing RH. Although the difference in penetration results between the 90 and 95% RH tests was not significant, the difference between these results and those from the 70% RH tests were statistically significant. This data indicates that, if a two-hour challenge time had been used for the IC, some differences in test results at different humidities would have been observed. Further increases in the length of challenge or testing the samples with equilibration would undoubtedly increase the differences observed in penetration results as a function of RH.

The lack of any effect of RH on the IC used carbon penetration results under the test conditions prescribed allowed an independent evaluation of the effects of other parameters on the test results. The interlaboratory differences observed must have been due to variations in parameters other than RH. INEL sensitivity testing indicated that the parameter most likely to have caused these differences was flow, or superficial face velocity. This testing indicated that a 15% reduction in the specified flow was required to obtain penetration values near the 18% values reported by three laboratories. Although measurement errors of this magnitude seemed unlikely, other explanations for the observed discrepancies were not obvious.

Second Workshop on Activated Carbon Testing

An NRC/INEL Workshop on Activated Carbon Testing was held in Annapolis, Maryland on June 5-6, 1985. The purpose of this workshop was to report the results of the IC to the participating laboratories and other interested parties and to discuss problems with the testing and potential solutions in light of the INEL sensitivity testing and commercial laboratory experience. INEL testing indicated that many of the laboratories might have been operating outside the ASTM specifications for RH and flow. The general conclusion reached was that most of the interlaboratory variance observed might have been caused by differences in calibration of critical parameter measuring devices.

Each of the laboratories represented at the workshop was asked to present any data, results or opinions obtained from their own testing experience which could possibly help to explain the large interlaboratory variance of IC results. These presentations and associated discussions suggested additional factors which may have affected the IC results or their interpretation. The most significant factors noted included: 1) changes in RH during equilibration which would affect the penetration results and might not correlate well with the FMC of the carbon (RH instability and hysteresis); 2) the misapplication or miscalculation of correction factors using incomplete or erroneous information; 3) the presence of water aerosols in the gas stream which would not be detected by a dew point hygrometer but would significantly change the moisture content of the carbon; 4) the chemical purity of the methyl iodide; 5) the lack of uniformity of face velocity or flow at the test bed; 6) the lack of uniformity of the methods used to determine the IMC of the carbon; 7) differences in test bed density and packing methods; 8) differences in the pretreatment of air used to remove potentially important contaminants; and 9) inhomogeneous mixing of the methyl iodide with the main air stream ahead of the test bed.

Each of these factors was subsequently addressed by sensitivity testing at the INEL. Those factors which were shown to exibit significant influence on the penetration results have been addressed by including specific recommendations or requirements in the INEL Standard Test Method for Nuclear-Grade Activated Carbon which has been included in this paper as Appendix A.

NBS Calibration Workshop

The results of the IC and the INEL sensitivity testing indicated that one of the most important causes of the lack of agreement among the participating laboratories was likely the inaccurate measurement of the critical test parameters. To facilitate measurement accuracy and thus promote interlaboratory agreement, a Calibration Workshop was held at the INEL on September 10-12, 1985. All U.S. carbon testing laboratories were invited to observe and participate in the calibration exercise by bringing their own flow and RH measuring devices to the INEL laboratory for in-line comparisons with secondary standards calibrated by the NBS. Two technical experts from the NBS were present to observe and guide these comparisons and to discuss individual problems or comments with the laboratory representatives present.

Comparisons of the commercial laboratory RH measuring devices were directed and observed by Mr. Saburo Hasegawa, the technical specialist in charge of RH measurements at the NBS.(3) These comparisons were performed by placing each commercial laboratory instrument individually in series with the NBS calibrated unit in the INEL test system. These calibrations served to explain some, but not all, of the variations observed in the IC penetration and FMC results.

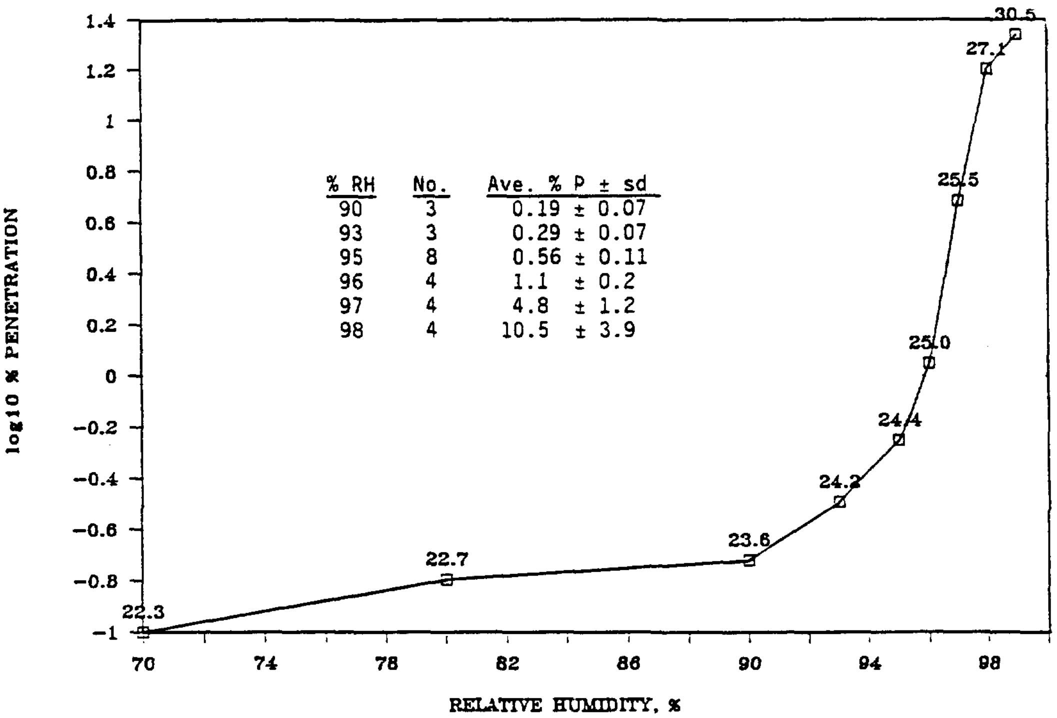
The calibration of flow measuring devices used by the commercial laboratories was accomplished by connecting all the devices in series in the INEL test system. Mr. George Mattingly, the NBS technical expert in the measurement of gas flow, brought an NBS owned and calibrated flowmeter which provided the reference measurements of actual standard flow. The results showed variations in flow calibrations from -4 to +8% of the NBS certified standard flow. This 12% relative difference in flow could account for a 30% difference in penetration results for the IC new carbon based on INEL sensitivity testing. Other problems with the application of flow measurements became obvious through discussions with commercial laboratory personnel. These included: 1) measurement of the exact diameter of the test bed which is used to calculate the flow required to maintain the specified face velocity; 2) the miscalculation of correction factors because of inaccurate measurements of temperature and pressure at the measuring device; 3) the miscalculation or ommission of correction factors required for the addition of gaseous water to the gas stream when "dry" air is actually being measured; and 4) incorrect placement of flow measuring devices behind the test canisters thus subjecting them to variable temperature and RH conditions caused by adsoptive heating of the carbon beds. These problems have been addressed on an individual basis with the commercial laboratories and in a more generic manner in the INEL Standard Test Method, found in Appendix A.

One-on-One Comparisons

Samples of a new carbon, designated 2N, were prepared using the same method as was used for the IC carbons. Samples of this carbon were distributed after the Annapolis workshop to each of the laboratories that participated in the IC. Following the NBS Calibration Workshop, the laboratories were requested to provide IC-type data to INEL personnel from at least one test of this carbon. It was hoped that the calibration of RH and flow measuring devices and the increased awareness by the laboratories of the problem areas identified would improve the agreement of test results. It was also hoped that tests of this carbon would aid the laboratories in attempts to improve their test system designs, instrumentation and operation.

A total of 21 tests were reported from five commercial U.S. laboratories. Penetration results ranged from 0.09 to 4.9%. Reported IMC ranged from 4.1 to 8% and reported FMC ranged from 21.6 to 27.9%. Much of this information was received by phone and is incomplete. Eight tests of the 2N carbon have been performed at standard conditions at the INEL. These tests yielded penetrations from 0.42 to 0.69 with a mean of 0.56 and a standard deviation of 0.11. The mean IMC was determined to be 4.12 ± 0.14 and the mean FMC was 24.4 ± 0.4. Additional INEL sensitivity testing of this carbon has produced a penetration versus relative humidity curve which clearly shows the extreme sensitivity of this carbon to changes in RH, Figure 1. This curve together with additional samples of this carbon may be used by the commercial laboratories as a reference for changes in performance.

The results of these one-on-one comparisons have indicated fairly good performance by some of the laboratories, while others have shown increasing agreement with INEL results. However, some laboratories have presented widely varying results which suggest a lack of parameter control which was not obvious



% RH	No.	Ave. % P ± sd
90	3	0.19 ± 0.07
93	3	0.29 ± 0.07
95	8	0.56 ± 0.11
96	4	1.1 ± 0.2
97	4	4.8 ± 1.2
98	4	10.5 ± 3.9

Figure 1. Results of sensitivity testing of new, co-impregnated, 2N carbon using the IC protocol and varying only RH. Numbers above points on plot indicate final moisture content as % water.

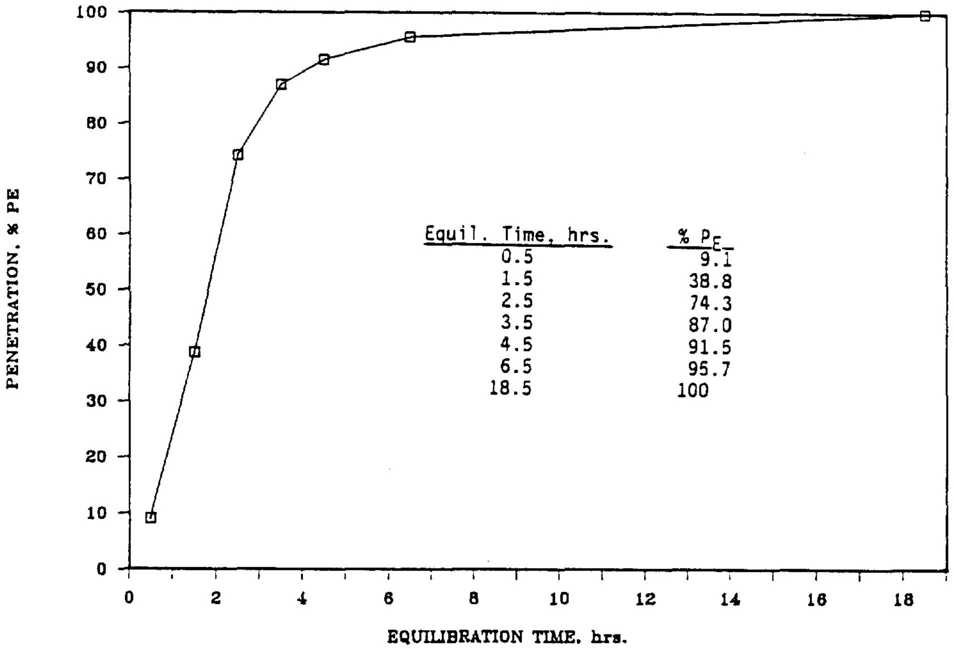
from the IC results, and several commercial laboratories have not participated in this program at all. The acceptability of the current state of U.S. carbon testing is, therefore, still very much in doubt.

Second NRC/INEL Interlaboratory Comparison

Eight U.S. laboratories, including the INEL, and eight foreign labs, one each from Canada, Spain, France, Germany(FRG), Italy, Netherlands, Finland, and Japan, have agreed to participate in the second NRC/INEL Interlaboratory Comparison (IC-2). Samples of one new and one used carbon, designated 3N and 2U respectively, were prepared in the same manner as the IC and 2N carbon samples. These samples were distributed to participating laboratories on June 6, 1986. A minimum of six equilibrated tests and two non-equilibrated tests are to be performed by each laboratory. All tests are to be conducted in accordance with the INEL Standard Test Method for Nuclear-Grade Activated Carbon, included here as Appendix A. Duplicate analyses of each carbon at each condition are required, but triplicate analyses are strongly encouraged. The new carbon is to be tested only at the standard condition, i.e. with equilibration, 95% RH, etc. The used carbon is to be tested at three conditions: 1) standard condition, i.e. with equilibration, 95% RH, etc.; 2) at 90% RH, with equilibration and all other parameters as specified in the standard; and 3) without equilibration, 95% RH, and all other parameters as specified in the standard. Final results of these tests are to be reported in the format given in Annex 1 of the test method by September 1, 1986. The results obtained from the IC-2 should provide a clear indication of: 1) the progress made toward interlaboratory reproducibility of results through this voluntary program; 2) the acceptability of commercial U.S. carbon testing; and 3) the status of carbon testing throughout the world.

Additional Sensitivity Testing

Sensitivity testing was conducted on samples of a fairly good used carbon, designated 2U, by varying the length of equilibration. All tests were conducted at standard conditions, i.e. 30.0°C, 95% RH, 12.2 m/min. velocity, etc., using a 1-hour challenge duration. The equilibration time of the non-equilibrated test was considered to be one-half the challenge time or 0.5 hour. Likewise, the total equilibration time of equilibrated tests was considered to be 0.5 hour plus the actual equilibration duration. The penetration values for these tests are expressed as a percentage of the equilibrated value, P_E, because this carbon is still being evaluated in the IC-2. The results of these tests are shown in Figure 2. It may be observed that this curve is approximately exponential, as will be discussed in the recommendations section following.



Equil. Time, hrs.	% P_E
0.5	9.1
1.5	38.8
2.5	74.3
3.5	87.0
4.5	91.5
6.5	95.7
18.5	100

Figure 2. Penetration of a used carbon, 2U, with equilibration time at the standard IC-2 conditions, i.e. 30°C, 95% RH, etc. The penetration is given as a percentage of that obtained with an 18-hour equilibration.

The Naval Research Laboratory (NRL) has proposed a depth profile method for evaluating the retention characteristics of activated carbon.(4) This method involves dividing the standard 2-inch test bed into four 1/2-inch sections. Each of the sections is counted separately after the standard ASTM test and a linear regression is performed on ln counts per section versus depth. The slope of this regression line, K_L, is then used to compare and evaluate the capability of the carbon. Three different carbons have been tested at the INEL using the IC protocol for new carbon to evaluate the validity and utility of this test method. The results of these tests are presented in Figure 3. The test bed penetration values obtained were 0.54%, 7.45%, and 60.2%, for the 2N, California used carbon, and IC used carbon, respectively. It was hoped that the correlation coefficient for the ln counts versus depth regression could be used as a criterion for the stability and acceptability of the test. Unfortunately, this is not the case.

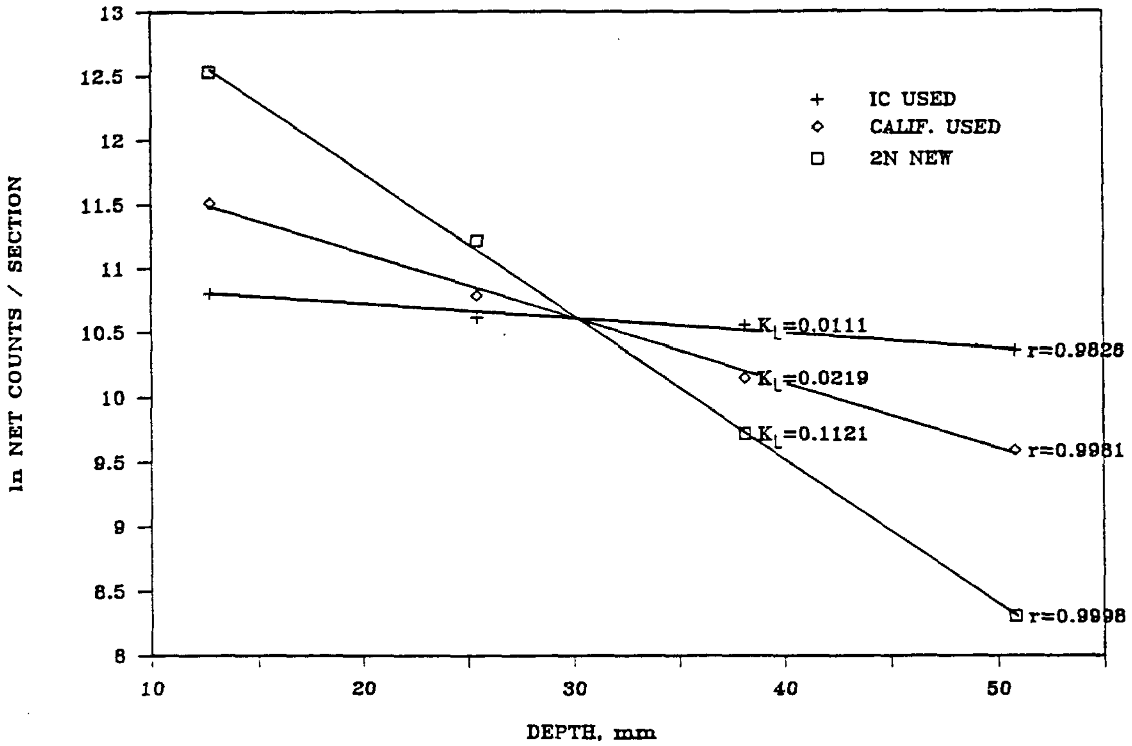


Figure 3. Results of depth profile evaluations of a new, 2N, and two used carbons, California and IC used, tested using the IC test protocol for new carbon.

During the equilibration phase of the test of the California used carbon, the temperature of the constant temperature cabinet dropped 0.6°C in response to a more drastic change in the laboratory. This decrease in cabinet temperature is known to result in a higher test bed RH even though the test gas temperature and RH just prior to the test bed remained at 30.0°C and 95.0% RH. This change in internal test bed RH was reflected in the FMC determinations made for each test bed section, which ranged from 27.4 to 29.6% water, and roughly indicated the time history of the cabinet temperature changes. This variation of a critical test parameter was not indicated by a significant reduction in the K_L correlation coefficient, although it was reflected in a somewhat higher penetration value than was obtained for a stable test under the same conditions. The depth profile method appears to offer no additional information on the activated carbon being tested because each K_L is associated with a unique penetration value measured at 2 in. depth and the general range of the correlation coefficient appears to be inversely related to the penetration value. This depth profile test method is, therefore, subject to all of the parameter stability and measurement problems associated with conventional ASTM carbon testing.

Recommendations

The recommendations presented represent the conclusions of nearly 3 years of laboratory research and extensive interaction with the NRC and members of the commercial carbon manufacturing and testing industry. These recommendations should be utilized by several separate but interrelated groups, including the NRC, commercial carbon testing laboratories, the ASTM D-28.04 committee, and the nuclear power industry. There is much overlap in the application and consequences of the basic findings of this program by the various concerned groups. The recommendations of this program are divided into three basic groups directed toward: 1) a standard test method; 2) the carbon testing laboratories; and 3) the NRC.

A Standard Test Method

A fundamental recommendation of this program must be the elimination of what is essentially "research" required from the commercial laboratories in order to meet the variety of testing requirements found in the nuclear power industry. A standard test procedure should be just that, a procedure which specifies standard test conditions which do not necessarily cover the entire range of power plant operating and accident conditions. If a power plant can show that the test conditions and acceptance criteria prescribed are too stringent for their applications, then research should be conducted to establish an acceptance criteria which is reasonable based on the results of the standard carbon test. In other words, if in-plant conditions do not match the test conditions, change the acceptance criteria rather than the test conditions. Quantitative evaluations of the effects of such things as temperature, flow rate, and carbon bed depth are available in the literature, and are probably more reliable than any single test at non-standard conditions. The reliable and accurate measurement of the penetration of methyl iodide through activated carbon is, obviously, a difficult enough task for the commercial laboratories given a single set of standard conditions.

Recommendations for changes to the ASTM D-3803-79 Standard, Method A have been incorporated into the INEL Standard Test Method for Nuclear-Grade Activated Carbon, included in this paper as Appendix A. These changes include a sweeping revision of the radio-analytical methods prescribed as well as fairly substantial changes to requirements for test procedures and instrumentation. The necessity of revision of the radio-analytical methods was generally accepted and these revised methods have been employed in most laboratories since the first IC. These methods are much less permissive than previous methods and will undoubtedly result in adequate precision in the radio-analytical portion of the test. The significant changes to the experimental portion of the test method are presented following with a brief justification for each.

Equilibration of Used Carbon Samples. Reactor accident scenarios vary widely because of differences in plant design and the exact sequence of events. It is difficult to postulate a scenario in which the occurrence of high humidity conditions and methyl iodide contamination are synchronous and of short duration. However, these are the conditions which are tested by ASTM D-3803, Method A. Methyl iodide insult to the carbon filters will likely follow a period of high humidity which might persist for an extended period of time, as might the iodide contamination. Even if methyl iodide and humidity occur simultaneously, their coexistance in the air challenging the carbon filters may extend for periods of days or even weeks. The resultant cumulative penetration of iodine through these filters approaches the value obtained for equilibrated used carbon.

Parametric studies performed at the INEL indicate that the non-equilibrated penetration results will asymptotically approach the equilibrated carbon result with time. For a fairly good used carbon, the penetration increases rapidly with increasing equilibration time or challenge time without equilibration. This increase in penetration correlates well with the adsorption of water by the carbon for approximately the first six hours, after which, other factors apparently cause the observed minor increase in penetration. Thus, if the carbon is tested without equilibration with the feed period extended to 18 hours, the instantaneous penetration, P_I, at 18 hours will equal the value obtained with equilibration, P_E, but the measured penetration will be the cumulative average of all instantaneous penetrations. The function of instantaneous penetration with time is illustrated in Figure 2, and is easily approximated by a simple exponential function in which the penetration rises rapidly and then levels out as it approaches the equilibrated penetration value. This exponential function has the form

$$P_I = P_E\ [1-e^{-0.5(t)}]$$

where: P_I = the instantaneous penetration, %,
P_E = the equilibrated penetration, %;
t = time since start of test, hours;
and 0.5 = an emperically derived time constant.

The penetration results for the first two hours of the real data are somewhat less than is predicted by this equation, probably due to the increase in test bed temperature and commensurate decrease in test bed relative humidity due to adsorptive heating of the carbon. However, this deviation does not significantly affect the conclusions which may be drawn from this equation. Given the function above, the cumulative penetration is simply the integral of the exponential with respect to t from 0 to 18, which results in a cumulative penetration for an 18-hour challenge test of approximately 89% of P_E. If the test is continued for an additional 18 hours, the resulting penetration would be approximately 94.3% of P_E. Obviously, as the duration of the unequilibrated test increases the resulting penetration value will asymptotically approach the equilibrated test penetration value. The equilibrated used carbon result should therefore be regarded as the best estimate of the long-term average iodine penetration.

Note that these calculations are based on stable 95% RH conditions, which are highly unlikely in a real reactor accident. Testing has shown that relative humidity excursions above 96% dramatically increase the methyl iodide penetration and require a great deal of time to return to the stable 95% RH value. This implies that the equilibrated used carbon test result might still be an underestimate of the true penetration of methyl iodide through activated carbon under accident conditions, but it is probably as good as can be achieved given the uncertainties in predicting actual reactor conditions. In addition, it will probably prove to be a much more accurate, reliable and equitable method for assessing the capability of used carbon.

The equilibration of used carbons prior to challenge can also be justified and indeed is required for the comparison of carbons exposed to different antecedent humidity conditions. Two identical samples of the IC-1 used carbon were each placed in desiccators. One desiccator contained anhydrous calcium sulfate, the other contained a saturated solution of potassium sulfate. The RH in the calcium sulfate desiccator was below 5% and the RH in the potassium sulfate desiccator was above 90%. After slightly more than a month of static equilibration, these carbon samples were tested on successive days using the IC-1 protocol for used carbon. The carbon exposed to low RH yielded a penetration result of 8.4%, while the carbon exposed to high RH yielded a penetration result of 54%. These tests show that identical carbons exposed to different RH conditions prior to testing give significantly different results. It is therefore not legitimate to compare non-equilibrated used carbon test results against a single standard change-out criteria. For example, carbon taken from a plant located on the gulf coast will generally give higher penetration results than carbon taken from the desert Southwest. In order to establish a valid standard test procedure and acceptance criteria, it is necessary to require equilibration for used carbon samples.

An additional benefit of equilibration of used carbon will be to expand the range of penetration results and increase the sensitivity of the method to the degradation of carbon performance. For example, a carbon which yielded an unequilibrated penetration of 25% yielded an equilibrated penetration of 60%. Although both values are well outside any reasonable acceptance criteria, a new standard change-out criteria will need to be established based on more extensive comparative testing. This new acceptance criteria, which should probably be between 10 and 20% penetration, will reduce the experimental and/or interlaboratory uncertainty currently associated with marginal samples.

The primary objection to the equilibration of used carbons has been that "exposure of used carbons to gas flow before challenge with radioactive contaminants may remove some adsorbed material and in effect 'regenerate' the carbon. The test could then show a higher performance than the carbon is actually able to provide." To date, there has not been a single carbon reported to show this enhanced performance with equilibration at 30°C. In fact, all carbons tested have shown significantly increased penetration with equilibration. If this "regeneration" phenomenon exists at all, it is obviously much less significant than the competitive exclusion of methyl iodide by the water added during equilibration. Indeed, the current ASTM test shows a higher performance than the carbon is actually able to provide on a long-term basis.

Equilibrated used carbon testing will increase the continuity of tracking the aging process of carbon. Because of the present specifications for testing, the initial used carbon test results obtained after installation often show an increase in efficiency over the results reported for the new material. This discontinuity has been a source of confusion for some utilities and will be alleviated by equilibration of used carbon samples.

<u>Changes in Duration of Equilibration, Feed, and Elution Periods.</u> Parametric studies performed at the INEL and in Germany indicate no significant differences in penetration results for equilibration durations of 16 and 18 hours, feed durations of 1 and 2 hours, or elution durations of 1 and 4 hours.(5) The changes in feed and elution durations were incorporated into the testing protocol for the first NRC/INEL Interlaboratory Comparison, which was agreed upon by all participating laboratories prior to testing.

The change of equilibration duration from 16 to 18 hours was made as a result of a survey of industry practices and in recognition of the fact that unattended control of critical parameters in the test systems is generally not as good as under close supervision. In the past, the most critical concern in running an equilibrated test was the possibility of test bed flooding during the night which would invalidate the test and cost the laboratory in terms of time and money. To ensure flooding did not occur, the relative humidity level might have been lowered slightly and then readjusted in the morning just prior to the feed period. This practice does not allow sufficient time for the carbon to adjust and results in significantly lower penetration results than those obtained with constant 95% relative humidity equilibration and feed. This change in equilibration time merely allows two additional hours for the carbon to reach a new equilibrium with the adjusted relative humidity. The additional two hour time period appears to be sufficient to reach a new equilibrium if the change in relative humidity is not too drastic.

Changes in Gas Velocity Variation and Absolute Pressure. The change in the permissible variation of gas velocity from 0.5 to 0.3 meters/minute was made to more closely agree with the specification for accuracy of flow measurement of 2%. This change was discussed at some length and agreed upon by all in attendance at the NRC Workshop on Activated Carbon Testing held in Annapolis, Maryland, June 5-6, 1985.

The change in absolute pressure from 104 kPa to 101 kPa was made in recognition of the existence of vacuum induced flow systems which at best can operate at standard atmospheric pressure (101 kPa). INEL testing has shown that over the range of 85 to 115 kPa no significant differences in penetration results so long as the pressure is held relatively constant. Variations in pressure in this range during a single test, however, will affect the water loading of the carbon and often result in increased penetration values.

Change in Maximum Permissible Temperature Variation. The change in the maximum variation of gas stream and constant temperature cabinet/sample bed assembly reflects the importance of temperature in controlling relative humidity and a reasonable judgement of the degree of control easily achievable with current off-the-shelf equipment. Temperature is not only a very important element in overall system control, it is also one of the most easily measured and controlled. Current state-of-the-art PID-type temperature controllers are in fact capable of much finer control than is specified. The INEL test system currently controls the cabinet temperature to ±0.1°C and the test bed inlet gas stream temperature to ±0.05°C. Tests using this system have indicated that even if the test bed inlet gas stream temperature and RH are constant at 30.0°C and 95%, measurable differences in penetration will result if the cabinet temperature and consequently the canister temperature varies by as little as 0.3°C. ASTM D-3803 allows a maximum temperature variation of 0.5°C which in fact exceeds its own prescribed limits for relative humidity if a constant 29.1°C dew point is assumed. Obviously, with simultaneous variations in flow and dew point, and errors associated with dew point hygrometer measurements, the variation due to temperature needs to be limited as much as possible to ensure compliance with the specifications for relative humidity.

The Carbon Testing Laboratories

Nearly all analytical laboratories require some type of internal quality assurance program as a means of maintaining acceptable performance. Even laboratories whose results are not "certified" must use standards as references to interpret their own analytical work. This is not true for carbon testing laboratories. Until the first IC, the common cry was "there is no such thing as a standard carbon". However, the laboratories have proven that a standard carbon can be produced by the intralaboratory reproducibility exhibited in the IC results. Nonetheless, while the rest of the analytical world generally requires a minimum of 10% QA/QC samples, each carbon testing laboratory somehow believes that their answers are the right ones, independent of anyone else. Obviously, a quality assurance program which consists of having their instruments calibrated every six months to NBS traceble standards is not a sufficient guarantee of the accuracy of their test results. It would be in their own best interest to set up an intra-industry quality assurance program with standard samples distributed to each laboratory on a routine basis. Lacking this, such a program will have to be set up by an outside agency. Given the lack of credibility of current carbon testing and the cost to the utilities of mistakes by a laboratory, it might be in the utilities best interest to approach an agency such as the Institute for Nuclear Power Operations (INPO) to implement a laboratory certification program. To date, the NRC has shown extreme patience and concern for the carbon testing laboratories and has given them every opportunity to improve their performance. It is unlikely that the NRC or any other agency involved will show this type of consideration in the future if the past poor performance is allowed to continue.

The NRC

It is recommended that the NRC: 1) adopt a new standard test method similar to the INEL Standard Test Method; 2) implement a mandatory quality control program for the carbon testing laboratories; and 3) re-evaluate and revise the nuclear power plant standard technical specifications for activated carbon performance to reflect the change in testing requirements.

The utilization of the INEL Standard Test Method, or something similar, would not only provide the laboratories with the guidelines they need to perform adequate testing, but would provide results together with supporting data to the utilities which could be evaluated. Allowing licencees to shop-around for a penetration value which meets their technical specification requirements only provides an incentive to those laboratories which tend to bend the testing requirements. The use of a single standard test method would also eliminate confusion by the power plants as to what conditions are to be tested. Indeed, it is entirely possible that carbon which will "pass" the 130°C test specified in Method C of ASTM D-3803 cannot provide the iodine retention capability which might be required of it under real plant accident conditions.

The NRC, as stated previously, has shown extreme patience with the carbon testing laboratories. Hopefully, the results and conclusions of this program will provide sufficient information to provoke some action. It appears that allowing the laboratories to pick and choose those portions of the standard or recommendations which they will implement on a voluntary basis will not solve the problems associated with carbon testing. The NRC cannot continue to allow licencees to fulfill their technical specification requirements by obtaining penetration values with no supporting data and simply trusting the laboratories to follow the insufficient guidelines of the ASTM Standard. A mandatory quality control program should be implemented with satisfactory performance rewarded by certification to test carbon samples for the utilities.

The technical specification requirements for activated carbon performance must be adjusted to reflect the results obtained from a new standard test method. The standard specifications may be set fairly soon if comparative testing proceeds without delay. However, a transition period will be required for implementation of the new requirements and should include reviews for plants whose requirements for performance of the carbon might be less stringent than the standard specifications because of plant design and/or operation.

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APPENDIX A

INEL STANDARD TEST METHOD FOR NUCLEAR-GRADE ACTIVATED CARBON

A Revision of ASTM D 3803-79, Method A.

1. Scope

1.1 This standard covers the most critical test method for establishing the capability of new and used activated carbon to remove radio-labeled methyl iodide from air and gas streams. A single test procedure is described for application to both new and used carbons. The conditions employed were selected to approximate operating or accident conditions of a nuclear reactor which would severely reduce the performance of activated carbons. Increased temperature or decreased relative humidity generally act to increase the efficiency of methyl iodide removal by activated carbon. This test method is a revision of the most stringent ASTM test of nuclear-grade activated carbon and, therefore, is recommended for the qualification of new carbons and the detection of degradation of used carbons.

2. Applicable Documents

2.1 ASTM Standards.
D 2652 Definitions of Terms Relating to Activated Carbon
D 2854 Test for Apparent Density of Activated Carbon
D 2862 Test for Particle Size Distribution of Granular Activated Carbon
D 2867 Test for Moisture in Activated Carbon
D 3195 Recommended Practice for Rotameter Calibration
D 3803 Radioiodine Testing of Nuclear-Grade Gas-Phase Adsorbents
E 300 Recommended Practice for Sampling Industrial Chemicals

2.2 Code of Federal Regulations.
CFR Title 49, Section 173.34, "Qualification, Maintainance, and Use of Cylinders"
CFR Title 49, Part 178, Subpart C, "Specifications for Cylinders"

2.3 Military Standards.
MIL-F-51068D Filter, Particulate High Efficiency, Fire Resistant
MIL-F-51079A Filter, Medium Fire Resistant, High Efficiency

3. Summary of Method

3.1 This test simulates normal containment operating conditions, accident conditions for some systems outside containment, and all conditions for control room atmosphere applications. Both new and used carbons are first exposed to humid air (pressure, approximately 1 atm.; temperature, 30.0°C; relative humidity, 95%) for an equilibration period of 18 hours. The first 16 hours of this equilibration period may be run unattended with the required parameter monitoring and control devices, but the final two hours must be closely monitored and controlled by qualified laboratory personnel. During the challenge or feed period, radio-labeled methyl iodide at a mass concentration of 1.75 mg/m^3 of humid air flow is passed through the beds for a period of 60 minutes. Following the feed period, humid air flow without test adsorbate is continued at the same conditions for a 60 minute elution period. Throughout the entire test, the effluent from the sample bed passes through two backup beds containing carbon having a known high efficiency for methyl iodide. The two backup beds trap essentially all the radio-labeled methyl iodide that passes the test bed, and provide a differential indication of their efficiency. At the end of the elution period, the gamma activity of ^{131}I in the test and backup beds is measured by a gamma counter, and the percent of adsorbate penetrating the test bed is determined.

4. Definitions

4.1 The following terms have special meanings for the purposes of this standard. Additional terms relating to this standard are defined in ASTM D 2652.

4.1.1 Penetration (P) - The percentage of the contaminant (CH_3I) which passes through the equilibrated test bed of standard depth, and is collected on the backup beds during the feed and elution periods under specified conditions.

4.1.2 Efficiency (E) - The percentage of the contaminant removed from a gas stream by an adsorption bed: E,% = 100 - P%.

4.1.3 Relative humidity (RH) - For the purpose of this test relative humidity is defined as the ratio of the partial pressure of water in the gas to the saturation vapor pressure of water at the gas temperature and pressure. At temperatures below 100°C, this is the normal definition and relative humidity can range from 0 to 100%.

4.1.4 Counter Efficiency (CE) - The fraction of the actual number of disintegrations of a radioactive sample that is recorded by a nuclear counter.

5. Apparatus and Materials

5.1 Sample Preparation Apparatus.

5.1.1 Riffle Sampler, in accordance with 30.5.2 of ASTM E 300, Recommended Practice.

5.1.2 Feed Funnel and Vibrator, in accordance with 2.2 and 2.3, respectively, of ASTM D 2854.

5.1.3 Balance, capacity > 200g, accurate to ±0.01g.

5.2 Sample and Backup Bed Assemblies.

5.2.1 The sample bed canister and backup bed canisters must each be either a single unit capable of containing carbon to a depth of 50mm or they may be assembled from two separate units each capable of containing carbon to a depth of 25mm. Two backup canisters, each of 50mm total depth, are required. Canisters may be reused after being decontaminated to remove residual radioactivity.

5.2.2 Clamping assemblies are needed for sample and backup beds. The only requirements for these assemblies are that they provide a smooth sealing face, uniform alignment of bed canisters, and sufficient clamping force so that the leak test in 8.2 can be met.

5.3 Test System - A single test system cannot be used for all the test conditions currently required by commercial nuclear power plants. Because of the range of conditions and accuracy of parameter measurement and control required, a minimum of two test systems are necessary, one for tests conducted below 100°C and near standard atmospheric pressure, and one for the higher temperature and pressure tests. As an example of a test system which can meet the parameter requirements of this test method as listed in Table A-1, a schematic of the INEL test system is shown as Figure A-1. This system is designed to operate at approximately 30°C and 95% RH, with a gas flow of 24.7 l/min at atmospheric pressure. If test conditions which differ significantly from these are required from the system, then separate calibrations and/or instrumentation may be required for use in these parameter ranges.

5.3.1 Saturator System - The system may be a controlled temperature saturator (bubbler) or spray chamber (environmental condition generator) or any other device of sufficient stability and capacity to supply the required mass flow of water vapor at test conditions.

5.3.2 Flow Generator - This system may be an air compressor upstream of the test system or a vacuum pump downstream of the test system. A dryer, carbon adsorber, and HEPA filter are required for either system to condition the inlet air. Flow measurement and control should be accurate and stable to within ±2%. System capacity shall meet or exceed the volumetric flow requirements as calculated from the specified face velocity. A surge tank and pressure control valve should be employed in either type of system to ensure stable and accurate flow measurement and control. For safety, it is important that the pressure system be equipped with a pressure relief valve. It is important that the pipe diameter and inlet air filters for a vacuum system be designed and maintained to minimize the pressure drop from ambient to ensure that the specifications for pressure at the test bed are met.

5.3.3 Moisture Separator - should be used to protect the HEPA filter by removing large quantities of entrained particulate water, if present, after humidification. A HEPA filter or equivalent is required to function as a final droplet trap to remove small amounts of fine particulate water from the carrier gas ahead of the test bed.

5.3.4 Test Adsorbate Supply - The system shall consist of a stainless steel cylinder, pressure gage, pressure regulator, and a flow regulator capable of providing a steady flow of the challenge gas, i.e. radio-labeled methyl iodide in dry nitrogen, for the duration of the test feed period. The point of injection into the main gas flow of the system must be such that the cross-sectional distribution of the adsorbate at the face of the test bed can be ensured to be homogeneous. A mixing chamber, baffles, glass beads, etc. should be used to acheive adequate mixing.

5.3.5 Constant Temperature Cabinet/Sample Bed Assembly - An enclosure and associated thermoregulatory system must be used that is capable of maintaining temperature to ±0.2°C. All tubing downstream of the moisture separator, the carbon bed canisters and holders, temperature and pressure ports and measurement devices upstream and downstream of the test bed, and an upstream port and tubing to the dew point sensor all must be included within the temperature controlled enclosure. In addition, it is highly recommended that a bypass line be included around the sample bed assembly to avoid exposing the sample to start-up conditions possibly outside those specified.

5.3.6 Air Flow Measurement and Control - Includes mass flow controllers, control valve and oriface meter, rotameter or any device with adequate stability and a demonstrated measurement accuracy of ±2% over the range of test conditions. All flow measuring devices must use correction factors for interpretation and application to actual test conditions. These factors must be carefully predetermined and documented. No flow measuring device should be located directly downstream of the test bed such that it is subject to variable temperature and humidity conditions during a test as a result of water adsorption by the carbon.

5.3.7 Interconnecting Tubing - Tubing beyond the point of methyl iodide injection shall be glass or stainless steel. No rubber, polyethylene, or other organic tubing should be used. Interconnections should be kept as short as possible to reduce the possibility of water condensation.

5.3.8 Temperature Measurement Devices - with certified accuracy and calibration to ±0.1°C are required, three or four wire platinum resistance thermometers (RTD's) are strongly recommended.

5.3.9 Pressure Measurement Devices - Absolute pressure measuring devices must be accurate to within ±2% at standard atmospheric pressure and be capable of digital or analog output to meet the specified recording requirements. The differential pressure device required for measurements across the test bed must be capable of detecting a 0.25 kPa pressure difference and be accurate to within ±2% at the normal operating ΔP.

5.3.10 Heaters and Temperature Controllers - Must be capable of maintaining the inlet gas stream temperature from the point of humidity control to the test bed, and the surface temperature of all carbon canisters within ±0.2°C.

5.3.11 Humidity Measurement - An optical dew point hygrometer with demonstrated accuracy and calibration to ±2% relative humidity at 95% RH and 30°C is required for measurement of RH of the gas stream immediately upstream of the test bed. A secondary check on this measurement device is required to ensure that calibration offset has not occurred. This secondary device may be another optical dew point hygrometer, wet bulb/dry bulb, or any other device capable of ±3% accuracy.

5.3.12 Data Recording - To meet the reporting requirements of 12.1.8-11, the use of potentiometric recorders or a data logger capable of recording temperatures, pressures, flow, and relative humidity data at a maximum of 5 minute intervals is required.

5.4 Gamma Detection System - Any reliable and efficient detection system for gamma rays of 365 keV energy is permissible, provided it produces actual counts of gamma photons and not an analog rate output, and provides adequate elimination of any interferences that might be present. Systems equipped with internal computers that make calculations or corrections for such things as dead time, counting efficiency, decay rates, etc. are also permissible provided they give accuracy equal to that required in this standard. In many cases, either thallium-activated sodium iodide well counters or single- or multi-channel gamma spectrometers that use thallium-activated sodium iodide, lithium-drifted germanium, or intrinsic germanium detectors can be used with appropriate professional guidance, proper shielding of at least 4 inches of lead, and preferably graded adsorbers of cadmium and copper to reduce the production of X-rays in the shielding. When significant gamma-emmitting interferences are absent and penetration of ^{131}I through the test bed is greater than a few tenths of percent, either the principal ^{131}I photopeak at 364.46 keV or the entire spectrum including the Compton continuum can be used. However, when the penetration is low, a multi-channel spectrometer with a germanium detector will be required for the most accurate measurements. This is necessary to identify the ^{131}I in the presence of the ^{214}Pb daughter of ^{226}Ra generally present in carbon, and to permit Compton correction for gamma-emitters such as ^{40}K and daughters of ^{226}Ra. The test bed, backup beds, and carbon backgrounds must all be counted under identical geometrical conditions. This requires the use of a jig on the detector to hold each counting bottle in identically the same position.

5.5 Materials

5.5.1 Air - Compressor, used for pressure systems, shall be of the oil-free type to minimize injection of hydrocarbons into the system. Line filters shall consist of a dryer, activated carbon and HEPA filters and shall be adequately sized and maintained.

5.5.2 Water - Deionized and/or distilled water must be used for water-vapor or steam generation.

5.5.3 Radio-Labeled Methyl Iodide - Shall be prepared and/or diluted with analytical grade chemicals and/or purchased from a reputable vendor. The methyl iodide solution should be stored in the dark below 0°C to slow its decomposition to I_2. The activity of the ^{131}I should be such that the total activity in the entire spectrum from the test bed is between 10^3 and 5×10^5 counts per minute.

5.5.4 Backup Bed Carbon - Shall have a penetration of no more than 2% when tested by this standard method. The calculation of the efficiency of the first backup bed is required for each test.

5.5.5 HEPA Filter Media - In accordance with MIL-F-51079. If a pleated filter is used in place of a flat sheet, it shall be constructed in accordance with MIL-F-51068.

6. Safety Precautions

6.1 Overpressure - The contaminant feed system makes use of dry nitrogen from standard high-pressure gas cylinders, a contaminant feed cylinder which is pressurized, and associated regulators and tubing for transport of the contaminant gas. This system must be designed with adequate saftey factors. Standards for the fabrication of such pressure vessels and associated fittings are contained in 49 CFR 173.34. Elastomeric seals must be replaced on a regular basis or if damaged to ensure system integrity.

6.2 Radioactivity - The radiotoxicity of ^{131}I is well documented. The species used in this test is very volatile and easily inhaled. Rigorous health physics procedures must be followed whenever handling the radioisotope and routine thyroid counting must be provided for laboratory personnel. The system must be adequately vented through a filter system capable of handling the maximum possible contaminant release. Radiation shielding and dosimetry must be provided to limit and monitor worker exposures in compliance with federal and state nuclear regulations. Personnel access to the system should be strictly limited and workers should be trained in health physics procedures.

7. Sampling

7.1 Guidance in sampling granular activated carbon is given in ASTM E 300, Recommended Practice.

7.2 Occasionally, samples received for laboratory analysis are not of sufficient quantity to fill the test canister to the standard depth of 5.08 cm (2 inches). If possible, another sample should be obtained. However, this is not always possible because of critical time constraints. If a substandard quantity of carbon must be tested, the resulting actual penetration value must be converted to the predicted penetration at the standard depth and noted as such on the report form. This conversion is based on the log-linear function of penetration with depth and has the form

$$P_s,\% = 100 \exp\{[\ln(P_a/100)](5.08/d)\}$$

where: P_s = the predicted penetration, in percent, at the standard depth;
P_a = the actual penetration, in percent, at the substandard depth;
and d = the substandard depth, in centimeters.

8. Preparation of Apparatus

8.1 Assemble the test apparatus making sure that the placement of RTD's is such that they accurately reflect the temperature of the gas stream and the temperature controlled cabinet or test canister, and are not subject to radiative heating.

8.2 Leak testing of the system designed to test carbon at standard atmospheric pressure should be performed on a routine basis, recommended prior to each test. This test should be a pressure decay test for pressure induced flow systems or a vacuum decay test for vacuum induced flow systems. The system should be pressurized to approximately 125 kPa or depressurized to approximately 75 kPa with filled test and backup cannisters in place. The system should then be isolated, i.e. sealed at all atmospheric connections, and the pressure change with time recorded. This rate of change should not exceed 5 kPa in 30 minutes to ensure safety and the accuracy of flow measurement.

8.3 To ensure the accuracy of relative humidity measurement, a check of the differential pressure between the test bed and the sensor of the optical dew point hygrometer should be performed initially and whenever the system is modified or semi-annually. This check should be performed with the test and backup canisters filled with carbon and with the system operating at the standard conditions specified, i.e. temperature, flow, RH, pressure, etc. This differential pressure should not exceed 1 kPa or must be corrected for either in the calculation of relative humidity, or preferably by modification of the test system to reduce the ΔP.

8.4 Correction factors for flow measurement devices, esp. rotameters, must be predetermined by the comparison of accurate pressure and temperature measurements made at the device and at the test bed under normal operating conditions. Correction factors to convert standard flow to actual flow at specified conditions, which may include the addition of a significant amount of water vapor, should be carefully determined for all measurement devices. No flow measuring device should be located directly downstream of the test bed such that it is subject to variable temperature and humidity conditions during a test as a result of water adsorption by the carbon.

8.5 From the determination of the "as received" apparent density (ASTM D 2854) and a knowledge of the exact volume of the test canister, determine the weight of carbon required to fill the test bed. Weigh this amount of carbon to the nearest 0.01g and record this weight and its final weight after the test on the report form as shown in Annex A-1. Determine the dry weight of carbon used in the test bed from the initial moisture content as determined using ASTM D 2867 Oven Drying Method, except using a 16 hour drying time. Record the initial and final sample and sub-sample weights and calculate the initial, adsorbed, and final moisture content, %, as described in section 11.1.

9. Calibration

9.1 RTD's, optical dew point hygrometers and other humidity measuring devices, flowmeters, pressure transducers, balances, radiation survey meters, and gamma detection systems shall be calibrated at intervals of not more than six months, or whenever a detectable change in performance occurs, with NBS traceable standards. Devices which are required to output data for recording should be calibrated together with the readout device to the accuracy specified.

10. Procedure

10.1 Stabilization Period - Install the filled test and backup canisters in the system. Perform the leak test described in 8.2 to ensure system integrity. Bring the system up to operating conditions, see Table A-1, and allow it to stabilize while bypassing flow around the test and backup beds. The duration of this stabilization period is recommended to be a minimum of two hours, during which the canisters and carbon must come to thermal equilibrium at the specified test temperature.

10.2 Equilibration Period (for new and used carbons) - Air with 95 ±2% relative humidity at a temperature of 30.0 ±0.2°C is run through the beds for 18.0 ±0.2 hours. This length of time ensures that the test bed carbon will reach equilibrium with the flow of humid air. There will be a sudden change in relative humidity at the start of equilibration that will produce a rapid temperature rise in the carbon caused by the heat of adsorption of water. The extent of this temperature rise cannot be controlled and depends upon the condition of the carbon. The conditions at the test bed inlet must be held at the specified conditions, Table A-1.

10.3 Feed Period (Challenge) - Humid air flow is already at the prescribed conditions, Table A-1, at the start of the feed period. Flow is maintained at 30.0 ±0.2°C at 95 ±2% relative humidity for 60 ±1 minutes with 1.75 ±0.25 mg/m^3 of radio-labeled CH_3I in the total system gas flow provided by the addition of a small and continuous flow of the challenge gas during the feed period.

10.4 Elution Period - To evaluate the ability of the carbon to hold the adsorbate once it is captured, flow is continued at the end of the feed period without change of the flow rate, relative humidity or temperature for a period of 60 ±1 minute. (See Table A-1.)

10.5 Monitor and record gas stream temperatures upstream and downstream of the test bed. A decrease in the downstream temperature is indicative of bed "flooding", the condensation of free water in the sample bed, and the test should be aborted. Monitor temperatures, pressures, humidity, and air flow at least every 5 minutes or continuously by means of a data logger or recorder. Also monitor the pressure drop across the bed. Erratic readings or a substantial increase in this differential pressure is an additional indication of test bed flooding.

10.6 At the end of the elution period, switch the system to bypass mode and shut down the system. Remove and disassemble test and backup beds. Transfer the carbon from the canister to a jar with a volume at least twice that of the carbon. Roll and tumble the jar gently until the carbon is thoroughly homogenized then transfer the blended carbon to a pre-tared plastic counting bottle sufficiently large to accomodate all of the carbon and tamp it down to some reproducible height. The counting bottle must be immediately sealed and reweighed to the nearest 0.01g. These weights should then be recorded on the report form.

10.7 Counting Conditions - It is never permissible to count the ^{131}I activity in the test and backup canisters directly as obtained from the test. The carbon from each canister must be counted in a plastic counting bottle having rigid vertical sides and uniform wall thickness and internal diameter, and then tamped down to a standard and reproducible height. The packing density is not particularly important for gamma counting within the range of densities likely to occur, but the geometrical angle subtended between the sample activity and the detector is of great importance if accurate results are to be obtained. Because penetration is simply a ratio of counting rates, absolute counting efficiencies are not necessary unless an independant determination of the total quantity of radio-iodine is desired. The carefully filled and weighed counting bottles should be placed on the detector in a jig that will guarantee reproducible positioning. Count for whatever period of time is necessary to obtain the desired sensitivity and precision. Calculate the results and propagate the statistical uncertainties as described below.

10.8 Gamma Count Corrections - If each test and backup carbon is homogenized and counted under identically the same conditions of height and geometry in identical counting bottles, no corrections are necessary for attenuation of the gamma rays by either the carbon or the counting bottle, or for geometry or counting efficiency. Corrections for dead time in the counter system are avoided by simply controlling the quantity of radioiodine used in each test. This simple and expedient method also minimizes costs of tracer, both internal and external dose to those operating the test system, and waste disposal. The principal corrections required are those for decay of the ^{131}I activity and for the carbon background, including the Compton contribution from higher energies when such interferences are present and a spectrometer must be used. When counting times can be kept short and all samples are counted with dispatch, even the decay correction can be made negligible, although this is an unnecessary limitation on the procedure.

10.9 Counting Efficiency - Determination of the counting efficiency is unnecessary as far as the measurement of penetration is concerned, and is undesirable because of the extra time and the standard ^{131}I solution that are required. However, if a separate determination of the quantity of ^{131}I used is desired, the counting efficiency can be determined rather simply. Fill a standard counting bottle with carbon to the standard height used in the test procedure. Determine the volume of water required to fill the interstitial voids just to the top of the carbon. Count this sample under the standard counting conditions to determine the blank. Measure an exact volume of a standard solution of ^{131}I of such activity that dead time effects are kept below about 1%. Dilute with water in a non-wetting plastic beaker to the volume determined previously to fill the carbon voids. Repack another counting bottle with carbon to the standard height and add the diluted iodine solution. Count under the identical conditions being used for the test samples, and as were used for the blank. The slight difference in attenuation of the gamma rays due to the water added will certainly be much less than the errors due to inhomogeneous absorption of small volumes of tracer in the carbon without water present. The counting efficiency, CE, is then

$$CE = (R_s - R_b)\ (\exp 0.003592\ t)/A_s$$

where: R_s = counting rate of ^{131}I standard, counts per minute;
R_b = counting rate of background, counts per minute;
A_s = activity of ^{131}I standard taken, as of time of standardization of original solution, disintegrations per minute;
t = length of time between standardization of original solution and counting, in hours;
and 0.003592 is disintegration rate per hour for 8.041-day ^{131}I.
for CE = net counts-per-minute per disintegration-per-minute of ^{131}I at the same time.

10.10 Decay Correction - If the carbon from different canisters from a given test are counted at significantly different times, they must each be corrected for decay to some common base time in order that the counting rates obtained be comparable. Although other times can be used for zero time, it is convenient to correct all counts back to midnight of the first day in which counting for a particular test was done. Using the 24-hour clock, times can be read directly from a watch to the nearest quarter hour, and the various beds can be counted in any order. For ^{131}I compounds, the correction is

$$R_0 = R_t \exp(0.003592\ t)$$

where: R_0 = equivalent counting rate at time zero (midnight);
R_t = counting rate at time, t;
and t = elapsed time between zero time and counting time, hours.

Generally, the counting interval will be small compared to the decay time so that the beginning of the count can be used to calculate the elapsed time. However, the midpoint of the counting interval gives better accuracy and is just as convenient to use. It should be emphasized that the decay correction should be applied to the net counting rate after correction for background, i.e. obviously the background does not decay with the halflife of ^{131}I.

10.11 Radioactivity and Counting Times - Corrections for dead-time losses of counting rate due to overloading the counting system by using too much activity can never be made as accurately or conveniently as avoiding such losses from the beginning. Such losses are particularly undesirable when the penetration is low and very large errors are incurred for the test bed with virtually no error from this source for the backup beds. Locating the test bed counting bottle some distance from the detector and counting only a small fraction of the total flux emitted to bring it within the proper range is neither desirable nor prudent. Consequently, the activity of the ^{131}I used in each test should be such that the test bed will not contain more than about 5 x 10^5 counts per minute of total activity incident upon the detector and associated electronics to avoid the increased uncertainties of making large corrections for dead-time effects. When gamma spectrometry is used, this applies to the total events being processed by the ADC for the entire spectrum, not just those of interest in the 365 keV photopeak. On the other extreme, the activity used should be kept sufficiently high to give 10^3 to 10^5 counts per minute in the test bed to keep the sensitivity and precision of the measurement high without requiring prolonged counting times, particularly when using just the photopeak in gamma spectrometry. Thus, the activity on the test bed can be measured with a relative standard deviation of a few tenths percent with counting times of a very few minutes. For carbon backgrounds and backup beds containing low activity, the counting times should be 30 minutes to 1 hour with gross counters or 1 to 2 hours with spectrometers using just the iodine photopeak. This will permit the iodine activity in the backup beds to be detected above the carbon background and the Compton continuum with reasonable statistical certainty.

10.12 Determination of Contaminant Mass - The efficiency factor can provide an independant means for determining the mass of the contaminant. The equation is

$$M = [\Sigma(R_t - R_b)]/(2.22 \times 10^6 E A_s)$$

where: M = mass fed during test, g;
R_t = count rate for test or backup bed, corrected to base time, counts per minute;
R_b = background count for canister corresponding to R_t, counts per minute;
E = efficiency factor for gamma counter.
and A_s = contaminant specific activity at base time, μCi/g;

11. Calculations

11.1 Initial, Adsorbed, and Final Moisture Content - Initial moisture content (IMC) as weight percent water is simply 100 times the difference in weight of the subsample of carbon before (W_b) and after (W_a) drying for 16 hours at 150°C divided by its initial weight, i.e.,

$$\text{IMC, \%} = 100(W_b - W_a)/W_b.$$

The percentage moisture absorbed during the test (MADT) is similarly 100 times the difference between the final weight (W_f) of carbon in the test canister after the test and the initial weight (W_i) of carbon in the canister before the test divided by the final weight, i.e.,

$$\text{MADT, \%} = 100(W_f - W_i)/W_f.$$

The final moisture content (FMC) is

$$\text{FMC, \%} = (\text{IMC,\%})W_i/W_f + (\text{MADT,\%}).$$

11.2 Penetration - All counting must be corrected for the corresponding background counting rates before other corrections are applied. The net activities are then corrected for decay from counting time to some common time zero before calculation of penetration. The halflife and disintegration constant of ^{131}I are 8.041 days and 0.003592/hour, respectively. Because counting efficiencies are not required when counting conditions are kept the same for all fractions, calculate percent penetration as follows:

$$P,\% = 100\ (B + C)/(A + B + C)$$

where: A = net counting rate of the ^{131}I activity collected in the test bed, cpm;
B = net counting rate of the ^{131}I activity collected in the first backup bed, cpm;
and C = net counting rate of the ^{131}I activity collected in the second backup bed;
for beds of equal depth,counted under identical conditions, and corrected for decay.

Obviously, efficiency, E, of the test bed in percent is

$$E,\% = 100 - P = 100(A)/(A+B+C).$$

The efficiency with which the ^{131}I activity passing the test bed was retained by the first backup bed is similarly

$$E_{bu},\% = 100\ B/(B + C)$$

This calculation is important in showing whether or not all the activity passing the test bed was collected, and whether or not the proper blank corrections are being made. When penetration is low and corrections for blanks and/or the Compton continuum are not made, "C" can be larger than "B" and the results will be grossly inaccurate. Specific equations are given in Annexes A-2 and A-3 for calculating both penetration of the test bed and efficiency of the first backup bed from the raw data obtained in a gross counter or in a gamma spectrometer, respectively.

11.3 Error Propagation - The uncertainty with which the measurement was made, expressed as one standard deviation, must be calculated for each measured value of penetration of the test bed and efficiency of the first backup bed. The uncertainty must include every statistical uncertainty incurred anywhere in the entire measurement process, all propagated to the final result by the well-known

Law of Propagation of Error. Thus, the standard deviation of percent penetration defined above is

$$S_P = 100 \frac{\{(B+C)^2(S_A)^2 + (A)^2[(S_B)^2 + (S_C)^2]\}^{0.5}}{(A+B+C)^2}$$

where A, B, and C have the same meanings as above and S is the estimate of the standard deviation of the corresponding quantities. It should also be noted that the standard deviation of efficiency by the test bed has the same absolute value as that of penetration of the test bed, i.e. $S_E = S_P$. Similarly, the standard deviation for percent efficiency of the first backup bed is

$$S_{E(bu)} = 100\ [C^2(S_B)^2 + B^2(S_C)^2]^{0.5}/(B + C)^2.$$

Specific equations are also given in Annexes A-2 and A-3 for calculating the standard deviations of both penetration of the test bed and efficiency of the first backup bed from the raw data obtained in a gross counter and in a spectrometer, respectively.

12. Report

12.1 Report the following information on a standard report form similar to that shown in Annex A-1 for each measurement of penetration:

12.1.1 Name, address, and phone number of laboratory making the test.

12.1.2 Name, signature and months of experience of technician performing test, and name and signature of supervisor approving test.

12.1.3 Date of test.

12.1.4 Source of sample including, for used samples, the original log number of the sample, the filter system and time for which it was exposed, if available.

12.1.5 Type of carbon, supplier name, grade designation, base material, impregnant(s), lot and batch numbers, if available.

12.1.6 Particle size distribution (new carbon only) in accordance with ASTM D 2862 method.

12.1.7 Apparent density for new and used carbons in accordance with ASTM D 2854 method, except determined "as received", i.e. not dried.

12.1.8 Maximum, minimum, average, and standard deviation for gas temperature immediately upstream of the test bed for each of the test periods.

12.1.9 Maximum, minimum, average, and standard deviation for pressure at the test bed for each of the test periods.

12.1.10 Maximum, minimum, average, and standard deviation for relative humidity as measured just prior to the test bed for each of the test periods.

12.1.11 Maximum, minimum, average, and standard deviation for the actual gas flow for each of the test periods.

12.1.12 Report the initial moisture content, %, of the test carbon together with the initial and final weights of the sample used for the moisture test. Also report the initial and final weights of the test bed carbon along with its adsorbed and final moisture content, %.

12.1.13 The duration of each of the test periods.

12.1.14 The penetration of the test bed and the efficiency of the first backup bed will be calculated for each separate measurement made. Every measured value will be reported as a finite number to the proper number of significant figures as indicated by the value of the standard deviation, including negative signs if obtained. No subjective judgements are permitted such as rounding negative results to zero or reporting results as "less than" some arbitrary figure. All raw data obtained will also be reported along with the calculated result, including total counts, counting times and decay times of the test bed, all backup beds, carbon backgrounds, etc., as illustrated in Annex A-1.

12.1.15 Every measurement of penetration of the test bed and efficiency of the first backup bed will be accompanied by an estimate of the statistical uncertainty with which each measurement was made, reported as one standard deviation of all random uncertainties incurred in the entire measurement process, not merely the standard deviation of sample counts.

Table A-1. Parameter Specifications for the INEL Standard Test Method for Nuclear-Grade Activated Carbon.

Parameter, unit	Specification ± Maximum Variation
Temperature, °C	30.0 ± 0.2
Relative Humidity, %	95 ± 2
Absolute Pressure, kPa	101 ± 5
Gas Velocity, m/min.	12.2 ± 0.3
Gas volumetric flow, l/min. (assuming 50.8 mm bed dia.)	24.7 ± 0.7
Bed Diameter & Depth, mm	50 ± 1
Equilibration Period Duration, hr.	18.0 ± 0.2
Feed Period Duration, min.	60 ± 1
Adsorbate Concentration, mg/m^3	1.75 ± 0.25
Elution Period Duration, min.	60 ± 1

Note: Temperature, relative humidity, pressure, and gas velocity are to remain constant within the specified maximum variations throughout the entire test, i.e. for each test period. Parameter excursions outside the specified limits during the last four hours of the test, i.e. the last two hours of equilibration and the feed and elution periods, will invalidate the test results. Parameter excursions during the first 16 hours of equilibration which are more than twice the specified variation shall invalidate the test results.

It must also be noted that testing has shown that unattended equilibration (16 hr.) of new carbon at ≥ 96% RH followed by two hours of attended equilibration at 95% RH results in significantly higher penetration values than those obtained with 18 hours of constant 95% RH equilibration. It is, therefore, very important to maintain the relative humidity below 96% during the 16 hours of unattended equilibration.

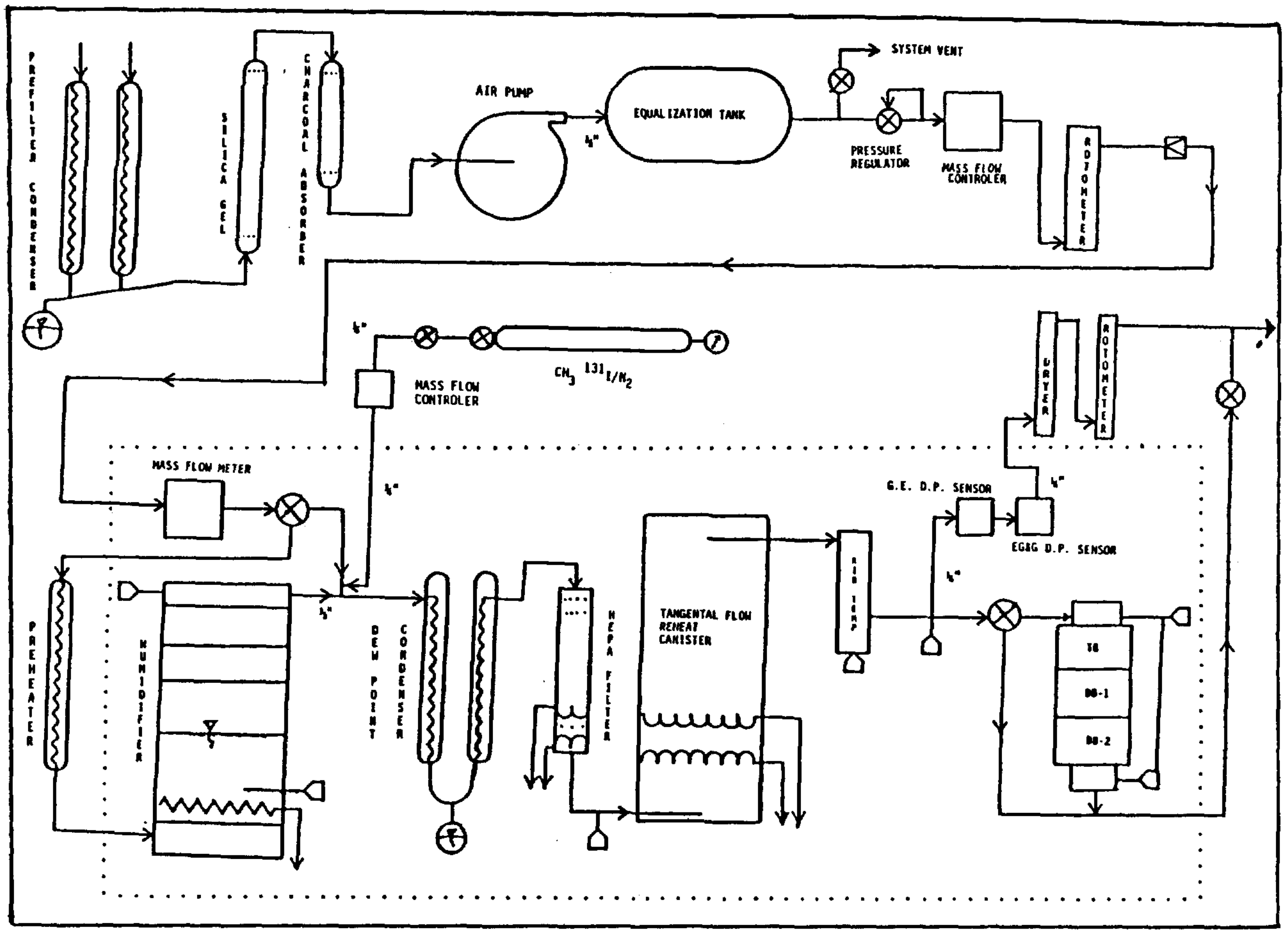

Figure A-1. A Schematic of the INEL Activated Carbon Test System, presented here as an example of a system design which will meet all of the specifications of this standard.

Annex A-1. Report Form for Results of INEL Modified Test Method.

Test Laboratory (12.1.1)
Name:________________________
Address:________________________
____
Telephone:________________________

(12.1.2 & 3) Test Date:__________
Technician
Name:________________________
Signature:________________________
Months operating test system:______.

Supervisor Name:________________________

Signature:________________________

Source of Sample (12.1.4) : New ___ or Used ___ ;
if used, Original Log Number:__________; Filter System:__________;
Time In Service:__________.

Type of Carbon (12.1.5) : Supplier Name:________________________
Grade Designation:________________________
Base Material:________________________
Impregnant(s):________________________
Lot Number:__________ Batch Number:__________

Particle Size Distribution (12.1.6, new carbon only) :

Apparent density (12.1.7) : Standard Volume:________________cc
Weight of Carbon:________________g
Density:________________________g/cc

Moisture Content Determinations (12.1.12) :

<u>Initial Moisture Content</u> (ASTM D 2854 Oven Drying Method, t = 16 hrs.)

(1) Weight of weighing bottle alone . . . . .__________g
(2) Weight of weighing bottle plus subsample of carbon . . .__________g
(3) Weight of subsample of carbon (2) - (1) . . . . .__________g
(4) Weight of weighing bottle plus carbon after drying . . .__________g
(5) Weight of moisture removed (2) - (4) . . . . .__________g
(6) Initial Moisture Content, 100 (5)/(3) . . . . .__________%

<u>Moisture Absorbed During Test</u>

(7) Weight of weighing bottle alone . . . . .__________g
(8) Weight of weighing bottle plus sample of carbon . . . .__________g
(9) Weight of sample of carbon (8) - (7) . . . . .__________g
(10) Weight of weighing bottle alone . . . . .__________g

(11) Weight of weighing bottle plus carbon after test . . . .__________g
(12) Weight of sample of carbon after test (11) - (10) . . .__________g
3) Moisture Absorbed During Test, 100 [(12) - (9)]/(12) . .__________%

Final Moisture Content (see section 11.1 for calculations)
(14) Final Moisture Content, (6)(9)/(12) + (13) . . . . . . .__________%

Test Canister Information: Diameter, ±0.1 mm ________mm
Depth, ±1 mm ________mm
Volume, ±0.1 cc ________cc

Summary of Test Parameters (12.1.8-11)
Equilibration Period:

First 16 hours of equilibration:
Duration ________hrs., Monitoring Frequency ________/hr.

Parameter	Minimum	Maximum	Average	Std.Dev.
Temperature, °C				
Relative Humidity, %				
Absolute Pressure, kPa				
Actual Gas Flow, l/min.				

Last 2 hours of equilibration:
Duration ________hrs., Monitoring Frequency ________/hr.

Parameter	Minimum	Maximum	Average	Std.Dev.
Temperature, °C				
Relative Humidity, %				
Absolute Pressure, kPa				
Actual Gas Flow, l/min.				

Feed Period:
Duration ________min., Monitoring Frequency ________/hr.

Parameter	Minimum	Maximum	Average	Std.Dev.
Temperature, °C				
Relative Humidity, %				
Absolute Pressure, kPa				
Actual Gas Flow, l/min.				

Elution Period:
Duration ________min., Monitoring Frequency ________/hr.

Parameter	Minimum	Maximum	Average	Std.Dev.
Temperature, °C				
Relative Humidity, %				
Absolute Pressure, kPa				
Actual Gas Flow, l/min.				

Note: The actual gas flows indicated are at the test conditions, i.e. corrected for temperature, pressure, and water vapor. These values may be converted to superficial face velocity by dividing by the test bed cross-sectional area, and making the proper unit conversions.

Counting Information (12.1.14-15)

Type of Instrument ____
(If gamma spectrometer, give energy region used)

Type and Size of Detector ____

Results:

Test Bed, Total Counts.............. ______________________________

Test Bed, Counting Time............. ______________________________ min.

Test Bed, Time Since Midnight....... ______________________________ hours

1st Backup Bed, Total Counts........ ______________________________

1st Backup Bed, Counting Time....... ______________________________ min.

1st Backup Bed, Time Since Midnight. ______________________________ hours

2nd Backup Bed, Total Counts........ ______________________________

2nd Backup Bed, Counting Time....... ______________________________ min.

2nd Backup Bed, Time Since Midnight. ______________________________ hours

Background Test Bed, Total Counts... ______________________________

Background Test Bed, Counting Time.. ______________________________ min.

Background BU Beds, Total Counts.... ______________________________

Background BU Beds, Counting Time... ______________________________ min.

Penetration ± 1sd, Test Bed......... ________________ ± ____________ %.

Efficiency ± 1sd, First Backup Bed.. ________________ ± ____________ %.

Note: When a gross gamma counter is used, there will be only a single figure to be entered in the above blanks for total counts. However, when a spectrometer is used, three numbers are required for each blank asking for total counts. The first number in each "count" blank is the total count obtained in the given energy interval. The second number, which will be subtracted from the first, is the background count expected in that interval from extrapolation of the Compton continuum. Both numbers are required for proper error propagation. The third number is the difference between the first and second, or the Compton-corrected net counts that will be used in the calculation of penetration. This method of reporting data from spectrometric measurements is shown in the following example.

Example of Counting Information

Type of Instrument ND-66 Gamma Ray Spectrometer, 360-370 keV
(If gamma spectrometer, give energy region used)

Type and Size of Detector Ge(Li), 75ml

Results:

Test Bed, Total Counts.............. 475626 - 14890= 460736
Test Bed, Counting Time............. 10 min.
Test Bed, Time Since Midnight....... 8.5 hours
1st Backup Bed, Total Counts........ 140685 - 8682 = 132003
1st Backup Bed, Counting Time....... 60 min.
1st Backup Bed, Time Since Midnight. 9.5 hours
2nd Backup Bed, Total Counts........ 3195 - 487 = 2708
2nd Backup Bed, Counting Time....... 120 min.
2nd Backup Bed, Time Since Midnight. 13 hours
Background Test Bed, Total Counts... 492 - 451 = 41
Background Test Bed, Counting Time.. 120 min.
Background BU Beds, Total Counts.... 485 - 492 = -7
Background BU Beds, Counting Time... 120 min.

In this example, the penetration of the test bed and its standard deviation obtained using the Compton-corrected values are 4.619 ±0.014%, and for the efficiency of the first backup bed are 98.969 ± 0.020%.

Annex A-2. Calculation of the Penetration of the Test Bed and Efficiency of the First Backup Bed and their Associated Uncertainties from Data Obtained Using a Gross Gamma Counter without Energy Discrimination.

Defining A, B, and C to be the net counting rates of the single test bed and two consecutive backup beds, respectively, at the same time and under identical counting conditions:

$$\text{Penetration, } P\% = 100\ (B+C)/(A+B+C);$$

$$\text{Efficiency, } E\% = 100\ A/(A+B+C) = 100 - P\%;$$

$$\text{Standard Deviation} = S_E\% = S_P\%$$

$$= 100\ \frac{\{[(B+C)^2(S_A)^2] + A^2[(S_B)^2+(S_C)^2]\}^{0.5}}{(A+B+C)^2}$$

where: $A = (X/t_x - BG1/t_{bg1})\exp(0.003592\ T_x);$

$B = (Y/t_y - BG2/t_{bg2})\exp(0.003592\ T_y);$

$C = (Z/t_z - BG2/t_{bg2})\exp(0.003592\ T_z);$

$$(S_A)^2 = [X/(t_x)^2 + BG1/(t_{bg1})^2] \exp(0.007184\ T_x);$$

$$(S_B)^2 = [Y/(t_y)^2 + BG2/(t_{bg2})^2] \exp(0.007184\ T_y);$$

$$(S_C)^2 = [Z/(t_z)^2 + BG2/(t_{bg2})^2] \exp(0.007184\ T_z);$$

and X, Y, Z, BG1, BG2, t_x, t_y, t_z, t_{bg1}, t_{bg2}, T_x, T_y, and T_z are the total counts, counting times, and decay times of the test bed, backup beds and backgrounds, respectively. The constant 0.003592 is the disintegration constant per hour for ^{131}I using a halflife of 8.041 days. The constant 0.007184 is the disintegration constant multiplied by two to square the exponential. "S" is the estimate of the standard deviation of a single measurement from counting statistics corrected for decay and background. For the distribution between the two backup beds, efficiency of the first backup bed in percent is 100 B/(B+C), and the standard deviation in percent is

$$100\ [C^2(S_B)^2 + B^2(S_C)^2]^{0.5}/(B + C)^2$$

Annex A-3. Calculation of the Penetration of the Test Bed and Efficiency of the First Backup Bed and their Associated Uncertainties from Data Obtained Using a Gamma Spectrometer with Energy Discrimination.

Using the same definitions given in Annex A-2, and defining X_c, Y_c and Z_c to be the Compton corrections for X, Y and Z, respectively, the following equations should be used to obtain the penetration of the test bed, the efficiency of the first backup bed and their respective uncertainties.

$$A = \{[(X-X_c)/t_x] - [(BG1-BG1_c)/t_{bg1}]\} \exp(0.003592\ T_x);$$

$$B = \{[(Y-Y_c)/t_y] - [(BG2-BG2_c)/t_{bg2}]\} \exp(0.003592\ T_y);$$

$$C = \{[(Z-Z_c)/t_z] - [(BG2-BG2_c)/t_{bg2}]\} \exp(0.003592\ T_z);$$

$$(S_A)^2 = \{[(X+X_c)/(t_x)^2]+[(BG1+BG1_c)/(t_{bg1})^2]\} \exp(0.007184\ T_x);$$

$$(S_B)^2 = \{[(Y+Y_c)/(t_y)^2]+[(BG2+BG2_c)/(t_{bg2})^2]\} \exp(0.007184\ T_y);$$

$$(S_C)^2 = \{[(Z+Z_c)/(t_z)^2]+[(BG2+BG2_c)/(t_{bg2})^2]\} \exp(0.007184\ T_z).$$

Note: All counts must be made under identical counting conditions or corrections must be made for the different conditions. The Compton correction must be estimated from the average of at least five channels each above and below the peak. The ^{131}I activity must be distributed homogeneously throughout the carbon and a standard height used. Used carbon might have a different background than the new carbon in the backup beds and should be determined separately. Both backgrounds must be constant. Air backgrounds are unnecessary unless the activity in the carbon is to be evaluated.

DISCUSSION

HOLUB: How did you measure humidity and did you make intercomparisons between various humidity meters?

SCARPELLINO: We used two dew-point hygrometers. One was calibrated within two weeks of our tests at the National Bureau of Standards. We also used a dew point condensing device for which the temperature is controlled by a monitored circulating water bath.

JACOX: I have a philosophic question. You made reference to the fact that the commercial labs were carrying out research functions rather than simply performing a standardized test. It appears to me that either I was very confused as to the initial intent of the INEL contract and round robin laboratory comparison, or else you have been doing a lot of research, too. It seems to me that the real problem is simply reproducibility. We agree that there are flaws, and, perhaps, overly loose tolerances in the ASTM method and that some labs are probably not able to meet strict tolerance requirements. Therefore, I am very curious why, instead of simply trying to find the systematic errors that are present and suggesting tighter tolerances to the ASTM, you are developing a new standard that seems to me to involve the same research effort you are decrying when it is performed by the commercial labs. This seems to me to be a contradiction.

SCARPELLINO: We are not a commercial lab and we are employed by the NRC to do some research work. I think there is a need for a standard test. I think we need to standardize the most critical test, the 30°C test, and then establish criteria based on it. If the laboratories have such a difficult time performing the 30°C test, who knows what happens at 80°C, and, especially, 130°C. The latter tests do not evaluate carbon satisfactorily from the research I have seen. I have done no testing at the several temperatures myself. However, some of the data suggest that the carbon performs better as you increase temperature. We want the final standard test procedure to place the greatest demands on the carbon. Using that test, it will be possible to set whatever criteria you want for your carbon.

JACOX: I agree with what you just said. I also think most people would agree that 30°C is the most critical test when conducted at 95% RH with methyl iodide. But why has there not been more effort to find the systematic errors that obviously exist under D-3803, rather than asking for additional test parameters related to loading, post-sweep, and pre-equilibration? All could be analyzed in an R&D mode, but at the moment, the industry needs to have everyone get the same answer on a single test. It seems we have just added more variables rather than trying to reduce them.

SCARPELLINO: We have only tightened restrictions on some of the variables. The major changes were changes in duration of feed and equilibration periods, which our parametric investigations and those of Deuber, in W. Germany, indicate should make no difference in the equilibrated test result. Whether you challenge for an hour or two hours or whether you equilibrate the sample for an hour or four hours, the measurable differences are insignificant. The changes are stated in the paper. Justifications for some reflect current practices within the commercial industry.

RIGBY: I have an observation and a question. For anyone interested, I have with me the figures of a roundrobin exercise conducted in the United Kingdom. I was very interested in your discussion about equilibrating used carbon at 95% RH before testing. I think it is a very, very good idea. I think it would also be very sensible to measure the level of moisture on the used carbon before equilibration, because the adsorption isotherms when water is on the carbon are a bit knotty anyway. I don't say it would show anything by the end of the day but I think it would be useful to know the initial level of moisture on the carbon before pre-equilibration.

SCARPELLINO: What you recommend would be a useful exercise. However, it is probably more important for research purposes than for routine analysis. I think the commercial labs will say that they simply will not have enough sample for the standard test if they take a subsample to measure the initial moisture content. That is not their fault, it is a fact of life.

RIGBY: Get them to get larger samples.

SCARPELLINO: Yes, I agree. It was put into our test method.

BELLAMY: One point I would like to make is that I do not agree that the technical specification should be based on the most critical test. I think the thing that we should all be concerned with here can be summed up in one word, reproducibility. I think the purpose of a test specification, in fact, the purpose of any test on used carbon, is to verify that, should we need that carbon to perform its intended function in the event of an accident, it will do so. Personally, I don't care whether the used carbon test is equilibrated or not equilibrated. I think it is more important that we get reproducibility into the system. So I guess I agree with what Mr. Jacox said.

The other point I want to make is that I think we have to be very careful about public perception. Some of Dr. First's comments this morning on Pilgrim are very appropriate because I have been at Pilgrim recently in front of some public meetings and, yes, we are getting to the point where we need those "flack jackets" regularly, believe me. If we come out now with a proposal to change the standard test and lower acceptance criteria for carbon, I think we will be in trouble because when you propose changing the standard test specification you are exposing yourself to a public hearing. I, for one, do not want to stand up in front of a public audience and say, "Yesterday we tested the carbon to 95% but today the acceptance criterion is only 90% or 80%." Even though I could explain technically why there was a change, and you could explain technically why there was a change, the people in the audience would have already made up their minds. My point is that I think reproducibility is the key to the solution.

SCARPELLINO: I am not sure it would require much of a technical explanation. I think the general public would be willing to except the fact that you made the test tougher. That is all you really need to say. The test is tougher, and our results are more reliable, so therefore we are going to change it. This does not mean any more iodine is ever going to go through the carbon. I know I wouldn't want to do it personally either.

Let me answer your first comment. I agree that a carbon test should be reproducible. However, we cannot sacrifice the ability to discriminate between good and bad carbon for the sake of reproducibility. If we were to set the standard carbon test conditions at 130°C, 95% RH, and challenge the carbon with elemental iodine, we would, undoubtedly, obtain interlaboratory reproducibility. Those tests would probably all result in penetration values of 0.01 to 0.1%. These results would also be good P.R. for the nuclear industry. In actuality, however, we would have lost the ability to detect poor carbons. A test which produces higher values of penetration can better discriminate between carbons and can reduce the uncertainties associated with determining whether a carbon is 99.0% efficient or 98.9% efficient, which often is the difference between acceptance and failure.

SCHOLTEN: I agree that we need a standard method for testing carbon. However, the actual conditions in a plant will differ from those of the standard test. Therefore, we have to transform the laboratory results to plant conditions. Has any parametric study been done, or planned, to make this transformation possible?

SCARPELLINO: Yes, INEL has performed some parametric investigations, and will, I hope, be able to continue and expand these investigations. I am aware of two other parametric studies. One published by Deuber and Gerlach in Nuclear Safety in 1985, which is cited in my paper, and another study by the Japanese, which was published much earlier.

NUCLEAR-GRADE, GAS-PHASE ADSORBENT IODINE RETENTION TEST

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Abstract

This paper describes the Nuclear-Grade Adsorbent Test Laboratory recently established by CRNL. Adsorbents are tested with various radioiodine species under closely controlled environmental conditions. This testing is required as part of the quality assurance testing program of the new LOCA emergency stand-by filter-adsorber installation, for the NRU Research Reactor. The primary feature of the laboratory is the use of aqueous sulphuric acid solutions to achieve and maintain 95% relative humidity. This test equipment has proven to be both simple to use and capable of producing consistent and repeatable test results.

I. Introduction

The Chalk River Nuclear Laboratories (CRNL) has recently established a Nuclear-Grade Adsorbent Test Laboratory. In this laboratory, the efficiency of adsorbents for the removal of various radioiodine species (CH_3I and I_2) can be evaluated under defined, closely controlled conditions.

The laboratory was set up as part of the quality assurance testing program for the new 8 $m^3.s^{-1}$ (16000 CFM) LOCA emergency stand-by filter-adsorber installation, built for the NRU Research Reactor. As well as providing exhaust air filtering for the NRU Reactor in the event of a LOCA emergency, the new filter installation will also be used for reactor operations during special experiments. Adsorbers had always been leak tested in-situ with I-131 tagged elemental iodine; however, it was always realized that the actual iodine retention characteristics of the carbon were not proven by this test. The routine replacement of adsorbent material practiced on small adsorber installations with less than 100 kg of carbon could not be considered economical for a system with more than 1600 kg of carbon. Therefore, laboratory testing of the carbon adsorbent, in addition to in-situ leak testing with methyl iodide-131, was considered necessary for economic reasons as well as assuring the carbon's performance over time.

In order to obtain representative carbon samples for laboratory analysis, bypass lines were installed in parallel with the carbon beds on six of the sixteen parallel filter trains.

Each bypass line contains one 50 mm deep adsorbent test bed canister. The bypass system is shown in Figure 1. A mock-up of the bypass system was tested in the laboratory to ensure leak tightness and proper face velocity through the canister. Measurements confirmed that the air flow through the canisters can be controlled to yield the design face velocity of 20 $cm.s^{-1}$, equal to that in the actual carbon adsorber. These representative adsorbent samples will then be removed at pre-determined intervals and the radioiodine adsorption performance determined over the anticipated life of the carbon.

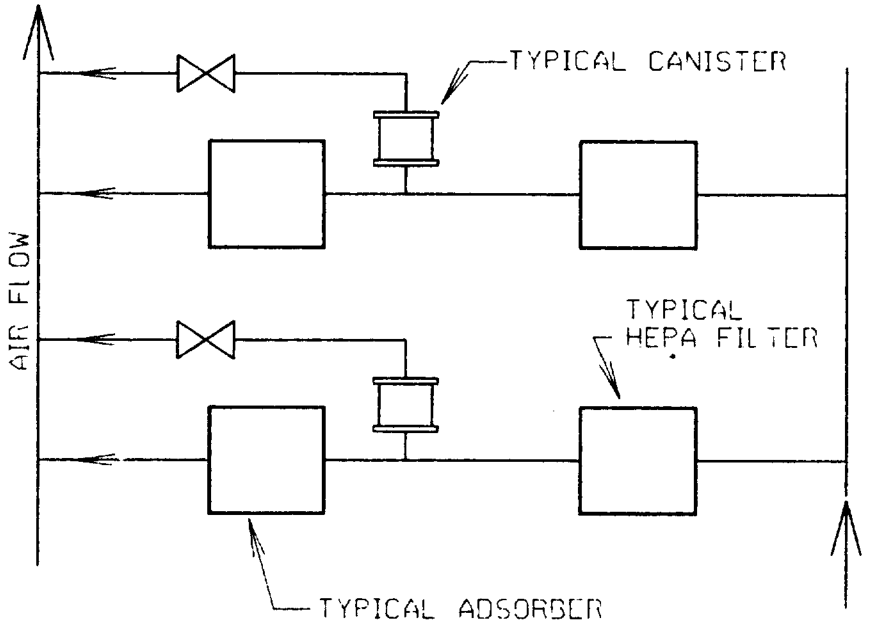


FIGURE 1
Bypass Canister System for 50 mm Deep
Pleated Bed Adsorber Cell

II. Test Specifications

Test Principle

Carbon testing is performed in accordance with Test Method A, ASTM D3803, 1979, "Standard Test Methods for Radioiodine Testing of Nuclear Grade Gas Phase Adsorbents", and CSA N288.3.2 Standard, "High Efficiency Nuclear Air Cleaning Systems for Normal Operations".

A representative sample of adsorbent is equilibrated with air (equilibration period), at the design face velocity, to temperature and relative humidity conditions for 16 hours. The equilibrated adsorbent is then challenged with a radioiodine (CH_3I or I_2) and humid air mixture (feed period) for 120 minutes. Following the feed period the carbon sample is purged with the humid air (elution period) for 240 minutes. Radioiodine, retained in both the test and back-up bed adsorbent, is radiometrically evaluated and the iodine removal performance of the tested adsorbent is then calculated for the specified depth values.

Test Conditions

In accordance with CSA Standard N288.3.2, the environmental conditions for the testing of adsorbents are as follows:

Temperature	-	25	±	1°C
Relative Humidity	-	95	±	2%
Face Velocity	-	20	±	$1\ \mathrm{cm.s^{-1}}$

Approximate adsorbate concentrations in the challenge gas stream are as follows:

CH_3I	-	$1.75\ \mathrm{mg.m^{-3}}$
I_2	-	$1.0\ \mathrm{mg.m^{-3}}$

III. Test Equipment

A functional diagram of the test assembly is shown in Figure 2. The system is composed of the following functional components:

- Environmental chamber with temperature control
- Constant humidity control
- Adsorbate gas generator and injection line
- Adsorber column
- Challenge gas recirculation line
- Radiometric analysis system
- Computing unit.

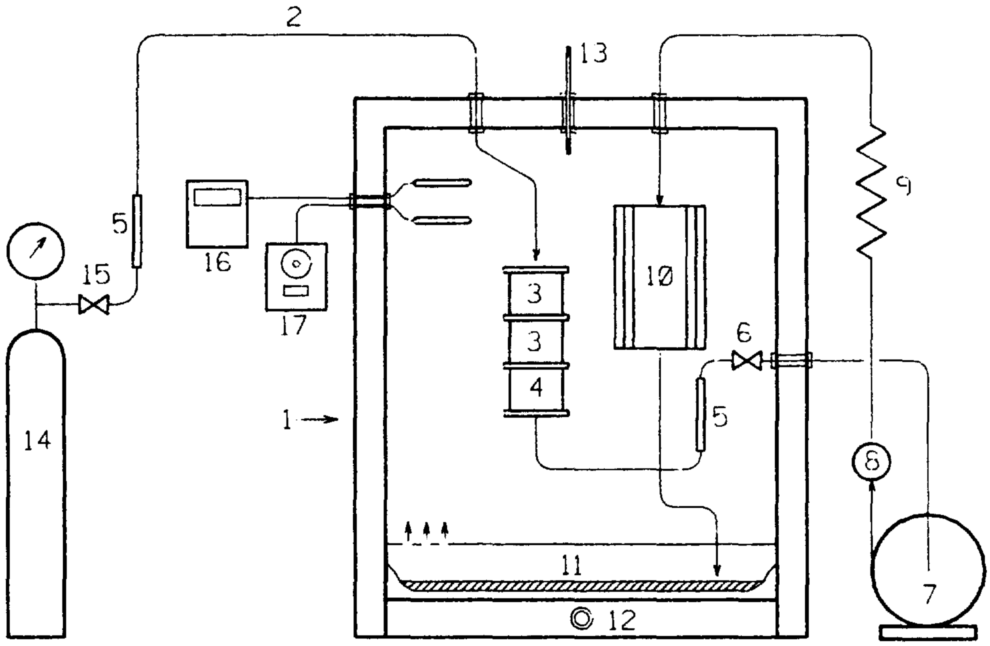
Environmental Chamber

The environmental chamber is a biological type incubator. The internal temperature of the test chamber is controlled, within 0.5°C of the temperature setpoint, with a direct acting thermostat.

Constant Humidity Control

The control of relative humidity within the test chamber is based on the standard method ASTM E 104-51 (1971), "Standard Recommended Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions". This standard describes three possible solutions to control humidity; namely, sulphuric acid, glycerin and salt solutions. Sulphuric acid solution is the only suitable alternative for maintaining 95% RH, as both glycerin and salt solutions are not sufficiently stable and are messy. This method has two distinct advantages: 1) the resulting humidity level is not significantly affected by moderate fluctuations of temperature, and 2) any required relative humidity can be established and maintained simply by preparing the appropriate concentration of sulphuric acid for the tray in the chamber. It is estimated in the ASTM Standard E 104 that the relative humidity levels in the test chamber can be maintained constant within ± 0.1%, under proper environmental conditions.

The relative humidity over aqueous solutions of sulphuric acid are given in Table 1 (excerpt from ASTM E 104 Standard).



1. Environmental Test Chamber
2. Injection Line
3. Stainless Steel Test Bed Canisters
4. Stainless Steel Back-Up Bed Canisters
5. Flowmeter
6. Flow Control Valve
7. Oil-Less Air Pump
8. Line Filter
9. Air-Cooled Discharge Line
10. Heat Exchanger
11. Sulphuric Acid Bath
12. Temperature Controller
13. Thermometer
14. CH_3I Challenge Cylinder
15. CH_3I Feed Control Valve
16. Cole Parmer Digital Hygrometer
17. Honeywell Relative Humidity Readout Instrument

FIGURE 2
Carbon Test Assembly Functional Diagram

Table 1. Relative Humidity Over Sulphuric Acid Solutions.

Density (25°C) g.cm^{-3}	Relative Humidity (%) At 0°C	25°C	50°C	75°C
1.0300	98.4	98.5	98.5	98.6
1.0641	95.9	96.1	96.3	96.5
1.0997	92.4	92.9	93.4	93.8
1.1368	87.8	88.5	89.3	90.0

From this table it can be seen that, when the solution and air temperature in the chamber are the same, the equilibrium value of RH is not sensitive to temperature fluctuations at higher humidity values. By interpolation of the above data the density of the aqueous sulphuric acid solution required to maintain a relative humidity of 95% is 1.0765 g.mL^{-1}. Because about 2% of the water will evaporate from the solution, to equilibrate both the chamber air and the carbon to 95% RH, 2 L of solution with an initial density of 1.075 g.mL^{-1} is used.

The temperature and relative humidity of the air in the chamber are monitored by two independent temperature/relative humidity electronic measuring devices. These instruments are regularly checked to ensure they are reading correctly. The method of checking involves drawing a known volume of the humid air in the chamber through a freezing coil cooled with dry ice. Knowing the volume of air sampled, the mass of the water collected, atmospheric pressure, air stream temperature, and the relative humidity and temperature downstream of the freezing coil, the relative humidity in the chamber can be accurately calculated. The computer program and algorithms used for these calculations are shown in the appendix. The calculated value can then be compared to the measured value.

Air Circulation Loop

The air circulation system is a closed loop system. The air pump draws conditioned air (during equilibration and elution period) and a challenge gas (during feed period) from the environmental chamber, through the test and back-up adsorbent beds, and recirculates it back into the chamber.

The challenge gas is a mixture of conditioned air (25°C, 95% RH), with I-131 labeled I_2 vapor or CH_3I. This adsorbate gas is carried by nitrogen from the generating system through an injection line to the test bed inlet, mixed with air and passed through the test bed and back-up bed (which removes all radioiodine), rotameter, flow control valve and air pump. A line filter is installed at the pump outlet for particulate removal. Air temperature, which is increased due to the work done on the air by the pump, is reduced within the air cooled discharge line to the ambient temperature of the room. The air stream is then passed through a heat exchanger in the test chamber to equilibrate it again to 25°C. Finally, the air is discharged into the tray and passes over the surface of the H_2SO_4 solution, and is equilibrated to 95% RH before being returned to the chamber.

The flow capacity of the recirculation loop and air pump is such that two carbon tests can be performed simultaneously, simply by installing an additional test column, flow meter and rotameter in parallel with the existing set.

Test Bed Assembly

The test bed assembly consists of a set of 50 mm deep stainless steel canister beds manufactured to the ASTM D3803 standard specifications. The test rings are individually sealed with rubber O-rings, and held in the test position with bolted stainless steel flanges. This set allows the installation of up to three, 50 mm deep rings with tested charcoal in series. For the compliance testing of 50 mm deep adsorber beds and new carbon, only one 50 mm deep test bed canister and one back-up bed canister are used in series.

Adsorbate Gas Generator and Injection Line

Either CH_3I or I_2 vapor can be used in the challenge gas stream. The methods of generation of these two species are as follows:

CH_3I tagged with I-131 is produced by an isotopic exchange process using stable CH_3I and aqueous, NaI-131 in NaOH/0.02M Na_2So_4 solution. The generation method is designed to yield 1 μCi* of I-131 per mg of stable CH_3I. The I-131 labeled CH_3I is then placed in a 2.25 L stainless steel cylinder and pressurized with N_2. The N_2/CH_3I adsorbate gas is then metered to the inlet of the test column to yield a mass concentration of 1.75 $mg.m^{-3}$ in the challenge humid air stream.

Elemental iodine, I_2, is generated in the environmental chamber, close to the test column inlet, in order to minimize its loss due to surface deposition. The I_2 vapor, labeled with I-131, is generated at a controlled rate and purged from a slightly acidic solution of elemental I-127 and NaI-131 with N_2.

Radiometric Analysis System

The radioiodine counting system is located in a low background area. The system consists of a Ge(Li) spectrometric detector in a shielded castle and a multichannel analyzer with automatic background subtraction. For this application, a counting geometry which keeps detector dead time loss below 10% is chosen.

Computer Unit

Penetration, statistical accuracy valves, and calculations to check the accuracy of the humidity reading instruments are performed with a microcomputer and printed with an attached printer.

Technical Specifications of Test Equipment

The range and accuracy of the operational parameters, their control and monitoring and the test requirements from the CSA N288.3.2 standard are shown in Table 2.

Table 2. Technical Specifications of Test Equipment.

	Temp. (°C)	RH (%)	Test Flow ($L.min^{-1}$)**
Control Range	25 - 65	40 - 98	15 - 50
Monitoring Range	0 - 100	0 - 100	2 - 50
Control of System Parameters	25 ± 0.5	95 ± 1.9	24.3 ± 1.0***
Monitoring of System Parameters	25 ± 0.25	95 ± 1.0	24.3 ± 0.75
CSA Standard Requirements	25 ± 1.0	95 ± 2.0	24.3 ± 1.2

---

* 1 μCi = 37 GBq

** Standard Pressure

*** Corresponds to a face velocity of 20 ± 1 $cm.s^{-1}$

IV. Operational Experience

Not a great deal of carbon testing experience has been gained to date due to the short time the laboratory has been fully operational. The test results obtained thus far, however, are encouraging. Also the problems overcome and the experience gained while achieving and maintaining a 95% RH level may be interesting to someone considering this method for this, or similar applications.

Constant Humidity Control

The use of aqueous sulphuric acid solutions to control relative humidity at 95% has been found to be both simple and accurate. Once the relative humidity level in the chamber reaches the equilibrium value, as determined by the sulphuric acid concentration, it remains very stable for the duration of the test. Figure 3 shows a typical response curve of chamber relative humidity versus time, with time zero representing the moment the air circulation pump is switched on. From this curve it can be seen that approximately 80 minutes are required for the chamber to reach 95% RH. This lag period may be viewed as a disadvantage due to the additional time added to an already lengthy procedure. Experience has shown, however, that the time required for the chamber to reach test relative humidity conditions can be included in the 16 hour equilibration period without compromising the test. This is verified in Figure 4, which shows temperature differential across the test and back-up carbon beds (measured by thermocouples placed in the inlet and outlet airstreams of the canister assembly) versus time. From this figure it is seen that even with the initial lag in relative humidity the adsorption of water on the carbon reaches equilibrium with the 95% RH airstream in 6-7 hours.

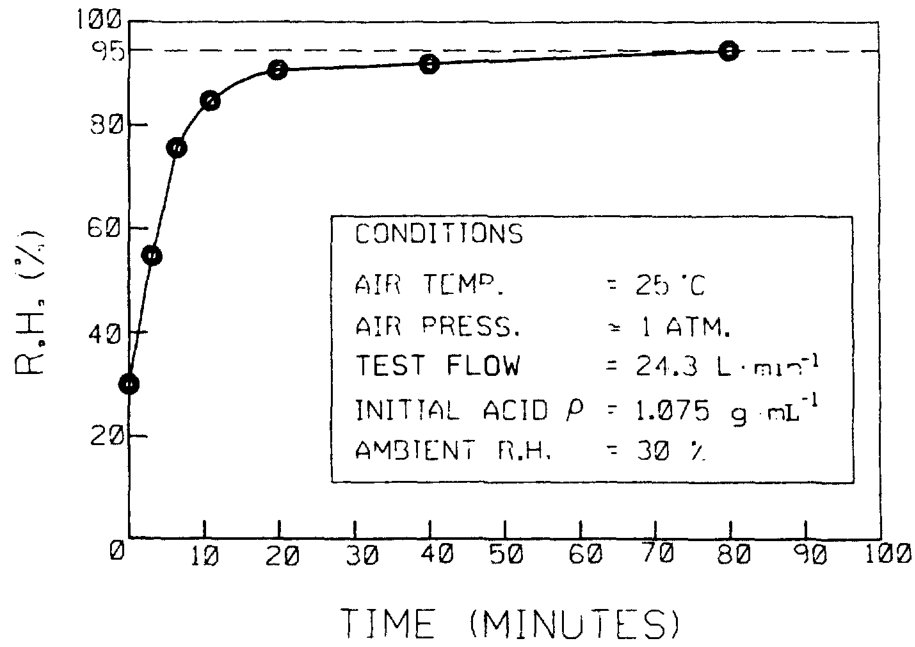


FIGURE 3
Typical Response Curve of Chamber
Relative Humidity Versus Time

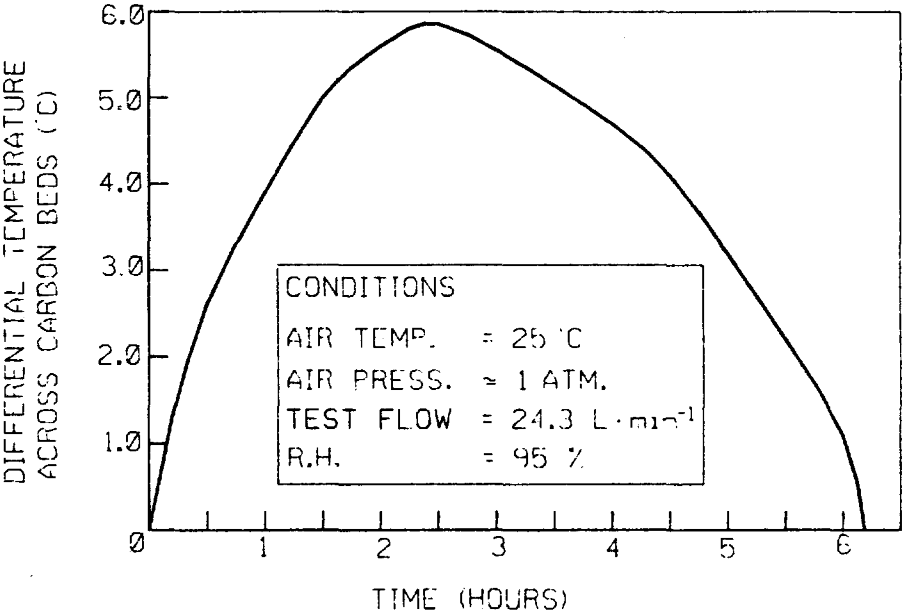


FIGURE 4
Typical Time Required for Adsorption of Water on Carbon to Reach Equilibrium with 25°C, 95% RH Airstream

A potentially serious problem with this method of humidity control is condensation within the chamber. Even a small amount of condensation will result in a loss of humidity control. The air temperature in the room in which the chamber is kept must be carefully controlled, and drafts in the room must be minimized to avoid condensation problems. To maintain temperature control, room temperature was initially kept at 20-22°C, to provide an ample temperature gradient for the dissipation of pump heat in the air cooled discharge line. At these temperatures condensation was forming on the walls and heat exchanger in the test chamber. This problem was completely solved by adding some additional insulation between the inner glass door and outer insulated door of the test chamber, and raising the room temperature. The room temperature now cycles between 22.5-24°C. This temperature range appears optimum to maintain temperature control and avoid condensation problems.

It is also important to keep the environmental chamber essentially airtight to avoid moisture loss. This is simply accomplished by sealing any through holes in the chamber with plasticine and ensuring that the inner glass door is adequately sealed.

Experience also has shown that careful attention must be paid to the temperature of the acid solution. Acid solutions of the proper density are normally prepared in advance and stored in the laboratory. The solutions of course achieve temperature equilibrium with the air (approximately 23°C). It was found that if the acid solution was not warmed to test temperature prior to starting the test, the temperature of the solution would take an unacceptably long time to reach test temperature in the chamber, and 95% RH would not be reached. This is attributed to inefficient heat transfer between the solution and chamber air and the heat loss through evaporation from the solution. To accommodate the heating of the solution a variable speed pump is used to circulate the acid solution external to the chamber through a glass coil immersed in a warm water bath. Circulation rate and bath temperature are adjusted to maintain bath temperature at 25°C. The acid solution is circulated for the first 20 minutes of the equilibration period, or when the relative humidity in the chamber reaches about 90%. The pump has also proved useful for loading and unloading the sulphuric acid solution into and out of the tray.

Carbon Testing

As mentioned earlier, only a limited amount of carbon testing experience has been gained to date, all for new 5% TEDA impregnated, activated, coconut based carbon. Test results are presented in Table 3. The carbon samples tested were from the same manufacturer and the same production lot.

Table 3. Results of Laboratory Testing of Carbon Adsorbent with CH_3I-131 in Air at 25°C and 95% RH*.

Sample No.	Retention and Accuracy (%)
1**	97.23 ± 0.05
2	98.42 ± 0.04
3	98.88 ± 0.04
4	98.31 ± 0.06
5	99.16 ± 0.04
6	98.92 ± 0.02
7	99.31 ± 0.02
Carbon Manufacturer's rating	99.00 minimum

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* Tests performed in accordance with ASTM standard D3803-Test Bed Depth = 50 mm.

** Conditions for this test were 25°C, 100% RH.

The retention results range from 97.23% to 99.31%. Sample No. 1 was rejected because the relative humidity in this test reached 100% due to a condensation problem in the chamber. Measures described previously were taken to eliminate this problem in subsequent tests. The actual range of retention results are thus 98.31% to 99.31%. The mean value of the retention and its precision is 98.82% ± 0.34%. The accuracy and repeatability of the results are considered very good and are in agreement with the carbon manufacturer's rating. The calculated accuracy (0.34%) is the result of random errors caused by slight differences in many variables, including: the mass of carbon in the test samples, the mass of CH_3I introduced, the amount of TEDA.

impregnate on the carbon, and the relative humidity and temperature of the chamber air. Counting errors make only a minor contribution (0.04% avg.) to the above accuracy value.

V. Conclusions

Even with the limited testing experience and data gained thus far, the following conclusions and comments can be made on the testing equipment in use at CRNL.

- The method using aqueous solutions of sulphuric acid to control relative humidity has proved to be quite simple and capable of maintaining 95% RH in the environmental chamber for the duration of the test.
- The test assembly is simple in design with a limited amount of required instrumentation and hardware, and replacement costs of the components are low.
- When the procedures outlined in ASTM Standard D3803, Method A, are closely followed (only deviation is 25°C test temperature in place of 30°C) the test equipment is capable of producing repeatable results with good accuracy.

VI. Acknowledgements

The authors would like to thank Mr. Brian Latouf (summer student) for writing the software to perform the relative humidity calculations, and Mr. Wayne Keuhl for his valuable contributions to the commissioning of the laboratory and for performing the actual carbon testing.

Appendix

Programmed Psychrometric Calculation

This program provides the psychrometric calculation required for the calibration of the humidity meter used in the adsorbent iodine retention test. All moist air property algorithms are from ASHRAE Handbook of Fundamentals, 1981, Chapter 5.

Program Operation

The program is written in BASIC for a TRS-80 Radio Shack pocket computer. It has approximately 1.5 kilobytes of memory, an attached printer and a cassette storage device. To use the programs simultaneously they must both be loaded onto the computer's current memory banks (see TRS-80 Manual for loading procedure). Definition mode "Shift A" will start the program. All input is manual and echo printed. The "Enter" bar must be hit after each input to keep the program running.

Program Nomenclature

The following variables are used in the program. The TRS-80 pocket computer has a memory limitation of 26 elements; thus, a definition of each variable is needed.

A: Mass Flow Rate of Air in Kilograms Per Minute
D: The Air Density in Kilograms Per Cubic Metres
E: The Mass of Water in the "Freeze-Out" Air in Kilograms
G: The Relative Humidity of the Air Accurate to Two Decimal Points
I: The Relative Humidity of the Dry Air After the "Freeze-Out" in Percent
K: The Relative Humidity of Air, Unrounded
L: New Total Partial Water Pressure
M: Time of Flow in Minutes
O: Accuracy to Goal of the Rounded-Off Relative Humidity
P: Atmospheric Pressure in Kilopascals
Q: The Water Mass in Kilograms
R: The Humidity Ratio of the Air in kg Water/kg Air
S: The Saturation Pressure of the Air in Pascals
T: The Dry-Bulb Temperature in Celsius
U: The Humidity Goal for Error Comparison
V: The Air Flow Rate in Cubic Centimetres Per Minute
W: The Water Mass "Freeze-Out" in Grams
X: Intermediate Calculation for the Saturation Pressure
Y: Intermediate Calculation for the Saturation Pressure
Z: The Dry-Bulb Temperature in Kelvin

Psychrometric Calculation Program List

```
10  REM EXPERIMENTAL ANALYSIS TO CALCULATE RELATIVE HUMIDITY
20  REM DEFINE THE PROGRAM AS "A"
30  "A"
40  REM INPUT AND ECHO PRINT ALL OF THE VARIABLES NEEDED
```

```
 50   INPUT "TEMPERATURE?(CEL)";Z
 60   PRINT "TEMP(CEL)=";Z
 70   INPUT "ATMOS.PRESS?(KPa)";P
 80   PRINT "PRESS(KPa)=";P
 90   INPUT "WATER MASS?(GRAMS)";W
100   PRINT "WATER(GRAMS)=";W
110   INPUT "AIRFLOW?(CC/MIN)";V
120   PRINT "FLOW(CC/MIN)=";V
130   INPUT "TIME FOR FLOW?(MIN)";M
140   PRINT "TIME?(MIN)=";M
150   INPUT "R.H.DRY AIR?(%)";I
160   PRINT "R.H.DRY(%)=";I
170   INPUT "HUMIDITY GOAL?(%)";U
180   PRINT "GOAL(%)=";U
190   REM CALL UPON THE SATURATION PRESSURE SUBROUTINE
200   GOSUB 800
210   REM CALCULATE THE AIR DENSITY USING IDEAL GAS EQN.
220   D=P/((8.3144/28.97)*T)
230   REM CONVERT WATER MASS IN GRAMS TO KILOGRAMS
240   Q=W/1000
250   REM FIND THE MASS FLOW RATE OF THE AIR IN KG/MIN
260   A=V/100^3*D
270   REM CALCULATE THE AMOUNT OF WATER IN THE CAPTURED DRY AIR
280   E=I/100*S*.62198/(P*1000-S)*A*M
280   REM ADD THE CAPTURE DRY AIR WATER VAPOR TO THE WATER COLLECTED
300   REM AND CALCULATE THE HUMIDITY RATIO
310   R=(Q+E)/(A*M)
320   REM FIND THE NEW PARTIAL WATER PRESSURE
330   L=P/(1+.62198/R)
340   REM FIND THE ACTUAL RELATIVE HUMIDITY FROM FREEZE OUT
350   K=L*1000/S*100
360   REM ROUND OFF BOTH THE R.H. AND FIND ITS % OFF FROM GOAL
370   O=(INT(ABS(U-K)*100))/100
380   G=(INT(K*100))/100
390   REM PRINT OUT THE RESULTS AND PROVIDE A RERUN ALTERNATIVE
400   BEEP3:  PRINT "R.HUM=";G;"%+-";O;"%"
410   INPUT "START OVER?(Y/N)";X$
420   IF X$ = "Y" THEN 50
430   INPUT "CONTINUE?(Y/N)";G$
450   END
800   REM SUBROUTINE FOR CALCULATING SATURATION PRESSURE
810   REM FOR A GIVEN TEMPERATURE
820   T = Z + 273.15
830   X = (-5800.2206/T) + 1.3914993 - (.048640239*T)
840   Y = X + (.4176478 E - 4) * T^2 - (.14452093 E - 7)*T^3 +
6.5459673*LN(T)
850   S = EXP(Y)
860   RETURN
```

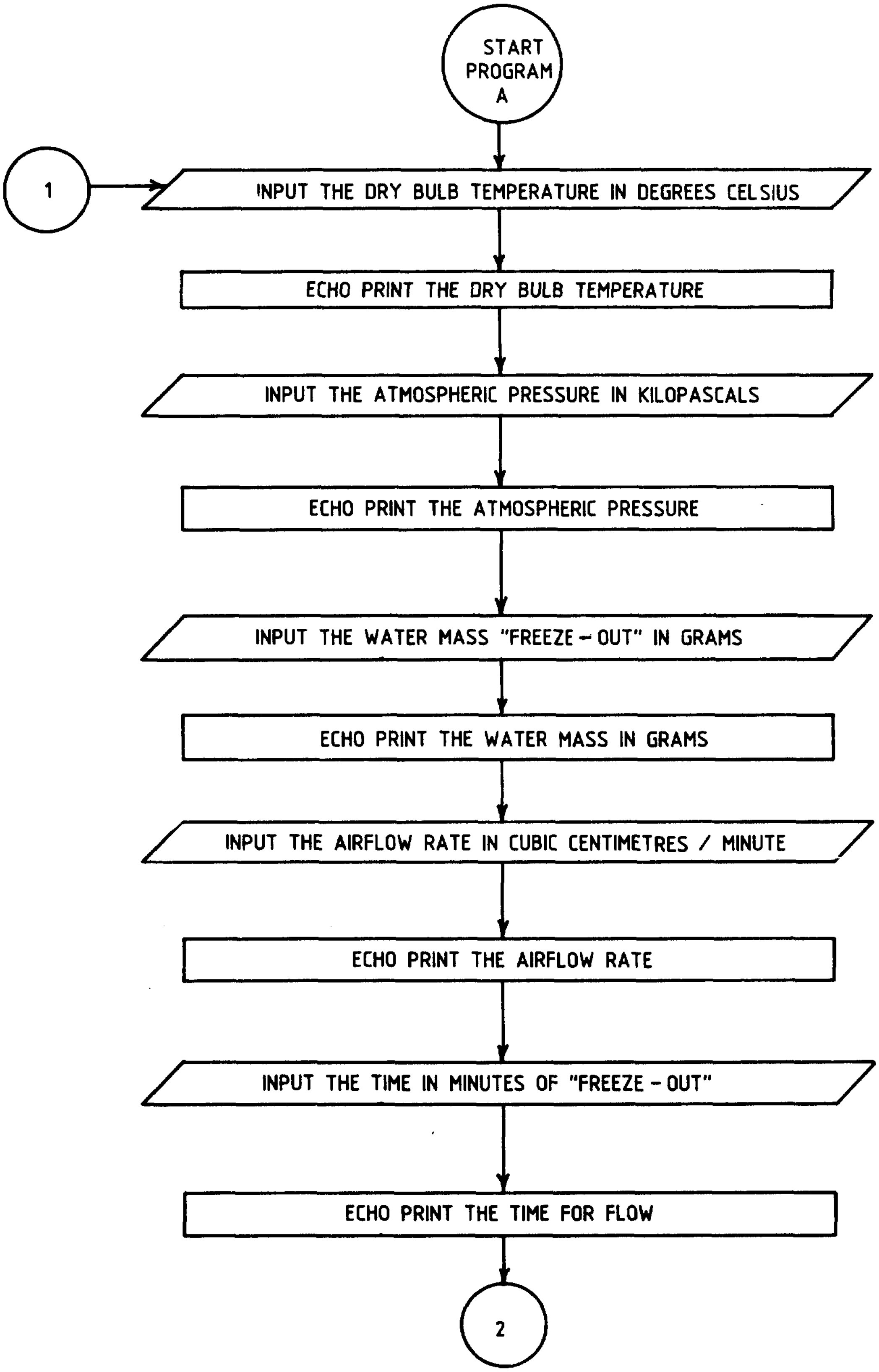

Figure A1. Program Flowsheet

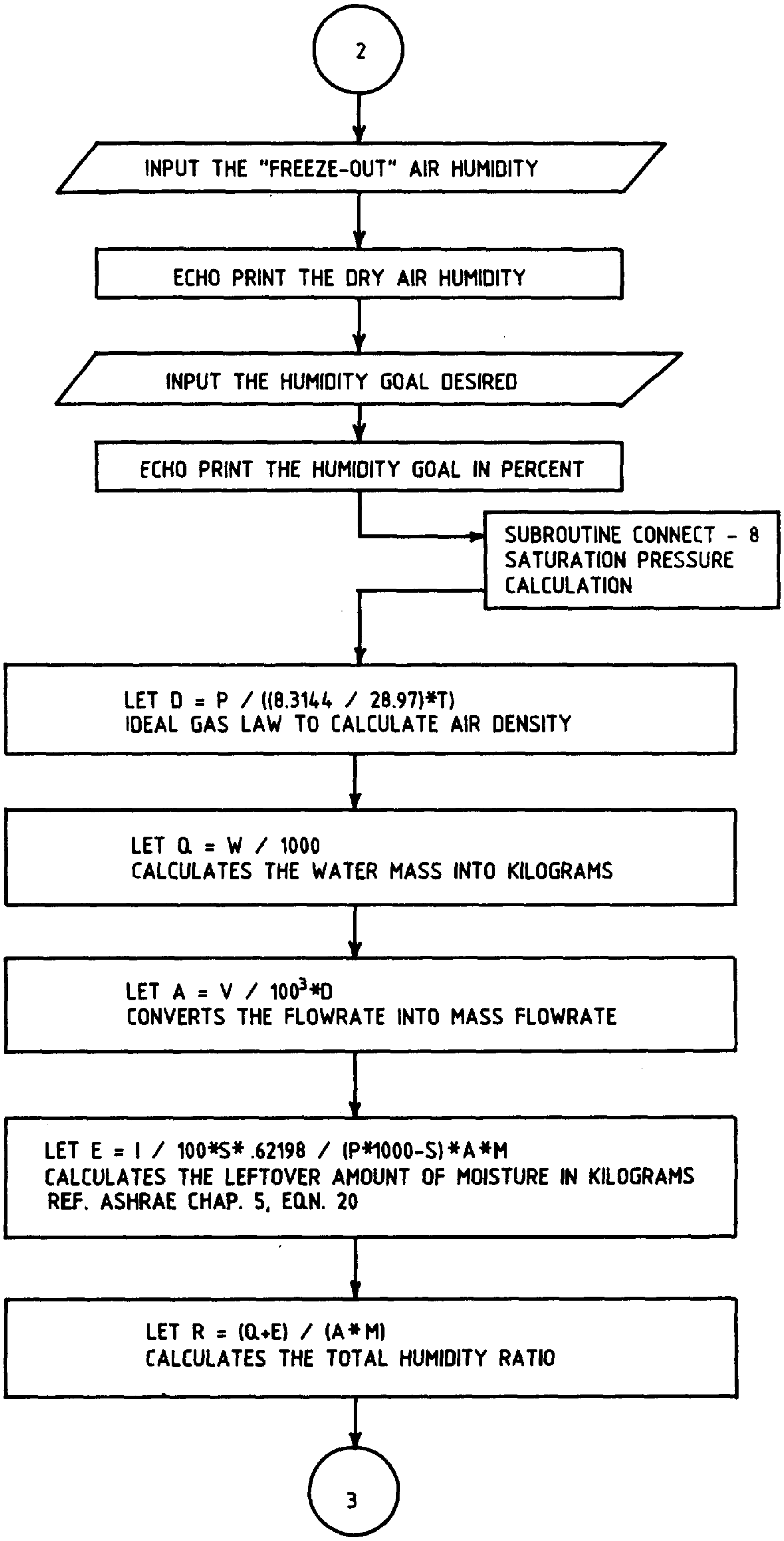

Figure Al Con't. Program Flowsheet

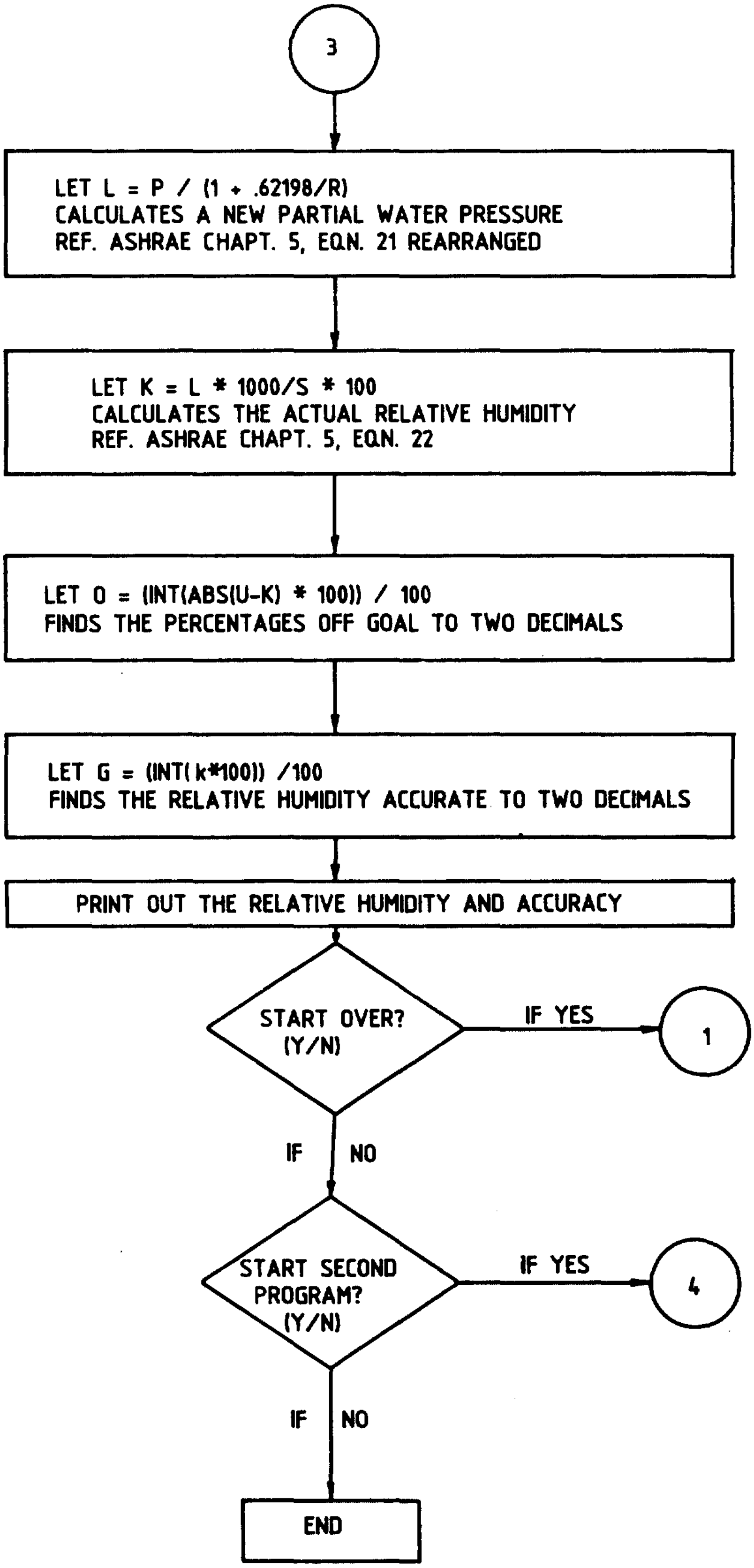

Figure A1 Con't. Program Flowsheet

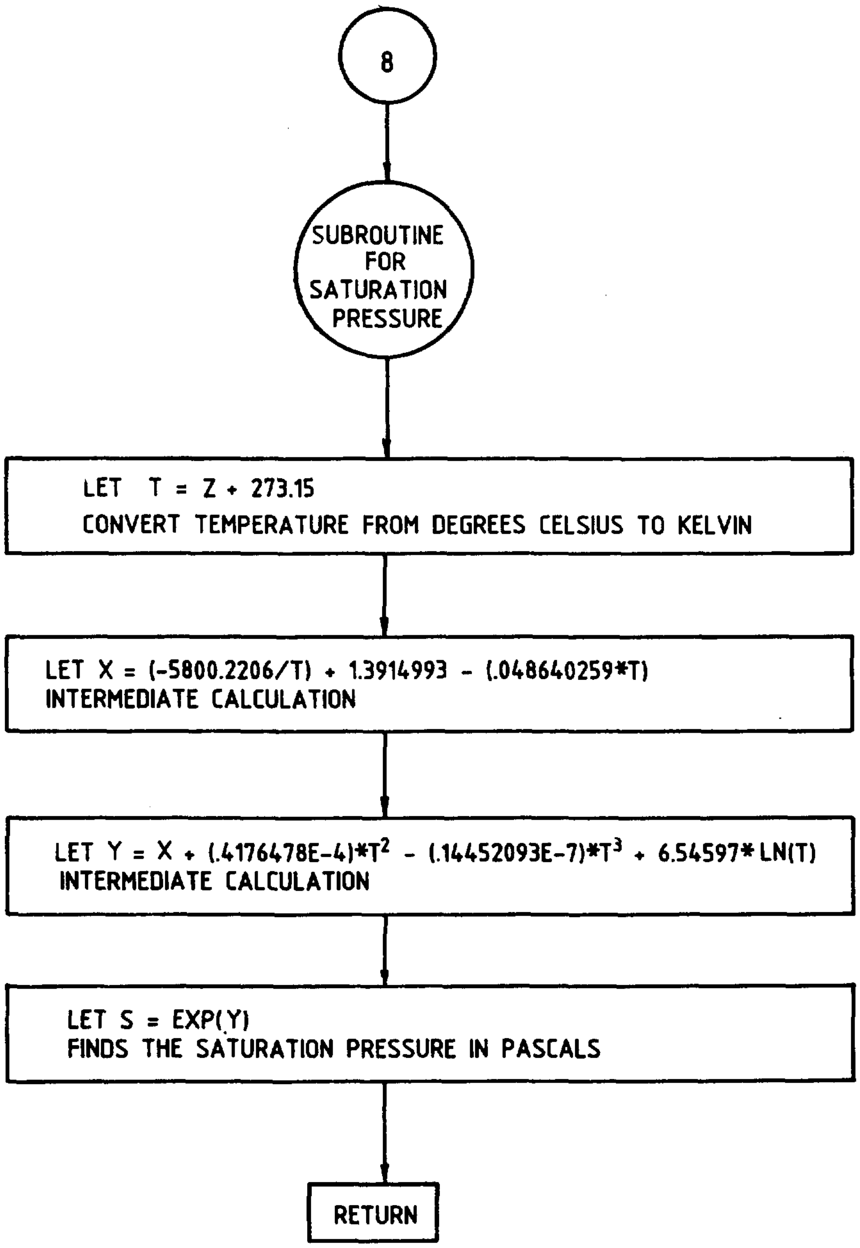

Figure A1 Con't. Program Flowsheet

THE U. V. SPECTROMETRIC METHOD OF ANALYSING CHEMICAL IMPREGNANTS OF A NUCLEAR GRADE ACTIVE CARBON AND ITS APPLICATIONS FOR MANAGING THE CARBON FILTER AT A NUCLEAR REGULATORY LAB. AND PLANTS.

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Abstract

A simple and convenient method of analysing chemical impregnants of a nuclear grade active carbon (i.e. TEDA, TEDA + KI, and KI_x) is described by means of ultraviolet spectrometry. The absorption maxima of each impregnant (TEDA, KI, and I_2) were determined in acetonitrile solvent and absorbance was plotted against concentration to afford a good linearity, which could well be applied as an analytical curve. Special considerations were exerted to confirm the influence of the coexistent element or compound to be analyzed such as TEDA in case of TEDA + KI and iodine in case of KI_x. The method was found useful to be practiced at a regulatory lab. or a nuclear power plant to identify or monitor the quality of an impregnated active carbon. Some typical examples of applying this analytical method at the regulatory lab. in this country (This lab.) were shown. The deterioration of TEDA in the used sample collected at the power plant of this country was observed by checking the variation of λ max against the concentation of acetonitrile extract of the sample and this data are referred to monitor the quality of the carbon in practical use. The replacing sample of the carbon sample in use at the domestic power plant was collected before installation in the filter system and the sample was analyzed for its impregnants. This data are the basic standard to follow the carbon during the course of active use at the power plant. This method could also be applied for monitoring the impregnation pattern of chemical species impregnated in a base active carbon sample for a research purpose. In this laboratory, the adsorption efficiency of both used and new carbon samples collected at the domestic power plants were tested for the regulatory purposes. In order to assure the testing results, samples were analyzed for their chemical compositions in advance of testing. Examples of the analysis and testing results were described. It is concluded that the method is of very simple and practical, which may open various applications besides described hereto for a nuclear regulatory lab. or power plants for managing their carbon filter systemes.

1. Introduction

In Korea, 4 PWRs and one CANDU power plants are now under routine operation and another 2 PWRs will be in routine operation within a year. Additional 4 or 10 nuclear power plants are going to be constructed by the end of this century. These power plants are operated by the Korean Electric Power Co., and this institute, as the National Laboratory, has been concerned with regulatory and R & D works to support the safe operation of these power plants.

Impregnants of a nuclear grade active carbon for power plants or hot facilities are generally known as KI + I_2, TEDA, TEDA + KI, and tertiary amine + iodine salts. The amount of the impregnants applied for a nuclear grade active carbon is usually indicated by the manufacturer on its technical data grossly without showing any definite analytical data. It was, therefore, necessary to confirm the definite quantity of chemical impregnants contained in the commercial samples in active use at the power plant to assure their quality. Since new carbon samples are sometimes non uniformly impregnated, which may influence the adsorption efficiency of that sample(1), the analysis of chemical impregnants of a nuclear grade active carbon was considered to be essential to guarantee the adsorption quality of the product. Furthermore, the chemical impregnants in a nuclear grade active carbon are liable to be deteriorated during the period of routine operation. According to recent literatures, iodate was formed in the deteriorated sample which decrease the adsorption efficiency(9) and hydroxide of TEDA, which may be formed by the deterioration of TEDA under a serious moisture, showed less adsorption efficiency than those of the corresponding iodide and TEDA itself(2). These findings warrant to trace chemical composition of the nuclear grade active carbon during the period of its routine use to assure the quality of chemical status of the impregnants, if it is possible to be traced by means of a simple and convenient analytical method.

A simple and convenient method of analysing chemical impregnants of an activated carbon was, therefore, developed by this laboratory. Microquantities of iodine dissolved in 5% aqueous potassium iodide could be analyzed by means of spectrometric method at the ultraviolet range(3), but the method of analysing chemical impregnants of a nuclear grade carbon sample had not been reported in literatures. The absorption maxima for each impregnant was determined in acetonitrile solvent, which was the best suitable solvent in the present cases, by ultraviolet spectrometric method and the influence of coexistent elements or compounds in the acetonitrile extract of a sample carbon was closely studied. The absorbance at λ max. of each impregnate was plotted against concentration to afford a good linearity which may well be applied as an analytical curve. Samples collected from domestic power plants were analysed by this method to monitor the quality of the samples in a chemical sense. The method was found useful to be practiced at a regulatory lab. or nuclear power plant. In this paper, details of the analytical procedure were presented and the feasibility of this method was discussed with special regards to qualify the chemical impregnated active carbon at a nuclear power plant.

During the course of this investigation, interlaboratory comparison of adsorption efficiencies of IC samples sponsored by US NRC had been conducted and this lab. participated to this comparison works. Results obtained in analysing IC samples and their absorption efficiencies were also reported in this paper to review the correlation between chemical uniformity of IC samples and their absorption efficiencies, if there are any. Some research results obtained during the period of impregnating base active carbon with TEDA, TEDA + KI, and KI_x were reported to introduce the use of this analytical method in this field.

2. Experimental Procedure

2.1 Moisture Determination of the Sample

In order to determine the moisture content of sample, ASTM Method D 2867, oven drying method #5 for determining moisture content of a nuclear grade active carbon, was adopted by use of a forced circulated drying oven. The results were summarized in table 12.

2.2 Extraction of the Sample

In a 200 ml., Erlenmeyer flask, a definite amount of the sample carbon weighed nearest 0.001g, 100 ml. of acetonitrile (ACS(GR) Grade, Tedia Co. USA) and a magnetic strring bar were placed and the flask was stoppered by means of a tappered glass joint, and it was stirred magnetically at a definite temperature and time. The mixture was filtered and the filtrate was reserved for further analysis. The filtered carbon was dried in a forced circulated oven and it was reserved for further testing as described in the later paragraph.

2.3 TLC Testing of the Acetonitrile Extract of the Sample

The acetonitrile extract of the sample was examined by means of a TLC for checking its major chemical compositions and purity as follows.

Plate : DC-Pastikfolien, Kiselgel 60 F_{245}, MERCK Art 5735.
Developing Temperature : 24-25°C
Solvent Front : 10.0cm.

A. Developing Solvent : 95% Ethyl Alcohol

The TLC studied by means of 95% ethyl alcohol as the developing solvent showed R_f values as follows.

R_f Values / Chemical Species	R_f Values *Coloring Agent	Spots	**Coloring Agent	Spots
TEDA	(1)	0.00	(2)	0.00
TEDA + KI	(1)	0.00, 0.75(Faint)	(2)	0.00, 0.75
KI_x	(1)	0.75(Faint)	(2)	0.75

* Coloring Agent : 0.2g. of ninhydrin were dissolved in the mixture of 95ml. of n-butanol and 5ml. of 10% aq. solution of acetic acid.
Coloring Method : The sprayed plate was heated for 20 minutes at 105°C.
** Coloring agent : 2.0% alcoholic solution of silver nitrate.
Coloring Method : The sprayed plate was heated to a dryness and it was exposed under sunlight.

B. Developing Solvent : 1-propanol + 33% ammonia water (4:1 V/V)

The TLC studied by means of the predescribed solvent showed R_f values as follows.

2.4 Ultraviolet Spectrometric Analysis of the Sample

A. Instrument

The following instrument and conditions were adopted through the entire experiments of the present study.

(1) Instrument : Safas, 170 D/DF, Monaco.
(2) Absorption Cell : 1cm width, Rectangular Cell.
(3) Conditions : Lamp Source ; H-Lamp
Slit Width ; 10cm. nm
Scan Speed ; 40nm/MN.
Chart Speed ; 25nm/MN.
Enr ; x1

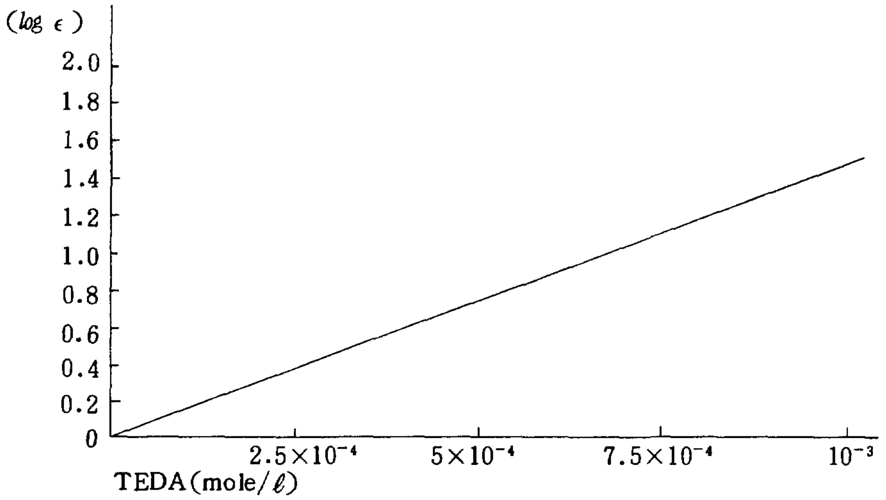
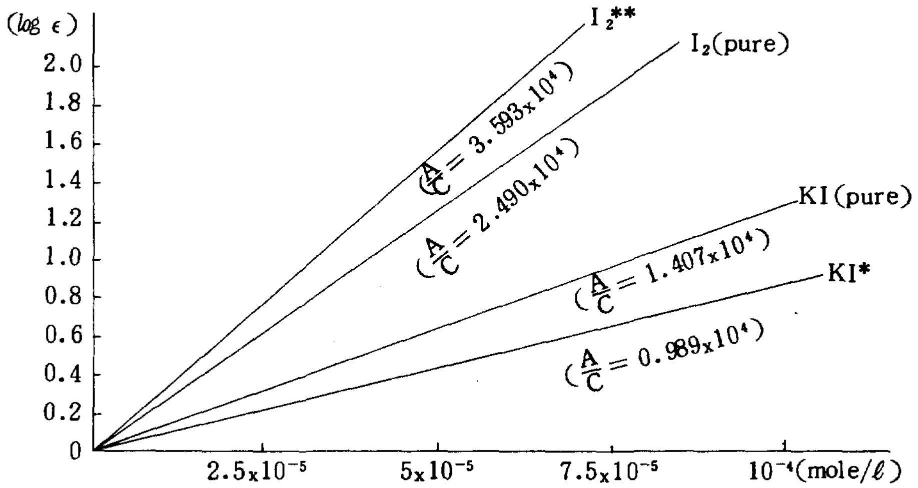


Fig.1. U.V. Spectrometric Calibration Curve of TEDA in Acetonitrile.



* In presence of I_2. ** In presence of KI.

Fig.2. U.V. Spectrometric Calibration Curve of KI_x in Acetonitrile.

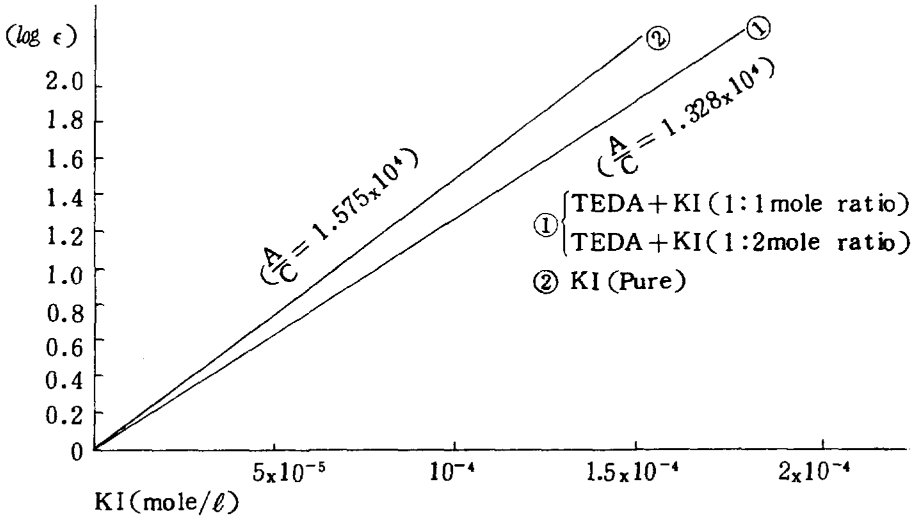


Fig.3. U.V. Spectrometric Calibration Curve of TEDA + KI in Acetonitrile.

R_f Values / Chemical Species	R_f Values			
	*Coloring Agent	Spots	**Coloring Agent	Spots
TEDA	(1)	7.0	(2)	7.0
TEDA + KI	(1)	7.0, 6.5(Faint)	(2)	5.5, 7.0
KI_x	(1)	6.5(Faint)	(2)	5.5

* Coloring agent and method were the same as above (1).
** Coloring agent and method were the same as above (2).

B. Measurement of λmax. of Each Component in Presence of Coexistend Element or Compounds

The acetonitrie extract of the sample was examined for its λmax. at ultraviolet region. The results were summarized in the table 1. The chemical compositions of the extract were identified by means of TLC testing as described in 2.3. The measured λ max. was confirmed as compared to those of authentic samples of each system in acetonitrile solvent.

Table 1. Absorption Maxima of the Major Components of the Acetonitrile Extract of the Sample.

Impregnant's System	λ max.	ε max.
	nm	
KI	256	1360
	302	990
TEDA	237	1426
TEDA + KI	*256	1080

* The λ max. of TEDA could not be observed due partly to the side peaks of KI at 230-240nm.

C. Plotting the Curve of Absorbance v.s. Concentration

In order to confirm the influence of coexistent element or compound on the spectrometric absorption pattern of a system of the acetonitrile extract of the sample, authentic sample solutions of TEDA, KI, and I_2 in acetonitrile were mixed in various molar ratio and the absorbance were plotted against concentrations as shown in figures 1, 2, and 3, respectively.

D. Typical Examples of Analysing the Sample

(1) KI_x Impregnated Sample

Sample Source	:	Kori No.1 Plant (PWR, Replacing sample in 1985)
Extraction	:	0.504g./100ml. of acetonitrile, 5 hrs. at 22-25°C. and left overnight at that temperature.
TLC Data	:	KI and I_2 were identified.
Trade Name	:	5 KI_3, 208 C

KI_3 %	:	8.62
I_2 (Free) %	:	0.15

(2) TEDA + KI Impregnated Sample

Sample Source	:	Kori No.2 Plant (PWR, 16 June, 1984)
Trade Name	:	
Extraction	:	0.250g, 100ml. of acetonitrile, 5 hrs. at 20-22°C and left overnight at that temperature.
TLC Data	:	TEDA and KI were identified.
U.V. Data	:	λ max. 256nm (No distinct peak was identified at 230-240nm.)
KI %	:	1.45%
TEDA %	:	Since there observed no distinct absorption maxima at 235-240nm region due to the side peaks of iodide, TEDA % was measured as follows : The observed KI molar concentration was half divided to result the reacted TEDA molar concentration and excess amount of KI solution was added dropwise to the sample solution until the absorbance of the solution was corresponded to the concentration of KI on the calibration curve. This value of excess adding KI molar concentration was half divided to result unreacted TEDA molar concentration. The total molar concentrations of reacted and unreacted TEDA were converted to weight % to give 1.45% TEDA (%) in this case.

2.5 Checking the Chemical Status of TEDA Impregnated Active Carbon in Active Use

In order to trace the chemical status of TEDA impregnated active carbon, samples used for a year were collected from KORI POWER PLANT (PWR) and checked their U.V. λ max. variation depending on their concentrations in actonirile solvent. It was confirmed that variation of λ max. was observed in cases of hydrophilic solvents such as methanol, ethanol, and water, whereas there are none variation in case of n-hexane and acetonitrile solvents, if the compound is pure enough. The results were summarized in the table 2. In cases of the samples collected at KORI POWER PLANT a considerable variation of λ max. were observed depending on the dilution factors as shown in the table 3.

Table 2. UV Absorption Maxima of Authentic Sample of TEDA in Various Solvents

Solvent λ max nm Sample	MeOH	95% EtOH	n-Hexane	Aceton-itrile	H_2O	Remarks
TEDA	247 245 243 242 239 233 229 223 222	240 236 233 232 225	240	237	(Conc. mol/ℓ) 240(10^{-2}) 236(6.7×10^{-2}) 234(5×10^{-3}) 288(2.5×10^{-3}) 220(1.25×10^{-3}) 216(6.25×10^{-4}) 215(5×10^{-4}) 210(2.5×10^{-4})	

Table 3. Variation of λ max. Against the Concentration of Acetonitrile Extract of the Active Carbon Used at the Kori Power Plant for a Year.

Source of Sample	Initial λ max.	Variation of λ max.	
	nm	Dilution Factor	nm
Kori Plants Sample			
# 1.	232	2	216
# 2.	231	2	220
# 3.	230	2	223
#4.	228	3	215

2.6 Examination of Samples Impregnated for Research Use

In order to confirm the feasibility of the present method of analysing chemical impregnants and to examine the impregnation pattern of the sample prepared for research use, base carbon (Physical Properties; ASTM D 2862,3802,3467,2854, 2866,3466,2867, and 3838, respectively.) was impregnated in aqueous solution of TEDA, TEDA + KI, and KI + I_2, respectively. The detailed profile of the impregnation process will be reported elsewhere, but the analytical process of checking the impregnation pattern was only reported here as follows.

A. TEDA Impregnation

A definite quantity of base carbon was placed in a 200ml. Erlenmeyer flask and a definite amount of TEDA aqueous solution was mixed with carbon by stirring it for a time and at a temperature. The resulting mixture was filtered and the filtered carbon was dried by menas of a drying oven. An aliquot of carbon was extracted as shown in 2.2, and the extract was analyzed for its chemical composition as shown in 2.4. The results were summarized in the table 4. Emphasis was laid on checking the effective extraction time.

Table 4. Impregnated Active Carbon in Aqueous Solution of TEDA.

*Extracted Time (Hrs.)	TEDA Content in the Sample Analysed (%)	**Recovery (%)
2	4.67	93.40
3	4.83	96.60
4	4.97	99.40
5	4.94	98.80

* 0.5g level of the carbon in 100ml. of acetonitrile was used for extraction. Extraction Temp. : 20-22°C.

** The weight increase of impregnated carbon after being dried was compared to the original weight of the base carbon. The weight increase was averaged to 5.00% in these cases.

B. TEDA and KI Impregnation

The impregnation process and analytical procedure were the same as above. Emphasis was laid on the correlation between the amount of carbon extracted and recovery rate. The results were summarized in the table 5.

Table 5. Impregnated Active Carbon in Aqueous Solution of TEDA and KI.

Exp. No.	Weight Increase of Impregnated Carbon. (%)	*Extracted Carbon g./100ml. of Acetonitrile	Analytical Value KI (%)	TEDA (%)	Recovery %
1	12.29	1.001	4.91	4.98	80.47
2	1.40	0.503	0.58	0.59	83.57
3	6.15	0 253	2.70	2.73	88.29

* Extracted for 5 hrs. and left overnight at 22-25°C.

C. KI and I_2 Impregnation

The impregnation process and analytical procedure were the same as stated above. Emphasis was laid on checking the effective extracted temperature and confirming the correlation between the amount of carbon extracted and recovery rate. The results were summarized in the table 6.

2.7 Analytical Study of IC Samples and Testings

IC samples distributed by EG & G Idaho Inc. were analyzed for their chemical impregnants according to the procedure described as above. In these cases, the moisture content of each sample was measured as described in 2.1 and the analytical values were calibrated for moisture contents. The results were summarized in tables 7 and 8.

Table 6. Impregnated Active Carbon in Aqueous Solution of KI and I_2.

Exp. No.	Weight Increase of Impregnated Carbon.(%)	*Extracted Carbon g./100ml. of Acetonitrile	Analytical Value KI(%)	I_2(%) (Free)	**I_2(%) (Bound)	Recovery %
1	10.65	1.003	0.78	0.07	1.19	37.93
2	2.88	0.505	0.67	0.57	1.02	78.47***
3	2.64	0.503	0.83	0.54	1.26	99.62

* Extracted for 5 hrs. and left overnight at 20-22°C.
** Calculated on basis of the molecular formula, KI_3. Detailed was explained in discussion.
*** Extraction temp. was accidently above 25°C.

Table 7. Analytical Data of Impregnants Contained in IC Samples. (New Cabon).

Sample No.	Iodide* (wt%)	TEDA (wt%)	Remarks
N3-14	2.75	2.78	
N3-15	2.30	2.33	
N3-16	1.76	1.78	
N3-17	1.93	1.95	
N3-18	2.29	2.32	
N3-19	2.03	1.99	

* λ max. 256nm (KI).

Table 8. Analytical Data of Impregnants Contained in Samples. (Used Carbon)

Sample No.	Iodide (wt.%)*	Iodine (wt.%)**	Indicated Testing Method	Remarks
U7-1	0.243	1.083	30°C	
U7-4	0.188	1.113	RH 95%	
U7-7	0.216	0.885		
U7-10	0.206	0.897		
U7-13	0.205	0.893		
U7-2	0.246	1.042	30°C	
U7-5	0.189	1.425	RH 90%	
U7-8	0.194	0.914		
U7-11	0.208	0.988		
U7-14	0.213	9.830		
U7-3	0.226	0.959	30°C	
U7-6	0.200	0.662	RH 70%	
U7-9	0.201	0.951		
U7-12	0.209	1.000		
U7-15	0.196	0.995		

* λ max. 256nm (KI)
** λ max. 302nm (I_2)

The standard deviation of analytical values were calculated and the uniformity of samples were evaluated as summarized in the table 9.

Table 9. Evaluation of the Uniformity of Impregnants in IC Samples.

Indicated Testing Methodes	Iodide Mean ± Std. Dev. %	Iodine Mean ± Std. Dev. %	TEAD Mean ± Std. Dev. %
A. Used Carbon*			
RH 70%, 30°C	0.202 ± 0.005(2.6%)	0.902 ± 0.13(14.4%)	
RH 90%, 30°C	0.201 ± 0.010(5.0%)	1.04 ± 0.23(24.0%)	
RH 95%, 30°C	0.204 ± 0.014(6.8%)	0.947 ± 0.10(10.2%)	
B. New Carbon			
RH 95%, 30°C	2.16 ± 0.66(25.3%)		2.19 ± 33(15.1%)

* U7-1, U7-2 and U7-3 were not included in this evaluation because of their deviated values. (ref. table 8.)

According to the testing protocol of EG & G Idaho Inc., the new and used carbon samples were tested for their adsorption efficiencies as summarized in tables 10 and 11.

Table 10. A Study on Penetration* of Radio-methyl Iodide through Activated Carbon (New Carbon).

Sample No.	Relative Humidity, %	Penetration Test Bed, %	Test Bed Density g/cm^3
N3-14	95	5.36	0.5060
N3-15	95	8.79	0.5021
N3-16	95	11.14	0.4882
Mean ± Exp. Std. Dev.		8.43 ± 2.38(28%)	0.499 ± 0.008(2%)

* Equilibration time was set as one hour for study purpose.

3. Results and Discussion

3.1 Moisture Determination

In table 12. the results of determining moisture of IC samples were summarized for reference. According to these results, moistures in new carbon samples were usually below than 3.0%, which may not be significant enough to effect the analytical results, since there are some more moisture adsorption during the course of sample handling process. However, in case of used carbon, the moisture contents were usually around 20% level, which may have a serious influence on the analytical results, though there may also be some moisture adsorption during the course of sample handling process. These points were seriously dicussed in the last NRC workshop for interlaboratory comparison of

Table 11. Interlaboratory Comparison Penetration of Radio-methyl Iodide through Activated Carbon (Used Carbon).

Sample No.	Relative Humidity, %	Penetration Test Bed, %	Test Bed Density g/cm^3
U7-1	95	24.18	0.5749
U7-4	95	*(27.70)	0.5690
U7-10	95	24.34	0.5737
Mean ± Exp. Std. Dev.		24.26 ± 0.08(0.3%)	0.573 ± 0.002(1%)
U-2	90	25.00	0.5629
U7-5	90	*(27.55)	0.5677
U7-11	90	23.22	0.5671
Mean ± Exp. Std. Dev.		24.11 ± 0.9(4%)	0.566 ± 0.002(1%)
U7-3	70	*(18.00)	0.5682
U7-6	70	24.10	0.5601
U7-12	70	22.87	0.5634
Mean ± Exp. Std. Dev.		23.49 ± 0.6(3%)	0.564 ± 0.003(1%)

* Deviated values were partly due to high or low contents of impregnants contained in samples (ref. tables 8 and 9.)

adsorption efficiencies, which showed a significant difference depending the initial moisture content of the IC sample. The adopted method of drying to measure the moisture content was ASTM-Method D 2867, in which an effective forced circulated oven was recommended for drying instrument. Some local excess drying seemed to cause some volatilization of impregnant, if an effective drying oven is not available or if there are some deviations on drying temperature. It is recommended that preliminary investigation on the moisture content of used sample may be necessary in case of analysing used sample providing an effective forced circulated oven, whereas the moisture determination process may not be essential to analyse the new sample.

Table 12. Moisture Content of IC samples.

Sample	Moisture Content (%)	Sample	Moisture Content (%)
* U-1	19.60	U-10	19.30
U-2	19.46	U-11	19.18
U-3	19.44	U-12	20.09
U-4	19.79	U-13	19.42
U-5	19.31	U-14	19.46
U-6	19.51	U-15	20.22
U-7	19.84	* N-14	2.85
U-8	19.73	N-15	2.88
U-9	19.15	N-16	2.86

* U : Used samples
N : New samples

3.2 Extraction Process

In extraction process, the choice of an effective solvent for extraction was very important to be considered. 10 solvents including water are known to be useful which are transparent in near ultraviolet region.(i.e. 200-360nm) Preliminary investigation to check the solubility of TEDA, TEDA + KI, and KI + I_2 showed that acetonitrile was the most useful for the present study. Water and alcoholic solvents showed better solubility, but these solvents could not reveal the constant λ max, which were varied depending on the dilution factor as shown in table 2 for TEDA case. Next problemes were extraction time and temperature. In case of TEDA, the extractibility was excellent after being stirred for 5 hrs. at 20-22°C, as shown in Table 4. In a TEDA + KI system, the extraction was greatly promoted when the concentration of base carbon was decreased to 0.25g/ 100ml acetonitrile level as shown in Table 5. In a KI + I_2 system, extraction temperature should be kept at a constant level as shown in Table 6. Detailed discussion on extraction time and temperature would better be described in the later paragraph (3. 4.) in conjunction with the chemical behaviors of these systems in the acetonitrile solvent.

3.3 TLC Study

Basically, TLC study on the acetonitrile extract of the sample to be analysed may not be necessary to identify its major chemical composition, if the specification of the sample is clear enough to indicate the composition. However, maker's specifications are sometimes not distinct enough to identify the composition. U.V. spectrometric examination of absorption maxima of the extract may also be useful for this purpose, but there are unclear case such as TEA + KI, TEDA absorption maxima of which could not be identified due to the side peaks of KI. TLC study was, therefore, conducted to confirm the composition in advance of analysis process. As summarized in 2.3, TEDA and KI could clearly be identified. It is recommended that both developing solvents listed in 2.3. would better be adopted to check spots closely. TLC study may also be very useful to check impurity caused by the deterioration of the sample, if any. There may be some other effective instrumental methodes of identifying the composition such as I.R., N.M.R., and others, but TLC was very simple and convenient to be used in an ordinary laboratory practice.

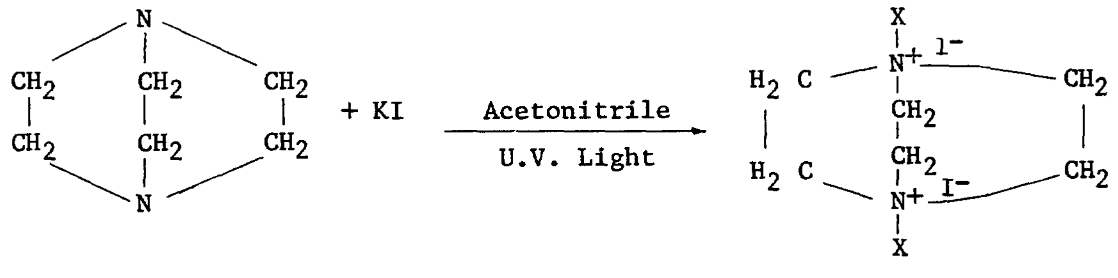
3.4 U.V. Spectrometric Analysis of the Sample

A. TEDA in the Sample

As summarized in table 1. and Fig.1, TEDA in the acetonitrile extract revealed the clear λmax at 237nm and the plot of λmax v.s. concentration showed a good linearity, which was useful as the analytical calibration curve. The extractibility of TEDA impregnated in a carbon was excellent and the recovery rate in the extracted acetonitrile solvent was close to the saturation, when the extraction mixture was stirred for 5 minutes at 20-22°C as summarized in the table 4. However, TEDA in the extract showed a variation of λmax depending on the dilution factor, if TEDA in the sample is deteriorted chemically as indicated in table 3. It is, therefore, recommended that the preliminary examination of the variation of λmax should be conducted in advance of the analytical process. If there are some variations of λmax depending on the dilution factor, the TEDA in the sample had already been deteriorated and hence it should be replaced as discussed in the later paragraph. Judging from the data of table 4, analytical accuracy of this method was 98-99%. The standard deviation of the analytical data was less than 2.0%.

B. TEDA and KI in the Sample

It was observed that the gradient of the curve of KI in this system was varied depending on the concentration of the coexistent TEDA in the system. Thus, gradients of curves of KI were colse together and they were lower than that of the pure KI, when the molar ratio of TEDA and KI adjusted to 1:1 and 1:2, as shown in figure 3. When the molar ratio of TEDA and KI was adjusted to 1:3 or more, gradients of curves were close to that of the pure KI. When the molar ratio was adjusted to 2:1 or more, gradients of curves were colse to that of the curve of the molar ratio of 1:1 and not varied much. On the other hand the λmax of TEDA in this system could not be observed at 237nm region, though there are some side peaks near at this region. These observations suggested that there may be the formation of a compound of TEDA and KI in acetonitrile under U.V. irradiation. It had been known for quite long time that alkyl iodies(5) or iodine(6) could form a salt quantitatively in a polar solvent with TEDA. These salts were prepared by the author to confirm their λmax in acetonitrile solvent, which showed a single λmax without showing TEDA peak at 237nm region. This finding led the author to expect



......(1)

the above compound in the system under U.V. irradiation. For the chemical structure of X in the above chemical formula, further extensive investigations may be necessary to identify it, but this assumption did not incur a serious analytical error as discussed in the following.

On basis of the above observations, the analytical procedure was developed as described in 2.4.D. Thus, the amount of KI in this system was analyzed on basis of the calibration curve of KI of the molar ratio of 1:1 in fig.3. For TEDA, the amount contained in the system was classified in two category such as reacted and unreacted TEDA with KI under U.V. irradiation. The reacted TEDA was calculated by dividing in a half of the molarity of KI analyzed. The unreacted TEDA was analyzed by adding the excess amount of KI solution of the known concentration until the final molar ratio of the TEDA and KI became close to 1:2 as described in 2.4.D. To confirm the feasibility of this method, the impregnated carbon sample was examined and the recovery rate could be amounted to 88.29% at present. This value will, however, be able to be promoted by improving the extraction process.

This method may be said to be too complicate and the analytical accuracy is not high at present for TEDA content, but it can show the KI amount accurately. For used carbon, TEDA may be liable to be evaporated or deteriorated chemically during the course of routine operation. If the amount of KI analyzed by this method is unreasonably high as compared to that of the original sample unused, the evaporation or deterioration of TEDA may be very serious in the sample. Further investigation along this line is now under progressing. In conclusion, this method is of very complicate to check the amount of TEDA, but it may still be worthwhile to be practiced in regulatory lab. to confirm the quality of the carbon sample.

C. KI and I_2 in the Sample

As shown in fig.3, the gradient of the curve of KI in presence of I_2 was lower than that of pure KI solution, whereas it was higher in case of I_2. In order to confirm the influence of the coexistent I_2 or KI on the gradient of the curves, the molar ratio of KI and I_2 in the sample solution was adjusted to 1:1, 1:2, and 2:1. In cases of the molar ratio of 1:1 and 1:2 or more, the curves of KI and I_2 are close to the curves shown in fig.2 as the analytical curves. In case of the molar ratio of 2:1 or more, the curves of KI and I_2 were close to those of pure KI and I_2. These observations led the author to postulate the following sequence of chemical reactions in the analytical solution under U.V. irradiation. Thus, KI_3 and I_2 may be formed initially and the resulting KI_3 may further be decomposed to KI and I_2 depending on the analytical condition. Since anhydrous acetonitrile was used and temperature was kept below than 25°C, the decomposition of KI_3 in the analytical system may be not serious enough to liberate the significant quantity of I_2 in the analytical solution.

$$\begin{tikzcd}
KIx \arrow[r, "CH_3CN", "U.V."'] & KI_3 \arrow[dr, shift left] & + \ (X-3) \cdot I/2 \cdot I_2 \\
& & KI \ + \ I_2 \arrow[ul, shift left]
\end{tikzcd}$$

Further extensive studies on these aspects of chemical reactions may be necessary, but the analytical procedure was developed on basis of this postulation at present as described in 2.4. The measured concentration of KI in the sample solution may indicate the presence of the equivalent amount of I_2 bound to KI and that of I_2 may also indicate the presence of free iodine present in the system. To confirm this approach of analysis, impregnated carbon with the mixed aq. solution of KI and I_2 were examined as summarized in the table 6 and 99.62% of recovery was obtained, when 0.503g of the sample carbon was extracted in 100ml. of acetonitrile at 20-22°C. The extraction temperature was very important in this case. If the temperature is higher than 25°C, lower recovery rate was observed. The method was of simple and convenient to be practiced in an ordinary laboratory. According to the recent literature,(7) impregnation on charcoal that contain KI_x as part of the formula could have the following reaction and liberated iodine may further be volatilized during the stage of the routine purge of the carbon filter system by moist air.

$$K^+ I_3^- + H_2O \longrightarrow K^+ I^- + I_2 \cdot H_2O$$

When this analytical method is applied to examine the compositions of this type of partly deteriorated carbon, the measured KI value may indicate unreasonably higher value than that of the original sample of this carbon unused, since the coexistent I_2 and bound I_2 are partly volatilized to increase the gradient of the calibration curve shown in the fig.2. Research along this line may result an efficient way of checking the deterioration pattern of this type of nuclear grade carbon in active use.

3.5 Checking the Chemical Status of TEDA Impregnated

The samples collected at Kori No.1 plant, which had been used for a year and had been experienced some water floggings in the filter system, were dried and examined for their compositions as summarized in table 3. The λ max. observed was lower than that of pure TEDA in acetonitrile solution. The sample solutions were diluted and the diluted solutions were examined again to indicate lower λ max than those of the previous cases. In parallel with these observations, λ max of TEDA in various solvents were examined to select the best solvent suitable for the analysis and it was found that hydrophilic solvents showed a solvent effect varying λ max, whereas acetonitrile solvent gave a definite λ max at 237nm. in acetonitrile solvent, when it was well dried. These observations suggested that TEDA in Kori No.1 samples deteriorated and hence their U.V. λ max were varied depending on dilution factor. Presumably, TEDA deteriorated to its hydroxide or equivalent and this caused the observed λ max variation. It was considered that the examination of TEDA impregnated carbon by this method may be one of the effective method to check the chemical status of the carbon in active use.

3.6 Examination of Samples Impregnated for Research Use

Examination of samples inpregnated in the present study was mainly focussed to confirm the feasibility of the present analytical method as discussed in 3.4. Detailed features of the impregnation processes will be reported elsewhere. It can be said that the present study of examining the chemical composition of an impregnated carbon was very useful to trace the impregnation pattern, which could indicate the optimum condition for preparing a carbon sample of the desired specification.

3.7 Analytical Study of IC Samples and Testings

Since new carbon samples are sometimes non uniformly impregnated(7) due to the inadequate mixing process or deterioration during the course of storage, IC samples received from EG & G were analysed for their impregnants. The results were summarized in table 7. For used carbon samples, the same analytical study was conducted and results were summarized in table 8. These analytical data were further evaluated to confirm their uniformity of impregnants contained.

As shown in table 9. used carbon samples were generally uniform in regards to their impregnants of iodide, which may be main active composition for adsorption of radio-methyl iodide, except several cases of U7-1, U7-2, and U7-3. Experimental standard deviations (relative) for groups of samples classified by the testing conditions were 2.6%, 5.0%, and 6.8%, respectively. For new carbon samples, standard deviations (relative) of each active component of IC samples were amounted to 25.3% for iodide and 15.1% for tertiary amine (TEDA), respectively. Being aware of these analytical data, this laboratory conducted testing works as summarized in tables 10 and 11. Testing works were conducted according to the Standard Method, D-3803-79 and IC testing protocol of INEL. Exceptionally deviated penetrations were observed in cases of U7-3 and U7-5, which may possibly be due to the high or low contents of the impregnant in the sample as compared with the rest of samples in the group. It was, therefore, considered to be deviated testing data and hence they were neglected of the evaluation of the reproductibility. Since experimental standard deviations (relative) of impregnants contents of new carbon samples as summarized in table 7 were too high to be penetration tested, it was condidered worthwhile to study the relative error propagation of penetrations on basis of data in table 9. Results shown in table 10 had indicated that there seemed to exist a correlation between the impregnant's contents and penetrations. (i.e. exp. standard deviation (relative) for penetration, 28% and those for impregnants, 25% and 15%, respectively) Further experimental data would better be accumulated to confirm this relation, but it may be said at present that the preliminary analytical study on the chemical impregnant of a testing sample would be worthwhile to be conducted to assure the testing result itself.

4. Conclusion

The present study on analysing chemical impregnants of a nuclear grade active carbon could result a simple and convenient method to be practiced at an ordinary laboratory by means of ultraviolet spectrometric method. This method may be applied to trace chemical behavior of a carbon sample in active use. The method is also applicable to check the impregnation pattern of a nuclear grade carbon during the course of impregnation process, which will be able to check the optimum condition of preparing a sample of the desired specification. The postulations described in discussion may further be investigated to confirm their detailed insides, but the analytical accuracies were very high except that of TEDA and KI, which was around 88% at present. It is expected that some more applications for managing the carbon filter may be possible in the near future.

Acknowledgement

The author express his sincere appreciation for U.V. spectrometric analytical works conducted by Mrs. S.W. Kim throughout this study.

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REMOVAL OF ORGANIC IODINE COMPOUNDS FROM FLOWING AIR STREAMS

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Organic radioiodides other than methyl iodide have been identified by several investigators in the past. However, only limited parametric studies have been performed to evaluate the challenge of these organic compounds toward the currently installed adsorbent beds. Initial evaluation of adsorbents has indicated that the removal properties of commercial adsorbents is different for organic compounds other than methyl iodide. Tests were performed using di-iodomethane, iodoethane, iodopropane and iodo benzene.

Adsorbents evaluated included stable iodine alone, amine alone and coimpregnated carbons. The results indicated that there are significant differences (i.e., lower removal efficiencies) for these compounds compared to methyl iodide and also for the individual species depending on the impregnant.

An explanation for these differences is offered based on isotope exchange rates for the various species and the fact that one or several of these species may be responsible for the "penetrating iodine species" suspected to be present by others in the past.

I. Introduction

Current official source term calculations assume that gas phase elemental iodine and organic iodide exist in addition to the solid (particulate) phase cesium iodide in reactor containment gases. The origin of organic iodides under reactor accident conditions has not been clearly established. However, without exception, the organic form of iodine presumed by all agencies is represented by methyl iodide. This also applies to adsorbents used to control radioiodine where removal efficiency is established using methyl iodide as the most penetrating species of organic iodide. This is contrary to results reported by others (1)(2) where a more penetrating form of (organic) iodide was suspected but not identified. While it is well established that in the case of a nuclear accident, fission product iodine is released mainly as cesium iodide (3)(4), various other chemical mechanisms are possible, including reactions at surfaces, reactions in the aqueous phase, reactions in the gas phase and radiation induced reactions in both the aqueous and gaseous phase leading to production of organic iodides. The potential and actual presence of various organic iodine species is well known (5)(6). However, since the establishment that one of these species was methyl iodide, practically all research work focused on evaluating adsorbents using methyl iodide. Based on a knowledge of the removal mechanism using activated carbon adsorbents, commonly used impregnated carbons were evaluated using I-131 tagged organic compounds other than methyl iodide.

II. Organic Iodide Isotope Exchange with Organic Iodides

The major removal mechanism for radioactive organic halides is isotope exchange with stable iodides on activated carbon carriers (7)(8). This is also the major removal mechanism for tertiary amine impregnated carbon which form stable iodine complexes which then further exchange with the radioactive organic iodides (9)(10).

The isotope exchange of organic halides with homologeous inorganic iodides or other organic halides has been extensively studied in the last fifty years. (11)(12)(13)(14)(15)(16)(17)(18). While these studies were not based on data obtained on systems using high surface area carbon supported components, their conclusions are important in the evaluation of the ease or difficulty of isotope exchange between the components involved.

Reaction rate and activation energy data from several investigators is shown on Tables 1 through 3.

The data from these Tables indicate that the isotope exchange of I^- with RI for normal aliphatic iodides decreases with increasing number of carbon atoms in the radical, at least up to four carbon atoms. One paper indicates that $n\text{-}C_4H_{11}$ I has a slightly higher isotope exchange rate than $n\text{-}C_4H_9I$. (12) At least for the isopropyl and butyl groups it is also shown that isotope exchange is significantly slower for the iso than for the normal iodide (13)(14)(15)(16).

There is also a significant decrease in the rate of isotope exchange with increasing substitution of halogens for hydrogen at least up to the point where at least one hydrogen atom is present (14)(18)(19).

One reference was found where isotope exchange between inorganic halides and CI_4 showed higher rate constants than CH_2I_2 or CHI_3 and the corresponding halide (18)

These exchange rate constant differences cannot be explained solely by the differences in activation energies of the isotope exchange process. It is suspected ΔS, the entropy of formation of the intermediate complex, is also an important parameter influencing the resulting rate constant (19).

There are indications in the literature also that olefinic equivalents exchange at a higher rate than the same carbon number parafins (18)(20).

Based on this literature review, it was decided that the use of methyl iodide--on an arbitrary basis--for the determination of the decontamination efficiency of currently used impregnated carbons may not be the most conservative method.

III. Experimental Procedures

The I-131 tagged organic iodides were obtained commercially from ICN.

ASTM D3803 method A was used with the exception that the loading time was one hour. The base carbon in all cases was US 8X16 mesh, 60 carbon tetrachloride capacity coconutshell carbon. The following impregnations were made:

1. KI, 5%
2. TEDA, 5%
3. KI, 2% + TEDA, 2%
4. Tetra Butyl Ammonium Iodide, 2.5%

The tetrabutyl ammonium iodide impregnated carbon was also used as the backup or guard bed carbon during the tests. The results of the tests are presented in Table 4.

Table 1

Isotopic Exchange Rate Constants for Alkyl Iodides with Iodide Ions at 100°C

R	Rate Constant $k\times10^5$ liter mole^{-1} sec^{-1}	Activation Energy kcal/mole.
CH_3I	120,000	15.4
C_2H_5I	17,500	19.0
C_3H_7I	10,000	19.3
C_3H_7I	1,000	--
CH_2I_2	230	21.7
CHI_3	120	22.3

Data from Ref. 16

Table 2

Rate Constants and Activation Energies for the Isotope Exchange of Alkyl Iodides with Iodide Ions at 25°C

	Solvent	Rate Constant $kX10^5$ liter $mole^{-1}$ sec^{-1}	Activation Energy kcal/mole.
CH_3I	Ethanol	400	16.5
C_2H_5I	Ethanol	17.4	22.3
n-C_3H_7I	Ethanol	14.0	18.4
i-C_3H_7I	Ethanol	0.62	21.2
n-C_4H_9I	Ethanol	9.8	18.4
i-C_4H_9I	Ethanol	1.28	18.8
sec-C_4H_9I	Ethanol	0.71	21.8

Data from Ref. 12

Table 3

Isotopic Exchange Rate Constants at 20°C for Alkyl Iodides with Iodide Ions ($kX10^5$ liter $mole^{-1}$ sec^{-1})

CH_3I	630
C_2H_5I	13
n C_3H_7I	10

Data from Ref. 13

Table 4

Organic Iodide-131 Removal Efficiency of Various Impregnated Carbons

Impregnant	MeI	EtI	PrI	MeI_2	IB
KI	97.89	91.70	97.59	99.83	99.91
TEDA	98.82	95.31	99.60	99.95	99.99
KI + TEDA	99.19	93.25	99.11	99.90	99.91
TBNI	99.10	95.92	99.58	99.99	99.81

IV. Evaluation and Discussion of Results

The removal efficiencies indicate (see Table 4) a drop in removal efficiency for the iodoethane (compared to methyl iododide) with a gradual increase in removal efficiency going from iodopropane to iodobenzene. This confirms preliminary results obtained by this laboratory and reported elsewhere (21).

This seems to somewhat contradict what would be expected based on isotope exchange rates. However, when the contribution of physical adsorption of these species is taken into account, the results can be explained. The boiling point for the iodomethane, iodoethane, iodopropane, diiodomethane and iodobenzene are 42, 71, 101, 181 and 188 C respectively. Thus we have a high removal efficiency for iodomethane, where the relatively low physical adsorption is offset by the fast isotopic exchange rate. A minimum is obtained in the removal efficiency with iodoethane where the increased physical adsorption cannot offset the slower exchange rate. This trend reverses with iodopropane where physical adsorption begins to dominate compared to the exchange rate. The net effect of the increased physical adsorption is to increase the residence time on the carbon and thus to allow enough time for isotopic exchange to take place even though the rate of exchange is considerably slower.

Work is continuing in this laboratory to look at the effects of loading and postsweep time on the removal of these organic iodides and also to look at their branched chain analogs.

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INVESTIGATIONS ON THE AGING OF VARIOUS ACTIVATED CARBONS IN THE EXHAUST AIR OF A PWR OVER AN EXTENDED PERIOD OF TIME

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Abstract

With 15 different commercial impregnated activated carbons aged in the containment exhaust air of a PWR over periods of up to 9 months, a tendency for a relatively low penetration by CH_3I-131 was observed for the carbons impregnated additionally or exclusively with a tertiary amine (e.g. TEDA or derivative). It is concluded that in particular for iodine filters of large bed depths comparatively long stay times should be obtained with amine containing carbons under the conditions investigated.

I. Introduction

Nuclear power plants are equipped with iodine filters containing impregnated activated carbons to keep the release of airborne radioiodine as low as reasonably achievable.

Impregnated activated carbons are known to age, i.e. to deteriorate in performance with respect to the retention of radioiodine, particularly in iodine filters that are continuously operated (e.g. containment exhaust air filters of pressurized water reactors). The aging of carbons in iodine filters is essentially due to the adsorption of organic compounds (e.g. solvents) and of inorganic compounds (e.g. O_x, SO_2, NO_x). In the first case the effective surface of the carbon is lowered. In the second case reactions with the carbon (and the impurities such as sulphur) as well as with the impregnant can occur. The alkalinity of the carbon can be reduced in this case.

In iodine filters various impregnated activated carbons are used differing e.g. in base material, grain size and impregnant. In recent years new impregnated activated carbons were developed (see below). Therefore we have performed investigations to provide comparative data on the aging of a variety of commercial impregnated activated carbons from several countries under relevant conditions. The data relate to the retention of methyl iodide (CH_3I-131).

In the present paper, investigations are covered on the aging of 15 different impregnated activated carbons in the containment exhaust air of a typical German pressurized water reactor (PWR 3) over periods of up to 9 months. Data on the aging of 5 carbons in the containment exhaust air of a similar pressurized water reactor (PWR 4) over periods of up to 3 months have already been published. /1/

II. Former Investigations

Numerous investigations have been performed on the aging of impregnated activated carbons in the exhaust air of nuclear power stations. /2,3,4/ It is difficult, however, to judge from these investigations the aging of different carbons in the exhaust air of other nuclear power stations. This is particularly due to the complexity of the aging process and to the differences in type and concentration of the pollutants in the exhaust air.

It must also be mentioned that mostly carbons of small bed depths (residence times (t): less than 0.5 s) were used in these investigations. However, it is not possible to reliably extrapolate to large bed depths (t : > 0.5 s) which, to obtain a long stay time, are used for iodine filters in some countries.

Because of these reasons it is only mentioned here that in studies performed under various conditions, often a good aging behavior with respect to the retention of CH_3I-131 was found with carbons impregnated additionally or exclusively with TEDA (triethylene-diamine) or another tertiary amine. /5,6,7/ Also during the storage of carbons (in closed containers), in which the aging is relatively small, the best aging behavior was observed with a TEDA-impregnated carbon. /8,9/

In our investigations on the aging of 5 carbons in the containment exhaust air of PWR 4 over periods of up to 3 months, also comparatively low penetrations by CH_3I-131 were observed for carbons impregnated additionally or exclusively with a tertiary amine. /1/ However, it was also found that the change in penetration due to aging can be stronger for amine-impregnated carbons than for e.g. KI-impregnated carbons.

Earlier aging investigations in German nuclear power plants were almost exclusively conducted with KI-impregnated carbons, essentially in order to identify the pollutants and optimize the layout of iodine filters. /10,11/

There are some doubts on the suitability of TEDA-impregnated carbons for use in iodine filters of nuclear power plants because of the low ignition temperature and high vapor pressure of TEDA. By using derivatives of TEDA ("heavy TEDA"), possibly together with antioxidants, fire hazards can be reduced. /12,13/ It is mentioned here that in recent comparison tests with a KI- und a TEDA-impregnated carbon at 180 °C, no difference with respect to the retention of CH_3I-131 was observed. /14/

III. Experimental

Data regarding the activated carbons investigated are contained in Table I. Three main groups of impregnants can be distinguished:

(a) KI or KI + I_2;
(b) KI + tertiary amine;
(c) tertiary amine.

Moreover, a carbon impregnated with an organic iodide was investigated.

Most of these carbons were developed in recent years. Efforts were made to include more recently developed carbons in order to cover even a broader range of carbons. However, the companies contacted were not able to supply these carbons in time.

The investigations covered in this paper were essentially performed as those conducted earlier. /1/ The carbons, mounted in sectioned beds, were challenged with the containment exhaust air of PWR 3 over periods of 3, 6 and 9 months, respectively, during power operation of the reactor. The periods did not overlap. The operating conditions of the carbon beds corresponded largely to the operating conditions of the iodine filters in German nuclear power stations in normal situations and were essentially identical with those in the subsequent laboratory tests with CH_3I-131. The parameters of the laboratory tests are given in Table II.

The tests with CH_3I-131 were run with both fresh and aged carbons. In the second case, the original arrangement of the carbons was maintained. Thus, the geometric course of the aging within the sectioned beds could be ascertained. As indicated in Table II, the aged carbons were preconditioned over a period of 1 h only to minimize the desorption of pollutants. (This duration should be sufficient due to the largely identical conditions during aging and testing.)

More details on the performance of the tests with CH_3I-131 are to be found in the literature. /4/ The reproducibility in these tests is excellent in general. /15/ The minimum detectable penetration, determined with NaI detectors, was 10^{-5} to 10^{-4} %.

As in our previous investigations, an additional bed of the carbon 207B (KI) was simultaneously challenged with the exhaust air to determine both the loading of the bed with organic compounds (mainly by gas chromatographic analysis of the CCl_4 extract) and its alkalinity (by pH value measurement of the H_2O extract).

IV. Results

In this chapter first the results are presented of the investigations on the retention of CH_3I-131 by the 15 carbons contained in Table I under the conditions indicated in Table II.

The results are given in terms of penetration by CH_3I-131. Tables III to V contain the penetration for fresh carbons (aging time: 0 months) and aged carbons (aging time: 3,6 and 9 months, respectively) at 3 bed depths (12.5, 25.0 and 37.5 cm equivalent to residence times (t) of 0.25, 0.5 and 0.75 s, respectively). Figures 1 to 15 display the same values up to the maximum bed depth (50 cm). Finally, Figures 16 to 18 show the results for the maximum aging time (9 months) for the above-mentioned 3 bed depths.

Figures 1 to 15 show that, using a semilogarithmic plot, with the fresh carbons the usual linear decrease of penetration with increasing bed depth was found. With the aged carbons, a nonlinear course of the penetration curves was obtained: flat at low bed depths and steep at large bed depths, in some cases nearly parallel to the penetration curve of the respective fresh carbon. This form of the penetration curves corresponds to a decrease in aging with an increase in bed depth, with a negligibly small aging in the above-mentioned cases of nearly parallel penetration curves.

Figures 1 to 15 also show that there is a tendency for the same penetration at aging times of 3 and 6 months. (In some cases the penetration at an aging time of 3 months was nominally even higher than at 6 months). Since the aging periods did not overlap, this is possible implying e.g. that the concentration of pollutants in the exhaust air was relatively low during the aging period of 6 months. Some results may also be attributable to experimental errors.

Apart from a few exceptions, the main results obtained for both fresh and aged carbons may be summarized as follows, considering a small bed depth (12.5 cm, t = 0.25 s) and a large bed depth (37.5 cm, t = 0.75 s), respectively:

(a) Fresh carbons:
At a bed depth of 12.5 cm a penetration of between 10^{-4} and 10^{-2} % was found for carbons with KI or KI_3 as the impregnant and of below 10^{-4} % for carbons with the other impregnants. At a bed depth of 37.5 cm the penetration was below 10^{-4} % for all the carbons.

(b) Carbons aged 3 or 6 months:
At a bed depth of 12.5 cm a penetration of about 10^1 % was observed for carbons with the KI or KI_3 impregnants and of between 10^{-1} to 10^1 for carbons with the other impregnants. At a bed depth of 37.5 cm the values were $\leq 10^{-4}$ to 10^{-1} % for the KI impregnant and $< 10^{-4}$ to 10^{-3} % for both the KI_3 and the other impregnants.

(c) Carbons aged 9 months:
At a bed depth of 12.5 cm the penetration was always between 10^1 and 10^2 %. However, at a bed depth of 37.5 cm, a penetration of 10^{-1} to 10^0 % was found for the KI impregnant, of 10^{-4} to 10^{-2} % for the KI_3 impregnant and of $< 10^{-4}$ to 10^{-2} % for the other impregnants.

The main exception was the carbon BPJ which, compared with the other carbons, showed a very high penetration after aging.

The results show a tendency for a comparatively low penetration for the carbons impregnated additionally or exclusively with TEDA or another tertiary amine (or an organic iodide). It is only at the maximum aging time and at low bed depths that this tendency is not evident. The implication of this finding is that the aging of amine-impregnated carbons was stronger than e.g. of KI-impregnated carbons (except for BPJ). The tendency for a comparatively low penetration for the amine-impregnated carbons after aging was consequently due to a better performance prior to aging. This is in agreement with our previous findings. /1/

As for the base materials and grain sizes of the carbons, it is believed that from the investigations performed one should not tempt to draw conclusions on their influence on the aging behavior of the carbons.

As for the additional investigations mentioned above, Figure 19 shows the loading of 207B (KI) with organic compounds of different volatility at an aging time of 9 months. This loading was obtained by gas chromatography. Whereas the compounds of high volatility were found on all the beds, the compounds of low volatility were only observed on beds 1 through 8. The former compounds consisted in particular of toluene, xylene and nonane, the latter compounds of decane and dodecane. Mass spectrometric measurements of the low-volatile compounds revealed methyl and ethyl derivatives of these hydrocarbons and, additionally, of benzene. As the alkalinity of the aged 207B (KI) was found to be unchanged, it is obvious that, in agreement with former measurements, the adsoprtion of organic compounds was a main reason for the aging.

V. Summary and Conclusions

Investigations were performed on the aging of 15 different commercial impregnated activated carbons from several countries in the containment exhaust air of a typical German pressurized water reactor (PWR 3) over periods of up to 9 months. The aging was determined with respect to the penetration by CH_3I-131 under the in-situ conditions (30 °C, 40 % R.H.).

A tendency for a comparatively low penetration was observed for the carbons impregnated additionally or exclusively with a tertiary amine (e.g. TEDA or derivative). This applies in particular to large bed depths (residence times: > 0.5 s) where the good performance of these carbons when fresh is dominant.

Based on the comprehensive data obtained it is concluded that in particular for iodine filters of large bed depths comparatively long stay times should be obtained with amine containing carbons under the conditions investigated. Taking into account the ignition temperature and vapor pressure of amines, derivatives of TEDA are more eligible than TEDA.

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Table I: Data of the activated carbons investigaded

Name	Impregnant	Base material	Size [a]	Supplier
207B	KI	coal	8 - 12 mesh	Sutcliffe Speakman
207B PA	KI	coal	8 - 12 mesh	Sutcliffe Speakman
SA 1565	KI	coal	1.6- 4 mm	Ceca
BPJ	KI	peat	1 - 2 mm	Degussa
727	KI, I_2	coconut shell	8 - 16 mesh	Barnaby and Cheney
463563	KI, I_2	coconut shell	8 - 16 mesh	Mine Safety Appliances
207B	KI, TEDA	coal	8 - 12 mesh	Sutcliffe Speakman
208C	KI, TEDA	coconut shell	8 - 12 mesh	Sutcliffe Speakman
G615	KI, TEDA	coconut shell	8 - 16 mesh	Pica
RI 180	KI, TEDA	coconut shell	1.6- 4 mm	Pica
787	KI, TEDA	coconut shell	8 - 16 mesh	Barnaby and Cheney
Kiteg II	KI, amine [b]	coconut shell	8 - 16 mesh	Nucon
207B	TEDA	coal	8 - 12 mesh	Sutcliffe Speakman
Q	amine [c]	coconut shell	8 - 16 mesh	Nucon
X	org. iodide	coconut shell	8 - 16 mesh	Nucon

[a] 8 - 12 mesh: 2.0 - 1.4 mm (BS 410); 8 - 16 mesh: 2.4 - 1.2 mm (ASTM D2862)

[b] amine: alkyl derivative of TEDA (also additional impregnants)

[c] amine: quinuclidine

Table II: Parameters of the tests with CH_3I-131

Parameter	Unit	Value
Temperature	°C	30 [a]
Relative humidity	%	40 [a]
Throughput	m^3/h	0.88 [a]
Face velocity	cm/s	50 [a]
Preconditioning time	h	1 [b]
Injection time	h	1
Purging time	h	2
Bed depth	cm	50 [a, c]
Residence time	s	1 [a]
I-131 injected	mCi	0.01 - 0.1
I-127 injected	mg	1

[a] Value (largely) identical with that during the aging in the nuclear power plant

[b] $\geq$ 16 h with fresh carbon

[c] 20 beds of a depth of 2.5 cm (diameter: 2.5 cm); sequence identical with that during the aging in the nuclear power plant

Table III: Penetration of various impregnated activated carbons by CH_3I-131 at different bed depths and aging times

(Data of activated carbons: Table I; test data: Table II)

Name	Impregnant	Bed depth (cm)	Penetration (%) [a]			
			0 months	3 months	6 months	9 months
207B	KI	12.5 25.0 37.5	2.8 (-3) - -	2.2 (+1) 1.1 (0) 3.6 (-2)	1.6 (+1) 3.8 (-1) 8.1 (-3)	4.2 (+1) 4.3 (0) 3.5 (-1)
207B PA	KI	12.5 25.0 37.5	9.6 (-4) - -	1.2 (+1) 1.0 (-1) 2.2 (-4)	1.5 (+1) 3.9 (-1) 1.1 (-3)	5.0 (+1) 5.5 (0) 3.8 (-1)
SA 1565	KI	12.5 25.0 37.5	3.3 (-4) - -	1.1 (+1) 1.2 (-1) 2.0 (-4)	1.8 (+1) 2.6 (-1) -	4.8 (+1) 1.8 (0) 8.9 (-2)
BPJ	KI	12.5 25.0 37.5	4.6 (-3) - -	5.5 (+1) 4.0 (0) 4.6 (-2)	7.4 (+1) 2.0 (+1) 4.1 (-1)	9.3 (+1) 5.7 (+1) 1.4 (+1)
727	KI, I_2	12.5 25.0 37.5	1.5 (-3) - -	1.1 (+1) 1.0 (-1) 1.2 (-4)	1.8 (+1) 2.8 (-1) 8.7 (-4)	5.2 (+1) 2.4 (0) 3.3 (-3)

[a] 2.8 (-3) = $2.8 \cdot 10^{-3}$ etc;
-: penetration lower than minimum detectable penetration (10^{-5} - 10^{-4} %)
(also in Tables IV and V)

Table IV: Penetration of various impregnated activated carbons by CH_3I-131 at different bed depths and aging times

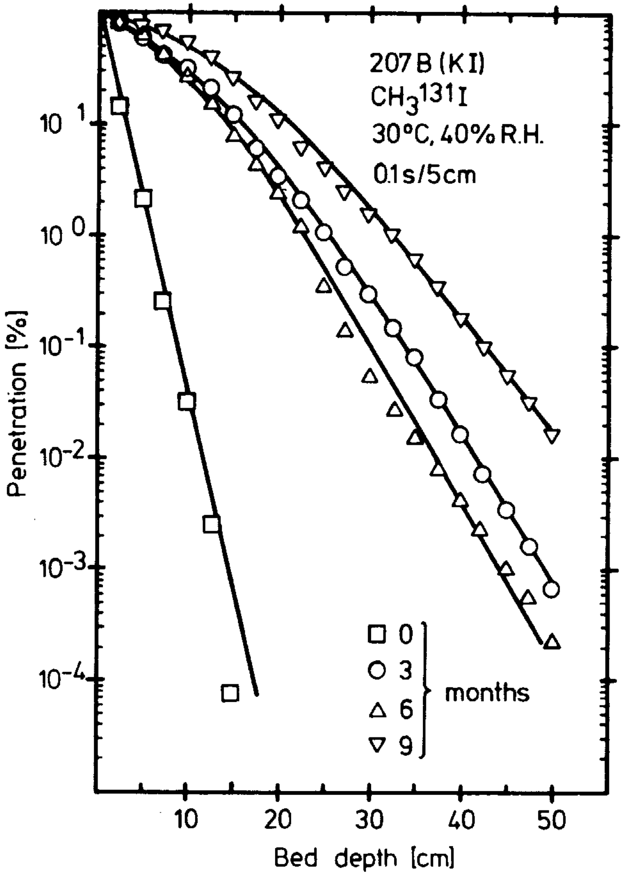
(Data of activated carbons: Table I; test data: Table II)

Name	Impregnant	Bed depth (cm)	Penetration (%)			
			0 months	3 months	6 months	9 months
463563	KI, I_2	12.5	3.8 (-4)	6.9 (0)	6.8 (0)	5.1 (+1)
		25.0	-	2.1 (-2)	3.1 (-3)	1.6 (0)
		37.5	-	-	-	1.2 (-4)
207B	KI, TEDA	12.5	-	2.4 (0)	1.4 (+1)	3.4 (+1)
		25.0	-	1.0 (-3)	1.5 (-1)	1.9 (0)
		37.5	-	-	5.2 (-4)	4.1 (-2)
208C	KI, TEDA	12.5	-	2.2 (-1)	1.1 (0)	1.7 (+1)
		25.0	-	-	-	1.3 (-2)
		37.5	-	-	-	-
G 615	KI, TEDA	12.5	-	4.8 (0)	1.6 (0)	3.2 (+1)
		25.0	-	4.2 (-2)	1.6 (-4)	6.1 (-1)
		37.5	-	5.8 (-4)	-	6.8 (-4)
RI 180	KI, TEDA	12.5	-	4.2 (0)	5.2 (0)	3.3 (+1)
		25.0	-	1.1 (-2)	4.8 (-3)	4.3 (-1)
		37.5	-	-	-	1.1 (-4)

Table V: Penetration of various impregnated activated carbons by CH_3I-131 at different bed depths and aging times

(Data of activated carbons: Table I; test data: Table II)

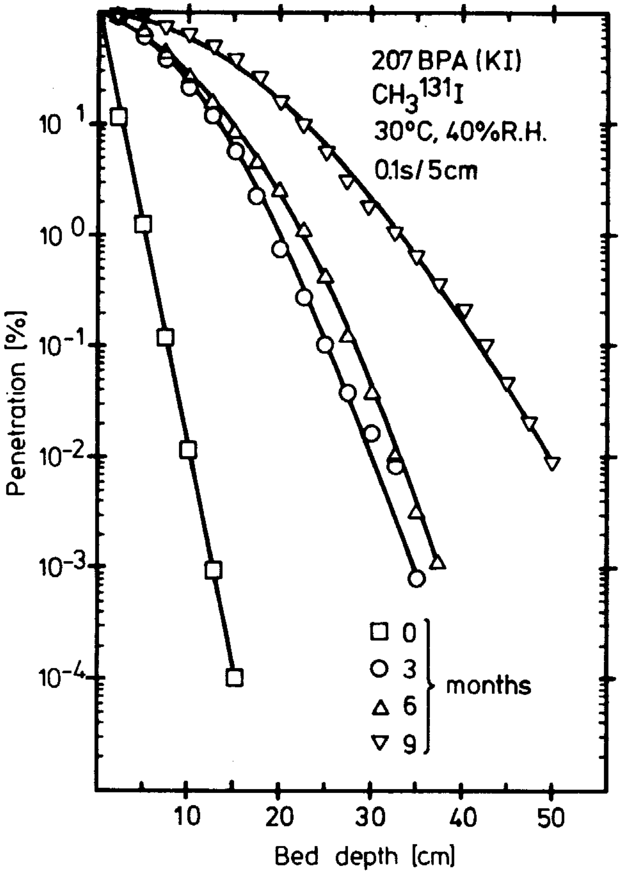
Name	Impregnant	Bed depth (cm)	Penetration (%)			
			0 months	3 months	6 months	9 months
787	KI, TEDA	12.5	-	2.9 (-1)	2.4 (0)	2.0 (+1)
		25.0	-	-	8.0 (-5)	7.8 (-2)
		37.5	-	-	-	-
Kiteg II	KI, amine	12.5	3.6 (-5)	5.8 (0)	1.8 (1)	5.8 (+1)
		25.0	-	2.7 (-2)	2.3 (-2)	1.8 (0)
		37.5	-	-	-	2.3 (-3)
207B	TEDA	12.5	-	9.9 (-1)	2.8 (0)	2.5 (+1)
		25.0	-	-	9.1 (-4)	1.2 (-1)
		37.5	-	-	-	-
Q	amine	12.5	5.4 (-5)	5.3 (0)	1.5 (+1)	4.9 (+1)
		25.0	-	7.1 (-3)	1.4 (-2)	8.0 (-1)
		37.5	-	-	-	1.7 (-3)
X	org. iodide	12.5	-	4.9 (0)	5.1 (0)	4.4 (+1)
		25.0	-	8.8 (-3)	4.6 (-3)	2.6 (-1)
		37.5	-	-	-	-



LAF II D861E

Penetration as a function of bed depth
at different aging times

Fig. 1 [a]

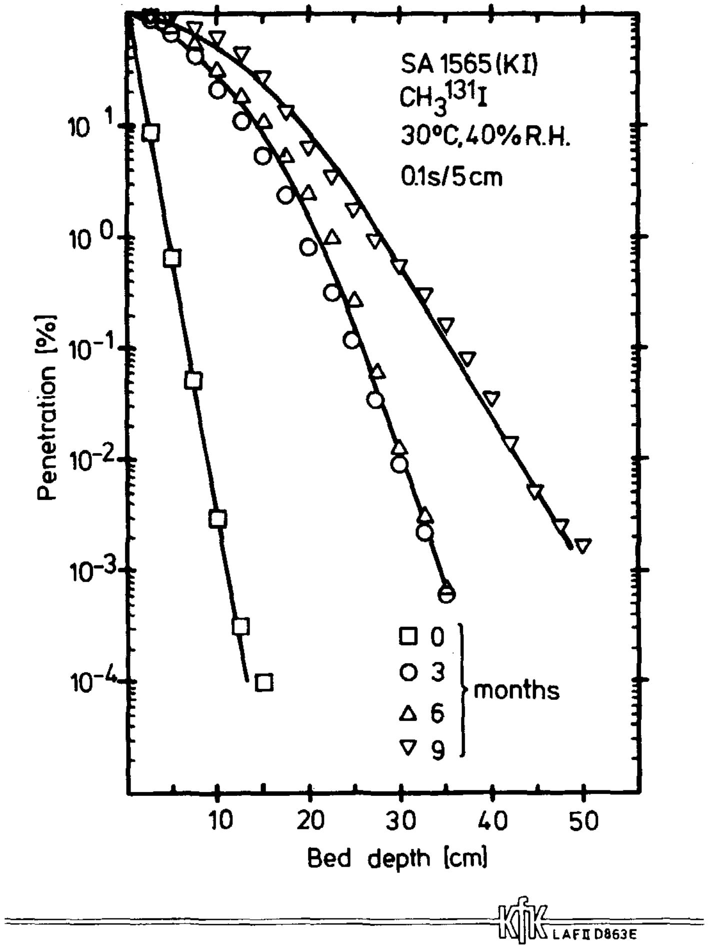


LAF II D862E

Penetration as a function of bed depth
at different aging times

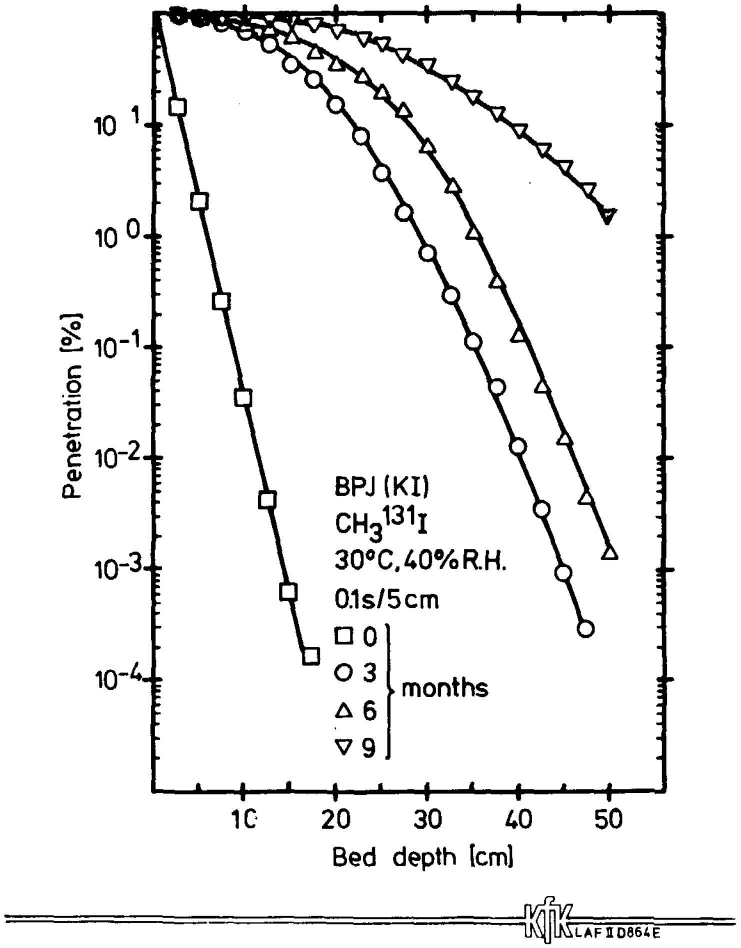
Fig. 2 [a]

[a] No overlapping of the aging periods (also in Figs. 3 - 15)



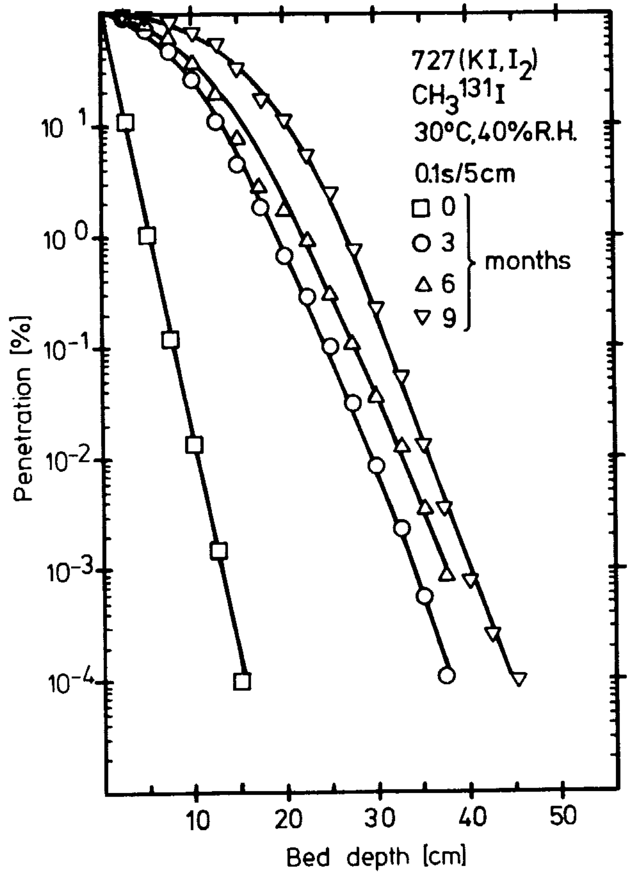
Penetration as a function of bed depth at different aging times

Fig. 3



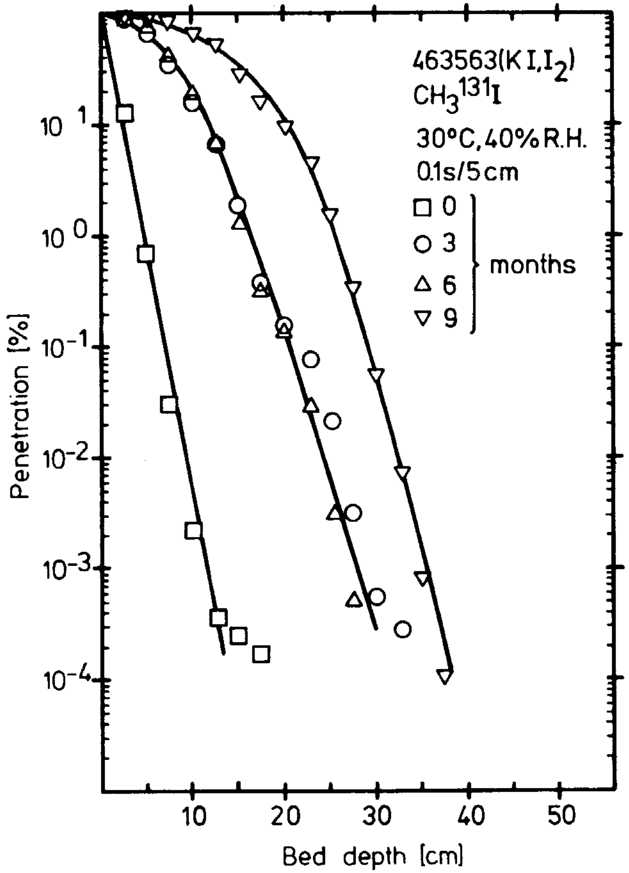
Penetration as a function of bed depth at different aging times

Fig. 4



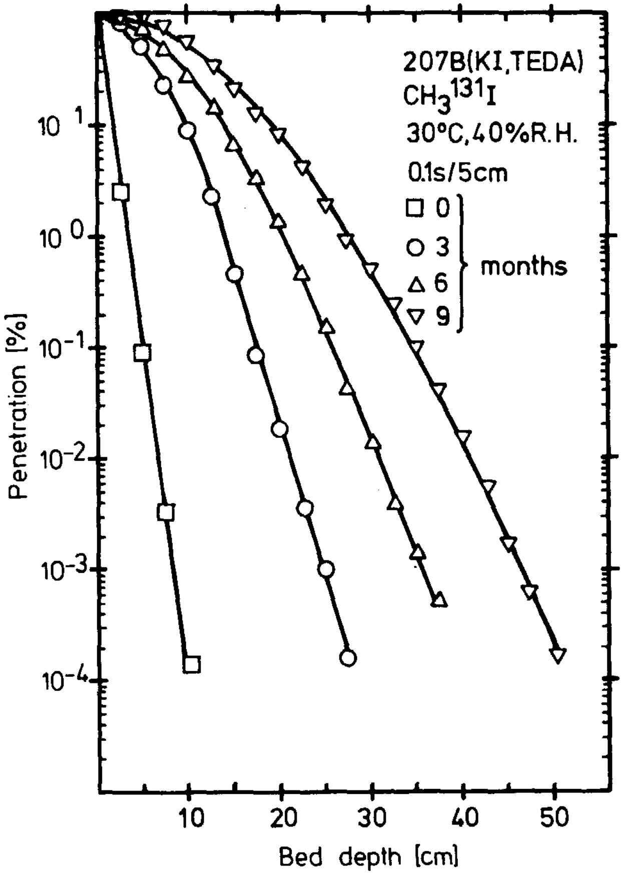
Penetration as a function of bed depth
at different aging times

Fig. 5



Penetration as a function of bed depth
at different aging times

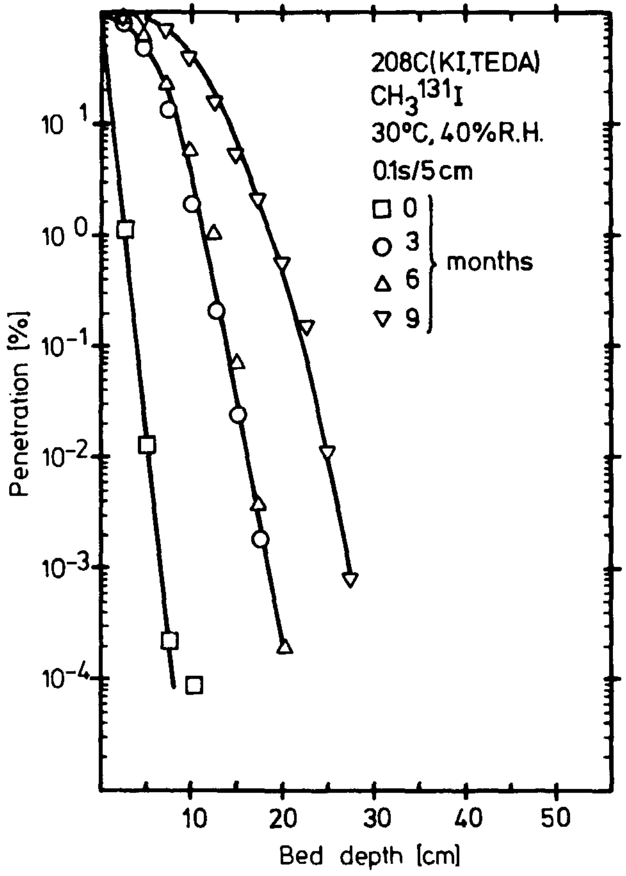
Fig. 6



KfK LAF II D867E

Penetration as a function of bed depth at different aging times

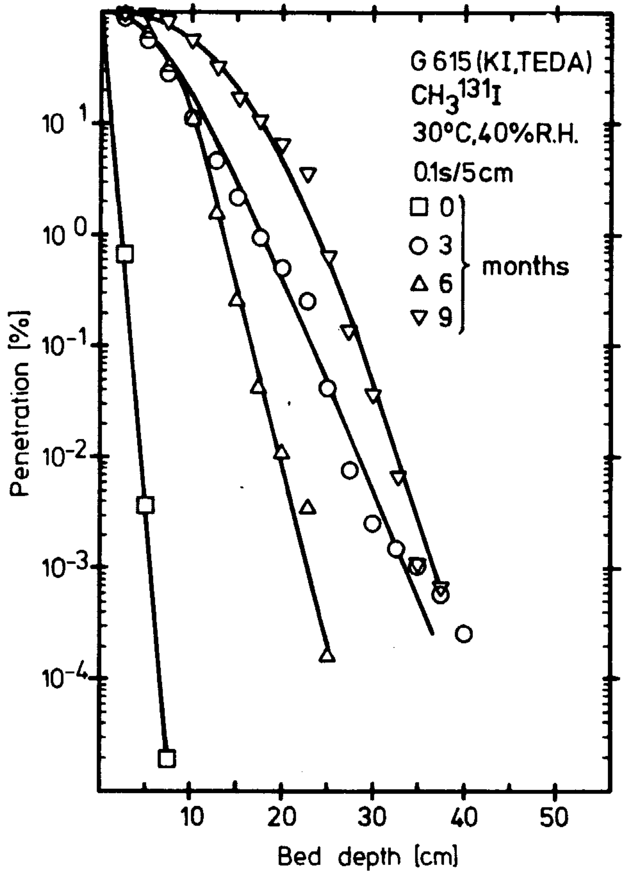
Fig. 7



KfK LAF II D8613E

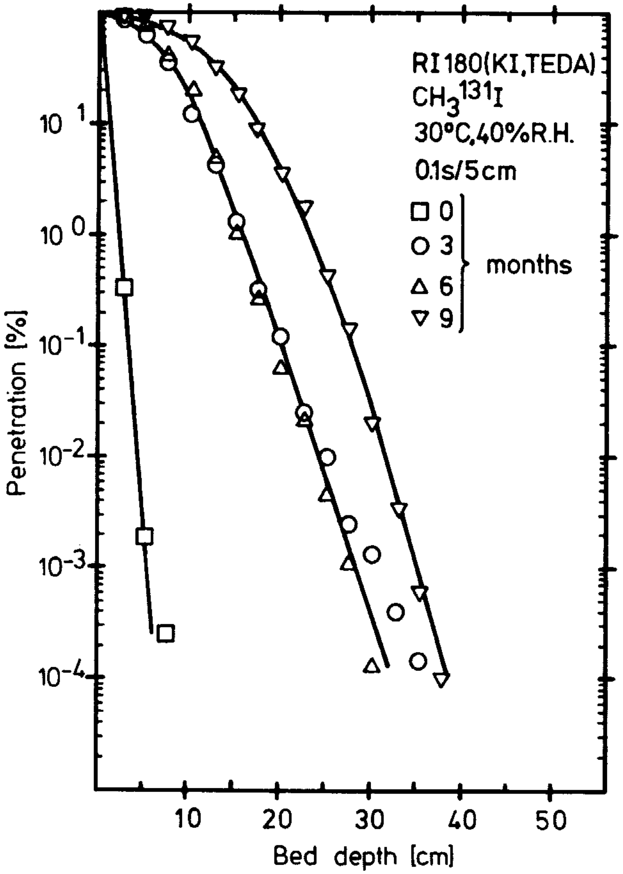
Penetration as a function of bed depth at different aging times

Fig. 8



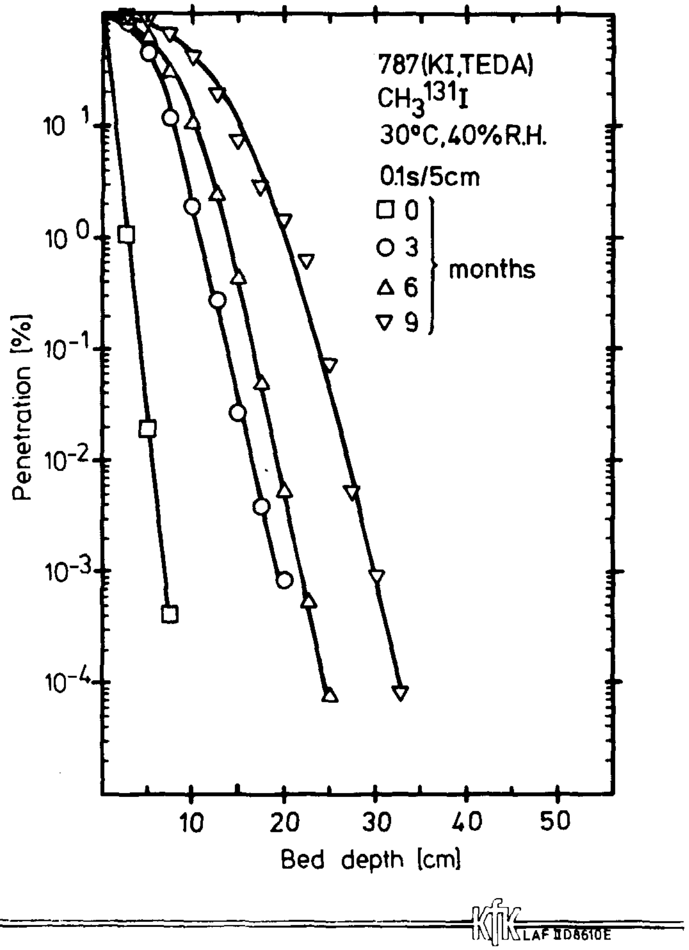
Penetration as a function of bed depth
at different aging times

Fig. 9



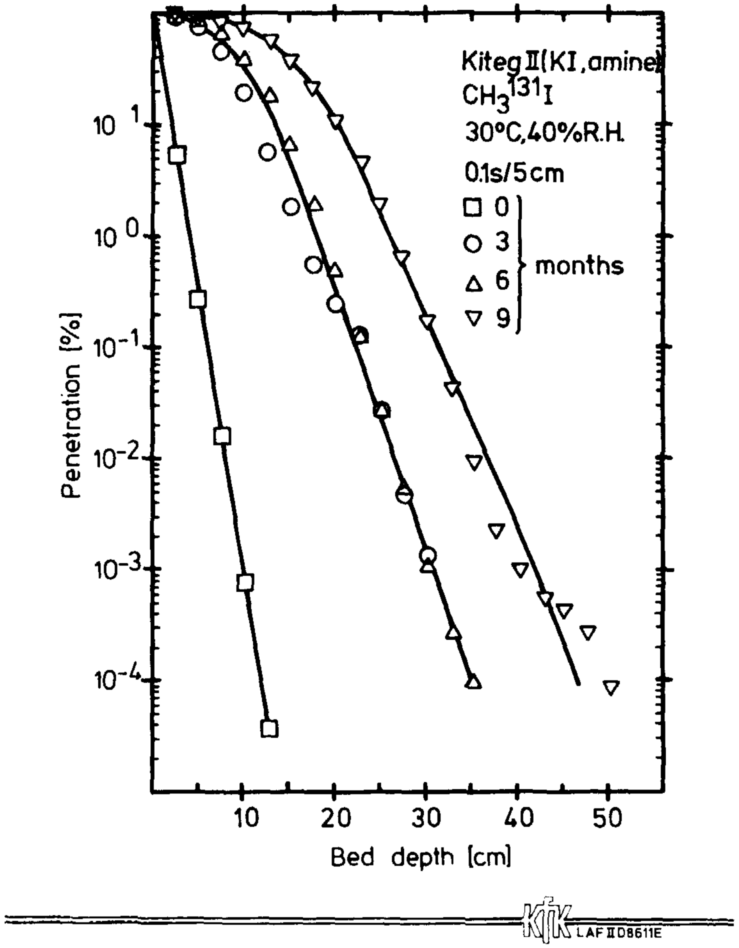
Penetration as a function of bed depth
at different aging times

Fig. 10



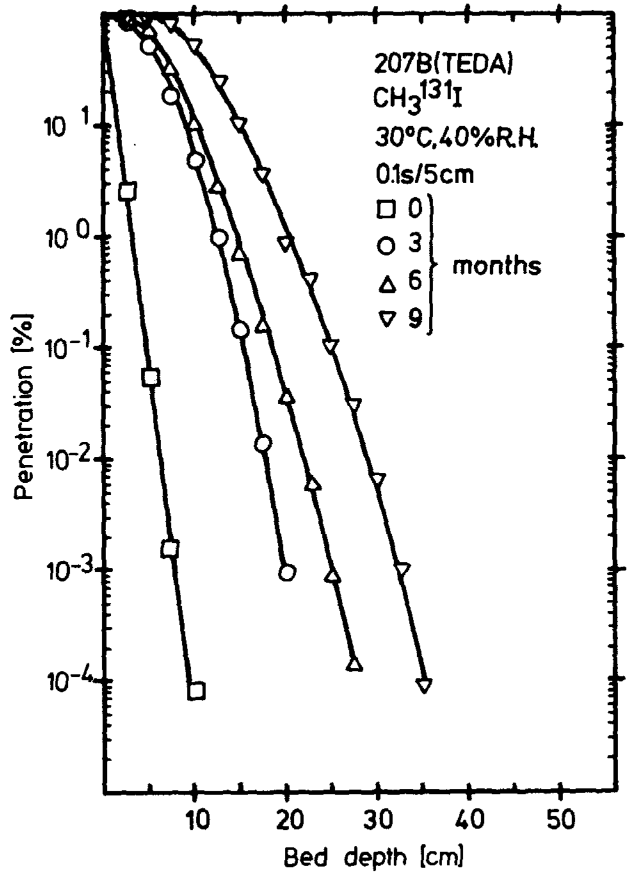
Penetration as a function of bed depth
at different aging times

Fig. 11



Penetration as a function of bed depth
at different aging times

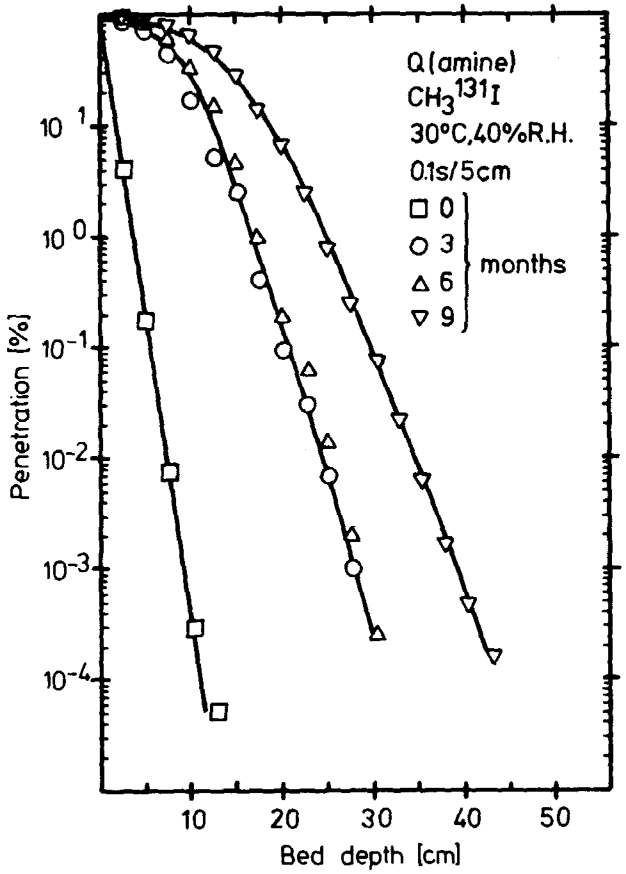
Fig. 12



LAF I D8612E

Penetration as a function of bed depth
at different aging times

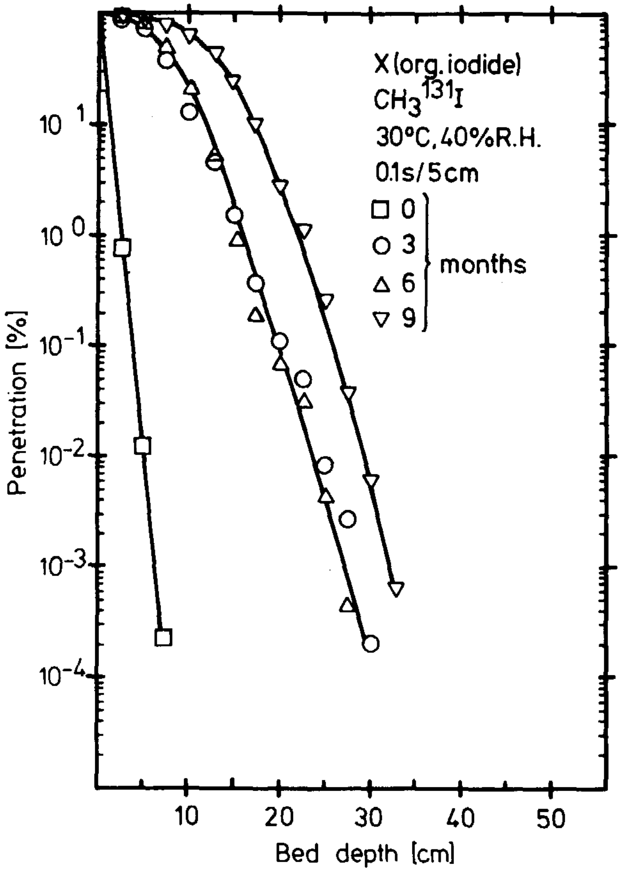
Fig. 13



LAF II D8614E

Penetration as a function of bed depth
at different aging times

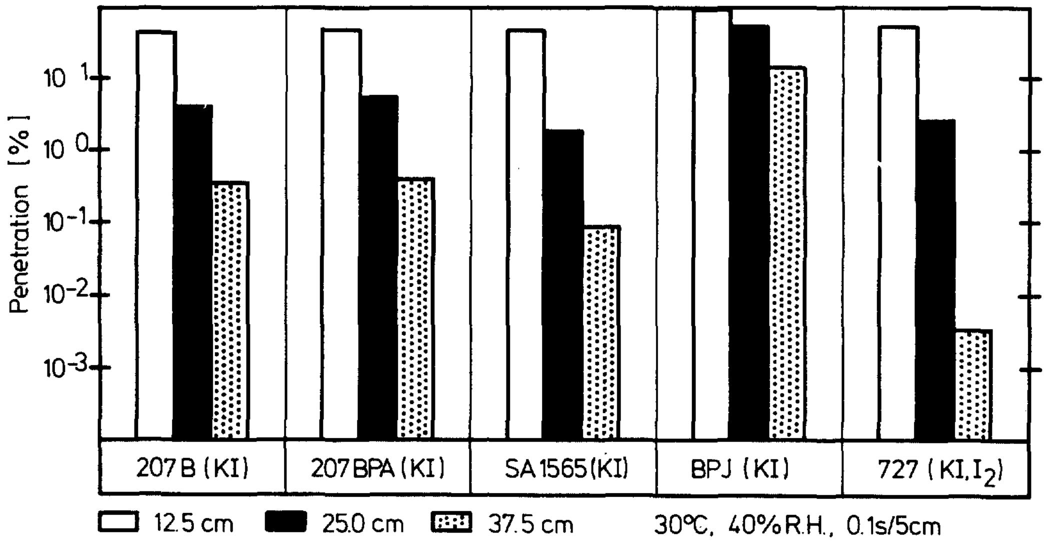
Fig. 14



LAF II D8615E

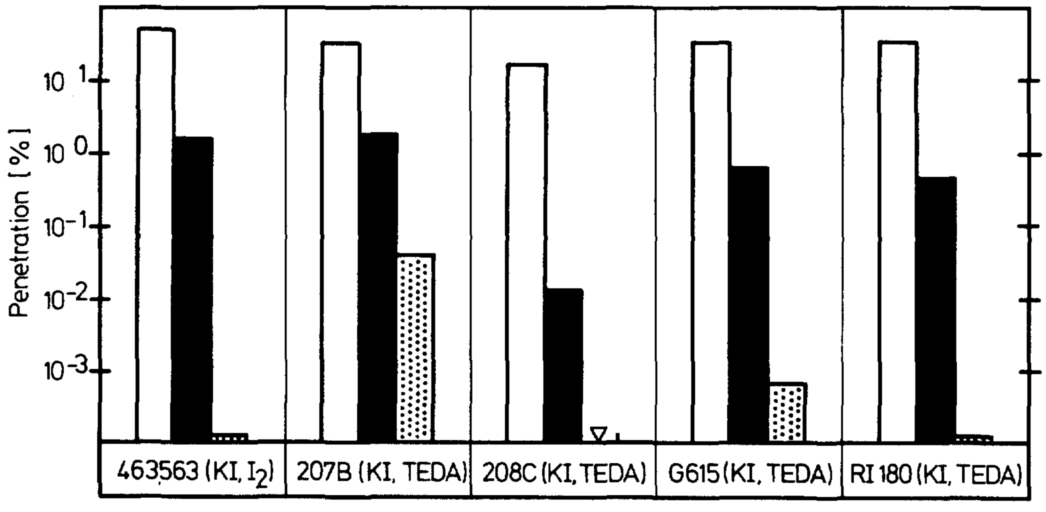
Penetration as a function of bed depth at different aging times

Fig. 15



Penetration of various impregnated activated carbons by $CH_3{}^{131}I$ at different bed depths (aging time: 9 months)

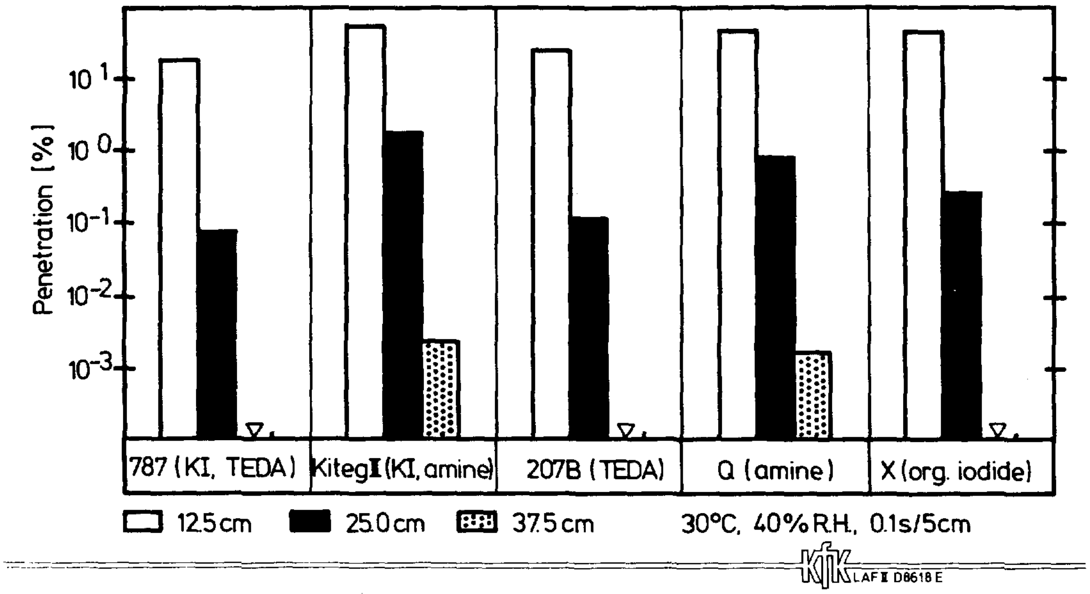
Fig. 16



Penetration of various impregnated activated carbons by $CH_3{}^{131}I$ at different bed depths (aging time: 9 months)

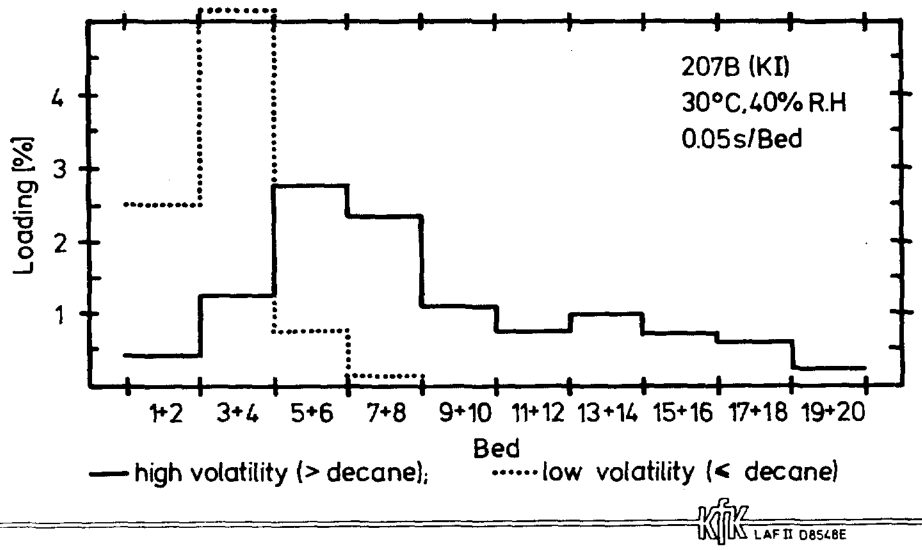
Fig. 17 [a]

[a] ∇: penetration lower than 10^{-4} % (also in Fig. 18)



Penetration of various impregnated activated carbons by $CH_3{}^{131}I$ at different bed depths (aging time: 9months)

Fig. 18



Loading of activated carbon beds with organic compounds of different volatility at an aging time of 9 months

Fig. 19

DEPTH PROFILE OF METHYL IODIDE-131 IN THE TESTING OF USED AND REGENERATED ACTIVATED CARBONS

by

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Introduction

The capability of nuclear grade carbons to remove radioiodine is slowly reduced after being placed in service. The methyl iodide-131 penetration measurements to be described in this paper were obtained for such used carbons obtained from different nuclear power installations and after known exposures to flows of outdoor air.

The retention of radioiodine within a carbon bed can be characterized by a depth profile, i.e., by the radioiodine count as a function of depth along the line of flow. In the measurements to be described the sample was thoroughly mixed and the carbon bed (50.8 mm) divided into four equal sections, separated by disks of glass filter paper. After the test each section was removed and counted; the depth profile was calculated from the counts of the four sections. The percent penetration was also determined after mixing the four sections thoroughly and counting the mixture with the same geometry as the backup beds. The calculation was as follows:

$$P = \frac{\text{counts of the backup beds x 100}}{\text{counts of total sample + backup beds}}$$

It will be shown that the depth profile contains information that is additional to the penetration and can be used as an index of the need to replace the carbon in the carbon adsorber.

Experimental

The sources of the used carbons are given in Table 1. All carbons were significantly degraded as judged by the penetration of methyl iodide-131 determined at 30°C and 95% RH. The samples were not prehumidified before the determination. Some of the carbons had been exposed to an unfiltered flow of outdoor air at different locations for known duration (1). The kinetic parameters of the ASTM D-3803 test procedure (2) were used in these measurements.

Table 1. Sources of Used Carbons and Penetration of Methyl Iodide-131 at 30°C and 95% RH.

NRL Number	Exposure	DURATION (months)	% Penetration 30°C
5337	After continued use in Carbon Adsorber	22	49.2
5338	In use in Spent Fuel Vent. System	6	26.7
5339	Removed from Spent Fuel Vent. System	~36	53.5
5340	Removed from Spent Fuel Vent. System	~36	58.6
	Continuous Flow of Unfiltered Outdoor Air		
5226	KI BC 727	15	6.0
5229	KI BC 727	32	22.4
5239	KI BC 727	40	9.5
5214	KI + TEDA BC 787	9	10.0
5235	KI + TEDA BC 787	27	10.1
5151	KI + TEDA KITEG-II	24	38.9
5170	KI + TEDA G-615	20	23.4
5169	5% TEDA on Coal Base	20	76.6
5208	5% TEDA on Coal Base	5	24.4
5208A	5% TEDA on Coal Base	5	30.6

The percentage of total counts of methyl iodide-131 retained in each section are given (Table 2) arranged in the same sequence as the samples in Table 1. The ordering of counts in the inlet to outlet sections decreased in many cases; it remained constant in others, and actually increased for five samples exposed to continuous flows of outdoor air. The behavior shown, Figure 1, for a 5% TEDA impregnated carbon had been exposed for 163 days in Simi Valley, CA (May 14 to October 24). Two determinations were made in order to check this surprising result. The behavior is quite different than that reported for new carbons where the penetration is exponential with depth.(3) Since the carbon test sample was uniformly introduced, the radioiodine-131 must have migrated from the inlet to the outlet

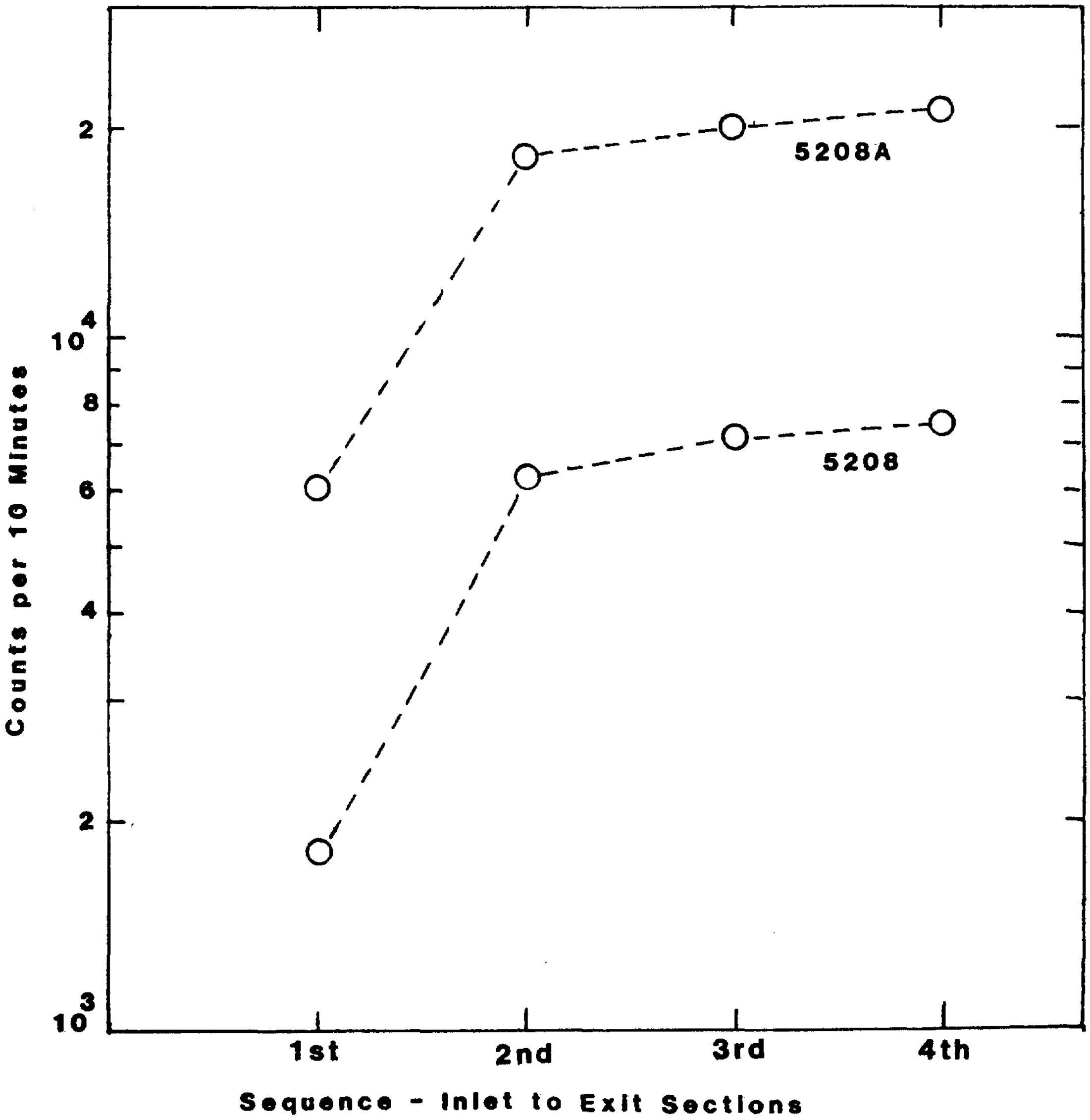

Figure 1. Migration of Methyl Iodide-131 During the Test of a 5% TEDA Charcoal After 163 Days Exposure to an Outdoor Airflow (Simi Valley, CA).

section during the test period. The concentration of methyl iodide-127 in the dose is approximately 10^9 times that of methyl iodide-131 and together with the iodine -127 in a KI impregnated carbon constitutes for new carbons a very large mass-action factor in favor of a successful iodine isotope exchange. However, the radioactive iodine can migrate in used carbons.

Table 2. Percentage of the Total Radioiodine-131 Counts in the Four Layers.

NRL Test	Penetration %	Layer 1	Layer 2	Layer 3	Layer 4
5337	49.2	48.2	24.2	16.1	11.5
5338	26.7	35.9	28.6	19.1	15.7
5339	53.5	25.0	24.1	25.1	25.8
5340	58.6	24.7	25.6	25.7	24.0
Continuous Flow of Unfiltered Outdoor Air					
5226	6.0	44.6	24.2	21.0	10.2
5229	22.4	42.8	23.5	18.0	15.7
5239	9.5	54.3	24.8	12.7	8.3
5214	10.0	16.5	46.5	21.7	15.2
5235	10.1	44.8	22.6	23.6	9.1
5151	38.9	1.6	27.7	37.3	33.4
5170	23.4	2.3	28.8	39.2	29.7
5169	76.6	0.9	4.6	7.1	87.5
5208	24.4	7.9	27.8	31.2	33.0
5208A	30.6	9.3	27.8	30.7	32.2

Discussion

A carbon adsorber is exposed to a variety of environmental contaminants during a long service life without regeneration. The slow degradation of the iodine trapping is due in part to the loss of adsorption, to the loss of chemical reactivity, and above all to the loss of iodine isotope exchange efficiency.

The contaminants that do accumulate can influence a methyl iodide-131 penetration test in several ways. Those that are involved in an iodine isotope exchange mechanism can be divided into two main groups:

Group I: Regenerated by chemical reduction.

Group II: Exposed to high molecular weight compounds and cannot be regenerated.

It has been found that many used carbons of Group I, but not all, can be regenerated by a chemical reaction with hydrazine (N_2H_4)(4). In one mode of degradation the iodide ions (the site of the iodine isotope exchange) are oxidized with the formation of compounds such as IO_x. These sites can be regenerated by a chemical reduction with hydrazine vapor at room temperature. An example of Group A (Figure 2) is a TEDA-impregnated carbon removed after 22 months service of

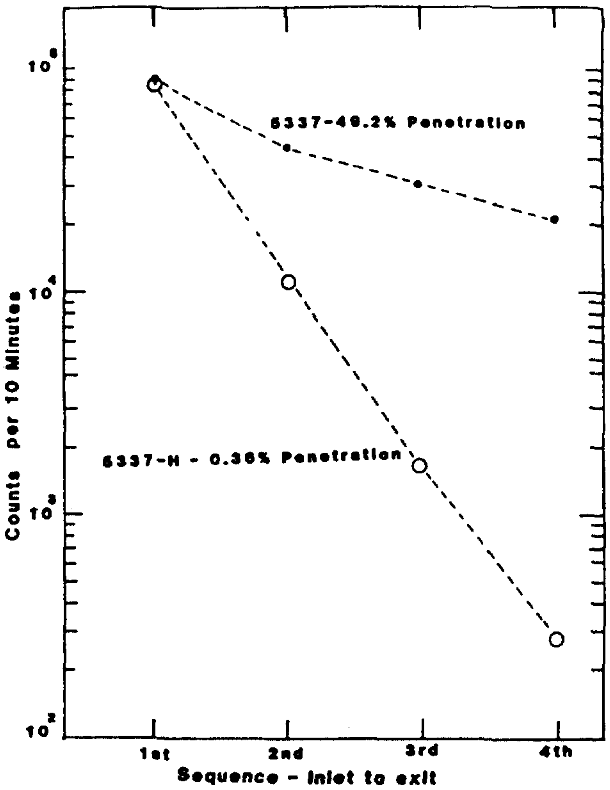

Figure 2. Depth Profile Through a TEDA-Carbon Removed From a Plant-Scale Carbon Adsorber (Before and After Hydrazine Treatment).

continuous use in a plant-scale carbon adsorber. The gradient of counts in the bed after regeneration is quite steep relative to that before regeneration.

Group II of used carbons are those that have adsorbed high molecular weight vapors during service, such as diesel exhaust gases, and these sites cannot be regenerated at room temperature by chemical reduction. The surface areas are very small and presumably the isotope exchange sites have been covered by the adsorbed vapors. One example (Figure 3) is for a carbon removed from the spent fuel handling ventilating system. There appears to be a point of no return for a heavily degraded carbon. The gradient of counts through the bed

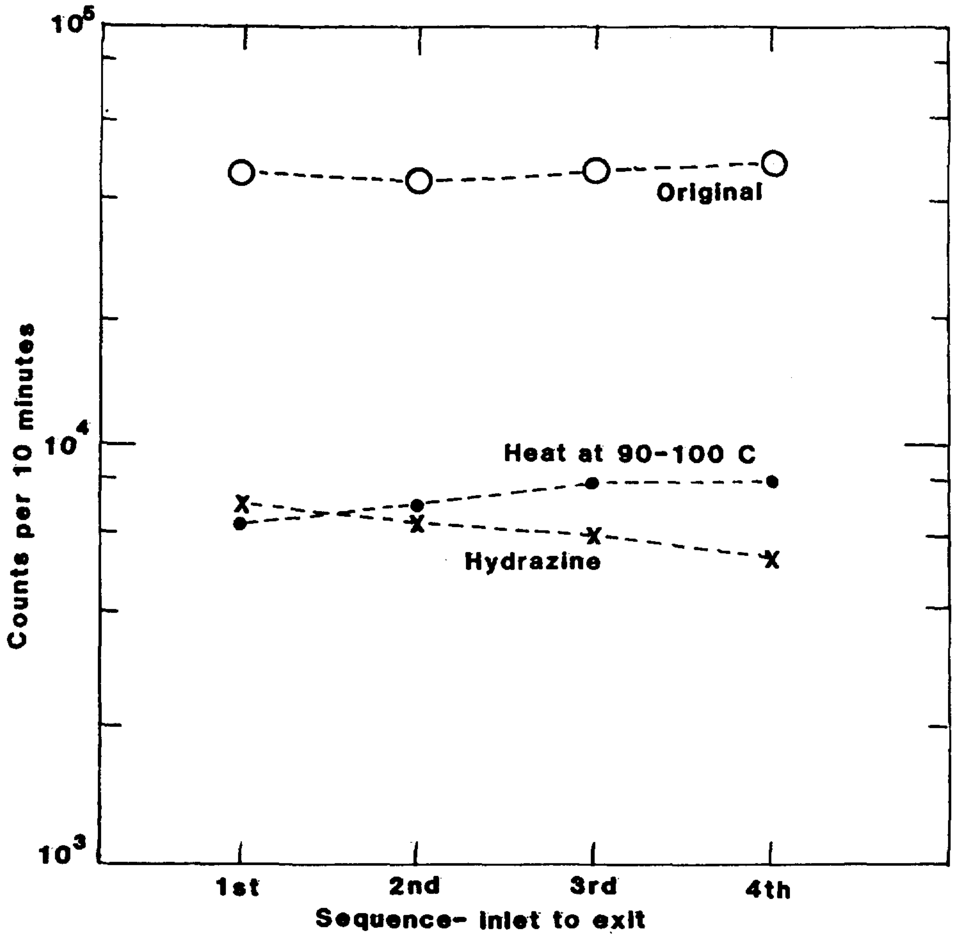

Figure 3. Depth Profile Through a KI-Carbon Removed from a Spent Fuel Ventilating System-Before and After Hydrazine Treatment and After Heating at 100°C for 48 Hours. (NRL 4339).

is obviously quite small. The sample (4339H) after hydrazine treatment was placed in the oven for about 50 hours (90-100°C). This furthered the degradation to almost completion, namely 84.3% penetration (Figure 3). Apparently, the mobility of the contaminants can further lead to the loss of the isotope exchange properties of certain used carbons.

In order to emphasize the uniqueness of iodine isotope exchange in the trapping of methyl iodide-131, three tertiary amine salts were prepared with methyl iodide-127 (Table 3A). Aliquots of the coconut shell charcoal (NACAR G 210-S) were impregnated with 2 wt.% of each salt. The methyl iodide-131 penetration was determined for each preparation and also the percentage of the total counts retained in each section (Table 3B).

Table 3A. Preparation of Methyl Iodide Salts of Three Tertiary Amines

Impregnant	MP °C	Iodine % calcd.	Iodine % obsd.
Quinuclidine · CH_3I	385	50.2	49.9
TEDA · 2 CH_3I	275	64.14	64.07
Hexamethylenetetraamine · CH_3I	205	45.04	45.0

Table 3B. Penetration of Methyl Iodide-131 and the Percentage of Total Counts in the Four Sections (Prehumidification at 95% RH for 16 Hours).

	Percentage of Total Counts 1	2	3	4	Penetration %
Quinuclidine · CH_3I	79.0	19.9	1.01	0.03	0.0
5299 TEDA · $2CH_3I$	71.4	18.7	7.4	2.4	0.38
5307 " "	80.5	14.6	3.6	1.2	0.23
5307 " "	95.6	3.7	0.26	0.09	0.03
Hexamethylenetetra-amine · CH_3I	73.5	20.9	4.7	0.86	0.23

The measurements show a very high iodine isotope exchange efficiency. Since all of the tertiary amine was tied up in the salt and not available to trap methyl iodide-131, and the physical adsorption of carrier methyl iodide was reversible, the trapping was limited to an iodine exchange with the iodide ion of the impregnated salt. The gradient of counts within the test column was quite steep as previously reported for new carbons.(3) However, the slope of the log count vs depth was not linear for these impregnations (Figure 4) and very little I-131 was found in the outlet sections.

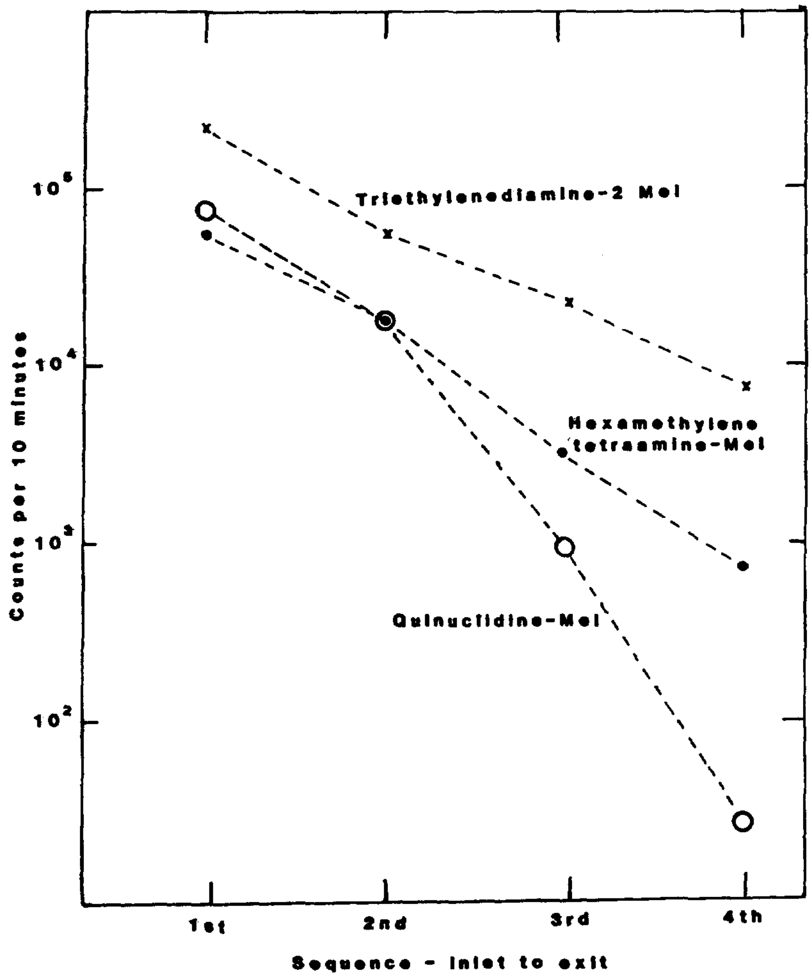

Figure 4. Counts per 10 minutes of Methyl Iodide-131 in the Four Sections of the Test Beds (Salts of MeI and Tertiary Amines on NACAR G-210S).

To determine if the methyl iodide-127 in the dose might react with either a KI or a TEDA impregnation, the adsorption of the vapor was determined. A KI-impregnated coconut shell charcoal (MSA 463563) and a TEDA-impregnated charcoal (S8S 5% TEDA) were used (Figure 5). The adsorption on the KI-carbon was Langmuir-type and that on the TEDA-carbon had a less-sharp knee and followed the Type II isotherm. Of greater importance is the fact that the methyl iodide can be desorbed from new carbons in the observed pressure range with no significant retention by either impregnation. The system was moisture-free in the above measurements. However, the adsorption of methyl iodide-127 on used carbons is not reversible in many cases.

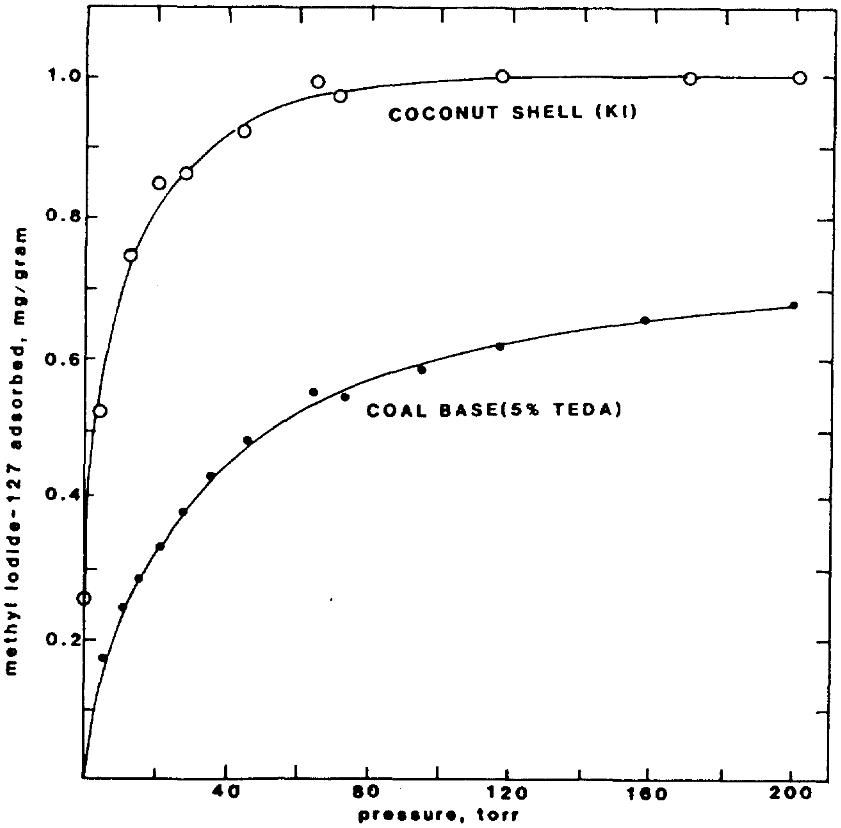

Figure 5. The Adsorption of CH_3I-127 Vapor at 31.7°C on Two New Impregnated Activated Carbons.

A mechanism is required to account for the migration of methyl iodide-131 to the lower sections of a uniformly-packed test column of used carbon. The possibility can be raised that chemical species are present that could react to form elemental iodine and thus move the trapped iodine-131 down the column as $I^{131} - I^{127}$. The changing surface composition of used carbons has developed as follows: First, the KI-impregnated sites have been oxidized during its service forming IO_x groups which do not enter into iodine isotope exchange. Second, in used carbons the acidity of the carbon surface has increased as shown by the low p^H of the water extracts. Third, in the relatively high concentration of methyl iodide-127, addition compounds to contaminants can form yielding iodide species at various places along the length of the column. The stage is thus set for the liberation of molecular iodine:

$$I^- + IO_x \longrightarrow I_2 + IO_{x+1}$$

The exchange reaction forming $^{131}I - {}^{127}I$ can then move the activity down the column. Preliminary experiments indicate these reactions are present in testing used carbons.(5)

The BET surface area of a carbon (NRL 5338) in use in a Spent Fuel Ventilation system was 1040m^2/g and this increased after hydrazine treatment to 1540 m^2/g. On a carbon removed earlier from the same system (NRL 5339) had a surface area of 670 m^2/g and did not improve with hydrazone treatment. Hence, there are varied and significant structural changes during the life of a used carbon.

Concluding Remarks

1. The depth profiles of CH_3I-131 in a carrier of CH_3I-127 show complex behavior in testing for the penetration of used nuclear-grade carbons. The carbons obtained from nuclear power plants and those from weathering in a continuous flow of unfiltered outdoor air show similar properties.

2. The depth profiles of the CH_3I-131 retained in the test beds of used carbons were either negative, zero, or positive for different samples. The isotope-exchanged iodine located in the entering section can definitely migrate down the bed during the dose period in the presence of methyl iodide-127. This does not happen for new carbons and the explanation must reside in the influence of certain contaminants that accumulate in the carbon.

3. Migration of I-131 takes place along the line of flow due to the formation of adsorbed elemental iodine from the adsorbed impurities. The exchange product ^{131}I $-^{127}I$ can then move the activity down the column.

4. Obviously, one cannot improve the performance of a carbon adsorber until a satisfactory procedure is developed for testing used carbon. A test should reveal the residual life as well as the existing penetration. A used carbon from a carbon adsorber has become so, not only because of contact with water vapor, but after contact with the many local and atmospheric contaminants. The combined influence on the carbon and its impregnation can lead to profound

changes that must be taken into account in a test procedure. The influence of water vapor in itself does not have sufficient generality to be useful in evaluation of used carbons.

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DISCUSSION

RIGBY: I would like to ask your opinion. When we talk about the aging of carbon, two different things can happen. One is oxidation due to oxygen and humidity. The second is organic contaminants. The first has been studied in depth. But very little work has been done on what happens with organic vapors. Do you think there is any merit in putting a sacrificial guard bed of unimpregnated activated carbon in front of the impregnated carbon bed? I mention this in particular because the Central Electricity Generating Board, in England, following studies last year, are in fact doing that at one of their power stations.

DEITZ: The contaminants of the air are of constant supply and invariably lead to the degradation of nuclear-grade carbons by weathering. Organic vapors (from solvent spills, paint vehicles, and lubricant sources) are more variable. These vapors, of course, must be sufficiently volatile to reach the carbon filter. A guard bed of activated carbon is not a permanent sink for organic vapors physically adsorbed. For example, benzene vapor may be adsorbed by activated carbon at a low relative humidity (below 50% RH) only to be released by an air flow at a higher relative humidity. Also, a bed of activated carbon acts like a chromatographic column and the incident pulse of organic vapor will eventually be in the effluent during long service in a power station. It is dubious, in my opinion, if a guard bed of activated carbon would be cost effective when placed in front of the nuclear-grade carbon.

MULTIPLE USE FILTER CELL - COMPARATIVE MEASUREMENTS

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Abstract

A new activated carbon filter cell has been developed that will yield higher decontamination factors for iodine and smaller leakages in the housing in comparison with other filter cell type units. This type of filter cell can be used several times by simply replacing the charcoal and the sealing.

The measured decontamination factors are given and compared with the values of other cells.

I. Introduction

In German nuclear power stations the relevant activated carbon filters are of the deep bed filter type. But filter cells are also used in small iodine filter systems such as for example in laboratory vent air. There are disposable filter cells and multiple use filter cells. The latter offer the advantage that they help to minimize the amounts of waste and hence require less expenditure for eliminating the smaller activity loadings to be expected.

The application of this type of multiple use reuseable filter cells implies a cleaning of the housing and mere replacement of the sealing and the sorption material.

Disposable filter cells and replaceable filter cells offered on the market have been investigated and examined with a view to removal efficiencies. It has appeared that some of the values obtained are far below the values to have been expected from the carbon used and the residence times evaluated. The plots of decontamination factors which, in part, run horizontally or have an extremely flat course while the face velocity undergoes variations, are an indication of mechanical leaks between the upstream and downstream filter sides.

II. The Problem

Considering these results, a new activated charcoal filter cell should be developed which should reduce the number of drawbacks listed above and produce higher decontamination factors than the multiple use filter cell.

As a first step, the greatest carbon volume possible should be enclosed, the carbon should be capable of the highest possible degree of utilization, and the pressure loss should be at a minimum. Carbon compaction in transit and during operation which cannot be ruled out, should be compensated for in order to avoid potential leakages.

III. Design Concept

A major improvement consisted in moving the lid for filling the filter cells to the rear (downstream side), in order to avoid leakages through the lid (Fig. 1). By appropriate design of the boundary zone it has been ensured that the air path through the filter cell is always equivalent to the thickness of the filter layer.

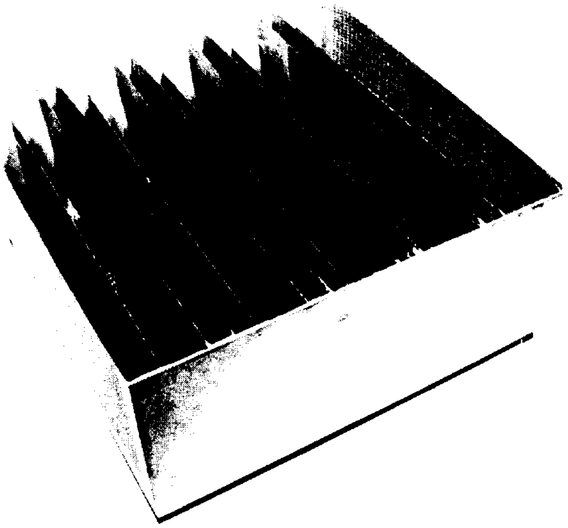

Fig. 1

For this reason, the slits have been arranged up to a distance equivalent to 2.5 cm border periphery for the case of 5 cm filter layer thickness (Fig. 2). The front faces of the V-pleats, except for the outermost entrance faces, are likewise slitted on the upstream and downstream sides in order to avoid that there are carbon zones not passed by the flow.

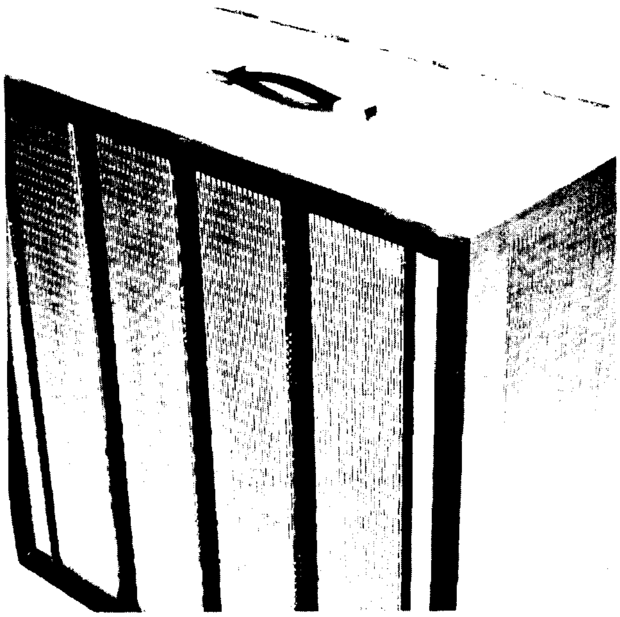

Fig. 2

For this reason, a permanent, elastic, air-transparent fleece has been placed on the lid side which on account of its high elasticity at the same time applies pressure onto the carbon (Fig. 3). Spacers are used to arrange the V-pleats in such a way that the distance between them is always the same. The spacers are equipped with threaded holes on the downstream side for lid mounting and pressing (Fig. 4).

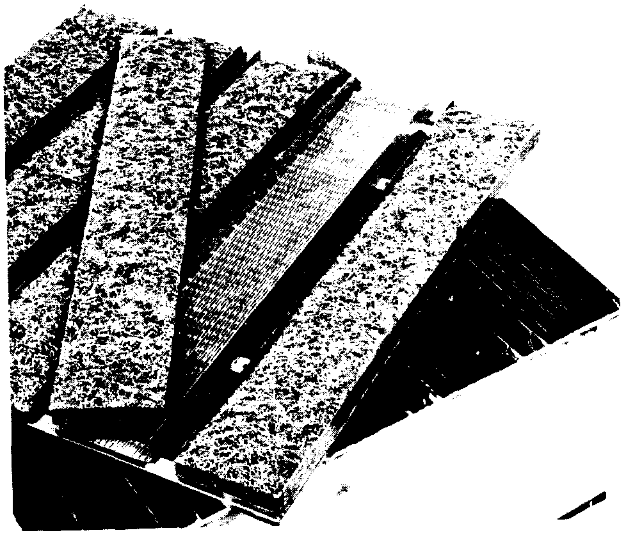

Fig. 3

The elastic material consists of rubberized hog's bristles which are permanently elastic up to 80 °C and cover the rear carbon filling holes.

The cell sealing is glued onto the cell and replaced in each refilling step. The cell is made completely of stainless steel and hence readily amenable to decontamination if necessary (Fig. 5).

The coal fill amounts to about 85 l of activated carbon whose granulation should not be smaller than 1.2 mm because for reasons of fabrication technology the slits are 1 mm in width. During the design stage particular attention was paid to avoiding any sharp edges which ensures that the carbon filters, like the HEPA filters, can be replaced in the plastic bag replacement mode, should the need arise.

The dimensions conform to the current filter cell sizes of 610 x 610 x 292 mm = 24" x 24" x 11.5". By an increase of the face area the pressure drop has been reduced to extremely low values and the volumetric flow rate has been increased, respectively.

Fig. 4

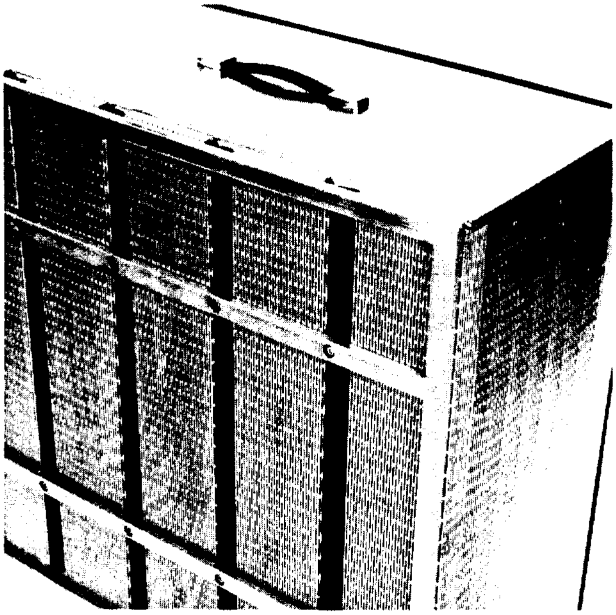

Fig. 5

IV. Test Equipment and Method of Measurement

The tests for determination of the decontamination factor were performed in the TAIFUN test bench under standard conditions at 1 bar, 30 °C, 70% relative humidity, using radioactive methyl iodide CH_3I-131 as the tracer /1/.

The decontamination factor can be calculated from the ratio of upstream air activity to downstream air activity which is determined with a Ge-Li detector.

V. Conducting the Experiment

The filter cells were tested for flows between 800 - 1500 m^3/h in the circulated air mode. The tracer is introduced into the central part of the piping, at several meters distance upstream of the test section (about 2 mCi within 5 minutes).

Upstream and downstream of the filter to be tested samples were collected from a gas stream using a perforated tube frame extending over the whole cross section of the test section, and the samples were transferred to activated carbon filters. The samples were measured and evaluated.

VI. Results

Fig. 6 shows the results of cells tested until now. Fig. 7 shows the improvements made, measured on the first prototypes.

It is to be seen, that the decontamination factors in the Karlsruhe Nuclear Multiple Use Cell are higher by the factor of approximately 10 than the decontamination factors of the welded and the multiple use filter cells, respectively, of different designs.

This is achieved, on the one hand, by the greater carbon volume, and, on the other hand, by the better utilization of the carbon caused by the greater face area in the increased perforated zone.

Comparison of pressure loss plots

Measurements on an industrial scale Karlsruhe Nuclear Multiple Use Cell yielded pressure drops of approximately 1.1 mbar at 800 m^3/h. These values are still below the level of pressure losses of welded disposable cells, despite the higher carbon volumes as can be seen in Fig. 8.

VII. Conclusions

The results show, that the new filter cell will give higher decontamination factors with a lower pressure drop using some simple construction ideas. It is expected, that the number of times such filter units can be reused will be greater than 20. So we use 2 sets of filter cells in our installation. One is under operation, the other set has time for decaying of the iodine and time, thereafter for cleaning and refilling with new charcoal.

VIII. References

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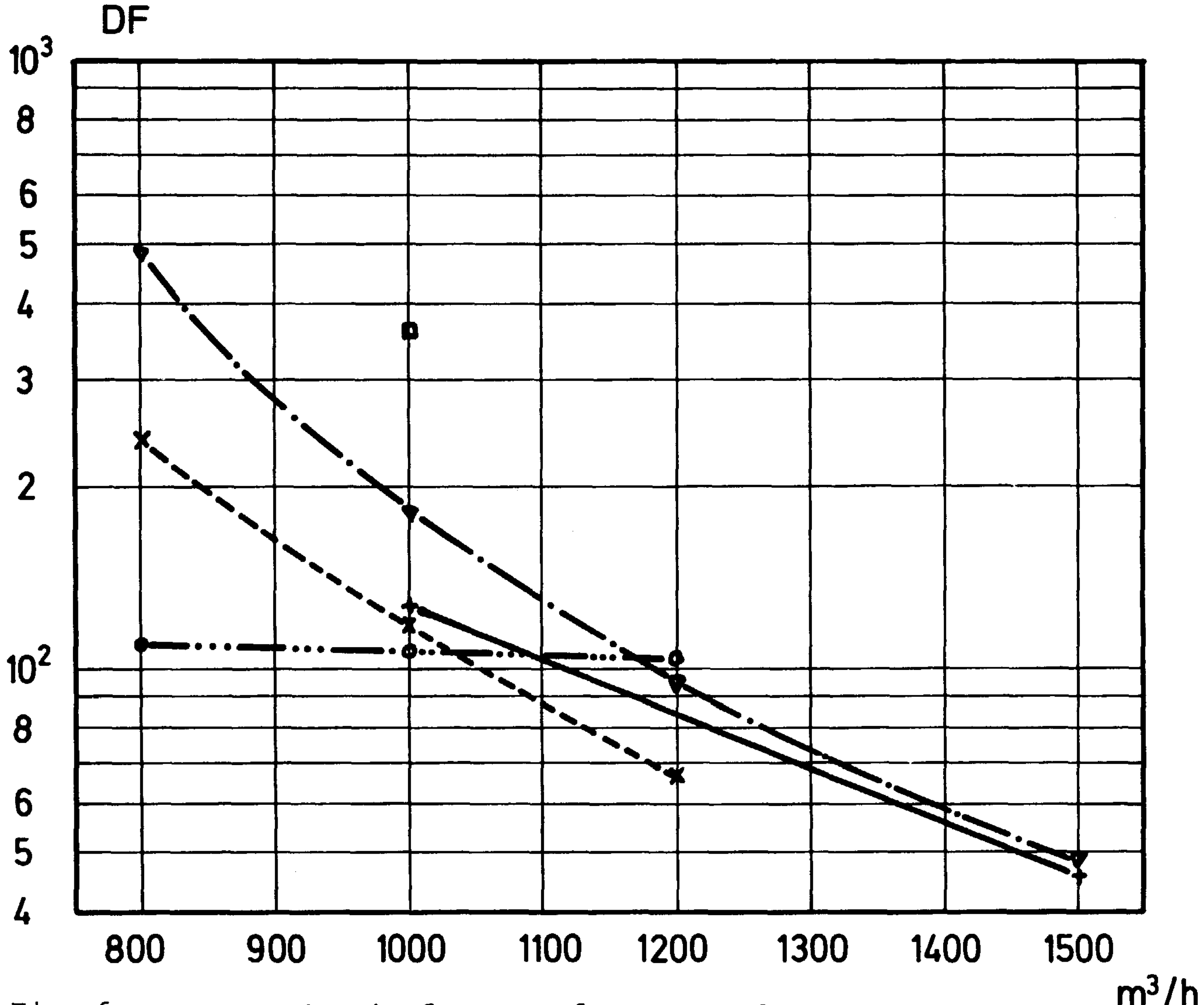

Fig. 6: Decontaminationfactors of commercial charcoal filters as a function of air flow rate

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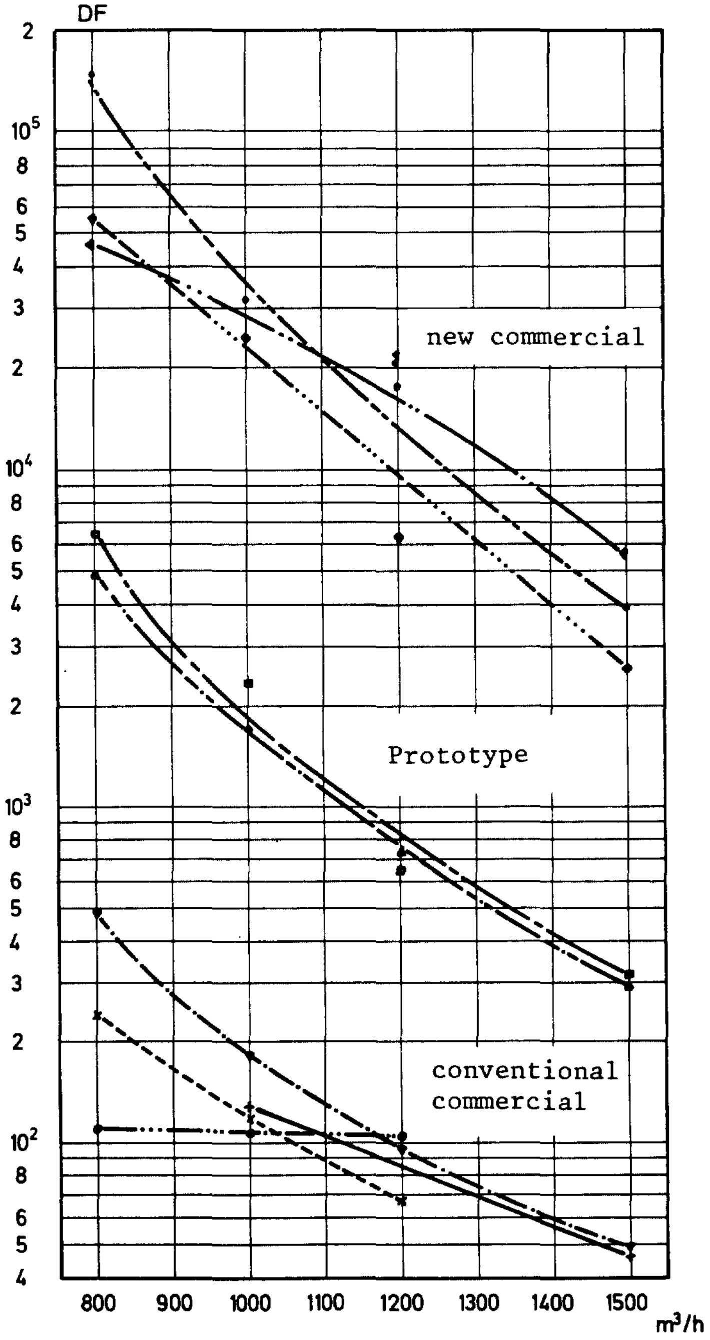

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Fig. 7: Decontaminationfactors of conventional commercial and new commercial charcoal filter cells as a function of air flow rate. Each test with the same carbon.

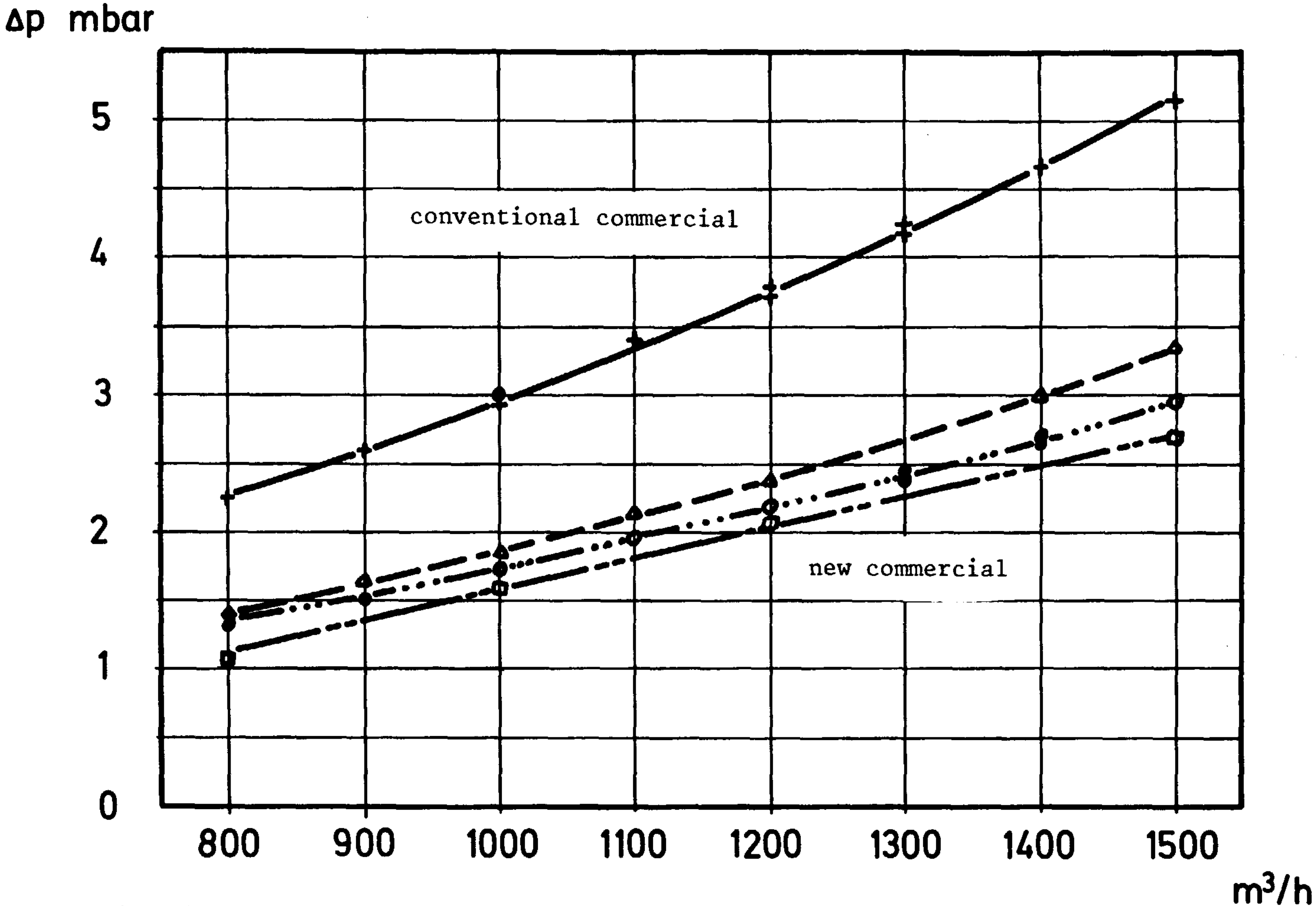

Fig. 8: Pressure drop of industrial and new charcoal filter cells as a function of air flow rate.

DISCUSSION

KOVACH: 1). Was there a difference in DF between the filter cell and an equal bed depth laboratory test?
2) If yes, do you attribute the difference to non-uniformity of flow or non-uniformity of packing?

DILLMAN: 1) Yes, there is a difference in the DF between the laboratory charcoal test and the cell test.
2) The difference may come from:
- a) the sealing of the cell.
- b) variations in the thickness of the charcoal bed, leading to nonuniform flows.
- c) non-uniformity of the charcoal size distribution during filling.
- d) the ratio between the enclosure surface of the housing duct and the charcoal volume, compared with a laboratory test or a deep-bed filter.

PERFORMANCE STUDY ON ACTIVATED CARBON FILTER SYSTEMS AT THE US ARMY CHEMICAL AGENT MUNITIONS DISPOSAL SYSTEM (CAMDS)

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Abstract

The US Army has been actively involved in the development and application of activated carbon filter systems for many years. In recent years, this work has expanded to include control of toxic gases generated in industrial activities. Ensuring that plant emissions were controlled and complied with all appropriate state and federal requirements has been a major part of this program.

This paper presents the results of a study of the performance of activated carbon filters used at the US Army Chemical Agent Munitions Disposal System (CAMDS). The filters (constructed with two adsorber banks in series) were installed, tested, and put in continuous service the late 1970's. A wide range of contaminants (e.g., paint solvents and common industrial compounds) as well as the chemical of concern (sarin) passed into the filter systems. Filter performance was monitored on a continuous basis for any detectable sarin breakthrough. It was expected that trace readings would appear and gradually approach a predetermined level at which time the filters would be serviced.

This study was prompted by the appearance of service level readings on a transient basis. An extensive set of data was collected and then charted in various ways to show the performance of the filter banks. The most useful presentation is one which plots the bank performance (C_i/C_o) against inlet concentration (C_i). The performance ratio was calculated when there were readings both upstream and downstream of a bank (a data set).

The plots, including data taken over an extended period, showed that high inlet concentrations tended to yield high filter efficiencies. When inlet concentrations were low however, the performance trended low.

These results are in agreement with general theory for adsorber performance. The operational data cover a wide range of concentrations, thereby extending the total data base over the wider range of high to very low concentrations found in many industrial plants.

However, the results conflict with the commonly accepted value of performance of 10^4 for carbon filter banks. The proper application of adsorbents must consider each compound; its unique characteristics, expected range of concentration. Careful investigation will become increasingly important when low concentrations of high toxicity or valuable compounds are of critical concern.

I. Introduction

The CAMDS facility is serviced by a number of filter systems to provide containment of any toxic vapors released as a result of the plant process. Each filter unit consists of a prefilter bank, a high performance particulate air (HEPA) filter bank, two activated carbon filter banks (in series), and another HEPA bank. A continuous (data averaged over one hour intervals) monitoring system is used to check the levels of toxic contamination within the filter train. The monitoring system is capable of detecting selected vapor contaminates in the parts per trillion(ppt) range. For the purposes of this study, the inlet, midbed and outlet concentrations of the toxic chemical sarin were tracked.

The performance of the filter systems was certified by testing to have a removal performance in excess of 99.99% per carbon bank. This corresponds to a reduction of the inlet concentration by a factor 10,000 (10^4). For the two banks in series a combined reduction of the inlet concentration by 10^8 was expected. The estimates of performance were assumed to apply for any inlet concentration.

Data from several filters at CAMDS was analyzed. The results of the study show that a single bank can not be expected to reduce the agent concentration by the 10^4 factor under all conditions at all times. The data indicate that the filter performance is widely variable and is expected to be a function of many factors. Of particular note was the significant effect of inlet concentration.

II. Discussion

The performance of high performance filters has been studied by many people. These studies have identified the influence of the most common variables including; adsorbent properties, gas flow rates, temperature, contaminant properties, moisture levels and time in service. A number of other minor items may also affect the performance. The point of this study was that the filters did not meet the expectations of the operating personnel and an explanation was desired.

Data Correlation. The monitoring data was examined in an effort to find a correlation. Many of the variables listed above were considered, but did not seem to provide an adequate explanation. The obvious items of time in service, accumulated bed loading and weather conditions were present and seemed to account for some of the events. However, there were enough unexplained events to create an interest in further investigation.

Data Selection. The analysis in this study was complicated by the large volume of data. All data had to be extracted by hand and cross matched with weather, operating and maintenance parameters. It was also complicated by the normal problems of erroneous or missing data.

In an effort to simplify the data extraction, several short time periods were selected for closer study. Within these time periods, only those data sets which met the criteria of having both inlet and outlet readings at the same time were extracted. This resulted in a large reduction in the data. In particular, it eliminated any data point for which there was a high inlet but no measurable outlet. This feature of the data extraction placed an upper bound (UB) on the data that can be expressed in terms of the maximum performance which can be reported. This upper bound is shown on the data plots. Efficiencies above this line exist, but can not be measured. In the case of sarin, this limit is approximately 1×10^{-5} mg/m^3. From this value it can be shown that, depending on the inlet concentration (usually less than 10 mg/m^3), the reportable performance will be less than 10^6.

Data Presentation. It was decided to plot the data on log-log paper. Using the inlet concentration as the base and the performance for the ordinate, each data point was plotted. The results of this effort provided graphic evidence of the relationship between filter performance (efficiency) and inlet concentration. Although this data is related to a specific compound, the results should be representative of adsorber performance in general and therefore merits close study when applying adsorber technology.

Operational Data / Performance Ratio. Figures 1&2 are graphs of performance ratio versus inlet concentration for selected Type II filters (with 2 inch beds). The effect of accumulating challenge is seen by the slight shift (downward) of the lines representing different time periods (increasing time) in Figure 1. Figure 2 compares two filters operating in parallel on the same facility (but with different flow rates). Figure 3 is a graph for a Type III filter (with 4 inch beds) and shows the same general trend as seen in Figure 1. Figure 4 compares the characteristics of the TYPE II AND Type III. Figure 5 combines all the data to illustrate the similarity of the several filters regardless of their application or service conditions. The two factors which all units have in common are that they have been in continuous service and have been challenged with widely variable concentrations of sarin.

The performance ratio (PR) is calculated by dividing the inlet concentration by the outlet concentration of that bed. Since the CAMDS filters are constructed with two bed in series, the space between beds is labeled as the mid-bed. Table 1 illustrates this process using typical values.

TABLE 1. Calculation of Performance Ratio PR = C_i/C_o

Sarin Level			Calculated Eff.	
Inlet Reading	Midbed Reading	Outlet Reading	Inlet/Midbed $\frac{C_i}{C_o}$	Midbed/Outlet $\frac{C_i}{C_o}$
1.1×10^{-1}	BDL	BDL	NA	NA
3.6	9.4×10^{-5}	BDL	3.8×10^{4}	NA
2.1	8.8×10^{-5}	7.9×10^{-5}	2.4×10^{4}	1.1

All concentrations are in mg/m^3
BDL indicates Below Detectable Limits (approx. 1×10^{-5})
NA indicates that the ratio is Not Available
because the outlet reading is BDL

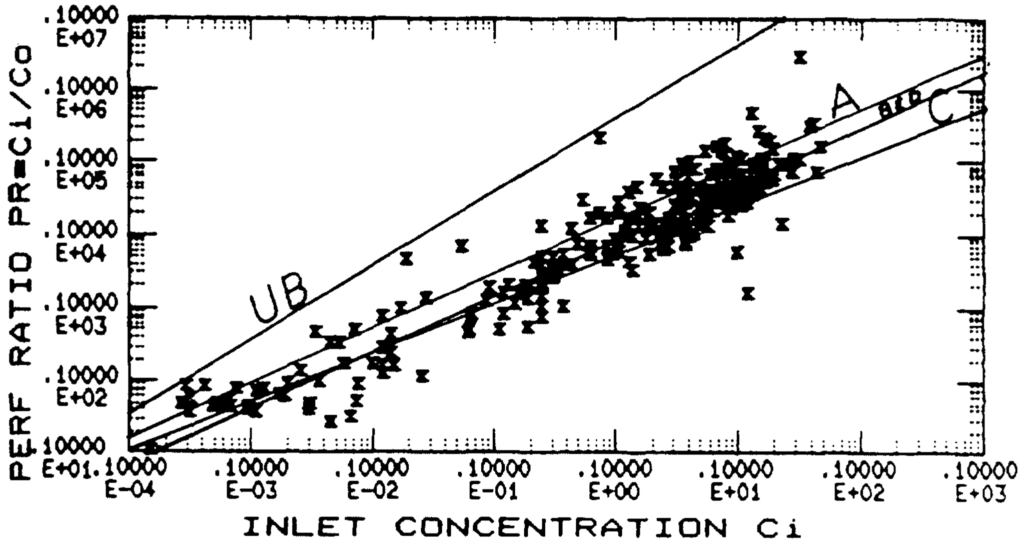

FIGURE 1. TYPE II ADSORBER (PDF)DATA SETS FOR; A=JAN 82 B=APR 82, C=JUL 82, D=COMBINED.

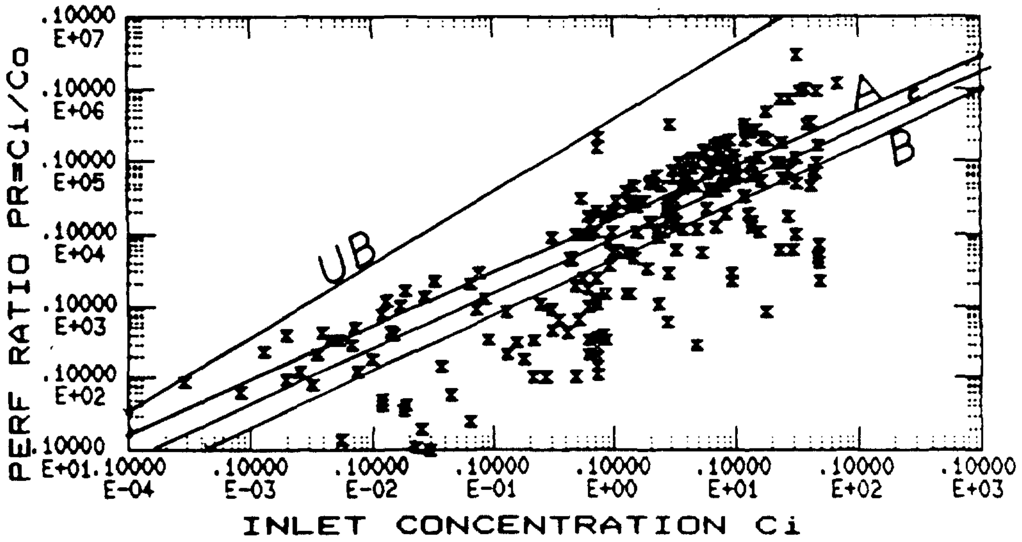

FIGURE 2. COMPARISON OF TWO TYPE II FILTERS IN PARALLEL SERVICE AND EQUAL TIMES (A=PDF, B=PPD, C=COMBINED).

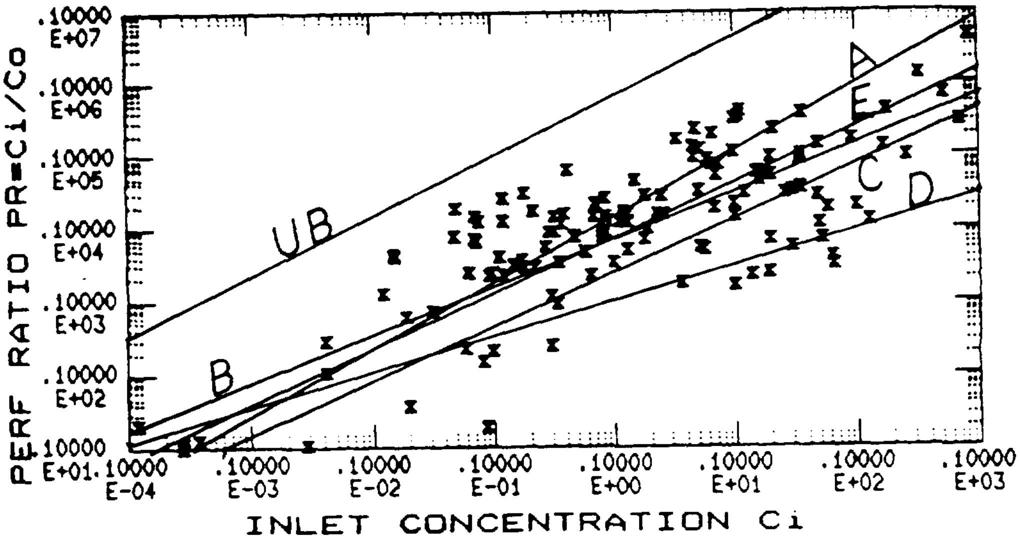

FIGURE 3. TYPE III FILTER (RLS) PERFORMANCE DATA SETS COVERING AN EXTENDED PERIOD; A=FEB 85, B=JUN 85, C=JUL 85, D=SEPT 85, E=COMBINED.

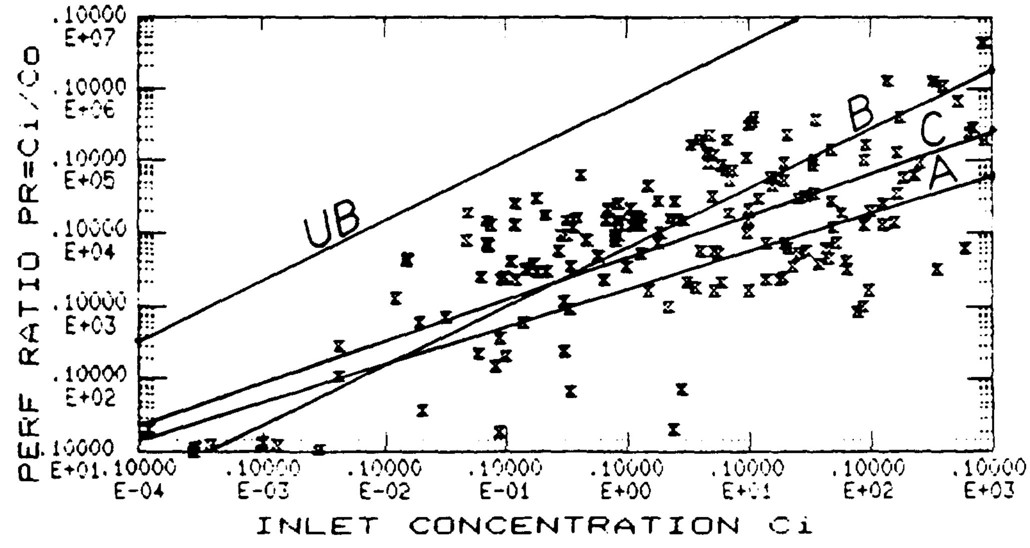

FIGURE 4. COMPARISON OF TYPE II (A=RII) AND TYPE III (B=RLS) FILTERS IN SIMILAR SERVICE (C=COMBINED).

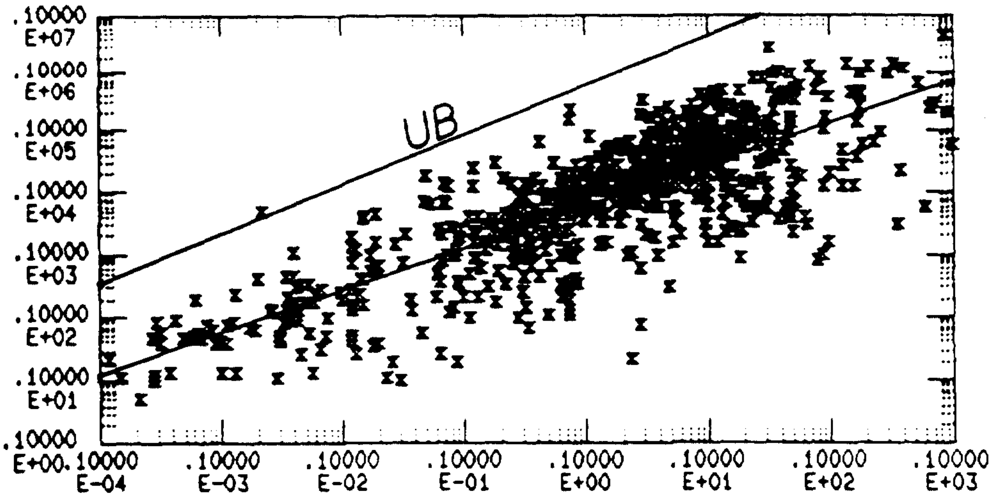

FIGURE 5. COMBINED DATA FOR TYPE II AND TYPE III FILTERS; A=PDF, B=PPD, C=RLS, D=RII, E=LIC, F=COMBINED(737 pts).

Filter Performance Extrapolation. The data points on the graphs show the general trend of decreasing performance ratio at lower inlet concentrations. The lines shown were fitted through the points using the least squares method. The fact that some of the data sets are quite small and contain only those points which met the screening criteria helps explain the wide scatter of the data. However, when there are enough points, the trend becomes apparent.

The equation for this line is expressed quite simply by:

$$PR = C_i/C_o = A(C_i)^B$$

Values for A and B were developed for the selected data sets. Table 2 shows the results of this exercise.

Table 2. Line Fit Coefficients For Combined Data

Figure #	A	B	# of Points
1 (Type II)	5026	0.76	286
2 (Type II)	4019	0.83	231
3 (Type III)	3966	0.72	139
4 (Type II/III)	2029	0.58	188
5 (Type II/III)	3153	0.69	737

At inlet concentrations ranging from $1x10^0$ mg/m^3 and higher, the performance ratios were generally 10^3 or greater. This corresponds to the bulk of experience in previous performance estimates. At lower inlet concentrations,the performance ratio is seen to decrease significantly. This raises the question of why there are no data points wherein the inlet was high and there was a low PR. It can be seen that this is never allowed to occur because this represents the condition in which the bed is saturated and has exhibited a massive breakthrough. Usually, the filters are changed before this happens.

Filter Service Life. With the general understanding that the life of a filter is limited, it remains for us to develop a means of predicting the service life of a filter system. Since it has been shown that this life is dependent on the type of service it sees, we should be able to apply the existing theory for adsorbents in this effort. However, it is also apparent that the expected operating conditions must be included as a fundamental part of this analysis.

The performance of carbon filters (expressed as PR) will decrease over time as the carbon matrix becomes loaded with contaminates. The data shown here does not directly show this. However, the data used for Figure 1 & 3 has been broken down into subsets (of time) and then a line fitted to each subset. These lines (A,B,C,etc) illustrate the effects of time on the filter performance (a decreasing PR). Since the filters were in continuous operation, with the inlet challenge varying over a wide range, the data sets represent a combination of adsorption and desorption occurring simultaneously. These processes were being influenced by changes in weather, plant operations and time. They show that given any filter with an indeterminate amount of loading, and letting the process variables drift as they will, the PR of the filter will roughly correspond to the inlet concentration. It should not be unexpected to see PR numbers ranging from greater than 10_4 to less than 1.

III Factors Affecting Filter Performance

It has been shown in many studies that a number of factors affect the overall performance of carbon filters. These include temperature, pressure, challenge concentration, accumulated loading, humidity, the presence of other contaminants, etc. The outlet concentration (of any species of interest) is a complex function of all these factors.

The carbon adsorbers described in this paper are designed in accordance with standard industry practices. The air velocity through the beds is about 40 ft/min. The tray type filter elements have a standard 2 inch bed depth which gives about 0.25 seconds of residence time. The Type III filter with its 4 inch beds would have a 0.5 second residence time (per bed) at rated flow. As a matter of convenience, to allow balancing of the associated ventilation systems, all of the filters were operated below their rated flow. In some cases they were operated at less than 50% of rated flow. This was expected to enhance their performance and extend their service life. The derating does not appear to have had much effect on the overall performance or service life.

The results presented in this paper illustrate the complex nature of the processes occurring within the filter. They extend the experimental data into regions where the adsorption/desorption equilibrium phenomena become a controlling factor.

IV Comparison With Previous Kinetic Studies

Kinetic studies of adsorption of chemical agents using carbon filters have been performed by the US Army at Edgewood Arsenal for many years. For these previous studies, the inlet concentrations have ranged from $5x10^2$ to as high as $6x10^3$ mg/m^3. The operational performance ratios were over 10^4 as previously expected.

As technology has improved and the environmental regulations have become more stringent, the operational limits of processing plants has decreased significantly. In 1985, the inlet challenge from newly developed processes was generally less than 10 mg/m^3. On the other hand, the allowable outlet concentrations had been reduced to $1x10^{-4}$ mg/m^3. This is just above the "best technology detectable limit" of $2.7x10^{-6}$ mg/m^3. It is also several orders of magnitude below the values previously used to predict filter performance in this type of service. It is therefore reasonable to assume that previous estimates of adsorption capacity, the adsorption rate constants, and the equations developed for predicting breakthrough time are suspect at these lower operating ranges.

V Conclusions

First, filter performance has been shown to be a function of inlet concentration. The inlet concentration integrated over time accounts for the total accumulated dosage. As this load increases, the contaminant (through desorption) starts to appear in the outlet stream. Although the scatter of the data points is quite broad, the trend of the data supports this conclusion. By tracking this trend, it should be possible to anticipate the need for service of the filter system.

Secondly, at inlet concentrations greater than 10 mg/m^3, the performance will generally be greater than 10^4. There are times however when due to combinations of factors discussed here that the performance ratio will be reduced to less than 10. It was expected that the type III filter with its 4 inch beds would outperform the type II units. However, the increased bed depth available in the type III units does not appear to represent a significant barrier to low concentrations passing through, even though the deeper bed will contain significantly more contaminant at high concentrations. The design of a filter bed to retain low level concentrations will require greater attention in the selection of adsorbents and flow rates.

The work reported here is part of a development program aimed at the safe disposal of outdated military munitions. In this respect, the Army has insisted on the highest standard of performance. But it has been able to achieve this only by constant monitoring and judicious timing of carbon bed changes.

VI Acknowledgments

This paper is the result of a long term study in the application of activated carbon to the treatment of process air resulting from the US Army CAMDS program at the Tooele Army Depot, Tooele, Utah.

DISCUSSION

GUEST: You didn't tell us what chemicals you were removing. Can we assume that the mechanism is physical adsorption rather than chemical reaction?

GLADDEN: We used unimpregnated carbon of a nuclear grade, the same grade that is specified in N509 and N510. The primary mechanism is physical adsorption. These were organic phosphates. Chemically the name is Sarin, nerve agent GB. It is not classified. It is to our advantage to use standard nuclear grade carbon because it is readily available. The Sarin compound breaks down with time. At low concentrations (C_i), the desorption of some compound is expected and this increases with time and accumulated total dose.

KOVACH: By the way, organic phosphates also react well with methyl iodide, so if you are interested, you can evaluate your used carbon as a feed stock for methyl iodide.

CLOSING COMMENTS OF SESSION CO-CHAIRMAN KOVACH

I would like to summarize by saying that there are still a lot of things we don't know. We have iodine forms that we have not identified, we have erratic behavior of various impregnated carbons that act one way at one time and differently at another and we are not exactly sure why. I think we still have to do a lot more learning before we can really educate others. The one thing I can plead for is an open information exchange between people so we can find out who is doing what, because one lifetime is not long enough for one place to generate all the information that is still needed. This type of cooperation is needed. I think we have to learn from each other as much as we teach each other. This may be a very unconventional summary, but that is my message.