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LONG-TERM EFFECTS ON RADIOIODINE TRAPPING BY CHARCOAL*

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Abstract

The Oak Ridge National Laboratory maintains systems which are designed to provide fission product containment, in the event of accidental release, by continually exhausting air from the containment volume, through HEPA filters and charcoal adsorbers. Present practice is to replace charcoal when in-place test results indicate less than 99.9% retention of I_2 for two hours. It is considered possible that a proven capability of trapping $CH_3^{131}I$ may be required in the future. A program of tests is underway to determine the $CH_3^{131}I$ efficiencies of some commercial impregnated charcoals as a function of time exposed to reactor off-gas. A TEDA-impregnated charcoal retained a high $CH_3^{131}I$ trapping efficiency (> 90%) during six months service whereas an iodized charcoal retained that efficiency for only about one month. The $CH_3^{131}I$ trapping efficiency test was performed at 90% R.H. with a loading of about 0.4 mg I as CH_3I/cm^3 of bed. This test loading is about ten times larger than the maximum total iodine loading estimated to be possible in ORNL off-gas systems and additional tests are underway to determine whether the trapping efficiencies for a more realistic loading will be maintained for a longer service period.

A second, more urgent problem is related to the slow release of iodine from charcoal beds. The ORNL need is to provide a method of predicting, from a short-term, in-place test result, the fraction of iodine which would be retained over a period of several weeks under accident and post-accident conditions. The results of some long-term (28 day) iodine retention tests are presented and compared with previous results (from ORNL and elsewhere). The releases are larger than acceptable under some conditions. The release depends on at least four environmental parameters: (1) the prevailing relative humidity, (2) the service history, (3) organic contamination in the air and (4) ionizing radiation. Additional tests are in progress to demonstrate the magnitude of the first three of these parameters. It is anticipated that the results of the planned tests, along with those from the Savannah River Laboratory program pertaining to the effects of radiation, will provide an outline of the magnitude of possible iodine releases from adsorbers under ORNL usage. It is suggested that a program of basic studies of the mechanisms involved in iodine trapping and release would help to provide the quality of arguments which may become necessary to defend the efficacy of containment adsorbers.

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I. Introduction

The Oak Ridge National Laboratory maintains systems which are designed to provide fission product containment, in the event of accidents, by continually exhausting air from the containment volume through HEPA filters and charcoal adsorbers. Impregnated (in most cases iodized) charcoal is employed and in-place tests (1) of $\text{CH}_3^{131}\text{I}$ trapping efficiencies are performed. In-place I_2 trapping efficiencies (1) are also periodically measured, and the charcoals are replaced when the in-place I_2 trapping test indicates less than 99.9% retention of I_2 for two hours. The ORNL containment adsorbers are not expected to have to cope with large temperature increases above normal ambient temperature.

It is considered possible that a capability to retain $\text{CH}_3^{131}\text{I}$ may be required sometime in the future. This would impose two new requirements: (1) a commercially available charcoal which would retain a high $\text{CH}_3^{131}\text{I}$ trapping capability for a reasonably long period of service and (2) a dependable means for demonstrating, with in-place test data, the efficacy of an adsorber. In an effort to find an adequate, commercially available charcoal which could provide $\text{CH}_3^{131}\text{I}$ trapping capability for an acceptable service time, we have a program in progress with the objective of demonstrating the relative $\text{CH}_3^{131}\text{I}$ trapping efficiencies of a TEDA (triethylenediamine) impregnated charcoal and an iodized charcoal as a function of time in reactor off-gas service. Some data from the program are presented.

Another and more urgent problem arises because of the failure of some charcoals, under certain conditions and service history, to retain iodine (I_2) with high efficiency for several weeks (i.e., for the several ^{131}I -half-lives that might be required). We need to understand enough about the processes of long-term iodine release from charcoal to predict the long-term retention efficiency from reasonably short-term in-place observations. We have a program of tests in progress which have the objective of demonstrating the magnitude of the effects of various conditions (such as relative humidity, hydrocarbon contamination in the sweep gas, hydrocarbon contamination on the charcoal, and service time) on the iodine release over a 28-day period after iodine loading. Some data from this program are also presented.

II. Poisoning of $\text{CH}_3^{131}\text{I}$ Trapping Capability

A. Procedure

A series of samples of TEDA-impregnated and of iodized charcoal were exposed to reactor off-gas air streams. Samples were removed at two-month intervals; the $\text{CH}_3^{131}\text{I}$ trapping efficiencies and B.E.T. surface areas were measured.

A series of samples of NAC-G618 (which is a TEDA-impregnated, coconut charcoal prepared by the North American Carbon Company) and a series of samples of NAC-G617 (which is an iodized, coconut charcoal also prepared by the North American Carbon Company) were exposed to LITR-BSR off-gas (air) beginning in April 1970. A series of samples of the NAC-G617 charcoal were also exposed to HFIR off-gas during the same time period.

Each sample was contained in a test-bed holder of the kind shown in Fig. 1; these holders were sections of 1-in. diameter glass pipe which retained, with a system of screens and bands, two 1-1/8-in. deep beds of the charcoal to be tested. Two batteries of charcoal test-beds were mounted on separate racks with an appropriate system of valves and piping. One battery of test-beds was installed so

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as to expose the charcoal to off-gas sampled upstream of the LITR-BSR containment adsorber and the other was similarly installed relative to the HFIR containment adsorber. The air velocity through each test-bed was controlled with a separate valve to a value of 40 fpm.

The LITR-BSR ventilation system exhausts air from both the BSR (the Bulk Shielding Facility which is a swimming pool type of reactor) and the LITR (the old Low Intensity Test Reactor which is no longer operating). The air from the LITR is added for humidity control. The LITR-BSR ventilation system contains a long metal duct, upstream of the charcoal adsorbers which is exposed to the weather; consequently, this off-gas stream undergoes large daily fluctuations in temperature and relative humidity. Figure 2 shows the daily maximum and minimum values of temperature and relative humidity during the period of exposure. Generally the range of the daily temperature variation was about 20°F. The range of the daily relative humidity variation was larger during the first two months than it was later; it commonly varied within a 35-65% R.H. range.

The HFIR (High Flux Isotopes Reactor) off-gas system exhausts conditioned air through a filter-adsorber system which is reasonably well insulated from the weather. The temperature and humidity do not, therefore, undergo very large daily oscillations.

A set of test-beds was removed from the exposure systems at two-month intervals. The specific days at which test-beds were removed are indicated on Fig. 2. The test-beds were installed in a laboratory-test system without disturbing the charcoal and the efficiency for trapping $\text{CH}_3^{131}\text{I}$ was measured.

The laboratory-test system consists of a gas train in which the temperature and relative humidity of the air stream is adjusted (to 25°C and 90% R.H.), and then passed through the test-bed at 40 fpm, and finally through a series of collection beds of charcoal. After passing the conditioned air through the gas train for a period of time to allow equilibration of the charcoal to the test relative humidity, an amount of $\text{CH}_3^{131}\text{I}$ (corresponding to 0.4 mg of I as CH_3I per cm^3 of charcoal bed) was injected. The air stream was continued for an afterpurge period. Finally, the relative count rates for the ^{131}I on each of the two 1-1/8-in. test bed sections and the collection beds were determined and the fraction of the ^{131}I retained on the first 1-1/8-in. test-bed section and on the whole 2-1/4-in. test bed was calculated. Values of experimental conditions are listed in Table 1.

After the $\text{CH}_3^{131}\text{I}$ trapping test, the first of the two 1-1/8-in. test bed sections was removed from the samplers and mixed. The B.E.T. surface area was measured on a portion of this mixed sample.

B. Results and Discussion

The B.E.T. surface area values are plotted on Fig. 3 as a function of service time for each combination of charcoal and exposure conditions. The decreases in surface area with time in service on the LITR-BSR off-gas system were about the same for the TEDA-treated and the iodized charcoals. The loss of surface area by the iodized charcoal was less during service on the HFIR system than on the LITR-BSR system. The temperature and humidity fluctuations in the LITR-BSR off-gas may be responsible for the more rapid decrease in surface area. The rate of loss in surface area for the samples exposed to the HFIR off-gas was similar in magnitude to that observed by Evans(2) in unimpregnated charcoals after exposure to Savannah River Reactor off-gas (air).

Max. & Min. Temperature (°F)

Max. & Min. Humidity (% RH)

Maximum and Minimum Temperature

and Relative Humidity of

Fresh Air Stream at the

~~Filter~~ ~~BSR~~ OGG - Gen at the LTR - BSR

Filter System

Filter - Adsorption System

Pressure (psia)

Pressure (psia)

Pressure (psia)

May

June

July

Aug

Sept

Oct

Nov

REDUCTION IN BET SURFACE AREA WITH SERVICE TIME

Surface Area, m^2/g

K&E 10 X 10 TO THE INCH 46 0780
7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

BET

400

1200

1600

- NAC-G-617(KI₃)
exposed to LITR-BSR off-gas
- NAC-G-618(TEDA)
exposed to LITR-BSR off-gas
- △ NAC-G-617(KI₃)
exposed to HFIR off-gas

— — — unimpregnated charcoal
exposed to Savannah River
Reactor off-gas (Ethane)

Service, months

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Table 1. Conditions for Methyl Iodide Decontamination Tests on LITR - BSR- and HFIR-Exposed Samples

Each test bed section: Two 1-1/8-in. deep beds in series, 1-in. bed diam.

Each collection bed section: four 1-in. deep beds of MSA 85851, 8 x 16 mesh (U.S.), in series; 1-in. bed diam.

Methyl Iodide Test Conditions:

Temperature, pressure: approximately 25°C, 1 atm

Air face velocity: 40 fpm

Superficial residence time for each 1-1/8-in. depth: 0.14 sec

Relative humidity: 90%

Preequilibration time: around 18 hr

Methyl iodide injection time: 2 hr

Afterpurge time: 4 hr

Inlet CH_3I concentration: around 17 mg/m^3

Weight I as CH_3I injected per volume of charcoal in 2-1/4-in. depth: around 0.4 mg/cm^3

The $\text{CH}_3^{131}\text{I}$ fractional penetrations are shown in Fig. 4 as a function of bed depth and service time for three combinations of charcoal and service. The zero exposure data, in each case, show the commonly observed linearity between the logarithm of the fractional penetration and bed depth.(3) This relationship can be predicted with a homogeneous bed. After a period of time in service, the linear relation fails; the logarithm of the fractional penetration through the first half of the bed is relatively higher than that through the second half. This is consistent with the postulate that the loss of $\text{CH}_3^{131}\text{I}$ trapping capability is due to poisoning by contaminants in the air; the front half of the bed removes some of the contaminants and partially protects the back half of the bed.

A major practical point is that a considerable loss of $\text{CH}_3^{131}\text{I}$ trapping efficiency (or increase in fractional penetration values) was observed in all three cases after only six-months service. The iodized charcoal (NAC-G617) showed a small difference in rate of poisoning at the two off-gas systems. The LITR-BSR off-gas (which undergoes large daily temperature and relative humidity fluctuations) resulted in somewhat faster loss of $\text{CH}_3^{131}\text{I}$ trapping capability.

A comparison of the results for the iodized charcoal (NAC-G617) with those for the TEDA-impregnated charcoal (NAC-G618), both exposed to the same gas stream, reveals that the TEDA-treated material retained a trapping efficiency in excess of a given value for a longer service time than did the iodized charcoal. For instance, the TEDA material retained a $\text{CH}_3^{131}\text{I}$ trapping efficiency greater than 90% for six months service, whereas the iodized charcoal retained that efficiency for about one month.

MODEL

DATE

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The $\text{CH}_3^{131}\text{I}$ trapping test conditions are not considered to be excessively conservative in comparison to accident conditions except in regard to the loading. The maximum accident iodine loading for some ORNL off-gas system adsorbers is about $3 \times 10^{-2} \text{ mg/cm}^3$ which is about an order of magnitude less than the CH_3I loading employed. Further tests are in progress to determine rates of poisoning on the basis of $\text{CH}_3^{131}\text{I}$ trapping tests made at lower loadings.

There is a qualitative correlation between the effects of exposure conditions (i.e., LITR-BSR off-gas vs HFIR off-gas) on the rate of loss of B.E.T. surface area and on the rate of loss of $\text{CH}_3^{131}\text{I}$ trapping efficiency. Without more basic descriptions of the $\text{CH}_3^{131}\text{I}$ trapping mechanisms than are available one can only speculate as to the possible significance and/or usefulness of this correlation.

III. Release of Iodine from Charcoal Beds

A. Procedure

These tests are being done on a laboratory gas train system having three test bed sections in parallel. In this system the air stream was first adjusted to the desired temperature (27°C) and relative humidity. The air was passed through the 2-in. (or in some cases, 1-1/8 or 2-1/4-in.) deep, 1-in. diameter test beds of charcoal followed by a series of charcoal collection beds. The controlled air was first passed through the train for about 22 hours to allow equilibration of the charcoal with the air. An amount of ^{131}I -labeled I_2 was put into the gas stream and air continued to pass through the system (at 40 fpm). At intervals of time during a 28-day period, the collection beds were replaced. Counting of the test bed and collection beds provided the information from which was calculated the fraction of iodine retained after each interval of time. In most of the tests, one branch of the gas train contained a test bed section of unimpregnated charcoal (BC-416), the second branch contained a test bed section of iodized charcoal (Witco-42) and the third branch contained a test bed section of TEDA-impregnated charcoal (NAC-G618).

In the tests done thus far, the relative humidity was 0% R.H. in one experiment and 90% R.H. in another. In a third test, at 90% R.H., the vapors from a mixture of hydrocarbons (benzene, toluene, cyclohexane and heptane) were included, at a concentration of 0.0018 volume percent, in the purge air starting immediately after the I_2 was loaded into the bed. The hydrocarbons were added to simulate impure ambient air.

B. Results from This Study and Comparison with the Results of Others

The results are presented in Figs. 5, 6, and 7 along with previously reported results which also pertain to iodine release from charcoal beds at room temperature.

Figure 5 is a presentation of data pertaining to release of iodine from unimpregnated charcoals. The results from this study show that the release from new, unimpregnated charcoals was greater into air of 90% R.H. than into air of 0% R.H. Only a slight further increase was observed for release into 90% R.H. air containing hydrocarbon vapor at a concentration of 0.0018 volume percent. In all three cases the releases were small; they were less than 10^{-4} of the total loading.

FRACTION OF IODINE RELEASED,

IODINE DESORPTION
FROM UNIMPREGNATED
CHARCOAL

FRACTION OF IODINE RETAINED

TIME, hours

A | This Study | BC-4116 | 8x16 | Coconut | 90 | 2 | 40 | 4x10⁻² | 0.0015% HCl's in Surfactant

Symbol	Reservoir	Designation	Mesh (U.S.)	Base	R.H. (%)	Depth (in.)	Velocity (ft/min)	Loading (mg/ft ²)	Remarks
□	This Study	Witco-42	8x16	Pet.	0	2	40	4x10 ⁻²	Continuous Loading
○	Cavan et al.	TS	8x16	Coal	15	2	60	0.2	
△	This Study	Witco-42	8x16	Pet.	90	2	40	4x10 ⁻²	Continuous Loading
○	Cavan et al.	TS	8x16	Coal	90	2	60	0.2	
▽	This Study	Witco-42	2x16	Pet.	90	2 1/4	40	0.1	~ 1 yr Service Time
△	This Study	NAC-6617	8x16	Coconut	90	1 1/2	40	0.2	
△	Pope et al.	BC-727	8x16	Coconut	Imbibit	1	43-63	2x10 ⁻³	0.07% Dieth. P. Acetate in Sump Gas
X	Adams et al.	BC-727	8x16	Coconut	65	1	40	0.9	
X	Adams et al.	BC-727	8x16	Coconut	65	1	40	0.9	AMSCO 125-52 in Sump Gas
△	Evans et al.	—	8x16	Coconut	10	1	68	2	

TIME, hours

▽ This Study Witco-42 8x16 Pet. 90 2 40 4x10⁻² 0.0018% H-C's in Sump Gas

FRACTION OF IODINE RELEASED

FRACTION OF IODINE RETAINED

Normal
IODINE DESORPTION FROM TEDA-
IMPREGNATED CHARCOAL

Symbol	Researcher	Designation	Mesh (U.S.)	Base	P.H.	Depth (in)	Velocity (ft/min)	Loading (mg/cm ²)	Remarks
□	This Study	NAC-G618	8x16	coconut	0	2	40	4×10^{-2}	
■	"	NAC-G618	8x16	coconut	90	2	40	4×10^{-2}	
△	"	NAC-G618	8x16	coconut	90	1½	40	0.2	
▽	"	NAC-G618	8x16	coconut	90	2	40	4×10^{-2}	0.0006 HC's in Swamp Gas

TIME, hours

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Caron et al. (4) did a series of experiments in which charcoal beds were exposed continuously for about two weeks to an air stream containing $1 \text{ mg I}_2/\text{m}^3$. Under these conditions, low release values were observed at low (15%) relative humidity but quite high release values were observed into 90% R.H. air. This observation may have resulted from some fraction of the iodine being in the form of organic iodides, since there is an apparent tendency in experimental systems, for a significant fraction of iodine at low concentration to become organic iodide (3).

The results of Evans et al. (5) are also plotted on Fig. 5. They show the relatively large releases which were observed from a bed of new charcoal while exposed to a $1.5 \times 10^7 \text{ rad/hr Co-60}$ gamma field and the even larger releases observed from a bed of charcoal which had seen three years service prior to the test of release during exposure to the gamma field.

The results from this study with iodized charcoal are shown on Fig. 6, along with results from other studies. In this study, one test with an iodized charcoal prepared from petroleum coke (Witco-42), showed very low release into 0% R.H. air. Two tests of the same charcoal showed almost the same release into 90% R.H. air. One test with a shallower bed (namely 1-1/8-in. as compared to the 2 or 2-1/4-in. beds in the previously mentioned tests) on iodized coconut charcoal (NAC-G617) also resulted in low releases (i.e., $< 10^{-4}$ of the total). One test in which a bed of iodized petroleum coke charcoal (Witco-42) was subjected to 90% R.H. air containing 0.0018 volume percent of hydrocarbon, resulted in a significant increase in the release but the release was still quite low (i.e., well below 10^{-4} of the total).

For comparison, results from Caron et al. (4), who did tests in which the test beds were continuously exposed to a low concentration of I_2 for a long-time, are also plotted on Fig. 6. At both low and high relative humidity, Caron et al. observed low releases which compare well with the observations from the present study.

Adams et al. (6) subjected an iodized, coconut charcoal (BC-727), after loading with iodine, to a gas stream containing quite high concentrations of hydrocarbons. In one experiment the gas stream contained about 0.07 volume percent diethylbenzene; in the other experiment Amsco 125-82 vapor at a concentration which was probably of the same order of magnitude was employed. The concentrations corresponded to an estimated 40% saturation. These experiments resulted in high releases, well over 10^{-3} of the total loading in 48 hours.

Pope and Smith (7) experimented with a 2 ft x 2 ft, pleated bed adsorber module which contained iodized coconut (BC-727) charcoal and which had been in service for about a year. They loaded the bed with a quantity of iodine and then swept it with ambient air. As can be seen by reference to Fig. 6, 10^{-3} of the loading was released in an hour and about 3.5×10^{-3} of the loading was released in two weeks.

A result from the experiments of Evans et al. (5), of iodine release from an iodized coconut charcoal bed while exposed to a $1.5 \times 10^7 \text{ rad/hr Co-60}$ gamma field is also plotted. The observed release in this experiment was high; it exceeded 10^{-3} of the total loading in a few days.

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Figure 7 is a presentation of the results from the present study with TEDA-impregnated, coconut charcoal. The results show an increase in the release into 90% R.H. air over that observed in 0% R.H. air. The release observed into the 90% R.H. air containing 0.0018 volume percent hydrocarbons was slightly less than that observed with 90% R.H. air without hydrocarbons. The difference may not be significant.

C. Discussion

Our ultimate objective is to provide a defensible way to predict, from an in-place measurement of the release into ambient air during a several hour period, the release that could occur over a period of several weeks under accident conditions. It seems to be clear from a survey of the results on Figs. 5 and 6 that accident releases could be greater than 10^{-3} of the total loading from a charcoal bed which had been indicated by an in-place test to release less than 10^{-3} of the total in two hours. (The 10^{-3} value is the allowable fractional release from ORNL containment adsorbers.) It appears that the release depends on at least four environmental parameters: (1) the relative humidity, (2) the service history, (3) organic contamination in the air and (4) ionizing radiation. The experiments, which we have in progress, have the objective of demonstrating the magnitude of the effects of the first three of these parameters. It is anticipated that the results of these experiments along with those from the Savannah River Laboratory program pertaining to the effects of radiation (5,8), will provide an outline of the magnitude of possible iodine releases from charcoal adsorbers under ORNL usage.

It is suggested that an effort toward a more basic understanding of iodine trapping on adsorbers or by other means should be in progress. Although the testing of commercial products under specific conditions anticipated in use is obviously necessary, a better understanding of the processes involved may also become necessary to the development of arguments to adequately defend the efficacy of containment adsorbers.

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Max. & Min. Humidity (% RH)

Max. & Min. Temperature (°F)