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AEC RESEARCH AND DEVELOPMENT REPORT

IODINE AND NOBLE GAS RETENTION STUDIES

PROGRESS REPORT: OCTOBER 1966 - DECEMBER 1968

R.C. MILHAM - L.R. JONES

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Savannah River Laboratory

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Reactor Technology
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IODINE AND NOBLE GAS RETENTION STUDIES

PROGRESS REPORT: OCTOBER 1966 - DECEMBER 1968

by

Robert C. Milham and Larry R. Jones

Approved by

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August 1969

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ABSTRACT

The removal of iodine from activated carbon by flowing air was measured to evaluate various carbons and to evaluate the effects of variables, such as service, temperature, partial regeneration, iodine loading, and face velocity on iodine desorption.

The effect of gamma radiation on the adsorption of iodine and methyl iodide on activated carbon exposed to flowing mixtures of steam and air was measured. Test conditions simulated a postulated loss-of-coolant accident where adsorption of radioiodine on carbon beds in the confinement system would produce an intense gamma field.

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INTRODUCTION

Removal of radioiodine from reactor confinement systems is of special importance because it is the fission product potentially most hazardous to the surroundings of a nuclear reactor. At the request of the AEC Division of Operational Safety, a continuing program is in progress at the Savannah River Laboratory (SRL) to evaluate the performance of carbon for removal of iodine under adverse operating conditions and to develop techniques to enhance its reliability and efficiency.

This report summarizes the work done at the Savannah River Laboratory during the period from October 1966 through December 1968 on (1) carbon ignition temperature, (2) desorption of iodine from carbon at high temperatures, (3) methyl iodide radiolysis, (4) iodine desorption detection and noble gas retention, and (5) alternatives to carbon for iodine adsorption. Earlier studies reported in DP-1075[1] were directed toward selection of a carbon with a higher ignition temperature.

SUMMARY

A standard procedure for the measurement of the ignition temperature of activated carbon was developed and is being reviewed by ASTM for adoption.[2] Ignition temperature studies at SRL have been concluded.

Tests of the desorption of iodine[2,3] showed:

Unimpregnated activated carbon (Type 416) desorbed much less iodine than impregnated carbons (Types 727, 592, and 117).*

The desorption of iodine at 200°C increased significantly with service life in the Savannah River Plant (SRP) confinement system.[4,5,6] However, the useful life of carbon can be extended by partial regeneration.

The rate of desorption of iodine from carbon with 30 months service life increased:

Exponentially with temperature (65 to 200°C)

Linearly with face velocity (20 to 100 ft/min)

Linearly with iodine concentration (0.8×10^4 to 6.2×10^4 $\mu g/m^3$)

Linearly with iodine loading (0.36 to 6.5 mg I/g C)

Up to 90% of the methyl iodide contained in a steam-air mixture was decomposed as the mixture flowed through activated carbon and was exposed to a gamma radiation field of $\approx 2 \times 10^7$ rads/hr.[7] Decomposition decreased with increased face velocity and with increased relative humidity.

Testing and evaluation of the carbon canister in the SRP filter breakthrough monitor showed that noble gases would be held up for 0.35 minute, thus hindering detection of small iodine leaks (0.1 to 1%) from the confinement system for about 25 minutes.

In a single test of a silver zeolite prepared by the Idaho Nuclear Corporation (INC), the measured iodine penetration was 0.41% which is significantly greater than that of Type 416 activated carbon (0.01%).

* Products of Barnebey-Cheney Co., Columbus, Ohio.

DISCUSSION

CARBON IGNITION TEMPERATURE

The procedure developed at SRL for the measurement of the ignition temperature of activated carbon was sent to the ASTM for adoption as a standard procedure. In this procedure, a 1-inch-diameter by 1-inch-thick bed of carbon in a quartz apparatus is heated by flowing air until the carbon spontaneously ignites. The proposed procedure was approved in June 1968 by Subcommittee III - Nomenclature and Definition of Terms of Committee D-28 on Activated Carbon and was sent to Subcommittee IV - Gas Phase Application Tests for consideration.

No further work on ignition temperature is planned.

HIGH TEMPERATURE DESORPTION OF IODINE FROM CARBON

Apparatus and Procedure

The apparatus shown in Figure 1 was used to measure the desorption of iodine from activated carbon. In this apparatus, a test carbon bed (2-inch-diameter by 1-inch-thick) is loaded by adsorbing elemental iodine tagged with ^{131}I from ambient air or from a steam-air mixture at 65°C. Then air, purified of dust and vapors at the desired temperature, is passed through the test bed and any desorbed iodine is adsorbed on backup carbon beds. The ratio of the ^{131}I on the backup beds to that loaded on the test bed is the fraction of iodine desorbed.

Before the iodine is adsorbed, the test bed is equilibrated with moisture by flowing a steam-air mixture at 65°C through the bed for 10 minutes at a velocity of 68 ft/min. Iodine is vaporized from a glass frit, passed through a particulate filter, and adsorbed on the test bed at a face velocity of 68 ft/min over an interval of about 60 minutes. The air temperatures upstream and downstream of the test bed, the pressure upstream of the test bed, and the pressure drop across the bed are measured.

Any iodine that penetrates the test bed during the loading step is collected on backup beds, and the accumulation of iodine on the backup beds is monitored continually with a gamma detector.

The sections of the apparatus through which iodine passes were built of glass and "Teflon"* coated stainless steel. These materials minimize the deposition of iodine on surfaces for better material balance and easier cleaning. Operating temperatures are limited to about 220°C to avoid decomposition of the "Teflon."

* Du Pont's trademark for its fluorocarbon resins.

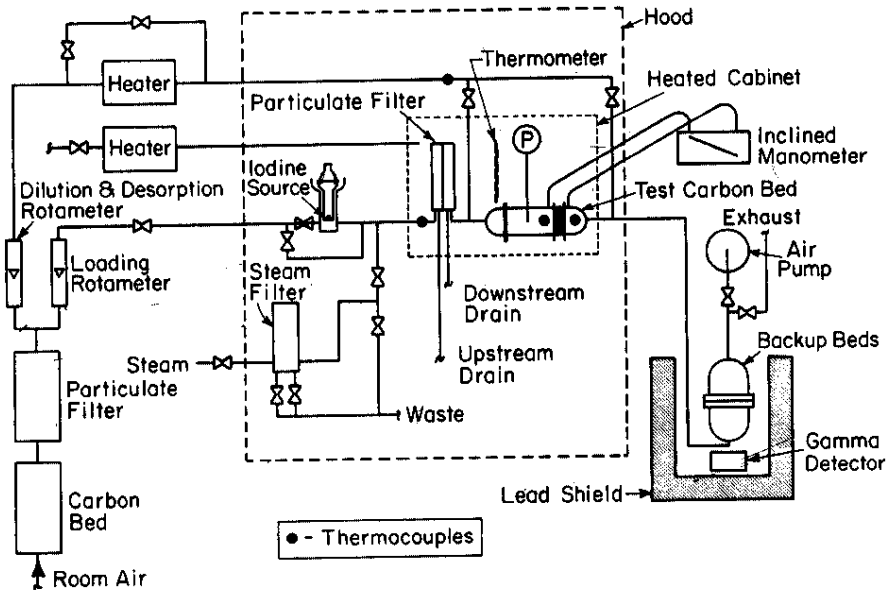


FIG. 1 ADSORPTION-DESORPTION APPARATUS

Comparison of Different Carbons

Unimpregnated, activated carbon (Type 416) desorbed much less iodine than impregnated carbons (Types 727, 592, and 117) as shown in Table I. An insignificant amount of iodine (<0.01%) was desorbed from previously unexposed Type 416 carbon when the iodine was loaded from a steam-air mixture at 65°C and desorbed at 200 ±10°C for 110 minutes. An excessive amount of iodine (0.05 to 28%) was desorbed from the commercial impregnated carbons.

Evaluation of test beds of Type 592 carbon in the SRP confinement system has been discontinued. Type 592 carbon was under study because of its high ignition temperature.

TABLE I

Desorption of Iodine from Various Unused Carbons

Carbon Type	Iodine Loading, mg I/g C	Desorbed in 110 Minutes at 200°C, %
416	0.77	<0.01
727	0.60	0.05
592	0.63	2.0
117	0.42	28

All of these carbons are made from a coconut shell base. Type 416 is unimpregnated and is used in the SRP confinement system. Type 727 carbon is impregnated with about 5% iodine for applications that require removal and retention of methyl iodide. Type 592 carbon is specially processed and impregnated to produce a high ignition temperature (530°C, at a face velocity of 105 ft/min). Type 117 carbon is impregnated in a proprietary manner to have a relatively high ignition temperature (405°C, at a face velocity of 70 ft/min) and to retain iodine at high temperatures.

Effect of Temperature

The percent desorption of iodine from Type 416 carbon increased exponentially with increasing temperature from 90 to 200°C as shown in Figure 2. An insignificant amount of iodine (<0.02%) was desorbed from previously unexposed Type 416 carbon when the iodine was loaded from dry air at ambient temperature. The rate of desorption decreased with time at high temperature, and after about 30 minutes the rate was negligible. The iodine desorption in two tests at 140°C agreed within 25%.

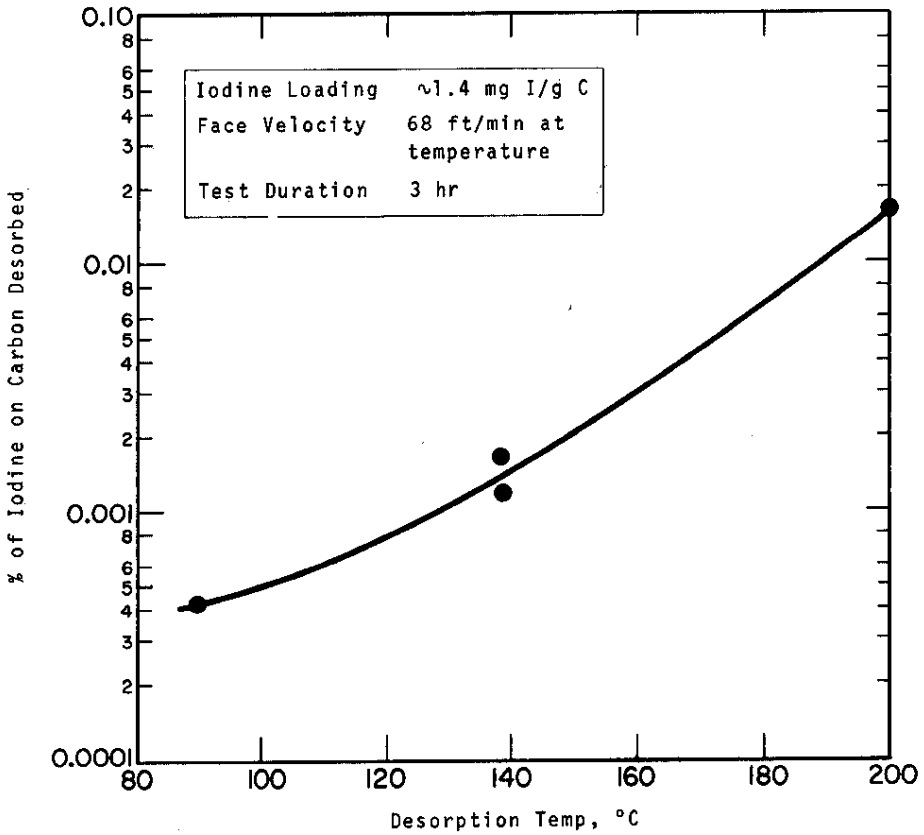
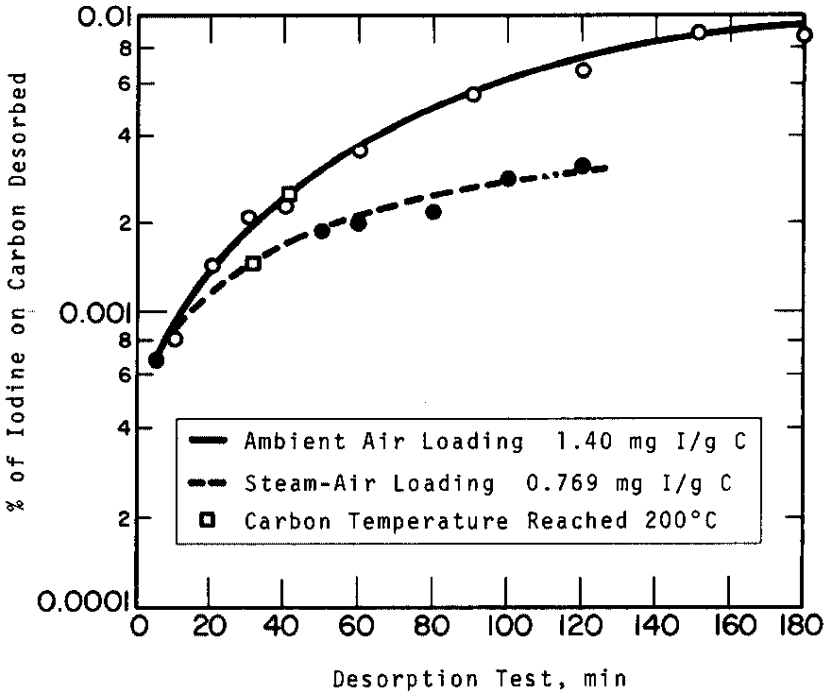


FIG. 2 DESORPTION OF IODINE FROM UNUSED TYPE 416 CARBON

Effect of Steam - Air Loading

The presence or absence of steam during iodine loading on previously unexposed Type 416 and Type 592 carbons had an insignificant effect on the desorption of iodine at 200°C at a face velocity of 68 ft/min. As shown in Figure 3, <0.01% of the iodine was desorbed from Type 416 carbon with or without steam during loading. The higher iodine desorption from carbon that was loaded from ambient air may be caused by the heavier iodine loading.



New Type 416 carbon loaded in ambient air and 68 ft/min, and loaded in steam air at 65°C and 68 ft/min followed by desorption in dry air at 200°C and 68 ft/min.

FIG. 3 COMPARISON OF THE EFFECT OF STEAM-AIR AND AIR LOADING ON THE DESORPTION OF IODINE FROM UNUSED TYPE 416 CARBON

Figure 4 shows that a large amount of iodine (~6%) was desorbed from Type 592 carbon when the test bed was loaded from ambient air and then desorbed at 200°C and a face velocity of 68 ft/min. This result confirms the excessive desorption from Type 592 carbon that was observed with steam-air loading.

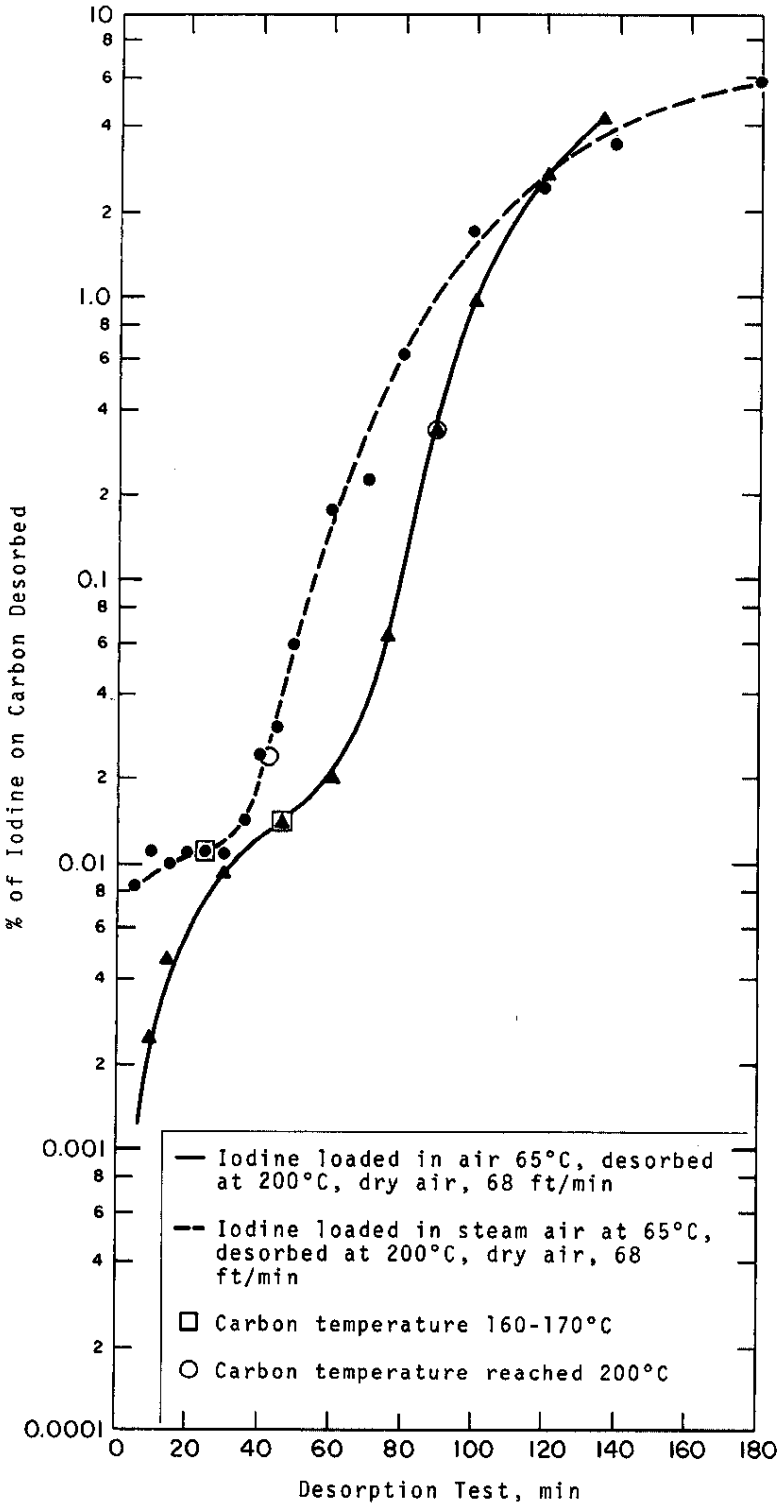
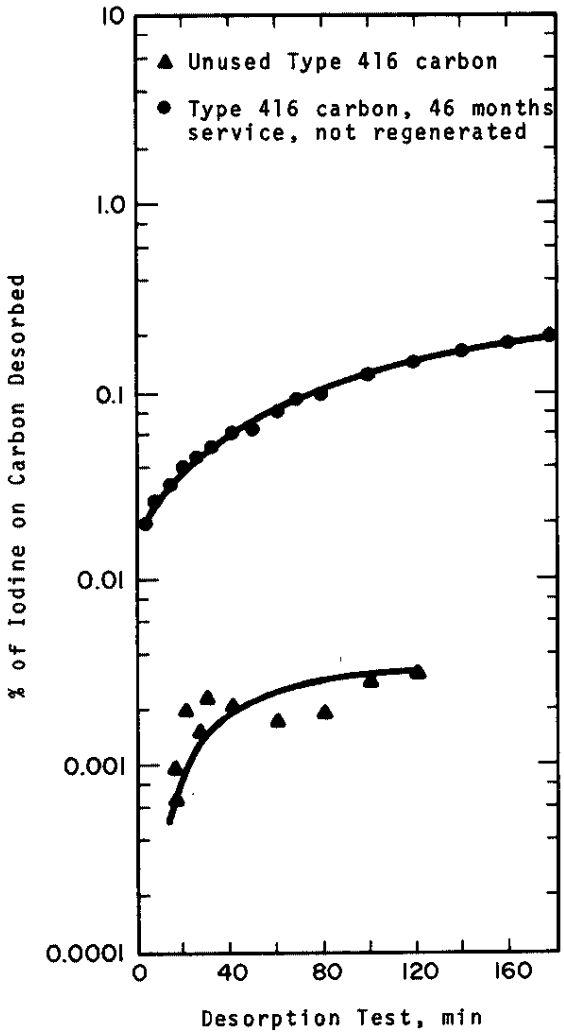


FIG. 4 COMPARISON OF THE EFFECT OF STEAM-AIR AND AIR LOADING ON THE DESORPTION OF IODINE FROM UNUSED TYPE 592 CARBON

Effect of Service

As expected, the effectiveness of activated carbon for retaining iodine at high temperature decreases with service life in the confinement system. After 46 months service in the SRP confinement system, Type 416 carbon desorbed a significant amount of iodine at 65°C as shown in Figure 5 in comparison with unused carbon. The test data shown in Figure 5 were obtained from samples with no regeneration.



Loaded from steam air at 65°C and desorbed in air at 65°C and 68 ft/min

FIG. 5 EFFECT OF SERVICE ON DESORPTION OF IODINE FROM TYPE 416 CARBON AT 65°C

Effect of Partial Regeneration

The useful life of carbon in the confinement system can be extended by partial regeneration. The carbon in the SRP confinement system is partially regenerated annually as a part of an unrelated test program. Prior to the on-line "Freon"* leak test,[8] carbon in the confinement system is heated to about 60°C for at least 48 hours with a face velocity of 5 to 10 ft/min. This treatment removes moisture that interferes with the leak test and coincidentally provides a partial regeneration of the carbon.

In the laboratory, samples are partially regenerated to mock up the treatment of carbon in the SRP confinement system. The test bed is heated to 60°C for at least 48 hours with purified air at a face velocity of 7.5 ft/min.

The decrease in desorption after partial regeneration is shown in Figure 6 for a carbon with 46 months service in the confinement system. The unregenerated carbon desorbed about 0.2%, and the identical carbon regenerated at 60°C desorbed only 0.013%. The desorption from unused carbon is shown for comparison. The scatter in the data points for small desorption is caused by measurements at the lower limit of sensitivity of the counting equipment.

Effects of Variables on Type 416 Carbon with 30 Months Service

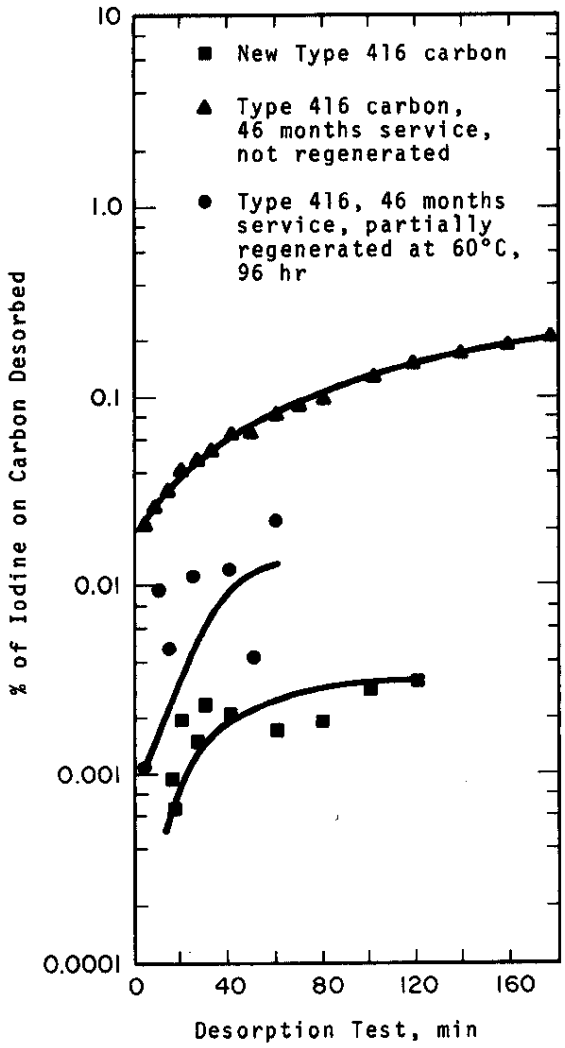
Temperature and face velocity had the most significant effect on desorption of the variables tested. Iodine loading on the test bed and the concentration of iodine vapor during loading had smaller effects on desorption. These results show the sensitivity of iodine desorption to iodine release rates and ventilation system variables.

In each of the following tests, Type 416 carbon with 30 months service was used. Each test bed was partially regenerated by passing air purified of dust and vapors at a temperature of 60°C and a face velocity of 7.5 ft/min through the bed for at least 48 hours.

Temperature

In tests up to 200 ±10°C, the rate of desorption of iodine from Type 416 carbon with 30 months service increased exponentially with temperature (Figure 7). This behavior is similar to that measured on new Type 416 carbon (Figure 2) and, as would be expected, the rate was much higher from carbon with 30 months service. These results demonstrate the necessity of maintaining moderate carbon bed temperatures in the event of a nuclear accident.

* Du Pont's trademark for its fluorinated hydrocarbons.



Loaded from steam air at 65°C and 68 ft/min and desorbed in air at 65°C and 68 ft/min.

FIG. 6 EFFECT OF PARTIAL REGENERATION ON DESORPTION OF IODINE FROM TYPE 416 CARBON AT 65°C

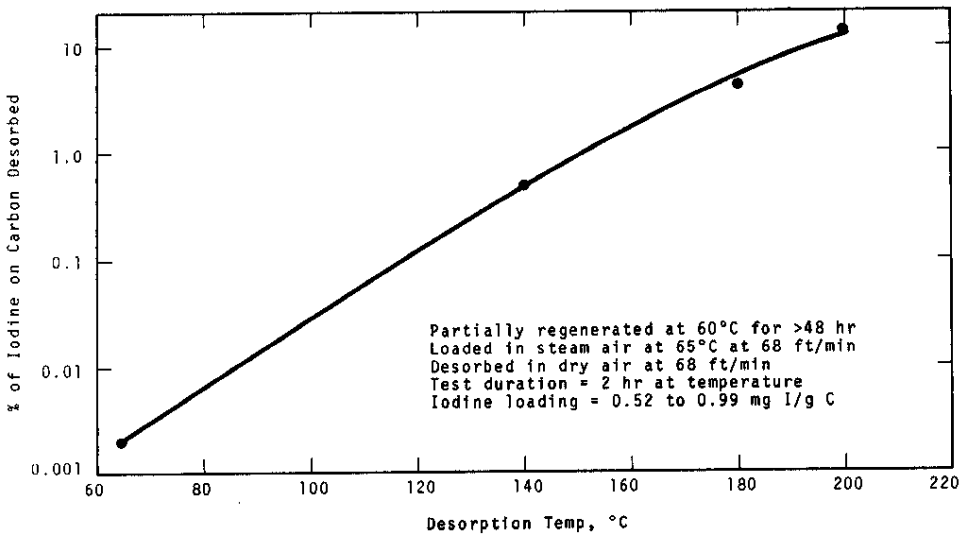


FIG. 7 EFFECT OF TEMPERATURE ON IODINE DESORPTION FROM TYPE 416 CARBON WITH 30 MONTHS SERVICE

Face Velocity

In tests at 140°C, the desorption of iodine from Type 416 carbon with 30 months service increased linearly as the face velocity increased from 20 to 100 ft/min (Figure 8). Thus, if ventilation flow decreased following a fuel meltdown and if constant temperature could be maintained in spite of the decreased ventilation flow rate, iodine desorption would decrease.

Iodine Concentration

In tests at 200°C, the desorption of iodine from Type 416 carbon with 30 months service increased as the average concentration of iodine in the inlet steam-air mixture at 65°C and 68 ft/min increased from 0.8×10^4 to 6.2×10^4 $\mu g/m^3$ (Figure 9). Some of the scatter in the data was caused by variations in the iodine concentration during the test.

Loading

In tests at 200°C, the desorption of iodine from Type 416 carbon with 30 months service increased as the loading was increased from 0.36 to 6.7 mg I/g C as would be expected (Figure 10). The desorption at as small a loading as 0.3 mg I/g C at 200°C was unacceptably great. In tests at 65°C, the desorption of iodine from Type 416 carbon with 30 months service was acceptably small (<0.08%) for loadings up to 8.9 mg I/g C.

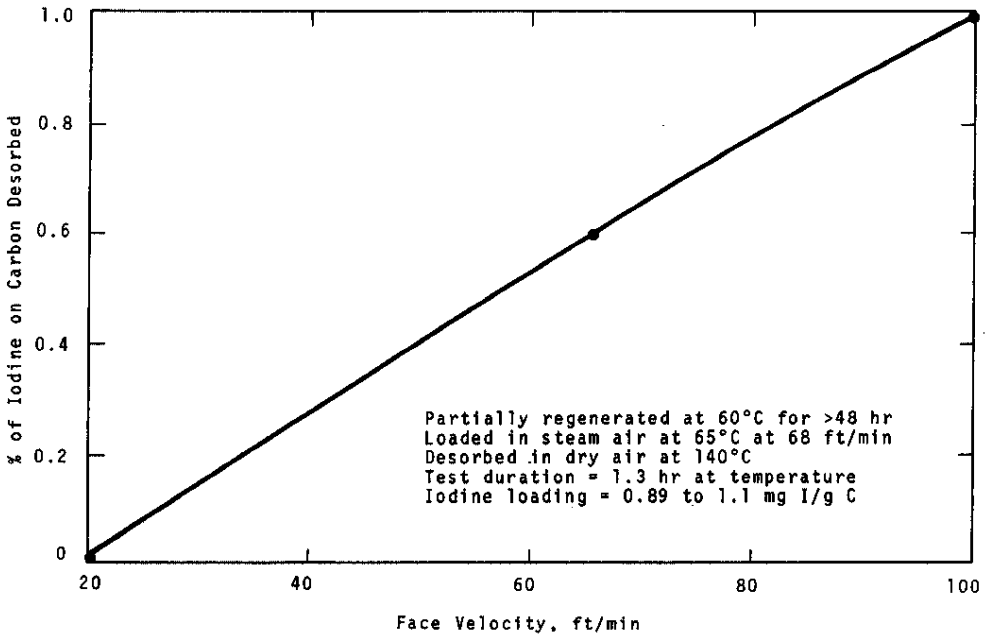


FIG. 8 EFFECT OF FACE VELOCITY ON IODINE DESORPTION FROM TYPE 416 CARBON WITH 30 MONTHS SERVICE

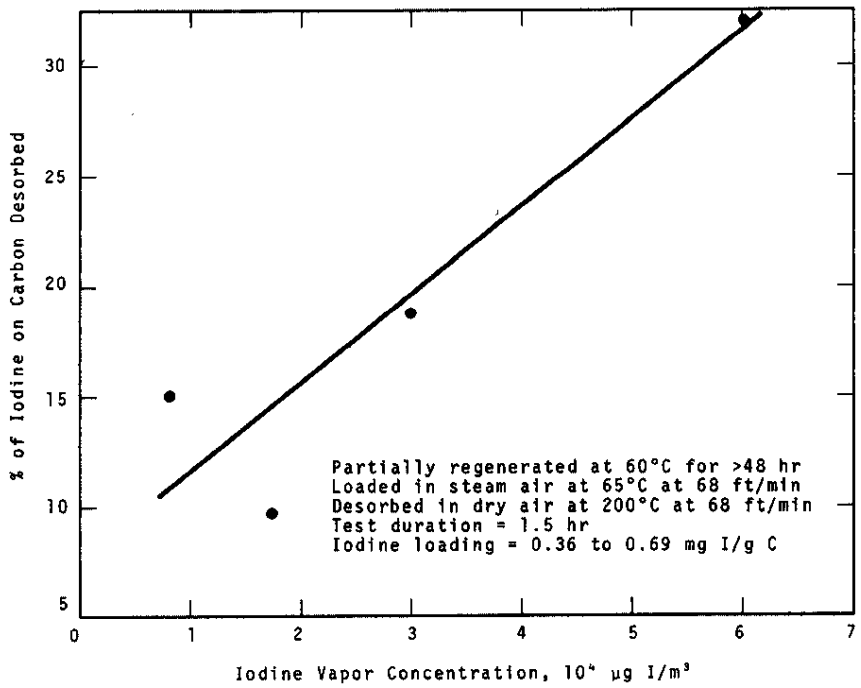


FIG. 9 EFFECT OF IODINE CONCENTRATION ON IODINE DESORPTION FROM TYPE 416 CARBON WITH 30 MONTHS SERVICE

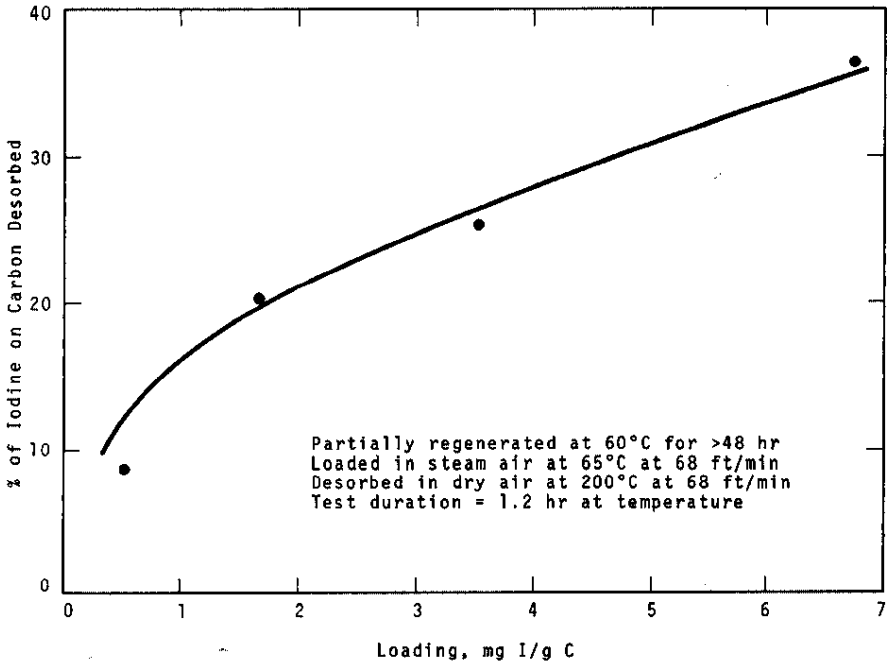


FIG. 10 EFFECT OF LOADING ON IODINE DESORPTION AT 200°C FROM TYPE 416 CARBON WITH 30 MONTHS SERVICE

Program for Desorption Study

Additional work needed includes:

Correlating iodine desorption characteristics with the basic properties of carbon

Determining the significant contaminants and their effects

Investigating methods to minimize contaminants and reduce the sensitivity of the adsorbent to them

Devising an accelerated service life test and method of measurement

Investigating the variables that determine the effectiveness of partial regeneration

METHYL IODIDE RADIOLYSIS

Results

The conditions under which radiolysis tests were run and the results are given in Table II. Figure 11 shows a plot of methyl iodide penetration as a function of relative humidity. The gamma radiation field of ≈2 x 10^7 rads/hr reduced methyl iodide penetration of the test carbon bed by a factor of 10 in tests at a velocity of 11 ft/min and 50% relative humidity. The radiation field reduced penetration by a factor of 3 in tests at a velocity of 11 ft/min and 65% relative humidity. Two tests in the radiation field at 55 ft/min showed no apparent effect of radiation. Radiation is expected to have less effect on adsorption as velocity increases because residence time is shortened and absorbed dose is reduced.

TABLE II

Test Conditions and Results of Methyl Iodide Radiolysis

Test	Gamma Field, rads/hr	Velocity, ft/min	Average Relative Humidity, %	CH_3I Loading, mg CH_3I/g carbon	Penetration, % (CH_3I only)
1	0	55	48	0.407 x 10^{-2}	14.1
2	0	55	78	1.845 x 10^{-2}	47.3
3	0	55	78	0.598 x 10^{-2}	62.6
4	0	11	78	1.106 x 10^{-2}	49.3
5	0	55	95	0.199 x 10^{-2}	89.8
6	0	11	68	0.596 x 10^{-2}	46.7
7	0	11	50	0.903 x 10^{-2}	19.8
8	2 x 10^7	55	65	1.490 x 10^{-2}	42.7
9	2 x 10^7	11	64	0.279 x 10^{-2}	14.8
10	2 x 10^7	55	65	0.169 x 10^{-2}	64.5
11	2 x 10^7	11	50	0.660 x 10^{-2}	2.4
12	2 x 10^7	11	50	1.980 x 10^{-2}	1.5

Relative humidity was chosen as the primary variable for preliminary tests because methyl iodide penetration is so greatly affected by it (Figure 11). Other variables were held constant except for velocity which is coupled to relative humidity because of gamma heating of the carbon in the test carbon bed.

Heat generated in the test carbon bed by gamma absorption resulted in temperature differences across the bed of from ≈10°C at a velocity of 55 ft/min to ≈30°C at a velocity of 11 ft/min. Relative humidity of steam-air mixtures decreased from 78% upstream of the test carbon bed to 23% downstream of the test bed at a velocity of 11 ft/min. Average values of relative humidity were used for comparison of tests.

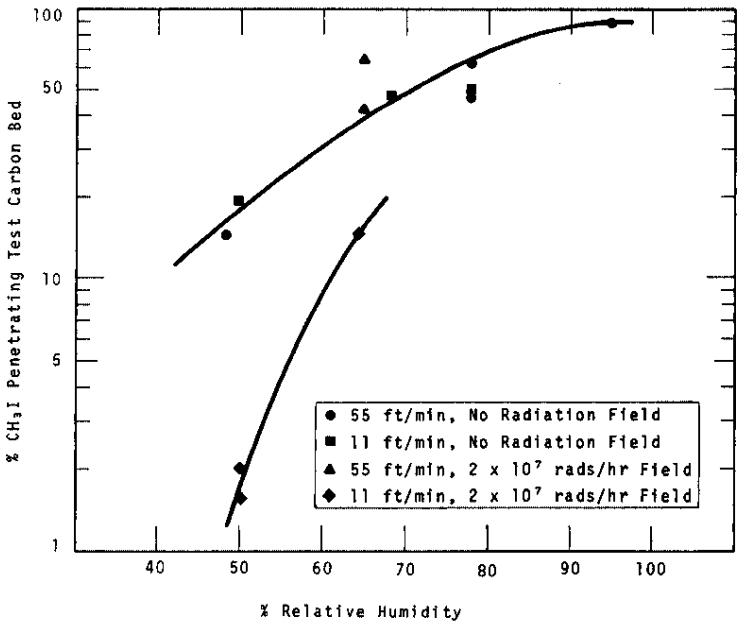


FIG. 11 EFFECT OF GAMMA RADIATION, RELATIVE HUMIDITY, AND VELOCITY ON METHYL IODIDE PENETRATION

Program for Radiolysis Study

The effects of absorbed gamma dose, relative humidity, velocity, temperature, organic impurities, iodine, and methyl iodide loading on the carbon, type of carbon, carbon service life, and sample injection rate should be examined. Only relative humidity and velocity have been investigated. Additional tests would use:

Lower methyl iodide injection rates to simulate a more intense radiation field and/or longer residence time

Higher velocities to determine the effect of velocity of the gas stream on residence time of the methyl iodide

Only elemental iodine

Iodine and methane to determine the effect of radiation on formation of methyl iodide

Impregnated carbons and carbon having three years service in the SRP confinement system

Better separation of variables is expected with improved apparatus.

IODINE DESORPTION DETECTION AND NOBLE GAS RETENTION

Filter breakthrough monitors are provided to detect any significant desorption or leakage of iodine from the SRP reactor confinement system. The monitors function by drawing about 2 ft^3/min of air from the effluent of the confinement system carbon beds. Any iodine in this air flow is adsorbed on a cylindrical canister of activated carbon. Radioactivity in the carbon is monitored by a detector mounted on the axis of the canister.

The intense gamma radiation from noble gases (that are not confined) might interfere with the detection of iodine leakage by the filter breakthrough monitor. Tests were made to determine the efficiency of carbon from the filter breakthrough monitor to retain iodine and xenon. The retention of krypton was calculated from theory and the measured xenon results.

Tests were made to determine the effect of background radiation from noble gases and the ability of the filter breakthrough monitor to discriminate against iodine. These tests show that the holdup time of xenon ranges from 0.25 minute at a face velocity of 2$\frac{1}{7}$ ft/min to 6 minutes at 2$\frac{3}{7}$ ft/min for a 1-inch-thick bed of Type 416 carbon.

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ALTERNATIVES TO CARBON FOR IODINE ADSORPTION

At the request of the AEC, a silver zeolite (prepared and supplied by the Idaho Nuclear Corporation) was tested by measuring the iodine penetration and the iodine desorption. The measured iodine penetration of the zeolite (0.41%) was higher than for activated carbon (0.01%).

There was barely measurable desorption of iodine (0.0005%) from the zeolite in 70 minutes at 200°C with a dry air flow of 68 ft/min at temperature. The desorption of iodine reached equilibrium very rapidly. With Type 416 activated carbon, desorption reaches equilibrium after about 3 hours and is typically about 0.005%. Further study is required to determine whether the material might have application at elevated temperatures or for extended exposure service.

A comparison of the Savannah River Laboratory test and the Idaho Nuclear Corporation test is shown in Table III.

No further SRL tests are scheduled at this time.

TABLE III

Adsorption Efficiency of Silver Zeolite

	Measured by	
	INC	SRL
Concentration of iodine in inlet stream, $\mu g/ft^3$	1	350
Flow rate, ft^3/min	0.05	1.5
Face velocity, ft/min	164	68
Duration of test, min	15 ±5	60
Bed dimension		
Depth, cm	4	1.3
Diameter, cm	0.6	5.1
Mesh size	10-20	10-20
Iodine loading, mg I/g adsorber	~0.0009	1.2
Measured efficiency, %	100	99.59

REFERENCES

1. R. C. Milham. High Temperature Adsorbents for Iodine - Progress Report: January 1965 - September 1966. USAEC Report DP-1075, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1966).

2. R. C. Milham. "High Temperature Properties of Activated Carbon: Part I - Desorption of Iodine, Part II - Standard Method for Ignition Temperature Measurement." Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes. New York, New York, August 26-30, 1968. Paper SM-110/49 (1968).

3. R. C. Milham. "Charcoal Post Treatment; Heat Degradation and Service Life." Proceedings of the Tenth AEC Air Cleaning Conference. New York, New York, August 28, 1968. CONF-680821, p 167 (1968).

4. W. S. Durant, R. C. Milham, D. R. Muhlbaier, and A. H. Peters. Activity Confinement System of the Savannah River Plant Reactors. USAEC Report DP-1071, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1966).

5. W. S. Durant. Performance of Activated Carbon Beds in SRP Reactor Confinement Facilities - Progress Report: September 1962 - September 1965. USAEC Report DP-1028, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1966).

6. G. H. Prigge. Application of Activated Carbon in Reactor Containment. USAEC Report DP-778, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1962).

7. L. R. Jones. "Effect of Gamma Radiation on Adsorption of Iodine and Methyl Iodide on Activated Carbon." Proceedings of the Tenth AEC Air Cleaning Conference. New York, New York, August 28, 1968. CONF-680821, p 204 (1968).

8 D. R. Muhlbaier. Standardized Nondestructive Test of Carbon Beds for Reactor Confinement Applications - Final Progress Report: February to June 1966. USAEC Report DP-1082, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1967).