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CONFINEMENT OF AIRBORNE RADIOACTIVITY

Progress Report: January – December 1975

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AIKEN, SOUTH CAROLINA 29801

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

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by

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Approved by

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ABSTRACT

Efforts are underway at Savannah River Laboratory (SRL) and the Naval Research Laboratory (NRL) to develop new carbon-impregnant formulations suitable for use in nuclear power plants as well as in the SRP system. Emphasis has been placed on carbons derived from domestic raw materials and impregnated with an amine having lower vapor pressure, higher flash point, and lower cost than triethylenediamine (TEDA). Promising results have been obtained with carbons derived from coal, petroleum, wood, and coconut and impregnated with a combination of iodine salts and hexamethylenetetramine (HMTA). Service-aging of several of the HMTA-iodine salt carbons is also being studied.

A separate study of the ability of sodium thiosulfate and potassium hydroxide to retain iodine in aqueous solutions in the presence of high-intensity gamma radiation show that concentrations of ∿1 wt % thiosulfate are required to reduce iodine evolution to less than 1%. A 0.05 wt % addition of potassium hydroxide has about the same effect. These studies revealed that lower concentrations of thiosulfate actually appear to promote evolution of both iodine and an unidentified species of iodine that is capable of penetrating several inches of carbon adsorber. The unidentified iodine compounds are, however, efficiently retained by a HEPA filter. This result suggests that the penetrating iodine may exist in the form of a particulate or aerosol.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

CONFINEMENT OF AIRBORNE RADIOACTIVITY

Progress Report: January – December 1975

INTRODUCTION

This report describes work during 1975 as part of a continuing program to provide adequate confinement of airborne radioactivity in the highly unlikely event of a major Savannah River Plant (SRP) reactor accident.[1] An accident of concern is a loss of coolant accompanied by severely degraded performance of the emergency cooling system. This accident sequence could result in significant melting of fuel accompanied by release of airborne fission-product activity such as radioiodine. Some of the iodine would volatilize into the air in the reactor building, and some might be dissolved in emergency cooling water and transferred to a retention basin. Because the retention basin is not confined, iodine could evolve into the environment.

Airborne iodine is confined within the reactor building by beds of activated carbon. This report describes the continuing program to improve the confinement capabilities of these beds. A second part of this report describes the laboratory evaluation of additives that could retard volatilization of iodine from aqueous solutions.

CARBON STUDIES

Carbon Testing

Previous confinement studies at Savannah River 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, and radiation exposure to iodine-bearing carbon in the beds.[2-15]

To improve the performance of the confinement system, unimpregnated carbon that had been used as an iodine adsorber for many years was phased out of service and replaced by Type GX-176 carbon*, a coconut carbon coimpregnated with potassium iodide and triethylenediamine (TEDA).[13] Changeover to the new carbon was completed in 1975.

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

The use of impregnated carbon necessitated development and implementation of new quality assurance tests to confirm vendor compliance with purchase specifications. Neutron activation analysis and pH measurements[15] were used to ensure both proper iodine salt impregnation level and a proper balance of I, K, and pH for optimum performance in the system. A TEDA extraction procedure was developed for use with the QA tests. Details of this procedure are reported in the Appendix.

Installation of the new type of carbon required aging studies to determine the iodine retention of this carbon in service. Improved performance of the new carbon was demonstrated during 18 months of continuous service. These service-aging studies will be continued.

Studies are also in progress to develop an impregnant formulation that will overcome the disadvantages of TEDA-impregnated coconut carbon: high cost, relatively high TEDA vapor pressure, relatively low TEDA flash point, and dependence on foreign sources for raw materials. Cooperative efforts between the Savannah River Laboratory (SRL) and the Naval Research Laboratory (NRL) indicate that several carbon-impregnant combinations that use domestic base carbons with iodine salts and hexamethylenetetramine (HMTA) may be as effective as the TEDA-KI-coconut carbon combinations.

Service-Aging Studies

Changeover from the unimpregnated carbon to Type GX-176 carbon[13] began in May 1974 and was completed in July 1975. Service-aging studies on the new carbon were started early in 1974 when small samples were installed in test beds in the Carbon Test Facility (CTF) in the P reactor area, and periodic sampling of full-sized carbon beds was also begun. Carbon with up to 18 months exposure to reactor building air was tested for iodine penetration with the SRL radiolytic desorption test.[10] All samples of Type GX-176 carbon performed better in a radiation environment than did the unimpregnated carbon with no service exposure.

Significant differences in service-aging rates were noted between CTF-aged samples and carbon removed from the confinement system. Type GX-176 carbon in the confinement system continues to outperform both the CTF carbons and samples of Type G-615 carbon* exposed earlier in the confinement system.[13] Test data

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

for Type GX-176 carbon are shown in Table 1. Data for Type G-615 carbon and unimpregnated Type 416 carbon* are shown in Table 2. These data are also presented in Figure 1. Reasons for the more rapid deterioration of Type G-615 carbon and the CTF samples of Type GX-176 carbon are discussed below.

TABLE 1

Effect of Service on Type GX-176 Carbon

Service Age, Months	*Compartment Number*	*Iodine Penetration, %*[a,b]
0	(Control)	0.025 ±0.01
6	K-2	0.052 ±0.03
6	P-2	0.062 ±0.04
8	P-2	0.051 ±0.03
12	K-2	0.060 ±0.04
12	P-6	0.055 ±0.03
18	K-2	0.090 ±0.02
6	CTF	0.129
7.5[c]	CTF	0.249
12	CTF	0.156
15[c]	CTF	0.207
18	CTF	0.375

---

a. Determined by radiation desorption test: 1 hour loading, 4 hours desorption at 80°C and 95% relative humidity in a radiation field of >1.5 x 10^7 rads/hr absorbed dose rate in carbon.

b. Average and standard deviations given for replicate determinations for confinement carbons. Single determinations given for CTF carbons.

c. Carbon exposed at flow rate of 67 FPM (1.25 x normal flow rate). Service age is estimated by assuming linear relationship between flow rate and service.

TABLE 2

Effect of Service on Other Carbon Types

Carbon Type	*Service, Months*	*Compartment Number*	*Iodine Penetration, %*[a]	
416[b]	0	(Control)	0.33	±0.04
416	21	C-2	0.61	±0.10
416	33	P-2	1.04	±0.20
416	35	P-3	3.61	±0.80
416	46	K-3	4.38	±1.20
G-615[c]	0	(Control)	0.03	±0.01
G-615	6	C-2	0.07	±0.04
G-615	9	C-2	0.129	±0.05

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[a] See Table 1, footnote *a*, for test conditions; values listed are averages with standard deviations.

[b] Unimpregnated carbon formerly used in the confinement system.

[c] An 8 x 16 mesh carbon containing 2% TEDA (Type GX-176 carbon is a 10 x 16 mesh carbon containing 1% TEDA). Both Type G-615 carbon and Type GX-176 carbon contain 2% KI and 1% fire retardant.

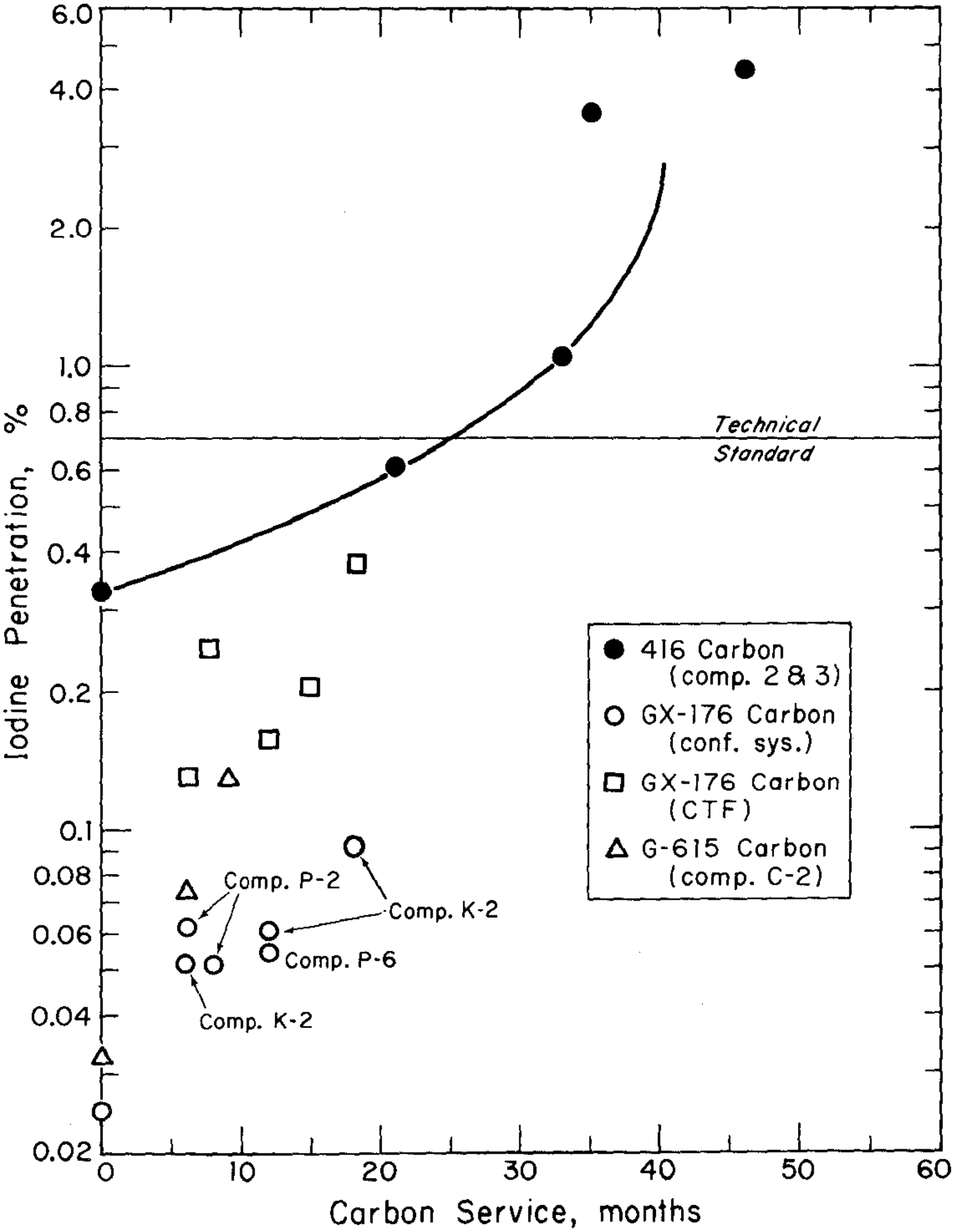

FIGURE 1. Iodine Penetration vs. Carbon Service

Particle-Size Distribution Effects

Three types of impregnated carbon have received service exposure in the SRP confinement system:

- Type G-618 carbon**, an 8x16 mesh coconut carbon impregnated with 5% TEDA.
- Type G-615 carbon, an 8x16 mesh coconut carbon impregnated with 2% TEDA and 2% KI (plus a flame retardant).
- Type GX-176 carbon, a 10x16 mesh coconut carbon coimpregnated with 1% TEDA and 2% KI (plus a flame retardant).

Types G-618 and G-615 carbons were removed from service after exposure of only 6 months and 9 months, respectively, because of the possible risk of carbon ignition.[12] Initial samples of a prototype Type GX-176 carbon were installed in the CTF along with Type G-615 carbon samples. Later, production lots of Type GX-176 carbon with a finer mesh size were placed in the confinemens system.

As discussed in the previous section, the full-sized confinement-system beds of the production lot of Type GX-176 carbon with 18 months exposure have continued to perform better than either the Type GX-176 carbon exposed in the CTF or the Type G-615 carbon exposed in the confinement system for 9 months.

Sieve analyses indicate that differences in performance of the three carbons (Type G-615, prototype GX-176, and confinement Type GX-176) may be due to variations in their particle size distributions. The data in Table 3 show that both Type GX-615 carbon and the prototype lot of Type GX-176 carbon contain a larger weight fraction of particles greater than 1.40 mm in diameter (the nominal opening in a U.S. Standard number 14 sieve) than does the production lot of Type GX-176 carbon. Although other factors (to be discussed in subsequent paragraphs) may affect the performance of the CTF carbons, aging rates of carbon types GX-176 and G-615 are probably affected more by particle size distribution of carbon granules than by impregnant content.

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* Product of Barnebey-Cheney Company, Columbus, Ohio

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

TABLE 3

Particle Size Distributions of Impregnated Carbons

Sieve Size[a]	*Type G-615*[b]	*Type GX-176 (prototype)*[c]	*Type GX-176 (confinement)*[d]	*Purchase Specification*[e]
On No. 8 Sieve	4.8	0.0	0.0	≤0.1
On No. 10 Sieve	24.6	7.9	0.1-0.6	≤5.0
On No. 12 Sieve	37.1	5.3	6.5-8.4	-
On No. 14 Sieve	25.8	61.3	34.1-37.2	-
On No. 16 Sieve	6.5	24.1	50.4-54.8	≥90.0
On No. 18 Sieve	0.9	1.4	2.2-4.5	≤5.0
Through No. 18	0.3	0.0	0.1-0.2	≤1.0

---

a. U.S. Standard ASTM E-11 series sieves.

b. Production lot exposed in C-2 compartment April through December 1972.

c. CTF carbon.

d. Production lot installed in confinement system beginning May 1974. Values given are the range of values obtained from the 16 sublots comprising the full purchase order.

e. This specification did not apply to the Type G-615 or prototype Type GX-176 carbons.

Moisture Condensation Effects

During the first six months of operation of the CTF with the prototype GX-176 carbon installed, moisture condensation and corrosion problems were experienced. In one case, moisture condensation corroded the stainless steel retaining screen and the aluminum test-bed body and leached impregnants from the carbon. The combined effects of impregnant leaching and contamination of the carbon with corrosion products probably contributed to rapid deterioration of the CTF carbon during the first six months (Table 1). The CTF data (Table 1) show that the carbon deteriorated more slowly between 6 and 12 months (when less condensation occurred due to warmer weather).

To resolve the differences between aging rates in the CTF and in the confinement systems, production lots of Type GX-176 carbon were installed in the CTF, and the test beds were thermally insulated to minimize moisture condensation. Use of production lots of Type GX-176 carbon in the CTF will also permit evaluation of the particle-size distribution effects because exposure conditions and impregnant levels will be the same in the CTF for both the production and prototype GX-176 carbon.

Quality Assurance Tests

Earlier studies at SRL have show the importance of proper balance of iodine, potassium, and pH for optimum carbon performance[14,15] and the need for control of TEDA content to reduce the hazard of carbon ignition.[13,14] Present studies indicate that close control of particle size distribution is also needed. The effect on performance of each of these parameters is great enough to dictate extensive quality assurance tests of all carbons installed in the SRP confinement system.

Type GX-176 carbon used at SRP was subjected to a variety of chemical, physical, and iodine-penetration tests before it was installed in the reactor off-gas cleanup system. Among the tests performed were: sieve analyses, pH analyses, iodine and potassium analyses (by neutron activation analysis), iodine-penetration tests using both the high temperature (180°C) test and the radiation test, and ignition temperature tests on each of the 16 sublots of carbon received.

TEDA Analysis of New Confinement Carbons

When the carbon was purchased, no quantitative analytical procedure was available for ascertaining whether the material met the TEDA content specifications. Ignition temperature tests on the carbon indicated that none of the sublots contained sufficient TEDA to cause premature ignition under adverse operating conditions, so installation in the confinement system was started without a specific TEDA analysis. However, an analytical procedure was developed and all sublots of carbon were analyzed before the installation was completed. The procedure involves measurement of infrared absorbance of TEDA that is extracted into CCl_4.

TEDA concentration ranged from 0.86 to 1.08 wt % with an average value of 0.99 wt % and a standard error of 0.08 wt %. The purchase specification for TEDA concentration on the carbon was 1.0 wt % with a range of ±0.1 wt % (an agreed-upon range pending specific analytical data to show the actual range). Apparently the manufacturing controls were effective because only two sublots fell below the minimum range (one by 0.03 wt % and another 0.04 wt %).

TEDA Analysis of Used Carbons

Determination of TEDA by infrared absorption is possible only in the absence of other hydrocarbons (see the Appendix). During the analysis of the new carbons, spectrum shapes were scanned visually for evidence of interference by other compounds. The absorption spectra were consistent with those observed for pure TEDA in CCl_4. To determine applicability of the procedure to used carbons, a sample of Type GX-176 carbon that had service-aged for 6 months in the confinement system was analyzed. The spectrum shape was considerably different; it had a stronger peak at a wave length below 3.3 μm than did pure TEDA. The calculated concentration of TEDA (based om absorbance at 3.74 μm) was 1.61 wt % compared to 1.03 wt % TEDA for the same sublot before confinement-system exposure. The different spectrum shape and the increased TEDA concentration indicate that the method cannot be used in its present form to determine TEDA in service-aged carbons.

No further development work to adapt the procedure to used carbons is planned. The quantitative loss of TEDA from carbon dried at 140°C suggests that a procedure based on thermal stripping rather than solvent extraction may be possible. Gas chromatography could be used to separate TEDA from the atmospheric contaminants.

New Impregnant Developments

Although the use of TEDA as an impregnant to enhance methyl iodide retention by carbon has been established,[9,10] TEDA charcoals have the disadvantage of the high cost of TEDA (~$8.00/pound in bulk lots), potential ignition hazards,[13,14] and the stripping of TEDA from the charcoal at temperatures as low as 140°C. For these reasons, studies are continuing both at SRL and NRL to develop other effective impregnants or impregnant combinations for organic iodide trapping.

British studies have shown that other amine compounds (pyridine, morpholine, piperidine, and others) are also effective as carbon impregnants.[16] However, like TEDA, these compound have relatively low melting and/or boiling points (ranging from 106 to 157°C[16]) and are not suitable impregnants for applications at elevated temperatures.

Preliminary data on carbon impregnated with triethanolamine (TEA, bp 277 to 279°C) were given in the previous progress report.[15] Subsequent data from both SRL and NRL show that TEA is not as effective as TEDA, particularly for methyl iodide trapping. Therefore, a search was undertaken at NRL for other amine compounds having both a low vapor pressure at 100°C and sufficient tertiary amine functional groups to react with methyl iodide. The compound hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) was found to have both thermal stability (it sublimes at 267°C) and adequate iodine retention properties when combined with inorganic iodine salts and potassium hydroxide.

HMTA is used commercially as an accelerator in vulcanizing rubber, in the manufacture of formaldehyde-type resins, and as a poison-gas absorber. It is used medically as a urinary antiseptic and has been used as an anlytical reagent for the determination of allyl halides. The price of HMTA is about $2.25 per pound in bulk lots (less than one-third the cost of TEDA). Even though HMTA is also used commercially as fuel for some types of camp stoves, carbon ignition temperature is not lowered by HMTA impregnation levels as high as 6%.

One-Step Impregnations

Preliminary studies at NRL showed that HMTA-impregnated carbons are effective for trapping methyl iodide only when the impregnants are combined in a specific sequence before the impregnation step is begun.[17] First, the HMTA and I_2 must be intimately mixed (ground together with a mortar and pestle or in a laboratory ball mill). Then potassium hydroxide, water and KI (when used) are added, and the slurry is stirred until a solids-free solution is obtained. Stirring for several hours is frequently necessary. The clear, solids-free solution can then be added to the carbon by drip or spray addition techniques that uniformly impregnate all the carbon granules. The total volume of solution added must be carefully controlled to saturate, but not flood, the carbon.

Earlier work with iodine salt impregnations (with or without TEDA) showed that the volume of water in the impregnation solutions should be the amount of water required to saturate the carbon (with proper allowance for rinse solutions to transfer all the impregnants to the carbon). The HMTA solutions, however, must be prepared with about two-thirds the water to avoid carbon flooding in this single-solution impregnation technique (use of ∿0.4 ml water/g carbon for a charcoal normally requiring 0.6 ml/g for saturation). The reason for the lower saturation volume has not been investigated, but the carbon micropore structure is probably partially plugged by the large hydrated, iodinated HMTA molecule.

SRL participation in the HMTA carbon development effort has been directed toward adapting the impregnation techniques to a variety of base carbons. Studies were initiated with Type G-210 coconut-base carbon* (∿1100 m^2/g surface area, 8 x 16 mesh particle size distribution). Previous studies at SRL have shown the necessity of proper balance among iodine, potassium, and alkalinity.[15] Thus, all the SRL formulations are based on an iodine-to-potassium weight ratio of 2:1 (atom ratio of 0.6:1) which was found most effective in the earlier studies. Because no data were available on optimum impregnation levels for the HMTA-iodine combination on coconut carbon, two series of samples were prepared. The first series consisted of systematic variation of the iodine content and form from 1% to 3% with a constant 5% HMTA. Samples prepared for this series were made with and without flame retardants to study the effect of the flame retardants on ignition temperatures and iodine penetrations of HMTA formulations. After the samples were tested for methyl iodide penetration at NRL, the optimum combination of iodine-iodine salts (1% iodine as I_2, 1% iodine as I^-) was used to prepare the second series in which the HMTA content was systematically varied from 1% to 6%.

Test data from the first sample series (Table 4) show that methyl iodide penetration on samples without flame retardants (first 5 samples) is lowest at 2% total iodine with half the iodine in the elemental form (I_2) and half the iodine in salt form (I^-). Data on samples incorporating flame retardants also show that the I_2-I^- combination is best and that monobasic sodium phosphate ($NaH_2PO_4 \cdot H_2O$) is a better additive than the dibasic salt ($Na_2HPO_4 \cdot 2H_2O$).

Test data from the second sample series (Table 5) show that 2% HMTA impregnation is the best HMTA concentration for methyl iodide retention (lowest penetration values) even though the thermal penetration test data are higher for this combination. Data for Type G-615 carbon (a commercial product of the same base carbon containing 2% TEDA) are shown for comparison.

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

TABLE 4

One-Step Impregnations of Coconut Carbon[a] With Constant HMTA

Impregnation Levels, %					Ratio (I/K) pH[c]	Ignition Temp., °C	*Iodine Penetration, %*	
HMTA	I_2	I^-[b]	KOH	Other			I_2[d]	CH_3I[e]
5.0	1.0	-	0.7	-	0.024	275	0.00061	9.32
5.0	1.0	1.0	0.7	-	0.041	325	0.00031	1.33
5.0	2.0	-	1.4	-	0.037	265	0.00041	2.53
5.0	3.0	-	2.1	-	0.043	265	0.00045	2.61
5.0	1.0	2.0	0.7	-	0.050	315	0.00060	2.39
5.0	2.0	-	1.4	1.0[f]	0.036	355	0.00060	3.05
5.0	1.0	1.0	0.7	1.0[f]	0.038	390	0.00052	1.86
5.0	1.0	1.0	0.7	1.0[g]	0.045	355	0.00057	3.18

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[a] Type G-210 base carbon (see text for description).

[b] As KI. Addition calculated on the basis of weight percent iodine added.

[c] Determined from analyses of carbons after impregnation (Reference 15).

[d] SRL Thermal Desorption test (see text for test conditions).

[e] NRL methyl iodide test data. Test run at 25°C, 95% relative humidity, 5 mg CH_3I/g C loadings and 0.25 second stay time in 2-in. deep carbon bed.

[f] $NaH_2PO_4 \cdot H_2O$ (monobasic sodium phosphate) flame retardant added.

[g] $Na_2HPO_4 \cdot 2H_2O$ (dibasic sodium phosphate) flame retardant added.

TABLE 5

One-Step Impregnations of Coconut Carbon[a] With Constant Iodine

Impregnation Levels, %					*Ratio*	*Ignition*	*Iodine Penetration, %*	
HMTA	I_2	I^-[b]	*KOH*	*Other*	*(I/K)/pH*[b]	*Temp., °C*	I_2[b]	CH_3I[b]
1.0	1.0	1.0	0.7	1.0[c]	0.034	350	0.00067	0.99
2.0	1.0	1.0	0.7	1.0[c]	0.038	370	0.00141	0.65
3.0	1.0	1.0	0.7	1.0[c]	0.029	415	0.00105	1.19
4.0	1.0	1.0	0.7	1.0[c]	0.036	422	0.00092	1.37
5.0	1.0	1.0	0.7	1.0[c]	0.038	390	0.00052	1.86
6.0	1.0	1.0	0.7	1.0[c]	0.037	435	0.00076	1.76
2.0[d] (TEDA)	- (2.0 KI)	-	-	1.0[e]	0.039	360	0.0060	0.79

---

a. Type G-210 base carbon (see text for description).

b. See Table 4 for details.

c. $NaH_2PO_4 \cdot H_2O$.

d. G-615 Carbon (2% TEDA).

e. Proprietary flame retardant.

Two-Step Impregnation

Work at NRL has shown that application of the iodine compounds and HMTA in two separate impregnation steps produces a charcoal with equal or better methyl iodide retention properties than the carbons produced by the single-step impregnation technique.[18] Since the iodine-iodine salt mixture along is freely soluble in water, as is the HMTA alone, the separate impregnation solutions can be prepared in a few minutes (without the lengthy stirring required in the one-step impregnation). The iodine salt mixture dissolved in about one-half the volume of water required to saturate the carbon is added to the carbon first. The HMTA in an equal volume of water is then added. It is not necessary to reduce the water volume as it was for the one-step impregnations. Proper control of the pH of the two impregnation solutions is required, however, to obtain a final product in the desired pH range (≤ 9.5). Thus, both solutions must be titrated to approximately the same pH before the impregnation step. Titres depend on the base charcoal used. Low pH carbons, such as coal and petroleum, require more KOH addition than do the highly alkaline coconut and wood charcoals.

Two series of test carbons have been prepared at SRL by the two-step impregnation technique. The first series was prepared before test data in Table 5 were available and contained 5% HMTA. Test data on this series of two-step impregnations are shown in Table 6. The second series of two-step impregnations was prepared with 2% HMTA. Test data were unavailable at the end of the report period.

The data in Table 6 show that the two-step impregnation technique produces a product about equivalent to the one-step technique with coconut base carbon (1.74% methyl iodide penetration for the two-step method vs. 1.86% methyl iodide penetration for the one-step method). These data also indicate that 5% HMTA retains methyl iodide more effectively on all the non-coconut base carbons (particularly coal carbons) than on the two coconut charcoals tested.

TABLE 6

Two-Step Impregnations[a] of Different Carbon Types

Base Carbon Data				*Iodine Penetration, %*	
Type No.	*Source Material*	*Ratio (I/K)/pH*	*Ignition Temp., °C*	I_2[b]	CH_3I[b]
G-210[c]	Coconut	0.030	398	0.00289	1.74
G-212[c]	Coconut	0.027	335	0.00231	2.47
G-352[c]	Coal	0.090	450	0.00141	0.50
BPL[d]	Coal	0.086	433	0.00337	0.53
337[e]	Petroleum	0.095	425	0.00721	0.73
GX-202[c]	Wood	0.045	436	0.00150	0.99

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[a] 5% HMTA, 1% I_2, 1% I^-, 0.7% KOH, 1% $NaH_2PO_4 \cdot H_2O$ (see text for impregnation details).

[b] See Table 4 for test details.

[c] Product of North American Carbon Company, Columbus, Ohio.

[d] Product of Pittsburgh Activated Carbon Division, Calgon Corporation, Pittsburgh, Pa.

[e] Product of Witco Chemical Corporation, New York, N. Y.

HMTA Carbon Service Aging Studies

Since HMTA is a new impregnant, service-aging effects on HMTA-impregnated carbons are uncertain. Thus, studies will be conducted on the effect of service on the iodine retention properties of the HMTA carbons before such carbons are recommended for use in off-gas cleanup systems. Additional studies are needed on the service attrition rates of the non-coconut base carbons. The first test program is in progress. Samples of coconut carbon containing 5% HMTA were installed in the CTF in 1975 and are scheduled for removal after 6, 12, and 18 months exposure. The first sample is scheduled for removal in April 1976.

Additional HMTA carbons are scheduled for installation in the CTF as test positions become available (April 1976). Testing of coconut-, coal-, petroleum-, and wood-base carbons impregnated with 2% HMTA are included in the service-aging schedule so that both iodine retention properties and service attrition properties can be evaluated.

IODINE EVAPORATION STUDIES

A loss of coolant accompanied by severely degraded performance of the emergency cooling system could result in melting of fuel and dissolution of fission products in the emergency coolant. Volatile fission products such as iodine could subsequently evolve from the emergency coolant and be released to the environment. One method to reduce the potential for such evolution is the use of additives that would retain the volatile, fission-product iodine in solution.

In earlier SRL studies[15] of possible additives, sodium thiosulfate appeared to be the most promising. Laboratory-scale experiments in the absence of a radiation field showed that iodine release could be reduced by 10^4 with a sodium thiosulfate concentration of 8×10^{-4}M in a 5.5×10^{-5}M aqueous solution of iodine. Other work[19,20] indicated that although the combined effects of temperature and radiation would destroy a portion of the thiosulfate, sufficient additive could probably be maintained to keep the iodine in solution. These tests, however, evaluated only the stability of thiosulfate in the radiation field, not the iodine-thiosulfate-radiation combination. To examine the combined effect, laboratory-scale experiments were performed with the SRL ^{60}Co Irradiation Facility to obtain radiation doses of 10^7 to 10^8 rad, doses comparable to those expected during the hypothetical accident. During these experiments, a combination of additive and radiation field was found that generated an iodine species that could not be trapped by carbon beds but could be collected on a HEPA filter. Attempts to identify the volatile species have been unsuccessful to date.

Experimental Equipment

The SRL ^{60}Co Irradiation Facility[21] which provides 2.7×10^7 rads/hr was used to irradiate aqueous solutions of KI to doses of 10^8 rads. The KI in each experiment was "tagged" with ∿1 mCi of ^{131}I, and scintillation counting equipment was used to measure the volatilization of the ^{131}I as a function of radiation dose imparted to the solution. Typically, 4 liters of solution in a stainless steel vessel was irradiated for ∿5 hr while air flowed over the solution surface at 13 l/min. The volatilized ^{131}I was transported by the flowing air and collected on activated carbon that was monitored with a scintillation counter (Figure 2). An inventory (material balance) was made of the ^{131}I activity of all system components after each test. Pre-irradiation pH was typically about 7, and in several experiments this was increased to >10 by adding KOH. The solutions were not buffered. Solution temperature during irradiation was ∿50°C.

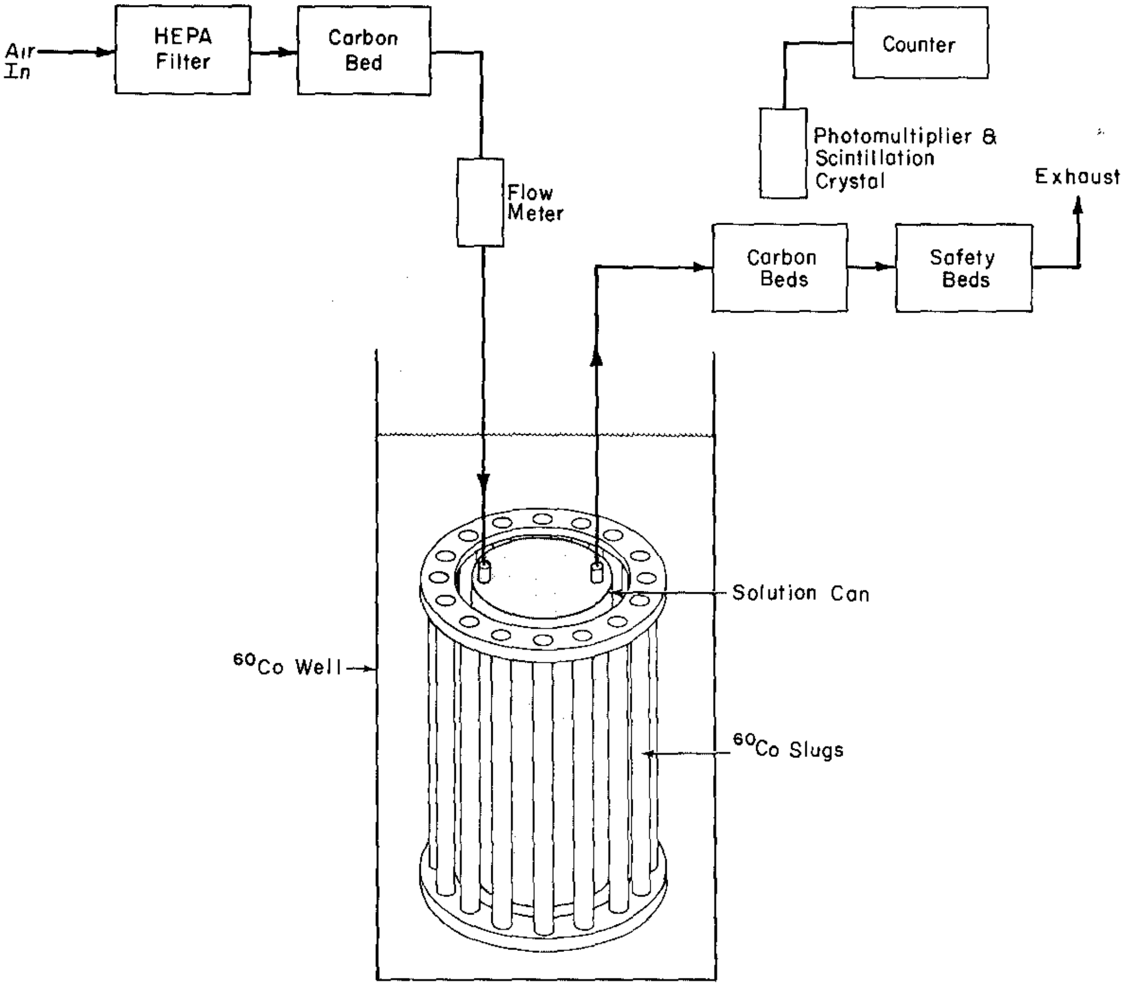

FIGURE 2. Experimental Arrangement

Experimental Results

Experimental results are given in two parts: 1) the effect of additives, and 2) the attempts to identify a penetrating form of iodine that was found during the experiments.

Influence of Additives on Iodine Evaporation

Investigation of the influence of additives on iodine retention included nine experiments, one with no additives, two with sodium thiosulfate, four with sodium thiosulfate and KOH, and two with KOH.

No Additives. Irradiation of a water solution containing KI (5.6×10^{-4}M) to a dose of 10^8 rad caused the evaporation of 14.6% of the iodine (Experiment 1). This result compared with 16 to 34% evaporation of iodine[15] from a solution containing elemental iodine ($\sim 1.5 \times 10^{-4}$M) in the absence of radiation. These results indicate that radiation converts ionic iodide to volatile iodine, most probably through OH radical attack of the iodide

$$OH + I^- \rightarrow I + OH^- \qquad (1)$$

The OH radicals result from the radiolysis of the water. Further, because the iodine evaporation is about equivalent in the two experiments, the conversion of iodide to iodine is thought be be almost quantitative.

Sodium Thiosulfate. When sodium thiosulfate was added at a molarity (5.5×10^{-4}) approximately equal to that of the KI, an almost quantitative release of the iodine occurred (94% in one experiment and 96% in another). The ineffectiveness of the thiosulfate at this concentration is thought to be due to the radiolysis of thiosulfate by the reaction[19]

$$S_2O_3^{2-} + 4(O) + H_2O \rightarrow 2SO_4^{2-} + 2H^+ \qquad (2)$$

augmented by acid decomposition of the thiosulfate by the reaction[19]

$$S_2O_3^{2-} + H^+ \rightarrow HS_2O_3^- \rightarrow HSO_3^- + S \qquad (3)$$

However, if all of the thiosulfate were destroyed, the iodine release should be about equivalent to the non-additive release. This was not the case, and the degradation of the thiosulfate or the degradation products is assumed to actually promote the release of iodine from solution.

An unexpected result of this experiment was that about 11 to 15% of the iodine evolved was a penetrating form that passed through the 3 in. of activated carbon designed to collect the iodine. Some of this activity was stopped in a 1-ft-thick backup bed of carbon, but a large portion penetrated it.

Sodium Thiosulfate + Potassium Hydroxide. To reduce possible acid decomposition of the thiosulfate, KOH (10^{-3}M) was added to increase the preirradiation pH of the solution from ∿7 to >10. Some improvement was found in that iodine evaporation was reduced to 30%. The penetrating iodine was found again.

With the same KI and KOH concentrations, the thiosulfate concentration was increased to 0.1 wt %. Almost quantitative release of the iodine occurred, but there was no evidence of generation of the penetrating form. When the thiosulfate concentration was increased to 1 wt % with the same KI and KOH concentrations, iodine evolution was significantly reduced to 0.044% in one experiment and 0.55% in another. There was no evidence of the penetrating form.

The first of these experiments with KOH added indicates that the KOH served to partially neutralize the reaction product ($2H^+$) of Equation 2 thus reducing acid decomposition by Equation 3. However, when the thiosulfate was increased to 0.1 wt %, the KOH was either ineffective in neutralizing the larger quantity of decomposition products ($2H^+$) or was depleted in neutralizing the lower pH solution resulting from the larger addition of thiosulfate. In the case of the 1 wt % addition of thiosulfate, sufficient thiosulfate was apparently present, even with decomposition, to maintain iodine essentially in the nonvaporizable iodide form by

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \qquad (4)$$

Potassium Hydroxide. The alternatives to thiosulfate as an additive for iodine retention are limited. One that has been suggested is KOH. The rationale behind the use of KOH is that it serves two purposes: 1) it promotes formation of the nonvolatile iodide by

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

and, 2) it increases solution pH to prevent the OH radical attack of the iodide[22]

$$OH + I^- \rightarrow I + OH^- \qquad (1)$$

which occurs in neutral or acidic solutions. In alkaline solution, the OH radicals are dissociated by the reaction[22]

$$OH \rightarrow H^+ + O^- \quad (6)$$

The effectiveness of KOH as an additive was briefly examined. With the same KI concentration as previously used, experiments were performed with KOH concentrations of 10^{-3}M and 8×10^{-3}M (0.05 wt %). The iodine evolutions measured were 2.5 and 1.2%, respectively.

A comparison of these results with the thiosulfate results indicates that 0.05 wt % KOH is almost as effective as 1 wt % thiosulfate. In addition, the change in iodine evolution is slight for an almost 10-fold change in KOH; a 100-fold change in iodine evolution occurs for a 10-fold change in thiosulfate concentration.

The additive experiments are summarized in Table 7. Figure 3 shows iodine evolution as a function of radiation dose.

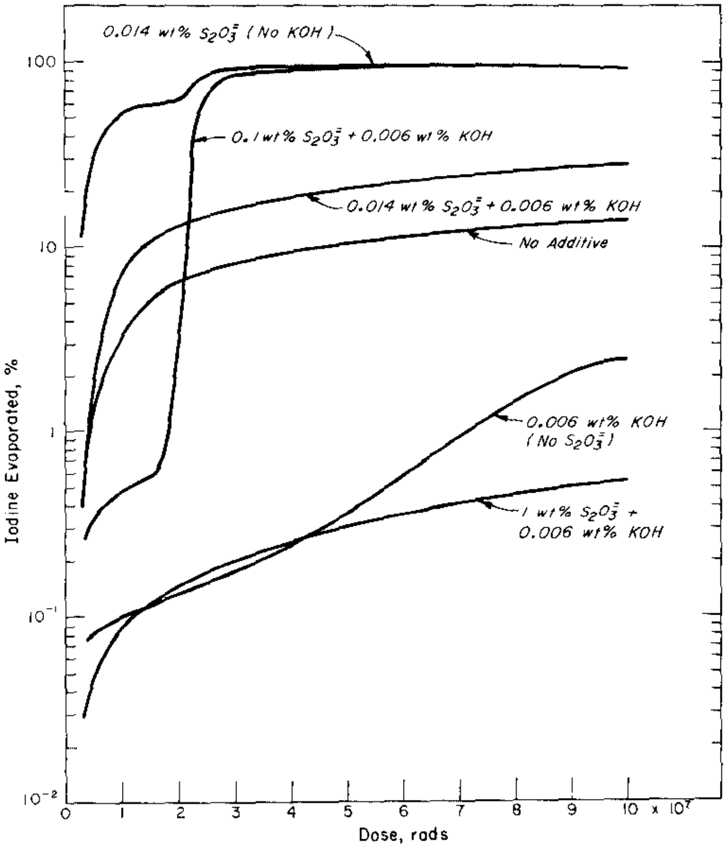

FIGURE 3. Effect of Additive and Radiation Dose on Iodine Evaporation (5×10^{-4}M Solution of KI)

TABLE 7

Iodine Evaporated After Exposure to 10^8 Rads

Type Experiment	*Concentrations, wt%*			*Iodine Evaporated, %*
	KI	*$Na_2S_2O_3$*	*KOH*	
No Additive	0.010	-	-	14.6
Thiosulfate	0.010	0.014	-	94[a]
	0.010	0.014	-	96[a]
Thiosulfate and KOH	0.010	0.014	0.006	30[a]
	0.010	0.1	0.006	96
	0.010	1.0	0.006	0.044
	0.010	1.0	0.006	0.55
KOH	0.010	-	0.006	2.5
	0.010	-	0.050	1.2

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[a] Experiments that gave the penetrating iodine species.

Penetrating Form of Iodine

As previously noted, several thiosulfate additive experiments produced significant quantities of an iodine form capable of passing through several inches of activated carbon. Tests were conducted to identify the penetrating iodine species and to determine whether the species might be produced in systems that use activated carbon for removing radioiodine.

Nine experiments were performed in the ^{60}Co irradiation facility in an attempt to obtain a sample of the penetrating iodine for analysis and identification. The experimental equipment shown in Figure 4 was designed to freeze out a sample. Nitrogen was also substituted for air as the flow gas to avoid freezing out oxygen. After seven such experiments with KI and thiosulfate concentrations equal to those that had previously given the penetrating iodine, the penetrating iodine was not formed in a nitrogen atmosphere. Oxygen apppears to be a prerequisite for its formation.

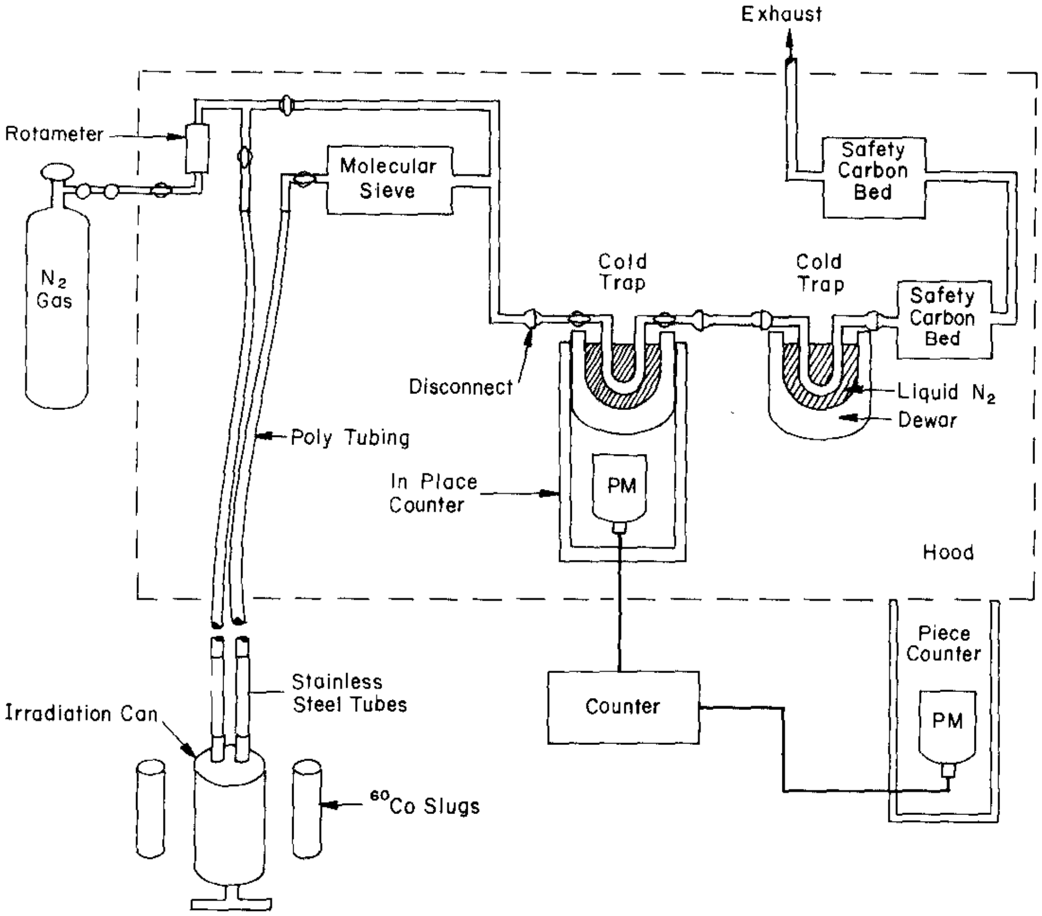

FIGURE 4. Schematic of Iodine Penetration Experiment

Two experiments were then performed with flowing air and a cold trap containing dry ice and trichloroethylene (-70°C) substituted for the liquid nitrogen trap. In both experiments, the penetrating iodine was generated, but the trap was incapable of freezing out a sample. Two experiments were performed to determine if the decomposition products of thiosulfate (SO_4^{2-} and S) were involved in the formation of the penetrating iodine. One experiment used KI plus Na_2SO_4 in the radiation field and the other used KI plus sulfur. Neither experiment produced the penetrating form of iodine.

Two additional experiments, with HEPA filters in the air stream, showed that the penetrating iodine was readily removable. This result suggests that the penetrating iodine may exist in the form of either a particulate or an aerosol. Both of these forms can pass through activated carbon beds. In the absence of a suitable analytical technique to apply to the material collected on the HEPA, identification work was halted.

Conclusions

The additive systems examined to date (with the exception of 1 wt % thiosulfate), do not greatly reduce iodine evolution from aqueous solutions in an intense radiation field. The 1 wt % thiosulfate additive offers the largest reduction but requires the largest amount of material.

A penetrating iodine species observed during the tests has not been identified. The present studies show that air is necessary for its formation and that thiosulfate in relatively low concentrations promotes its formation. Whether it is formed in the absence of thiosulfate is unknown. Although the decomposition products of thiosulfate did not promote the formation of the penetrating species in these experiments, they may do so at a different pH.

APPENDIX - TEDA ANALYSIS

Several possible analytical methods for determination of TEDA in carbon were investigated. These included thermogravimetric analysis, differential thermal analysis, Kjeldahl nitrogen analysis, and solvent extraction followed by infrared absorption analysis of the extract. The solvent extraction procedure proved most satisfactory for analysis of the extract. The solvent extraction procedure proved most satisfactory for analysis of new carbons. The other methods either failed to provide specific TEDA content or lacked sensitivity for determining TEDA at the 1 ±0.1% level.

TEDA is dissolved from carbon in a Soxhlet extractor with CCl_4 as the solvent. In the absence of calibrated standards, carefully prepared laboratory-impregnated carbons were used to determine the extraction efficiency (81.0 ±6.0% confidence interval). The TEDA content of the extract is determined with a calibrated infrared spectrophotometer. The infrared absorption band at 2880 cm^{-1} was chosen for determination of TEDA (see Figure A1) because the most reproducible data were obtained at this frequency.

Careful attention to detail is necessary to obtain reproducible data with this method.

Carbon History

The 2880 cm^{-1} (3.47 μm wavelength) absorption band results from infrared absorption by carbon-hydrogen bands in the TEDA molecule. Any solvent-soluble hydrocarbon present as a contaminant in the carbon will interfere with the determination of TEDA; the method is therefore only useful for new charcoals which have not been exposed to organic chemical vapors.

Sample Preparation

Water and dust must be removed from the carbon before TEDA extraction. The carbon dust and fines concentrate in the extract along with the TEDA and decrease infrared transmission. Water, even in small quantities, also causes infrared interference. In addition, water deposits in the extraction solution remove some of the TEDA from the CCl_4 because of preferential solubility in the aqueous phase. Dust can be removed by blowing an air jet through a sample of the carbon suspended between two small, fine sieves (3-in.- series, 40-60 mesh).

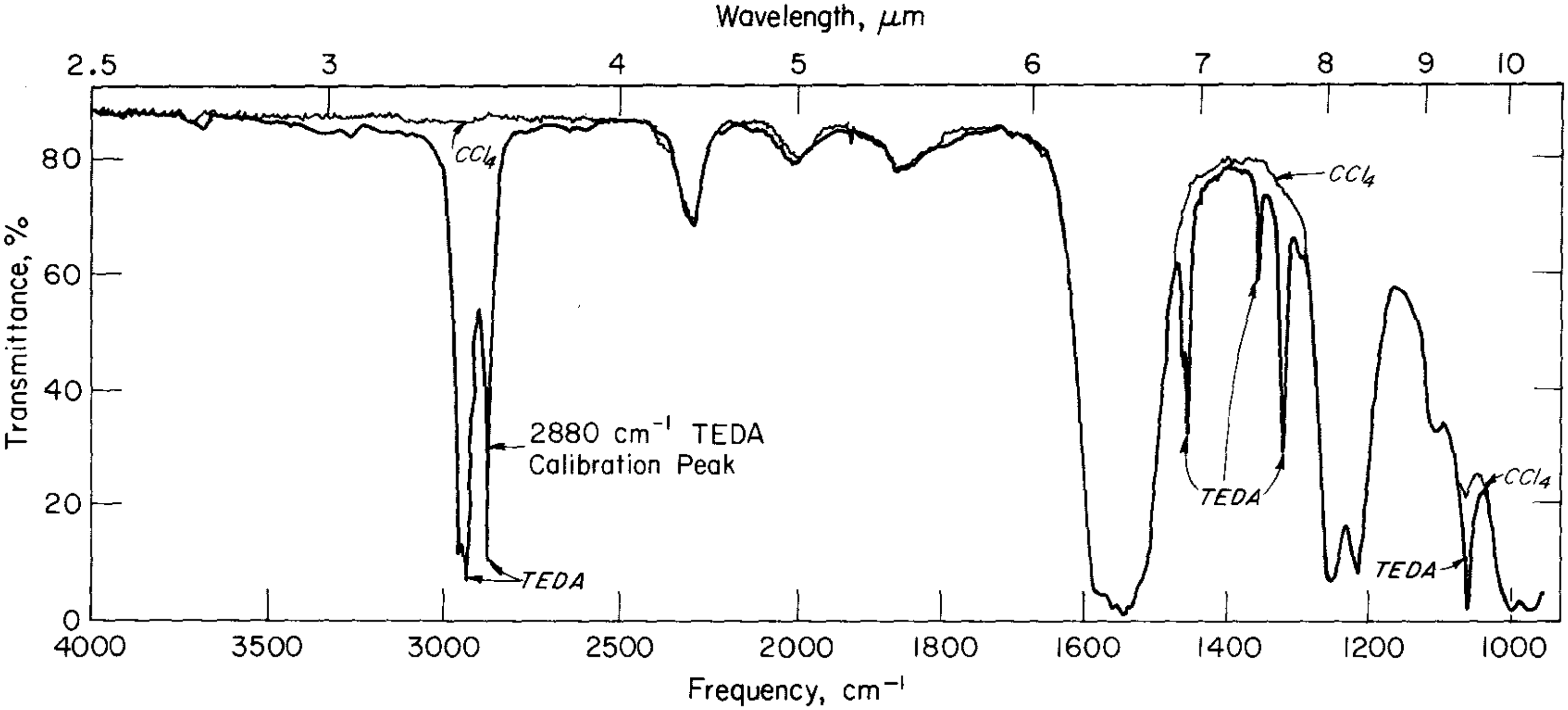

FIGURE A-1. Infrared Absorption of Spectrum of TEDA Extract

Drying the sample requires considerable care. Three methods were evaluated: heated drying, desiccant drying, and an intert gas purge. The most consistent results were obtained when a dry nitrogen purge at room temperature was used. TEDA losses into the dry nitrogen gas stream were not measurable (based on the lack of weight gain of a liquid nitrogen cold trap downstream of the carbon drying chamber). Laboratory-prepared standards were dried in the same manner, so that all data are reported relative to nitrogen-dried samples.

TEDA losses into heated air or nitrogen gas streams ranged from a 10% loss in 2-1/2 hr at 100°C to quantitative loss (>99%) in 2 hr at 140°C.

Desiccant drying was also unsatisfactory. Approximately 2 wt % moisture remained in carbon samples stored in a desiccator over molecular sieves (Type 4A, predried at 600°C) for 96 hr.

Once dried in the nitrogen gas stream, carbon samples can be stored over molecular sieves in a desiccator without appreciable weight gain.

Because of the rapid absorption of moisture from laboratory air by dry carbon (>1 mg/min for a 2-g sample on a humid day), rapid transfer and weighing techniques must be used. Although a "dry-box" would be desirable to minimize moisture pickup during this phase of the operation, it was not found essential.

Sample Extraction

TEDA was dissolved from the carbon in a modified "Pyrex" micro extraction apparatus (Fisher Catalog #20-650). Modifications included a larger boiling flask for larger solvent volumes and a wire mesh basket to contain the carbon sample.

The sample is extracted for about 240 cycles (a cycle is the accumulation of a full extraction chamber of solvent in contact with the carbon in spectrographic-grade carbon tetrachloride (MCB #CX-415 or SQ-2601). Spectrograde CCl_4 is required to minimize interference in the infrared measurement. Thermal degradation of TEDA in the boiling flask was observed when cycle times were shortened below 45 seconds or when extraction times longer than 3 hours were used. Thermal degradation is a function of the heating rate and the concentration of TEDA in the residual CCl_4 in the boiling flask (the concentration in this flask increases as the solvent is evaporated into the extraction chamber). Thus, the initial CCl_4 addition must be varied with the TEDA content to avoid exceeding a total TEDA concentration of about 1 mg/ml. An initial volume of 20 ml of CCl_4 was satisfactory for Type GX-176 carbon (1% TEDA). A 40-ml volume would be required for Type G-615 carbon (2% TEDA). Larger boiling flasks may be required for carbons containing 4-5% TEDA. A thermal shield extending from the hot plate to the top of the extraction chamber was also found useful in avoiding thermal degradation. Lower heating rates could be used with the thermal shield because it prevents air swept through the fume hood from cooling the apparatus. Toxicity of CCl_4 precludes its use outside a fume hood.

When the extraction is complete, the extract is transferred with clean-CCl_4 washings, to a volumetric flask whose volume depends on the TEDA content of the carbon and the volume of solvent used in the extraction. For Type GX-176 carbon, a 25-ml flask was used.

Precautions must be taken in handling the final solutions to avoid evaporative losses of CCl_4, which can occur even through the ground glass stopper of the volumetric flask. If infrared analysis is inaticipated the same day as the extraction, an ice bath is recommended. Overnight storage should be in a refrigerator. Periodic cleanup of all glassware with chromic acid is also necessary to remove residual TEDA or TEDA degradation products.

Concentration Determinations

As noted earlier, the 3.74 μm-wavelength absorptions peak gave the most consistent data. A CaF_2 cell with a 1.0-mm path length was found necessary for the analysis because the less-expensive NaCl cells fog and retain TEDA. Careful cleaning of the cell after each determination is necessary to remove residual TEDA.

The spectrophotometer (a Perkin-Elmer Model 521) was calibrated against samples of known concentrations of commercial TEDA (98% purity). Three separate calibration runs were made, and a least squares fit of the data points was calculated to obtain a "standard" curve.

The overall accuracy of the procedure is limited by uncertainties in the extraction efficiency but is estimated to be within ±10% of the concentration determined at the 90% confidence level. Replicate determinations of the same carbon yielded values within ±10% of each other at the 95% confidence level.

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