ADSORBENTS FOR IODINE REMOVAL

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KOVACH: Ladies and gentlemen: we are opening the afternoon session of the 10th Air Cleaning Conference and it is also my position to be the first one to speak after a most enjoyable portion of the meeting. I will be followed by R. C. Milham, Savannah River Laboratory, R. D. Ackley, Oak Ridge National Laboratory, W. J. Maeck, Idaho Nuclear Corporation, and L. R. Jones, Savannah River Laboratory. We prefer that all questions be held until after presentation of the five papers.

This session will deal with "Adsorbents for Iodine Removal" and after we discuss the removal of particular materials in various sizes and by various means, we arrive at the rather gray area and that is the removal of gases components in containment purification systems.

ADSORBENTS; REVIEW AND PROJECTION

By

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INTRODUCTION

The method of iodine removal by adsorbents depends on both the chemical
and physical properties of the iodine compound and the chemical and physical
properties of the adsorbent employed.

Although recently a large amount of data was reported on the types and
properties of various iodine forms, the properties of adsorbents and the
forces controlling adsorption were often ignored.

It is worthwhile here to review the gas-solid interaction and draw
attention to parameters influencing the iodine removal efficiency of adsorbents.

GAS PHASE ADSORPTION

In any heterogeneous system consisting of atoms, molecules or ions,
the interaction between the phases begins with chemical or physical inter-
action at the phase interface. When a molecule under kinetic motion hits
the surface (as an example of phase boundary) from a random direction, it
can either bounce back from the surface elastically with the angle of reflec-
tion equalling the angle of incidence, or the molecule may stay at the
surface for a period of time and come off in a direction unrelated to that
from which it came. Generally, the latter is the case, the residence time
depending on the nature of the surface and molecule, the temperature of the
surface and the kinetic energy of the molecule.

The interaction at the interface involving transition of a molecule
from one phase to another can be considered the sorption of the molecule
by the given phase. The type of interaction between phases of a heterogen-
eous system depends on the properties and composition of all of the components
of the system. On the standpoint of the distribution of the substances to be
sorbed, two types of sorption can occur: adsorption and absorption. Adsorp-
tion takes place when the molecules or atoms sorbed are concentrated only at
the interphase, while absorption takes place when the molecules or atoms are
distributed in the bulk of the interacting phases.

The adsorption of atoms or molecules on a solid from the gas phase is a spontaneous process, and as such it is accompanied by decrease in the free energy of the system. The process involves loss of degrees of freedom. Therefore, there is also a decrease in entropy, and the adsorption process is always exothermic regardless of the type of forces involved.

The number of molecules present on the surface at any one time is dependent upon the number of molecules reaching the surface and on the residence time of these molecules on the surface. If "n" molecules strike a unit area of the surface per unit time and remain there for an average time of "t", then "σ" number of molecules are present per unit area of the surface.

$$\sigma = nt \tag{1}$$

Using cm^2 as a unit surface and seconds as unit time, n is the number of molecules striking 1 cm^2/sec. Using the Maxwell and Boyle-Gay Lussac equations, the following number for n can be obtained

$$n = 3.52 \times 10^{22} \times \frac{p}{\sqrt{MT}} \tag{2}$$

where

p = pressure in Hg mm,

M = molecular weight,

T = absolute temperature, $^{\circ}K$

By comparing results obtained from this equation with the number of molecules occupying unit surface area under equilibrium conditions, it is evident that the adsorption process in itself is instantaneous.

The Frenkel equation

$$t = t_o e^{Q/RT} \tag{3}$$

where

t_o = time of oscillation of molecules in the adsorbed state,

Q = the heat of adsortion. (Expressing the energy of adsorption.)

expressing the magnitude of the molecule residence time shows the residence time t dependence on the magnitude of Q.

As it will be later discussed in commercial adsorbents, the rate controlling process is diffusion.

ADSORPTION FORCES

Forces causing adsorption are the same ones which cause cohesion in solids and liquids, and which are responsible for the deviation of real gases from the laws of ideal gases. The basic forces causing adsorption can be divided into two groups: intermolecular or van der Waals, and chemical, which generally involves electron transfer between solid and the gas.

Depending upon which of these two forces plays the major role in the adsorption process, it can be classified as physical adsorption (van der Waals) or chemisorption, where heteropolar or homopolar forces cause adsorption. Thus, if in the process of adsorption the individuality of the adsorbed molecule (adsorbate) and of the surface (adsorbent) are preserved, we have adsorption. If electron transfer or sharing occurs between the adsorbate and the adsorbent, or if the adsorbate breaks up into atoms or radicals which are bound separately, then we are presented with chemisorption.

While the theoretical difference between physical adsorption and chemisorption is clear, in practice the distinction is not as simple as it may seem. The following parameters can be used to evaluate an adsorbent-adsorbate system to establish the type of adsorption.

1. The heat of physical adsorption is in the same order of magnitude as the heat of liquefication, while the heat of chemisorption is of the same order as of the corresponding chemical reaction. It has to be pointed out here that the heat of adsorption varies with surface coverage, because of lateral interaction effects. Therefore, the heat of adsorption has to be compared at corresponding levels.

2. Physical adsorption will occur under suitable temperature and pressure conditions in any gas-solid system, but chemisorption takes place only if the gas is capable of forming a chemical bond with the surface.

3. A physically adsorbed molecule can be removed unchanged at a reduced pressure at the same temperature where the adsorption took place. The removal of the chemisorbed layer is far more difficult.

4. Physical adsorption can involve the formation of multimolecular layers, while chemisorption is always completed by the formation of a monolayer. (In some cases physical adsorption may take place on top of a chemisorbed monolayer.)

5. Physical adsorption is instantaneous, (It is the diffusion into porous solids which is time-consuming.) while chemisorption may be instantaneous, but it generally requires activation energy.

A typical example of complications arising when trying to classify a particular process is the use of I-127 impregnated carbons to adsorb both elemental iodine and decontaminate CH_3I^{131} by isotope exchange. Small amounts of elemental I_2 chemisorb on carbon surfaces particularly when surface oxides or water is present on the carbon surface. As the iodine concentration on the surface increases, physical adsorption takes place. Thus, there is both chemisorbed and physically adsorbed iodine present on the carbon surface. When the CH_3I^{131} molecule contacts the surface it has to be chemisorbed for various lengths of time to facilitate the $^-I^{131} \rightleftharpoons {}^-I^{127}$ exchange. When the elemental I_2^{131} molecule contacts the surface, it will be physically adsorbed on the already present layers of iodine.

Although as illustrated the process involving the use of I_2 impregnated carbons for the removal of both I_2^{131} and isotope exchange is complicated, it is still necessary to investigate the various steps involved to enable the optimization of the carbon and treatment for this purpose.

EXCHANGE REACTIONS

It is attempted here only to briefly cover isotope exchange reactions in their relation to the surface chemistry of iodine adsorbents.

The primary exchange reaction involved is the

$$CH_3{}^{131}I + {}^{127}I^- \text{ (on surface)} \quad CH_3{}^{127}I + {}^{131}I^- \text{ (on surface)} \quad (4)$$
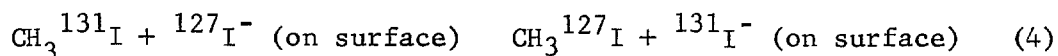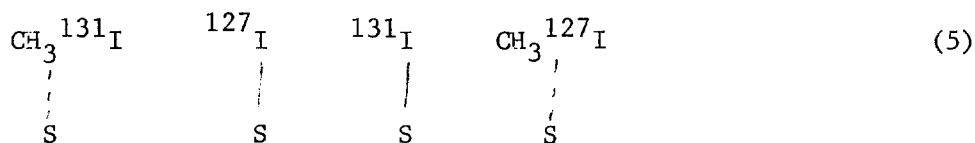
No doubt longer chain alkyl halides do behave in the same manner although some fouling can be expected due to the better retention of both isotope forms of the halide. The reaction also takes place in case of higher halogenated compounds.

It is important also to realize that these reactions are reciprocal and the equilibrium constants approximate the values expected from the relative ratio of the random distribution of $^{127}I_2$ and $^{131}I_2$ isotopic species of iodine.

Possible Mechanisms

1. The alkyl halide molecule is not chemisorbed except during the actual exchange which takes place with a chemisorbed iodine atom (or ion).

$$
\begin{array}{cccccc}
CH_3{}^{131}I & & {}^{127}I & {}^{131}I & CH_3{}^{127}I & (5) \\
| & & | & | & | & \\
S & & S & S & S &
\end{array}
$$

where S represents the surface.

2.   The mechanism may be dissociative and involve adsorbed radicals (or ions) of the type CH_3.

Different mechanisms could occur in case of unsaturated alkyl halides, but is not discussed here.

Kinetics

When as an example dealing with the $CH_3{}^{131}I \rightleftarrows {}^{127}I_2$ exchange it can be assumed that the following species take place in the reaction:

      a.   physically adsorbed methyl iodide
      b.   chemisorbed methyl radicals
      c.   chemisorbed ^{131}I atoms
      d.   chemisorbed ^{127}I atoms (bulk physically adsorbed at high I_2 loading.)

Let's assume first that no elemental ^{127}I is present on the carbon surface, but it is introduced with the $CH_3{}^{131}I$ in vapor form. After the reactants are introduced to the carbon the following will take place:

1.   The surface concentration of each of the four kinds of species will build up and reach equilibrium value.

2.   The exchange reaction will commence and will lead to isotopic equilibrium between the species in the system, including the gas phase.

Naturally, step No. 2 cannot be completed until all of the methyl iodide is adsorbed and desorbed. The only factor which reduces the rate of exchange from the intial value is the increase of the ^{131}I loading to that of the ^{127}I concentration. Thus, the rate determining step (as long as ^{127}I excess is present) is the rate of adsorption and desorption of methyl iodide. In case of methyl iodide, no difference in adsorption rates can be expected between $CH_3{}^{131}I$ and $CH_3{}^{127}I$ because the relative size and polarity of the molecules is identical. Thus, both processes occur at the same rate and a convenient form of "adsorption/desorption" can be used.

Due to the fact that activated carbon retains relatively high quantities of iodine, both ^{127}I and ^{131}I will be retained on the carbon surface. This permits the preloading of carbons with $^{127}I_2$.

In actual practice further complication arises from the presence of H_2O on the carbon surface which competes with the CH_3I for available adsorption sites.

It is evident from the above description that the $CH_3{}^{131}I$ concentration and rate of adsorption is critical to establish "residence times" for carbon systems. This criticality is somewhat lessened by the indiscriminate $^{127}I_2$ loading of carbons, but this practice introduces other problems which will be discussed later.

ADSORPTION RATE IN POROUS ADSORBENTS

As it is shown in the previous discussion, the boundary layer is the most important in the phase interaction. Therefore, to achieve a high rate of adsorption, it is expedient to create the maximum obtainable surface area within the solid phase. High surface area can be produced by creating a large number of micro capillaries in the solid. All commercial adsorbents, such as activated carbon, silica gel, alumina, etc. are prepared in this manner.

While, as it was described in the previous paragraphs, adsorption is nearly instantaneous, the passage of molecules through capillaries (pores) may involve some time. There have been observations that in rare cases it took several days to reach adsorption equilibrium

The movement of molecules into the pores is a diffusion process. Regardless of the mechanism used, a correlation between σ , the number of molecules adsorbed per cm^2 at a given pressure and temperature, and time t_r required to complete the adsorption process:

$$\sigma_t = (1 - e^{-k_d t_r}) \tag{6}$$

where

σ_t = value of o at time t_r

= the equilibrium value of o

k_d = a constant which is inversely proportional to the square of the distance which the molecules have to travel, and proportional to the diffusion constant D, which can be obtained from the following equation:

$$D = D_o e^{-Qd/RT} \tag{7}$$

where

D_o = a constant

Q_d = the energy of activation

The temperature dependence of the diffusion constant and the temperature dependence of constant k_d in equation (6), and of the whole phenomenon of the rate of reaching adsorption equilibria depends on the activation energy Q_d. The molecules may proceed in three major manners within the pore structure. They may collide with the wall of the capillary and bounce off immediately

according to the cosine law, collide again, etc. In this case, there is no activation energy.

Secondly, the molecules may collide with the wall, stay there for time t, reevaporate, collide again, et. The energy of activation will then be equal with the heat of adsorption. Thirdly, the molecules may migrate along the wall of the capillary during a sufficiently long time t, or they might make hopping movements as described by deBoer. The energy of activation is then given by the fluctuations in the heat of adsorption ΔQ_a. As an example, the rate of adsorption of ethane on activated carbon gives an energy of about 3 kcal/mole, which is roughly half of the value of the heat of adsorption.

ADSORPTION EQUILIBRIUM

Adsorption equilibrium is defined when the number of molecules arriving on the surface is equal to the number of molecules leaving the surface into the gas phase. As it was discussed previously the adsorbed molecules exchange energy with the structural atoms of the surface, and provided that the time of adsorption is long enough, they will be in thermal equilibrium with the surface atoms. In order to leave the surface, the adsorbed molecule has to take up sufficient energy from the fluctuations of thermal energy at the surface so that the energy corresponding to the vertical component of its vibrations surpasses the holding limit.

As an example, the efficiency of the dry carbon bed toward CH_3I in a dry atmosphere when at equilibrium with the CH_3I will be zero. However, for initial selection of the adsorbent it is important to know which adsorbent will hold the maximum amount of CH_3I under equilibrium conditions.

Adsorption Isotherms

When studying the adsorption of a particular gas on the surface of a particular adsorbent, we may start by inserting into equation (1) the generalized values for n from equation (2) and values for t from equation (3):

$$\sigma = \frac{N_p}{\sqrt{2 \quad MRT}} \times t_o e^{Q/RT} \qquad (8)$$

because the adsorbent and the adsorbate are defined, M and t_o are constants, thus we get:

$$\sigma = \frac{kop}{\sqrt{T}} \, e^{Q/RT} \qquad (9)$$

in which $\quad ko = \dfrac{Nto}{\sqrt{2\pi MR}} \qquad (10)$

If we consider the temperature constant, we arrive at the simplest form of adsorption isotherm.

$$\sigma = k_T p \qquad (11)$$

which shows that the amount of gas adsorbed will be directly proportional to the pressure.

Adsorption isotherms thus show the free energy charge as a function of the amount of molecules adsorbed. Under real conditions where the mutual interaction of the adsorbed molecules takes place and at an increasing coverage, the adsorption energy Q changes and deviation from equation (11) takes place.

A large number of equations were developed to follow the actual detail of the adsorption equilibrium process. Those most often used are the Brunauer, Emmett, Teller (BET), Polanyi (in various modified forms) and Langmuir equations. These are not discussed here. They can be found in the appropriate references. (1,2,3)

Isotherms as measured under existing conditions can yield qualitative information about the adsorption process and also give indication to the fraction of surface coverage; thus, with certain assumptions to the surface area of the adsorbent.

It is important to point out that the slope of the adsorption isotherm depends both on the adsorbate and the adsorbent properties. Brunauer (4) classified adsorption isotherms into five basic groups. These represent monolayer formation, multilayer formation, molecular interaction in the monolayer, finite multilayer formation and the combination of molecular interaction causing concave isotherms with a formation of finite multilayers. The slope of the adsorption isotherm showing equilibrium capacity as an example for iodine depends not only on the base material such as carbon, but on the structural form of the carbon also.

Utilizing various adsorption isotherms available, surface area determinations can be made for commercial adsorbents. These fall in the following typical ranges.

Activated alumina	50 - 400 m^2/g
Silica gel	200 - 600 m^2/g
Molecular sieve	600 - 800 m^2/g
Activated carbon	500 - 1600 m^2/g

ADSORPTION DYNAMICS

The application of adsorbents for iodine adsorption in engineered safeguard systems involves the use of a dynamic system. The adsorbent is generally used in a fixed bed and the contaminated air is passed through the adsorbent bed. Although isotherms are indicative of the efficiency of an adsorbent for iodine removal, they do not supply data to enable the calculation of contact time or the amount of adsorbent required to reduce the iodine concentration below the required limits.

It is necessary here to evaluate the dynamic capacity of a system in more detail. When a fluid is passing through a bed of adsorbent, most of the adsorbate is initially adsorbed at the inlet part of the bed and the fluid passes on with little further adsorption taking place. When the adsorber inlet end is at equilibrium, the adsorption front moves along the bed until

"breakthrough" and then equilibrium conditions are achieved at the outlet end. While the equilibrium holding capacity of the bed is a function of the adsorbent used and the temperature at which it is operated, the dynamic capacity is also dependent on the operating conditions such as fluid flow rate, pressure, particle size, bed depth, etc. The dependence is caused by the effect of these factors on the overall mass transfer rates. Of particular importance is the relative sizes of the saturated and unsaturated zones when breathrough occurs. If the unsaturated zone where mass transfer takes place (mass transfer zone MTZ) is longer than the adsorbent bed, immediate breakthrough will be observed.

The following factors play the most important role in the dynamic adsorption.

The type of adsorbent used.

Most porous solids are capable of adsorbing both organic and inorganic gases and vapors. However, their preferential adsorption characteristics and other physical properties make each one more or less specific for a particular application. As an example, silica gel, alumina and molecular sieves will adsorb water preferentially from a gas phase mixture of water vapor and methyl iodide. Activated carbon behaves similarly but to a lesser extent, its surface properties and H_2O selectivity somewhat dependent on the type of surface oxides present on the carbon surface. In addition, at high instantaneous water loadings alumina, silica gel and molecular sieves are structurally weakened by contact with water droplets.

As it was shown before, adsorption takes place at the interphase boundary, therefore the surface area of the adsorbent is an important factor in the adsorption process. Generally, the higher the surface area of an adsorbent, the higher is the adsorption capacity for any compound. However, the surface area has to be available in a particular pore size within the adsorbent. At low partial pressures (concentration) the surface area in the smallest pores into which the adsorbate can enter is the most efficient in retaining the adsorbate. At higher concentration multilayers can form only in larger pores, while near saturation conditions capillary condensation can take place within the pores and the total micropore volume is the limiting factor. Thus, at different iodine concentrations a different type of adsorbent will show optimum capacity or an adsorbent satisfactorily holding methyl iodide may not be the optimum material for elemental iodine removal.

Due to the same structural differences, the adsorption isotherms on three carbons identified only as primarily small micropore containing, intermediate micropore containing and large micropore containing can cross over at various concentration ranges, the large micropore containing having the highest equilibrium capacity at high concentration and the small micropore containing at low concentrations. Thus, it is important to perform empirical adsorption studies in the concentration ranges expected under actual conditions.

The above discussion related primarily conditions influencing the actual adsorption process. As discussed previously, the molecule which is to be adsorbed (to be retained, to react or to exchange) has to diffuse first into the porous solid through macropores which are the interconnecting channels in the adsorbents. These are also the pores which influence adsorbent life in catalytic processes where molecules have to be adsorbed, converted and desorbed such as in the case of $CH_3{}^{131}I \rightleftharpoons {}^{127}I$ isotope exchange.

The lesser fouling of the 207B impregnated carbon as observed by Adams (5) compared with MSA 85851 and B-C 727 could be caused by the presence of a considerably larger amount of micropores in the 207B.

These micropores present in alumina and molecular sieves can enhance catalytic reactions between I_2, CH_3I and metallic impregnates on the substrate.

Therefore, thorough knowledge of the internal structure of the adsorbent has to be evaluated before selection or even more, before optimization can take place. To the awareness of the author such an investigation has not been performed yet.

The Effect of Particle Size

The dimension and shape of particle size effects both pressure drop through the adsorber bed and the diffusion ratio into the particles. External mass transfer increases inversely with the diameter $d^{3/2}$ and the internal adsorption rate inversely with d^2. These effects are also often ignored. To dramatize the particle size influence on the efficiency of adsorbent systems it is worthwhile to show a specific example from Collins, et al.(6) Methyl iodide penetration on 0.5% KI impregnated 207B at an 0.2 sec. residence time showing $CH_3{}^{131}I$ penetration in % at a 100 μg CH_3I/g carbon loading:

8 - 12 mesh	0.175%
12 - 16 mesh	0.01%
18 - 30 mesh	0.0005%

It is evident that everything else being equal, adsorbent beds consisting of smaller particles, although causing higher pressure drop, will be much more efficient, because sharper and shorter mass transfer zones will be obtained. This factor is particularly amplified when the MTZ is close in length to the adsorbent bed depth.

The Depth of the Adsorbent Bed

The effect of bed depth on adsorption mass transfer is twofold. First, it is important that the bed is deeper than the length of the transfer zone which is unsaturated. The second is that any multiple of the minimum bed depth gives more than proportional increased capacity. In general, it is advantageous to size an adsorbent bed to the maximum length which is allowed by pressure drop considerations. The determination of the depth of the transfer (MTZ) zone or unsaturated depth may be determined by experiment

$$MTZ = \frac{\text{Total bed depth}}{t_2/(t_2 - t_1) - x} \tag{12}$$

where

t_1 = time required to reach breakpoint

t_2 = time required to saturation

x = the degree of saturation in the MTZ

or,

$$\text{MTZ} = \frac{1}{1 - x} \; D_1 \; \left(1 - \frac{C_1}{C_s}\right) \tag{13}$$

where

D_1 = bed depth

C_1 = breakthrough capacity of bed D_1

C_s = saturation capacity

x = the degree of saturation in the MTZ

C_s of the above equation can be obtained by measuring the breakthrough capacities of two beds and using the following equation

$$C_s = \frac{C_2 D_2 - C_1 D_1}{D_2 - D_1} \tag{14}$$

where

C_1 is breakthrough capacity for bed length D_1

C_2 is breakthrough capacity for bed length D_2

Direct methods for the calculation of the MTZ are also available using transfer units, however, particularly for multicomponents systems, the calculation becomes very tedious.

Gas Velocity Effects

The length and rate of movement along the bed of the MTZ is directly proportional with the fluid velocity. Thus at high air velocities the unsaturated zone not only moves faster, but also becomes elongated. As an example, an MTZ which is 2" long at 40 fpm can be 3" long at 70 fpm. Due to this elongation effect, the term "residence time" lately wide spread in the iodine adsorber studies has to be used with caution and its limits fully understood.

Elemental I_2 adsorption as a velocity function was extensively investigated by Prigge. (7)

Temperature effects

As it was discussed in the basic adsorption theory, physical adsorption decreases with increasing temperature. (At the same time it has to be remembered that diffusion rates increase at higher temperature and high temperature is required for some forms of chemisorption to take place.) Thus, while physical adsorption of iodine will take place preferentially at lower temperatures, the reaction between iodine and silver coated surfaces increases at higher temperature, or it is required for chemical exchange with KI to take place. (8)

It also has to be remembered that the adsorption process is exothermic. As the adsorption front moves through the bed, a temperature front also proceeds in the same direction. This increase in temperature during the adiabatic operation of the adsorber will decrease the capacity of the adsorbent. At the low I_2 and CH_3I concentrations encountered in reactor safety work this temperature rise is insignificant. However, the heat of adsorption of the accompanying water vapor in case of steam release will raise the bed temperature initially to a higher temperature, thus lowering the relative humidity of the adsorber.

The adiabatic temperature rise can be calculated by assuming that there is a thermal equilibrium between the fluid and the bed, and that the temperature of the outlet gas stream is essentially the same as that of the adsorbent.

$$\Delta t = \frac{6.1}{(S_g/C) \times 10^5 + 0.51 \ (S_A/W)} \tag{15}$$

where

Δt = temperature rise, ^{o}F

W = saturation capacity of bed at $t + \Delta t$, ^{o}F

C = inlet concentration, p.p.m.

S_g = specific heat of gas, B.T.U./ft.^{3}/^{o}F

S_A = specific heat of adsorbent, B.T.U./lb/^{o}F

Value of S_A for common adsorbents are under ambient conditions:

    Activated Carbon   0.25

    Alumina   0.21

    Molecular Sieve   0.25

When adsorbing iodine[131] additional heating will occur due to decay heat which may cause ignition in carbon beds or possible desorption of iodine from the adsorbent. This desorption effect becomes very significant when high [127]I loadings are present in the adsorbent. Due to the fact that ignition of carbon adsorbers takes place at a higher temperature than where they still hold iodine, this problem became a vicious circle. If due to decay heat the iodine will desorb from the carbon (reaching equilibrium adsorption under the particular conditions at a lower capacity level), then there will be no decay heat to ignite the carbon. Thus, high ignition carbons are required only if they also have high temperature iodine retention capacities. The same effect can lessen the problem of spot overheating on the carbon bed because as soon as a particular adsorbent face becomes overheated the iodine will migrate and distribute the heat load more uniformly in the adsorber cell.

If other oxidizing contaminants such as ozone or NO_x are present, the use of carbon is dangerous and real fire and explosion hazards may occur. In these cases only noncombustible adsorbents should be used.

High temperature iodine and methyl iodide adsorption and conversion results are available elsewhere. (7,10,11,12,13)

The Concentration of Adsorbate

The adsorption capacity of adsorbents is directly proportional to the concentration of the adsorbate. The reasons for this were discussed under the equilibrium adsorption part. The concentration of the adsorbate is inversely proportional to the length of the MTZ. Thus everything else being equal, a deeper bed will be required to remove a lower concentration contaminant with equal efficiency than to remove the same contaminant at higher concentrations. As an example, Adams and Browning (9) showed efficiencies for a three-stage system, each 0.75 inches deep of 99.99, 74.6 and 14.5% respectively. Naturally, the outlet concentration was lower from each stage. Even if elusive CH_3I contributed to this effect, it is still significant to demonstrate the point. Similar data can be obtained from a number of 1" and 2" deep carbon bed efficiencies recently reported. (10)

The Presence and Concentration of Other Contaminants

It is important to stress the fact that some portion of all gases present will be adsorbed on the adsorbent surface. Because these gases or vapors also compete for the available surface area and/or pore volume, their effect will be the lowering of the adsorption capacity for the particular adsorbate, which is to be removed. Under ambient conditions, very little (10-20 mls STP/g) air is adsorbed on commercial adsorbents. However, moisture or carbon dioxide has a more significant effect. Although activated carbon is less sensitive to moisture than silica gel, alumina and molecular sieves, its adsorption capacity can be considerably lower than adsorption from a dry air stream. This is well known from the past few years' methyl iodide adsorption problem.

The reverse is true for some impregnated adsorbents, where moisture can enhance the reaction because they take place in solution rather than on a dry surface. In these cases, it is advantageous to use polar adsorbents retaining sufficient water for the reaction to take place.

Pressure Effects

Generally, the adsorption capacity of an adsorbent increases with increasing pressure, if the partial pressure of the contaminant increases. However, at high pressures (over 500 psig) a decrease in capacity will be observed due to retrograde condensation and a decrease in the fugacity of the more easily adsorbed compound and increased adsorption of the carrier gas.

Removal Efficiency of the System

Due to the shape of the MTZ and longitudinal dispersion of the adsorbate, it is evident that non-proportionally deeper beds are required to increase single pass efficiency from 99 to 99.9% efficiency. The knowledge of the MTZ shape under the particular conditions can only assure the optimum bed depth for the required removal efficiency.

It is also imperative that all parameters are investigated, including the optimum particle size and adsorbent properties to enable satisfactory packing of the adsorbent beds.

The removal efficiency of the adsorbent is not identical to the removal efficiency of the system. There is no substitute to the evaluation of unit adsorbers constituting a building block in the system. Such problems as flooding, channeling and wall effect (particle size/container diameter ratio) occur to a different degree in tube tests than in full size adsorber units. The Savannah River Lab work on adsorbers, the WAPD test facility and the LRL heated wind tunnel tests show significant contributions toward solving scale-up problems.

Decomposition or Reaction of the Adsorbate on the Adsorbent Surface

Even unimpregnated commercially available adsorbents contain various amounts of impurities which influence the overall efficiency of iodine removal.

Coconut shell carbons contain alkali, potassium and sodium salts which react with elemental iodine and increase retention even at very high temperatures such as exist in HTGR coolant purification systems. (14,15)

One possible reason for the higher CH_3I loadings on 207B obtained by Collins and Eggleton (16) lies in the ash constituents of 207B. Several compounds including hydrosulfides catalyze the decomposition of methyl iodide. The 207B type coal carbons contain sulfur compounds, while coconut shells don't. Even this advantage does not show up at high humidity and at higher CH_3I concentrations, (17) thus, very often the impurity effect becomes significant only at low concentrations while at higher concentrations, the prime process washes out differences caused by impurities.

However, knowing this effect, it can be put to work as in the example of amine loaded carbons (18, 19, 20) which form quaternary compounds with CH_3I.

The decomposition of CH_3I can take place by non-chemical induced means also, such as gamma radiation on the surface of ^{131}I loaded carbon. (21)

The use of various metal salts or metal impregnated adsorbents also utilizes the same effect. (22,23,24,25)

While preparing and evaluating various treatments of adsorbents, care has to be taken to realize the possible detrimental effects of the treatment also. As an example, K_2CO_3 or silver salt loaded activated carbons catalyze the hydrolysis of methyl iodide

$$CH_3I + HOH \xrightarrow{K_2CO_3} CH_3 - OH + KI + H_2O \qquad (16)$$
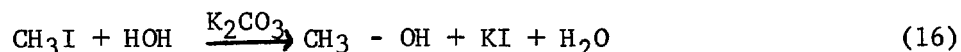
Both catalysts significantly lower the ignition temperature of the carbon also.

The Effect of Adsorbent Hardness

It is unnecessary to explain that if the adsorbent generates dust while the air flows through the adsorbent beds due to mechanical vibration or due to movement caused by air flow, the efficiency of the system will be less and an extra set of downstream particulate filters will be necessary. In addition to this, settling may occur in the adsorbent beds causing significant reduction in integrity. Prigge presented data to show differences which may occur in identical base adsorbents. (7)

The Effect of Aging and Weathering

Both the adsorption capacity and the rate of adsorption (or reaction, isotope exchange, etc.) can be affected by the altering of the surface or by the coadsorption of impurities. As an example, prolonged exposure of an unimpregnated carbon, even to low concentrations of NO_2 will alter the surface oxides on the carbon surface presenting different conditions than the surface of virgin carbons. The coadsorption of various organic compounds on top of the iodine layer in some impregnated carbons lowers the isotope exchange rate, thus also the efficiency. (26)

Silver coated adsorbents when oxidized showed considerable loss in elemental iodine removal efficiency.(although this can be regenerated by converting the oxides to sulfides) (25) Very few of the current iodine adsorbent systems are so designed as to permit in situ regeneration. Unfortunately, it is not easy to correlate accelerated weathering to actual conditions, thus only time will completely solve the degree of weathering occurring under various conditions.

Intermittent Loading of the Adsorbent

This is a particular problem that is faced by adsorbers used in hot cell or fuel reprocessing plant operations, where the adsorbers are used periodically or the concentration of iodine greatly varies depending on the periodic discharge of iodine species. The performance of the adsorbent may be impaired under these conditions due to variations in the MTZ at different times and the desorption-readsorption migration causing diffusion deeper into the adsorbent bed.

It may be concluded that short periods of intermittent operation do not impair the overall capacity,if the system bed depth equals several MTZ lengths, but in an originally undersized system, serious decrease in adsorbent life will take place.

CONCLUSIONS

All of the above listed parameters require investigation. It is very difficult to single out one which is more important than the other. Unfortunately, although very large amounts of results are available on various adsorbents for iodine removal under various conditions, it is difficult to make correlations because significant parameters were either ignored or not reported. Normally, basic research precedes the technology, but in case of iodine adsorbents, the requirement for materials that work even if they work only now and have limitations, bypassed the basic research part and we are suffering the results now. Adsorbents are available for various conditions, but optimization is very difficult and empirical in most cases.

Even within the current scope of adsorbent use technology, it is necessary to fill in the gaps in the information available concerning properties of the adsorbents to optimize systems. The requirement for this can be demonstrated by current practice of using over a ton of ^{127}I as an impregnant to remove $CH_3^{131}I$ from a reactor where the total halogen inventory in the core is approximately 10 kg.

Closer working relationship is required between the adsorbent manufacturers and those evaluating adsorbents to exchange and make available information concerning the properties of adsorbents which are certainly non-proprietary.

Even when the optimum adsorbent is developed which has high retention or exchange capacity for all forms of iodine under accident conditions, it will have to be compatible with the hardware in which it is used. Only the system's efficiency is important as an engineered safeguard, and it can be measured only in place.

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CHARCOAL POST TREATMENT; HEAT DEGRADATION AND SERVICE LIFE

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PRESENT STATE OF KNOWLEDGE

It is well known, that service in a reactor confinement system degrades activated carbon. At the Savannah River Plant (SRP), activated carbon must be replaced after 3 to 5 years to insure that its iodine absorption efficiency meets the required design (99.85% removal). This activated carbon in on-line continuously with a flow of about 100,000 cu ft/min. The environment of the confinement system is relatively pure since the nearest industrial area is at least 15 miles away. Analysis of the air upstream of filters showed:

~ 0.02 ppm NO_2

< 0.002 ppm SO_2

An analysis of used carbon from SRP showed:

3.5 mg SO_2 per g carbon

5.0 mg NO per g carbon

This supports the observation that carbon is degraded by impurities in the air.

To extend the life of carbon at SRP, it is partially regenerated annually by passing air at about 60°C through the carbon at a velocity of 5-10 ft/min for a minimum of 48 hours. This treatment is primarily intended to prepare the carbon for a "Freon"* leak test. Partial regeneration produces a significant improvement in the iodine adsorption efficiency of carbon that has had service in the SRP confinement system (1).

Current work is aimed at measuring the penetration of iodine while it is being absorbed on carbon from a steam-air mixture at 65°C and an air flow of 68 ft/min. Tests have been made on Type 416 which is used in the SRP confinement system and on Type 592 carbon which has an unusually high ignition temperature (~ 500°C).

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*Trademark of the Du Pont Company

In these tests, a small scale test bed, 1-inch thick by 2-inches in diameter is tested. The bed was designed to mock up a full sized SRP carbon bed. The temperature, steam-air mixture and flow are chosen to be as close to actual accident conditions as possible.

The penetration of iodine during loading at 65°C with an air flow of 68 ft/min was:

new Type 416 carbon	-	0.0001%
30 months service Type 416 carbon	-	0.01%
46 months service Type 416 carbon	-	0.1%
new Type 592 carbon	-	0.001%
22 month service Type 592 carbon	-	0.1%

The desorption of iodine after the test bed is loaded will be discussed in detail tomorrow at the IAEA Symposium. Briefly the following amounts of iodine were desorbed at 200°C with an air flow of 68 ft/min at temperature:

new Type 416 carbon	~0.02%
30 months service Type 416 carbon	12%
45 months service Type 416 carbon	20%
new Type 592 carbon	6%
22 months service Type 592 carbon	50%

Therefore, it is extremely important to have adequate cooling of the exhaust ventillation air so that low temperatures are maintained in the carbon beds.

PRESENT PROGRAM AT SRL

A detailed study of the variables that affect the desorption of iodine from activated carbon is in progress. The effects of service, temperature, face velocity, iodine loading, impregnation and partial regeneration are being determined. By optimizing the partial regeneration conditions we expect to extend the service life of the carbon.

An analytical study is in progress of the impurities that are adsorbed on activated carbon during normal operation of the confinement system. By identifying these impurities adsorbed on the carbon during normal service, we expect to develop an accelerated test of carbon quality of exposing carbon to high concentrations of these key impurities for shorter times than during confinement operation.

We will continue to monitor the quality of carbon in the SRP confinement system periodically to insure that it meets design specifications.

The Freon leak test will be made annually to insure that no air by-passes the carbon beds.

RECOMMENDATIONS FOR TESTING CARBON QUALITY

1. The quality of the carbon should be established from small scale tests of representative samples.

2. Full size beds should be leak tested in place.

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AGING AND WEATHERING OF IMPREGNATED CHARCOALS USED FOR TRAPPING RADIOIODINE
(AN INTERIM REPORT)*

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ABSTRACT

Aging, weathering (exposure to flowing air), and poisoning are processes which might adversely affect charcoal performance, especially with regard to trapping radioiodine in the form of methyl iodide (CH_3I). Accordingly, some effort has been applied toward investigating the effects of the above processes. The bulk of the data thus far obtained correspond to three different types of charcoal. Two types are iodized, to provide isotopic exchange capability, and the other is triethylenediamine-impregnated. The influences of the processes were examined by observing the variation in ^{131}I of $CH_3^{131}I$ removal capability for the iodized charcoals or in CH_3I removal capability for the amine-impregnated charcoal. The results, which were generally in accord with expectation, indicated the following: (1) aging per se has little or no effect on impregnated charcoal performance; (2) weathering with air at around 50% relative humidity has an appreciable effect; and (3) poisoning of iodized charcoal can have a large effect.

INTRODUCTION

A significant proportion of airborne radioiodine may exist as methyl iodide (CH_3I), which readily penetrates beds of the usual types of activated charcoal if the prevailing relative humidity is greater than, say, 30%. Investigation prompted by this potential problem has resulted in the discovery or development and subsequent use of certain types of impregnated charcoal which are effective for decontaminating air streams transporting $CH_3^{131}I$ even at relative humidities as high as 90%. The impregnated charcoals under consideration here may be described as either (1) iodized, to provide ^{131}I, ^{127}I exchange capability or (2) amine-impregnated of which triethylenediamine-impregnated charcoal is the most notable example. Recent information concerning the use of impregnated charcoals for trapping radioiodine together with references to earlier, and, in some cases, more detailed reports may be found elsewhere.[1,2,3]

Aging, weathering (or exposure to continued air flow), and poisoning are processes which, conceivably, may deleteriously affect impregnated charcoal performance, particularly its performance with respect to trapping the radio-iodine occurring as CH_3I. Accordingly, an effort has been directed toward investigating the severity of these three processes. The majority of the data

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thus far obtained and those to be presented herein correspond to three different types of impregnated charcoal; also, the data for each type were all obtained using charcoal having the same lot number. Identification of the charcoal types follows: MSA 85851 (lot 93066), 8-14 mesh (Tyler), from Mine Safety Appliances; BC-727 (lot 01345), 8-14 mesh (Tyler), from Barnebey-Cheney; and 5% TEDA (UK)(lot W/310B), 8-12 mesh (BSS), from Sutcliffe, Speakman via United Kingdom Atomic Energy Authority researchers. The MSA 85851 and BC-727 types are iodized and the 5% TEDA (UK) is triethylenediamine-impregnated. Additional information on these charcoals is given in the references already cited.

PROCEDURE

Results from a standardized radioactive methyl iodide removal test were used to indicate aging, weathering, and poisoning effects. The conditions of the test, in which $CH_3^{127}I$ labeled with $CH_3^{131}I$ is employed, is given in Table 1. From each test two removal efficiencies were calculated, one for the first or upstream 1-in. test bed and one for the two 1-in. test beds in series.

The effect of aging, in the absence of weathering, has not been studied formally. However, a number of applicable results have been obtained in conjunction with other objectives, and those that were obtained under the Table 1 conditions will be employed herein. These results correspond to charcoal stored in closed containers with an air atmosphere and at room temperature.

For investigating weathering, two setups for exposing charcoal to flowing air are employed. One is located in a laboratory and the other, in the Oak Ridge Research Reactor (ORR) Building. The charcoal holders used, and there are six per setup, are glass tubes, 1-in. I.D., and each contains two 1-in. depths of charcoal separated by a distance of about 1 in. The same type of holder is used in the tests corresponding to Table 1, so that reloading of the weathered charcoal is avoided. In the laboratory, the charcoal is exposed to treated process air under the conditions of, approximately, 40 fpm (superficial velocity), $78^{\circ}F$, and 50% relative humidity (R.H.). The treatment of the air consists of having it flow through a bed of charcoal followed by a high efficiency filter and then over a pool of distilled water. In the ORR building, the exposure is to flowing air taken directly out of the interior of the building near the reactor, and the conditions are (approximately) 20 fpm, $78^{\circ}F$, and 50% R.H. Considering the two differing velocities and based on this one aspect, the intensity of the laboratory exposure was greater than that for the ORR exposure. Periodically, one or more charcoal holders are withdrawn from the weathering setups, and the weathered charcoal is subjected to the removal test corresponding to Table 1. Also, once charcoal is withdrawn, it is not returned to either weathering setup. In the case of iodized charcoal, the removal efficiency thus obtained refers to that for the ^{131}I of $CH_3^{131}I$, and this ^{131}I removal is accomplished via the combined effect of isotopic exchange and the usual sorption processes. For brevity, the result is termed, albeit inaccurately, as $CH_3^{131}I$ removal. In the case of triethylenediamine-impregnated charcoal, the removal efficiency can be regarded simply as that for CH_3I.

Table 1. Conditions of Radioactive Methyl Iodide Removal Test*

Test beds: two 1-in. depths in series, 1 in. diam.

Air velocity (superficial): 40 fpm

Temperature and pressure: 25°C and 1 atm

Relative humidity (R.H.): 65%

Time for preequilibration (to 65% R.H.): $\geq$ 16 hr

Duration of CH_3I injection: 2 hr

Duration of additional air flow: 4 hr

Inlet CH_3I concentration: around 17 mg/m^3

Amount of CH_3I injected per cm^3 of charcoal: 0.5 mg

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*Refers to ^{131}I (of $CH_3{}^{131}I$) removal in the case of iodized charcoal.

The first group of weathering results to be presented is for one of the types of iodized charcoal, MSA 85851, and corresponds to a year or more of exposure. After terminating that phase of the work, the decision was made to investigate a greater variety of charcoals and, of necessity, the planned maximum exposure times were reduced (to 4 months). A schedule was arranged providing for the obtaining of 2- and 4-month data points for each type of charcoal to be involved. In order to be able to relate the newer and older results, type MSA 85851 was again included along with types BC-727 and 5% TEDA (UK), and the corresponding results are reported herein. Two additional charcoal types, along with BC-727 for comparison purposes, are currently being weathered.

RESULTS AND DISCUSSION

The data collected to exhibit the effect of aging alone are shown in Figs. 1-3. In Fig. 1, no trend is apparent, but in each of Figs. 2 and 3 there is a suggestion of a slight decrease in removal efficiency with time. If the decrease is real, it would be more prominent for the 1-in. removal efficiencies, and such is the case here. Obviously, however, the number of data points for Figs. 2 and 3 are insufficient to provide the basis for firm conclusions on the effect of aging on either of the two charcoal types involved.

The earlier weathering results are given in Figs. 4 and 5 for 1- and 2-in. depths, respectively. The upstream 1-in. depth during weathering is also upstream during the $CH_3^{131}I$ removal test. When compared on either an exposure time or cumulative flow basis, the ORR building-exposed charcoal (actually, building air-exposed) exhibits a much larger effect due to weathering than does the laboratory-exposed charcoal (actually, treated process air-exposed). This observation is, of course, in accord with expectation, since the ORR building air would not normally be as free of impurities as the treated process air used in the laboratory setup. Thus, the data for ORR building-exposed charcoal are very likely indicative of poisoning. In view of the magnitude of the overall decrease in the 1-in. removal efficiency for ORR-exposed charcoal, the decrease being from 90 to 50%, poisoning would appear to represent a potentially serious problem, even when the conditions of exposure are not regarded as severe. Whether the apparent recovery of $CH_3^{131}I$ removal capability indicated by the 15-month data point in Fig. 5 is real or spurious is not known. The positions of that point and the analogous one of Fig. 4 can be explained by assuming that, while the first 1-in. depth adsorbed additional impurities during the period involved, the second 1-in. depth, on balance, desorbed impurities. At least as likely, the explanation is associated with a slight difference in physical locations of the charcoal holders or a slight aberration in experimental technique. The relatively low rate of decrease observed for the laboratory-exposed charcoal may be due to mild poisoning and/or due to some more subtle process.

The more recent weathering data are shown in Figs. 6-8, where the abscissa is time rather than integrated flow as was used in Figs. 4 and 5. Also, the removal efficiencies corresponding to both 1-in. and 2-in. depths for a given type of charcoal are displayed on the same graph. The results for the three
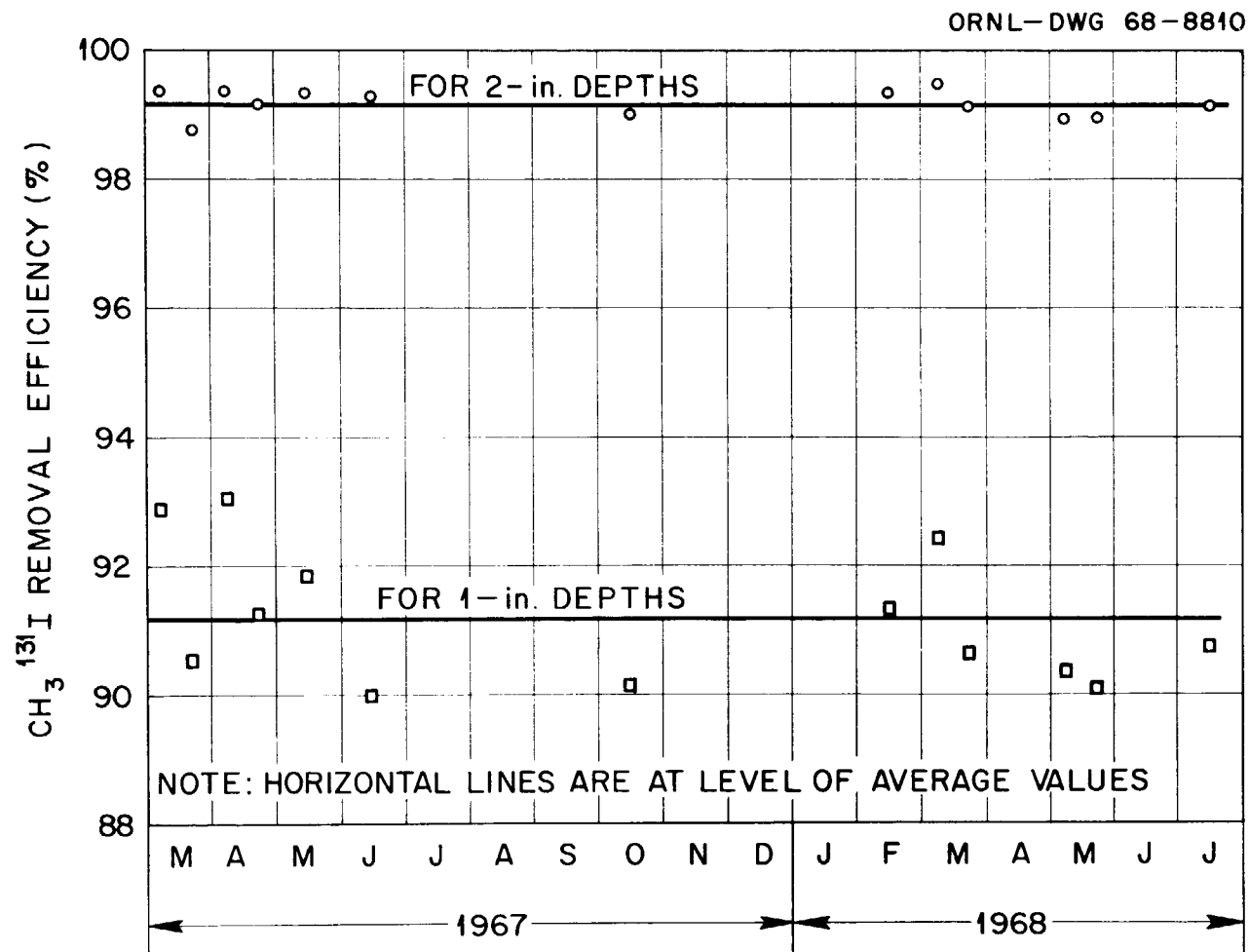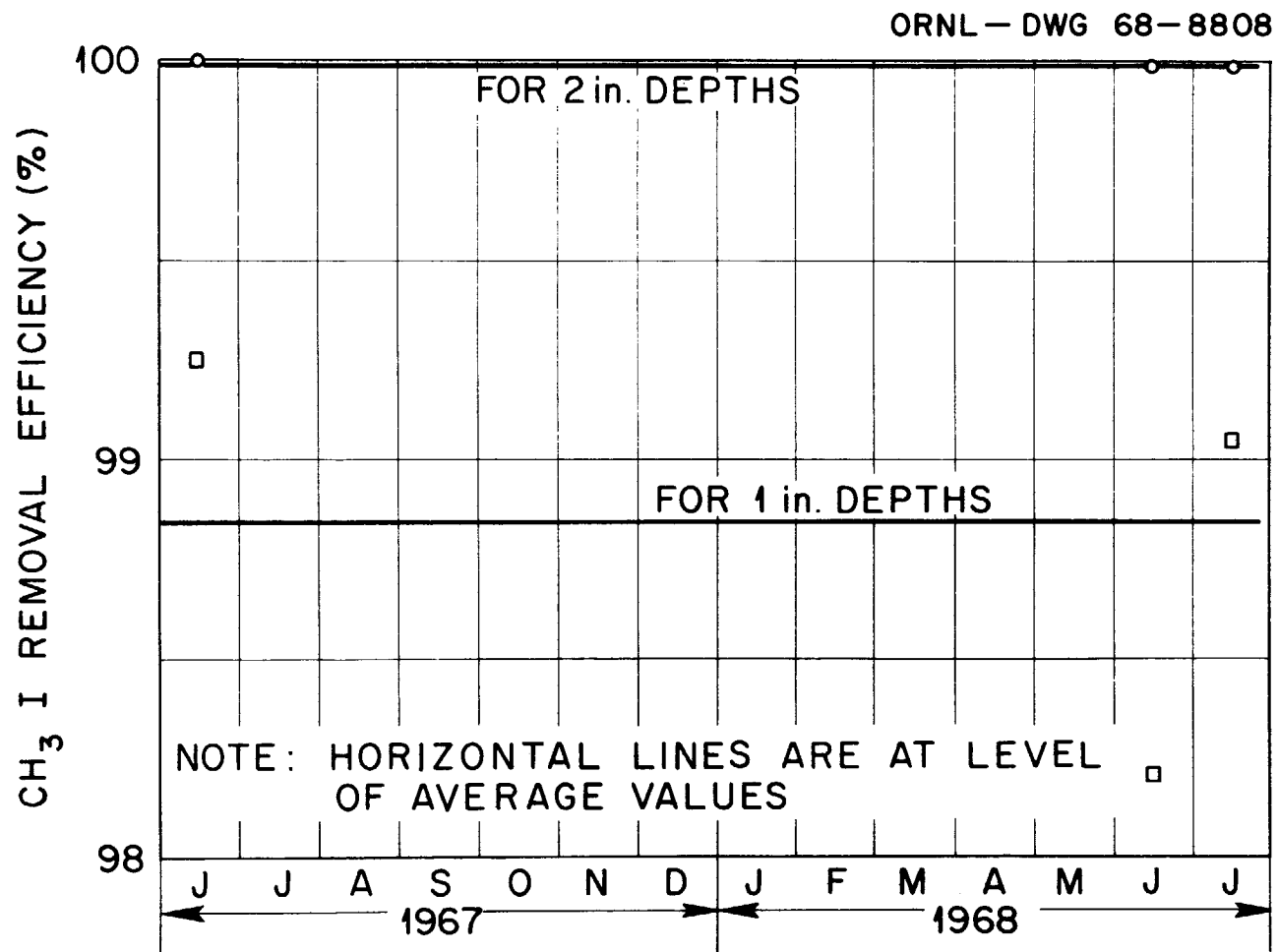
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Effect of Aging on $CH_3 {}^{131}I$ Removal Capability of Iodized Charcoal, Type MSA 85851 (Lot 93066).
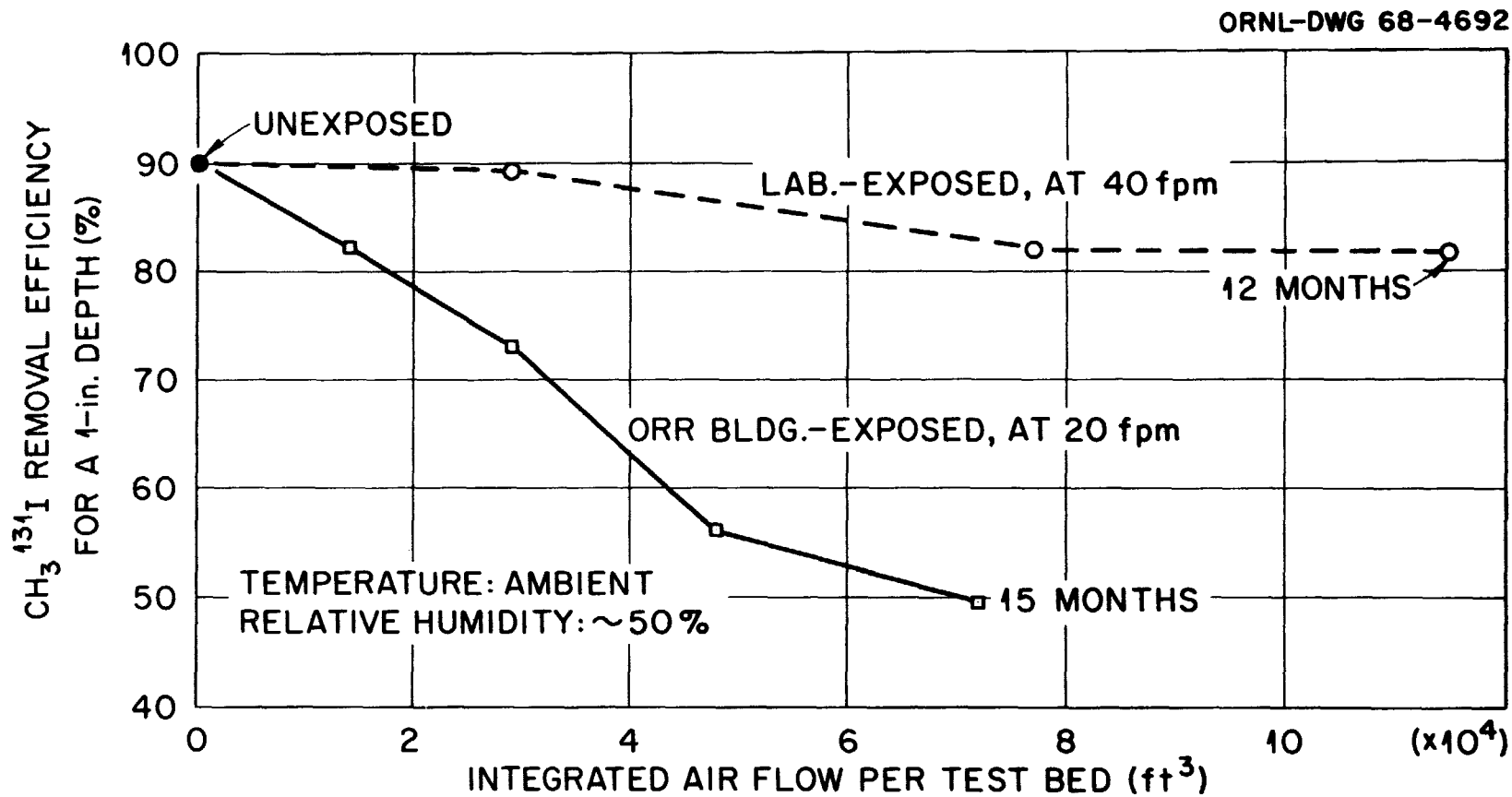
Fig. 1
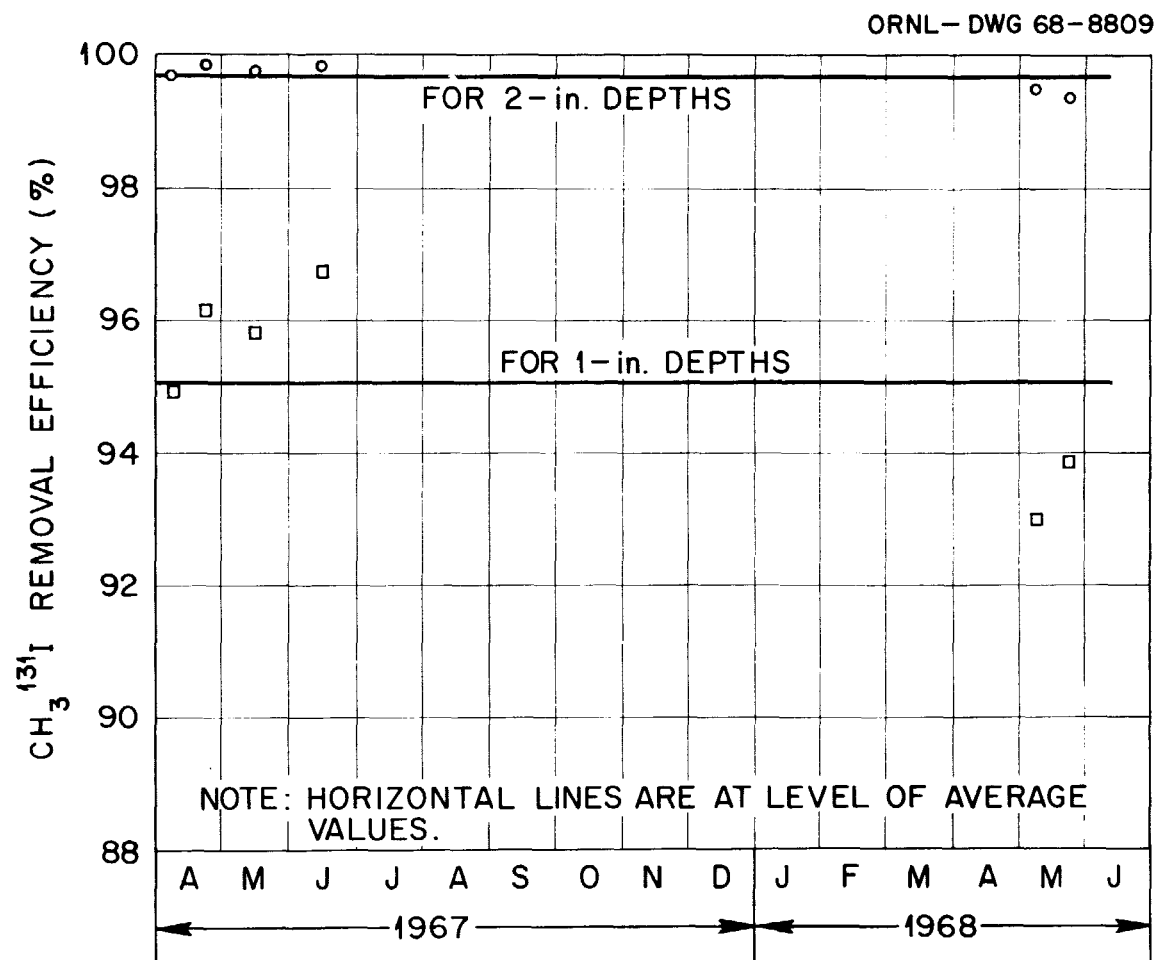
Effect of Aging on $CH_3{}^{131}I$ Removal Capability of Iodized Charcoal, Type BC-727 (Lot 01345).
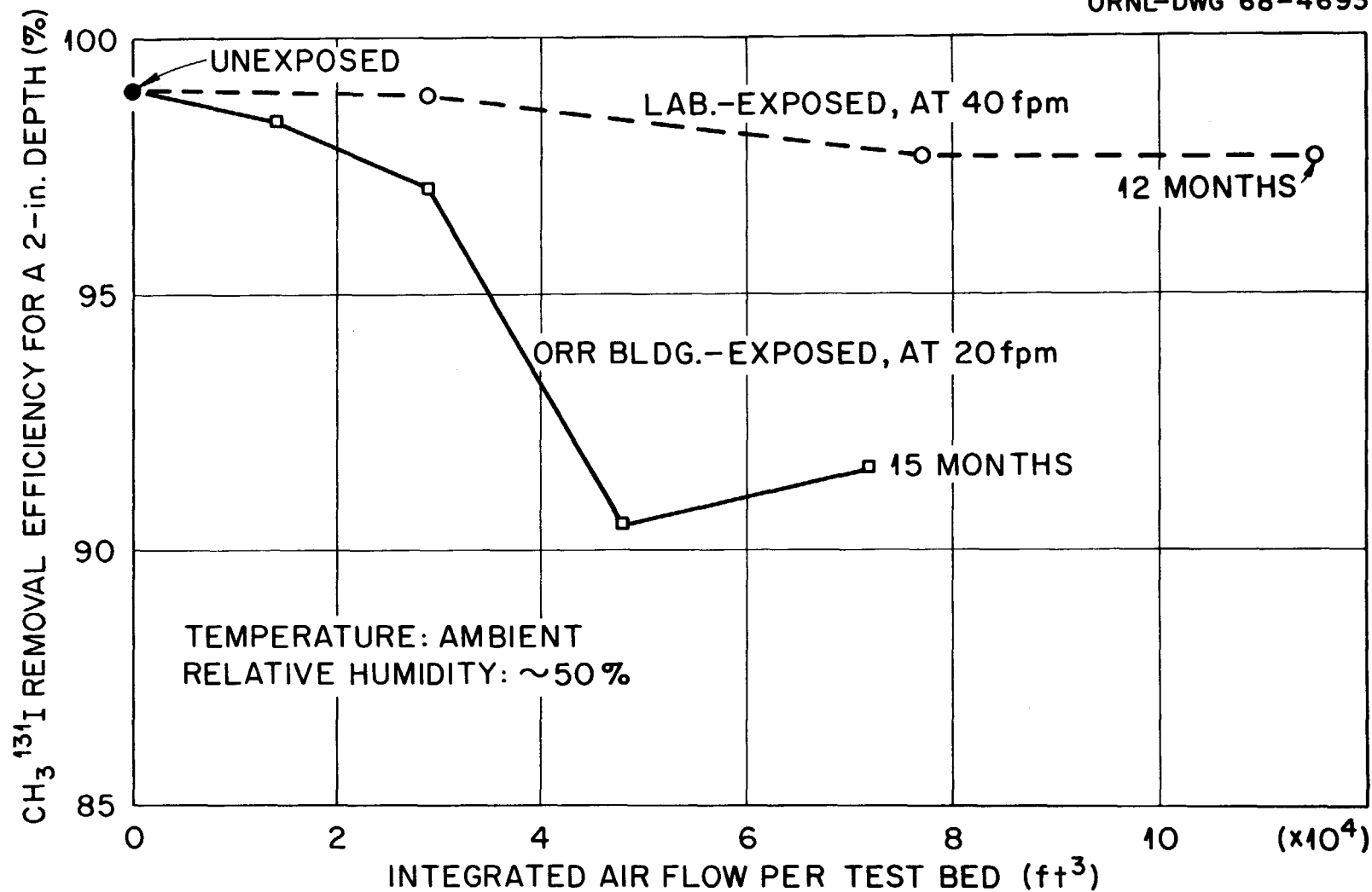
Fig. 2

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Effect of Aging on CH_3I Removal Capability of Triethylene-diamine – Impregnated Charcoal (5 % , UK , Lot W/310 B)
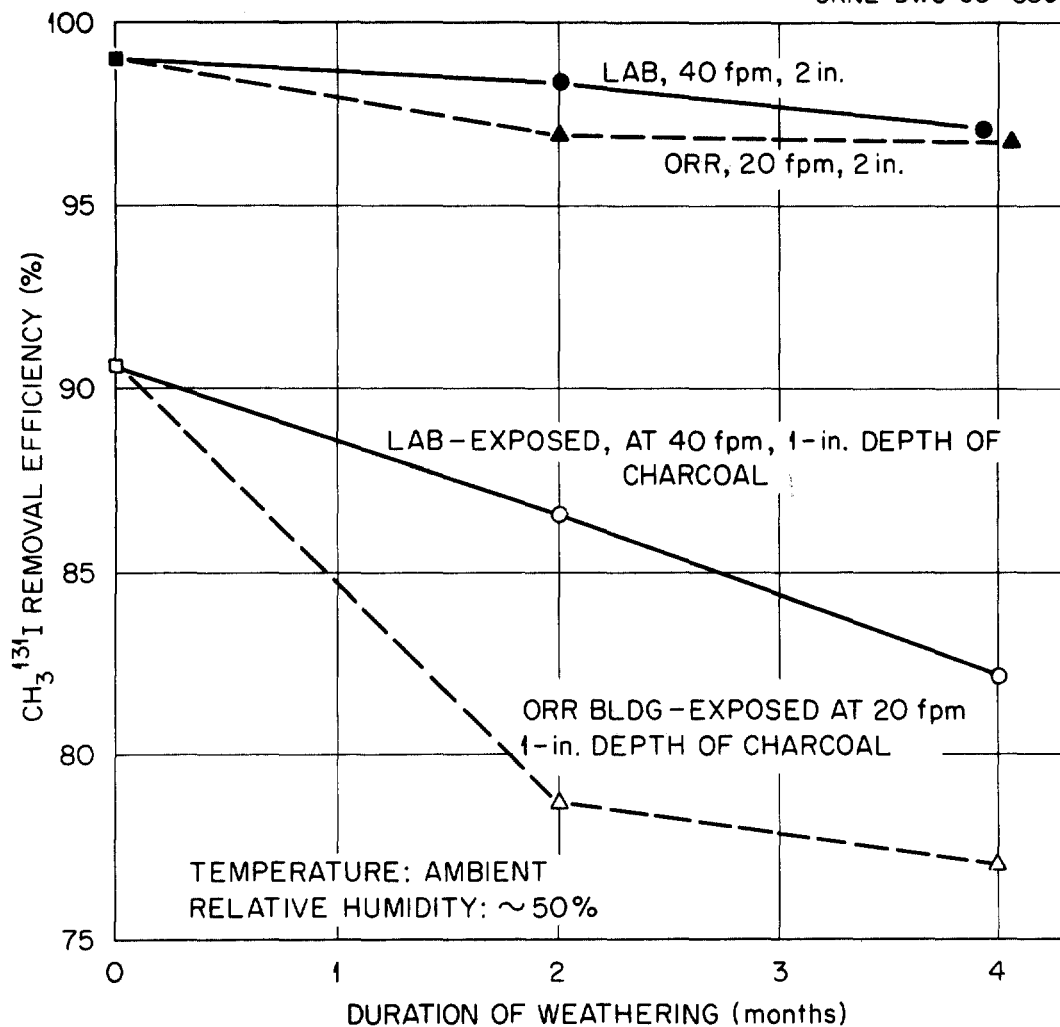
Fig. 3

Effect of Weathering on CH_3 ^{131}I Removal Capability of MSA 85851
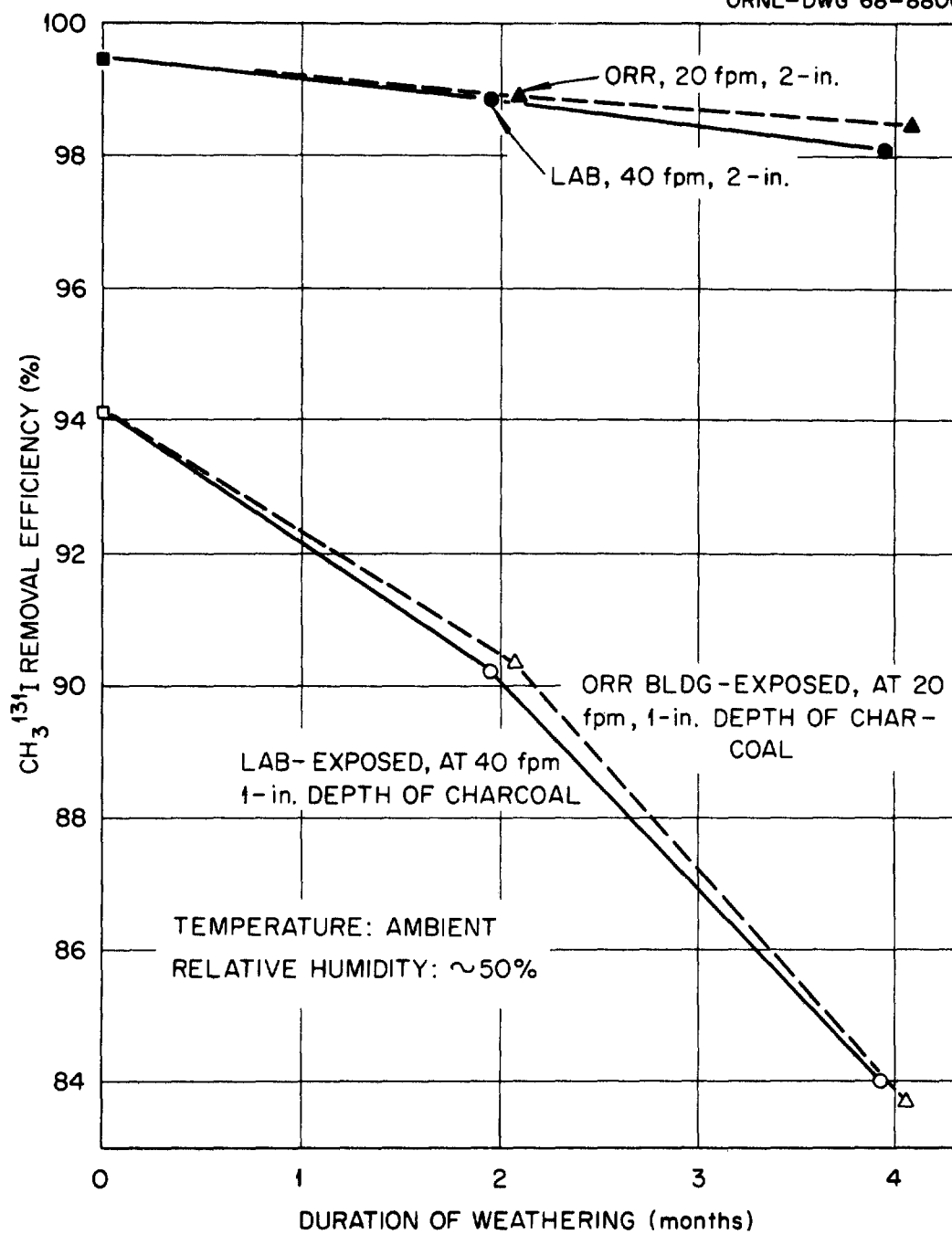Iodized Charcoal (1-in. Depth).

Fig. 4

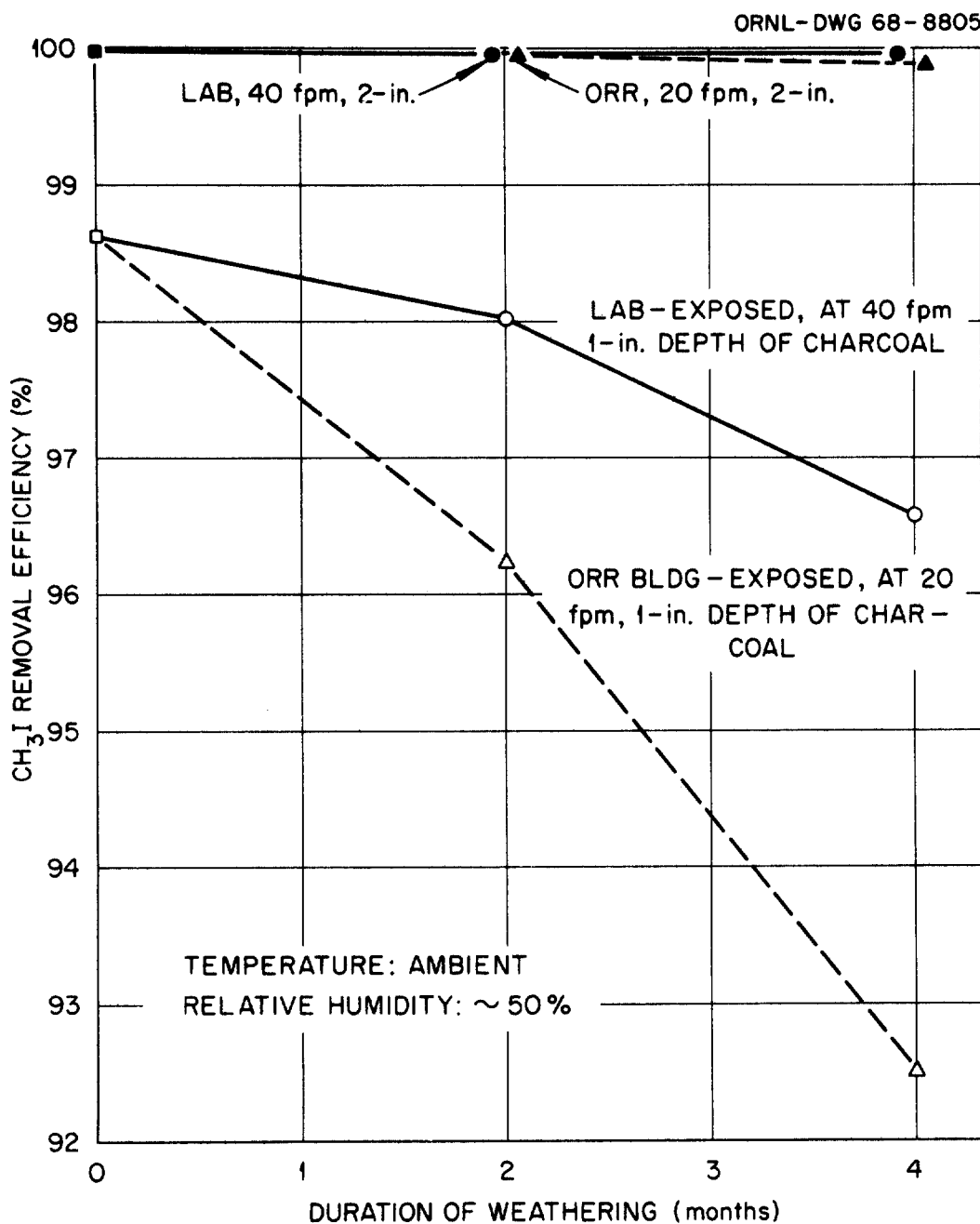Effect of Weathering on CH_3 ^{131}I Removal Capability of MSA 85851 Iodized Charcoal (2-in. Depth).

Fig. 5

Effect of Weathering on $CH_3{}^{131}I$ Removal Capability of Iodized Charcoal, Type MSA 85851 (Lot 93066).

Fig. 6

Effect of Weathering on $CH_3{}^{131}I$ Removal Capability of Iodized Charcoal, Type BC -727 (Lot 01345).

Fig. 7

Effect of Weathering on CH_3I Removal Capability of Triethyl-enediamine –Impregnated Charcoal (5%, UK, Lot W/310 B).

Fig. 8

different charcoal types should be comparable since the various types in their holders were side by side in the weathering setups during the same periods of time. (In comparing the graphs with each other, note should be taken of the differences in ordinate scales.) As may be observed from the data for 1-in. depths, the behavior of type BC-727 charcoal during weathering is indicated to be somewhat different from that of the other two types in that the effects of the two variations in weathering produced virtually the same decreases in $CH_3^{131}I$ removal efficiency for BC-727 charcoal over the time periods involved, while for each of the other two types the extents of decrease differed appreciably for the two variations in weathering. Type BC-727 is also included among the types currently being weathered so additional information on this point may be available at a later date.

A summary of the weathering data in Figs. 4-8 is shown in Table 2 which gives the overall rates of decrease in percent per month. A disturbing feature of these results is the disagreement between the rates calculated from the older and newer data pertaining to laboratory-exposed MSA 85851 charcoal. Possible reasons for this disagreement are under investigation. In Table 2, the relatively low rates of decrease for the triethylenediamine-impregnated charcoal, 5% TEDA (UK), indicate that it withstands the effects of these variations of weathering very well, although, to some extent, this is related to its initially high CH_3I removal capability. In this connection, mention might be made that the application of triethylenediamine-impregnated charcoal would appear to be limited to situations where the possibility of the charcoal reaching a more than moderately elevated temperature would be virtually zero, since, as demonstrated in ignition experiments on this charcoal, the impregnant volatilizes at a temperature of about $190^\circ C$ and occasionally ignites.[2]

The available results on weathering and poisoning of impregnated charcoal, including other results not presented here, demonstrate that adequate consideration should be given to these effects in the design and operation of adsorbers containing impregnated charcoal for trapping that radioiodine occurring as CH_3I along with the radioiodine occurring as I_2. Obviously, where possible, adsorbers should not be subjected to extended air flow except when the need to trap radioiodine arises. In those cases where continued air flow is required, an additional upstream bed of unimpregnated charcoal to bear the brunt of poisoning due to impurities in the air would be helpful; alternately, an increased depth of impregnated charcoal might be employed. In addition, in the majority of applications, particularly if continued flow pertains, fairly frequent and appropriately designed in-place tests to determine $CH_3^{131}I$ removal capability would appear to be required.

CONCLUSIONS

1. Aging of itself has little or no effect on the performance of impregnated charcoal with respect to trapping $CH_3^{131}I$.

2. Weathering with air at around 50% relative humidity results in appreciable reduction in $CH_3^{131}I$ removal capability.

Table 2. Rate of Decrease in CH_3I or $CH_3{}^{131}I$ Removal Efficiency During Weathering

Charcoal Type	Rate of Decrease (%/month)			
	Lab-Exposed		ORR-Exposed	
	1-in.	2-in.	1-in.	2-in.
MSA 85851 (older data)	0.72	0.11	2.7	0.50
MSA 85851 (newer data)	2.1	0.45	3.4	0.54
BC-727	2.5	0.32	2.6	0.23
5% TEDA (UK)	0.51	0.001	1.5	0.02

Note: 1-in. and 2-in. refer to depths of charcoal.

3. Poisoning of iodized charcoal may result in a drastic reduction of $CH_3^{131}I$ removal capability.

4. Installed beds of impregnated charcoal should be protected from the effects of poisoning and, if feasible, from the effects of weathering. In-place tests should be conducted periodically, with a frequency governed by individual circumstances.

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A HIGHLY EFFICIENT INORGANIC ADSORBER FOR AIRBORNE IODINE SPECIES
(Silver Zeolite Development Studies)

By

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ABSTRACT

A synthetic zeolite, Linde Molecular Sieve 13X, converted to the silver form strongly adsorbs inorganic and organic species of airborne iodine. As a filter material for the cleanup of iodine from reactor containment atmospheres, it has ideal properties of non-flammability, high temperature operability with adsorption of iodine up to 500°C, retention of iodine up to 1000°C, and a rapid reaction time. Retentions of greater than 99.98% have been measured for elemental iodine and for methyl iodide for a variety of conditions varying from dry flows at room temperature, dry flows at 500°C, and steam-air mixtures. Other promising applications of this type of material to the nuclear industry include (a) cleanup of dissolver off-gas from chemical processing plant operations, (b) filter materials for health physics safety devices such as face masks and air monitors, and (c) adsorbing filters in sampling devices.

INTRODUCTION

In the reactor safety program, the cleanup of reactor containment atmospheres for fission products, especially the volatile iodine species, is of major importance. Charcoal (potassium iodide impregnated) currently is the material commonly used for the cleanup systems; however, it has disadvantages of iodine desorption at relatively low temperatures, flammability, and unsatisfactory performance with steam atmospheres.

A more promising approach is the use of inorganic adsorbers in which the reaction mechanism involves the formation of a stable iodine compound. With selected inorganic materials the preferred properties of nonflammability, high temperature operability, rapid reaction rates with various iodine species, and a high tolerance to steam atmospheres can be obtained.

DISCUSSION OF PRELIMINARY WORK

As part of the LOFT-ECCS sampling and analysis program[a], Idaho Nuclear Corporation is investigating a variety of materials, both for the retention of total iodine and for the differentiation of iodine species.

Both organic and inorganic materials, with the latter emphasized, were investigated for the uptake of I-131 tagged elemental iodine and methyl iodide from water-saturated air at room temperature and steam-air mixtures. The results for the retention of the two iodine species are summarized in Tables I and II. In addition to retention, the distribution of the adsorbed species as a function of bed length was measured with a gamma-ray scanning device. Many of the materials adsorbed only elemental iodine, and several adsorbed both elemental iodine and methyl iodide. None were selective for methyl iodide.

Of the materials that adsorbed both iodine species, Linde Molecular Sieve 13X converted to the silver form has the best overall properties It is inorganic, easily and reproducibly prepared, stable up to high temperatures with no desorption of iodine, and stable to moisture with no loss of silver. It has high capacity, and a rapid rate of reaction with both elemental iodine and methyl iodide such that the adsorbed species is tightly bound at the entrance of the bed. Significant features of the material are its high surface area-to-volume ratio and the incorporation of the silver in a reactive state throughout the crystal lattice. The silver form is prepared simply by passing a silver nitrate aqueous solution through a column of the 13X zeolite material suspended in water, washing it free of silver nitrate, and drying it under a heat lamp. The capacity is 0.4 grams of silver per gram of received material.

Much other information is presented in Tables I and II, such as the effect of mesh sizes of the various materials and the effect of silver nitrate loadings on inactive supports. Particularly interesting is the increased retention of iodine with increasing pore size of the molecular sieves from the 3Å pore size of the 3A material to the average 10Å pore size of the 13X material. In fact, the 13X material will adsorb methyl iodide with no additive; however, the methyl iodide desorbs with an air purge. This methyl iodide adsorption by the 13X material

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[a] The Idaho Nuclear Corporation is providing technical support to the Phillips Petroleum Company.

provides residence time for the reaction between methyl iodide and silver to go to completion.

EXPERIMENTAL

A simple apparatus (Figure 1) was designed to evaluate Linde Molecular Sieve 13X in the silver form (LMS-13X-Ag) as the filter material for the cleanup of reactor atmosphere containments. In these tests, the test beds and backup beds were 4 in. long in 1-in. diam x 6-in. long stainless steel pipe nipples. Barnebey-Cheney-151 potassium iodide impregnated charcoal was used for the backup beds. The retention and the distribution of elemental iodine and methyl iodide were determined for a variety of atmospheric conditions. In these experiments, the percent retentions were calculated as the activity on each bed divided by the sum of the activities on both beds.

TABLE I

RETENTION OF ELEMENTAL IODINE ON VARIOUS MATERIALS

Experimental Conditions:

Conc of I_2 in flowing stream, 1 μg/ft^3
Flowrate, 0.05 ft^3/min for 15±5 min
Dimensions of bed, 0.6-cm diam, 4-cm long
Atmosphere composition of flowing stream –

1. Water-saturated air at 25°C
2. Steam

Material [a] and Treatment	Atmosphere Composition	Elemental Iodine Retention, %
Activated Al_2O_3-Bi metal mixture	1,2	100[b],100[b]
Activated Al_2O_3-Bi metal mixture, heated (partial conversion to Bi_2O_3)	1	100
Activated Al_2O_3 (coated with hydrazine sulfate)	1	100
Activated Al_2O_3 (coated with $AgNO_3$)	1	100
Linde Sieve 13X-Bi metal mixture	1	100[b]
Linde Sieve 13X-Ag form	1,2	100, 100
Bi_2O_3-ZrO_2 mixture	1	76[b,c]
Chromosorb-P, (as received)	1	43[b]
Chromosorb-P, Bi metal mixture	1	100[b]
Dowex-1x8 (20-40 mesh)	1	98[b]
Ce$(IO_3)_4$, as received	1	95[b]
Zirconium molybdate (converted to Ag form with $AgNO_3$ and washed)	1	100
Hydrous zirconium oxide (as received)	1	98[b]
Hydrous zirconium oxide (converted to iodide form with KI, washed and dried)	1	100[b]
Hydrous zirconium oxide (converted to iodide form with HI, washed and dried)	1,2	100[b],100[b]

[a] Mesh sizes: Al_2O_3, 60-80; Linde Sieve 13X, 60-80; Chromosorb-P, 80-100.

[b] Does not retain CH_3I

[c] Easily purged from support with air.

TABLE II

RETENTION OF METHYL IODIDE ON VARIOUS MATERIALS

Experimental Conditions:

Conc of CH_3I in flowing stream, submicrogram carrier-free except where noted
Flowrate, 0.05 ft^3/min for 15±5 min
Dimensions of bed, 0.6-cm diam, 4-cm long
Atmosphere composition of flowing stream

    1. Water-saturated air at 25°C.
    2. Steam

Treatment of Material	Material[a]	Atmosphere Composition	Methyl Iodide Retention, %
None	Silver molybdate, 0.25 ml H_2O per g	1	25
	Magnesium perchlorate	1	<1
	Ceric iodate	1	<1
	Linde Sieve 13X (60-80)	1	31
	Bi_2O_3	1	<1
	Activated Al_2O_3	1	<1
	Activated Al_2O_3-Bi metal mixture	1	<1
	Activated Al_2O_3-Bi metal misture, heated (partial conversion to Bi_2O_3)	1	<1
	Activated Al_2O_3coated with hydrazine sulfate	1	<1
	Chromosorb-P (80-100)	1	<1
	Chromosorb-P (80-100)-Bi metal mixture	1	<1
	Dowex-1x8 (20-40)	1	<1
	Dowex-50x8 (50-100)	1	<1
	Silver chloride	1	<1
	Silver periodate	1	10
	Silver benzoate	1	<1
	Zinc metal	1	<1
	Auramine-O	1	<1
	Triethylenediamine	1	<1
	Hydrous zirconium oxide	1	<1
	Zirconium molybdate	1	<1
	Dowex-1x8 (50-100) (mixed with PbO_2)	1	<1
Coated with $AgNO_3$	Activated Al_2O_3	1	100
	Activated Al_2O_3 11 mg CH_3I	1	100
	Activated Al_2O_3, 0.4 ml H_2O per g	1	92
	Activated Al_2O_3, contacted with HF and dried	1	3
	Activated Al_2O_3	2	99
	Linde Sieve 5A (40-60)	1	11
	Linde Sieve 5A (60-100)	1	42
	Linde Sieve 13X (60-80)	1	100

TABLE II (Con't)

Treatment of Material	Material[a]	Atmosphere Composition	Methyl Iodide Retention %
Coated with AgNO$_3$ (Cont)	Linde Sieve 4A (40-60), 8 mg CH$_3$I	1	11
	Linde Sieve 4A (60-100), 7 mg CH$_3$I	1	89
	Linde Sieve 13X (60-100), 9 mg CH$_3$I	1	100
	Dowex-50x8 (50-100)	1	99
	Dowex-50x2 (100-200)	1	99
	Dowex-50x16 (20-40)	1	50
	Chromosorb-P (80-100) (damp)	1	100
	Chromosorb-P (80-100) (1 ml H$_2$O added to 2 grams adsorber)	1	97
	Chromosorb-P (80-100) (bone dry bed and air)	1	<1
	Chromosorb-P (80-100)	1	100
	4 grams contacted with 20 ml Ag(I) solution, filtered, no H$_2$O wash, slightly damp 500 g/l Ag(I).		
	125 g/l Ag(I)	1	100
	25 g/l Ag(I)	1	25
	6.2 g/l Ag(I)	1	10
	1.2 g/l Ag(I)	1	3
	0.25 g/l Ag(I)	1	<1
Coated with BiONO$_3$	Activated Al$_2$O$_3$	1	<1
	Chromosorb-P (60-80)	1	<1
	Linde Sieve 13X (60-80)	1	<1
Coated with Hg(NO$_3$)$_2$	Activated Al$_2$O$_3$ (air dried)	1	94
	Activated Al$_2$O$_3$ (damp)	1	10
	Chromosorb-P (damp)	1	96
Placed in Ag form	Linde Sieve 3A (60-80)	1	33[b]
	Linde Sieve 4A (60-80)	1	100
	Linde Sieve 13X (60-80)	1	100
	Linde Sieve 13X (60-80), vacuum dried	1	100
	Linde Sieve 13X (40-60)	1	100
	Linde Sieve 13X (30-60)	1	100
	Linde Sieve 13X (20-30)	1	99
	Linde Sieve 13X (10-20)	1	99
	Linde Sieve 3A (60-80), contacted with HI and dried	1	49
	Linde Sieve 13X (60-80), contacted with HI and dried	1	97
	Linde Sieve 13X (60-80)	2	100
	Linde Sieve 13X (60-80), bed completely water saturated with steam before sample passed through.	2	97

TABLE II (Con't)

Treatment of Material	Material[a]	Atmosphere Composition	Methyl Iodide Retention, %
Placed in different metal forms	Linde Sieve 13X (60-80), Cu form	1	<1
	Linde Sieve 13X (60-80), Cu form, contacted with HI and dried	1	13
	Linde Sieve 13X (6 C-80), Hg(I) form	1	1
	Linde Sieve 13X (60-80), Pb form	1	2
	Linde Sieve 13X (60-80), Pb form, then contacted with HI and dried	1	10
	Linde Sieve 13X (60-80), Tl(I) form	1	100
	Linde Sieve 13X (60-80), Tl(I) form, after 10-min air purge	1	90
	Hydrous zirconium oxide, iodide form	1	<1
	Hydrous zirconium oxide, $Cu(NH_3)_4^{++}$ form	1	<1
	Hydrous zirconium oxide, Bi(III) form	1	1
	Zirconium molybdate, Ag(I) form	1	100
	Zirconium molybdate, Ag(I) form (1 ml H_2O added to 6 g adsorber before test)	1	25
	Dowex-2x8 (50-100), dichromate form	1	<1
	Dowex-2x8 (50-100), permanganate form	1	<1
	Dowex-2x8 (50-100), thiosulfate	1	<1
	Dowex-50x8 (50-100), 80% conversion, Ag(I) form	1	5

[a] Mesh size is given in parenthesis. Mesh size of Al_2O_3 is always 60-80.

[b] Retention band not sharp.
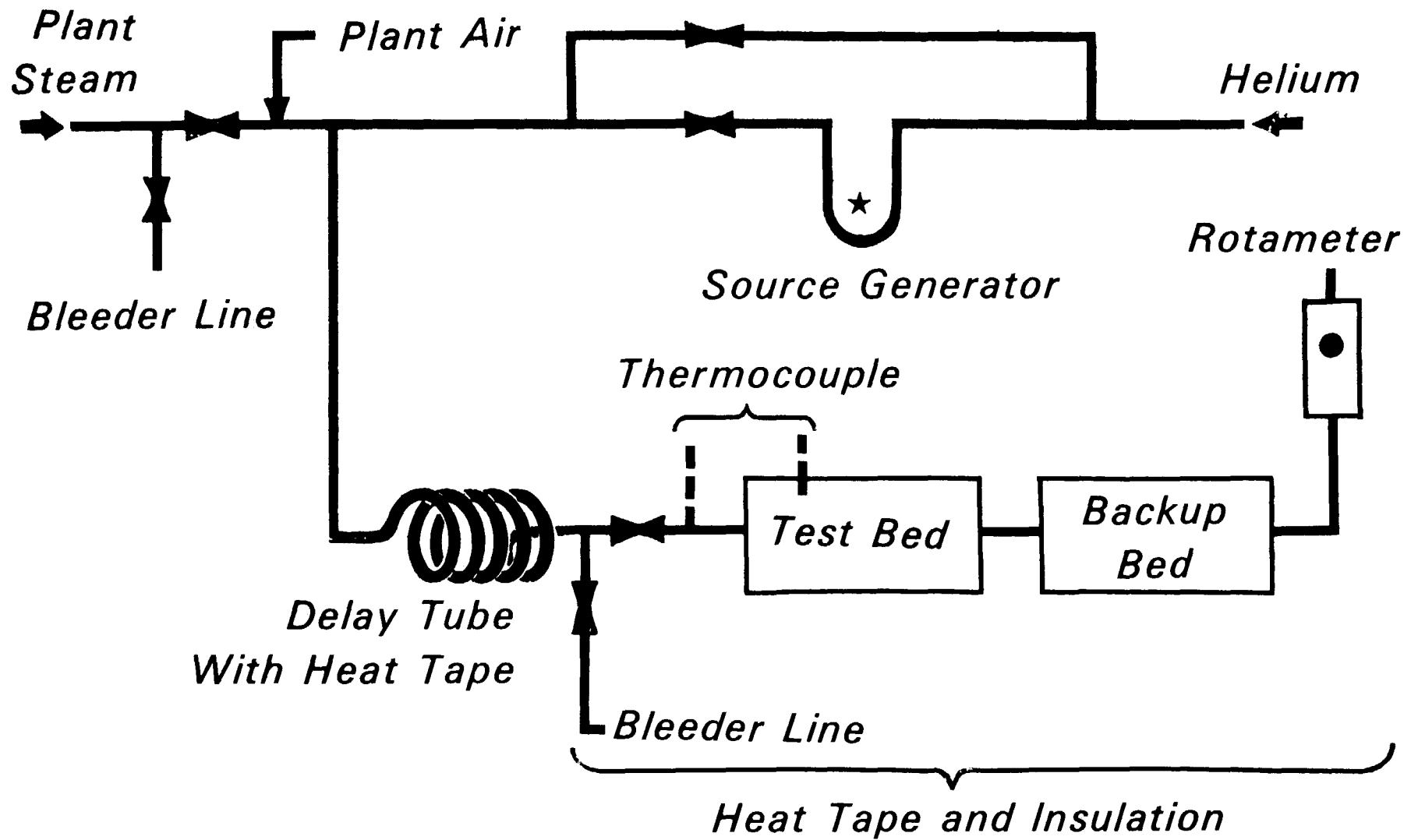
Figure 1. High Volume Experimental Apparatus

For elemental iodine at room temperature and a high flow rate of 8 cfm, the holdup time in the LMS-13X-Ag test bed was 17 msec and the retention was 99.98%. The distribution of the iodine on the test bed, measured with the gamma scanning device, was a sharp band at the entrance (Figure 2). The band did not move and no iodine was desorbed by a 19-hr purge at 25°C.

The retention of elemental iodine from heated (113°C) air onto a heated (95°C) LMS-13X-Ag test bed is shown in Figure 3. A 20-hr 100°C air purge followed by a 12-hr purge with 262°C air did not move the band nor desorbe any iodine from the bed. Of the total iodine on the two beds, 99.98% was sharply adsorbed on the front of the test bed.

The retention of methyl iodide from dry air at 135°C on the LMS-13X-Ag test bed was 99.99%, and it was adsorbed as a sharp band on the front of the bed (Figure 4). A 16-hr air purge at 145°C followed by a 2.5-hr purge with 362°C air did not move the band nor desorb any iodine from the test bed.

The adsorption of methyl iodide at 500°C also was studied (Figure 5). In this test, the LMS-13X-Ag material was placed in a quartz tube in a tube furnace at 500°C with an air-cooled backup charcoal bed located downstream. After heating the bed for 30 min, an air-helium-methyl iodide mixture was introduced. Greater than 99.9% of the iodine activity adsorbed on the LMS-13X-Ag bed. At this temperature, it is believed that methyl iodide thermally decomposed to elemental iodine which adsorbed on the bed.

The high temperature desorption properties of LMS-13X-Ag were studied by placing the material traced with I-131 in a furnace. The sample was heated for 1-hr periods at 100°C increments starting at 400°C. After each heating period, the material was removed from the furnace, cooled, and counted. The first loss of iodine occurred at 1000°C and was 5%. Desorption in a flowing air stream was studied in a similar manner using a 1-in. diam tube furnace at an air flow rate of 1 ft^3/hr. The first loss of iodine occurred at 900°C and was 2%.

The result of flowing a methyl iodide-steam atmosphere at 150°C onto a 190°C heated bed of LMS-13X-Ag is given in Figure 6. Under these conditions, the bed remained dry and the methyl iodide retention was 99.99%. The significance of this is that the effect of moisture can be overcome by the use of heated beds.

The retention of methyl iodide on water-saturated LMS-13X-Ag and charcoal beds in a steam atmosphere are given in Table III.
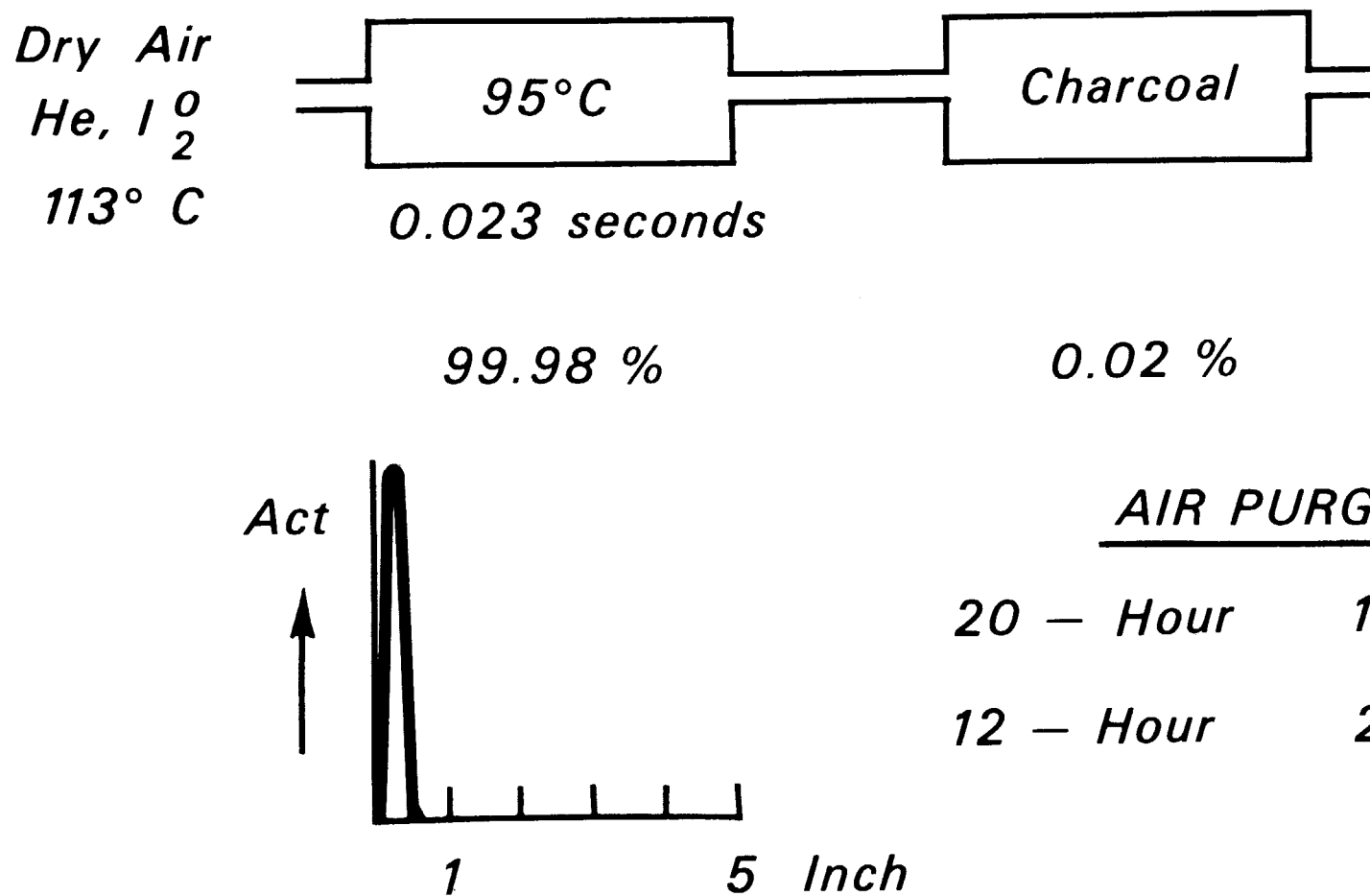
Dry Air
He, I$_2^o$

8 cfm   0.017 seconds

Charcoal

99.98 %   0.02 %

Act

19 — Hour Air Purge

1   5 Inch
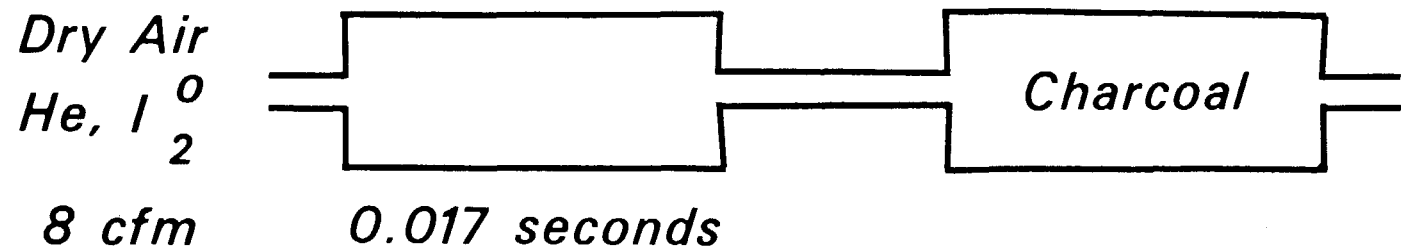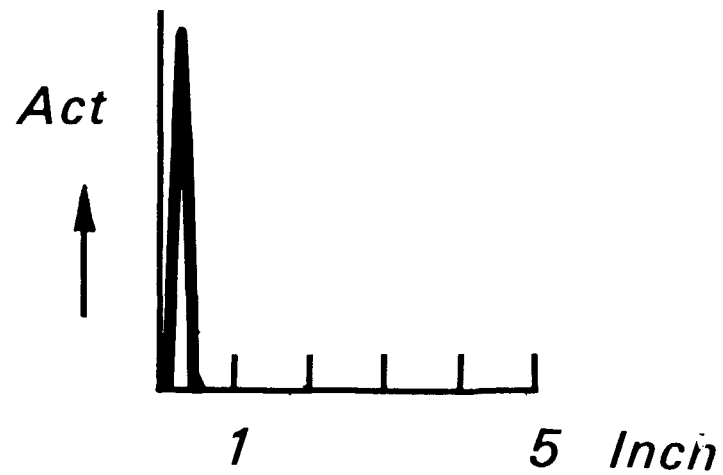
Figure 2. Distribution of Elemental Iodine on LMS-13X-Ag at Ambient Conditions

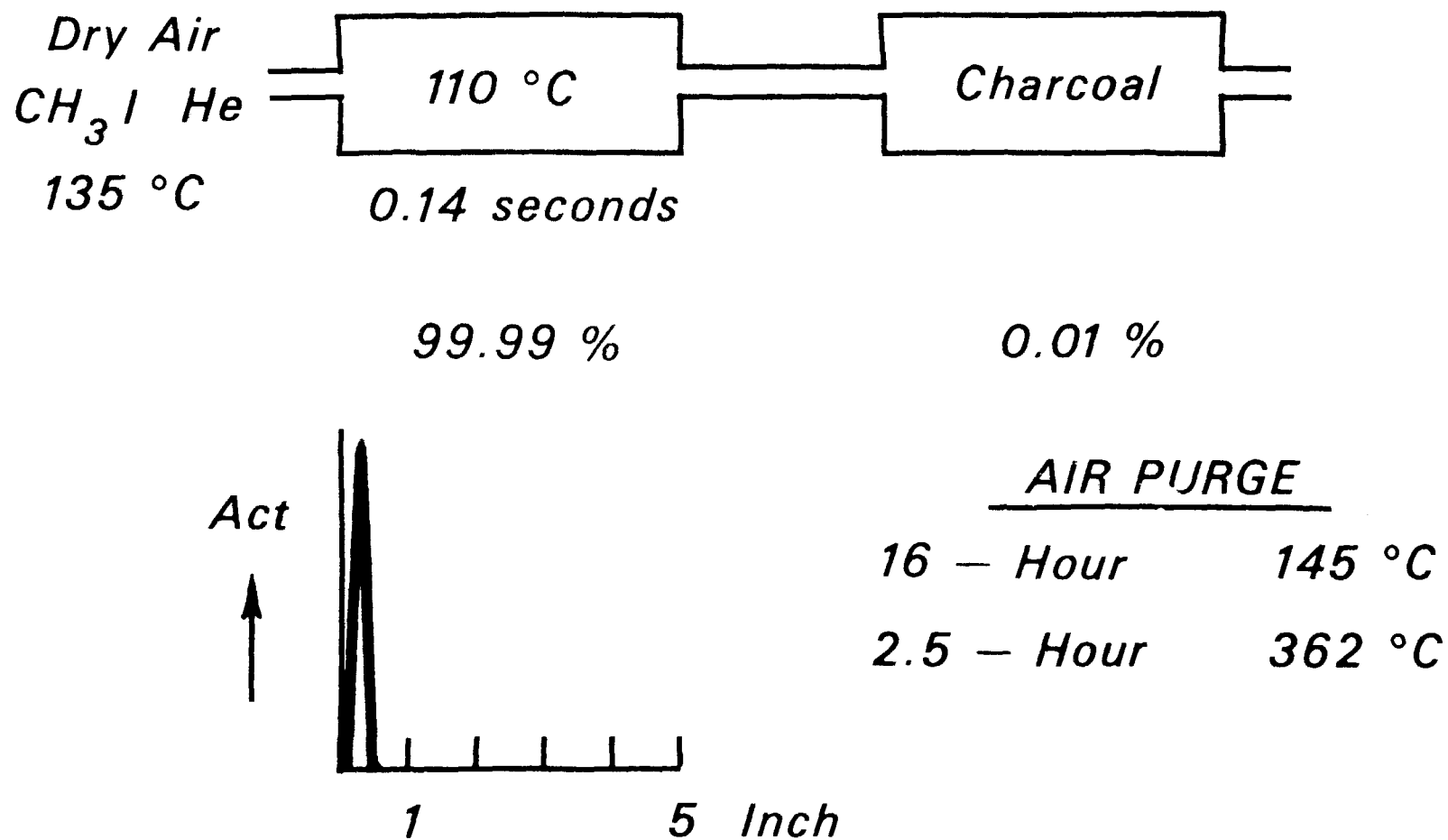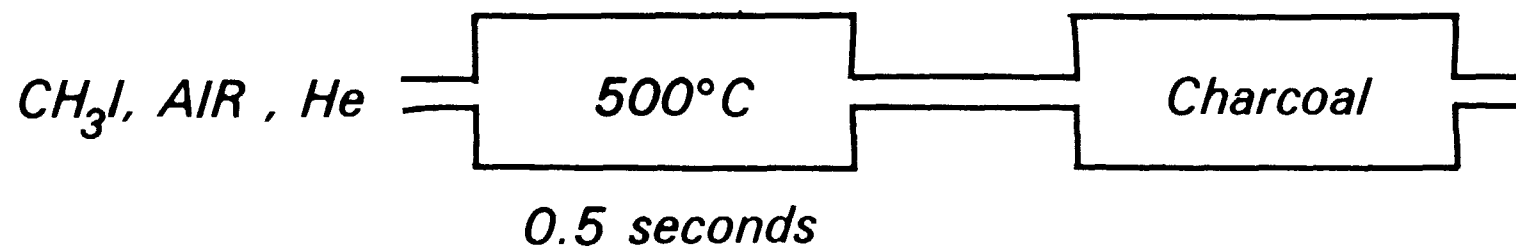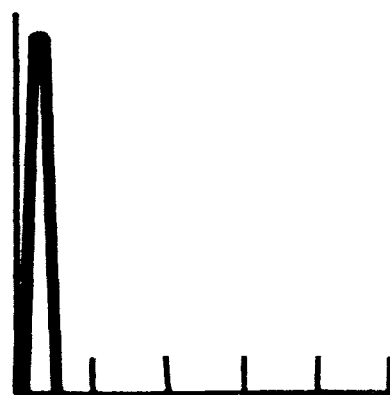Figure 3.   Distribution of Elemental Iodine on LMS-13X-Ag from Heated Air on a Heated Bed

Figure 4. Distribution of Methyl Iodide on LMS-13X-Ag from Heated Air on a Heated Bed

CH$_3$I, AIR , He ⟹ | 500°C | ⟹ | Charcoal |

0.5 seconds

99.9%   0.1%

Act.

↑

Consider for gas
cooled reactors

1   5   Inch

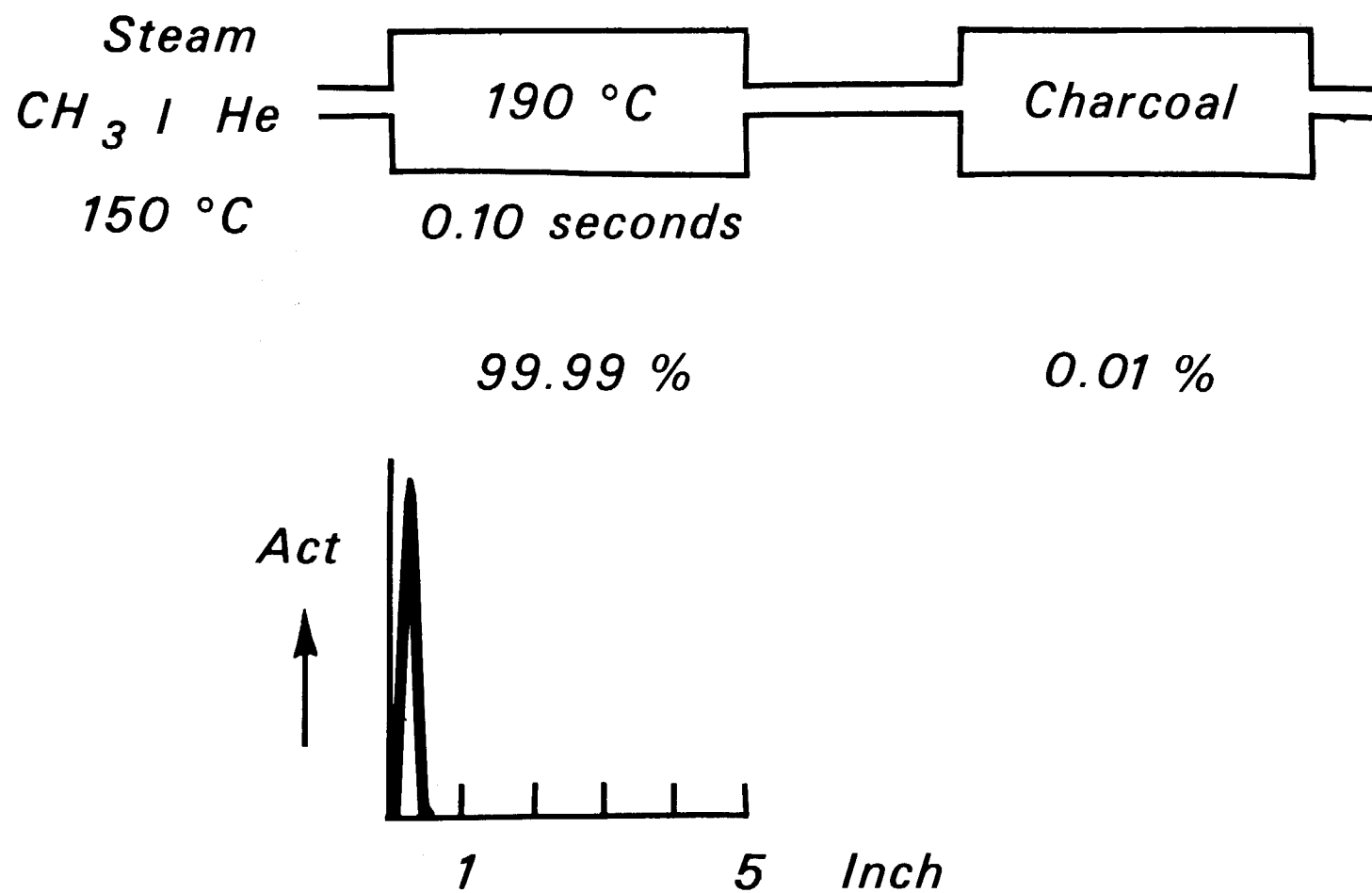Figure 5. Distribution of Methyl Iodide on LMS-13X-Ag at 500°C

Figure 6. Distribution of Methyl Iodide from Steam on Heated LMS-13X-Ag

Table III

DISTRIBUTION OF METHYL IODIDE ON STEAM-SATURATED BEDS
OF LMS-13X-Ag AND CHARCOAL

Test	Test Bed at 113°C	Backup Bed Heated
	Charcoal	13X (Ag)
1	9.1%	90.9%
2	13X (Ag) 55.3%	Charcoal--13X 44.7%

The beds were equilibrated with 113°C steam for 1 hr. The backup beds
were externally heated; however, the temperature was not high enough to
prevent condensation in the bed. After equilibration, a methyl iodide-
steam mixture at 113°C was introduced on the test bed. Two tests were
run under these conditions; one with LMS-13X-Ag as the test bed and
charcoal as the backup bed, the other with the order reversed. The
adsorption of methyl iodide on LMS-13X-Ag was several times better than
on charcoal. In both tests, water ran from the test beds upon disassembly
of the equipment.

The relative adsorption of methyl iodide on steam-saturated beds of
LMS-13X-Ag and charcoal in a steam atmosphere was further investigated.
Alternate 0.5-in. layers of charcoal and LMS-13X-Ag were used as the test
bed. The bed was saturated with steam, then exposed to a mixture of
methyl iodide and steam. The results are shown in Figure 7. This test
confirms the previous experiment in that LMS-13X-Ag is several times
better than charcoal for this condition.

COMPARISON TO CHARCOAL

A comparison of the adsorption of elemental iodine and methyl iodide
for LMS-13X-Ag and charcoal along with a comparison of other physical
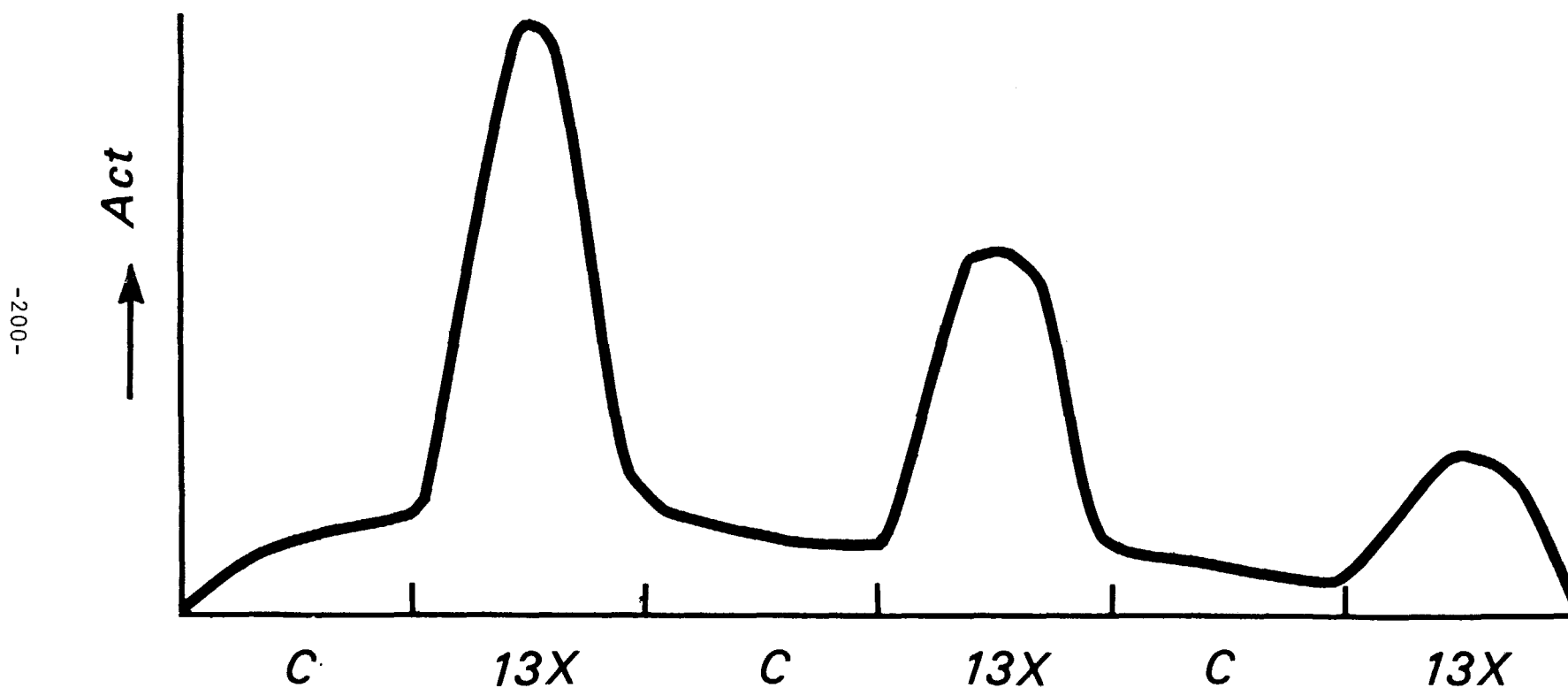properties is summarized in Table IV.

Figure 7. Relative Adsorption of Methyl Iodide on Steam-Saturated Alternate Beds of Charcoal and LMS-13X-Ag from a Steam Atmosphere Flow

Table IV

COMPARISON OF LSM-13X-Ag AND KI-IMPREGNATED CHARCOAL

Adsorption Efficiency	13X-Ag	Charcoal
Dry Air (amb) I_2, CH_3I	Equal	
Hot Air (dry) I_2, CH_3I	Better >250°C	
Sat'd (steam) CH_3I	Approximately 5 times better	
Residence Time (sec)	0.01-0.1	0.2
Pressure Drop (10-20 mesh)	Equal	
Temperature Stability (fire hazard)	900°C	250°C
Shelf Life	To be determined	

Under ambient conditions, both LMS-13X-Ag and charcoal retain elemental iodine and methyl iodide equally well. At increased temperatures, charcoal fails; it starts to desorb iodine about 250°C and ignites about 300°C.

For steam conditions LMS-13X-Ag is 5 to 6 times better than charcoal. The required residence time is shorter for LMS-13X-Ag. The pressure drop across a 2-in. bed is the same for equal mesh sizes. The high temperature stability of LMS-13X-Ag is very important because it increases the applications of the material. Of prime importance is the nonflammability combined with the high temperature adsorption capabilities for use as heated beds and for use in gas-cooled reactor systems.

Because of the short period of time that this material has been available, prolonged aging studies have not been made. However, we believe that the shelf life of the material should be long because the silver is directly incorporated into the crystal lattice. Prolonged heating under a bright heat lamp did not darken the material.

FUTURE STUDIES

Areas of future work are:

1. Iodine uptake as a function of silver concentration:

    Preliminary studies were made with fully converted silver zeolites. Partially converted zeolites and the best method of preparation will be investigated.

2.   Evaluate LMS-13X-Ag with other metal additives:

The addition of those ions known to react with iodine
will be studied. These include Cu, Hg, Tl, Pb, Bi, Sb,
and Sn.

3.   Particle size and shape:

Iodine uptake as a function of the physical size and shape
of the bed particle will be investigated.

4.   Temperature:

Iodine uptake and desorption will be investigated as a
function of temperature.

5.   Moisture:

Iodine uptake in humid atmospheres will be more fully
investigated. The use of heated beds to reduce the
moisture effect will be stuided.

6.   Flow Rates:

Correlate iodine uptake and desorption with temperature
and moisture at varying flow rates.

7.   Shelf Life:

Study shelf life with respect to temperature, moisture,
light, radiation, and atmospheric composition.

8.   Poisons and Containments:

Study the effect of various atmospheres on iodine uptake
and shelf life. Determine the effect of He, CO_2, organic
vapors, etc.

9.   Study the retention of high molecular weight organic iodides.

10. Study Base Material Composition:

Determine the effect of alkali metal and alkaline earth
ratios to aluminate and silicate. Also, investigate other
mineral exchangers for use as support.

11. Preparation of Adsorbant:

> Determine the preferred method of preparing the adsorbant.
> (Ion exchange replacement or direct buildup in manufactur-
> ing process). Consider new manufacturing processes such
> as crystal growth and calcination. Study the effect of
> pore size.

OTHER APPLICATIONS

Preliminary laboratory studies indicate that the silver form of LMS-13X can be effective for the removal of iodine from dissolver off-gases from nuclear fuel reporcessing plant. Long exposures of the bed to water-saturated air and NO_2 and CO_2 did not reduce the bed's efficiency for iodine removal.

EFFECT OF GAMMA RADIATION ON ADSORPTION
OF IODINE AND METHYL IODIDE ON ACTIVATED CARBON

By

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ABSTRACT

The effect of gamma radiation on the adsorption of iodine and methyl iodide on activated carbon exposed to flowing mixtures of steam and air is being measured at the Savannah River Laboratory. The steam-air-iodine mixtures are exposed to a radiation field of $\approx 2 \times 10^7$ rads/hr while flowing through a bed of test carbon. Preliminary tests, in which only relative humidity and velocity have been varied, show that the radiation field decomposed up to 90% of the methyl iodide. Test conditions simulated a postulated loss-of-coolant accident where adsorption of radio-iodine on carbon beds in the confinement system would produce an intense gamma radiation field.

INTRODUCTION

Radioactive iodine must be confined if released during an unlikely reactor accident because of the potential hazard to the surroundings if released to the atmosphere. If there were a loss-of-coolant accident, enough radioiodine would adsorb on carbon beds in the confinement system to produce an intense gamma radiation field. Therefore, the effect of gamma radiation on the adsorption of iodine and methyl iodide on activated carbon is being measured at the Savannah River Laboratory (SRL) as part of a continuing program[1,2] in support of the reactor confinement facilities at the Savannah River Plant (SRP). This report presents results of tests to determine the effect of relative humidity, velocity, and gamma radiation on the adsorption of iodine by carbon beds.

SUMMARY

Up to 90% of the methyl iodide contained in a steam-air mixture was decomposed as the mixture flowed through activated carbon and was exposed to a gamma radiation field of $\approx 2 \times 10^7$ rads/hr. Decomposition decreased with increased face velocity probably because of shorter residence time and smaller total absorbed dose. Decomposition also decreased with increased relative humidity. At a face velocity of 11 ft/min and 50% relative humidity, the amount of methyl iodide penetrating the carbon bed decreased from 20% for tests with no gamma radiation field to $\approx 2\%$ for tests in the gamma radiation field. At 65% relative humidity, penetration decreased from 47% out of the radiation field to 15% in the field. No detectable decrease in penetration was measured at 65% relative humidity when the face velocity was increased to 55 ft/min.

BACKGROUND

Elemental iodine and hydrogen iodide are very reactive and are adsorbed and retained from air by activated carbon, under a wide variety of adverse conditions, with efficiencies >99.9%; however, methyl iodide is not as efficiently adsorbed.[3] Atkins and Eggleton[4] identified methyl iodide as the most penetrating form of iodine that could be released during a reactor accident. Collins, Taylor, and Taylor[5] found that retention of methyl iodide by activated carbon was especially poor when the relative humidity of the gas carrying the methyl iodide was >80%.

Under reactor accident conditions, methyl iodide would be exposed to an intense gamma radiation field generated by fission products adsorbed on the carbon beds. Decomposition of methyl iodide by radiolysis was investigated by Tang and Castleman.[6,7] Mixtures of methyl iodide and dry air were placed in sealed bulbs and irradiated under static conditions. Additional tests were also run with mixtures of methyl iodide and moist air. Deomposition was dependent on total absorbed radiation dose and independent of dose rate. Results from tests with methyl iodide and moist air showed that water vapor inhibits the decomposition of methyl iodide by radiolysis.

APPARATUS AND TECHNIQUES

The methyl iodide radiolysis apparatus is shown in Figure 1. A mixture of ambient air, iodine, methyl iodide tagged with ^{131}I, and steam was passed through a test bed of Type 416* unimpregnated

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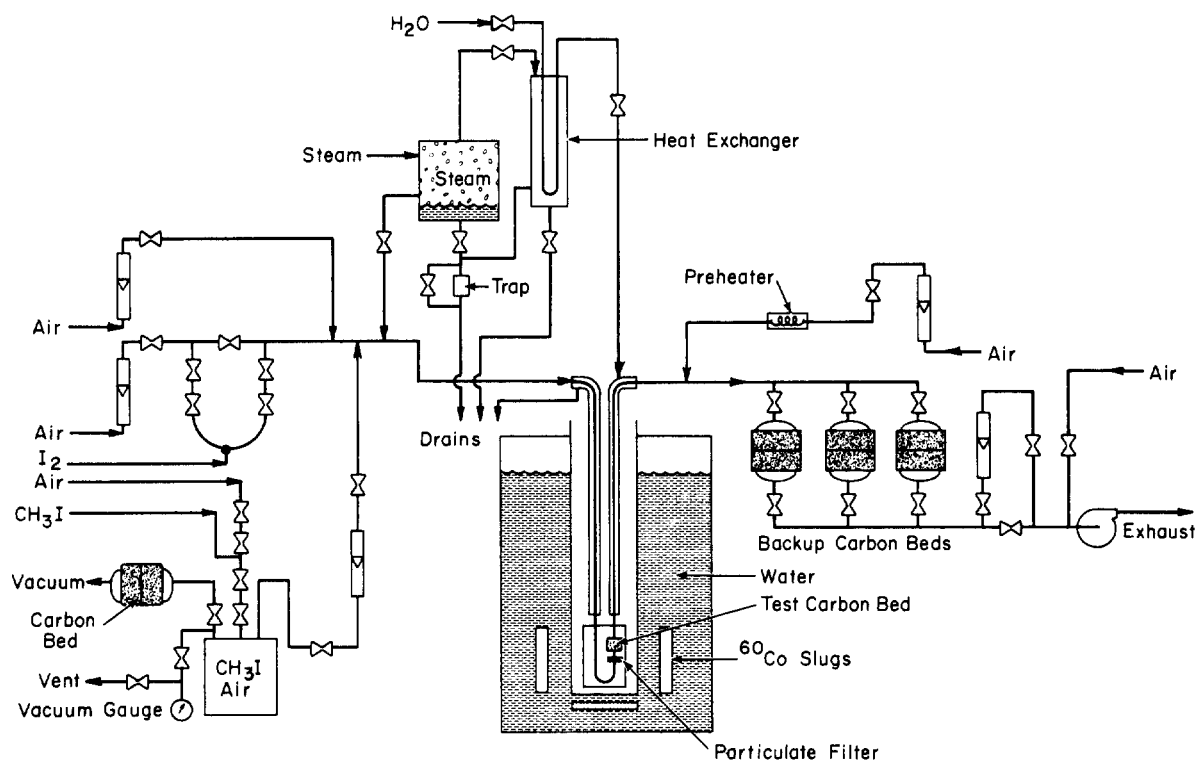
* Product of Barnebey Cheney Co.

FIG. 1 APPARATUS TO DETERMINE RADIOLYTIC DECOMPOSITION OF
METHYL IODIDE ON ACTIVATED CARBON

carbon positioned in the gamma field and then through one of three sets of backup carbon beds. Each set of backup beds consisted of three one-in.-thick beds in series containing impregnated carbon especially treated to retain methyl iodine. Each set monitored methyl iodide penetration for a specific time interval.

The gas stream was prepared by mixing steam at $100^\circ C$ with ambient air at $\approx 25^\circ C$. A volumetric ratio of air to steam of 4:1 and 6:1 produce slightly supersaturated steam-air mixture temperatures of 50 and $60^\circ C$, respectively. The steam-air-iodine mixture flowed to and from the test carbon bed through tubing insulated with a jacket through which water flowed at $65^\circ C$. Dry air at $100^\circ C$ was added to the steam-air-iodine mixture immediately upstream of the backup carbon beds to reduce relative humidity to $\leqslant 10\%$.

Elemental iodine was injected into the gas stream by passing ambient air at constant velocity through a glass frit containing solid iodine.

Liquid methyl iodide tagged with ^{131}I was placed in a short length of tubing valved off at both ends. After warming the liquid to room temperature, the methyl iodide vapors were flushed into a large reservoir tank which was then pressurized to 15 in. of mercury with compressed air. Initial flow of methyl iodide-air mixture out of the reservoir tank and into the system was set so that the pressure in the reservoir tank was reduced to atmospheric pressure in 60 min. One-third of the original methyl iodide sample was injected into the system in an exponentially decreasing concentration on the basis that the methyl iodide completely mixed with the air in the tank. The remaining two-thirds of the sample was discarded. Therefore, material balance calculations were based on one-third of the original methyl iodide sample.

"Teflon"* tubing was used in the apparatus, and all stainless steel pieces except for the test section were "Teflon" coated to minimize iodine deposition. The test section was not coated with "Teflon" because it decomposes in an intense gamma radiation field.

Each test ran four hours. The system was pre-equilibrated with a steam-air flow at the test conditions for the first two hours. Then elemental iodine and methyl iodide samples were injected with total flow passing through the first set of backup beds. After seven minutes, the total flow was diverted to the second set of backup beds. At the end of one hour, the total flow was diverted to the third set of backup beds and both sample flows and the steam flow were terminated, leaving only dry air flowing through the system for the remaining hour of the test.

* "Teflon" - trademark of Du Pont.

The test section was housed in an air-filled pipe surrounded by ^{60}Co slugs and a large volume of circulating water (Figure 1). The temperature of the test section was controlled by adding water to this pipe to conduct heat generated by gamma absorption away from the test section and into the circulating water on the outside of the pipe.

After each test, major parts of the apparatus were disassembled. The amount of ^{131}I tracer on each piece was determined by counting in a gamma detector. A computer program converts these counts to mass of CH_3I and calculates penetration of the test carbon bed, material balance, methyl iodide loading on the test carbon bed, and methyl iodide adsorption on other pieces of the apparatus.

Initial concentrations of methyl iodide were $\approx 10^3$ $\mu g/m^3$. Elemental iodine loading on the test carbon bed was ≈ 0.7 mg $^{127}I_2$/g carbon. Methyl iodide loadings varied from 0.001 to 0.02 mg CH_3I/g carbon because of the high volatility of methyl iodide and the minute quantity required for each sample. A better technique for preparing these high specific activity samples is being developed.

DISCUSSION OF RESULTS

The conditions under which the tests were run and the results are given in Table 1. Figure 2 shows a plot of methyl iodide penetration vs. relative humidity. The gamma radiation field of $\approx 2 \times 10^7$ rads/hr reduced methyl iodide penetration of the test carbon bed by a factor of 10 in tests (7, 11, and 12) at a velocity of 11 ft/min and 50% relative humidity. The radiation field reduced penetration by a factor of 3 in tests (6 and 9) at a velocity of 11 ft/min and 65% relative humidity. Two tests (8 and 10) in the radiation field and at 55 ft/min show no apparent effect of radiation. Radiation is expected to have less effect on adsorption as velocity increases because residence time is shortened and absorbed dose is reduced. Results of test 8 may be in error because relative humidity could have been higher than that reported due to condensation of water vapor during one stage of the test.

A reduction in penetration by a factor of 10 corresponds to a 90% decomposition of methyl iodide by gamma radiolysis. Data from Tang and Castleman's[6] work on decomposition of methyl iodide by radiolysis in dry air are shown in Figure 3. At a methyl iodide concentration of 10^3 $\mu g/m^3$, 90% decomposition would require an absorbed dose of 5×10^5 rads. Residence time required for absorption of 5×10^5 rads from a 2×10^7 rads/hr field is ≈ 1.5 min. Data from Tang and Castleman's[7] work on decomposition of methyl iodide by radiolysis in moist air, shown in Figure 4, were cross-plotted at SRL to show more directly the effect of moisture upon absorbed dose required for decomposition. Above about 5% relative

TABLE 1

TEST CONDITIONS AND RESULTS OF METHYL IODIDE RADIOLYSIS

| Test	Gamma Field, rads/hr	Velocity, ft/min	Average Relative Humidity, %	CH_3I Loading, mg CH_3I/g carbon	Penetration, % (CH_3I only)
1	0	55	48	0.407×10^{-2}	14.1
2	0	55	78	1.845×10^{-2}	47.3
3	0	55	78	0.598×10^{-2}	62.6
4	0	11	78	1.106×10^{-2}	49.3
5	0	55	95	0.199×10^{-2}	89.8
6	0	11	68	0.596×10^{-2}	46.7
7	0	11	50	0.903×10^{-2}	19.8
8	2×10^7	55	65	1.490×10^{-2}	42.7
9	2×10^7	11	64	0.279×10^{-2}	14.8
10	2×10^7	55	65	0.169×10^{-2}	64.5
11	2×10^7	11	50	0.660×10^{-2}	2.4
12	2×10^7	11	50	1.980×10^{-2}	1.5
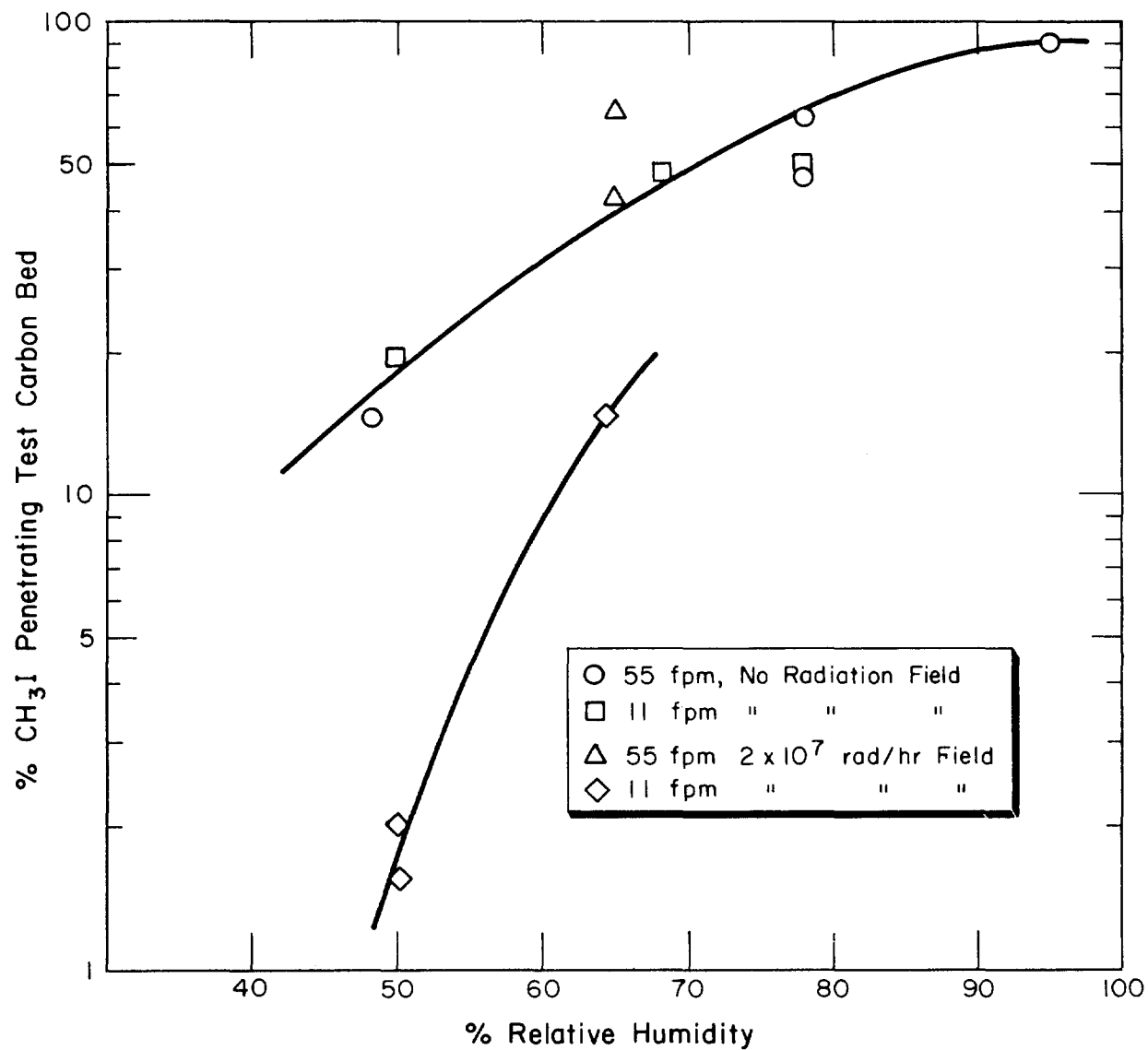
FIG. 2 EFFECT OF GAMMA RADIATION, RELATIVE HUMIDITY AND
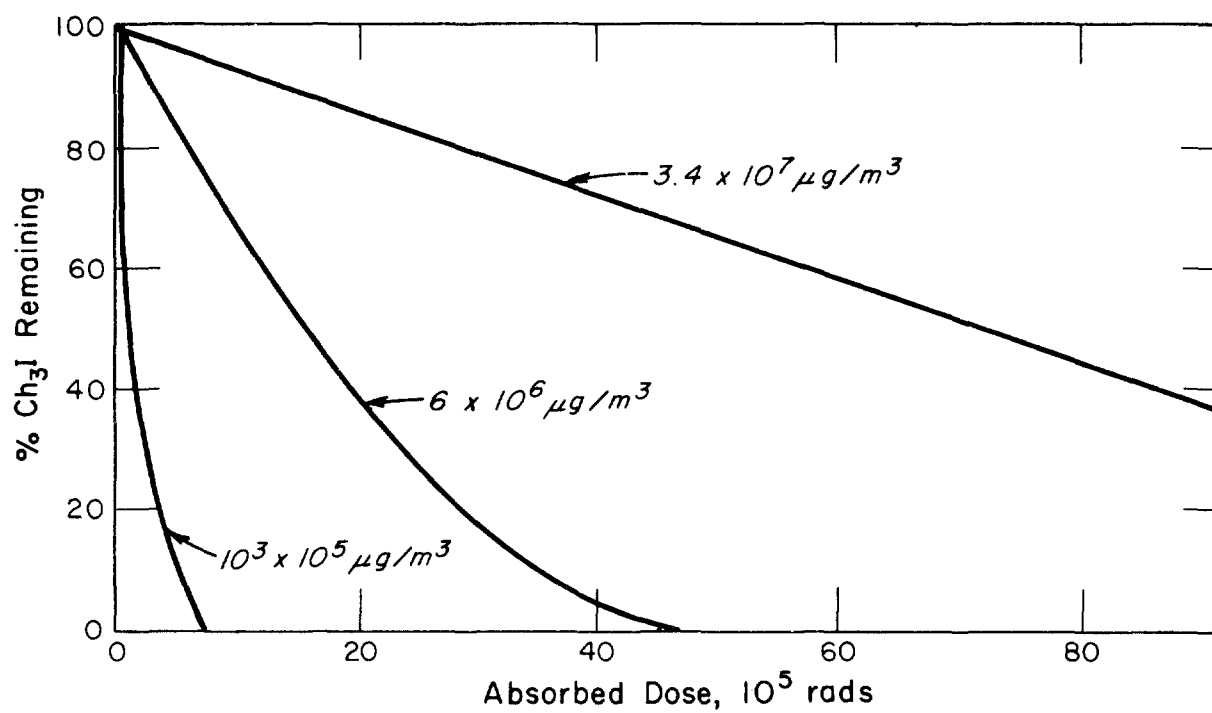VELOCITY ON METHYL IODIDE PENETRATION

FIG. 3 GAMMA-INDUCED DECOMPOSITION OF CH₃I IN DRY (VAPOR PRESS. H₂O 0.1 mmHg) AIR - Tang and Castleman, Jr., Brookhaven National Laboratory.
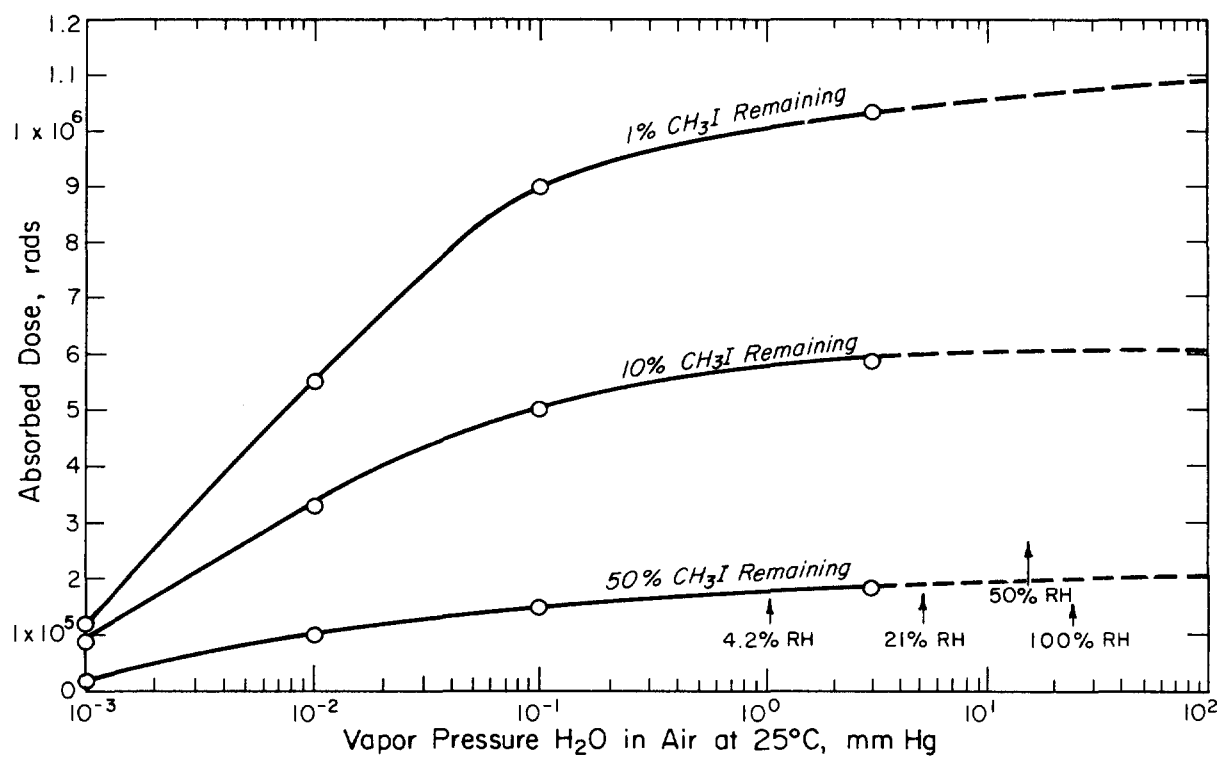
FIG. 4 GAMMA-INDUCED DECOMPOSITION OF CH_3I AIR-WATER VAPOR MIXTURES
CH_3I Initial Concentration from 10^3-10^5 $\mu g/m^3$ by Tang and Castleman, Jr.,
Brookhaven National Laboratory

humidity, absorbed dose remains nearly constant. However, the absorbed radiation dose required for 90% decomposition of methyl iodide is increased to 6×10^5 rads by the presence of the water vapor in the air. The corresponding residence time in the 2×10^7 rads/hr field is ≈ 1.8 min. It is postulated that water molecules competing with methyl iodide molecules for gamma absorption result in less decomposition of methyl iodide for a given dose.

The presence of elemental iodine molecules and a large mass of carbon in the system should decrease decomposition rate several-fold; for the same total decomposition the residence time must be increased. Test results indicate an average residence time of 5.5 min at the beginning of the tests.

Relative humidity was chosen as the primary variable for preliminary tests because methyl iodide penetration is so greatly affected by it (Figure 2). Other variables were held constant except for velocity which is interrelated with relative humidity because of gamma heating of the carbon in the test carbon bed.

Heat generated in the test carbon bed by gamma absorption resulted in temperature differences across the bed of from $\approx 10^\circ C$ at a velocity of 55 ft/min to $\approx 30^\circ C$ at a velocity of 11 ft/min. Relative humidity of steam-air mixtures decreased from 78% upstream of the test carbon bed to 23% downstream of the test bed at a velocity of 11 ft/min. Average values of relative humidity were used for comparison of tests.

Tests were run with and without carbon in a special apparatus (Figure 5) to measure the gamma heating. It was found that about one-third of the heat generated in the methyl iodide apparatus was from gamma absorption in the carbon. It was concluded that the remaining heat was generated in the stainless steel test section that holds the test carbon bed. The gamma heating of the carbon alone was calculated from the experimental data as ≈ 65 Btu/(hr)(lb) of carbon. This value agreed well with the 74 Btu/(hr)(lb) of carbon calculated from theory.

All tests were run at an average test carbon bed temperature of $65^\circ C$, the temperature at which maximum moisture is entrained in the steam-air mixture.[8] Practically all of this entrained moisture was removed by the particulate filter located immediately upstream of the test carbon bed.

FUTURE WORK

Of the important variables—absorbed gamma dose, relative humidity, velocity, temperature, organic impurities, iodine, and methyl iodide loading on the carbon, type of carbon, carbon
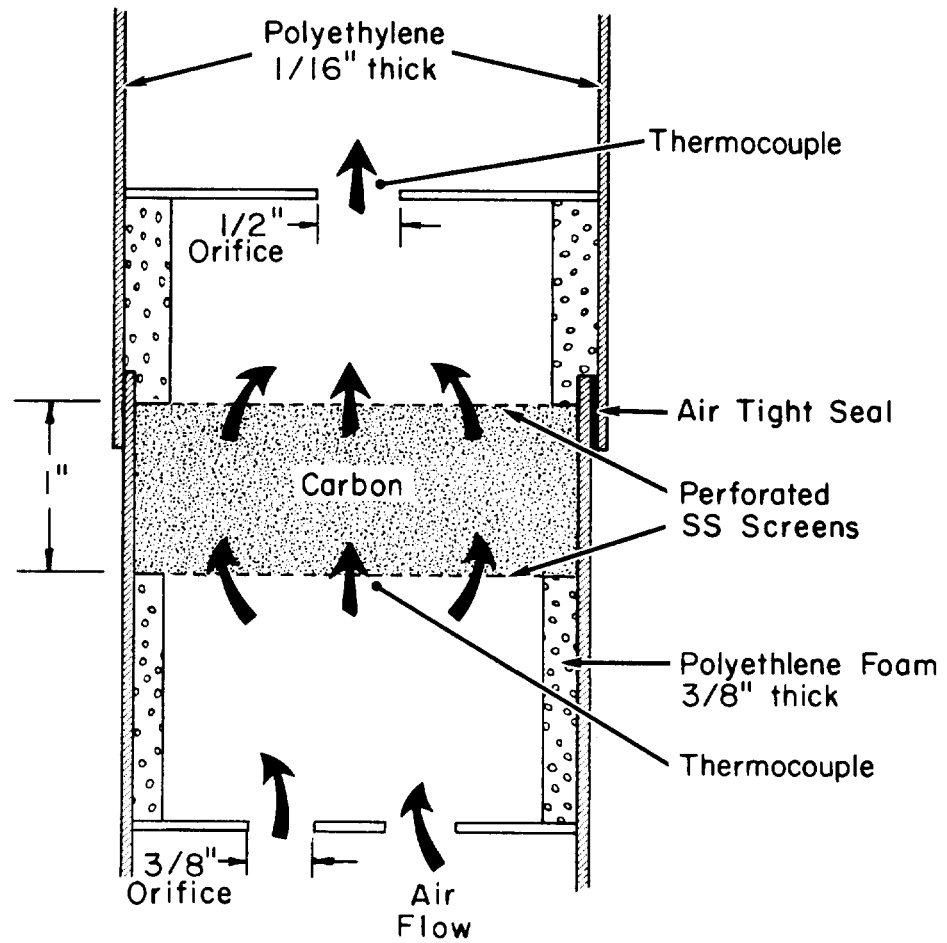
FIG. 5 SPECIAL APPARATUS FOR GAMMA HEATING TESTS

service life, and sample injection rate—only relative humidity and velocity have been investigated. Tests are required 1) at slower methyl iodide injection rates to simulate a more intense radiation field and/or longer residence time, 2) at higher velocities to determine the effect of velocity of the gas stream on residence time of the methyl iodide, 3) using only elemental iodine, 4) using iodine and methane to determine the effect of radiation on formation of methyl iodide, and 5) using impregnated carbons and carbon having three years service in the SRP confinement system.

ACKNOWLEDGMENTS

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KOVACH: I would like to congratulate our speakers, not only on the excellent work that they did, but also on the extraordinary discipline they showed in keeping within the time limit. And, for this reason, it appears that we do have reasonable time for a question period.

ETTINGER: I'd like to ask Mr. Ackley whether he has any estimate as to the magnitude of weathering or poisoning for impregnated charcoals when tested with elemental iodine.

ACKLEY: (ORNL) We have not done any work on the effect of weathering using elemental iodine. All tests were with methyl iodide, mainly because we feel the various effects are far more pronounced with methyl iodide.

ETTINGER: I was wondering if it is conceivable that by going to impregnated charcoals, you do very well on methyl iodide to start with, but you lose so much effectiveness on weathering and poisoning that in the long run you're worse off than if you use non-impregnated charcoals.

ACKLEY: I believe you would have to protect the impregnated charcoals, perhaps more so than you would unimpregnated charcoals.

ETTINGER: You mean protected with another bank of charcoal filters that are not impregnated, or something like that?

ACKLEY: Perhaps, or keep them offstream until you actually need them.

ETTINGER: Thank you.

FIRST: This is addressed to Mr. Milham. Did you do any experiments with your carbons to determine whether they could be returned to their original retention capacity by steam reactivation or some such process that charcoals are normally subjected to?

The interest, of course, is whether a bed which has deteriorated could be reactivated by some simple method in place. Even though it might have some adsorbed radioactivity, it would be possible at least to bed the reactivation stream into a supplementary unit to pick up the radioactivity and get your bed back into a high efficiency state once again.

MILHAM: We have done no work on regeneration processes other than that associated with our "Freon" test program that I described.

THAXTER: Dr. Maeck, with respect to your zeolite, I recognize and recall you said you've only worked with it for a few months so I'll ask you to guess.

Would you hazard a guess as to the, shall we say, the short term aging characteristics of this type of material in a bed in the presence of organic test vapors, such as say hydrochloric acid?

MAECK: We have done some experiments passing NO_2 vapors through the material as we understand there can be some breakdown of the zeolite in acidic atmospheres. This was actually done in connection with trying to evaluate material for use in processing plants. We dropped a solution of sodium nitrate into a boiling nitric acid solution and generated about a mole of NO_2 which we allowed to pass through a condenser and on to a one inch bed of the zeolite filter pack. After the NO_2 had passed through the pack, we then dissolved a piece of aluminum metal and introduced an iodine tracer into the dissolver. The iodine retention under those conditions was still greater than 99 per cent.

I might add that our condenser was not as efficient as it could have been. We actually had nitric acid percolating up in the bed, however this did not appear to impair efficiency of the bed for trapping iodine.

We also passed 500 liters of propane through the bed; 500 liters of oxygen and 100 liters of CO_2 and so forth. None of these had any serious effect on the bed for the retention of iodine.

VILES: I have three questions for Mr. Maeck. I assume that since you didn't mention the obvious presence of silver iodide downstream of the zeolite that none occurred. Is that correct? You did notice this in charcoal in steam atmospheres?

MAECK: That's right.

VILES: Another question is, did you run elemental iodine at $900^{\circ}C$ in air?

MAECK: No, not 900! The highest test temperature that we used to evaluate iodine uptake was 500° and this was for methyl iodide flowing on to the bed.

I have a feeling that under the test conditions that methyl iodide would decompose before it even reached the bed. Because as it goes down the tube furnace it would start to heat up, and would probably decompose, thus essentially only elemental iodine would be going on to the bed at $500^{\circ}C$.

VILES: The reason why I asked the question is the possibility of oxidation. We know this occurs with hydrogen iodide in the presence of oxygen and feel that this would probably be enhanced at elevated temperatures and I was wondering if this occurs with silver iodide in the zeolite? There's the possibility that you might not have oxidation in the case of iodine.

MAECK: In the test for iodine desorption at 1,000°C. After the iodine was adsorbed on the bed at low temperatures, the bed was dissembled and the bed materials placed in a small cup and put in a muffle furnace and heated at 100° increments and after each heating the sample was taken out of the furnace and counted. This procedure was continued until we observed a decrease in activity.

The first apparent loss of iodine occurred by 1,000°C.

Duval in his work indicates breakdown or decomposition of silver iodide at about 960°C.

VILES: Do you know for a fact that it is silver iodide?

MAECK: Let me back up one minute.

We did some experiments of coating aluminum oxide with silver nitrate such that we had a solid silver nitrate coating on the alumina surface. We put large amounts of iodine on to the bed and it turned the characteristic yellow color of silver iodide.

X-ray analysis showed that this was indeed silver iodide.

We did the same experiment with the silver loaded zeolite, but we could not confirm the silver iodide x-ray pattern. The material did turn yellow. We have the feeling that perhaps the bonding is a long chain type structure of aluminate, silicate, silver, iodide, silicate, aluminate--kind of following the actual structure of the zeolite.

VILES: Which is a very complex structure.

MAECK: Yes.

LOUROS: My question is directed to Mr. Maeck. Have you considered, or did you consider, comparing your silver zeolite with activated carbon impregnated with silver at the same levels?

MAECK: No, you're talking now about silver reduced on the surface of the carbon?

LOUROS: Yes.

MAECK: No, we did not.

KOVACH: I would like to make a comment to this question.

This was done concerning some HGDI work and it was found that silver coated carbon tends to be a real good explosive, so to those who want to make explosives, I recommend against using it! Obviously you can run it in strictly a helium or no oxygen atmosphere.

BURLEY: My question is addressed to Mr. Milham. Do you have any data on the shape of the time dependent concentration vs. desorption curve at a constant temperature?

MILHAM: At 65°C, the desorption curve for new Type 417 carbon shows a leveling off after two hours. There is no measurable desorption from new carbon after about two hours.

If we continue heating Type 592 carbon to about 200°C there is a break in the curve at about 140°C indicating an apparent leveling off of desorption.

At about 160 or 170°C, there seems to be another sudden increase in desorption.

The data I quoted is time dependent. At 200°C it takes about an hour and a half to two hours before desorption levels off. The time dependence will be described in greater detail in my paper SM-110/49 at the IAEA Symposium.

BURLEY: Is this essentially linear or do you get this initial curve and then the leveling off?

MILHAM: The desorption appears to follow an exponential behavior until the desorption levels off at its final value.

GOLDMAN: I have a question for Mr. Maeck. He seems to be getting a lot of play! In view of the complications of the methyl iodide reaction on your zeolite, have you had an opportunity yet to make an estimate of the mass loading that these beds could take?

MAECK: No, other than we have taken several hundred milligrams of iodine crystals and passed air over the iodine allowing the air-iodine mixture to flow onto the bed to the point where the bed turned a bright yellow color right on the leading edge.

Now, it's my feeling that the capacity is extremely large. We might be talking of capacities on the order of say 100 milligrams per gram of material.

GOLDMAN: Thank you.

ERLEBACH: I have a question for Mr. Jones. I wonder whether you have made an estimate of the beta dose which would pass into the gas once the methyl iodide is adsorbed on the charcoal? It seems to me that this may be a very substantial contribution.

JONES: Yes, we have. Of course in our cobalt facility it would be absorbed in our facility before it reached our carbon bed. However, we have just begun to study this in our full-size confinement system and it seems to be a substantial fraction, perhaps 40 per cent.

ADAMS: I would like to address several comments to Mr. Maeck. We also use the same method for determining adsorber efficiency in our laboratory studies and we feel that it's a useful method only if you trap all of the iodine penetrating your test adsorber.

MAECK: Right!

ADAMS: We find that one must take pains to ensure that the backup traps are capable of collecting all the iodine passing through the adsorber bed under test.

MAECK: Yes.

ADAMS: Looking then at Fig. 2 in your paper, you indicate that there is a 17 microseconds delay time in your silver zeolite test adsorber and that the backup charcoal bed is of the same size; do you know that the charcoal backup bed, operating with only a 17 microsecond delay time, was picking up all of the iodine penetrating the silver zeolite bed and that none of the iodine might have passed completely through the charcoal and consequently lost from your experimental apparatus?

MAECK: That's a very good point which has been brought up several times. We have run an experiment at a flow of about two cubic feet per minute which is four times less than the test you mentioned. Two charcoal backup beds were used in which the backup-backup bed was chilled. We observed no activity on that chilled bed.

                    My feeling is that if there was any significant breakthrough of the first bed, we would not observe the sharp retention band at the front of the bed that we see all the time. You might expect a trailing of the adsorption band if there were any significant leaks. Either that or we are encountering a completely different species.

ADAMS: A further question. You mentioned Barnebey-Cheney 151 charcoal used in the backup charcoal beds. I'm not familiar with that material.

MAECK: Our charcoal people tell us that Barnebey-Cheney grade their types of charcoals as to whether it's impregnated or unimpregnated and also according to mesh size and this particular number was 151. Mr. Cartan, is that the same as the 727 with a different mesh size?

CARTAN: It's the same charcoal with 2% $KI-IO_2$.

ADAMS: We noted your first announcement of the silver zeolite material in the Idaho Nuclear Company progress report and we made up some of the material for study in our laboratory. I'm sure that our preparation was different from yours since our material only produced a methyl iodide efficiency,

under humid conditions, of around 92 percent, which is comparable to the efficiency of MSA 85851 charcoal under the same conditions. May I request that we exchange samples?

MAECK: Yes.

ADAMS: One last comment. From the results of your work, I feel that we may finally have a solution to the iodine control problem, in that we have a non-combustible material which would take out 99.98 percent of the iodine and charcoal to take the last 0.02 percent; so, we now have a 100 percent system.

MAECK: You don't give up easily!

KOVACH: As long as you are standing right here, Dr. Maeck, I also have a question which relates somewhat to a previous one. You were showing very good efficiencies when you used the charcoal backup but when you put another silver zeolite downstream of the charcoal, suddenly you picked up a relatively large concentration there also. Would you comment on this?

In most of these samples that you were running, the particle size was considerably smaller than those in the conventional systems. I'm wondering why on your apparatus I didn't see a particulate filter or anything downstream.

Could the filters have been picking up some particulate forms here because of your much smaller particle size?

MAECK: There was a glass fiber particulate filter on the leading edge of the bed and when the bed is counted that particulate filter is removed and it's only the actual bed material which is counted. This applies to both the charcoal bed and the silver zeolite bed.

As far as the charcoal backup trap is concerned, we have also run this experiment with a second silver zeolite bed.

KOVACH: Well, I'm referring to Figure 7. The question is was there considerable amounts of iodine that ended up on the second zeolite which was downstream of your carbon?

MAECK: Oh, yes. This bed was dripping wet with water and we're not making any claim that a bed which is dripping with water will have a sharp retention band or that one bed dripping wet is as efficient as when it is dry, but under similar conditions we do feel that the silver zeolite is better than charcoal.

WILHELM: How does the removal efficiency for methyl iodide at higher humidity of this type of charcoal you used compare with a type of charcoal mostly in use in the United States, or is it the same as MSA 85851 or the English

charcoal SS 207B because the removal efficiency of those types of charcoal is pretty well known and I don't know anything about the charcoal you mentioned? I don't know anything about the efficiency of this charcoal type you used to compare.

KOVACH: Would the Barneby representative care to comment?
(No comment.)

WILHELM: I really would like to know. When we compare two components, I have first to know how good one is. I don't know.

Well, the second question is in the experiment with saturated steam in Table 4, it is written that your zeolite type was approximately five times better than charcoal.

On what basis is this calculated? Is this considering the stay-time or considering the decontamination factor?

MAECK: No, this is just relative data. This is just adding up total activity on both tests and then calculating that fraction on each bed.

For instance, in the first test the charcoal bed was followed by the 13X bed and 9 per cent of the total activity on both beds was on the charcoal bed.

I think the experiment is shown better with the series of mixed beds.

WILHELM: I would just like to check with you if I may. When you say it's five times better you mean that from the total amount of activity trapped it was five times greater on zeolite than on charcoal type?

MAECK: Yes, that's generally what we're implying there.

WILHELM: And, because the total amount which was trapped was nearly 100 per cent, it will be five times better in removal efficiency too?

MAECK: Our equipment was such that we could not generate all the types of atmosphere that we desired.

As I said, we've not had a lot of time to work on this material, but I still feel that based on the work done on the multiple packing of carbon, 13X, carbon, 13X, carbon, 13X, that this experiment does show that the silver zeolite is performing better than charcoal under similar conditions.

WILHELM: Thank you.

VILES: Dr. Maeck again. You mentioned about the displacement of the charcoal bed downstream of the zeolite bed at some distance, particularly where you had temperature differences and you wanted to show that you had good removal by the charcoal.

Did you scan the pipe tubing and so forth to see if any iodine had been removed in the tubing, etc. ?

MAECK: Yes, it was glass tubing and we did take it out and look at it.

PARKER: I have to pick a hole a little bit in this too!

MAECK: It's all in the family!

PARKER: We observed that type displacement, particularly where we had water condensing in the bed which you appear to acknowledge. It really results from the aqueous leaching of the KI and carbon system and its being carried down to other parts of the bed. It doesn't really represent rapid transfer of methyl iodide; at least it didn't in our case.

I want to ask if you're aware that MSA oxidation catalyst "Hopcalite" does a very similar job as far as converting methyl iodide and holding it at elevated temperatures as long as it's not water-logged. I'm sure the same is true with silver zeolite.

MAECK: We have run the zeolites with a lot of water on them and they still seem to function.

I have heard about the "Hopcalite" work and I would not like to make a comparison at this time, but I guess that as long as the pores of the sieve are open that the methyl iodide can get into the sieve that the reaction should go on.

PARKER: I'm aware of a case in which the "Hopcalites" are being used because of the presence of other organics which have poisoning properties.

I have one question for Mr. Ackley and that is, is there an effort being made to theorize the mechanics of deterioration of the impregnated carbons ?

ACKLEY: (ORNL) Are you referring to the effects of poisoning?

PARKER: The aging process--do you have a theoretical analysis as to what happens?

ACKLEY: (ORNL) We have some thoughts on how to approach this, but I rather doubt that we will have time to do much along that line.

DEITZ: About ten years ago, a considerable amount of work was undertaken to study the shelf life of charcoal. We found that it made a real difference as to whether or not the package was vented to ambient and this was traced to the loss of CO_2 by the charcoal. It could not be simply reversed by

subsequently passing CO_2 through the charcoal, but it could be considerably suppressed by storing the sample in a closed can, or by maintaining it in an atmosphere of CO_2. Once the activity was lost, it was necessary to use both heat, CO_2, and water vapor in some proper combination to recover the activity. In short, one must "activate" the charcoal.

I wish to suggest that an atmosphere of CO_2 might be maintained in the charcoal bed to prevent the loss in activity of the charcoal.

KOVACH: You are talking here about the chemisorbed surface oxides coming off the carbon?

DEITZ: The adsorption complex on activated charcoal is very complicated. On storage this complex slowly decomposes into CO_2 and water.

KOVACH: I think some people will go along with CO_2 here as long as it doesn't have any methane in it.

KRATEL: I have a question for Mr. Milham. You give the desorption data after a period of use of four months and you compare these data with desorption data obtained from fresh charcoal. Are desorption data available for a period of one week or a couple of days because such data would be more reliable for comparison?

MILHAM: Our data is obtained from samples of the carbon beds used in the plant. These samples are available only after several months of operation. The shortest service life we have tested is 22 months.

PETERSON: I have a two-part question for Mr. Ackley and Mr. Jones. It seems that taking impregnated charcoals are very efficient for adsorbing methyl iodide but I was wondering about radiated decomposition of these impregnants leading to the formation of organic iodide.

ACKLEY: (ORNL) Are you asking have we done any work on it? No, we have not.

We have proposed some, but as yet, funds have not been made available.

KOVACH: Are there any British colleagues here who would like to comment on the possibility of creating methyl iodide from the TEDA methyl iodide complex?

ABBEY: As far as I know, I am the only one from the U. K. here. So I felt I was safe in getting on my feet. So far as I know, nothing has been done on this.

KOVACH: Thanks to the discipline of the questioners we are finishing on time. We can now close the discussion on adsorbents. I would like to add one more comment. On the basis of some of the work presented here, it appears that at times we had better look and evaluate principles rather than products--at least, first the principles and then the products and make sure the particular processes which we are evaluating do work the way we say they work.