

SESSION 5

ADSORPTION

TUESDAY: August 23, 1988
CHAIRMAN: A.G. Evans
T.R. Thomas

OPENING COMMENTS OF SESSION CHAIRMAN EVANS

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CARBON ADSORBERS**

V. Friedrich

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OPENING COMMENTS OF SESSION CHAIRMAN EVANS

This morning we are going to talk about activated carbon and it is appropriate as activated carbon has been the mainstay of iodine retention materials used in reactors for as many years as adsorbers have been used. Mainly what we will be discussing this morning are the characteristics of the carbon and what happens to it on aging.

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KINETIC STUDIES OF THE RETENTION OF RADIOACTIVE GASES BY ACTIVATED CARBON ADSORBERS

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ABSTRACT

A bimolecular reaction model containing the physico-chemical parameters of the adsorption process (adsorption and desorption rate constants, specific surface area of the adsorbent and concentration) has been developed to describe the kinetics of a continuously operating adsorption column. An analytical solution of the model was found for low inlet gas concentrations and a cascade-type numerical method was used for calculations at higher inlet concentrations. When calculating accumulation and break-through curves using the cascade method the results show a strong concentration dependence at higher inlet concentrations but with decreasing concentration the curves asymptotically tend to the curve calculated by the analytical solution which is not concentration-dependent. Adsorption and desorption rate constants (K_F and K_B) and "active site concentration" (A_0) were determined by fitting theoretical curves on experimentally measured break-through curves. The values of K_F , K_B and A_0 were $3 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $2.5 \times 10^{-4} \text{ s}^{-1}$ and $2.3 \times 10^{-3} \text{ mol cm}^{-3}$, respectively, for the system composed of methyl-iodide vapour as adsorbate and granuled activated carbon as adsorbent. Adsorption isotherms measured under dynamic conditions and at various temperatures were of Langmuir-type. From the temperature-dependence of the kinetic parameters the activation energy was calculated by the help of the Arrhenius-equation and the process was found exotherm with an activation energy of 67 kJ mol^{-1} (16 kcal mol^{-1}).

I. INTRODUCTION

Industrial practice and laboratory experiments show that the performance of continuous flow adsorption columns has a dynamic character, i.e. the removal efficiency changes (decreases) in time, and this process is effected by many parameters such as temperature, air humidity, gas concentration and composition, geometry of the column, face velocity, e.t.c. In the nuclear industry, granuled activated carbon adsorbers are widely used to control the release of radioactive gases (e.g. radioiodine) into the environment. In this case, even a relatively small deterioration in the removal efficiency can cause harmful release of radioactive material^(1,2). It is, therefore, important to understand and model the physico-chemical processes resulting in the retention of airborne radioactive material in charcoal adsorbers. Within the last two decades, investigations have been performed on the dynamic character of gas adsorption on granular carbon adsorbents^(3,4,5). Experimental studies on the influence of various parameters have also been reported^(6,7). However, pertinent data for the physico-chemical parameters (rate constants, isotherms) are still not

available and therefore the validation of various models and the extrapolation of experimental test results for long term operation and accident conditions is difficult⁽⁸⁾.

Since physical adsorption plays an important role in the removal of gases and vapours even if the efficiency of the adsorbent is increased by special impregnants (e.g. KI or TEDA for the removal of CH₃I), the aim of this work was to develop a simple model for the description of the adsorption process and to carry out experiments for model validation. The dynamic adsorption of CH₃I vapour on granulated activated charcoal was experimentally studied. The time-dependent accumulation and break-through of methyl iodide and the dynamic saturation capacity of the adsorbent was measured and the adsorption and desorption rate constants as well as the "effective active site concentration" of the adsorbent were determined by fitting the break-through curves calculated by the theoretical model on the experimental results. Adsorption isotherms were measured in the temperature range of 20-80° C and the activation energy was also calculated.

II. THEORETICAL

Assuming that the adsorption mechanism can be represented by the reversible processes of adsorption and desorption Jonas and Svirbely⁽⁹⁾ investigated the kinetics of adsorption of carbon tetrachloride and chloroform from air mixtures by activated carbon. The Wheeler and Robell⁽¹⁰⁾ adsorption equation for gas breaking through or penetrating a bed of charcoal, modified by Jonas and Rehrmann⁽¹¹⁾ was used by the authors as well as by others^(3,4,8) for the evaluation of experimental results. This model, besides experimental parameters (such as bed weight, bulk density of the bed, bed weight, adsorption capacity of the bed, concentrations), contains a pseudo-first-order adsorption rate constant, which is valid for a certain range of adsorbent loading, assuming, that the adsorbent surface occupied by adsorbate is much less than the free surface being still available for the adsorption.

The model, briefly reported by Friedrich and Lux⁽¹²⁾ does not use this assumption and contains both adsorption and desorption rate constants as follows:



where g is a gas molecule, a is a free active site on the adsorbent, e is an occupied active site, k_F is the adsorption rate constant and k_B is the desorption rate constant. The rate of the process can be described by the following Eq.:

$$\frac{dE/x,t/}{dt} = k_F \cdot G/x,t/ \cdot A/x,t/ - k_B \cdot E/x,t/ \quad (2)$$

where G , A and E are the concentrations of the gas, free active sites and occupied active sites, respectively, that depend on time t and distance x measured from the inlet side. Because of the conservation of /free+occupied/ active sites we have

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$$A = A_0 - E \quad (3)$$

where A_0 is the concentration of the active sites /that is proportional to the specific surface of the sorbent/.

An approximate numerical solution of Eq. /2/ is obtained in the following way. The column of a finite length X is divided into N layers and the continuous time variable is represented by periods of length

$$\Delta t = X/NV \quad (4)$$

where V is the linear face velocity. /This model will be called the cascade model./ Assuming that the inlet gas concentration is constant, i.e. $G(0,t) = G_0$, and denoting the values at the function in Eq. /2/ in layer i and in period j by $E_{i,j}$ and $G_{i,j}$ a recursive solution of Eq. /2/ is given by the equation system

$$E_{i,j} = \frac{k_F \cdot A_0 \cdot G_{i-1,j}}{Q} /1-P/ + E_{i,j-1} \cdot P \quad (5)$$

$$G_{i,j} = G_{i-1,j} - E_{i,j} \quad (6)$$

where $Q = k_F G_{i-1,j} + k_B \quad (7)$

$$P = e^{-Q \cdot \Delta t} \quad (8)$$

and the initial conditions read $G_{1,j} = G_0$ and $E_{i,0} = 0$.

Computing step by step the values $E_{i,j}$ and $G_{i,j}$ using Eqs /5/ and /6/ for $i=1 \rightarrow N$ and $j=0 \rightarrow j_{max}$, the $G_{N,j}$ vs. time curves will show the concentration breakthrough and

$$\sum_{i=1}^N E_{i,j}$$

vs. time curves the adsorbate accumulation. The value of j_{max} can be defined as the time when the difference between inlet and outlet concentrations is less than some small ϵ value or the increment of the accumulation is less than ϵ . With increasing number of layers the accuracy increases but so does the computing time too. When searching an analytical solution for the problem of the column of finite length, the following system of partial differential equations is to be solved. Again Eq. /2/ describes the rate of the process.

$$\frac{\partial E(x,t)}{\partial t} = k_F \cdot G(x,t) \cdot A(x,t) - k_B \cdot E(x,t) \quad (9)$$

Equation /3/ gives the active site conservation

$$A(x,t) = A_0 - E(x,t)$$

while gas conservation calls forth the relation

$$\int_0^x [E/y, t/ + G/y, t/] dy = V \cdot G_0 \cdot t - V \cdot \int_0^t G/x, t' / dt' \quad (10)$$

where V is the linear face velocity, x and t are variables for distance and time. Equation /9/ describes the reaction rate, Eq. /10/ represents the mass balance for the continuous flow column of finite length. This system of partial differential equations can be solved after introducing new variables:

$$v = \frac{x}{V}; \quad \tau = t - \frac{x}{V}. \text{ Denoting } \bar{F} / v, \bar{\tau} / = F/x, t/,$$

the initial conditions for Eqs /9/ and /10/ read

$$\bar{G} / 0, \bar{\tau} / = G_0 / \bar{\tau} /; \quad \bar{G} / v, 0 / = \bar{E} / v, 0 / = 0 \quad / v \geq 0 /.$$

In the analytical solution we assume that A/x, t/ in Eq. /9/ can be replaced by its maximum value A₀. It can be seen that this assumption is equivalent to the approximations

$$D / v, \bar{\tau} / \equiv k_F \cdot G / v, \bar{\tau} / / k_B \ll 1 \quad (11)$$

By the help of the Laplace-transformation the following solutions were found:

$$\bar{E} / v, \bar{\tau} / = \beta \cdot G_0 \cdot e^{-\beta v} \int_0^{\bar{\tau}} [e^{-k_B \cdot t} \cdot I_0 / 2 \cdot \sqrt{\alpha \cdot t \cdot v} /] dt \quad (12)$$

$$\bar{G} / v, \bar{\tau} / = G_0 \cdot e^{-\beta v} [e^{-k_B \cdot \bar{\tau}} I_0 / 2 \cdot \sqrt{\alpha \cdot \bar{\tau} \cdot v} / + k_B \cdot \int_0^{\bar{\tau}} [e^{-k_B \cdot t} I_0 / 2 \cdot \sqrt{\alpha \cdot t \cdot v} /] dt \quad (13)$$

where

I₀ is the zero order Bessel-function

$$\alpha = k_F \cdot k_B \cdot A_0 \quad (14)$$

$$\beta = k_F \cdot A_0 \quad (15)$$

III. EXPERIMENTAL

A simplified scheme of the laboratory apparatus is shown in Fig. 1.

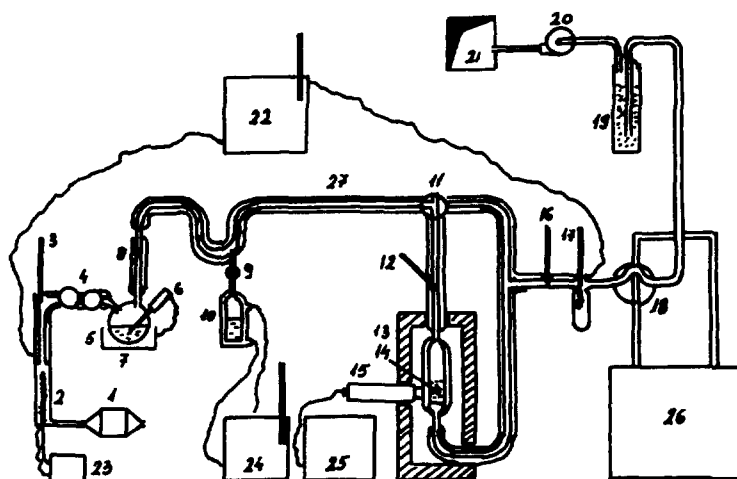


Fig.1. The laboratory apparatus
 1-inlet air filter, 2-electric air heater, 3-thermometer, 4-air flow regulator, 5-steam generator, 6-contact thermometer, 7-electric heater, 8-rotameter, 9-valve, 10-CH₃I generator, 11- two-way valve, 12-upstream thermometer, 13-lead shielding, 14-test bed, 15-scintillation detector, 16-dry thermometer, 17-wet thermometer, 18-gas sampling valve, 19-safety charcoal bed, 20-air pump, 21-ventilation system, 22-ultrathermostat, 23-temperature regulator, 24-ultrathermostat, 25-impulse scaler, 26-gas-chromatograph

The vapour of CH₃I labelled with ¹²⁵I was produced from liquid CH₃I. The concentration of gaseous CH₃I was adjusted by the temperature of the thermostat and the air flow. The CH₃I concentrations were in the order of 1×10^{-7} - 8×10^{-7} mol cm⁻³. Accumulation curves were observed using ¹²⁵I labelled CH₃I and measuring the ¹²⁵I activity on the column by scintillation detector and impulse-scaler, breakthrough curves were recorded by means of a gas chromatograph /using flame-ionization detector/. The first experiments were carried out at ambient temperature and 25-30 % relative humidity. When investigating the temperature dependence of the adsorption process, both bed and vapour temperatures were 17.5, 25, 30, 40, 50, 60, 70 and 80° C. The adsorbent was granulated activated carbon (type SKT-6, made in USSR), with a specific surface area of 1125 m²/g determined by BET method. The bed depth was 4 cm, diameter 2 cm, face velocity of the air-CH₃I vapour 3 cm s⁻¹. The adsorbent was preconditioned with CH₃I-free air at the temperature of the experiment up to constant weight (about 1 hour). The weight of the carbon was also measured after reaching the dynamic saturation (i.e. inlet and outlet CH₃I-concentrations were equal).

IV. RESULTS AND DISCUSSION

In evaluating the calculational models above it is remarkable that the analytical solution is proportional to the inlet concentration G_0 but no other concentration dependence appears in Eqs/12/ and /13/. On the other hand, Eqs /5/ and /6/ show an explicit concentration dependence of E/G_0 . This contradiction is due to the approximation, Eq. /11/ in the analytical method. In fact if $D_0 = k_F \cdot G_0 / k_B \ll 1$, then the G_0 -dependence of the cascade method also vanishes. Dependence of the breakthrough curves on inlet

concentration as calculated by the cascade method is given in Fig.2.

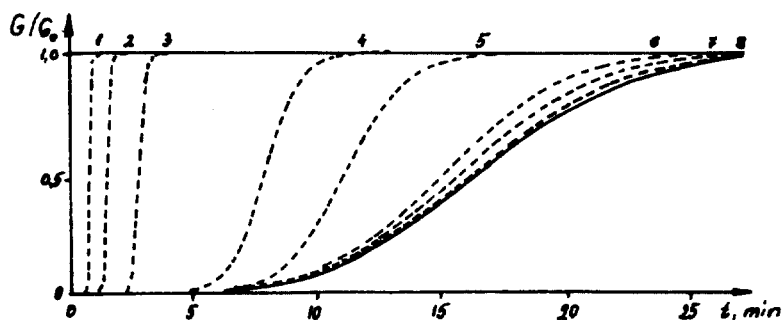


Fig. 2. Breakthrough curves calculated by the cascade method /-----/ and the analytical solution /-----/ Eq./16//. In the cascade method $N=100.0$, $\Delta T = 0.01$ s, and $D_0 = 20.0, 10.0, 5.0, 1.0, 0.5, 0.1, 0.05$ and 0.01 for the curves No 1, 2, 3, 4, 5, 6, 7 and 8, respectively. For both cascade and analytical calculations $\alpha = 0.4$ and $\beta = 20.0$

It is seen that with decreasing inlet concentration the curves asymptotically tend to the analytical curve and at $D_0 = 0.01$ the two curves practically coincide. The purpose of these calculations was to test the mathematical equations and the numerical method, therefore the values of α , β , D_0 were fictive.

Experimentally measured break-through curves are shown in Fig. 3.

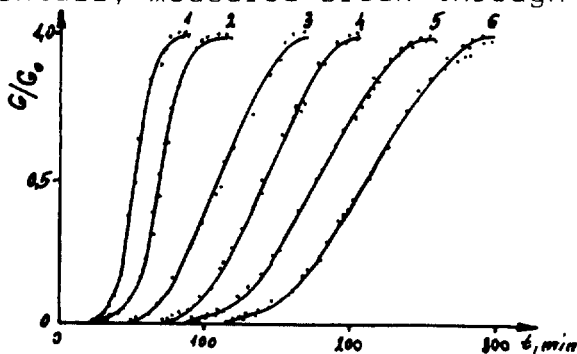


Fig. 3. Methyl-iodide break-through curves measured at 25°C and 25-30 % relative humidity. Inlet concentrations (G_0) were 6.76, 6.31, 4.17, 3.15, 2.20 and 1.80×10^{-7} mol cm^{-3} for curves No. 1, 2, 3, 4, 5 and 6, respectively.

A remarkable concentration dependence can be seen in Fig. 3. The laboratory experiments were carried out with relatively high inlet concentrations for the purpose of reaching dynamic saturation in a reasonable time period. At such high concentrations approximation /11/ is not justified, i.e. the analytical solution of the model does not apply. When fitting break-through curves calculated by the cascade method with the experimental results the physico-chemical constants k_F , k_B and A_0 were determined:

$$k_F = 3.0 \pm 0.3 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_B = 2.5 \pm 0.2 \times 10^{-4} \text{ s}^{-1}$$

$$A_0 = 2.3 \pm 0.3 \times 10^{-3} \text{ mol cm}^{-3}$$

Adsorption isotherms were constructed by plotting the weights of CH₃I uptake at dynamic saturation as a function of inlet concentrations. Isotherms determined at three different temperatures are seen in Fig. 4.

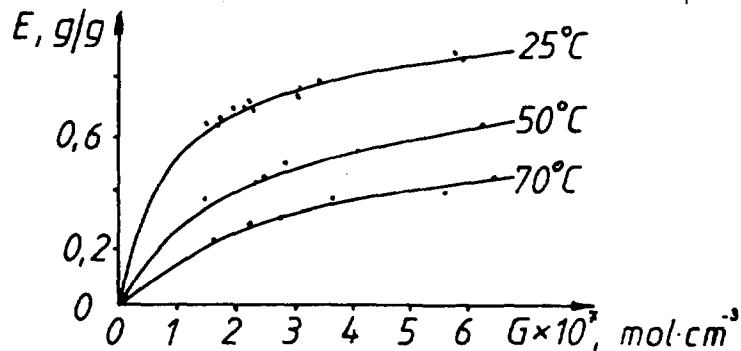


Fig. 4. Adsorption isotherms at different temperatures

The isotherms shown in Fig.4. can be well described by the Langmuir equation, which can also be expressed in the terms of thermodynamic parameters:

$$E = \frac{L \cdot \frac{k_F}{k_B} \cdot G_0 \cdot A_0}{\frac{k_F}{k_B} G_0 + 1} \quad (16)$$

where E = adsorbate uptake /g/g/

$$L = M_{\text{CH}_3\text{I}} / \rho_{\text{carbon}}$$

By the help of the linearized form of Eq. 16 the ratio k_F/k_B and A_0 can be calculated from the measured CH₃I uptakes at different inlet concentrations (G_0). The following values were found at 25° C:

$$\frac{k_F}{k_B} = 1,25 \times 10^7 \text{ cm}^3 \text{ mol}^{-1}$$

$$A_0 = 2,67 \times 10^{-3} \text{ mol cm}^{-3}$$

which are in good agreement with those determined by break-through curve fittings ($k_F/k_B = 3 \times 10^3 / 2,5 \times 10^{-4} = 1,2 \times 10^7$ and $A_0 = 2.3 \times 10^{-3}$). When calculating the product of k_F and A_0 , this results in a pseudo-first order adsorption rate constant, which can be compared with the pseudo-first order rate constant k_v used by the Wheeler and Robell equation(10). The product of k_F and A_0 using the above data is about 7 s^{-1} which is in the same order of magnitude as the values for k_v determined by Deitz and Jonas(3) and Vikis and al.(8). This can be considered as a good agreement, taking into account the differences between the types of charcoal used by the different investigators.

The influence of temperature on the kinetics of CH₃I adsorption on charcoal was also investigated, when measuring break-through and

dynamic saturation capacity at different temperatures (17-80°C). It was established, that the higher the temperature the faster the break-through occurred and the lower dynamic saturation capacity was found. The temperature dependence of the ratio k_F/k_B (calculated by Eq. 16) in the form of Arrhenius-plot is shown in Fig. 5.

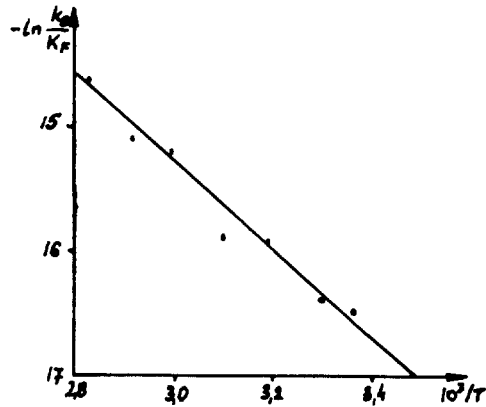


Fig.5. Arrhenius-plot of the ratio k_F/k_B

From the slope of the straight line the activation energy of the adsorption process was calculated by the help of the Arrhenius-equation, and the process was found exotherm with an activation energy of 67 kJ mol^{-1} (16 kcal mol^{-1}).

It is interesting to note that a temperature dependence of A_0 (active site concentration) could also be observed as it is shown in Fig. 6.

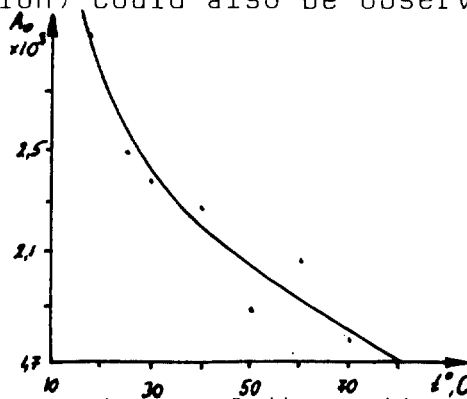


Fig.6. The temperature dependence of the active site concentration (A_0)

This observation suggests that the number of active sites (or the specific surface area) available for the adsorption under given thermodynamic conditions has also dynamic character and is influenced by temperature through the two-dimensional motion of the adsorbate molecule(s) on the surface.

V. CONCLUSIONS

A bimolecular reaction model was used to describe the adsorption process in continuous flow columns filled with solid adsorbents. The analytical solution of the model for low gas concentrations and a cascade-type numerical method for higher gas

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concentrations were developed. The experimental results on the adsorption of CH_3I on activated carbon showed the applicability of the model. The laboratory experiments were performed at relatively high gas concentrations while industrial (especially nuclear) applications usually assume very low concentrations.

The link provided by the cascade method between the two extreme concentration cases gives a viable strategy of experimental investigations of industrial processes. Namely by numerical /cascade-type/ reproduction of the experimental results the material constants are determined and with these constants analytical calculations prognosticate industrial functioning.

This strategy makes high-concentration laboratory experiments possible that have the advantage that the process of reaching dynamic saturation is significantly faster. From the obtained breakthrough and/or accumulation curves the physico-chemical parameters $/k_F, k_B, A_0/$ can be calculated. The sorbent material can be characterized by these parameters since they are independent of the experimental conditions.

ACKNOWLEDGEMENTS

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DISCUSSION

KABAT: Could the reaction kinetics of chemisorption be incorporated into the equations to make them applicable for impregnated adsorbents?

FRIEDRICH: We plan to extend the model with parallel adsorption processes (H_2O vapor, poison gases) and with chemisorption (impregnants). I am not sure if an analytical solution could be found since even to get a solution for the most simple case we had to make a significant approximation (Eq. 11 in the text). Using the cascade-type numerical method, the problem can probably be solved, but it will significantly increase the computing time which is rather long already.

WREN: All of the experiments were carried out at a flow velocity of 3 cm/s. This flow velocity is far smaller than that used in nuclear air cleaning applications. At high flow velocity, not the adsorption-desorption processes but the mass transfer may be the rate determining step for CH_3I adsorption on charcoal. At what flow velocity does the author think this transition occurs? Can your model be used at high flow velocities such as 20 cm/s?

FRIEDRICH: I think that gas-phase mass transfer cannot be the rate-determining step even when the linear flow rate is an order of magnitude higher. On the contrary, the adsorption rate increases and becomes more and more close to a final value due to the loss of an air film surrounding the particles, as it was reported by Deitz and Jonas (see ref. 3 in the paper). So I think our model can apply to higher flow rates (i.e. lower residence times), as well.

THOMAS, T.: One of the assumptions you used was that E was much, much less than the activated site concentrations (A_0). Yet all your curves are based on going to saturation. I was wondering if that is an improper assumption? Since you are running your experiments to saturation, could that cause some error in the analytical fit, or solution?

FRIEDRICH: We had to make this assumption, otherwise we couldn't solve the partial differential equation.

THOMAS, T.: But it is in direct conflict with the type of experiment which you ran, which was to go to saturation.

FRIEDRICH: You are right, but we did not use the analytical solution for evaluating our experiments. All the experimentally measured curves were evaluated by curve fitting using the step by step cascade method. When fitting the break-through curves calculated by the cascade-type numerical method we were not able to use a least square routine because of the long computing time and the limited speed of our computer. So we had to adjust the k_f , k_B , and A_0 values practically manually, because even to calculate several break-through curves took rather long computing time. When fitting the Langmuir-equation (Eq. 16 in the text) on the measured isotherms, we used a linear least square routine to optimize the values of k_f , k_B and A_0 . The experimental errors of the determined physico-chemical constants were approximately 10% (see the numerical results in Chapter IV of the text). The analytical solution does not apply to all cases. When the concentration range is too high, we can not use it. But for the case of a nuclear power plant, for example, where the concentration is very, very low, I am sure this equation can be applied.

THOMAS, T.: You say that with your curve fitting methods you were able to establish the forward and backward rate constants k_f , k_B , and A_0 . Did you do any repetitive measurements with the same type of charcoal but from a different batch? Did you get another batch and repeat the experiment to see if you got the same A_0 . Do you have some feeling for the reproducibility of these three constants?

FRIEDRICH: Yes, we repeated the measurements many times. We used a lot of batches and so the error, as I indicated in the paper, is computed from all those experiments.

THOMAS, T.: The reason I asked is that usually these types of rate constants are not very repetitive, at least in catalysis. If you get different material, even from the same supplier but at a different time, you can not get good repetition on these values. Also, I would think that the three values would vary in the presence of other constituents such as water vapor, CO_2 , etc.

FRIEDRICH: We did not investigate the influence of different batches on the physico-chemical constants. We took the charcoal samples from two different filters in our NPP, and it was unknown for us whether they originated from the same batch or not. Since the purpose of our experiments was to verify our model and to see the reproducibility of the constants, we mixed the samples and used them as one batch. Also, for the above reason, we did not investigate the influence of H₂O vapor and other air components but we intend to do so, as soon as we can extend the model on parallel (or competitive) processes. If the extended model is correct, any components in the air should influence the value of A₀ (i.e., the available specific surface area) but not that of the rate constants k_f and k_g.

CURRENT PROBLEMS IN THE ASSESSMENT
OF THE EFFECTIVENESS OF RADIOIODINE RELEASE CONTROL

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Abstract

In the opening session of the 19th DOE/NRC Nuclear Air Cleaning Conference R.M. Bernero (1) demonstrated the environmental significance of iodine releases from normal operations and supported it with results of numerous field investigations. The behaviour of airborne radioiodine in BWR and PWR operations, as presented in this paper, was similar in many aspects to its behaviour observed in operational areas and gaseous effluent of PHW reactors. While the identity of airborne "non-I₂, non-CH₃I" species has not yet been conclusively identified, there cannot be any doubt on their presence in areas and effluent of nuclear facilities. Since only iodomethane and elemental iodine tests are currently available for the performance testing of radioiodine absorbers, the test results may not properly represent the adequacy of radioiodine effluent control under certain operational or release conditions. Data from field measurements of radioiodine at PHWRs are compared with data from similar measurements taken at US power plants, in order to relate the behaviour pattern of airborne radioiodine and to assess the need for its effluent control under both typical operations and accidental conditions in nuclear power plants.

I. Introduction

An effective control of the release of radioiodine at the source (reactor fuel, reactor and auxiliary systems, such as primary coolant purification and fuel handling systems) and within operational areas is the most effective way of reducing radioiodine releases in both liquid and airborne forms. A proper combination of engineering controls, operational procedures and chemical methods of iodine volatility control can effectively maintain low radioiodine releases under normal operating conditions. However, the occurrence of minor operational incidents, causing increased levels of airborne radioiodine in ventilated areas, has been sufficiently frequent to justify the installation of radioiodine absorbers in effluent pathways for normal operations. While the airborne radioiodine release scenarios can be reasonably well defined for the normal operations and minor incidents, they are extremely complex and practically impossible to be specified for the whole range of potential reactor accidents under which the range of fractional release of the core inventory of radioiodine can vary from negligible to substantial.

II. Basic Aspects of Effective Control of Radioiodine Emissions

Generic Requirements

Selection and design of appropriate absorber systems, their proper operation and testing:

The absorbers design should be based on proper assessment of all potential release scenarios for normal operations, minor radioiodine release incidents and/or emergency release situations;

Operational personnel should be provided with equipment and comprehensive work procedures for maintaining the absorber's operational parameters within design specifications;

Appropriate absorbers testing program with corresponding procedures must be implemented to assure their compliance with performance standards and regulatory requirements.

Monitoring of Radioiodine in airborne effluent.

To demonstrate the compliance of normal plant emissions with regulatory limits quantitative monitoring of the "gross" radioiodine emissions should be performed in effluent pathways which have the potential of exceeding a significant portion (e.g. 0.1 %) of annual release limit. The dynamic range should be from the Lower Limit of Detection up to the Derived Emission Limit levels during normal operations;

For proper assessment of the public hazard from accidental releases selective measurement of chemical forms of radioiodine in airborne effluent should be performed when its levels exceed its emission limit.

III. Current Situation

At present we only know that significant portions of radioiodine species, other than I_2 and CH_3I , occur in effluent pathways. No generally acceptable characterization of their chemical behaviour and absorption properties has been gained from prior theoretical and experimental identification attempts. The findings on their origin, physical and chemical properties have remained controversial among air cleaning experts.

- The performance specifications in absorber design have been limited to I_2 and CH_3I removal.
- Several methods of the hydrolysis product(s) generation were applied in experimental investigations. No one has been generally accepted for absorbers testing.
- A few selective sampling systems have been developed which have given sufficient evidence of distinct chemical properties of the hydrolysis product(s). They have been applied in operational field and environmental determination of airborne radioiodine species, however, reservations have been expressed on the validity of the results.

IV. Volatile Species of Radioiodine

It can be safely assumed that the reactivity of elemental iodine is considerably enhanced under reactor operating conditions. The major factors are:

- it is formed as a monatomic decay product in highly active state
- within the fuel in operating reactors its reaction equilibrium with materials and other fission products is likely to be restrained by thermal dissociation and radiolysis processes.
- subsequent to its release from the fuel in a reactor or shortly after discharge it reacts with liquid or gaseous media. The reaction rate depends on chemical affinity of reaction components and on reaction conditions, such as temperature, pH, the presence of chemical additives and/or impurities, etc.

Chemical Origin

The presently unproven species may be of at least two types:

- products of iodine hydrolysis and/or subsequent reactions, which are formed through a limited time period after the release of elemental iodine from leaking fuel into aqueous media;
- gaseous organic species other than iodomethane, formed through extended time periods by direct reaction of iodine or its compounds with organic materials in gaseous, liquid or solid forms. They may also result from the decomposition (e.g. radiolysis) of nonvolatile organic compounds of radioiodine.

A number of experimental investigations have been performed with volatile forms of radioiodine, generated from very diluted aqueous solution of elemental iodine. Because of their low stability and existence is limited to very low concentration, their experimental identification was extremely difficult and could not have been completed within the allocated time period.

Several attempts have been made for theoretical assessment of the volatility of HOI. Several investigators initially calculated that HOI was highly volatile from its aqueous solution. However, from a more recent theoretical assessment it was suggested that HOI was not volatile from its aqueous solutions.

Although the possibility of HOI release from aqueous solutions of iodine has been opposed by several investigators, no other substantiated interpretation for the volatile species has been offered.

Field Investigations - Normal Operations

Some of the results of more recent investigations, performed in light water power reactors and summarized in references (1), (2) and (3) have been consistent with results of field measurements at heavy water power reactors.

A brief comparison of the results follows.

Fractional species distribution

A fuel pool was classified in ref. (3) as one of more common major sources of airborne radioiodine in LWR nuclear power plants. It also had the highest measured portion (58%) of "HOI" in PWR plants.

This has been consistent with the following findings from CANDU plants, reported in publication (4):

- The primary coolant heavy water was not a major source of gaseous iodine forms.
- Major release of gaseous forms of radioiodine occurred in the spent fuel transfer system area and spent fuel inspection bay. Only minor portion of airborne radioiodine has been found as I_2 and CH_3I immediately after the discharge of defective fuel from the reactor. The major form of radioiodine, measured in the Spent Fuel Bay atmosphere, was associated with the hydrolysis of elemental iodine. Its time dependence, in relation with the concentration of iodine ions in bay water, is illustrated in Figure 1.

The volatility of this species has been very rapidly diminished by the addition of hydrazine into spent fuel bay water.

Chemical change of iodine species

The observation was reported in reference (3), that "as aging of radioiodine occurs, the chemical species change from reactive forms (I_2 and HOI) to less reactive form (organic)". Data in Table 4, show that the portion of HOI decreased in 27 days from 54 to 9 %, while the portion of organic forms increased from 35 to 86 %. The same pattern was also shown in other parts of reference (3) and in reference (2).

Similar observation, made in CANDU plants, was reported in publication (5). Table 1 shows that the range of initial "HOI" portions of 55-75 % decreased within a few weeks period to the range of 30-40 %, while the portion of organic iodine increased from 10-20 % to 40-60 %.

Collection efficiency of impregnated adsorbents

High efficiency of HOI removal by charcoal (the impregnate was not specified) has been demonstrated in Table 6, reference (3). The reported Decontamination Factors have been, with one exception, significantly higher for HOI than for CH_3I . However, the reported DF values of AgX are consistently lower for HOI than for CH_3I in Tables 2 and 3 of reference (2). Results of measurements, reported in (4), have shown that AgX efficiently absorbed HOI at low humidity, but its efficiency was rapidly reduced under high humidity conditions. Charcoal, impregnated with TEDA, was also found much more efficient than AgX for the removal of HOI.

Radioiodine Release from Reactor Accidents.

Of the three major north-american reactor accidents in the past, only the TMI 2 accident scenario was relevant to the reactor accident source terms for commercial LWR nuclear power plants. Therefore, there has been a tendency to interpret its airborne release scenario as being typical for US power reactors. As a result of relatively low radioiodine release from this accident suggestions were made that the iodine hazard rating in WASH 1400 was substantially overestimated and doubts were expressed on the need for radioiodine absorbers in nuclear power plants. A brief discussion on two essential aspects of radioiodine release from TMI follows.

Radioiodine Release Scenario at TMI.

The TMI plant has been built with particularly strong reactor containment buildings. The integrity of Unit 2 containment building remained perfect during the accident. This was the fundamental factor in restraining the release of gaseous radioiodine. Its gaseous forms remained hermetically sealed in the containment building and the portion of iodine which was released from damaged core into cooling water and process liquids was chemically fixed (by the addition of NaOH and possibly $\text{Na}_2\text{S}_2\text{O}_3$) before it was transferred to Auxiliary Building tanks and spilled on its floors.

Such an iodine release scenario may be quite typical for accidents in which the integrity of the reactor containment remains unimpaired. However, in other nuclear power plants which have not had their containment built to such a stringent safety standards, hydrogen explosion or other pressure transient could cause a damage to the containment integrity, with very pronounced effect on the fission products release scenario. Any impairment of the containment integrity would require that its negative pressure be maintained by sufficient ventilation flow. The ventilation stream from the reactor containment would contain substantially higher activity of radioiodine than the atmosphere of Auxiliary Building at TMI 2, which would be reflected in proportionally higher effluent levels.

Research of Radioiodine Source Terms

Experimental research has been performed at ORNL on the release of fission products from irradiated LWR fuel at high temperatures. Fuel elements were punctured at elevated temperatures and released iodine (essentially 127 + 129 isotopes) were analyzed with a thermal gradient tube. Cesium iodide was the major iodine species, while negligible portion of highly volatile species was found downstream of the tube. This finding was suggested as an interpretation of low radioiodine release from TMI-2. On several occasions, e.g. in reference (6) it was also suggested as a basis for major re-definition of Reactor Accident Source Terms.

There is no doubt that the results of this experiment have been quite accurate and the conclusion on extensive formation of particulate fission products was correct. However, there has been a question if the equilibrium of iodine forms, measured in irradiated fuel after 2 years of storage at normal temperature, can represent the distribution of chemical forms of iodine continuously formed in the fuel at full reactor power.

Few examples of field data, which are further briefly described, give enough evidence on the existence of significant portion of gaseous forms of radioiodine in fuel and consequently in operational areas atmosphere during and shortly after its on-power operation in a reactor.

1. Release of Iodine from Fuel into Operational Systems

The release of radioiodine from defective fuel into primary coolant has been a commonly known phenomenon. It also has been known for many years that iodine activity spikes occur in the primary coolant after each power transient.

- It has been reported in reference (7) that bursts of ^{131}I

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were "about one to few percent of the fuel element inventory" under these conditions. This effect has also been occurring in Ontario Hydro power reactors. The fluctuations of ^{131}I activity in primary coolant of DPGS through August 1970 are illustrated in Figure 2 which was reproduced from reference (8).

- It was also demonstrated in reference (9) that there was a continuous leak of radioiodine into primary coolant, corresponding to 5-10 % of its production rate at steady reactor power from significantly defected fuel elements.

2. Release of iodine from fuel into atmosphere.

The composition of airborne radioiodine in operational areas and gaseous effluent of Ontario Hydro nuclear power plants was measured, using a species selective sampler, described in reference (12). A glass fibre filter was used as the first element of this samples for the collection of particulate radionuclides, including particulate forms of radioiodine. Results of the measurements, reported in reference (5), are listed in Table 1.

- The Table shows that up to 300 MPC_a (6×10^6 dpm/m³), of ^{131}I were measured in the operational areas atmosphere. Approximately 85 % of this activity penetrated the particulate filter into the sampler components for the collection of gaseous species.
- No detectable ^{137}Cs / ^{134}Cs was collected on the particulate sampler. Easily detectable activity of Cs (in the order of 10^2 - 10^3 dpm) would have been measured if the 15 % of ^{131}I , collected on the filter, was present as CsI.
- Significant portion of ^{131}I on the particulate filter was apparently collected by the adsorption of I_2 vapour or "HOI" on the filter because the retention of 5-10 % of these forms was measured in previous laboratory testing of this type of filter.

Release of Radioiodine at Chernobyl

The Chernobyl accident scenario excluded any use of air cleaning systems. It would hardly have any similarity with a potential scenario of any PWR, BWR or PHWR credible accident. However, some environmental data may be applicable as a factual basis for cultivating our comprehension of iodine release terms under reactor core meltdown conditions. It was reported in reference (10) that radioiodine was released in the largest amount of any fission product, with the exception of noble gas radioisotopes. "It was estimated that 25 % of the Chernobyl inventory of radioiodine was released at lower levels over six days from April 26 to May 2". The essential fact, from the release scenario point of view, was that 75-85 % of airborne radioiodine, sampled in the vicinity of the plant, penetrated through particulate sample collectors into charcoal cartridges. Data from reference (11) are presented in Table 2 which show that the same portion of gaseous forms of radioiodine was also measured in the listed countries.

The iodine data from this reactor disaster are consistent with

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the above observations on the presence of significant portion of radioiodine, in gaseous forms with high release potential, in reactor fuel.

V. Summary

Comparison of field data and experimental results from several sources was performed in this paper. The results were generally in good agreement. The need has also been demonstrated for further clarification of certain areas in order to improve the control of radioiodine in airborne effluent of nuclear power plants under both normal and emergency release conditions. The current radioiodine control could be significantly improved in following areas:

1. Achieving a unified position on Radioiodine Source Terms and on the need of radioiodine absorbers in nuclear power plant ventilation systems:
 - It has been evident from the iodine release data from Chernobyl that substantial portion of radioiodine in gaseous form could be released from a melted core to reactor containment atmosphere.
 - Also, it has been evident from results of field measurements taken during normal reactor operations and irradiated fuel handling that a significant portion of radioiodine is being released in gaseous forms, other than I_2 or CH_3I , from the fuel into primary coolant, spent fuel handling systems and areas.
2. Including all gaseous forms of radioiodine, which can be present in significant portions in airborne effluent under normal and emergency release conditions, into the Radioiodine Source Terms, absorbers design and their performance testing.

A good agreement has been found between the results of two major independent field investigation programs, in which different analytical methods were applied:

 - major sources of airborne radioiodine, identified in different types of power reactors, followed a similar pattern;
 - Similar pattern of chemical behaviour of airborne radioiodine species was identified in operational areas. Significant portion of radioiodine occurred in chemical forms other than I_2 or CH_3I . These forms were usually generated in areas with aqueous solutions of radioiodine;
 - Similar ratio of the species absorption in impregnated charcoal and AgX was measured in preliminary tests.
3. Providing appropriate capability for the analysis of iodine species in nuclear power plant areas and effluent.
 - two commercially available systems for selective sampling of airborne radioiodine species, were used in previous field investigations with reasonably comparable results.

VI. References

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Measured Airborne ¹³¹ I		Relative Content - %		
Concentration - MPCa	Particulate	I ₂	"HOI"	Organic
25 - 300	~ 15	1 - 5	55 - 75	10 - 20
~ 2	~ 10	~ 5	50 - 65	20 - 30
~ 0.1	~ 5	30 - 40	40 - 60	

Table 1
Average composition of Airborne Radioiodine Species in PHWR Operational Areas

Monitoring Location	Total ¹³¹ I - Bq d/m ³	Gaseous ¹³¹ I - %	Particulate ¹³¹ I - %
RISO, Denmark	9.03	70	30
MOL, Belgium	19.80	67	33
JAERI, Japan	2.40	20	80
STUDSVIK, Sweden	74.95	80	20
ROMA, Italy	26.43	70	30
PETEN, Netherlands	35.70	NA	NA
MUNICH, FRG	102.40	77	23
BERLIN, FRG	51.65	77	23
OAK RIDGE, USA	0.12	77	23
RICHLAND, USA	0.62	92	8
THARAPUR, India	0.12	83	17
HELSINKI, Finland	270.00	85	15
BUDAPEST, Hungary	51.10	73	27

Table 2
Atmospheric ¹³¹I Concentrations from Chernobyl Accident

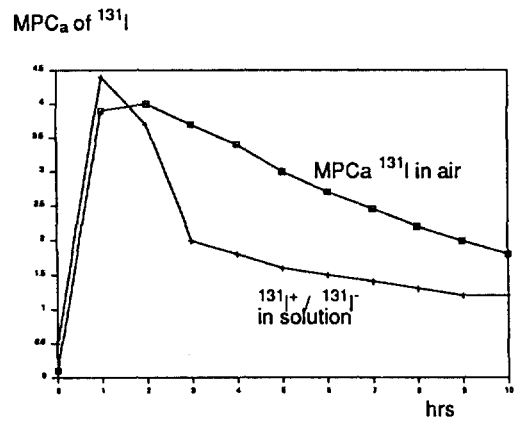


Figure 1
Time dependence of airborne ^{131}I in Spent Fuel Bay atmosphere

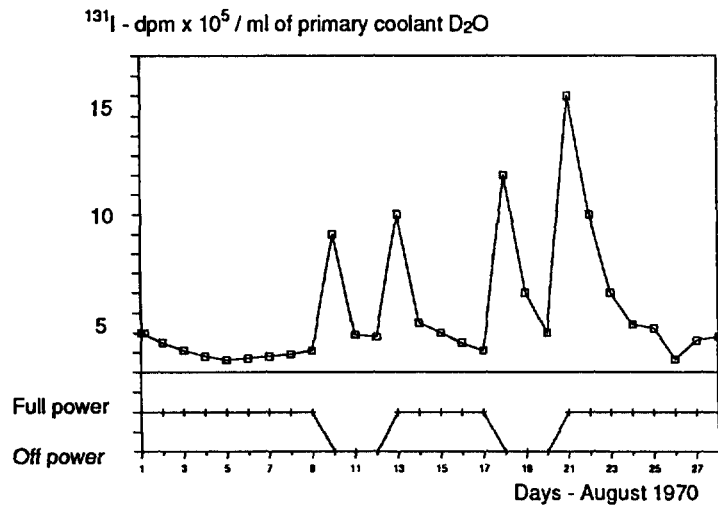


Figure 2
Emission of Radioiodine from fuel to primary coolant, following reactor power transients

DISCUSSION

HULL: One comment and then a question. In the collection of numerous post-Chernobyl samples, I saw one or two data for species separation for iodine. It appeared that about 30% was particulate, and that 60-70% was not particulate. Of that about half was elemental and about half organic. I noticed, if I read your paper correctly, that you think TEDA-treated charcoal is a more efficient medium for collecting the hydrolysis product HOI, than is silver impregnated zeolite. Is that correct?

KABAT: 1) Yes, I would expect elemental and organic iodine to be the major species occurring under the "dry release" conditions at Chernobyl. 2) TEDA impregnated charcoal is presently the best adsorbent for airborne radioiodine under normal release conditions. However, it is not recommended for use under reactor accident conditions when high temperature of effluent gas and decay heat could cause significant desorption of TEDA and consequently the penetration of radioiodine.

HULL: I was thinking of it from the post-accident monitoring standpoint, where it seems to me, we may be involved in a contradiction. Silver zeolite is the preferred medium because it has lower retention of gases which can confuse the picture. It is standard to use zeolite in a situation where you may have radioactive noble gases. Are we likely to miss the hydrolysis products if we go that route?

KABAT: The preference has been given to AgX for iodine sampling under emergency release conditions because of its low adsorption of noble gas. Radioisotopes of noble gas, primarily Xe, would interfere with the detection of radioiodine in the cartridge. However, we found that a charcoal cartridge can also be used if it is sufficiently purged with pure air before its radiometric analysis. It is a relatively easy procedure, we ran about 40 volumes of air through the sample cartridge in a few minutes and reduced the xenon content down to less than 10% of the original content.

EVANS: In the environmental monitoring area, if you are only looking for iodine (not in a post-accident situation) probably the TEDA-carbon is preferred. In the immediate post-accident situation, silver impregnated materials are recommended because xenon and krypton retention by the charcoal would confuse the iodine interpretation. I think that is the reason we have gone that way in this country.

GUEST: I did not fully understand the point you were making about it during the talk, but I was under the impression that this HOI thing had been laid to rest. I do not know if there is anybody in this room that still believes in HOI, but to the best of my knowledge there is not a shred of evidence anywhere that demonstrates that HOI exists in the gas phase.

KABAT: It was not the purpose of this presentation to extend discussions on the existence of airborne HOI or any other specific problem of iodine chemistry. Data were submitted in

this paper to demonstrate that

- a sufficient portion of gaseous radioiodine can be released from nuclear fuel to cause a major population hazard during nuclear power plant accidents,
- a significant portion of airborne radioiodine has occurred in chemical forms other than I_2 or CH_3I in operational areas and gaseous effluent of nuclear power plants. The present knowledge of these species is not sufficient for their proper monitoring and effective effluent control.

In general, three different approaches have been taken in the rating of radioiodine hazard:

1. Estimated iodine release from the TMI accident shows that radioiodine release from reactor accidents does not cause a major population hazard.
2. Radioiodine hazard assessment is to be based only on I_2 and CH_3I . The presence of significant amounts of airborne species other than I_2 or CH_3I in areas and effluents from nuclear facilities is not considered.
3. Radioiodine has a major hazard potential and a significant portion of its airborne forms have been found to be different from I_2 and CH_3I . Proper effort should be made to identify and characterize these species, develop the capability for their proper monitoring and effluent control.

The objective of this presentation was to summarize available field data in order to stimulate our awareness of the potential radioiodine hazard rather than taking too optimistic approaches. In the conclusion, I have suggested (in other words) that rather than saying "there is not enough evidence on the other species - so what," we should ask "---what we ought to do about it."

GUEST: I think everybody agrees that iodine chemistry is quite complex and that some hydrolysis products may get into the air occasionally. But the data you presented are about 20 years old, and as you pointed out, the problem was fixed almost 20 years ago just by adding hydrazine to the cooling water. I do not know why we need to do massive research trying to find femtograms of some compound that is transient and really does not cause much of a problem anymore.

KABAT: The main point of the presentation was that results of measurements we made almost 20 years ago are consistent with similar measurements done in Idaho four years ago for different reactors using different sampler systems.

WILHELM: I would like to comment on the medium we use to test carbon. Worldwide, it is done with methyl iodide. When you look at the amount of radioactive iodine released to the environment and look at the deposition velocity under normal operating conditions of a reactor, the effect of methyl iodide, an organic iodine compound, released to the environment, is nearly nothing because the deposition velocity is orders of magnitude lower than for elemental iodine. All the filters are tested with methyl iodide and when the methyl iodide test results are too low you exchange the carbon. That is the situation under normal operating conditions. There are very well known compounds which are harder to trap than methyl iodide, for example, ethyl iodide. For low iodine releases under normal reactor operational conditions, the environmental effect

is practically zero because of their low deposition velocity on pasture. Ingestion of milk is the only important path for health physics considerations because the effect of inhalation is at least two orders of magnitude lower than that of ingestion. So, testing iodine filter systems during normal reactor operations with more penetrating iodine compounds does not make sense. It will increase the amount of carbon needed for removal and in this way increase the amount of contaminated waste carbon after use. For emergency standby filter systems, the situation is quite different. For high iodine releases to the environment during an accident, inhalation is also an important path for the body burden. In this case, iodine compounds like ethyl iodide with a low deposition velocity may add significantly to the dose received because they are retained. Ingestion can be stopped, inhalation not.

KABAT: The information on higher penetration of ethyl iodide is consistent with data published by other investigators and also with my (non-published) observations. In our preliminary measurements all, ethyl iodide, methylene iodide, propyl iodide and iodobenzene, penetrated impregnated charcoal more rapidly than iodomethane. While the deposition velocity of the pure compounds on vegetation is low, I do not believe that we have sufficient data on their stability in the open atmosphere. Likely, their decomposition products would significantly contribute to the overall iodine deposition under normal release conditions. This may be sufficient reason for their monitoring in normal releases. I agree that the hazard from their inhalation is similar to the hazard from other airborne iodine species.

WREN: Your speculation is based on sampling by various adsorbers. Since the adsorption efficiency of these adsorbers, in general, depends on the challenge concentrations, I assume that you have calibrated the efficiency of these adsorbers as a function of gas concentrations. In your actual sampling, I suspect, the concentrations are quite small. Any comment?

KABAT: Data presented in this paper were extracted from several previous publications, which contain specific information on the applied sampling methods, sample collectors, calibration, etc. If I have correctly understood, this question relates to possible concentration dependence of selective collectors for airborne radioiodine species. In general, the collection efficiency of selective collectors was calibrated at iodine concentrations similar to airborne concentrations in operational areas. Their species selectivity was frequently confirmed by performing regression analysis of penetration profiles from several sections of the sample collector columns.

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TRAPPING PERFORMANCE OF 1.5% KI 207B CHARCOAL FOR METHYL IODIDE IN CO₂ AT HIGH TEMPERATURE AND PRESSURE

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Abstract

Recent experimental work is reported on the trapping performance of current UK potassium iodide impregnated coal based charcoal for methyl iodide in CO₂ at pressures up to 42 bar (4.2 MPa) and temperatures up to 275°C. The aim of the work is to underwrite the performance of the iodine adsorption plants in the blowdown systems of the UK Commercial Advanced Gas-cooled Reactors (CAGRs).

The current results, which are consistent with earlier data, show that an increase in pressure at constant gas staytime leads to a reduction in trapping performance and that above about 200°C the performance is further reduced as a result of increased desorption of iodine species. Tests carried out with I-131 labelled KI impregnant indicate that flowing gas can remove iodine from the impregnant, the rate of loss increasing exponentially with temperature (activation energy ~90 K Joules/mole) and linearly with flowrate. After passing CO₂ gas through a charcoal bed at 244°C for 30 days some 40% of the impregnant was found to have been removed from the charcoal.

The effect of variations in methyl iodide loading (up to a maximum of 0.02 g CH₃I per g charcoal) and gas face velocity (from 10 cm/s to 70 cm/s) have also been investigated. The trapping performance can be characterised by a K value defined by $DF = 10^{K \cdot t}$, where DF is the Decontamination Factor and t the staytime of the gas within the charcoal bed. A significant reduction in K value was observed at high methyl iodide loadings greater than 200 µg CH₃I/g charcoal. The K value was also found to vary as (gas velocity)^{0.6}, this result suggests that the trapping performance is mainly controlled by mass transfer from the flowing gas to the surface of the charcoal granules. This mechanism has been used as the basis of a predictive model of the trapping process. An analysis of all the experiments carried out to date has shown that the model satisfactorily predicts most of the K value dependence on pressure at temperatures below 150°C. Subsidiary measurements of the detailed distribution of trapped iodine through the charcoal test bed has indicated the presence of a small amount of a penetrating iodine species. This result suggests a breakdown of the simple single iodine species K value concept for deep beds.

It is concluded that the CAGR iodine adsorber plants will perform satisfactorily over the required range of operating conditions and that only minimal changes in performance will arise from any in-service loss of impregnant.

I. Introduction

Part of the United Kingdom's nuclear power programme is based upon the Advanced Gas-cooled Reactor (AGR). The essential features are: graphite moderator; carbon dioxide coolant (40 bar pressure); a post-stressed concrete pressure vessel inside which is housed not only the core but also the coolant circulators, heat exchangers and reactor control mechanisms. The fuel is slightly

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enriched uranium dioxide pellets contained inside transverse ribbed stainless steel cans, with 36 pins making up a fuel element.

The operating licence for the reactor site includes the requirement that no release of radioactive material to the atmosphere should exceed the authorised limits negotiated between the reactor operators and the Authorising Ministries. To meet this requirement gas clean up plants are installed which include particulate filters as well as adsorbers to remove radio iodine species of which the most important is the less easily trapped methyl iodide-131 (8 day half life). The gas clean up plants can be divided into two main types: those handling reactor coolant (pressurised CO₂), and those associated with air cleaning systems. Details of both types of plant in use in UK AGRs are given in Reference 1. A typical layout for a reactor gas blowdown system is shown schematically in Figure 1. The iodine adsorbers in both systems incorporate beds of impregnated granulated activated charcoal; for beds handling air the impregnant used is triethylenediamine (TEDA, 5% by weight), and for those handling high temperature pressurised CO₂ potassium iodide (KI, 1.5% by weight) is used. The trapping mechanisms is different for the two types of impregnant, for TEDA it is by chemical reaction and for KI it is mainly by isotopic exchange.

For a number of years the UKAEA carried out an on-going programme of laboratory experiments aimed at underwriting the performance of KI impregnated charcoal for trapping methyl iodide at the high temperature, high pressure conditions under which the reactor gas blowdown adsorber beds are operated. The programme has concentrated on the trapping of methyl iodide since this had been shown to be the most penetrating iodine species. The present paper gives the results obtained in a recent series of experimental tests.

II. Experimental Programme

Previous Work

In the previous work ⁽²⁾ attention was focussed on investigating the main parameters affecting charcoal performance as shown in Table 1.

Table 1.

	<u>Range</u>
Pressure	1 to 27 bar
Temperature	20°C to 300°C
Water vapour	100 to 6000 vpm

The data obtained were used as the basis for the design of the early AGR plants. Further work ⁽³⁾ looked in greater detail at the species of iodine desorbing from the charcoal at temperatures in the range 200°C to 275°C at a fixed pressure of 31 bar. The results showed the expected trend of increasing iodine penetration with increasing temperature. Increasing the water vapour concentration of the CO₂ gave improved performance at the higher temperatures studied. The major fraction of the desorbing iodine species was found to be of a form which was readily adsorbed on silver or copper surfaces. It was concluded that these materials showed potential for improving plant performance at high temperatures if used in combination with the charcoal.

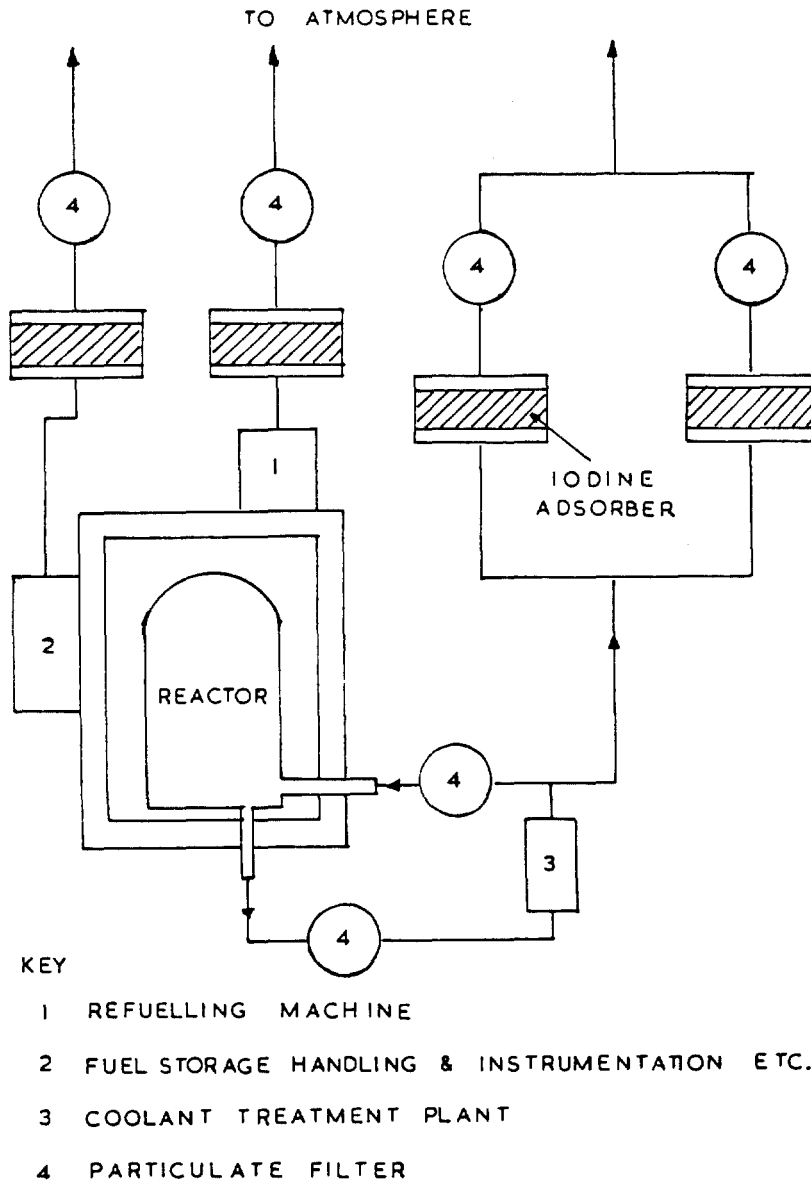


FIG 1. REACTOR BLOWDOWN SYSTEM

Current Work

The design data for the more recent UK AGR plants (ie Heysham 2 and Torness) are given in Table 2. It can be seen that the maximum operating pressures are significantly higher than the 31 bar maximum of the earlier experimental work. To extend the matrix of data, further performance tests have been carried out at a pressure of 42 bar over the temperature range 130°C to 250°C.

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Table 2. Design data for iodine adsorbers

<u>Adsorber</u>	<u>Reactor blowdown</u>	<u>Recirculation system</u>	<u>Auxiliaries*</u>
Charcoal) diameter:	1175 mm	1175 mm	770 mm
bed size) depth:	480 mm	480 mm	1120 mm
Process gas	reactor coolant	reactor coolant	CO ₂
Maximum gas flow	20 kg/s	10 kg/s	1 kg/s
Maximum pressure	32 bar	40 bar	45 bar
Maximum gas temperature	200°C	200°C	100°C
DF**	200	200	200

*ie: refuelling machine, fuel storage tube, instrument and circulator vents.

** Minimum Decontamination Factor (DF) used in activity release assessment.

All the previous high pressure tests were carried out at the then normal plant operating gas face velocity of 36 cm/s (defined as volumetric flowrate/cross sectional area occupied by the charcoal bed). There is now a design requirement for an increase in gas velocity through the charcoal bed. Evidence from References 4 and 5 indicate that; under dry air or CO₂ at atmospheric pressure, below 30°C and at a constant staytime within the bed, the index of performance parameter K varies as (velocity)^{0.5}. The current experimental programme has included further tests to determine the velocity dependence at 31 bar and 150°C.

In the United Kingdom, charcoal beds are designed assuming a maximum methyl iodide loading of 50 µg CH₃I/g charcoal. This loading limit is based on tests at atmospheric pressure (6) which showed a progressive reduction in performance at loading levels above this value. The present paper includes the results of a recent study of the effect of iodine loading over the range 0.04 to 20,000 µg CH₃I/g at 31 bar and 150°C. Also presented are the results obtained from an investigation of the effect of increasing the water vapour concentration from 200 to 1100 vpm. This series of tests, carried out at 31 bar over the temperature range 50°C to 275°C, also gave data on the desorbing iodine species.

Two series of supplementary tests have also been carried out at atmospheric pressure in a special low pressure/high temperature test rig. This rig was built to provide greater flexibility and control over test parameters. In the first series of tests, the desorption of iodine species from I-131 labelled KI impregnated charcoal was investigated over a range of temperatures and gas flowrates. The aim of the second series was to provide data on the detailed distribution, at 190°C, of trapped methyl iodide along a 20 cm deep charcoal bed which was subdivided into 12 separate units. Iodine migration along the bed was investigated by varying the gas purge period. The current test programme is summarised in Table 3.

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Table 3. Summary of Latest Tests

<u>Test</u>	<u>Parameter</u>	<u>Pressure</u>	<u>Temperature</u>
A	High pressure	42 bar	130°C to 250°C
B	Gas velocity (18 to 53 cm/s)	31 bar	150°C
C	CH ₃ I loading (0.04 to 20,000 µg/g)	31 bar	150°C
D	Water vapour (200 and 1100 vpm) Iodine desorption	31 bar	50°C to 275°C
E	Desorption from KI	1 bar	75°C to 244°C
F	Iodine migration	1 bar	190°C

III. Experimental Method

The high pressure test rig used for the experiments is described in detail elsewhere (³). The essential features, shown schematically in Figure 2, consist of a charcoal test bed (made up of 8-12 BSS mesh KI impregnated 207B type material prepared by Sutcliffe Speakman) through which a downward flow of CO₂ is passed. The flow can be either once through or recirculated, the latter mode of operation is normally used to conserve CO₂. There is provision for injecting, over a 3 minute period, a known quantity of methyl iodide labelled with the isotope I-131. The rig can be operated at up to a pressure of 45 bar and temperature of 300°C.

The charcoal test bed arrangement (see Figure 3) consists of a 13 mm diameter x 190 mm deep bed of charcoal which is subdivided into 5 separate units. A heated 'guard ring' system is used to maintain a uniform temperature along the charcoal bed (gradient normally less than 2°C). A sixth unit comprising a number of discs of silver-plated copper mesh is positioned immediately downstream of the bed. This unit is used to determine the amount of the more reactive iodine species penetrating or desorbing from the bed. Two traps, fitted with high efficiency, vacuum dried fine mesh (18-30 BSS) KI impregnated 207B charcoal, are fitted in parallel further downstream of the test section. Stop valves and purge lines are provided to permit alternate use of the traps on recirculation mode without interruption of the flow in the main charcoal bed. The traps are changed periodically (6 x 10 minutes and 7 x 30 minutes) throughout the 4.5 hour purge following the injection of methyl iodide. Instrumentation is provided to measure pressure, temperature, flowrate and the concentration of water vapour and oxygen in the CO₂ gas.

At the end of the test run, the rig is depressurised, cooled overnight to ambient temperature and the 5 charcoal units and silver/copper mesh unit removed. Standard γ spectrometry methods are used to measure the I-131 activity of the test bed units, the silver/copper mesh, the downstream charcoal traps and appropriate sections of the stainless steel test rig.

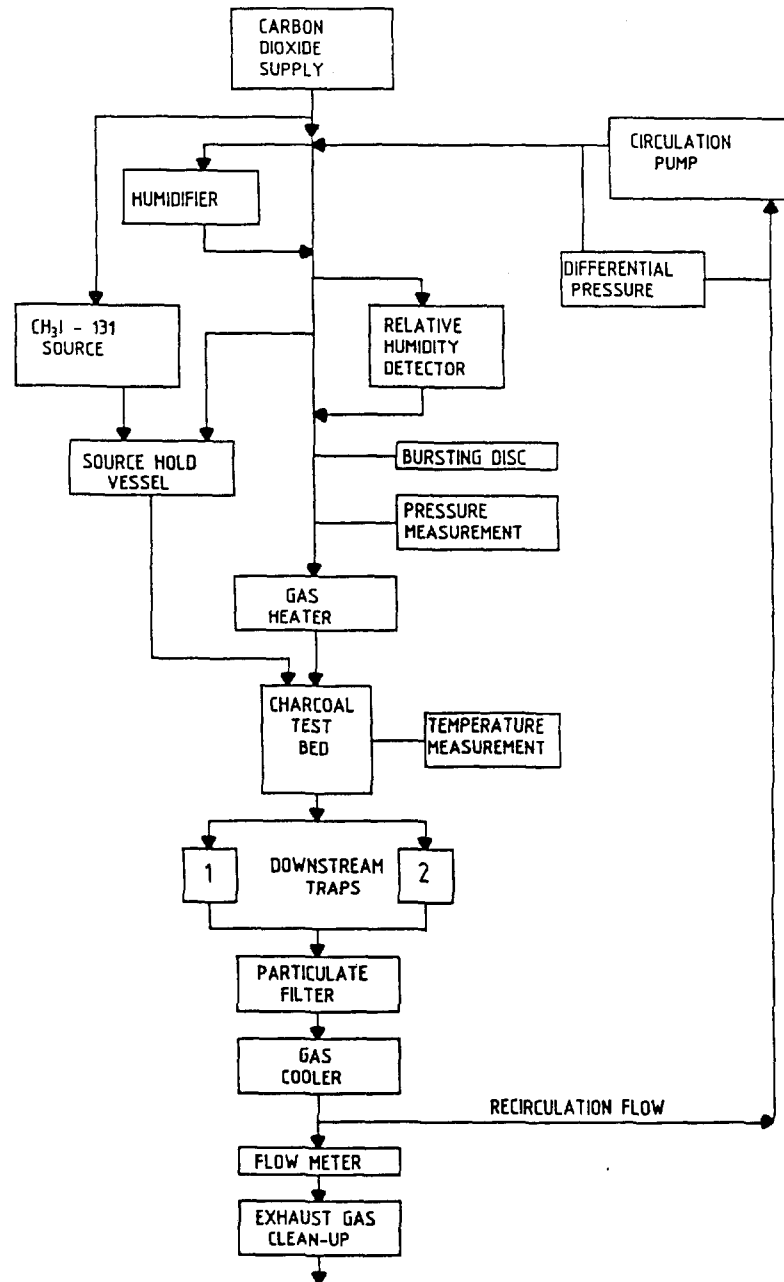


FIG 2. TEST RIG (SCHEMATIC)

To extend the flexibility and ease of carrying out some of the experiments, use was made of a specially built low pressure high temperature test rig. The general design of this rig, which could be operated at atmospheric pressure and up to 300°C, is very similar to that of the high pressure rig. The fact that glassware rather than stainless steel was predominantly used to construct the rig minimised the plate-out of iodine onto rig surfaces. In order to measure the distribution of trapped iodine in greater detail, the 108 mm deep charcoal test bed was subdivided into 12 separate units. To provide data on the species of iodine desorbing from the charcoal, a freezing chain was inserted between the test bed and the usual downstream silver/copper mesh and charcoal traps. The chain contained three cooling coils immersed (sequentially) in ice/water at 0°C, carbon tetrachloride at -22°C and trichloro-ethylene at -70°C.

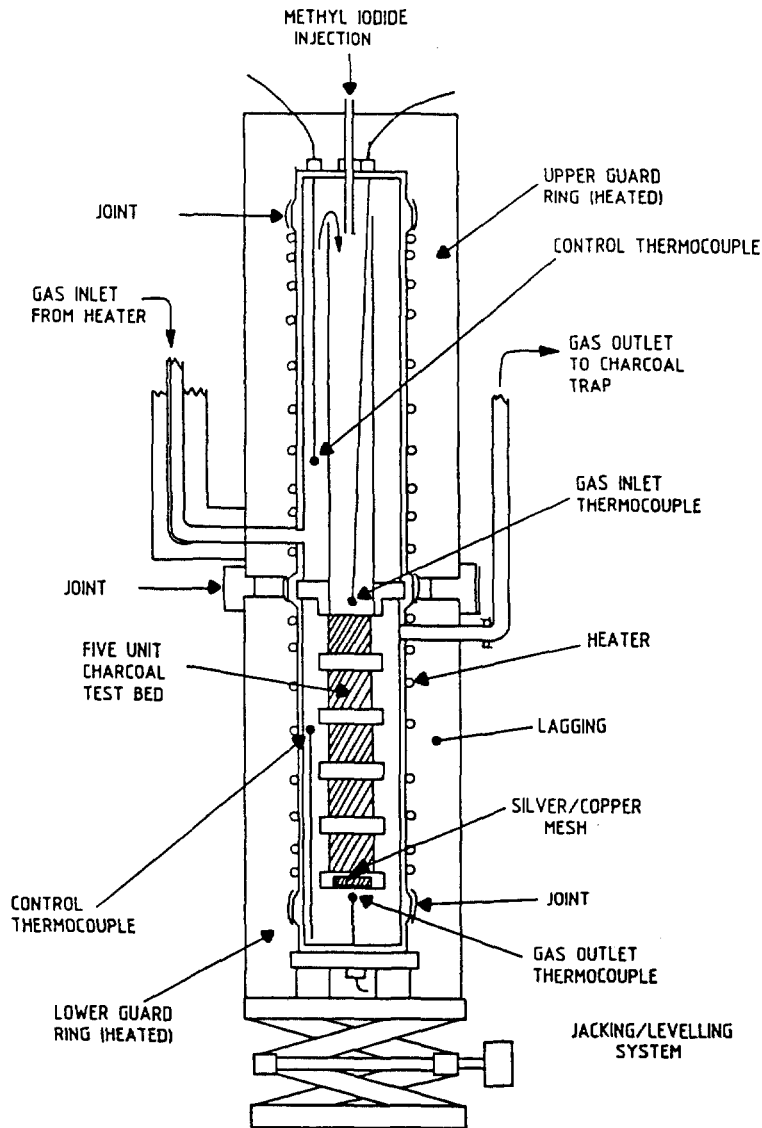


FIG 3. CHARCOAL TEST BED

Analysis of Data

The trapping performance of impregnated charcoal for gas-borne iodine species can be characterised by a K value defined as:

$$K \text{ value} = (\log_{10}(DF))/T^t \quad (1)$$

where DF = Decontamination Factor

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$$= \frac{\text{iodine concentration in upstream gas}}{\text{iodine concentration in downstream gas}}$$
$$T' = \text{staytime (in seconds)} = \frac{\text{bed volume}}{\text{gas flowrate}}$$

The K value can also be derived from the distribution of trapped iodine (I) along the charcoal bed;

$$K \text{ value} = \frac{-d}{dT'} (\log_{10}(I)) \quad (2)$$

The purchasing contract for charcoal normally requires that a quality control check is made of the charcoal's trapping performance for methyl iodide. In addition, checks are required to monitor possible deterioration in the performance of operating plants. The performance is assessed from a K value measurement on a sample of charcoal carried out under standard conditions. In the UK these are: downward flowing moist air at 98% relative humidity, atmospheric pressure, temperature of 22°C and gas face velocity of 36 cm/s. In the present paper Kstd value refers to the above standard conditions, other quoted K values are as measured at the particular test condition. For the high pressure rig tests, DF values were calculated for each test bed unit and expression 1 then used to determine the appropriate unit K value.

$$DF(\text{unit } n) = \frac{(\text{Un..U5}) + \text{Ag} + \text{Traps}}{(\text{Un-1..U5}) + \text{Ag} + \text{Traps}} \quad (3)$$

where (Un..U5) = sum of I-131 activity units n to 5

Ag = I-131 activity on silver/copper mesh

Traps = sum of I-131 activity on all charcoal traps

Between test comparisons are based on the mean K value of the 5 units.

IV. Results and Discussion

Test A - Effect of Pressure and Temperature

Five runs were carried out at a pressure of 42 bar over the temperature range 140°C to 250°C, the water vapour concentration in the CO₂ carrier gas was about 200 vpm. Following the 3 minutes injection of I-131 labelled methyl iodide, the flow through the test bed was maintained for a further 4.5 hours at a face velocity of 36.4 cm/s (equivalent to a staytime of 0.1 second per unit). The methyl iodide loading on the charcoal for runs A1 to A3 was 22 µg CH₃I/g, a higher value of 88 µg/g was used for runs A4 and A5.

The derived K values are given in Table 4 and plotted in Figure 4 together with earlier data obtained at pressures of 7 bar, 14 bar and 31 bar. It can be seen that pressure has little effect on charcoal performance at temperatures above 200°C. The tendency for K-value to fall with increasing temperature suggests that the trapping process at high temperatures is controlled by the desorption of iodine species from the charcoal. As the temperature is reduced below 200°C there is a progressive reduction in charcoal performance with increasing pressure. Evidence is presented later in the paper that this trend is due mainly to the trapping process being controlled, in this temperature region, by mass transfer

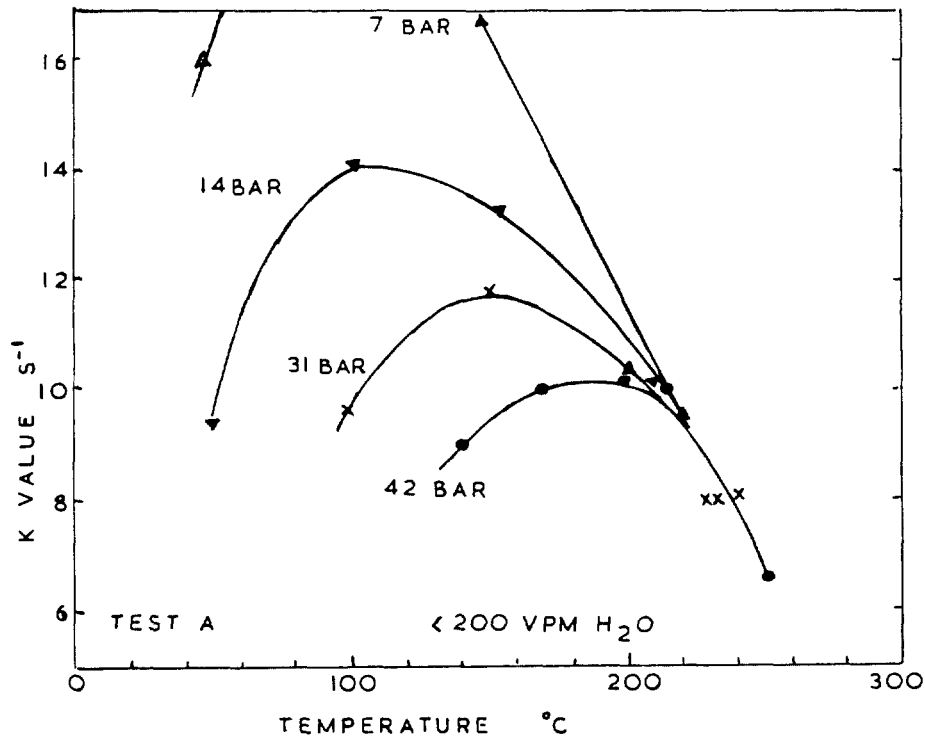


FIG 4. EFFECT OF PRESSURE & TEMPERATURE

from the flowing gas to the surface of the charcoal granules. There may also be some reduction in the effective surface area of the charcoal as a result of adsorption of CO_2 ; the amount adsorbed will tend to increase with increasing pressure and lower temperatures. Evidence to support this adsorption effect may be provided from a future investigation of CO_2 adsorption isotherms.

The experimental data is also given in Figure 5 in a form useful for the designers and operators of reactor blowdown iodine adsorbers. The shaded area in the figure represents the pressure and temperature operating region for which an acceptable trapping performance can be achieved, ie K value greater than 10 s^{-1} .

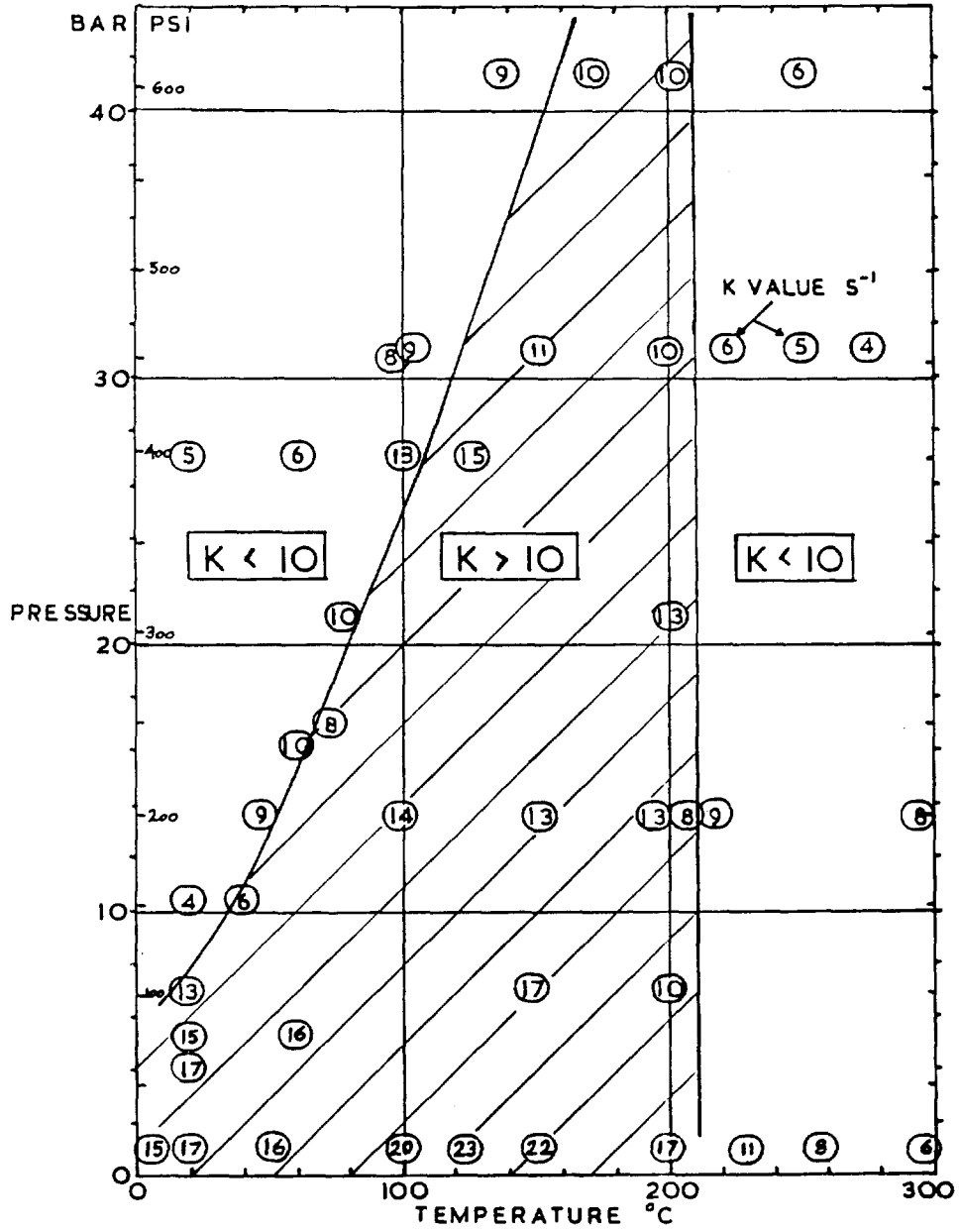


FIG 5. CONTOUR DIAGRAM OF K VALUES FOR PRESSURE AGAINST TEMPERATURE, KI CHARCOAL IN CO₂

Test B - Effect of Gas Face Velocity

This series of measurements were designed to investigate the dependence of K value on the face velocity of the gas flowing through a charcoal bed (ie face velocity = volumetric flowrate/cross sectional area occupied by the bed). The rig operating conditions were: pressure 31 bar, temperature 150°C. An initial series of measurements, covering a velocity range from 12 cm/s to 73 cm/s, indicated that K value was proportional to (velocity)^α where α = 0.8. There was a significant error in the measurement which arose from the inability to keep other operational parameters constant over the wide range of face velocity tested. In the lowest face velocity test a significant temperature gradient occurred over the test bed. The highest face velocity test was carried out using the straight-through mode of operation due to the limiting range of the recirculation pump. The large volume of gas used in this test required frequent changes of gas supply bottles which resulted in significant step changes in the oxygen and water vapour content of the CO₂ gas passing through the rig.

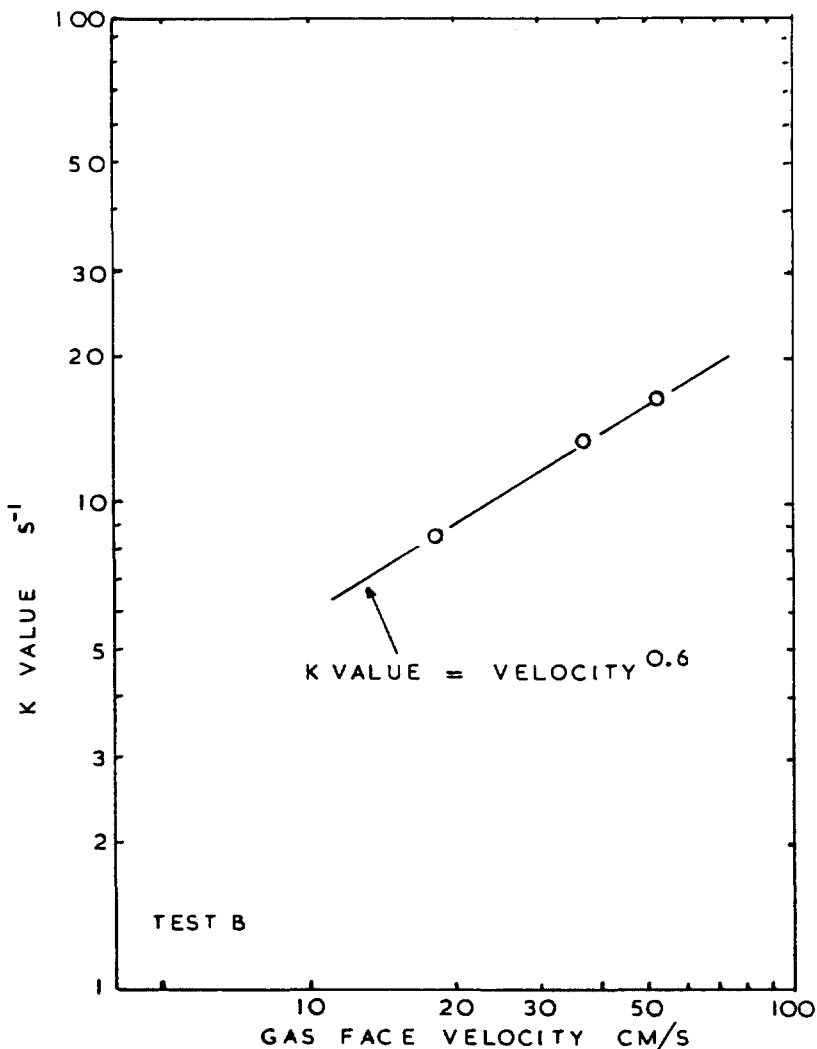


FIG 6. EFFECT OF FACE VELOCITY

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The measurements were repeated over a more restricted velocity range of 18 to 53 cm/s for which the rig conditions could be more closely controlled and monitored. The results, given in Table 5 and plotted in Figure 6, produce a value of α of 0.60 ± 0.05 which is very similar to the value of 0.5 obtained for dry air or CO₂ at atmospheric pressure and up to 30°C (4,5). The velocity dependence of the mass transfer coefficient (K_m) associated with gas flow through packed beds is quoted (7) as K_m proportional to (velocity)^{0.6}. The fact that a similar velocity dependence is obtained for the K value of charcoal suggests that, under dry gas conditions at both 1 bar 22°C and 31 bar 150°C, the trapping process for iodine species is controlled by the mass transfer of iodine from the flowing gas to the surface of the charcoal granules. It is worth noting that the velocity dependence is much lower, K value proportional to (velocity)^{0.2}, for wet gas conditions - 98% relative humidity. Hence, for these conditions, the trapping process is more diffusion rate and/or chemical rate controlled.

Test C - Effect of Methyl Iodide Loading

To investigate the effect of methyl iodide loading on the charcoal trapping performance, six tests were carried out in which the mean loading on the test bed varied from 0.04 µg to 20,000 µg CH₃I/g. From the measured I-131 activity distribution, the mass loading and the K value were derived for each of the individual test bed units. The results and run conditions are given in Table 6 and the variation of K value with loading plotted in Figure 7. It can be seen that, as expected, K value reduces as the iodine loading is increased and by an amount which becomes progressively larger at higher loadings.

Also included in the figure are the data from Reference 6 for 98% relative humidity air or CO₂ at 22°C. The trend for this data is for K value to be

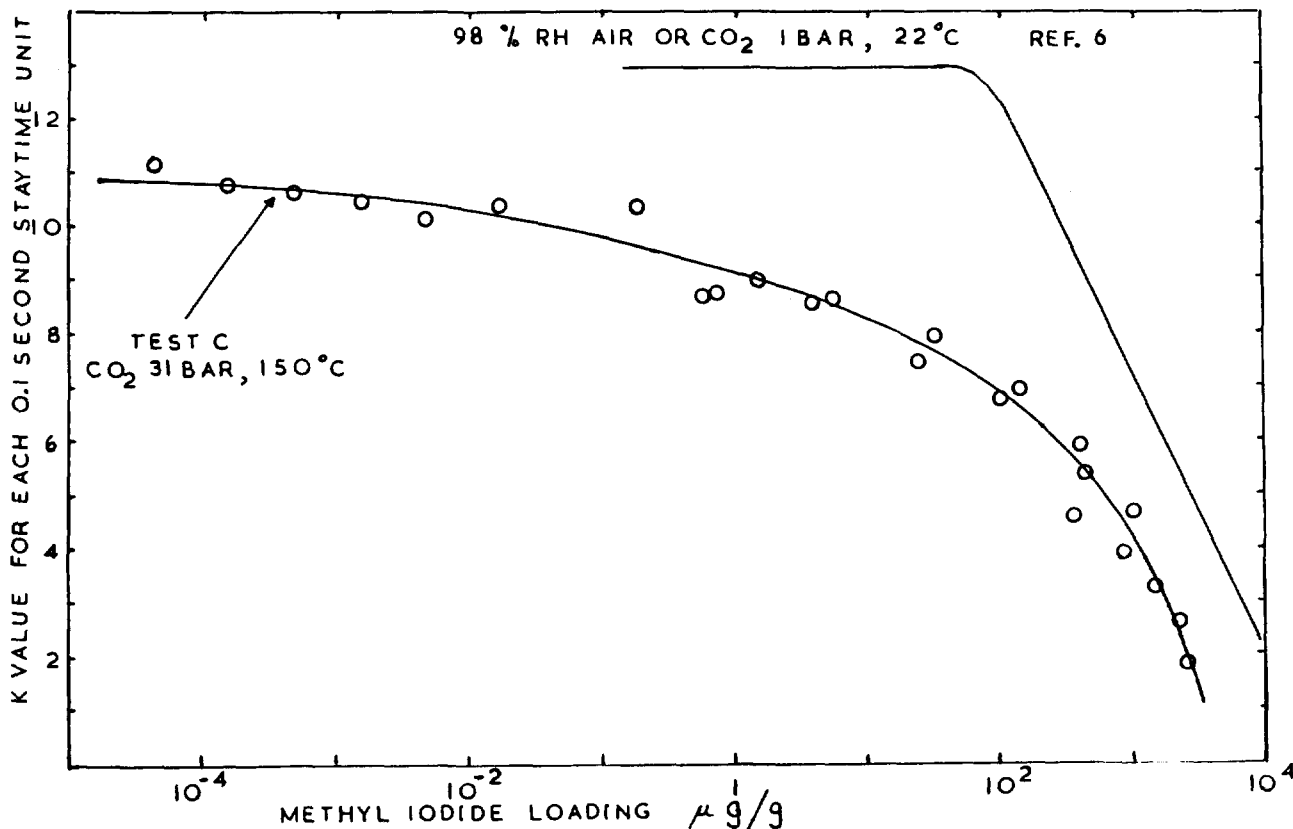


FIG 7 EFFECT OF METHYL IODIDE LOADING

independent of iodine loading up to $50 \mu\text{g CH}_3\text{I/g}$, and then to fall by 5 s^{-1} for every tenfold increase in loading. It was on the basis of this early data that an upper limit of $50 \mu\text{g CH}_3\text{I/g}$ was recommended for charcoal bed design purposes. The parametric data from the previous high pressure - high temperature tests have all been obtained at a mean test bed loading of approximately $50 \mu\text{g CH}_3\text{I/g}$. The use of this data will lead to a significant margin of safety being built into the design. This follows from the present results which show that the trapping performance can improve in the downstream parts of the bed where the loading levels are less than this value.

Test D - Effect of Water Vapour

A large amount of data exists on the effect of water vapour on the performance of KI impregnated charcoal at up to 98% relative humidity at atmospheric pressure and ambient temperatures (⁶). For reactor blowdown bed application, data is required at 32 bar, temperatures up to 275°C and water vapour concentrations in the range 20 vpm to 1100 vpm. The majority of the previous high pressure - high temperature data was obtained at about 200 vpm H_2O . In the present series of tests, which has covered a temperature range from 50°C to 275°C , data have been obtained at 200 vpm and 1100 vpm. The K value results derived are listed in Table 7 and plotted as a function of temperature in Figure 8. It can be seen that, below 200°C the K value is independent of water vapour concentration. However, above 200°C the increase to 1100 vpm H_2O produces some improvement in charcoal performance.

In this series of experiments further data has been obtained on the species of iodine desorbing or penetrating the test bed. The gas emerging from the charcoal test bed passes first through a series of silver plated copper meshes which remove the chemically reactive iodine species (eg elemental iodine or hydrogen iodide). Any methyl iodide present in the gas will pass through the mesh and be trapped on the downstream charcoal traps. A 'species ratio' can be defined as $(\text{I-131 trapped on silver})/(\text{I-131 trapped on charcoal trap})$ and will represent the reactive iodine to methyl iodide ratio.

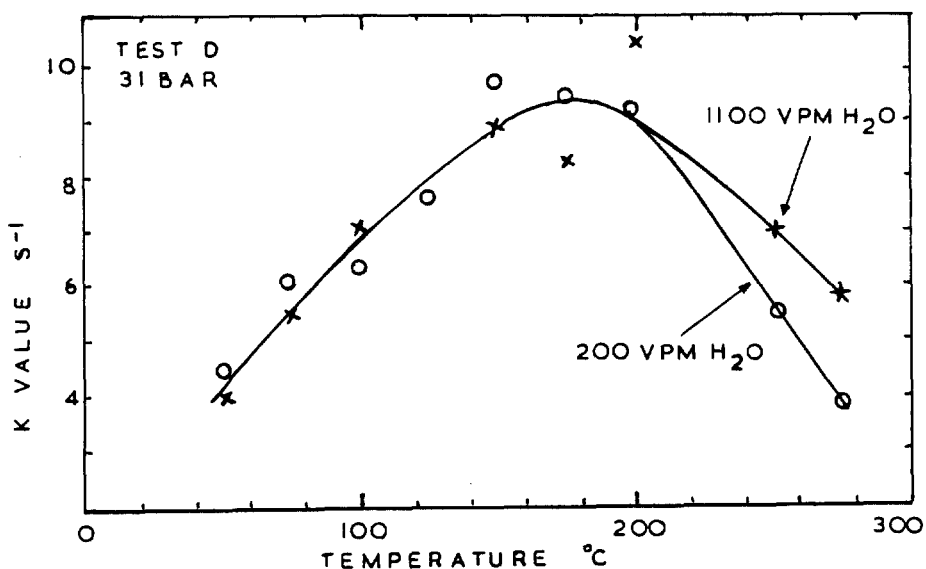


FIG 8. EFFECT OF WATER VAPOUR

Previous results (3) had shown that progressively more iodine is trapped on silver as the temperature is raised above 200°C. The above species ratio has been calculated for the present tests and the values listed in Table 7. The ratios are plotted against reciprocal temperature in Figure 9a. In general, the species ratio for both water vapour concentrations are very similar and increases with increasing temperature. The trend has an associated activation energy of 76 ± 5 K Joules/mole. At high temperatures (ie $1000/T^{\circ}K$ less than 2.1 (or T greater than 200°C)) the two water vapour concentrations give different results, with less silver mesh activity occurring at 1100 vpm H₂O. Hence, the improvement in K value above 200°C with 1100 vpm H₂O appears to be associated with a reduction in the amount of reactive iodine desorbing from the charcoal bed.

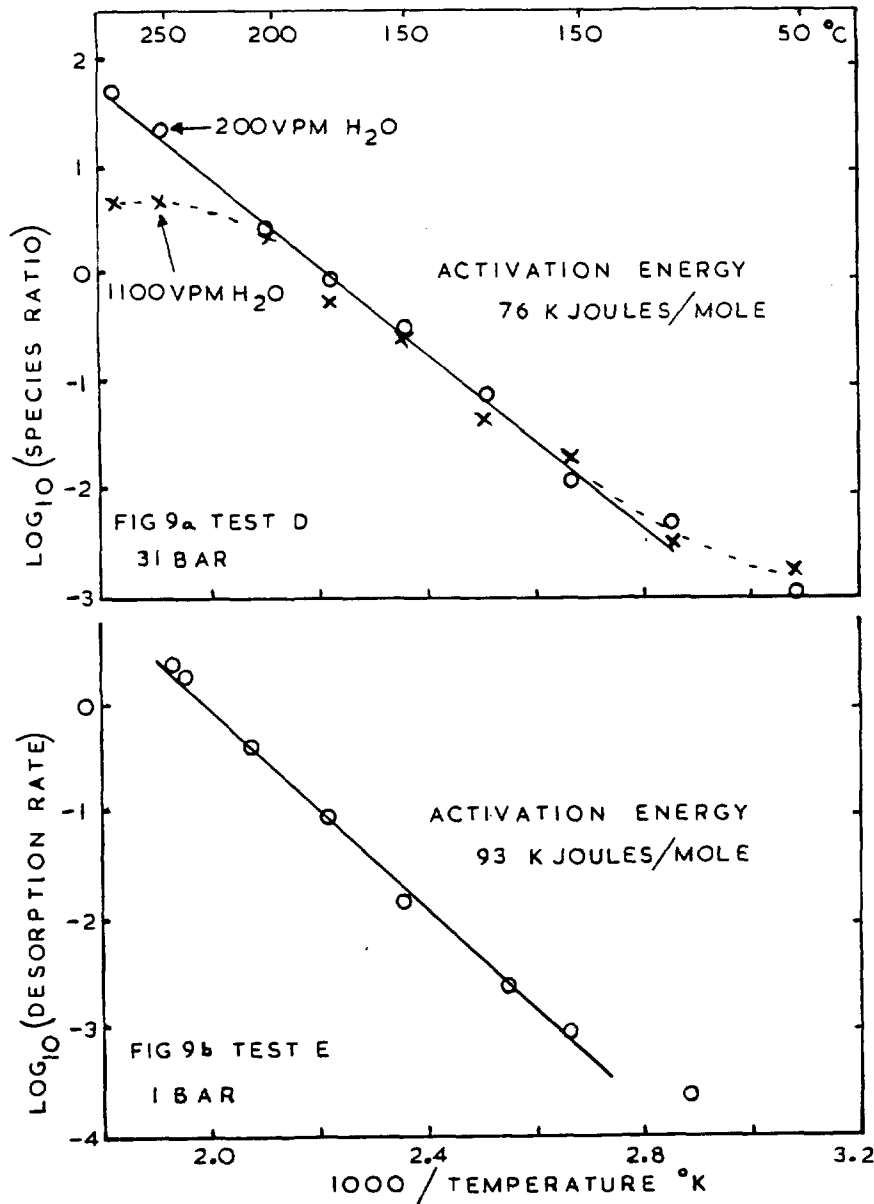


FIG 9. TEMPERATURE DEPENDENCE OF IODINE DESORPTION

Test E - Desorption from KI Charcoal

The high pressure rig tests have indicated the presence of at least two iodine species which desorb from a charcoal bed. In order to investigate further the source and identity of these species a series of tests were carried out in a specially built atmospheric test rig. The rig employed a freezing chain downstream of the heated charcoal test bed. In an initial test, the charcoal bed was heated to 250°C and I-131 labelled methyl iodide injected into the CO₂ purge gas. The bulk of the penetrating I-131 was associated with material frozen out in the main trapping coil at -65°C. Within the first hour after injection, black crystals of metallic lustre were seen to be developing in the coil and by the end of the 4.5 hour run they completely covered the surface of the coil. This material was subsequently identified as elemental iodine. The mass of this iodine was estimated to be at least 50,000 times greater than the amount present in the injected CH₃I. The main source of this iodine could, therefore, only be the KI impregnant. It was further established that this elemental iodine was readily trapped on the surface of silver-plated copper mesh.

Further runs were carried out to determine the temperature dependence of the desorbing elemental iodine. In these tests, pure CO₂ was passed through a bed of KI impregnated charcoal - the KI impregnant being labelled with I-131. The rate of loss of I-131 from the bed was measured at different temperatures in the range 73°C to 244°C at a fixed gas flowrate (face velocity 36 cm/s - bed staytime 0.4 seconds).

The results are listed in Table 8 and plotted as a function of reciprocal temperature in Figure 9b. It can be seen that the rate of loss of iodine from the bed increases exponentially with increasing temperature, rising from 2 x 10⁻⁴% per 24 hours at 73°C to 2.4% per 24 hours at 244°C. The activation energy associated with the process is 93 ± 2 K Joules/mole. It is worth noting that this activation energy is similar to the value of 75 K Joules/mole obtained for the variation in species ratio for the Test D results at 31 bar. If isotopic exchange takes place between the KI impregnant and the incident CH₃I-131 then radio iodine can be released by thermal breakdown of the impregnant. This mechanism is the main contributor to the reduced performance of KI impregnated charcoal at high temperature.

Further tests were carried out in the atmospheric rig at combinations of 4 flowrates (giving bed staytimes of 0.3, 0.4, 0.8 and 1.6 seconds) and 4 temperatures (152°C, 181°C, 212°C and 244°C). The results showed that the rate of loss of iodine at each temperature increased linearly with flowrate, ie doubling the flowrate doubled the iodine loss. Hence the concentration of iodine in the gas emerging from the bed is independent of flowrate. To determine the extent to which iodine could desorb from KI charcoal the test bed was continuously purged with CO₂ at 244°C for a period of 30 days. At the end of this time, it was established that the amount of iodine lost from the bed varied from 53% for the upstream quarter to 32% for the downstream quarter. Since the operating period of a reactor blowdown plant in any one year is relatively short, it is unlikely that sufficient impregnant would be lost to significantly reduce the trapping performance of the plant.

Test F - Iodine Migration

This series of tests in the atmospheric rig was aimed at investigating the detailed distribution of trapped iodine along a charcoal bed. The 200 mm deep bed was subdivided into 12 separate units by the use of discs of stainless steel mesh.

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The experimental method followed the standard procedure: establish temperature (in this case 190°C) and flow conditions; inject I-131 labelled methyl iodide (over a few minutes); continue to purge with CO₂. The final I-131 distribution along the bed was determined at three different purge durations (20 minutes, 3.5 hours, and 23 hours). From the results, which are plotted in Figure 10, it can be seen that the measured distributions can be divided into two regions. For units 1 to 7 there is a simple exponential variation having K values of 52 s⁻¹ and 46 s⁻¹ for the 20 minute and 3.5 hour runs respectively. There is some flattening of the variation at the front end of the bed in the 23 hour run (K value increases from 34 s⁻¹ for unit 1 to 44 s⁻¹ for unit 7). This indicates that there was some

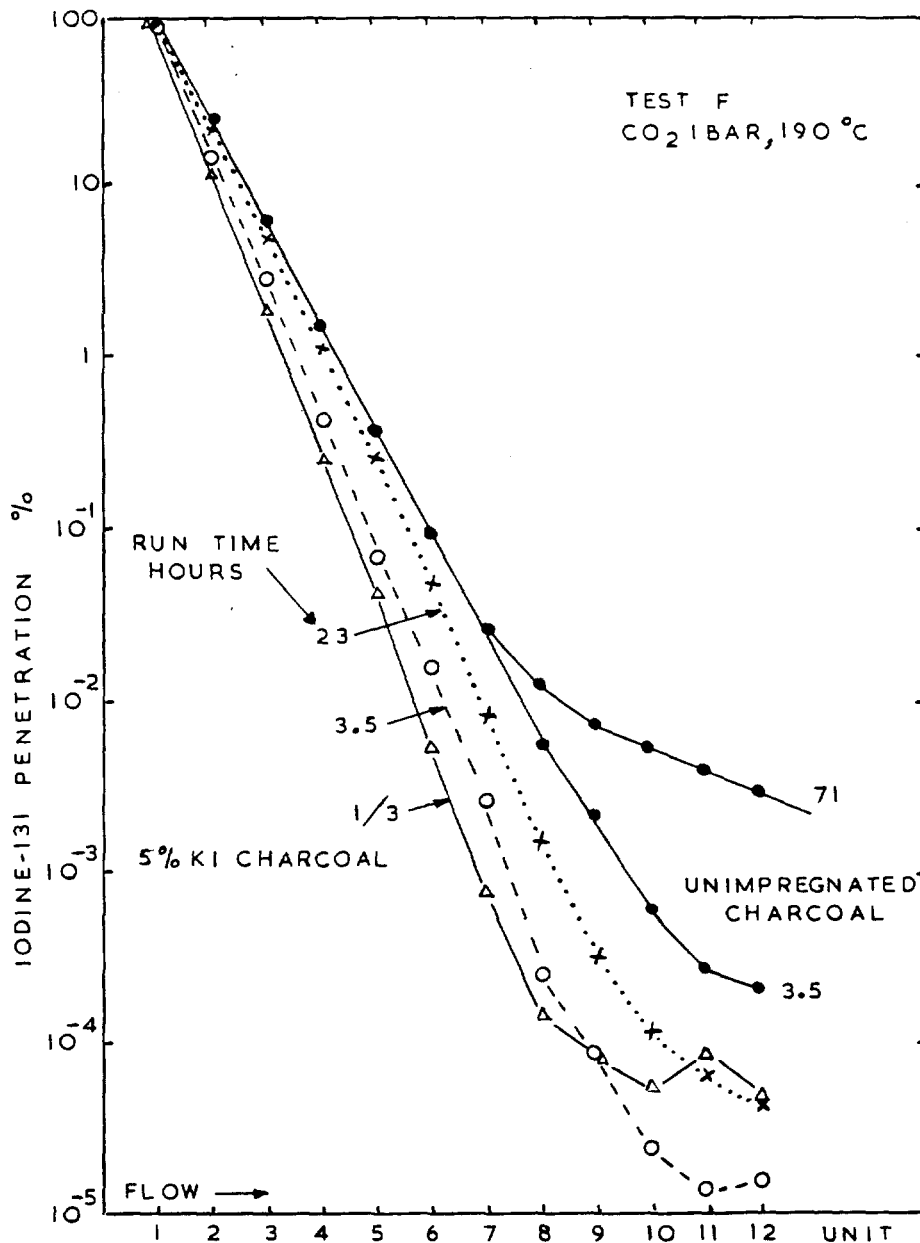


FIG 10. I-131 DISTRIBUTION ALONG TEST BED

migration of iodine along the bed, although the amount is not large.

There is evidence from the much flatter variation in the downstream part of the bed (units 8 to 12) of the existence of a penetrating iodine species. Although the K value for this species could not be accurately determined, it is estimated that it is less than 10 s^{-1} . The fact that the distribution in the downstream part of the bed was unaffected by the insertion of silver-plated copper mesh between units 7 and 8 indicates that the species is not elemental iodine. Further work is required to chemically identify this species, and to determine whether or not it is present as an impurity in the injected methyl iodide.

The results of two additional tests with unimpregnated charcoal are also included in Figure 10. The K value of the front part of the bed is slightly lower than that for KI impregnated charcoal, ie 35 s^{-1} compared to 46 s^{-1} . The penetrating iodine species is also seen to be present in both tests. The 71 hour test results suggest this species has a K value of 8 s^{-1} . Both tests demonstrate that, even though hot flowing gas can remove the KI impregnant, an acceptable trapping performance can be achieved even if all the impregnant is lost.

Development of a Mechanistic Model

The original aim of the early experimental programme was to provide a matrix of parametric data which covered the range of plant operating conditions. The key parameters being pressure, temperature and water vapour concentration. The data now available also includes the effects of gas velocity and iodine loading. Elemental iodine and small amounts of an unidentified penetrating iodine species have also been shown to be present in the gas emerging from a charcoal bed. It was decided that some effort be devoted to the development of a mechanistic model which could be used to predict plant performance.

The model assumes that surface adsorption of methyl iodide is so rapid (under AGR plant conditions) that the rate controlling step is the movement of methyl iodide from the gas phase to the surface of the charcoal granules. The process is therefore 'mass transfer' limited. The adsorbed methyl iodide can either undergo isotopic exchange with the KI impregnant, or be desorbed and re-adsorbed further down the bed. Some elemental iodine-131 can also be transferred along the bed due to thermal breakdown of the impregnant.

The K value of a particular iodine species can be written as

$$K \text{ value} = S \cdot K_m \quad (4)$$

where S = sticking probability
 K_m = mass transfer coefficient

For charcoal beds operating in CO_2 , the following expression is used for K_m

$$K_m = B \left(\frac{P}{T^2}\right)^{-0.39} \cdot \left(\frac{V(1-e)}{de}\right)^{0.61} \quad (5)$$

where B = constant of proportionality
 P = pressure
 T = temperature °K
 V = gas velocity
 e = bed voidage
 de = characteristic granule diameter

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This expression is based on that obtained by Colquhoun-Lee and Stepanek for flow through packed beds (?).

The model, which is still in the early stage of development, has been used in a single iodine species form to check that the process is indeed mass transfer limited. The analysis has, therefore, been restricted to that of methyl iodide only, ie to data at temperatures below 150°C.

It was found that the model satisfactorily predicts the K value dependence on pressure and temperature. The sticking probability S, which is expected to be independent of temperature, varied from 0.55 at 22°C to 0.70 at 150°C. This variation may be due to the model not taking account of changes in the effective surface area of the charcoal as a result of CO₂ adsorption. This adsorption is known to be pressure and temperature dependent. Further experimental work is required to quantify the effect.

Further development of the model will include a treatment of the production and adsorption of both elemental iodine and the penetrating species, together with an extension to 275°C.

V. Conclusions

From the present study of the trapping performance for methyl iodide by 5% KI impregnated 207B charcoal in CO₂, the following conclusions can be drawn:

1. The results at a pressure of 42 bar are in line with earlier data (^{2,3}) at 7, 14 and 31 bar. Above 200°C the charcoal performance (ie K value) is independent of pressure but falls markedly with increasing temperature. Below 200°C there is a progressive reduction in K value with increasing pressure.
2. The K value at 31 bar, 150°C was found to vary as (gas face velocity)^{0.6}. This dependence is similar to that observed previously (⁴) for dry gas (less than 30% relative humidity) at atmospheric pressure and 22°C. The results suggest that the charcoal trapping mechanism is mass transfer limited under these test conditions.
3. Data obtained over a wide range of methyl iodide loadings, from 0.04 µg to 20,000 µg per gram of charcoal, indicate that K value reduces as the iodine loading is increased. The trend is more gradual than that observed previously at atmospheric pressure and 22°C. The present results do not suggest any change to the 50 µg CH₃I/g loading limit currently recommended for charcoal bed design purposes in the UK.
4. Over the temperature range 50°C to 200°C, increasing the water vapour content of the CO₂ from 200 vpm to 1100 vpm has no effect on charcoal performance. The increase to 1100 vpm gives a small improvement at temperatures above 200°C.
5. A series of tests in an atmospheric pressure rig has shown that two additional iodine species are present in the gas emerging from a charcoal bed. The main species has been identified as elemental iodine which is produced by thermal breakdown of the KI impregnant with an associated activation energy of ~90 K Joules/mole. This species has also been shown to be present at high pressure - high temperature conditions and is produced with a similar activation energy

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(75 K Joules/mole). Of smaller importance, at levels of about 2×10^{-4} per cent of the incident methyl iodide, is a penetrating species which has a K value (at 1 bar, 190°C) of 8 s^{-1} . The chemical identity of this species is not known.

6. At a temperature of 244°C and gas face velocity of 36 cm/s, some 10% of the KI impregnant was found to have been removed from the charcoal bed over a 30 day purge period. However, since the operating period of a reactor blowdown plant is relatively short in any one year, it is unlikely that sufficient impregnant would be lost to significantly reduce the adsorbers trapping performance.
7. There is some evidence that trapped methyl iodide can migrate along the bed, although the effect is not large. Further work is required to extend the data to the full blowdown period of 16 hours.
8. A start has been made to develop a mechanistic model to predict charcoal bed performance. An initial test of the model has shown it can adequately predict the methyl iodide K value dependence on pressure (1 bar to 42 bar) and temperature (22°C to 150°C).
9. The experiments carried out to date have shown that there are a number of factors which affect charcoal trapping performance: pressure, temperature, iodine loading, gas velocity, purge time, loss of impregnant, and the presence of iodine species other than the incident methyl iodide. The minimum Decontamination Factor required of a blowdown iodine adsorber is ~ 200 . The main conclusion to be drawn from the results to date is that the actual value could greatly exceed 10^4 , provided of course that there is no by-pass leakage of gas.

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Table 4. Results for Test A - effect of temperature at 42 bar

<u>Conditions</u>		
Gas:	CO ₂ recirculation	
Pressure:	42 bar	
Face velocity:	36.4 cm/s	
Staytime:	0.1 second per unit	
Water vapour:	less than 200 vpm	
Run duration:	4.5 hours	

<u>Run</u>	<u>Temperature</u> °C	<u>K value</u> seconds ⁻¹
A1	140	9.0
A2	170	10.0
A3	200	9.8
A4	214	10.0
A5	250	6.5

Note: the Kstd value of the stock material = 7.5 s⁻¹

Table 5. Results for Test B - effect of face velocity

<u>Conditions</u>		
Gas:	CO ₂ straight through	
Pressure:	31 bar	
Temperature:	150°C	
Water vapour:	25 vpm	
Oxygen	3 vpm	
CH ₃ I loading	0.3 µg/g	
Run duration:	70 minutes	

<u>Run</u>	<u>Face velocity</u> cm/s	<u>K value</u> seconds ⁻¹
B1	18.2	8.6
B2	36.0	13.5
B3	53.0	16.3

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Table 6 Results for Test C - effect of methyl iodide loading

Conditions

Gas: CO₂ recirculation
 Pressure: 31 bar
 Temperature: 150°C
 Face velocity: 36 cm/s
 Water vapour: 200-350 vpm
 Run duration: 4.5 hours
 Unit staytime: 0.1 second

<u>Run</u>	<u>Charcoal Unit</u>	<u>Loading</u> <u>µg CH₃I/g</u>	<u>K value</u> <u>seconds⁻¹</u>
C1	1	3.20 E-2*	8.38
	2	4.92 E-3	10.16
	3	4.80 E-4	10.59
	4	4.24 E-5	11.16
	5	3.15 E-6	9.87
C2	1	1.44 E+0	8.94
	2	1.91 E-1	10.37
	3	1.75 E-2	10.38
	4	1.61 E-3	10.46
	5	1.46 E-4	10.79
C3	1	4.67 E+2	5.32
	2	1.54 E+2	6.93
	3	3.30 E+1	7.93
	4	5.40 E+0	8.53
	5	7.70 E-1	8.61
C4	1	1.08 E+3	4.64
	2	4.24 E+2	5.94
	3	1.14 E+2	6.79
	4	2.48 E+1	7.41
	5	4.70 E+0	8.60
C5	1	2.85 E+3	1.83
	2	2.46 E+3	2.63
	3	1.56 E+3	3.25
	4	8.20 E+2	3.88
	5	3.68 E+2	4.49

*3.2 E-2 ≡ 3.2 10⁻²

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Table 7. Results for test D - effect of water vapour

Conditions

Gas: CO₂ recirculation
 Pressure: 31 bar
 Face velocity: 36 cm/s
 Run duration: 4.5 hours

Dry CO₂: less than 200 vpm water vapour

<u>Run</u>	<u>Temperature</u> °C	<u>K value</u> <u>seconds⁻¹</u>	<u>Species*</u> <u>ratio</u>
D1	275	2.77	50.4
D2	250	5.44	22.0
D3	200	9.07	2.33
D4	175	9.50	0.878
D5	150	9.86	0.314
D6	125	7.56	0.0654
D7	100	6.40	0.0125
D8	75	6.14	0.0049
D9	50	4.59	0.0011

Wet CO₂: 1100 vpm water vapour

<u>Run</u>	<u>Temperature</u> °C	<u>K value</u> <u>seconds⁻¹</u>	<u>Species*</u> <u>ratio</u>
D10	275	5.86	4.39
D11	250	6.93	4.72
D12	200	10.51	2.01
D13	175	8.19	0.506
D14	150	8.85	0.251
D15	125	7.55	0.0417
D16	100	7.35	0.0197
D17	75	5.41	0.0031
D18	50	4.01	0.0018

*ratio of I-131 on silver/copper mesh
I-131 on charcoal trap

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Table 8. Results for test E - desorption from KI impregnant

<u>Conditions</u>		
Gas:	CO ₂ recirculation	
Pressure:	1 bar	
Face velocity:	36 cm/s	
Water vapour:	less than 20 vpm	
Oxygen:	~ 5 vpm	

<u>Run</u>	<u>Temperature</u> °C	<u>% loss I-131</u> <u>per day</u>
E1	73	0.00022
E2	103	0.00078
E3	120	0.0024
E4	151	0.0150
E5	180	0.0867
E6	209	0.412
E7	240	1.98
E8	244	2.37

DISCUSSION

HYDER: I was very interested in your results on the loss of impregnant from carbon that had been in service for a long time. I reported some years ago, (European ACC paper) using a SEM device, that I saw a loss of impregnants from samples that had been in service in our reactor for a long time. I was not able to determine what happened, but in the work which I will be talking about in the next paper I did get another very old sample from the Naval Research Lab, and found to my surprise, on doing some analyses with it, that it actually contained a small amount of methyl iodide. This is aged carbon, KI-impregnated, that had never seen any radioiodine or anything like that. So it may be that the penetrating species which you observed could be an organic iodide.

COLLINSON: It is comforting to learn of other results which support our findings. I assume that your carbon is also KI-impregnated. We did some tests whereby we knew that iodine was passing through the bed and we inserted silver mesh through the bed which should have removed any elemental iodine. The material still came through the back end so we decided that it certainly was not elemental iodine. But, as you suggest, it could very well be some organic iodine. The other possibility that we mentioned is the fact that we need to be certain there is not any impurity in the methyl iodide source that we inject. This is one thing we need to check.

KOVACH, J. L.: I would like to caution the generalization that bulk diffusion is the rate controlling step. The rate controlling step can change with velocity.

COLLINSON: I realize that we have to specify the velocity range over which we must apply the data. The plant operating range of face velocity falls within the range tested. It is over this range that we consider bulk diffusion is the rate controlling mechanism at temperatures below 150°. I thank Mr. Kovach for his comment that we should not necessarily assume the mechanism is dominant at all velocities outside this range.

EFFECT OF ORGANIC MATERIAL ON CARBON AGING

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Introduction

Activated carbon is used in the confinement systems for the Savannah River Plant reactors to retain elemental or organic radioiodine in the reactor building effluent air. In this application it is exposed to an airflow of seven or eight bed volumes per second for many months. During this time, its ability to retain organic iodine slowly degrades, as a result of reactions with air and airborne materials. At these flow rates, even small traces of impurities in the air can have an important cumulative chemical effect over the service life of the carbon. Many aspects of the aging and deterioration of the carbon have been characterized by studies at Savannah River and elsewhere.⁽¹⁻⁴⁾ The surface of the carbon becomes acidic, and its ability to retain iodine from methyl iodide falls off as it ages.

Traces of organic vapors are ubiquitous, and the accumulation of organic material on the carbon surface might play a significant role in the aging process. Activated carbon is an effective sorbent for concentrating and retaining many organic vapors. However, the accumulation of organic impurities in the carbon at Savannah River had not been previously measured, although procedures have long been in place to limit releases of organic vapors in the reactor buildings. The study reported here was undertaken to quantify the effect of organic accumulations on the aging process, and to provide a basis for limiting the use of volatile organic materials in the area ventilated by the confinement system.

Quantitative studies of the effects of sorbed organic materials on methyl iodide retention had been reported by other investigators.^(4,5) These studies confirmed that sorbed organic materials degrade carbon performance, and that this effect varies from one organic compound to another. However, these studies were generally conducted with new carbon, and the relative importance of organic accumulation to the aging process under the conditions existing at Savannah River could not be inferred. The studies reported here were undertaken to determine the practical importance of organic accumulation as compared to other aging mechanisms. In addition, the effect of organic accumulations on the radiolytic release of iodine was investigated. Radiolytic release of iodine from carbon is a principal concern in the analysis of potential accident sequences at SRP, and this had been investigated in earlier studies without a knowledge of whether any organic material was present.⁽¹⁾

Three types of investigation were conducted. In the first, the amount of organic material accumulated on carbon during service was measured in a large number of carbon samples from the reactor confinement system, using liquid extraction and quantitative gas chromatography. The resulting data were correlated with methyl iodide retention measurements and statistically examined to determine the importance of the organic content to the aging process. In a few samples additional organic material (xylene) was added to the organics already present, and the methyl iodide retention was measured before and after this addition, to determine the differential effect of the added material.

The second set of experiments dealt with a single compound, bromotrifluoromethane ("Halon"®), a fire extinguishing agent used in large quantities in automatic protective equipment in the reactor building. Its possible persistence on the carbon following a release was of concern because of the quantities involved. The loading and release of this compound from new and used carbons was measured experimentally.

Finally, the effect of organics on the release of iodine from carbon in a radiation field was investigated. The release of organic iodine from a variety of carbon samples was measured before and after the addition of iodine to the carbon. The experiments included studies in which this was measured before and after adding organic material to the samples.

Experimental

Carbon Samples

Carbon samples were obtained from routine sampling of the confinement system at the Savannah River Plant. The carbon used there is North American Carbon Co., type GX-176, coconut shell charcoal with a surface area of about 1000 m²/g as received. This is impregnated with 2.0% potassium iodide and 1% triethylenediamine (TEDA) by weight. Methyl iodide retention in this carbon involves both exchange with the iodide impregnant, and chemical fixation with the TEDA. After several months, most of the TEDA has disappeared, and the exchange process dominates. In the radiolysis studies carbon samples from other sources were also used for comparison; these included two samples obtained from Dr. V. Deitz of the U.S. Naval Research Laboratory, and a sample of used carbon from the interlaboratory round robin comparison coordinated by EG&G-Idaho.⁽⁶⁾ The USNRL samples, identified as samples 5338 and 5340, had been aged 6 and 36 months, respectively, in a spent fuel ventilation system facility.⁽⁷⁾ The EG&G sample was identified as 2U8-2. Additional information on the carbon samples is provided in the discussion section and the associated tables.

Methyl Iodide Retention

The samples were characterized by measurement of methyl iodide retention in a one-inch-thick test bed using Method B, ASTM Standard D3803. According to this method the temperature was maintained at 80°C and the relative humidity at 95%. These measurements were made by the Nuclear Containment Systems Co, Inc., Columbus, Ohio. In the samples with added xylene the samples with and without the added material were run simultaneously in a parallel arrangement that ensured identical conditions for both samples throughout the analysis.

Measurement of Organic Content

The organic content of carbon was measured by extracting 1.0 g of carbon with 3.0 ml of methylene chloride, CH₂Cl₂ in a sealed vial. The contact time was approximately 24 hours at room temperature. Spectroscopy-grade normal heptane (0.1 ml) was added to the resulting solution as an internal standard, and the total amount of organic material present determined by gas chromatography. The separation was made on a 6 ft by 1/8 inch 20% SP 2100 Supelcoport® column, coupled to a flame ionization detector. The column, initially at 75°C, was held at this temperature for two minutes and then heated at the rate of 20°C per minute to 150°C. The column was then held at this temperature for ten minutes to ensure that all material mobile at this temperature was eluted. Separate experiments without heptane ensured that no significant peaks were obscured by the standard. As a test, samples were also run with benzene as an internal standard; the results obtained were similar within experimental error, and the response of the system to heptane and benzene was consistent with the quantities added. A representative chromatogram is shown in figure 1. The chromatograph automatically integrated peak heights; the heights of the unknown were compared to those of the internal standard, and the amount of unknown calculated directly from this comparison. Separate studies for identification of the organic materials were made using a gas chromatograph fitted with a mass spectrograph detector.

Carbon Samples with Added Organic Material

Three samples were prepared in which additional xylene was added to determine its differential effect on carbon properties. In each of these, the carbon sample was placed overnight in a bell jar containing an open pan of xylene. The carbon was then allowed to air dry before analysis and use, so that any condensed xylene not held by surface forces would evaporate.

A sample of carbon with dodecane added was prepared for the radioanalysis studies by pouring 2 ml of mixed dodecanes over 55 g of carbon in a beaker. In order to distribute the dodecane over the carbon, a watch glass was put on top of the beaker, and the system was gently warmed on a hotplate for about an hour. Subsequent analysis of a well-mixed sample showed about 0.3 weight % of dodecane, indicating that only part of the dodecane had been retained.

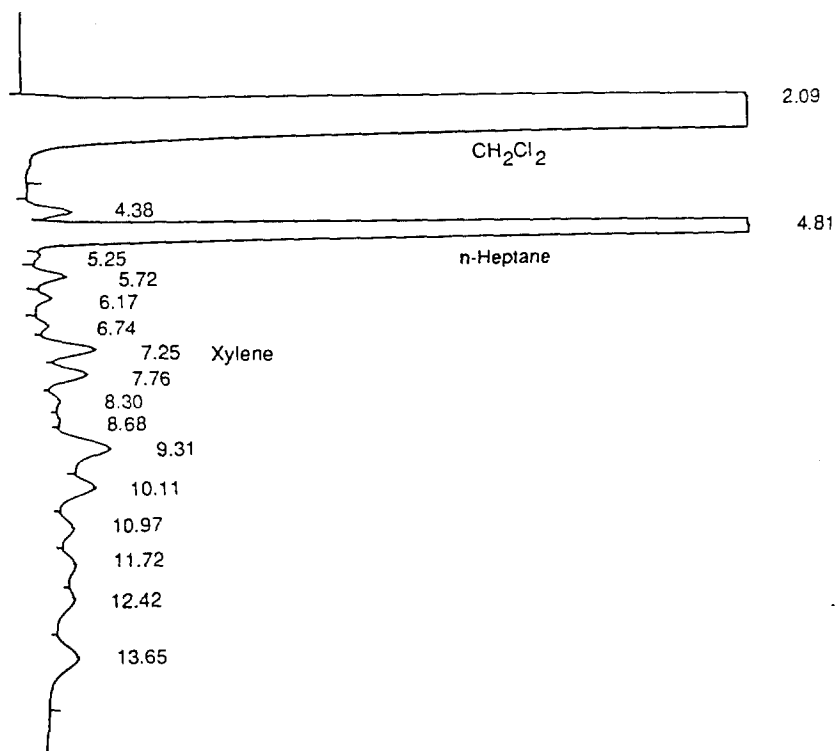


Figure 1. Chromatogram of the organic extract from a SRP carbon sample. CH_2Cl_2 is the extracting solvent; n-heptane is added as an internal standard. Numbers show elution times in minutes.

Bromotrifluoromethane Studies

The residence time of bromotrifluoromethane on the carbon was measured in experiments in which the pure gas was blown through a bed of the carbon of interest for a period long enough to ensure that the surface was saturated, and then air was blown through the bed at a measured velocity. Flow rates up to and including that used in the SRP filter compartments were tested. Carbon samples were removed periodically and analyzed for CF_3Br by neutron activation of bromine. Additionally, loaded samples were removed and stored for various periods of time before measurement. The results from these stored samples showed that the loss of CF_3Br from the carbon was negligible during the period of time required for analysis.

Irradiation Studies

Irradiation studies were performed at the Neely Nuclear Research Center of the Georgia Institute of Technology ("Georgia Tech"). The equipment used is shown schematically in Figure 2. The carbon sample of interest is placed in a ^{60}Co radiation field of about 3.8×10^6 R/hr (10.6 Gy/sec) in a pool irradiator. A stream of air, dry or humidified as desired, is circulated at approximately 0.0046 m/s through the carbon continuously. A portion of the effluent stream is sampled for organic iodides. After a period of time in which a background sample is taken, a low concentration of iodine is added to the air stream and accumulated on the carbon over a period of about an hour. The total iodine added is about 0.05 g/g carbon. The system is sampled during this time. Airflow is then maintained for about two additional hours, and another sample is taken during the last half hour. Sampling involved contacting a side stream of the effluent from the carbon cell with toluene for 30 minutes to concentrate organic material in the toluene solution; the resulting solution was then analyzed by gas chromatography with an electron capture detector in the Georgia Tech analytical laboratories. Standards of many simple organic iodides were used to calibrate the apparatus and to ensure that they would be detected. Of all the simple organic iodides tested, only methyl iodide was consistently observed as a significant product. For most samples only this material is reported as a radiation product.

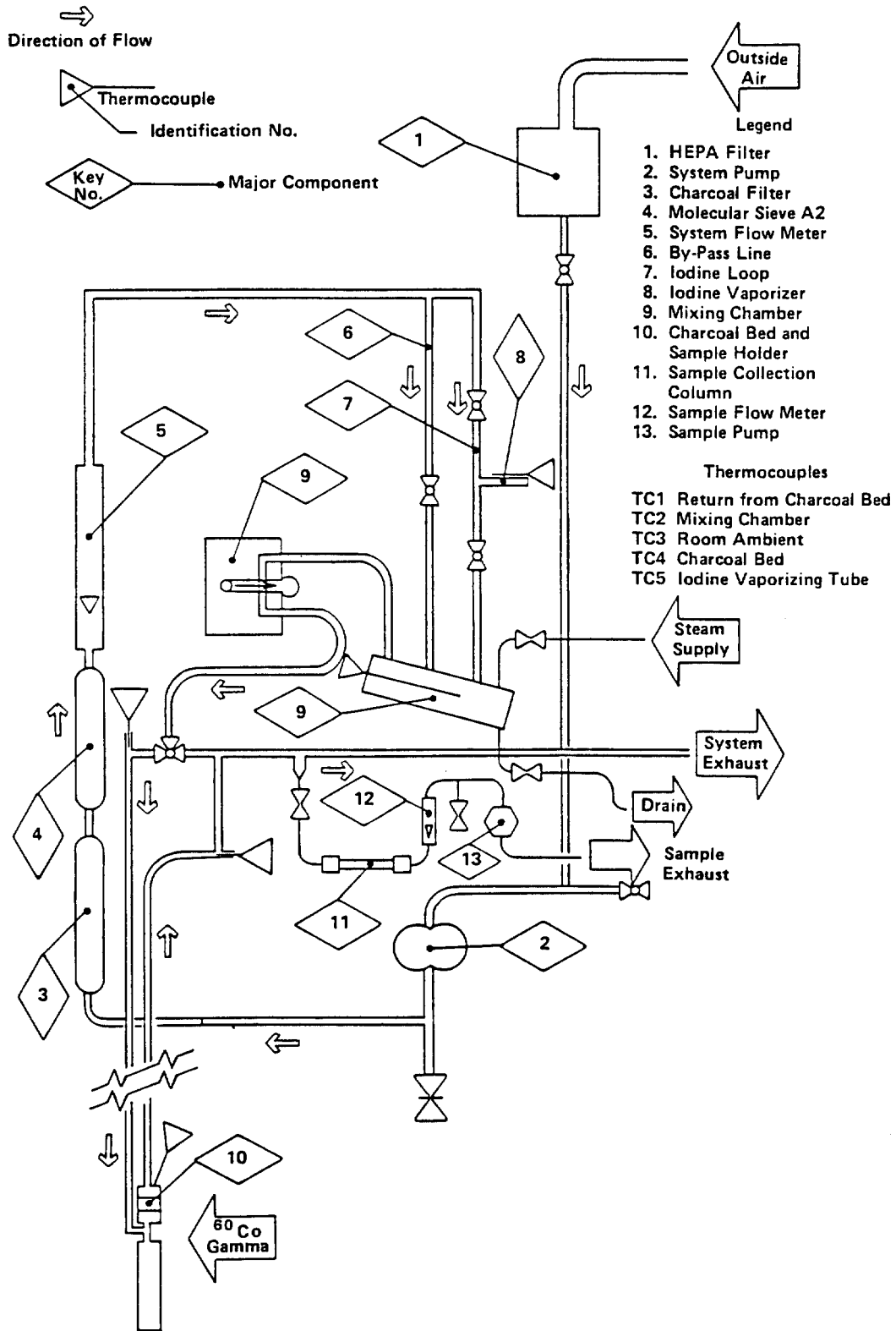


Figure 2. Experimental apparatus for radiolysis experiments.

Results and DiscussionTypical Organic Contents

Figure 3 shows the organic content of the carbon samples studied as a function of time in service. The figure shows that most samples follow a trend of gradual accumulation of organic material up to around 1% at 30 months, but also shows some samples lying outside this trend. These outliers include an older sample from C reactor and several more recent samples obtained from K reactor. They can be explained by the unintentional exposure of these samples to organic material as the result of its release to building air during maintenance operations. The amount of organic material required to contaminate the carbon in one of the five filter compartments (approximately 1700 lb) to three weight per cent is only about 50 lb. Thus fairly modest amounts of paint, adhesives, etc., can significantly cause significant organic loadings.

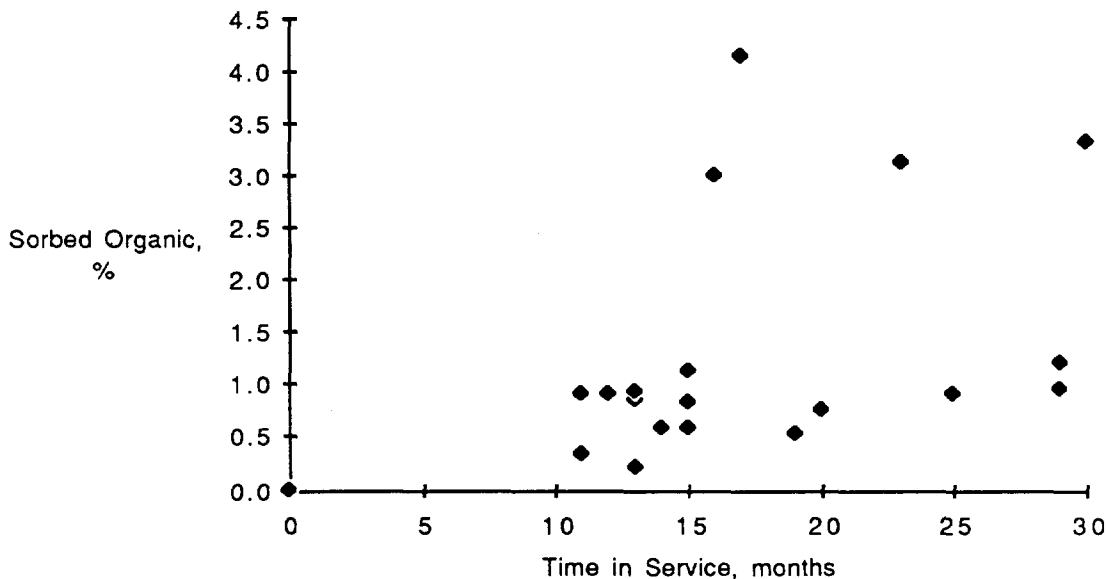


Figure 3. Organic content as a function of service time.

The nature of the organic compounds found was consistent with this hypothesis. Xylene was identified in nearly all samples, on the basis of its characteristic elution position and the dual peak produced by the three isomers present in the commercial solvent. Compounds eluting ahead of xylene were found only in a few carbon samples, and are presumed to have desorbed from the carbon. Further identification of the organic vapors sorbed on some of the carbon samples was undertaken with the GC/MS equipment. Xylene was confirmed; the other compounds were principally saturated hydrocarbons as indicated by their fragmentation patterns. They were not further identified. Some chromatograms of samples high in organic content were very similar to chromatograms of vapors obtained from paints used at the site. The principal exception was that the more volatile components of these solvents were missing on the carbon samples from the reactors. These presumably diffused through the carbon bed and been lost during the time between their original release and sampling.

Figure 4 correlates organic content and methyl iodide retention in the samples studied. Methyl iodide retention generally decreases as the organic content increases, but it is difficult to separate this from the effect of other aging processes on methyl iodide retention. To test the possible effect of organic content, these data were subjected to a statistical analysis performed by R. L. Postles of SRL. He fitted the data to a linear model, and found that he could best fit them with the equation

$$R = 92.1 - 2.0T - 7.0S \quad (1)$$

where R is methyl iodide retention in percent, T is service time in months, and S is sorbed organic

material in weight per cent. From his statistical analysis Postles concluded that the effect of sorbed organic is real, but that the "uncertainty" of the data is large enough to make more elaborate analysis of the data unjustified. Over a service time of thirty months, during which the carbon typically sorbs 1 to 3 weight % of organic, the organic effects are less important than other aging processes; i.e., the effect of the S term is about half that of the T term.

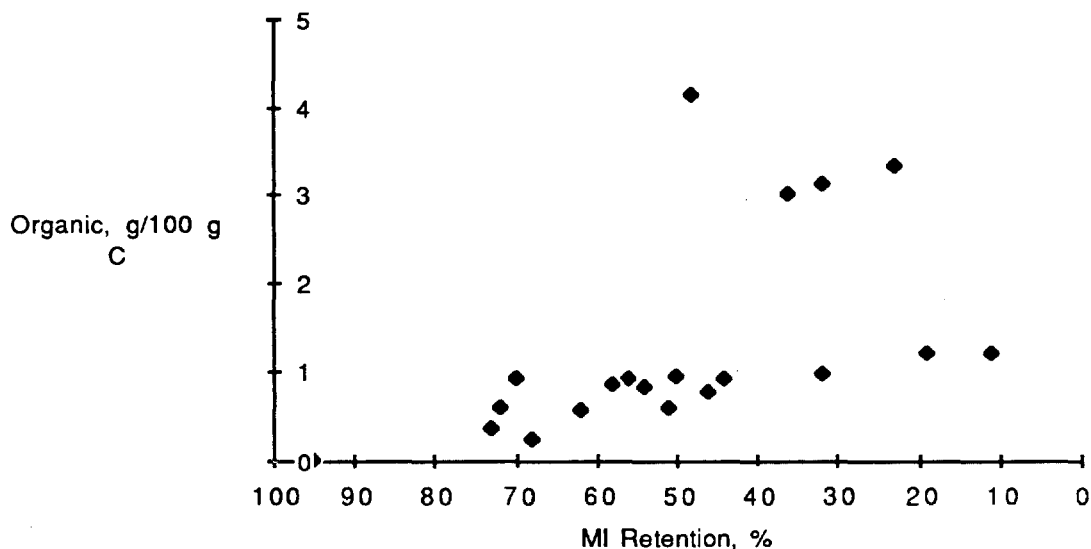


Figure 4. Correlation of organic content with methyl iodide retention.

Two experiments were performed in which used carbons were deliberately loaded with xylene vapor and then subjected to the methyl iodide test. One of these (15732) had been quite low in organic content before the test; the other (15021) was relatively high. The results are shown in Table 1. The parallel arrangement previously described was used to directly compare the untreated and treated carbon samples of each batch. (Note that the organic contents shown are only approximate. At the time these experiments were done the method for organic analysis was still under development, and the heptane internal standard was not used.) Although xylene was identified by Broadbent⁽⁴⁾ as a material which has a relatively large effect on carbon performance, its effect on these used carbons is small or nonexistent.

Table 1. Methyl iodide retention in samples with and without xylene.

Sample	Xylene, wt%	Methyl Iodide Retention:	
		Without Xylene	With Xylene
15021	6	48	49
15732	7	51	48

Methyl iodide retention measured at 80°C, 95% relative humidity, one inch bed thickness.

The results of these experiments, together with the statistical analysis previously described, show that the effect of organics on carbon performance is limited. Although sorbed organics decreased somewhat the methyl iodide retention by carbon, the carbon still retains much of its effectiveness even in the presence of rather large amounts of sorbent.

Some inference is possible regarding the mechanism by which sorbed organics affect methyl iodide retention. In these used carbon samples, all of the impregnant TEDA has been lost by evaporation or reaction. Methyl iodide retention depends on the availability of the potassium iodide impregnant for exchange with the methyl iodide. Other aging processes chemically alter this impregnant⁽²⁾ or remove it,⁽³⁾ but the sorbed organics do neither. Their effect may be simply to make it more difficult for methyl iodide to reach the impregnant.

Sorption and Desorption of Bromotrifluoromethane (Halon®)

The fire extinguishing agent Halon® (CF_3Br) is used at SRP and elsewhere in the nuclear industry for fire protection of important electrical equipment that would be ruined by water flooding. Over a thousand pounds may be present in a given reactor area. An inadvertent discharge of part of this inventory raised questions of its persistence on the carbon and its possible deleterious effect on carbon performance in an accident. The first question was answered by experiments of its loading on carbon and desorption into an air stream. Some results from these studies are shown in Figure 5.

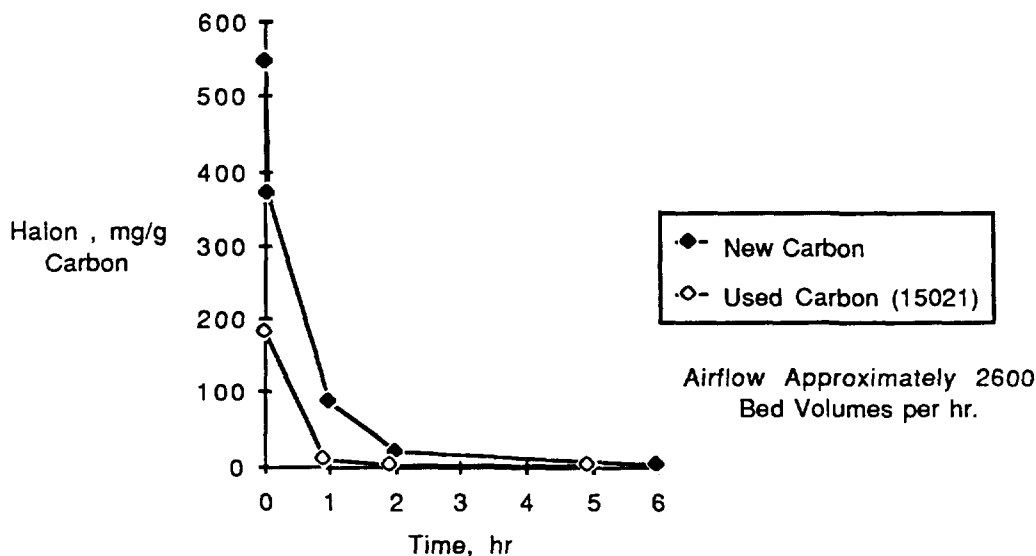


Figure 5. Halon® elution from carbon.

As the figure shows, about 0.5 g of bromotrifluoromethane per g carbon is sorbed on carbon from an atmosphere of the pure material. Used carbons sorb less than new carbon, in approximate proportion to the surface area as measured by the BET method. As the figure shows, desorption of the carbon in flowing air is rapid. Several experiments conducted at high airflows, similar to those used in the SRP filter compartments, indicated a half-life for the sorbed CF_3Br of slightly less than ten minutes.

These data indicate that so long as airflow is maintained, any CF_3Br loading will be transient. The maximum amount that could be released in the building is in the range of 15% to 20% of the weight of the carbon in the filter compartments. The data obtained on other organic materials, as described above, indicate that a loading in this range is not likely to decrease the methyl iodide retention very much. Actual loadings would be lower, because the CF_3Br would be diluted into a large volume of air. Consequently, it would reach the filter compartments over a period of time comparable to its desorption half-life.

Radiolysis Studies

Evans^(1,8-10) studied the radiolysis of iodine-loaded carbon using radioiodine tracers. He reported that the radiolysis of iodine-loaded carbon releases some of the iodine in the form of organic iodides, and that amount released increases with service time. This increase was not only the result of the decreasing retention of organic iodides by the used carbon; evidently changes in the chemistry at the carbon surface were increasing the rate at which the organic iodides were synthesized. Evans studied this effect at high dose rates (>30 Gy/sec) and found the yield of organic species to be independent of dose rate in this range, but dependent on total dose; the rate decreased markedly within a few hours.^(8,9) Evans found a correlation between methyl iodide retention in carbon and radiolytic iodine production over a range of aging times,⁽¹⁾ but he did not identify the specific aspects of surface chemistry that were responsible for the radiolytic processes.

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The radiolysis study was undertaken to try to clarify the reaction mechanisms that produce organic iodides in irradiated carbon. A specific goal was to be able to use simple tests to characterize a carbon in terms of its potential for releasing iodine under accident conditions of high temperature, humidity, and radiation. Evans' measurements were too difficult to be used routinely as a quality control method. A working postulate for this study was that the presence of sorbed organic vapors on the carbon surface might have a major effect on the radiolytic release of iodine from the carbon. It appears from the results, however, that any such effect is fairly small. This result was reassuring, in that organic contamination of carbon prior to an accident will not increase iodine releases by a large factor. However, the larger questions of radiolytic mechanisms and of identifying useful parameters for characterizing partly used carbons are still unresolved.

In contrast to the work by Evans, the current studies were not conducted by the radioiodine labeling technique. Rather, unlabeled organic iodides were concentrated and measured by purely chemical methods. The radioiodine labeling technique used in previous work corresponds more closely to the behavior of the system in containing radioiodine in an actual release, but the technique chosen shows other processes involving the inactive iodine impregnant. As will be seen, such processes are significant.

Irradiations were performed at low humidities (<18% relative humidity) and at humidities exceeding 90% relative humidity. The results are tabulated in Tables 2 and 3, respectively. Information on the carbon samples is tabulated in Table 4. For each carbon sample four measurements are shown, each representing a thirty-minute sample period. These are as follows:

1. A background sample with the carbon in place, but without irradiation.
2. A sample with the carbon-containing cell in place in the radiation field, but no iodide added.
3. A sample taken during iodine addition to the irradiation cell.
4. A sample taken approximately 90 minutes after iodine addition was terminated.

Table 2. Methyl Iodide Production at Low Humidity.

Sample	Methyl Iodide Recovered, ppb:		Irrad + I ₂	Residual
	Background	Irradiated		
5338	ND	0.17	ND	ND
5340	0.40	3.1	5.1	2.4
2U8-2	ND	ND	ND	ND
15021	ND	0.45	0.40	ND
15732	ND	0.31	0.80	0.58
K2084	ND	0.40	2.1	2.1
P3046	0.14	0.07	0.03	0.07

Carbon temperature 60°C to 70°C during and after iodine addition. Relative humidity <18% in all samples.

Table 3. Methyl Iodide Production at High Humidity.

Sample	Methyl Iodide Recovered, ppb:		Irrad + I ₂	Residual
	Background	Irradiated		
5338	0.44	0.44	3.1	4.2
5340	5.9	12.6	53	155
2U8-2	ND	0.5	0.5	0.5
15021	ND	0.75	2.9	4.8
15732	ND	1.2	3.0	1.5
K2084	ND	1.0	2.6	2.7
P3046	ND	1.2	2.5	2.5
L3126	ND	.002	.028	.062

In L3126 a trace of iodotoluene was observed during iodine addition. Relative humidities were >90% in all cases.

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Table 4. Carbon Samples.

Sample	Source Months Service	Organic Content Wt. %	Methyl Iodide Retention, %
5338	NRL, 6	0.6	73 (a)
5340	NRL, 36	1.9	41 (a)
2U8-2	INEL	0.7	82 (b)
15021	SRL, 17	4.4	48 (c)
15732	SRL, 14	0.6	51 (c)
K208	SRL, 16	2.0	38 (c)
P3046	SRL, 29	1.2	15 (c)
L3126	SRL, 19	0.5	62 (c)

- a. 30°C, two-inch bed; see Ref. 9.
- b. 30°C, two-inch bed. NCS methyl iodide value shown (Ref. 6)
- c. 80°C, one-inch bed

These are tabulated in Tables 2 and 3 for each test. As anticipated, the yield of methyl iodide from the samples irradiated at high humidities was greater than that from samples irradiated in dry air. Methyl iodide is retained more strongly by the carbon in dry air, and some was no doubt so retained during this experiment. Table 3, showing the high humidity results, is therefore of more interest, for more of the methyl iodide was released.

The first interesting result observed was that significant amounts of methyl iodide were generated from most samples during the period before any iodine was added to the irradiation cell. Some methyl iodide was recovered during this phase from all samples in the high humidity irradiations. The amount generated during this period was lowest for the three low-service samples INEL 2U8-2, NRL 5338, and L3126, all of which were also low in organic contamination. The methyl iodide yield was highest from the NRL carbon sample 5340. This material, which had undergone the most service, 36 months, generated more methyl iodide than the others in all phases of the test; it even appears to have contained some methyl iodide prior to irradiation. The remaining samples, which varied both in length of service and in organic content, showed no clear trend.

As expected, the rate of methyl iodide generation increased in nearly all samples during the period when iodine was added. It remained high 90 minutes after iodine addition ceased. Some carbons, in fact, showed increased yields of methyl iodide at the time. The same sort of general trend is observed during these periods as was observed before iodine was added. Sample 5340 gives very high yields, the low-service samples 5338 and 2U8-2 give low yields, and the others are somewhere in between. The tables show no clear correlation of organic content (as separated from other aging parameters) with methyl iodide retention.

To address directly the question of the effect of added organic material on the methyl iodide yield during irradiation, portions of carbon batch L3126 were loaded with additional organic material (dodecane or xylene) before irradiation. This carbon had a rather low organic content, 0.54 pm, prior to loading the added material. The xylene loading was quite high, approximately 17 weight per cent. However, as previously noted, the added organic in the dodecane-treated sample was only about 0.3 weight per cent.

Results from the irradiation experiments are shown in Table 5. The observed methyl iodide recoveries are low and scattered, but it is clear that the massive amount of added xylene does not produce a correspondingly high iodine loss. The scatter may be due in part to the high humidities during this experiment. Iodoxylene was not observed; if produced, it was probably retained on the carbon.

These results indicate that radiolytic releases of iodine are more dependent on general aging processes than on the organic contamination of the surface. These aging processes are detected and defined by the methyl iodide retention of the carbon. Thus the results support the customary Savannah River method of evaluating carbon degradation by methyl iodide retention.

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Table 5. Irradiation of Organic-Treated Samples.

Sample	Methyl Iodide Revocered, ppb:		Irrad + I2	Residual
	Background	Irradiated		
L3126 Untr.	ND	0.002	0.028	0.062
L3126 + Dodecane	ND	0.007	0.010	0.020
L3126 + Xylene	ND	0.022	0.035	0.022

Humidities near 100% during this experiment.

Acknowledgements

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DISCUSSION

WREN: We have also studied the effect of contaminants on TEDA charcoal. We found that inorganic acids such as NO_2 or SO_2 are most detrimental, not organic molecules. This is because TEDA is a Lewis base. Maybe your results can be interpreted from this point of view.

HYDER: As a matter of fact, we are not exactly dealing with TEDA charcoal, as I said here, because the TEDA has been reacted or lost. That may be one of the reasons we do, in fact, see large uptakes of inorganic gases over this period of time. I looked at the amounts of NO_x and sulfur oxides retained on aged carbons but could not correlate the results with methyl iodide retention. However, our earlier work at SRL showed that NO_x has a strong effect on aging. I guess that is another study, but I am not prepared to talk about it right now.

KOVACH, J. L.: I have two questions. Is it fair to generalize the contaminants as organics? There are certainly great differences between halogenates of organic compounds. I think it is known in general organic chemistry that some things are much easier to halogenate than others. So, in both organic formation and in correlation of activity, I think it is too much of a generalization to just call it organics.

HYDER: That is a fair question. We are not seeing everything organic that could be on the carbon. The method will not show every kind of organic. On the other hand, what we are seeing are many of the common solvents which are used in paints, adhesives, and liquid lubricants in the operation of the reactor buildings. We can see them and they are the ones which we are trying to characterize. They may differ somewhat in their individual effects, we have not attempted to resolve this, Broadbent did.

KOVACH, J. L.: Is the 80°C CH_3I test representative of the SRP operating or accident condition?

HYDER: The question you are raising is, "Would we have an 80°C temperature or a higher or lower one in the accident analysis?" We have done a variety of accident analyses rather recently as part of our safety analysis for the reactors. Yes, we do get a variety of temperatures and a variety of humidities; it depends on the course of the accident. All I can say is that the conditions chosen are within the range, or envelope, of possible accidents and conditions that might occur.

FURRER: I am a little astonished that you found no influence after impregnation of charcoal with organics. Have you analyzed the loaded charcoal after the CH_3I test for its xylene content? We observed in former tests that the organics were blown out during the CH_3I test and water vapor saturated the charcoal.

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HYDER: Yes, we have analyzed the carbons by two methods. We used the GC method, as I suggested, but at the loadings we used one can use simple gravimetry to find out how much xylene is there. That was the basis for the numbers which I cited when I added the xylene to the literature. We weighed it before and after. I came to realize afterwards that this method may not be quite fair because the xylene may be replacing something else that was adsorbed, namely water vapor. It may not be an exact method but, on the other hand, it does indicate that we put a lot of xylene on the carbon and we did not see the effect we were looking for. We did not analyze for xylene after the CH_3I test. I have found that smaller amounts of xylene are retained under the conditions of the test.

FRECHETTE: Will we ever have enough data to remove the requirement now in Plant Technical Specifications to do methyl iodide testing after paint/chemical contaminating events?

HYDER: I believe so. We are developing requirements of this type for our plant.

THE EFFECTS OF TEMPERATURE AND HUMIDITY ON THE AGEING
OF TEDA IMPREGNATED CHARCOALS

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Abstract

Samples of triethylene diamine (TEDA) impregnated 207B carbon have been aged for up to 1000 hours at temperatures in the range 40° to 70°C and at relative humidities of 50% and 90%. The rate of ageing (in terms of methyl iodide-131 trapping efficiency) increases progressively as the temperature is raised above 50°C and also as the relative humidity is increased; below 50°C however the ageing rate is relatively low, even at 90% RH.

A parallel examination by temperature programmed desorption of the growth of surface oxygen groups with ageing indicates that, unlike KI impregnated carbons, the groups formed on the TEDA carbons are not linked to the decline in performance. Also, the presence of an amine, which, as a group, are generally regarded as anti-oxidants, does not reduce the rate of surface oxidation.

The rate of ageing of TEDA carbons has been shown to follow the increase in the partial pressure of water above the sample and it is proposed that TEDA carbon ageing could be caused by loss of TEDA either by a process akin to steam distillation, or by reaction with or catalysis by water, to form a less efficient impregnant.

1. Introduction

It has been found that KI impregnated charcoals, which are very effective at trapping radio-iodine compounds in CO₂ cooled systems, rapidly lose efficiency when exposed to high humidity air (Broadbent, 1985).

Research has shown that this deterioration was mainly caused by oxidative ageing of the carbon surface and that the more acidic groups formed, e.g. carboxylic acid groups, were particularly deleterious (Billinge, Docherty and Bevan, 1984). The rate of oxidative ageing also increases with increasing humidity of the air (Billinge and Evans, 1984), while additional deterioration is caused by adsorption of trace organics which poison active surface sites (Broadbent, 1985).

Similar carbons impregnated with the amine triethylene diamine (TEDA) show a much reduced rate of ageing under ambient conditions and are consequently becoming more widely used in this application e.g. in irradiated fuel dismantling areas (Broadbent, 1985). The ageing rate is still appreciable, however, but for reasons which are not, as yet, clear.

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Amines are a class of compounds well-known for their anti-oxidant properties so TEDA carbon may age more slowly than KI material because the rate of formation of organo-oxygen surface groups is reduced; a second possibility is that the basic properties of the amine neutralize any surface acidity formed. A separate problem with TEDA is its comparatively high vapour pressure which may result in an increasing loss of impregnant as operating temperatures rise above ambient. The work reported here examines the effect of exposure of TEDA impregnated carbons at various times, temperatures and relative humidities on (1) the K value (or methyl iodide trapping efficiency factor), measured under standard conditions; (2) the level of surface oxygen groups, measured by temperature programmed desorption of the surface groups as CO₂ and CO into a flow of helium.

2. Experimental

Materials

Samples of Sutcliffe-Speakman Ltd. 207B coal based carbon (8-12 BS mesh) impregnated to a nominal 5% TEDA were taken from a single batch held by OED(N) S&T.

Ageing - Description of Apparatus and Method

A dynamic ageing rig (Fig. 1) has been constructed to study ageing at temperatures up to 100°C and relative humidities up to 100%. Four charcoal samples of approximately 100 ml each can be accommodated in parallel in the rig. The relative humidity of the air flowing through the samples for a given bath temperature is controlled by the temperature of the water cascading down the saturator column against the upward air flow, mist and water droplets being effectively removed by a double coiled condenser. At dew points above ambient, condensation is avoided by using trace heating on the air flow line between the saturator column and the water bath. Relative humidity is measured by a heated cell dew point hydrometer (EG&G mirror condensation type). The airflow of about five litres per minute per sample is measured on a GAP meter after removal of excess moisture in a cold water condenser. This flow is induced by an extraction pump drawing from a manifold connected to the outlets of each flow meter. The inlet air is cleaned by passing through an activated charcoal bed.

Ageing runs were carried out for periods of up to 1000 hours for each set of conditions of temperature and RH. These conditions were set up at the start of each run when about 100 ml of "as received" charcoal is loaded into specially designed sample vessels (Fig. 2) and then attached to the rig via flexible tubing. Samples were removed from the rig at predetermined intervals up to the end of the run. Test conditions were then changed and a further run started. Once removed from the rig the charcoal samples were quickly transferred to air tight polythene bottles (125 ml) and stored for K factor determination, which was carried out within a few days to minimize the chance of any further ageing.

Rig for the Measurement of the Index of Performance (K factor) of Charcoal

The Index of Performance of charcoal is a measure of the efficiency of a charcoal bed for the adsorption of methyl iodide vapour contained in a flowing stream of air under standard conditions of sample size, air flow, temperature and relative humidity. These standard conditions have been established by the UKAEA at Sellafield and have been applied in a rig developed by them.

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The relative humidity is controlled in the range 97%-99%. The methyl iodide (traced with I-131) is loaded onto the sample by deposition from the vapour phase, over a 10 minute period, to yield a loading of 50 micrograms per gram of charcoal. Following the injection of the methyl iodide, the airflow is continued for a further two hour period. Any methyl iodide penetrating the test bed is collected on two traps containing small grain size charcoal. The overall decontamination factor for the sample is determined by counting the I131 activity on the sample and in the traps. The K factor or index of performance is then calculated from the expression

$$K = \frac{\log_{10} DF}{t}$$

when DF is the decontamination factor, which is the ratio of the initial methyl iodide charge to that released from the bed and t is the gas residence time in the carbon bed (in seconds).

The rig constructed for the present study (see Fig. 3) was originally designed for a dual purpose and differs in a number of ways from the standard rig developed by the AEA. It was intended to be used as a standard K factor rig and also as a rig on which the dependence of K factor on relative humidity, temperature and gas residence time could be determined.

A saturator system similar to that used for the ageing rig provides air to the sample at a relative humidity in the range 97%-99%. The sample temperature is controlled at 20°C by the use of a water bath. Normally duplicate samples are measured together. Although there are slight deviations from standard conditions, the K factors determined for three reference charcoals agreed very well with the determinations from other laboratories taking part in an inter-laboratory comparison exercise and using the AEA rig design (see Taylor and Billinge (1985)).

Measurement of Surface Oxygen by Temperature Programmed Desorption

Some of the samples removed from the ageing rig were dried for two hours at 373 K and were then crushed and sieved to the range 211-600 μm . About 0.5 g was packed into a silica U tube and retained in place with a silica wool plug. The tube was placed in an electric furnace and the temperature held at 150°C overnight in a controlled flow of purified helium to remove as much of the TEDA impregnant as possible and thus reduce interference with the gas chromatographic analysis of CO and CO₂, which forms the basis of establishing the extent of surface ageing.

The sample temperature was then raised at a linearly programmed rate of 5 K min⁻¹. The helium carrier gas, together with any desorbed gases, passed through the sample loop of a gas chromatograph fitted with a katharometer detector. The sample valve was actuated automatically every 213 seconds and the levels of desorbed carbon dioxide and monoxide were determined using a 2 m "Porapak Q" column held at 40°C. The evolution of these two gases, as vpm, was plotted against temperature to give a characteristic desorption pattern. The total oxygen desorbed in carbon dioxide, designated [O(CO₂)] and in carbon monoxide [O(CO)] was evaluated by integration.

3. ResultsEffect of Ageing on K Values

Samples of TEDA carbon were exposed at two levels of humidity, 50% RH and 90% RH, and three temperatures, 40°C, 60°C, 70°C for periods up to 1000 hours. A plot of K value against exposure time (Fig. 4) shows that, at 50% RH, ageing increases with temperature, e.g. 1000 hr K value at 60°C is $\sim 11 \text{ s}^{-1}$, at 70°C is $\sim 9 \text{ s}^{-1}$. As the level of humidity is raised its impact becomes more significant; at 90% RH, the 1000 hr K value at 60°C is $\sim 6.0 \text{ s}^{-1}$, the 70°C figure is $\sim 4.5 \text{ s}^{-1}$. In contrast, the 40°C/90% RH material remained at K $\sim 11.0 \text{ s}^{-1}$ from 200 to 1000 hours, which is consistent with previous results (Broadbent, 1985) where humidity was found to have only a small effect on K up to 50°C.

In summary, at 40°C even relative humidities as high as 90% have little effect on the ageing of TEDA carbons. At temperatures above 50°C humidity has a considerable and progressive effect i.e. at any given temperature 90% RH causes much faster ageing than 50% RH.

Effect of Ageing on Surface Oxide Growth Measured by Temperature Programmed Desorption

A typical desorption pattern from a fresh TEDA/207B carbon is shown in Fig. 5a with that from an aged sample (Fig. 5b). Patterns from an unimpregnated carbon and a KI-carbon are included for comparison (Fig. 5c and 5d). The characteristics of the TEDA carbon patterns are close to those of the unimpregnated charcoal, differing mainly in the low temperature evolution $< 500^\circ\text{C}$ ($< 773 \text{ K}$) of CO in the TEDA cases. In contrast KI impregnation (Fig. 5d) causes a change in shape of the second CO_2 peak and the creation of a new CO peak at 750°C (1023 K). These points indicate less interaction between TEDA and the support carbon than is the case with KI.

The desorption pattern from the aged sample (Fig. 5b) shows how the peaks grow with ageing. The quantities of oxygen evolved from the surfaces of fresh and aged TEDA carbons are presented in Table 1, columns three to six, for the first CO_2 peak, ($\text{OCO}_2(1)$) up to 455°C (728 K); the second CO_2 peak from 455°C (728 K) to completion ($\text{OCO}_2(2)$); the first CO peak also to 455°C (728 K) ($\text{OCO}(1)$); the second CO peak from 455°C (728 K) to peak maximum ($\text{OCO}(2)$).

In columns eight to 11 the increases in size of each peak over that of the fresh material are given (Δ). Column 7 shows the K factors of each sample.

The Δ values for the two CO_2 peaks are shown in Fig. 6. Considering the 60°C and 70°C results only, the curves fall into two groups with the 90% RH runs showing a far greater increase in surface oxygen than the 50% RH runs, which show little change over the 1000 hours ageing period. This is a parallel trend to the effect of ageing on K value (3.1. above) where the higher humidity causes a faster decline in K. The $40^\circ\text{C}/90\%$ RH results show an intermediate pattern. The K value shows little change over the ageing period of these runs but the increase in surface $\text{O}(\text{CO}_2)$ lies between that for the higher temperatures at 50% RH and 90% RH.

The Δ values for the CO peaks are shown in Fig. 7 and 8. The first CO peak points (Fig. 7), while exhibiting some scatter, do not vary greatly for all the humidities and temperatures examined. Variation of RH and temperature has no appreciable effect on the growth of the first CO peak, although it does increase

slowly with ageing. The second CO peak (Fig. 8) shows a qualitatively similar pattern of behaviour to CO₂; the 90% RH results show a greater increase than the 50% RH results. The 40°C/90% RH results follow the same general trends, the first CO peak following the same curve as the 60°C/70°C, 50% RH results, the second CO peak falling close to the 60°C/70°C 90% RH results. In summary, the growth of all peaks except the first CO peak is very sensitive to RH.

4. Discussion

The Effect of Exposure at Temperatures <50°C on Methyl Iodide Trapping Efficiency

For KI impregnated carbons previous work (Billinge et al., 1984, Billinge and Evans, 1984) clearly demonstrated at temperatures below 50°C links between (1) the rate of oxidative ageing of the carbon surface and relative humidity and (2) the increase in acidic surface groups and the deterioration in methyl iodide retention efficiency (K values). In contrast, the present study (Fig. 4) together with previous work (Broadbent, 1985) found that below 50°C/90% RH, similar carbons impregnated with triethylene diamine (TEDA) showed only a small decline in performance with time compared with KI carbons and no relationship between this decline and temperature or humidity. Explanations can be offered in terms of the difference in chemistry of the two systems: in the KI/carbon system, adsorption of CH₃I initially requires scission of the C-I¹³¹ bond followed by isotopic exchange with I¹²⁷ from the KI impregnant. The coal carbon surface catalyses the C-I scission step but acidification of the surface by oxidation to carboxyl or lactone groups inhibits this step, causing a fall in the rate of reaction; on the other hand with TEDA the mechanism is significantly different. TEDA is a cage-structure tertiary diamine, the stereochemistry of which makes the lone pair electrons on each nitrogen atom very accessible. CH₃I-131 is trapped by the formation of quaternary groups.

The chemistry is not totally divorced from that of the underlying carbon surface, however, as demonstrated by UKAEA workers (Evans and Hillary, 1986) who showed that TEDA on low ash coconut shell carbon has a K value of only 6.7, compared with 12.7 for the same quantity of impregnant on a coal-based carbon. Whether this difference can be equated with variations in mineral content or surface oxidation state still remains to be settled but the latter is a less likely explanation since (1) amines in general have anti-oxidant properties which may be expected to inhibit carbon surface oxidation and (2) the basicity of the amine impregnant might be expected to neutralize any acidic groups formed and so reduce their effect.

The Effect of Exposure at Temperatures ≥50°C on Methyl Iodide Trapping Efficiency

Examination of the desorption patterns (Fig. 5) of TEDA and KI carbons shows a clear similarity in the first CO₂ peak, which reaches a maximum at ~250°C (523 K) in both cases. It has previously been found that, for KI carbons this peak is due to acidic oxy-groups which are a major cause of ageing. It is therefore informative to consider this peak in relation to TEDA ageing.

Results obtained previously up to 50°C/90% RH (Broadbent, 1985) and those reported here at 40°C/90% RH show only a small fall in K value up to 1000 hours ageing but the TPD results at 40°C/90% (Table 1, Fig. 6) show there has been a considerable increase in the quantity of CO₂-forming groups in that time

CO₂(1) maximum value is 0.27%). There are no comparable figures for KI carbon

under these conditions but it appears that the presence of amine is not significantly suppressing the formation of surface carboxyl groups and, in contrast to KI carbon, these groups are not greatly affecting the K value of TEDA carbon under this condition.

The results at 60°C/50% RH and 70°C/50% RH show a greater decline in K value than do the 40°C/90% RH results (Fig. 4 and Table 1) but the maximum increase in first peak O(CO₂), 0.16%, (70°C/50% RH, 1004 h) is a factor of 1.7 less than the maximum for the 40°C/90% RH sample (800 h 0.27%), i.e. the samples showing the greater increase in surface oxygen show the lesser decline in K factor. This indicates no linkage between K value and acidic surface oxygen groups in TEDA carbons.

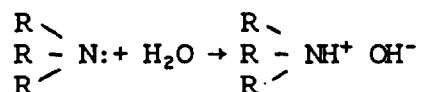
The results at 60°C/90% RH and 70°C/90% RH show the largest decline in K and also the greatest increase in the first CO₂ peak (Fig. 6). One comparable result on KI carbon is available at 60°C/85% RH. After 400 h the first CO₂ peak oxygen increased by 0.31% which agrees well with the TEDA figure at 60°C/90% RH/430 h of 0.31%. This is confirmation that the presence of TEDA is not interfering appreciably with the rate of growth of oxy-acidic groups on the surface and, coupled with the 40°C/90% results, confirms that combined surface oxygen is not the primary cause of ageing in TEDA carbons.

At a given temperature, the rate of growth of surface oxygen groups increases with increasing relative humidity on KI carbons (Billinge and Evans, 1986). Assuming TEDA carbons behave similarly, the expected order of increasing surface oxygen would be 60°C/50% RH < 70°C/50% RH < 60°C/90% RH < 70°C/90% RH for the samples examined here, with the position of the 40°C/90% RH samples depending on the relative effects of temperature and humidity. By comparison of the 60°C/50% RH with 60°C/90% RH or 70°C/50% RH with 70°C/90% RH it is clear that this increase in relative humidity has a much greater effect than the 10° temperature change. Therefore the position of the 40°C/90% RH surface oxygen levels between 70/50 and 60/90% is not anomalous. This is consistent with the formation rate of surface oxygen-groups being dependent on the quantity of water absorbed on the surface which itself is governed by relative humidity. As it has already been argued that no relationship exists between the rate of TEDA carbon ageing and surface oxygen level, the cause of ageing is still an open question. The most probable answer is a loss of the impregnant itself or its conversion to a less active entity.

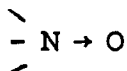
Further examination of Fig. 4 shows that the rate of decline in the K value with ageing time follows the sequence 40/90% < 60/50% < 70/50% < 60/90% < 70/90%. It can be seen, from Table 2, that this order is coincident with one of increasing water vapour partial pressure. Furthermore a plot of water vapour pressure against 1000 hr. K values (from Fig. 4) shows a linear relationship (Fig. 9). The vapour pressure of TEDA impregnated on activated carbon is not known but values for the pure compound at 298 and 323 K have been reported by Deitz (1981) as 0.6 and 2.9 torr respectively. Using the simplified Clausius-Clapeyron equation and plotting log p against 1/TK enables values of 1.6, 5.3 and 8.5 torr to be deduced at 313, 333 and 343 K. Thus the combined TEDA and water vapour pressures also maintain the same order of increase (Table 2) and linearity against K (Fig. 9). It is therefore probable that a mechanism of TEDA removal similar to that of steam distillation, is in operation with the rate of TEDA removal being dependent on the combined partial pressure of TEDA and water vapour above the carbon surface.

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An alternative possibility is that a direct reaction between TEDA and water occurs to form another compound, or that water catalyses the oxidation of TEDA by air, as it does the carbon surface. Such reactions could result in the formation of a quaternary hydroxide:



or an amine oxide, i.e.



either of which may be less effective than TEDA itself for trapping methyl iodide.

Further work is required to substantiate which of these mechanisms is important but it is clear that a mechanism dependent on water vapour pressure only should cause a similar decline in performance of TEDA carbon in wet inert gas as in wet air. Minimal decline in K value in humidified inert gas would indicate that chemical reactions of the TEDA molecule itself were the more important. Total nitrogen analysis on aged samples would show whether TEDA was being lost or converted to another N-compound. These investigations will be the subject of a later report.

The First CO Peak

The major difference in the TPD pattern of TEDA carbon compared with those of KI or unimpregnated carbon is the appearance of a CO peak over the same temperature range as the first CO₂ peak (Fig. 5). This near coincidence might suggest that the two emanate from the same source and some interaction between TEDA and the carbon surface offers a possible explanation. However, the behaviour of the two peaks under ageing conditions is very different. The first CO peak (Fig. 7) shows only slow growth over 1000 hours which is insensitive to changes in humidity and temperature; the first CO₂ peak also shows low growth at low (50%) humidity (Fig. 6) but raising the humidity causes a large increase as also happens with KI carbons, so the temperature coincidence of the two peaks seems fortuitous. Even so the fact that this CO peak is present only on TEDA carbons does indicate that it is linked to the TEDA impregnant in some way and may be due to the slow degradation of that compound with time.

5. Conclusions

(1) The decline in methyl iodide trapping efficiency (K) of TEDA impregnated carbons in moist air is slow at temperatures below 50°C and relatively unaffected by humidity.

(2) At 50°C and above K declines with temperature but is more susceptible to increasing relative humidity from 50 to 90%.

(3) The rate of growth of surface oxygen groups with ageing increases with relative humidity throughout the temperature range so that the level of surface oxygen at 40/90% RH exceeds that formed at 70/50% in spite of which the K values samples exposed at 40/90% exceed those at 70/50%.

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(4) In contrast to KI carbons, no relationship between the ageing rate of TEDA carbon and surface oxygen group growth has been established. Furthermore, there is no indication that the presence of this base inhibits the formation of acid surface oxygen groups.

(5) The K value declines linearly with increasing partial pressure of water which favours a removal mechanism of TEDA by physical 'steam distillation' related to the combined water + TEDA vapour pressure over the surface as the most probable cause of ageing. An alternative possibility is that chemical reaction, either by hydroxylation of TEDA or oxidation of TEDA catalysed by water, forms a less efficient product.

6. Acknowledgements

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Table 1: TPD Results: Total and Decremental Surface Oxygen Desorption Values

1 Sample	2 Time hours	3 *OCO ₂ (1)	4 *OCO ₂ (2)	5 +OCO(1)	6 +OCO(2)	7 K	8 ΔOCO ₂ (1)	9 ΔOCO ₂ (2)	10 ΔOCO(1)	11 ΔOCO(2)
Fresh 60C/50%RH	0	0.12	0.09	0.07	0.96	14.05				
	272	0.18	0.10	0.15	1.00	12.89	0.06	0.01	0.08	0.04
	400	0.18	0.11	0.14	1.09	12.33	0.06	0.02	0.07	0.13
	619	0.21	0.14	0.14	1.12	11.11	0.09	0.05	0.07	0.16
	985	0.22	0.12	0.18		10.84	0.10	0.03	0.11	-
70C/50%RH	290	0.22	0.12	0.18	0.97	11.00	0.10	0.03	0.11	0.01
	597	0.23	0.16	0.18	1.07	10.00	0.11	0.07	0.11	0.11
	1004	0.28	0.19	0.22	1.16	8.63	0.16	0.10	0.15	0.20
60C/90%RH	175	0.26	0.12	0.13	1.01	11.59	0.14	0.03	0.06	0.05
	285	0.32	0.20	0.14	1.11	11.32	0.20	0.11	0.07	0.15
	430	0.43	0.32	0.15	1.16	8.74	0.31	0.23	0.08	0.20
	600	0.45	0.33	0.16	1.10	7.76	0.33	0.24	0.09	0.14
70C/90%RH	480	0.45	0.32	0.24	1.35	6.70	0.33	0.23	0.17	0.39
	937	0.55	0.46	0.25	1.23	4.56	0.43	0.37	0.18	0.27
40C/90%RH	213	0.28	0.17	0.13	1.01	10.87	0.16	0.08	0.06	0.05
	405	0.34	0.24	0.14	1.15	11.00	0.22	0.15	0.07	0.19
	667	0.38	0.26	0.15	1.24	10.32	0.26	0.17	0.08	0.28
	800	0.39	0.28	0.16	1.24	10.73	0.27	0.19	0.09	0.28
	1000	0.27	0.25	0.12	1.22	11.05	0.15	0.16	0.05	0.26

* OCO₂(1) and (2) - % oxygen evolved in CO₂ from dry, ash-free carbon

+ OCO(1) and (2) - % oxygen evolved in CO from dry, ash-free carbon

Table 2: Absolute Partial Pressure of Water at Various Temperature/Relative Humidity Conditions and Vapour Pressure of TEDA

Expt. Conditions		P_{H_2O} mm Hg	P_{TEDA} mm Hg
T°C	RH%		T°C
40	90	49.8	25 0.6
60	50	74.7	40* 1.6
70	50	116.9	50 2.9
60	90	134.4	60* 5.3
70	90	210.3	70* 8.5

* Deduced from the Clausius-Clapeyron equation

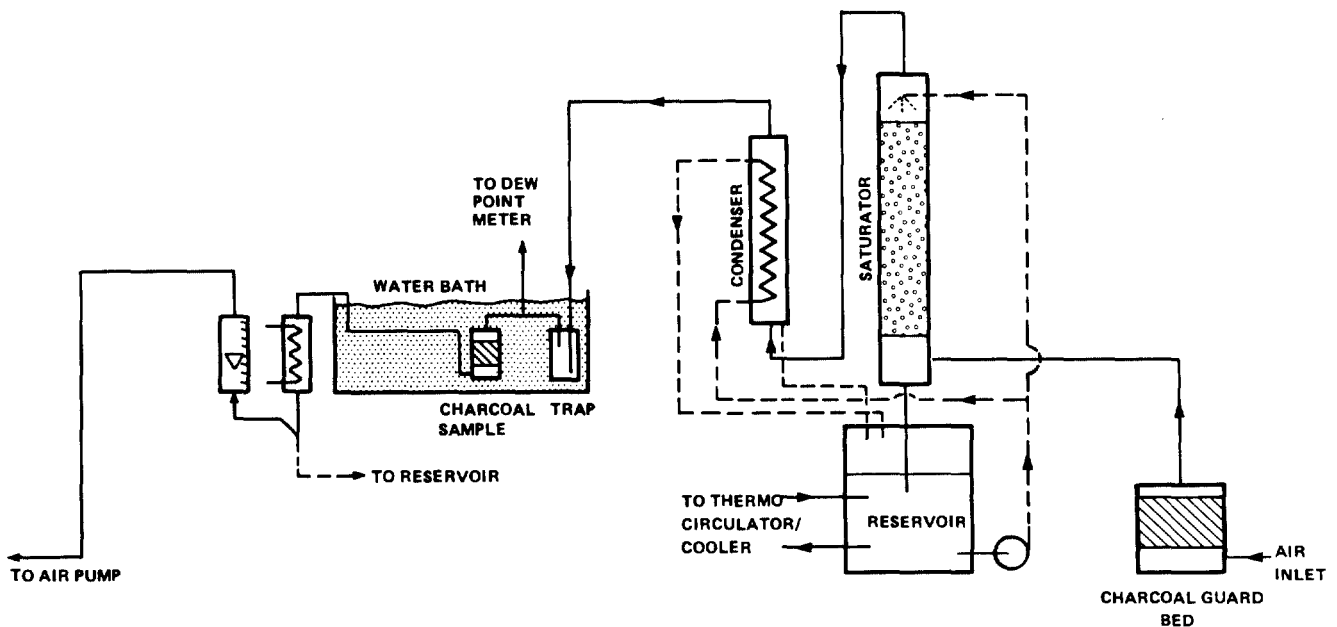


FIG. 1 DYNAMIC ACCELERATED AGEING RIG

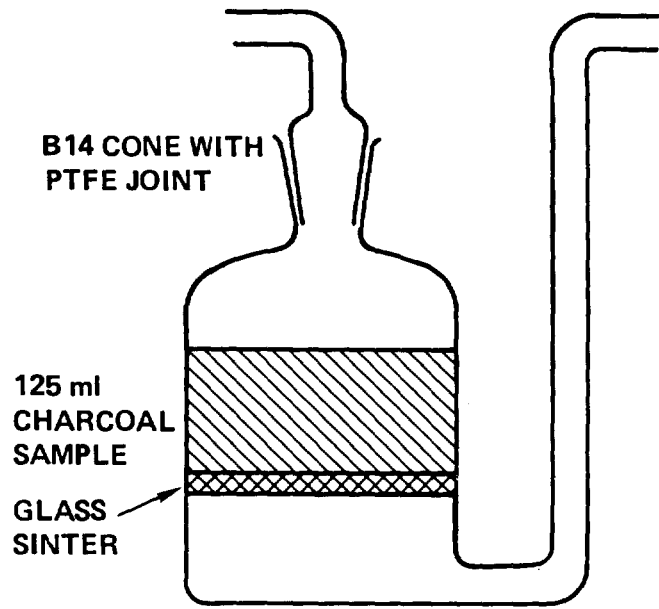


FIG. 2 CHARCOAL SAMPLE VESSEL-AGEING RIG

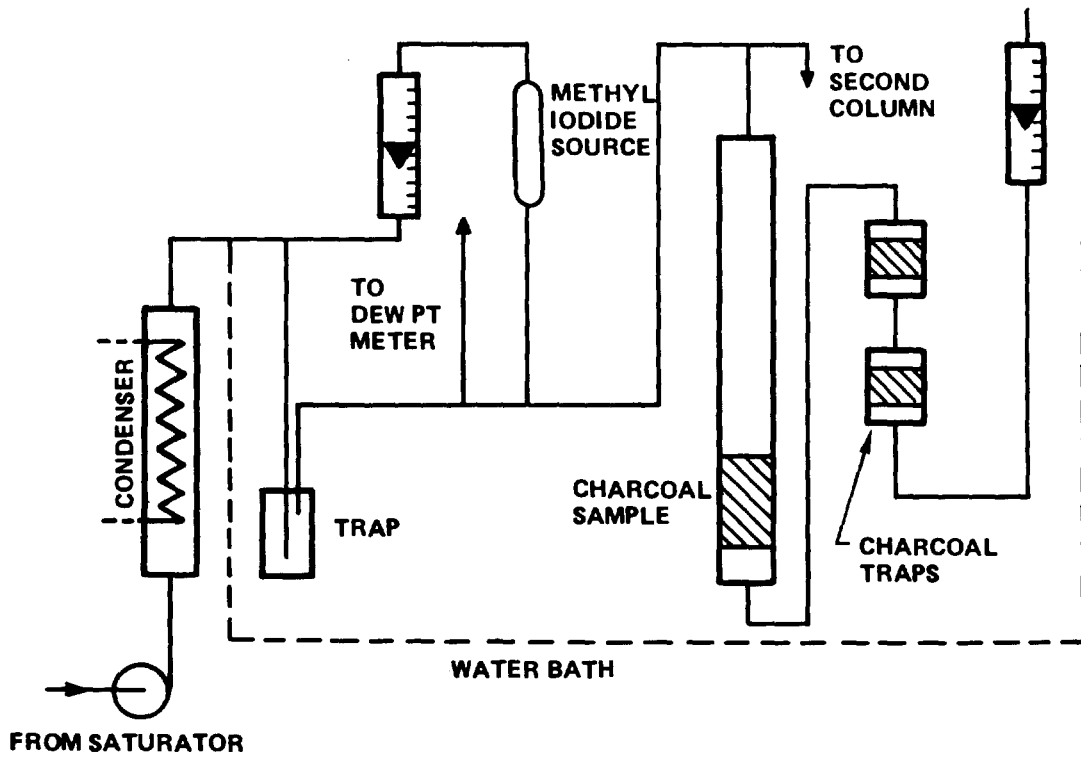


FIG. 3 CHARCOAL K FACTOR RIG

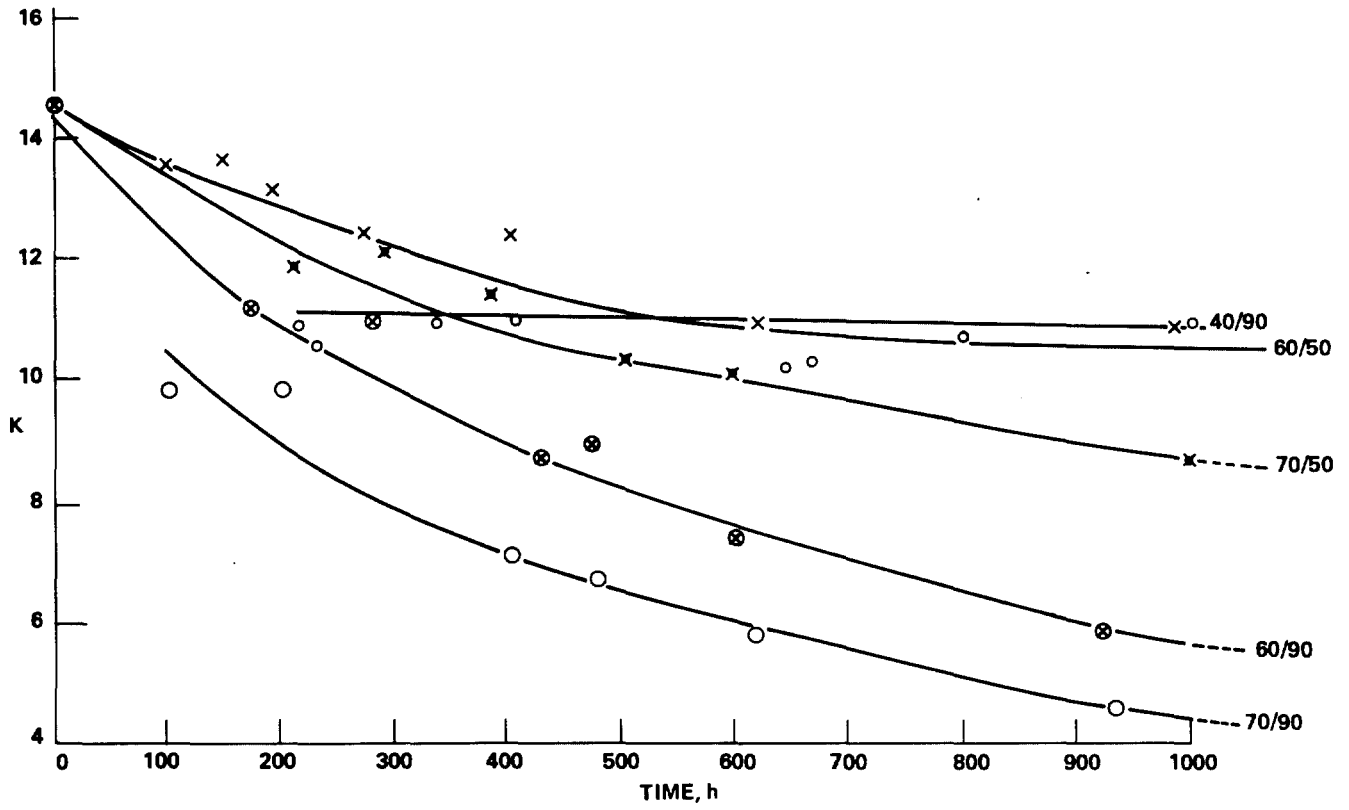


FIG. 4 DECLINE IN K WITH EXPOSURE TIME

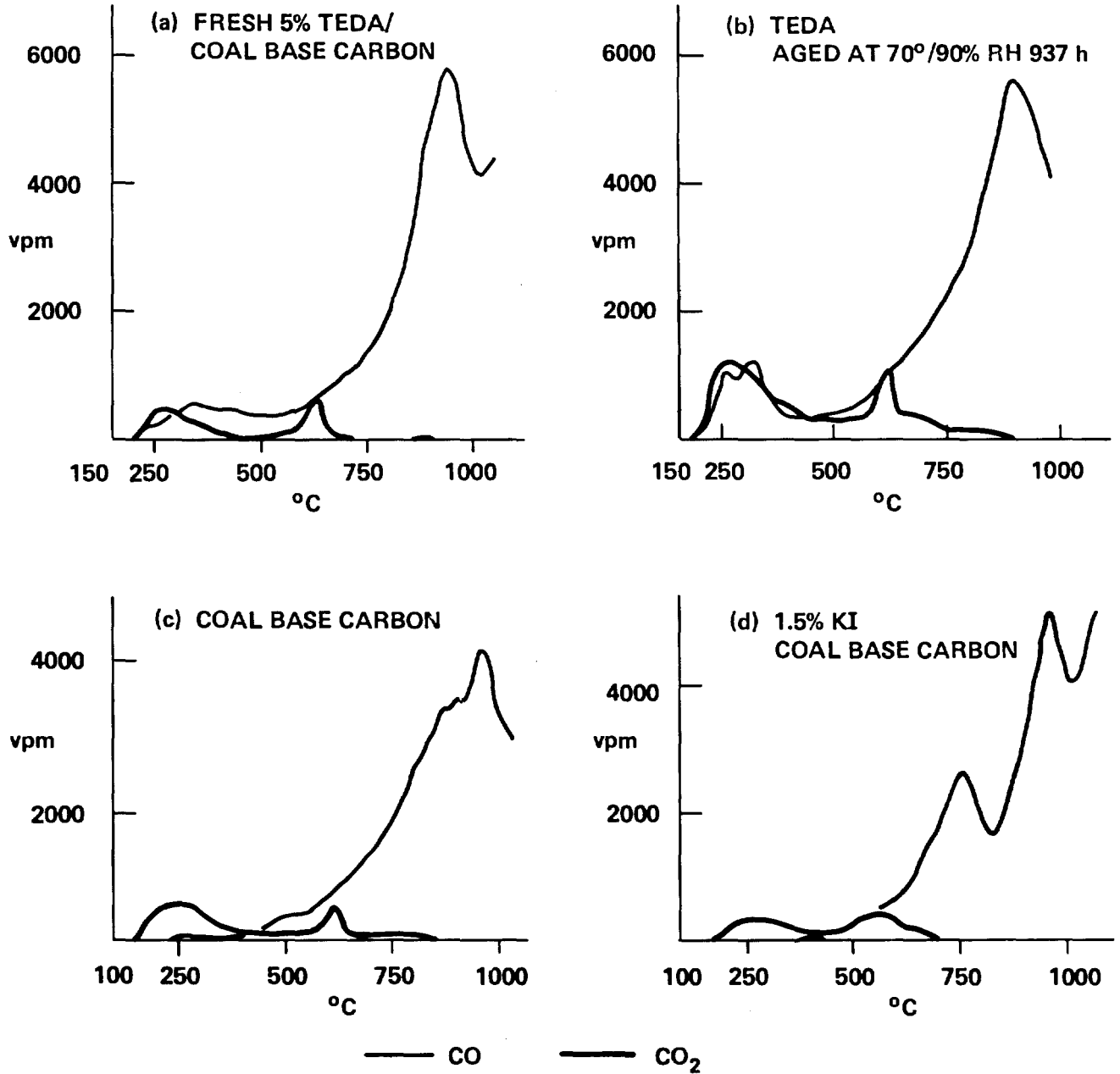


FIG. 5 TEMPERATURE PROGRAMMED DESORPTION PATTERNS

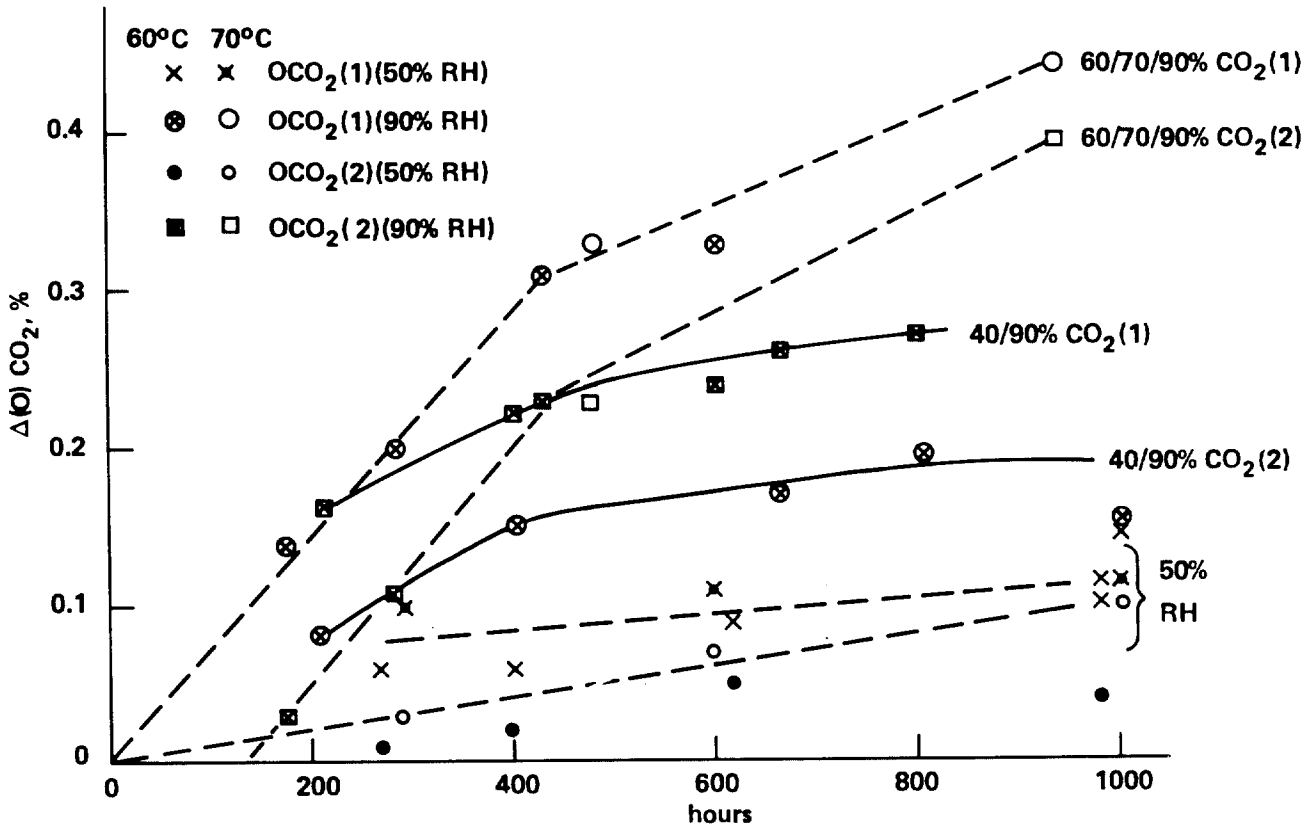


FIG. 6 INCREASE IN CO₂ EVOLVED vs. AGEING TIME

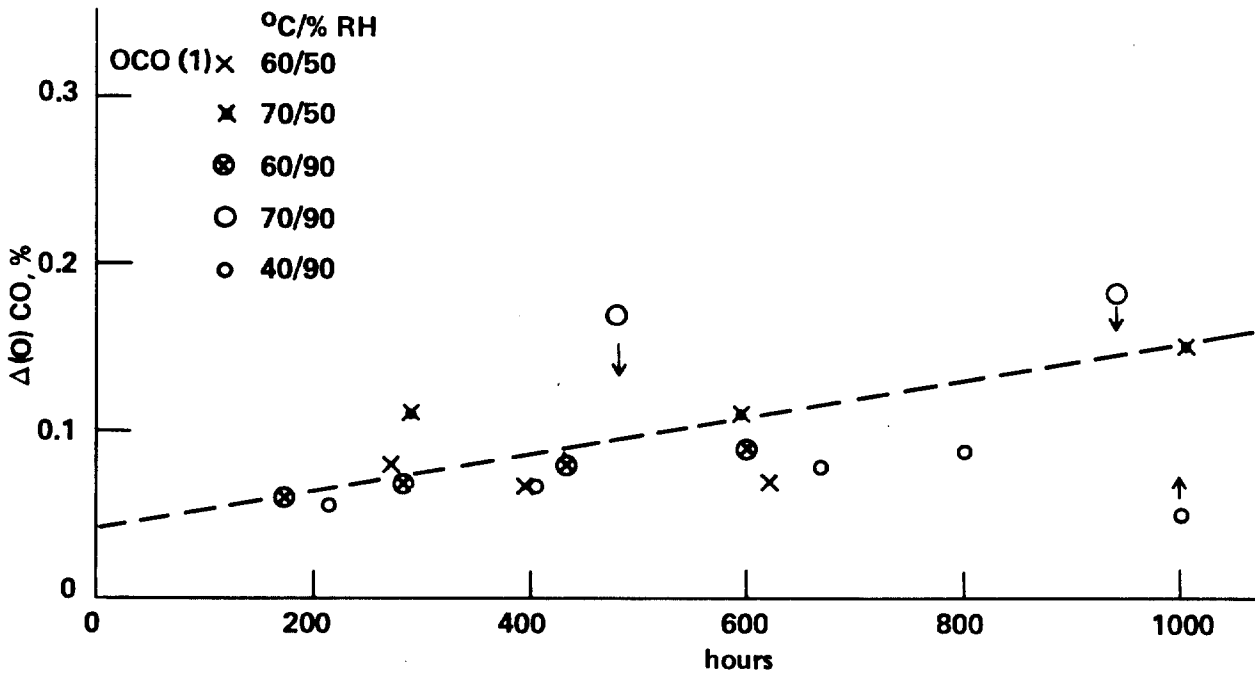


FIG. 7 INCREASE IN CO EVOLVED vs. AGEING TIME FOR 1st CO PEAK

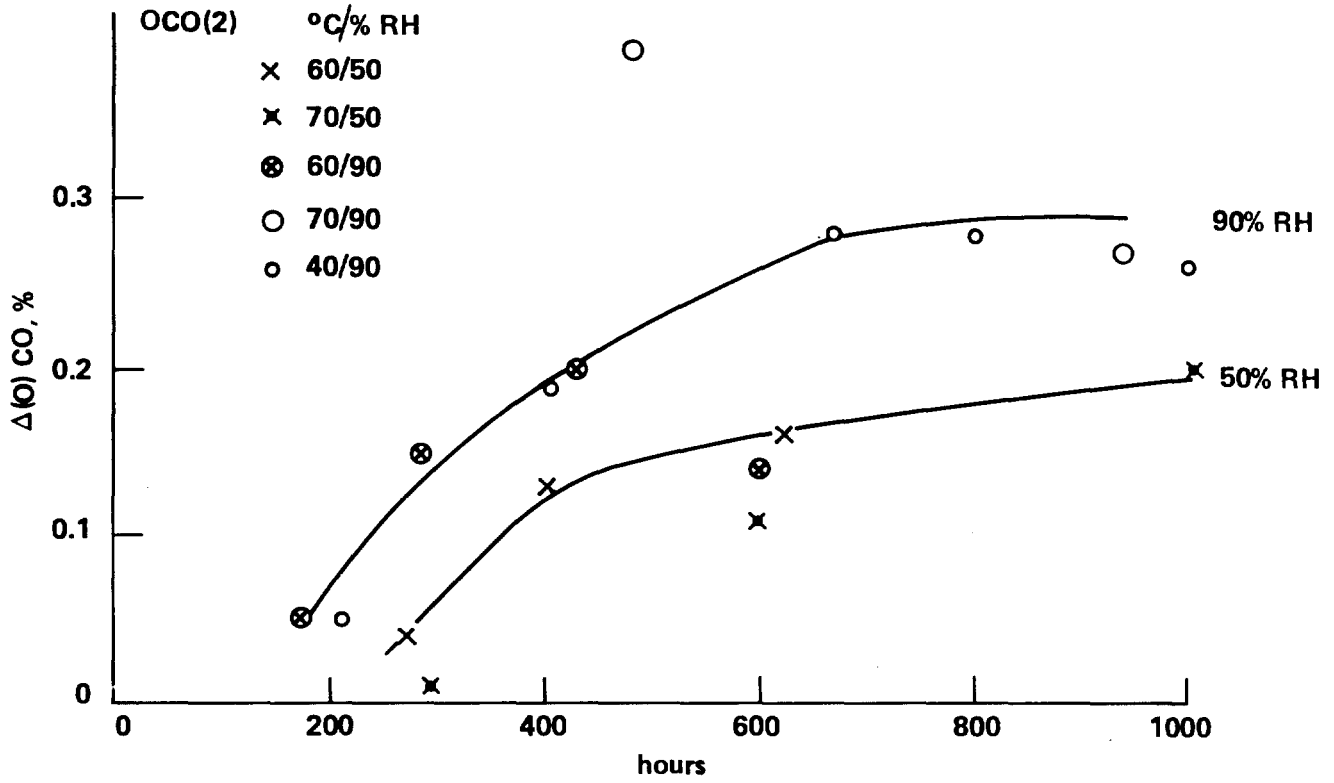


FIG. 8 INCREASE IN CO EVOLVED vs. AGEING TIME FOR 2nd CO PEAK

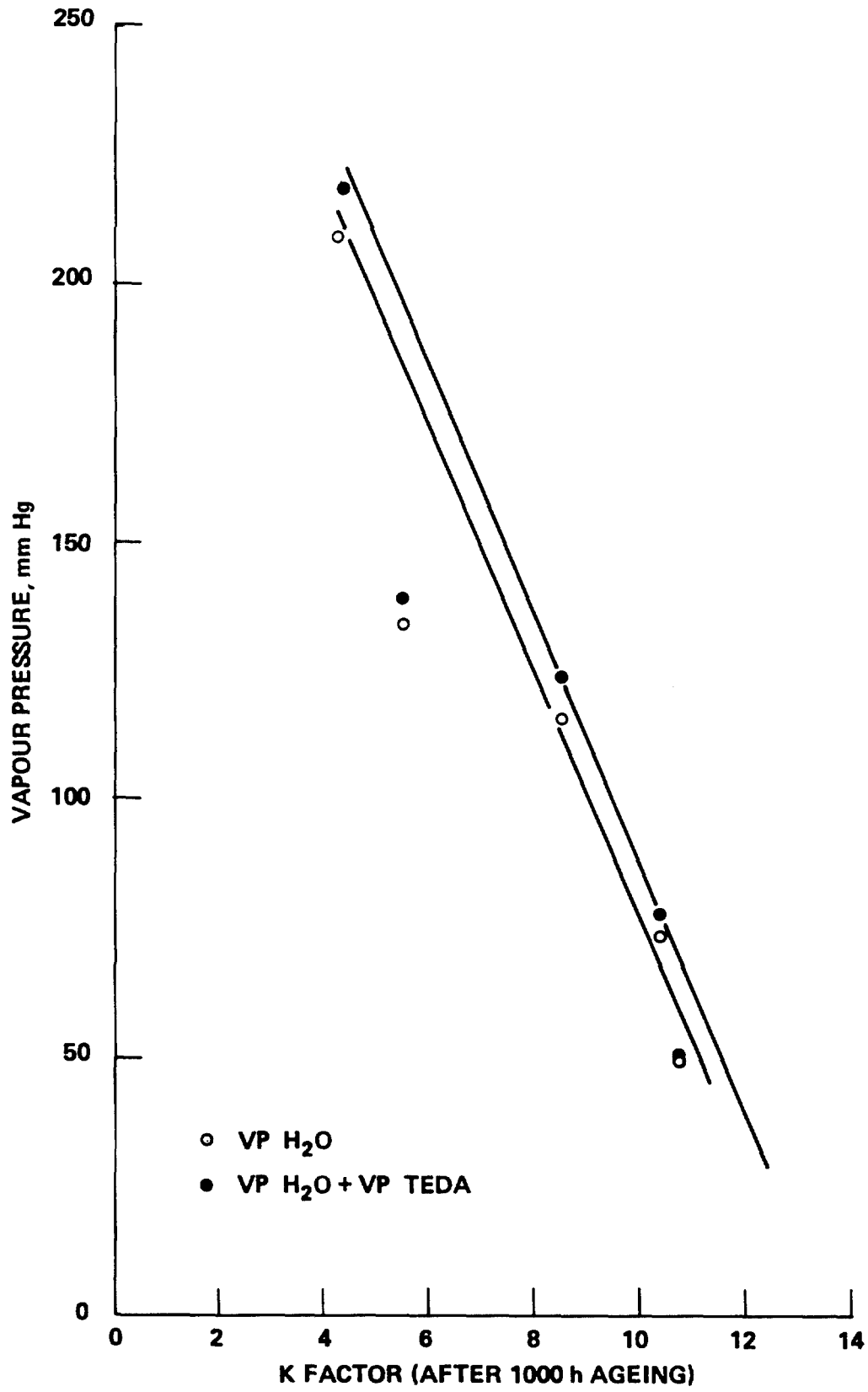


FIG. 9 ABSOLUTE VAPOUR PRESSURE OF H₂O AND H₂O + TEDA vs. K

DISCUSSION

KOVACH, J. L.: I think somebody made a terrible mistake. What is your definition of aging for this work? How would 40-70°C storage be postulated? I think somebody told you in the U.K. that the typical temperature would be 40-70 degrees and you switched from fahrenheit to centigrade. Where in the U.K. would you be storing carbon between 40 and 70°C.

BILLINGE: Your definition of aging is not our definition of aging. For our own purposes we define aging as the deterioration of carbon performance solely due to the interaction of its surface with moist air. This can occur in storage under poor conditions or under any air cleaning service condition. In service, there is additional deterioration due to strongly sorbed trace species, e.g., organics, SO_x, NO_x, which we label poisoning. The two effects may be separated in service by the use of guard beds.

KOVACH, J. L.: You refer to both aging and weathering.

BILLINGE: Weathering covers both reasons for decline.

KOVACH, J. L.: When you were first talking about aging I thought this was a project started before you switched temperature scales and you just kept the same numbers.

BILLINGE: No, we are interested in the use of TEDA at higher temperatures for the same reasons everybody else is. We have only gone up to 70°C so far; no doubt we need to go higher.

WREN: We have also studied the release of TEDA using a mass spectrometer. We observed not only the release of TEDA but also the release of pyrimidine. We think pyrimidine is the decomposition product of TEDA. Our charcoal was coconut-shell based carbon. Did you observe any other species released beside TEDA? One additional comment is that pyrimidine, being similar to TEDA, may still have high removal efficiency for CH₃I. This we have not examined yet.

BILLINGE: In our mass spectroscopy work the major mass peaks we saw were those of TEDA. There were other peaks present which might possibly be assigned to piperazine rather than pyrimidine but I have not examined them in detail. I think my UKAEA colleagues did look at pyrimidine as an impregnant many years ago and they found it quite efficient but since it has a higher vapor pressure than TEDA, it deteriorated more quickly at high temperatures.

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CHEMICAL ANALYSIS OF NEW AND USED 5% TEDA - IMPREGNATED CARBON

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Ron Massey
Ontario Hydro Research Division

ABSTRACT

All radioiodine filters in Ontario Hydro's nuclear generating stations use 5% triethylene diamine impregnated carbon as an absorbent. Because replacement carbon, management of used carbon from the filters, and labor to change the carbon are expensive, increased service-life is desirable. Methods to optimize the quality of the new carbon, including analysis methods for new supplies, are described. Analysis of carbon samples taken from filters, to try to determine the reason for deterioration in service, are also discussed.

INTRODUCTION

Ontario Hydro currently relies on nuclear generating units to produce about fifty percent of the power needs of the province of Ontario. This percentage will increase when the Darlington NGS-A station units start to come on-line in 1989. The nuclear generating stations are listed in Table 1.

All air effluents from areas which can potentially be contaminated by radioiodine are filtered through carbon and standby carbon filters are provided for emergency use. The mass of carbon used per station is listed in Table 2 and a typical break-down by system is listed for Bruce NGS-B in Table 3. All carbon used in all systems is now 5% triethylenediamine (TEDA) impregnated coconut. The 240 Mg total of Table 2 represents a major capital outlay. Assuming an optimistic service-life of 2 1/2 - 3 years for continuous operation filters, adding low-level waste management costs of \$275 per drum and an estimate of labour costs of carbon change-out, the annual operating costs for carbon filters are in excess of 1 M\$ US. This provides a major inducement to attempt to lengthen the useful service-life.

STEPS TAKEN TO LENGTHEN SERVICE LIFE

Procurement

In the past, the nuclear stations purchased carbon individually. They were required to go through a tendering process which required several months of

lead time. Consequently the stations often purchased in bulk and stored supplies on site, sometimes for long periods of time, and not always under optimum conditions. When stored at the station, deterioration in storage has occurred. Central procurement has been initiated with purchases based on projected needs. This has reduced storage times markedly.

Storage

Storage that is required is now provided at a central supply facility in space designed for computer paper. This is a dust-free, climate controlled atmosphere. Deterioration in storage should be minimized by providing this atmosphere and by the reduction of the storage time.

Specifications and Testing of New Supplies

Formerly, new carbon supplies were only required to be the correct mesh size and to pass the ASTM D3803 test for radioiodine absorption: mesh sizes were not checked. Now, new carbon supplies are required to meet the specification listed in Table 4.⁽¹⁾ A certificate is required from the vendor detailing ash, hardness, density and the carbon tetrachloride activity of unimpregnated material. Pre-shipment and as-received samples are tested for moisture, mesh size, TEDA content and by ASTM D3803. Other parameters are spot-checked. The shipment may be rejected if it fails to meet specification at either stage of testing.

It has been found that if all other parameters are correct, the material easily passes the D3803 test. If the data continue to demonstrate this, the D3803 test for new supplies may be dropped at some time in the future.

In-Service Testing

It is hoped that more accurate testing of in-service carbon may reduce premature changing of the material. This testing is the subject of another paper to be presented later in this conference.

TEDA ANALYSIS

Methods

The testing of new supplies is performed by standard, well-documented methods, with the exception of the TEDA analysis. There is a draft ASTM method which involves extraction of TEDA with dilute sulphuric acid, followed by gas-chromatography of the extract.⁽²⁾ As we were unaware of this draft procedure when it was determined that this analysis should be performed, a similar procedure was developed independently. Extraction of TEDA from the carbon was attempted using common organic solvents. Methanol was found to extract the TEDA quantitatively. Gas-chromatography of the extract gave an accurate analysis of spiked samples.

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Further confirmation of the accuracy of the analytical method has been obtained by cross-checking against a totally independent method; total kjeldahl nitrogen (TKN) analysis. Samples of unused impregnated carbon and the base carbon before impregnation have been analyzed by TKN. The difference in nitrogen concentration, which must be due to the impregnant, can be used to calculate a TEDA concentration.

Results for New Carbons

Analytical data for unused commercial samples are shown in Table 5. Table 5 shows good agreement between the two methods. TKN analyses are only performed now as a back-up confirmation for marginal supplies.

Results For Carbon Taken Out-Of-Service

A limited number of used or aged carbon samples have been analyzed for TEDA by both methods. The results, listed in Table 6, show that the TKN method has a very high bias. The first two results (which are averages of analyses of six discrete samples from each of the filters tested) are for carbons which have failed the D3803 test badly. As we are very confident of the analytical data in Table 6, it is concluded that the excess TKN over TEDA by MeOH extraction demonstrates that nitrogen compounds other than TEDA are present. These compounds may be decomposition products of TEDA. It has been suggested that these may have some methyl iodide trapping capability. This would agree with the observations of Dietz⁽³⁾ that "the TEDA is gone but it's memory lingers on."

It could be speculated that the most likely nitrogen compounds which may trap methyl iodide are amine (TEDA) salts which undergo an exchange reaction with radioiodine. As described below, we have failed to isolate measurable quantities of such compounds, with the exception of a trace of pyrazine (Table 8).

The original concentration of TEDA in these used carbons is unknown, therefore it is not known if some TEDA has sublimed in-service or if the carbon contained less than the required 5% when new.

The third carbon in Table 6 was unused but had been stored in a station environment for over a year. Again, the original TEDA concentration is not known, but this analysis appears to indicate that some TEDA decomposition may have occurred during storage. More data are required to confirm this observation.

CHEMICAL ANALYSIS OF USED CARBON

As our objective is to obtain longer service life from the carbon, we have attempted to determine the cause of deteriorated performance in our plants by analyzing some carbons which have failed and been taken out of service. There was a concern over how to obtain a representative sample for analysis.

Most of the filter-beds in use are of the very common welded, gasketless type shown in Figure 1. Depending on flow patterns and on packing, the individual cells may be subjected to different air-flows and therefore contain carbon of varying quality. It also seemed possible that as the carbon settled, there may be less flow through more densely packed carbon at the bottom of the cell than through the looser top strata. To investigate this, samples were taken from a filter before the carbon was removed. A grain-sampler was used to take samples from three depths of two cells spaced across an extremely poor filter unit. Each of the six samples were analyzed for TEDA content, pH of aqueous extract, organics and radioiodine retention by D3803. The results of these analyses are presented in Table 7.

Table 7 data indicate that the D3803 test performance deteriorated with decreasing TEDA content and decreasing pH. Again, as the TEDA content of the original carbon was unknown, it is not known how much or if any TEDA has sublimed during service. The pH of new 5% TEDA carbon aqueous extract has consistently been found to be in the range 9.0 to 10.0. As used carbon pH has been found to be much less than 7.0, it seems unlikely that this results solely from loss of TEDA. It seems that some acidic component accumulates in-service. It is unknown if the acid results from carbon oxidation to form acid groups as suggested by Billinge et al⁽⁴⁾, by absorption of ambient acid gases from ventilation air or by other means.

No correlation of D3803 result with the concentration of organics was observed. The organic constituents were analyzed by gas chromatography-mass spectrometric methods. Components found are listed in Table 8. The only potential decomposition product of TEDA found was pyrazine. This was present in low concentration in three out of six samples. The major components listed in Table 8 indicate that the major source of the organic contamination is probably cleaning (degreasing) solvents used in the station eg, "Varsol".

It was considered that the correlation of D3803 performance with TEDA content and pH had potential for providing a method to determine the need for carbon change without performing the D3803 test. Similar samples were taken from another filter which was due to be changed. The results, listed in Table 9, show essentially no correlations. It is planned that one more filter will be analyzed by these methods, but the possibility of using a simple chemical test, such as pH of the aqueous extract, to determine the need for carbon change appears unlikely.

From Tables 7 and 9 it can be seen that the D3803 test of the composite sample, prepared by mixing grab samples from six places in the filter gave similar results to the average of the individual samples. This composite grab sample value was much better than the test canister value. It is now our policy that wherever possible, composite grab samples are used for analysis rather than test canisters, as this is felt to give a more representative result.

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CONCLUSIONS

- (1) By improvements to the procurement, storage, and testing of new carbon supplies, the quality of the carbon being installed has been improved. More time is required for proof, but there are strong indications this is leading to longer service-life and hence, major cost savings.
- (2) There are good indications that the D3803 test may be unnecessary for new TEDA impregnated carbons if other quality criteria are met.
- (3) A simple accurate extractive method for TEDA analysis has been developed and this can be cross-checked for marginal new supplies by analyzing for Total Kjeldahl Nitrogen.
- (4) The reasons for carbon performance deterioration in service are still not understood, but some characteristics of the deterioration of carbon used in Ontario Hydro's nuclear facilities have been determined.

REFERENCES

- (1) Ontario Hydro Standard Specification M-661M-84.
- (2) Proposed ASTM D 28.04-7 "Standard Method of Analysis of TEDA Impregnant in Activated Carbon"
- (3) V. Dietz, Proc of 18th DOE NACC (1984).
- (4) B.H.M. Billinge, J.B. Docherty, M.J. Beran, Carbon V22, No. 1 (1984).

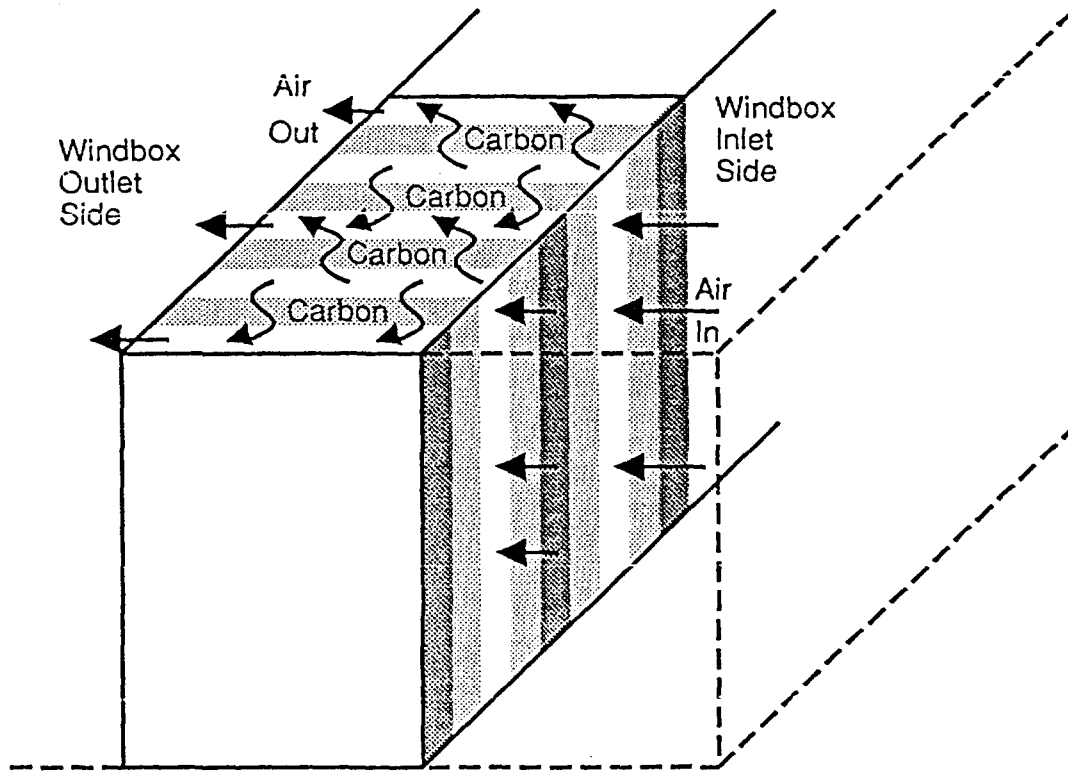


FIGURE 1

Table 1

Ontario Hydro Nuclear Generating Units

<u>Station</u>	<u>Units</u>	<u>Unit Size MWe (NET)</u>	<u>In-Service Date</u>
Pickering NGS-A	4	514	1971-1973
Bruce NGS-A	4	769	1977-1979
Pickering NGS-B	4	516	1983-1986
Bruce NGS-B	4	837	1984-1987
Darlington NGS-A	4	881	1989-1993

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Table 2

Total Carbon Inventory Per Station

<u>Station</u>	<u>Mass of Carbon Mg</u>
Pickering NGS-A	5.0
Bruce NGS-A	37.5
Pickering NGS-B	9.5
Bruce NGS-B	52.5
Darlington NGS-A	<u>136.0</u>
TOTAL	<u>240.5</u>

Table 3

Carbon in Station Systems: Bruce B

<u>Station System</u>	<u>System Function</u>	<u>Mode of Operation</u>	<u>Mass Carbon (Mg)</u>
Reactor Building Ventilation	All air from active areas of Units	Continuous Once-through	35
Irradiated Fuel Bay Ventilation	Air from Irradiated Fuel Bay Building	Continuous Once-through	8.8
Vault D ₂ O Vapor Recovery	Drier circuit for D ₂ O recovery	Continuous Recirculating	6.5
Emergency Filtered Air Discharge	Emergency Use Only	Standby	2.0

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Table 4 (a)

Absorbent Physico-Chemical Properties

<u>Property</u>	<u>Limits</u>	<u>Test</u>
CCl ₄ Activity, by weight (a)	50% to 70%	ASTM D3467
TEDA or Equivalent Impregnant Content (c)	5% minimum	Note b
Moisture Content, by weight	5% to 14%	ASTM D2867
Ignition Temperature, °C	330 minimum	ASTM D3466
Ash Content, by weight (a)	15% maximum	ASTM D2866
Hardness	92 minimum	ASTM D3802
Particle Size Distribution	See Table 4(b)	ASTM D2862
Apparent Density, kg/m ³	380 minimum	ASTM D2854
Radioiodine Penetration	See Table 4(c)	Note d
Overall Requirements	Must Pass	ASTM D4069 Note e

-
- a Test is performed on base material before impregnation.
- b Proposed ASTM D 28.04-7 "Standard Method of Analysis of Triethylenediamine (TEDA) Impregnant in Activated Carbon."
- c On occasion KI₃ impregnant may be required at 5% minimum by weight, as specified in ASTM D28.04-25.
- d CSA N288.3, No. 4 "Operation Testing of Nuclear Air Cleaning Assemblies," ASTM D 3803 may be used until CSA N288.3, No. 4 is issued.
- e Test covers performance requirements of "as received" impregnated activated carbon.

Table 4 (b)

Particle Size Distribution

<u>Sieve*</u>	<u>Percent</u>
Retained on No. 6 sieve	0.1% maximum
Retained on No. 8 sieve	5.0% maximum
Through No. 8 retained on No. 12 sieve	60.0% maximum
Through No. 12 retained on No. 16 sieve	40.0% minimum
Through No. 16 sieve	5.0% maximum
Through No. 18 sieve	1.0% maximum

*Sieves per ASTM E11

Table 4 (c)

New Absorbent Performance

<u>Test Conditions</u>		<u>Absorbate</u>	<u>Maximum Penetration (%)</u>
Absorbent depth minimum (mm)	50.0 ± 2.5	I ₂	0.05
Temperature (°C)	25.0 ± 1.0	CH ₃ I	1.0
Relative humidity (%)	95.0 ± 2.0		
Gas face velocity (m/s)	0.2 ± 0.01		

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Table 5

Comparative TEDA Analysis of New Coconut Carbon

<u>Sample Number</u>	<u>TKN (TEDA %)</u>	<u>MeOH Extract (TEDA %)</u>
1	6.6	7.1
2	5.6	5.5
3	5.3	5.4
4	5.3	5.4
5	3.4	3.5
6	3.3	3.6
7	3.3	3.5
8	3.3	3.4
9	4.4	4.7
10	4.1	4.1
11	4.2	4.3
12	4.0	4.2
13	5.7	4.8
14	5.0	5.0
15	5.0	5.0
16	6.0	5.9
17	5.9	5.9

Table 6

Comparative TEDA Analysis of Used Coconut Carbon

<u>Sample</u>	<u>TKN TEDA (%)</u>	<u>MeOH Extract TEDA (%)</u>
Carbon removed from service*-Bruce A Unit 1	2.7	1.1
Carbon removed from service*-Bruce B Unit 4	2.7	1.1
New carbon stored for ~ 1 year on site	7.0	4.0

*Poor performance carbon as measured by ASTM D3803 radioiodine test.

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Table 7

Analysis of Used Carbon From BNGS-A 4-7322-FR3

Sample	Penetration by D3803 %	TEDA MeOH Ext wt%	pH	Total Organics (wt %)
Cell 4 MID	76.7	0.5	4.1	2.2
Cell 13 TOP*	20.4	0.9	4.6	3.7
Cell 13 BOT*	19.0	1.0	6.0	6.5
Cell 13 MID	11.9	1.1	6.8	7.1
Cell 4 BOT	11.2	1.3	7.0	2.5
Cell 4 TOP	<u>9.7</u>	1.4	7.6	3.6
AVERAGE OF ABOVE	<u>14.8</u>			
COMPOSITE OF ABOVE	15.0			
TEST CANISTER	93.0			

Top refers to samples taken ~ 2 feet below the top surface of the carbon.
 Mid refers to samples taken ~ 4 feet below the top surface of the carbon.
 Bot refers to samples taken ~ 6 feet below the top surface of the carbon.

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Table 8

Analysis of Organics Extracted From Spent Carbon

Compound Found	Sample Concentration mg/g					
	Cell Number 4			Cell Number 13		
	Top	Mid	Bot	Top	Mid	Bot
AROMATICS						
toluene	2.6	0.9	0.9	--	--	--
ethyl benzene	3.6	3.0	3.2	4.0	--	5.6
xylene	16.6	13.9	17.7	14.9	17.1	31.9
1-ethyl - 2-methyl benzene	3.8	1.1	0.6	8.4	4.4	9.1
styrene	3.2	0.9	--	9.0	4.9	5.9
total aromatics	29.8	19.8	22.4	36.3	26.4	52.5
ALIPHATICS						
C9	1.9	--	1.1	2.9	--	3.2
C10	--	0.6	--	3.7	17.4	5.8
C11	4.2	1.4	1.2	3.9	7.4	3.1
C12	--	--	--	--	15.9	--
C13	--	--	--	--	4.2	--
total aliphatics	6.1	2.0	2.3	10.5	44.9	12.1
ALCOHOLS						
2-pentanol, 2-methyl	--	--	1.0	--	--	--
3-cyclohexen-1-ol,	--	--	.9	2.7	--	4.9
4-methyl						
total alcohols	--	--	1.9	2.7	--	4.9
NITROGEN*						
pyrazine	1.7	0.5	0.5	--	--	--
triethylenediamine+	11.0	3.8	8.2	--	8.0	7.2
total nitrogen	12.7	4.3	8.7	--	8.0	7.2
TEDA MeOH ext'n - GC	14.0	5.3	13.0	8.8	11.0	10.0

*Semi-quantitative test by thermal desorption from solid sample into GC/MS.

+TEDA

Table 9

Analysis of Spent Carbon From BNGS-A 1-7322-FR6

Sample	Penetration by D3803 (%)	TEDA MeOH Ext(%)	pH
Cell 10 MID	15.9	1.3	7.6
Cell 10 TOP	8.4	0.6	8.1
Cell 4 MID	8.3	1.5	8.0
Cell 4 TOP	4.9	0.9	8.8
Cell 10 BOT	3.9	0.7	8.6
Cell 4 BOT	3.4	1.6	8.5
AVERAGE OF ABOVE	7.5		
COMPOSITE OF ABOVE	6.9		
TEST CANISTER	4.9		

DISCUSSION

KOVACH, J. L.: Have you measured air flow uniformity through your Type 3 adsorber beds?

GUEST: Yes, we have. I will present the data in a paper tomorrow.

JONAS: Since TEDA impregnated onto carbon probably deposits in the large macropores of the carbon is it possible that a TEDA reaction with carbon would produce a gaseous product which, if then adsorbed in the small micropores of the carbon, could be difficult to extract by your chemical analyses?

GUEST: If TEDA decomposes by reaction with carbon or any other means, it is no longer TEDA. Therefore it does not matter if it extracts or not.

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A STUDY ON ADSORPTION CHARACTERISTICS AND DETERIORATION PATTERNS OF AN IMPREGNATED ACTIVE CARBON UNDER A SIMULATED SERVICE CONDITION OF THE FILTERING SYSTEM AT A NUCLEAR POWER PLANT.

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Abstract

In order to study the relative adsorption pattern of organic iodides with an impregnated active carbon, organic iodides were reacted with TEDA (Triethylenediamine) in presence of methanol or hydrocarbons. 1:2 organic salts were formed in case of methanol solvent, whereas 1:1 addition complexes were formed in case of hydrocarbon solvents except the case of methyl iodide which formed 1:2 complex. The chemical structure of salts or complexes were identified by means of TLC, NMR, and elemental analysis. The yields of salts or complexes were decreased in order of carbon numbers of the organic iodide. The prepared salts or complexes were subjected to the radioisotope exchange reaction with $\text{CH}_3^{131}\text{I}$, which could show the tendency of these compounds towards an isotopic exchange reaction. 1:1 organic salts were further prepared to confirm the adsorption pattern of an impregnated carbon (TEDA + KI system) under a dried air flow at 50°C. Methyl iodide formed a mixture of mono and di complex with impregnated carbon, whereas under a moist condition it formed the corresponding salts. Ethyl iodide showed the similar tendency, but the formations of di derivative were markedly decreased. Impregnated active carbons such as KI₃, TEDA + KI, and Dimethyl iodide of TEDA were subjected to the deterioration study under ASTM D 3803-86 conditions. A severe deterioration was observed in case of KI₃, whereas it was relatively minor in cases of TEDA + KI and Dimethyl iodide of TEDA. The deteriorated samples were subjected to the study of radioactive methyl iodide penetration. Under the condition of ASTM D 3803-86 method A, the deteriorated sample could not show the penetration higher than that of the none deteriorated sample, but the penetration of the former sample was markedly increased as the methyl iodide's concentration was increased, which indicated a significant damage of the adsorption characteristics of the former. Three kinds of impregnated carbon such as TEDA + KI, Dimethyl iodide of TEDA, and monomethyl iodide of TEDA were prepared and their feasibilities of being applied for a ESF filter system were discussed comparing their physical and adsorption characteristics.

1. Introduction

In Korea, 6 PWRs and one CANDU power plants are now under the routine operation and another two PWRs will be in the routine operation within a year. Additional 2 PWRs are now under construction. These power plants are operated by Korea 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 plants. During the course of performing regulatory works, it has frequently been experienced that many types of impregnated active carbons were offered by many manufacturers to the company to replace the used carbons at the facilities and the selection of the most suitable carbon has always been under a serious discussion in regards to its effectiveness, stability, price, and others based on the manufacturer's quality statements. It was, therefore, considered to be essential to perform a study on adsorption characteristics and deterioration patterns of an impregnated carbon under the operational condition of a plant simulated in the laboratory, which may be able to afford more definite conceptions for selecting an impregnated carbon

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A (the simulated normal condition of a plant) and higher adsorbate concentration (the simulated DBA situations). The results obtained by these studies were further extended by means of evaluating di and mono methyl iodides of TEDA for deterioration patterns under the similar condition described as above.

Finally, three types of impregnated carbon such as TEDA + KI, Dimethyl iodide, and Monomethyl iodide of TEDA were considered to be the effective impregnated carbon for the use of a nuclear plant, especially for ESF filter system, and their feasibilities for the practical application were discussed comparing their physical and other related properties.

2. Experimental Procedures

2.1 Preparation of Alkyl Iodides of TEDA

The preparation of alkyl iodides of TEDA was performed on basis of the reported procedure(11). Results were summarized in the table 1-A.

2.2 Preparation of Addition Complexes Formed between Alkyl Iodides and TEDA

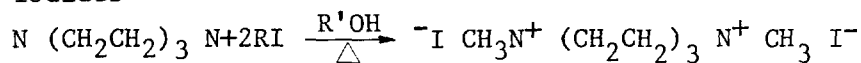
The preparation of addition complexes formed between alkyl iodides and TEDA was conducted by means of the procedure reported for preparing the charge-transfer complex formed between iodine and TEDA(12). Results were summarized in the table 1-B.

2.3 NMR Identification of Alkyl Iodides and Complexes of TEDA

Prepared compounds as described in 2.1 and 2.2 above were subjected to NMR identification by means of Bruker AM-300 NMR Spectrometer. In cases of complex compounds, deuterium alcohol was applied as the solvent in order to minimize decompositions of the product in a strong polar solvent such as D₂O. Results were summarized in the table 2.

Table 1. N-Alkylated Triethylenediammonium Iodides and Addition Complexes Formed between TEDA and Alkyl Iodides

A. Iodides

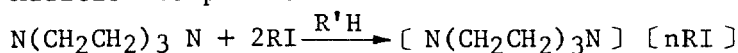


TEDA g(mole)	R	RI g(mole)	R'	ROH (ml)	RX Time (hr)	Yield	m.pt.of the product(°C)	Remarks
5.6(0.05)	-CH ₃	14.2(0.1)	-C ₂ H ₅	50	3	100	260	
2.8(0.025)	-C ₂ H ₅	7.8(0.05)	-CH ₃	"	"	76	228	
2.8(0.025)	-C ₃ H ₇	8.6(0.05)	"	"	"	54	218	
5.6(0.05)	-C ₄ H ₉	18.4(0.1)	"	"	6	43	221	
2.8(0.025)	-CH(CH ₃) ₂	8.6(0.05)	-C ₂ H ₅	"	"	27	179	
2.8(0.025)	-CH(CH ₃) (C ₂ H ₅)	9.2(0.05)	"	25	8	17	*260(dec.)	
5.6(0.05)	-(CH ₃) ₃	18.4(0.1)	"	"	N.R.	"		

* The product was identified as decomposed materials. (See NMR data in table 2.)

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B. Addition Complexes



TEDA g(mole)	R	RI g(mole)	R'	R'H (ml)	TX Time (hr)	Yield (%)	**Dec. Pt. of the Product(°C)	Remarks
1.4(0.0125)	-CH ₃	3.6(0.025)	-C ₆ H ₁₃	60	3	100	238-40	n=2
"	-C ₂ H ₅	3.9(0.025)	"	"	"	62	168-70	n=1
"	-C ₃ H ₇	4.3(0.025)	"	"	"	47	148-50	n=1
"	-C ₄ H ₉	4.6(0.025)	"	"	6	40	140-2	n=1
"	-CH(CH ₃) ₂	4.3(0.025)	-(CH ₂) ₆	50	"	9	*231(dec.)	
"	-CH(CH ₃) (C ₂ H ₅)	4.6(0.025)	"	"	8	5	*220(dec.)	
"	-C(CH ₃) ₃	4.6(0.025)	-C ₆ H ₁₃ or -(CH ₂) ₆	60		N.R.		
"	-CH ₃	1.8(0.0125)	-C ₇ H ₁₅	60	1.5	69	206-8	mix. of n= 1&2

* The product was identified as decomposed materials. (See NMR data in table 2.)

** The products were unstable and they were converted to the corresponding iodides by treating them in a hot solution of ethyl alcohol.

Table 2. Chemical Shifts of Reaction Products Formed between TEDA and Alkyl Iodides.

Type of Type	Compounds R	Solvent	δ-CH ₃	δ-CH ₂	δ-CH ₂ -N	δ-CH ₂ -N (TEAD*Ring)
	-CH ₃	D ₂ O	-	-	3.42(s)	4.12(s)
	-C ₂ H ₅	CD ₃ OD	1.5(t)	-	3.55-3.9(q)	4.07(s)
	-C ₃ H ₇	CD ₃ OD	1.02(t)	1.6-2.0(q)	3.45-3.8(q)	4.1(s)
	-CH(CH ₃) ₂	D ₂ O	1.3-1.6(t)	-	3.82(s)	3.94(s)
	-CH(CH ₃) (C ₂ H ₅)	D ₂ O	-	3.55(s)	-	-
	-CH ₃ (n=2)	D ₂ O	-	-	3.4(s)	4.15(s)
	-C ₂ H ₅ (n=1)	CD ₃ OD	1.4(t)	-	3.17-3.43(m)	
	-C ₃ H ₇ (n=1)	CD ₃ OD	1.0(t)	1.5-2.0(q)	3.1-3.25(m)	
	-CH(CH ₃) ₂ (n=1)	D ₂ O	1.6-1.1(d)	-	3.23-3.3(m)	
	-C ₄ H ₉ (n=1)	D ₂ O	0.95(t)	1.2-1.9(m)	2.95-3.55(m)	
	-C ₃ H ₇ (n=1)	D ₂ O	0.8-1.1(t)	1.5-2.1(q)	3.00-3.37(m)	
	-CH(CH ₃) (n=1) (C ₂ H ₅)	D ₂ O	-	3.23(s)		

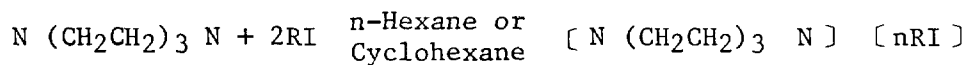
* TEDA in D₂O : δ-CH₂-N2.74(s), TEDA in CD₃OD : δ-CH₂-N2.80(s)

2.4 Elemental Analysis of Complex Compounds

Since the complex compounds formed between alkyl iodides and TEDA were not appeared in literature, elemental analysis of complexes were performed by means of Perkin-Elmer 240 C Elemental Analyzer to confirm the chemical structure identified in 2.3 above. Results were summarized in the table 3.

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Table 3. The CHN Analysis of the Products Formed between TEDA and Alkyl Iodides in Hydrocarbon Solvents



n	R	Calc.			Found		
		N, %	C, %	H, %	N, %	C, %	H, %
2	-CH ₃	7.07	24.24	4.55	7.72	24.42	4.49
1	-C ₂ H ₅	10.45	35.82	6.34	10.21	34.57	6.19
1	-C ₃ H ₇	9.93	38.30	6.74	9.45	37.60	6.65
1	-C ₄ H ₉	9.46	40.54	7.09	8.87	40.46	7.16

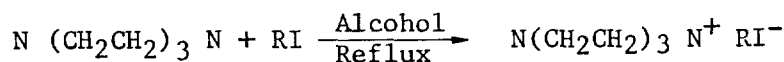
2.5 Preparation of 1-Alkyl-4-Aza-1-Azoniaiodo Bicyclo [2,2,2,] Octane

Since the intermediate compound formed between an impregnated active carbon of TEDA or TEDA + KI and radioactive methyl iodide under a humid air flow is considered to be a mono adduct and the preparative procedure of this type of adduct was not clearly reported in literatures, mono adducts formed between alkyl iodides and TEDA were prepared by means of modifying the procedure adopted in 2.1. Alkyl iodide dissolved in a solvent was added as slow as possible to the solution of TEDA. Results were summarized in table 4. Prepared compounds were identified by means of NMR and CHN analysis as described above.

2.6 Radioactive Isotope Exchange Reaction

Into a erlenmeyer flask equipped with a magnetic stirrer and stopper, a definite quantity of the salt or the complex was dissolved in 100ml of anhydrous methanol under stirring at the room temperature and a definite quantity of radioactive methyl or ethyl iodides was added to the solution. The resulting mixture

Table 4. Preparation of 1-Alkyl-4-Aza-1-Azoniaiodo Bicyclo [2,2,2,] Octane



TEDA (g)	R	RI (g.)	Alcohol (ml.)	RX. Time (hrs.)	Yield (%)	*m.pt. of the product (°C)	Remarks
11.3	-CH ₃	14.0	250	4	92.90	211	(Methanol)
8.4	-C ₂ H ₅	12.0	350	3	86.76	177	(Ethanol)
2.8	-C ₃ H ₇	4.0	150	3	70.59	161	(")
2.8	-C ₄ H ₉	4.0	150	3	52.94	149	(")

* EX. R = -CH₃, ¹H NMR(D₂O): δ = 3.40 (t, 6H, TEDA Ring-CH₂ -), 3.20(t, 6H, TEDA Ring-CH₂-), 3.05(s, 3H, -CH₃): CHN Anal. Calc. for C₇H₁₅N₂I; C% 33.07, H% 5.90, N% 11.02, Found; C% 32.50, H% 6.05, N% 10.90. All other products were identified both by NMR and CHN analysis.

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was well stirred at the room temperature, and it was stoppered well and kept at 25-30°C for a definite time. The radioactivity of the solution was measured by the r-counter (EG&G, Ortec 7050-7000 series, Ge-Li Detector.) The stopper was removed and the flask was heated over a hot plate under stirring and unreacted alkyl iodide was completely removed. The radio-activity of the residual solution was measured and it was compared to the original radioactivity of the solution to calculate the percentage of isotope product formed. Results were summarized in tables 5 and 6.

Table 5. Removal of Radioactive Methyl Iodides by N-Alkyltriethylenediammonium Iodides and Addition Complex Formed between TEDA and Alkyl Iodides*

EXP.No.	Type of Compounds	R	wt. (g)	CH ₃ ¹³¹ I + CH ₃ ¹²⁷ I (μI)	RX. Temp. (°C)	RX. Time (hr)	Isotope Product (%)
1.	(TEDA)	-	0.025	50	25-30	38	38.52
2.	R	-CH ₃	0.12	50	25-30	38	54.28
3.		-C ₂ H ₅	"	100	25-30	14	35.00
4.		-C ₃ H ₇	"	"	25-30	14	30.00
5.		-CH(CH ₃) ₂	"	"	25-30	18	31.20
6.		-C ₄ H ₉	"	"	25-30	14	39.70
7.		-CH ₃	"	"	25-30	14	42.20
8.		-CH ₃	"	"(n=2)	25-30	18	37.20
9.		-C ₂ H ₅	"	"(n=1)	25-30	18	36.10
10.		-C ₃ H ₇	"	"(")	25-30	38	36.60
11.		-CH(CH ₃) ₂	"	"(")	25-30	14	38.30
12.		-C ₄ H ₉	"	"(")	25-30	14	35.10

* Reactions were run in 100ml of anhydrous methanol.

Table 6. Removal of Radioactive Ethyl Iodide by N-alkylated Triethylenediammonium Iodides*

Types of Compounds	R	wt (g)	C ₂ H ₅ ¹²⁷ I + C ₂ H ₅ ¹³¹ I (μI)	RX. Temp. (°C)	RX. Time (hrs.)	Isotope Product (%)	Remarks
	-CH ₃	0.4	50	25-30	18	36.55	
	-C ₂ H ₅	0.4	50	25-30	18	29.23	
	-C ₃ H ₇	0.4	50	25-30	18	29.55	

* Reactions were run in presence of a solution of 30ml. of ethanol and 10ml. of water.

2.7 Identification of the Intermediates Formed between the Impregnated Active Carbon (TEDA + KI) and Alkyl Iodides under an Air Flow

A. Dry Air Flow

ASTM D 3467-76 (CCl₄ Activity) was applied for the adsorption of alkyl iodides with the impregnated active carbon. (TEDA + KI) The adsorbed carbon sample was eluted under the similar air flow as above until the weight of the carbon sample becomes constant. It was further dried in an oven until the decrease of the weight becomes constant. The dried sample was extracted with n-Heptane and anhydrous methanol successfully. The methanol solution was examined through TLC (Developing solvent; n-propanol: ammonia solution (4:1 v/v)). The methanol solution was concentrated and resulting solid products were examined by means of decomposition point, and NMR comparing these data with those of the authentic samples prepared in 2.1, 2.2, and 2.5 as described above. Qualitative results obtained were illustrated in the Fig.1.

B. Humid Air Flow

Adsorptions were performed on basis of ASTM D 3803-86 except adsorbate concentrations. Adsorbate concentration was increased as compared with that of ASTM 3803-86 in order to facilitate the isolation and identification of the formed intermediate. The eluted carbon sample was treated as described in A above. Qualitative results obtained were illustrated in the Fig.1.

Fig.1. Adsorption Pattern of Alkyl Iodides on an Impregnated Active Carbon (TEDA (2%) + KI (2%))

Carbon (20g) N(CH ₂ CH ₂) ₃ N + KI	CH ₃ I (Saturation)*	(N(CH ₂ CH ₂) ₃ N) (CH ₃ I)
	50°C, RH 0%	+
		(N (CH ₂ CH ₂) ₃ N) (2 CH ₃ I)
		(Complex mix.)
	C ₂ H ₅ I (Saturation)*	(N (CH ₂ CH ₂) ₃ N) (C ₂ H ₅ I)
	50°C, RH 0%	(Complex)
	CH ₃ I (43.3mg/2hrs)**	N (CH ₂ CH ₂) N ⁺ CH ₃ I ⁻ (Salt)
	30°C, RH 90%	Trace of ⁺ N(CH ₂ CH ₂) ₃ N ⁺ 2CH ₃ I ⁻
	C ₂ H ₅ I (35.6mg/2hrs)**	N ⁺ (CH ₂ CH ₂) ₃ N C ₂ H ₅ I ⁻ (Salt)
	30°C, RH 90%	Trace of ⁺ N(CH ₂ CH ₂) ₃ N ⁺ 2C ₂ H ₅ I ⁻
	CH ₃ I (43.3mg/2hrs)**	N (CH ₂ CH ₂) ₃ N ⁺ CH ₃ I ⁻ (Salt)
	80°C, RH 90%	& Little of ⁺ N(CH ₂ CH ₂) ₃ N ⁺ 2CH ₃ I ⁻

* Adsorptions were performed on basis of ASTM D 3467-76 (CCl₄ Activity) Carbon Samples were extracted with hydro-carbon and alcoholic solvents, and the products were isolated and identified by their dec. points, TLC, and NMR.

** Adsorption was performed on basis of ASTM D-3803-86. The methods of isolating and identifying the products were the same as above.

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2.8 Deterioration of an Impregnated Active Carbon under a Humid Air Flow

An impregnated active carbon was examined for the deterioration of its impregnant under a humid air flow equivalent to those of ASTM D 3803-86 method A and method C, respectively. The carbon sample was exposed to a humid air flow for a definite time and it was dried until the weight decrease become constant. The dried sample was extracted with acetonitrile and the extract was examined by means of U.V. spectrometry. Results were summarized in table 7-10. In case of the carbon impregnated with TEDA + KI, the sample was extracted with anhydrous ethanol and the extract was refluxed with the excess quantity of methyl iodide to form the corresponding dimethyliodide of TEDA. From the quantity of dimethyl iodide formed, the amount of TEDA deteriorated was back calculated. Results were summarized in table 9. Data on TEDA + KI and methyl iodide of TEDA studied under a humid air flow of 30°C, RH 90% did not show any deterioration of impregnants and hence they were not summarized in a table.

Table 7. Variation of Absorbance of Deteriorated Sample of KI + I₂ Series at λ max*

Type of carbon sample	State of sample	Absorbance (log e) of equivalent conc. of extracts at λ max*	Remarks
KI ₃	Original	0.588	
"	Air Flow, at 30°C RH 80% for 10hrs	0.514	
"	Air Flow at 30°C, RH 80%, for 16hrs	0.599	

* At 247nm

Table 8. Variation of Absorbance of Deteriorated Sample of KI + I₂ Series at λ max*

Type of carbon sample	State of sample	Absorbance (log e) of equivalent conc. of extracts at λ max*	Remarks
KI ₃	Original	1.420	
"	Air Flow at 80°C, RH 80% for 1hrs.	1.730	
"	Air Flow at 80°C, RH 80% for 14hrs.	**1.940	

* At 247nm.

** CH₃ ¹³¹I Penetration(%) 3.35. (Under ASTM D-3803-86, Method A., Test adsorbate conc. 2.3 x 10⁻²mg/min.) (Ref. table 12).

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Table 9. Variation of Absorbance of Deteriorated Sample of TEDA + KI Series at λ max*

Type of carbon sample	State of sample	Absorbance (log e) of equivalent conc. of extracts at λ max*	**TEDA deteriorated (wt. %)
TEDA + KI	Original	0.162	-
	Air Flow at 80°C, RH 90% for 7.5hrs.	0.179	9.5
	Air Flow at 80°C, RH 90% for 15hrs.	0.217	20.0

* At 247nm.

** The alcoholic extract of the sample was reacted with an excess amount of methyl iodide and the amount of TEDA in the sample were calculated on basis of dimethyl iodide formed.

Table 10. Variation of Absorbance of Deteriorated Samples of Dimethiodide of Triethylenediamine at λ max*

Type of carbon	State of the sample	Absorbance (log e) of equivalent conc. of the extract at λ max*	Remarks
Dimethiodide of triethylenediamine	Original	2.70	
"	Air flow, 80°C, RH 90%, 8hrs.	2.70	
"	Air flow, 80°C, RH 90%, 16hrs.	2.65	

* At 274nm.

2.9 Penetration Test of the Deteriorated Carbon Samples

Deteriorated carbon samples evaluated in table 7-10 were subjected to the penetration test for radioactive methyl iodide under the condition of ASTM D 3803-86, method A. The test was further extended to confirm the penetration pattern of a deteriorated sample under a rigid condition of DBA or the equivalent by means of increasing the adsorbate concentration as shown in table 11. Typical results were summarized in table 11.

2.10 Comparative Study of Physical and Other Related Properties of Three Types of Impregnated Carbon Suitable for a ESF System

In order to evaluate the feasibility of an impregnated carbon for being applied at a ESF system of a plant, three types of impregnated carbons were prepared in this laboratory. In table 12, results of examining their physical and other related properties were summarized together with experimental procedures adopted.

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Table 11. Examples of CH₃ ¹³¹I Penetration* of Deteriorated Carbon.
(TEDA (2%) + KI (2%) Impregnated)

Deteriorated Conditions °C RH(%) Time(hrs.)			Introduced Amount of Test Adsorbate		CH ₃ ¹³¹ I	Penetration (%)
			mg/min.	Total (mg)		
None deteriorated			1.8 x 10 ⁻²	2.2		<0.01
"			4.2 x 10 ⁻²	5.7		0.08
80	90	4.5	3.8 x 10 ⁻²	5.7		0.03
80	90	7.5	3.6 x 10 ⁻²	5.4		0.09
80	90	15.0	(1) 2.9 x 10 ⁻²	2.7		<0.01
			(2) 2.2 x 10 ^{-2**}	2.7		0.50
80	90	15.0	3.6 x 10 ⁻²	5.4		0.29
None deteriorated			35.7 x 10 ⁻²	42.8		5.30
80	90	15.0	14.7 x 10 ⁻²	17.6		51.00

* Based on ASTM D 3803-86, Method A except the test adsorbate concentration and total input of the adsorbate as shown in the table.
(Sample bed : 33mm, Depth 50mm)

** The test adsorbate was introduced successively after checking the penetration of the previous test.

Table 12. Comparison of Properties of TEDA and Its Derivatives and Activated Carbons Impregnated by These Chemicals

Type of Compound	N(CH ₂ CH ₂) ₃ N ⁺	⁺ N(CH ₂ CH ₂) ₃ N ⁺	N(CH ₂ CH ₂) ₃ N
	CH ₃ I ⁻	CH ₃ I ⁻	+ KI
1. m pt. (°C)	211	260	TEDA 158
2. pH of aq. sol.	6.8 ²⁾	5.3 ²⁾	TEDA : 10.2 ¹⁾ KI : 6.0 ¹⁾
3. Isotope product formed by CH ₃ ¹³¹ I (%) ³⁾	81.86	84.85	TEDA = 78.85 KI = 66.12
4. Impregnated carbon			
a. Impregnated (wt %)	4.43	4.38	3.84 (TEDA = 2.14 KI = 1.70)
b. pH ⁴⁾	9.0	7.6	9.6
c. Deterioration at 80°C, RH 90%, 15hrs.	None	None	TEDA deteriorated ca. 20%
d. CH ₃ ¹³¹ I ⁵⁾ penetration (%)	0.08	0.09	0.08

- 1) Aq. sol. of 0.2g samples in 100ml of water (pH of water : 6.3).
- 2) Aq. sol. of 0.4g samples in 50ml of water (pH of water : 6.3).
- 3) In presence of 30ml MeOH and 10ml of water, sample : 0.3g, 0.4g, 0.1g, and 0.3g, respectively. Reaction time 72hrs. Reaction Temp. 25-30°C.
- 4) According to ASTM D-3838-80.
- 5) According to ASTM D-3803-86, method A.

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3. Results and Discussion

3.1 Dialkyl Iodides of TEDA

As shown in table 1-A, 2 moles of alkyl iodides could react with 1 mole of TEDA in presence of alcoholic solvents to form the corresponding dialkyl salts as reported(11) for ethyl, methyl, and butyl iodides. In case of methyl iodide, the formation of the salt was almost quantitative which could be applied as a quantitative analytical reaction of confirming the amount of TEDA as described in 3.6. However, tertiary butyl iodide could not form the salt, whereas isobutyl analogue decomposed TEDA to various mixtures as shown in the NMR datum. This may be due to the steric hindrance of the bulky structures of iodides used. Yields of salts were decreased in order of the carbon number of the iodide, which may also be elucidated by means of the steric structures of TEDA and iodides.

3.2 Complexes of TEDA

Even though 2 moles of iodine had formed the 1:2 charge transfer complex with 1 mole of TEDA and 1 mole of the iodine could form the 1:1 complex in the reported literature,(12) 2 moles of alkyl iodides had formed the 1:1 addition complex as summarized in table 1-B. In case of methyl iodide, 2 moles of the iodide had formed the 1:2 complex whereas 1 mole of it formed a mixture of 1:2 and 1:1 complexes as listed in table 1-B. The complexes were colored compounds and they decomposed along a broad temperature range which are the characteristics of an addition complex.(13) These differences of the complex as compared with those of iodine complex were probably due to the steric structure of iodides, which hindered the formation of the 1:2 complex around nitrogen atoms of TEDA molecule. Methyl iodide, which has a less bulky structure, could form the 1:2 complex. The structure of the complex was examined by means of TLC, NMR, and analysis as listed in tables 1 and 3, and they supported the formation of 1:1 complex. The complex was easily converted to the corresponding salt by treating it in a hot solution of ethyl alcohol which indicated the unstability of its structure as compared with that of a charge transfer complex. At present, the structure of the complex is considered to be an addition type rather than a charge transfer judging from the observations described hereto, but it should further be identified by means of other instrumental analysis than NMR. Isopropyl and isobutyl iodides had formed a mixture of decomposed products and tertiarybutyl iodide had shown no reactivity with TEDA. These may again be due to the steric structures of iodides and TEDA itself.

3.3 Mono Alkyl Iodides of TEDA

Mono alkyl iodides of TEDA could be formed as listed in table 4. Yields of the product were decreased in order of the carbon number of the alkyl iodide. Products were identified by means of both NMR and CHN analysis. In case of methyl iodide, methanol solvent could form the mono salt at its refluxing temperature, but ethyl, propyl, and butyl iodides could form the mono salt only in ethanol solvent of the higher refluxing temperature than that of methanol. An excessive reaction time afforded a small quantity of the di salt in case of methyl iodide whereas ethyl, propyl, and butyl iodides could form cleanly mono salt even in a prolonged reaction time. These differences of the reactivity of each alkyl iodide may be attributed the steric structure of each iodide which may hinder the formation of the salt around the nitrogen atom of the TEDA molecule. This tendency of an alkyl iodide was also observed in the radioactive isotope exchange reaction described in the following 3.4. According to the literature,(14) the marked deactivation of the tertiary nitrogen atom in a mono quaternized TEDA was experienced,

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and it was explained that the positive charge present on the quaternized nitrogen atom deactivated the reactivity of the tertiary nitrogen atom. The convenient formation of the mono iodide described above was explained duly by this trend of the reactivity of the TEDA molecule, and this may also be a good reference point to the formation of mono adduct when an impregnated carbon (TEDA + KI) is treated with methyl iodide under a dry or humid air flow as shown in fig.1.

3.4 Radioactive Isotope Exchange of Methyl or Ethyl Iodides with Salts or Complexes

Comparative study data on the radioactive isotope exchange reaction of methyl iodide with dialkyl salts or complexes of TEDA were listed in table 5. Generally, the yield of the isotopic product was decreased in order of the carbon number of alkyl iodide as expected from its steric structure. This trend was, however, not distinct enough in cases of complexes, which may be due to the structure of the complex. Presumably, the moiety of the tertiary nitrogen atom involved in the complex molecule is less sterically hindered than that of the salt. In table 6, data on the radioisotope exchange reaction of ethyl iodide with alkyl iodides of TEDA were summarized. The yield of the isotopic product was decreased as compared with that of the corresponding methyl iodide reaction and the decrease of the yield was also observed in order of the carbon number of the alkyl group of the salt molecule. More quantitative data on the determination of the rate constant of the reaction may further be searched in the near future to elucidate these steric effects observed in details, but the following informations are obtainable at the present stage.

A. Radioisotopic exchange of methyl iodide with TEDA itself is less prominent than that of its methyl iodide. This tendency had already been observed in the system of tertiary amines.(3).

B. The same reaction with dialkyl iodides of TEDA showed a steric hindrance effect to decrease the yield of the isotopic product which was depended on the structure of the iodide.

C. The same reaction with complexes of TEDA showed a less steric hindrance effect than that of B above, which may be due to the less steric crowded moiety of the nitrogen atom involved. These informations may be useful to understand the effectiveness of an impregnated carbon (TEDA series) adsorbing radioactive methyl iodide or high molecular weight iodides on basis of the structure of the formed intermediate discussed in the following 3.5.

3.5 Adsorption of Methyl Iodide or Ethyl Iodide with an Impregnated Carbon (TEDA + KI)

Results obtained in the study on the isolation and identification of the intermediate compounds formed between methyl iodide or ethyl iodide and an impregnated carbon (TEDA + KI) under a dry or humid air flow were illustrated in Fig.1. Under a dry air flow at 50°C, the carbon formed a mixture of di and mono complexes of TEDA, which was identified by means of examining the isolated product for its decomposition point, TLC, and NMR comparing these data with those of the authentic samples prepared above. The formation of the mono adduct was dominant, though the carbon was saturated with methyl iodide. The adsorption of ethyl iodide with the carbon under the similar condition above had formed the mono adduct exclusively. The adsorption of methyl iodide with the carbon under a humid air flow at 30°C (ASTM D 3803-86, Method A.) had formed a mixture of mono and di methyl

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iodides (salts) of TEDA. The formation of mono adduct was dominant again. (ca. 99%) The ethyl iodide under the similar experiment had exclusively formed the mono ethyl iodide of TEDA. (ca. 99.5%) These trends of adsorptions had indicated that the reactivity of the impregnant in the carbon could not be high enough to form a significant amount of the di adduct, though the concentration of iodides introduced in the system was of extreme high, (ca. 20 times of that of ASTM D-3803-86 Method A.) The adsorption of methyl iodide with the carbon at 80°C, (RH 90%, ESF filter's operational condition) had shown some increase of di adduct, but it was not significant enough to be noticed, which indicated that the adsorption pattern of alkyl iodides was not influenced much by the change of the temperature.

The difference of the structure of intermediates formed under a dry and a humid air flows may duly be explained by the fact that complexes of TEDA could be formed in non polar solvents whereas the salts were in polar solvents as shown in 3.1 and 3.2 above. Probably, the structure of the intermediate will be varied from the complex to the salt depending on the moisture content of the air flow. However, the formation of mono adduct even under the condition of an extreme high concentration of iodides and a high temperature (80°C) suggested the following conceptions, which may be essential to evaluate the adsorption effectiveness of TEDA in an impregnated carbon.

A. The upper layer of the sample bed used in this experiment may contain a higher concentration of dialkyl iodides than that of the down layer, which was formed at the later stage of the dose period. According to Deitz, (15) a sudden decline of the concentration, the concentration of $^{127}\text{I}-\text{CH}_3$ penetrated through a new or slightly used carbons containing TEDA, was observed at the end of the dose period. This observation may partly be explainable by the present observation that the dialkyl iodide of TEDA was formed at the end of the dose period even in a trace quantity at the upper layer, which consumed methyl iodide a great deal.

B. Under a normal operation condition of a plant (25-30°C, RH 70-95%) with a relatively minor concentration of radioactive methyl iodide, TEDA in an impregnated carbon may be limited in its reactivity to form the mono adduct through its service time. One of two tertiary nitrogen atoms in the TEDA molecule has, therefore, no direct effect to trap radioactive iodides except some influences on the formation of mono iodide itself or the radioactive exchange of the formed mono adduct by the bond through interaction of σ electrons of nitrogen atoms. (16) The steric structure of TEDA had played a steric hindrance effect on the formation of alkyl iodides and the radioactive exchange reaction of the formed iodides as discussed in 3.5 above. Under this situation, the advantage of TEDA compared to that of other impregnant should be limited to the electronic structure of the bicyclic molecule itself, which may further be investigated in details.

C. Under a DBA or other serious accidents, a sudden increase of the radioactive iodide's concentration and temperature of the effluent may be expected to enhance the formation of dialkyl iodides which may trap more quantity of radioactive iodides, but results of the present study had shown the formation of a trace quantity of dialkyl iodides under the air flow containing methyl iodide of an extreme high concentration at the operation temperature of an ESF filter system. It may be reasonable to estimate that the reactivity of TEDA under a DBA or other accident situation may not be beyond the formation of the mono adduct. The removal efficiency of radioactive iodides in this situation will also be depended on one of two nitrogen atoms for trapping and mono quaternized iodide ion as described above. Furthermore, the steric considerations on the structure of TEDA discussed in 3.5 above may become a significant factor to be evaluated in a ESF filter system, as the effluent released under the accident situation is known to be

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contaminated with high molecular weight iodides. In this laboratory, further researches to define a quantitative correlation between the formed intermediate and the adsorbate concentration are under progressing and results obtained may be applied for developing an impregnant of higher trapping ability than that of TEDA or its analogue.

3.6 Deterioration of the Impregnant in an Impregnated Carbon under a Humid Air Flow

Under the normal operational condition of a plant, KI_3 showed an increase of absorbance at its λ max. as shown in table 7, which was an indication of the loss of elemental iodine in the system according to the previous study of this laboratory.(10) TEDA + KI and dimethyl iodide of TEDA didn't show any increase of absorbances at their λ max. Under the ESF filter operational condition, KI_3 and TEDA + KI had shown some increases of absorbances at their λ max as summarized in tables 8 and 9. In case of TEDA + KI, the increase of the adsorbance was the indication of loss of TEDA in the system.(10) The quantitative measurement of the amount of the loss of TEDA in the system had shown 9.5-20.0% loss of TEDA during the period of 7.5-15.0 hrs. intervals as listed in table 9. However, dimethyl iodide of TEDA did not show any increase of absorbance at its λ max as listed in table 10. These observations afforded the following informations.

A. KI_3 is subjected to a deterioration of its iodine content even under a normal operation condition and hence it should be checked time basis for its iodine content in order to maintain its quality of adsorption.

B. Under the ESF operational condition, the loss of iodine in a KI_3 carbon was very severe even for 1 hour interval and hence this type of carbon should not be operated at this condition. The evaporation of adsorbed iodine in a KI_3 carbon at a high temperature had already been pointed out in many literatures.

C. Under the ESF filter operational condition, TEDA + KI showed a relatively minor loss of TEDA, but it was still significant to be evaluated. The operational time intervals of 7.5-15.0 hrs. shown in table 9 may ordinarily not be experienced in a DBA situation except an extreme fatal accident, but ESF filter system should be checked for its operational condition for a hour at least once a month through its service life. During the course of this checking operations, total operation time accumulated may reach the listed time intervals, when the loss of TEDA in the carbon may be significant as listed in table 9.

D. The impregnant of dimethyl iodide of TEDA did not show any deterioration even under the ESF filter operational condition for 16 hours and hence this type of impregnant seemed to be useful for an ESF filter system provided that all other relevant characters required for a nuclear grade impregnated carbon were sufficed to be useful.

3.7 Penetration Tests for Deteriorated Carbon Samples

In case of KI_3 carbon, the deteriorated sample at 80°C, RH 80% for 14 hours penetrated 3.35% of radioactive methyl iodide under the condition of ASTM D-3803-86, Method A as shown in the foot note of table 8. As discussed in 3.6, this type of impregnated carbon may not be stable enough to be used in an ESF filter system.

In case of TEDA + KI carbon, the deteriorated samples under the ESF filter operational condition were closely checked for their penetrations of radioactive methyl iodide as summarized in table 11. Under the test condition of ASTM D-3803 Method A, they showed the permissible penetration defined in the technical

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specification of a plant, but the penetrations were gradually increased as compared with those of none deteriorated sample when the introduced amounts of the test adsorbate were doubled. The penetrations had become very serious amounts as compared with those of none deteriorated sample when the total input of the test adsorbate was increased remarkably. These observations had indicated that the deteriorated samples prepared in this study could maintain the permissible penetration of radioactive methyl iodide under the test condition of ASTM D-3803-86, Method A., but the adsorptivity of the samples had, doubtlessly, been damaged judging from the data obtained for the loss of TEDA listed in table 9 and the high penetration rate observed under the increased input of the test adsorbate in table 11. It may, therefore, be reasonable to recommend that TEDA + KI carbon used for a ESF filter system should be checked for its TEDA content after being operated more than 15 hours to confirm the quality status of the carbon. Some other types of impregnant such as dimethyl iodide structure, which was stable under the ESF operational condition, would be more desirable for the ESF filter system and further efforts to develop this type of impregnant may be anticipated in the near future.

3.8 Comparative Study on Three Types of Impregnated Carbons Suitable to a ESF Filter System

In table 12, physical and other relevant properties of three types of carbon of TEDA + KI, mono methyl iodide of TEDA, and dimethyl iodide of TEDA were summarized. Judging from these data together with discussions described hereto, TEDA + KI carbon has the following disadvantages to be used for a ESF filter system.

A. Deteriorated under the ESF filter operational condition during the period of 7.5-15.0 hours.

B. One of two nitrogen atoms in the TEDA molecule had only been effective to trap radioactive methyl iodide.

C. The steric structure of TEDA had played a steric hindrance effect to the formation of alkyl iodide of high carbon number. The effluent of a DBA situation is liable to be contaminated with high molecular weight iodides.

Dimethyl iodide or monomethyl iodide carbon has the following advantages to be used for a ESF filter system.

A. Under the ESF filter operational condition, no deterioration had been observed even for 16 hours interval.

B. Iodide ion in the molecule was very reactive to the radioactive isotope exchange reaction and it was more reactive than TEDA or KI in presence of anhydrous methanol as shown in table 12.

C. The steric hindrance effect exerted by the iodide towards the radio-isotopic exchange reaction of high molecular weight iodides was not so high as compared to that of the formation of alkyl iodides of TEDA.(see tables 1,4,5 and 6.)

However, the following disadvantages should be evaluated.

A. pH of the water solution of dimethyl iodide of TEDA is low to result the pH of the water extract of the impregnated carbon as 7.6, which should be alkalized by adding a buffer reagent to the carbon. On the other hand, the acidity of the iodide itself may result an oxidative decomposition of iodide ion during the course

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of a prolonged service time.

B. pH of the water solution of monomethyl iodide is high enough to result the pH of the water extract of the impregnated active carbon as 9.0, but the possibility of the decomposition of the iodide ion by a prolonged exposure with oxygen is still to be considered.

It may be the future research problemes to developpe an impregnant of stable, less steric, high trapping ability, and effective radioactive isotope exchange reactivity under a ESF filter operational condition, but an impregnant of having monomethyl iodide structure is recommendable as one of the effective impregnant or coimpregnant for a ESF filter system on basis of data in table 12.

4. Conclusion

Results obtained in this study could afford valuable conceptions to understand the adsorption pattern and deterioration profiles of impregnated carbon of TEDA + KI, KI₃, dimethyl iodide of TEDA, and monomethyl iodide of TEDA, respectively. These conceptions may further be extended in future research to developpe an impregnant of stable, less sterically hindered, high trapping ability, and effective radioactive isotope exchange reactivity for a ESF filter system of a nuclear power plant.

Acknowledgement

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DISCUSSION

WREN:

You are concerned about steric effects based on your experiments in solution phases. On surfaces, adsorbed TEDA is likely to be oriented in a specific way. In addition, the iodine species is also adsorbed with a specific orientation. Is it too hasty to extrapolate the results observed in solution to those of adsorbed phases.

KIM:

Basically, results obtained in reactions of a solution state should be reconfirmed further in reactions observed in a gaseous-solid phase. I am now doing some work to confirm these aspects and results observed may be presented in a subsequent paper. Thank you for your kind comments.

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ACTIVE CHARCOAL FILTER IGNITION TESTS

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Abstract

Activated charcoal filters have wide applicability for gas adsorption system in nuclear or conventional plants.

Such filters, where used for radioactive gas delay, may undergo some ignition risk due to decay heat and/or to self combustion process.

A test system was set up to find out correlation between ignition point and charcoal physical parameters such as mean and bulk density, dynamic adsorption coefficient, surface area.

This test system was realized in conformity with ANSI/ASTM D 3466 and the charcoal to test was prepared according to ANSI/ASTM D 2854 and in conformity with recommended Practice E 300.

This paper reports experimental equipment, instruments and test procedure adopted along with an analysis of the data obtained.

Results of the limits of these correlation and their applicability area are indicated.

I. Introduction

In the event of a disfunction of a system for lack decay heat removal, loss of air flow, there may be some ignition risk for active charcoal filters due to decay heat and/or to self combustion process.

Activated charcoal production is seldom provided with standard test methods and the certificated physical parameters are not always prepared in conformity with ANSI-ASTM standards. Therefore it may be necessary to verify such parameters or useful to test them to design adsorption systems.

The most significant parameters to take into account are:

- surface area
- granular density
- bulk density
- adsorption coefficients
- ignition temperature.

II. General considerations on relevant parameter correlations

In previous papers (1, 2) the behaviour of activated charcoal has been widely investigated to find out correlations between physical parameters.

The aim was to minimize the number of parameters to verify for a first selection of activated charcoals or the number of tests to

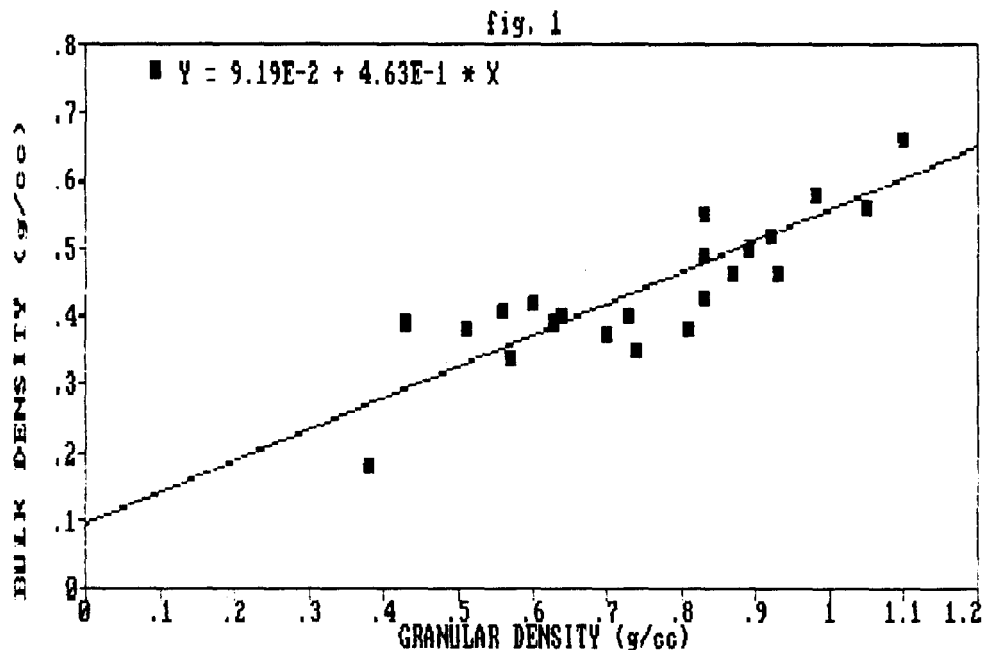
perform for the acceptance of a selected type of charcoal.

To minimize tests means at last, to minimize time waste and costs.

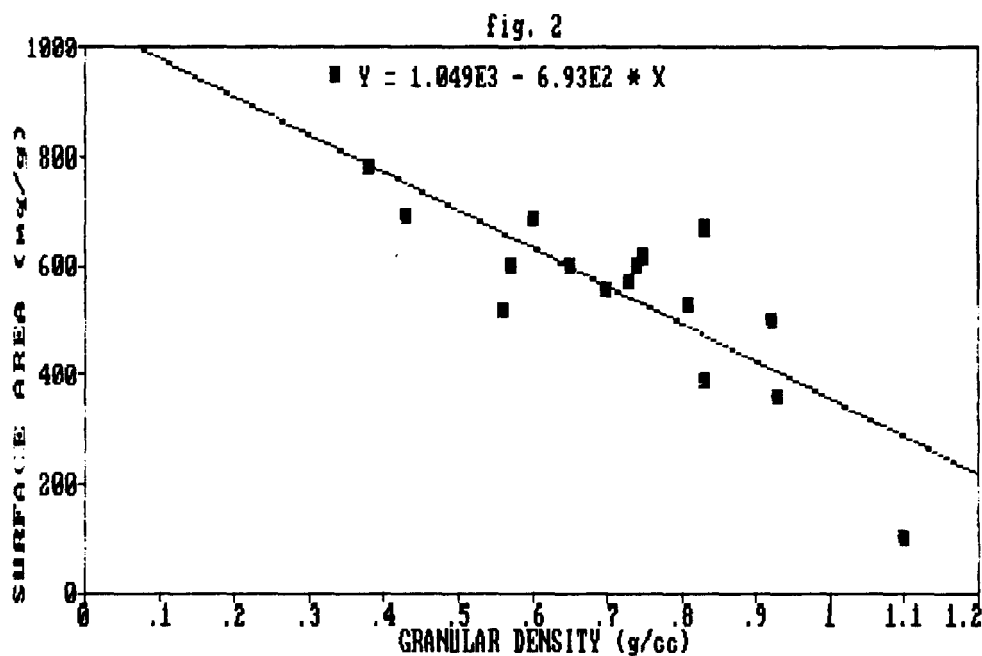
The most useful correlations found out in tests performed on different samples of activated charcoal are reported in fig. 1, 2 and 3.

From these it point out:

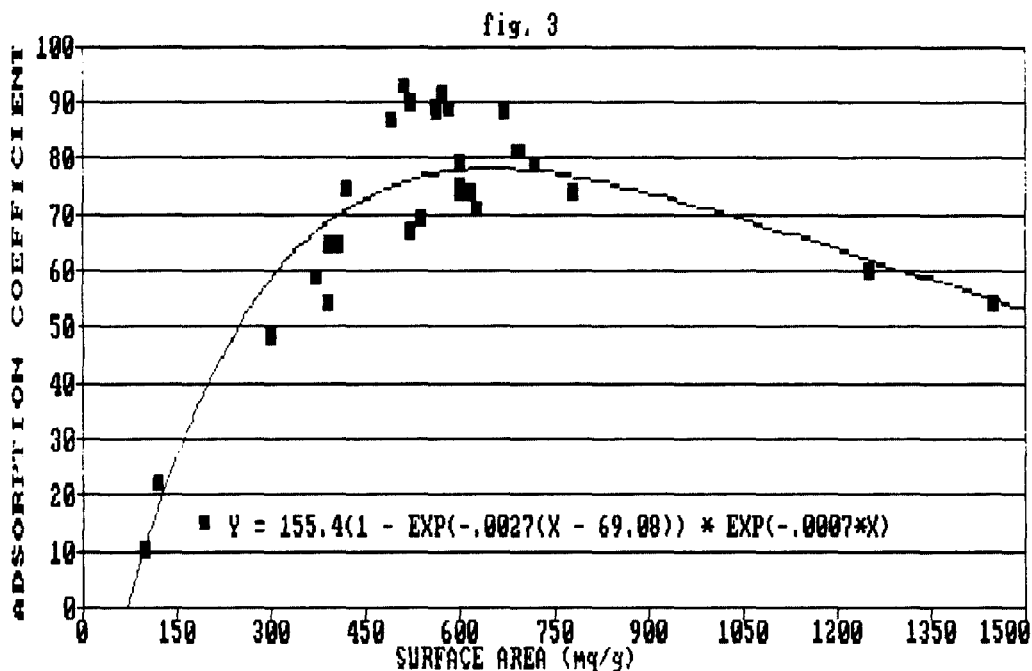
- there is a linear dependence between bulk and granular density (fig. 1) and between surface area and granular density (fig. 2)



- from experimental data reported in fig. 3 a semiempirical relation for the dynamic adsorption coefficient of Kr vs surface area was calculated.



Most of activated charcoal sampler tested, after all, fit on with these relationships quite well, within experimental errors.



III. Ignition test

The aim of this test is to determine when and how a granular activated charcoal may reach the ignition temperature in flowing air and to examine if there is same relationship between ignition point and physical parameters.

A sample of charcoal is exposed to a heated air stream, the temperature of which is slowly increased until the charcoal ignites.

The test apparatus and procedures are accomplished according to the ANSI-ASTM Test Method D 3466-76.

In fig. 4 the assemble apparatus is shown: the air supplied by a blower (1) is passed through a air dryer (2), a HEPA filter and a filter of activated charcoal (3).

The flow is regulated by the valve (4) and controlled by the flowmeter (5). There is a control of relative humidity too (6), to verify R.H. be less than 5% at 25 °C.

The sample of charcoal to test (8), obtained in conformity with ASTM Recommended Practice E 300, is introduced into the quartz ignition tube (7) using the procedure described in Test Method D 2854.

The sample is covered with quartz beads to prevent fluidization of the charcoal bed.

The heating mantle is taped around the ignition tube and surrounded by a heat insulator.

The temperature is measured by termocouples T₁, T₂, T₃.

A supply of compressed nitrogen is provided to quench the fire when there is the sudden temperature rise at ignition.

There is an automatic temperature programmer to increase

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the temperature of the air stream and an automatic system to cut off air flow immediately at ignition and to introduce nitrogen.

The temperature vs time measured by thermocouples T₁ and T₂ are recorded and the ignition point calculated.

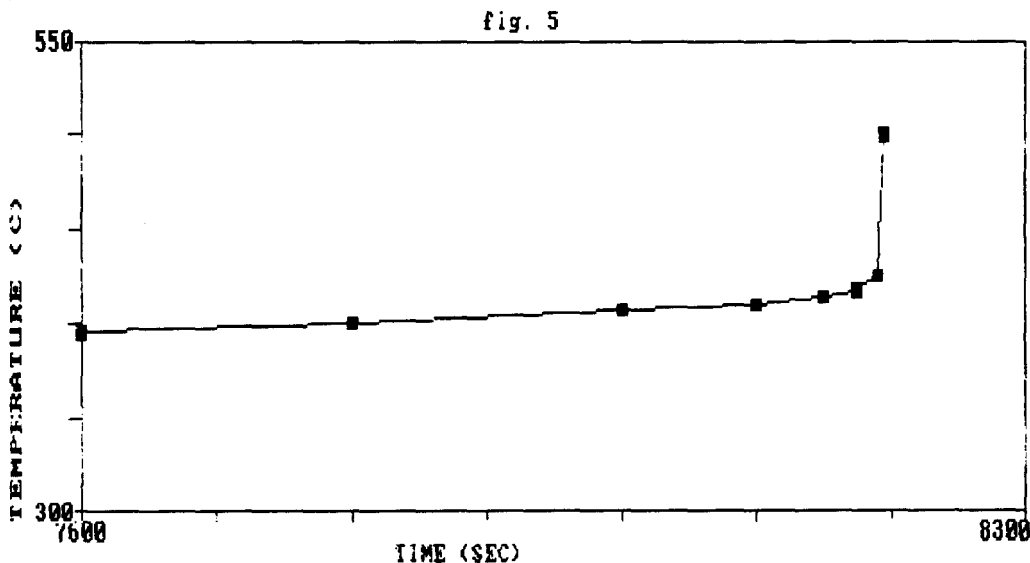
IV. Experimental results

Fifteen samples of activated charcoal from different manufactures were tested under the same following conditions:

- air flow rate was adjusted to 14.7 ± 0.3 l/min
- temperature rise control was programmed to increase the temperature of the air stream at a rate of 10 °C/min, until T indicated about 150 °C.
At this point the temperature controller reduced the air heating to 3 °C/min
- temperature rise rate was maintained at 3 °C/min until ignition was achieved, as indicated by a sudden rise in T₁ or T₂ value
- on ignition air flow was cut off immediately by valve (9) and nitrogen was introduced by valve (9) to quench fire.

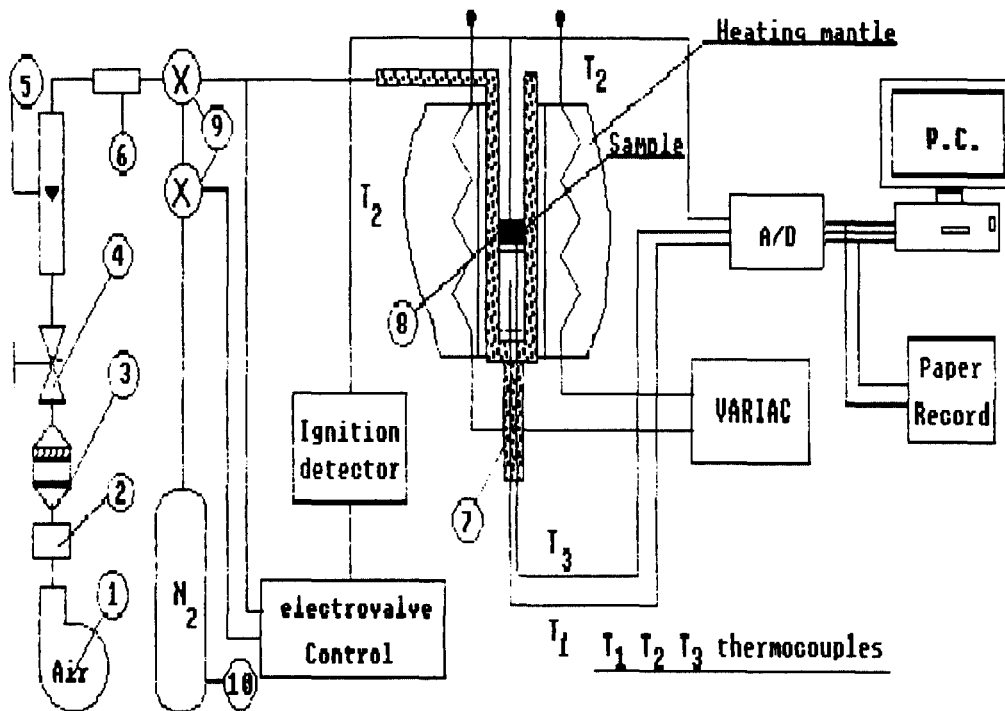
A typical time-temperature plot is reported in fig. 5 for one of the runs.

This plot was obtained from recorder both for thermocouples T₁ and T₂.



The ignition temperature is defined from the signal which first shows sudden rise, that is ignition, drawing tangents to the heating curves before and after ignition.

The resulting values are the average ignition temperatures between T₁ and T₂.



LEGEND

- | | |
|-------------------------------------|------------------|
| 1 - Blower | 6 - Higrrometer |
| 2 - Air dryer | 7 - Quartz tube |
| 3 - HEPA filter and charcoal filter | 8 - Sample |
| 4 - Damper | 9 - electrovalve |
| 5 - Flowmeter | 10 - Nitrogen |

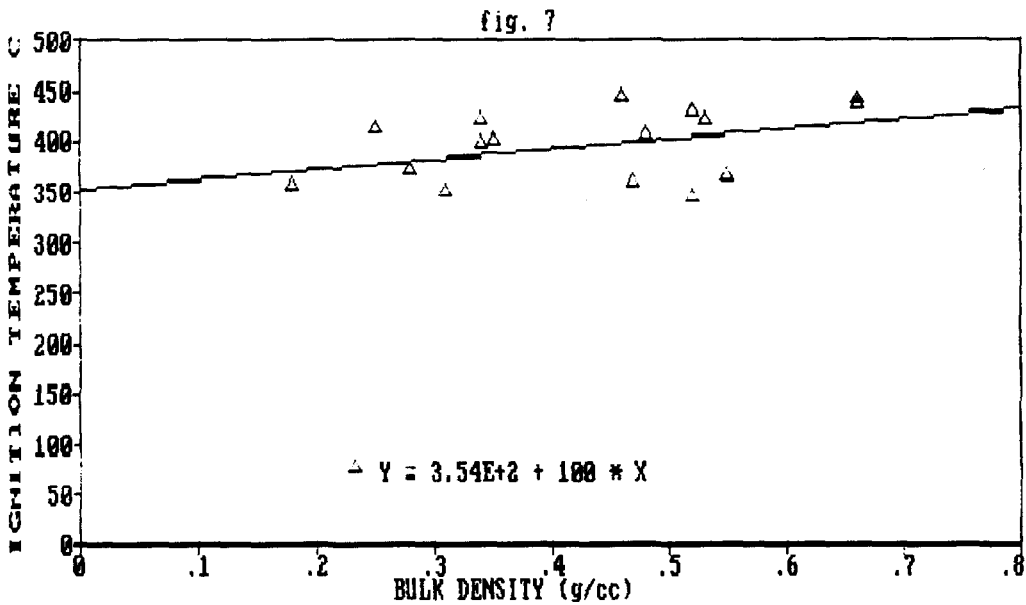
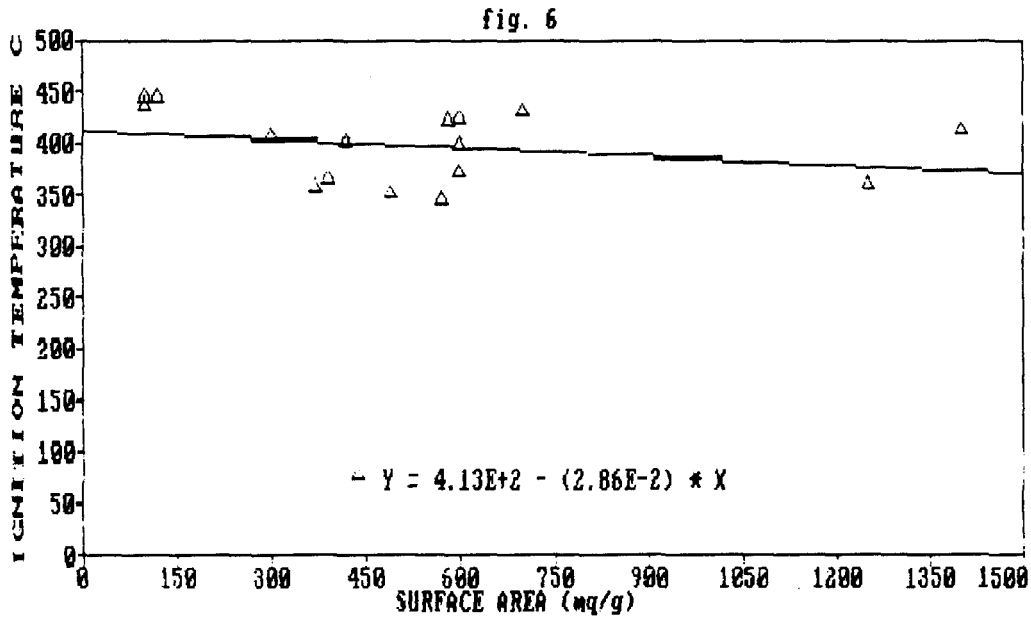
Fig. 4 - Ignition Apparatus

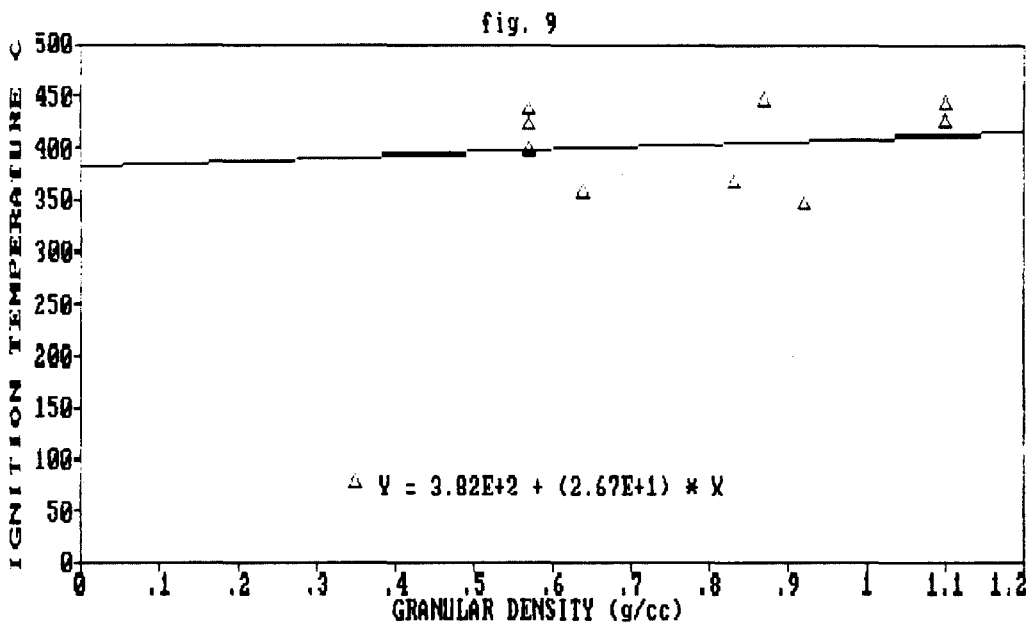
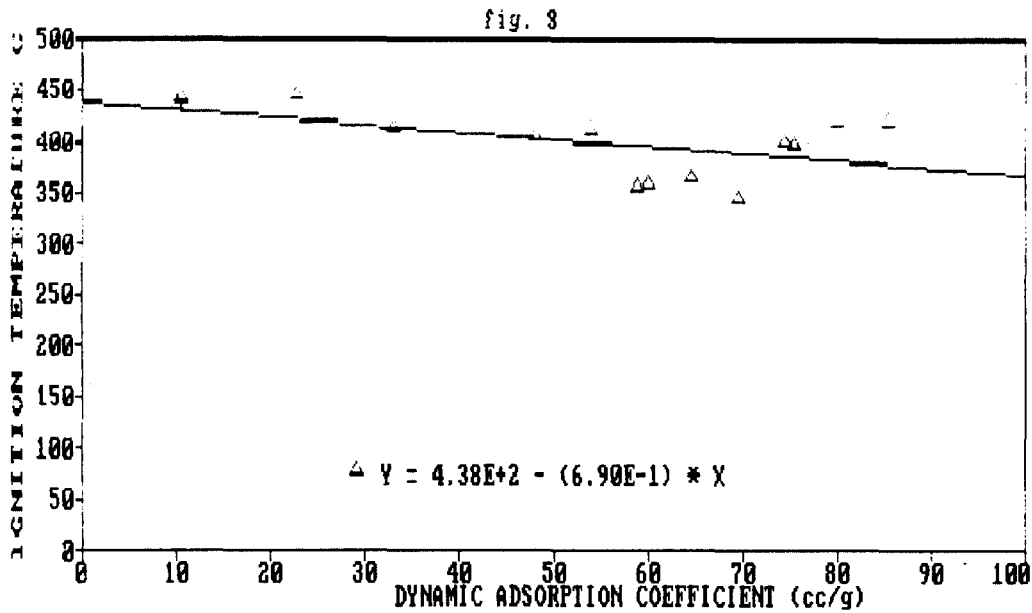
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Charcoal sample to test were selected among a wide range of available types.

Most of them were acceptable for nuclear use on the basis of their physical characteristics, some had extreme values of relevant parameters and were tested to fulfil an overall investigation.

Results are reported in figures from 6 to 9, where ignition temperature is plotted vs surface area, bulk and granular density and dynamic adsorption coefficient for a typical gas (Kr⁸⁵).





From the analysis of data obtained it point out that there isn't a strong dependence of ignition point from any of physical characteristics usually taken in account, not even from surface area.

The difference emerging ranging from 100 to 1400 mg/g in fig. 6 may be considered within experimental errors.

The same conclusions result from the analysis of correlations found for the other physical parameters.

A conservative value of 350 °C for ever type of unused activated charcoal is recommended in design of an adsorption system. Anyway the presence of contaminants such as impurities or solvents may change such conservative value along the life of a charcoal filter and further work should be done to investigate the behaviour in

working conditions.

V. Acknowledgments

This work performed in the frame of E.N.E.A. safety research programme.

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CLOSING COMMENTS OF SESSION CHAIRMAN THOMAS

In this morning's session, four papers on charcoal adsorbers were presented covering kinetic studies, current problems, trapping performance at high temperature and pressure, and effects of organics on aging. Each paper indicate that additional research is needed to elucidate the mechanisms by which adsorbers work as intended or fail prematurely.

Dr. Friedrich fitted Langmuir-type equations in terms of adsorption and desorption rate constants, active site concentrations, and inlet concentrations to adsorption isotherms of methyl iodide at different temperatures. More research in this area is needed especially with respect to the effect of different carbon batches and on aging and the reproducibility of observed kinetic parameters.

Dr. Kabat reviewed current operational problems with charcoal filters in reactors and concluded that more research is needed to characterize penetrating iodine species. Test results based on iodomethane and elemental iodine may not represent the true in situ iodine removal efficiency because of unidentified penetrating species.

Mr. Collinson fitted a pseudo first order kinetic expression which is a function of stay time to experimental data on the trapping performance of methyl iodide at high temperature and pressure in carbon dioxide. The test results indicated that trapping performance is mainly controlled by mass transfer from the gas to the solid surface. The presence of a penetrating iodine species was also suggested.

Dr. Hyder measured the organic contaminants in several used carbon samples from nuclear reactors and conducted methyl iodide retention tests. No correlation between contaminant loading and iodine retention was observed. This seems to contradict the common perception that adsorption of organic contaminants leads to aging and reduced retention.

CLOSING COMMENTS OF SESSION CHAIRMAN EVANS

We are beginning to realize from CO-CO₂ evolution measurements that oxidation of the surface of the charcoal may have something to do with the aging process. Exactly what, we are not sure. A couple of the papers talked about trying to develop fundamental new impregnants to use on charcoals. I think that is grounds for fertile exploration. There is a suggestion (sort of an undercurrent) based on what we have seen that perhaps TEDA is reacting to form iodine compounds and that this is the reason we do not see TEDA as TEDA on the charcoal anymore. It would behoove us to explore this a little bit further. It is unfortunate that we do not have the opportunity to discuss the ignition temperature tests with the authors. They were not able to come here. One of my first questions would be, "What is the impact of aging on charcoal?" From my experience we know that the ignition temperature decreases as the charcoal ages. The measurement of the ignition temperature of new charcoals is not nearly as important as what it might be for charcoal that has been in service for a period of time.