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CONFINEMENT OF AIRBORNE RADIOACTIVITY PROGRESS REPORT: JULY - DECEMBER 1973

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SUMMARY

Confinement system studies to determine basic gas-phase reaction mechanisms of iodine with activated carbon indicate that potassium plays a significant role in high-temperature iodine retention. Low-potassium charcoals (such as coal and petroleum-base carbons) retain iodine less effectively than coconut-shell charcoal, which has a high natural K^+ content. Iodized (KI, I_2, or KI-I_2 impregnated) coconut-shell carbons tend to perform more poorly when the atom ratio of iodine to potassium (I/K) exceeds a value of approximately 0.4. High-temperature (180°C) iodine penetration of some commercial iodized charcoals exceeds 1% when the I/K ratio exceeds 1.0. Carbons of high pH also tend to retain iodine better than low pH carbons; thus, the basic reaction mechanism in iodine retention is probably the conversion of I_2 to an I^- complex.

The high-temperature desorption test (I_2 loading followed by 4 hours desorption at 180°C) can be used as a quality control performance test for commercial iodized carbons.

Small HEPA filters, designed for 10 to 15 cfm air flow, were irradiated by an ~3 x 10^7-rad/hr ^{60}Co source before their performance characteristics were measured in a new test facility containing a "Teflon"*-stainless steel moisture separator upstream of the test filter. Accident conditions were simulated by brief exposure of the filter to mixtures of steam and air at several times filter design flow capacity followed by ~5-hour exposure to steam and air at decaying temperatures; flow was limited by pressure drop across the test filter. Similar test filters, fabricated from filter media with 7 to 48 months service in the confinement system, were exposed to the same test conditions. Although measured pluggage with moisture of test filters made from service-aged media was more severe than pluggage of irradiated filters, potential reduction of confinement system air flow from filter pluggage during an accident would not prevent adequate removal of radioiodine decay heat from carbon adsorbers in the system if at least 3 to 5 filter compartments were on line and radioiodine adsorption was distributed evenly among the on-line compartments. More severe test conditions were required to rupture a test filter than could be postulated during any Savannah River reactor accident.

DISCUSSION

CARBON TESTING

High-Temperature Desorption Tests

The high-temperature desorption test was initially designed as a screening test to aid in selecting potential carbon types suitable for use in the confinement system.[9] The test conditions (10-minute loading of elemental iodine at ambient temperature and humidity followed by 4 hours desorption at 180°C) were selected to prevent damage to the "Teflon"-coated test apparatus and "Neoprene"* "O"- rings used as seals in the apparatus. The 180°C temperature is also the upper limit of usefulness for TEDA-impregnated carbons because TEDA boils at 174°C and flashes at ~190°C.[12]

In the original test series,[10] 13 of the 21 candidate adsorbers were subjected to the high-temperature test and had penetration values ranging from 0.003% to 18.08% (Table I). The values fall into three broad penetration catagories: (1) very low (<0.010%), which were coconut charcoals either unimpregnated or impregnated with TEDA or TEDA + KI; (2) intermediate (<0.10%), which were coconut carbons impregnated with I_2, KI_3 or PbI_2; and (3) very high (>1.0%), which were some coconut carbons impregnated with KI_3 and petroleum-base carbons with KI_3 or TEDA impregnation. The anomaly in the data is that four of the 1500-m^2/g coconut-shell carbons impregnated with KI_3 use the same source of base carbon, yet the penetration values range from 0.023% to 18.08% (the extremes are two different lots from the same vendor).

Preliminary investigation of the cause of differences in the performance of the KI_3 carbons indicated that different methods of impregnation were used by the three vendors;[10] however, confirmation of the techniques used could not be obtained because of the proprietary nature of the processes. Variation in the iodine content of the different carbons is also a possible cause (particularly because the greatest performance variation was observed between different lots from a single vendor). The sodium, potassium, and iodine content of each sample was determined by neutron activation analysis. The results of these analyses indicated a

* Registered tradename of E. I. du Pont de Nemours and Company.

TABLE I

High-Temperature Test Data[a]

Mfg	*Base Carbon*	*Surface Area, m^2/g*	*Impregnant*	*Iodine Penetration,*[b] *%*
A	Coconut	1100	None	0.004
A	Coconut	1500	KI_3	0.052
B[c]	Coconut	1100	None	0.004
B	Coconut	1500	KI_3	0.028
B	Coconut	1100	KI_3	0.056
B	Coconut	1100	I_2	0.070
B	Coconut	1500	PbI_2	0.084
B[c]	Coal	1300	PbI_2	0.420
B	Coconut	1100	KI • TEDA	0.006
B[c]	Coconut	1100	KI • TEDA	0.006
B	Coconut	1100	TEDA	0.003
C	Coconut	1500	KI_3	18.08
C[c]	Coconut	1500	KI_3	0.023
D	Coconut	1500	KI_3	2.412
E	Petroleum	1500	KI_3	6.484
E	Petroleum	1100	TEDA	12.03
E	Petroleum	1500	TEDA	4.560

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a. Source of data is Reference 10, except where noted.

b. See text for test conditions.

c. New data.

strong correlation between the atom ratio of iodine to potassium and iodine penetration during the high-temperature test. The sodium content of the impregnated carbons was consistently <0.2 wt % and was not related to penetration.

Chemical Analysis of Carbons

Results of the neutron activation analyses of several of the KI and KI$_3$ carbons are shown in Table II. Iodine and potassium contents are compared with the iodine penetration values from Table I and with pH values for water extracts of each carbon (5 g carbon extracted with 20 ml distilled water; pH measured after 10 minute contact time). The comparison between I/K ratios and iodine penetration is shown graphically in Figure 1.

TABLE II

Comparison of Chemical Analysis with pH and Iodine Penetration

Carbon	Iodine,[a] wt%	Potassium,[a] wt%	Atom Ratio I/K	pH[b]	Iodine Penetration,[c] %
A[d]	3.78	1.75	0.665	9.36	0.052
B-1[e]	3.02	1.55	0.601	9.62	0.028
B-2[f]	1.31	1.04	0.386	9.86	0.006
B-3[g]	<0.01	2.09	$<1.5 \times 10^{-3}$	9.98	0.003
C-1[h]	4.01	0.96	1.26	7.05	18.08
C-2[i]	4.23	2.23	0.586	9.02	0.023
D[j]	4.42	1.14	1.19	9.56	2.412
E[k]	3.12	0.96	1.00	8.78	6.48

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a. Activation analysis of undried sample.

b. See text for method.

c. High-temperature test.

d. KI$_3$ on 1500-m^2/g coconut carbon, manufacturer A.

e. KI$_3$ on 1500-m^2/g coconut carbon, manufacturer B.

f. KI + TEDA on 1100-m^2/g coconut carbon, manufacturer B.

g. Unimpregnated 1500-m^2/g base carbon of the same type used to prepare samples B-1, C-1, C-2, and D.

h. KI$_3$ on 1500-m^2/g coconut carbon, manufacturer C - first lot tested.

i. KI$_3$ on 1500-m^2/g coconut carbon, manufacturer C - second lot tested.

j. KI$_3$ on 1500-m^2/g coconut carbon, manufacturer D.

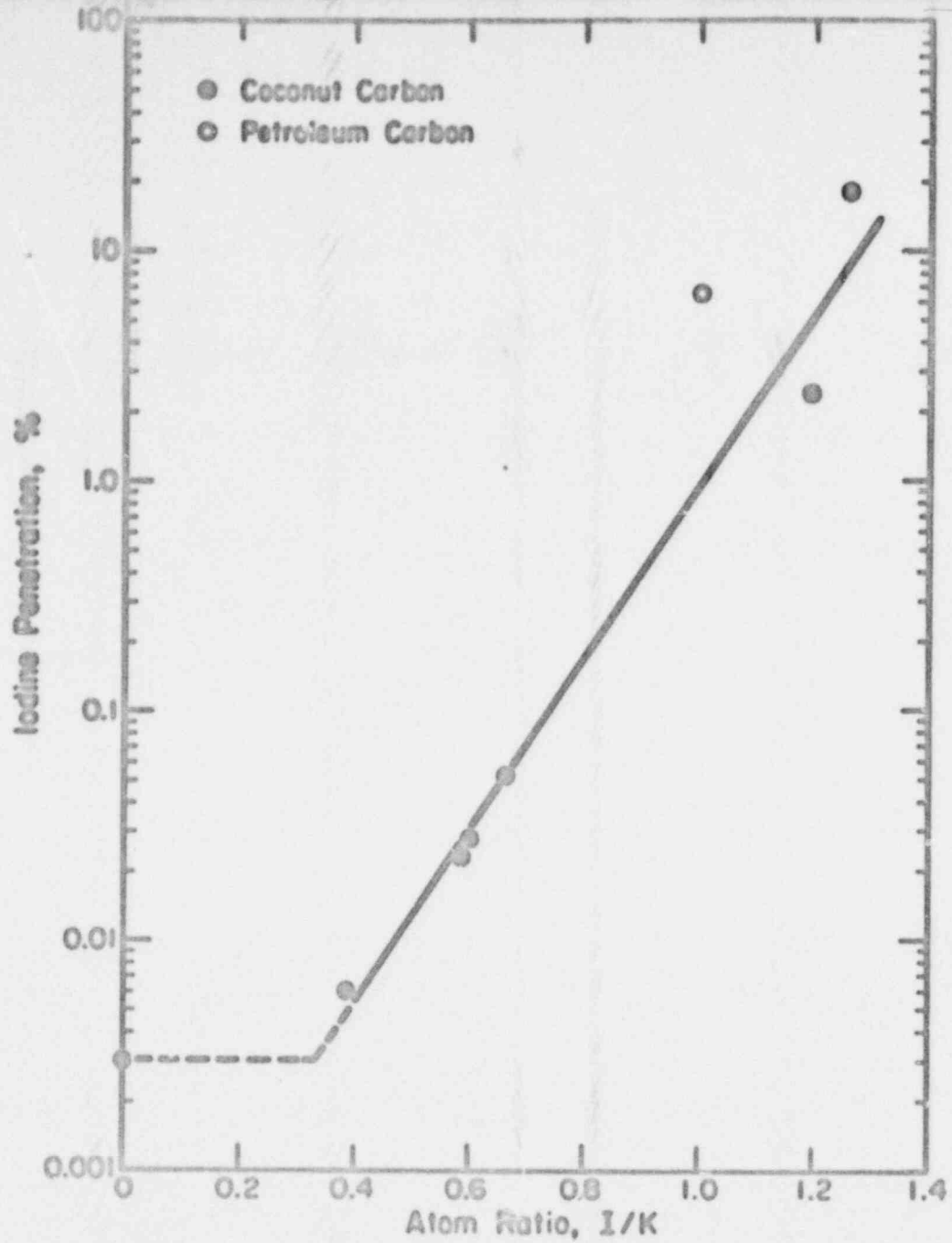

FIGURE 1. Effect of I/K Ratio on High-Temperature Iodine Penetration

Figure 1 indicates a logarithmic increase in high-temperature iodine penetration with a linear increase in the I/K ratio (above a threshold of ~0.35) and suggests that potassium plays a significant role in iodine retention mechanisms. This probably explains why coconut-shell charcoals (which are rich in K^+) are more effective for iodine removal than coal or petroleum-base charcoals. Because variability in performance between different manufacturing lots of KI_3-impregnated carbons could be caused by variations in K^+ content of base carbons as well as differences in impregnation technique, samples of base carbons from 10 different manufacturing lots from the same vendor (covering a 5 year period) were analyzed for potassium content (again by neutron activation analysis). Results are summarized in Table III.

TABLE III

Chemical Content of Coconut-Shell Base Carbons

Approximate Surface Area, m^2/g	pH[a]	K^+, wt %	Na^+, wt %
1100	10.0	0.99	0.13
1100	9.9	1.18	0.51
1100	9.9	0.86	0.06
1100	10.1	0.79	0.18
1100	10.1	0.99	0.07
1500	9.9	1.13	0.11
1500	10.0	1.17	0.07
1500	9.9	1.19	0.08
1500	9.9	1.30	0.09
1500	10.3	1.27	0.06

a. See text for description of method.

The data in Table III indicate that there is little variability in the base carbon, particularly the 1500-m^2/g carbon from which the commerical KI_3 carbons are manufactured. Thus, the variability in performance (and the I/K ratio) is probably a function of impregnation technique. The best carbons are those with a pH greater than 9 and which have I/K ratios less than 0.7.

To validate these conclusions, a series of four iodine solutions were prepared with reagent grade I_2, KOH, and KI. Three solutions were prepared with a constant I_2 content (6.2 grams in 100 ml water) and a varying KOH concentration. The fourth solution was made by dissolving 10.5 g KI in 100 ml water. The first two solutions (4.6 g KOH with I/K = 0.47 and 5.8 g KOH with I/K = 0.60) were predictably clear and colorless (even after standing in fluorescent light for 3 weeks in a sealed polyethylene bottle) because of the absence of the I_3-complex or free I_2 in solution. The pH of both solutions was 12.3. The third solution (2.9 g KOH with I/K = 0.95) was a very dark brown

color (characteristic of I_3^- solutions) which stained the plastic bottle on standing and had a pH of 8.9. The fourth solution (KI with I/K = 1.0, pH = 7.3) was initially clear and colorless, but gradually turned a faint brown color on standing in the light.

The solution behavior of the iodine strongly suggests a similar reaction on the carbon surface where some I_2 may be liberated on heating and accounts for poorer performance of the high I/K ratio carbons. The high pH solutions favor formation of I^- complexes which are relatively nonvolatile. High pH carbons (such as coconut carbon) should favor I_2 to I^- conversion, whereas low pH carbons (neutralized coconut or coal and petroleum carbons) should favor the formation of less stable I_3^- complexes, particularly when the I/K ratio exceeds 1.

Several samples of new and service-aged carbons were tested for pH and high-temperature iodine penetration to determine if any correlation existed between residual alkalinity (available excess K^+) and iodine retention. The results are shown in Table IV.

A good correlation between pH and iodine penetration is not shown by the data except for the general trend toward higher penetration with lower pH (Figure 2).

While the I/K ratio in service-aged carbons does not change significantly with time, the pH does change with the accumulation of acidic atmospheric pollulants (such as NO_2 and SO_2). In addition, other atmospheric pollutants (such as hydrocarbons) accumulating on the service-aged carbon are competing with iodine for reactive sorption sites (or compounds in the carbon which will react with I_2). Thus, the rapid decrease in performance (Figure 3) appears independent of carbon type, and an impregnated carbon (G-615, KI + TEDA) deteriorates as rapidly in service as an unimpregnated carbon (416) when evaluated by the high-temperature desorption test.

Use of the High-Temperature Desorption Test

The high-temperature desorption test has been a valuable aid in selecting an impregnated carbon for use in the Savannah River confinement system. The test should prove equally valuable for other investigators interested in screening potential containment system carbons. In addition, the test can be used as a quality control test by carbon manufacturers. Because the I/K ratio correlations are still in the development stage, direct measurement of the carbon performance is the preferred method of evaluation of different lots of carbon. The high-temperature test has been proposed for inclusion in the ASTM and ANSI standard