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DP-1259

AEC RESEARCH AND DEVELOPMENT REPORT

IODINE RETENTION STUDIES

PROGRESS REPORT

JANUARY - JUNE 1970

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Aiken, South Carolina

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by

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May 1971

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ABSTRACT

In tests simulating exposure conditions of the confinement system following power surge and loss-of-coolant accidents, the iodine retention efficiencies of carbon samples were measured. In both tests, the iodine retention efficiency decreased with increased carbon service, but was within specification for up to 42 months of service. In methyl iodide radiolysis tests, a gamma radiation field of ~1.7 x 10^7 rads/hr did not significantly extend the effectiveness of carbon for methyl iodide adsorption.

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INTRODUCTION

The activity confinement system for each Savannah River production reactor is designed to collect radioactive gases and particles that might be released in the unlikely event of a reactor accident. At the request of the AEC Division of Operational Safety, a continuing program is in progress at the Savannah River Laboratory to evaluate the performance of the carbon used in the confinement system for iodine removal under adverse operating conditions and to develop techniques to enhance its reliability and efficiency.

Previous reports summarize the progress from January 1965 to December 1969.[1-4] This report summarizes the iodine retention studies at the Savannah River Laboratory from January to June 1970.

SUMMARY

The iodine retention efficiencies of carbon samples were measured in tests simulating the exposure conditions of the confinement system following power surge and loss-of-coolant accidents. Iodine retention decreased with increasing carbon service, but remained within specification (99.85% removal of elemental iodine) for up to 42 months of service. No significant differences were found in aging effects when comparing the two tests. No satisfactory method of extending the useful life of carbon (by partial regeneration) has been developed.

Methyl iodide penetration through Type 416 unimpregnated carbon was reduced by up to 50% as a mixture of methyl iodide, elemental iodine, steam, and air at >20% relative humidity flowed through a 1-in.-thick test carbon bed exposed to a gamma radiation field of $\sim$1.7 x 10^7 rads/hr. In tests at less than 5% relative humidity, the radiation did not affect penetration.

The presence of carbon significantly inhibits the formation of nonpenetrating forms of iodine from methyl iodide in a radiation field. The radiation field is most beneficial at high relative humidity where methyl iodide adsorption efficiency is low, and least beneficial at low relative humidity where efficiency is high. Therefore, the radiation field does not significantly extend the effectiveness of carbon for methyl iodide adsorption.

DISCUSSION

RETENTION OF IODINE UNDER ACCIDENT CONDITIONS

Test Modifications

The iodine adsorption efficiency test,[3] used to determine whether or not iodine removal in the Savannah River confinement system is within specification (>99.85% removal), was modified to evaluate carbon performance under accident conditions. The original test[3] measured the iodine adsorption efficiency of carbon and showed the effects of service, iodine loading, and partial regeneration on iodine adsorption efficiency. The modified test determines carbon performance under two simulated reactor accident conditions: a power surge and a loss of coolant. The term iodine retention efficiency is used in this report because both adsorption and desorption determine how much iodine is retained by carbon.

Power Surge Test

In a power surge accident, the temperature of the reactor would increase rapidly, and a burst of steam would be released to the ventilation air. After a brief interval, the fuel would begin to melt, and fission products would be released in a steam atmosphere. Hence, in a power surge accident carbon in the confinement system would first be exposed to a steam-air mixture, then to a steam-air-fission product mixture, and then to ambient conditions.

In the power surge test, the apparatus (Fig. 1) with the test bed in place is heated to 80°C in about 30 minutes to equilibrium temperature. To minimize regenerative effects, no air is passed through the test bed during this heating. The apparatus is kept at 80°C to minimize moisture entrainment while a steam-air mixture at 80°C flows (at a face velocity of 65 ft/min) through the test bed for 5 minutes. Iodine is then loaded on the test bed by passing a steam-air-iodine (tagged with ^{131}I) mixture through the test bed for 10 minutes. After the iodine is loaded on the test bed, air at 40°C and ~80% relative humidity flows through the apparatus for 15 minutes. Any iodine that penetrates the test bed is collected on backup beds. The iodine retention efficiency is the ratio of the iodine remaining on the test bed to the iodine loaded on the test bed. Carbon can be evaluated by the power surge test either before or after annual partial regeneration.[2-4]

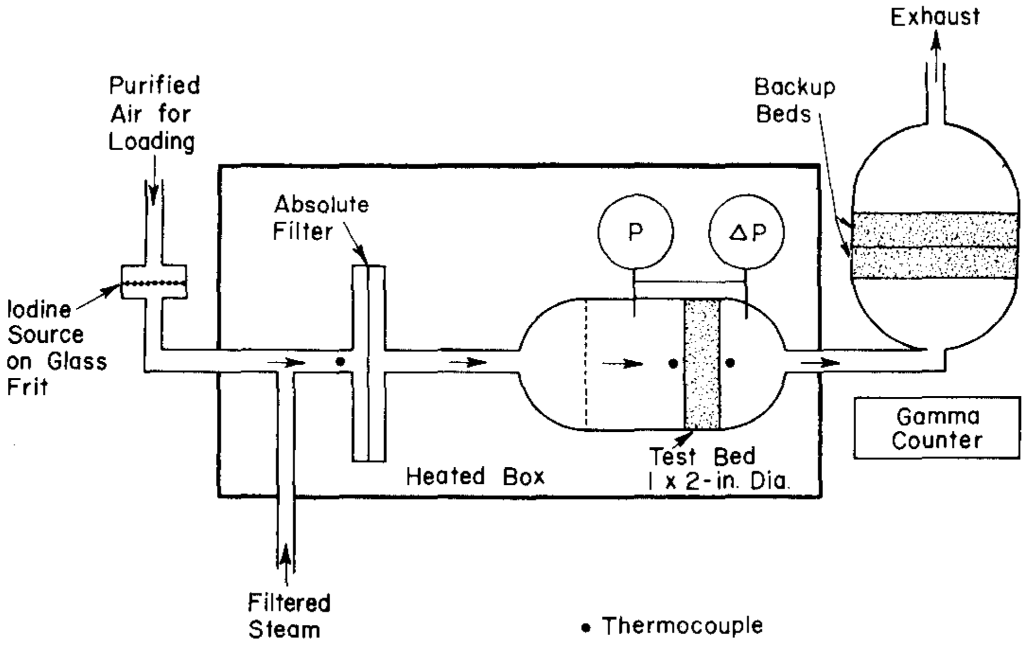

FIG. 1. SCHEMATIC OF DESORPTION APPARATUS

The test procedure used during the previous report period[4] was modified slightly to reflect more accurately the exposure conditions expected in Savannah River reactors in the unlikely event of a power surge accident. The modifications include reducing the premeltdown steam-air equilibration period (before iodine loading) from 10 to 5 minutes, and increasing the temperature of the postmeltdown air stream (after iodine loading) from 23 to 40°C.

Loss-of-Coolant Test

In a loss-of-coolant accident, coolant would drain suddenly from the reactor, and the temperature of the fuel would increase rapidly. If the emergency core cooling system failed to operate promptly, the fuel would melt and release fission products to the ventilation air. Possible subsequent quenching of the hot fuel with water could release a burst of steam to the ventilation system. Hence, in a loss-of-coolant accident, carbon in the confinement system would be exposed to fission products in ambient air (possibly followed by a steam-air mixture) and then to prevailing ambient conditions.

In the loss-of-coolant test, iodine (tagged with ^{131}I) is loaded on the test bed in 10 minutes in ambient air at a face velocity of 65 ft/min. The air flowing through the apparatus is heated to 80°C for 10 minutes, and then a steam-air mixture at 80°C flows through the test bed at a face velocity of 65 ft/min for 5 minutes. After the steam-air treatment, air at 40°C and 80% relative humidity flows through the test bed at a face velocity of 65 ft/min for 20 minutes. Iodine that penetrates the test bed is collected on backup beds. The iodine retention efficiency is the ratio of the iodine remaining on the test bed to the iodine loaded on the test bed. Carbon can be evaluated by a loss-of-coolant test either before or after the annual partial regeneration.[2-4]

As indicated in the previous report,[4] the iodine retention efficiency of any carbon is influenced most significantly by the length of exposure to steam-air mixtures (Fig. 2). A critical evaluation of conditions expected in the Savannah River reactors in the unlikely event of a loss-of-coolant accident shows that steam evolution after core meltdown is expected to last less than 5 minutes. Thus, the 5-minute steam-air exposure period in the loss-of-coolant test represents an upper limit for iodine desorption time at the higher (80°C) temperature. An extended exposure period at 40°C and 80% relative humidity is expected to follow the steam evolution period.

Results

The retention of iodine by activated carbon in the Savannah River confinement system decreases with increasing service life. No significant differences in the effects of aging were found between the two tests simulating accident conditions at Savannah River (Fig. 3). Thus, the carbon in this system remains within specification (99.85% iodine retention) for up to 42 months of service.

No credit is taken for the higher iodine retention efficiencies that sometimes result from partial regeneration of carbon during the annual "Freon"* leak check. Data reported previously[4] indicate that the regeneration effects are of short duration and do not significantly improve the subsequent performance of the carbon (see also later section of this report).

Iodine retention efficiency decreases with increased service because impurities such as SO_2 and organic matter are adsorbed, and because oxides of nitrogen destroy active adsorption sites for iodine.[3]

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* Registered trademark of Du Pont.

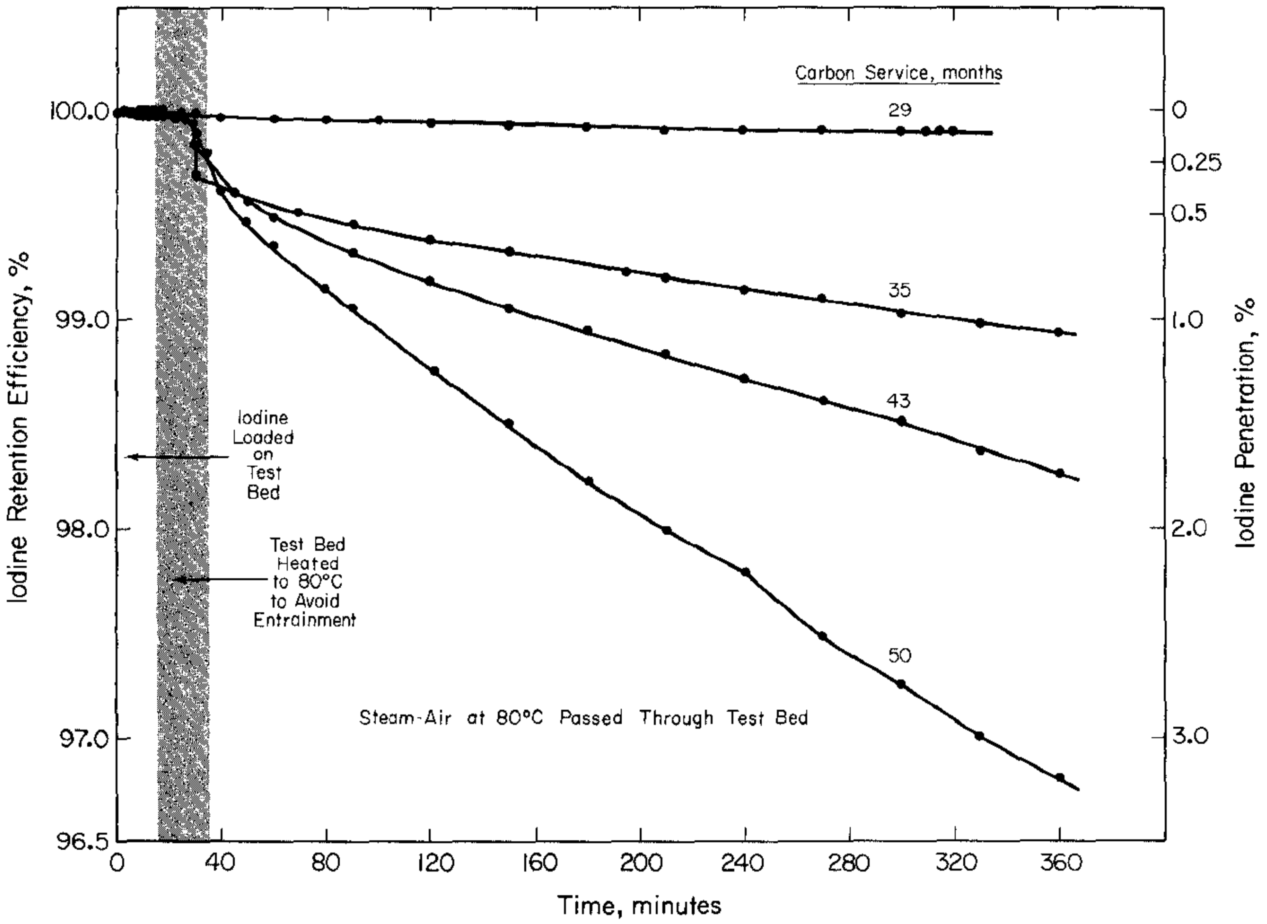

FIG. 2 EFFECT OF STEAM-AIR EXPOSURE TIME ON IODINE RETENTION EFFICIENCY

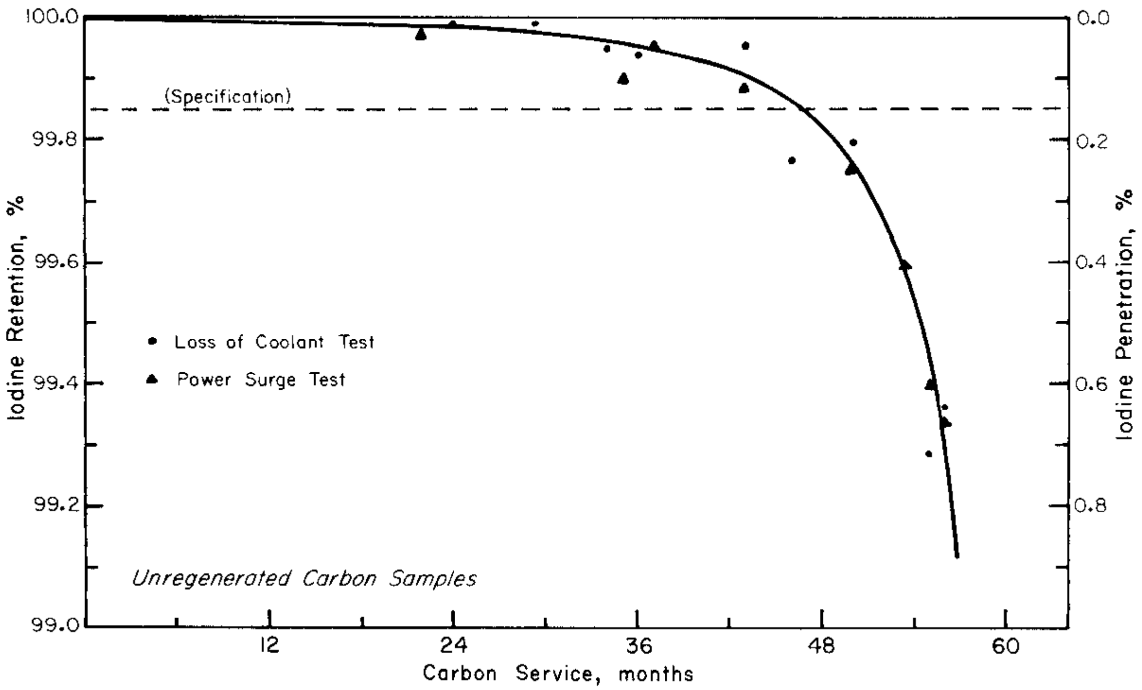

FIG. 3 EFFECT OF SERVICE ON CARBON

In the power surge test, nearly all of the iodine penetrated the test bed during iodine loading (Fig. 4). After the iodine is adsorbed on the carbon from steam-air at 80°C, air at 40°C at 80% relative humidity did not cause further iodine desorption.

In the loss-of-coolant test, most of the penetration resulted from desorption of iodine during the 80°C steam-air exposure period (Fig. 5). Again, extended exposure to air at 40°C and 80% relative humidity resulted in no further desorption of iodine.

Additional tests to demonstrate the effect of temperature and moisture on the desorption of iodine from carbon are summarized in Figure 6. In these tests (not under postulated accident conditions), air at 80°C (saturated or dry) desorbs significant iodine from carbon with 50 months service. Saturated air (steam-air) desorbs nearly twice as much iodine as dry air at 80°C. Exposure to air at 40°C (saturated or dry) caused no further desorption after the initial desorption by air at 80°C.

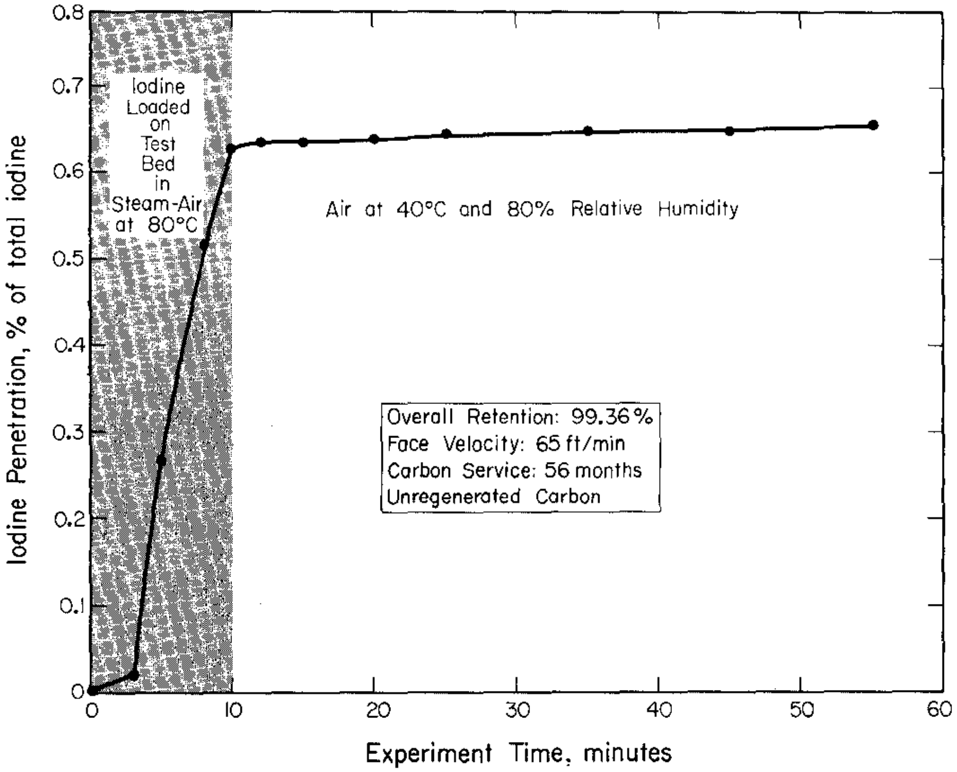

FIG. 4 IODINE PENETRATION DURING POWER SURGE TEST

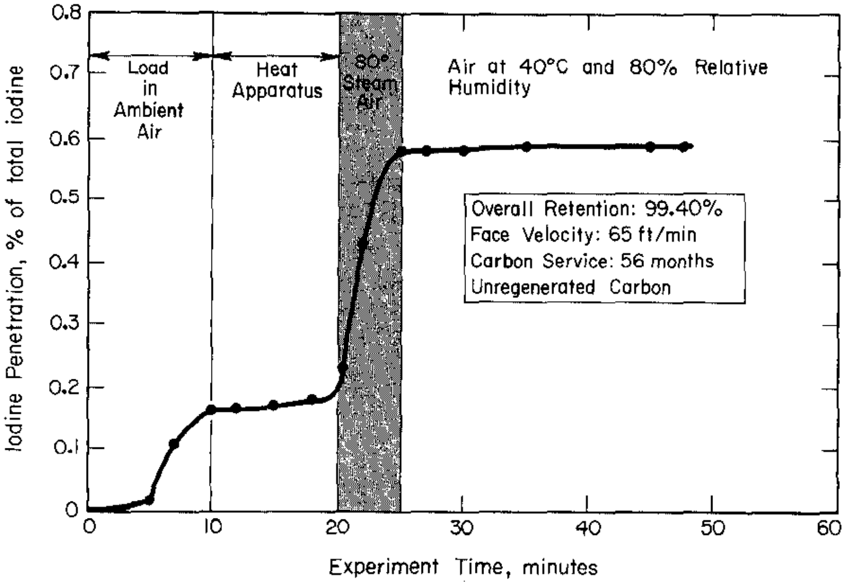

FIG. 5 IODINE PENETRATION DURING LOSS-OF-COOLANT TEST

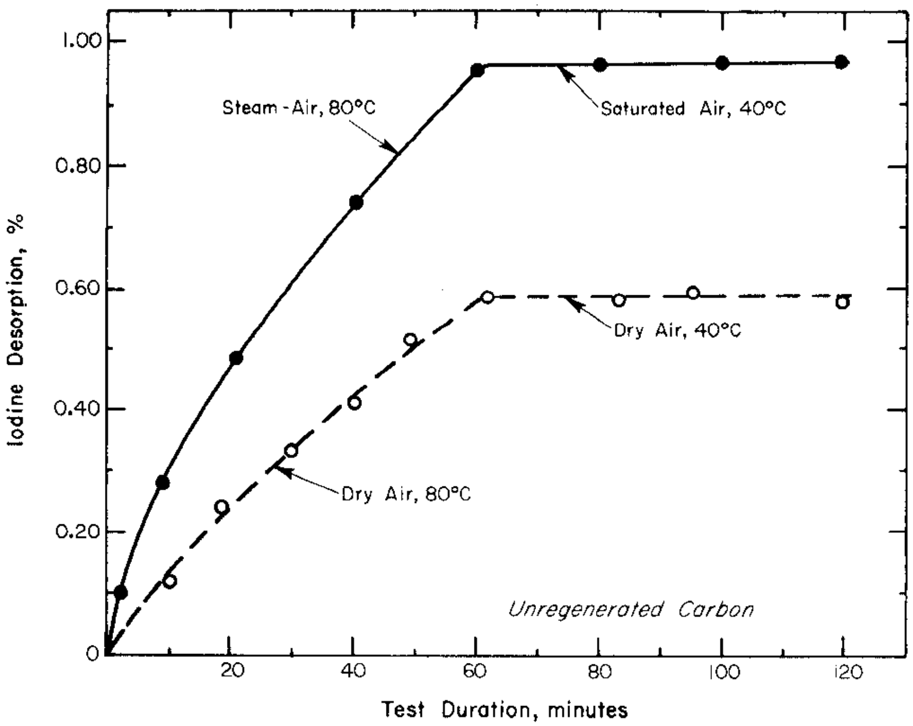

FIG. 6 EFFECT OF MOISTURE AND TEMPERATURE ON CARBON WITH 50 MONTHS SERVICE

PARTIAL REGENERATION OF CARBON

Investigation of partial regeneration of carbon by heating and addition of a denitrating agent (formaldehyde) continued. Data reported earlier[4] indicated a significant improvement in iodine retention efficiency by passing dry air at 60°C through the carbon bed. 60°C was chosen because that is the approximate temperature attained in the confinement compartments during leak testing operations in the summer months. Heat losses through the uninsulated walls and limited heating capacity in the compartments restrict regeneration temperatures to about 40°C during the winter months, however. As shown in Table I, partial regeneration of used carbons at 40°C results in little or no improvement in iodine retention. Measured surface areas of regenerated and unregenerated carbon are shown for comparison with iodine retention efficiency.

TABLE I

Iodine Retention Efficiency and Surface Area of Carbon After Partial Regeneration

Carbon Service, months	Regeneration[a]	Surface Area, m^2/g	Power Surge Test Efficiency, %	Loss-of-Coolant Test Efficiency, %
24	None	490	99.97	99.94
24	40°C	470	99.97	99.91
24	60°C	600	99.98	99.95
34	None	450	99.89	99.95
34	40°C	620	99.97	99.99
34	60°C	780	99.99+	99.99+
37	None	480	99.95	99.94
37	40°C	350	99.95	99.87
37	60°C	540	99.99+	99.97

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[a] 48 hours exposure to dry air stream at a face velocity of 7.5 ft/min.

Attempts to regenerate used carbon samples with a denitrating agent (formaldehyde) indicate that this method of reclaiming carbon is unsatisfactory because it reduces iodine retention (Table II).

TABLE II

Effect of Heat and Formaldehyde on Carbon

Carbon Service, months	Formaldehyde Added, mg/g C	Regeneration Temperature, °C	Iodine Retention Efficiency,[a] %
50	None	None	97.65
50	None	40	99.31
50	0.37	40	98.75
50	3.7	40	99.24
50	None	60	99.85
50	0.37	60	99.77
50	3.7	60	99.62
New	None	None	99.996
New	0.37	None	99.993
New	0.37	40	99.987
New	0.37	60	99.989

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[a] Retention after exposure to 80°C steam-air mixture for 60 min.

Further studies of aging and regeneration effects on carbon will be directed toward developing accelerated aging techniques (such as exposure to elevated concentrations of NO_2, organics, etc.) and installing carbon bed exposure facilities in the reactor building exhaust air stream. The latter test facility (in parallel with the confinement system) will permit in-service exposure of small test beds containing samples of special carbons (new or regenerated) without disturbing the confinement system.

METHYL IODIDE RADIOLYSIS TESTS

Under reactor accident conditions, methyl iodide would be exposed to an intense gamma radiation field generated by fission products adsorbed on the carbon beds.

The effect of gamma radiation on the adsorption of iodine and methyl iodide on activated carbon is being measured as part of a continuing program,[1-4] in support of the reactor confinement facilities at Savannah River.

This report presents results of tests to determine the effects of relative humidity, face velocity, methyl iodide loading on the carbon, and methyl iodide concentration.

Apparatus and Techniques

The methyl iodide radiolysis apparatus is shown in Figure 7. A mixture of ambient air, elemental iodine, methyl iodide tagged with ^{131}I, and steam was passed through a test bed of carbon positioned in the gamma field and then through three backup carbon beds. Each backup carbon bed was one inch thick and contained impregnated carbon treated in a proprietary manner to retain methyl iodide.

A gamma detector was mounted three inches from the backup beds and connected to a scaler. Methyl iodide penetration of the test bed as a function of time during each test was measured by taking a one-minute count every two minutes during the methyl iodide loading and every ten minutes during the remainder of the test.

The gas stream was prepared by mixing ambient air at ~25°C with saturated steam at 100°C. A volumetric ratio of air to steam of 2.28:1 produces a slightly super saturated steam-air mixture with a temperature of 65°C.[5] The steam-air-iodine mixture flowed to and from the test carbon bed through tubing insulated with a jacket through which water flowed at 70°C. Dry air at 100°C was added to the steam-air-iodine mixture immediately upstream of the backup carbon beds to reduce relative humidity to <10%. Elemental iodine was injected to the gas stream by passing ambient air at constant velocity through a glass frit containing solid iodine.

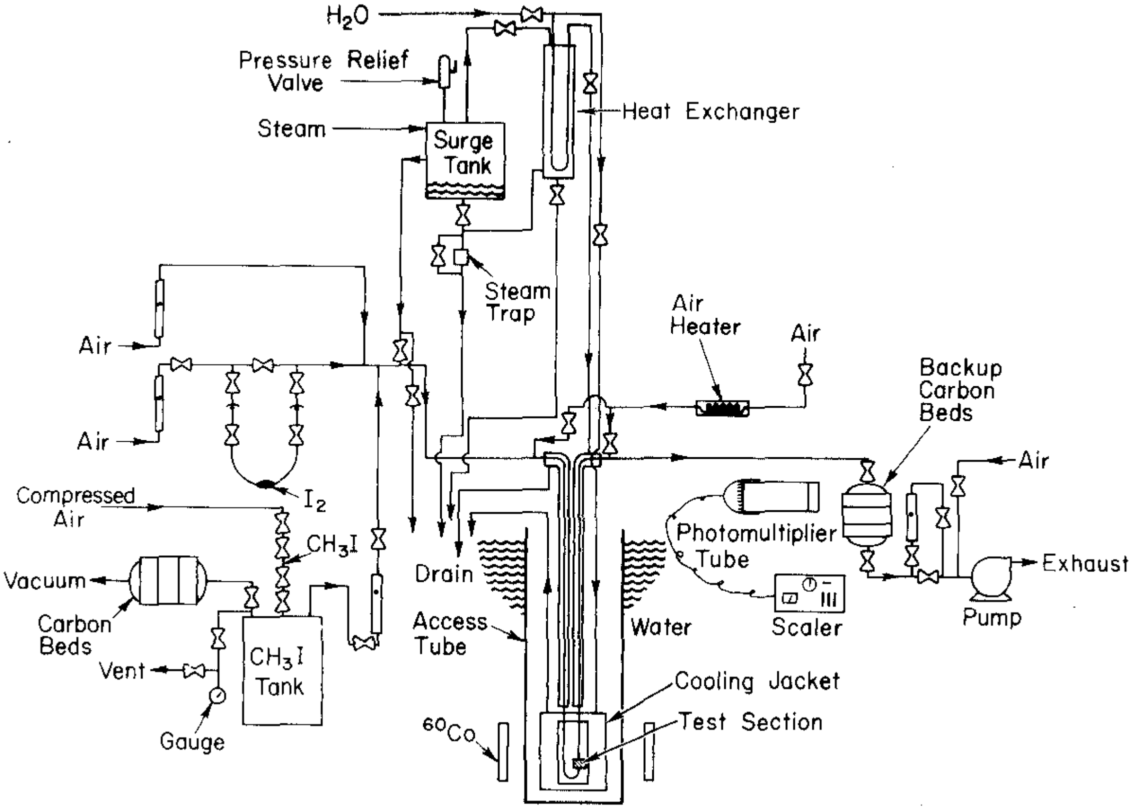

FIG. 7 METHYL IODIDE RADIOLYSIS APPARATUS

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

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

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* Registered trademark of Du Pont.

Samples of particulate filter media and other materials used in filter construction were irradiated in the test carbon bed assembly during some tests in the radiation field. Physical properties of these materials before and after irradiation are being determined at the Naval Research Laboratory in Washington, D. C.

The test carbon bed assembly and jacketed tubing were inserted into one of the two six-inch-diameter air-filled aluminum tubes leading to the ^{60}Co source (Fig. 8). The source (Fig. 9) consists of ~750,000 curies of ^{60}Co in 44 slugs (22 slugs surrounding the base of each of the two tubes). Shielding is provided by 24 feet of water. The gamma radiation field inside the test carbon bed assembly was determined to be $\sim 1.7 \times 10^7$ rads/hr by dosimetry methods described in Reference 6.

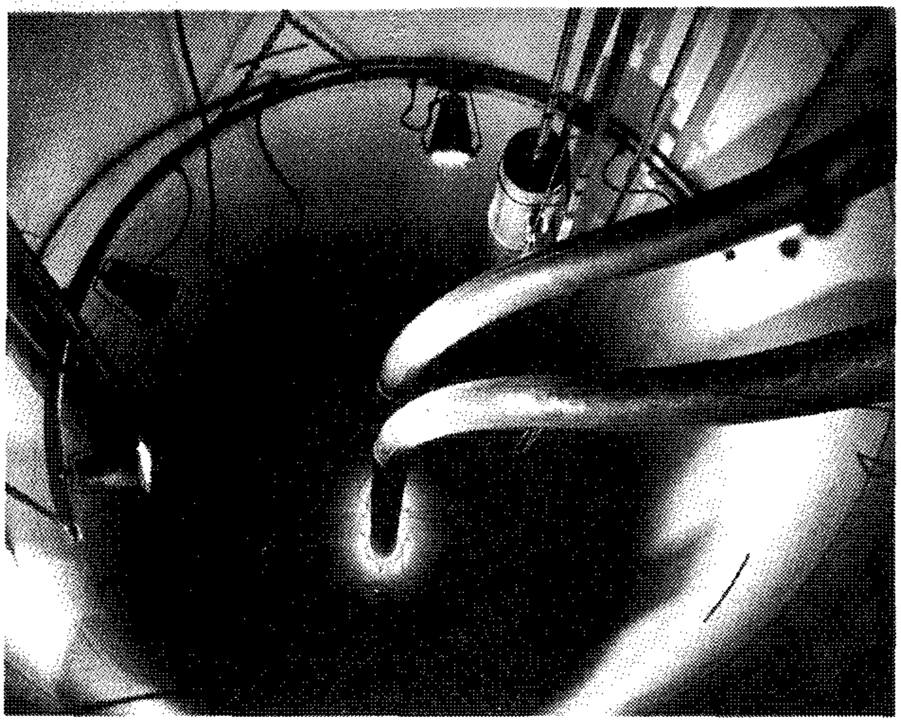

FIG. 8 ALUMINUM TUBES LEADING TO ^{60}Co SOURCE

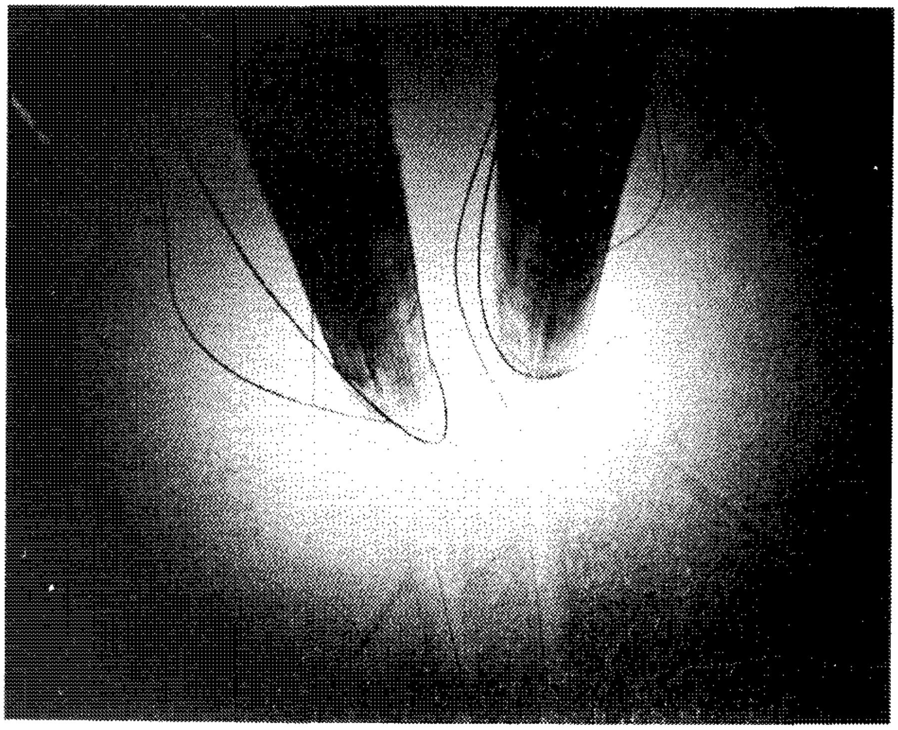

FIG. 9 ^{60}Co SOURCE

In tests in the gamma radiation field, the temperature of the test carbon bed assembly was controlled by flowing water through a jacket surrounding the assembly to remove heat generated by gamma absorption. In tests out of the gamma radiation field, the test bed assembly was heated by flowing hot air through the jacket.

Each test lasted three hours. The system was preheated with a dry air flow at 65°C for 30 minutes. Then the system was pre-equilibrated with a steam-air flow at 60°C for 30 minutes. When pre-equilibration was complete, 17% of the air flow was diverted through the elemental iodine source holder to begin elemental iodine sample injection. Five minutes later methyl iodide sample injection was started and continued for 60 minutes. After 60 minutes of loading, both sample holders and steam were valved off. Ambient air flow was continued through the system for 60 minutes with the temperature of the test carbon bed reduced to ~40°C.

After each test, major parts of the apparatus were disassembled. The test carbon bed, particulate filter support (perforated metal cylinder), particulate filter container, and cooling water jacket are shown in Figure 10. The amount of ^{131}I tracer on each piece was determined by counting in a gamma detector. A computer program converts these counts to mass of CH_3I and calculates penetration of the test carbon bed, material balance, methyl iodide loading on the test carbon bed, and methyl iodide adsorption on other pieces of the apparatus.

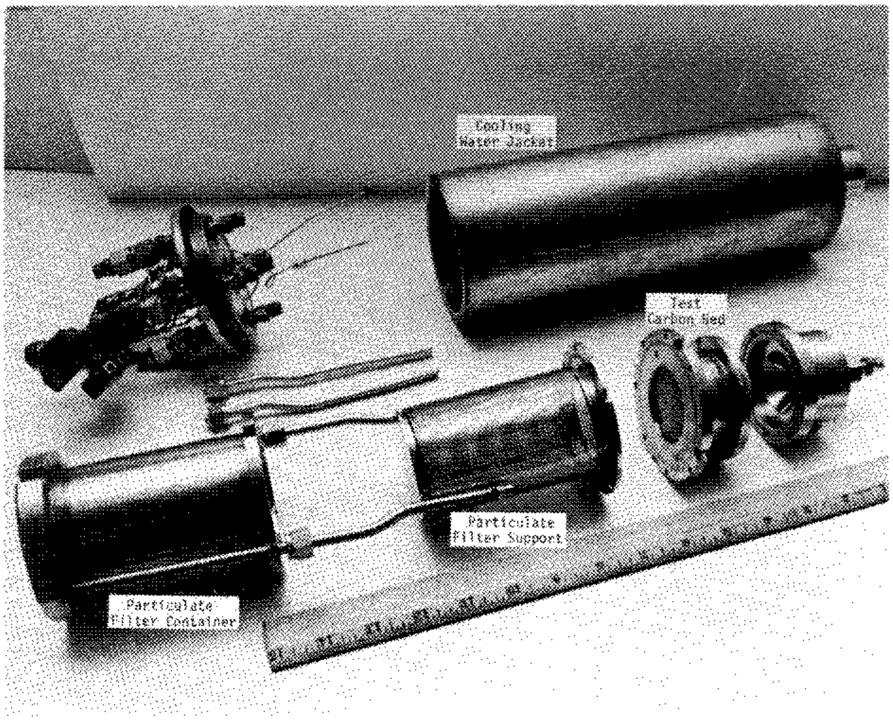

FIG. 10 TEST CARBON BED ASSEMBLY AND WATER COOLING JACKET

Results

Effect of Relative Humidity

In tests with and without the gamma field, relative humidity and face velocity were test variables for Type 416 unimpregnated carbon* at constant iodine loading and injection rate. As shown in Figure 11, methyl iodide penetration of the test carbon bed increased with increasing relative humidity. Penetration increased from 9.8% in the radiation field to 19.5% with no radiation field at 55 ft/min face velocity and 27% relative humidity.

Tests at <5% relative humidity at both velocities resulted in penetrations which indicated no effect of the radiation field. More data would be needed at 10 to 30% relative humidity to adequately predict penetration as a function of relative humidity at both velocities. Average methyl iodide loading on the carbon was ~0.10 mg/g carbon.

Effect of Face Velocity

Results of tests with and without the gamma field with face velocity as the test variable are shown in Figure 12. The radia-

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* Product of Barnebey-Cheney Company, Columbus, Ohio.

tion field reduced penetration by ~5% at 55 ft/min velocity and by ~25% at 11 ft/min velocity. The reduction in penetration became larger as face velocity was reduced, probably because of increased methyl iodide residence time in the gamma field at the lower velocity.

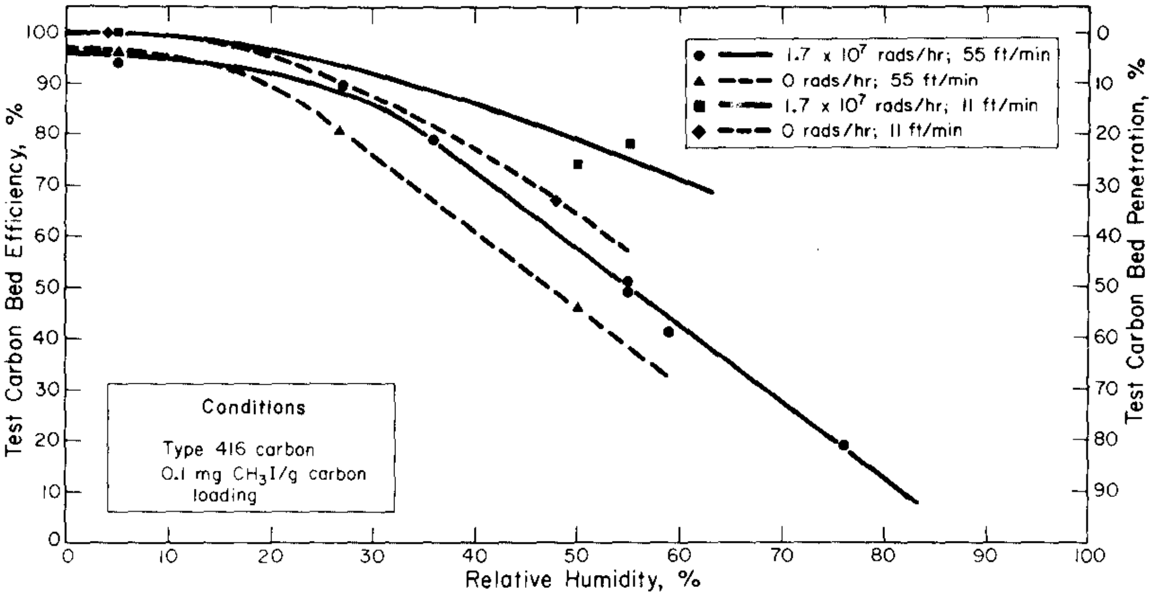

FIG. 11 EFFECT OF RELATIVE HUMIDITY ON EFFICIENCY OF TEST CARBON BED

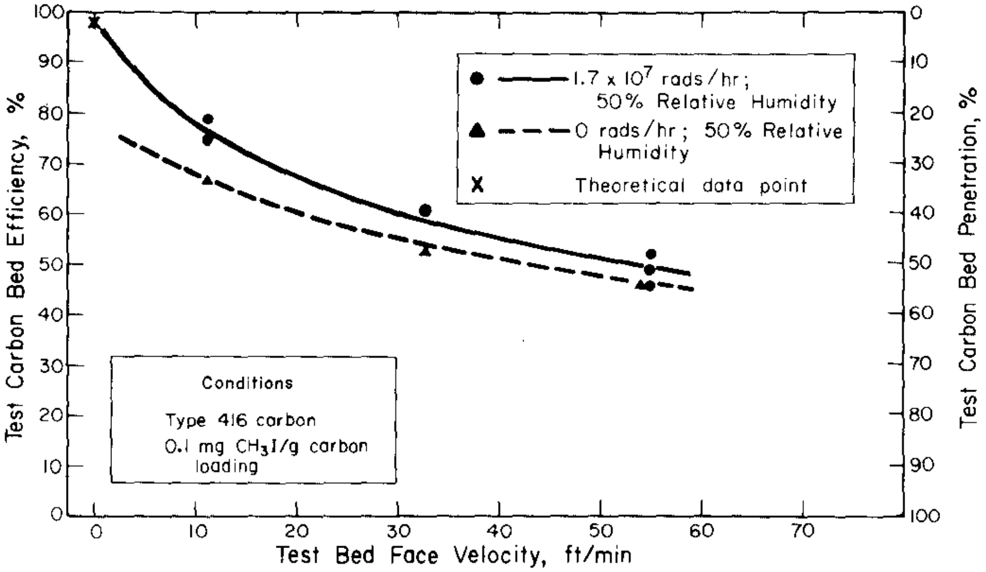

FIG. 12 EFFECT OF FACE VELOCITY ON EFFICIENCY OF TEST CARBON BED

Based on the assumption that the reduced penetration in the radiation field was the result of radiolytic decomposition of the methyl iodide, a theoretical point was placed at zero velocity. At zero velocity, residence time and radiation dose to the methyl iodide would approach infinity. Concentrations of air, steam, and methyl iodide ($\sim 10^3\ \mu g/m^3$) would strongly favor greater than 99% decomposition of the methyl iodide. Data reported by Tang and Castleman[7,8] indicate that an absorbed dose of less than 10^6 rads would produce greater than 99% decomposition. Thus, a penetration of less than 1% would be expected at zero velocity. These data were obtained in the absence of carbon with static test conditions.

Typical data on penetration versus time during tests at 55 ft/min velocity and at 11 ft/min velocity are shown as the lower curves in Figures 13 and 14, respectively. The upper curves show percent of the methyl iodide sample which has been injected into the system as a function of time during the test. The percent of the total methyl iodide sample adsorbed on the test carbon bed at any time during the test is the difference of the two curves at that time.

Residence times are shown also in Figures 13 and 14. Residence time in the radiation field was determined at both velocities by subtracting calculated residence time in tubing carrying the sample to and from the radiation field from the measured delay in arrival of initial penetration at the backup beds.

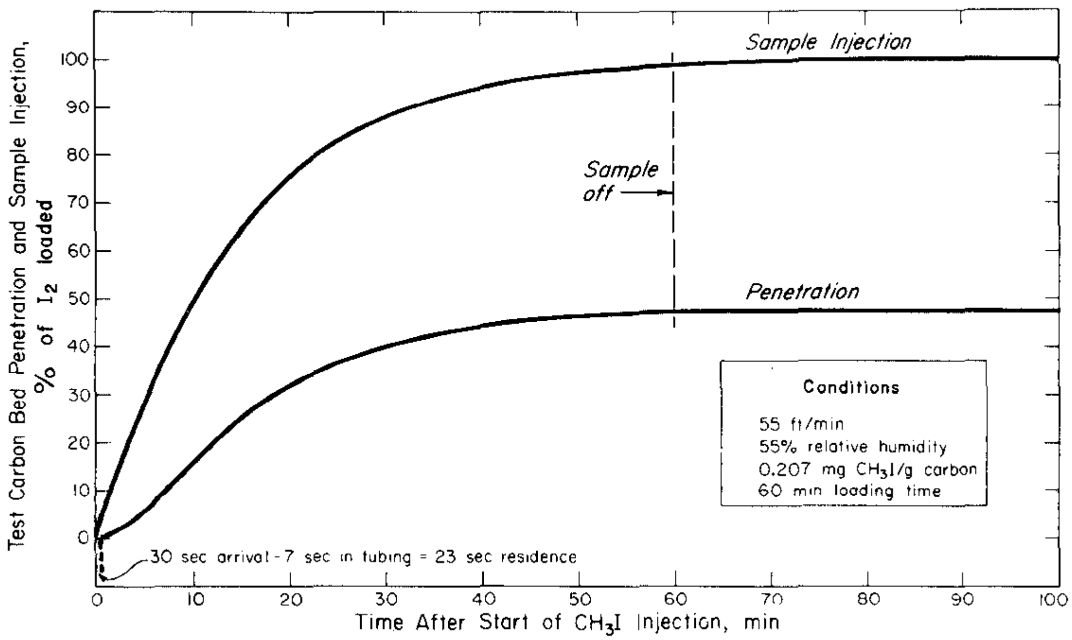

FIG. 13 PENETRATION OF METHYL IODIDE AS A FUNCTION OF TIME (Face Velocity, 55 ft/min)

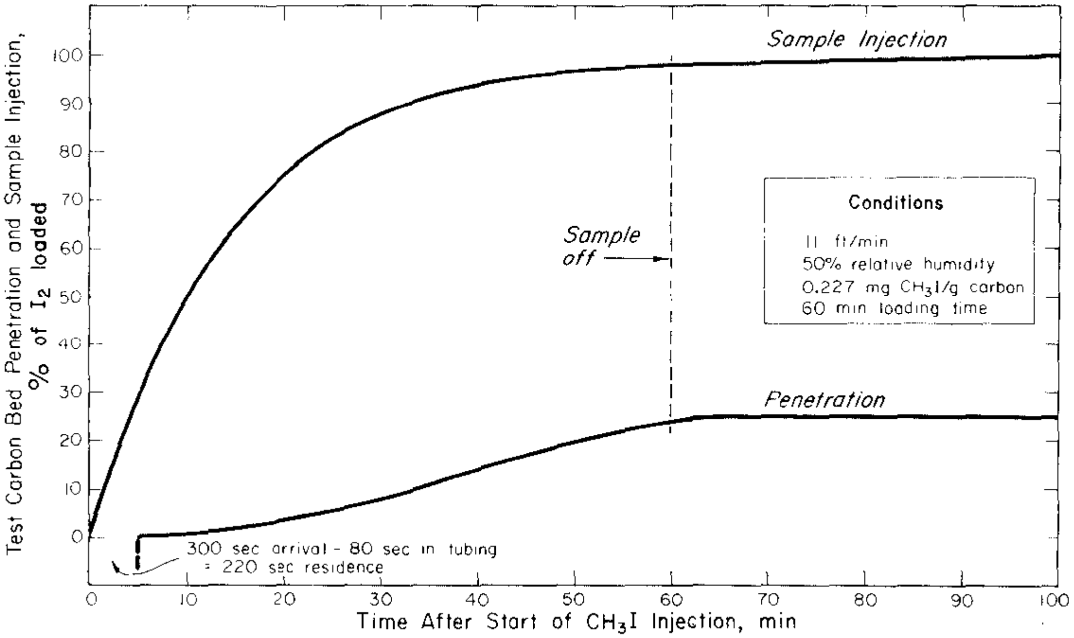

FIG. 14 PENETRATION OF METHYL IODIDE AS A FUNCTION OF TIME (Face Velocity, 11 ft/min)

Effect of Methyl Iodide Loading on Carbon

The results of tests in which methyl iodide loading on the carbon was the test variable are shown in Figure 15. The percent reduction in penetration caused by the gamma field varied from approximately zero at loadings greater than 0.12 mg of CH_3I/g of carbon to 35% at a loading of 0.02 mg of CH_3I/g as shown by the difference in the curves in Figure 15. Penetration decreased with decreasing methyl iodide loading on the carbon in tests both in and outside the radiation field.

Effect of Methyl Iodide Concentration

Tests were run in which the methyl iodide loading time in steam-air was reduced from 60 minutes to 15 and 5 minutes. The methyl iodide concentration in the steam-air mixture was 2.4×10^3 μg/m^3 for loading in 60 minutes, 9.6×10^3 μg/m^3 for loading in 15 minutes, and 28.8×10^3 μg/m^3 for loading in 5 minutes. Loadings were approximately the same in all cases. Results, shown in Figure 16, indicate little sensitivity to methyl iodide concentration over the range investigated.

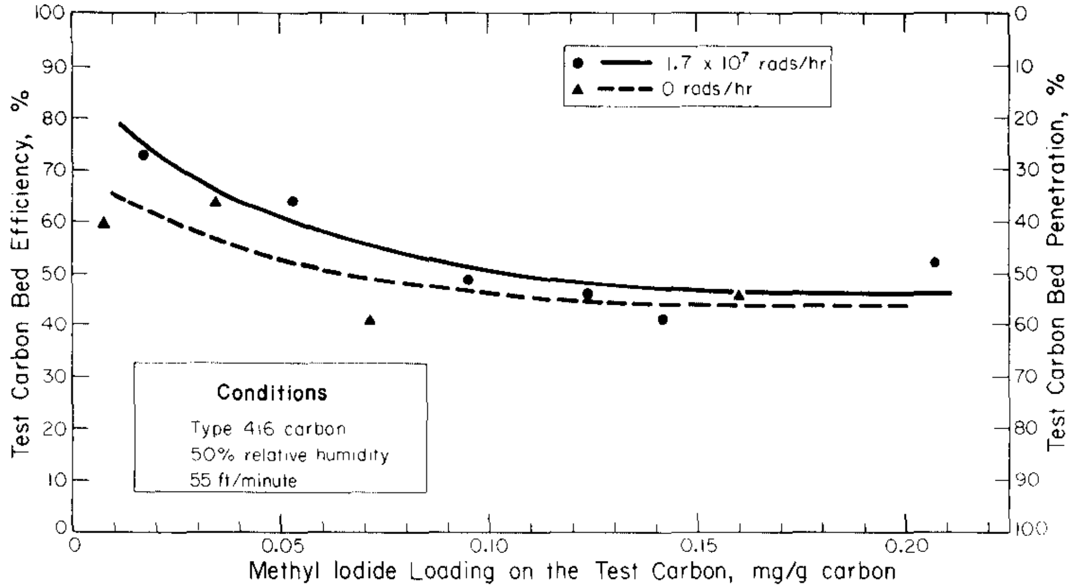

FIG. 15 EFFECT OF METHYL IODIDE LOADING ON CARBON BED EFFICIENCY

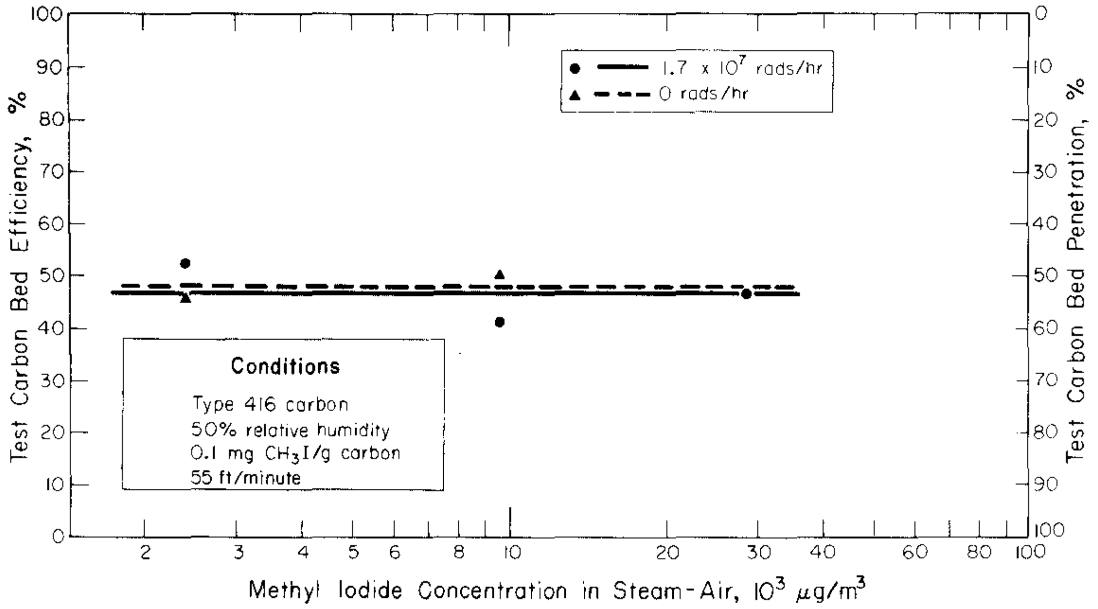

FIG. 16 EFFECT OF METHYL IODIDE CONCENTRATION ON CARBON BED EFFICIENCY

Radiolytic Decomposition of Methyl Iodide

Based on the assumption that radiolytic decomposition of the methyl iodide into non-penetrating forms of iodine was the only factor causing the reduced penetration measured in the gamma field, decomposition was calculated and compared with published data. Tests at 27% relative humidity and 55 ft/min face velocity (23 seconds residence time indicate 50% decomposition. Data by Tang and Castleman[7,8] indicate that 50% decomposition should be expected at a residence time of slightly less than 30 seconds in a field of 1.7×10^7 rads/hr.

Tests at 11 ft/min velocity and 50% relative humidity (220-seconds residence time, Fig. 14) indicate ∿35% decomposition. Data by Tang and Castleman[7,8] indicate that >99% decomposition should be expected at a residence time greater than 120 seconds.

The carbon may inhibit the radiolytic decomposition of methyl iodide. During most of the residence time in the gamma field, the methyl iodide must be temporarily adsorbed on the surface of the test carbon. If a methyl iodide molecule is decomposed, the ions formed are not in the free gaseous state where they are likely to collide and react with other ions or molecules; they are in a partially immobilized adsorbed state where they are most likely to recombine because of their proximity. Thus, decomposition is inhibited.

In a discussion of data on radiolysis of methyl iodide adsorbed on silica gel reported by Sagert, Reid, and Robinson,[9,10] the authors attribute the observed long lifetime of CH_3I^- to a back reaction accelerated by caging effects of narrow pores in the silica gel. The authors postulate that this caging keeps methyl radicals and negative iodide ions close together after decomposition favoring recombination to form CH_3I^-.

Immobilization of methyl iodide molecules by adsorption on the carbon surface must greatly increase at low relative humidities (<10%) as evidenced by very low penetration. Failure of data at <5% relative humidity to indicate any decomposition might be attributed to this reduced freedom of the ions to react with other molecules or ions to form stable non-penetrating species.

In future tests, the effects of gamma dose and relative humidity on methyl iodide and elemental iodine retention by several adsorbers will be studied.

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