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Charcoal Performance Under Accident Conditions in Light-Water Reactors

Final Report

Prepared by V. R. Deitz

Naval Research Laboratory

Prepared for
U.S. Nuclear Regulatory
Commission

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ABSTRACT

Nuclear-grade activated carbons have a limited life in regard to satisfactory performance in trapping radioactive methyl iodide. Carbons from different sources and impregnations were systematically degraded by exposure to unfiltered outdoor air and all were found to degrade with respect to radioactive methyl iodide trapping efficiency. The same carbons, exposed to air flows of known contaminant species and concentrations under controlled laboratory conditions, behaved similarly. Evidence was found from both the laboratory and outdoor exposure tests that air flows above 70% RH degrade the carbon efficiency significantly. An adverse synergistic influence of moisture and hydrocarbon vapors was observed. Local meteorological conditions of high humidity combined with atmospheric pollutants in the test vicinity contributed jointly to the degradation of the trapping efficiencies of impregnated carbons.

When service activated carbons were exposed to radiation levels of 10^7 to 10^9 rads, the iodine isotope exchange capacity was regenerated. The recovery increased with the increase of atmospheric contaminants directed to the carbon adsorber during service. While the efficiency for iodine isotope exchange was vastly improved, the removal of cold methyl iodide-127 was only slightly improved or not at all. It was also found possible to regenerate the iodine isotope-exchange efficiency by reaction with airborne chemical reducing agents such as hydrazine with little or no improvement in methyl iodine-127 retention. Chemical regeneration was successful for carbons exhausted with known contaminants as well as for many carbons removed from nuclear power operations.

The gradient in methyl iodide-131 penetration through a bed changes from a simple exponential profile for new carbons to a non-linear exponential profile for weathered and service-aged carbons. The behavior is attributed to the chromatographic distribution of the contaminants that accumulate in the bed. The thermal stability of KI_x impregnated carbons was studied for the retention of the iodine of impregnation; weathered KI_x carbons were observed to be considerably less stable than new material.

The removal of radioactive iodine from air flows passing through impregnated activated carbons depends on a minimum of three distinguishable reactions: (1) adsorption on the carbon networks of the activated carbons, (2) iodine isotope exchange with impregnated iodine-127, and (3) chemical combination with impregnated tertiary amines when present. When a carbon is new, all three mechanisms are at peak performance and it is not possible to distinguish among the three reactions by a single measurement; the retention of methyl iodide-127 is usually equal to the retention of methyl iodide-131. After the carbon is placed in service, the three mechanisms of iodine removal are degraded by the contaminants of the air at different rates; the adsorption process degrades faster than the other two.

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TABLE OF CONTENTS

CONTENTS (Cont'd)

EXECUTIVE SUMMARY

1. The activated carbon in the carbon adsorber units of engineered-safety-feature atmosphere clean up systems degrades slowly during its long service. The behavior is attributed to the atmospheric contaminants (ozone, sulfur dioxide, and nitric oxides) in outdoor make-up air and to local solvent spills within the installation.

2. Water vapor influences the degradation of a nuclear-grade carbon which correlates best with the dew point and duration of the air flow. The trapping efficiency remains good up to dew points below about 30°F.

3. KI_x carbons weathered in intermittent flows of outdoor air may yield etration of methyl iodide-131 than when subjected to continuous weathering with the same total volume of air. Weathered samples of carbon cannot be regenerated at ambient temperature by a continuous air purge alone.

4. Commercial activated carbons with TEDA (triethylenediamine) and potassium iodide in the impregnation formulation, after exposure to the common contaminants in unfiltered outdoor air, exhibit less penetration of methyl iodide-131 than do the carbons with only potassium iodide + iodine as the impregnant. The impregnation formulation of nuclear grade carbons is a critical choice to high efficiency and long service life.

5. The winter months with air flows of low average dew points have minimum influence in the weathering of nuclear grade carbons. The pattern of air contaminants (ozone, sulfur dioxide and nitric oxides) 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.

6. Consideration should be given to and a cost effective analysis made for the use of controlled inlet air heaters to maintain the prevailing relative humidity below 90% RH.

7. Based on the experimental results, it appears that reactor-grade activated charcoal can satisfy the stipulation in Regulatory Guide 1.52 that requires successful trapping of radioiodine during a DBA with radiation levels up 10^9 rads.

8. The exposure of service activated carbons to radiation levels of 10^7 to 10^9 rads regenerates the iodine isotope exchange capacity. The observations validate the directive in Regulatory 1.52 that atmospheric cleanup systems must operate in a DBA of an average radiation level of 10^9 rads for iodine buildup on the adsorber. There is little or no change in the adsorption of cold methyl iodide.

9. A service carbon of low efficiency can be regenerated at room temperature by contact with hydrazine vapor or spray. The chemical reduction process accomplished the same end product as the radiation exposure to 10^7 to 10^9 rads, namely, it restores the iodine isotope exchange efficiency. Both KI and TEDA service carbons can be regenerated with hydrazine vapor or spray.

10. An activated carbon in service having both KI and TEDA impregnation can trap methyl iodide-131 by three independent mechanisms: (1) adsorption to the carbon network, (2) isotope exchange and (3) chemical combination with the tertiary amine. Improvement in isotope exchange appears to be the outstanding factor for the maintenance of efficient iodine trapping in used and service grade carbons.

11. A canvas of 80 individual units of 46 utilities has shown that over 3 million pounds of nuclear-grade activated carbon are in place. In view of the cost of the carbon and the labor costs of replacement, in situ studies are justified to evaluate the cost effectiveness of the regeneration process based on the hydrazine reaction.

12. It is recommended that the study of carbon regeneration be extended to a Pilot Plant Scale with the inlet air derived from a refueling and storage building or its equivalent.

1.0 Loss of Iodine Trapping - Weathering

1.1 Introduction

At any stage in the service life of an activated carbon adsorber that is used in nuclear air cleaning applications, the carbon must have the capability to retain a designated fraction of the airborne radio-iodine that may be liberated under accident conditions. Specifically, the retention of radioactive iodine, while it decays to xenon, is the prime objective of these air cleaning units. During normal operations there is a slow and continuous degradation in the efficiency of a service carbon due to exposure to containment and atmospheric contaminants (1). When accident conditions are superimposed, additional problems can be expected. These include possible radiation damage to the physical structure of the activated carbon, the desorption of adsorbed materials, induced radioactivity after exposure to the accident radiation, and chemical changes in adsorbed contaminants.

The objective of the present work was to investigate the performance of activated carbons in removing airborne radioiodine under light water reactor accident conditions. The effects of in-service weathering were to be assessed, the exposure to relevant contaminants and to intense radiation doses, all judged by the retention of radioiodine-131 by the carbon.

The continuous exposure of charcoals to environmental contaminants has a pronounced influence on the trapping efficiency for methyl iodide, the species generally considered to be representative of the organic iodides present in nuclear power operations. It may be generated from a series of surface chemical reactions between elemental fission iodine and the organic contaminants present in a containment space and other structures. The adsorption capability of the charcoal can be reduced due to the weathering process. The adsorption sites of a charcoal can be blocked by atmospheric contaminants; also, the particular chemical sites between the charcoal and the impregnates, where chemical reactions with methyl iodide molecules can take place, can be damaged or destroyed by the contaminants. Both processes occur during the "weathering" of charcoal.

The term "weathering" is used to differentiate among several mechanisms which result in reduced capability of carbons to remove radioiodine. First, the term "ageing" of a carbon connotes possible shelflife of the carbon, stored as it must be in closed containers in a given environment. Thus, ageing would be restricted to a sealed static testing operation. Second, "service-aged" carbon indicates the exposure of a carbon to the actual air flow from a confined system such as a reactor building, fuel-handling building, etc. including any make-up air. In fact, the term itself suggests exposure under a relevant set of conditions. Third, "weathered" carbon is a subgroup of service-aged carbon and signifies an exposure to the atmospheric contaminants in either a flow of outdoor air at a given location, or under some laboratory set of conditions in which a controlled exposure can be realized. From the above point of view, a weathered carbon is a special, and relevant, case of service-aged carbon. Under normal operating conditions, the two cases can be identical.

1.2 Atmospheric Contaminants

Large volumes of outdoor air are used in a nuclear air cleaning operation and a contaminant concentration of 1 ppm becomes a significant insult when accumulated over the total lifetime of a carbon adsorber. The atmospheric contaminants include the volatile hydrocarbons, ozone, sulfur dioxide, nitric oxides, and carbon monoxide, all of which are widely distributed. Local contaminants are also drawn into the air ducts as a result of solvent spills, evaporation of lubricating agents, and volatilization of paint components. The prolonged exposure of carbons to these contaminants has a degrading influence on the trapping efficiency for methyl iodide-131, which, as mentioned above, is the species generally considered as the most difficult radioiodine to remove from a nuclear power plant atmosphere.

Using a typical carbon module as an example, an air flow of 30,000 cfm for 90 days (3.9×10^9 cu. ft.) may be directed through the adsorber which contains approximately 3750 pounds of activated carbon (2-inch depth). Based upon 3 years of measurement of atmosphere contaminants at the Naval Research Laboratory (NRL), the typical quantities of contaminants thus introduced to the carbon adsorber are listed in Table 1.1.

Table 1.1 Atmosphere Contaminants Passing into a 30,000 cfm Carbon Adsorber (3750 lbs)

	Concentration ppm 3-year av. at NRL (4)	Weight in 30 days (lbs)	Weight in 90 days (lbs)	Wt.-% of Charcoal
Ozone	0.019	3.3	10	0.27
SO_2	0.023	5.3	16	0.43
NO_2	0.043	7.0	21	0.56
CO_2	1.37	139.	416	11.0
Hydrocarbons (non-CH_4)	0.23	71.3	214 (hexane)	5.0

Using the NRL Air Quality Data for 1977, 1978, and 1979 Table 1.2 (4), the monthly average concentrations of five airborne contaminants may be seen to have common trends. The NO_2 concentrations were fairly uniform over the year; the SO_2 was somewhat greater in the first quarter than in the remainder of the year; the total hydrocarbons including methane were fairly uniform over the year. The oxidants (mainly ozone) were higher in the second and

Table 1.2 Monthly Average of Pollutant Concentrations (ppm) during 1977, 1978, 1979 - NRL

	O_3			SO_2			NO_2			RHC			CO		
Month	1977	1978	1979	1977	1978	1979	1977	1978	1979	1977	1978	1979	1977	1978	1979
Jan.	0.007	0.013	0.006f	0.052	0.028	0.028	0.018	0.011	0.024	0.28	0.04	0.06	1.92	1.45	1.42
Feb.	0.010	-	0.009	0.028	-	0.019	0.055	-	0.028	0.48	-	0.04	1.22	-	1.67
Mar.	0.012	-	0.006	0.023	-	0.026	0.079	-	0.026	0.24	-	1.02	3.77	-	1.80
Apr.	0.013	0.034	0.032	0.023	0.016	0.017	0.051	0.087	0.021	0.40	0.02	0.95	0.63	1.10	1.75
May	0.015	0.037	0.027	0.020	0.013	0.015	0.047	0.031	0.010	0.22	0.10	0.12	0.32	1.24	1.08
June	0.020	0.052	0.032	0.020	0.014	0.013	0.116	0.006	-	1.06	0.05	0.28	0.98	1.06	0.98
July	0.040	0.035	0.034	0.023	0.014	0.013	0.078	0.025	0.035	0.07	0.07	2.53	0.95	1.06	1.59
Aug.	-	0.038	0.034	-	0.015	0.012	-	0.011	0.019	-	0.06	0.32	-	1.25	0.96
Sept.	-	0.030	0.023	-	0.024	0.013	-	-	0.022	-	0.02	0.26	-	1.14	1.26
Oct.	0.018	0.055	0.016	0.015	0.024	0.015	0.073	-	0.023	0.08	0.09	0.32	1.14	1.56	1.63
Nov.	0.013	0.012	0.017	0.015	0.029	0.018	0.028	-	0.033	0.04	0.28	0.44	1.17	2.25	-
Dec.	0.012	0.006	0.013	0.022	0.017	0.0282	0.061	0.015	-	0.06	0.89	0.23	1.62	1.52	1.99
Year	0.014	0.031	0.021	0.024	0.019	0.018	0.058	0.027	0.024	0.25	0.16	0.55	1.33	1.36	1.47

NRL Memo Report 3764, "The 1977 NRL Air Quality Data" by A. Stamulis, 27 pp.

NRL Memo Report 4010, "The 1978 NRL Air Quality Data" by A. Stamulis, 19 pp.

NRL Memo Report 4228, "The 1979 NRL Air Quality Data" by A Stamulis, 35 pp.

third quarters. These are some of the facts that have to be recognized in any attempt to correlate the weathering behavior of charcoals in a flow of outdoor air during long periods of exposure.

Possibly the most important constituent of the air is the water vapor which in magnitude far exceeds the mass of the above-mentioned contaminants. Since the initiation of these investigations, the moisture content of outdoor air encountered at NRL has been recorded for the four seasons of 1977, 1978, 1979 and 1980. The absolute humidity (dew point), Fig. 1.1, has been maximum in July and August and minimum in January and February (5). The yearly trends are similar and appear to be a general characteristic of the climatological location of NRL which is located close to the Washington National Airport. The monthly-averaged dew points are below 50°F for about half of the year.

The ambient air temperature, relative humidity, and dew point are related as follows:

Let t = the ambient temperature, ^{o}F
p = the partial pressure [illegible] water vapor at $t^{o}F$
p_o = the vapor pressure of water at $t_o{}^{o}F$

$$r = \text{relative humidity} = \left(\frac{p}{p_o}\right)_{t^{o}\,F} \qquad (1)$$

$$\text{dew point (d.p.)} = \text{temperature } t_o \text{ at which } p = p_o \qquad (2)$$

$$t^{o}\,F = (t^{o}\,C \times 1.8) + 32 \qquad (3)$$

$$\log_{10} p_o = 8.10765 - \frac{1750.286}{235.0 + t_o{}^{o}C} \qquad (4)$$

Using equations (1), (2), (3) and (4), any one of the three parameters (r, d.p. (^{o}F) or t(^{o}F)) can be expressed as a function of the other two. However, the calculation of d.p. from r and t and of r from d.p. and t are the most useful.

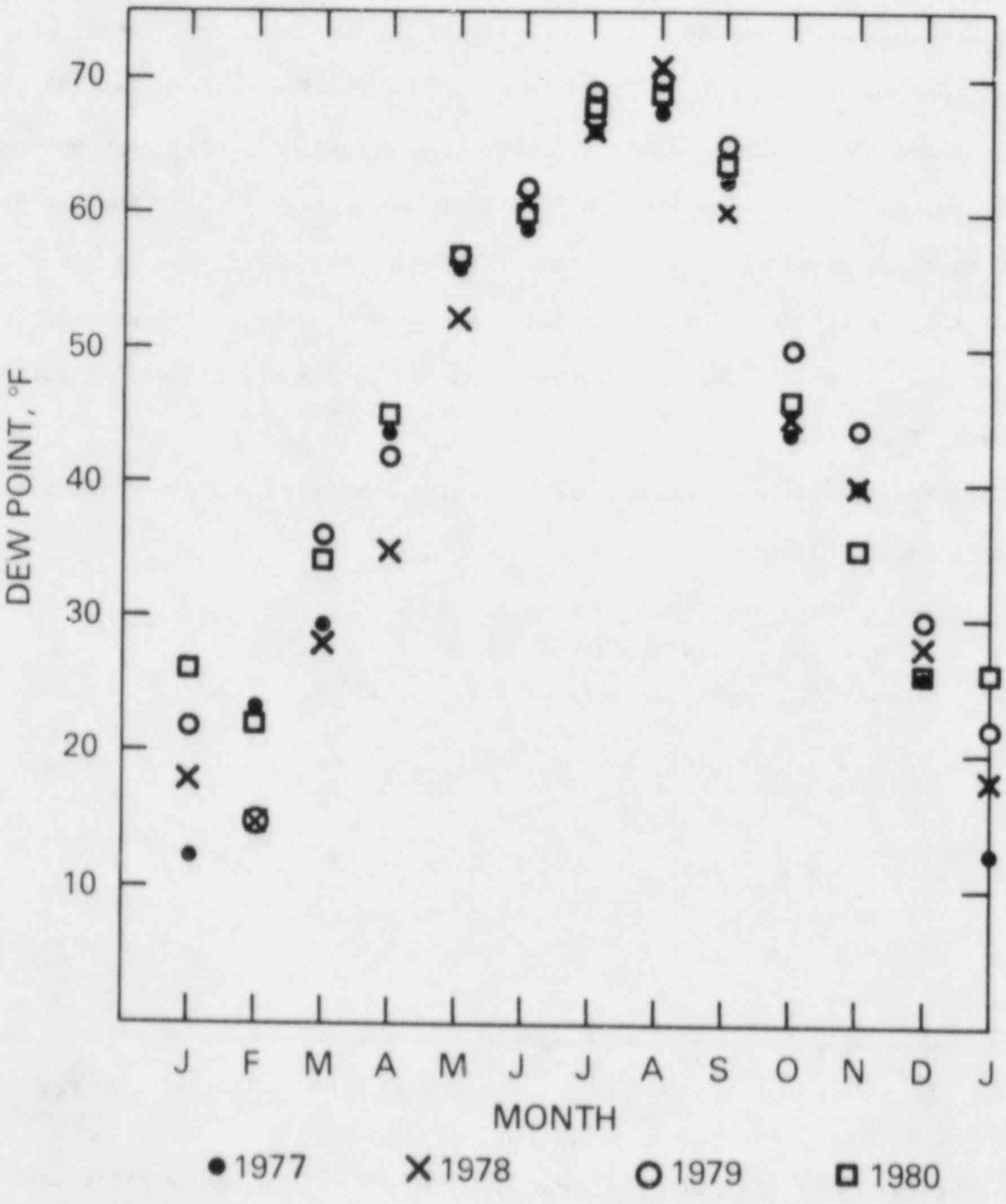


Figure 1.1 Monthly Average of Dew Points Observed at Washington National Airport (1977, 1978, 1979, 1980)

The weathering of activated carbon involves slow chemical changes in both the carbon networks of the activated carbon and in the chemistry of the impregnation. A working model of the carbon is that of a continuous carbon network of distorted, intertwined ribbons of graphite-like layers which are 3-10 Å thick. This structure is based on a simultaneous analysis of the low and high angle x-ray diffraction studies by Konnert and D'Antonio (6). The carbon network also contains smaller quantities of hydrogen, oxygen, nitrogen, and sulfur and these vary with the source material and the method of manufacture. Nuclear grade carbons have been based to-date on either coconut shell or coal.

Early in the application of the carbon adsorber to air cleaning process, it was found that a base charcoal was not sufficient for trapping organic iodides. The KI and the KI_x impregnations were then introduced and in 1967 TEDA was added. The impregnation chemicals are subject to a twofold degradation: 1) at the interface between the carbon networks and the impregnants and 2) on the surface of the exposed impregnants. Due to the large surface area of the carbon and the known quantity of impregnation (1 to 5 wt.%), the surface coverage by the latter is fractional. The commercial impregnated activated carbons used by the nuclear industry include both coconut shell and coal as source materials. The impregnations include a mixture of potassium iodide and elementary iodine and tertiary amines, either separately or as co-impregnants. In the presence of water vapor at high dew points the impregnant can adsorb considerable water; originally, the impregnant was very soluble in water. Upon repeated hydration and dehydration of a carbon adsorber in service clustering can occur and make larger crystals of, for example KI or TEDA, and thus decrease the contact area with the carbon support. In addition, the presence of the atmosphere contaminants can modify the processes.

The results of this study reflect the properties of test carbons with particular impregnations rather than endorsements or recommendations of any particular manufacturer's product.

1.3 Methyl Iodide-131 Test Results

In determinations of the methyl iodide-131 trapping efficiency (2,3) of new charcoals, a gradient in penetration of the iodine is established along the line of flow and the profile is known to be logarithmic with depth. During the weathering of a charcoal, however, independent gradients of the retained contaminants are slowly established along the line of flow and these gradients greatly complicate the interpretation of a subsequently measured iodine trapping efficiency. The gradient was observed by dividing the 2-inch depth of activated charcoal into four equal parts and by making the iodine penetration measurement on each section. While new carbon presents a uniform adsorbent packing to the test gas, namely CH_3I-131, a weathered bed is non-uniform (Figure 1.2). The greatest penetration for weathered carbons is through the inlet layer of the carbon; the penetration through each of the remaining beds tends toward a constant value, but the magnitude of penetration was considerably more than for the original new carbon. The lack of an exponential gradient in the penetration through a weathered carbon can be directly attributed to a gradient in adsorbed contaminants that developed during weathering. For example, the BC 727 (Figure 1.2) had been exposed to a flow of unmodified outdoor air for three months (July, August and September) at NRL. As previously mentioned, this period is highest in atmospheric contaminants. In general, it is difficult to anticipate such

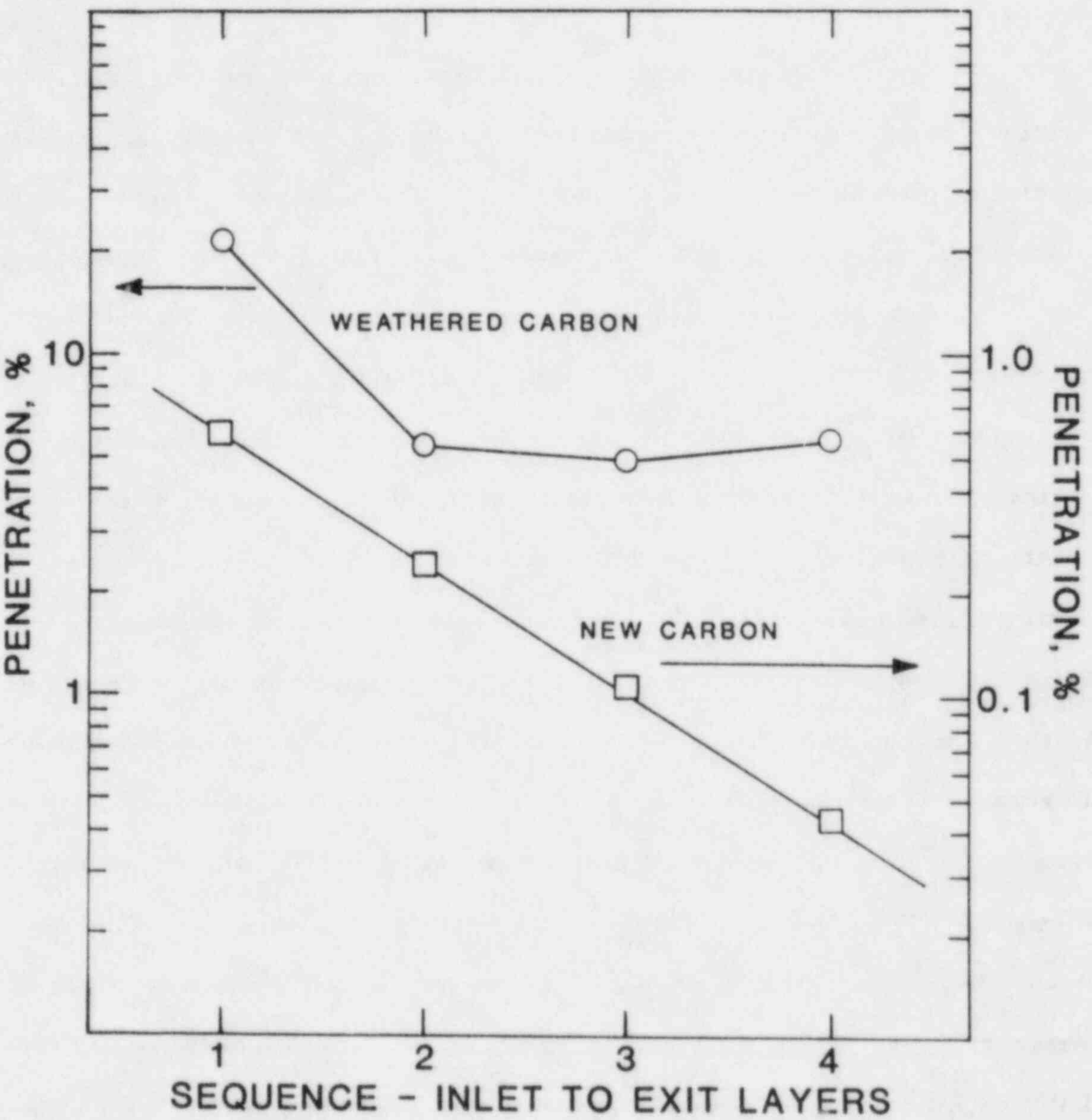


Figure 1.2 Observed Depth Profiles in the Penetration of CH_3I-131 through New and Weathered Carbons. The Weathering of the Same Carbon (BC 727) Took Place in a Flow of Unmodified Outdoor Air for 3 Months

information, but a knowledge of the gradient that does exist within a carbon adsorber in service is important in an estimate of residual capacity and service life.

It has been suggested that a preliminary carbon bed be installed before a carbon adsorber in order to protect or guard the iodine trapping property against atmospheric contaminants. The behavior of such a "guard layer" is quite unpredictable in view of the variable flow of contaminants. Moreover, the guard bed would require the same handling as the carbon adsorber and the process may well not be cost effective.

Weathering exposures of impregnated carbons have been made using outdoor air at NRL, the Atmospheric Physics facilities of the Argonne National Laboratory, Argonne, IL, 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 (1). Measurements with the carbons from these sites broadened the data base of important parameters that contributed to the weathering reactions that degrade the efficiency of the carbon for trapping radioactive methyl iodide.

An overview of all exposures is summarized in Figure 1.3 in which the penetration of $^{131}ICH_3$ (percent) is plotted as a function of the exposure duration (months) (1). The values can be divided into two groups on the basis of the impregnation on the carbon. The commercial carbons for nuclear power installations are of two types: (A) KI_x (i.e., $KI + xI_2$) and (B) KI + TEDA (triethylenediamine) or some other tertiary amine. The methyl iodide-131 penetration of the carbons after weathering followed in general the sequence KI + TEDA better than KI_x under conditions existing at the three exposure sites. The open circles of Figure 1.3 designate carbons with KI_x

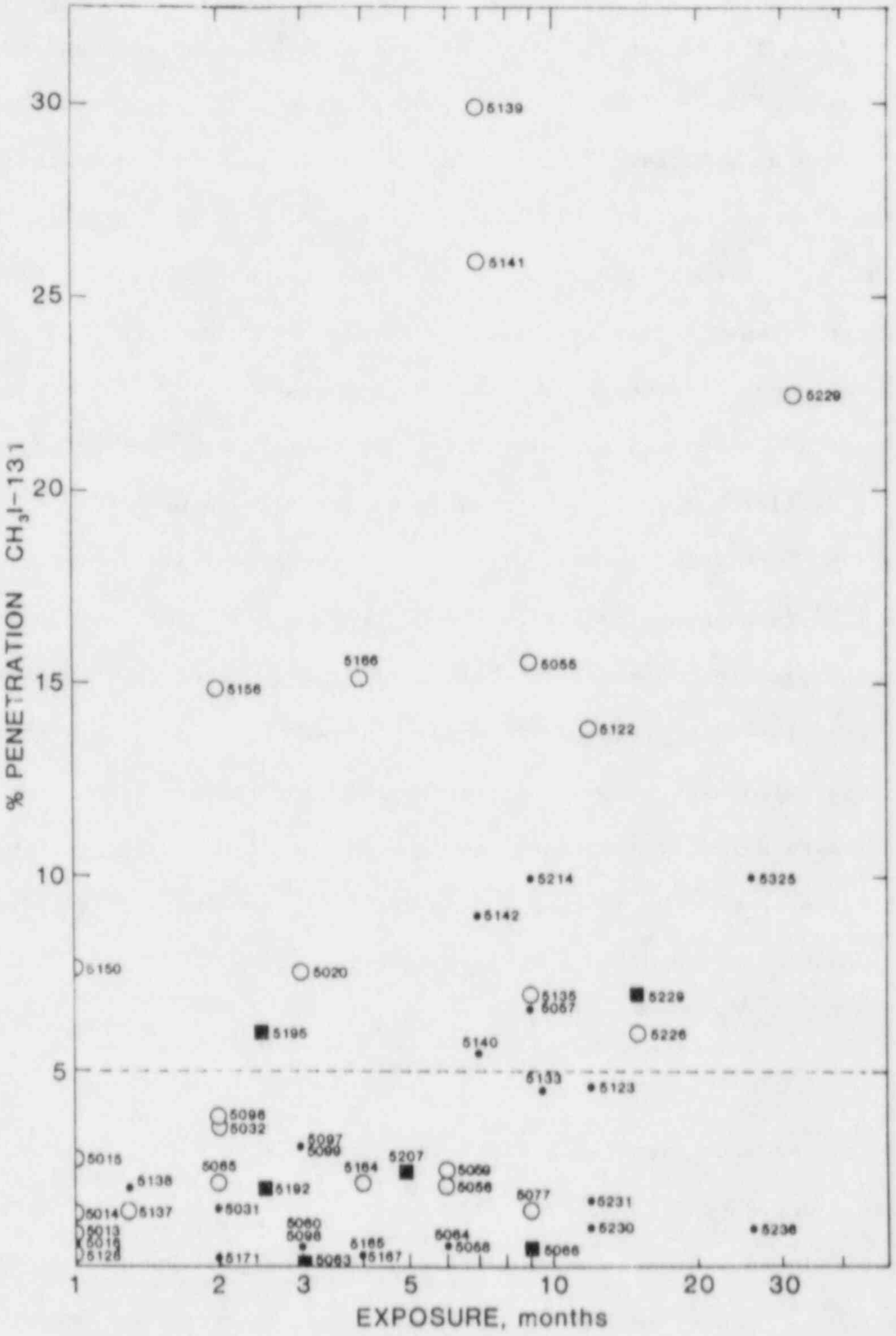


Figure 1.3 The Dependence of Penetration of Methyl Iodide-131 on the Duration of Outdoor Air Flow: Open Circles Designate KI_x, Closed Circles KI + TEDA, and Closed Squares TEDA Alone. The Numbers are NRL Designations for the Penetration Tests.

impregnations, the closed circles are carbons with KI and TEDA and the closed squares are with TEDA alone. The horizontal line at 5% penetration of methyl iodide-131 is an arbitrary division in the performance of the weathered activated carbons. All of these evaluations were made at 95% RH in the 2-inch bed specified by ASTM D 3803 (3). However, the laboratory tests for representative service samples given in Regulatory Guide 1.52 (13) specifies 70% RH. Although a 2-inch bed, designed to operate outside the primary containment at 70% RH, is restricted to less than 1% penetration of organic iodide, a similar bed inside the primary containment is permitted up to 10% penetration. Activated carbons with both impregnations are found (Figure 1.3) to be above and below the 5% penetration level, but in general, the KI_x impregnation degrades in shorter exposures. Based on these data it appears that the bi-impregnated formulations may be the desirable choice towards realizing high-removal efficiency and long service life.

An alternate way of presenting the weathering performance of activated carbons has been used by Hillary and Taylor (17). An index of performance, K, for a particular sample was defined as follows:

$$K = t^{-1} \log_{10} \frac{100}{\%\ \text{Penetration}}$$

where t is residence time (seconds). The magnitude of K decreased as the performance degraded. The results previously given in Figure 1-3 are also presented (Figure 1-4) in a plot of K as a function of exposure time. It is again seen that the bi-impregnated activated carbon (●) shows better performance than the KI_x impregnation (○).

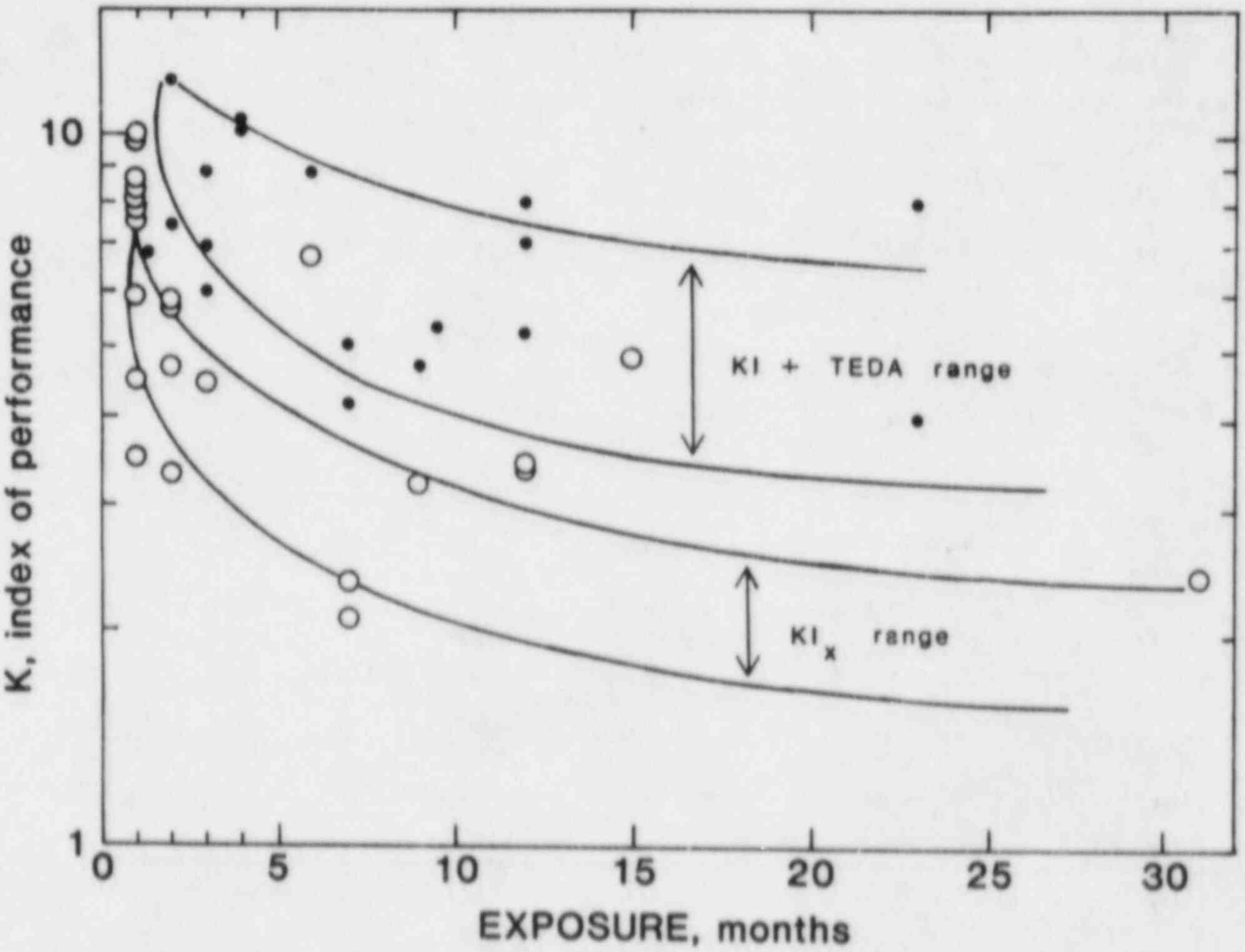


Figure 1.4 K-values for Weathered KI_x Impregnated (○) and Weathered KI + TEDA Co-impregnated (●) Coconut Shell Charcoals

A statistical analysis of the above penetration results for weathered carbons is rendered very difficult by the many experimental parameters of weathering in outdoor air flows. Obviously, the number of exposures under similar meteorological conditions are rather few. An attempt has been made to compare the three types of impregnation by a calculation based on the percent penetration per month. All of the results for a given impregnation are pooled for the purpose of the calculation. The following definitions were used as an index of weathering:

$$\text{average rate of degradation} = \frac{\sum p/t}{\sum n}$$

$$\text{change in rate of degradation} = \frac{\sum p/t}{\sum t}$$

where p = % penetration methyl iodide-131

t = exposure time

n = number of exposures

The input data are summarized in Table 1.3 and the results in Table 1.4. The rate of degradation is greatest with the KI_x impregnation, it is not as great for TEDA alone, and it is least with the bi-impregnation of KI + TEDA. A similar sequence is obtained for the change in the rate of degradation. There appears to be a synergistic influence in the bi-impregnation of activated carbon in as much as a nonadditivity effect is present relative to each component.

Table 1.3: Comparison of Three Impregnations

KI + TEDA			KI_x			TEDA (5%)		
time (months)	p%	K	time	p%	K	time	p%	K
1	0.72	8.57	1	1.30	7.54	1	0.90	8.18
2	1.41	7.40	1	1.13	7.79	1	.05	13.20
3	1.84	6.94	1	0.92	8.14	1	.02	14.80
3	3.13	6.02	1	0.69	8.64	1	.02	14.80
3	0.59	8.92	1	0.83	8.32	1	.13	11.54
3	3.10	6.03	1	13.2	3.52	1	.39	9.64
6	0.61	8.86	1	3.31	5.92	3	.18	10.98
9	6.62	4.72	1	0.81	8.37	6	.82	8.34
9.5	4.54	5.37	2	3.56	5.79	9	.46	9.35
12	4.82	5.27	2	6.84	4.66	2.5	1.88	6.90
1.3	1.97	6.82	2	3.79	5.69	2.5	2.19	6.64
7	5.44	5.06	3	7.59	4.48	5	2.34	6.52
4	0.30	10.09	6	2.08	6.73	2.5	5.97	4.90
7	8.98	4.16	9	15.6	3.23	2.5	3.82	11.07
4	0.25	10.41	12	14.1	3.40	5	24.4	2.45
2	0.10	12.00	1	0.73 0.07	8.55 12.62	5	30.6	2.06
4	0.22	10.63	1	0.81 0.29	8.37 10.15	2	0.18	10.98
23	10.0	4.00	1 1	0.35 7.62	9.82 4.47	15	7.0	4.62
23	1.0	8.00	2 31	14.86 25.0	3.31 2.41			
12	1.7	7.08	12	13.8	3.44			
12	1.0	8.00	15	6.0	4.89			
			7	30.0	2.09			
			7	26.0	2.34			

Table 1.4: Rate of Degradation of Three Types of Impregnated Nuclear-Grade Carbons

Impregnation	Rate of Degradation	Change in Rate	Number of Exposures to Air
KI_x	2.23	0.607	28
TEDA	1.07	0.337	18
KI + TEDA	0.502	0.070	21

Fourteen exposures were made, each for 1 month, in connection with the weathering of BC-727, a KI_x impregnated activated carbon. The results were used to demonstrate the influence of seasonal variations on the penetration of methyl iodide-131 (Fig. 1.5). The seasonal influence on the dew point of the outdoor air has been noted previously in this report (Fig. 1.1). These results at constant exposure time have been used to determine an upper and lower confidence level for the values observed for the methyl iodide-131 penetration. The mean of the 14 values was 2.29 and the variance $\sigma^2 = 12.63$, using the t-distribution tables for $\eta - 1 = 13$ degrees of freedom, the confidence interval for 95% and 90% were calculated, viz.:

$$95\% \quad 0.62 \leq \mu \leq 4.0$$

$$90\% \quad 1.0 \leq \mu \leq 3.6$$

An examination of Figure 1.5 indicates that these values appear to be reasonable.

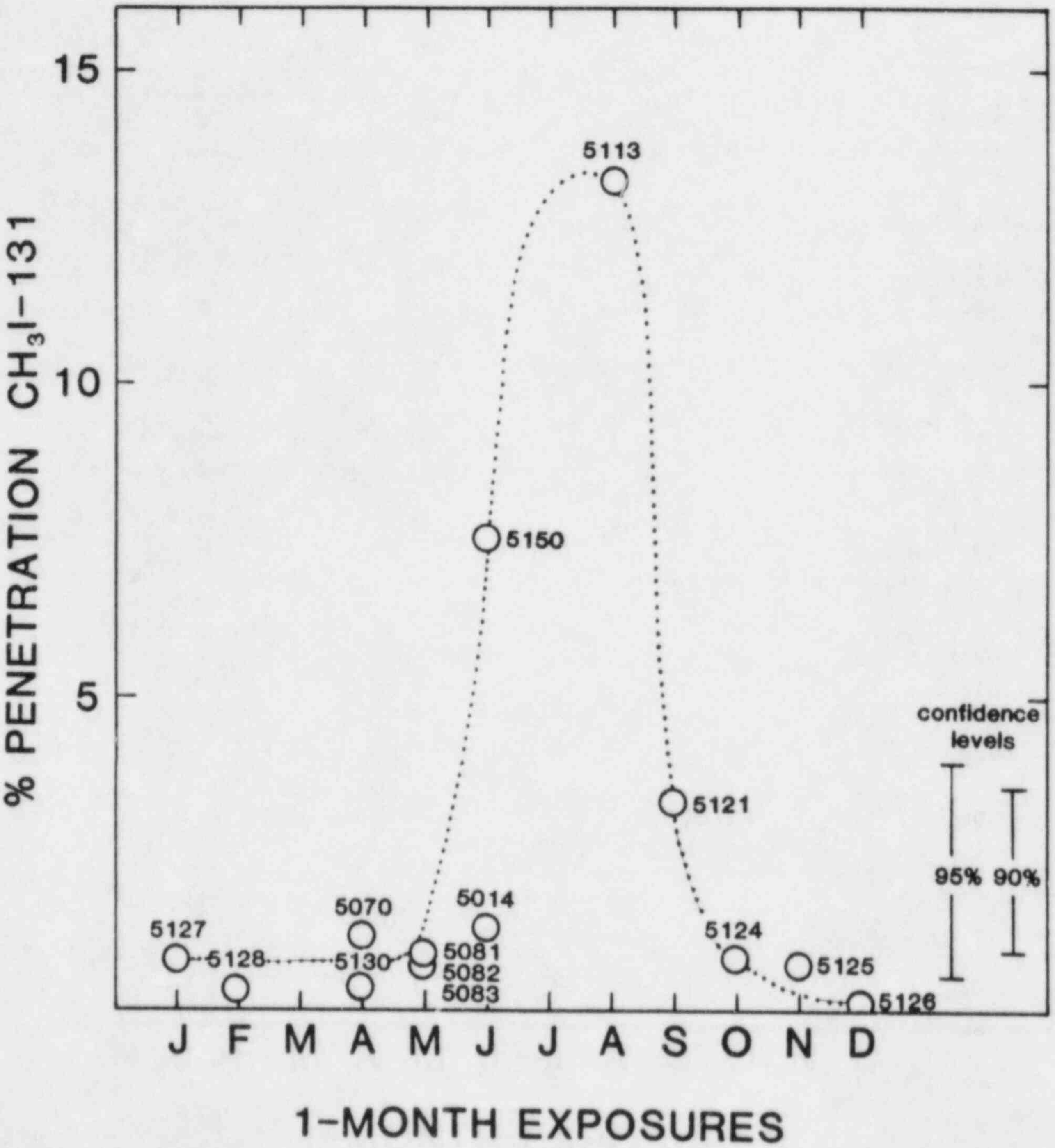


Figure 1.5 Seasonal Variation in the % Penetration of CH_3I-131 for 1-Month Exposures to Unmodified Outdoor Air at NRL

Based on established ASTM procedures, the testing of weathered nuclear-grade carbons is frequently not subjected to the 16-hour prehumidification with 95% RH air that is prescribed for new material. The elimination of prehumidification as part of the test is thought to be relevant to accident conditions where a carbon adsorber must be ready at all times to play its role as an engineered safety feature. Several investigators do not recommend any pretreatment that would bring about a partial regeneration of the carbon and thus increase the measured trapping efficiency. Should the regeneration be appreciable, the test results would be invalidated. The accumulated experiences with weathered service carbons at NRL (16) indicate that the prehumidification at 95% RH and 30°C before testing lowers the value observed for trapping efficiency relative to that observed without the prehumidification. Thus, a prehumidification of weathered service carbons could confuse the interpretation of the results for $^{131}ICH_3$ trapping efficiency.

There are several possible changes that could occur in test carbons during a prolonged exposure to high humidity air flows. Chemically, there are hydrolytic reactions and hydration changes among the impregnation constituents. Physically, the base carbon adsorbs water vapor in a strongly increasing amount with increase of relative humidity above 50% (1).

The above considerations and previous reports (1,9,14,19) may be summarized as follows:

(1) The penetration of methyl iodide-131 through a nuclear-grade carbon adsorber weathered in outdoor air flows is dependent on the moisture content of the carbon both in the testing and in actual service operations.

(2) When exposed to unfiltered outdoor air, the moisture content of the carbon at the end of the exposure period contributes strongly to the results for iodine penetration in the laboratory test.

(3) The separate impacts of adsorbed contaminants and water vapor and the synergistic influence between these components during weathering are critical factors that determine the efficiency at any given time during service.

(4) The dew point, relative humidity, or moisture (g/M^3) of the air flow constitute alternative pairs of parameters which correlate with the observed penetration of methyl iodide-131.

(5) Intermittent air flows through test carbons results in the degradation of the trapping efficiency of the carbon. The particular impregnation of the carbon appears to control the amount of degradation.

(6) The inlet layer 0.5 inch of a 2-inch bed serves as a "<u>guard</u>" for the remaining carbon. The depth profile for new carbons show a simple exponential attenuation in the methyl iodide-131 penetration, but the profile in weathered or service-aged carbon is variable and quite unpredictable.

1.4 Chemical Reactions during Weathering

The principle contaminants of the air that degrade nuclear-grade carbons are ozone, nitric oxides, and sulfur dioxide, combined synergistically with water vapor. The stepwise oxidation states of iodine that could be derived from a KI impregnation include the following species:

$$I^-,\ I_2,\ IO^-,\ IO_3^- \text{ and } IO_4^-$$

The exchange of radioiodine-131 in solution with some of these species has been studied by several investigators. An early observation (7) was the free exchange of I_2 and I^- when mixed in aqueous solutions to form I_3^-. However, I_2 and IO_3^- do not exchange with appreciable speed. Only when I_2 was mixed with IO^- in hot 20 N sulfuric acid and then cooled and separated was some exchange observed. A more detailed study of the kinetics of the iodine-iodate isotopic exchange reactions (8) showed that there was no measurable exchange in neutral solutions over a period of 1600 hours (exchange half time was 5×10^5 hr). Other experiments showed that pentavalent iodine retained its identity. Hence, when a KI impregnation on activated carbon is oxidized during weathering, the methyl iodide-131 trapping efficiency of the carbon can be seriously impaired.

It may be noted that some oxidation products formed on a nuclear-grade carbon may or may not agree with those observed in corresponding solution reactions. This is due to the possible adsorption of the products by the carbon. Some of the products are sufficiently mobile in solution reactions and the fragments can diffuse away. However, the reverse chemical reactions in gas-solid systems are restricted by desorption considerations.

Carbons exposed to air flows react strongly with atmospheric SO_2 and are markedly degraded for trapping radioactive iodine as a result of the adsorption. Using direct probe mass spectrometry at NRL, an estimate of the total sulfur uptake has been made in weathered carbons (10). This method involves loading 1 to 2 mg of the carbon in a glass capillary tube on a probe tip and inserting the probe into the ion source of a quadrupole mass spectrometer. The sample is heated at a given rate from 30 to 300°C and the desorbed species are ionized and mass-analyzed. Among the most abundant ions were SO_2^+ ($m/z=64$) and SO^+($m/z=48$). Figure 1.6 shows a plot of the percent of the total ion current attributed to SO^+ and SO_2^+ versus the duration of the exposure to outdoor air. There is a linear dependence of total sulfur accumulation on weathering time.

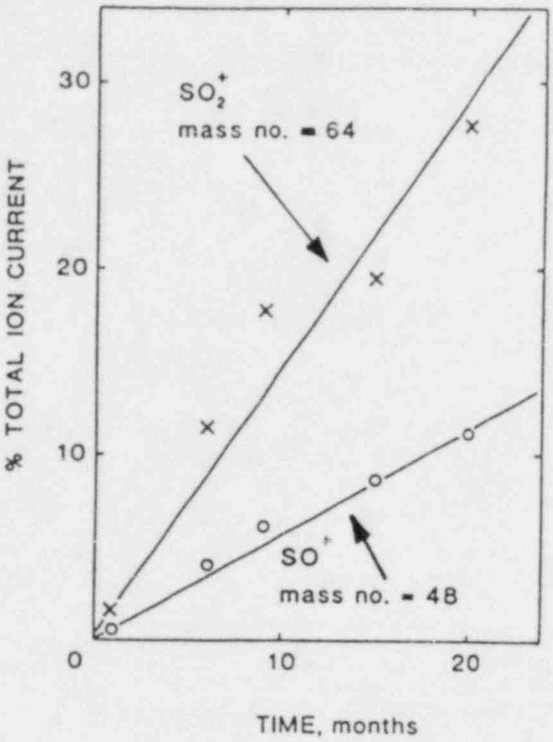


Figure 1.6 Accumulation of m/z 48 and 64 in Weathered TEDA (5%) Coal Base Charcoals (10)

The retention of radioactive iodine by KI_x impregnated carbons in service is the bottom-line property. Should elemental iodine be retained by physical adsorption, it would be readily desorbed by small temperature increases. Iodine, however, held by chemical combination with the carbon network, would require a higher temperature to decompose a carbon-iodine covalent bond (20) and liberate iodine. A chemical modification of the carbon network and/or iodine-containing impregnants by weathering can also adversely influence the chemical retention capability since the carbon surface chemical composition is modified by the contaminants.

The weathering of KI_x carbon in outdoor air modifies the thermal stability and during heating causes a greater emission of elemental iodine at lower initial temperatures. Similar behavior was observed with service-aged GX-176 which can be correlated with the measured penetration for both CH_3I-131 and elemental iodine-131.

Thermal analyses of new and of service-weathered KI_x carbons can be used to observe changes in iodine bonding to the base carbon network. Laboratory tests (19) showed the release of iodine to the air flow in addition to the gasification of carbon (CO and CO_2). A temperature gradient of 3°C/min. was used and the upward air flow through the carbon bed (2.54 cm diameter and 2.54 cm depth) was 5 L/min (contact time = 0.15 sec). The effluent elemental iodine from the heated carbon sample was determined, and the effluent from an independent sample was converted completely to elemental iodine by passage of an aliquot of the flow through a hot quartz tube before the iodine measurement (16). The organic iodide was determined by difference.

Typical thermal emissions of elemental iodine (mg/M^3) from the above KI_x carbons are given in Fig. 1.7 as a function of the exit gas temperature. The emission from service carbons exceeded that from the new MSA carbon also with a KI_x impregnation; the emission began to increase more rapidly at a lower temperature for the service carbon than for the new carbon. It is concluded that the iodine in a KI_x impregnation of the carbons is subject to chemical change as a result of the weathering process.

In order to demonstrate a correlation between weathering and the degradation processes to which these KI_x impregnated carbons were subjected, the total iodine (mg) gasified at 180°, 221°, and at the spontaneous ignition

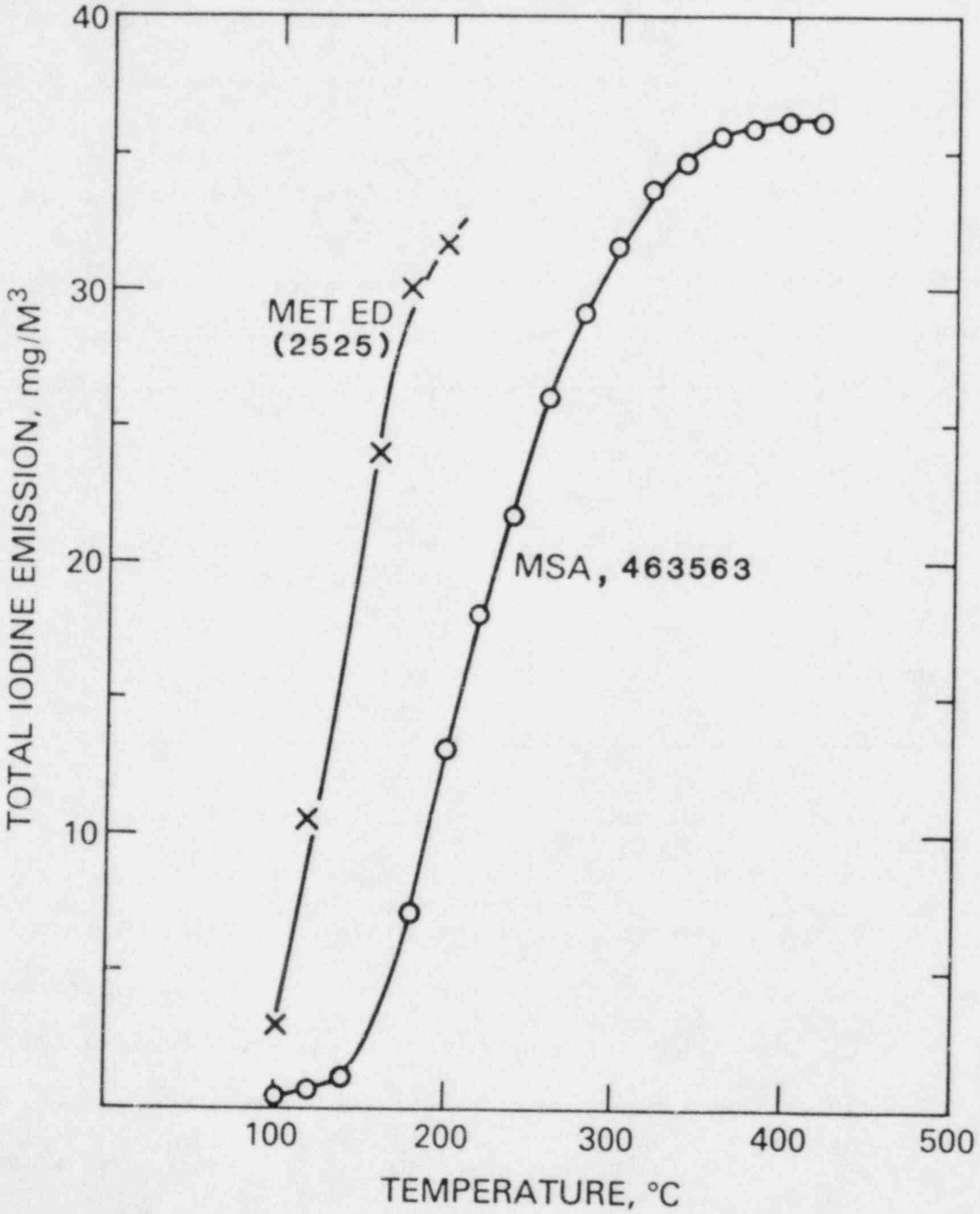


Figure 1.7 Rate of Elemental Iodine (I_2) Emission with Temperature Programmed at 3°/min [MET ED 2525 service carbon and new MSA 463563, both KI_x impregnations]

temperature (SIT) were determined (Table 1.5). The sequence is shown to have the same alignment at the SIT as does the corresponding determination of methyl iodide-131 penetration. The anomaly is service carbon #4.

Table 1.5 Comparison of the Penetration of Methyl Iodide-131 with Iodine Emission

Carbon	CH_3 I-131 Penetration	Total Iodine Emission		
		180°C	211°C	SIT
	%	mg	mg	mg
1	50.9	2.71	4.50	18.5
2	44.0	2.03	3.56	-
3	30.5	0.63	2.0	14.0
4	24.5	1.60	3.07	13.9
New MSA				
5	0.13	0.24	0.82	9.7

Organic compounds containing iodine are known to be subject to pyrolysis in the gas phase by abstraction of HI and/or primary decomposition leading to elemental iodine. Investigations on the pyrolysis of iodides adsorbed on charcoal have not been reported, but the present work has shown that organic iodides and molecular iodine are among the low temperature (100 to 200°C) products. In gas phase pyrolysis the various substituents in organic iodide molecules are reported to be very marked and are reported to depress the activation energy below the value corresponding to the iodine bond energy. A similar behavior for organic iodides adsorbed on charcoal can be expected.

Organic iodine compounds were present in the evolved fraction during the early stages of the heating cycle, but the amounts were small relative to elemental iodine. This observation agrees with previous results with a KI_x-impregnated carbon (2701) which did not form significant amounts of organic iodides as gas-phase products in an air oxidation environment (9).

In all of the samples analyzed, the iodine released was accompanied by carbon oxidation to form CO and CO_2. The amount of carbon burn-off (i.e., the carbon contained in the CO + CO_2) was qualitatively proportional to the elemental iodine evolved. The behavior has been explored in some detail since it would suggest the rupture of a chemical bond between impregnated iodine and the carbon networks of a KI_x impregnated carbon. The total carbon gasified using a service carbon and a new carbon is plotted in Fig. 1.8 as a function of the elemental iodine released. The X-coordinate is turned back after 3 decades and then continued in the upper section to cover three additional decades. The stoichiometric ratio of total carbon gasified to iodine released first leveled off as the temperature increased to about 160°, and then the ratio increased at higher temperatures. The behavior is compatible with a model in which there is a threefold increase of I_2 up to 160°C and less than a one-fold increase in total carbon; this could be termed desorbed or easily decomposed iodine. In the temperature range 160-400°C, there is an additional threefold increase of I_2 and about a threefold increase in gasified carbon; this behavior indicates the difference between the desorption of iodine and the decomposition of a stronger iodine-carbon bond (20). In all cases, the weathering of a carbon realized during service enhanced the release of iodine from the KI_x impregnation.

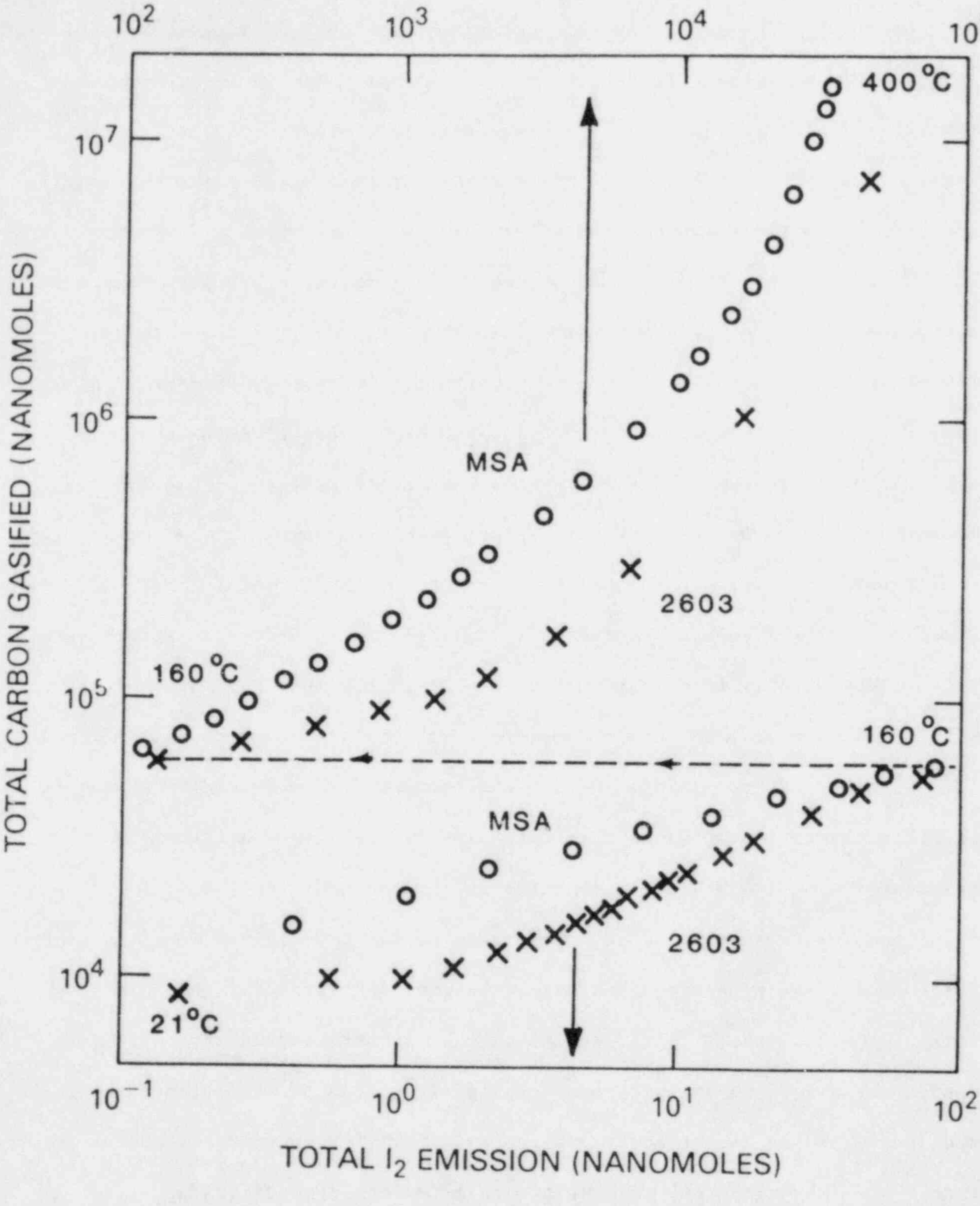


Figure 1.8 Correlation of Carbon Gasified with the Release of I_2 for MET ED 2603

New KI_x carbons have the same general behavior in carbon burn-off and iodine release, but they differ in degree. The increase of I_2 (two decades) from 26 to 50°C with relatively little carbon burn-off is compatible with physical desorption of I_2, but at the higher temperatures, there is steady carbon burn-off along with iodine release.

The commercial nuclear carbon GX-176 is impregnated with both KI_x and TEDA and a series of these carbons was provided by the Savannah River Laboratory (11,12) after having been service-aged in the confinement system which received reactor building air (linear velocity of 15.8 m/min). The results demonstrate that the quantity of iodine emitted is greater in magnitude than in new material and occurs earlier in the heating cycle for the service-aged carbon. Iodine could be detected at 50°C for the aged carbon as compared to 175°C for the new material.

A comparison is made (Figure 1.9) between new GX-176 and the same carbon after 12-months service. The Y-coordinate is the integrated amount of iodine in micrograms that is emitted up to the designated temperature. During the thermal analysis test, the heating rate was 5.6°C/min. and the linear air flow was 10 m/min.

The thermal instability of impregnated iodine induced by service ageing of GX-176 can be correlated with the measured penetration for both CH_3I-131 and I_2-131 (12). The results (Table 1.6) show that the two penetration values increase in about the same ratio (50 to 60). The thermal instability, as measured by the integrated iodine emission, is several magnitudes greater for the 12-month service-aged GX-176 than for the new material.

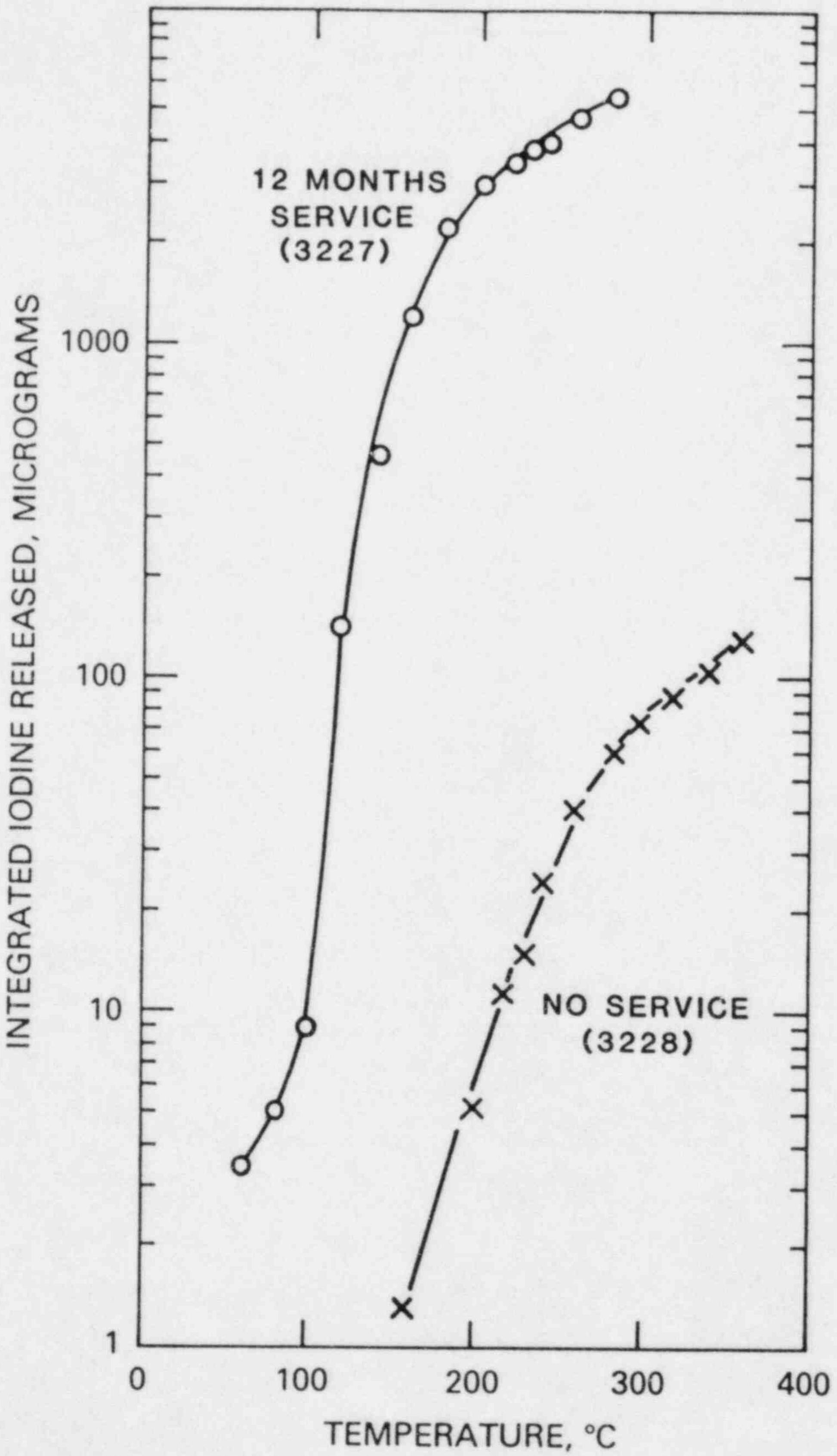


Figure 1.9 Emission of Iodine During Programmed Heating (5.6°/min.) of GX-176 (KI and TEDA Impregnation)

Table 1.6 Properties of Service-Aged GX-176 (12)

	New	Aged 12-month
Penetration CH_3I-131, %	0.45	28
Penetration I_2-131, %	0.002	0.093
Iodine Emission:		
Integrated to 180°C, μg	1.3	2200
Integrated to 200°, μg	5.2	3300
Integrated to 250°, μg	31.0	4400

1.5 Formation of Organic Iodine Compounds

The direct formation of organic iodides by the reaction of elemental iodine and an activated carbon is an important fact to establish. It is necessary to use a base carbon alone in order to remove the contribution of the impregnation chemicals.

A mixture of elemental iodine (0.5 wt.%) and an unimpregnated activated carbon (BC Type 177) from coconut shells was heated (6.7°C/min.) in a flow of purified air at a linear velocity of 10m/min. Elemental iodine was detected almost immediately and organic iodide was detected as low as 100-125°C. Two other activated carbons - BPL 10x16, a coal base carbon, and GX 32, a petroleum base carbon - were also treated. A comparison was made (Table 1.7) of the released iodine products integrated to 180° and also to 260°C: coconut carbon at 180°C released only 0.00055 wt.% elemental iodine; the coal base carbon released about four times more, 0.0023 wt.%; and the petroleum carbon base material released ten times more. However, the formation of organic iodides was in the reverse order, in that the coconut carbon emitted ten times more organic than elemental carbon, the coal base carbon emitted only 30% more, and the petroleum base less than 10% more. When the release was integrated to 260°C, the pattern was about the same.

Table 1.7 Thermal Release of Iodine from Mixtures of I_2 and Base Carbons

	Detection	Initial I_2	Integrated to 180°C		Integrated to 260°C	
		mg	mg	Wt.%	mg	Wt.%
BC 177	I_2	25.6	.00014	.00055	.0043	0.017
BC 177 (coconut)	I_2 + Organic	25.6	.00194	.0076	.0269	0.11
BPL 10x16	I_2	29.5	.000682	.0023	.0316	0.11
BPL 10x16 (coal)	I_2 + Organic	29.5	.000891	.0030	.0366	0.12
GX 32	I_2	17.1	.00408	.024	.0596	0.35
GX 32 (petr. coke)	I_2 + Organic	17.1	.00442	.026	.0694	0.41

The above complex behavior may be summarized as follows:

1. A KI_x-impregnated carbon is modified in the weathering process and this causes a greater emission of iodine during heating to elevated temperatures.

2. The carbon is gasified at high temperature to CO and CO_2 and the increase is proportional to the iodine evolved.

3. The magnitudes of the CH_3I-131 penetration of 30°C of corresponding samples are in the same sequence as the total iodine emissions when the latter are compared at the same temperature.

4. The total iodine released, integrated up to the SIT, is considerably less than that contained in the impregnation formulation.

5. The dominant iodine species in the thermal emission from KI_x species is present on the carbon as a molecular entity, a simple decomposition would take place:

$$KI_x \rightarrow KI + I_2$$

If the iodine in KI is oxidized, another species in the carbon must be reduced. The process may be formulated as follows:

$$2\ KI + \text{carbon-oxidized} \rightarrow I_2 + \text{carbon reduced}$$

A sink for the K^+ in KI is most likely the carbonate of bicarbonate salts that are present. However, the actual mechanism is most likely quite complex due to the great heterogeneity of a carbon surface composition. The heat of dissociation of a carbon-iodine bond varies with the molecular species; the value in CH_3I is 50 kcal/mole. The decomposition of all iodine species on a weathered KI_x impregnated carbon should lead to a steady and continuous emission of iodine.

1.6 Laboratory Weathering with Selected Contaminants

A methyl iodide-131 penetration test of a carbon weathered in a flow of outdoor air deals with a gradient of contaminants in the carbon of uncertain composition. In laboratory experimentation with selected contaminants, use was made of a known challenge mixture to the sample in the same container that was used for outdoor air (1).

Seven commercial activated carbons were exposed to filtered air flows at three levels of relative humidity (50, 70, 90% RH). The purified air flow was continuous at a rate of 100 L/min. for 100 hours. 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 detrimental influence of water vapor on iodine trapping has no simple explanation. At high relative humidity, physical adsorption of water vapor can influence the available porosity and block some adsorption sites for trapping iodine. However, extended exposures to water vapor have additional detrimental effects and these can continue to degrade the carbon. The methyl iodide-131 penetrations (Table 1.8) 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 seven different carbons vary to some extent, but it is important to remember that these measurements are based on a single production sample (25 lbs.) of each type. The behavior of the S&S (5% TEDA) according to these measurements, is outstanding for weathering in water vapor only. Mixtures of pollutants and water vapor will be discussed in another section.

Table 1.8. Dependence of Methyl Iodide-131 Penetration on the Relative Humidity of Controlled Laboratory Air Flows

Carbon	Relative Humidity	pH (av)	Average of Weight Increase	Methyl Iodide-131 Penetration
	%		%	%
BC 727	50	9.5	25.8	1.69
	70	8.7	45.4	6.3
	90	8.9	47.6	13.6
G 615	50	9.9	20.0	0.50
	70	9.4	28.6	1.8 ± .04
	90	9.3	29.9	2.0
MSA 463563	50	8.3	21.4	4.66 ± .09
	70	8.1	36.1	8.6 ± .09
	90	8.3	39.0	9.27 ± .06
S&S (5% TEDA)	50	8.4	15.4	0.01
	70	8.4	26.7	.03
	90	8.7	31.9	.04 ± .01
AAFR 2701	50	9.1	18.9	0.24 ± .02
	70	8.6	43.6	3.29 ± .04
	90	8.7	51.5	7.21 ± .05
G 617	50	9.4	20.3	1.10 ± .02
	70	9.2	57.4	6.20 ± .05
	90	9.6	61.5	9.10 ± .13
KITEG	50	7.7	18.6	0.25 ± .03
	70	7.7	29.1	2.45 ± .03
	90	7.7	40.0	4.37 ± .27

The general behavior of the above test carbons was found to be reproducible. For example, one sample of BC 727 was exposed in August 1977 and another sample in October 1978; the results are given in Table 1.9. The good reproducibility obtained for BC 727 may be due in part to the close control possible in laboratory weathering and to the good reproducibility of the carbon samples withdrawn from the master samples.

Table 1.9 Reproducibility of Laboratory Weathering (BC 727)

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 contaminant mixtures listed below were also used in laboratory measurements. In all cases, charcoal filtered compressed air was used at a linear flow of 40 ft/min. prior to the addition of controlled contaminants (1).

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

During the weathering stage, no trace of ozone or sulfur dioxide was detected in the exit gases during the test period (100 hrs.) and no change in CO concentration was detected in passing through the carbon. This indicates, the high adsorption capacity of the carbon for ozone and sulfur dioxide, and no detectable adsorption for carbon monoxide.

The methyl iodide-131 penetration was determined for each of the four half-inch layers of the weathered bed (Table 1.10). It is obvious that the inlet layers have been influenced to the greatest degree by the insult gases (excepting CO) and the penetration of methyl iodide-131 was always greater therein than in the subsequent layers. The sulfur dioxide + water vapor and the ozone + water vapor mixtures exceed the influence of water vapor alone. The exposures to the mixtures of ozone or sulfur dioxide with water vapor resulted in a large adsorption of water vapor within all four layers of a test, but the ozone or sulfur dioxide interaction was confined to the first layer. This is due, in part, to the large difference in concentration of the two components introduced; ozone about 2.5 ppm, sulfur dioxide 0.5 ppm, and water vapor about 200,000 ppm. However, it does demonstrate that humidified carbons present strong adsorption sites for the two contaminants considered. Carbon monoxide appears indifferent and does not influence the methyl iodide-131 penetration.

Table 1.10 Penetration of Methyl Iodide-131 in Laboratory Weathering

	Test Number				Test Number			
	5030	5035	5036	5037	5025	5027	5028	5029
Insult	Water Vapor				SO_2 + water vapor			
Carbon	BC727	G615	BC727	G615	BC727	G615	BC727	G615
% RH	70	70	90	90	70	70	90	90
Time (hrs.)	100	100	100	100	115	75	100	100
Volume (m^3)	600	600	600	600	690	450	600	600
*P(CH_3I) inlet	16.3	2.4	12.7	2.0	37.5	7.2	66.0	16.0
Second	13.2	1.6	5.1	nd	11.2	1.6	nd	nd
Third	15.2	1.6	7.3	nd	9.9	1.2	nd	nd
Fourth	10.7	1.8	3.4	2.1	10.9	2.1	17.0	2.6

	Test Number				Test Number
	5043	5044	5045	5046	5038
Insult	O_3 + water vapor				CO + water vapor
Carbon	BC727	G-615	BC727	G-615	G-615
% RH	90	90	70	70	90
Time (hr.)	53	108	95	100	100
Vol (m^3)	318	648	570	600	600
*P(CH_3I-131) inlet	19.0	3.1	18.3	1.9	3.0
Second	11.7	1.4	7.7	nd	1.5
Third	13.9	3.0	11.0	nd	1.8
Fourth	21.5	0.7	12.2	2.9	1.2

*P(CH_3I-131) = percent penetration of methyl iodide-131
nd = not determined
BC727 represents a KI_x impregnated carbon
G615 represents a KI + TEDA impregnated carbon

The two commercial carbons, BC 727 and NACAR G-615, have shown different behaviors in the weathering experiments to date. These are two of the six coconut-base carbons studied and a better judgment can be made when the impregnation is included. There was a different impregnation on carbon BC 727 (KI_x) than on carbon NACAR G-615 (KI + TEDA) and the response to the chemical reactions of weathering can be expected to differ. The distribution of certain components of a given impregnation among the carbon particles depends in part on the volume of the air flow and the mobility of these compounds. A formulation containing triethylenediamine (TEDA) may slowly lose this component by its volatility (the vapor pressure of TEDA is 2.9 torr at 50°C and 0.6 torr at 25°C) and a formulation containing KI_x may lose iodine by decomposition into elemental iodine. It is not known how TEDA adsorbed on an activated carbon is desorbed in the presence of air + water vapor, especially after weathering has occurred.

The adverse influence of extraneous organic materials on methyl iodide-131 penetration has been reported (18). The current weathering exposures (Table 1.9) involve the combined mixture of organic vapor and 95% RH air flowing continuously into the carbon bed for 100 hours at a flow of 100 L/min. The weathering was followed by the determination of methyl iodide-131 penetration. The compounds included n-hexane, methanol, carbon tetrachloride, and methylethylketone, each at different concentrations. New samples of BC 727 (KI_x impregnation) or NACAR 615 (KI + TEDA) were used for each case. The test cell for the penetration measurement was layered in the same sequence as in the usual weathering cell (1).

To prepare the air-vapor mixtures, a small glass trap containing the organic liquid was thermostated and a small controlled flow of air was introduced using all-glass or Teflon tubulation. This flow was injected into the main air flow (100 L/min.) which passed through a mixing chamber. A small aliquot of the effluent from the mixing chamber was directed through the sampling loop of a 5710 Hewlett Packard Chromatograph having an FID detector. The air flow through the organic liquid was then adjusted in order to reach the desired concentration of the organic vapor in the combined air flow. Calibrated permeation tubes were used in these experiments as standards in the calibration of the gas chromatograph.

Prior to placing a test carbon sample in the laboratory weathering apparatus, the air flow was adjusted to 100 L/min. and the desired concentration of contaminant was obtained at the regulated relative humidity. After the system reached a steady state, the container of carbon was placed in position and the air flow readjusted to 100 L/min. to compensate for the resistance to flow through the carbon.

The control realized is shown by examples for the low-level insult of carbon tetrachloride (NRL Tests 5180 and 5181, see Table 1.11). Over the 100-hour period, 41 chromatographic data points were obtained. For NRL 5180 the mean concentration was 2.4 ppm carbon tetrachloride with a standard deviation of 0.35 ppm; for NRL 5181 with an equal number of data points, the mean concentration was 3.0 ppm with a standard deviation of 0.72.

Table 1.11 Penetration of CH_3I-131 after Exposure of Impregnated Carbons to Organic Vapors at 95% Relative Humidity for 100 hrs. in an Air Flow of 100 L/min.

Carbon	Vapor	Test	Wt.%	Penetration, %	Carbon	Concen. Vapor	Test	Wt.%	Penetration, %
727	MeOH	5199			727	CCl_4	5182		
	5 pm	1	30.4			15 ppm	1	34.2	
		2	30.5				2	33.8	
		3	30.5				3	33.6	
		4	30.6	2.1			4	33.4	6.22
615	MeOH	5198			615	CCl_4	5181		
	0.5 ppm	1	28.3			3.0 ppm	1	34.3	
		2	28.0				2	35.6	
		3	26.9				3	36.1	
		4	26.0	0.15			4	35.5	2.08
615	MEK	5189			727	CCl_4	5180		
	4.5 ppm	1	31.1			2.4 ppm	1	39.72	
		2	31.0				2	39.12	
		3	30.9				3	38.84	
		4	30.4	1.47			4	38.70	1.83
727	MEK	5188			615	Hex	5179		
	3.5 ppm	1	32.6			0.30 ppm	1	35.1	
		2	32.7				2	35.1	
		3	32.7				3	34.9	
		4	32.9	0.09			4	34.4	0.21
615	MEK	5185			727	Hex	5178		
	1.9 ppm	1	31.3			17 ppm	1	35.9	
		2	31.3				2	35.9	
		3	31.3				3	36.1	
		4	30.8	0.76			4	36.4	8.72
727	MEK	5184			727	Hex	5174		
	1.9 ppm	1	35.2			17 ppm	1	38.5	
		2	35.2				2	38.5	
		3	35.3				3	38.2	
		4	35.4	2.0			4	38.2	5.77
615	CCl_4	5183			615	Hex	5173		
	2.0 ppm	1	30.4			0.4 ppm	1	28.7	
		2	30.4				2	28.6	
		3	30.2				3	28.6	
		4	30.4	1.84			4	29.7	1.35

MeOH = methyl alcohol; MEK = methylethylketone; CCl_4 = carbon tetrachloride; Hex = n-hexane

The observed penetrations of methyl iodide-131 were found to increase in proportion to the amount of organic vapor introduced. The weight increases (Table 1.9) are due to both the water vapor and the organic vapor. Both impregnations were on a coconut shell charcoal, not of the same Lot number. However, it again appears that the bi-impregnation of KI and TEDA shows less penetration of methyl iodide-131.

The methyl iodide-131 trapping efficiencies in four additional experiments were determined with and without prehumidification after a hydrocarbon contamination. The objective was to demonstrate the synergistic influence of water vapor and the hydrocarbon. Without prehumidification, there is an increase in penetration relative to the original carbon (Table 1.12), but the efficiencies remained within acceptable performance requirements of nuclear grade carbons. However, after the prehumidification, the penetration was markedly increased beyond that for prehumidification alone plus organic vapor alone.

Table 1.12 Influence of Prehumidification on Trapping Efficiency after Contamination with Octane (M.W.=114) or with Tetradecane (M.W.=198)

Carbon	*Prehumidification	BC 717	BC 727	MSA 463563	G 615
Orig.	No	.05	.014	0.13	0.05
Orig.	Yes	1.0	4.8	2.5	0.27
Orig. + 10 wt.%	No			0.37	
Octane	Yes			9.2	
Orig. + 10 wt.%	No	1.2	0.33	0.80	
$C_{14}H_{30}$	Yes	5.3	15.6	15.9	
Orig. + 2 wt.%	No	0.63	0.63	1.01	0.18
$C_{14}H_{30}$	Yes	8.8	9.5	7.5	1.5
Orig. + 0.2 wt.%	No				0.09
$C_{14}H_{30}$	Yes				0.81

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

The results for the carbon exposures to air flows of two sequential levels of relative humidity are summarized in Table 1.13. The known hysteresis of the water adsorption and desorption isotherm is a strong factor in determining the final water content of adsorbent carbon. Accordingly, the observed penetration of methyl I-131 for both carbons after 100 hours in air of 90% RH is more than twice that after 50 hours of 50% RH plus 50 hours at 90% RH. Previously, the weight gains were found to be approximately equal for both carbons at 100 hours at 90% RH and the greater penetration after 100 hours at 90% RH appears to be independent of weight-gain behavior.

Table 1.13 Results after Exposure at Two Sequential Levels of Relative Humidity (Total time 100 hrs.)

Carbon	Exposure Time(hrs.)	% RH	pH	Total Wt. Change %	% Penetration CH_3I-131
G 615	50	50			
	50	90	9.5	38.8	0.66 ± .02
G 615	50	90			
	50	50	9.4	34.8	0.69 ± .06
G 615	50	90			
	50	dry air	9.3	0.84	0.06 ± .01
G 615	100	90	9.3	29.9	2.00
G 615	100	50	9.9	20.0	0.50
BC 727	50	50			
	50	90	9.2	50.1	5.88 ± .05
BC 727	50	90			
	50	50	9.0	46.9	3.95 ± .04
BC 727	50	90			
	50	dry air	8.9	0.78	1.02 ± .05
BC 727	100	90	8.9	47.6	13.6
BC 727	100	50	9.5	25.8	1.69

Moreover, the results for penetration after 50 hours at 90% RH + 50 hours at 50% RH are approximately the same as 50 hours at 50% RH + 50 hours at 90% RH. Apparently, only the exposure to air at 90% RH is the degrading factor for methyl iodide-131 penetration.

The exposure of the test carbons to two levels of relative humidity only approximates the great variability encountered in practice. A service carbon is subjected to variable periods of high and low relative humidity; periods of dry air could be favorable to high methyl iodide-131 trapping efficiency and periods of wet weather would steadily increase the moisture content and decrease trapping efficiency. These preliminary results indicate that it could be advantageous to introduce a flow of air in dry weather to dehydrate effectively those adsorbers which otherwise may not be in operation at that time. This subject will be discussed in Chapter IV in connection with preheaters in humid weather or in accident situations where the charcoal may have to operate near 100% RH.

1.7 Solvent Spills and Water Flooding

Two accident situations of some importance to the efficiency of a carbon adsorber are solvent spills that can occur and the flooding of the adsorber by water with the release of radioactive compounds. In order to estimate the order of magnitude of such effects on the trapping of iodine, some preliminary measurements were made at NRL. These experiments using methyl iodide-131, can be subjected to many future refinements.

Benzene Vapor

All samples (2" diameter and 1" height) were prehumidified for 16 hours at 98% RH and 25°C in an air flow of 5.5 L/min. The first dose of CH_3I-131 was followed by air flow at 11 L/min. for four hours. After counting the activity of the carbon sample and the two back-up beds, the system was reassembled and known quantities of benzene vapor were introduced. The carbon and back-up beds were again counted. Finally, a second dose of $CH_3{}^{131}I$ was introduced and the penetration again determined.

The results for 3 samples (Table 1.14) indicate that the injection of benzene vapor following the first addition of $CH_3{}^{131}I$ did not significantly move the trapped iodide, but the subsequent dose of methyl iodide-131 showed an increase in penetration.

Table 1.14 Penetration of CH_3I-131 through a 5% TEDA Carbon after a Benzene Spill

Injection	4101	4102	4103
50 μg CH_3I/g	1.9%	1.1%	1.7%
1 ml C_6H_6	1.6	1.0	2.0
6 ml C_6H_6	2.1	-	-
11 ml C_6H_6	2.2	-	-
50 μg CH_3I	2.9	2.4	3.9

Acetone Vapor as a Solvent Simulant

Acetone vapor (CH_3COCH_3) was used to determine if the pre-adsorbed methyl iodide-131 would migrate. The test sample was assembled in 1/4 inch layers separated by stainless screens in order to count the charcoal in each layer. No residual radioactivity on the screens was subsequently detected. Two charcoals were used:

Sample 4104	5% TEDA, 1% sodium silicate on a coal base carbon
Sample 4021	Commercial, 1.5% KI and I_2, coal base carbon

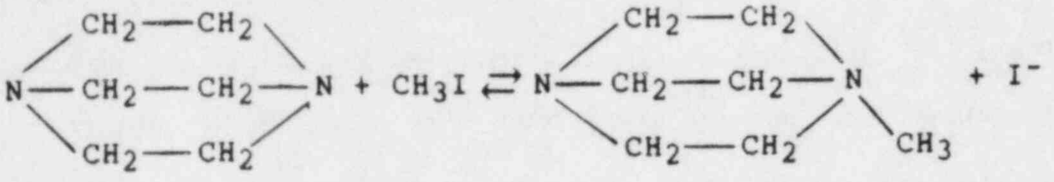
The samples were prehumidified for 16 hours at 98% RH. After the $CH_3{}^{131}I$ injection and subsequent counting, the columns were reassembled and acetone vapor injected in 2.15 hours. Subsequently, the air flow was continued for two hours at 11 L/min. (96% RH). Each section was again counted. It appears possible to induce the migration of adsorbed methyl iodide-131 through a charcoal bed with a solvent vapor such as acetone; the previous experiments with benzene did not do so.

A second series of measurements using acetone vapor were undertaken in which a 2-inch deep bed (2" diameter) was separated into 8 layers. The weight of charcoal (5% TEDA, 1% sodium silicate on a coconut charcoal) was 52.6g. The charcoal was humidified 16 hours (96% RH) before dosing with $CH_3{}^{131}I$, 50µg per g charcoal (0.203 microcurie total). After counting, the assembled system was further humidified for 18 hours. The acetone vapor was introduced in an air flow (96% RH) for 4.3 hours using 10 ml liquid acetone (7.91g). The second count was made immediately thereafter.

Table 1.15 Acetone Vapor after Methyl Iodide Injection (50µg/g) (all counts for 2 minutes) (0.328µ Ci)

Section	$CH_3{}^{131}I$ 19 Nov.	Corrected 20 Nov.	After acetone 20 Nov.	Difference
1st quarter inch	3675	3373	2321	-1052
2nd	1022	938	1256	+ 318
3rd	350	321	600	+ 379
4th	320	294	296	+ 2
5th	126	116	170	+ 54
6th	48	44	90	+ 46
7th	45	41	96	+ 51
8th	25	26	42	+ 16

The results in Table 1.15 show in detail how the acetone vapor drives the $CH_3{}^{131}I$ into deeper layers of the 2" charcoal bed. There is an almost linear behavior of log count vs. depth before and after the acetone. The results suggest that the quaternerization reactions may be reversible, for example:



Removal of Activity by Water Flooding

Regulatory Guide 1.52 (June, 1973) in Section 3.j stipulates that the design of the adsorber section "should provide for water sprays to inhibit adsorber fires." In order to explore the possible removal of adsorbed methyl iodide-131 by liquid water, the following experiments were made.

Methyl iodide-131 was introduced into a volume (53 ml) of a commercial 5% TEDA impregnated sample using charcoal filtered ambient air. The sample (2" diameter, 1" high) was mixed thoroughly and divided into four parts for counting; the total was 59,924 counts per 2 minutes. Distilled water (50 ml) was then contacted with the sample bed and after a 5-minute contact, 5 ml of the water extract was decanted onto a 13 ml sample of unexposed charcoal (background counted) contained in a suitable planchet and immediately counted.

Decanted aliquot	590 counts (2 minutes)
Total estimate in water	5900 counts (2 minutes)
Estimated extracted activity	10%

A second experiment was then made with the object of estimating the portion of the extracted activity among the charcoal, water, and the gas phase. As before, the CH_3I (.00116 ml with a total activity of 0.222 microcuries) was introduced to the charcoal (5% TEDA impregnated) using ambient filtered air and a non-humidified sample. The air flow

(10.5 L/min.) was continued for 2 hours and the charcoal was then thoroughly mixed, divided into 4 parts for counting.

The sample was then returned to location A (Figure 1.10) and distilled water (100 ml) was slowly injected. Air was passed continuously (10.5 L/min.) through the water-charcoal mixture and the effluent air stream was directed to the charcoal at location B. The water flowed into the Dowex 1-X8 (15 ml volume) at C and accumulated in the reservoir D. The distilled water was introduced in 13 minutes and the air flow was continued for an additional hour. The counting results are summarized below:

Table 1.16 Distribution of MeI-131 after Flooding a Charcoal Column with Water

	Counts per 2 minutes
Total activity introduced into charcoal	19819
Residual activity in charcoal, A	18563
Water-extracted CH_3I, D	1256
Activity of Resin Bed, C	364
Effluent air through charcoal, B	80
Unaccounted activity	812

In the above short exposure to liquid water, about 6.3% of the CH_3I was extracted. The solubility of CH_3I in water is reported as 1.8 in 100 parts water (15°C); however, the solubility of the complex TEDA-CH_3I may be expected to be greater in common with the known water solubility of tetraalkylammonium salts in general. A similar enhancement would occur with a soluble KI_x impregnation.

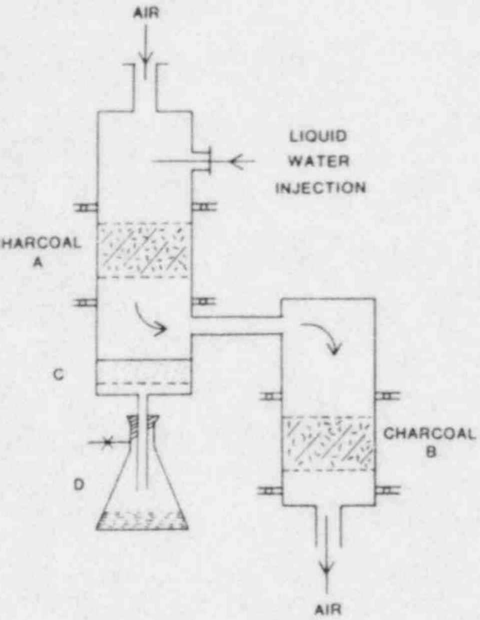


Figure 1.10 Laboratory Apparatus to Estimate the Distribution of CH_3I-131 Between the Charcoal, Water, and the Gas Phase

The unaccounted fraction is in part located in the water that passed the ion exchanger and some in the O-rings used to join the flanges.

The following may be concluded from the above accident scenarios:

1. The retention of methyl iodide-131 is adversely influenced by the pre-adsorption of organic solvent vapors.

2. In one case, acetone vapor, the adsorption of the vapor caused pre-adsorbed methyl iodide to move into deeper layers of the charcoal bed.

3. Water flooding of charcoal containing adsorbed methyl iodide brings about a partition of the iodine among the original charcoal, the water and in the gas phase. Obviously, this is strongly dependent on the details of the water flooding and warrants additional studies under better controlled conditions.

1.8 Concluding Remarks

1. Commercial activated carbons with TEDA (triethylenediamine)and potassium iodide in the impregnation formulation, after exposure to the common contaminants in unfiltered outdoor air, exhibit less penetration of methyl iodide-131 than do the carbons exposed similarly with only potassium iodine + iodine as impregnant.

2. The penetration of methyl iodide-131 as a measure of carbon-filter performance rises rapidly in air flows of greater than 70% relative humidity.

3. The observed influence of water vapor on the degradation of impregnated carbons correlates best with the dew point of the air flow. The trapping efficiency remains good at dew points below about 20°F.

4. The prevailing dew point-temperature-relative humidity at the completion of weathering have a strong influence on the test results. The exposed samples were evaluated for the penetration of methyl iodide-131, weight gain, and the pH of the water extract.

5. Initially, the common air contaminants (ozone, sulfur dioxide, nitrogen oxides, hydrocarbons) adversely influence the inlet layer of a carbon filter bed. The contaminants then migrate to lower depths with increase of length of service.

6. Accidental exposures of a carbon filter to the vapors from solvent spills or to organic vapors from plant operations, contribute to the degradation process more strongly at higher humidities than at lower humidities.

7. Exposures of KI_x carbons to intermittent flows of outdoor air may yield more penetration of methyl iodide-131 than continuous operations with the same total volume of air.

8. Weathered samples of carbon cannot be regenerated at ambient temperature by a continuous air purge alone.

9. The laboratory studies indicate that the interaction of ambient concentrations of ozone, sulphur dioxide, or the nitric oxides with impregnated carbons may be of second order importance relative to the insult of water vapor-organic compounds.

10. The ASTM test procedures to qualify new impregnated activated carbons for the penetration of iodine-131 or methyl iodide-131 cannot be applied without ambiguity to weathered or service carbons. Additional research is needed to develop such a standard.

1.9 References

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2.0 Accident Scenario

2.1 Introduction

In a nuclear power accident mode, the concentration of airborne radioactive iodine (elemental, organic iodides, cesium iodide) will increase manyfold above that during normal operation. The rates of chemical reactions based on these species will increase in ventilation systems and more iodine may reach the adsorbers. The reaction involves the base carbon, the adsorbed contaminants, and the impregnation chemicals. The reaction of the iodine with the carbon networks of activated carbon can lead directly to the formation of organic ^{131}I within the carbon bed; the ^{131}I trapped within the carbon networks can then form the more volatile methyl iodide and "bleed" into the effluent air. The rate will be dependent on the weathering of the carbon adsorber (including dew point), the impregnation chemicals, and the magnitude of the radiation.

The small radiation present in the non-accident mode has no influence on the carbon adsorber, and the efficiency of the carbon adsorber is controlled only by the accumulated intake of atmospheric and/or local contaminants and the relative humidity. The object of the adsorber units of an engineered-safety-feature (ESF) atmosphere clean up system is to operate successfully under postulated DBA (design basis accident) conditions.

The regulatory guides of the U.S. Nuclear Regulatory Commission present requirements for the design, testing and maintenance of atmospheric clean up systems during normal plant operations (1) which differ from requirements for those systems to be used for post-accident use (2). At present the test procedures for <u>new</u> activated carbon which is added to both systems are the same. The activated carbon adsorber is required to be leak tested with a gaseous halogenated hydrocarbon (3) to ensure that by-pass leakage is less than 0.05%. The laboratory testing criteria for activated carbon (2) are summarized in Table 2.1. A representative sample is defined (2) and constitutes a difficult goal to attain. The testing is performed initially and at least once per 18 months thereafter for systems maintained in a standby status or after 720 hours of system operation. The testing, of course, must also follow painting, fire, or chemical release in any ventilation zone communicating with the system. The activated carbon is to be replaced if the representative sample fails to pass the applicable test in Table 2.1.

Table 2.1 Laboratory Tests for Activated Carbon (2)

Activated Carbon Bed Depth	Assigned Activated Carbon Decontamination Efficiencies	Laboratory Tests for Representative Sample
2 inches. Air filtration system designed to operate inside primary containment	Elemental iodine 90% Organic iodide 30%	Test for a methyl iodide penetration of less than 10%
2 inches. Air filtration system designed to operate outside the primary containment and relative humidity is controlled to 70%	Elemental iodine 95% Organic iodide 95%	Test at a relative humidity for a methyl iodide penetration of less than 1%
4 inches or greater. Air filtration systems designed to operate outside the primary containment and relative humidity is controlled to 70%	Elemental iodine 99% Organic iodide 99%	Test at a relative humidity of 70% for a methyl iodide penetration of less than 0.175%

The present investigation is relevant to an accident period in which the radiation sources would be the radioactive gases passing through the carbon adsorber. It is not possible to expose activated carbons in the laboratory to a radioactive gas at the high Curie level of an accident. However, the carbons can be exposed to equivalent radiation levels (γ and/or β sources) and at the same time the activated carbon can be subjected to gas flows of non-radioactive species in order to study the chemistry of the resultant degradation reactions.

Typical accident conditions for a clean up of airborne radioactive materials have been established (2). The average radiation level is given as 10^6 rads/hr in the primary atmospheric clean up system and a dose from iodine build-up on the adsorber of 10^9 rads. In the secondary atmospheric clean up system, the corresponding values are 10^5 rads/hr and 10^9 rads (Table 2.2). The environmental conditions of the DBA for a given ESF system are determined for each plant, but those for typical cases have been specified by the Nuclear Regulatory Commission (2). In addition, primary systems are designed to withstand the radiation dose from water and plateout sources in the containment and also the corrosive effects of chemical sprays.

Table 2.2 Typical Accident Conditions for ESF Atmosphere Cleanup Systems (2)

Environmental Condition	Atmosphere Clean up System	
	Primary	Secondary
Pressure surge	Result of initial blowdown	Generally less than primary
Maximum pressure	60 psig	~atmospheric
Maximum temperature of influent	280°F (138°C)	180°F (82°C)
Relative humidity of influent	100% plus condensing moisture	100%
Average radiation level		
For airborne radioactivity	10^6 rads/hr[a]	10^5 rads/hr[a]
For iodine buildup on adsorber	10^9 rads[a]	10^9 rads[a]
Average airborne iodine concentration		
For elemental iodine	100 mg/m^3	10 mg/m^3
For methyl iodide and particulate iodine	10 mg/m^3	1 mg/m^3

[a] This value is based on the source term specified in Regulatory Guide 1.2 (Ref. 5) or 1.4 (Ref. 6), as applicable.

The radiation sources available at NRL include a 1-MeV Cobalt-60 irradiation facility and a 45 MeV Linear Electron Accelerator (LINAC). These sources presented an opportunity to examine the influence of the radiation dose rates as well as the total radiation dose. To obtain the desired exposures mentioned above, the radiation exposure was estimated (Figure 2.1) for the different sources. The geometry of the LINAC was maintained constant and the Co-60 exposures could be conveniently varied by the distance from the source.

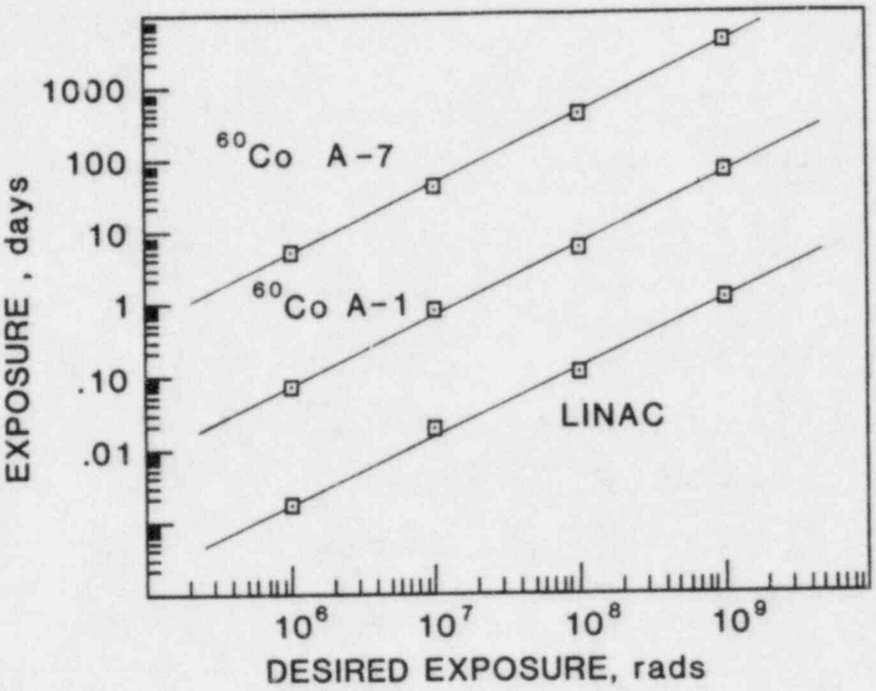

Figure 2.1 Variation of Exposure with Different Sources as a Function of Desired Exposure

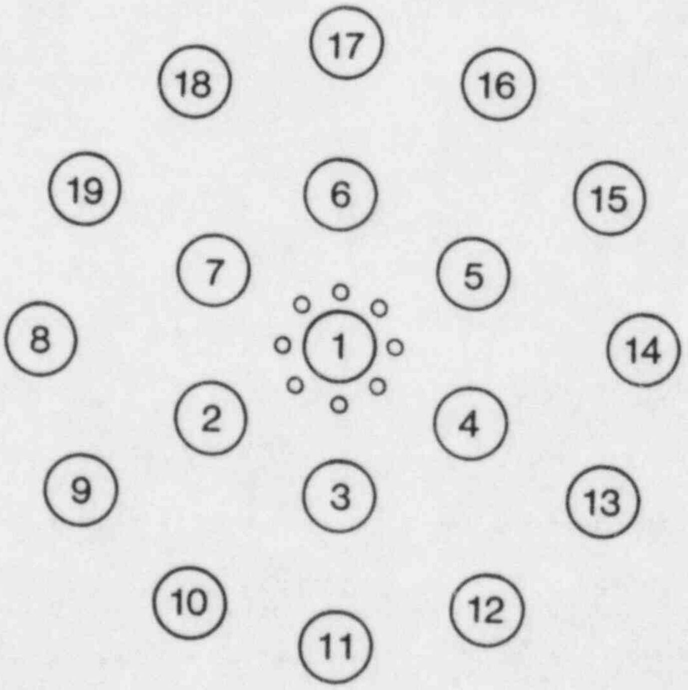

Figure 2.2 Position Array for Samples Around the Cobalt-60 A-Source at NRL. The A-1 position is located within the cylindrical array of eight cobalt-60 rods as shown above.

2.2 Static Exposure of Carbons to the γ-Source ^{60}Co

The position for samples around the Cobalt-60 A-source at NRL is shown in Figure 2.2. The static exposures of the carbons have made use of the positions A-1, A-3, A-5, and A-7. The A-1 position is located as shown within the cylindrical array of eight Co-60 rods and the remaining positions are outside of this array. Because the half-life of Co-60 is 5.2 years, the exposure rate was essentially constant at each position over the duration of each exposure. The dose rate decreases rapidly with distance from the source and, therefore, there is a gradient through the carbon sample, mostly as a result of distance. Each position was calibrated at the center of each sample hole in the array. The radiation field at position 1 is fully symmetric, see Fig. 2.2, and that at the outer rings of the array is not symmetric through the carbon samples. The calibrated dose rates of the three groups of position were:

A-1	7.5×10^5 rads per hour
A-2 to A-7	1.4×10^4 rads per hour
A-8 to A-19	2.5×10^3 rads per hour

The sample container was of stainless steel, 3 in. (7.62 cm) i.d., and the useful height in the radiation field was ±2.5 in., (±6.35 cm), measured from the center. This permitted a sample volume of 580 cm^3. The closure at the top was made with a new 3 in. (7.62 cm) O-ring (synthetic rubber) and the assembly was lowered through a depth of 12 ft. (3.66 meters) in water 22°C to the desired location. The gas inlet and outlet tubing (1/4 inch stainless) was provided with several right angle bends for radiation safety.

2.2.1 New Carbons

The moisture retained by new, unused impregnated carbons on prehumidification before a methyl iodide-131 penetration test influences on subsequent test results (15). It was considered worthwhile, therefore, to irradiate several new carbons for about 100 hrs (with and without the added moisture to the carbon and without air flow) in the γ-field of Cobalt-60 and to determine the subsequent penetration of methyl iodide-131. The results, Table 2.1, were obtained with dried carbons irradiated in the period 20-24 November 1981 and after prehumidification in an air flow of 90% relative humidity (21-24 November) and then irradiated for the period 24-28 November 1981. The total radiation flux was approximately the same in both cases, namely 1.4×10^7 rads. In the subsequent penetration tests with methyl iodide-131, the ASTM procedure D-3803 was used (4).

The radiation effect on the above new carbons, as measured by methyl iodide-131 penetration, was not significant and the penetration remained below the permissible level (ASTM Standard D4069-81). In two of the three carbons, prehumidification before the Co-60 radiation gave the same difference in penetration behavior as previously observed for prehumidified and non-prehumidified samples of new carbons.

Table 2.3 Penetrations of Methyl Iodide-131 Through New Carbons After Exposure to a Total γ-radiation Flux of 1.4x10^7 Rads.

Carbon*	Irradiation Conditions NRL Test	Irradiation Conditions Exposure Time hrs.	Irradiation Conditions Total Rads	Penetration %
	Carbons as received			
615	5217	98	1.5x10^7	0.27±.02
727	5218	98	1.4x10^7	0.30±.11
S and S	5219	98	1.5x10^7	0.08±.06
G-615	5228	52.15(days)	9.0x10^8	0.07±.05
	Prehumidified Carbons			
615	5221	96	1.4x10^7	0.10±.08 0.16±.08
727	5222	96	1.3x10^7	1.40±.84
S and S	5223	96	1.4x10^7	1.51±.84

*See Appendix II for characteristics of these carbons.

A total exposure of 10^9 rads was completed with a sample (G-615, KI and TEDA impregnation) placed in the A-1 position. The integrated intensity for the 52.15 days (7.22x10^5 rads/hr, av.) was 9.03x10^8 rads and the penetration of methyl iodide-131 was only 0.07±.05%. This value is of the same order of magnitude previously observed for other samples of G-615 without radiation. It was concluded at this point in time that a new carbon that passed the ASTM qualification test (4) was not subject to significant degradation under the conditions of the radiation exposure alone.

Previous to the present investigation a few studies were published (see Table 2.4) on the influence of radiation on the properties of some carbon solids. It was reported that there were insignificant changes in surface area of carbon blacks (5) irradiated at 5x10^{18} to 1.4x10^{19} neutrons/cm^2 and with γ-radiation of 4x10^{22} to 8x10^{22} rads. Microcrystalline graphites and charcoal (6,7,8) showed very little or no change after irradiation in water vapor, oxygen, argon, krypton, or xenon adsorption. Neutron irradiated graphite (up to 7.53x10^{20} nvt total) was shown (9) to decrease in surface area, density and pore shrinkage. Apparently, the graphite crystallites, in expanding upon neutron irradiation, occupy the voids in their immediate vicinity, thus causing the changes in surface properties.

It may be concluded that the carbon networks derived from a large variety of source materials are stable physically and chemically in the radiation fields specified in typical accident conditions (Table 2.2). The well known Wigner effect is observed in a much higher radiation flux when graphite is used as a neutron moderator.

Table 2.4 Influence of Radiation on Some Properties of Carbon Solids

	Radiations	Property	Ref.
	neutrons/cm^2		
Spheron 6, original	none	107 m^2/g surface area	(5)
	5.7x10^{18}	106	
	8.8x11^{19}	110	
Spheron 6, heated	none	86	
	1.4x10^{19}	87	
	8.9x10^{19}	87	
Sterling FT, original	none	13.6	
	1.4x10^{19}	12.1	
Sterling FT, heated	none	14.4	
	1.4x10^{19}	13.4	
	γ-radiation		
Spheron 6, original	none	107 m^2/g	(5)
	8.2x10^{22}	107	
Spheron 6, heated	none	86	
	4.1x10^{22}	87	
Sterling FT, heated	none	14.4	
	8.2x10^{22}	14.6	
Pile Graphite	BEPO operations	No change in water adsorption	(6)
Graphite dust	4x10^{19}n/m^2	No change in O_2 or Argon adsorption	(7)
S and S 208	4x10^{11} rads (fast electrons)	No change in Kr, Xe adsorption	(8)
Artificial graphite	Neutron bombardment	Surface area decrease	(9)

2.2.2 Exposure of Used Carbons

Since all carbon adsorbents accumulate a variable amount of contaminants during the time in service, it was thought that the ionization of some of these adsorbed contaminants could influence the retention of iodine compounds in a relevant radiation field. The two service carbons described below were first irradiated in the Co-60 facility each to a total of 10^7 and 10^8 rads. The penetration of methyl iodide-131 was determined before and after the irradiation (Table 2.5).

The NRL sample 5143 was a service carbon removed from a utility operation where it had been in place for four years. The moisture content was 19.7% and the pH of the water extract was 7.3. It had been installed as a KI_x-impregnated coconut shell carbon. The NRL sample 5233 had been used for two years in a glove box operation in which iodine-125 was used to prepare organic preparations for medical treatments. The pH of water extract (6.9) showed no significant change after exposure to Co-60 radiation. The material when new was NACAR G 615, a co-impregnation of TEDA (triethylenediamine) and KI (potassium iodide) on coconut shell carbon. A decrease in pH of the water extract of a charcoal usually accompanies the degradation of iodine change upon weathering. The fact that none occurred on irradiation indicates little or no chemical change of the similar type.

Table 2.5 Penetration before and after ^{60}Co Irradiation

NRL Sample	% Penetration of Methyl Iodide-131*		
	Original	10^7 rads	10^8 rads
5143	31.0	16.4	6.3
5233	30.1	11.7	7.2

*Standard Test ASTM/ANSI D3803-79

The exposure of the above two samples to the γ-radiation of ^{60}Co actually decreased the subsequent penetration of methyl iodide-131. In other words, the efficiency for the removal of methyl iodide-131 was increased. This is a remarkable observation and was further supplemented by additional results for different used carbons at several radiation levels (10^7,10^8 and 10^9).

2.3 LINAC Irradiation of Carbon Samples

Since the times required to reach 10^9 rads in the available positions of the ^{60}Co facility were excessively long, the NRL LINAC facility was used (the cooperation of Dr. K.M. Murray was very much appreciated). A description and the operating characteristics of the NRL LINAC are given in Appendix 2. The aluminum sample container for the activated carbon exposures was 11 cm. diameter and 11 cm. high. The total volume of approximately one liter was divided into four equal sections (to accommodate four different samples) by inserting thin aluminum partitions having a snug fit with the inside diameter and with the inside height. Each section held about 210 ml of carbon. The container was mounted on a rotating base operating at 5 rpm.

In order to determine the dose rate, three short tests (see Figure 2.3) were made. In the first two tests, an array of nine TLD's was placed first at a distance of 50 cm and than at 75 cm from the exit slit for about three seconds at each location. The 75cm location resulted in a more uniform dose distribution than did that at 50 cm and was chosen as the final location. The dose count distribution as a function of distance is shown in Table 2.6; the standard deviation at 50 cm was 830 and that at 75 cm was 330.

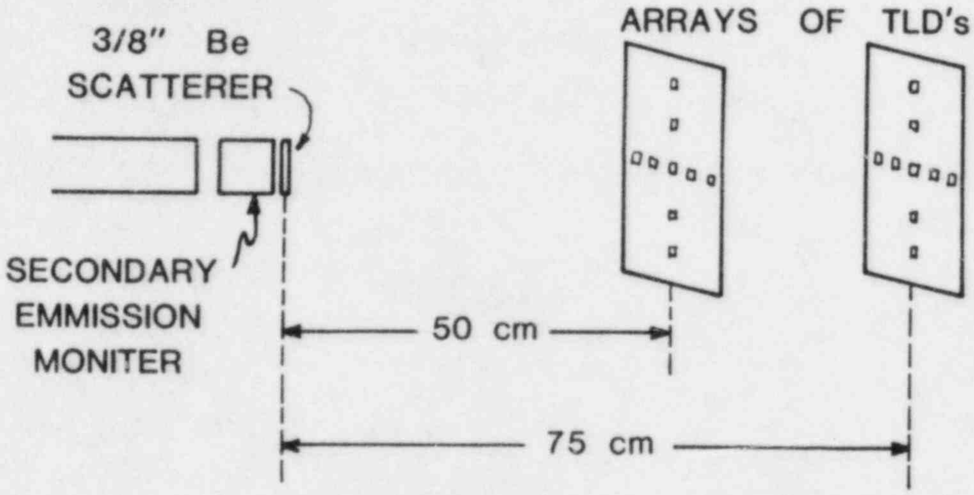

Figure 2.3 Alignment for Determination of the Dose Rate

Table 2.6 Dose Count of an Array of Nine TLD on Container

	50 cm	75 cm
TOP OUTER	1281	779
TOP INNER	3408	1427
RIGHT OUTER	2124	931
RIGHT INNER	2776	1458
BOTTOM OUTER	1987	793
BOTTOM INNER	3441	1119
LEFT OUTER	1503	700
LEFT INNER	2878	1249
CENTER	-	1573

To calibrate the beam monitor, a secondary emission monitor, SEM (see Figure 2.4), was used and three pairs of TLD's were placed in the sample which was rotated at 5 RPM. The sample was placed 75 cm from the scatterer and irradiated for ten seconds. The average current from the SEM for this period was 20 μA. This was integrated as shown below using a Keithley Model 610 CR electrometer, a voltage-to-frequency converter (VFC) and a scaler. With the VFC set at 100 HZS/V, the total count was 362.

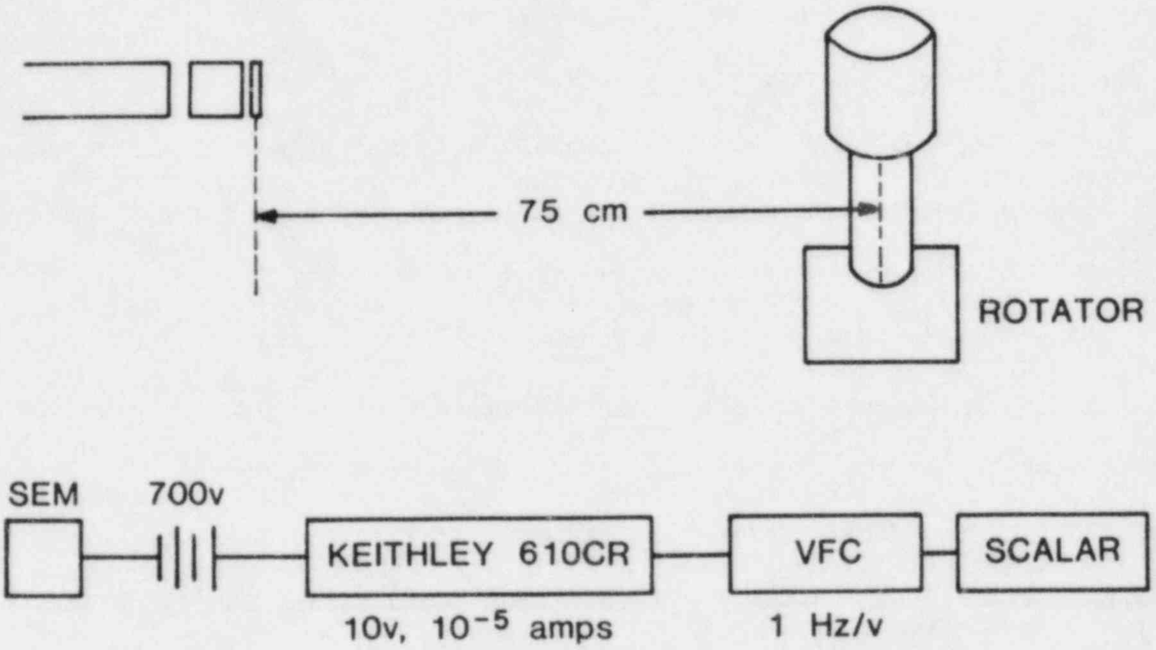

Figure 2.4 Calibration of Beam with a Secondary Emission Monitor SEM

	Dose on Each TLD		
	1	2	Avg.
CENTER TLD	27.0 Krads	28.0 Krads	27.5 Krads
MIDDLE TLD	17 Krads	20 Krads	18.5 Krads
TOP TLD	11 Krads	11 Krads	11 Krads

Choosing a dose of 20×10^3 rads as representative of most of the sample, the value of 5.5×10^3 rads per count was obtained with the VFRC set at 1 HZ/VOLT. The following counts correspond to the designated total rads that were desired:

1.8×10^5 counts	10^9 rads
1.8×10^4 counts	10^8 rads
1.8×10^3 counts	10^7 rads
1.8×10^2 counts	10^6 rads

2.3.1 Induced Activity after Irradiation

The first samples irradiated continuously on the NRL LINAC, resulted in 191,000 counts on the beam monitor. This corresponded to a total dose of 1.05×10^9 rads.

The irradiated samples were found to be radioactive. The presence of this activity raised a problem of interference in subsequent penetration tests with iodine-131 when crystal counting is used. Approximately one gram from each of the four samples was taken for analysis of the induced activity. The spectrum of each sample was found to be dominated by the gamma rays from I-126, as shown below:

1.	KI + TEDA (G-615)	0.25μCi/g	50.9μCi/sample
2.	KI + TEDA (G-615)	0.25μCi/g	46.7μCi/sample
3.	KI + TEDA (BC-787)	0.27μCi/g	43.1μCi/sample
4.	KI + TEDA (KITEG II)	0.14μCi/g	23.4μCi/sample

LINAC exposures have also been made at 10^8 and 10^7 rads. Table 2.7 summarizes the results for the formation of radioiodine-126 which decreased about tenfold for each tenfold decrease in total rads of exposure.

The iodine-126 was attributed to a γ,n nuclear reaction with ^{127}I. In addition to I-126, low level I-124 and C-11 were detected. The half-life of each of the above radioactive species is:

I-126	13 days
I-124	4 days
C-11	20.5 minutes

Table 2.7 Formation of Iodine-126 in LINAC Exposures

Date	Irradiation NRL	Measured μC_i	Measured Date	Calculated to $t = 0$ μC_i
10-11 Aug 81 at 10^9 rads	5242	21.71	27 Aug	50.9
	5243	20.99	26 Aug	46.7
	5244	18.39	27 Aug	43.1
	5245	10.52	26 Aug	23.4
20 Oct 81 at 10^8rads	5251	2.02	3 Nov	4.26
	5252	1.73	5 Nov	4.06
	5253	1.99	2 Nov	3.98
	5254	2.00	3 Nov	4.22
20 Oct 81 at 10^7rads	5255	0.174	12 Nov	0.593
	5256	0.314	2 Nov	0.628
	5257	0.166	12 Nov	0.566
	5258	0.242	5 Nov	0.567

The initial intensity of iodine-126 A(o) was calculated from the measured value A(t) at time t as follows: $A(t) = A(o)e^{-kt} = A(o)e^{-0.693\ t/t_{1/2}}$, where $t_{1/2}$ is the half-life. Sufficient iodine-126 activity was found to invalidate a penetration measurement based on a sodium iodide crystal counting procedure. This is due to the interference of the Compton Scattering from ^{126}I into the channel used for the ^{131}I measurement.

Gamma-ray analyses were carried out utilizing 10% efficient Ge-Li detectors and a Canberra Series 80 multichannel analyzer system used in conjunction with a PDP 11/34 computer (10).

2.3.2 Exposure of Used Carbons

A number of used carbons from service were exposed on the LINAC facility to an accumulated value of 10^9, 10^8 and 10^7 rads. The penetrations of methyl iodide-131 were determined using the Ge-Li detector and the results are given in Table 2.8.

Table 2.8 Penetration of Methyl Iodide-131 before and after LINAC Irradiation

Sample Number	Original Carbon	Previous Exposure	Initial	% Penetration After LINAC 10^7rads	10^8rads	10^9rads
5233	NACAR G-615	Continuous use for 2 years in glove box with I-125 compounds	30.1	7.87	1.37	.039
5234	NACAR G-615	Ditto for 1 year service	10.5	2.0	0.10	.033
5143	KI_x Coconut Charcoal	Removed from Nuclear Power Plant after 4 years	31.0	21.6	8.9	-
5214	BC 787	Weathered at NRL 286 days (0.77 yr.)	9.9			.03
5151	NUCON KITEG II	Weathered at NRL 757 days (2.07 yrs.)	38.9			.002
ARK	Coconut Charcoal, KI_x	Removed from Nuclear Power Plant	3.93	2.5	2.4	
FSV	BC-727	Removed from Nuclear Power Plant	28.3	32.3	24.0	
SRL P-2 (14)	GX-176	14 months in compartment P-2, SRL	28.0	12.2	0.21	
SRL P-2 (19)	GX-176	19 months in compartment P-2, SRL	55.4	46.6	14.0	
SRL K-2 (18)	GX-176	18 months in compartment K-2, SRL	41.1	10.6	0.16	
SRL K-5 (15)	GX-176	15 months in compartment K-5, SRL	48.6	-	3.2	
SRL C-3 (15)	GX-176	15 months in compartment C-3, SRL before paint fumes (12)	41.3	-	33.5	
SRL C-3 (15a	GX-176	Ditto after exposure to paint fumes, SRL (12)	69.0	65.6	41.2	

The NRL sample 5233 has been described above in connection with Co-60 irradiation. The NRL sample 5234 had been used for one year in a glove-box operation in which I-125 was used to prepare organic-iodine preparations for medical treatments. The original material was NACAR-G615, having a co-impregnation of TEDA (triethylenediamine) and KI (potassium iodide) on coconut shell carbon.

NRL sample 5143 had been removed from a nuclear power plant where it had been in service for four years. The moisture content was 19.7% and the pH of the water extract was 7.2.

NRL sample 5214 had been weathered at NRL by passing outdoor air ($1.05\text{x}10^6$ cubic feet) from 17 Sept 1980 to 25 June 1981 (0.77 year). The pH of the inlet layer was 4.2 and that for the exit layer was 9.5. The original material was BC 787 which had been impregnated with TEDA and KI on coconut shell carbon.

NRL sample 5151 had been weathered at NRL by passing outdoor air ($2.75\text{x}10^6$ cubic feet) from 30 May 1979 to 25 June 1981 (2.07 years). The pH of the inlet layer was 4.1 and that for the exit layer was 8.0. The original material was designated as NUCON KITEG II, Lot 024.

The reactivation of service carbons by irradiation increased steadily with increase in the integrated radiation (Figure 2.5). The improvement appears to depend on the nature and amount of accumulated contaminants which produced the initial high penetration. It should be noted that all of these carbons contained iodine-127 as a component in the impregnation and the significance will be discussed below (Chapter 3).

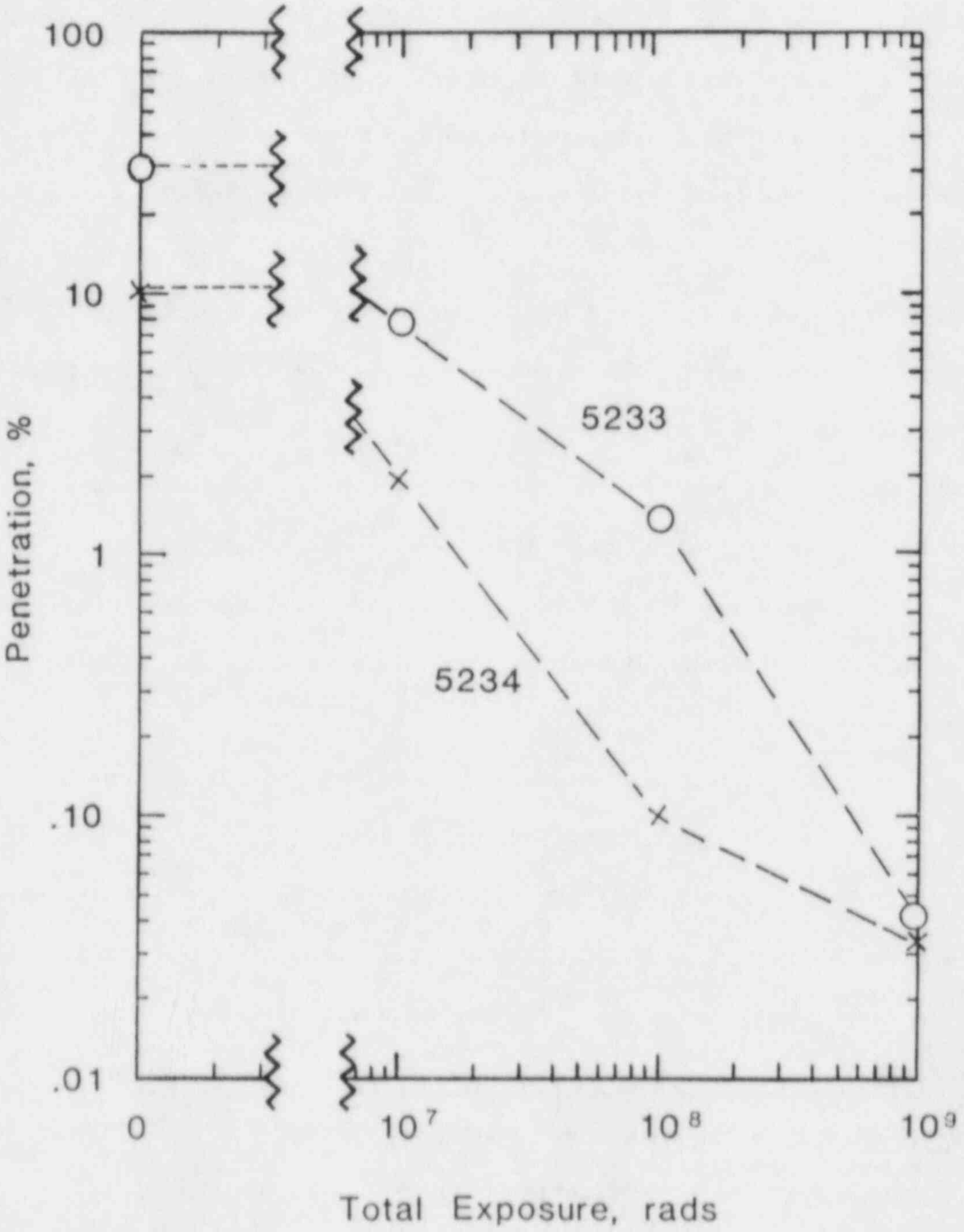

Figure 2.5 Decrease in Penetration of Methyl Iodide-131 with Increased Total Exposure on the NRL LINAC

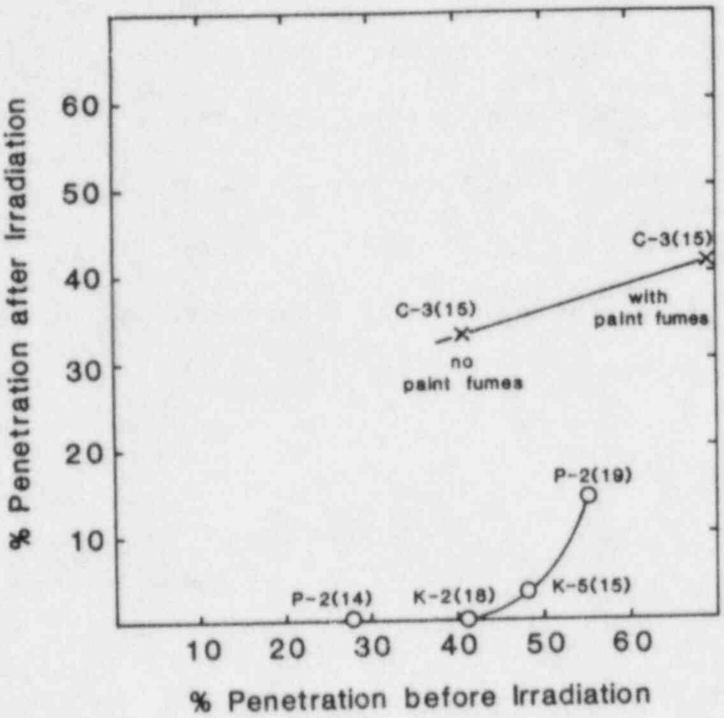

Figure 2.6 Penetration of Methyl Iodide-131 before and after Irradiation at 10^8 Rads on the NRL LINAC

The six SRL samples (11) are a valuable source of comparative data because these were used at the same plant with the same starting carbon. The results (See Figure 2.6) indicate that on the exhaustion of the carbon (14 to 19 months) some contaminants accumulated that limited the extent of recovery upon exposure to LINAC radiation for a total of 10^8 rads. In particular, the carbon from the C-3 compartment (15 month) (12) received an additional intentional exposure to volatile paint solvents resulting from painting operations in the reactor space. As evident in Figure 2.6, the C-3 (15) sample exposed to paint fumes decreased penetration from ~70 to 40%; the same sample without paint fumes showed a penetration change from ~40 to 34. Hence, the carbon exposed to paint fumes had better percent recovery from irradiation than the carbon which was not exposed. It can certainly be concluded that exposure of the carbon to paint fumes degraded the carbon performance and this was not totally recovered by irradiation to 10^8 rads.

The recovery of carbon efficiency for trapping methyl iodide-131 varies with some exceptions with the quality of contaminants added during service. Another way to display the change is to plot the ratio of the penetration of the initial carbon to that observed after irradiation (Fig. 2.7). A trend is evident relating the improvement of the carbon with its service time before the irradiation.

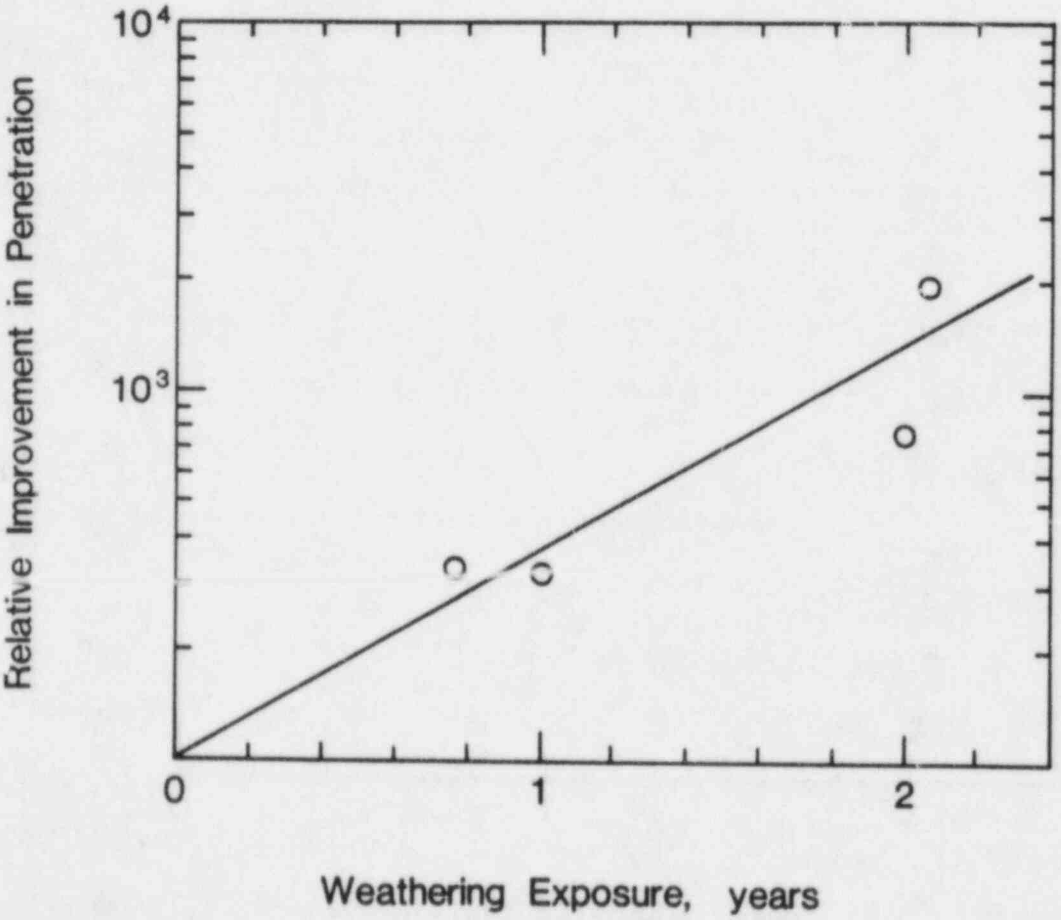

Figure 2.7 Ratio of the Penetration of Initial Carbon (KI Impregnation) to that Observed after Irradiation (10^9 rads on LINAC) as a Function of Time in Service

During the methyl iodide-131 penetration measurements (ASTM D-3803, 79), it was found that some of the induced I-126 was detected in the two back-up beds. The amounts (see Table 2.9) are small, but they are evident of the presence of isotope "scrambling" among the species ^{126}I, ^{127}I, and ^{131}I present on the carbon during the test procedure. The mechanism is quite complex and involves both gaseous and adsorbed species.

Table 2.9 Migration of Induced ^{126}I during the Test Procedure (ASTM D-3803) for Trapping Methyl Iodide-131(30°C)

NRL Sample No.	Post-test Count for ^{126}I (μCi)			Counting Date
	Test Sample	Back-up A	Back-up B	
5233	16.13	8.89(-3)	3.29(-5)	31 Aug
5234	18.14	1.98(-3)	<5.6(-5)	31 Aug
5214	13.45	4.89(-3)	2.54(-5)	1 Sept
5251	9.38	2.48(-3)	2.67(-5)	28 Aug

Measurements were made by Nuclear Environmental Services, 3 Choke Cherry Road Rockville, Md 20850

2.3.3 LINAC Irradiation of 5% TEDA Carbons

Activated carbons impregnated with KI with and without TEDA (triethylenediamine) were weathered and the results (Fig. 1.3) indicated that a bi-impregnation using both impregnants is the preferred choice to maintain high iodine-131 removal efficiency. In order to demonstrate how a TEDA impregnation alone might behave upon irradiation, a series of weathered carbons containing 5% TEDA were irradiated on the LINAC to 10^8 rads. The results (Table 2.10) show that the penetration of methyl iodide-131 with three of the six samples (weathered for 30, 151 and 278 days) actually increased somewhat after irradiation; three (weathered for 150, 443 and 595 days) showed considerable decrease in penetration upon irradiation. The second group may have contained a group of contaminants different than the first group and was more vulnerable to the radiolysis reactions. With the exception of the 595 day exposure, the penetration of the irradiated samples increased steadily with the duration of the exposure (see Figure 2.8) to outdoor air.

Table 2.10 5% TEDA Carbons Irradiated on LINAC to 10^8 Rads

NRL Sample	Previous Exposure	Penetration % Initial	Penetration % Irradiated
5080	Weathered at NRL, 30 days	0.02	0.43
5208	Weathered at Simi Valley, 150 days	24., 31	0.88
5064	Weathered at NRL, 151 days	0.82	1.1
5066	Weathered at NRL, 278 days	0.46	3.7
5227	Weathered at NRL, 443 days	32.	9.0
5169	Weathered at NRL, 595 days	76.	3.1

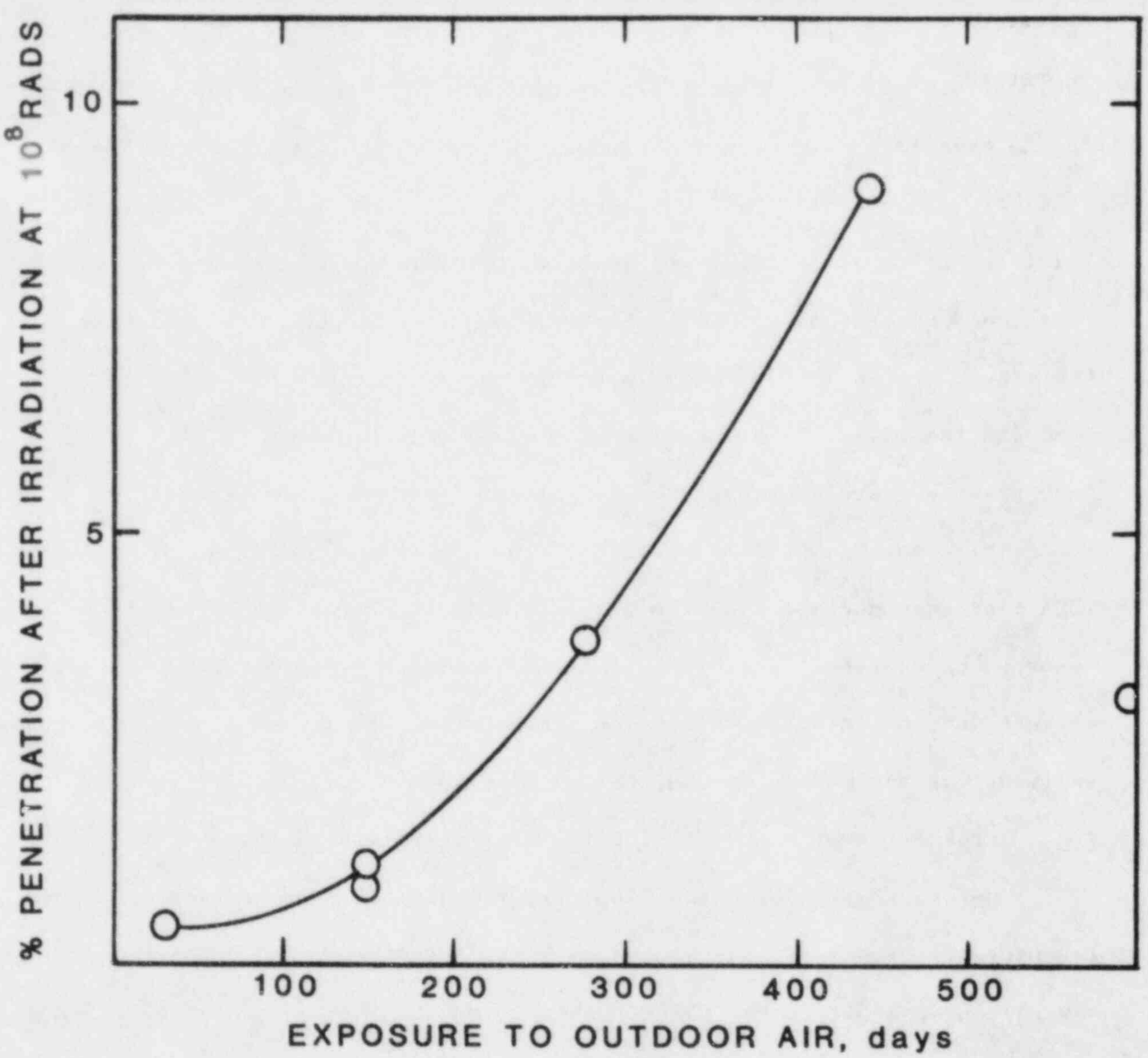

Figure 2.8 Penetration of Methyl Iodide-131 After LINAC Exposure (10^8 Rads) as a Function of the Time of Weathering

A decomposition reaction of TEDA adsorbed on a coal-base charcoal has been studied by a mass spectrometry technique (13). This method involved selection of one m/z value ion with the first magnetic sector, collision induced dissociation of the mass-selected ions between the two sectors, and the analysis of the decomposition products with the second (electric) sector. In the experiment a desorption product at 60-70°C from a TEDA-impregnated coal-base charcoal (5 wt.%) was found to be m/z = 80. It was identified as being one of three isomers: pyridazine, pyrimidine, or pyrazine (ortho-, meta-, and para-diazine). The charcoal was then heated in the ion source, the m/z 80 ion mass selected as mentioned above, and the decomposition products identified. The most abundant ions were m/z of 53, 52, 51. The pure diazines were each analyzed in the same manner. Comparison of relative intensities established the pyrazine structure to the m/z of 80 formed on the TEDA impregnated charcoal. The above experiment demonstrates that TEDA adsorbed on charcoal is subject to decomposition reactions. The possibility of such decomposition on desorption from charcoal should be kept in mind when analyses for adsorbates on charcoals are performed.

2.4 Interaction of Methyl Iodide-127 with Irradiated Carbons

The penetration of methyl iodide-127 was first used to determine the trapping efficiency of new carbons by Deitz and Romans (14). The results for new carbon agreed with the values determined using methyl iodide-131. It is now known that the penetration of methyl iodide-131 through used reactor grade carbons (see Table 2.6) is markedly decreased as the result of the irradiation. Penetration measurements have also been made using methyl iodide-127 on the same samples and the results demonstrate an important new aspect of iodine-trapping which will now be discussed.

2.4.1 Penetration with Methyl Iodide-127 after LINAC Irradiation

The sample NRL 5233 was weathered in glove box operations and the initial penetration of CH_3I-131 after weathering was 30.1%. After LINAC irradiation to 10^9 rads, the penetration decreased to 0.03%. A second sample, GX-176 weathered for 18 months in the K-2 compartment was obtained from the Savannah River Laboratory. The initial penetration of CH_3I-131 was 41.1%. After LINAC irradiation to 10^8 rads the penetration decreased to 0.16% (Table 2.11).

The results for CH_3I-127 penetration are shown in Figures 2.9 and 2.10. The penetration is reported (Table 2.11) after the dose period of 120 minutes and after the 4-hour air purge (total 360 minutes). The large penetration of CH_3I-127 after the LINAC irradiation contrasts strongly with the very small penetrations of CH_3I-131. The penetration at the end of the dose for NRL 5233 indicated improvement from 85 to 25, but by the end of the purge (360 minutes) the total penetrations were about equal.

Table 2.11 Penetration Tests with Methyl Iodide-127 after LINAC Irradiation of Two Used Carbons

		Penetration, %		
Sample	% RH	CH_3I-127 Dose 120 min	Air Purge of 240 min	CH_3I-131*
Original 5233	95	85	92	30.1
Irradiated 10^9	95	25	87	0.03
Original SRL K-2	90	-	-	41.1
Irradiated 10^8	90	36	70	0.16

*Determined by ASTM D-28 3803 (1979)

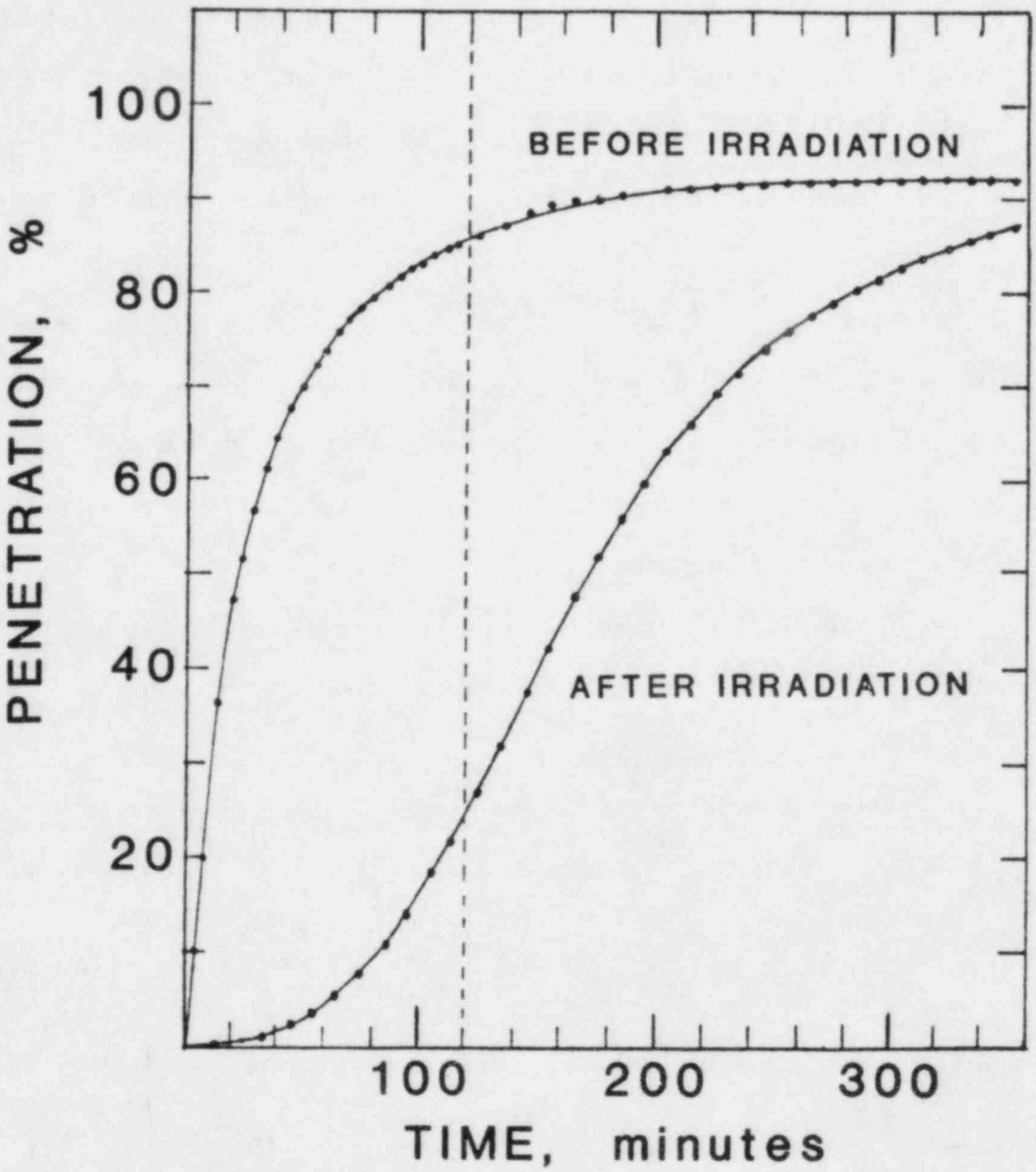

Fig 2.9 The On-line Penetration of Methyl Iodide-127 in the Testing of the Original and the Irradiated (LINAC at 10^9) Sample NRL 5233 (Air Flow of 90% RH (Run 3427)

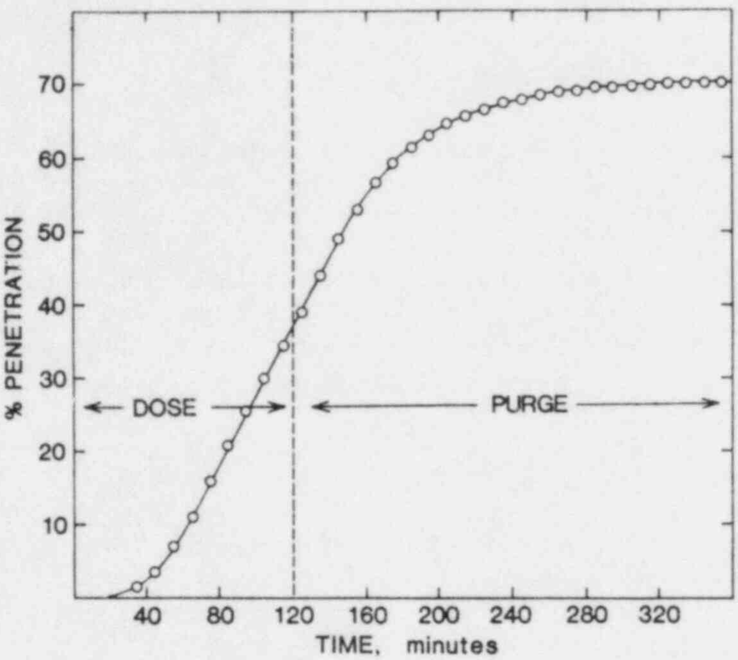

Figure 2.10 Penetration of Methyl Iodide-127 after LINAC Irradiation to 10^8 Rads of SRL K-2, 18 months (Run 3428)

2.4.2 Penetration with Methyl Iodide-127 after Irradiation in the Co-60 Facility

The sample NRL 5234, weathered in glove box operations, had an initial penetration of CH_3I-131 was 10.5%. After exposure to γ-radiation of Co-60, the penetration decreased to 1.9%. A second sample NRL 5143, weathered in utility operations, had an initial penetration for CH_3I-131 of 31.0%; after a Co-60 irradiation to 10^8 rads, the penetration decreased to 4.45 in one sample and to 3.84 with a duplicate sample (Table 2.12).

The results for NRL 5234, irradiated to 10^7 rads on the Co-60 facility, are shown in Figures 2.11 and 2.12. The penetration was observed either with dry air (2% RH) as the carrier,or using a second sample with humidified air (95% RH). The results show the pronounced influence of the water content of the carrier air. Dry air (2% RH) decreased the CH_3I-127 penetration of both the original and the irradiated sample to about the same extent. The penetrations observed at the end of the dose (120 min.) and at the end of the purge (360 min.) are summarized in Table 2.10. Note that all methyl iodide-131 penetrations were determined in an air flow of 95% RH.

Sample NRL 5143 was examined in duplicate for all operations with good reproducibility (Table 2.12). The original sample was also tested with dry air (2% RH) and wet air (95% RH) and the adsorption of CH_3I-127 was greater with dry air as the carrier air.

Table 2.12 % Penetration Tests with Methyl Iodide-127 before and after Co-60 Irradiation to 10^8 Rads

Sample		RH	Penetration		
			$^{127}I\text{-}CH_3$		$^{131}ICH_3$*
			Dose 120 min.	Dose & Air Purge Total 360 min.	
5143	original	2	7.9	60.0	31.0
5143(1)	after 10^8 rads	2	9.3	60.8	4.45
5143(2)	after 10^8 rads	2	10.0	50.4	3.84
5143	original	95	70.0	101.0	-
5143	ditto, 5-day dry air purge	2	10.4	81.0	-
5234	original	95	82	138	10.5
	original	2	11	15	
5234	after 10^7 rads	95	79	103	1.9
		2	14	18	-

*Determined by ASTM D-28 3803 (1979)

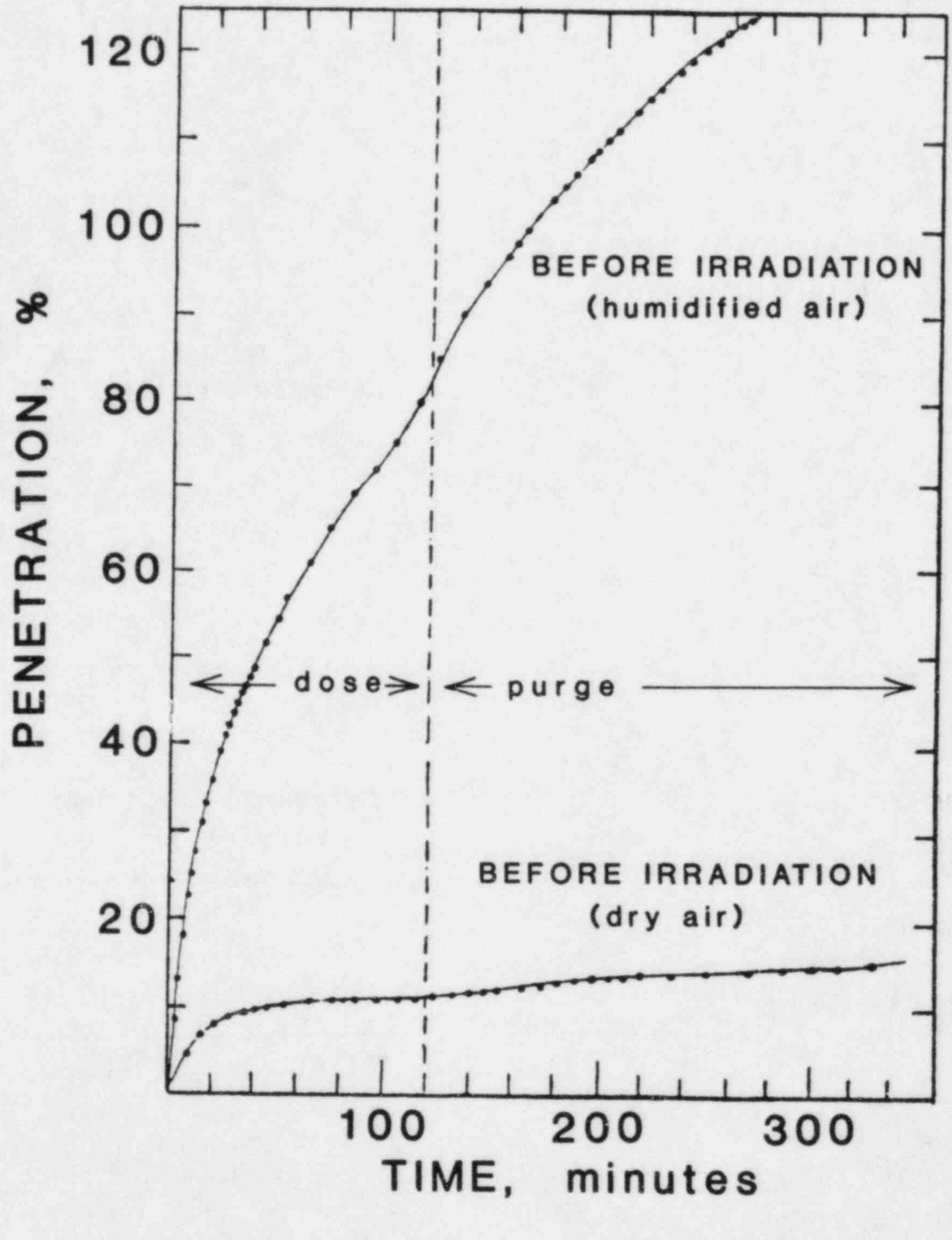

Figure 2.11 The On-line Penetration of Methyl Iodide-127 on Irradiated Carbon (NRL 5234) (at 10^7 rads) with Dry Air (2% RH) and Humidified Air (90% RH)

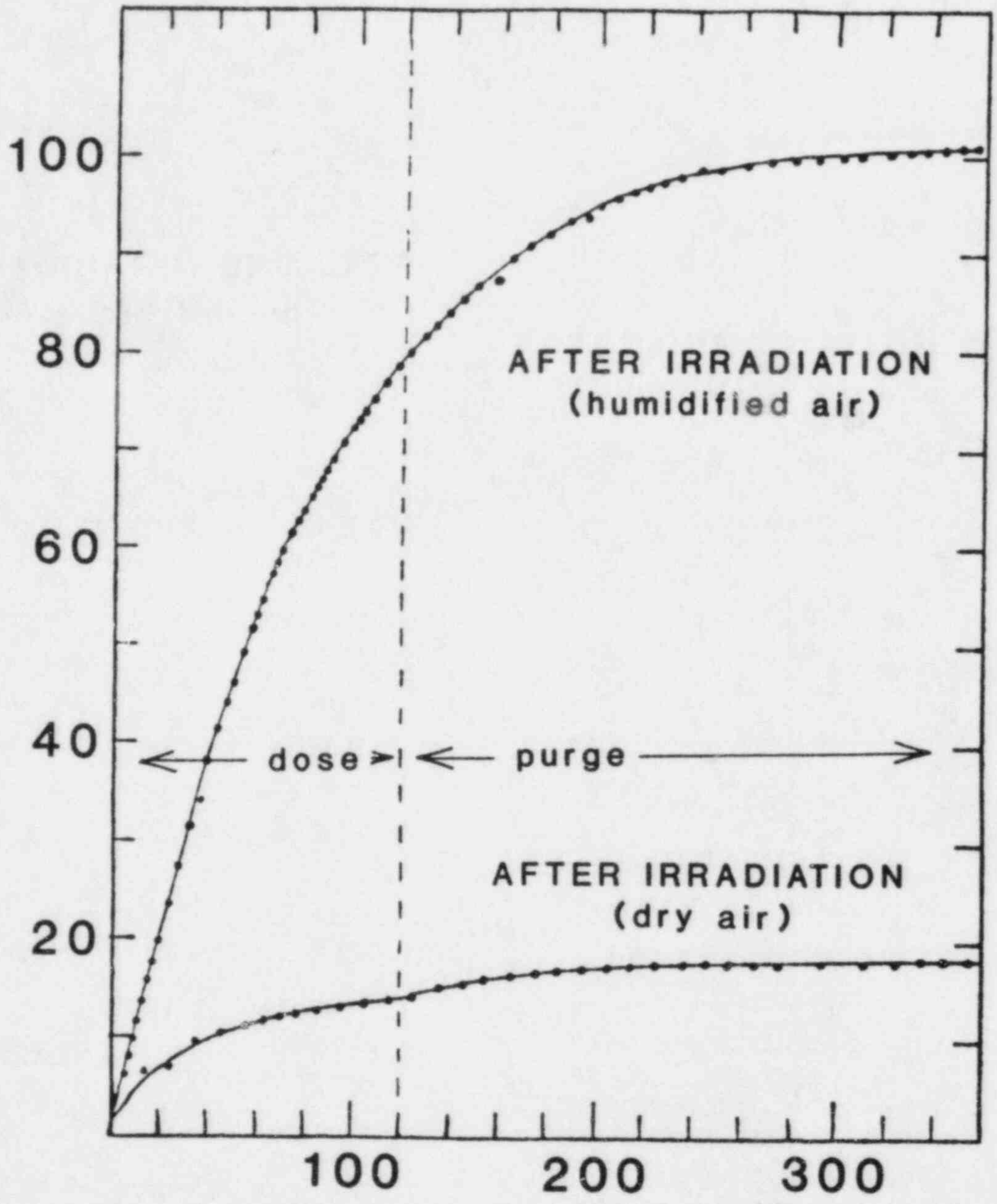

Figure 2.12 The On-line Penetration of Methyl Iodide-127 on the Irradiated Carbon (NRL 5234) with Dry Air (2% RH) and with Humidified Air (90% RH)

The results for used and in-service carbons demonstrate a great disparity between the trapping of the radioactive species and methyl iodide-127. It is apparent that the capacity for isotope exchange has been vastly improved by the irradiation and that for adsorption only slightly influenced or not at all. The significance of this fact will be discussed further in other sections in which the basic chemical changes of radiolysis are examined. The chemical changes promote iodine isotope exchange.

2.5 Interaction of Methyl Iodide-127 during Continuous Irradiation

The penetration of methyl iodide-131 through used carbons has been shown to increase with the duration of the flow of humidified (95% RH) air (15) and to decrease with the exposure times to a radiation source. The combined influence of these factors was studied with exposure times of 100 hours to gamma radiation of ^{60}Co accumulated to 10^6, 10^7 and 10^8 rads. Changes in methyl iodide-127 penetration were followed daily by gas chromatography (electron capture detector) using a dose period of 2 hours and a purge period of 4 hours.

The equipment required to expose the weathered carbons in the ^{60}Co facility consisted of the container, a controlled humidified air flow, a source of methyl iodide-127, the portable chromatograph, and sufficient stainless steel tubing to place the container under 12 feet of water and to return the flow to the chromatograph.

The stainless steel container (Figure 2.3) had an inside diameter and height of 3 and 9.5 inches, respectively. The inlet and outlet stainless steel (1/4-inch) tubings were welded to the container lid. The closure was made with an O-ring and four bolts to the main body. A spring-lock connection welded to the center of the lid provided the means to lower the assembly into position using a 15-foot aluminum rod. The outlet 1/4-inch tube connection was welded directly to a concentric close-fitting stainless tube with a perforated steel bottom (see Figure 2.13) in which the carbon sample was placed. An additional leg touching the inside bottom of the container was welded to the bottom to provide a support for the carbon container. The air flow was charcoal filtered and the rate was 20 liters per minute at 90% RH and 22°C.

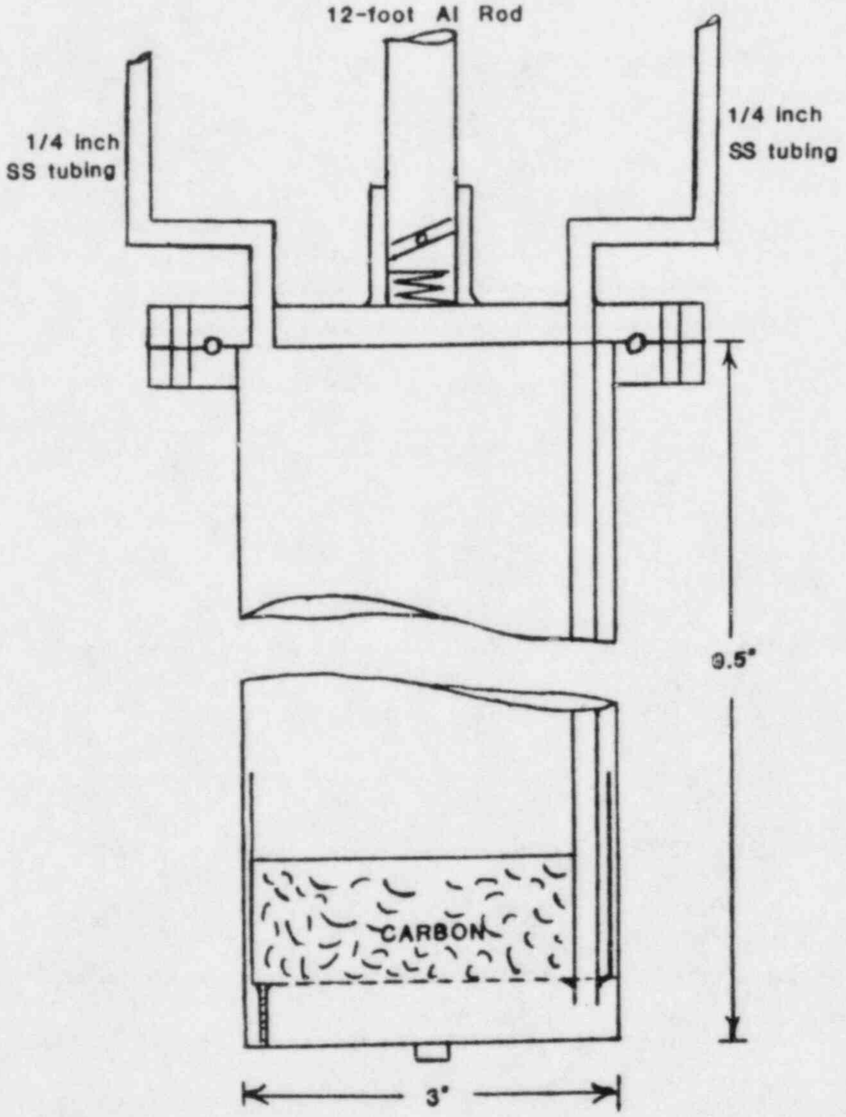

Figure 2.13 Sketch of the Container Used to Position the Carbon Sample in the Cobalt-60 Radiation Source at NRL

The measurements include a run without irradiating the carbon, then the container was lowered into the A-7 position of the ^{60}Co facility where it remained for the designated time. Upon removal from the radiation field a test run was then made with CH_3I-127. The sample of carbon was NRL 5234, a KI-TEDA impregnated carbon which had been used for one year in glove box preparations of biological compounds containing ^{125}I.

The average flow rate of air was maintained at 15 L/min. Since the volume of the sample was 103 ml, the contact time was (103x60)/15,000 = 0.41 sec. Table 2.13 gives the level of radiation, the exposure times, and the carrier mixture. The A-7 position at the time of these exposures averaged 1.29 E5 rads/hr.

Table 2.13 Experimental Procedure for Series I using NRL Sample 5234 in the A-7 Position (Test 3419)

Test	Date	Radiation (rads/hr)	Time Irradiated	Carrier
			hrs.	
A	2 Feb	None	-	Dry air
Irradiated	9 Feb at 13:45		0	Humidified Air
B	10 Feb	1.29 E5	23	Humidified Air
C	11 Feb	1.29 E5	51	"
D	12 Feb	" "	71	"
E	14 Feb	" "	125	"
Removed	14 Feb at 18:30			
F	16 Feb	None	-	Dry Air
G	18 Feb	None	-	Humidified
A repeat	22 Feb	None	-	Humidified

Total Radiation Exposure = 5 day and 5 hours = 125 hours
Total Rads = 125x1.29 E5 = 1.61 E7

The flow of humidified air (charcoal treated) was continuous. The total dose of methyl iodide-127 was varied 10-fold. The effluent was observed at 10-minute intervals and the values at 120 minutes (end of dose) and at 360 minutes (end of 4-hour purge) are given in Table 2.14. It had been shown in previous work (14) that the penetration of methyl iodide-127 at 120 minutes for <u>new</u> carbons correlated well with the penetration values determined with methyl iodide-131.

Table 2.14 Penetration (%) of Methyl Iodide-127 (Series I) using NRL 5234 in the A-7 Position of the ^{60}Co Radiation Field

	Carrier	Integrated DOSE Total (120)	Integrated Effluent		P_{120} %		P_{Total} %
			120	Total			
A	Dry Air	4.35	0.490	0.698	11		15
B	Humidified	16.0	3.88	3.88	24	-	24
C	"	24.8	6.81	6.81	27	-	27
D	"	33.9	8.56	8.56	25	-	25
E	"	10.6	4.97	4.97	47	-	47
F	"	4.27	.562	.786	13		18
G	"	4.19	3.24	4.57	77		101
H repeat	"	2.98	2.28	4.21	77		138

<u>Discussion</u>

Long exposure times of impregnated carbons to humidified (>90% RH) flowing air have an adverse influence on the subsequent methyl iodide-131 trapping (15). Although the gain in weight of the carbons leveled off in about 24 hours, the penetration of methyl iodide after further contact with humidified air continued to increase. The quantity of adsorbed water appeared not to be the controlling factor and it does not appear to be a question of filling the porous structure or a blocking of water adsorption sites.

When the above water-vapor degradation is combined with the irradiation improvement, variable degrees of balance can be expected between the two opposing tendencies. The penetrations (Table 2.11) are plotted in Figure 2.14 as a function of the irradiation time and in Figure 2.15 as a function of the integrated dose. Humidified air was the carrier gas in all tests except A and F in which dry air was used. The sharp drop in penetration during irradiation may be interpreted as improvement exceeding degradation. As the irradiation continued, the penetration gradually increased as the degradation begins to exceed the improvement. Variation in the relative humidity due to insufficient control may have been a factor.

A significant behavior is shown in Figure 2.16 in which the effluent methyl iodide during the purge period is shown to be suppressed to almost zero. At this stage of the test, there are a sufficient number of adsorption sites that retained the methyl iodide-127 normally desorbed when no radiation field is present.

An activated carbon having both KI and TEDA impregnation has at least three independent mechanisms for trapping radioactive iodine:

1) adsorption to the carbon network of the carbon,
2) isotope exchange,
3) chemical combination with the tertiary amine.

For new carbons all three mechanisms are at peak performance and it is not possible to distinguish readily among them. However, as the carbon is weathered, each mechanism is subject to its characteristic degradation process or processes. The present results suggest that any impregnation or operation procedure that would maintain the iodine isotope exchange capacity is greatly to be desired, since the bottom line in the nuclear application is the retention of radioactive iodine by the carbon bed.

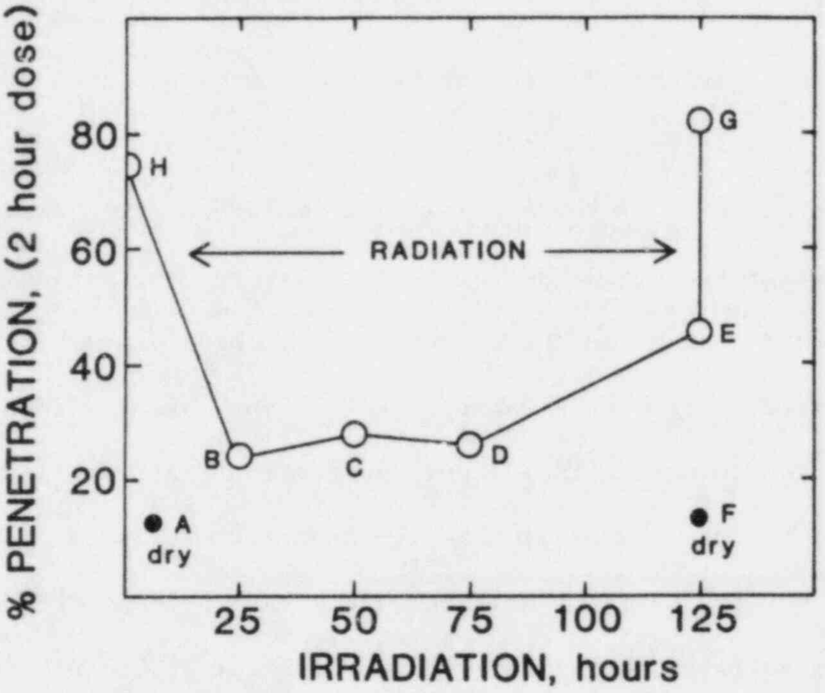

Figure 2.14 The Penetration of Methyl Iodide-127 as a Function of ^{60}Co-radiation (● = dry air, ○ = humidified air) NRL-5234 (Run 3419)

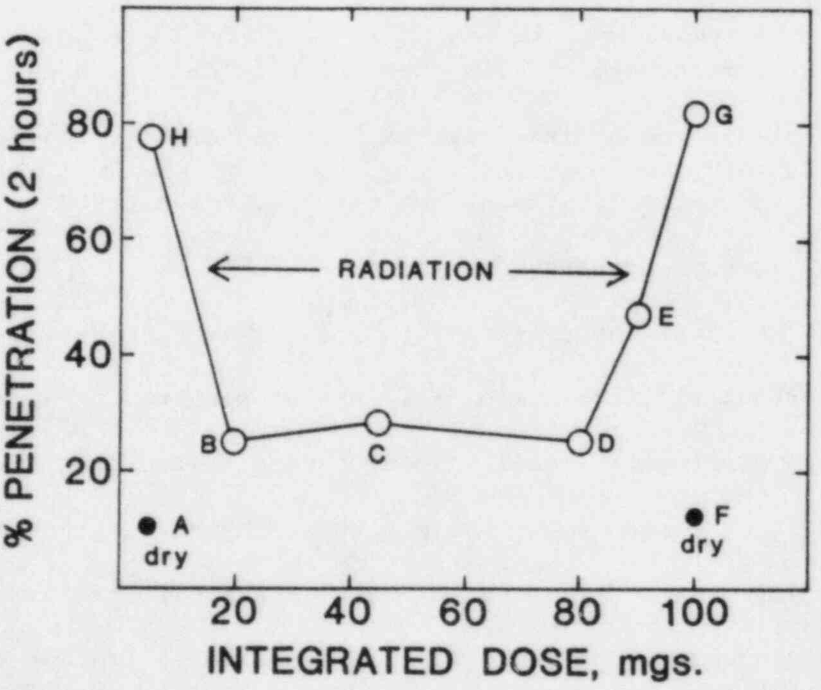

Figure 2.15 The Penetration of Methyl Iodide-127 as a Function of the Integrated Dose (● = dry air, ○ = humidified air) Series I

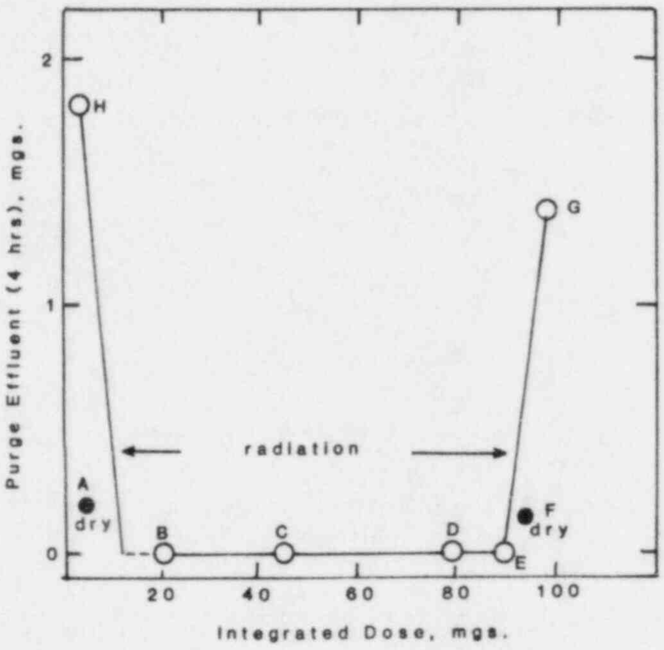

Figure 2.16 Suppression of Methyl Iodide Effluent during Purge (4 hours). NRL 5234 (● = dry air, ○ = wet air)

Radiolysis in Presence of Ar and Kr

The exposure of service carbons to γ-radiation from a Co-60 source (1.17 and 1.33 MeV) has been shown to increase the efficiency for trapping methyl iodide-131. Since krypton and xenon may be present in postulated accidents, radiation studies in presence of these gases are relevant. Although a radiolysis enhancement in some chemical reactions has been reported,it has to be shown if the same is true for adsorbed contaminants on nuclear-grade carbons.

Progress has been made in exposure of one service carbon (NRL 5143) to γ-radiation in rare gas environments. A slow flow of the gas through the carbon was maintained during the entire time required to accumulate 10^8 rads. The results to date, summarized in Table 2.15, show that the presence of either argon and krypton has little influence on the penetration of methyl iodide-131.

Table 2.15 γ-radiation (Cobalt-60 source) Influence on NRL 5143 Carbon in Rare Gas Environment (%P = Percent Penetration of Methyl Iodide-131)

	AIR	ARGON	KRYPTON
Initial %P	31.0	31.0	31.0
Radiation, hrs	141	175	190
Total Rads, $\times 10^8$	0.94	1.0	1.1
Final %P	6.3	27.1	34.
NRL Test	5249	5296	5298
Absorption coef. 10^{-24} cm^2/atom	1.5	3.77	7.7

One explanation of the absence of any effect in the presence of argon and krypton might be in the increased gamma-ray total absorption coefficient for the energy of the source. The absorption coefficients for the elements increase uniformly and because of the increased absorption, less γ-radiation might reach the carbon. However, the density of the gas is far less than that of the carbons and, hence, more than 99% of the γ-ray absorption must be attributed to the carbon and less than 1% to the rare gas. A different species may account for the radiolysis results. Hydrogen atoms produced in the primary reaction between the radiation and the contaminant, including the water content, may be the effective species, but the continuous flow of the rare gas may have removed the source of the hydrogen atoms required for the beneficial radiolysis reactions.

2.6 Concluding Remarks

1. The exposure of service activated carbons to radiation levels of 10^7 to 10^9 rads regenerates the iodine isotope exchange capacity of the carbons as measured by the removal of methyl iodide-131.

2. The radiation influence on new carbons was not significant and the penetration remained below the permissible level (ASTM Standard D 4069-81).

3. Iodine-126 was formed from KI-127 impregnated carbon when subjected to LINAC radiation in direct proportion to the dose level.

4. There is a great disparity for used and in-service activated carbons between the trapping of the radioactive species and the removal of methyl iodide-127. The efficiency for iodine exchange was vastly improved by the irradiation and that for adsorption only slightly influenced or not at all.

5. An activated carbon having both KI and TEDA impregnation has a minimum of three independent mechanisms for trapping methyl iodide-131: (1) adsorption to the carbon network, (2) isotope exchange, (3) chemical combination with the tertiary amine. Isotope exchange appears to be the outstanding factor for improvement and maintenance of iodine trapping.

6. The increasing relative humidity of the carrier air and duration of the exposure high humidity are degrading factors in methyl iodide-13 trapping efficiency.

7. Prehumidification of test samples at 30°C always resulted in an increase in the penetration of methyl iodide-131.

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3.0 The Regeneration Process

3.1 Introduction

Rather than "radiation damage", it has been demonstrated that there can be "radiation improvement" (insofar as the trapping of methyl iodide-131 is concerned) when used nuclear-grade activated carbons are exposed to radiation fields of 10^7 to 10^9 rads. The original carbons contained either KI_x impregnation or KI + TEDA impregnation. It is well known (11) that chemical changes take place in organic polymers upon irradiation and the improved strength and stability is based on the formation of highly crosslinked networks. These covalent chemical bonds are formed at room temperature. However, the modifications to be reported for service activated carbons are based on different and more subtle chemical changes in the adsorbed contaminants with either no or little apparent change in structure or stability of the activated carbon support.

For most high-energy radiation sources of practical interest, the energy transferred to the medium is through the release of fast electrons. The interactions of these high-energy electrons with the atoms and molecules of the medium provide the mode of excitation; a complicated series of reactions result. The radiation-induced scission of a primary chemical bond is called radiolysis.

The chemical changes during the irradiation of nuclear-grade carbons from service also include significant changes in the component structures of the impregnation chemicals as well as the contaminants adsorbed on the activated carbons. There are examples where chemical reactions, not normally expected, may take place in a reactor system in the presence of a radiation flux (1). The magnitude of the energy that could be transferred far exceeds the chemical bonding energies and could lead to complex degradation reactions. A detailed literature survey has not revealed references to products formed when service activated carbons are irradiated (see Table 2.2).

The radiolysis products from the exposure of known organic chemical species (organic compounds, polymers) have been widely studied. These will be reviewed for clues that might be relevant to service grade carbons after these are exposed to high radiation levels (up to 10^9 rads). The exposures have been made in the gas phase or in liquid and solid states. The latter appear to be more relevant to the present work due to the lower mobility of some of the products formed when adsorbed on nuclear-grade carbons.

It has been reported that the most immediate processes (ionization, excitation, and electron capture) are not influenced to any significant extent by the viscosity of the medium. Also, the processes that follow excitation and ionization, namely molecular dissociation and reaction without mass transport, are not greatly influenced by the rigidity of the medium or molecular size. Similar radiological reaction products are formed either in polymers or in low molecular weight analogs. For example, the analysis of the gases liberated on pile irradiation of polyethylene and in alpha particle irradiation of hexadecane are strikingly similar (11). In the limiting case of very slow diffusion, the steady state description for liquids cannot be applied to solids and similarly to strongly adsorbed contaminants on activated carbons.

3.2 Review of Radiolysis of Known Compounds

The available knowledge in radiation chemistry does permit some generalization as to the sites of principal radiolytic atack on carbon species (3). The radiolysis yield, G, is defined as

$$G = \frac{\text{number of molecules formed}}{\text{100 eV of energy absorbed}}$$

Although the results (Table 3.1) were obtained using specific organic compounds, the main radiolytic attack was at the specific functional group present in the molecule. It can be assumed that some of these functional groups are adsorbed in the boundary surface of a service carbon removed from a nuclear plant adsorber. The principal attack, aside from C-H cleavage, is at its point of attachment to the rest of the molecule. G_{-M} (Table 3.1) signifies the decrease in yield of group M.

Table 3.1 Chemical Bonds Broken in Radiolysis (3)

Compound type	Main Attack Site	Approx. G_{-M}
Hydrocarbons:		
Saturated	C-H, C-C bonds	6-9
Unsaturated	C-H, C-C bonds; polymerization or cross linking	11-10
Aromatic	C-H bonds; side chain C-C bonds	0.2-1
Alcohols	H-COH, C-COH bonds	3-6
Ethers	C-H, C-OR bonds	~7[a]
Aldehydes and ketones	C-H, C-$\overset{O}{\overset{\|}{C}}$ bonds	~7[a]
Esters	C-H, $\overset{O}{\overset{\|}{C}}$-OR bonds	~4[a]
Carboxylic acids	C-H, C-$\overset{O}{\overset{\|}{C}}$OH bonds	~5[a]
Halogen compounds:		
Fluorides	C-H, C-C bonds	~3
Others	C-H, C-X bonds	~3

(a) Tolbert, B.M. and Krinks, M.H., "Chemical Effects of Ionizing Radiation on Pure Organic Compounds," Radiation Research, Supp. 2, 586 (1960).

In the radiolysis of organic iodides, the bond between carbon and iodine is preferentially broken. A summary of the product yields from several alkyl iodides is given in Table 3.2. These results are pertinent since most nuclear-grade carbons are impregnated with KI or KI_x and it is probable that C-I bonds are formed with the carbon networks by the chemical reactions of weathering.

Table 3.2 Radiolytic Yields from Liquid Alkyl Iodides (4)

Compound	Methyl iodide		Ethyl iodide		n-Propyl iodide	Isopropyl iodide
Dose, 10^6 rads	0.1	16	0.1	16	0.2	0.2
Radiation	X	γ	X	γ	X	X
G_{I_2}	1.2	1.26	3.03	2.12	1.44	2.55
G_{HI}		0.01		0.33		
G_{H_2}	0.08	0.060	0.20	0.23	0.26	0.25
G_{CH_4}	0.57	0.77	0.007	0.01	0.015	0.015
$G_{C_2H_2}$	0.03		0.11	0.09	0.04	0.00
$G_{C_2H_4}$	0.08	0.081	2.00	2.20	0.13	0.004
$G_{C_2H_6}$	1.05	1.11	1.12	1.92	0.005	0.004
$G_{C_3H_6}$	0.001		0.00		1.27	2.25
$G_{C_3H_8}$	0.005		0.007	1.03	1.89	
G_{R_uH}*	0.57	1.12	1.03	1.89		
$G_{R\ H}$			2.00		1.27	2.25
G_{isomer}					0.28	0.06
G_{R_2}	1.05	1.11		0.33		

*R_u = Unsaturated Alkyl Iodide

It is to be noted that low radiation doses were employed for all studies in radiation chemistry and careful product analyses were made. At high radiation doses possible in a DBA, the radiolysis products are surely of greater complexity. Nevertheless, a trend in the products formed can be expected.

One result of the atmospheric degradation of a KI impregnated carbon is the loss of isotope exchange between I-127 and I-131. Oxidation reactants such as ozone can gradually convert the I^- present on the boundary surface of a carbon to a higher oxidation state such as IO_3^-. It was reported by Meyers and Kennedy in 1950 (5) that the iodine isotope exchange between NaI-131 and $NaIO_3$ at 50°C in nearly neutral solution was not measureable after 1600 hours (estimated exchange half-time $>5 \times 10^5$ hr.). One can infer that once the iodine on charcoal is oxidized, the product would be quite resistant to isotope exchange. More recently (1976), N. Ikeda (12) reported no indication of isotopic exchange between $^{131}I^-$ and IO_4^- or between $^{131}I_2$ and IO_4^- in weak solutions of nitric acid.

The radiolysis reactions of potassium iodate are quite complex and appear to be dependent on whether air is present or absent in the irradiated solutions. With unfiltered 250 KEV X-rays elemental iodine may form at low pH along with H_2O_2 (6), the latter complicating the iodine analysis. The products also depend on the magnitude of the radiation as shown by the formation of iodine-128 and iodine-130 by neutron capture in KIO_3 crystals (7), the radioactive iodine appearing as iodide, iodate and periodate ions on analysis of alkaline aqueous solutions of the irradiated solids. The relative concentrations of the radioiodine oxidation states varied with the time and temperature of the neutron irradiation.

As mentioned above the effects of radiation on polymers have been studied in considerable detail. The chemical reactions produced when polymers are subjected to high energy radiation are not basically different from those which occur when simple organic compounds are irradiated (2). To change a hydrocarbon molecule, for example, that contains 20 chemical bonds requires a change of at least one bond per molecule, or a 5% change. In a long chain polymer with perhaps 10^5 bonds, a change of only one bond may double or halve this structure; the chemical change is only 0.001%. However, this minute change can produce drastic modification in physical properties of the polymer.

Studies of radiation-induced chemical reaction in aqueous solutions have shown that dissolved oxygen has played an important role. In air-free solutions radiation causes a <u>chemical reduction</u> of solute (8). For example, in neutral and alkaline solutions of KIO_3 exposed to 0.16×10^6 rads (250 KEV x-rays), the iodate reduction was increased by 25 to 80% following the removal of air. The hydrogen atoms which are formed in the primary radiochemical process (9) are lost by recombination and partly by the solute molecules; the presence of O_2 further decreases the available H atoms for chemical reduction by HO_2 formation which can lead to H_2O_2, a product which has been widely reported.

3.3 Radiolysis of Potassium Iodate Impregnated on Activated Carbon and Equivalent Chemical Reactions

The above brief review shows the need to observe the radiolysis of a few relevant pure compounds adsorbed on activated carbons at radiation levels pertinent to the present study. The improvement in methyl iodide-131 trapping observed after exposure of service carbons to radiation levels of 10^7 to 10^9 rads must in some way be related to the reversal of chemical reactions initiated by the weathering or to additional reactions which compensate for the degradation reactions during weathering.

It was first considered instructive to compare the radiolysis of KIO_3 crystals and KIO_3 solutions, with that of KIO_3 adsorbed on activated carbon. This has been reported for crystals and solutions but not at comparable energy inputs. For example, crystalline KIO_3 subjected to neutron capture forms iodide, iodate and periodate ions in alkaline aqueous solutions of the irradiated solids. These are drastic changes relative to that which may happen in the radiation radiolysis at 10^9 rads. The changes observed in solutions of KIO_3 in high x-ray radiation may be more comparable to the possible radiolysis of KIO_3 adsorbed on carbons.

The atmospheric contaminants that chemically degrade nuclear-grade carbons include ozone, sulfur dioxide and the nitric oxides. Special attention has been directed to ozone. The reaction in a weak alkali solution is known to be as follows:

$$3O_3 + I^- \rightarrow 3O_2 + IO_3^-.$$

If the same reaction takes place on a KI-impregnated carbon, one would expect to find KIO_3 in a weathered carbon with an accompanying decrease in iodine exchanges. In order to test this model, a coconut shell carbon (GX-212) was impregnated with aqueous KIO_3 (2 wt%). The penetrations of air mixtures of methyl iodide-127 and of methyl iodide-131 with methyl iodide-127 were determined before and after irradiation to 10^8 rads on the NRL LINAC. The radiolysis reactions during the irradiation reduced the iodate and a significant decrease in methyl iodide-131 penetration was observed (Table 3.3). However. there was little change in the methyl iodide-127 penetration, determined under similar dynamic conditions (using an electron capture detector). The results (Figure 3.1) indicate little change in the adsorptive properties, for methyl iodide-127. This is in strong contrast to the improvement observed in the iodine isotope exchange behavior (Table 3.3).

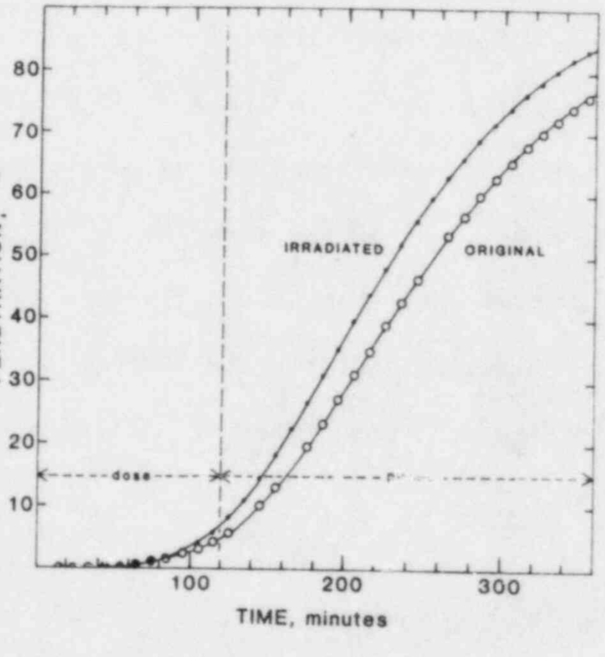

Figure 3.1 Penetration of Methyl Iodide-127 through the Original Preparation of KIO_3 on Coconut Shell Charcoal (•) and that after LINAC Irradiation (○) (10^8 rads)

The results (Table 3.3) are consistent with the observations reported in Chapter 2. Since the original carbon was new, i.e., not weathered, the methyl iodide-131 penetration agreed with that for methyl iodide-127. After irradiation, there was a 100-fold decrease in methyl iodide-131 penetration, but that for methyl iodide-127 was about the same. It can be concluded that the KIO_3 of the impregnation is converted by radiolysis into a chemical species that exchanged more readily with the methyl iodine-131.

Table 3.3 Penetration of Methyl Iodide Through a New Coconut Carbon Impregnated (2 wt.%) with KIO_3 (Preparation 1)

Exposure	Test Gas	% Penetration
Original	MeI-131	6.0
LINAC at 10^8 rads	MeI-131	0.80
Original	MeI-127	5.0
LINAC at 10^8 rads	MeI-127	6.9

There are several organic compounds available that chemically reduce KIO_3 in solution (in vitro) and one of these, hydrazine, is reported to react as follows (10):

$$2\ KIO_3 + 3N_2H_4 \rightarrow 3N_2 + 2KI + 6H_2O$$

In order to detect the chemical reduction by hydrazine, a second quantity of impregnated activated carbon (2.1% KIO_3 dry basis, NACAR G-212) was prepared and the methyl iodide-131 penetration determined for three cases:

(1) original impregnation,

(2) after irradiation to 10^8 rads on the NRL LINAC, and

(3) after chemical treatment with a dilute hydrazine solution.

The aqueous solution of hydrazine was sprayed into a rotating cylinder containing the carbon and the product air dried in a glass tray. The results (Table 3.4) indicate a close correlation in the results of the chemical reactions in the radiolysis during the LINAC exposure and the chemical reduction to form KI by hydrazine of the KIO_3 impregnated on the activated carbon.

Table 3.4 Comparison of Radiolysis and Chemical Treatments of KIO_3 (2 wt. %) Impregnated Carbon (Preparation 2)

Exposure	Test Gas	% Penetration
Original KIO_3 Impregnation	MeI-131	4.4
LINAC at 10^8 Rads	MeI-131	0.13
Chemical Treatment	MeI-131	0.3

The depth profiles of methyl iodide-131 retained in the test beds of carbon after hydrazine treatment were exponential. The gradients are given in Figure 3.2 as counts per 10 minutes for each of the test beds before and after the chemical treatment. The example is for the second preparation of KIO_3 impregnated carbon (NRL Sample 5297). Previous work with new activated carbons has shown that this behavior is indicative of the uniformity of the impregnated material as introduced into the test column

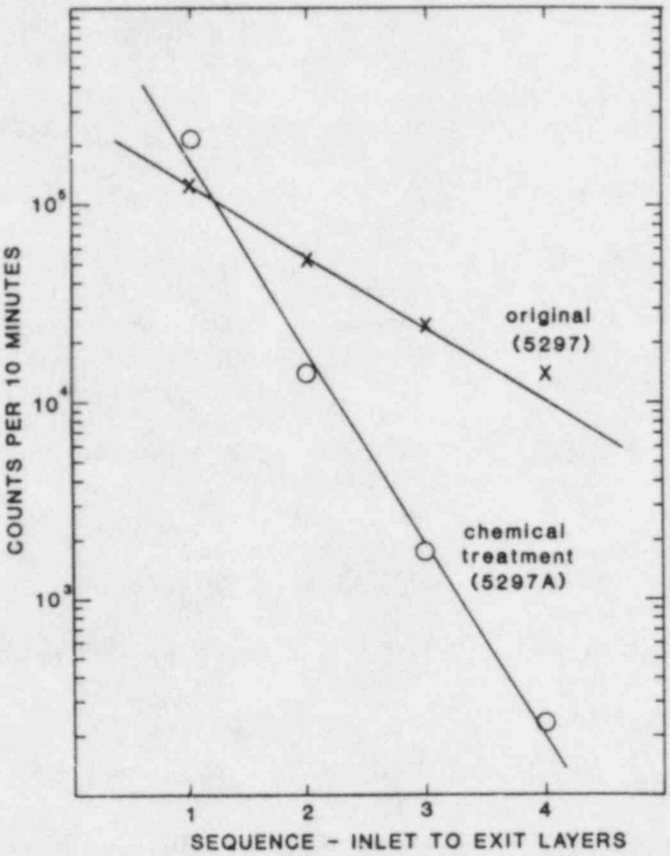

Figure 3.2 Gradient of Methyl Iodide-131 Retained in the Test Bed before and after Chemical Treatment. (NRL 5297) (2nd preparation of KIO_3 Impregnated Carbon)

The oxidized species derived from impregnated potassium iodide on charcoal does not necessarily have to be an iodate ion (IO_3^-). The known oxyacids of iodine are listed by Downs and Adams (26) as follows:

HOI	Short life in aqueous solution
HIO_2	Perhaps identified in solution
HIO_3	Vapor phase, solid phase, aqueous solution
HIO_4	Vapor phase, solid phase
$H_7I_3O_{14}$	Solid phase
H_3IO_6	Solid phase, aqueous solution

As indicated above reasonably stable crystalline salts have been isolated, except for iodites and hyperiodites. The existence of HIO_2 and IO_2^- as more than transient species in solution is doubtful. Because of the interest shown in the assumed existence of the HOI molecule, it is noted that the equilibrium constants for the disproportionation of the hypohalites (OX^-) in alkaline solution have been determined (where X = halogen):

$$3\ OX^- \rightleftarrows XO_3^- + 2X^-$$

OCl^- persists for days in solution, OBr^- decomposes in hours, and OI^- disappears almost instantaneously. The stability of HOI adsorbed on charcoal, however, is not known.

The HOI molecule does exist under special experimental conditions. Walker, Tevault and Smardzewski (27) reacted oxygen atoms and ozone with hydrogen iodide in dilute argon matrices at 8°K and used the infrared absorption peaks at 3597, 1103 and 575 cm^{-1} to identify HOI. The oxygen-18 and deuterium isotopic frequencies and associated band assignments were also observed and these isolated H-O and O-I stretching modes which established the HOI structual arrangement.

In order to demonstrate the oxidation and the reduction of I^-, a stream of ozone in oxygen was directed through a new KI-impregnated activated carbon (MSA 463563) for 10 hours. No odor of ozone was detected at any time in the effluent. Aliquots of the ozone-treated carbon were then treated with hydrazine in one case and methyl hydrazine in the second. The results (Table 3.5) indicate improvement despite the limited ozone treatment of the new carbon. In other examples (28), extended ozone pretreatments were made in presence of water vapor and these lead to degradation levels for similar new carbons of 10-20% penetration of methyl iodide-131.

Table 3.5 Chemical Treatments of Ozone-Treated Carbons having KI Impregnation.

Pretreatment	Methyl Iodide-131 % Penetration
None	0.05
Ozone	1.0
Ozone, hydrazine	0.52

It may be concluded that the above behavior demonstrates that the two independent processes - irradiation and chemical reduction - lead to the formation of iodide ion (I^-) and thus convert the original iodate, or other oxidized iodine species, into one that readily exchanges with I-131.

In general, chemical reactions in solution (in vitro) are subjected to different constraints than between the same reactants adsorbed on activated carbon (in carbono). The radiolysis of chemical species in vapor and liquids can differ from the same reactants adsorbed on activated carbon. Some basic reasons for this behavior are given below:

I. The activation energy may be different in each of the modes, i.e. bond-breaking in the gas phase may be less probable than in a liquid at the same concentration and temperature.

II. The entropy changes may be different in each mode because: (1) the adsorption of products in carbono; (2) the molecular orientation in the adsorbed phase relative to random orientations in solution.

III. The concentration gradients may influence the extent of attainment of steady states from a mass action point of view.

IV. The molecular complexes in solutions may not be present in gas or vapor mixtures.

V. Dimensional changes in the adsorbed mode on activated carbon are different than volume changes in vitro.

Lieser (29) showed that heterogeneous iodine exchange reactions can involve both the surface and the interior of the crystal. The iodine-131 exchange between sodium iodide crystals and gaseous methyl iodide was studied between 160 and 255°C and this involved deeper layers of the crystal with increase of temperature. The iodine exchange mechanism will be discussed in Section 4.1. However, a regeneration conducted at room temperature will most probably be limited to surface reactions.

3.4 Chemical Treatment of Nuclear-Grade Carbons Removed from Service

The service carbons removed from commercial adsorbers have been exposed to a large variety of contaminants, some of which are oxidants like ozone, and the presence of these and other contaminants could slow the rates of chemical reduction with hydrazine. As an example a sample of service carbon that had been removed from service (NRL 5291) was treated with different amounts of hydrazine. The initial material had a penetration of methyl iodide-131 of 38.5% when not prehumidified and 42.2% when prehumidified (16 hours at 95% RH). The carbon was rotated slowly in a horizontal cylinder with lifting vanes while a small volume of solution containing the hydrazine was gradually sprayed into the cylinder. The activated carbon retained a free-flowing appearance after the addition.

Each sample was then tested for methyl iodide-131 penetration and the results (Figure 3.3) showed an improvement in direct proportion to the amount of hydrazine introduced. The reproducibility is shown by the two points at "C" in Figure 3.3, namely 8.0 and 7.8% respectively. The carbon before removal had been in service for about four years and, as mentined above, the penetration of methyl iodide-131 was considerable. Had the carbon been treated periodically, for example, after about 6 months service, the recovery might have been more complete.

A second carbon sample removed from service in another reactor site (NRL 5143) improved from 31.0% to 3.0% after hydrazine treatment. The same sample was also treated in a different experimental arrangement and the penetration

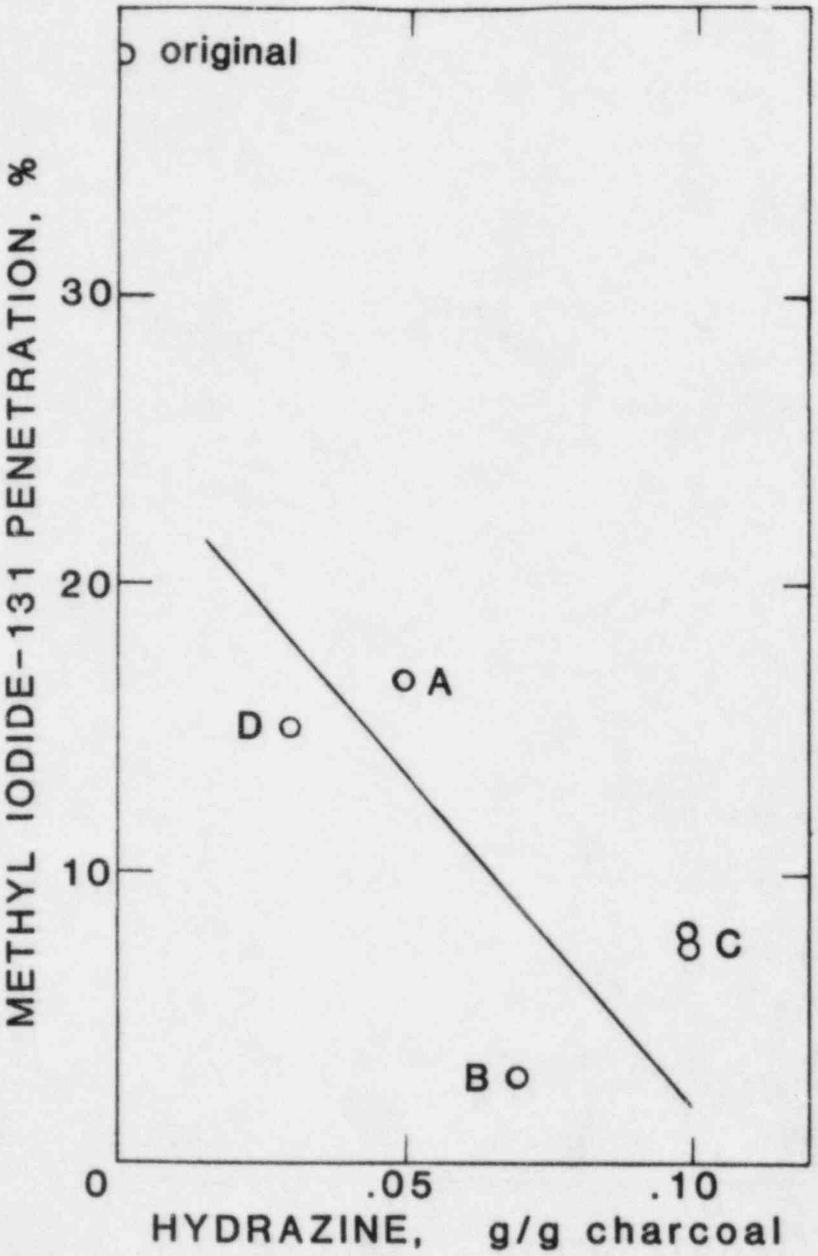

Figure 3.3 Improvement in Methyl Iodide-131 Penetration after Hydrazine Treatment

of methyl iodide-131 improved from 31.0% to 2.2%. The test bed had been prepared in four equal layers and each was counted before and after the test. The depth profiles (Figure 3.4) of the methyl iodide-131 retained in the test samples after the treatments were not quite as linear as they were for uniform sample packing and it is not clear at this point in time the reason for the behavior (see Chapter 4).

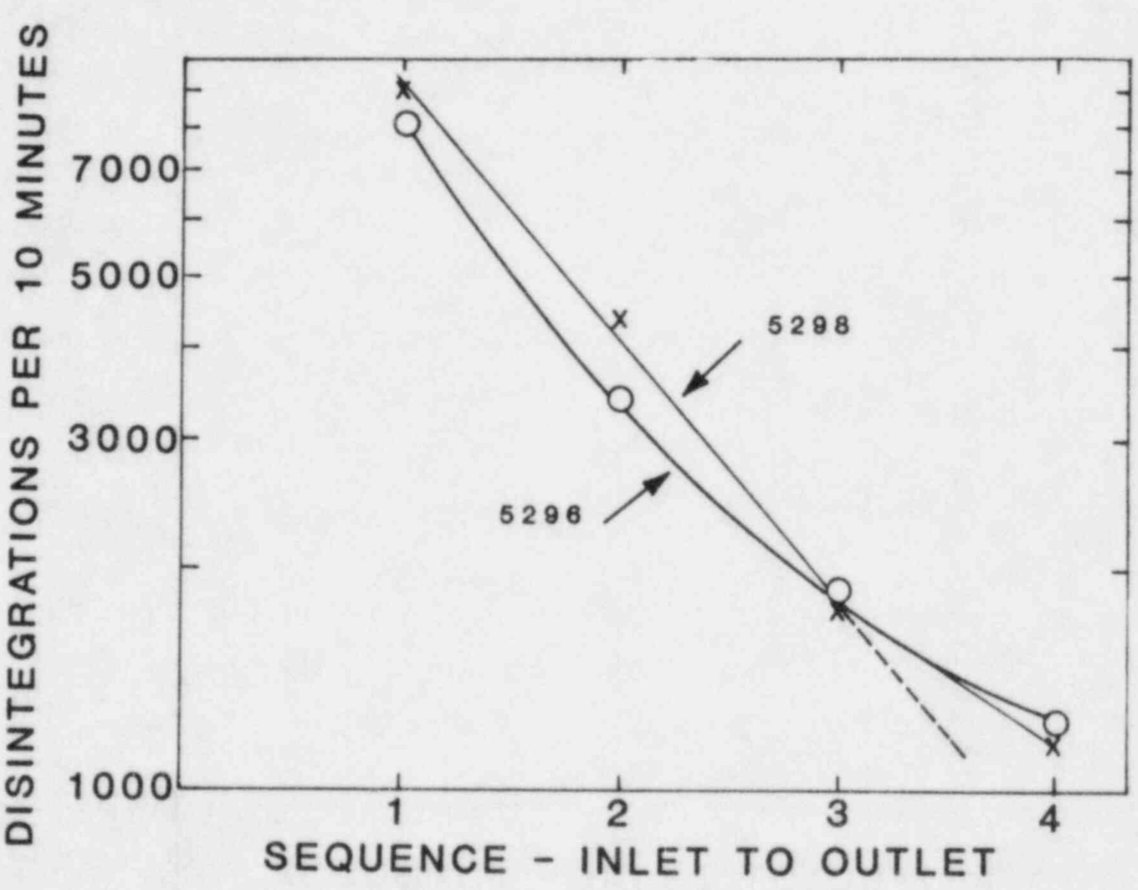

Figure 3.4 Depth Profile after Chemical Treatment

Three additional samples of GX-176 (30) removed from service (Savannah River Laboratory) were treated with hydrazine and the results (Table 3.6) are compared with the starting material and with LINAC irradiation samples.

Table 3.6 Methyl Iodide-131 Penetration with GX-176 Samples Removed from Service (Savannah River Laboratory)

	Penetration, %		
	Original	10^8 Rads	Hydrazine
C-3 compartment, 30 months	69	41	7.4
K-2 compartment, 18 months	41	0.16	1.9
P-2 compartment, 14 months	28	0.21	9.0

3.5 Chemistry of Some Airborne Reducing Agents

Some important requirements of airborne reducing agents for the regeneration of the iodine-isotope exchange capacity of nuclear-grade carbons include the following:

(1) Wetting of the carbon surface

(2) Chemical reducing powers

(3) Mobility on the carbon surface

(4) Rapid desorption of products

(5) Reaction at ambient temperatures

A reducing agent to be used in this application is not intended in itself to remove radioiodine that might be released from nuclear reactors. Such a scheme was proposed in 1966 (13,14) and entailed the formation of a stable aerosol by the gas phase reaction of hydrazine (or its unsymmetrical dimethyl derivative) with released radioiodine, followed by the filtration of the aerosol. The present objective is to reform the isotope-exchange properties of the surface sites of the impregnated activated carbon. The carbon will then continue to function in isotope exchange after the reducing agent has been depleted.

The heterogeneous decomposition of hydrazine has been studied when contacted with many metals as powders, carrier supported, wire filament, or deposited thin films (15). A practical catalyst (Shell 405), iridium on alumina, has been widely studied in space engine technology. The hydrazine decomposition on platinized carbon electrodes in alkaline solutions (16) appears to proceed by progressive dehydrogenation of N_2H_4 without rupture of the N-N bond. Activated carbons have been used as a support for Ir, Rh, Ru, Pt and Pd, and the first spontaneous hydrazine decomposition catalyst (Shell Development Co.) was a Ru-Ir (2.1-28% metal) on activated carbon (17). Of particular interest is the fact that this catalyst was very active, but it was later found that carbon carriers became hydrogenated to methane during prolonged use in space power-engine operation. It has also been demonstrated that oxidants such as I_2O_5 can be used to initiate single-start catalysts for the decomposition of monomethyl hydrazine as well as hydrazine (18). This fact is pertinent to the use of hydrazine to reduce the oxidized forms of iodine that develop in weathered KI impregnated activated carbons.

The removal of oxygen from boiler-feed water with hydrazine is widely used. Filtration on activated carbon in the presence of N_2H_4 in the condensate reduced the oxygen content to 13 to 5% of the original concentration (19). The kinetics of hydrazine elimination from steam and condensate using activated carbon showed that the rate of the reaction was controlled by the temperature, initial concentration of hydrazine, and the type of activated carbon (20). The oxygen content of the medium had little influence on the rate of hydrazine elimination. It is noted that boiler water treatment with hydrazine is widely used in the steam generation of nuclear power plants

There are many catalytic processes in the chemical industry in which the catalyst supported on activated carbon uses hydrazine for hydrogenation (21). For example, 1% Pt on activated carbon (aq. suspension) formed 99.6% 2-$ClC_6H_4NH_2$ from $2ClC_6H_4NO_2$ (157 min at 90° and 10 atm.). In the partitioning of high-level liquid wastes, hydrazine with active charcoal as a catalyst increased the rate of reduction of Pu(IV) and Fe(III) in HNO_3 solutions, indicating its potential use in fuel reprocessing for decreasing the amount of waste (22). Chromates have been effectively removed from aqueous $K_2Cr_2O_7$ using $N_2H_4 \cdot H_2O$ and activated carbon wherein the reduced Cr(III) was readily precipitated as $Cr(OH)_3$ at pH 5.5-7 (23). The activated carbon promoted the rate of reduction and aided in coagulation of the precipitate.

In addition to the degradation of iodine-isotope exchange by exposures to ozone, contact with sulfur dioxide has been shown to be detrimental to the trapping process (see Chapter I). It is known that sulfur dioxide is partially reduced by hydrazine and the sulphites yield thiosulfate (24):

$$2\ NaHSO_3 + N_2H_4 \longrightarrow Na_2\ S_2O_3 + 2\ NH_3 + H_2O$$

Also, SO_3 can be reduced to thiosulfate by action of hydrazine. Corresponding chemical changes are known for exposures to high level radiation, but little is known concerning the complex radiolysis reactions of sulfur and nitrogen compounds. There have been studies in which the radiolysis of normal heptane is inhibited by dibenzyl sulfide (25), but what happens to the latter is not known.

In general, chemical reactions in solution (in vitro) are subjected to different constraints than between the same reactant on activated carbon (in carbono). This applies to the reaction of hydrazine with known compounds compared to the same reaction on activated carbon. The two categories may approach each other with increasing amounts of water on the carbon which occurs at high relative humidities.

3.6 Concluding Remarks

1. Chemical changes during radiation are responsible for the regeneration of used nuclear-grade activated carbons by a series of complex radiolysis reactions.

2. Chemical reducing agents such as hydrazine can react with used nuclear-grade carbons to regenerate the iodine isotope exchange property. No change was observed in the adsorptive property of the carbon.

3. Hydrazine reacts with a KIO_3-impregnated carbon and improves the iodine-isotope exchange efficiency.

4. Either radiation or chemical reduction leads to the formation of iodide ion (I^-) which can readily exchanges with methyl iodide-131.

3.7 References

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4.0 Test Considerations

4.1 The Iodine Isotope Exchange

An isotope exchange is a chemical reaction in which the atoms of a given element interchange between two or more chemical forms of the element (1). The example in this study is the interchange of iodine atoms between methyl iodide and the iodide ion in a KI impregnation of activated carbon. A continuous exchange of iodine atoms is presumed to occur in a homogeneous mixture, but it is not observed unless one of the reactants is altered by including the radioactive isotope which then appears in the second reactant, thus permitting the progress of the exchange to be followed.

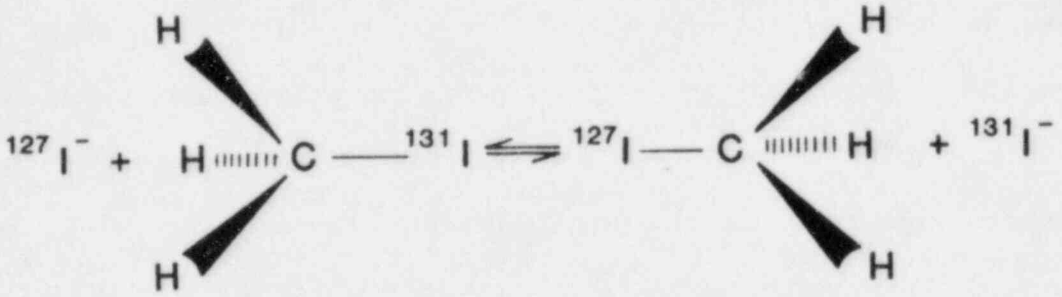
The thermodynamic justification for the exchange reaction is based on the following considerations. The enthalpy (ΔH) for the exchange process is zero. However, there is an increase in entropy of the system as the exchange proceeds towards a steady state where all the isotopes are randomly distributed. Due to the entropy of mixing, the free energy (ΔF) of the system decreases by the amount calculated for equilibrium conditions from the entropy change, viz.

$$\Delta F = - T\Delta S$$

The usual exchange mechanism is one in which the slow step is the decomposition of a transition state. The two species must interact to form a transition state which can then decompose either to the initial state or to the exchanged state. An illustration is the reaction of molecular iodine with an iodide ion, the tri-iodide being the transition state:

$$({}^{127}I - {}^{131}I) + {}^{127}I^{-} \rightleftharpoons ({}^{127}I - {}^{127}I - {}^{131}I)^{-} \rightleftharpoons {}^{131}I^{-} + ({}^{127}I - {}^{127}I)$$

The kinetic data for isotope exchange in a tetrahedral carbon-iodine compound, such as methyl iodide, have been explained by the Walden inversion mechanism. The greatest probability for substitution occurs when the entering group



approaches the carbon atom along the bond line joining the carbon atom to the group to be replaced. Hence, the new group is in a position that is the mirror image of the displaced position. The rate of substitution will, in general, depend strongly on steric factors.

The above considerations have been applied in the past to various homogeneous systems. For heterogeneous-exchange reactions the rate is frequently determined not only by the exchange rate between the reactants but also by the rates at which the exchange products become dispersed in the two phases. In the case of methyl iodide-131 approaching the surface of a $K^{127}I$-impregnated activated carbon, it is not likely that a uniform iodine isotope distribution is present over the carbon phase. The mixing of methyl iodide-131 and the carrier methyl iodide-127 is very rapid in the gas phase relative to the actual exchange process; the latter on the other hand, is rapid relative to the diffusion across the interface into the porous structure of the carbon containing the impregnated KI.

Experimentally, gas-solid exchange reactions are simpler to study than homogeneous-exchange reactions because the two reactants are in different phases and separation has already taken place. In solution-solid systems,

I. Kolthoff et al (2) found that the lack of equilibrium between the interior of a solid and the solution (aging of precipitates) had a strong influence on the fraction isotope exchange. A similar complicating factor may exist for the KI-impregnated carbons when in contact with an air flow of variable high moisture content (~95% RH). The exchange sites on the KI crystals may suffer changes in the crystal surface area in the presence of multiple layer coverages of adsorbed moisture. Cycles of hydration and dehydration could thus modify the isotope-exchange properties of the available iodide ion.

An important concern in iodine exchange is the chemical behavior of iodine at very low concentrations. As pointed out by Kahn and Wahl (4) in 1953, trace impurities can oxidize the iodine into species that do not exchange under conditions of the measurements. The stable isotope added as a carrier is at macro concentrations which are not noticeably modified by the oxidant impurities. It is estimated that in the iodine penetration test of ASTM D3803 the ratio of the concentration of $^{131}ICH_3$ to the carrier $^{127}ICH_3$ is 10^{-9} and, therefore, the problem observed in solutions by Kahn and Wahl is pertinent to the chemistry of the test standard.

Using three iodine species ^{125}I, ^{127}I and ^{131}I, experiments at NRL to be described have demonstrated considerable scrambling among all iodine isotopes during a radioiodine test for the trapping efficiency of an activated carbon. As discussed above, the reactants in the isotope exchange reactions first form a transition state which then decomposes into products that depend on the initial concentration of each available isotope at the surface site. The exchange does not necessarily depend on the total amount of iodine in the impregnation on the carbon, only that available on the surface. Lieser (3) investigated the iodine isotope exchange between crystals of NaI and gaseous methyl-iodide and showed that increasing the temperature led to a participation of more and more surface layers in the rapid surface exchange. The activation energy for the exchange with the deeper lying layers rose continuously. At present, the configuration of the NaI or KI impregnation in the surface of an activated carbon is not known, i.e. the crystal size on the surface is unknown.

The following penetration tests using ^{125}I, ^{127}I and ^{131}I made use of the ASTM D-3803 test parameters and the results are described below.

4.1.1 Iodine Test 619 (BC 727)

The test gas was the usual mixture of CH_3I-131 and CH_3I-127 introduced at 30°C into the air flow of 12.2 m/min and 95% RH. The sample (39.5g) was BC 727, a widely used KI_x-127 impregnated coconut shell charcoal. It was additionally impregnated with KI-125 in an aqueous solution (4 ml). This was introduced as a fine spray on the charcoal using a DeVilbiss atomizer and the sample was then mixed thoroughly. After the penetration test, the sample bed and the two back-up beds (containing new NACAR G-618) were counted for I-131 and I-125 in similar geometry. The following ratios were calculated:

$$p\ (125) = \frac{^{125}\text{I of both backup beds - background}}{^{125}\text{I of sample + backup beds - background}}$$

$$p\ (131) = \frac{^{131}\text{I of both backup beds - background}}{^{131}\text{I of sample + backup beds - background}}$$

The I-125 background was 2.6 cpm in a 500-minute count and the I-131 background was 23 cpm in a 100-minute count. The results are summarized in Table 4.1.

Table 4.1 Summary of Test 619 (BC 727) with Iodine-125, 127 and 131

	Isotope	cpm			Penetration %
		Sample	Backup #1	Backup #2	
1. Addition of NaI	^{125}I	*1.33(5)	-	-	-
2. Prehumid. 16-hr	^{125}I	-	25.9	3.6	0.02
3. Addnl. 2 hr.	^{125}I	-	3.7	2.1	0.004
4. Feed 2 hr.	^{125}I	-	3.72(3)	1.86(1)	2.7
of CH_3I-131 in					
CH_3I-127	^{131}I	-	8.63(2)	2.12(1)	6.1
5. Purge 2 hr.	^{125}I	1.38(5)	7.02(2)	3.4	0.51
	^{131}I	1.36(4)	1.80(1)	1.7(1)	0.26
Total Penetration of ^{125}I					3.23
Total Penetration of ^{131}I					6.4

* 1.33 (5) = 1.33 x 10^5

The penetration of ^{125}I from the NaI-125 addition to the charcoal was barely detectable during the 18 hours of pre-humidification with 95% RH air. Both ^{125}I and ^{131}I isotopes were present after the 2 hour feed with CH_3I-131 and CH_3I-127. There was also a significant penetration of both isotopes after the 2 hour air purge. In this experiment three of the four initial exchange reactions were demonstrated:

NaI-125 (S) + MeI-131 (g)

NaI-125 (S) + MeI-127 (g)

NaI-127 (S) + MeI-131 (g)

NaI-127 (S) + MeI-127 (g)

The radioactive counting is, of course, blind to the process dealing with exchange among the ^{127}I sites. Some models of the exchange process, as shown previously, assume that this does take place despite the lack of a thermodynamic justification of the system based on the entropy of mixing.

The magnitude of the total ^{131}I penetration is twice that of ^{125}I. Since the iodine transfer in both cases was via the gas phase, the surface mobility of CH_3I-131 may be a factor in the overall mechanism.

4.1.2 Iodine Tests with NRL 5175 (BC 727)

In a second experiment the feed flow consisted of cold methyl iodide, i.e. CH_3I-127 in 95% RH air flow. The radio-activity was first introduced into the carbon sample in one case as NaI-131 and in the second case as methyl iodide-131. The first sample was impregnated with NaI-131 solution as a fine spray, mixed thoroughly and the resultant activity was 0.868 μCi. The second sample was treated with methyl iodide-131 in methyliodide-127, mixed thoroughly, and gave a resultant activity of 5.57 μCi. The sample and back-up beds were counted after the prehumidification of 16 hours, the feed flow of 2 hours, and the air purge of 4 hours. In laboratory 1, the background was 18.1 cpm and in laboratory 2 the background was 13 cpm. The results are summarized in Table 4.2.

Table 4.2 Summary of NRL 5175 by Two Laboratories with I-127 and I-131

	Sample	Backup #1	Backup #2	Penetration %
	Laboratory 1 (µCi)			
1. Addition of NaI-131	*8.68(-1)			
2. Prehumidification, 16 hrs.	-	1.02(-2)	2.81(-5)	1.16
3. Feed, 2 hrs CH_3I-127	-	5.59(-3)	6.67(-4)	0.72
4. Purge, 4 hrs air	6.76(-1)	1.61(-3)	1.02(-4)	0.20
		Total Penetration		2.08
	Laboratory 2 (cpm)			
1. Addition of CH_3I-131	5.57 µCi	-	-	-
2. Prehumidification, 16 hrs.	6.32(5)	5.34(3)	4.4	0.84
3. Feed, 2 hrs	6.32(5)	1.70(3)	3.8	0.27
4. Purge, 4 hrs air	6.32(5)	5.12(2)	1.9	0.081
		Total Penetration		1.19

*8.68 ($^{-1}$) = 8.68 x 10^{-1}

The penetration of ^{131}I was detected during the prehumidification of the NaI-131 sample (1.16% penetration) and was also significant with the CH_3I-131 sample (0.84% penetration). During the 2-hour feed of cold methyl iodide, both laboratories reported the penetrations of 0.72% and 0.27%, respectively. The magnitude of the penetration using NaI-131 in the sample was about twice that reported for the CH_3I-131 sample.

4.1.3 Iodine Tests with NRL 5333

A third set of measurements were concerned with radio-activity introduced in one case directly into the carbon and in a second case into the sample via the gas phase. Both carbon samples were MSA 463563, a KI-127 impregnated coconut shell charcoal, and both sets of measurements were made identically. Sample 1 was impregnated with NaI-131 solution as a fine spray, mixed thoroughly and the resultant activity was 2.23 μCi. Sample 2 received a cold feed of two hours following the 16 hours prehumidification. This was followed by a customary feed of CH_3I-131 in CH_3I-127 for two hours, and finally by an air purge of four hours. The results are summarized in Table 4.3.

Table 4.3 Isotope Exchange with $^{127}ICH_3$ in Feed and either ^{131}INa or $^{131}ICH_3$ in the Impregnated Carbon (MSA 463563)

	Sample	Backup #1	Backup #2	Penetration %
		NaI-131 Added		
1. Addition of NaI-131	2.23μCi			
2. Prehumidification, 16 hrs	2.39(0)	2.90(-3)	5.81(-4)	0.14
3. Feed CH_3I-127,2 hrs	2.36(0)	4.51(-3)	5.03(-4)	0.21
4. Purge, Air, 4 hrs	2.47(0)	3.47(-3)	5.80(-4)	0.16
			Total	0.51
		CH_3I-131 Added in Feed		
1. Prehumidification, 16 hrs				
2. Feed CH_3I-127, 2 hrs				
3. Feed CH_3I-131, 2 hrs	1.01(-1)	3.12(-4)	8.40(-6)	0.32
4. Air Purge, 4 hrs	9.37(-2)	5.40(-2)	0	0.55
			Total	0.87

The penetration in the two cases after the feed periods were equal, 0.35 and 0.32, respectively. However, a significant difference was indicated after the air purge, the CH_3I-131 dosed sample having the larger penetration.

The penetration observed during the three stages of the test are summarized in Table 4.4. Altogether, there were three different samples as noted and two of these were in duplicate. In two cases, the maximum penetration occurred during the 16-hour prehumidification, in three cases during the 2-hour dose, and in one case during the 4-hour air purge. The mean and standard deviation for the penetrations through BC-727 was 3.23% and 2.27%, respectively. This includes the variations among sample aliquots, two radio-isotope additions, and two different laboratories.

Table 4.4 Penetration (%) at Specified Iodine Radioisotope Addition

Sample	Isotope Addition	Lab	Penetration (%)			
			Prehumid.	Dose	Purge	Total
BC727	NaI-125	1	.024	2.7	0.51	3.23
	CH_3I-131	1	-	6.1	0.26	6.4
BC727	NaI-131	1	1.16	0.72	0.20	2.1
BC727	CH_3I-131	2	0.84	0.27	0.08	1.2
MSA	NaI-131	1	0.14	0.21	0.16	0.51
MSA	CH_3I-131	1	-	0.32	0.55	0.87

It may be concluded from the above three sets of independent experiments that there is considerable scrambling among all iodine isotopes during the radioiodine test procedure. The possibility exists that a reaction product of the exchange, trapped on the charcoal in the early stage of the dose, may then be gasified at a later stage of the dose period. If this happens, the details of the test procedure as they are conducted in different laboratories, become very important. It is to be noted that all samples were new materials, i.e. not weathered to any extent.

4.2 Radioiodine Testing of Nuclear-Grade Activated Carbons

The need for standards in radioiodine testing was apparent following the pioneering work at the Oak Ridge Laboratory (1960-1970) on the trapping of radioactive iodine by KI and KI_3 impregnated charcoals. In particular, there was a need to evaluate the competing commercial activated carbons offered as new materials for the iodine application.

The present test evolved from work centered in the RDT Standard office at Oak Ridge and four editions of this test were issued during the interval 1970-1977. The development of the standard was supervised by C.L. Burchsted of the Oak Ridge Standards Laboratory who was aided by a Technical Review Committee of 12 persons: W.L. Anderson, H. Barnebey, B. Bird, H. Cotabish, J.F. Fish, H. Gilbert, R.T. Goulet, J.L. Kovach, R.I. Marble, J. Mecca, R.D. Rivers and F.R. Schwartz.

The earliest version of the RDT M16-1 test was published in June 1970 under the title, "Activated Carbon, Impregnated for Gas Adsorption" and apparently it was to serve as both a test procedure standard and a material standard (1,2). It was associated from the beginning with pertinent standards of the D-28 Subcommittee on Activated Carbon of ASTM and included definitions and test standards for apparent density, particle size distribution, moisture and ignition. In addition, the Supplement No. 1 to US AEC Report TID-7015 and Military Specification MIL-C-17605B were considered. The following four laboratory procedures designated as "Iodine-attenuation Tests" were to serve for the Type-Qualification of activated carbons:

(A) Elemental iodine in air (25°C and 90% RH) containing radioactively-tagged iodine (1 mg per M^3) with 2 hours dose and 2 hours air purge (triplicate parallel tests).

(B) Elemental iodine in air (80°C and 50% RH) containing tagged I_2 (85 mg per M^3) with iodine injection for 10 minutes and saturated steam-air at 80°C for 10 minutes (triplicate parallel tests).

(C) Methyl iodide in air (25°C and 90% RH) containing tagged methyl iodide (17 to 18 mg per M^3 air) with 2 hours dose and 2 hours air purge (triplicate parallel tests).

(D) A desorption test in which air (25°C and 50% RH) containing tagged iodine (85 mg per M^3) was introduced in 10 minutes and followed by air purge at 200°C for 3 hours (triplicate parallel tests).

Pre-equilibration in flowing air was specified for at least 12 hours before the start of a test. The test and backup beds were specified at 5 cm (2-inch) diameter and 2.54 cm (1-inch) depth. It is to be noted that each test was based essentially on models or some aspects of a postulated accident, but the principal objective was to serve as a procurement standard for new nuclear-grade carbons.

The second draft of RDT M16-1 standard, December 1970 (3), was concerned with two types of activated carbon: Type I for trapping elemental radioiodine, and Type 2 for both elemental and organic iodine. There was a strong emphasis on the material standard aspect, terms and definitions, and quality assurance requirements. Five iodine tests were stipulated: (1) elemental iodine efficiency at 25°C and 90% RH; (2) methyl iodide at 25°C and 90% RH; (3) elemental iodine at 80°C and 50% RH loading and 80°C and 100% RH purge; (4) methyl iodide at 80°C and 50% RH loading and 80° and 100% RH purge, and

(5) a radioactivity retention test for both Type 1 and Type 2 carbons with 10 minute loading of elemental iodine (85 mgs/M^3 air) and an air purge at 200°C for 3 hours. Pre-equilibration was specified in all tests and no details as to counting radioactivity were given.

In the January 1972 edition of RDT M16-1T(4), the title was changed to "Gas Phase Adsorbents for Trapping Iodine and Iodine Compounds" and the title remained the same in the future editions. The emphasis on definitions, material standard specification, Type 1 and Type 2 carbons, and the five iodine decontamination efficiency tests were unchanged.

The edition of June 1972 of RDT M16-1T(5) contained some important notes as to the conduct of the tests. The sample beds, 5 cm in diameter, were to be 5 cm deep for the methyl iodide tests and 2.54 cm deep for elemental iodine. The radioactivity present in test and back-up beds was to be determined with gamma spectrometry at the 0.3645 MeV energy peak of the pulse-amplitude spectrum of ^{131}I. The five radioiodine tests were to be:

(1) Elemental iodine at 25°C and 70% RH, challenged for two hours and purged for 2 hours.

(2) Pre-equilibrate at 130°C, 95% RH, challenge with elemental iodine for 1.5 hours and purge for 1.5 hours.

(3) Same as (1) with methyl iodide-131.

(4) Same as (2) with methyl iodide-131.

(5) Retention test with methyl iodide-131 (0.025 C_i of ^{131}I) with 2 hour challenge at 25°C, 70% RH and four hour purge with air at 180°C.

(6) In RDT M16-1T, October 1973 the adsorbents to be tested were specified as only those chemically treated to enhance the trapping of organic iodine compounds.

The base materials were classified: (1) Coconut-base activated carbon, (2) activated carbon made from other base materials, and (3) mineral base, polymer, or other noncarbonaceous base adsorbents. Technical requirements, more properly concerned with a material standard, were still specified. Although the impregnant and impregnation method might be proprietary, sufficient information was to be furnished (1) to verify that a shipment was identical to the lot examined in the original qualification test, and (2) to establish the uniformity of the shipment. There were few changes made in the five iodine penetration tests presented in the June 1972 version. It may be noted that the relative humidity stipulation was steadily raised from 50% at the beginning to 95% RH in 1972.

An important meeting was held in November 1974 (Augusta, GA) to resolve differences among the requirements of RDT M16-1, ANSI N509 and N510, U.S. Regulatory Guide 1.52, and the proposed ASTM standard being developed in the D28.04 Subcommittee (7,8). As a result, the number of tests required for qualification was reduced and the test requirements applied to the characteristics of the adsorbent and the application.

Accordingly, the draft of 30 May 1976 (9) developed by the ASTM D28.04 Committee (Standard Test Methods for Radioiodine Compound Adsorption of Activated Carbon), was limited to the adsorption efficiency of activated carbons. The five tests, now also presented in tabular form, were designated.

(1) Methyl iodide efficiency test at 25°C and 95% RH

(2) Methyl iodide efficiency test at 70°C and 95% RH

(3) Methyl iodide Loss of Coolant Accident, 130°C and 95% RH

(4) Elemental iodine test at 25°C and 95% RH for 2 hours
and air purge at 25°C and 95% RH

(5) Elemental iodine, high temperature retentivity test, feed at 25°C and RH < 50% for 10 min followed by air purge at 180°C for 4 hours.

Extensive detail for making the above tests and for counting were given. The type of canisters to contain the sample and backup beds and a test system schematic were described.

The RDT M16-1T draft, dated June 1976 (10) contains little that is different from the October 1973 version. However, one new consideration was introduced, i.e. used adsorbents. It was stipulated that these could be tested as with new material except (1) the material shall not be pre-equilibrated before testing, and (2) performance (acceptance) requirements shall be as specified by the purchaser or by the regulatory agency having cognizance of the purchaser's operations.

The last version of RDT M16-1T, dated December 1977, contained the following Foreword which signified a major change in policy:

"This standard supersedes the October 1973 issue of RDT M16-1 T and incorporates the following major changes to that issue:

1. Provision for two classes of adsorbent. The earlier issues of the standard provided for a single class of maaterial intended primarily for reactor in-containment applications. This issue adds a Class B adsorbent suitable for reactor ex-containment systems (e.g., standby gas treatment, fuel pool skimmer, auxiliary building and laboratory offgas and ventilation exhaust systems, and other applications where the adsorbent is not exposed to a steam-air environment.

2. The radioiodine test of the earlier issues has been removed from the body of the standard (to Appendices C, D and E) and has been rewritten to conform with the proposed ASTM standard for those tests. When the ASTM standard is published, Appendices C, D and E will be dropped from this standard.
3. Appendix F for the ball-pan hardness has been rewritten to conform with the proposed ASTM standard for that test; the appendix will be dropped when the ASTM standard is published.
4. Appendix G has been added for pH of water extract. An ASTM standard for pH has been initiated; when published, Appendix G of this standard will be dropped."

In a second draft of the iodine test [ASTM, D28.04. dated 25 July 1977 (12,13)] the applicability of the iodine tests to used carbons was also mentioned. However, the prehumidification period was to be omitted for used carbon and instead, the sample brought to the test temperature without air flow. The ambient test temperature was increased from 25° to 30°C for all stages of the test, and the medium temperature from 70 to 80°C for all stages of the test. The high temperature remained 130°C. The significance of the tests was justified by an assumed scenario following a DBA. It was claimed that the tests "provide a reasonable picture of the effectiveness of an activated carbon for radioiodine and its organic iodides under normal and post-DBA conditions" (13).

In the interval between Draft 1 and Draft 2 of the D28.04 radioiodine test standard, the text was subjected to a grueling examination by many qualified investigators in the field. There were questions raised as to humidity and temperature control, counting gamma activity and the statistical treatment, back-up bed strategy, inconsistencies in the table and text, and some "soul-searching" in regard to the significance of the test as to its relevancy for an adsorbent bed in actual use following a DBA in inside and outside containment systems. A compromise was finally developed and the test was approved by ASTM in 1979 as D-3803 "Standard Method for Radioiodine Testing of Nuclear Grade Gas-Phase Adsorbents". Since the ASTM iodine test standard has been published (D-3803-79), the RDT M16-1T is no longer concerned with that topic. It became simply a material standard for the procurement of the gas phase adsorbents.

In 1977 it was suggested that ASTM develop a materials standard for the special case of nuclear-grade activated carbon. Such a standard would detail the procurement requirements of nuclear-grade carbons and could specify the test method already developed for the radioiodine test standard. The preparation of the material standard was subjected to five drafts in the period between 31 July 1978 and 23 June 1980.

The ASTM D28.90 Executive Subcommittee had a special meeting on June 18, 1979 with Joseph Grady, ASTM President, George Atkinson, Staff Director of Standards Development, and James Dwyer, D28 Staff Manager. The purpose was to inquire whether the proposed Standard Specification for Impregnated Activated Carbon Used to Remove Gaseous Radioiodines from Gas Streams could or should require that a purchaser verify the certification of performance and physical properties furnished by the producer or supplier. The subcommittee concluded that not only could the specification require such verification, but it was recommended that it do so. Accordingly, two resolutions were offered and unanimously approved, as paragraphs 13.2 and 13.2.1 of the proposed specification, requiring the proposed specification be submitted to simultaneous subcommittee and committee ballot.

The proposed standard was balloted simultaneously to both D28.04 and D28 on Letter-Ballot D2801 (79-1) dated September 14, 1979. The final results of the D28.04 ballot were 7 affirmative votes, 1 negative vote and 2 abstentions. The negative vote, which is quoted below, objected to the combination of actions required by the supplier and purchaser in the same Section 13.

"The vote is negative for the following reasons:

1. While the supplier is required to mark product that product meets the requirement of subject specification, paragraph 13.2 shows required action by the purchaser.

2. The supplier has no control over what the 'purchaser shall..' do with product after receipt.

3. Therefore, supplier cannot mark product prior to 'purchaser shall...'action...".

In order to satisfy this objection, editorial changes were made in the June 19, 1980 revision to clearly separate the actions required by the supplier from those required by the purchaser.

Accordingly, the proposed standard was then accepted by the ASTM and has been published under the designation: D 4069-81 with the following title: "Standard Specification for Impregnated Activated Carbon Used to Remove Gaseous Radioiodines from Gas Streams".

During the above time-consuming steps in the developments of D-3803 an investigation was in progress at NRL concerned with the impregnation of activated carbons from various source materials. The study pursued in 1977 required many measurements for the penetration of methyl iodide-131. Some of these tests were sent to different laboratories as a guide to NRL of the reproducibility of penetration results; the measurements were made according to the then available RDT M-16 Test Procedures. A special tertiary amine impregnation was used on five coal-base activated carbons from different sources and the measurements were made at four temperatures (20, 30, 80, and 130°C).

The sources of the five activated carbons (not-impregnated) were Union Carbide Corp., Sutcliff-Speakman, Ltd., Calgon Corp., Westvaco Corp., and Witco Chemical Corp. The measurements were made by Environmental Engineering and Testing, Nuclear Environmental Services, Nuclear Consulting Services, American Air Filter Co., Windscale Laboratory, Great Britain and the Naval Research Laboratory.

A summary of the overall results are presented graphically (Figure 4.1). The penetrations (%) of methyl iodide-131 are grouped according to the activated carbon and the numbers in Figure 4.1 designate one of the 6 laboratories, not in the sequence given in the previous paragraph.

The values reported at 20° and 130°C varied over wide limits; those at 30° and 80°C were more consistent. Several groupings of the results were analyzed as shown in Tables 4.5, 4.6 and 4.7. With a few exceptions the mean and standard deviations were of the same magnitude. Table 4.5 indicates more variations among laboratories than among carbons.

The methods used by Laboratory 1 gave consistently high results in terms of penetration. This can be attributed to the use of a relative humidity above 95% RH. Table 4.7 also includes the mean and standard deviation for the five carbons evaluated at 30° and 22°C excluding the results in duplicate from Laboratory 1. These observations raised important questions, namely, should close attention be paid to individual laboratories as sources in the procedural variations in the method? Is there a fundamental problem in the chemistry of the testing procedure?

In 1977, and in fact today, the cost per measurement of a methyl iodide-131 penetration was a considerable item in a research budget. Perhaps this may be one explanation for the scarcity of radioiodine penetration data for activated carbons. Many problems still exist in an evaluation of weathered carbons that remain or are removed from service and considered more investigation is warranted.

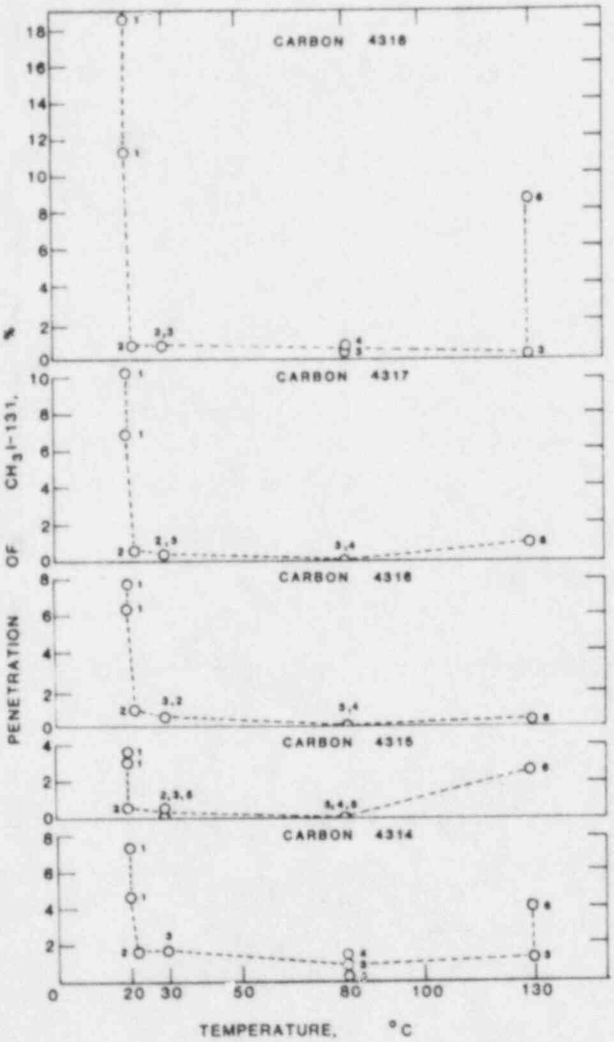


Figure 4.1 Summary of Measurements on the Penetration of Methyl Iodide-131 Conducted at NRL with Five Coal Base Charcoals

Table 4.5 Penetration (%P), of Methyl Iodide-131 at Various Test Temperatures for Five Different Carbons (4314-4318) at One of Six Laboratories (1-6)

20°C			30°C			80°C			130°C		
Carbon	%P	Lab	Carbon	%P	Lab	Carbon	%P	Lab	Carbon	%P	Lab
4314	4.6	(1)	4314	1.73	(3)	4314	0.36	(3)	4314	4.1	(6)
4314	7.4	(1)	4315	0.14	(3)	4314	0.51	(3)	4315	2.6	(6)
4315	3.6	(1)	4316	0.48	(3)	4315	0.00	(3)	4316	0.31	(6)
4315	3.0	(1)									
4316	7.8	(1)	4317	0.33	(3)	4316	0.00	(3)	4317	0.98	(6)
4316	6.4	(1)	4318	0.70	(3)	4317	0.03	(3)	4318	8.7	(6)
4317	0.3	(1)	4315	0.05	(5)	4318	0.39	(3)	4314	1.34	(3)
4317	6.9	(1)	4315	0.24	(4)	4314	1.44	(4)	4318	0.093	(3)
4318	8.6	(1)	4315	0.53	(4)	4315	0.04	(4)			
4318	11.3	(1)				4316	0.00	(4)			
4314	1.54	(2)				4317	0.14	(4)			
4315	0.26	(2)				4318	0.74	(4)			
4316	0.90	(2)									
4317	0.46	(2)									
4318	0.72	(2)									
Mean	5.51			0.52			0.33			2.59	
Std. Dev.	5.2			0.53			0.44			3.03	

Table 4.6 Variation of Methyl Iodide-131 Penetration (%) with Laboratory (1-6) and Temperature (22-130°C) for a Given Carbon

Carbon 4314		Carbon 4315		Carbon 4316		Carbon 4317		Carbon 4318	
%P	Lab	%P	Lab b	%P	Lab b	%P	Lab	%P	Lab
4.6	(1)	3.5	(1)	7.8	(1)	10.3	(1)	18.6	(1)
7.4	(1)	3.0	(1)	6.4	(1)	6.9	(1)	11.3	(1)
1.54	(2)	0.26	(2)	0.17	(2)	0.60	(2)	0.60	(2)
1.73	(3)	0.14	(3)	0.90	(2)	0.46	(2)	0.72	(2)
0.36	(3)	0.00	(3)	0.48	(3)	0.33	(3)	0.70	(3)
0.515	(3)	0.04	(4)	0.00	(3)	0.03	(3)	0.39	(3)
1.44	(4)	0.05	(5)	0.00	(4)	0.14	(4)	0.74	(4)
4.1	(6)	2.6	(6)	0.31	(6)	0.98	(6)	8.7	(6)
		0.24	(4)					0.093	(3)
1.34	(3)	0.53	(4)						
Mean 1.56		0.48		0.31		0.42		1.71	
Std. Dev. 1.16		0.87		0.34		0.34		3.09	

It must be recognized that the relevancy of the ASTM D-3803 iodine test is open to question for the performance of a service carbon during an accident scenario. Neither the Windscale Incident (October 1957) nor that at Three Mile Island (March 1979), the latter involving a much lower iodine escape, bear any resemblance to the assumed scenario of the present iodine test. After an extensive study one must conclude that an adequate understanding is lacking concerning the properties of the carbon during and after long service in air cleaning adsorbers, during which time the carbon filters must always be ready to trap the iodine liberated during the assumed accident.

Table 4.7 Grouping of Carbons using Results for Methyl Iodide-131 Penetration (%) Obtained at 30° and 22°C

			Carbon		
Laboratory	4314	4315	4316	4317	4318
3	1.73	0.14	0.48	0.33	0.70
5		0.05			
4		0.24			
4		0.53			
2	1.54	0.26	0.90	0.46	0.72
1	4.6	3.6	7.8	10.3	18.6
1	7.4	3.0	6.4	6.9	11.3
Mean	3.82	1.12	3.90	4.50	7.83
Std. Dev.	2.77	1.51	3.7	4.94	8.7
EXCLUDE Laboratory (1)					
Mean	1.64	0.24	0.69	0.40	0.71
Std. Dev.	0.13	0.18	0.30	0.091	0.014

A recent program of round robin measurements for the penetration of methyl iodide-131 was conducted by CONAGT (ASME Committee on Nuclear Air and Gas Cleaning Technology) and made use of the test procedure given in ASTM D-3803-79. The results reported by First (14) showed a considerable spread for each of the four carbon samples distributed to 15 different laboratories. The lack of reproducibility could be attributed to any one of three factors, or some combination thereof:

(1) Non-adherence of the laboratory to important details of the test procedure.

(2) Inherent lack of particle uniformity within the master sample.

(3) Poor sub-division from the master sample.

The heterogeniety among particles of new material is further compounded when the gradients of contaminants are introduced into a carbon in service.

4.3 Sampling of Activated Carbon and its Influence on Measured Properties

The errors of analyses come from two general sources, the analytical procedure and the selection of the sample. For a material as heterogeneous as activated carbon, it was felt that a considerable part of the error in various analyses might be due to the sample itself. For example, in any given carbon supply there are variations in particle size, shape and density and these may not be uniformly distributed in the sample. The sources of the heterogeneity may be traced to many factors in the manufacturing and distribution processes.

4.3.1 Separation by Specific Gravity

In order to demonstrate a measure of the heterogeneity among various carbon samples, a separation by specific gravity was made using the device called Whippet (8). This is a triangular vibrating table on which the charcoal is introduced at one corner and slowly discharged over the opposite side. The table can be tilted, the air flow that lifts the particles can be varied, and the table vibrated at a specified frequency. The effluent charcoal falls into six equally spaced chutes and for a given quantity introduced, the weights and volumes from each chute may be determined and the bulk densities calculated. A typical separation for a coconut shell charcoal is shown in Figure 4.2 (9). The mean bulk density was 0.41 g/ml and the standard deviation 0.067. The distribution was not normal and indicates the supplier's adjustments to meet specifications on a 8x16 nominal size. Obviously, care must be exercised that the particles not be segregated during the sampling procedure.

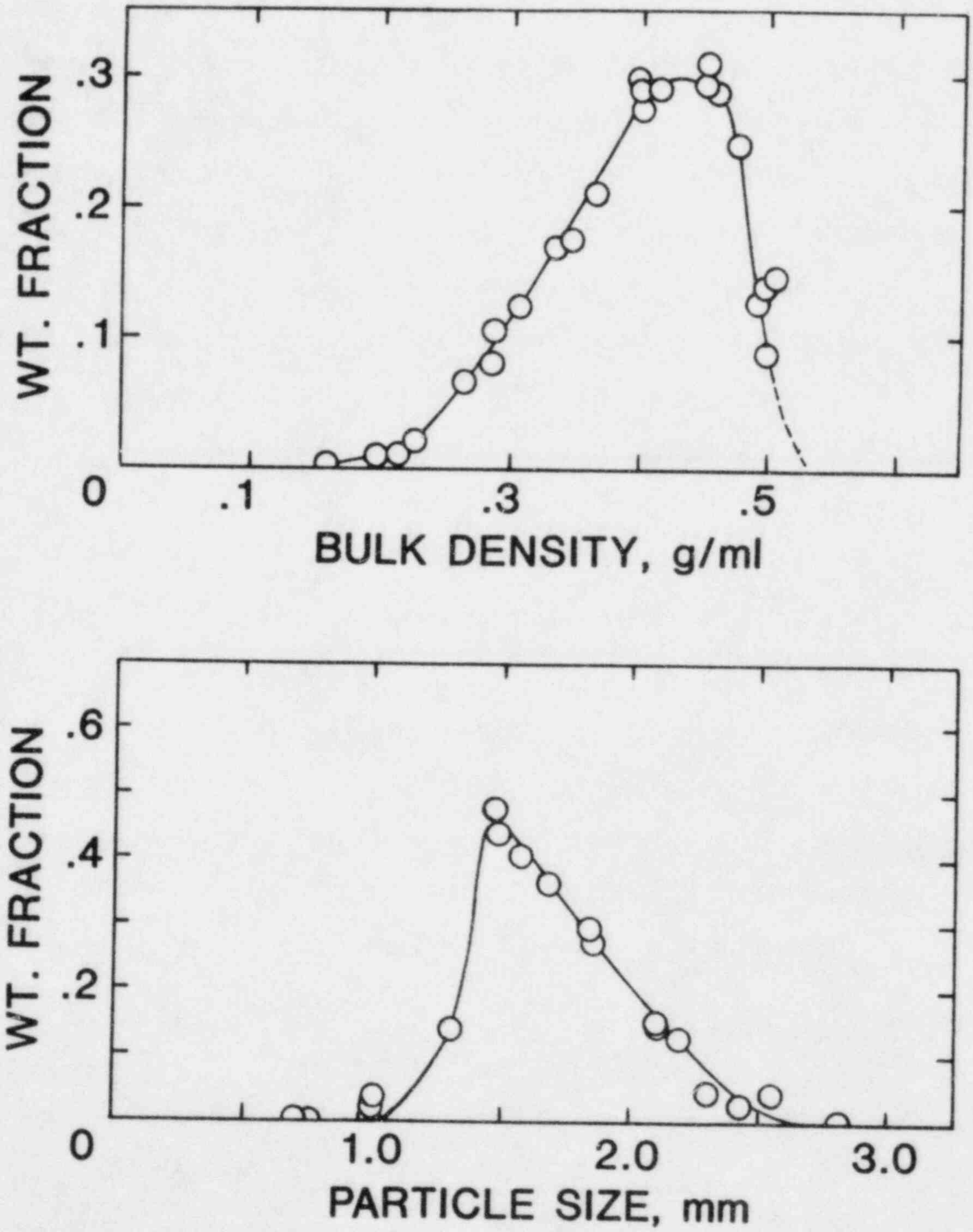


Figure 4.2 Distribution of Particle Density and Particle Size for a Coconut Shell Charcoal (8 x 16) (four series of measurements included)

4.3.2 Theoretical Model of Sampling

A novel approach to the problem of sampling heterogeneous granular adsorbents was reported by F.G. Carpenter (5) who treated the subject from a fundamental point of view and applied the results to several measurable properties. He calculated the minimum weight of sample which should be used in a test procedure from a knowledge of the desired precision, the average value of the property being tested, the distribution of this property among the particles, and the weight of the individual particles. In the practical problem, the equations were solved for the weight of sample which would give the desired precision with a given heterogeneity in hand. Since actual sampling methods are never perfect, the calculated weight is a minimum weight and should be increased in accordance with the imperfection of the sampling procedure.

The properties of the particles of an activated carbon are assumed to be essentially continuous variables within wide limits and the individual particles to be imbued with the property to different extents. Strictly speaking, therefore, there are no two particles in any finite amount of material which are absolutely identical. However, in order to formulate a mathematical treatment, the material will be considered to be composed of a mixture of only a relatively few different types of particles. All particles whose property lies within a certain narrow range will be considered to be of one type characterized by the mean of the range.

Carpenter assumed $\underline{m}$ different types of particles and the values of the property corresponding to the various types indicated by g_1, g_2, $\ldots g_i$, $\ldots g_m$. The fraction by weight of the various types was indicated by f_i. The mean value of the property will then be:

$$\bar{g} = \sum_{1}^{m} g_i f_i \qquad (1)$$

If it were possible to select a sample with the same fraction of each of the different types of particles from the parent lot, the relative amounts of each (f_i) would then remain the same and $\bar{g}$ would be the same for both parent lot and sample. In practice, it is not possible to select a sample with the same fraction of each of the different types of particles; therefore, the next best thing is done. Each particle in the entire parent lot is given the same probability of being chosen for the sample. Such a procedure on the average amounts to the same thing, but the concept of probability permits fluctuations in individual cases.

The random fluctuation in the number of particles of the various types is carried over into random fluctuations in the weighted average value of the property. The magnitude of this variation can be approximated by:

$$s_{\bar{g}}^2 = \frac{1}{W} \sum_{1}^{m} (g_i - \bar{g})^2 k_i f_i \qquad (2)$$

where

$s_{\bar{g}}$ = standard deviation of $\bar{g}$

W = weight of sample

m = number of types of particles

$\bar{g}$ = average value of the property

g_i = value of the property of the i'th type

k_i = weight per particle of the i'th type

f_i = fraction by weight of the i'th type

The standard deviation of $\bar{g}$ given by equation 2 is the theoretical sampling error. When expressed as relative error (or coefficient of variation, CV) and solved for W, the result becomes:

$$W = \frac{1}{(CV)^2} \sum_{1}^{m} \left(\frac{g_i}{\bar{g}} - 1 \right)^2 k_i f_i \qquad (3)$$

The weight of sample (W) in equations 2 and 3 is that required to reduce the sampling error to $s_{\bar{g}}$ or CV under ideal sampling conditions. Any errors in the test or analysis would necessarily be added to the sampling error.*

4.3.2.1 Determination of Smallest Weight of Sample

Carpenter (5) applied equation 3 to the practical problem of determining the smallest weight of sample that could be used in a test. This required a knowledge of the desired precision (CV), the mean value of the property $\bar{g}$, the distribution of this property among the particles (g_i and f_i), and the weight of the individual particles (k_i).

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*Note: The standard deviation, s, as used here is a measure of variation from the average. An estimate of the standard deviation may be obtained from a series of n measurements by computing differences between each measurement and the mean. Each of these differences is squared and the squares are summed over all n measurements. This sum is then divided by one less than the number of measurements, i.e. by (n-1), and the square root of the quotient is an estimate of the standard deviation. It is common practice to express the standard deviation as a fraction of the mean and this quantity is called the coefficient of variation, CV.

The average weight per particle is related to the density (ρ), diameter (D), and shape factor (S) of the particles by the relationship: $k_i = \rho_i S_i D_i^3$. However, it also can be simply evaluated directly by counting and weighing 100 or 1000 particles. As an example, various properties of the sieve fractions of Char 32 (a service bone charcoal) were examined (see Table 4.8). The average values of the properties and the weights of sample required for either 1 percent or 0.1 percent coefficient of variation were evaluated from equation 3. It is of interest to note that a sample of a few grams was sufficient for a precision of 1 percent in all of the test reported, but, if a coefficient of variation of 0.1 percent was required, samples of as much as 150 grams are needed in some cases.

If the nature of the property under test is such that particle size and shape have no effect, the sample can then be ground. As a result there is a very great reduction in k_i and the size of the sample can be reduced accordingly.

Table 4.8 Properties of Sieve Fractions of a Service Bone Char (Char 32)

f_i Wt. Fraction	k_i mg per Particle	Carb %	Insoluble %	N %	Area m^2/g	Color Removal %/g	Ash Removal %/g
0.135	2.56	6.8	0.8	0.54	70	82	31
0.263	1.35	6.8	0.4	0.42	60	82	40
0.242	0.452	7.8	0.5	0.32	54	79	44
0.167	0.173	8.6	0.4	0.35	49	77	38
0.124	0.0648	9.2	0.5	0.38	45	77	37
0.069	0.0117	9.3	0.5	0.33	42	76	36
Value of $\bar{g}$		7.81	0.50	0.39	55.0	79.4	38.7

Desired Precision		Minimum Weight of Sample in Grams					
1%	.01	0.16	1.49	0.60	0.297	0.0080	0.238
0.1%	.001	15.9	149	60	29.7	0.80	23.0

4.3.2.2 Application to Sieve Analysis

If the test is concerned with the presence or absence of some feature, the theory is also applicable. One such example is a sieve analysis where the fraction within a certain size range is sought.

Let the i'th type of particle be the one having the desired attribute, then in terms of the previously given definitions $g_i = 1$ and $g_{j \neq i} = 0$. From equation 1, $\bar{g} = f_i$ and from equation 2 the following is obtained:

$$W = \frac{1}{s_f^2} \left[(1 - 2 f_i) k_i f_i + f_i^2 \sum_1^m k_i f_i \right] \qquad (4)$$

W in equation 4 gives the minimum weight of sample required to obtain a certain precision (s_f) in the fraction by weight (f_i) of material of the i'th type. Equation 4 is the same as those given by Buslik (6) and Gayle (7) for error of sieve analyses.

Equation 4 was applied to the calculation of the weight of sample required to obtain a certain precision in a sieve analysis. The sieve analysis of a 8x16 coconut shell carbon is given in Table 4.9 along with all the necessary calculations to obtain the weight of sample required for a standard deviation of 0.001 in the fraction on the various sieves.

As might reasonably be expected, the coarsest fractions having the largest weight per particle and fewest number of particles require the largest sample size. The very coarsest sizes require less sample because f_i, which is also a factor, is small.

It should also be pointed out that the sample weights listed in Table 4.9 presume that there is absolutely no error in sieving. If samples of the indicated size were used, the variations found would always be greater than 0.001 because the sieving error would have to be added to the sampling error.

Table 4.9 Sieve Analysis of a Coconut Shell Carbon (8x16)

Sieve Fraction	f_i	Particle weight k_i	$1-2f_i$	$k_i f_i$	f_i^2	Calculated wt. CV=0.1%
		mg		mg		(g)
8x10	0.135	4.3	0.730	0.581	0.0182	465
10x12	.299	2.8	0.402	.837	.0894	542
12x14	.405	1.8	0.190	.729	.164	516
14x16	.143	1.0	.714	.143	.0204	150
16x20	.018	0.6	.964	.0108	.00032	11
20x30	.001	0.2	.998	.0002	.00000	-

4.3.2.3 Evaluation of Sampling Procedures

Having a theory to predict the error which will occur in an unbiased sampling procedure, Carpenter (5) examined practical sampling procedures. Since sampling is essentially a particle-handling operation, particle properties can be easily discriminated against during the sampling. The contributing factors, as mentioned previously, are particle size, density, and shape. The theoretical treatment gives the error for independent samples when the size of the sample is much smaller than the parent lot. This requirement is met for practical purposes when the sample is 1/8th or less of the parent lot.

A special mixture containing two sieve fractions was prepared consisting of 200 grams of a fraction through No. 12 and on No. 20 sieve and 200 grams of a fraction through No. 40 and on No. 60 sieve. The sieve analysis of the mixture indicated no particles present of a size near that of the opening of a No. 30 sieve and this sieve was used, therefore, to separate the two fractions in subsequent analyses. Hence, the sieving was completed in a very short time with no error. It is important that the sieving error be eliminated in order to prevent confounding the sampling error.

The average weight per particle was determined for the two fractions by weighing 1000 particles of each. For the coarse fraction $k_1 = 1.28$ milligrams per particle, and for the fine fraction $k_2 = 0.062$ milligrams per particle.

This particular mixture of particles was sampled by the following procedures, each sample sieved, and the percentages of coarse and fines computed: (1) Boerner sampler, both regular and small size; (2) riffle; (3) coning and quartering; (4) grab sampling. The standard deviations of the percent fines estimated from the experimental data were compared with the theoretical values obtained from equation (2) in order to determine whether the sampling method was unbiased.

The Boerner samplers are standard equipment and require no special operating techniques. The riffle was used in two ways, either with all possible precautions or in a careless manner. The only differences between the two uses of the riffle were in the prior mixing of the char and in the manner in which it was introduced onto the riffle. When the riffle was operated with all precautions, the char was mixed by tumbling in a container whose capacity was about 10 times the volume of the char. It was then poured very slowly onto the riffle from a scoop in a stream that was about two-thirds as wide as the riffle. When the riffle was operated carelessly, no prior mixing was used, and the char was simply dumped from the container (whatever it was) onto the riffle. No attempt was made either to spread the stream evenly over most of the riffle or to pour it slowly. The careless operation of the riffle is about what one would expect from an inexperienced and uninstructed laborer who is frequently employed in industry for such sampling operations.

The coning and quartering was done on a large piece of stiff wrapping paper on a smooth table. The cone was formed with the use of a funnel. A wide-blade spatula was used for flattening the cone and for quartering. The last traces of fines were swept up with a brush.

The grab samples were taken from a pile of mixed char by use of a small cylindrical cup holding about 12 milliliters. The cup was deeply inserted into the pile in an effort each time to scoop up a representative sample.

The results of the tests (Table 4.10) are listed in a sequence of decreasing accuracy. The regular Boerner sampler and the riffle give essentially theoretical results and can be considered as unbiased sample dividers. The small Boerner is not quite as good as theory. This is probably because the width of the individual pockets is only about twice the diameter of the larger pieces of bone char. The design and construction of the small Boerner are identical with the regular model and there is no reason to suspect that it should not be as accurate. It was, however, designed for fine particles and would doubtlessly be as good as theory if used only for particles of the size intended. Particles finer than about a No. 20 sieve would probably be accurately sampled with this device.

Table 4.10 Comparison of Sampling Procedures for Precision

Procedure: 400 g of char reduced in three steps to 8 samples of 50 g each. The char consisted of 50% fines and 50% coarse.

Procedure	Standard Deviation of Percent Fines
Theoretical	0.18
Regular Boerner	0.25*
Riffle	0.28*
Small Boerner	0.32
Riffle (careless)	2.57
Coning and Quartering	4.04
Grab**	12.5

* Not significantly greater than theory (at the 5% level)
**Eight samples of 12 grams each were obtained. Theoretical standard deviation = 0.37.

Table 4.10 also shows that careless use of the riffle can easily result in 10 times as much variation as careful use. The process of coning and quartering shows up very poorly. It should be pointed out that a mixture of very fine and very coarse particles is an extreme test of this procedure. If the particles were more nearly the same size, coning and quartering would then do a better job. Nevertheless, the procedure of coning and quartering still falls far short of theory.

The grab sampling was expected to give poor results and, indeed, it was so poor as to be absolutely useless.

In conclusion, the sampling of a stock of granular activated carbon requires great care. The cost of most measurements is an increasing quantity and an inadequate sample, not representative of the whole, obviously detracts from the overall value of the measurement. The sampling problem becomes particularly acute when a sample is sought to be representative of full-scale adsorber. Further discussion is presented in the following section.

4.3.3 Sampling of Carbon Adsorbers (10)

The testing of nuclear air-cleaning systems for iodine penetration is closely associated with the freon-aerosol leak test designed to prove the mechanical integrity of the unit. Unless this integrity is established, it is not possible to separate the quality of the adsorbent from mechanical leaks in the system. Progress in developing a satisfactory in-place test is slow in this country because of the present restrictions on introducing radioactive materials into plant equipment. The present tests, therefore, are made on representative samples of adsorbent removed from the system.

In order to infer satisfactory efficiency for a system from measurements on the carbon sample, ANSI/ASME N510-1980 (10) states several requirements:

1. "The sample is actually representative of all of the cells in the system;
2. All of the cells are filled properly in accordance with a qualified, filling procedure which will ensure a 'tight pack';
3. There are no leaks or by-passes in either the individual cells (factory tests) or the installed system (field tests);
4. Tests are to be made of samples withdrawn periodically from the installed adsorbers in accordance with the procedures in ASTM D-3803.

A laboratory test of D-3803 requires a sample volume of 104 ml. Obviously, it is not practical to fulfill all of the above requirements. Two basic sampling techniques were outlined in ANSI N509 (Appendix A) (11):

(a) An entire adsorber cell may be removed from an operating system. The adsorbent is removed from the cell, sampled and analyzed.

(b) Special test canisters may be installed in parallel with the adsorber.

Method (a) raises questions as to which one of the cells should be removed from the adsorber unit. Also left unspecified is the procedure for sample reduction to 104 ml that is required for the laboratory test D-3803. Method (b) demands careful control of the air flow so that the parallel behavior through the canister and adsorber is in the correct ratio. Perhaps a simple gas meter on the effluent side of the canister to monitor the air flow would be in order as used in the weathering studies (see 1.0).

Hillary (12) and Hillary and Taylor (13) concluded that it was essential to carry out both full-scale and laboratory iodine testing. In the former case, the methyl iodide-131, sealed in a silica capsule, was introduced in quantities of about 1 mg with a nominal activity at the millicurie level to give adequate sensitivity for full-scale testing. The tests first showed that poor performance was due mainly to by-passing the carbon units; attention to values and by-pass lines successfully eliminated the leaks. Penetrations of 0.015 to 0.022% were associated with new carbon; at a later time the values increased to 0.08 to 0.1% at plant flow rates of 1000 cfm (30 M^3/min). The laboratory test results were found to correlate with plant-scale results. The former being conducted at 98% RH with 16 hours pre-humidification with a contact time of 0.4 sec.

A safety consideration in the conduct of a plant-scale radioiodine test is the escape of methyl iodide-131 should a leakage or poor carbon be present. Experimentation at NRL indicates that a preliminary test with cold methyl iodide could warn against this possibility. The following four situations could be present:

1. Good carbon and mechanical integrity
2. Good carbon and mechanical by-passing
3. Poor carbon and mechanical integrity
4. Poor carbon and mechanical by-passing.

The introduction of pulsed flows of methyl iodide-127 was shown to have the following corresponding behavior:

1. Steady low-level release with no indication of pulsed input;
2. Prompt indication of pulsed input in the effluent;
3. Steady release at higher level than case 1 with no indication of pulsed input.

4. Prompt indication of pulsed input in the effluent with little diminution in the pulses.

In view of the difficulties in removing a representative sample from a carbon adsorber for laboratory tests, it is possible that a plant-scale test can be devised with the above safety considerations in mind. From the point of view of a DBA, the mechanical integrity of a carbon installation is as serious a problem as the degradation of the carbon itself. The experimental results obtained by the Windscale observations are very valuable indeed.

4.4 References

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5.0 Concluding Remarks

The activated carbon adsorbers in Engineered Safety Features for air cleaning systems are intended to prevent the release of radioactive iodine at any stage in the service life. The present report has been concerned with factors which degrade the carbon during service and with additional factors pertinent to the superposition of a DBA on the performance. The implication of the results to reactor operation and to an accident scenario is now discussed.

5.1 Significance to Present Installations

Sizable amounts of atmospheric contaminants accumulate in a year's operation of nuclear-grade activated carbon adsorbers and carbon degradation thus becomes a very important factor in the design and operation of the adsorber. One important problem is to define the permissible degradation in efficiency without jeopardizing the operating requirements for the removal of radioactive iodine.

Initially, the common air contaminants (ozone, sulfur dioxide, nitrogen oxides, hydrocarbons) adversely influence the inlet layer of a weathered activated carbon bed. The contaminants then migrate to lower depths with increase of service time. The retention of methyl iodide-131 is strongly influenced by the pre-adsorption of organic solvent vapors. In one case, acetone vapor, the adsorption of the vapor caused pre-adsorbed methyl iodide to move into deeper layers of the charcoal bed. Water flooding of a carbon containing adsorbed methyl iodide brings about a partition of the iodine among the original charcoal, the water and the gas phase. Obviously, this is strongly dependent on the details of the water flooding and warrants additional studies under better controlled conditions.

Accidental exposures of the activated carbon adsorber to the vapors from solvent spills or to organic vapors in plant operations, contribute to the degradation process and the degradation occurs more strongly at higher than at lower relative humidities. 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. The laboratory studies indicate that the interaction of ambient concentrations of ozone, sulphur dioxide, or the nitric oxides with impregnated carbons may be of second order importance relative to the insult of water vapor-organic compounds.

The depth profile for new carbons show a simple exponential attenuation in methyl iodide-131 penetration, but after weathering or with service-aged carbons, the depth profile is quite unpredictable. The behavior is attributed to a chromatographic distribution of the contaminants that accumulate in the carbon bed.

The weathering of KI_x carbons decreases the thermal stability and enhances the thermal emission of iodine at initial temperatures, which may be observed below 100°C.

There is a seasonal correlation of the observed penetration of $^{131}ICH_3$ with the dew point (°F). The winter months with air flows of low average dew points have minimum influence in the weathering of a nuclear grade 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.

Ackley, Adams and Browning(1) recommended that some provision be provided in the $^{131}ICH_3$ removal system to maintain the prevailing relative humidity below 90% RH. A simple procedure to accomplish this would be to pre-warm the air flow to the carbon. To reduce 95% RH air at 77°F to 50% RH requires a temperature increase of 18°F, and to reduce 95% RH air to 70% RH requires 9°F (see Fig. 5.1). The disadvantage is, of course, the heating cost of the large volume of air in process. Heating estimates to reduce the relative humidity of inlet air for time periods at designated relative humidities and to reach target values of 70 to 50% RH are summarized in Table 5.1. Since the inlet air is not always at 95% RH, some consideration should be given to the use of controlled inlet air heaters on ventilating systems based on a technical and economic analysis of the engineering factors.

Table 5.1 Heating Estimate to Reduce the Relative Humidity of Inlet Air to Either 50 or 70% RH for a Carbon Unit of 30,000 cfm

Fraction of Inlet Air at Designated Relative Humidity			Required Heat (BTU) to Reach Designated Target	
95% RH	70% RH	50% RH	50% RH	70% RH
1.0	0	0	3.96×10^9	1.98×10^9
.5	.5	0	2.97×10^9	0.99×10^9
.25	.5	.25	1.98×10^9	0.50×10^9
.20	.4	.40	1.58×10^9	0.40×10^9
.10	.40	.50	1.18×10^9	0.20×10^9

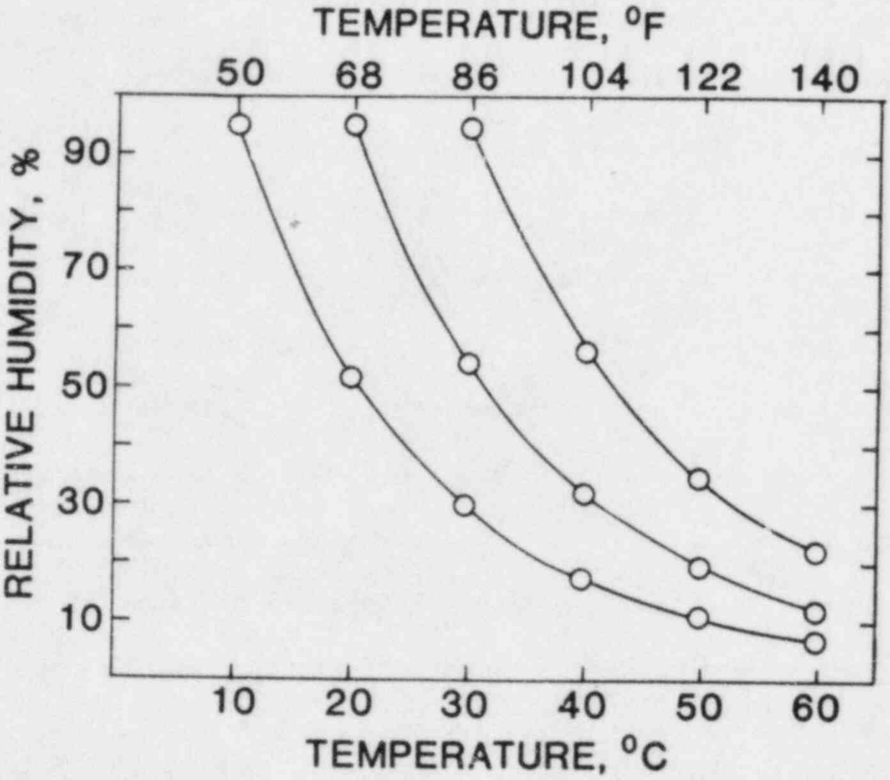

Figure 5.1 Decrease in Relative Humidity on Heating Air Initially at 95% RH at the Designated Temperature

The exposure of service activated carbons to radiation levels at 10^7 to 10^9 rads regenerates the iodine isotope-exchange capacity of the carbons as measured by the trapping of methyl iodide-131. The influence of radiation on new carbons was not significant nor relevant since they soon become weathered. The recovery of the efficiency for trapping methyl iodide-131 at ambient conditions is outstanding. Since all carbons accumulate a considerable amount of contaminants during the time in service, the ionization of some of these contaminants in the radiation field generates the exchange sites for radioiodine compounds. The recovery of the isotope-exchange appears to increase with the quantity of contaminants directed to the carbon adsorber during service and there is a definite trend relating the improvement of the carbon with the service time. Regulatory Guide 1.52 (Revision 2, March 1978) stipulates that the carbon in Atmosphere Cleanup Systems must operate in a DBA of an average radiation level of 10^9 rads for iodine buildup on the adsorber. Since service carbons exposed to radiation levels of 10^7 to 10^9 rads actually improved on the iodine isotope exchange, the directive is obviously valid.

The irradiated samples showed little or no improvement in the adsorption of methyl iodide-127. The disparity in the trapping of the radioactive species and the removal of methyl iodide-127 by used and in-service activated carbons is a very important observation. The efficiency for iodine exchange was vastly improved by the irradiation and that for adsorption of methyl iodide-127 only slightly influenced or not at all. The behavior establishes the existence of at least three completely independent reactions that can take place within the domain of impregnated activated carbons:

(1) adsorption on the carbon networks of the activated carbons,
(2) iodine isotope exchange with impregnated iodine-127,
(3) chemical combination with impregnated tertiary amines when present.

When a carbon is new, all three mechanisms are at peak performance and it is not possible to distinguish among the three by a single measurement; the retention of methyl iodide-127 in new carbon is usually equal to the retention of methyl iodide-131. After the carbon is placed in service, the three mechanisms of iodine removal are degraded by the contaminants of the air at different rates; the adsorption process degrades faster than the other two.

Iodine-126 was formed from KI-127 impregnated carbons when subjected to LINAC radiation in direct proportion to the dose level. Other experiments with $^{125}ICH_3$, $^{127}ICH_3$ and $^{131}ICH_3$ using new impregnated carbons showed that there is considerable scrambling among all iodine isotopes during a radioiodine test procedure. The possibility exists that a reaction product of the exchange, trapped on the charcoal in the early stage of the dose, may then be gasified at a later stage of the dose period. If this happens, the details of the test procedure as they are conducted in different laboratories, become very important.

It is possible to regenerate the iodine isotope exchange efficiency of a used carbon by reaction with air-borne chemical reducing agents at ambient temperature. The same kind of chemical changes taking place during radiation and which are responsible for the regeneration of used nuclear-grade activated carbons, take place with chemical reducing agents such as hydrazine. These react with used nuclear-grade carbons to regenerate the iodine isotope exchange property. No change was observed in the adsorptive property of the carbon.

As an example, hydrazine reacted with a KIO_3-impregnated carbon and improved the iodine-isotope exchange efficiency. Either high level radiation or chemical reduction at room temperature lead to the formation of iodide ion (I^-) which readily exchanged with methyl iodide-131. In general, chemical reactions between gas reactants adsorbed on activated carbon (<u>in carbono</u>) are subject to different constraints than between the same reactants in solution (in vitro). Also, the radiolysis in vapor and liquids can be different than with the same reactants adsorbed on carbon.

The above results have been derived from what are essentially laboratory experiments. It is essential that many of these measurements, especially those on hydrazine regeneration, be repeated and extended on a pilot plant scale. There is a real possibility that a carbon adsorber can be regenerated in situ, thus creating savings in new material and labor.

Prehumidification of test samples at 30°C always resulted in an increase in the penetration of methyl iodide-131.

5.2 Additional Knowledge Gaps to be Investigated

The ASTM test procedure D-3803 to qualify new impregnated activated carbons for the penetration of iodine-131 or methyl iodide-131 cannot be applied without ambiguity to weathered or service carbons. Additional research is needed to develop such a standard.

For the majority of new carbons, and new carbons only, the penetration of $^{127}ICH_3$ is equivalent to the penetration of $^{131}ICH_3$. Some economy in the testing of new carbons would be realized by its use. Nevertheless, $^{131}ICH_3$ would be required for used- and in service- nuclear-grade carbons.

The experimental results in the present report were obtained by laboratory scale methods. Pilot plant scale work is required to verify the properties of air flows through carbon beds as a function of the particle characteristics of the carbon. The boundary area of carbon particles per unit volume can be measured and there is need to correlate this parameter with the adsorptive properties of the carbon bed.

5.3 References

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APPENDIX I

NRL LINEAR ACCELERATOR
U.S. Naval Research Laboratory
Washington, DC 20375

CHARACTERISTICS

The Naval Research Laboratory (NRL) LINAC is a three-section, S-band accelerator which operates in the energy range 5 to 65 MeV. At maximum efficiency the beam energy is 42 MeV and peak beam current is 0.5A. Pulse width can be varied from 0.03 to 1.4 µs.

TEST PARAMETERS

LINAC parameters and operating characteristics are typically very flexible. Data presented here are representative of normal operations. The experimenter can arrange with the NRL LINAC supervisor for operation of the LINAC in other than routine modes.

OPERATING CHARACTERISTICS

Operating characteristics of the NRL LINAC are given in Table 1.

TABLE 1. Operating Characteristics

Microwave Frequency	2858 MHz
Number of Accelerating Sections	3
Energy Range	5 to 65 MeV
Maximum Efficiency Operation:	
Beam Energy	42 MeV
Peak Beam Current	0.5 A
Rated Average Power	8 kW
Beam Pulse Width (FWHM)	0.03-1.4 µs
Pulse Repetition Rates per Second (single pulses are available within width range)	5, 15, 30, 60, 180, 360
Average Beam Current	
Port 1	250 µA
Port 2	100 µA (max)
Port 3	100 µA
Port 4	100 µA
Energy Spread, $\Delta E/E$(a)	0.4 to 10%
Transient Mode Operation:	
Beam Energy (ave)	30 MeV
Peak Beam Current	1 ampere
Beam Pulse Width (FWHM)	50 ns

(a) Value sensitive to beam energy and current.

Electron-Beam Loading

Electron-beam loading characteristics are given in Figure 1 and the floor plan of the LINAC laboratory in Figure 2.

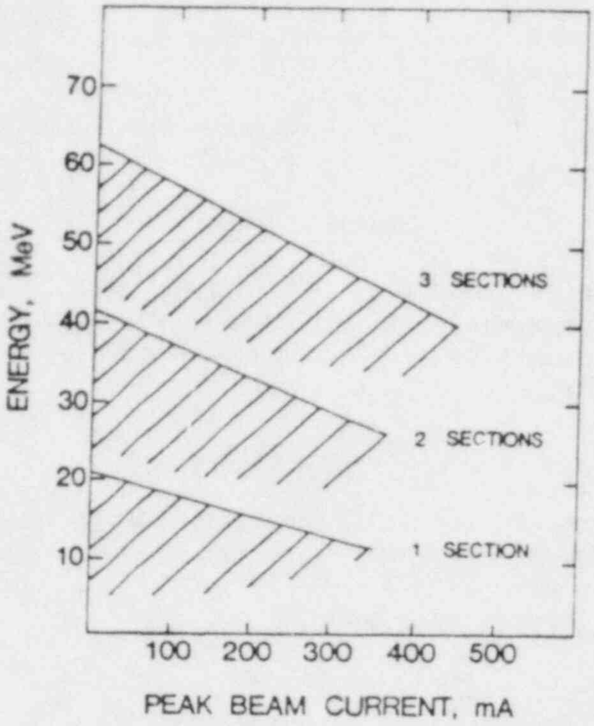

Fig. 1 - Beam Loading Characteristics

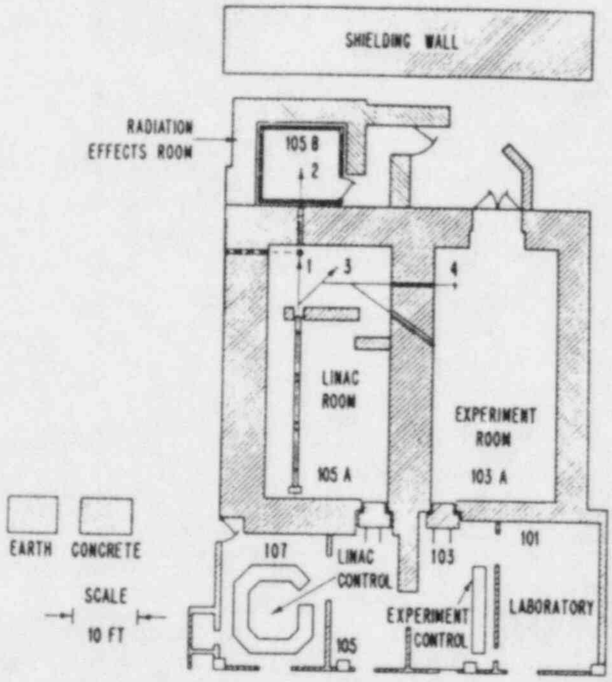

Fig.2 - Floor Plan of NRL LINAC Laboratory

As with all LINACS, the electron current available over the entire energy range is not constant, being maximum near the center of the range and approaching zero at the upper limit. In the case of the NRL LINAC, energies below 5 MeV are nearly impossible to obtain, and at 5 to 7 MeV unanalyzed beam currents are limited to 100-200 mA, peak. Due to the fact that the energy spread of the raw beam may be as large as 15 to 20 percent (FWHM), deflection and collimation of the beam reduces the available current.

Pulse Shape

The pulse shape for longer pulses (0.5 - 1.4 μs) in beam one are approximately rectangular. As the pulse length is reduced the shape is more triangular. Pulses appearing in beams 3 and 4 are somewhat less regular in shape due to the energy-time relationship within the duration of the pulse. Best rise time achieved on short pulses is 14 ns, although this could be improved with sufficient demand.

Repetition Rate and Pulse Predictability

Repetition rates are given in Table 1. Single pulses can be delivered for any pulse width within the normal pulse width range.

Pulse reproducibility and predictability are excellent. For example, on single pulse exposures, pulse amplitude predictability of ± 5 percent is typical with dark current background radiation less than 0.5 percent for a single 4×10^4 rads (Si) pulse.

Electron-Beam Geometry and Energy Spread

The size and shape of the beam spot depend on the energy, the current, the particular beam port employed, and the amount of focusing used. Spot diameter is typically in the range 0.2 to 1.0 cm. The shape of the spot can be made round or elliptical through the use of quadrupole focusing lenses. Extra large spot sizes can be produced by scattering from a foil.

The experimenter should be aware that radiation dose values quoted as characterizing the environment output are directly related to beam spot size; higher values are associated with smaller beam diameters.

Beam energy width E/E (FWHM) of the raw beam is 10 percent at 38 MeV and 1.0 percent at 56 MeV for the equilibrium mode. The energy width of deflected beams is adjustable by means of slits in the magnetic analysis system. The transient mode featuring high peak currents of short duration would exhibit an FWHM of 20 percent to 30 percent.

Neutron Irradiations

A compact target of water-cooled tantalum plates is available for neutron irradiations. To emphasize fast neutrons, a minimum of water is used. Three to four inches of lead is employed to reduce gamma contamination. Preliminary spectral measurements indicate a broad peak at about 1 MeV, with a differential flux of about 7×10^{12} neutrons/cm^2

per coulomb of LINAC beam at a point 90° to the center of the target. Gamma contamination at this point is about 4×10^4 rads (Si) per coulomb of LINAC beam.[a] A coulomb of 42 MeV electrons is collected in about 6 hours. (See Reference (3)).

ENVIRONMENT

The NRL LINAC electron beam can be used directly as a radiation source, converted to X-rays by means of a bremsstrahlung target, or converted to neutrons by means of a photoneutron target.

Output Characteristics

The electron beam emerges through a water-cooled stainless steel window and can be used directly or converted to X-rays and neutrons. By appropriate experimental techniques either of these three components can be emphasized and their effect on various media studied.

TABLE 2. Environment Characteristics

Electrons	
Peak current (50 ns pulse)	1 amp
Peak current (1.4 μs pulse)	0.5 amp
X-Rays (10 cm from converter plate)	1×10^3 rads (Si)/pulse
Neutrons	1×10^6 1 MeV equivalent neutron/cm2/pulse

Measurement Techniques and Errors

Electron beam current measurements are made in two ways. One of these consists of a current transformer through which the electron beam passes just before emerging from the water-cooled exit window. The second involves Faraday cup techniques employed after the beam has emerged through the window. Both give results having errors less that ± 5 percent. (See Reference (4)).

Absorbed does measurements are made using thermoluminescent detectors and reverse biased silicon diodes. These are calibrated against an absolute silicon calorimeter (5) or a ^{60}Co source.

Neutron intensity measurements are available using sulfur disks that give neutrons per cm^2 for energies above 3 MeV. Neutron spectrum information is also available. Dose measurements for neutrons are made using Li^6 and Li^7 enriched TLD's (Li^{6}F$_2$, Li$^7{}_2$).

For the dose measurements involving use of the reverse biased silicon diode, digital readout is available giving total integrated dose for each pulse.

(a) Measured 11.5 cm from center of target and behind 4-inch lead gamma ray shield.

Electrical Noise

The electrical noise within the LINAC laboratory space can be separated into two general categories:

1. Noise not synchronous with LINAC radiation pulse, and
2. Noise synchronous with LINAC radiation pulse.

Each of these categories can be subdivided into

(a) Radiated noise, and
(b) Conducted noise.

Nonsynchronous Noise

The most significant source for noise in this category is that associated with the silicon controlled rectifiers (SCR's) used in the waveguide cooling system for the LINAC. The conducted component appears as several "gliches" of about 4 volts amplitude and 50 s duration appearing on the 115 VAC service lines.

The typical radiated component is such that a signal having a maximum amplitude of 3 millivolts peak-to-peak, a characteristic frequency of 4 kHz and lasting for 5 milliseconds is induced in a 60-foot length of semi-flexible, 1/2 inch-diameter coax cable with the cable terminated at its input end with 50 ohms.

Synchronous Noise

The most predominant source of noise synchronous with the LINAC radiation pulse is that associated with the klystron modulators. The conducted component appears on the 115 VAC service lines with a maximum amplitude of 5 volts peak to peak with an average frequency of about 1.5 MHz and lasting for 20 μs.

The radiated component will induce a signal in an inductive loop 5 inches in diameter and terminated in 50 ohms having a maximum amplitude of 15 millivolts with a frequency of 14 MHz and lasting for 10 μs.

By various means periodic improvements in all of these noise levels have been made and will continue to be made.

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APPENDIX II

IMPREGNATED NUCLEAR CARBONS INVESTIGATED

Nuclear Carbon	Nominal Size	CCl_4 Activity*	Source	Impregnation
BC 787	8x16	60	Coconut	Iodine salts and tertiary amines
BC 727	8x16	90	Coconut	KI + I_2
BC 717	8x16	60	Coconut	KI + I_2
G 615	8x16	60	Coconut	KI + TEDA
G 617	8x16	95	Coconut	KI + I_2
MSA (463563)	8x16	60	Coconut	KI + I_2
AAF 2701	8x16	60	Coconut	KI + I_2
KITEG	8x16	60	Coal	(Iodine Salts (and tertiary amines
KITEG II, NUSORB	8x16	60	Coconut	
Sutcliffe, Speakman & Co.	8x16	60	Coal	5% TEDA

*ASTM D3467; TEDA = triethylenediamine.

APPENDIX III

FIGURES

FIGURES (Cont'd)

FIGURES (Cont'd)

APPENDIX IV

TABLES

TABLES (Cont'd)

TABLES (Cont'd)

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16. ABSTRACT (200 words or less)

Nuclear-grade carbons were systematically degraded by exposure to unfiltered outdoor air with decrease in radioactive methyl iodide trapping. Local meteorological conditions of high humidity combined with atmospheric pollutants in the test vicinity contributed jointly to the degradation. When service carbons were exposed to radiation levels of 10^7 to 10^9 rads, the iodine isotope exchange capacity was regenerated. The adsorptive properties were only slightly improved. It was possible to regenerate the iodine isotope-exchange efficiencies by reaction with airborn chemical reducing agents such as hydrazine for carbons removed from nuclear power operations. The depth profile in methyl iodide-131 penetration changed from simple exponentional through new carbons to a non-linear profile for weathered and service aged carbons. The behavior is attributed to the chromatographic distribution of the contaminants that accumulate in the bed. The removal of radioactive iodine depends on a minimum of 3 distinguishable processes: adsorption on the activated carbon, iodine isotope exchange with impregnated iodine-127, and chemical combination with impregnated tertiary amines when present. When a carbon is new, all 3 mechanisms are at peak performance. After the carbon is placed in service, the 3 mechanisms degrade at different rates; the adsorption process degrades faster than the others.

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