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CONFINEMENT OF AIRBORNE RADIOACTIVITY

PROGRESS REPORT: JANUARY - DECEMBER 1976

A. G. EVANS

SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801

PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

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A. G. EVANS

Approved by

G. F. Merz, Research Manager
Reactor Engineering Division

Publication Date: August 1977

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ABSTRACT

Service aging studies conducted at the Savannah River Laboratory (SRL) show that Type GX-176 carbon has a useful life of at least 30 months as a halogen absorbent in the airborne-activity confinement system for the Savannah River production reactors. The studies also show that elemental iodine retention by this carbon at high temperature (180°C) is more a function of the pH of the service-aged carbon than of the length of time in service. Type GX-176 carbon is a 10 x 16 mesh coconut shell charcoal impregnated with potassium iodide and triethylenediamine.

Studies of new absorbent formulations at SRL show that coal-, coconut-, and wood-base carbons can be impregnated with hexamethylenetetramine (HMTA) and combinations of iodine, iodine salts, potassium hydroxide, and phosphate salts to obtain methyl iodide penetration values of less than 1%. Consistent penetration values of less than 0.5% have been obtained with two coal-base carbons when the total iodine and HMTA were added at the 2% level. Three phosphate salts ($NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$, and $Na_3PO_4 \cdot 12\ H_2O$) have been used successfully as pH buffers and ignition retardants. Boric acid was found to be an unsatisfactory ignition retardant.

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INTRODUCTION

The airborne-activity confinement system for each of the Savannah River Plant (SRP) production reactors is a continuously online, off-gas cleanup system designed to collect halogens and particulates that could be released in the highly unlikely event of a reactor accident.[1] Active components in the system include moisture separators to remove entrained moisture droplets, HEPA filters to remove particulate radioactivity, and beds of activated carbon to remove halogens. All air from the process areas of the reactor buildings passes through the confinement system before being exhausted to the atmosphere.

The Savannah River Laboratory (SRL) has conducted a continuing program to characterize and improve the performance of the confinement system components. This report summarizes (1) work during 1976 to evaluate the performance of carbon in the confinement system and (2) research efforts to develop improved carbon types to further enhance iodine retention capabilities.

Previous confinement studies at SRL[2-16] have shown that iodine retention on activated carbon is greatly influenced by impregnants on the carbon, temperature of the carbon beds, length of time the carbon has been in service, moisture content of the air passing through the beds, radiation exposure received by the carbon as a result of the decay of trapped iodine, and the particle size distribution of the carbon granules.

To improve the performance capabilities of the system, the unimpregnated carbon that had been used as an iodine absorber for many years was replaced by an impregnated carbon. The new carbon, Type GX-176,* is a 10 × 16 mesh (U.S. Sieve Series) coconut shell charcoal impregnated with potassium iodide and triethylenediamine (TEDA). Changeover to Type GX-176 carbon was completed in 1975.

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* Product of North American Carbon Company, Columbus, Ohio.

SERVICE AGING STUDIES

Studies to characterize the performance of carbon Type GX-176 in service were begun in 1974. Samples of the carbon were installed in the Carbon Test Facility (CTF) for accelerated aging tests before full-sized beds were placed in service in the confinement system. The confinement system carbon has also been sampled routinely by periodic removal of beds of carbon from the confinement compartments.

Service-aged carbon from the CTF and the confinement compartments are tested for iodine retention under simulated accident conditions using the SRL radiolysis test to assure performance within design specifications. The radiolysis test consists of loading elemental iodine onto the carbon (0.7 mg I/g carbon) in a humid air stream (∿95% relative humidity) at 80°C in the presence of an intense radiation field (at least 1.5×10^7 rads/hr absorbed dose rate in the carbon) and measuring the amount of iodine desorbed from the carbon during the five-hour test period (one-hour loading period followed by four-hour desorption period).

Other tests performed on the carbon include measurement of iodine penetration at a higher temperature (180°C), determination of the pH of the carbon, and measurement of the carbon ignition temperature. Selected samples have also been analyzed for residual impregnant levels and for methyl iodide penetration.

Radiolysis Tests

Results of radiolysis tests on Type GX-176 carbon exposed in the confinement system are shown in Table 1. Radiolysis test data on the same type of GX-176 carbon exposed in the CTF are shown in Table 2.

CTF-aging data is compared to confinement-system aging data by assuming a linear relationship between the flow rate of air through the carbon and the rate of deterioration of carbon performance. Since air flow rate is proportional to linear face velocity, the aging rate should be proportional to the linear face velocity as well. Carbon in the confinement system is exposed to reactor building air with a linear face velocity of about 52 feet per minute (fpm). Carbon samples in the CTF are exposed with a linear face velocity of about 65 fpm in the "normal-flow" test positions and about 81 fpm in the "accelerated-flow" test positions. Thus, the CTF samples in the "normal-flow" positions should be accumulating pollutants from reactor building air at rates approximately 1.25 times greater than those of carbons exposed in the confinement compartments, and the aging rates in the CTF "accelerated-flow" positions should be about 1.56 times greater than those in the confinement compartments.

TABLE 1

Iodine Penetration of Service-Aged Type GX-176 Carbon

Service Age, months	*Compartment Number*[a]	*Iodine Penetration,*[b] *%*
0	(Control)	0.028
6	K-2	0.052
12	K-2	0.060
18	K-2	0.090
24	K-2	0.176
30	K-2	0.335
7	P-2	0.062
9	P-2	0.051
14	P-2	0.121
19	P-2	0.228
27	P-3	0.359
12	P-6	0.055
24	P-6	0.145
30	P-6	0.165

a. Confinement compartment number where the carbon was exposed.

b. SRL radiolysis test. See Text for test description.

TABLE 2

Iodine Penetration of CTF-Aged Type GX-176 Carbon

Exposure Period, months	*Face Velocity, fpm*	*Equivalent Service,*[a] *months*	*Iodine Penetration,*[b] *%*
0	(Control)	0	0.028
6	65	7.5	0.129
6	81	9.4	0.249
12	65	15.0	0.156
12[c]	65	15.0	0.169
12	81	18.8	0.207
18	65	22.5	0.375
19[c]	81	30.0	0.741
24	65	30.0	1.374

a. Assumes linear relationship between linear face velocity and service aging rate. See Text for explanation.

b. SRL radiolysis test. See Text for test conditions.

c. Production lot of Type GX-176 carbon. Other samples listed were prototype samples installed before the production lot was available. See Text for discussion.

Data from Tables 1 and 2 are shown graphically in Figure 1. Radiolysis test data for service-aged, unimpregnated Type 416* carbon (the type formerly used in the confinement system) are shown for comparison.

Examination of Figure 1 shows that Type GX-176 carbon exposed for 27-30 months in confinement compartments P-3, P-6, and K-2 retains iodine as well as Type 416 carbon does with no service exposure. The data also show that carbon exposed in compartment P-2 deteriorates somewhat more rapidly than carbons exposed in other compartments. Extrapolation of the data shows a minimum useful service life at SRP of about 30 months. Even though carbon in other confinement system compartments performs better for longer periods, all the Type GX-176 carbon in the system is being replaced after approximately 30 months' service. Installation of new Type GX-176 in all compartments began in November 1976. Used carbon from all confinement system compartments will be tested to determine whether some carbon can be safely used for longer periods of time.

Earlier service aging studies on CTF samples indicated that the prototype sample of Type GX-176 carbon first installed in the facility aged more rapidly than the production lot of Type GX-176 installed in the confinement system. Tests performed on production-lot carbon installed later in the CTF show that no difference in iodine penetration is evident after 12 months' exposure (15 months equivalent confinement exposure), but that penetration through the prototype carbon is nearly twice that of the production lot after 30 months equivalent service (Table 2). As indicated in earlier publications,[16,17] iodine penetration differences are caused by differences in the particle size distributions of the two carbons. The particle size distribution of the new production lot of Type GX-176 is essentially the same as that of the Type GX-176 in the confinement system. Samples of the new lot of carbon are being installed in the CTF for further aging studies.

High-Temperature Tests

Earlier studies[3,5,14] at SRL showed that the ability of carbon to retain iodine at elevated temperatures declines rapidly with increasing service. Data presented in Table 3 and Figure 2 show that at 180°C, iodine penetration is lower in service-aged Type GX-176 carbon than in either Type 416 carbon or Type G-615** carbon (a TEDA-, KI-impregnated carbon exposed experimentally in the SRP

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

** Product of North American Carbon Company, Columbus, Ohio.

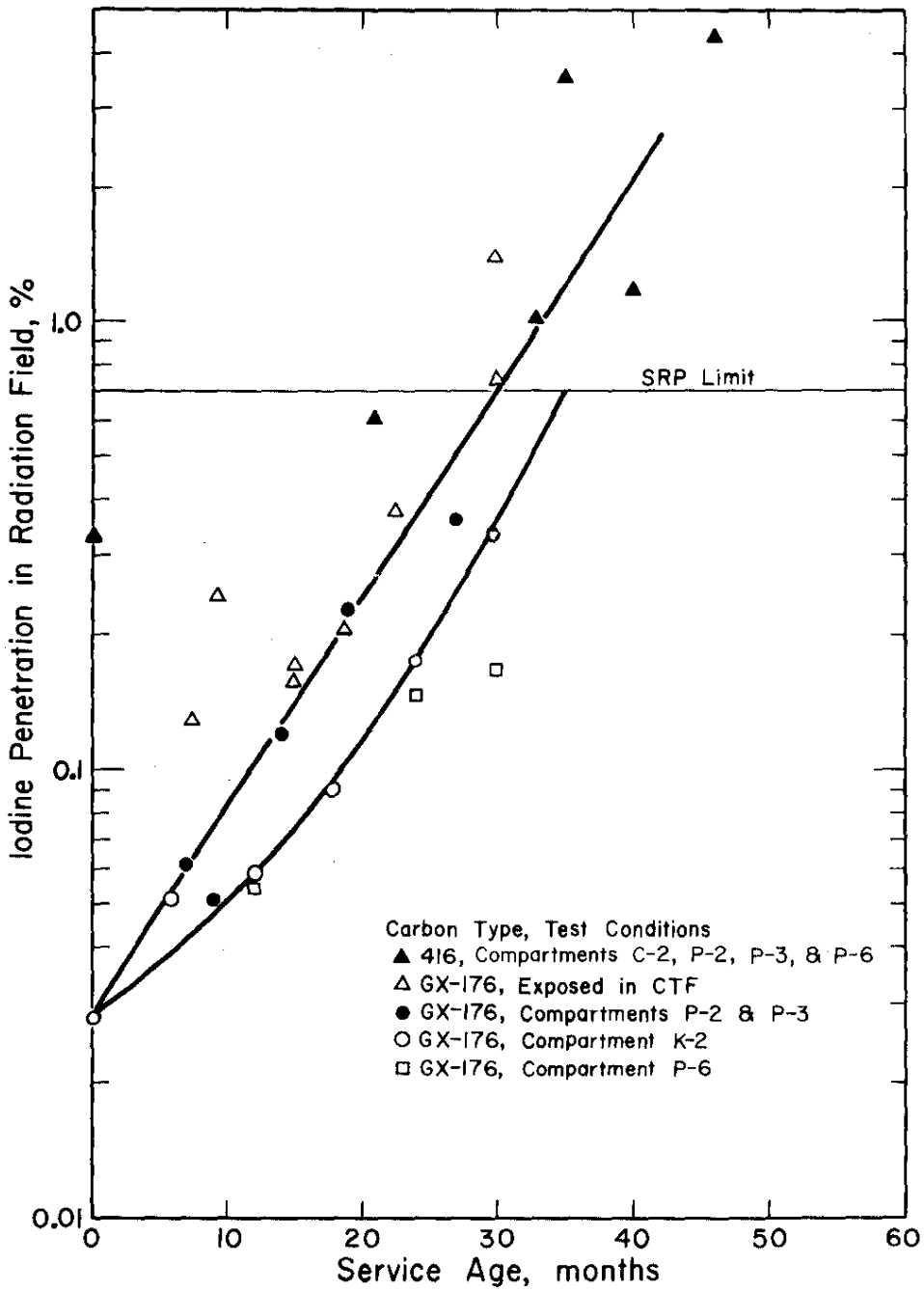

FIGURE 1. Radiation Test Data

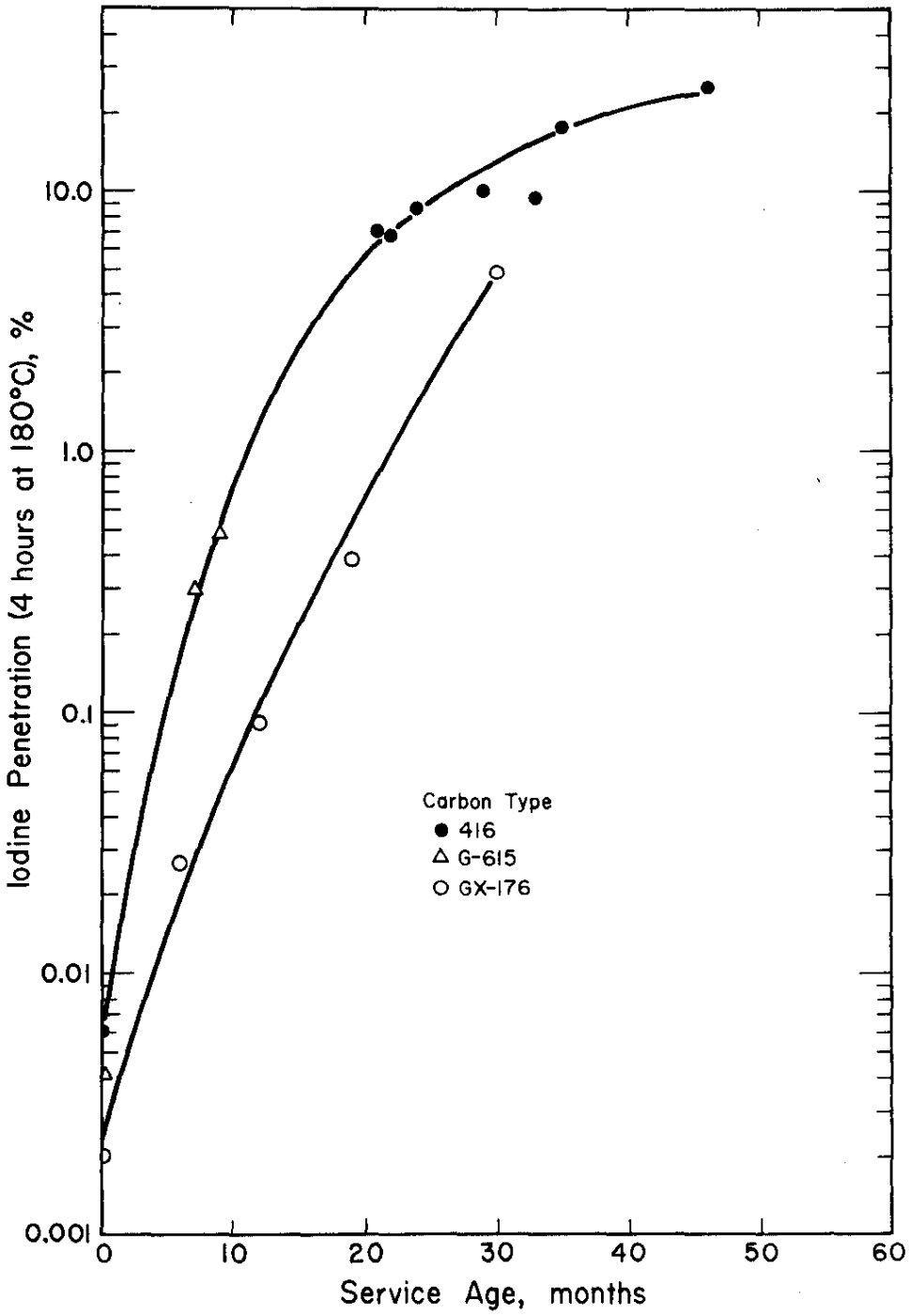

FIGURE 2. High-Temperature Iodine Penetration as a Function of Service

TABLE 3

High-Temperature Test Data for Confinement System Carbons

Carbon Type	*Service Age, months*	*Compartment Number*	*Iodine Penetration at 180°C, %*[a]
416	0	--	0.006
	21	C-2	7.22
	22	P-2	6.84
	24	L-2	8.59
	29	P-3	10.2
	33	P-2	9.48
	35	P-3	17.7
	46	K-3	25.2
G-615	0	--	0.004
	6	C-2	0.295
	9	C-2	0.474
GX-176	0	--	0.002
	6	K-2	0.027
	12	K-2	0.093
	18	K-2	0.392
	19	P-2	1.97
	30	K-2	5.05

a. Elemental iodine loaded at room temperature, then desorbed for 4 hours at 180°C.

confinement system).[13] Examination of Figure 2 shows that high-temperature iodine desorption rates for Types 416 and G-615 carbons are similar, despite the fact that Type G-615 is an impregnated carbon. The superior performance of Type GX-176 is attributed to the combination of impregnants and the particle size distribution of the carbon.

pH Determinations

pH tests are performed on carbon by measuring the pH of water extracts of the carbon. The SRL test consists of placing a 5-g carbon sample in 50 ml of cold, distilled water, heating the slurry to boiling, then cooling to room temperature in a sealed flask. Carbon granules are removed from the water by decanting the liquid from the carbon after cooling and before the pH measurement. Data obtained by this method (Table 4) show a rapid decrease in pH with increasing service exposure.

As indicated earlier, Types G-615 and 416 carbon show similar high-temperature proportions of iodine desorption, while Type GX-176 carbon deteriorates more slowly. When the high-temperature

TABLE 4

pH of Service-Aged Carbons

Carbon Type	*Service Age, months*	*Compartment Number*	*pH of Water Extract*[a]
416	0	--	9.59
	21	C-2	4.80
	22	P-2	4.75
	33	P-2	4.33
	35	P-3	3.99
	46	K-3	3.01
G-615	0	--	9.86
	6	C-2	7.20
	9	C-2	6.63
GX-176	0	--	9.70
	6	K-2	7.60
	12	K-2	6.60
	18	K-2	6.46
	24	K-2	6.15
	30	K-2	5.20
	7	P-2	7.70
	14	P-2	6.89
	19	P-2	6.06
	12	P-6	7.15
	24	P-6	6.70
	30	P-6	5.36

a. See Text for description of method.

desorption data for Types GX-176, G-615, and 416 carbons are compared with the reciprocal of the carbon pH (1/pH instead of service age), all three carbons appear to behave similarly, as shown in Figure 3. Earlier studies on new carbons showed a similar pH effect on high-temperature iodine retention and indicate that one of the principal mechanisms for high-efficiency iodine retention is the conversion of elemental iodine to ionic iodine on the charcoal.[15]

Other Tests

Determinations were made of the ignition characteristics of carbons exposed in the confinement system. The data for impregnated carbons show an initial increase in carbon ignition temperatures for the first few months of service followed by a decrease to values well below those obtained for new carbons. The total iodine content of selected samples of Type GX-176 carbon in service in the confinement system also show an initial increase followed by a slight decrease. Ignition temperature and total iodine content data are shown in Table 5.

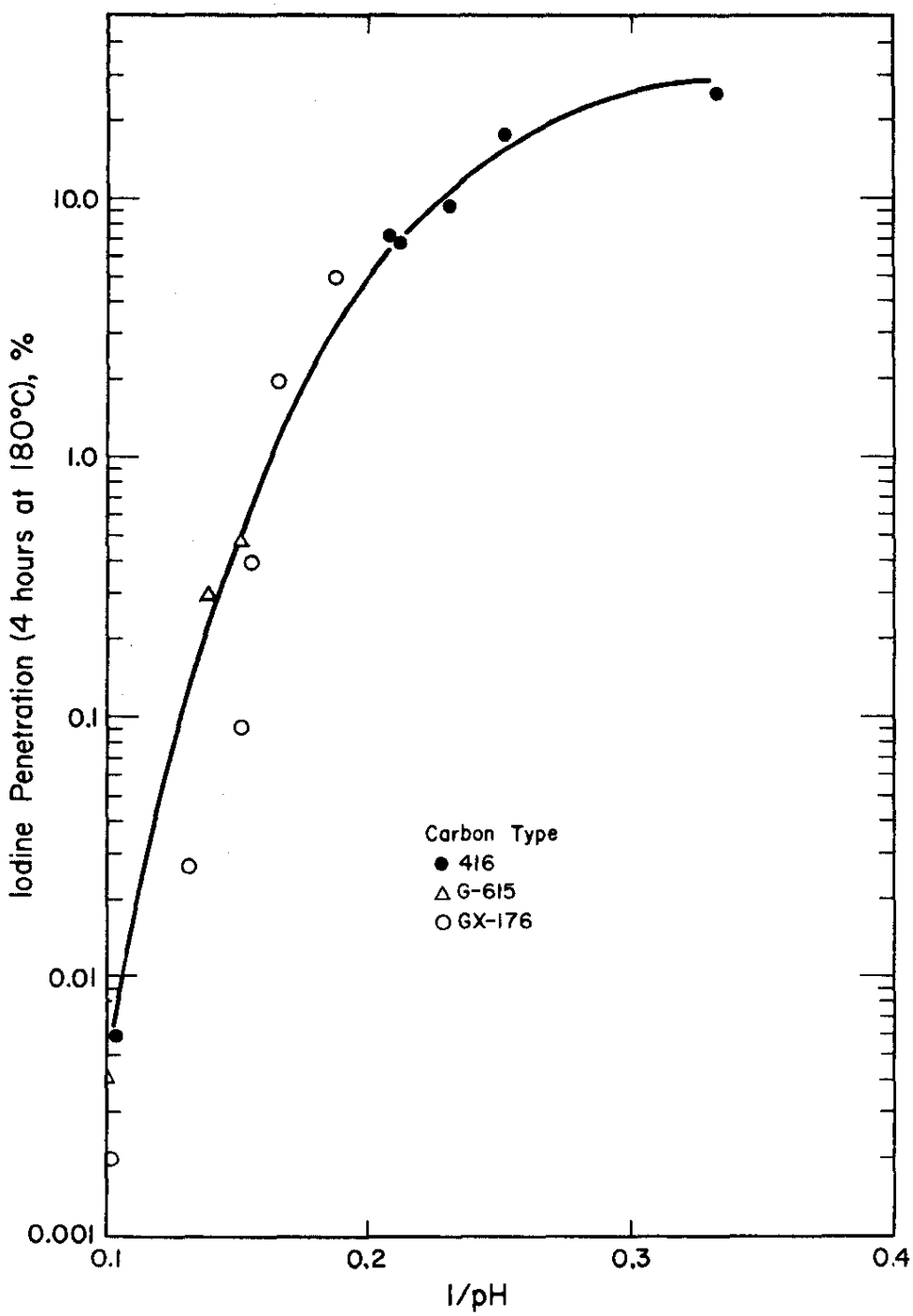

FIGURE 3. High-Temperature Iodine Penetration as a Function of carbon pH

TABLE 5

Other Properties of Service-Aged Carbons

Carbon Type	*Service Time, months*	*Compartment Number*	*Ignition Temp,*[a] *°C*	*Total Iodine,*[b] *wt %*
416	0	(Control)	340	--
	43	K-3	275	--
G-615	0	(Control)	360	--
	6	C-2	420	--
	9	C-2	415	--
GX-176	0	(Control)	386	1.41
	6	K-2	437	1.72
	12	K-2	322	1.59
	18	K-2	312	1.59
	24	K-2	297	--
	30	K-2	295	--
	7	P-2	420	--
	9	P-2	415	--
	14	P-2	336	--
	19	P-2	287	--
	12	P-6	333	--
	24	P-6	320	--

a. As measured in a standard ASTM quartz ignition-temperature apparatus at a heating rate of 5°C/min and a linear face velocity of 55 fpm at 300°C.

b. Determined by neutron activation analysis.

Selected samples of carbon were also sent to the Naval Research Laboratory (NRL) where methyl iodide penetration tests were performed. NRL test conditions were 25°C temperature, 95% relative humidity, 0.25-second residence time (2-inch-deep carbon bed), 0.1 mg CH_3I/g carbon loading, and a total test time of 4 hours (2 hours loading, 2 hours desorption) following a 16-hour pre-equilibration period at 25°C and 95% relative humidity. This test is intended as a qualification test for new carbons and is not necessarily indicative of expected carbon performance under accident conditions. Results of methyl iodide penetration tests at NRL are summarized in Table 6.

Type 416 carbon was not tested because of the known poor methyl iodide retention properties of unimpregnated carbons. The initial lower methyl iodide penetration and slower rate of deterioration during the first 6 months of service obtained for Type GX-176 indicates the importance of particle size distribution in initial performance and in service aging rates, as discussed in References 16 and 17.

TABLE 6

Methyl Iodide Penetration of Confinement-System Carbons

Carbon Type	*Service Time, months*	*Methyl Iodide Penetration, %*[a]
G-615[b]	0	0.79
	6	11.4
	9	22.3
GX-176[c]	0	0.45
	6	5.82
	12	28.5
	18	32.1

a. NRL test data courtesy V. R. Deitz.

b. Service exposure in the C-2 compartment.

c. Service exposure in the K-2 compartment.

NEW IMPREGNANT DEVELOPMENTS

Joint studies have continued at NRL and SRL to develop new impregnant-carbon combinations for efficient trapping of methyl iodide in reactor off-gas cleanup systems. The purpose of these studies is twofold. First, effective impregnant combinations are being sought to replace formulations containing TEDA. While the TEDA has been proven to be an effective additive for trapping and retaining many forms of radioiodine, the combined effects of high material cost, high vapor pressure, and low flash point necessitates caution in both the manufacture and use of TEDA-impregnated carbons.[16,18]

Research efforts were undertaken earlier at NRL to find a suitable substitute for TEDA in impregnation formulations. Results of these studies indicated that the compound hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) could be used effectively in combination with iodine salts and potassium hydroxide to retain methyl iodide.[19] Improved thermal stability of HMTA-impregnated carbons was demonstrated in earlier studies at SRL. These studies showed a systematic increase in carbon ignition temperature with increasing HMTA content up to about 4% added HMTA.[16]

The second purpose of the joint NRL-SRL studies is to demonstrate effective trapping of radioiodine compounds on carbons derived from domestic raw materials. Most of the reactors in the United States specify coconut-base carbon for their iodine trapping

systems because of the unique combination of physical hardness and chemical reactivity for iodine compounds. Excessive world demand for coconut-base carbon or unfavorable international political situations might conceivably limit availability of coconut-base carbon, thus requiring availability of substitutes.

Earlier studies at SRL[14,15,20] demonstrated that elemental iodine could be efficiently trapped on a variety of base carbons when excess potassium (as KOH or K_2CO_3) was added to the carbon. These studies showed that the mechanism for very efficient retention of iodine on carbon is a pH-sensitive chemical reaction in which I_2 is converted to ionic iodine salts (I^-, IO^-, IO_3^-). As indicated earlier in this report, iodine retention is a function of pH of the carbon, and a high pH is required to form the stable iodine salts.

Recent studies at NRL[19] indicate that efficient methyl iodide retention on iodized charcoals is also a pH-sensitive chemical reaction in which CH_3I is catalytically converted to methanol (CH_3OH) and potassium iodide (KI) as shown in the equations

$$CH_3I^* + K^+ + OI^- \rightarrow CH_3OI + KI^*$$

$$CH_3OI + OH \rightarrow CH_3OH + OI^-$$

where I* = radioactive species.

A high pH is required to stabilize the (OI^-) ion on the carbon and to complete the conversion of the intermediate product (CH_3OI) to methanol. Thus, efficient trapping of both elemental iodine and methyl iodide require a carbon with a high pH. Addition of KOH (or K_2CO_3) to impregnation formulations, however, lowers the ignition temperature of the resulting impregnated carbons.[20] Acceptable ignition characteristics can be obtained by the addition of phosphate salts to the impregnation solutions. When added in the right proportions, the phosphate salts also serve as pH buffers, thus maintaining favorable chemical conditions for retaining radioiodine on the carbon.

During the current report period, approximately fifty samples were prepared using several impregnation formulations on nine different charcoals. The charcoals used in the experiments are listed in Table 7.

The initial SRL impregnation formulations incorporating HMTA were used on coconut-base carbons. Methyl iodide penetration data for the resulting test carbons showed the optimum level of iodine and HMTA impregnation to be 2.0 weight percent (2% total iodine, 2% HMTA).[16] These early preparations were made using 1% iodine

from I_2 and 1% iodine from KI. Sufficient KOH was added to the impregnation solutions to assure an I/K atom ratio of 0.6 or less (see Reference 20). The elemental iodine added to the solutions was always converted to ionic salts in the high pH solutions according to the idealized reaction[21]

$$3I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$$

Other oxiodides are probably also formed in the iodine-caustic reaction as discussed in References 19 and 22.

Because consideration must be given both to cost and handling safety of reagents in adapting the formulations to commercial carbon production, most of the subsequent impregnations have been made with KI and KIO_3 salts rather than the more hazardous and expensive elemental iodine. Impregnation solutions are now prepared by adding total iodine at the 2.0% level, but with a 5:1 mole ratio of KI and KIO_3. KOH is still added in varying amounts to achieve favorable I/K ratios and to produce a carbon with a high pH.

Experimental carbons were subjected to a variety of analytical and iodine penetration tests to confirm the levels of impregnation and to determine optimum combinations for a given base charcoal. Tests performed include pH measurements, ignition temperature measurements, specific analyses for Na, K, and I (by neutron activation analysis), I_2 penetration tests (at 180°C), and methyl iodide penetration tests (performed at NRL).

TABLE 7

Base Carbons Used in Experimental Impregnations

Manufacturer's Designation	*Source Material*	*Vendor*
BPL[a]	Coal	Calgon Corporation, Pittsburgh, PA
BPX[a]	Coal	Calgon Corporation, Pittsburgh, PA
Witcarb 965[b]	Petroleum	Witco Chemical Corporation, New York, NY
MBV[c]	Coal	Union Carbide Corporation, New York, NY
207A[d]	Coal	Sutcliff Speakman & Co., Ltd., Bronxville, NY
G-352[e]	Coal	North American Carbon Company, Columbus, OH
G-210[b]	Coconut	North American Carbon Company, Columbus, OH
G-212[b]	Coconut	North American Carbon Company, Columbus, OH
GX-202[b]	Wood	North American Carbon Company, Columbus, OH

a. Sieved to a 10 × 16 mesh particle size distribution (U.S. Sieve Series).

b. 8 × 16 mesh particle size distribution.

c. 6 × 14 mesh particle size distribution.

d. 10 × 16 mesh particle size distribution.

e. Ground and sieved to a 10 × 16 mesh particle size distribution.

Coconut- and Wood-Base Carbon

HMTA was first applied to coconut-base carbons so comparisons could be made with TEDA-impregnated products. Systematic studies of ignition retardants were also begun on coconut-base carbon. Studies were then extended to other base carbons. Impregnation and test data for coconut- and wood-base carbons are shown in Table 8.

Three types of inorganic salts are commonly used as ignition retardants in treating combustible materials: (1) halide salts, (2) phosphorous salts, and (3) boron salts. The effect of all three types of materials can be seen by comparing ignition temperature data on Samples 3, 2, 7, 8, and 38 in Table 8. Sample 3 was prepared with elemental iodine (I_2) with no specific ignition retardant. Sample 2 was prepared with KI and I_2. The effect of half the iodine being added as the KI salt was to raise the ignition temperature from 265 to 325°C. Addition of 1% monosodium phosphate ($NaH_2PO_4 \cdot H_2O$) increased the ignition temperature to 390°C (Sample 7). When 1% disodium phosphate ($Na_2HPO_4 \cdot 2\ H_2O$) was added (Sample 8), the ignition temperature increased to 355°C, but methyl iodide penetration increased considerably. Addition of 0.8% boric acid (H_3BO_3) (Sample 38), reduced the ignition temperature to 275°C and increased the methyl iodide penetration to the highest value obtained in this sample series. Similar poor results were obtained when H_3BO_3 was used on a coal-base carbon and will be discussed later in this report.

The data in Table 8 indicate that combining 1.3% KI with 1.0% monosodium phosphate gives the best ignition retardant combination without significant sacrifice in methyl iodide retention. Additional studies on phosphate additives are discussed later under coal-base carbon impregnations.

Comparison of methyl iodide penetration data for Samples 28 and 35 indicates that HMTA is of some value in improving the performance of iodized Type G-210 carbon. However, the level of methyl iodide penetration of all the samples in Table 8 is generally greater than that obtained with TEDA-impregnated coconut-carbon (0.79% for new Type G-615 and 0.45% for new Type GX-176 - Table 6). The low penetration data obtained from Sample 22 (0.46%) indicates that a satisfactory impregnation formulation can be developed for the HMTA-coconut carbon combination.

Data obtained from the wood-base carbon indicate that the addition of 2% HMTA to the formulation does not improve methyl iodide retention (Samples 23 and 32). As with coconut-base carbon, further experimentation would be required to develop a product yielding consistent results.

TABLE 8

HMTA Impregnations of Coconut- and Wood-Base Carbons

Carbon Type and Number[a]		*Iodine Form*[b]	*Impregnation Level, weight %*				*pH*	*Ign. Temp, °C*	*Iodine Penetration, %*	
			HMTA	*Iodine*	*KOH*	*I.R.*[c]			CH_3I[d]	I_2[e]
G-210	3	I_2	5.0	2.0	1.4	None	10.40	265	2.53	0.41×10^{-3}
G-210	2	I_2, I^-	5.0	2.0	0.7	None	10.62	325	1.33	0.31×10^{-3}
	7	I_2, I^-	5.0	2.0	0.7	1.0	10.40	390	1.86	0.52×10^{-3}
	8	I_2, I^-	5.0	2.0	0.7	1.0[f]	10.20	355	3.18	0.57×10^{-3}
	18	I_2, I^-	5.0	2.0	0.7	1.0	10.66	398	1.74	2.89×10^{-3}
	22	I^-, IO_3^-	2.0	2.0	0.8	1.0	10.48	320	0.46	1.04×10^{-3}
	28	I^-, IO_3^-	2.0	2.0	0.4	1.0	10.30	375	2.59	0.88×10^{-3}
	40	I^-, IO_3^-	2.0	2.0	0.8	1.0	10.24	350	2.32	0.56×10^{-3}
	38	I^-, IO_3^-	2.0	2.0	0.8	0.8[g]	10.03	275	4.45	0.84×10^{-3}
	35	I^-, IO_3^-	0.0	2.0	0.4	1.0	9.09	377	4.10	0.79×10^{-3}
G-212	19	I_2, I^-	5.0	2.0	0.7	1.0	10.37	335	2.47	2.31×10^{-3}
	25	I^-, IO_3^-	2.0	2.0	0.4	1.0	10.20	335	0.91	1.20×10^{-3}
GX-202	15	I_2, I^-	5.0	2.0	0.7	1.0	10.21	436	0.99	4.50×10^{-3}
	23	I^-, IO_3^-	2.0	2.0	0.4	1.0	10.16	412	1.49	1.15×10^{-3}
	43	I^-, IO_3^-	2.0	2.0	0.8	1.0	9.72	425	2.39	1.34×10^{-3}
	32	I^-, IO_3^-	0.0	2.0	0.4	1.0	9.86	403	1.42	1.53×10^{-3}

a. See Table 7 for description of base charcoals. Sample numbers are laboratory identification numbers.

b. Designates source of iodine for impregnation solutions (see Text).

(I_2, I^-) = 1.0 wt % I_2, 1.31 wt % KI; (I^-, IO_3^-) = 2.18 wt % KI, 0.56 wt % KIO_3.

c. Ignition retardant. $NaH_2PO_4 \cdot H_2O$ used except where noted.

d. Methyl iodide test data courtesy V. R. Deitz (NRL). See Text for test conditions.

e. SRL high-temperature test (see Text), iodine penetration at 180°C.

f. $Na_2HPO_4 \cdot 2H_2O$.

g. H_3BO_3.

Petroleum-Base Carbon

Promising results have been obtained from HMTA impregnations of Witcarb 965 as shown in Table 9. The data indicate that the level of HMTA and KOH impregnation must be carefully controlled to obtain the optimum methyl iodide and elemental iodine retention.

Coal-Base Carbon

Coal-base carbons suitable for air cleaning applications are all manufactured by blending finely pulverized coal or coke with a binder, forming the plastic blend into pellets or cake, then burning the binders out to leave a porous material. The pore structure of the final product is affected by a number of manufacturing variables such as the mineral and volatile component content of the coal, the particle size range of the pulverized coal, the binder used, furnace conditions during carbonization (binder burn-off), and the degree of activation after carbonization. The pore structure, in turn, affects the iodine retention properties and the ability of the carbon to accept and retain impregnants added to enhance the iodine retention properties. Thus, it is necessary to select a coal-base carbon with a favorable pore structure as well as an optimized particle size distribution to produce a good iodine adsorber.

Five different coal-base carbons have been tested at SRL with iodine-salt, HMTA impregnation combinations. Two of the carbons tested (Types G-352 and 207A) are manufactured outside the United States. The remaining three (Types BPL, BPX, and MBV) are domestic carbons. The most consistent methyl iodide penetration data were obtained from impregnations of the foreign carbons. Test data are summarized in Table 10.

Experimental carbons prepared from Type G-352 (ground and sieved to 10 × 16 mesh) show methyl iodide penetrations consistently less than 0.5% with a number of different combinations of HMTA, iodine salts, and KOH. The only poor result was obtained when H_3BO_3 was used as an ignition retardant (Sample number 39, Table 10). This result confirms the earlier observation that H_3BO_3 is an unsatisfactory additive (see Sample 38, Table 8).

In earlier tests of ignition retardants, the monosodium phosphate salt ($NaH_2PO_4 \cdot H_2O$) was superior to the disodium salt ($Na_2HPO_4 \cdot 2H_2O$) when each was present at the 1.0 weight percent level (Samples 7 and 8, Table 8). Additional samples were prepared with Type G-352 using each of the three sodium phosphate salts ($NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$ and $Na_3PO_4 \cdot 12H_2O$). For these samples the total salt added was adjusted to obtain a constant phosphate ion (PO_4^{-3}) content of 0.69 weight percent. The potassium

TABLE 9

HMTA Impregnations of Petroleum-Base Carbons

Carbon Type and Number[a]	*Iodine Form*[b]	*Impregnation Level, weight %*				*pH*	*Ign Temp, °C*	*Iodine Penetration, %*	
		HMTA	*Iodine*	*KOH*	*I.R.*[c]			CH_3I[d]	I_2[e]
Witcarb 965									
17	I_2, I^-	5.0	2.0	0.7	1.0	8.54	425	0.73	7.21×10^{-3}
44	I^-, IO_3^-	2.0	2.0	0.8	1.0	10.10	425	0.72	1.06×10^{-3}
27	I^-, IO_3^-	1.7	2.0	0.8	1.0	10.10	415	0.44	6.92×10^{-3}
29	I^-, IO_3^-	2.0	2.0	0.6	1.0	9.77	432	1.10	0.41×10^{-3}
33	I^-, IO_3^-	0.0	2.0	0.8	1.0	10.08	425	1.09	1.73×10^{-3}

a. See Table 7 for description of base carbon. Sample numbers are laboratory identification numbers.

b. (I_2, I^-) = 1.0 wt % I_2, 1.3 wt % KI; (I^-, IO_3^-) = 2.18 wt % KI; 0.56 wt % KIO_3.

c. Ignition retardant, $NaH_2PO_4 \cdot H_2O$.

d. CH_3I penetration data courtesy V. R. Deitz, NRL.

e. SRL high-temperature test (180°C).

TABLE 10

HMTA Impregnations of Types G-352 and 207A Coal-Base Carbons

Carbon Type and Number[a]	*Iodine Form*[b]	*Impregnation Level, weight %*				*pH*	*Ign Temp, °C*	*Iodine Penetration, %*	
		HMTA	*Iodine*	*KOH*	*I.R.*[c]			CH_3I[d]	I_2[e]
G-352									
14	I , I^-	5.0	2.0	0.7	1.0	8.33	450	0.50	1.41×10^{-3}
24	I^-, IO_3^-	2.0	2.0	0.4	1.0	8.36	447	0.37	6.95×10^{-3}
27	I^-, IO_3^-	2.0	2.0	0.7	1.0	9.82	430	0.36	1.21×10^{-3}
48	I^-, IO_3^-	2.0	2.0	0.8	1.0	9.85	397	0.48	1.09×10^{-3}
31	I^-, IO_3^-	0.0	2.0	0.8	1.0	9.42	420	0.21	3.25×10^{-3}
39	I^-, IO_3^-	2.0	2.0	0.8	0.8[f]	9.12	395	1.17	1.60×10^{-3}
51	I^-, IO_3^-	2.0	2.0	0.8	1.0	10.20	419	0.48	11.1×10^{-3}
52	I^-, IO_3^-	2.0	2.0	0.4	1.9[g]	10.02	417	0.46	5.23×10^{-3}
53	I^-, IO_3^-	2.0	2.0	0.0	2.8[h]	10.00	440	0.51	5.11×10^{-3}
207A									
54	I^-, IO_3^-	2.0	2.0	0.8	1.0	9.24	400	0.21	1.82×10^{-3}
58	I^-, IO_3^-	1.5	2.0	0.8	1.0	9.53	400	0.22	2.14×10^{-3}
57	I^-, IO_3^-	0.98	1.9	0.8	1.0	9.54	400	0.35	0.77×10^{-3}
56	I^-, IO_3^-	0.5	2.0	0.8	1.0	9.48	390	0.38	1.04×10^{-3}
55	I^-, IO_3^-	0.0	2.0	0.8	1.0	9.32	395	0.21	1.55×10^{-3}

a. See Table 7 for description of base carbons. Sample numbers are laboratory identification numbers.

b. (I_2, I^-) = 1.0 wt % I , 1.3 wt % KI; (I^-, IO_3^-) = 2.18 wt % KI, 0.56 wt % KIO_3.

c. Ignition retardant; $NaH_2PO_4 \cdot H_2O$ except as noted.

d. CH_3I penetration data courtesy V. R. Deitz, NRL.

e. SRL high-temperature test at 180°C.

f. H_3BO_3.

g. $Na_2HPO_4 \cdot 7\ H_2O$.

h. $Na_3PO_4 \cdot 12\ H_2O$.

hydroxide content was adjusted to obtain a tribasic phosphate salt (NaK_2PO_4, Na_2KPO_4 or Na_3PO_4). Test results (Samples 51, 52, and 53, Table 10) show nearly equal methyl iodide penetration for each combination, and indicate that the phosphate ion content is more important than the salt form. The choice of reagents for production lots would thus be based on material costs and handling convenience.

Data reported earlier[16,18] showed an optimum HMTA content for coconut-base carbons of 1 to 2 wt %. A series of samples was prepared on Type 207A carbon in which the HMTA content was varied from 0.0 to 2.0 wt % as shown in Table 10. While all the samples showed low methyl iodide penetration, the samples containing 1.5 and 2.0% HMTA (Samples 58 and 54) were slightly better than those containing 0.5 and ∿1.0% HMTA (Samples 56 and 57).

Control samples (those containing only iodine salts with no HMTA) for both Types G-352 and 207A also showed very low methyl iodide penetration. Control samples for all other base carbons tested showed higher CH_3I penetration than their companion samples prepared with HMTA. These results suggest that the pore structures of Types G-352 and 207A carbons are well suited for methyl iodide adsorption and subsequent reaction of the CH_3I with the iodine salt impregnants. Service aging of Types G-352 and 207A should reduce the efficiency of the methyl iodide catalysis reaction, however, and the beneficial presence of HMTA would become more apparent by providing a second reaction mechanism for trapping the organic iodides.

Impregnation and test data for three other coal-base carbons (Types BPL, BPX, and MBV) are shown in Table 11. Examination of the data shows that satisfactory methyl iodide penetration data (less than 1% penetration) have been obtained with each carbon. The data show, however, that these carbons are more sensitive to minor variations in impregnation formulation (particularly the amount of KOH added). For a more extensive investigation of the effect of impregnation formulation on Type MBV carbon, see Reference 19.

TABLE 11

HMTA Impregnations of Types BPL, BPX, and MBV Coal-Base Carbons

Carbon Type and Number[a]	*Iodine Form*[b]	*Impregnation Level, weight %*				*pH*	*Ign Temp, °C*	*Iodine Penetration, %*	
		HMTA	*Iodine*	*KOH*	*I.R.*[c]			CH_3I[d]	I_2[e]
BPL									
16	I_2, I^-	5.0	2.0	0.7	1.0	8.99	433	0.53	3.37×10^{-3}
26	I^-, IO_3	2.0	2.0	0.6	1.0	9.99	420	0.69	1.84×10^{-3}
50	I^-, IO_3	2.0	2.0	0.8	1.0	9.77	412	1.28	12.6×10^{-3}
34	I^-, IO_3	0.0	2.0	0.8	1.0	9.90	392	1.30	0.79×10^{-3}
BPX									
36	I^-, IO_3^-	2.0	2.0	0.82	1.0	9.80	410	1.05	1.21×10^{-3}
47	I^-, IO_3^-	2.0	2.0	0.80	1.0	9.69	415	0.67	0.85×10^{-3}
37	I^-, IO_3^-	0.0	2.0	0.79	1.0	9.56	405	2.20	3.14×10^{-3}
MBV									
30	I^-, IO_3^-	2.0	2.0	0.7	1.0	9.88	445	0.75	14.8×10^{-3}
49	I^-, IO_3^-	2.0	2.0	0.8	1.0	10.34	435	0.44	21.0×10^{-3}

a. See Table 7 for description of base carbons. Sample numbers are laboratory identification numbers.

b. (I_2, I^-) = 1.0 wt % I_2, 1.3 wt % KI; (I^-, IO_3^-) = 2.18 wt % KI, 0.56 wt % KIO_3.

c. Ignition retardant; $NaH_2PO_4 \cdot H_2O$ used for all samples.

d. CH_3I penetration data courtesy V. R. Deitz, NRL.

e. SRL high-temperature test at 180°C.

Additional Tests

While satisfactory methyl iodide retention values have been obtained for several combinations of carbon and impregnants on newly impregnated carbons, the service aging characteristics and service attrition characteristics of the samples have yet to be determined. Small samples (about 300 g) of several of the carbons have been installed in the CTF for preliminary evaluation. The first of these samples is scheduled for removal in the spring of 1977. The test beds (especially the coal-base samples) will be examined for evidence of carbon loss, then tested for methyl iodide retention. NRL is currently considering the impregnation of larger samples (50 pounds each of several base carbons) for more detailed analysis. SRL will participate in both the service exposure and analysis phases of this program. Quantitative evaluation of the rate of wear of carbon granules in a flowing air stream (a service attrition test) must await development of a test method.

CONCLUSIONS

A variety of foreign and domestic base carbons have been impregnated with several combinations of iodine salts, KOH, HMTA, and ignition retardants. Acceptable methyl iodide retention (less than 1% penetration) has been obtained after impregnation of each type of base carbon tested. For some of the carbons, however, wide variations in methyl iodide penetration data were observed with only minor changes in the impregnation formulation. Consistent data were obtained for several impregnant variations on two types of coal-base carbon (Types G-362 and 207A), indicating that the impregnation formulations investigated at SRL are well suited to these particular carbons. Further development work will be required to determine the proper impregnant combinations for the other base carbons.

REFERENCES

1. 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 and Co., Savannah River Laboratory, Aiken, SC (1966).

2. W. S. Durant. *Performance of Activated Carbon Beds in SRP Reactor Confinement Facilities - Progress Report: September 1961 - September 1965*. USAEC Report DP-1028, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1966).

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

4. R. C. Milham and L. R. Jones. *Iodine and Noble Gas Retention Studies - Progress Report: October 1966 - December 1968*. USAEC Report DP-1209, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1969).

5. R. C. Milham and L. R. Jones. *Iodine Retention Studies - Progress Report: January 1969 - June 1969*. USAEC Report DP-1213, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1969).

6. R. C. Milham and L. R. Jones. *Iodine Retention Studies - Progress Report: July 1969 - December 1969*. USAEC Report DP-1234, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1970).

7. A. G. Evans and L. R. Jones. *Iodine Retention Studies - Progress Report: January 1970 - June 1970*. USAEC Report DP-1259, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1971).

8. A. G. Evans and L. R. Jones. *Iodine Retention Studies - Progress Report: July 1970 - December 1970*. USAEC Report DP-1271, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1971).

9. A. G. Evans and L. R. Jones. *Confinement of Airborne Radioactivity - Progress Report: January 1971 - June 1971*. USAEC Report DP-1280, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1971).

10. A. G. Evans and L. R. Jones. *Confinement of Airborne Radioactivity Progress Report: July 1971 - December 1971.* USAEC Report DP-1298, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1972).

11. A. G. Evans and L. R. Jones. *Confinement of Airborne Radioactivity - Progress Report January-June 1972.* USAEC Report DP-1316, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1973).

12. A. G. Evans. *Confinement of Airborne Radioactivity - Progress Report: July 1972 - December 1972.* USAEC Report DP-1329, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1973).

13. A. G. Evans and L. R. Jones. *Confinement of Airborne Radioactivity - Progress Report: January 1973 - June 1973.* USAEC Report DP-1340, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1973).

14. A. G. Evans and L. R. Jones. *Confinement of Airborne Radioactivity - Progress Report: July 1973 - December 1973.* USAEC Report DP-1355, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1974).

15. A. H. Dexter, A. G. Evans, and L. R. Jones. *Confinement of Airborne Radioactivity - Progress Report: January - December 1974.* USERDA Report DP-1390, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1975).

16. A. G. Evans and A. H. Dexter. *Confinement of Airborne Radioactivity - Progress Report: January - December 1975.* USERDA Report DP-1430, E. I. du Pont de Nemours and Co., Savannah River Laboratory, Aiken, SC (1976).

17. A. G. Evans, "Effect of Service Aging on Iodine Retention of Activated Charcoals." *Proceedings of the 14th ERDA Air Cleaning Conference,* Sun Valley, Idaho, August 2-4, 1976, p 251, USERDA Report CONF-760822, Technical Information Center, Oak Ridge, TN (1977).

18. A. G. Evans. "New Charcoal Impregnants for Trapping Methyl Iodide, Part II, Applications to a Variety of Base Charcoals." *Proceedings of the 14th ERDA Air Cleaning Conference,* Sun Valley, Idaho, August 2-4, 1976, p 310, USERDA Report CONF-760822, Technical Information Center, Oak Ridge, TN (1977).

19. V. R. Dietz and C. H. Blachly. "New Charcoal Impregnants for Trapping Methyl Iodide, Part I. Salts of the Iodine Oxacids with Iodide or Iodine and Hexamethylene-tetramine." *Proceedings of the 14th ERDA Air Cleaning Conference*, Sun Valley, Idaho, August 2-4, 1976, p 294, USERDA Report CONF-760822, Technical Information Center, Oak Ridge, TN (1977).

20. A. G. Evans. "Effect of Alkali Metal Content of Carbon on Retention of Iodine at High Temperatures." *Thirteenth AEC Air Cleaning Conference*, San Francisco, CA, August 12-15, 1974, p 743, USAEC Report CONF-74087, Vol. 2, Technical Information Center, Oak Ridge, TN (1975).

21. Therald Moellar. *Inorganic Chemistry*. John Wiley & Sons, Inc., New York (1952).

22. A. J. Downs and C. J. Adams. *The Chemistry of Chlorine, Bromine, Iodine and Astatine*. Pergamon Texts in Inorganic Chemistry, Vol. 7, Pergamon Press, New York (1973).