DP-MS-71-88

CONF-720614--10

DESORPTION OF RADIOIODINE FROM ACTIVATED CARBON IN AN INTENSE GAMMA RADIATION FIELD

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A Paper for Presentation at the 17th Annual Meeting
of the Health Physics Society
Las Vegas, Nevada
June 12-17, 1972

5/16/72

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ABSTRACT

Radioiodine adsorbed on activated carbon following a major reactor accident can be converted to organic iodides and desorbed in an intense radiation field. The rate of formation and desorption of the organic iodides is a function of radiation field strength, relative humidity, carbon type and service history, and possibly the operating temperature of the adsorber bed. Free radical reactions involving iodine, water, carbon, and an intense radiation field are proposed as the mechanism of organic formation.

Data are presented for desorption rates in humid air from several types of carbon and inorganic-base iodine adsorbers at a gamma dose rate of 1.5×10^7 rads/hour (^{60}Co source). Desorption rates from selected adsorbers are also given for lower dose rates and with varying purge gas compositions as well as under varying temperature and exposure conditions outside the radiation field.

* The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

INTRODUCTION

The activity confinement system for each Savannah River production reactor is designed to collect halogens and particles that might be released in the unlikely event of a reactor accident.[1] A continuing program is in progress at the Savannah River Laboratory to evaluate the performance of the confinement system for removal of airborne radioactivity under a variety of accident conditions and to develop techniques to enhance its reliability and efficiency.[2-10]

One of the parameters which could not be evaluated until recently was the effect of a high intensity radiation field on the iodine retention characteristics of carbon in the system. If a reactor accident did occur, the accumulation and decay of radioiodine on the carbon beds could result in radiation fields in excess of 10^7 rad/hr. Similar radiation fields could be encountered in the carbon filters used in the containment systems of most large reactors including power reactors.

FORMATION OF PENETRATING FORMS OF IODINE IN A RADIATION FIELD

Confinement system studies at Savannah River have shown that elemental iodine retention on activated carbon is most strongly influenced by the operating temperature of the filter beds, the moisture content of the air passing through the beds, and the length of time the carbon has been in service in the system. Extensions of the studies to include the effects of radiation on iodine retention revealed that organic iodides are formed when a system composed of elemental iodine, carbon, and moist air is exposed to an intense gamma radiation field. The extent to which the penetrating iodides are observed to be formed and desorbed from test carbon beds is a function of intensity and duration of irradiation, the carbon type and service history, the composition of the purge gas stream, and possibly the operating temperature of the carbon bed.

Radiation tests were performed in an irradiation facility containing approximately 300,000 curies of ^{60}Co arranged in two rings of slugs (Figure 1). Each ring of 22 slugs is positioned around a 6-inch-diameter aluminum access tube and housed in a 26-foot-deep pit filled with 10,000 gallons of demineralized water. Each tube was fabricated with an "S" bend beginning about 8 feet below the water surface to reduce the radiation dose rate at the top of the access tube to approximately 1 mr/hour. The absorbed dose rate

in the carbon in the test assembly (Figure 2) was 1.5×10^7 rad/hour. Elemental iodine, tagged with ^{131}I, was volatilized into a humid air stream, passed through a test bed containing carbon or other iodine adsorbers, and then passed through a series of backup carbon beds before release to the atmosphere (Figure 3).

Reaction Components

Tests were first performed to demonstrate that the simultaneous presence of carbon, iodine, moisture, and radiation are required for formation of the penetrating iodides. The test carbon was an unimpregnated coconut base carbon. Test data are summarized in Table I.

Formation and desorption of penetrating iodine compounds continues for at least 100 hours when irradiation continues as shown in Figure 4. Effect of carbon type and service history are also shown in Figure 4. Test conclusions are summarized below:

- Preirradiation of carbon caused no penetrating iodide formation.
- Irradiation of I_2-air-moisture mixture in absence of carbon caused no penetrating iodide formation.
- Desorption of penetrating iodides ceased when I_2-loaded carbon was removed from the radiation field.
- Desorption of iodine increases with increasing humidity in the purge gas stream.

- Desorption of iodine continues for at least 100 hours in a radiation field.

From the above, it can be concluded that the necessary components for the formation and desorption of penetrating iodine compounds are iodine, carbon, moisture, and an intense radiation field.

The radiation field strength and possibly the operating temperature of the carbon bed also effect the amount of iodine released as shown in Table II. Since all the dose rate tests were run for the same period of time (5 hours), the differentiation between the effects of total absorbed dose and dose rate cannot be made.

The rate of desorption of iodine in a radiation field as a function of time is shown in Figure 5. From these data, unimpregnated carbon has an initial desorption rate much higher than that of KI_3-impregnated carbon, but after about 15 hours the desorption rate is the same.

Reaction Products

Iodine compounds desorbed from the test carbon bed in the radiation field are passed through a series of backup carbon beds, which are located outside the gamma field. The backup beds are maintained at the same temperature or at higher temperatures than the test bed to prevent condensation of moisture in the backup beds and air lines. The first backup bed contains unimpregnated carbon; the next two backup beds contain KI_3-impregnated carbon.

The distribution of activity on the three backup beds varies with the operating temperature of the beds. When the system is maintained at about 80°C (the same temperature as the test carbon bed), the unimpregnated first backup bed retains 40 to 50% of the desorbed products, and the first impregnated carbon bed retains ∿99% of the activity passing through the first backup bed. Increasing the temperature of the air stream increases the fraction retained on the unimpregnated carbon. This behavior is consistent with that observed earlier[7] for methyl iodide, because increasing the temperature decreases the relative humidity of the air stream and increases the fraction retained on unimpregnated carbon.

Attempts to recover and analyze the activity trapped on the unimpregnated carbon backup beds have been only partially successful. Both inert gas purging and vacuum heating techniques have been attempted with a net removal of <20% of the activity on the bed. The gases removed from the beds are collected in liquid nitrogen cold traps and analyzed by gas chromatography.

Four organic iodides have been identified in the products collected from the backup beds: methyl iodide (CH_3I), methylene iodide (CH_2I_2), ethyl iodide (C_2H_5I), and vinyl iodide (C_2H_3I). Two noniodine compounds (methanol and nitromethane) are usually found, and as many as eight other as yet unidentified compounds are present in most samples. Other techniques for collection and identification of the desorption products are being investigated. The small sample size and large dilution factors make direct

specific analysis difficult (<40 μg of iodine desorbed into ∿8 m^3 of air containing ∿1.5 kg of H_2O during a typical 4-hour desorption).

Reaction Mechanisms

The experiments to date have been scoping studies designed to define the nature and magnitude of the phenomenon, rather than to establish specific mechanisms or rate constants. The data are sufficient, however, to identify the critical components in the system and, thus, to infer some general reaction mechanisms.

Moisture is apparently one of the critical rate controlling components in the system. Because the principal penetrating products appear to be organic iodides, the moisture content of the purge gas stream probably plays a dual role in iodine desorption:

- Radiolytic decomposition of water furnishes the hydrogen required to form stable alkyl iodides.
- The rate of desorption of organic iodides from the test bed is governed by the relative humidity of the purge gas stream.

In the highly energetic system existing in a radiation field of ∿10^7 rads/hour, the reaction mechanisms are probably all free radical reactions. Of the numerous free radical pathways available to form organic iodides, the simplest (and most probable) is the radiation-induced iodination of organic side chains on the basic carbon structure followed by reaction with hydrogen and hydroxyl free radicals to form organic iodides. Thus, for methyl iodide, the reactions

$$I_2 + RCH_3 \longrightarrow RCH_2I + HI$$

$$H_2O + RCH_2I \longrightarrow R\text{-}OH + CH_3I$$

can be postulated. Similar equations can be written for methylene iodide, ethyl iodide, and vinyl iodide.

Sequential hydrogenation of unsubstituted carbon to form methylene free radicals ($\cdot CH_2\cdot$) or methyl free radicals ($H_3C\cdot$) and subsequent reaction with sorbed or free radical iodine is also possible, but somewhat less probable because of the multiple reactions required.

Further evidence for the free radical mechanism postulate is provided by a series of tests in which nearly dry air, humid air, and humid N_2 were used as purge gases.

If the principal reaction mechanism for organic iodide formation is a free radical mechanism, oxygen in the purge gas stream should reduce the organic iodide yield by reacting with iodide precursors. The test results (Table III) show that more iodine is desorbed in N_2 gas than in air and indicate that the postulated free radical mechanism is correct.

Anhydrous air as a purge gas should inhibit organic iodide formation by restricting the supply of free hydrogen to complete the reaction. Equipment limitations prevented running an anhydrous test; however, reducing moisture with a dry air purge decreased iodine desorption more than a factor of ten. In the dry air test, approximately 70% iodine desorption occurred during the loading

phase when air was being drawn through a glass frit containing moist iodine crystals.

SCREENING TESTS FOR ALTERNATIVE IODINE ADSORBERS

The scoping studies previously discussed were designed to define the nature and extent of iodine penetration of activated carbon in the presence of an intense gamma radiation field. In the unlikely event of a major reactor accident, the radioiodine loading on the confinement system carbon could produce a radiation field of sufficient strength to desorb significant quantities of iodine. Consequently, a series of screening tests was undertaken to find alternative iodine adsorbers that are less sensitive to the radiation effects.

Three screening tests and a control test were designed to simulate a range of conditions to which carbon in the confinement system might be subjected in the unlikely event of a major reactor accident. The three conditions are: radiation exposure (as a result of adsorption and subsequent decay of radioiodine on the carbon); high temperature (180°C) exposure after iodine loading (assuming partial failure of emergency core cooling); and artificial weathering using NO_2 to simulate service weathering of the carbon.

Test Conditions

In all tests, 2-inch-diameter by 1-inch-thick test beds were used. Air filtered by a 1-foot-thick carbon bed followed by a

HEPA filter was used in all tests. The filtered air then passed through the test beds at a face velocity of 55 ft/min. Iodine loading was approximately 0.7 mg of I_2/g of carbon for carbon base adsorbers and approximately 0.35 mg of I_2/g of test material for inorganic adsorbers.

Control and Radiation Tests

Test conditions for the radiation screening tests were dictated by the physical size and dose rate obtainable in the ^{60}Co facility (1.5×10^7 rads/hour absorbed dose rate in the carbon) and by equipment design features of the test assembly (e.g., the absence of a condensate trap prevented running at high humidities). The control test was run under the same temperature and humidity conditions as the radiation test, but outside the ^{60}Co radiation field. Elemental iodine was loaded onto the carbon test bed over a 60-minute period in an air stream at 80°C and 50% relative humidity. Iodine was then desorbed for 4 hours at 80°C and 50% relative humidity. Iodine was loaded by vaporizing freshly precipitated $^{127}I_2$ tagged with ^{131}I into a prefiltered air stream.

High Temperature Test

Iodine was loaded onto the test carbon bed in 10 minutes in air at ambient conditions (23°C and ∿50% relative humidity) and desorbed for 4 hours with hot (180°C), dry air. The irradiation test apparatus was not designed to operate above 80°C; therefore the high temperature tests were run in the absence of the high-intensity gamma radiation field.

NO_2 Test

Samples of test carbon were artificially weathered in an NO_2-air stream as discussed in reference 8. Total NO_2 exposure was 91.1 mg of NO_2/g of carbon or the equivalent of 36 months of weathering in the SRP confinement system. Elemental iodine was loaded onto the test bed as described in the high temperature tests. Iodine was desorbed for 4 hours with 80°C air saturated with moisture. As noted in reference 8, the NO_2 weathering technique fails to simulate true service weathering when the test carbon bed is subjected to elevated temperature and airflow before iodine loading; therefore the NO_2 tests had to be run outside the radiation field.

Test Results

A total of 21 different iodine adsorbers were subjected to one or more of the screening tests. The primary objective of these tests was to select the best adsorbers for more detailed testing and eventual use in the confinement system. For this reason, some products that retained iodine poorly in one or more tests were not subjected to the complete series of screening tests.

All tests used new carbon as supplied by the vendors. Several conclusions are indicated by the test data shown in Table IV:

- The iodine retention efficiencies of coconut-base carbons impregnated with KI_3 varied widely from vendor to vendor, particularly in the high-temperature and NO_2 tests. In some cases the base carbon was the same, but different methods of

impregnation were employed. Thus, the method of KI_3 impregnation appears to affect the performance of the product for nuclear applications.

- Petroleum-base carbons had consistently poorer iodine retention properties in the high-temperature test than most coconut-base carbons, regardless of the impregnant.
- Triethylenediamine(TEDA)-impregnated carbons were among the better adsorbers both in the radiation test and the NO_2 test. One adsorber, a TEDA-impregnated coconut-base carbon, gave consistently better test results than all other adsorbers. A similar carbon impregnated with TEDA and KI performed nearly as well as the carbon impregnated with only TEDA in most of the tests.
- The iodized carbons (KI_3, PbI_2, and I_2) are more sensitive to temperature and simulated weathering than either unimpregnated or TEDA-impregnated carbons (the exception being the TEDA-KI combination).
- Use of insoluble PbI_2 instead of highly soluble KI_3 appears to have no benefit for iodine retention under the conditions used in this test series.
- All the impregnated adsorbers performed better in the radiation test than the unimpregnated coconut-base carbons. This is consistent with earlier findings that the principal mechanism of iodine penetration in an intense radiation environment is formation and subsequent desorption of organic iodides.

The two TEDA-impregnated coconut carbons (TEDA and TEDA + KI) have been selected as the best replacement carbons for the Savannah River confinement system. Full-sized beds of both types have been installed in one reactor confinement compartment to evaluate the weathering (service aging) characteristics of each.

SUMMARY

Elemental iodine will react with activated carbon and water in an intense radiation field to form organic iodides, which are poorly retained by unimpregnated carbons. Impregnated carbons, especially coconut shell carbons impregnated either with TEDA or TEDA and KI, retain the organic iodides better in the radiation environment than unimpregnated carbons. Weathering characteristics of these carbons are being determined.

PW:jeb

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TABLE I

Effect of Radiation and Moisture on Iodine Penetration

Iodine Penetration (5 hr), %	Test Conditions
<0.01	Control test, no radiation
<0.01	Preirradiated carbon, no radiation during test
<0.01	Irradiation of I_2, air, and moisture, but not carbon
0.02	Dry air loading and desorption in radiation field
0.14	Moist air loading, dry air desorption radiation field
0.15	Moist air loading in radiation field, desorption outside radiation field
0.30	Moist air loading, ambient desorption, radiation field
0.43	Moist air loading and desorption, radiation field

TABLE II

Iodine Penetration as a Function of Dose Rate and Carbon Type

Carbon	Iodine Penetration, %[a]		
	1.5×10^7 rad/hr at 80°C	1.5×10^7 rad/hr at 60°C	1.4×10^6 rad/hr at 60°C
Unimpregnated	0.296	0.318	0.0165
KI_3-Impregnated	0.0154	0.0083	0.0003

[a] 1-hour loading and 4-hour desorption in 50% relative humidity.

TABLE III

Effect of Purge Gas Composition on Iodine Desorption

Radiation Field, rads/hr	Purge Gas	Relative Humidity, %	Iodine Penetration, %[a]
1.5×10^7	Air	50	0.283
1.5×10^7	N_2	50	0.474
1.5×10^7	Dry Air	<1	0.020

a. 1-hour loading, 4-hour desorption, unimpregnated carbon.

TABLE IV

Screening Test Results

Mfgr.	Adsorber	Impregnant	Measured Iodine Penetration, %[a] Control	Radiation	NO_2	High Temp
A	coconut	none	<0.001	0.283[b]	0.061[b]	0.004
B	coconut	none	<0.001	0.299	-	-
A	coconut	KI_3	<0.001	0.017[b]	0.229[b]	0.052
A	coconut	KI_3	0.002	0.132[b]	-	-
B	coconut	KI_3	<0.001	0.014[b]	0.029[b]	0.028[b]
B	coconut	KI_3	<0.001	0.029	0.074	0.056
C	coconut	KI_3	0.001	0.030[b]	0.364	18.08
D	coconut	KI_3	-	0.045	0.552	2.412
E	petroleum	KI_3	0.011	0.058[b]	2.049[b]	6.484[b]
B	coconut	I_2	<0.001	0.021	0.043	0.070
A	coconut	PbI_2	0.009	0.046	0.117	-
A	coconut	PbI_2	-	-	0.029	-
B	coal	PbI_2	0.002	0.015	1.877[b]	-
B	coconut	PbI_2	<0.001	0.160[b]	0.433	0.084
B	coconut	KI + TEDA	<0.001	0.037[b]	0.046[b]	0.006[b]
B	coconut	TEDA	<0.001	0.003[b]	0.018[b]	0.003[b]
E	petroleum	TEDA	-	0.008	0.080	12.03
E	petroleum	TEDA	-	0.014	0.028	4.556
B	inorganic	Ag	-	0.168	-	-
B	inorganic	Ag	0.008	0.195	-	-
F	inorganic	Ag	0.002	0.011	-	-

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a. Test conditions are described in text.

b. Average of replicate determinations.

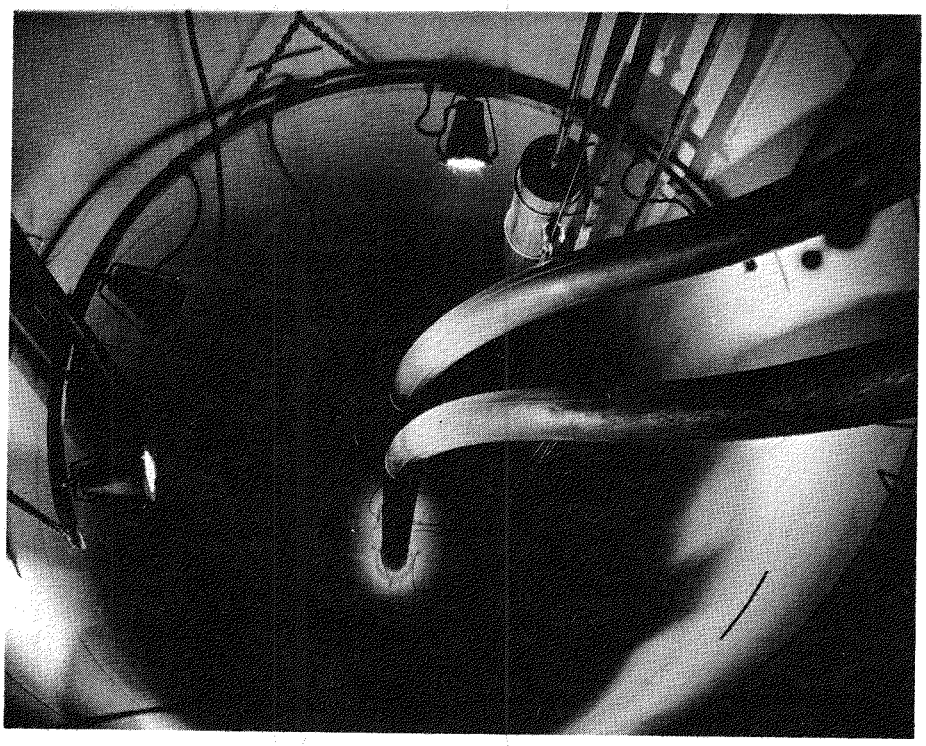

FIG. 1 ALUMINUM TUBES LEADING TO ^{60}Co SOURCE

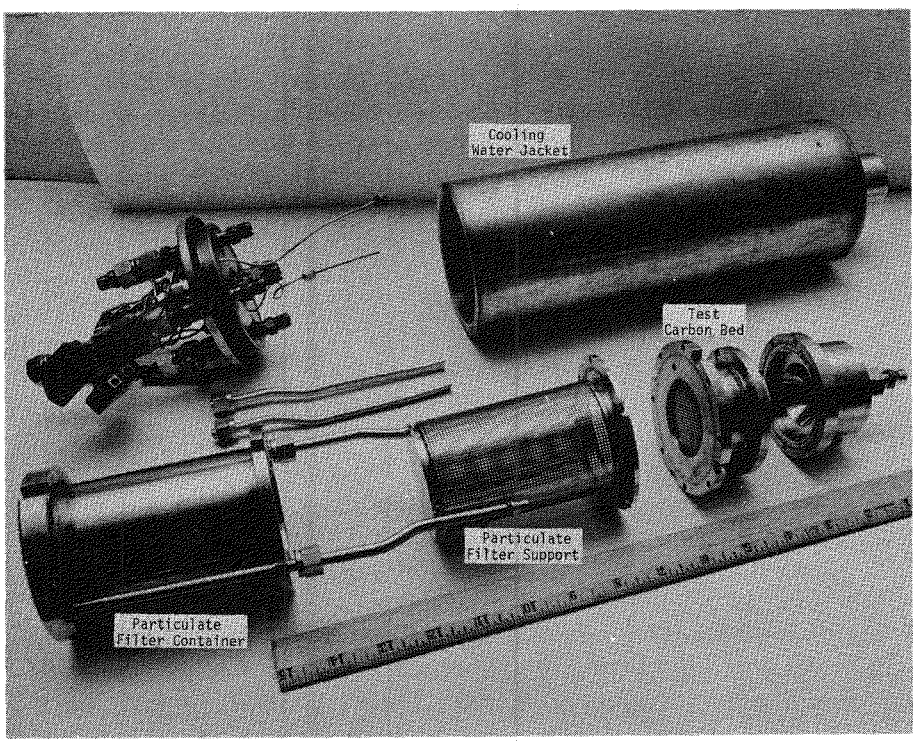

FIG. 2 TEST CARBON BED ASSEMBLY AND WATER COOLING JACKET

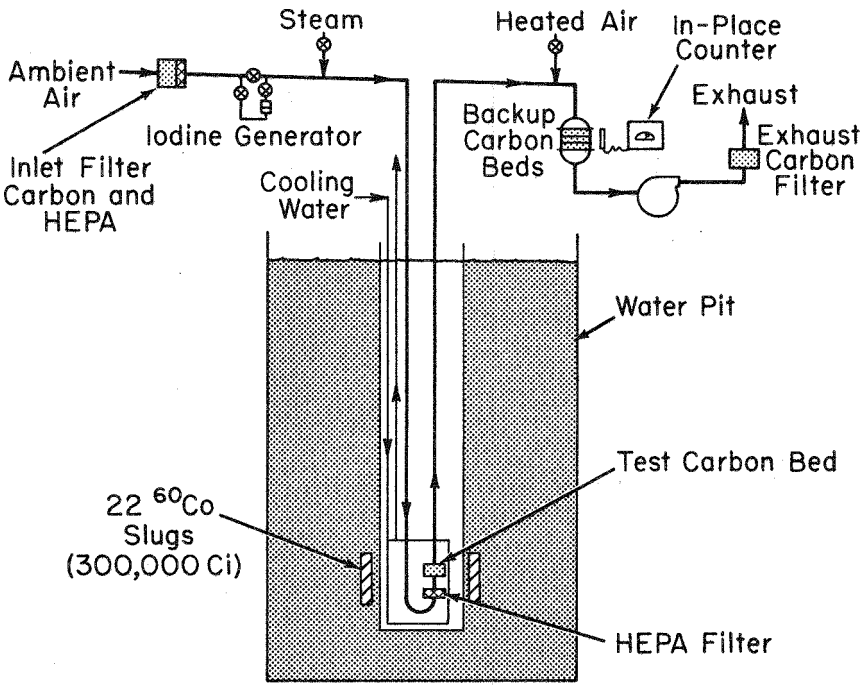

FIG. 3 IRRADIATION TEST EQUIPMENT

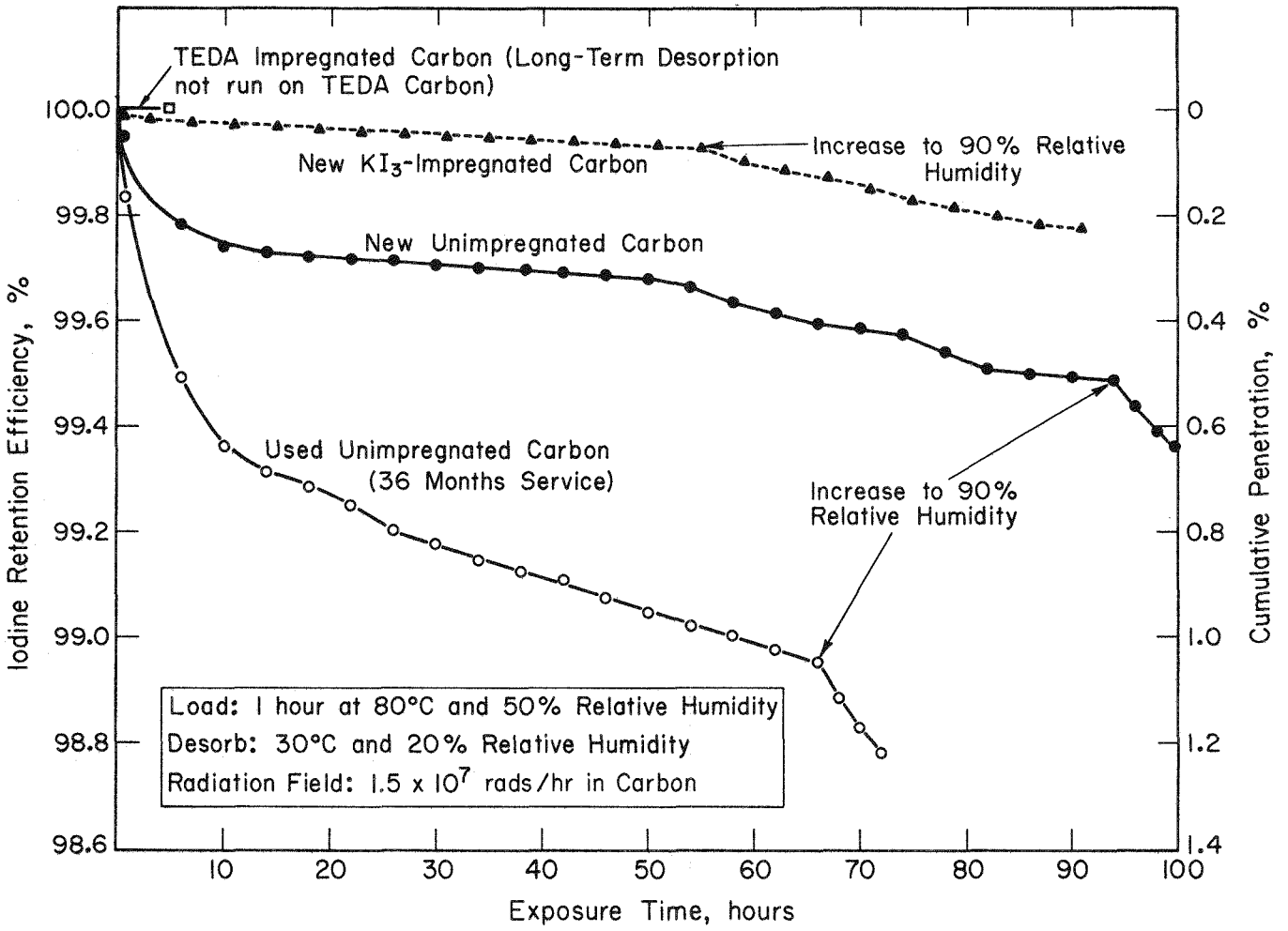

FIG. 4 EFFECT OF RADIATION ON IODINE RETENTION

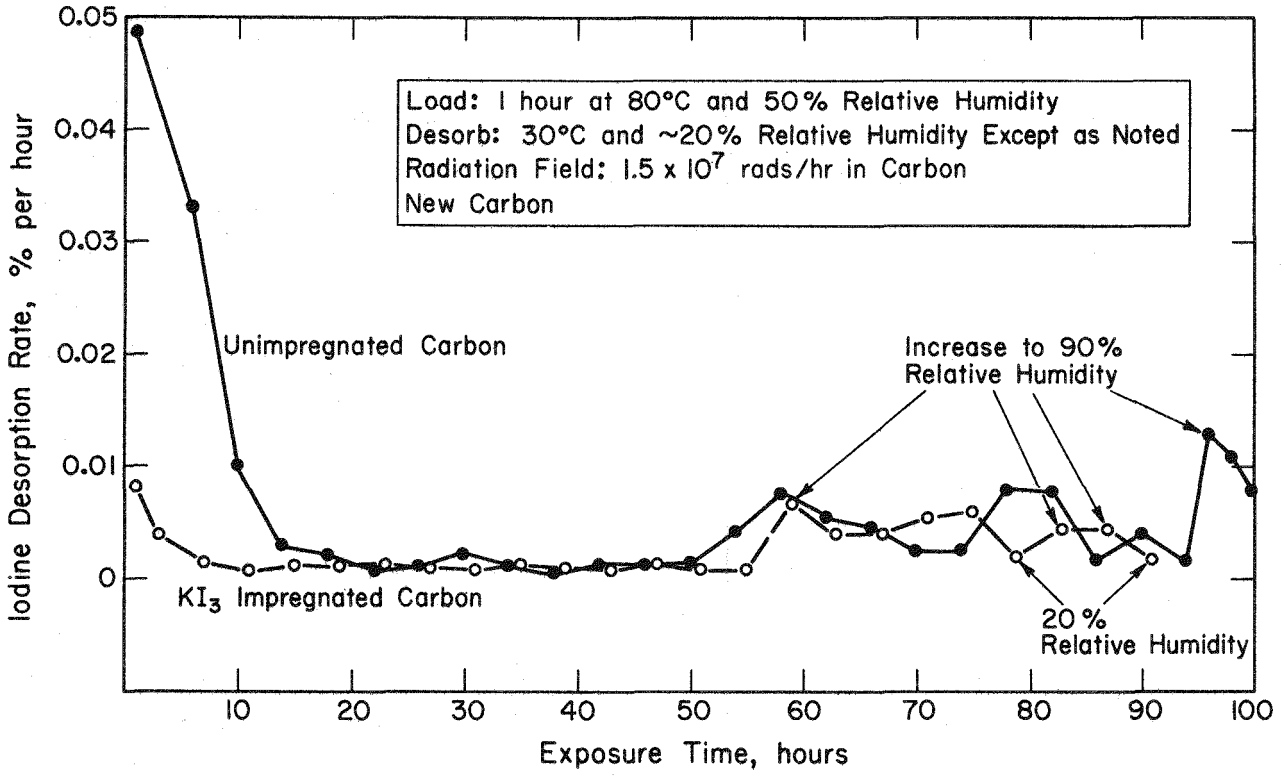

FIG. 5 IODINE DESORPTION RATE OF NEW CARBONS