Session 7

IODINE ADSORPTION

TUESDAY: October 21, 1980
CHAIRMAN: Richard D. Rivers
American Air Filter

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P. Hayn, H.-H. Stiehl, W. Mathewes

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OPENING REMARKS OF SESSION CHAIRMAN:

John Collins' keynote address yesterday morning and Louis Kovach's review last hour are both encouraging with regard to the matter of radioiodine, or iodide, removal, in that the results of the Three Mile Island event show that we do not have as much airborne iodine as the models predicted. However, at Three Mile Island there were iodine releases and the performance was not what we would have liked. It is not at all certain that the criteria that had been established for these systems are optimum. The removal efficiency of the various filter trains at TMI ranged from 50-80%, rather than the 90-99% the quality control data would have indicated. Whatever the reasons for this level of performance, it is inadequate, and Kovach was assuredly correct when he stated that optimum impregnants probably have not yet been found. Development of proper base carbon-impregnant combinations, which bring together the best of both properties, should be one of the research goals of the future. The titles of the papers in this session intimate that a little of the future is already with us. New materials are being developed, along with continuing studies of environmental effects and evaluation methods, both in the reactor containment area and in fuel processing fields. It should be a broad-ranging and interesting session.

Activated Charcoal filters and the test canisters

P. W. Hayn, H.-H. Stiehl, W. Mathewes

1. Introduction

Long-standing experience in installations with activated carbon filters in nuclear power plants today allow - with respect to the actual knowledge of the loading process, the composition and concentration of noxious matter, and considering the commissioning and testing regulations - to determine those criteria which must be met by such filters:

1. Distribution of the activated carbon.
2. Concentration of noxious matter.
3. Utilization of the loading capacity.
4. Efficiency over long periods.
5. Even loading in the charcoal filter and in the test canister.
6. Representative sampling method of the charcoal.
7. Possibility of multiple sampling.
8. Minimum volume of waste material.

By the beginning of the aera of nuclear power, the waste volume had not been considered sufficiently (comp. lecture during the 15th DOE Nuclear Air Cleaning Conference in Boston/USA). This philosophy also affected the design of the filters, which could not really utilize the loading capacity of the activated carbon; considerable lots of excess material was deposited as radioactive waste since the supervision and control of the loading conditions of the activated carbon was insufficient.

Together with the increasing number of nuclear power plants over the whole world, the problem of waste disposal became more and more pressing; those designs of activated carbon filters became interesting which promised a better utilization of the carbon - the consequence to be expected is less waste volume.

2. Review

The first filters consisted of filter cells with charcoal poured in. The filter cells of a maximum thickness of the layers of 50 mm therefore allowed only a limited volume flow. The filter cells were arranged either horizontally or vertically and penetrated once by the air stream which was loaded with noxious matter. Due to the uncertainty in determining the loading of the carbon without checking exactly the minimum efficiency of such filters a great portion of carbon was replaced which was not loaded with noxious matter, when replacing the activated carbon (figure 1).

The next step in the development of such filters are deep bed filters, the thickness of layer of which can be adjusted to any ratio. The replacing of the activated carbon is easier and safer than in the case of cell-type installations. It should be emphasized that, although the standstill periods of such plants are longer (because of the increased use of activated carbon), the utilization - related to the cells - is not more favourable. These filters can be designed to have circular, square, or rectangular cross-sections of flow. Since these filters are designed as two-layer-filters (two separate layers which are penetrated one after the other), the concentration of noxious material can be monitored between the layers so that the second layer can be protected from undue loading with noxious matter. Once a certain concentration of noxious matter was reached behind the first layer this was replaced. The volume of waste could therefore be reduced, compared to single-layer deep bed filters. However, also this system does not allow to utilize the maximum loading capacity of the activated carbon (figure 2).

Long years of development passed by, until another type of filters could be introduced which also used the principle of two filter layers which were penetrated one after the other. The advantage, compared to the two-layer system, becomes clear when considering the way of exchanging the activated carbon. The first layer is removed upon a certain concentration value; this layer then is replaced by the activated carbon of the second layer. The free space, which is obtained by this process, is filled with fresh activated carbon. This filter system which is also designated as multi-way filter, can better utilize the loading capacity of the activated carbon, than those systems which have been described above (figure 3).

When once more considering the loading and exchanging processes of multi-way filters, the following can be observed: A gas stream which is loaded with noxious matter penetrates a filter layer, is partly filtered, then penetrates another filter layer and is once more filtered so that it reaches the admissible clean gas concentration value. If a certain total filtering factor of both layers is underrun, the lower contaminated layer is removed and the upper - partly contaminated - layer replaces the removed layer of sorption material. This part of the layer then is exposed to another loading process. The sorption material involved is therefore loaded more than it would have been when being removed immediately.

To avoid unevenness of the layer of activated carbon, this is condensed in a mechanical process. Because of the construction height of the filter, the lower sections of the filter layers are exposed to a somewhat higher stress than the sections above which can cause a certain unevenness of the penetration and of the loading with noxious matter.

3. Development

The uneven density of the activated carbon does not become relevant if same conditions prevail at any point of the cross-section of flow which can be obtained by appropriate arrangement of the filter layer and by the determination of the direction of flow. This condition is fulfilled if the filter layers are arranged horizontally and if vertical gas stream is given. In this case, two directions of flow are possible:

1. Flow from bottom to top.
2. Flow from top to bottom.

In the first case, that layer which is most loaded with noxious matter is on the top of the filter layer. Replacing the filter layer upon reaching the maximum admissible filtering factor means that similar to the deep bed filter the whole filter layer would have to be replaced. The utilization rate of the activated carbon involved is not different in such case from that of a deep bed filter with vertical filter layer.

In the second case, however, the sorption material which is penetrated first is on the bottom. If the maximum loading capacity of the activated carbon has been reached in the bottom section of the filter layer, without underrunning the total precipitation factor of the filter, this part of the layer can be removed from the filter by letting off. If it can be guaranted that the gas stream which penetrates the filter layer does not whirl up the filter layer in the vicinity of the gas outlet, almost homogenous conditions can be obtained over the whole cross-section of the filter. Filters of this design allow to consider only a part of the filter material as waste which can be loaded with noxious matter until reaching the limits of its loading capacity. This allows a further reduction of the waste volume and of the activated carbon involved.

Picture 4 shows a filter of the described design. It becomes clear that the gas stream enters the layer of the activated carbon from the bottom, that it is distributed over the cross-section by means of roof-shaped inlet orifices, and that it leaves the filter through lozenge shaped outlet orifices within the layer. The arrangement and shape of the outlet orifices ensures that whirling effects of the activated carbon cannot occur during operation and after letting off parts of the layer. The activated carbon above the outlet orifices has been provided as reserve material, which is not penetrated - it is not involved in the filtering process - and its quantity allows for a twice partial letting off of the filter layer without replacing carbon. The material is let off by operating the gates which are arranged below the roof-shaped inlet orifices. The activated carbon then falls into the container below. The air inlet orifice cannot - due to its position - be obstructed by the activated carbon which has been let off. The geometrical design of the components of this filter ensures that, during the process of letting off, the carbon moves downwards with parallel faces.

4. Sampling

Precise data on the loading conditions is an absolute prerequisite for the determining of the loading of the layer of activated carbon with noxious matter. In the case of deep bed filters, test filters are provided in parallel with the filters; these test filters are periodically removed from the air stream and the loading conditions of the activated carbon tested in a laboratory. The provision of several of such test filters arranged in parallel which are tested in differerent intervals after the commissioning allows to draw the time curve of the precipitation factor and to determine the time for replacing the activated carbon.

Problems in the layout of such test filters cause misinterpretations of the actual loading conditions of the carbon in the main filter. This was often the reason for insufficient utilization of the sorption material in the main filter. Numerous investigations and sampling processes revealed that the same residence times must be provided for the test and main filters to precisely estimate the loading conditions.

This requires that the parallel test filters must be provided with measuring and control devices to align the test filters with the conditions of the main filter.

5. Standard type

The picture 5 show the construction of a test filter. This picture makes clear that the filter consists of two chambers of equal dimensions the size of which can be adjusted by strainers. On the one side, a volume stream measuring device in the form of a measuring screen has been provided, on the other side an adjustable choke to adjust the volume stream. Both measuring devices together allow to determine the residence time of the test filter and to adjust it to the residence time of the main filter. At present, the test filter of this design is a standard filter which is used in German installations for monitoring of deep bed filters.

6. New design

By-pass filter arrangements of the type described before cannot be provided for filters with filter layers changing during operation. It must be guaranteed with such filters that test material is available which has the actual loading conditions of the main filter. The exact information on the loading conditions of the activated carbon is obtained if the carbon is taken directly from the filter bed of the main filter.

In the case of the fluidised bed filter described, specimen are taken directly from the filter bed at different points - over the thickness of the layer - by means of a probe. The design of the spindle guarantees that, when taking the specimen, the layer above the spindle moves downwards with parallel faces. The slim contour of the spindle does not affect negatively the streaming process. The taken volume of activated carbon for one test corresponds to the volume of the spindle. Remote layers are not taken and do not influence the result of the test. The filter which has been described last, and the sampling method shall be tested, in the near future, in a power plant under operating conditions (figure 6).

7. Summary

Activated carbon filters are used with succes for adsorption of radioactive fission products in nuclear power stations. The designs known hitherto utilize the activated carbon with varying efficiency. New filter designs give good results of efficiency of the carbon used; a reduction of waste volume is possible compared to older filter designs.

Good utilisation of the loading capacity of the activated carbon can only be reached by close supervision and determination of its loading condition. The test adsorbers arranged in parallel and used on deep bed filters cannot be used for the fluidized bed carbon filter; on the latter carbon is sampled from the main filter for testing purpose by means of a spindel.

Safest adsorption of radioactive fission products is realized by using deep bed filters as on these the poisening phenomina of the activated carbon on the efficiency have little influence only.

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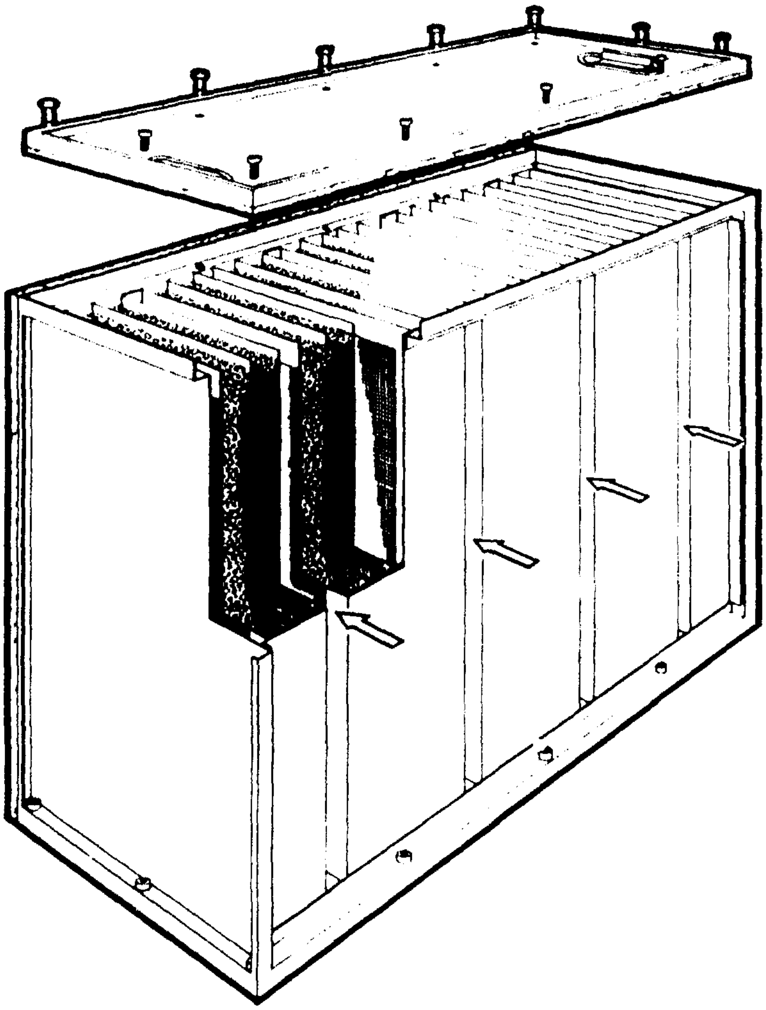


Figure 1 DELBAG filter cell with replaceable activated carbon layer, layer depth 50 mm

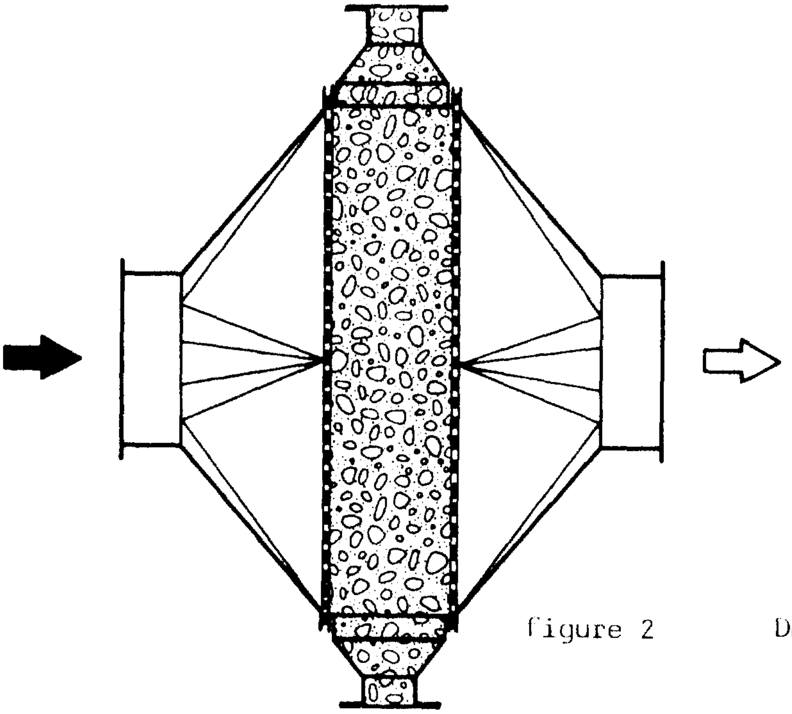


figure 2 Deep bed filter

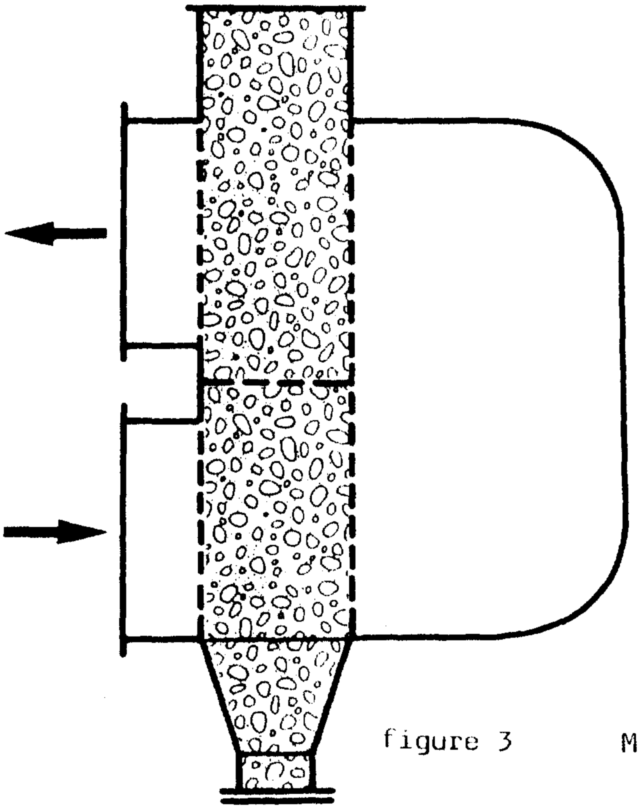


figure 3 Multi-way filter

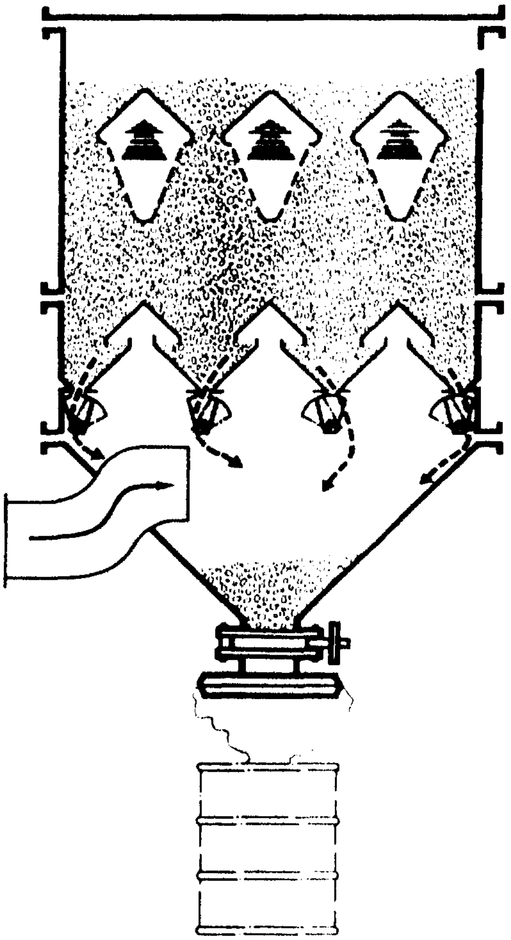
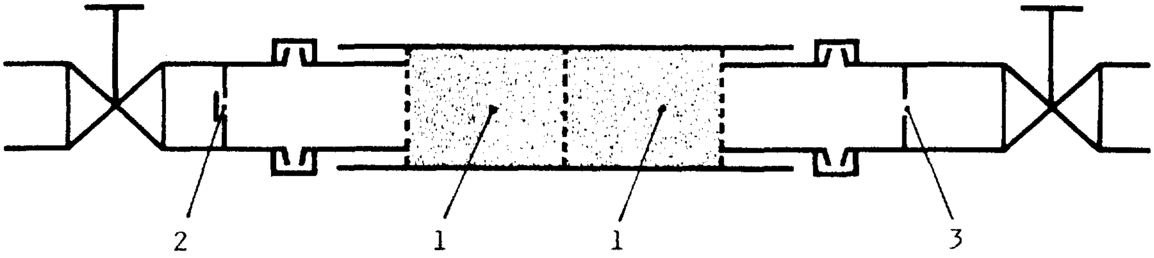


figure 4 Multi layer deep bed adsorptions filter operating-principle



1. Chamber
2. Adjustable choke
3. Orifice

figure 5 Sampling-adsorbent (bypass) for sorption-material

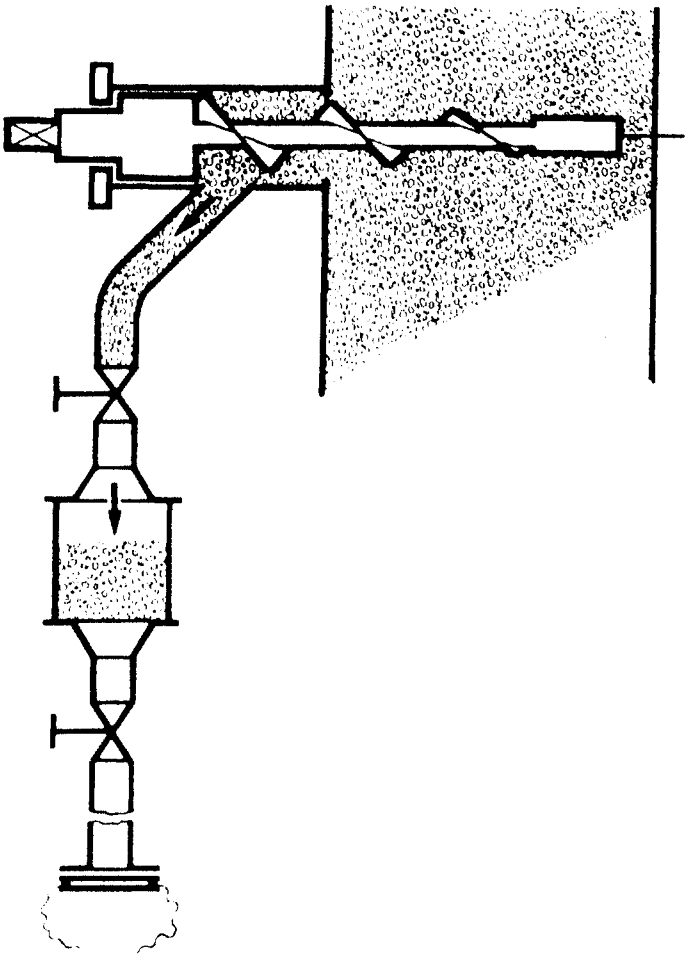


Figure 6 Sampling-device for sorption-material

DISCUSSION

RIVERS: Airflow appears to be able to leak in a number of regions, according to the figures you showed.

HAYN: It is sealed in the actual configuration, but it just does not appear so in the schematic diagrams I showed.

NONRADIOMETRIC AND RADIOMETRIC TESTING OF RADIOIODINE SORBENTS USING METHYL IODIDE*

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Abstract

A nonradiometric test of adsorbents and adsorbers with normal methyl iodide ($CH_3\,^{127}I$) is desirable. Use of methyl radioiodide ($CH_3\,^{131}I$) requires special precautions and facilities and results in bed contamination. However, first it must be established to what extent the removal of $CH_3\,^{127}I$ by adsorbents is indicative of the removal of $CH_3\,^{131}I$.

An experimental apparatus was built and used to simultaneously measure the penetrations of CH_3I molecules and the radioisotope in $CH_3\,^{131}I$ through charcoal adsorbent beds. Gas chromatography with electron capture detection was used to measure CH_3I. Radioiodine was measured using charcoal traps within NaI scintillation well crystals. Real time (5-min interval) radioiodine measurement provided immediate penetration results directly comparable to the real time penetrations of methyl iodide.

These penetrations were compared for typical charcoal adsorbents with these impregnants: a) 5% KI_3, b) 5% KI_3 + 2% TEDA, c) 5% TEDA, and d) metal salts (Whetlerite). Differences between CH_3I and $CH_3\,^{131}I$ penetrations observed for the two iodized charcoals were attributed to isotope exchange reactions. Equivalent penetrations were observed for non-iodized adsorbents and for iodized ones at initial time. First order rates were confirmed for reactions with TEDA and for isotope exchange. This was one more confirmation of the lack of a challenge concentration effect on efficiencies at low test bed loadings. In addition to other removal mechanisms, reversible physical adsorption was observed with all charcoals.

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I. Introduction

Testing of radioiodine adsorbents and adsorbers with nonradiometric vapors has several advantages. The test agents have lower toxicity, requiring fewer handling precautions, fewer special facilities, and no licensing for field use. Their use allows more frequent tests due to lower cost of the test agent. There is no radioactive contamination of the test bed and no release of radioactive vapor in the bed effluent.

One such nonradiometric test in current use is the in-place leak test of adsorber stages using a refrigerant tracer gas (Freon) and one or two gas chromatographs with electron capture detectors.(1) This procedure gives penetrations which are extrapolated to zero test time. An unusually high initial penetration value (>0.05%) indicates the need to locate and repair a leak and retest. Another example is the carbon tetrachloride activity test performed on activated carbon base materials to determine their surface areas and degrees of activation.(2)

Every compound has its distinctive adsorption or reactive behavior with a given adsorbent. Therefore, the most useful tests of removal efficiency involve the same vapor to be trapped. Radioiodine (^{131}I) tagged elemental iodine (I_2) and methyl iodide (CH_3I) are used for laboratory measurements of adsorbent efficiencies and retentions(3,4) and for in-place testing of adsorber banks.(5) These radioiodine species are the major vapor forms of ^{131}I identified in nuclear environments. Very sensitive measurements due to the high specific activity of ^{131}I allow determinations of small penetrations using small amounts of radioiodine vapors. A total efficiency value is obtained by an established test procedure involving bed humidification, loading, and elution for predetermined periods and conditions.

From time-to-time the possibility of using normal iodine (^{127}I) vapor species for efficiency testing has been proposed. Two papers at the 15th DOE Nuclear Air Cleaning Conference reported preliminary efforts at defining the usefulness of normal methyl iodide for this application. One paper by Wood, et al., showed experimental breakthrough curves due to methyl iodide loading on several types of charcoal adsorbents.(6) Effects of relative humidity, challenge vapor concentration, and linear velocity of air on breakthrough times were demonstrated. In retrospect, the breakthrough times were measures of bed capacities, rather than of efficiencies that are more appropriate to the negligible bed loadings usually expected for radioiodine. However, these results did point out that the total methyl iodide loading ($CH_3\,^{131}I$ + $CH_3\,^{127}I$) and not just the loadings of $CH_3\,^{131}I$ can affect the efficiency of an adsorbent.

The paper by Romans and Dietz(7) compared $CH_3\,^{131}I$ and $CH_3\,^{127}I$ penetrations using conditions representative of those in the RDT M16-1T standard test procedure. Good agreement was found between 2-h accumulated penetrations determined using $CH_3\,^{127}I$

and $CH_3\,^{131}I$ in separate tests. Penetrations agreed within a factor of 3 for a charcoal impregnated with KI_x and within a factor of 4 for a charcoal impregnated with KIO_3 + KI + K_3PO_4 + HMTA (hexamethylenetetramine). A more detailed report of this work has been published recently.(8)

A recent paper by Jonas, Dietz, and Romans contained additional data on a charcoal with the latter set of four impregnants.(9) Five tests with methyl radioiodide at three laboratories for 95% relative humidity and 16 h prehumidification resulted in an average penetration of 0.26% with a standard deviation of 0.16%. Measurements were again made under RDT M16-1T specifications. This average corresponds to a first order adsorption rate constant of 24 s^{-1}. In the one experiment using normal methyl iodide under similar conditions (16 h prehumidification at 90% relative humidity) an adsorption rate constant of 28 s^{-1} (1693 min^{-1}) was reported.

The agreements in these penetration and rate constant results are encouraging for using normal methyl iodide to indicate efficiency for methyl radioiodide. However, on deeper reflection, they are also puzzling. These adsorbents contain normal iodine in various forms to remove radioiodine by isotope exchange:

$$CH_3\,^{131}I + \underset{\text{(on adsorbent)}}{^{127}I} = CH_3\,^{127}I + \underset{\text{(on adsorbent)}}{^{131}I}$$

The normal methyl iodide formed is either trapped by another mechanism or passes out of the bed. Only if the isotope exchange rate is insignificant would equivalent removal efficiencies be expected for $CH_3\,^{131}I$ and $CH_3\,^{127}I$.

In an attempt to resolve this problem we have made extensive comparisons of $CH_3\,^{131}I$ and $CH_3\,^{127}I$ penetrations through test beds of four variously impregnated charcoals. The basic question addressed was: to what extent is the removal of methyl iodide by an impregnated charcoal indicative of the removal of methyl radioiodide?

II. Experimental Details

An experimental apparatus was constructed for periodic and simultaneous measurements of penetrations of both total methyl iodide (CH_3I) and methyl radioiodide ($CH_3\,^{131}I$) through test beds. Its components and design are shown in Figure 1. Compressed air was cleaned, filtered, regulated, and humidified before entering a 2.4-cm-i.d. glass flow system inside a glove box. An electronic mass flow meter (Datametrics 800-L) which monitored airflow was periodically checked using a dry test meter (Singer DTM-325) at the test bed location. Humidification was accomplished by passing air through the headspace over a heated water reservoir. A humidity monitor/controller (Phys-Chemical Research Corp.), which controlled water heating, was calibrated with a dew point hygrometer (EG&G 911) at the test bed location.

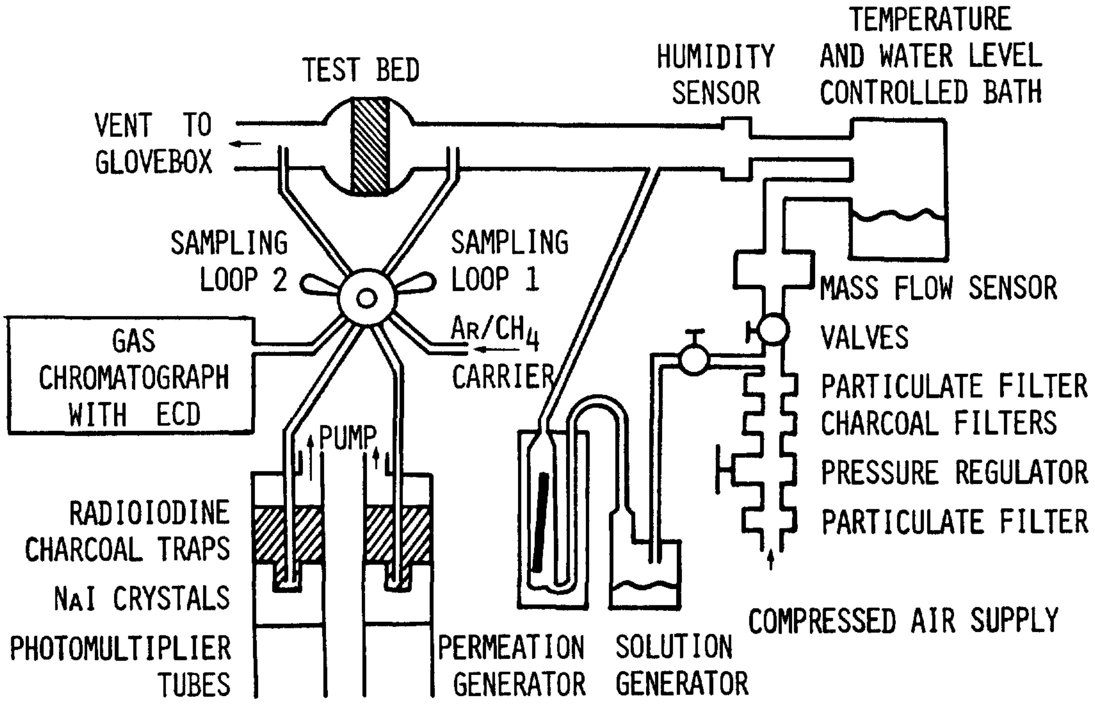

FIGURE 1

APPARATUS FOR SIMULTANEOUS CH_3I AND $CH_3{}^{131}I$ BED PENETRATION MEASUREMENTS

<u>$CH_3{}^{127}I$ + $CH_3{}^{131}I$ Vapor Generation</u>

Vapors for challenging test beds were generated in two ways: (1) Liquid methyl iodide containing $CH_3{}^{131}I$ was released at a steady rate by permeation through the walls of a sealed Teflon tube into a 500 cm^3/min airflow. Permeation rate was regulated by temperature control (25 - 76°C, ± 0.1°C) of the permeation tube in a Calibration System (Analytical Instrument Development, Inc., Model 303). The methyl iodide-radioiodide was ordered as 5mCi ^{131}I in 3 mL total CH_3I (ICN Chemical and Radioisotope Division, Irvine, CA). Two milliliters were used to fill a permeation tube. (2) Alternately, methyl iodide containing $CH_3{}^{131}I$ was generated from an aqueous solution. A syringe was used to inject 2 mL of solution (0.1% CH_3I in distilled water) into 100 mL of water in a glass container. The volatile methyl iodides in the stirred solution entered the headspace and were swept by 500 cm^3/min of air into the main airflow. These two generation methods represent two different situations in which radioiodine adsorbers are used. The steady, low level release of CH_3I from a permeation tube is typical of routine air cleaning situations. Generation from solution produces a spike of CH_3I concentration which drops exponentially with time, typical of an accidental radioiodine release.

Methyl Iodide Detectors

The detector for total methyl iodide was a gas chromatograph (Varian 1520) with a linearized ^{63}Ni electron capture detector (Tracor Instruments). Air from upstream and downstream of the test bed was drawn at 800 cm^3/min through matched Teflon sampling loops attached to a 10-port valve (Valco Instrument Co.) of Hastalloy-C (for inertness). This valve was pneumatically actuated by a digital valve sequence programmer (Valco Instrument Co.) to alternately inject the upstream and downstream air at 2.5-min intervals. The chromatographic column was 1.8-m x 4-mm-i.d. glass packed with 15% OV-7 on 100/120-mesh Chromosorb G. Operating conditions were 100°C and 20 cm^3/min 19:1 $Ar:CH_4$ carrier gas. An electronic peak integrator (Spectra Physics Minigrator) quantitated the methyl iodide peaks and recorded elapsed times. Calibrations used CH_3I permeation tubes whose outputs were determined by periodic weighings.

Methyl Radioiodide Detectors

The radiometric detectors collected and measured ^{131}I from the 800 cm^3/min air samples passing through the gas chromatograph sampling valve. Figure 1 shows the charcoal traps and 7.6-cm diam x 7.6-cm-thick NaI (Tl) well-type (52-mm deep x 29-mm-diam) scintillation crystals with integral photomultiplier tubes (Harshaw Chemical Co.). High-efficiency charcoal was used (5% TEDA impregnated Barnebey-Cheney CN 2762). The majority of radioiodine was collected at the bottom of the well, resulting in good detection efficiencies ($\sim$0.5) for the 0.364 MeV gamma-ray.(10) Each detector for upstream and downstream air had its own preamplifier, amplifier, single-channel analyzer, and counter (all from Ortec). They shared the power bin (Ortec), high voltage power supply (Canberra), timer (Ortec), and printer (Ortec). Linear-log rate meters (Mech-Tronics) were used for count rate monitoring. Detector counts were taken for 5-min intervals and printed together. Each detector trap and crystal was shielded by 5 cm of lead to reduce background counts. Fresh charcoal was placed in the detector traps for background counts before each new bed was tested. The detectors were calibrated almost daily for relative sensitivities by sampling the same radioiodine-containing air.

Test Beds

Charcoal test beds of selected depths were packed into 2.4-cm-i.d. glass tubing. The usual airflow rate was 1.8 L/min, which corresponds to 6.6 cm/s linear velocity and 0.75 s residence time for a 5-cm-deep bed. This residence time is three times that specified in the standard radioiodine test method.(3) However, this difference will not qualitatively affect the conclusions reached in this paper. Charcoals for testing were taken from air-purifying respirator canisters. Impregnations of the 8-16 mesh range charcoals were identified by the manufacturers (MSA = Mine Safety Applicances Company, Pittsburgh, PA; and Scott = Scott Health/ Safety Products, South Haven, MI) as given in Table I.

Table I. Experimental Charcoals

Canister		Charcoal Impregnants (Weight Percents)
Source	Designation	
MSA	GMR-I	5% KI_3 [a]
MSA	GMR-I[b]	5% KI_3 + 2% TEDA[c]
MSA	GMR-S	Metal and Ammonium Salts[d]
Scott	600252-75	5% TEDA

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[a] KI_3 = equal amounts of KI and I_2

[b] Canisters manufactured after July, 1979, through at least April 1980.

[c] TEDA = triethylenediamine, $N(CH_2CH_2)_3N$

[d] Whetlerite charcoal

III. Results: Iodized Charcoal without Amine Impregnant

Comparisons of CH_3I and $CH_3{}^{131}I$ Penetrations

To illustrate the type of results that were observed in 17 experiments with 5% KI_3-impregnated charcoal, we will first consider one test conducted under the following conditions:

3.75 cm-depth x 2.4-cm-diam bed
1.8 L/min airflow; 6.6 cm/s; 0.57 s bed contact time
86% RH; 2-h equilibration before testing
3.8 mg/m^3 CH_3I; 0.125 μCi/m^3 ^{131}I

Cumulative $CH_3{}^{131}I$ penetrations after successive 5-min intervals were calculated from the ratios of downstream and upstream (of the test bed) decay counts, corrected for relative detector sensitivities. Instantaneous CH_3I penetrations at 5-min intervals were calculated from the ratios of peak areas obtained from downstream and upstream sampling, corrected for relative sampling loop volumes. For comparisons, cumulative CH_3I penetrations were calculated by integrating the instantaneous penetrations over time using a trapezoidal approximation. The results of these calculations are shown in Figure 2. The first observation is that cumulative CH_3I penetrations and cumulative $CH_3{}^{131}I$ penetrations were not equal except at initial experimental time (t=0). They diverged increasingly with increasing time. Secondly, instantaneous CH_3I penetration began to exceed 100% at 88 min due to desorption of previously adsorbed vapor. At this same time instantaneous $CH_3{}^{131}I$ penetration was only 11%.

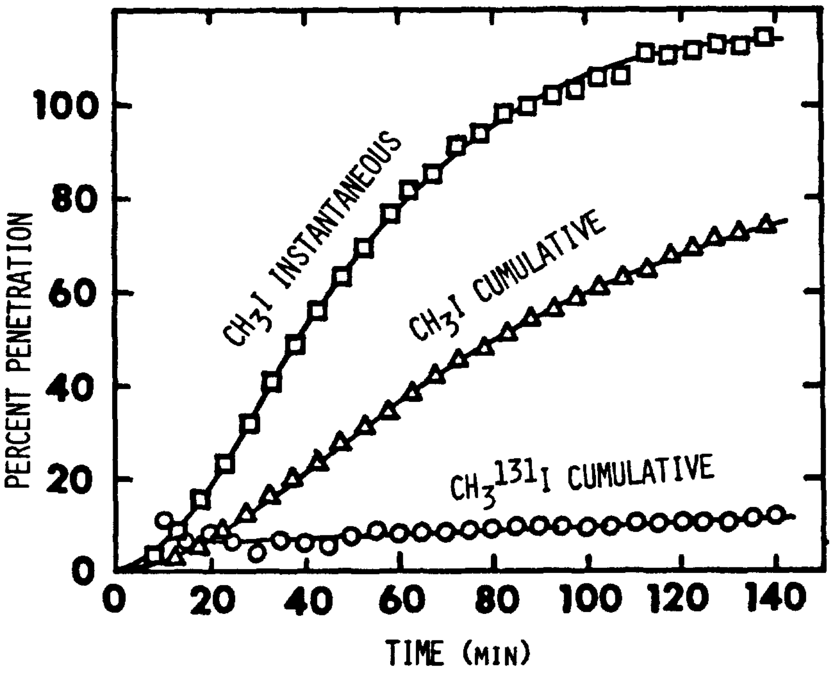

FIGURE 2

COMPARISONS OF PENETRATIONS FOR A TEST OF AN IODIZED (ONLY) KI_3 CHARCOAL

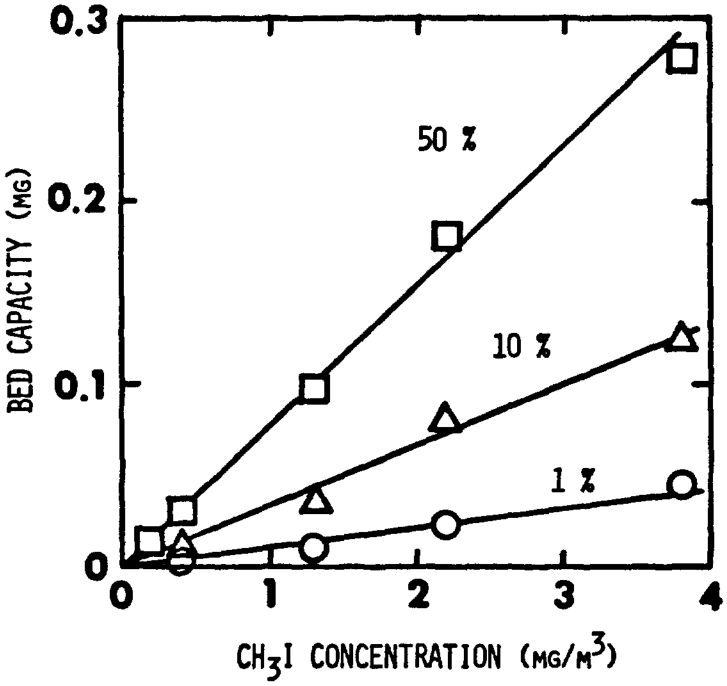

FIGURE 3

DYNAMIC ADSORPTION ISOTHERMS AT THREE INSTANTANEOUS PENETRATION PERCENTS FOR METHYL IODIDE AND THE KI_3 CHARCOAL

Effects of Challenge Concentrations

Five tests were made at the above conditions but with different challenge concentrations of CH_3I (0.19 - 3.78 mg/m^3) and $CH_3{}^{131}I$ (0.0061 - 0.125 μCi/m^3) varying over a factor of 20. Breakthrough times (t_B) for 1%, 10%, and 50% instantaneous penetrations were nearly the same for all challenge concentrations (Table II). Individual breakthrough times were used to calculate the breakthrough capacities (t_B C_o) plotted vs. challenge concentrations in Figure 3. The linearity of these plots indicates that CH_3I adsorption and desorption occurred according to a simple linear isotherm (Henry's law). Other charcoals which have been tested with CH_3I have not indicated linear isotherms.

Table II. Effects of Challenge Concentrations

CH_3I				$CH_3{}^{131}I$	
Conc.	Breakthrough Times (min)			Conc.	Percent
(mg/m^3)	$t_{1\%}$	$t_{10\%}$	$t_{50\%}$	(nCi/m^3)	Penetration[a]
0.19	6.8	18.0	39.6	6.1	12.3
0.41	2.4	14.7	41.5	13.6	16.0
1.29	3.8	15.4	41.8	42.6	9.7
2.19	7.4	20.5	45.8	72.3	15.4
3.78	3.4	15.1	38.7	124.7	11.5
Average	4.8	16.7	41.5	Average	13.0
Std. Dev.	2.2	2.5	2.7	Std. Dev.	2.7

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[a] Average instantaneous penetration after the initial period in which physical adsorption was significant.

The Wheeler adsorption equation predicts the logarithm of penetration as a linear function of time for low penetrations (< 15%), and such plots have been reported for CH_3I.(9) Other published data do not show this semilog relationship.(6) The penetration curves for the experiments reported here with the iodized charcoal consistently fit the Statistical Moments Theory (SMT) equations(6) and an empirical exponential $C/C_o = at^b$ equation better than the Wheeler equation. For example, four data sets from Figure 2 where penetrations were less than 15% yielded the correlations in Table III.

The consistent failure of the Wheeler equation to give the best fit of penetration results from many experiments brings to question its use in extrapolating to define initial penetration. However, it will always give a conservative (higher) initial value relative to the true one due to the curvature of the breakthrough curve. For this example, the Wheeler equation gave an initial penetration value of 0.33% (std dev = 0.18%) to be compared with the SMT initial value of 0.094%. One of the best fits of the breakthrough curves was for a $(C/C_o) = at^b$ empirical equation which has three difficulties: (1) It has no theoretical basis. (2) It does not allow extrapolation

Table III. Fits of Penetration Data to Equations

2 Equation		Linear Correlation Coefficient, r
Wheeler:	$\ln(C/C_O) = \ln a + b\ t_B$	0.9256
Exponential:	$\ln(C/C_O) = \ln a + b \ln t_B$	0.9999
SMT:	$\frac{t_B - m_1 + m_3/6m_2}{X_B} = -\sqrt{m_2} + \frac{m_3}{6m_2} X_B$	0.9999

of penetration to initial test time. (3) Extrapolated values vary rapidly at short times; for this example, 0.020% at 0.5 min, 0.073% at 1 min, and 0.265% at 2 min.

Effects of Bed Depth and Contact Time

Another series of experiments was performed in which bed depth of the KI_3 charcoal was varied from 1.25 cm to 5.0 cm for these conditions:

2.4-cm-diam bed.
1.8 L/min airflow; 6.6 cm/s linear flow velocity
86% RH; 2-h equilibration before testing
3.3 mg/m^3 CH_3I; 1.22 μCi/m^3 ^{131}I.

Ratios of cumulative CH_3I and $CH_3\ ^{131}I$ penetrations are plotted vs. time in Figure 4. These ratios increase from unity with increasing time and are larger for deeper beds. The intercept of unity resulted from physical adsorption, which is the same for $CH_3\ ^{131}I$ and $CH_3\ ^{127}I$, being the most effective removal mechanism initially. As the bed became loaded and desorption became significant, isotope exchange removal of $CH_3\ ^{131}I$, but not $CH_3\ ^{127}I$, became more important. Therefore, cumulative CH_3I penetration through an iodized charcoal such as this one, is not indicative of $CH_3\ ^{131}I$ cumulative penetration after an arbitrary period.

Average $CH_3\ ^{131}I$ penetrations were calculated for 17 experiments in which bed depths, concentrations, and linear flow velocities (6.6 - 13.3 cm/s) were varied. These are plotted vs. bed contact (t_C) time on a semilog graph in Figure 5. Bed contact time is bed depth divided by linear flow velocity. The results indicate a straight line with intercept of unity and a slope of $d \ln(C/C_O)/dt_C = -3.62\ s^{-1}$(std dev = 0.27 s^{-1}). These results indicate that $CH_3\ ^{131}I$ removal is by a simple first order reaction with a rate coefficient of 3.62 s^{-1}. Such kinetics are also confirmed by the lack of concentration dependence previously discussed above. The removal reaction must be isotope exchange, since total CH_3I is being removed much less efficiently.

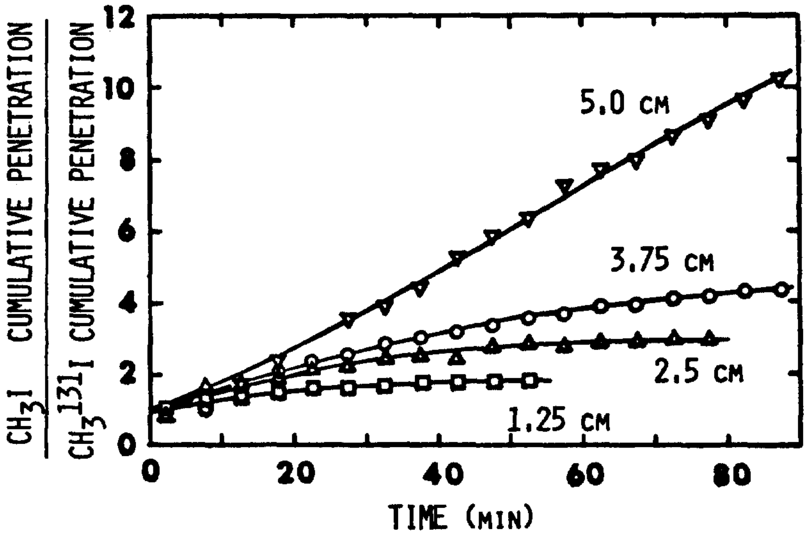

FIGURE 4

RATIOS OF $CH_3{}^{131}I$ AND CH_3I PENETRATIONS FOR FOUR DEPTHS OF AN IODIZED (ONLY) KI_3 CHARCOAL

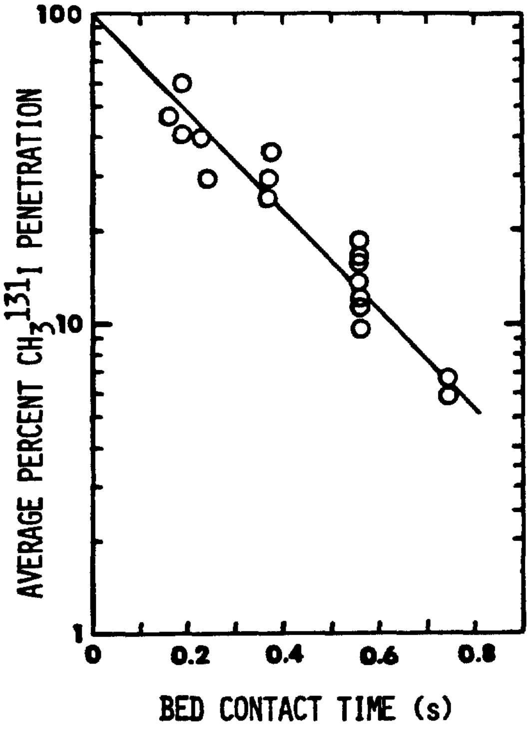

FIGURE 5

FIRST ORDER RATE PLOT FOR $CH_3{}^{131}I$ PENETRATION THROUGH IODIZED (ONLY) KI_3 CHARCOAL

IV. Results: Iodized Charcoal with Amine Impregnant

Comparisons of CH_3I and $CH_3{}^{131}I$ Penetrations

Ratios of cumulative CH_3I and $CH_3{}^{131}I$ penetrations for three bed depths of charcoal with mixed impregnants (5% KI_3, 2% TEDA) are shown in Figure 6. Experimental conditions were similar to those of the preceding section. The initial equivalence of CH_3I and $CH_3{}^{131}I$ penetrations is again attributed to physical adsorption which is the same for both species. During the first 30 min, adsorption sites become exhausted and the most efficient removal mechanisms become:

$$CH_3I + N(CH_2CH_2)_3N = N(CH_2CH_2)_3NCH_3{}^{+} I^{-}$$

for both species and

$$CH_3{}^{131}I + {}^{127}I^{-} = CH_3{}^{127}I + {}^{131}I^{-}$$

for methyl radioiodide only.

Effects of Bed Depth and Contact Time

Constant penetrations of CH_3I and $CH_3{}^{131}I$ after the initial physical adsorption period were averaged. Figure 7 shows semilog plots vs. residence time and bed depth (top scale). Again, straight lines with intercepts of unity resulted. The first order rate coefficient for total CH_3I removal by reaction with TEDA was 2.97 s^{-1} (std dev = 0.12). The one for $CH_3{}^{131}I$ removal was 4.88 s^{-1} (std dev = 0.15). The difference between these two values, 1.90 s^{-1}, must be the first order rate coefficient for isotope exchange.

V. Results: Amine (only) Impregnated Charcoal

Comparisons of CH_3I and $CH_3{}^{131}I$ Penetrations

Fourteen experiments were performed with the charcoal impregnated only with 5% TEDA. Bed depths (1.25 - 3.75 cm), relative humidities (75% or 86%), equilibration times (0 or 2 h), and generation methods (permeation tube or solution) were varied. Airflow velocity (6.6 cm/s) and bed diameter (2.4 cm) were constant. Challenge concentrations of CH_3I and $CH_3{}^{131}I$ varied widely, particularly during runs using vaporization from solution.

The penetrations of CH_3I and $CH_3{}^{131}I$ increased from zero to values constant with time. The initial period of efficient physical adsorption varied with relative humidity and period of bed equilibration prior to testing. Penetrations following the initial periods were averaged and compared in Figure 8. The plotted points

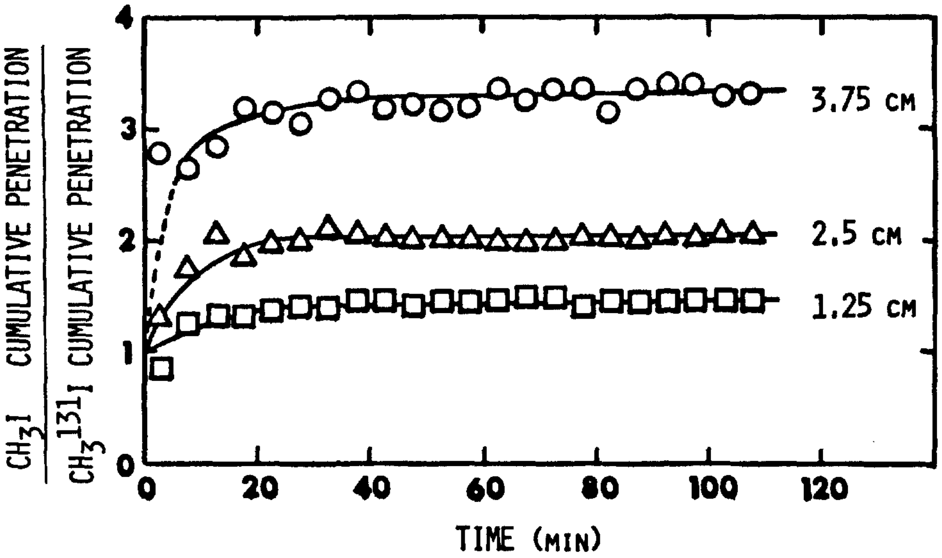

FIGURE 6

RATIOS OF $CH_3{}^{131}I$ AND CH_3I PENETRATIONS FOR THREE DEPTHS OF A MIXED IMPREGNANT (KI_3, TEDA) CHARCOAL

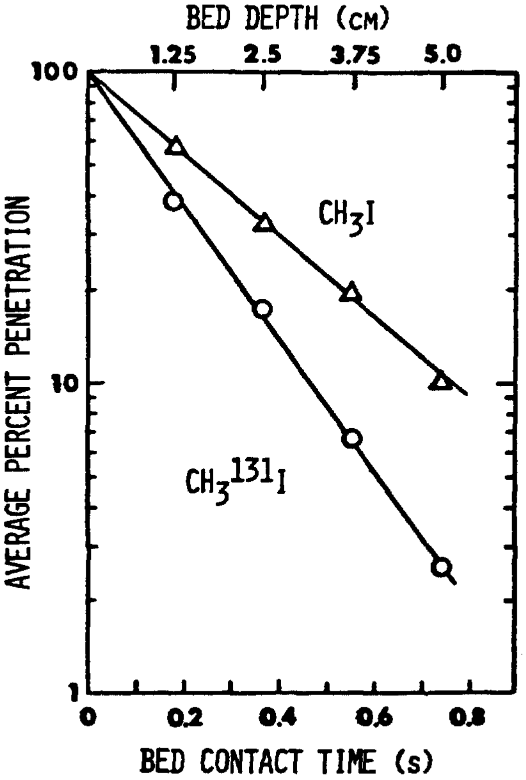

FIGURE 7

FIRST ORDER RATE PLOTS FOR $CH_3{}^{131}I$ AND CH_3I PENETRATIONS THROUGH A MIXED IMPREGNANT (KI_3, TEDA) CHARCOAL all fall close to the dashed equality line. Therefore, as expected, CH_3I and $CH_3\,^{131}I$ were removed at equal efficiencies and rates by reaction with TEDA.

Effects of Bed Depth and Contact Time

Once again, plots of ln (C/C_o) vs t_c or bed depth for both CH_3I and $CH_3\,^{131}I$ were linear with intercepts of unity. Calculated rate coefficients are given in Table IV. Within experimental uncertainties there are no differences between any of these rate coefficients.

Table IV. First Order Rate Coefficients for Removal

Species	Relative Humidity	Number of Points	Rate Coefficient (s^{-1}) Average	Std Dev
CH_3I	86	10	7.10	0.30
$CH_3\,^{131}I$	86	10	6.91	0.46
Both	86	20	7.00	0.27
CH_3I	75	4	7.44	1.27
$CH_3\,^{131}I$	75	4	7.06	0.86
Both	75	8	7.25	1.03

VI. Results: Whetlerite Charcoal

Duplicate experiments were performed with beds of Whetlerite charcoal under conditions similar to those of Section III, A., but without equilibration before testing. Instantaneous penetrations of CH_3I increased with time and even exceeded 100% as the vapor adsorbed at the beginning was displaced. This is typical of removal by physical adsorption only. Breakthrough times averaged 33 ± 3 min at 0.1%, 49 ± 6 min at 1%, and 68 ± 8 min at 10% penetrations.

Cumulative penetrations of CH_3I and $CH_3\,^{131}I$ are compared in Figure 9. The data points closely fit the equivalence line until 100% penetration, then deviate slightly in the direction of greater $CH_3\,^{131}I$ penetration. This deviation is explained as the result of forming volatile radioiodides other than $CH_3\,^{131}I$. The ^{131}I detector is not compound specific, but the GC is. Indeed, other GC peaks were observed, but not identified or quantitated.

VII. Conclusions

A. Differences between CH_3I and $CH_3\,^{131}I$ removal rates were observed for two iodized (5% KI_3) charcoals. The charcoal also containing 2% TEDA had a lower first order isotope exchange rate coefficient (1.9 s^{-1}) than the one without (3.6 s^{-1}).

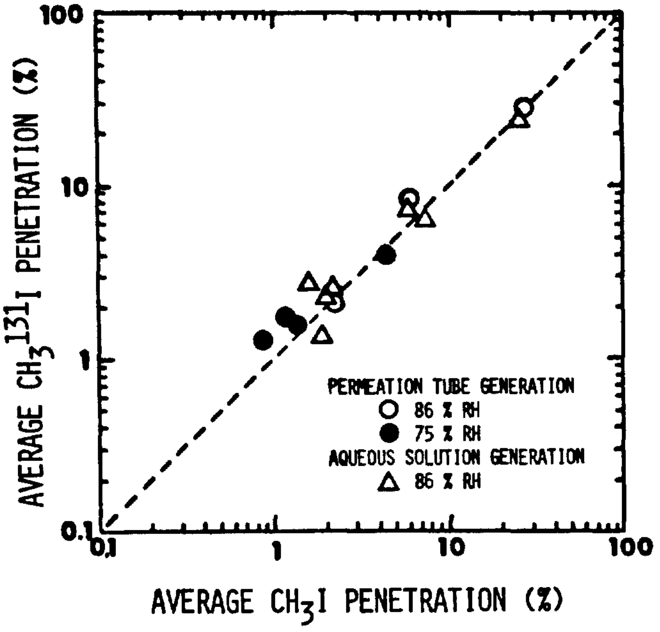

FIGURE 8

COMPARISONS OF $CH_3{}^{131}I$ AND CH_3I PENETRATIONS THROUGH BEDS OF AMINE (ONLY) IMPREGNATED CHARCOAL

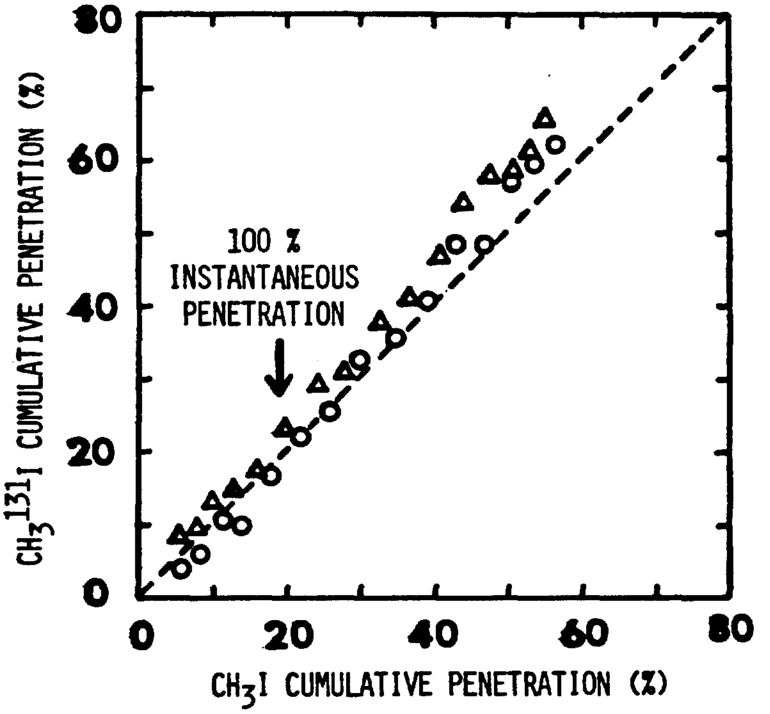

FIGURE 9

COMPARISONS OF $CH_3{}^{131}I$ AND CH_3I PENETRATIONS THROUGH BEDS OF A WHETLERITE CHARCOAL

B. Reactive trapping of CH_3I and $CH_3\,^{131}I$ was observed for two charcoals impregnated with TEDA. This was also by a first order rate mechanism with rate coefficients of 7.1 s^{-1} (5% TEDA) and 3.0 s^{-1} (2% TEDA + 5% KI_3).

C. Physical adsorption was also observed for all charcoals used. With KI_3 and/or TEDA impregnated charcoals, physical adsorption was more efficient than isotope exchange or reaction only at short times. Reversibility of physical adsorption results in cumulative penetrations approaching 100% unless these impregnants or similar ones are present.

D. CH_3I penetration is equivalent to $CH_3\,^{131}I$ penetration for

1. Iodized charcoals only at zero time;
2. Amine (only) impregnated charcoals at all times;
3. Charcoals without amine or ^{127}I impregnants at all times.

E. All experimental data indicated no effects of varying challenge concentrations on $CH_3\,^{131}I$ or CH_3I removal efficiencies by isotope exchange or TEDA reaction. The one iodized charcoal without amine showed no effect of challenge concentration on breakthrough times of CH_3I.

VIII. Applications of CH_3I as a Testing Agent

Laboratory Testing of Adsorbents

1. The efficiency of amine impregnation can be tested in the development of new sorbents, the acceptance testing of commercial ones, and the performance testing of used ones. Fewer precautions in handling and storage are required relative to the use of $CH_3\,^{131}I$. More rapid results are obtained by avoiding the need for decay counting.

2. Adsorption parameters for charcoals without amine impregnants can be determined. Methyl iodide can replace carbon tetrachloride in adsorbent qualification prior to impregnation.(2) Methyl iodide is more representative of reality than is carbon tetrachloride. The development of the breakthrough curve can be used to determine efficiency and capacity for total CH_3I ($CH_3\,^{127}I$ + $CH_3\,^{131}I$ + etc.).

3. When tagged with ^{131}I, CH_3I can be used as described above to determine the efficiency of ^{127}I impregnation for isotope exchange.

In-Place Testing of Adsorbers

1. Leak testing of installed adsorbers can be done with CH_3I as well as with the Freons currently in use.(1) The problem of the best way to extrapolate penetration to zero time must be further studied.

2. Total efficiency (adsorption plus desorption) testing of amine impregnation can be performed under actual use conditions of humidity, airflow rate, etc.

3. With iodized charcoals, as well as with amine impregnated charcoals, in-place CH_3I testing can be used to monitor the condition of adsorbers in use. Weathering and poisoning can be checked until the need for laboratory testing is indicated. This should reduce the frequency of the costly and difficult procedures of taking representative samples and laboratory testing.

X. References

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DISCUSSION

DEITZ: I would like to inquire as to the range of relative humidity during these tests.

WOOD: The relative humidities were high, at least 85% minimum and frequently up to 100%.

SIGLI: It is generally accepted that for high relative humidity, the mechanism of retention of iodine as methyl iodide is isotopic exchange. Can you explain how, if you test with non-radioactive methyl iodide on charcoal impregnated with KI_3, you can have such an isotopic exchange?

WOOD: That is right, and that is my point. You cannot measure isotopic exchange with normal methyl iodide. What you can do, is get an idea of the physical adsorption that is occurring. If you follow this over a period of time, it should give you some indication of effects such as weathering and poisoning. But it will not measure the isotopic exchange. That is the one limitation, I would say, of using normal methyl iodide.

BEHAVIOR OF GASKETLESS DEEP BED CHARCOAL FILTERS FOR RADIOIODINE REMOVAL IN LWR POWER PLANTS

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Abstract

The removal efficiency of radioiodine filters can be affected by mechanical leakage, aging and poisoning, desorption of radioiodine originally removed by the activated carbon and also by the occurrence of penetrating iodine compounds. To provide high decontamination factors only the gasketless deep bed filter type seems to be appropiate. The experience gathered and the data given in this paper are based on the surveillance testing of radioiodine filters in all German nuclear power plants and on laboratory research work which has been done over years to evaluate the operating behavior of deep bed radioiodine filters and to prove their reliability.

From the data measured it can be concluded that:

- Gasketless deep bed filters with activated carbon can be designed for extremely low leak rates resulting in a penetration of less than 0.001 %.
- Radioiodine filters with a life expectancy on the order of years in the stand by mode can be designed for a minimum removal efficiency of 99 % for organic iodine under accident conditions. The removal efficiency for elemental iodine is at least two orders of magnitude higher in laboratory tests.
- Radioiodine filters for continuous use can be designed for a minimum removal efficiency of 90 % during an operating period of more than one year.

1. Introduction

Since 1968, all filter testing in nuclear power plants within the Federal Republic of Germany has been done by the LAF of the Karlsruhe Nuclear Research Center. Testing has also been performed for a number of foreign plants. Therefore, a large body of experience and data could be compiled. Laboratory testing of the carbon for iodine removal and also in-place testing of iodine filters are normally performed with ^{131}I in the form of $CH_3{}^{131}I$ which is mixed with $CH_3{}^{127}I$.

Because there will be practically no desorption of radioactive methyliodide during in-place tests, testing and retesting of deep-bed filters can be done within short periods of time without restrictions. This could become necessary if a leak were discovered and repaired during testing. In-place testing with radioactive methyliodide on iodine filters continuously used will also give data on the performance of the carbon, because the measured penetration depends on the mechanical leak rate and the performance of the carbon under service conditions.

Gasketless deep-bed filters (GDBF) filled with impregnated activated carbon have been used for more than 20 years to remove radioiodine from the exhaust air of German nuclear power plants. Because leaks, quick aging and poisoning were often detected when cell type carbon filters were used, only iodine filters of the GDBF-type have been permitted since 1974 for exhaust air cleaning during or following emergency situations of nuclear reactors [1].

2. Behavior of deep carbon layers during continuous service in the exhaust air of a reactor building

Fig. 1 shows the penetration of deep layers of impregnated activated carbon when tested with radioactive methyliodide after 0, 4 and 10 months of continuous operation in the exhaust air of the containment of a German 1300 MW_{el} PWR(Fig.2). Also data are given in Tab. I in 2 months increments for a service life of up to 14 months.

Fig. 1 and Tab. I show the results of a quick degradation of the carbon, especially for low bed depths (for example for 5 and 10 cm in Tab. I), and irregularities in the region of high bed depths ($\geq$ 25 cm for 6 and 12 months), which may be related to recovery effects during operation. Based on Tab. I the bed depth of a layer of impregnated, activated carbon will be discussed with respect to its removal efficiency and service life.If a minimum removal efficiency of 90 % is required, a bed depth of 15 cm (0.3 s residence time) will allow only an service life of about 3 months, whereas 25 cm bed depth will give about 14 months of operation. For a minimum removal efficiency of 99 % the data are: 20 cm bed depth (0.4 s residence time) for about 2 months and 35 cm (0.7 s residence time) for about 10 months. Including the recovery between 10 and 12 months of service life, a 35 cm deep bed can be operated for about 14 months.

The poisoning with organic compounds can be seen in Fig. 3 which shows the concentration of organic compounds (mostly solvents) versus the bed depth of the carbon layer after service lifes of 2, 4 and 14 months.

After 2 months (Fig. 3a) considerable amounts of solvents with a higher volatility (like xylene and toluene) were adsorbed in the carbon layer up to about 20 cm; by contrast, compounds with a lower volatility (for example decane) were only found in the first 10 cm. After 4 months compounds with a higher volatility will have penetrated practically completely the 50 cm deep carbon layer, whereas the low-volatile compounds will be found in up to about 20 cm bed depth (Fig. 3b). After 14 months the total level of higher volatile organics shows some increase at greater bed depths, the low volatile organic compounds penetrated up to about 25 cm with a high loading in the bed sections of 5 - 10 and 10 - 15 cm (Fig. 3c). Their adsorption resulted in a gradual displacement of the higher volatile compounds. The total solvent content in the first few cm of the carbon layer decreases with time, possibly because the carbon is additionally degraded for adsorption processes by oxidation and other chemical reactions [2]. For example, the total loading in the section from 0 - 5 cm was 7 wt. % after 2 months, but only 1 % after 14 months of service life.

It may be mentioned that the samples used for the determination of the removal efficiency and gas-chromatographic measurements were aged in parallel in the PWR containment exhaust air and all samples were used only once. Therefore, no effects of earlier measurements influenced the data of samples aged over longer periods of time. For each measurement two independent samples were available. To avoid serious changes inside the carbon layer during preconditioning with wet air for the methyliodide test, the time for this operation was limited to one hour (the relative humidity during the service life and laboratory testing was roughly the same).

The results of these measurements are summarized in the following conclusions:

- The higher volatile organic compounds will penetrate also into deep carbon beds within a few months, leading to a maximum loading which depends basically on the concentration controlled adsorption-desorption equilibrium. This loading causes a reduced but relatively stable removal efficiency of the carbon in service.

- The retention time of higher volatile organic compounds on carbon is so short that the use of guard beds will not give protection for a reasonable period of time.

- To compensate for the reduced removal efficiency of carbon by higher volatile organic compounds, an increase of the bed depth of the impregnated, activated carbon is needed.

- The lower volatile organic compounds and the chemical reaction of the carbon (e.g. oxidation) will impair the removal efficiency of the carbon by processes starting mainly at the front end of the carbon layer and progressing slowly into the depth.

- A guard bed to trap lower volatile organic compounds, which could be made of non-impregnated,activated carbon, will give protection for a useful time of operation. The guard bed will give protection also with respect to chemical reactions for extended periods of time.

Because experiments 3) showed that impregnated carbon has practically the same protective effect as non-impregnated carbon for the process mentioned last, also a larger bed depth of the impregnated activated carbon may be used. Comparing both alternatives and having in mind the limited flow resistance acceptable for the guard bed plus iodine filter, the maximum time of useful filter performance will be reached only when the guard bed is also able to trap radioactive iodine compounds or when the bed depth of the iodine filter itself is extended. For comparison, in Tab. II data are given for the removal efficiencies as a function of service life for two successive test filters, each of 25 cm bed depth and filled with the same type of impregnated activated carbon (same conditions and set up as used for the data in Tab. I). The data show clearly the protective effects of the impregnated guard beds and also their additional removal efficiencies.

In a German PWR - power plant large deep-bed filter units (total volumetric flow rate 90,000 m^3/h) have been operating for about 2 years now with guard beds positioned below the iodine filter beds. The units are designed such that the impregnated carbon can first be used for iodine trapping and then inside the guard bed (multiway sorption filter 4)) to reduce the amount of carbon needed and therefore the contaminated waste.

3. Measurement of the organic compounds in the exhaust air of a PWR containment

Considering the importance of the adsorption of organic compounds on iodine filters, data should be available about their concentration in the air to be filtered. From the data given in Fig. 3a-c and Tab. I it can be concluded that the loss of removal efficiency of the carbon caused by the adsorption of lower volatile organic compounds is much larger than from those with higher volatility. Therefore, a qualitative and quantitative analysis of the organics in the exhaust air was performed. A continuously measuring gas-chromatograph was used to analyze the air upstream of the iodine filters of the PWR containment in which the carbon samplers mentioned before were aged.

The measurements were performed for a total time of 6 months with interruptions for service and calibrations and also in a period when the exhaust air flow through the filter was stopped during the refueling outage. During power operation, the whole exhaust air from the reactor containment was vented via the duct equipped with the sampling station, during refueling outage also other ducts and filters with a much higher flow rate are used; therefore the number of air changes inside the containment will be higher and the concentration of organics may be lower despite higher source terms.

The following organic compounds were measured: methylene chloride, acetone, benzene, toluene, butylacetate, ethylbenzene, xylene, nonane, decane. The time of gas-chromatographic measurements covered power operation, refueling outage and again power operation of the reactor station. The total concentrations of organic compounds in the exhaust air during power operation in the last week before refueling outage varied between 1.5 and 8 mg/m^3. During refueling outage an increase up to 34 mg/m^3 was measured which was mostly due to methylene chloride (up to 14 mg/m^3), xylene (up to 7 mg/m^3), acetone (up to 6 mg/m^3) and benzene (up to 3 mg/m^3). In the following power operation period,the concentration of all organics was higher than before the refueling outage. Peak values up to 63 mg/m^3 for the total concentration of the measured organics and often high values for methylene chloride, acetone, nonane and xylene were recorded.

To summarize, during and after refueling outage, including inspection and repair work,organic solvents were used in large amounts (e.g. as ingredients of products for cleaning, painting and leak detection). A compound with practically always high concentration (5 - 10 mg/m^3) during power operation and refueling outage was xylene. From the measurements mentioned above it can be concluded that a steep decrease of filter performance is to be expected within one or two months after refueling outage. Surveillance tests of the iodine filters should be performed within this period of time.

4. Desorption of solvents from deep bed carbon filters by hot air

From the results of the gas-chromatographic analysis of the adsorbed organic compounds and their distribution within deep carbon beds during service, it was exspected that a desorption process could restore the removal efficiency at least to a larger extent. Activated impregnated (KI_3) carbon aged and tested at high relative humidity showed improved removal efficiency for radioactive methyliodide after a few hours of sweeping with air of 90°C in some preliminary experiments. To prove the desorption effect under realistic conditions, impregnated activated carbon was aged in the PWR containment exhaust air mentioned before and desorbed. Again, two successive test filters, each of 25 cm bed depth in sections of 5 cm, were used. The aged filters were desorbed by sweeping with dry air of 90°C (linear flow velocity 50 cm/s) for 5 h. Previous experiments showed that the main weight loss of the aged carbon will occur within a time period of 5 h under the conditions used. To avoid a serious loss of organic compounds before testing, the sweep time with wet air before loading with radioactive methyliodide was limited to $\leq$ 0.5 h; therefore, the carbon beds are not in equilibrium with the H_2O vapor pressure in the sweep gas.

Data are given in Tab. III for the removal efficiencies of the desorbed filters and for filters aged in parallel, but not desorbed. The removal efficiencies of the test filters are improved by the desorption process, but are still far below the values to be expected for the new carbon. The relatively best results are measured for the second filters in series. Irreversible processes, e.g. oxidation, must have deteriorated the carbon seriously during aging and desorption. Judging the values of Tab. III, one must realise that the removal efficiency of the desorbed carbon would still decrease with increasing preconditioning periods with wet air.

In conclusion, when impregnated (KI_3) activated carbon was aged in the exhaust air of a reactor containment, only a moderate improvement by the desorption process with hot air could be detected regarding the removal efficiency for ^{131}I in the form of $CH_3{}^{131}I$. Desorption with steam was not tested because such a desorption process was not considered to be an in-place procedure which can be performed at justified expenditure on iodine filters in nuclear power plants.

5. Penetration of radioiodine through deep beds of impregnated, activated carbon

Tests were performed with deep beds consisting of new and aged carbon. The penetration of ^{131}I radioactivity was measured after a purging time of 2 and 336 h with air of 30°C and 40 % r.h. as the sweep gas. The linear flow velocity during loading and purging was 50 cm/s; ^{131}I in the form of elemental iodine was used as the test medium; the iodine concentration in air during the 1 h loading period was 1 mg/m^3, the carbon was KI_3 impregnated. Tests were performed with new and aged carbon.

Desorption of ^{131}I after conversion into organic iodine compounds (indicated by iodine species samplers) occurred within the beds of new and used carbon. The movement of the ^{131}I radioactivity resulted mainly in a flattened removal profile. The iodine desorbed from the first part of the carbon bed was nearly completely trapped by the successive carbon layers, the release of radioiodine from 25 cm deep carbon beds during the purging time of 14 d (which is equivalent to a radioactive decay of 70 % of the trapped iodine) was insignificant.

Fig. 4 shows the penetration of ^{131}I through the carbon layer of a by-pass sampler provided in an internal recirculation iodine filter of the PWR-containment, tested 1.25 y after the carbon was filled in (undisturbed layers, no mixing). The result of the movement of the ^{131}I radioactivity during the long purging period is obvious, but the decrease of total removal efficiency can be neglected for high bed depths. When new carbon is used, the effect of desorption is still lower.

The desorption experiments will be continued with different types of carbon, at higher temperatures and high relative humidity.

6. In-place tests of deep-bed iodine filters

The filters are tested regularly for leaks and performance after filling and refilling with carbon by use of radioactive methyliodide as the test medium. The measured penetration is caused by the total of mechanical leaks and an amount of the test medium which depends on the quality of the carbon 5).

In Tab. IV the results are given of all in-place tests performed since 1968 on standby iodine filters used for emergency air cleaning of the exhaust air of the annular rooms of the reactor containment. The measured penetration was normally below 0.001 %, in only three cases out of 17, a (small) leak was detected, but the penetration was so low (0.006 %, 0.003 %, 0.002 %) that the filter performance was still in accordance with 'regulations. The leaks did not depend on the special design of the iodine filters as can be seen from test results of earlier and later testing of the same filter units.

All deep-bed filters tested are designed for horizontal air flow; the carbon is arranged in a vertical layer with an excess of carbon to make up for settling. The radioactivity used for in-place testing has to be limited with respect to the environmental burden resulting from the $CH_3{}^{131}I$ discharged during testing. Therefore, the in-place tests are performed in two steps, pretesting with a small radioactivity for the detection of leaks $\geq$ 1 %, and final testing with a radioactivity normally high enough for leaks down to at least 0.001 % penetration. Because at some reactor stations only a leak rate of $\geq$ 0.01 % must be detected, the total radioactivity used was limited by regulations and a detection limit of 0.001 % could not be reached in all tests.

In-place tests on deep bed iodine filters for continuous use during normal power operation showed comparable results (Tab. V), but because of different local regulations not all such filters were tested after refilling; therefore, a complete report is not available.

The most realistic method of in-place filter testing is the measurement of the actual removal efficiency with respect to the reactor-generated radioiodine. This is possible when the radioiodine concentration in the exhaust air to be cleaned is high enough (e.g. $\geq 10^{-11}$ Ci/m^3) and meaningful when the operational conditions will not undergo many variations.

In Fig. 5 the results are given of 37 weeks of continuous testing of a deep-bed iodine filter (0.6 s residence time, activated carbon with 2.5 % KI_3) for the exhaust air of the equipment rooms of a PWR-containment. The tests were performed by measuring the radioiodine concentrations upstream and downstream of the filter using iodine species samplers [6]. The sampling periods were one week each. The measurements started two weeks after the new carbon was filled in. Most of the radioiodine reaching the iodine filter was converted into organic iodine compounds. Elemental radioiodine could be measured only upstream of the iodine filter; downstream of the filter the concentration was normally below the detection limit. Therefore, the plots given in Fig. 5 relate only to the total ^{131}I decontamination factors (elemental plus organic radioiodine concentration upstream versus organic radioiodine concentration downstream of the filter) and to decontamination factors for ^{131}I in the form of organic compounds. In the 4th week of filter operation a larger amount of primary coolant was released to the equipment rooms and the total ^{131}I concentration in the exhaust air increased from 5.4×10^{-11} (3rd week) to 1.6×10^{-9} Ci/m^3.

For total ^{131}I the decontamination factors (DF) decreased within 37 weeks from 1800 (removal efficiency $\eta = 99.944$ %) to 15.6 ($\eta = 93.7$ %) and for organic ^{131}I compounds from 1370 ($\eta = 99.927$) to 14.7 ($\eta = 93.19$ %). During the 4th week of filter operation, when the ^{131}I-concentration increased as shown before, a DF as high as 15,300 ($\eta = 99.993$ %) was measured for organic ^{131}I compounds.

Having in mind the failure potential inherent in aging and lab.-testing of by-pass samplers, the authors consider the in-place method of testing with iodine species samplers as the best test method available today. However, it is fully satisfactory for iodine filters only, which will not experience more unfavourable operational conditions during an emergency situation of the reactor station.

7. Laboratory tests of carbon from control filters

When newly filled, the deep-bed iodine filters are in-place tested for leaks and performance as shown before. In service, the performance of carbon is tested by use of so-called control filters. For this purpose, the deep-bed iodine filters are normally equipped with three control filters filled with the original carbon of the iodine filter. Care is taken that the number of air changes within the carbon volume of the iodine filter and of the control filter are the same; e.g., to compensate for differences in the flow resistance of the iodine filter and the control filter, the carbon layer in the control filter (divided by screens into at least two beds) will have a somewhat less bed depth than the main filter.

Tab. VI shows results of control filter tests for standby iodine filters which are used only in emergency situations. The air flows through these filters during testing only and due to the leak rate of the dampers. The carbon from the control filters is tested with ^{131}I in the form of $CH_3{}^{131}I$ at 30°C and at 98 - 100 or 95 % r.h. after 20 h of preconditioning. A minimum removal efficiency (η) of > 99 % was measured for each of the control filters listed in Tab. VI. (The only exception since 1968 was a control filter with η = 98.9 %. Due to an uncertain service life of the carbon (> 3 y) this figure is not included in Tab. VI.)In one case η = 99.90 % was reached after 10 months, in another case, η = 99.84 % was measured after 2 y and 1 month. Summing up, a minimum removal efficiency of > 99.9 % was measured for emergency stand-by filters in 21 out of 23 surveillance tests of aged carbon from control filters.

Some remarks may be added on the test conditions. The combination of low temperature (30°C) and extremely high relative humidity (98 - 100 %) is the most unfavourable expected. By purging with wet air during the time of preconditioning some of the organics may desorb from the carbon. Experiments showed that also long-time aged carbon samples had the lowest removal efficiencies after preconditioning with air of extremely high humidity.

In Tab. VII results are given of control filter tests for iodine filters for the exhaust air of the reactor containment. The different test conditions are due to the local conditions. To clean the exhaust air of the containment, two filter trains in parallel are provided. One of them is used continuously during power operation but no records are available to show the real operating time of a single filter train. On the basis of the data of Tab. VII it can be assumed that some filters were not used within the test periods because no decrease in the removal efficiencies was measured. In these cases (e.g. PWR No. 4, iodine filter No. 1, second operational period) the filter train in parallel must have been used permanently during the operational period indicated.

In conclusion, a removal efficiency of $\geq$ 90 % can be expected from the results given and from additional data not included in Tab.VII, for a service life of about one year. Only in one case a lower figure was measured (89.7 % after 10 months of operation). The reason may be an unusual high loading with filter poisons during refueling outage and revision.

8. General directions for the design of radioiodine filters

General directions for the design of radioiodine filters of nuclear power plants are published by the German Minister of the Interior 7).

A few recommendations in this general direction, which are of special interest within the theme of this paper, may be mentioned here.

- Iodine filters for use during and after a reactor emergency situation have to be built as gasketless deep-bed filters with a bed depth of at least 20 cm, even if the removal efficiency to be provided and the amount of excess carbon to compensate for aging would allow a smaller bed depth. (In the future, the minimum bed depth may be changed from 20 to 50 cm).

- The total amount of carbon to be provided for iodine removal has to include an excess of at least 2/3 of the amount necessary for reaching the minimum removal efficiency.

- The impregnated activated carbon should reach a minimum K-factor of 5 when tested with radioactive methyliodide at 30°C, 98 - 100 % r.h. and at the maximum linear air velocity of the original iodine filter.

$$K = \frac{\log DF}{t} ;$$

DF = decontamination factor
t = residence time

- The linear flow velocity within the original iodine filter should be in the range of 25 - 50 cm/s.

- The minimum removal efficiency for methyliodide under the most adverse conditions during or after a reactor emergency situation should be 99 % for radioiodine in form of methyliodide and 99.9 % for elemental radioiodine. (By recommendation of the German Advisory Committee on Reactor Safeguards, the permissible minimum removal efficiency for elemental radioiodine was recently increased from 99.9 to 99.99 % for the iodine filters provided to clean the exhaust air of the annulus of a PWR containment).

9. Conclusions

The following conclusions can be drawn regarding the design of reliable radioiodine filters for cleaning the exhaust air of nuclear power plants under normal and emergency conditions:

- The effects of aging and poisoning of the carbon and of the desorption of radioiodine can be limited to an acceptably low extent by the use of deep layers of activated, impregnated carbon.

- The amount of impregnated activated carbon needed for the operation of radioiodine filters above a given minimum removal efficiency and for longer operating periods decreases with increasing bed depth.

- Comparing a deep bed radioiodine filter and a filter train consisting of a prefilter of non-impregnated activated carbon in front of a radioiodine filter, the deep bed iodine filter will provide higher decontamination factors on the basis of equal flow resistance.

- Desorption of solvents from deep beds of impregnated, activated carbon with hot air as the sweep gas will give only a moderate improvement of the removal efficiency.

- Gasketless deep bed filters with activated carbon can be designed for extremely low leak rates resulting in a penetration of less than 0.001 %.

- Deep bed radioiodine filters with a life expectancy of several years in the stand-by mode can be designed for a minimum removal efficiency of 99 % for organic iodine under emergency conditions. The removal efficiency for elemental iodine is at least two orders of magnitude higher.

- Deep bed radioiodine filters for continuous use and a service life of about one year can be designed for a minimum removal efficiency of 90 % for organic iodine.

- Only deep bed radioiodine filters will provide the removal efficiencies mentioned above for operational periods acceptable both from the side of the reactor operation and safety consideration.

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7) Der Bundesminister des Inneren, Auslegungsrichtlinien und Richtwerte für Iod-Sorptionsfilter zur Abscheidung von gasförmigem Spaltiod in Kernkraftwerken (Feb. 1976).

Table I. Removal Efficiency of Impregnated Carbon as a Function of Bed Depth and Service Life in the Exhaust Air of a PWR Containment

Type of carbon : SA 1565, KI impreg., 8 - 14 mesh

Continuous air flow of 50 cm/s during service

Test conditions: Wet air of 40°C, 75 % r.h. and 50 cm/s linear velocity during 1 h of preconditioning, 1 h of loading and 1.5 h of sweeping

Test medium : $CH_3{}^{131}I + CH_3{}^{127}I$

Service life (mo.)	Removal efficiency in %									
	Residence time in s									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Bed depth in cm									
	5	10	15	20	25	30	35	40	45	50
0	93.7	99.6	99.97	99.996	99.999	++)	++)	++)	++)	++)
2	46.3 +)	86.3 +)	96.2 +)	99.3 +)	99.91 +)	99.990	99.9990	99.9999	++)	++)
4	23.3 +)	60.8 +)	86.0 +)	95.6 +)	98.7 +)	99.6	99.92	99.98	99.996	99.9990
6	16.6 +)	51.5 +)	81.1 +)	95.3 +)	99.1 +)	99.8	99.94	99.990	99.997	99.9996
8	14.5 +)	46.8 +)	71.8 +)	89.1 +)	95.4 +)	98.5	99.5	99.90	99.96	99.991
10	10.0	39.1	64.0	84.9	94.3	97.8	99.1	99.7	99.90	99.95
12	7.8	34.3	59.9	83.1	94.6	98.7	99.74	99.95	99.99	99.998
14	5.5	28.0	53.0	73.6	90.0	97.2	99.26	99.81	99.95	99.99

+) median value

++) penetration below detection limit

Table II. Removal Efficiencies of Two Successive Carbon Filters as a Function of Bed Depth and Service Life

Type of carbon : SA 1565, KI-impreg., 8 - 14 mesh

Air flow during operation: Exhaust air of a PWR containment, v_{lin} 50 cm/s

Test conditions : Wet air of 40°C, 75 % r.h., v_{lin} 50 cm/s during 1 h of preconditioning, 1 h of loading and 1.5 h of sweeping

Test medium : $CH_3{}^{131}I + CH_3{}^{127}I$

Filter-No.	Service life (mo.)	Removal efficiency in %				
		Bed depth in cm				
		5	10	15	20	25
I	0	93.7	99.6	99.97	99.996	99.999
II	0	"	"	"	"	"
I	2	46.3 +)	86.3 +)	96.2 +)	99.3 +)	99.91 +)
II	2 ++)	88.3	98.6	99.90	99.98	99.998
I	4	23.3 +)	60.8 +)	86.0 +)	95.6 +)	98.7 +)
II	4 ++)	72.6	93.8	98.5	99.7	99.92
I	6	16.6 +)	51.5 +)	81.1 +)	95.3 +)	99.1 +)
II	6 ++)	73.2	93.2	98.6	99.7	99.96
I	8	14.5 +)	46.8 +)	71.8 +)	89.1 +)	95.4 +)
II	8 ++)	66.7	90.0	97.2	99.2	99.8
I	10	10.0	39.1	64.0	84.9	94.3
II	10 ++)	61.8	85.0	94.0	97.6	99.1
I	12	7.8	34.3	59.9	83.1	94.6
II	12 ++)	76.1	95.2	99.1	99.8	99.97
I	14	5.5	28.0	53.0	73.6	90.0
II	14 ++)	72.1	92.6	98.1	99.5	99.90

+) median value

++) protected by the 25 cm guard bed of the same carbon

Table III. Regeneration of Aged Deep Bed Carbon Filters by a Desorption Process with Hot Air

Type of carbon : SA 1565, KI-impreg., 8 - 14 mesh

Air flow during aging: Exhaust air of a PWR containment, v_{lin} 50 cm/s

Test filters : Two filters in series, each with 25 cm bed depth

Desorption process : Dry air of 90°C and v_{lin} 50 cm/s as the sweep gas, duration 5 h

Test condition : Wet air of 40 or 30°C, 75 or 98 - 100 % r.h. as the sweep gas for $\leq$ 0.5 h before loading, 1 h of loading and 1.5 - 2 h of sweeping

Test medium : $CH_3{}^{131}I + CH_3{}^{127}I$

Filter		Test condition	Removal Efficiency in % +)				
No.	Condition			Bed Depth in cm			
			5	10	15	20	25
1	not desorbed	40°C, 75 % r.h.	14.3	36.3	53.9	70.3	82.8
1	desorbed	" "	19.0	47.1	69.2	83.1	91.6
2	not desorbed	" "	38.4	61.4	76.4	85.6	91.8
2	desorbed	" "	54.7	81.8	94.2	97.9	99.2
1	not desorbed	30°C, 98-100 % r.h.	10.4	21.5	32.1	44.2	50.7
1	desorbed	" "	15.5	31.6	46.0	60.4	69.7
2	not desorbed	" "	23.5	40.7	52.2	61.6	68.9
2	desorbed	" "	39.0	63.3	77.5	86.3	91.4

+) median values of two experiments

Table IV. Results of In-Place Testing of Iodine Filters for the Annulus Exhaust Air of a PWR Containment

All tests performed after filling with fresh carbon

Test medium: $CH_3{}^{131}I + CH_3{}^{127}I$

Filter-No.	Date of testing	Residence time (s)	Penetration (%)
I	April 68	approx. 1	≤ 0.0002
"	Oct. 70	" 1	0.006 +)
"	Jan. 73	" 1	0.0002
"	March 74	" 1	≤ 0.0003
"	July 76	" 1	≤ 0.0002
"	Aug. 78	" 1	≤ 0.0004
II	June 74	" 1	0.003 +)
"	March 75	" 1.3	≤ 0.0003
"	Oct. 78	" 1.4	≤ 0.003 ++)
III	Dec. 75	" 1.1	≤ 0.0002
"	June 79	" 1.1	≤ 0.0005
IV	July 71	" 1	≤ 0.0004
"	Sept. 73	" 1	0.0003
"	June 75	" 1	0.002 +)
"	May 77	" 1	≤ 0.0006
"	April 78	" 1	≤ 0.0007
"	June 78	" 1	≤ 0.0016 ++)
V	April 76	" 1	≤ 0.0003
"	Aug. 78	" 1.2	0.0005
VI	Oct. 76	" 1.2	≤ 0.007 ++)
"	April 79	" 1.2	≤ 0.002 ++)

+) Leak, penetration still in accordance with regulations.

++) Low radioactivity of test medium (limited by regulations)

Table V. Results of In-Place Testing of Iodine Filters for the Containment Exhaust Air of a PWR

All tests are performed after filling with fresh carbon

Test medium: $CH_3{}^{131}I + CH_3{}^{127}I$

PWR No.	Filter- +) No.	Date of testing	Residence time (s)	Penetration (%)
4	1	April 78	approx. 2.5	$\leq$ 0.0004
	1	May 79	" 1.3	$\leq$ 0.0008
	1	June 80	" 2.3	$\leq$ 0.0006
	2	April 78	" 2.5	$\leq$ 0.0007
	2	May 79	" 1.5	$\leq$ 0.0006
	2	June 80	" 2.3	$\leq$ 0.0006
5	1	Nov. 77	" 1.0	$\leq$ 0.0003
	1	July 79	" 1.3	$\leq$ 0.0008
	1	March 80	" 1.3	$\leq$ 0.0007
	1	Aug. 80	" 1.3	$\leq$ 0.0005
	2	Nov. 77	" 1.0	$\leq$ 0.0003
	2	Aug. 78	" 1.3	0.0014 ++)
	2	March 80	" 1.5	0.0012 ++)
6	1	April 79	" 0.6	$\leq$ 0.0028
	1	March 80	" 0.6	0.046 ++)
	2	April 79	" 0.6	$\leq$ 0.0029
	2	March 80	" 0.6	$\leq$ 0.0057

+) two filter trains in parallel.

++) Leak, penetration still in accordance with regulations

Table VI. Results of Laboratory Tests of Impregnated Carbon from Control Filters (representative of the stand by iodine filters of the PWR annulus exhaust air)

Test conditions: Residence time and bed depth during testing similar to original filter unit.
Wet air of 30°C and 98-100 % r.h. during 20 h of preconditioning, 1 h of loading and 2 h of sweeping

Test medium : $CH_3{}^{131}I + CH_3{}^{127}I$ + samples of carbon directly removed from filter ++ samples tested at 95 % r.h.

PWR No.	Residence time (s)	Typ of carbon	Fresh carbon	1. Control filter		2. control filter		3. control filter	
			η (%)	Time aged (mo.)	η (%)	Time aged (mo.)	η (%)	Time aged (mo.)	η (%)
1	1.0	Pellets, KI 2 mm Ø	> 99.99	10	99.961 +)	21	99.983 +)	33	99.949 +)
1	1.0	SS 207 B, KI 5-10 mesh	> 99.999	8	>99.999	-	-	-	-
2	1.0	Pellets, KI 1.3-2 mm Ø	> 99.9999	11	>99.9999	22	>99.9999	-	-
3	1.1	SS 207 B, KI 8-12 mesh	99.99992	4	>99.9999	13	>99.9999	26	>99.999
3	1.1	Pellets, KI 1.3 mm Ø	> 99.999	15	99.9946	-	-	-	-
4	1.0	Pellets, KI 2 mm Ø	99.998	11	99.96	———	carbon exchanged		———
4	1.0	"	99.965	6	99.948	———	carbon exchanged		———
4	1.0	SS 207 B, KI 5-10 mesh	> 99.999	7	99.9991	15	99.988	22	99.990
5	1.0	Pellets, KI 2 mm Ø	99.993	10	99.90	———	carbon exchanged		———
5	1.0	SS 207 B, KI 5-10 mesh	> 99.9999	11	>99.999	24	99.9961	-	-
6	1.1	SS 207 B, KI 8-12 mesh	> 99.9999++	7	>99.999++	19	99.961++	25	99.84++
6	1.1	"	> 99.9999++	8	>99.998++	23	99.986++	-	-

Table VII. Results of Laboratory Tests of Impregnated Carbon from Control Filters, (representative of the iodine filters of the PWR containment exhaust air)

Test conditions: Residence time and bed depth during testing similar to original filter unit

Test medium : $CH_3{}^{131}I + CH_3{}^{127}I$

PWR No.	No.	Iodine Filter Residence time (s)	Typ of carbon	Fresh carbon η(%)	1.Control filter Time +) aged(mo.)	η(%)	2.Control filter Time +) aged(mo.)	η(%)
4	1	2.0 ++)	SS 207 B, KI 5-10 mesh	> 99.9999	6	99.984	carbon exchanged	
	1	2.0 ++)	"	"(new fill)	9	>99.999	12	>99.999
	2	2.0 ++)	"	" "	7	99.989	carbon exchanged	
	2	2.0 ++)	"	" "	9	>99.999	12	>99.999
5	1	1.0 ++)	"	" "	6	>99.997	13	99.11
	1	1.0 ++)	"	" "	7	91.8	10	89.7
	2	1.0 ++)	"	" "	6	98.8	carbon exchanged	
	2	1.0 ++)	"	" "	5	99.97	11	99.88
6	1	0.6 +++)	SS 207 B, KI 8-12 mesh	> 99.9999	7	98.2	carbon exchanged	
	2	0.6 +++)	"	"	7	>99.999	carbon exchanged	

+) including stand by and purging operation,

++) wet air of 30°C and 98-100 % r.h. during 20 h of preconditioning, 1 h of loading and 2 h of sweeping,

+++) wet air of 30°C and 70 % r.h. during 20 h of preconditioning, 1 h of loading and 2 h of sweeping

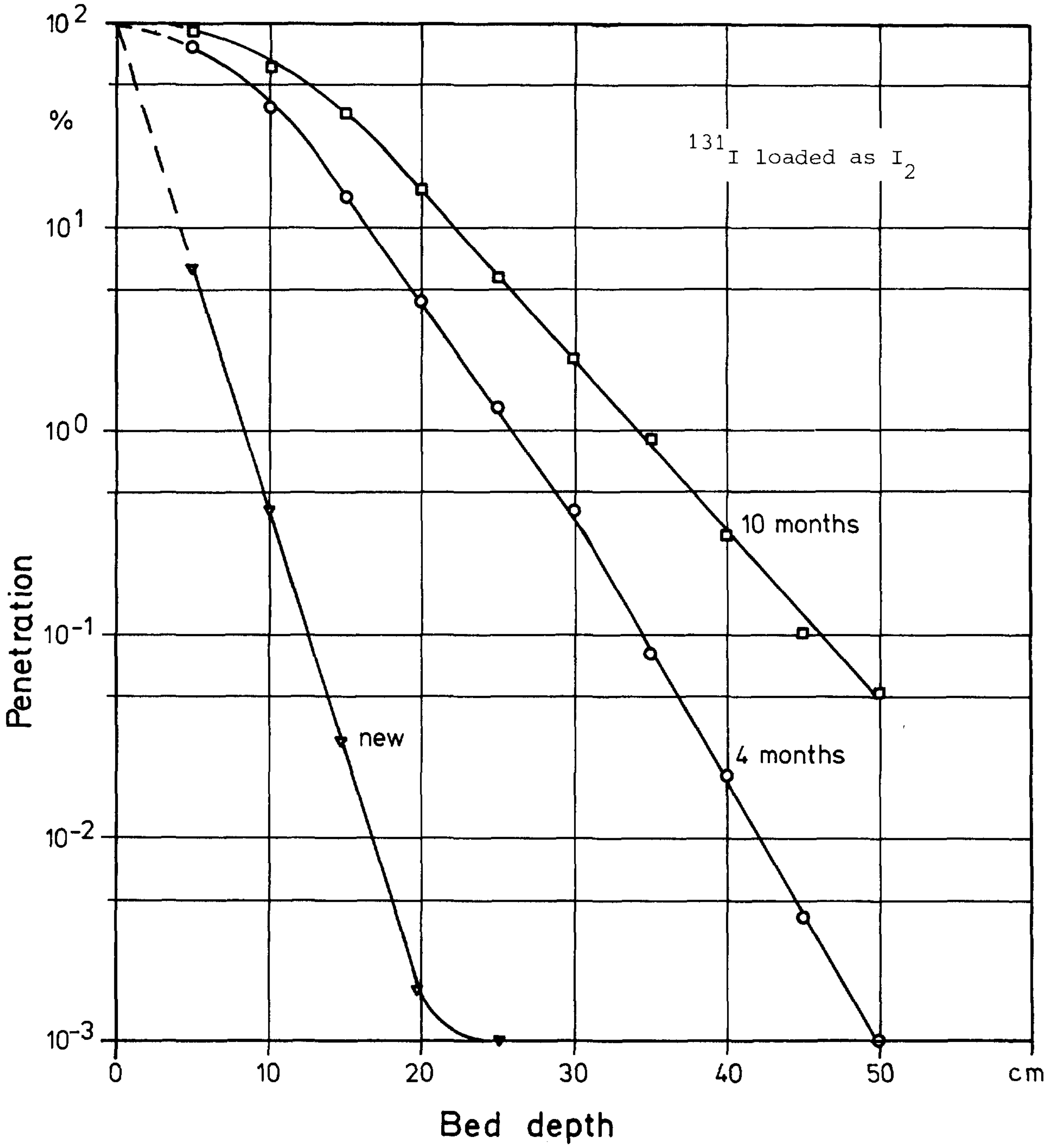

Fig. 1 Penetration of a deep bed carbon filter as a function of bed depth and service life

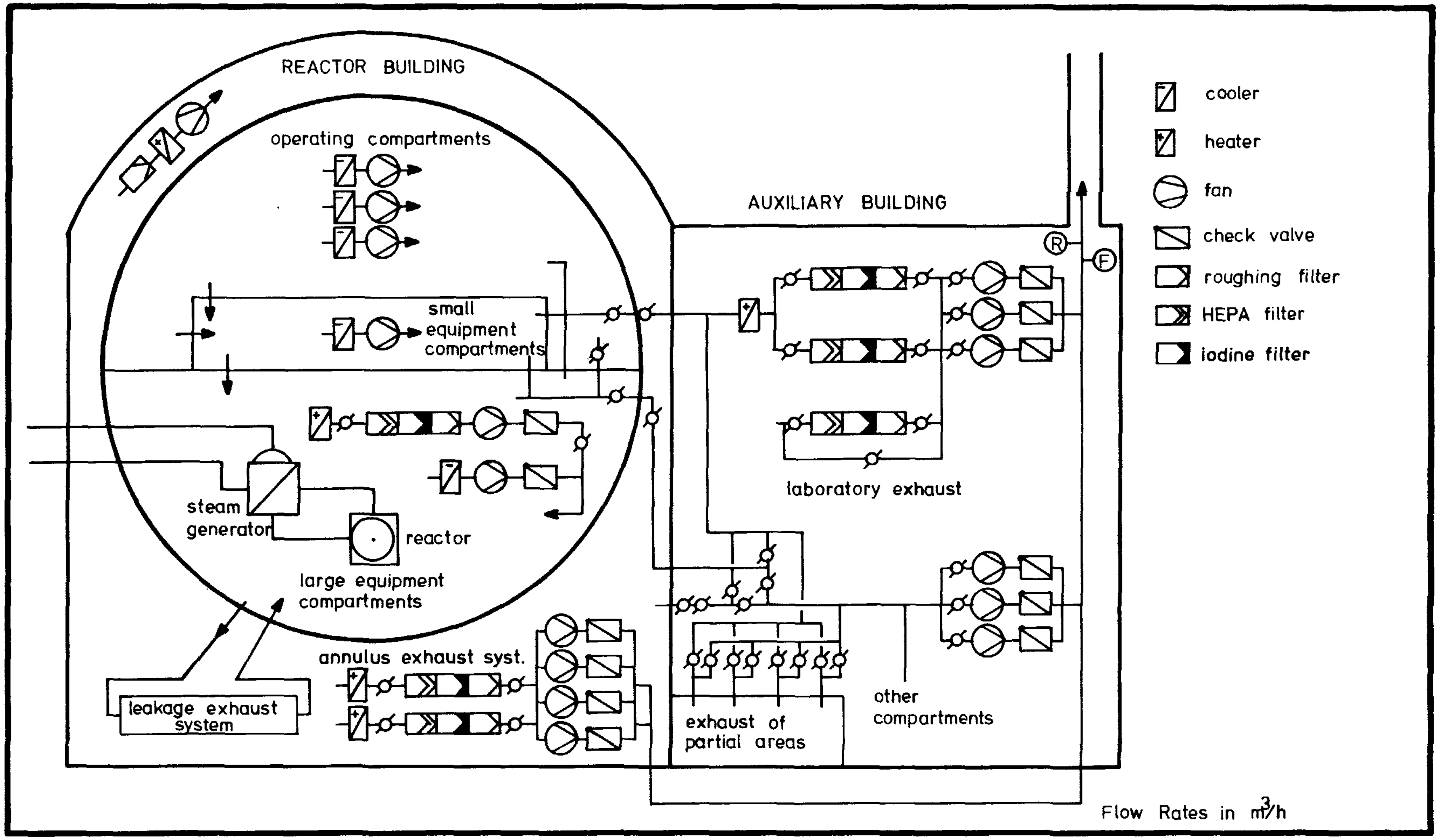

Fig.2: FILTER and VENTILATION SYSTEMS of a PWR POWER PLANT

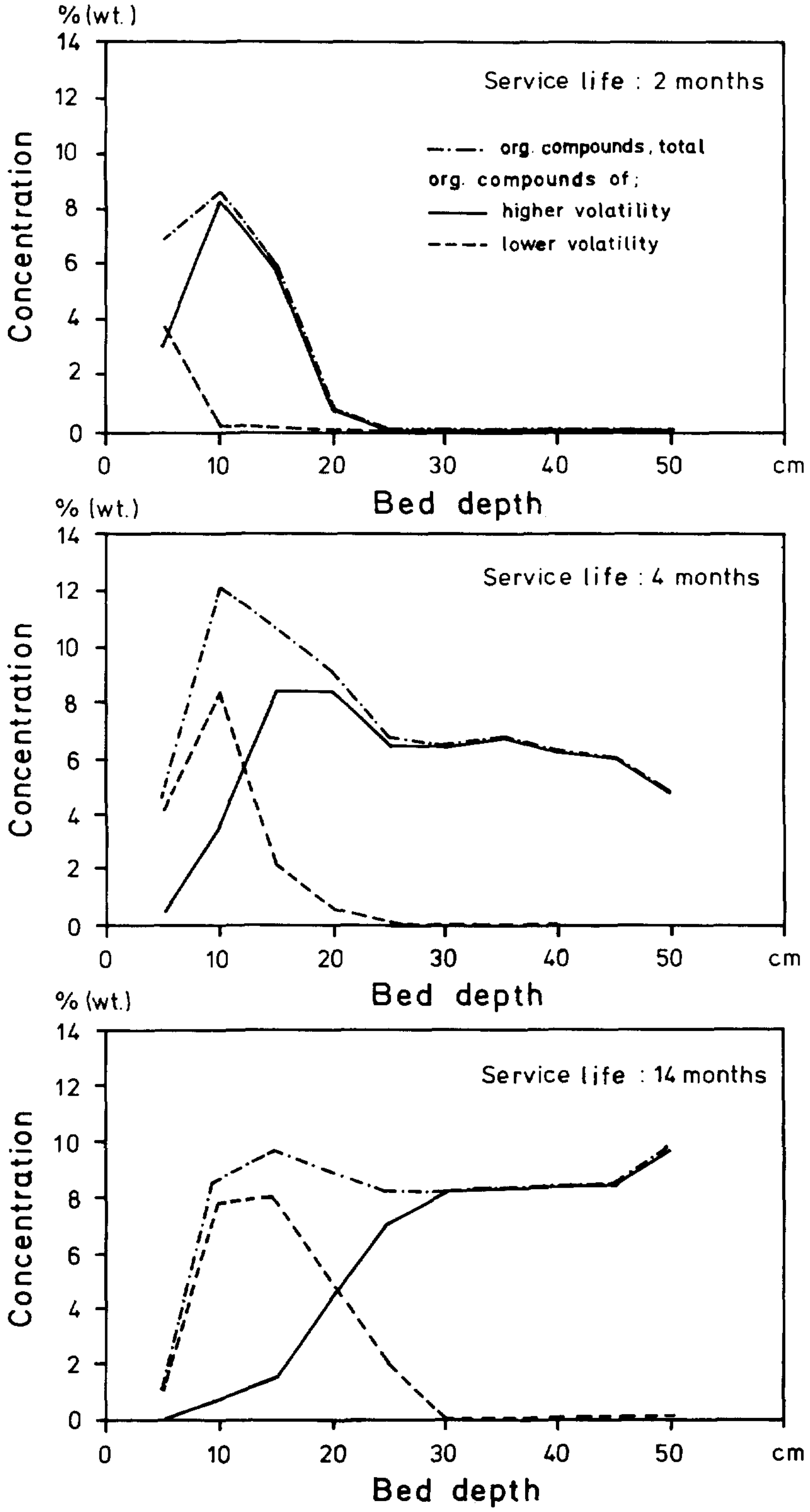

Fig. 3: CONCENTRATION of ORGANIC COMPOUNDS in IMPREGNATED ACTIVATED CARBON as a FUNCTION of BED DEPTH and SERVICE LIFE

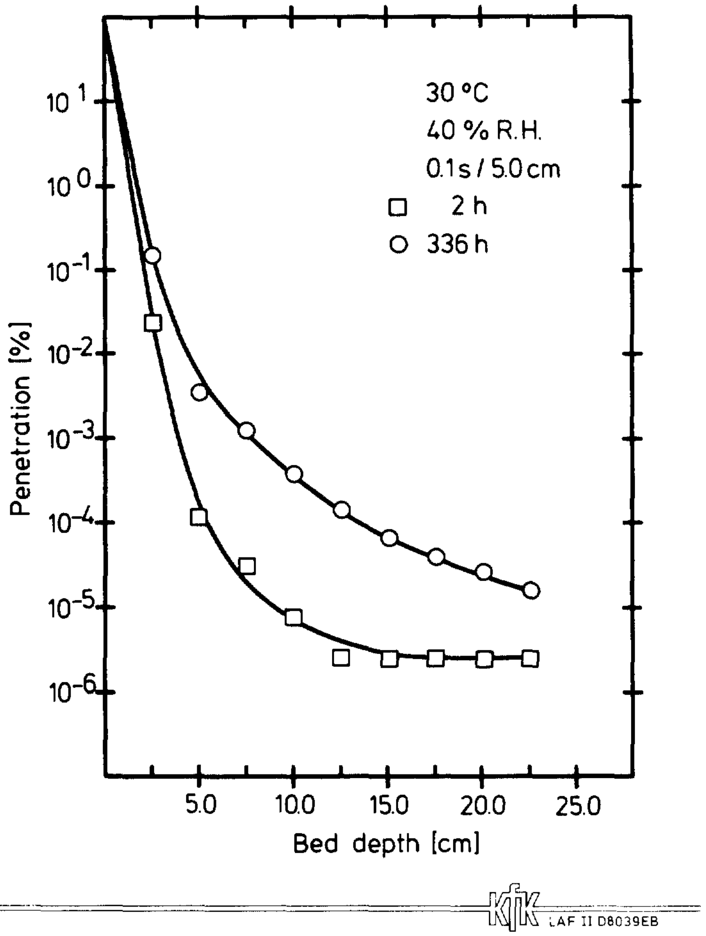

Fig. 4: Penetration of a deep bed carbon filter by ^{131}I as a function of purging time (^{131}I loaded as I_2)

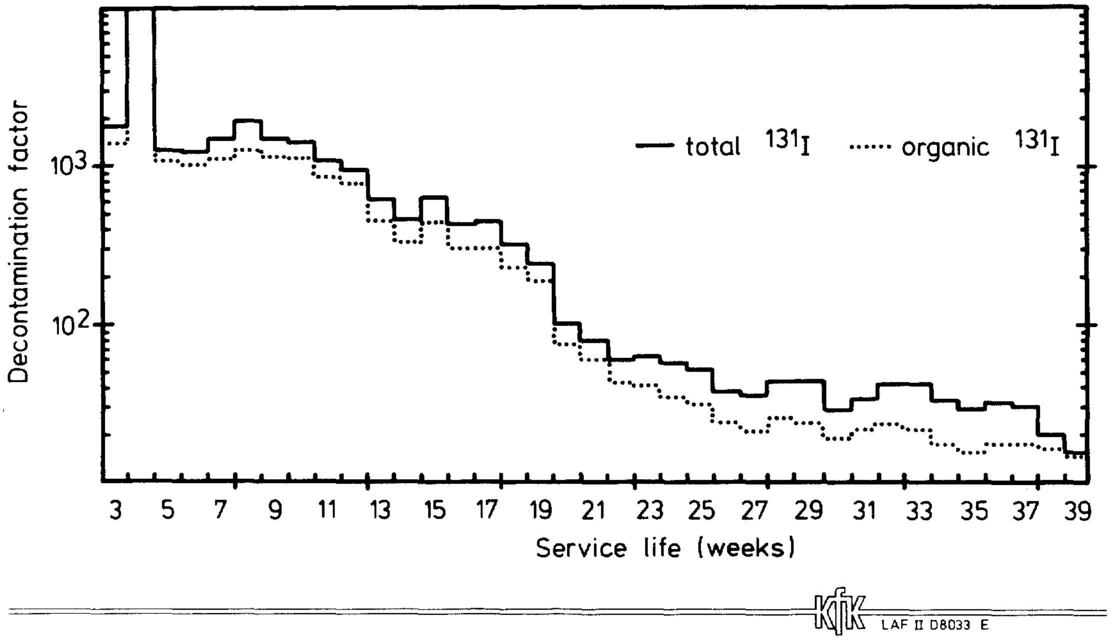

Fig. 5: Decontamination factor for ^{131}I as a function of service life (Exhaust air of a PWR equipment compartment)

DISCUSSION

DENNISON: You reported that you tested continuously the iodine generated by a reactor over a year's time. Did you see any seasonal variations from summer to winter? The reason I ask the question is because I am monitoring continuously with lower concentrations and thinner beds , and I see a difference in the decontamination factor. It varies over a range of 10 to 1. For example, a thousand for the winter and a hundred in the summer for approximately the same bed and the same conditions. Do you have any comment?

WILHELM: This may be the result of different relative humidities at winter and summer times of the air actually being filtered. Moreover, you have seen the variations I reported. Sometimes the decontamination factor was a little higher, sometimes a little lower. There was one case, I think it was in the second week after the startup of the measurements, where the decontamination factor exceeded any value measured in the very first period and later. This was at the time when we had a large release of primary coolant to the containment. In this case, the total concentration of iodine was higher. Maybe this added to a higher decontamination factor. But it is clearly not only a function of the concentration; we looked into this very carefully. Different factors are responsible.

EVANS: Would you care to comment on the type of impregnation in your charcoal?

WILHELM: All the carbons reported here were impregnated with KI_x because TEDA impregnated carbons are not accepted at this time in Germany due to the high volatility of TEDA. If we can find a better impregnation, we will be happy.

PRE-ACCIDENT WEATHERING OF IMPREGNATED CARBONS FOR IODINE REMOVAL

by

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Abstract

The atmospheric degradation of carbons, measured by increased penetration of methyl iodide-131, is an important factor in the operation and replacement of carbon filters. The commercial carbons are distinguished by three types of impregnations: (1) KI + xI_2 , (2) KI and a tertiary amine, and (3) the tertiary amine alone. A degradation of these carbons has been observed in continuous flows of outdoor air and this degradation has been found to decrease in the sequence (1) to (2) to (3) over exposure times of up to one year. It is concluded that the choice of impregnation formulation in nuclear-grade carbons is an important factor towards high efficiency and long service life.

The pattern of air contaminants observed in the above weathering at several locations was subject to considerable fluctuation. The atmospheric conditions, particularly relative humidity and dew point, are important factors when these are in a range in which the relative humidity is above 50%. The seasonal effect has been observed for monthly exposures of KI_x carbons. Weathering under laboratory conditions suggests that the expected life (24 to 30 months) of the carbon might be realized if only the normal contaminants of the air alone were present. In air flows above 50% RH, and when accidental solvent spills occur, the combined effect with the contaminants accelerates the degradation of the carbons.

A determination of iodine-131 penetration is obviously the decisive factor in safety performance. The test results provide a valid indication of the condition of the carbon at the time of the test and if the carbon proves to be unacceptable, the filter system has already operated for a period of time with degraded carbon. It is recommended that some on-line measurement be made that would anticipate a drastic drop in trapping efficiency. A routine in-line chromatographic test procedure with methyl iodide-127 (non-radioactive) may be one possibility.

I. Introduction

Studies on activated carbons and on impregnated carbons for use in nuclear air cleaning processes have been dominated during the last decade by a need to qualify new materials. Test procedures with this objective(1) have been developed. However, the technical evaluation of carbon in-service has proven to be a formidable problem. A carbon is exposed to a variety of environmental contaminants during a long service life without carbon regeneration and these contaminants accumulate and slowly modify the useful life of the carbon. The term "weathering" is used to describe these phenomena. There is no acceptable test whereby an operator of a carbon filter might anticipate a possible drop in the efficiency for trapping radioiodine. The critical penetration may not be observed until the residual iodine retention efficiency is quite low.

A twofold approach has been followed to obtain the necessary data(2,3,4). First, the nuclear carbon samples have been exposed to unmodified outdoor air for various periods of time and at different locations. These were then examined for changes in methyl iodide penetration with $^{131}ICH_3$, weight changes, pH of the water extract, and other pertinent chemical properties. This approach is representative of conditions which might exist during the normal service life of a carbon, but it does not allow control over the concentrations or type of atmospheric contaminant. Second, additional samples of the same nuclear carbons were exposed under controlled laboratory conditions to various known pollutant combinations.

The term "weathering" may be placed in better context by distinguishing three contributions which result in reduced capability of nuclear carbons for removing radioiodine. First, the term "ageing" of a nuclear carbon connotes possible shelf-life of a carbon, stored as it must be in closed containers in a given gaseous environment. Thus, ageing would be restricted to a static testing operation. Second, "service-aged" carbon could indicate the exposure of a nuclear carbon to the actual air flow from a confined system such as a reactor building, fuel-handling building, etc. In fact, the term itself suggests exposure under a pertinent and relevant set of conditions. Third, "weathered" carbon signifies an exposure to ambient contaminants in either a flow of outdoor air at a given location, or under some laboratory set of conditions, where a controlled exposure to a given contaminant can be realized. From the above point of view, a service-aged carbon is a special, and relevant, case of weathered carbon. Under normal operating conditions, the two cases can be identical.

In addition to exposures using outdoor air at NRL, several samples have been weathered at other locations: the Atmospheric Physics facilities of the Argonne National Laboratory, Argonne, Ill., the Simi Valley Monitoring Station of the Air Pollution Control District of Ventura County, CA., and in the Auxiliary Building of Unit 2 of the Three Mile Island Nuclear Power Plant, Middletown, PA. The pertinent objective for including these sites in these studies is to factor the important parameters that contribute to those weathering reactions that degrade the efficiency of the carbon for trapping radioactive methyl iodide. We are most grateful for the permission granted to use the above facilities.

II. Weathering of Nuclear Carbons in Outdoor Air

During exposure to very large volumes of air, a nuclear carbon interacts with many of the contaminants in the air. The individual contaminants may be less than 1 ppm; but the volume of filtered air is so huge that upon integration over an operating time, a sizable quantity of contaminant may enter the carbon filter. For example, a flow of 30,000 cfm for 90 days amounts to 3.9×10^9 cu.ft. through a filter containing approximately 3750 pounds of carbon (2-inch depth). The quantities of contaminants introduced to such a filter are listed in Table I.(5)

Table I. Some contaminants passing into a 30,000 cfm filter.

	Concentration ppm (V/V) (3-yr ave. at NRL)	Weight in 90 days (lbs)	Wt.-% of Carbon
Ozone	0.019	10	0.27
SO_2	0.023	16	0.43
NO_2	0.043	21	0.56
CO	1.37	416	11.0
Hydrocarbons (non-CH_4)	0.23	214 (hexane)	5.0

In determinations of methyl iodide-131 trapping efficiency of new nuclear carbons, a gradient is established along the line of flow and the profile is known to be logarithmic with depth. During the weathering of the carbon, independent gradients of the retained contaminants are slowly established along the line of flow and these gradients greatly complicate the interpretation of the subsequently measured trapping efficiency.

In the present studies, this factor has been taken into consideration by dividing the 2-inch depth of carbon into four equal parts; subsequent measurements were made on each section. The stainless steel test container was used for the weathering, shown in Figure 1, has an inside diameter of 4 inches and a depth of 2 inches. The bed is separated by perforated stainless steel discs (A) into four equal layers, each of which contains sufficient carbon for an ASTM test (conducted in a bed 2" diameter and 2" deep).(1) This configuration makes it possible to study the vertical profile of properties through the test sample. Two additional perforated discs (B) were installed at each end (B), separated by a spacer 0.5 inches high, in order to equalize the cross-sectional air flow.

The air flow was directed as follows: (1) From the air intake above roof (in close proximity to the NRL air analysis intake) to the 12-port manifold located on the top floor, (2) from each outlet port of the manifold through the samples of carbon, (3) integrating gas meter, (4) intake of air pump, and (5) to ambient air on the top floor. There is a separate gas meter and a separate pump for each sample container. The methyl iodide-131 test procedure followed essentially the RDT-M16 specifications. The contact time was 0.25 seconds and the linear flow rate 12 m/minute.

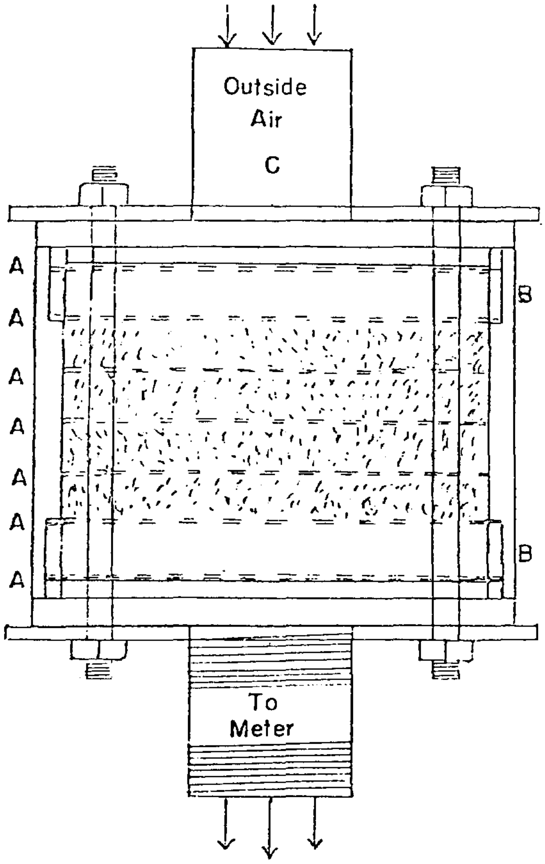

Figure 1.
Sample Container with Perforated Stainless Steel Separators (A) with Spacer Rings (B) at Entrance and Exit. Inlet and Outlet Tubes (C) 1.375 inch I.D.

There are many factors that can influence the reproducibility of the penetration in a weathered sample: the initial sampling of the nuclear carbon, the contaminant fluctuations in concentration during the exposure, the meterological conditions that exist at the close of weathering, and the testing procedure for penetration. Some factors may have greater influence than others. For example, results summarized in Table II are for a series of 1-month exposures of BC 727 over the indicated dates. Two of the 14 values were excessively high and only one was somewhat below the average. The mean of 12 values, is 0.94% penetration; the standard deviation is 0.82 and the variance 0.62.

Three of the exposures listed in Table II (5081, 5082, and 5083) were made simultaneously in the same period, 2 May to 2 June, 1978. The mean is 0.813, the standard deviation 0.11, and the variance is 0.009. Assuming these results are a measure of the overall reproducibility of the weathering experiment for the given carbon, it is possible to examine the individual exposures in Table IV for the presence of other interactions which contributed to the overall mean of 0.94.

Table II. The penetration of methyl iodide-131 after an exposure for one month at the indicated dates.

NRL No.	Penetration %	Exposure
5014	1.30	2 June - 30 June, 1977
5070	1.13	7 April - 2 May, 1978
5081	0.92	2 May - 2 June, 1978
5082	0.69	2 May - 2 June, 1978
5083	0.83	2 May - 2 June, 1978
5113	13.2	2 Aug. - 1 Sept., 1978
5121	3.31	1 Sept. - 13 Oct., 1978
5124	0.81	13 Oct. - 14 Nov., 1978
5125	0.73	14 Nov. - 18 Dec., 1978
5126	0.07	18 Dec. - 18 Jan., 1979
5127	0.81	18 Jan. - 21 Feb., 1979
5128	0.29	26 Feb. - 26 Mar., 1979
5129	29.7	26 Mar. - 26 Apr., 1979
5130	0.35	27 Apr. - 30 May, 1979

The high precision available in counting the radioactivity in carbon test beds is countered by the low reproducibility of the conditions that exist in weathering the carbons with outdoor air flows. High counting precision is, of course, very important in an estimate of activity that might be present in an iodine release collected by a canister of new carbon.

A correlation with the seasonal variation of dew point is a helpful parameter in studies of the interaction of water vapor with activated carbons. The penetrations of $^{131}ICH_3$ (Table II) were obtained after one-month exposures over the four seasons of the year and such a comparison is made in Figure 2(6). Obviously, both penetration and dew point have the same seasonal dependence in that the maxima for both parameters occur during July and August.

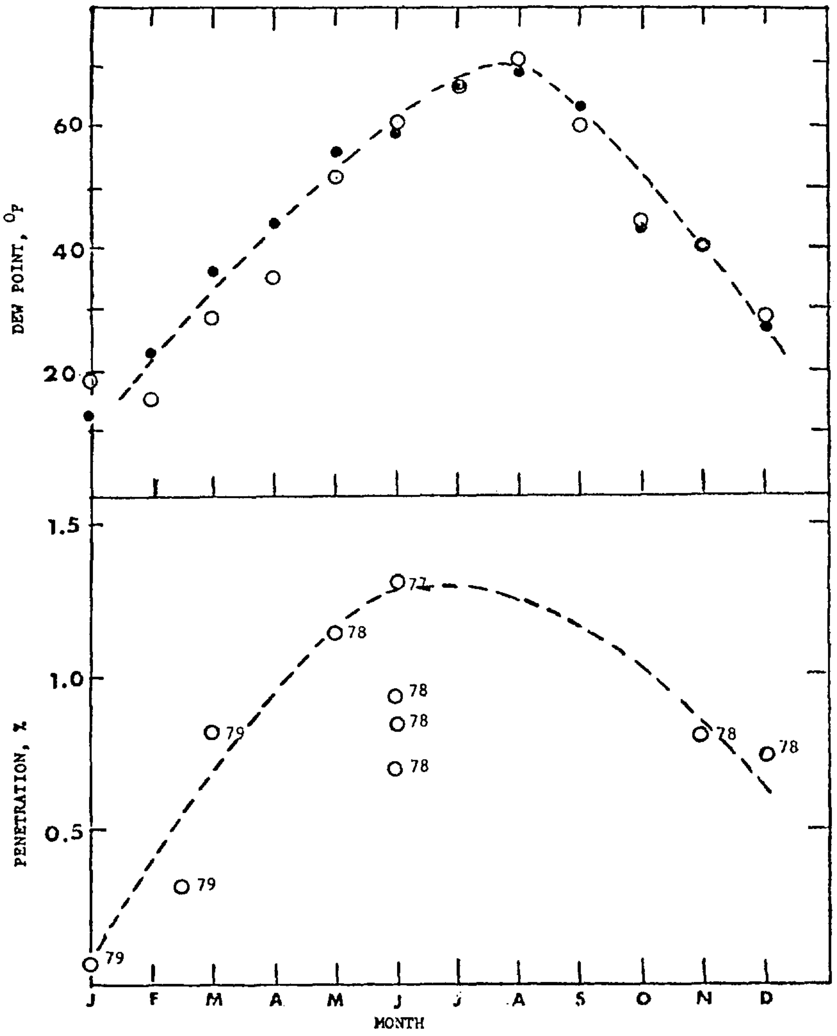

Figure 2.
Seasonal Correlation of the Penetration of $^{131}ICH_3$ with the Dew Point (°F) for Monthly Exposures with the Same Nuclear Carbon (BC 727)

The penetration results for locations outside of NRL are summarized in Table III. The correlation of penetrations with the existing contaminants and dew point variations requires that each exposure be treated on an individual basis. This will be done for typical cases but not for all exposure tests.

Table III. Penetration of $^{131}ICH_3$ through nuclear carbons weathered at sites outside NRL.

Test	Carbon	Time (mos)	pH of Water Extract				Penetration
			1	2	3	4	1,2,3,4 %
			Argonne National Laboratory				
5137	BC 727	1.3	7.9	8.7	8.7	8.7	1.35
5139	BC 727	7	6.8	9.0	9.1	9.0	30.02 ± .41
5164	BC 727	4	6.3	8.2	8.2	8.0	2.17 ± .16
5138	G 615	1.3	8.8	9.2	9.2	9.2	1.97
5140	G 615	7	6.8	9.5	9.5	9.6	5.44 ± .18
5165	G 615	4	7.0	8.3	8.3	8.3	0.30 ± .05
5192	S & S	2.5	6.8	7.6	7.6	7.6	1.88 ± .19 2.19%
5207	S & S	5	4.5	7.1	7.2	7.3	-
			Simi Valley, Ventura Co., Calif.				
5141	BC 727	7	6.5	8.1	8.7	8.7	25.9 ± .36
5166	BC 727	4	6.9	8.7	8.7	8.7	15.16 ± .62
5142	G 615	7	8.5	8.9	9.4	9.5	8.98 ± .21
5167	G 615	4	8.0	9.1	9.2	9.2	0.25 ± .08
5195	S & S	2.5	6.4	7.3	7.4	7.3	5.97 ± .48 11.07
5208	S & S	5.0	3.8	5.5	6.3	6.6	-
			Three Mile Island				
5172	S & S	2	7.4	7.6	7.8	7.9	0.18 ± .02
5171	G 615	2	8.05	9.10	9.07	9.05	0.10 ± .06
5190	G 615	4	9.0	9.1	9.1	9.1	0,22 ± ,07
5191	Nusorb-Q	4	9.0	9.1	9.1	9.1	0.01 ± .01

An overview of all exposures leads to the summary graph of Figure 3, in which the penetration of $^{131}ICH_3$ (percent) is plotted as a function of the exposure duration (months). The values can be divided into three distinct patterns, each corresponding to a type of impregnation on the carbon: (1) KI_x (i.e. $KI + xI_2$), (2) KI + TEDA, (3) TEDA or some other tertiary amine (TEDA = triethylenediamine). The penetration of the carbons after weathering decreased in the order (1) to (2) to (3) under the manifold conditions existing at the three exposure sites. It appears that the impregnation formulation of nuclear carbons is a critical choice toward realizing high removal efficiency and long service life.

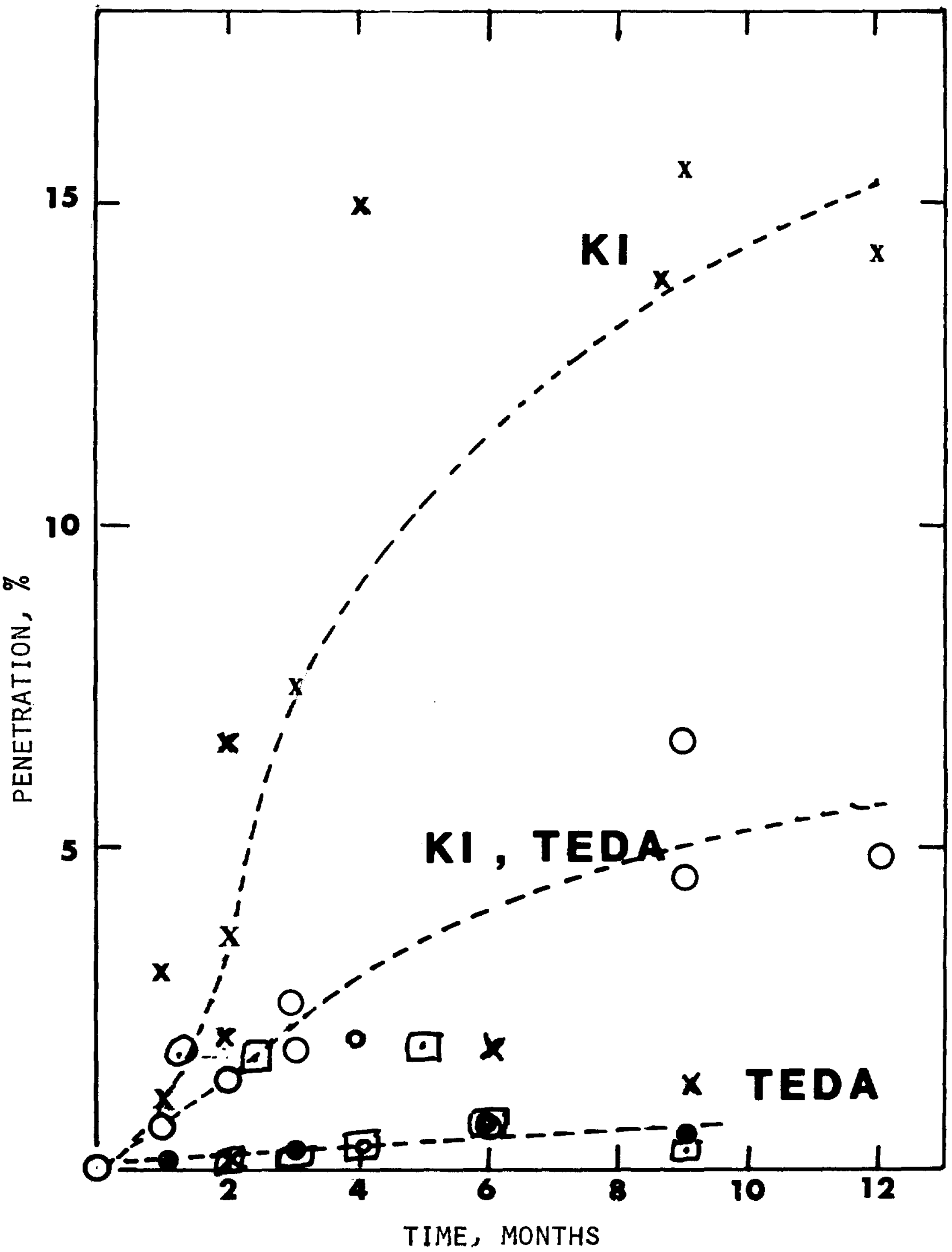

Figure 3.
Penetrations of $^{131}ICH_3$ After Exposure of Nuclear Carbons to Outdoor Air at All Locations.

The influence of the dew point can be shown for the results given in Table IV for BC 727 after exposures of two to 12 months. The points on Figure 3 that fall far off the indicated line can be associated with exposure periods of low dew point. Consequently, the air was dry and the aggravated influence of moisture and contaminants was minimum. For example, NRL 5137 was run between 12 February and 21 March 1979; the dew point was in the range 15-30°F and $^{131}ICH_3$ penetration was 1.35%. A similar situation was present in NRL 5164 in which the penetration after four months was 2.2%. However, NRL 5139 was exposed from 21 March to 22 October 1979, during which the dew point varied from 30 to 60 to 35; the penetration after seven months was 30%.

Table IV. Correlation of $^{131}ICH_3$ penetration with the dew point during exposure of BC 727.

NRL Test	Time (mo)	Exposure	Dew Point* Range (°F)	Penetration %
		Naval Research Laboratory		
5032	2	29 Jul - 30 Sep	70-60	3.6
5065	2	9 Feb - 7 Apr	25-45	6.8
5096	2	3 Jun - 1 Aug	60-70	3.8
5020	3	1 Jul - 30 Sep	65-65	7.6
5056	6	16 Nov - 1 May	40-40	2.1
5055	9	16 Nov - 16 Aug	30-70	15.6
5122	12	22 Sep 79 - 25 Sep 80	20-70	14.1
		Argonne National Laboratory		
5137	1.3	12 Feb - 21 Mar	15-30	1.3
5139	7	21 Mar - 22 Oct	30-60-35	30.0
5164	4	22 Oct - 27 Feb	35-20	2.2
		Simi Valley, Ventura County, CA.		
5141	7	23 Mar - 24 Oct	50-60-55	25.9
5166	4	24 Oct - 28 Feb	55-50	15.2

* Dew Points are monthly averages.

III. Confirmation by Laboratory Weathering Studies

The number of combinations of test gases and nuclear carbons that warrant investigation is obviously very large. Care and consideration are needed to select the laboratory systems for possible correlation with outdoor exposures. The contaminant mixtures listed below were selected in air flows of 50, 70, or 90% RH:

air + water vapor
air + water vapor + sulphur dioxide
air + water vapor + ozone
air + water vapor + carbon monoxide
air + water vapor + hexane vapor
air + water vapor + carbon tetrachloride vapor

air + water vapor + methylethylketone vapor
air + water vapor + methyl alcohol vapor

Seven commercial carbons were exposed to air flows at three levels of relative humidity (50, 70, 90% RH) at a flow rate of 100 L/min for 100 hours. The air was first humidified by bubbling the entire flow through water which was controlled at the desired temperature by a surrounding heat jacket. Humidities of 50, 70 and 90% RH were obtained by water temperatures of 11-12°C, 17-18°C, and 21-22°C, respectively. The residence time in the carbon bed was 0.25 sec. and the linear flow rate was 12.3 m/min. The total flow was thus 600 M^3 and the total weight of water (calculated at 22°C), to which each carbon was exposed, was 0.97, 1.74, and 2.61 kg at 50, 70, and 90% RH, respectively. The relative humidity in each of the two systems was monitored by a dewpoint hygrometer (General Eastern, Series 1211 P Sensor) and the air temperature was measured simultaneously with a platinum resistance thermometer (General Eastern, 1212 P).

The $^{131}ICH_3$ penetrations of the seven nuclear carbons were found to be reproducible in water vapor-air mixtures. For example, samples of BC 727 were exposed in August 1977 and in October 1978 and the results are given below:

Test	Exposure	RH%	CH_3I-131 % Penetration
5030	1-5 Aug 1977	70	6.3
5131	16-20 Oct 1978	70	6.12 ± .076%
5036	15-19 Aug 1977	90	13.6
5132	16-20 Oct 1978	90	13.7 ± .127%

The good reproducibility obtained is due in part to the close control possible in laboratory weathering and to the good reproducibility of the BC 727 carbon samples withdrawn from the master stock supply.

The methyl iodide-131 penetrations increased for all seven carbons with increase in the relative humidity of the air flow. The increase from 50 to 70% RH was greater than the increase from 70 to 90% RH. The differences among the different nuclear carbons, seen in Figure 4, vary and seem to depend on both impregnation and base carbon. The behavior of the S&S (5% TEDA), according to these measurements, is outstanding with respect to weathering in water vapor.(7) Mixtures of pollutants and water vapor present other problems.

The exposure of nuclear carbons to three levels of relative humidity only approximates the great variability encountered in practice. The carbon in service is subjected to variable periods of high and low relative humidity; periods of dry air could be favorable to high trapping efficiency and periods of wet weather would steadily increase the moisture content and decrease efficiency.

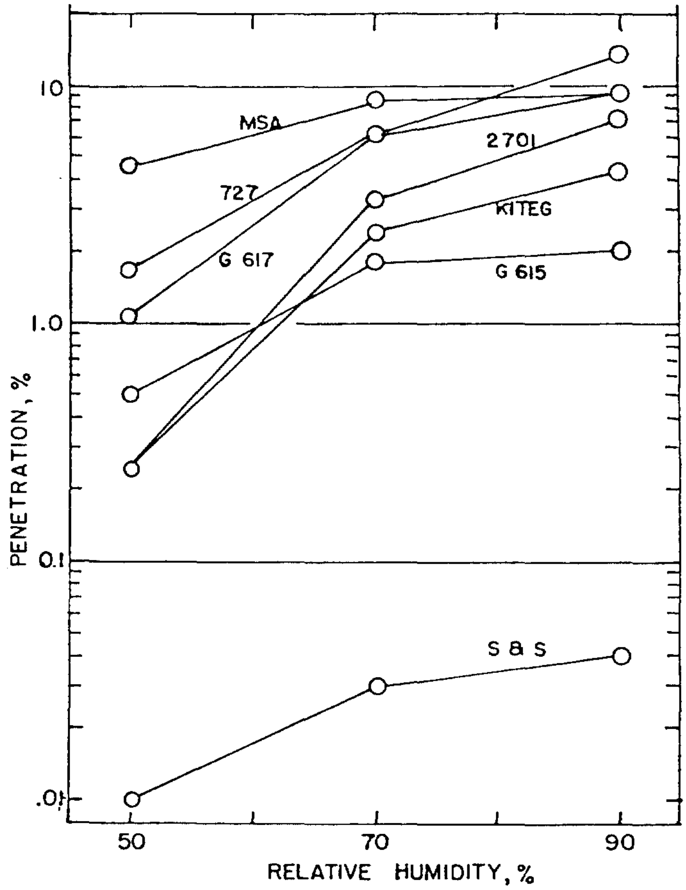

Figure 4.
Methyl Iodide-131 Penetration for Carbons Weathered at Constant Relative Humidity (21-23°C) for 100 Hrs at 100 L/min.

The results for carbon exposures to air flows having in sequence two levels of relative humidity are summarized in Table V. The subsequent $^{131}ICH_3$ penetration is dependent on the sequence of the exposure. The two exposures for each carbon of 50 hours of different relative humidity did not result in as much penetration as the 100-hour exposures. The increased penetration with increased times of prehumidification was quite unexpected when first observed(8) in 1976 with experimental carbons and it is important to note that the same effect is present for commercial carbons.

Table V. Results after exposure at two levels of relative humidity (total time 100 hrs)

Carbon	Exposure		Total Wt. Change %	Penetration %
	Time (hrs)	% RH		
G 615	50	50		
	50	90	38.8	0.66 ± .02%
G 615	50	90		
	50	50	34.8	0.69 ± .06
G 615	50	90		
	50	dry air	0.84	0.06 ± .01
G 615	100	90	29.9	2.00
G 615	100	50	20.0	0.50
BC 727	50	50		
	50	90	50.1	5.88 ± .05
BC 727	50	90		
	50	50	46.9	3.95 ± .04
BC 727	50	90		
	50	dry air	0.78	1.02 ± .05
BC 727	100	90	47.6	13.6
BC 727	100	50	25.8	1.69

Organic vapors in air mixtures without water vapor were added to one of the carbons to the high level of 11 wt.%. The results with no prehumidification are:

Test	Carbon	Contaminant	$^{131}ICH_3$ Penetration
-	BC 727	None	0.014
5114	BC 727	Hexane	2.04 ± .04
5115	BC 727	Methanol	0.77 ± .05
5116	BC 727	Methyl Isobutyl Ketone	1.19 ±.10

The addition of 11 wt.% of these compounds, quite a large amount, did not degrade the carbon below the allowable performance requirements. However, based on the results presented in Table VI, unacceptable methyl iodide-131 penetration can be expected when a combined flow of water vapor and organic vapor is allowed to enter the carbon. There is a synergistic influence of water vapor and a hydrocarbon. For example, the penetration for BC 727 was 4.8% for water vapor alone, and 0.63% for 2% $C_{14}H_{30}$ alone, but 9.5% for both water vapor and 2% $C_{14}H_{30}$. Also, the penetration for MSA 463563 was 2.5% for water vapor alone and 1.01% for 2% $C_{14}H_{30}$ alone, but 7.5% for both water vapor and 2% $C_{14}H_{30}$. Additional exposures have been made that involve the insult mixture of organic vapor and 95% RH air going continuously to the carbon bed. Subsequently, the determination of methyl iodide-131 penetration was made.

Table VI. Influence of prehumidification on trapping efficiency after hydrocarbon contamination.

Carbon	*Prehumidification	% Penetration $^{131}CH_3I$			
		BC 717	BC 727	MSA 463563	G 615
Orig.	No	0.05	0.014	0.13	0.05
Orig.	Yes	1.0	4.8	2.5	0.27
+10% Octane	No			0.37	
	Yes			9.2	
+10% $C_{14}H_{30}$	No	1.2	0.33	0.80	
	Yes	5.3	15.6	15.9	
+2% $C_{14}H_{30}$	No	0.63	0.63	1.01	0.18
	Yes	8.8	9.5	7.5	1.5
+0.2% $C_{14}H_{30}$	No				0.09
	Yes				0.81

* Prehumidification: 16 hrs., 25 L/min, 95% RH

IV. Depth Profile in Weathered Nuclear Carbons

As a function of exposure time, the depth profile through a carbon bed has demonstrated that the top layer serves as a guard layer for the remaining carbon. The pH of the water extract of the first half-inch layer of the two-inch bed becomes progressively acidic with time of exposure. The results in Table VII show that the pH may drop below 3.0 after a year's exposure at the NRL site.

Table VII. pH of the first half-inch layer of two-inch bed at NRL exposure.

Exposure (months)	G 615	BC 727	2701	KITEG	S & S	MSA 463563
1	9.3	8.3	7.6	6.7	8.0	7.5
2	8.2	7.6				
3	7.9	7.0	3.6	2.8	4.5	3.4
6	3.8	3.1	2.4	2.4	4.0	2.5
9	4.1	3.3	2.5	2.3	3.2	2.7
12	2.9	2.2				

The behavior of two of these carbons at two other weathering sites has been followed for a shorter time, but, as shown in Table VIII, the trend towards lower pH with exposure time is present.

Table VIII. Values of pH on first half-inch layer of a two-inch bed.

Time (mos.)	Argonne Site		Simi Valley	
	BC 727	G 615	BC 727	G 615
Original	9.5	9.8	9.5	9.8
1.3	7.9	8.8	-	-
4	6.4	7.0	6.9	8.0
7	6.8	6.8	6.5	8.5
	S & S		S & S	
Original	9.5		9.5	
2.5	6.8		6.4	
5	4.5		3.8	

The weight increase of a nuclear carbon in the first half-inch layer has no trend with exposure time since most of the weight change depends strongly on the moisture content of the air at the point in time of sample withdrawal. The behavior for six of the carbons under study is shown in Table IX.

Table IX. Weight increase of first layer of two-inch bed at NRL exposure.

Exposure (months)	G 615	BC 727	2701	KITEG	S & S	MSA 463563
1	21.7	3-46*	27.1	16.8	0 to 25.7	20-30
2	21.3	36.2**				
3	34.0	34.5	5.5	9.2	5.9	5.0
6	6.5	9.1	27.0	27.0	30.7	8.0
9	36.4	47.4	45.5	29.6	26.5	9.2
12	23.6	28.9				

* Range of many determinations.
** Averaged.

All new nuclear carbons show a linear exponential attenuation of $^{131}ICH_3$ penetration with depth. In weathered or service-aged carbons, the depth profile is quite unpredictable. As shown in Figure 5, the greatest penetration is through the inlet layer of the carbon and the penetration through each of the remaining beds tends to a constant value, but the penetration is considerably more than the original new carbon. This behavior is compatible with some uniformity in the degradation below the inlet carbon layer.

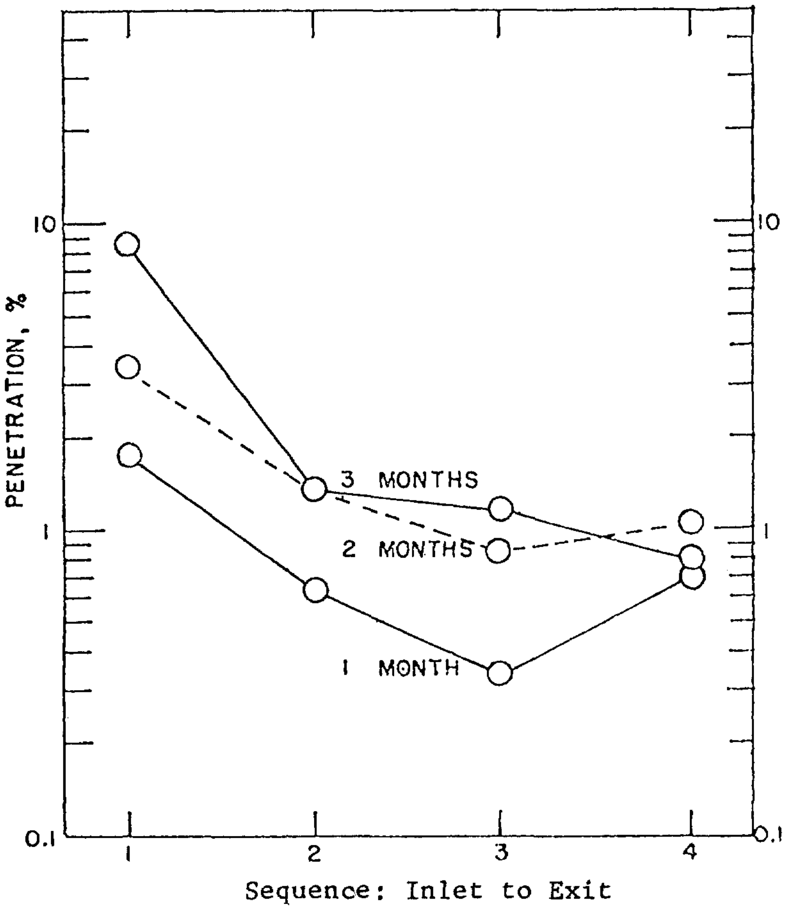

Figure 5.
Depth Profile in the Weathering of NACAR G 615 for One, Two, and Three Months in Unmodified Outdoor Air at NRL.

For exposures of short duration, for example the laboratory tests of 100 hours at 100 L/min, the depth profile (see Figure 6) indicates a fairly constant penetration value in layers 2, 3, and 4. The comparison is made for two carbons (BC 727 and G 615) using 70% RH air in one case and 70% RH and SO_2 in the second case. The standard deviation for the penetrations through the layers 2, 3 and 4 is within the overall experimental reproducibility of the measurements.

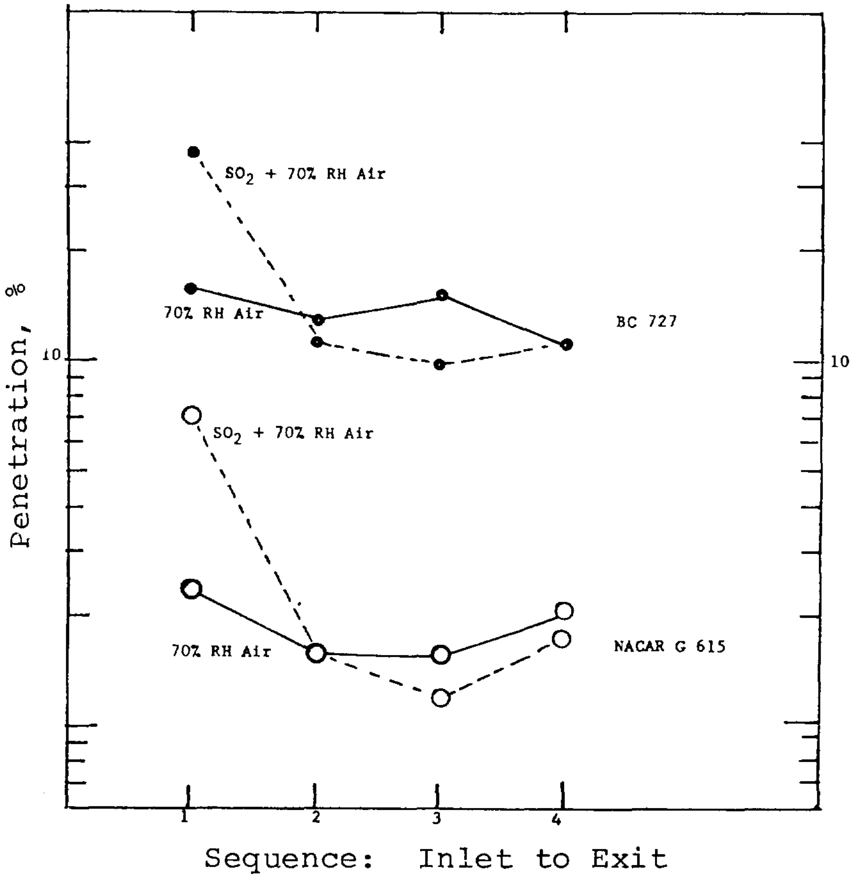

Figure 6.

Penetration Profile Developed in Laboratory Flows of 100 L/min for 100 hrs. with [70% RH + SO_2] and 70% RH Alone.

V. Concluding Remarks

1. The atmospheric degradation of nuclear carbons is a very important factor in the design and operation of carbon filters in nuclear installations. Sizable amounts of contaminants can accumulate in a year's operation of the carbon filter. One important question is concerned with the permissible degradation in efficiency without jeopardizing the operating requirements for radioactive iodine removal.

2. The impregnation formulation of nuclear grade carbons is a critical choice to high efficiency and long service life.

3. A seasonal correlation of the observed penetration of $^{131}ICH_3$ with the dew point (°F) has been observed. The winter months with air flows of low average dew points have minimum influence in the weathering of a nuclear carbon. The pattern of air contaminants in the vicinity of nuclear installations and that within the various buildings may be helpful in a prognosis of residual filter efficiency for trapping radioiodine.

4. There is a synergistic influence of water vapor and several contaminants which can result in unacceptable penetration values for methyl iodide-131. The weight increases of carbons exposed to humidified air flows is dominated by the water vapor adsorption.

5. The carbon in the inlet layer of a weathered carbon bed will be degraded to the greatest degree by the insult gases and to some extent behaves as a guard layer to the remaining depth of carbon.

Acknowledgement

The technical guidance of J. T. Collins and his staff and the overall program guidance of D. E. Salberg of the U.S. Nuclear Regulatory Commission are very much appreciated.

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AN OPERATIONAL SILVER ZEOLITE IODINE ADSORPTION SYSTEM

by

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ABSTRACT

This paper describes the rationale used to justify silver zeolite as the iodine adsorption medium in a single-housed multi-stage filtration unit to be used as the Loss-of-Fluid-Test (LOFT) containment vessel atmosphere cleanup system and reports the status of the system after two years of operation. The system is required to (1) remove entrained moisture, (2) reduce relative humidity, if necessary, (3) remove particulates both upstream and downstream of the adsorbent medium, and (4) remove iodine by adsorption in an 8,000-cfm system.

Cost analysis and feasibility studies were conducted and showed that a single-housed multi-stage filter train with a Type-13X silver zeolite gasketless adsorber was the most cost effective and practical concept.

Design, installation, and operational problems are discussed. The system efficiency test results are noted showing no degradation from the two years of operation. The operational problems have been minor and can easily be corrected in future units by making small modifications in the system design.

NOTICE

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I. Introduction

The mission and general objectives of the Loss-of-Fluid-Test (LOFT) Reactor Experimental Program at the Idaho National Engineering Laboratory include the following:

1. To provide data required to evaluate the adequacy of and to improve the analytical methods currently used to predict the response of large pressurized water reactors (LPWRs) to postulate accident conditions; the performance of engineered safety features (ESF) with particular emphasis on the emergency core cooling system (ECCS); and the quantitative margins of safety inherent in the performance of the ESF.

2. To identify and investigate any unexpected events or thresholds in the response of either the plant or the ESF and develop analytical techniques that adequately describe and account for the unexpected behaviors.

Since the Three Mile Island incident, the LOFT mission has been extended:

3. To evaluate and develop methods to prepare, operate, and recover systems and the plant for, and from, reactor accident conditions.

4. To identify and investigate methods by which reactor safety can be enhanced, with emphasis on the interaction of the operator with the plant.

This mission is being fulfilled by a facility which can intentionally place a 50 MW (thermal) reactor into accident conditions, measure responses, and recover. During the first two years of operation, power-escalation tests, two large-break experiments, and two small-break experiments have been conducted.

These types of experiments demanded the installation of an efficient and reliable radiological filter train to clean the reactor containment vessel atmosphere.

A single-housed filter train with silver zeolite was justified, designed, and installed and now has been in service for two years.

II. Justification

The original LOFT Containment Atmosphere Cleanup System was designed in the 1960's but was not intended to be installed until just prior to the loading of fuel in the LOFT reactor. In late 1975, with fuel loading approximately three years away, a task was begun to procure and install the system.

Initial review of this 8,000-cfm system indicated a very complicated and costly maintenance program. This prompted a state-of-the-art look at the entire design. By 1976 the use of 2.5-cm (1-in.)-deep pleated activated charcoal beds in series was no longer the optimum design, and Maeck, Pence, and Keller(1) had reported that silver zeolite was a highly efficient adsorber for iodine. In addition, the Power Burst Facility (PBF) at the INEL had gained some experience from a silver zeolite adsorption filter.

In-depth feasibility studies and cost analyses were performed. The conclusions of these studies showed that over a ten-year period a silver zeolite permanent single unit (PSU) or gasketless adsorber in a single multi-stage filtration unit was the most cost effective design.

The cost analysis considered three basic designs:

1. Completion of the original design, consisting of a housing containing a moisture separator, two parallel housings with four HEPAs each, and six housings in two parallel activated-charcoal banks (each housing with four pleated 2.5-cm bed cells per Institute of Environmental Sciences (IES) CS-8 type I(2)). Duct heaters would be installed between the moisture separator and the two HEPA housings for humidity control.
2. A single multi-stage unit with a moisture separator, humidity-control heaters, upstream HEPAs, a gasketless adsorber containing activated charcoal, and downstream HEPAs.
3. A single multi-stage unit with a moisture separator, humidity-control heaters, upstream HEPA, a gasketless adsorber containing Type-13X silver zeolite, and downstream HEPAs.

Tray-type adsorbers (IES CS-8 Type II) were not considered in the cost analysis because of accessibility and maintenance logistics.

The initial cost of the silver zeolite medium in the third design made it the most expensive, but only by about 10%. The necessity of a fire detection and suppression system required by local fire protection authorities for both charcoal designs was the factor that reduced the cost difference between the charcoal and silver zeolite designs.

With the installed-cost differences of the three designs relatively small, the cost of changing out and maintaining the adsorbers in each of the three designs was considered.

The following assumptions were used as the criteria for changing out the adsorbents in a standby system:

1. The useful life of installed activated charcoal as an adsorber is limited to three years as stated in the Nuclear Air Cleaning Handbook.(3)
2. The useful life of silver zeolite is expected to exceed an estimated facility life of 10 years.

The low maintenance requirement for silver zeolite gave the edge to the silver zeolite design because the charcoal designs would require a minimum of three changeouts in a 10-year period. The initial higher cost of the silver zeolite design would be recovered in three years (one changeout) compared to the charcoal pleated-bed design, and in six years (two changeouts), compared to the charcoal gasketless adsorber design.

The next consideration then was the feasibility of using silver zeolite in a large system, which came down to a comparison of advantages and disadvantages.

The advantages of using silver zeolite instead of activated charcoal that were considered are the following:

1. Non-flammability
2. Longer service life
3. Higher adsorption capacity (85 mgI/g)
4. Less humidity effects
5. No iodine desorption
6. Lower susceptibility to poisoning by contaminant gases
7. Opportunity to gain operating experience.

The disadvantages are the following:

1. High initial cost
2. If poisoned and not regenerable, more expense for replacement
3. Little previous operating experience in the industry.

When all of the above factors are considered, the selection of silver zeolite in a single-housed multi-staged train is the most cost-effective and practical choice. The recoverability of the silver was not included in the cost analysis or the feasibility study; however, it is a factor that should be considered.

III. Design

Due to the existence of the concrete-vault structures that were to contain the original multi-housing filter system, the design of a single-housed multi-stage unit was not straightforward.

Space and accessibility were the two prime factors hampering an American National Standards Institute (ANSI)-509N(4) standard design. The unit had to fit in an underground vault

5.79 m in length x 4.12 m in width x 4.72 m in height (19 x 13.5 x 15.5 ft), retain accessibility for inplace testing and maintenance work, and still have the basic characteristics of a typical 8,000-cfm, single-housing filter train using standard components (see Figure 1).

The available space could contain a housing of 5.33-m (17.5-ft) maximum length, including transition pieces on each end, and still contain a moisture separator, electric heaters for humidity control, HEPAs, a 5-cm (2-in.)-deep gasketless adsorber bed, and downstream HEPAs (see Figure 2).

The maintainability criteria of ANSI-509N was satisfied by reducing the standard internal spacing between components and providing side access for loading and unloading of the moisture separator and HEPA filter elements with bag-in, bag-out capability. Access to the adsorber is from the top for both fill and removal of the adsorbent. Manways were installed on each side of the housing to provide entry for inspection and cleaning.

The accessibility for inplace testing is provided by a remote station outside of the vault. Tubing connects the sample or injection points on the housing to the station. The accessibility of the sample canisters is provided by a separate housing mounted outside the vault; the housing has a flow path sized and designed to allow a representative air sample taken immediately upstream of the adsorber to pass through the sample canisters and return to the filter train immediately downstream of the adsorber. These sampling techniques allow complete annual testing of the adsorber without personnel having to enter the vault.

Figure 3 shows the filter train with the remote sample canister housing, filter train arrangement, and the remote station and connecting tubing for the inplace testing.

A procurement specification was written for the silver zeolite using RDT M 16-1T.(5) The RDT standard was modified to use only the sections and requirements that were applicable to silver zeolite. This modification allowed the purchase of an adsorbent material that had been manufactured per the RDT standard.

IV. Installation and Operation

During installation of the silver zeolite in May 1978, the importance of adequate support of the perforated retention screens in the gasketless adsorber was realized. The approved design allowed the screens to bulge between the supports, as shown in Figure 4. The added 0.13-m^3 (4.5-ft^3) volume created by the bulging had not been calculated in purchasing the quantity needed to fill the adsorber section. Fortunately the manufacturer had, in inventory, enough silver zeolite from

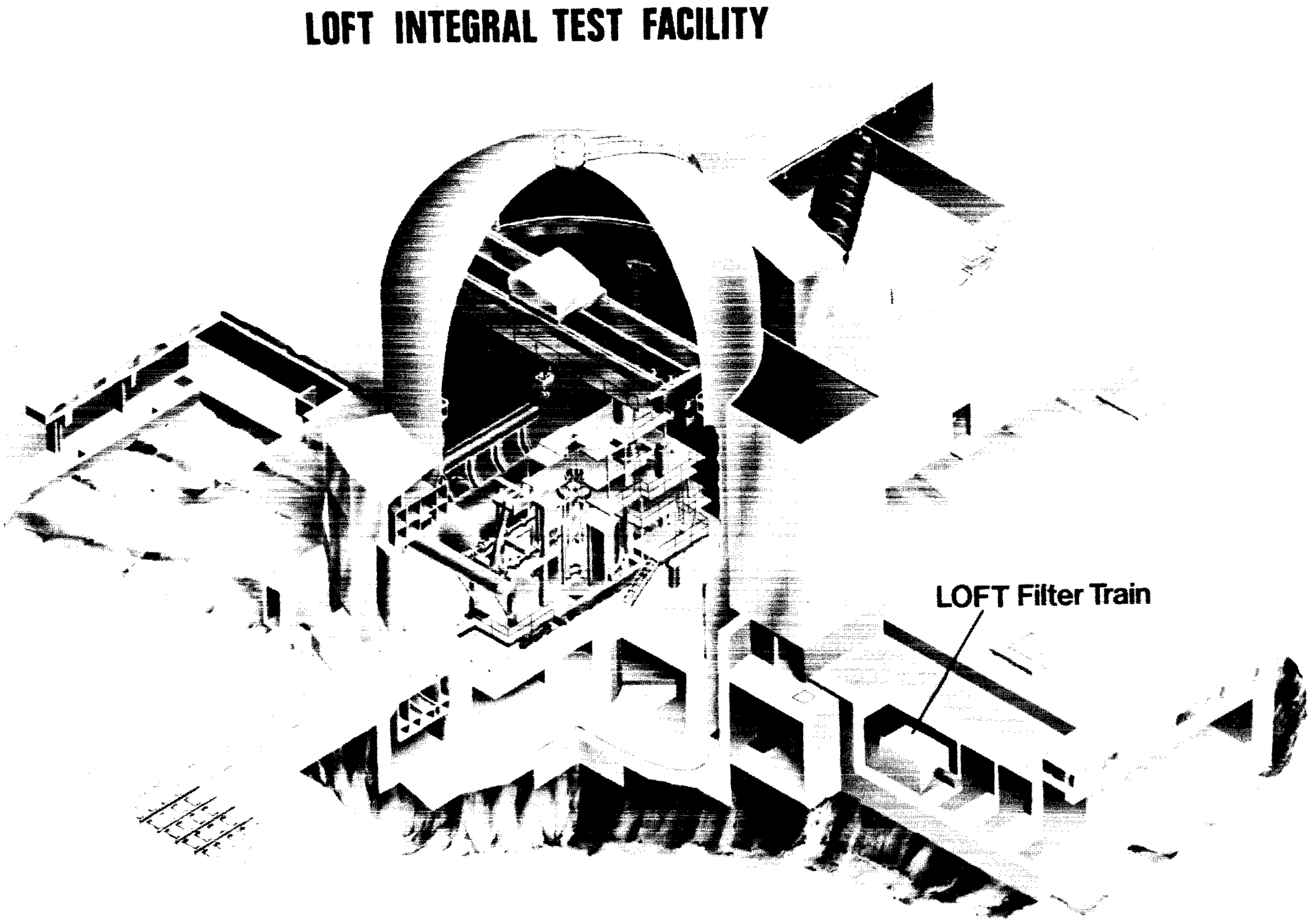

Figure 1. LOFT Integral Test Facility

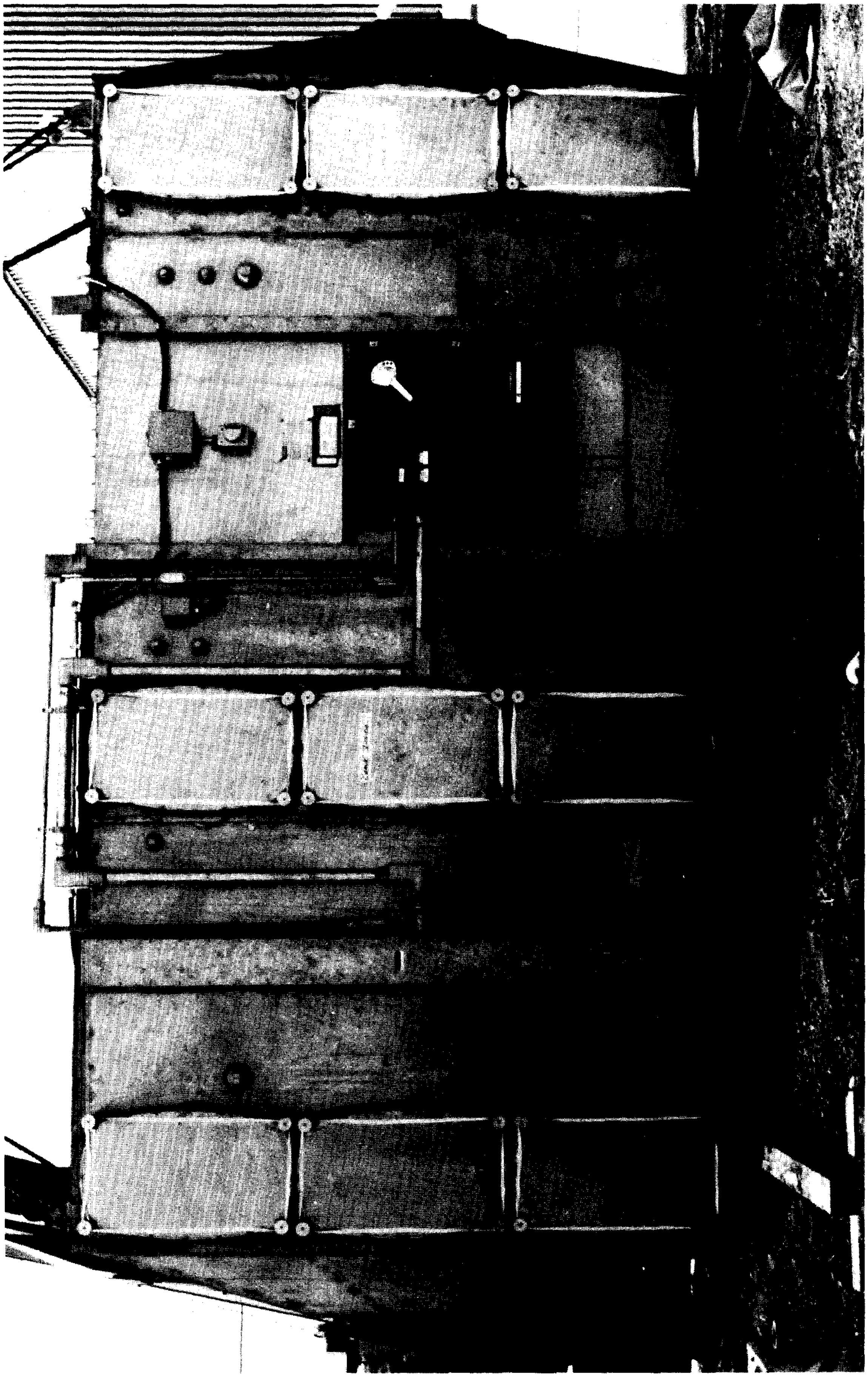

Figure 2. LOFT Filter Train

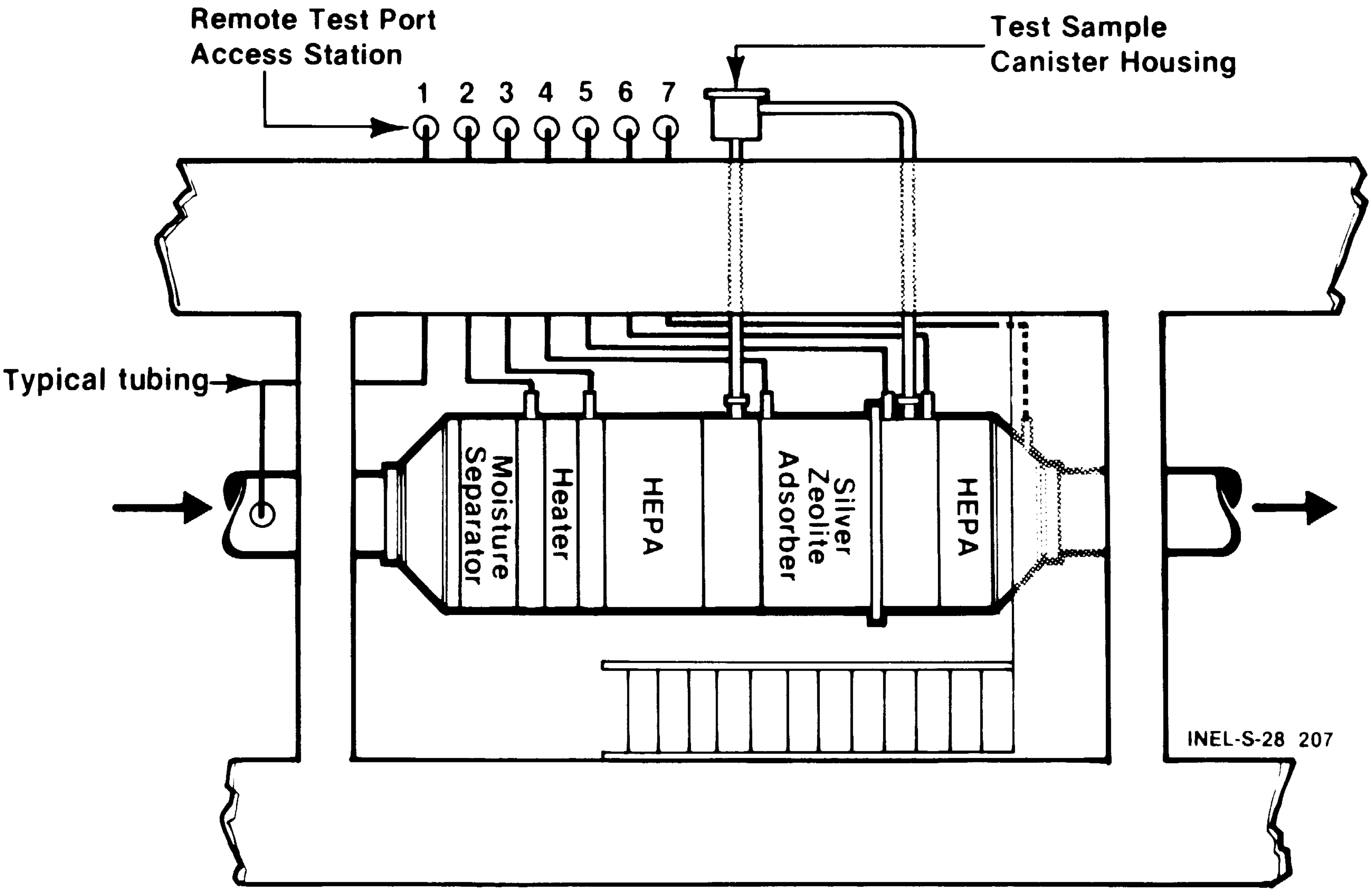

Figure 3. LOFT Filter Train Arrangement

Figure 4. Adsorber Air Slot with Bulged Retention Screens

the same production batch to supply the required quantity. Without the immediate delivery of this silver zeolite, the LOFT schedule would have been severely impacted.

Each channel of the adsorber section was filled, tamped, and packed to ensure that the maximum bulging had occurred. The unit then was sealed, and the initial inplace testing was conducted using a freon challenge gas. The initial inplace test results indicated an efficiency of 99.97%. These initial test results corresponded to the laboratory efficiency results of the virgin batch of 99.95% when challenged with radioactively tagged methyl iodide. This correspondence verified that the adsorber unit was full, and there was no break-through occurring.

The results from the first annual tests (June 1979) were 99.98% for the inplace test using a freon challenge gas and 98.3 ± 1.2% for the laboratory test. Because of the reported uncertainty from a new testing lab and because the inplace test corresponded to the initial test results, the credibility of the laboratory results was questioned.

However, the decision was made to inspect the adsorber section prior to the second annual tests to see if there was a problem with the adsorber. The vault was entered, and the examination found two problem areas.

The first problem was discovered when the top closure plate on the adsorber section was removed, revealing a lowered adsorbent level in four channels. Figures 5 and 6 show the condition of the top of the adsorber. Three of the channels had settled significantly, two of them exposing the retention screen and producing a leak path. Since the level of only four of the ten channels had dropped, the drop in level was attributed to additional creeping or bulging of the retention screens and not to settling of the spherical silver zeolite beads.

The adsorber section was refilled using the excess silver zeolite in the reservoir above each channel in order to retain the same batch of adsorbent material exposed to the air flow. New silver zeolite of a different production batch was then used to refill the reservoir portion and top off the adsorber section.

The second problem that was found during the investigation was improperly filled test canisters. Figure 7 depicts the possible consequences of a loosely packed canister; it was discovered that most of the silver zeolite had fallen out of the canister. It is very important that the canisters, as well as the adsorber unit, be filled properly.

All canisters were examined, and each loosely packed one was repacked using silver zeolite taken from the air flow region of the adsorber section. Then the canisters were re-installed for future use.

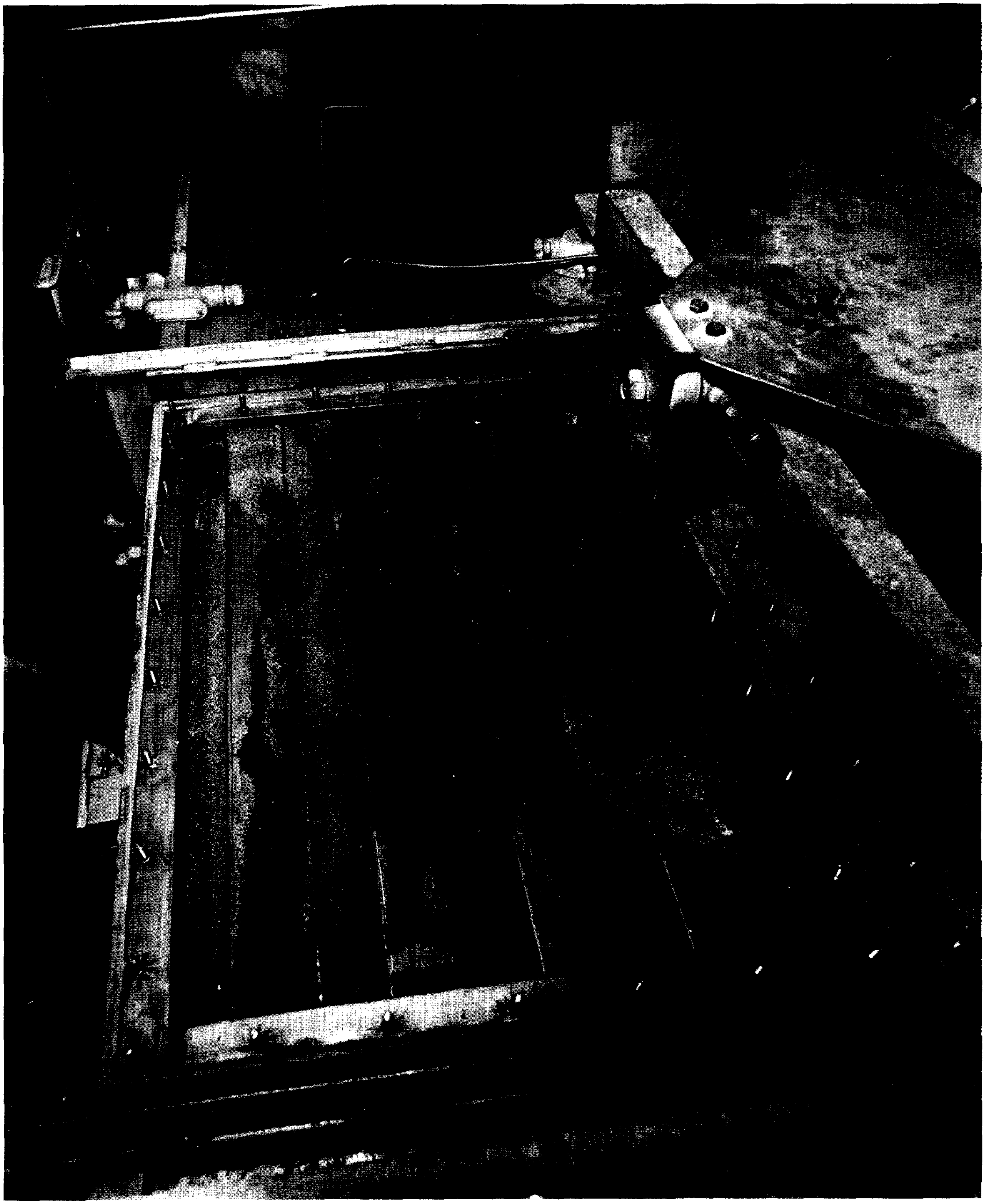

Figure 5. Adsorber with Top Closure Removed

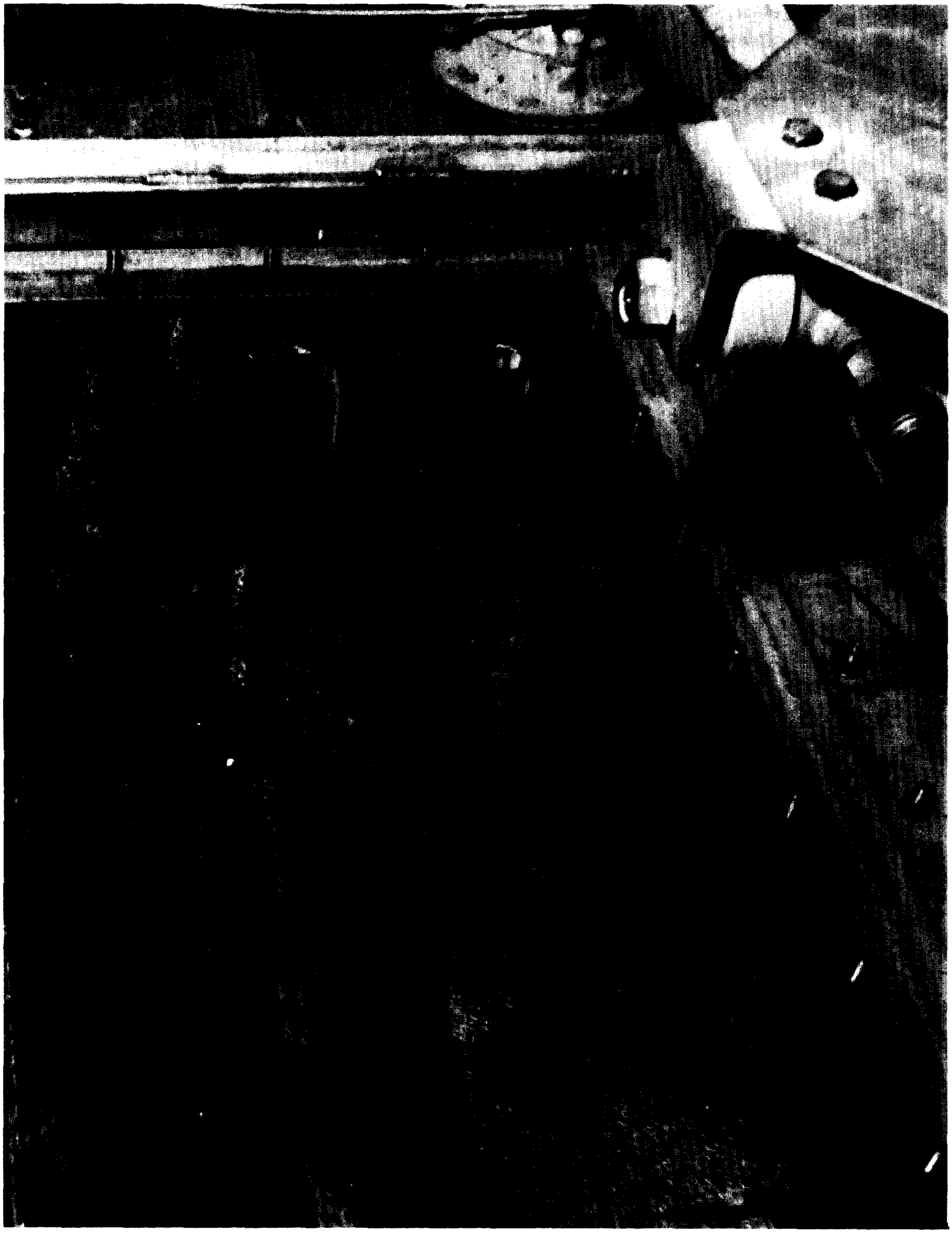

Figure 6. Close-up of Adsorber with Top Closure Removed

Figure 7. Consequence of Loosely Packed Sample Canister

The second annual inplace tests were conducted in May 1980 after the refilling and maintenance of the filter train were completed. The challenge gas for this test was radioactively tagged methyl iodide rather than the freon gas used in the previous tests. Using the methyl iodide challenge gas has the advantage of demonstrating the system inplace adsorption efficiency rather than merely testing for a leak path through the adsorber bed. At the same time, a sample canister was removed and sent out to a commercial laboratory for testing. The efficiency results after two years of operation in a predominantly standby mode were as follows:

Inplace test - 99.94% (uncontrolled conditions)

Laboratory test - 99.95% (at 70% RH, 30°C, 0.2 m/s or 40 fpm)

The filter train has been returned to service and is expected to remain in service for the projected life of the LOFT project.

V. Conclusion

The LOFT containment cleanup system, which uses silver zeolite as an adsorption medium in an 8,000-cfm system, has operated satisfactorily during two years of nuclear reactor experimental testing. Although the initial cost was more than the cost of traditional concepts, a relatively short payback period was realized due to reduced maintenance. Also, the silver zeolite system is less complicated because the fire detection and protection capability is not necessary. No indications of medium degradation have occurred during approximately 1000 hours of operation in the two-year period.

The operational problems have been minor and are easily corrected. More supports should be provided for the retention screens than were designed into the LOFT unit. The test canisters must be filled completely to prevent loosening of the retention screens.

The remote testing station makes the annual inplace testing faster and easier. This concept can also be incorporated into the traditional charcoal adsorber systems.

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ORGANIC IODINE REMOVAL FROM SIMULATED DISSOLVER OFF-GAS STREAMS USING SILVER-EXCHANGED MORDENITE*

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ABSTRACT

The removal of methyl iodide by absorption onto silver mordenite was studied using a simulated off-gas from the fuel dissolution step of a nuclear fuel reprocessing plant. The methyl iodide absorption of silver mordenite was examined for the effect of NO_x, humidity, iodine concentration, filter temperature, and filter pretreatment. The highest iodine loading achieved in these tests has been 73 mg CH_3I per g of substrate. This is approximately half the elemental iodine loadings. The experimental results indicate that a filter operating at a temperature of 150°C obtained higher iodine loadings than a similar filter operating at 100°C. Pretreatment of the sorbent bed with hydrogen rather than dry air, at a temperature of 200°C, also improved the loading. Variations in the methyl iodide concentration had minimal effects on the overall loading. Filters exposed to moist air streams attained higher loadings than those in contact with dry air.

A study of the regeneration characteristics of silver mordenite indicates limited adsorbent capacity after complete removal of the iodine with 4.5% hydrogen in the regeneration gas stream at 500°C.

1. INTRODUCTION

Iodine-129 is produced by both natural and man-made sources. The natural sources include the spontaneous fission of uranium and the interaction of cosmic rays with xenon in the atmosphere. The annual production through these natural paths is approximately 10 mg/year. With its long half-life, 1.6×10^7 years, ^{129}I tends to accumulate worldwide: as of 1940, the estimated accumulation has been reported to be 2×10^5 g.[1] A single light-water reactor (LWR) will produce 234 g of ^{129}I based on a uranium burnup of 30,000 MWd/t.[2] In handling the spent fuel, a single 5-t/d nuclear fuel reprocessing plant would have to process 3.2×10^5 g of ^{129}I/year.

In addition to ^{129}I, various amounts of other short half-life iodine isotopes are also produced. However, none of these appear in significant amounts after long (>200-d) decay times. On the other hand, in the reprocessing of liquid-metal fast breeder reactor (LMFBR) fuels, reducing the decay times to as little as 90 d might have economic incentive. This shorter decay time would mean that larger amounts of the short half-life isotope ^{131}I ($t_{1/2}$ = 8.05 d; specify activity, 1.24×10^5 Ci/g) would also become a significant factor.

During the past two decades, various systems have been studied to reduce the iodine released to the environment. Two liquid scrubber systems are currently available: the Iodox system and the mecuric nitrate-nitric acid (Mercurex) system. Solid sorbents have also been studied, either as secondary systems to provide final filtering following use of either the Iodox or Mercurex system or as primary systems to replace the liquid methods. These solid sorbents include silver faujasite, silver mordenite, alumina silicates, and macroreticular resins. Activated carbon has also been examined as a reference material. Activated carbon, however, cannot

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be considered as a primary sorbent for treating reprocessing plant off-gas because of its low ignition temperature and its adverse reactions with nitrogen oxide which could lead to the formation of explosive compounds and to poisoning by organic contaminants in the off-gas.

If high decontamination factors are required, one of the more promising systems to date for primary iodine removal is the Iodox system. Otherwise, solid sorbent-based processes tend to be favored. The Iodox system has already been tested on an engineering scale and has demonstrated good capabilities and operability. Decontamination factors (DF's) in excess of 10^6 have been obtained. There are, however, concerns about the long-term integrity of the materials of construction that come in contact with the 20 to 23 *M* HNO_3 scrub solution.

In comparison to liquid systems, silver-impregnated solid sorbents offer a much simpler iodine removal scheme. In this case, however, iodine DF's are limited to about 10^3, and high operating costs can be expected, particularly if the silver is not recovered. In the past few years, regenerable adsorbents have been receiving considerable attention.

At the 14th ERDA Air Cleaning Conference,[3] it was reported that silver-exchanged faujasite (AgX) loaded with elemental iodine could be regenerated in situ with a pure hydrogen stream at 500°C; however, a 50% loss in loading capacity was observed after five loading cycles. Silver-exchanged faujasite is capable of adsorbing iodine at temperatures as high as 500°C, and, like most other sorbents, it is adversely affected by water vapor, especially when condensation occurs. Faujasite is also adversely affected by acid vapor which would be found in the dissolver off-gas system. Average I_2 loadings were 100 to 200 mg I_2 per g AgX or 23 to 47% utilization of the available silver.

A silver-containing alumina silicate, AC-6120, also showed potential on a once-through basis. Silver utilizations of ~59% have been reported with AC-6120.

The high cost of silver, the lack of an available AC-6120 regeneration scheme plus limited regeneration potential, and the lack of acid resistance of the AgX make it less attractive than AgZ for large-scale use.

Similar studies with silver mordenite (AgZ) showed only a negligible reduction in loading capacity after eight cycles.[4] Average I_2 loadings were 100 to 130 mg I_2 per g AgZ or 42 to 55% utilization of the available silver. However, these tests were limited to elemental iodine loading.

The objectives of the solid sorbent studies reported here were to evaluate:

1. The suitability of silver-exchanged mordenite as a back-up or secondary iodine removal system for the Iodox process in nuclear fuel reprocessing plants;
2. The removal capabilities of silver-exchanged mordenite for organic iodides;
3. The use of dilute H_2 in the regeneration of silver-exchanged mordenites, thus reducing the explosion hazard.

2. EXPERIMENTAL PROCEDURE

Silver-exchanged mordenite (AgZ) was prepared by ion exchange with 0.16-cm-diam extrudates of the sodium form of Norton Zeolon 900; silver-exchanged faujasite (AgX) and lead-exchanged faujasite (PbX) were prepared from 0.16-cm-diam extrudates of Linde molecular sieve, Type 13X. Fifteen hundred grams of the unexchanged zeolite was loaded into an ion exchange column and batch contacted with 3 L of 1 *M* silver nitrate or lead nitrate solution at 40°C. At regular intervals the spent solution was replaced with fresh solution until no change in silver or lead concentration was detected. The solution was drained, and the exchanged zeolite was air dryed at 60°C for 24 h. Silver-exchanged mordenite was also purchased from Ionex Corporation under the trade name of Ionex Ag-900. The AgZ was pretreated in situ prior to sorbent tests. The bed was heated to 200°C and connected to either a dry air supply or to a gas cylinder containing 4.5% H_2–95.5% Ar. A flow rate of 5 L/min was maintained for 24 h. The bed was then isolated and allowed to cool to the operating temperature. The hydrogen pretreated bed is denoted as $\overset{\circ}{\text{Ag}}\text{Z}$.

Methyl iodide loading tests were conducted using an apparatus similar to that used by Staples et al.[3] A schematic of the equipment is presented in Figure 1, and operating conditions are listed in Table I. Heated air streams containing the desired amount of NO, NO_2, $^{127}CH_3I$ tagged with $^{131}CH_3I$, and water vapor were passed through the segmented filter bed located in the heated main filter enclosure. Initial studies were conducted using a glass filter casing.

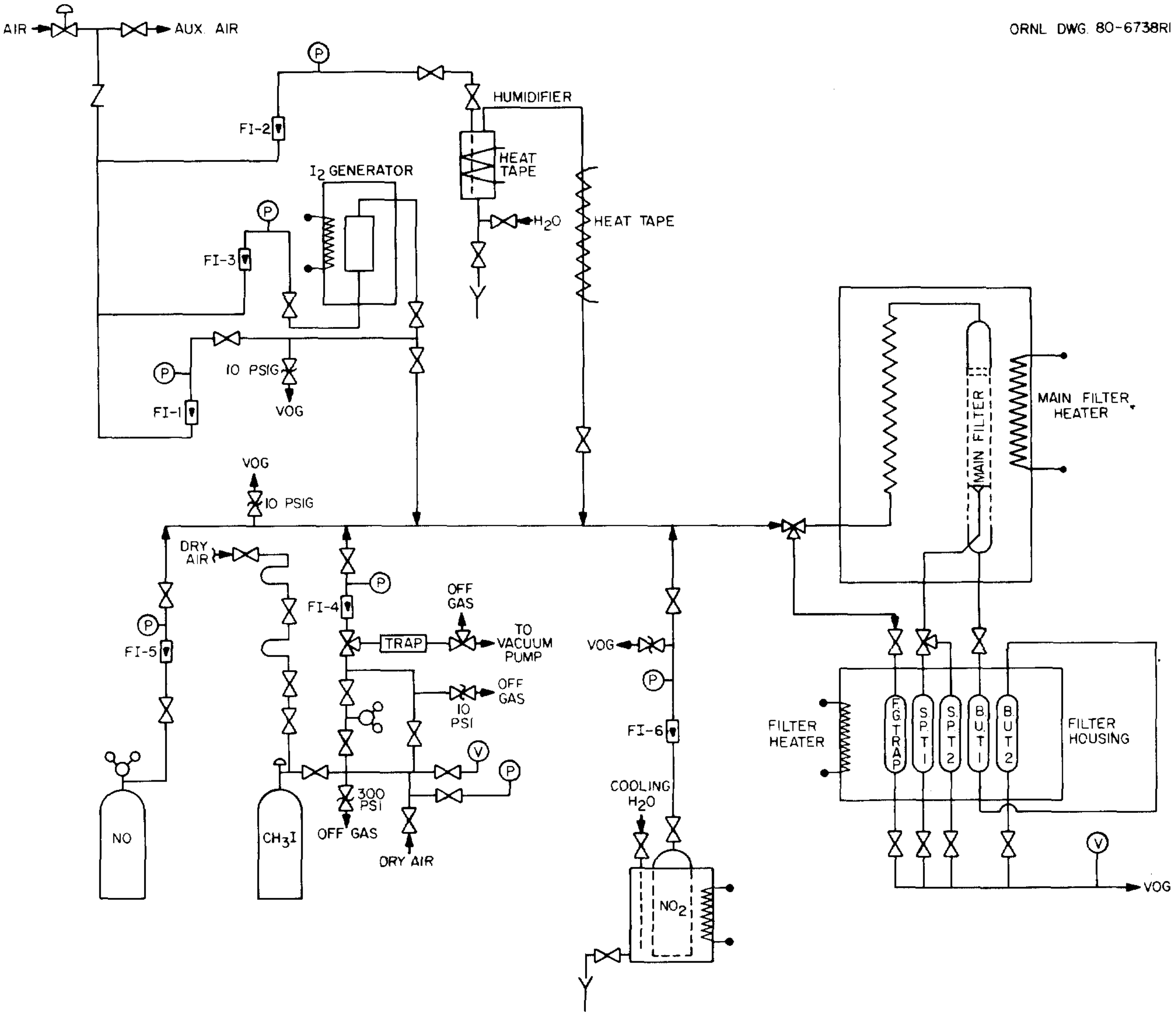

Figure 1
Test apparatus for methyl iodide loading studies

A stainless steel filter divided into six segments (see Figure 2) was used in later experiments. The breakthrough of the bed was monitored by collecting CH_3I on AgX from a slip stream port located downstream of bed 4. At regular intervals, this sample trap was removed and counted for ^{131}I. When $> 0.1\%$ of the iodine in the feed gas stream was found to be passing through bed 4, the run was stopped and the bed segments were counted for ^{131}I. The total amount of CH_3I loaded on the test bed was then calculated from the known ratio of ^{127}I to ^{131}I.

Maximum loading and regeneration tests were conducted in a similar manner. However, only 4 beds separated by 2.54-cm stainless steel spacers were loaded into a stainless steel filter casing. The degree of CH_3I loading was monitored by scanning the filter with a 7.6- by 7.6-cm

Table I. Experimental conditions for scoping studies

Variable	Unit
Bed weight, g	42.051
Bed diameter, cm	5.08
Bed thickness, cm	2.54
Number of beds	6
Carrier gas	Air
Superficial velocity, m/min	10.0
CH_3I concentration, mg/m^3	500 or 1000
NO concentration, %	0 or 3.1
NO_2 concentration, %	0 or 1.4
Relative humidity (dewpoint) °C	–54 or ~30
Pretreatment	Dry air or 4.5% H_2 in Ar for 24 h
Furnace temperature, °C	100 or 150

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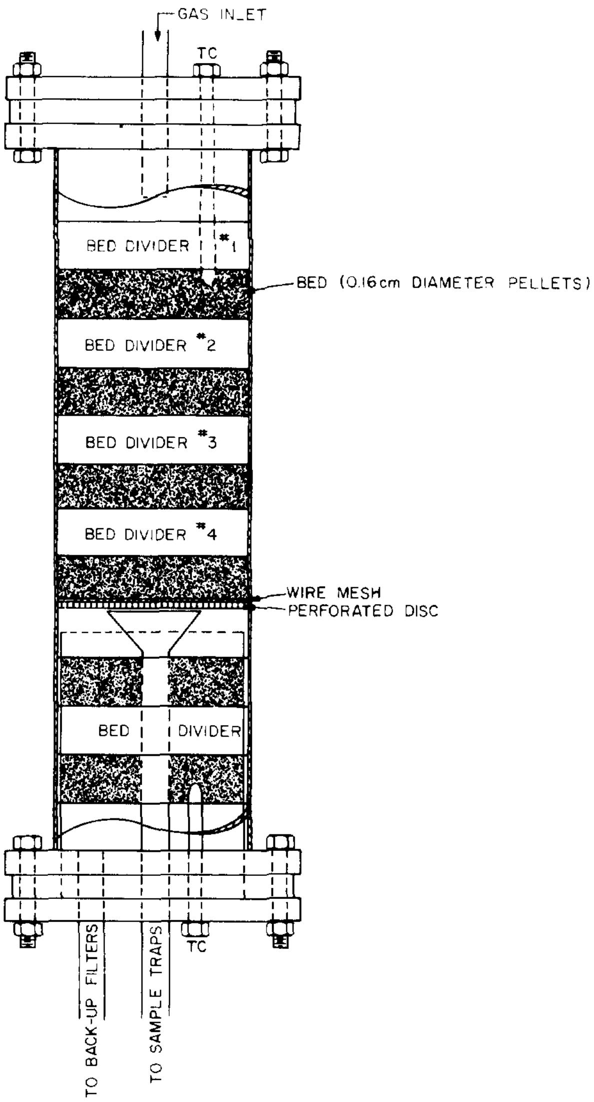

Figure 2
Stainless steel version of main filter

NaI detector with a 0.30-cm-wide slit collimater (Figure 3). Iodine-131 photo-peak counts were recorded as a function of filter position. During regeneration, similar scans were made to monitor the iodine removal without disturbing the beds.

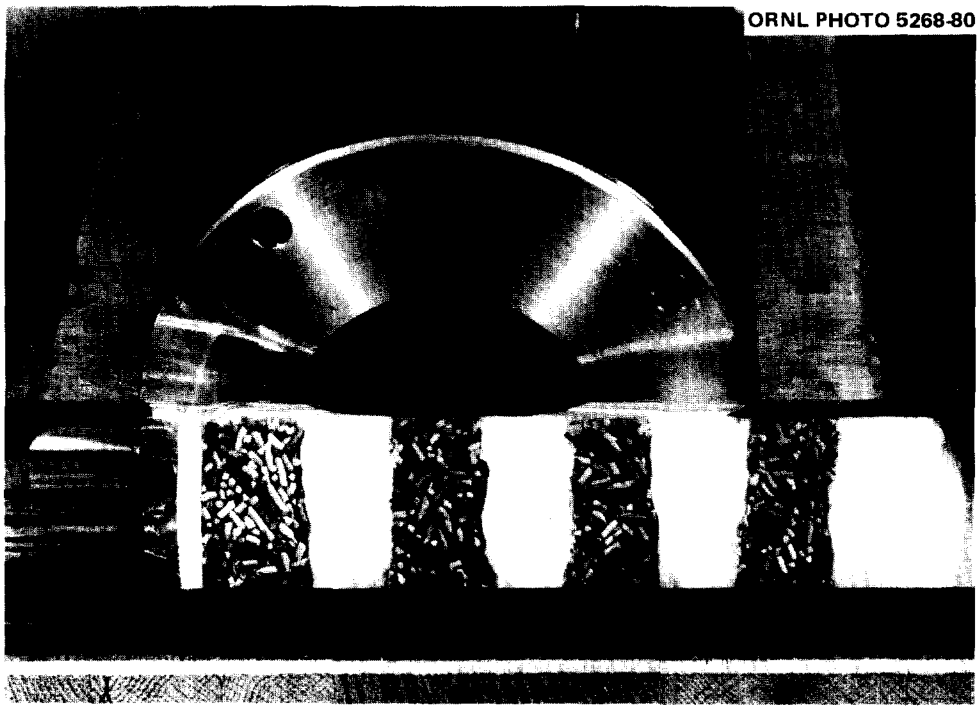

Figure 3
Detector and collimator for in situ ^{131}I measurements. A portion of the glass column is also shown.

3. EXPERIMENTAL RESULTS

Scoping Tests

The effects of NO, NO_2, humidity, pretreatment conditions, operating temperature, and CH_3I concentration on the loading capacity of silver-exchanged mordenite were evaluated using an eight-run fractional 2^n factorial-designed experiment. Each run was in duplicate, and the loadings for each bed were averaged between the two runs. The results for bed 1 are shown in Table II.

A response error for this experiment can be estimated using a dummy variable.[5] Using this technique, a value of 1.382 mg/g was obtained; however, this method probably overestimates the response error because of the interaction of the measured variables.

Analysis of the data has indicated that (1) pretreatment with 4.5% H_2–95.5% Ar at 200°C for 24 h improved loadings; (2) loadings were improved at higher operating temperatures; (3) loadings were improved in moist air conditions; and (4) the other variables, NO, NO_2, and CH_3I concentration, produced variations in loadings that were less than the response error.

Maximum Loading Tests

Three tests were conducted to evaluate the loading of Å̊gZ under what appeared to be optimum conditions (determined from the scoping study). The test conditions and bed loadings are listed in Table III. The results show little or no response in the loadings to changes in NO, NO_2, or CH_3I concentration, as predicted by the scoping experiments. Also, the loadings do not appear to be affected by the length of time of the moist air pretreatment to the bed. This indicates that while water is necessary to improve the loading of CH_3I, pretreatment of the bed with moist air prior to the run has no noticeable benefit.

Table II. Summary of screening runs[a]

Run	Bed 1 loading[b] [mg CH_3I/g (AgZ)]	NO (%)	NO_2 (%)	Dew Point (°C)	Temperature[c] (°C)	CH_3I concentration (mg/m^3)	Pretreatment	Dummy
1	7.307	0	0	54	100	1000	H_2	+
2	4.568	3.1	0	54	150	1000	Air	-
3	7.410	0	1.4	54	150	500	H_2	-
4	2.460	3.1	1.4	54	100	500	Air	+
5	7.085	0	0	37	150	500	Air	+
6	6.068	3.1	0	38	100	500	H_2	-
7	4.341	0	1.4	30	100	1000	Air	-
8	9.442	3.1	1.4	25	150	1000	H_2	+
Σ	48.681							
$\Delta\Sigma$		3.605	1.376	5.192	8.329	2.636	11.773	3.908
Effect	6.085	0.901	0.344	1.298	2.082	0.659	2.943	0.977

[a] Run conditions: six beds each, 2.54-cm-thick, 5.08 cm in diameter, face velocity of 10 m/min; pretreated 24 h at 200°C with dry gas (either 4.5% H_2 -95.5% Ar or air), average decontamination factor $>10^3$ through four beds.

[b] Loadings are based on a dry density of 0.85 g/cm.

[c] Furnace temperature.

Table III. Experimental conditions and loadings for maximum loading tests.

Conditions	Run 25	Run 26	Run 31
Temperature, °C (furnace)	150	150	150
Bed 1	~83	~83	~83
Pretreatment	4.5% H_2/24 h	4.5% H_2/24 h	4.5% H_2/24 h
NO, %		3.1	
NO_2, %		1.4	
CH_3I, mg/m^3	500	1000	1000
Moisture[a]	33°C (8-h pretreatment)	27.8°C (during run)	37.5°C (24-h pretreatment)
No. of beds	6	6	4
Bed No.	**Bed Loading, mg CH_3I/g AgZ**		
1	33.8	32.4	31.9
2	26.4	21.0	24.0
3	12.1	7.06	5.05
4	1.91	0.642	0.110
5	0.468	0.061	
6	0.0017	0.001	
Average for loadings beds 1–4	18.55	15.28	15.27

[a] Moisture content of gas stream as determined by the measured water utilization; pretreatment with moist air across bed at operating temperature for indicated times.

Following the scoping tests, the equipment was modified to allow monitoring of the inlet bed temperature. Previously, only the furnace temperature was measured. In relation to the furnace, the inlet bed operated at lower temperatures, depending on the feed gas flow rate. For example, the inlet bed operated at 59°C when the furnace was maintained at 100°C, and at 83°C with the furnace at 150°C, whereas the feed gas flow rate was 20 L/min. At a flow rate of 5 L/min used during pretreatment, only 6°C temperature difference was observed for a furnace temperature of 200°C. A stainless steel filter casing was constructed to allow three radial temperature measurements on the inlet bed and a single temperature measurement in the lower portion of the filter. Radial temperatures were within 3°C during subsequent tests. A large heated enclosure was constructed to house the filter and gas preheater. The new equipment, which replaced the original Linburg furnace and glass filter casing, allows a more uniform filter temperature regardless of feed gas flow.

Two additional maximum loading tests were conducted using a filter temperature of 150°C to examine the temperature effects. The feed gas conditions were 1000 mg CH_3I per m^3, a dew point of 31.1°C, and a total flow rate of 20 L/min. Average bed loadings were 40.16 mg/g $\mathrm{A\overset{o}{g}Z}$, which is more than double the average loadings for an inlet bed temperature of 83°C. The loading on bed 1 was approximately 73 mg/g $\mathrm{A\overset{o}{g}Z}$.

Preliminary tests were conducted to study the effects of temperature changes (noted in the scoping study) using a dry feed gas stream of 20 L/min containing 1000 mg CH_3I per m^3. Experiments were run at 75, 100, 125, 150, and 175°C. The average amount of CH_3I loaded on four 2.54-cm-thick beds is shown in Figure 4 as a function of temperature.

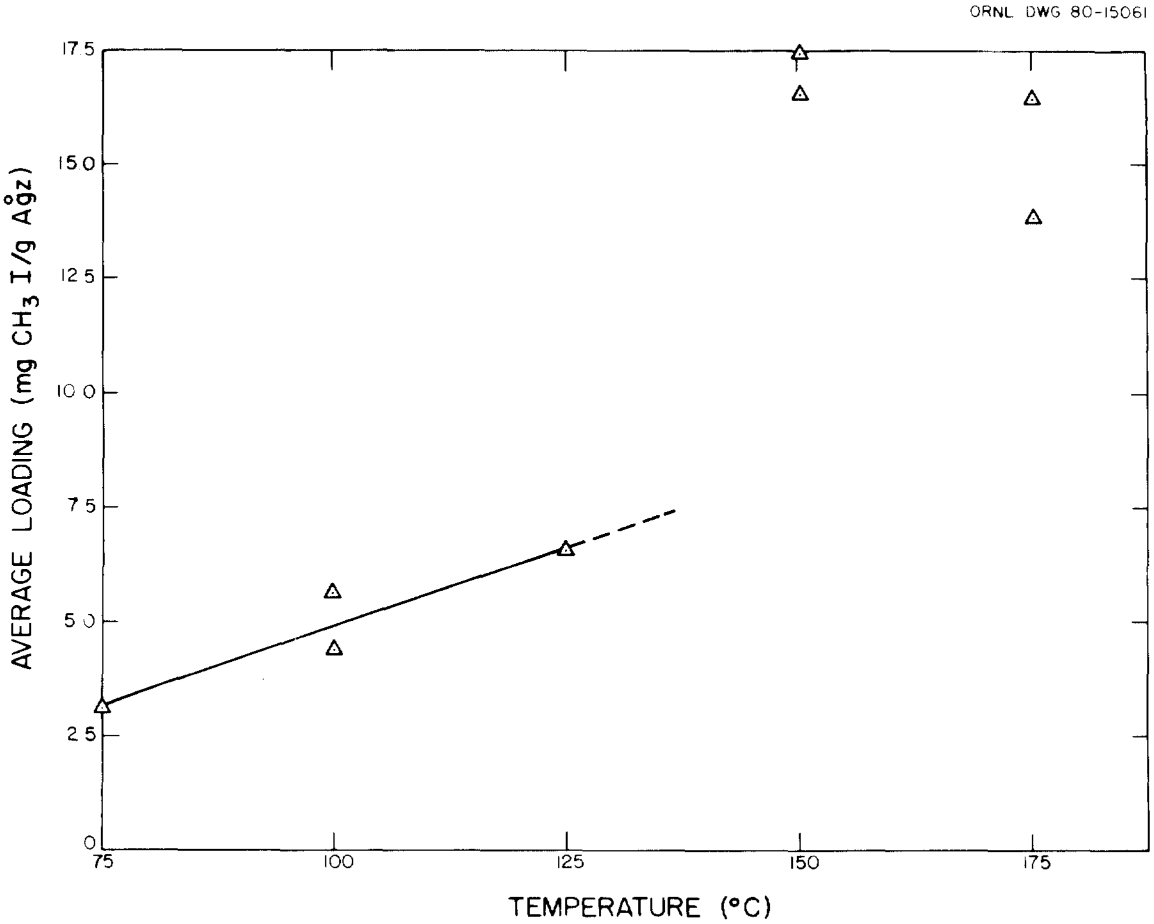

Figure 4

Average CH_3I loading from a dry feed gas stream (containing 1000 mg CH_3I per m^3) onto a 10.16-cm-deep bed of $\mathrm{A\overset{o}{g}Z}$ as a function of temperature

Below 125°C, small increases in loading can be obtained by increasing the temperature. Above 150°C, much higher loadings are achieved. The loading appears to slowly decrease as the temperature is increased above 150°C; however, higher temperature experiments must be completed before this trend can be fully analyzed. Studies are also planned to examine the gap in the loading profile between 125 and 150°C.

Regeneration Tests

Loaded AgZ beds were regenerated with equipment shown in Figure 5 using 4.5% H_2 – 95.5% Ar. Regeneration with low H_2 concentrations appeared to be feasible if the mechanism can be described by

$$1/2\,H_2(g) + AgI(s) \leftrightarrow Ag(s) + HI(g) \ .$$

Equilibrium vapor pressures of HI at 500°C for 5% H_2 and 100% H_2 are 26.5 and 119.1 Pa respectively. Following the initial loading, the test beds were removed from the main filter housing, counted, and returned to their original location in the filter. The filter was then placed back into the furnace. During later tests, the loading was determined by scanning the column. The H_2 gas line was connected to the filter housing at the lower end enabling the H_2 to pass from bed 4 up through bed 1 and on to the PbX bed where the HI was trapped. After 24 h of regeneration with 4.5% H_2, approximately 98 to 99.4% of the iodine originally loaded was removed. The second loading of the regenerated bed using the same feed gas conditions as the initial loading indicated a lower capacity than the first loading. Bed loadings before and after regeneration were as follows:

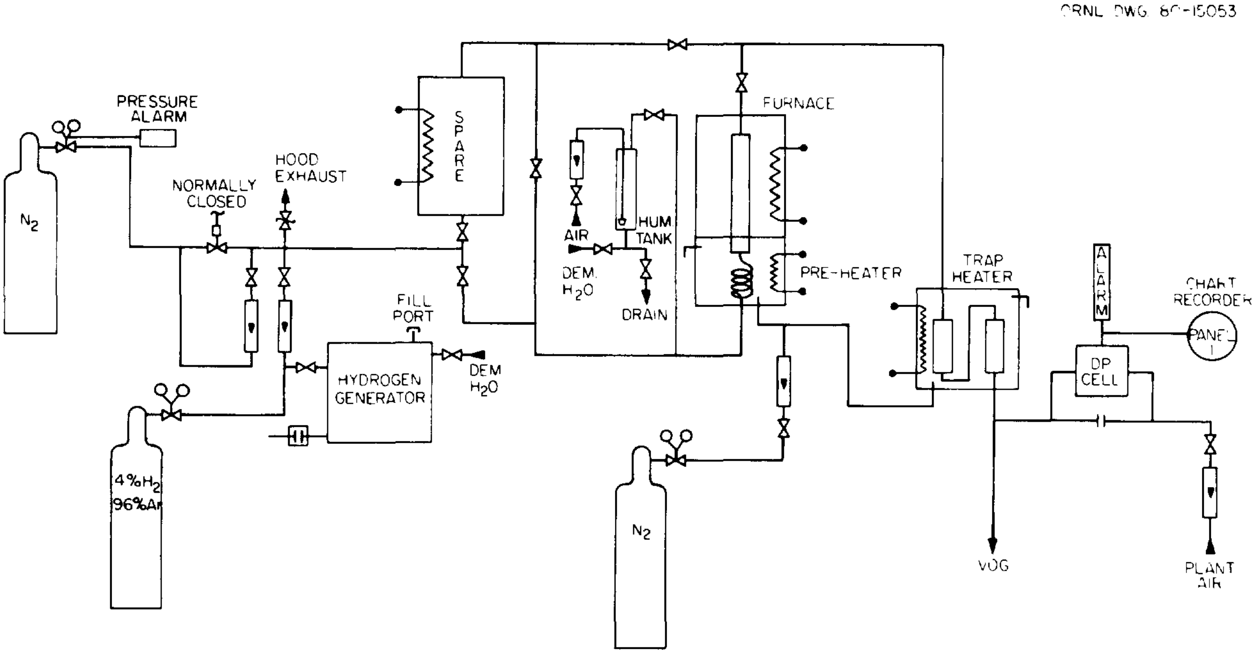

Figure 5
Hydrogen regeneration flowsheet for silver mordenite

Bed	Initial loading, mg/g	Reloading, mg/g
1	25.0	3.85
2	21.8	1.26
3	10.6	0.255
4	2.59	0.110

Since water vapor appears to be required for improved loadings, the reloaded bed 1 was placed in the inlet position of a second filter that had been pretreated with 4.5% H_2–95.5% Ar at 200°C. This filter was then exposed to a water vapor stream (dew point of 30°C) for 8 h to replace the water in the regenerated bed, which was probably driven off during regeneration. A feed gas of 1000 mg CH_3I per m^3 and a dew point of 30°C was passed across the filter at a rate of 20 L/min. The loading of the regenerated bed was increased to 8.95 mg/g AgZ. This indicates that water should be reintroduced into regenerated AgZ filters to improve the loading.

Effects of Hydrogen Pretreatment

Following the pretreatment of AgZ with 4.5% H_2–95.5% Ar at 200°C, free silver was detected by x-ray defraction. Prior to pretreatment with the hydrogen, free silver was not seen. A scanning electron micrograph (Figure 6) shows nodules suspected to be free silver on the surface of the zeolite structure. A similar photograph of AgZ without H_2 pretreatment, shown in Figure 7, shows no such nodules. Photomicrograph measurements show the silver nodules to be on the order of 2000 Å. The nodules are present on both the outside and the inside surfaces of the pellet. They are attached to the major crystalline structures and are accessible through the random pore structure. The silver map of Figure 6 (produced by induced electron fluorescence) indicates that additional silver, that is, silver not present in the nodules, still remains attached to the mordenite structure. This is inferred because silver locations are shown that do not correspond to the nodule locations. Similar results reported by Yates are further indications of the high mobility of the silver atoms.[6] Yates also reported that the average crystallite size of silver, when reduced at 250°C in pure H_2, was only 170 Å. The temperatures of interest are well below the melting point of silver (961°C), and the vapor pressure is extremely low (10^{-5} mm Hg at 757°C).

Another scanning electron micrograph of the regenerated AgZ material (Figure 8) shows very large nodules, which are suspected to be free silver. X-ray defraction shows a much stronger silver band for regenerated material than for original unregenerated AgZ. The large silver nodules probably account for the reduced loading capacity, since the number of silver sites available for reaction are significantly reduced.

An additional effect of hydrogen pretreatment is a change in the hardness of the mordenite structure. After being treated for 24 h at 200°C with 4.5% H_2–95.5% Ar, the pellets are more brittle than those exposed to air under the same conditions. The air-pretreated pellets are much more difficult to break or cut. This effect, however, has not been fully investigated.

Figure 6
Silver mordenite following 24-h pretreatment with a 4.5% H_2–95.5% Ar at 200°C. Note small nodules on the larger structure

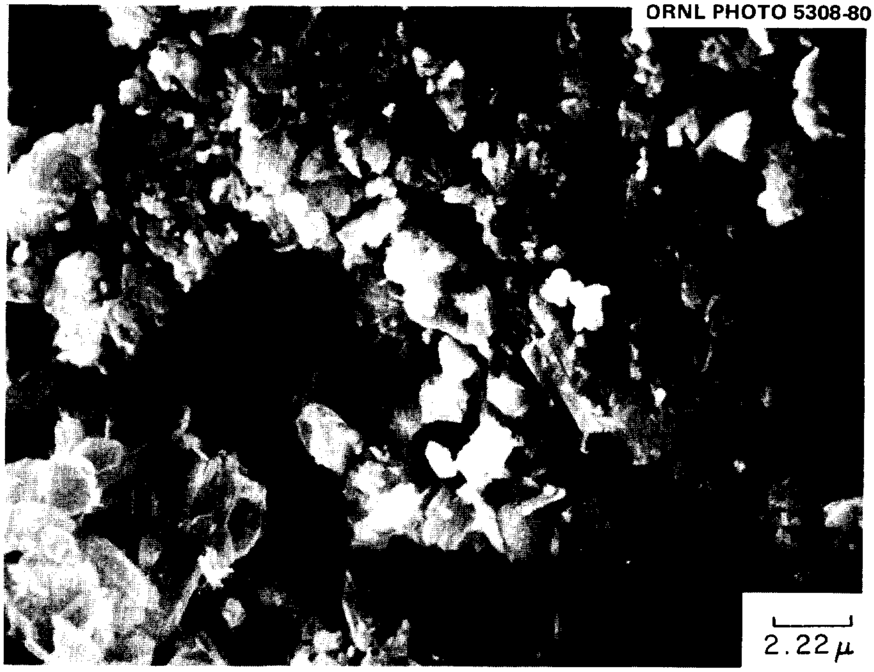

Figure 7
Silver mordenite following 24-h air pretreatment at 200°C.

ORNL PHOTO 5309-80

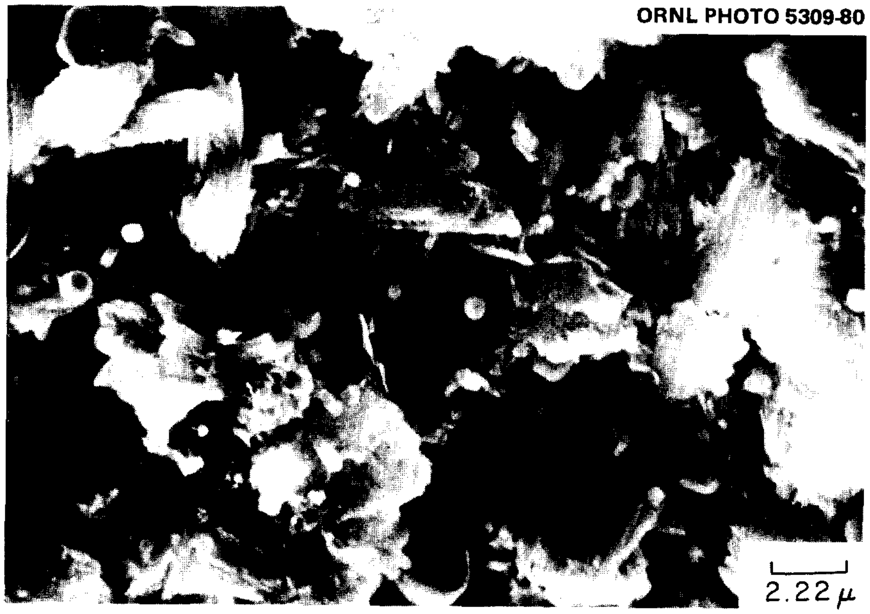

Figure 8
Silver mordenite following regeneration with 4.5% H_2–95.5% Ar at 500°C. The large smooth nodules on the structure are suspected to be free silver.

4. CONCLUSIONS

The following conclusions can be made from the experimental results and interpretation of the data:

1. Loadings of ~73 mg CH_3I per g of $\overset{o}{\mathrm{Ag}}$Z can be obtained. This represents a silver utilization of about 31%.
2. Bed temperature has a positive effect on the loading capacity of the $\overset{o}{\mathrm{Ag}}$Z and AgZ.
3. The pretreatment of AgZ with 4.5% H_2 improves the loading capacity of the material.
4. Free silver is detected only after hydrogen pretreatment. A noticeable difference in the appearance of the mordenite from untreated material is seen under the scanning electron microscope. Nodules approximately 2000 Å in diameter are visible on both the surface and cross section.
5. More than 98% of the iodine loaded on $\overset{o}{\mathrm{Ag}}$Z as CH_3I can be removed by a gas stream of 4.5% H_2–95.5% Ar at 500°C. However, regeneration apparently causes a dramatic loss in the bed loading capacity. This can be partially offset by the use of water vapor in the feed gas.
6. Following regeneration, very large nodules suspected to be free silver are seen in the AgZ structure.
7. Water vapor with a dew point up to 35°C has a positive effect on the bed loading for CH_3I.
8. NO, NO_2, and CH_3I concentrations have little or no effect on the CH_3I loading capacity of AgZ or $\overset{o}{\mathrm{Ag}}$Z.
9. Increasing the filter temperature from 83 to 150°C while using water vapor in the feed gas doubles the CH_3I loadings on $\overset{o}{\mathrm{Ag}}$Z.

Future plans include:

1. Further examination of the nodule formation.
2. Alternate regeneration schemes to improve reloading capacities.
3. Mixed I_2 and CH_3I loadings on $\overset{o}{\mathrm{Ag}}$Z.
4. Examination of the apparent role that water vapor has in CH_3I loadings.
5. Further examination of the temperature effects of CH_3I loadings.

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MODIFIED TEDA IMPREGNANTS FOR METHYL IODIDE REMOVAL

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ABSTRACT

One of the more successful impregnants for methyl iodide removal has been TEDA (Triethylene Diamine). The high activity of this compound owes as much to its rigid structure as to its basicity. Drawbacks to the use of TEDA as an impregnant have been 1) its vapor pressure and 2) that it is a solid and must be dissolved in water before applying to the charcoal. It is reported that the addition of C-Alkyl groups to the TEDA molecule can serve the purpose of decreasing the vapor pressure of the TEDA molecule. Thus improved performance at higher temperatures is expected when such modified TEDA compounds are used. Charcoals impregnated with C-Alkyl derivatives of TEDA are capable of retentions of more than 99% of the input methyl iodide under standard test conditions at 130°C, 95% R.H. Repeated tests of such charcoals have shown their ability, under standard test conditions, to retain greater than 99% methyl iodide at 25°C, 95% R.H.

I. Introduction

The most common method for the removal of radioactive iodine species has been the use of elaborate gas filtration systems containing beds of an absorbent material, usually activated charcoal. Various impregnants, including organic and inorganic compounds, have been added to these charcoal absorbents to improve their removal of methyl iodide. These impregnants can be either organic or inorganic. The common inorganic iodide impregnants have been found to age rapidly(1) and to promote corrosion of stainless steel filter holders(2). Because these problems appear to be inherent in the chemical nature of the iodine compounds, we have focused on the commercial development of charcoals using improved organic impregnants.

II. Linear Nitrogen Compounds

In 1967 Collins, et al.(3) reported the penetration of methyl iodide through charcoals containing various amine impregnants. Strong differences were found between the efficiencies obtained using different impregnants, but no detailed investigation was made regarding the effect of the basicity of the nitrogen atom on the results obtained. We have reanalyzed the data of Collins, et al.(3) and have shown in Table 1 and Figure 1 the reaction rate constant, k, as a function of the basicity of the amine impregnant. The reaction rate constant, k, was obtained from the penetrations reported by Collins, et al.(3) through the equation;

$$f = e^{-k t}$$

where: f = fractional penetration of methyl iodide, dimensionless
k = rate constant for the reaction of methyl iodide, sec^{-1}
t = contact time, sec.

The basicity of these nitrogen compounds (pK$_b$, the x axis in Figure 1) is the pH of the aqueous solution of that compound at which half the amine is ionized. The higher the pK$_b$, the more strongly basic the amine.

In Figure 1, although there does appear to be some increase in k as pK$_b$ increases, the results are highly scattered. Among the least successful compounds are those with a low value of pK$_b$, but it should also be noted that one of the least successful impregnants, guanidine, was the most strongly basic compound tested, having a pK$_b$ of 13.65. There must be some other factor or factors controlling the effectiveness of these organic impregnants. We strongly suspect that the most important factor is the geometry of the amine molecule.

III. Geometric Effects

The geometry of the amine molecule has an important effect on the value of k. Two molecules having a caged structure, hexamine and triethylene diamine (TEDA), gave superior removal efficiencies. The k value for the TEDA molecule was so high (46 sec^{-} that it was omitted from Figure 1. This geometric effect had been known for many year before the work of Collins, et al.(3) appeared. In 1946, Eldred(4) reported that the similar caged molecule, quinuclidine, reacts with methyl iodide 50 times faster and wi isopropyl iodide 700 times faster than does triethylamine. Another factor, doubtlessl caused by differences between a caged and uncaged structure, is the finding that quinuclidine forms a far more stable complex with trimethyl boron than does triethylamine.

The high activity of TEDA and quinuclidine can be attributed to their high symmet and insignificant bond strain. According to Yakhontov(5), in quinuclidine the nitroge lone pair electrons are sp^3 hybridized and are free from steric crowding. The same should be true of TEDA. These steric properties show up in the fact that in many cycl nitrogen compounds there is a "characteristic absorption at 2700-2800 cm^{-1} attributabl to interaction between the nitrogen lone-pair electrons and the neighboring axial CM bands"(5). These absorption bands are not present in either TEDA or quinuclidine(26,

A major difficulty with quinuclidine and TEDA has been their volatility. For example, "quinuclidine rapidly and completely sublimes on standing in the open air"(5). The volatility of TEDA probably accounts for the difficulty of TEDA impregnated charcoals in passing a standard test in which methyl iodide in air at 130°C, 95% R.H. is passed through a two inch thick bed for two hours, after which time there is a two hou elution period.

IV. C-Alkyl Derivatives of TEDA

It is reported here that the addition of one or more C-Alkyl groups to the TEDA molecule can serve the purpose of decreasing the vapor pressure of the TEDA molecule. Thus, improved performance at higher temperatures is expected when such modified TEDA compounds are used. Charcoals impregnated with C-Alkyl derivatives of TEDA are capabl of retentions of more than 99% of the input methyl iodide under standard test conditions at 130°C, R.H. 95%. (See Table 2, below.)

Another advantage of these derivatives is that they are either liquids or can be dissolved in the simpler members of this family (e.g., 2 methyl, 2 ethyl, 2 propyl) an applied directly to the adsorbent. This eliminates the use of water as a solvent and thereby eliminates the cost of drying the adsorbent subsequent to impregnation. The resulting impregnation is able to produce a monomolecular layer of amine and the adsorbents thus obtained have a high activity. Repeated tests of such charcoals have shown their ability, under standard test conditions, to retain greater than 99% methyl iodide at 25°C, 95% R.H., as shown in Table 2.

The basic TEDA molecule is unusually stable for an amine. It is known that samples of TEDA may remain white for years, whereas samples of nearly every other common amine will darken from atmospheric exposure within months. By using alkyl groups as an additive to the TEDA molecule, we have added one stable group to enhance the retention of another. We have determined that for each additional CH_2 attached to the TEDA molecule, the volatility is reduced by $\sim$30 percent, extending the retention of the modified TEDA molecule by a similar fraction. We also find that the ignition temperature of the impregnated charcoal can be increased by $\sim$18°C for each additional CH_2 group attached to the TEDA molecule.

V. Conclusions

Significant improvement in the removal of methyl iodide can be attained by careful attention to the physical chemistry involved in the interactions of the impregnants with methyl iodide. One approach has been demonstrated in this paper.

As a general rule in the nuclear industry, improved technology has consistently lead to higher standards. The development of improved adsorbents should lead to higher standards for the removal of methyl iodide.

(Patent protection is being sought for the new technology described herein.)

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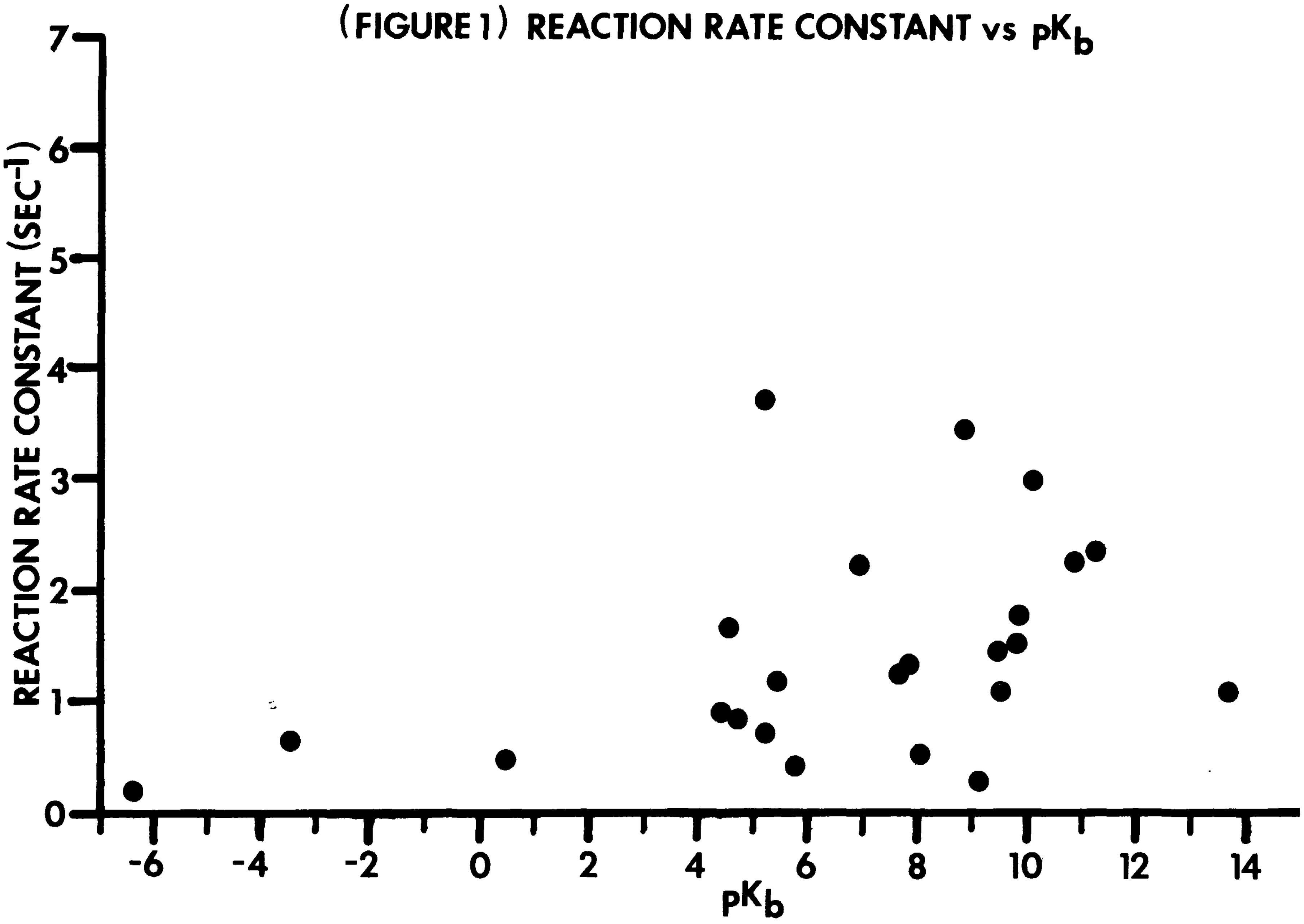

(FIGURE 1) REACTION RATE CONSTANT vs pK_b

Table 1

pKb and Reaction Rate Constants for Various Amines

Amine	Reaction Rate Constant, Sec^{-1}	$\mathrm{pK_b}$ Dimensionless	Reference
Isoquinoline	1.20	5.42	6
Pyrrole	0.65	-3.51	7
N Dimethyl p Phenylene Diamine	6.70	0.38	8
Quinoline	0.32	9.10	6
Hexamethylenetetramine	3.73	5.14	9
Diethanolamine	3.48	8.87	10
3 Diethyl Aminopropanol	2.95	10.10	11
Dicyclohexylamine	2.37	11.25	10
Tri N Butylamine	2.26	10.89	12
Iminazole	2.25	6.95	6
N Propanolamine	1.76	9.85	13
Succinimide	1.69	4.54	14
N 2 Aminoethyl Ethanolamine	1.54	9.83	15
Ethanolamine	1.48	9.50	16
Triethanolamine	1.33	7.77	8
Guanidine	1.18	13.65	17
Isopropanolamine	1.19	9.47	18
5 Aminoacridine	0.91	4.40	19
Sym Diphenylguandine	0.85	4.70	20
2 Amino 2 Methyl Propan-1:3 Diol	0.69	5.22	21
Acridine	0.59	5.58	6
p Amino N,N Diethylaniline	0.53	8.00	22
Dimethylformamide	0.49	0.45	23
Toluene p-Sulphonamide	0.20	-6.39	24
Ethylenediaminetetraacetic Acid	1.26	7.73	25
Triethylene Diamine (TEDA)	46.	11.05	26

Table 2

Test Results Obtained with Charcoal Impregnated with 2 Methyl Triethylene Diamine
(Commercial Grade, Radshield 25 type Impregnated Charcoal)

1. 25°C Test
Bed depth - 2 inches
Relative humidity - 95%
Air velocity - 12 meters/minute
Pressure - atmospheric
Methyl Iodide Concentration - 2 mg/m^3
Feed Duration - 2 hours
Elution period - 2 hours
Measured retention in sequential tests - 99.58
99.59
99.54
99.68
99.92

2. 130°C Test
Bed depth - 2 inches
Relative humidity - 95%
Air velocity - 40 feet/minute
Pressure - 42.5 psig
Methyl Iodide concentration - 1.75 mg/m^3
Feed duration - 2 hours
Elution Period - 2 hours
Measured retention - 99.76%