SESSION 11

ADSORBER TESTING AND ADSORBER PERFORMANCE

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A SIMPLIFIED TEST PROCEDURE FOR DETERMINING THE EFFECTIVENESS OF ADSORBENTS FOR THE REMOVAL OF METHYL IODIDE

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Abstract

ASTM Test Procedure D3803 measures the ability of nuclear-grade carbon to remove methyl iodide from a stream of humidified air. This test, unlike all the other procedures developed by ASTM Committee D28, has evolved to become extremely complex. The intricacy of this test as well as the great difficulty in obtaining interlaboratory agreement, creates doubt as to the actual meaning of the results. Here a far simpler test system is described in which thermodynamic principles are used to maintain a constant, reproducible test procedure. This paper describes a system implementing these elements, its cost to build, and the factors affecting its accuracy.

I. Introduction

A "standard" test system for determining the ability of nuclear-grade carbon to adsorb methyl iodide is described in ASTM Standard Test Method D3803.(1) However test systems built to meet these ASTM specifications have given results which differ widely, depending on the laboratory in which the measurements were made. One review of an earlier version of this test procedure states:(2)

> "The NRC is interested in developing a test method to evaluate a carbon's ability to adsorb iodine and methyl iodide. As a result, they have sponsored a program to evaluate D3803. Results from the second round robin series were presented to D28.04 by Chris Scarpellino of EG&G, Idaho.
>
> "According to Scarpellino, the results of methyl iodide adsorption tests by various laboratories varied by two orders of magnitude. Factors that contribute to the variance between laboratories include:
>
> * Problems with test equipment calibration.
> * Problems associated with measurement of relative humidity above 90%, and maintaining constant relative humidity.
> * Flow Measurement difficulties.
>
> "Other potential problem areas with the test method were discussed. McKee indicated moisture condensation in the pores at high relative humidity may be a problem. Physical-chemical effects other than adsorption may occur (Deitz, McKee) at high relative humidity. The effect of oven moisture measurement on impregnated carbons was also discussed."

Later in the same report, Scarpellino cites problem areas found through his contact with other test laboratories. Problems cited include:

> "It is difficult to avoid the conclusion that the <u>measurement</u> of relative humidity, and possibly flow, is inadequate in some or all of the test facilities. The <u>control</u> [of] these factors may be quite adequate, since the intralaboratory variances were quite small.
>
> "The test setups need to be examined for systematic errors, such as using a pressure for calculation that is actually measured at a different point in the system. The interlaboratory comparison had already revealed some such errors, and these had been corrected, or corrections were in progress.
>
> "Modern flow and RH measurement devices, particularly those involving electronics, are marvelous in speed of response and possibly sensitivity and accuracy - but they may lack a bit in stability. Classic methods, such as wet

bulb/dry bulb measurement and orifice meters, often give more reliable data; one can tell if a rotameter ball is stuck.

"At high humidities, one must guard against the creation of droplets; these must be filtered out of the system.

After considering the above information, ASTM Committee D28 concluded that:

"Based on the results to date, the Committee believes D3803 must be modified. No action will be taken by [ASTM Committee] D28.04 until the NRC sponsored program is completed."

The large number of problem areas cited above, along with the absence of any specific program to understand the root source of errors in the methyl iodide penetration test, indicates that both the NRC and ASTM Committee D28 are far from developing an adequate test system. The most important indication of how much needs to be done is that there is no "gold standard" by which interlaboratory differences may be explained. Thus it would appear that any two numbers, even were they to differ by two orders of magnitude, are equally "correct". Thus at this time, those who are trying to develop a standard test procedure for determining methyl iodide retention, do not even know what the results from such a test should be.

What is needed is a reproducible test procedure, based on simple thermodynamic principles, that defines precisely and exactly the test parameters. The principles behind such a test system are described next.

II. Basic Concepts

The two simplifying principles used in the design of this system are:

1. If the test apparatus is sufficiently small and operated isothermally, then the entire system can be contained in a well-stirred, temperature controlled water bath. Because of the very high heat capacity of water, in a well circulated water bath, temperature control within ±0.1°C is not difficult to maintain. Such systems are not only highly precise in their temperature control, but also inexpensive. If the system is based on thermodynamic equilibria, then temperature control is simplified enormously, as it is no longer necessary to build a system in which temperature differences are tightly controlled. We will use the saline concentration of the water in the bath to control the relative humidity in the system. This procedure is highly stable - for example, for the equilibrium relative humidity to be in error by **2.5%** (*i.e.* going from a 95% RH to a 97.5% RH), the saline concentration must be in error by **50%**.
2. The tagged methyl iodide can be injected with precision as its water solution using an infusion pump. With this scheme, it is no longer necessary to synthesize a pressurized air/methyl iodide mixture, and then monitor its input using a rotameter controlled air infusion system. This system also eliminates the interaction of the methyl iodide with the walls of the gas cylinder and associated plumbing.

III. The Basic System

Figure 1 lays out a test system built to incorporate these concepts. Note that it is simple to hold constant the predetermined the test parameters in this system because:

- The test temperature is controlled by the temperature of a single water bath.
- The relative humidity is controlled by the salt concentration.
- The contact time is controlled by the ratio of the volume of adsorbent to the minute volume of humidified air.
- A simple and precise procedure for injecting methyl iodide is used.

The operation of this system is as follows. Air passes into the opening shown on the left hand side of the drawing, being drawn by the air pump, "P2", at the opposite end of the system. The indrawn air first passes upward through bed "A", which is packed with berl saddles. In this bed it comes into close contact with sodium chloride solution drawn from the temperature regulated bath surrounding it, through small holes at the top of the bed, at a rate of about 1 lpm. The berl saddles in the bed give the large surface area necessary to permit equilibrium to be established between the gaseous and liquid phases flowing countercurrently to each other.

The number of transfer units required for 99.9% equilibrium with the vapor pressure of water in the saline solution (assuming presaturation to within 10% of the desired value) is ln(100) = 4.6. If it is further assumed that the HETU is 6 cm., then the minimum tower height is 30 cm., a height that will easily fit into a moderately sized bath.

Although not critical to the design of the system, the degree of air-saline water contact (conveniently described in terms of the number of transfer units) can be established by passing air containing tracer amounts of tritiated water through the tower and determining the fraction of the tritium that is removed. The natural logarithm of the ratio of the input concentration to the output concentration of tritium would be equal to the number of transfer units.

Saline solution is drawn off the bottom of bed "A" by a sump pump, "P1", and passed back into the water bath. In order to prevent flooding, the flow through pump, "P1", is set at a rate sightly higher than the expected flow of saline solution. The entrainment of a small amount of air by the pump, "P1", indicates that this pump is operating at a sufficient flow to prevent flooding of bed "A".

For operation at 30°C, the concentration of sodium chloride in the bath's water is maintained at a molality of 1.378, which is the concentration required to establish an equilibrium water vapor pressure equivalent to a RH of 95% over the saline solution at 30°C.(3,4) The salt concentration in the brine is monitored by a hydrometer and makeup water is added as required to maintain the molality.

The air from bed "A" is drawn through the bed "B", containing the carbon to be tested, by the pump, "P2", which in turn is controlled by a mass flow meter at the effluent end of the bed. The diagram also shows a second adsorption bed, needed to prevent any effluent ^{131}I from escaping from the system. All parameters except the air flow rate are governed by thermal or chemical equilibria that are easy to maintain. The air flow rate is the one parameter that requires critical monitoring. This is because the contact time is a dynamic rather than an equilibrium property and thus there is no way to establish this factor, as all the other factors were, by a known thermodynamic equilibrium.

By adding a trace of a dye (*e.g.* fluorescein) to the sodium chloride solution, one can, by wiping the joints after disassembling the apparatus, locate any water leaks. Actually in this system, unlike the test system described in ASTM D3803, small water leaks should have no effect, for introducing a small amount of extraneous sodium chloride solution for which the water vapor pressure is the same as that of the air passing over it, will have no effect on the humidity of the air passing over it.

Thus with this test apparatus, one can determine in a straightforward manner how these test variables effect carbon performance, and thereby obtain the necessary data for accident analyses. In contrast, the current ASTM procedure requires a preheater, humidifier, condenser, and a reheat canister all contained within a temperature regulated system. The allowable temperature tolerance in the ASTM procedure is ±0.2°C. Assuming that condenser is high by 0.2°C and that the beds are low by the same amount, then the RH at which the beds will be tested will be 97.3%. As it is well established that bed performance falls rapidly as a RH of 100% is approached, the severe interlaboratory disagreement found with this procedure seems readily understandable.

Although the system described here is for operation at 30°C, the parameters can be easily modified for operation at other temperatures. For example, with NaCl, a molality of 1.374 would be used to generate a 95% RH at 80°C. This slow drift in the desired saline concentration with temperature reduces any possible confounding effects of temperature and salt concentration.

Alternatively, lithium chloride (LiCl) may be used to reduce the vapor pressure of water, as excellent data on the equilibrium of water vapor pressures above LiCl solutions are available.(5,6) For a 95% RH at 30°C and 80°C, respectively, LiCl molalities of 1.195 and 1.238 would be used. The Appendix gives a BASIC program that uses a 25 parameter quintic equation developed earlier for the vapor pressure of water in equilibrium with 1.0-18.5*m* LiCl at temperatures from 25°C to 100°C. This program is included with this text because if the reader is not familiar with the thermodynamic terminology used by Gibbard, programming his lengthy equations is certain to be very time consuming.

IV. The Methyl Iodide Infusion System

In the system described here, the methyl iodide is dissolved in water and infused by a syringe pump into a midget impinger from which it is desorbed from a steam of air into the test system. This system has the advantages of being highly accurate - using a microsyringe, a precise amount of method iodide can be dissolved in an equally precise volume of water, and an infusion pump used to deliver a metered volume of the solution to be passed into the test system. Infusion pumps that will perform this service with a very high accuracy are readily available. This procedure avoids the problems in setting up concentrations of methyl iodide in compressed air, with wall adsorption of methyl iodide, and with accurately metering the compressed air containing the methyl iodide. Because in the procedure described here, the rate limiting step is the infusion of dissolved methyl iodide, the key to accuracy is knowing the concentration of methyl iodide dissolved in the water and the rate of infusion. The methodology proposed here, which is considerably refashioned from that described in ASTM 3803, was used earlier in the testing of impregnated charcoal for the removal of methyl iodide.(7) Although the results are not presented here, this water phase injection procedure was simple to use, accurate in its delivery of methyl iodide, and inexpensive to build and operate.

We next discuss the design parameters for this infusion system. Glew and Moelwyn-Hughes(8,9) recommend the following equation for calculating the solubility of methyl iodide in water:

$$\log_{10} (C_{sat}) = -110.278 + 37.621 \log_{10}(T) + 4823/T \qquad (1)$$

where C_{sat} is in moles/liter and T is in °K.

This equation gives a solubility of 1.40 gms of methyl iodide in 100 grams of water at 30°C. If it is assumed that 1.4 m^3 of air will pass through the test beds over an one hour injection period, then at a methyl concentration of 1.75 mg/l, the required weight of methyl iodide for the test is 2.51 mg. This amount of methyl iodide could be dissolved in 0.18 ml of water.

How long does it take to establish equilibrium between the influent and effluent methyl iodide in the midget impinger? The equilibrium time, t, required for establishment of a 95% equilibrium between the rates of infused and effluent methyl iodide is:

$$t = 3VK/q \qquad (2)$$

where V is the volume of water, K is the water-air partition coefficient (at 30°C), and q is the flow of air, ml/min.

The water-air partition coefficient (at 30°C) for ethyl iodide in the impinger, is required in order to use Eq. 2. Hasty recommends the following equation for the partition coefficient of methyl iodide between air and water:(9,10)

$$\log_{10}(K) = -4.82 + 1597/T \qquad (3)$$

where K is the water-air partition coefficient (dimensionless). At 30°C, $K = 2.8$.

Assume that the test is run with an initial 5 ml of water in the midget impinger and that the 2.51 mg. of methyl iodide is contained in 1 ml of water, which is infused into the impinger over the hour of the test. Further assume that a stream of air is passing through the bubbler at a rate of 50 ml/min. With these values, the equilibrium time, t, is ≈ 1 minute. If this short equilibrium period should be thought to cause any difficulty, then the effluent from the impinger can be vented around the test bed for one minute before starting the test.

Methyl iodide slowly hydrolyzes in water. Moelwyn-Hughes gives a value of 1.73×10^{-7} sec^{-1} as the first order rate constant for the hydrolysis of methyl iodide in water at 30°C.(9,11) At this rate, 16 hours would be required to hydrolyze 1% of the methyl iodide in an aqueous solution. The effect of hydrolysis can be reduced to an altogether unmeasurable level by storing the aqueous solution in a refrigerator, and adding a few copper beads to the impinger to scavenge any iodide that is formed.

V. Additional Considerations

In the test as described here, all but one factor - the flow of air through the test beds - is controlled by equilibrium. There is no possible way to remove this last time dependent factor, as the test itself is not a static measurement, but rather a measurement of the dynamic uptake of methyl iodide, with a rate constant described in terms of inverse seconds. This reliance on equilibrium - rather than temperature differences - results in a formidable decrease in the error expected in practice. Another advantage of the system described here is that in relying on thermodynamically basic factors, the results obtained should be more meaningful.

Finally the cost of the system is really quite low. Below are listed the major expenses that would be incurred in setting up the system.

Infusion Pump	$900
Water Bath	$300
Temperature Regulator	$500
Stirrer	$100
Air mover	$900
Sump Pump	$500
Mass Flowmeters for air measurement	$1,500
Glassware	$1,000
Total	$5,700

Appendix

Basic Program to Calculate the Molality of a Lithium Chloride Solution giving a Desired Relative Humidity at a Known Temperature.

```
10 'Basic Calculations:
20 D(1,4) = 9.947194E-02
30 D(2,4) = 8.226815E-03
40 D(3,4) = 2.238653E-04
50 D(4,4) = -7.046113E-05
60 D(5,4) = 1.982918E-06
70 D(1,0) = 53.28557
80 D(2,0) = 31.26828
90 D(3,0) = -3.094298
100 D(4,0) = .2368127
110 D(5,0) = -7.457059E-03
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120 D(1,1) = 1.764393
130 D(2,1) = -.3632635
140 D(3,1) = .0633694
150 D(4,1) = -4.792288E-03
160 D(5,1) = 1.201533E-04
170 D(1,2) = -.0194551
180 D(2,2) = 5.074271E-03
190 D(3,2) = 8.763426E-04
200 D(4,2) = -1.314343E-04
210 D(5,2) = 4.82115E-06
220 D(1,3) = 9.83248E-04
230 D(2,3) = -5.225767E-04
240 D(3,3) = 2.689426E-05
250 D(4,3) = 1.467403E-06
260 D(5,3) = -1.252579E-07
270 TS = 298.16'K
280 A = 1.5
290 INPUT "What are the desired temperature in degrees centigrade and relative
humidity";T,RH
300 TAU = T +273.16 - TS
310 FOR J= 1 TO 5
320 DCOEF(J) = D(J,4) - .2516103*(-(-D(J,0) + TS*D(J,1) -TS^2*D(J,2)/2 +
TS^3*D(J,3)/6)*TAU/TS^2/(1+TAU/TS) + (D(J,1) - TS*D(J,2) +
TS^2*D(J,3)/2)*LOG(1+TAU/TS) + (D(J,2) - TS*D(J,3))*TAU/2 +
D(J,3)*(2*TS*TAU + TAU^2)/12)
330 PRINT DCOEF(J)
340 NEXT
350 S = 1.17284 - 6202.357*TAU/TS^2/(1 + TAU/TS) + 54.42507*LOG(1 +
TAU/TS) - .161993*TAU + 8.596094E-05*(2*TS*TAU + TAU^2)
355 DELTI = 1
360 PRINT "S =";S: Print "Molality   Error"
370 I=DELTI+I
380 'I is the ionic strength measured in moles of solute per kilogram of solvent
390 X = A*I^.5
400 Z = (1 + X - 1/(1 + X) - 2*LOG(1 + X))/X^2
410 'PRINT "X =";X;" and Z =";Z
420 M=I
430 DM=0
440 FOR J = 1 TO 5
450 DM = DM+DCOEF(J)*M^J
460 NEXT
470 PHI = 1 - S*Z/A + DM
480 DIFFER = PHI+55.51*LOG(RH/100)/I
490 PRINT USING "#.####### ###.###";I/2, DIFFER/2'   NOTE: factor of 2 between
molality and ionic strength.  Molality is printed.
500 IF DIFFER >0 THEN I=I-DELTI: DELTI=DELTI/2:
510 IF DELTI < .000001 THEN STOP ELSE GOTO 370
```

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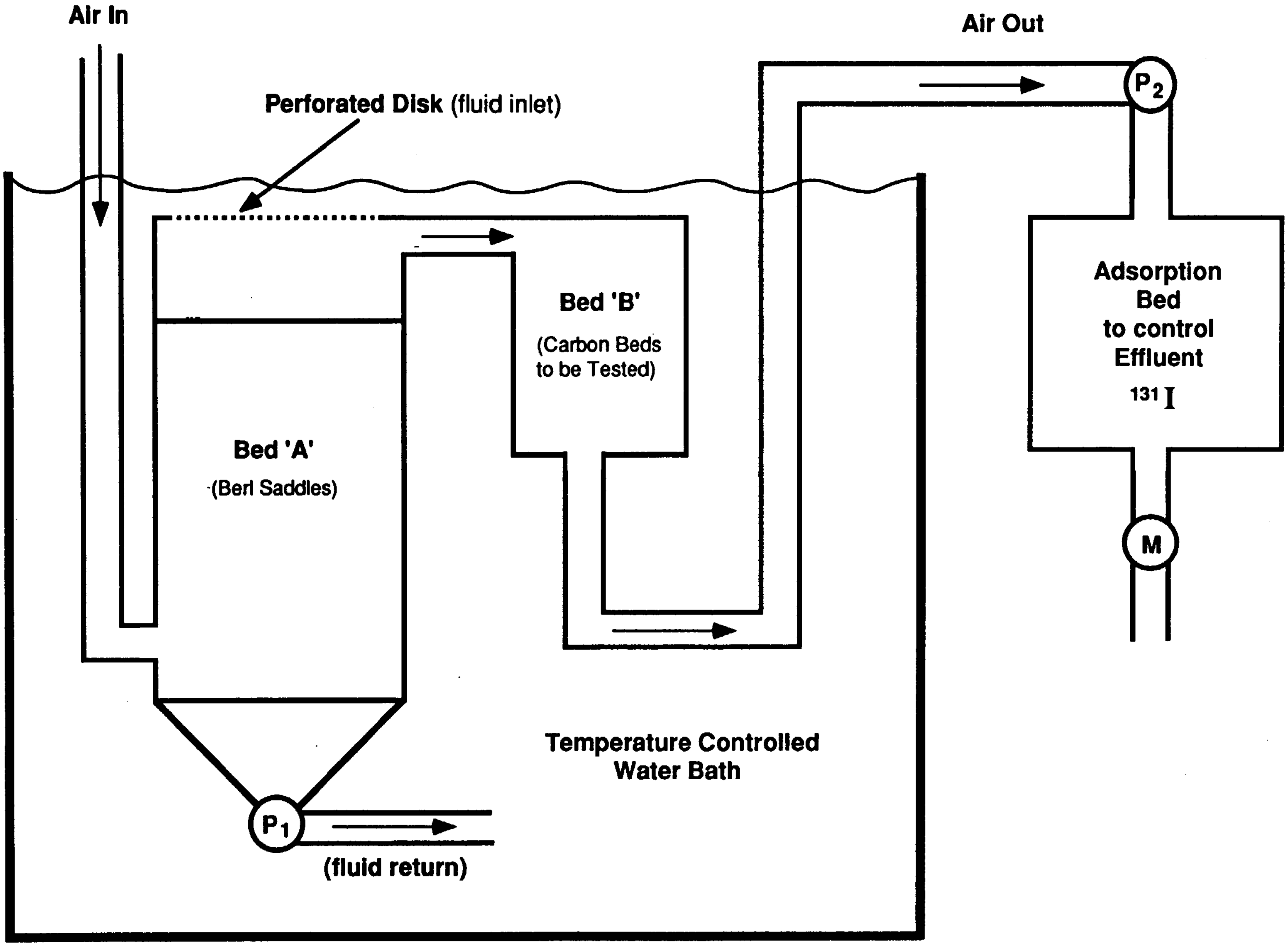

Figure 1: Proposed Test System for Retention of Methyl Iodide

DISCUSSION

FIRST: I don't think that citing that round-robin result buttresses your argument at all, because the whole purpose of the round-robin was to find out if the then standard was adequate. The round-robin did exactly what it was supposed to do. It showed that the description of the test was inadequate and that is why it underwent further study.

UNDERHILL: I think I can say that I can agree with that.

KOVACH: In that particular test loop, I have not seen anything other than so-called calculated verification of any of the parameters that are required for the test; for example, the precision of the temperature regulation or verification of humidity. We all believe that we are good engineers and we use engineering parameters, but, at the same time, these good folks who are called the Nuclear Regulatory Commission require us to verify these values; that we maintain the humidity and we maintain the temperature in a way to generate results that are based on thermodynamic principles. In the test loop that you described, I have not seen any of the verification instrumentation that shows that the parameters that you expect from handbooks, in fact, are being maintained in the system.

UNDERHILL: All I can say is, if you take a simpler test system and you try to verify it, you are better off than trying to verify the accuracy of the complex test system. I am just trying to strip the measurement of methyl iodide penetration down to its basics. This is just a proposal for that.

KOVACH: One additional comment to assist you in this endeavor. The old National Bureau of Standards has a booklet out on humidity measurement which has about 30 or 40 pages of humidity vs salt solution measurements and values reported. You may find that there is something that was cross-checked and verified under various conditions. Not that I want to take away anything from a PhD thesis.

PARAMETRIC STUDIES OF RADIOACTIVE IODINE, HYDROGEN IODIDE AND METHYL IODIDE REMOVAL

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Abstract

The recent evaluation of iodine fission product forms indicates that overall iodine concentration in the gaseous form would be significantly lower than currently assumed in US licensing documents and that the gaseous iodine forms would be elemental iodine, hydrogen iodide, and organic iodides. The removal mechanism of elemental iodine on carbon base adsorbents is primarily by physical adsorption, the removal of hydrogen iodide is by physical adsorption, chemical reaction and isotope exchange, while the organic iodides, best represented by methyl iodide, are removed by isotope exchange.

The methyl iodide removal efficiency of impregnated activated carbons is a complex process, which is influenced by the properties of the base adsorbent, the type of the impregnant and by the process conditions. A systematic study was performed evaluating the individual and combined effects of base carbon particle size impregnant type, temperature, superficial gas velocity, humidity, contact time and bed depth.

Parametric studies were also performed to confirm the removal mechanism of hydrogen iodide by currently used adsorbent types. The data generated permits selection of process conditions which permit the engineering design of radioiodine removal systems. The data indicates that current US regulation frozen designs are not necessarily the optimum conditions and further improvements can be made in the control of radioiodine releases.

Material and Methodology

All adsorbents were coconut shell based. The starting base carbon met the current U.S. quality requirements, i.e. 60% carbontetrachloride activity (CTC) and the particle size distribution required by ASME AG-1 Section FF.

Where special impregnation was used the process was from water solution and the impregnant quantities are indicated, where a standard commercial product i.e. NUCON® NUSORB® KITEG II which contains KI, tertiary amine, pH control and fire retardant impregnants it is from normal production samples.

The basic procedure utilized was the ASTM D3803 (1989) method, where deviation from the specific conditions was required to perform the test, the procedures and required control tolerances of the ASTM D3803 (1989) method were used.

$H^{131}I$ was prepared by isotope exchange between $^{131}I_2$ and $H^{127}I$ with removal of the excess $^{131}I_2$ after the isotope exchange took place.

Particle Size Effects on $CH_3{}^{131}I$ Removal

The 8x16 mesh base carbon was impregnated by 2.0 wt. % KI and 2.0 wt% KI and 2.0 wt. % tertiary amine (TEDA) solution and screened into five fractions. Each of the fractions was tested according to the ASTM D3803 procedure at 30°C and 95% RH.

The $CH_3{}^{131}I$ penetration data for each of the two impregnant types are shown on Tables 1 & 2 and the results are plotted on Figure 1.

In all cases, the coimpregnated carbons show significantly lower $CH_3{}^{131}I$ penetration than the solely KI impregnated carbons. Test beds were segmented into 2.0 inch (5.0 cm) and 4.0 inch (10 cm) depths for the 80 FPM tests and a single 2.0 inch (5.0 cm) deep bed was used for the 40 FPM test bed. In all cases, for both impregnated types at equal residence time (i.e. 0.25 seconds for 40 FPM - 2.0 inch and 80 FPM - 4 inch deep beds) the penetration was significantly lower at the high velocity, 80 FPM conditions than at 40 FPM. In all cases, for both impregnants the $CH_3{}^{131}I$ penetration decreased with decreasing particle size. Both of the two observations indicate that diffusion is a rate controlling step in the $CH_3{}^{131}I$ removal mechanism. Although there are differences in the mechanism between the single KI and the KI-TEDA coimpregnated carbons. This difference indicates that the KI and TEDA are deposited in different parts of the pore structure and the isotope exchange rate also affects the removal process. The main removal mechanism even for TEDA impregnants is the isotope exchange because the excess non-radioactive $CH_3{}^{127}I$ reacts with the TEDA first and then the $CH_3{}^{131}I$ - $CH_3{}^{127}I$ exchange can take place. The data also shows the difficulty in comparing adsorbents for $CH_3{}^{131}I$ removal when the particle size of the adsorbents is not identical.

The obtained results also show that the use of the K-factor for comparing adsorbents is not satisfactory when identical residence times and different carrier gas velocities are used, while it gives similar values at the same velocity different residence times, when the particles size is carefully controlled and the carrier gas velocity is in the 80 FPM (40 cm/sec) range.

Velocity Effects on $CH_3{}^{131}I$ Removal

Tests were performed using the ASTM D3803 (1989) test method and tolerances on 1.0 inch (2.5 cm), 2.0 inch (5.0 cm) and 4.0 inch (10.0 cm) bed depths at 20, 30, 40, 60 and 80 FPM carrier gas velocities. The adsorbent used were samples from commercial NUSORB KITEG II adsorbent. The data are shown on Table 3 and Figure 2. While the penetration is in inverse proportion to velocity for all three bed depths the diffusion control is clearly shown by comparing as an example the values at equal (0.25 sec) residence time at

20 FPM	1.0 inch bed depth
40 FPM	2.0 inch bed depth
80 FPM	4.0 inch bed depth

which clearly show that at equal residence but time higher velocity conditions the penetration as an example is more than an order of magnitude less at 80 FPM than at 20 FPM.

The data also show that at 60 FPM and above the rate controlling mechanism changes from that controlling below that velocity (for the standard particle size distribution adsorbent). The K values are comparable for velocities at and above 60 FPM regardless of residence time while below 60 FPM velocity the K values decrease with increasing bed depth.

Therefore, where the pressure drop consideration is not relevant a significantly smaller size air cleaning system can be designed operating with deeper beds at higher velocities. Considering the floor space costs for nuclear facilities this means significant cost savings, but such better performance, as an example, 4.0 inch deep bed at 80 FPM with the commensurate 0.25 second residence time, is not considered by current U.S. regulations and designs. The other clear indication is that equal residence time does not mean equal $CH_3{}^{131}I$ penetration.

Temperature Effects on $CH_3{}^{131}I$ Removal

Tests were performed using the ASTM D3803 (1989) test method and tolerances at 25, 30, 40, 60 and 80°C on 1.0 inch (2.5 cm), 2.0 inch (5.0 cm) and 4.0 inch (10.0 cm) bed depths on commercial NUSORB KITEG II adsorbent.

The data are shown on Table 4 and Figure 3.

The increased temperature is expected to increase both diffusion and isotope exchange rates and improve the $CH_3{}^{131}I$ removal within the temperature range tested. The performance improvement is much more significant on shallow adsorbent beds (1.0 inch) than for 2.0 inch and deeper beds, however, under all conditions the performance improved with increasing temperature.

It is important to point out that while 1.0 inch beds are rarely used in nuclear air treatment systems they are very commonly used in sampling cartridges monitoring iodine releases. Unfortunately, there were no detailed parametric studies performed to determine use variables on these cartridges, however, data presented here can be an indication of their performance.

As reported elsewhere in this conference, the temperature effects are more significant when testing used adsorbents than for new adsorbents.

Humidity Effects on $CH_3{}^{131}I$ Removal

Tests were performed using the ASTM D3803 (1989) test method and tolerances at 70, 80, 85, 90 and 95% RH on 1.0 inch (2.5 cm) 2 inch (5.0 cm) and 4.0 inch (10.0 cm) bed depths on commercial NUSORB KITEG II adsorbent.

The data are shown on Table 5 and Figure 4.

The detrimental effect of water coadsorption on $CH_3{}^{131}I$ removal is a well known fact and has been demonstrated in the past. However, the data shows that %RH variation is more significant for bed depths shallower than 4.0 inch deep at equal residence times.

For most systems the currently selected U.S. test condition of 95% RH is a conservative test for new adsorbent evaluation.

Screening Tests for $H^{131}I$ Removal

Tests were performed using the ASTM D3803 (1989) method and tolerances under three selected conditions on commercial NUSORB KITEG II adsorbent.

The data are shown on Table 6.

Under all conditions tested the penetration of $H^{131}I$ was higher than that of $CH_3{}^{131}I$. Therefore, if the current source time study indication of $H^{131}I$ presence is validated the $CH_3{}^{131}I$ test for adsorbents may not be conservative.

Conclusions and Recommendations

Most parametric studies reported in the past[1,2] were performed under different test conditions or covered only part of the parameters affecting the $CH_3{}^{131}I$ removal process[3]. The results generated indicate that for engineering design of nuclear air treatment systems and their current U.S. regulations[4,5] is not based on the best available performance conditions for the adsorbents currently available.

The assumption that $CH_3{}^{131}I$ penetration is the most conservative test for characterizing adsorbents is not shown by the results of $H^{131}I$ penetration.

Particularly where energy requirement is not critical it is more advantageous to use deeper beds at higher carrier gas velocity than currently practiced in the U.S.

References

1. Kovach, J. L. "Iodine Fission Product Mass Transfer in Adsorbent Media", 13th AEC Air Cleaning Conference CONF740807, pg. 736.

2. Deuber, H & Gerlach, K "Parametric Investigations on the Retention of Methyl Iodide by a KI Impregnated Activated Carbon", (KfK Karlsruhe) Reports KfK 3594 (1983) KfK 3594 (1984) and Nuclear Safety Vol 26. No. 2 pp 157-169 (1985).

3. Scarpellino, C.D. et al. "Technical Evaluation Report of Testing Procedures for Activated Carbon Adsorbers in Ventilation Filter Assemblies in Nuclear Power Plants", EG&G Idaho Report EGG-CS-7131 (1985) and Final Technical Evaluation Report for NRC/INEL Activated Carbon Testing Program EGG-CS-7653 (1987).

4. USNRC Regulatory Guide 1.52.

5. USNRC Regulatory Guide 1.140.

TABLE 1

PARAMETRIC STUDY OF PARTICLE SIZE EFFECTS ON $CH_3{}^{131}I$ PENETRATION AT 30°C, 95% RH

Impregnant: KI

Base Carbon: Coconut

		0.25 sec. Residence Time 40 FPM (20 cm/sec) velocity 2.0 inch (50 mm) bed depth		0.125 sec. Residence Time 80 FPM (40 cm/sec) velocity 2.0 inch (50 mm) bed depth		0.25 sec. Residence Time 80 FPM (40 cm/sec) velocity 4.0 inch (100 mm) bed depth	
US Sieve Mesh	Particle Size mm	Penetration %	K Value	Penetration %	K Value	Penetration %	K Value
8X10	2.38 - 2.00	3.900	5.64	11.18	7.61	1.745	7.03
10X12	2.00 - 1.68	1.980	6.81	10.27	7.91	0.901	8.18
12X14	1.68 - 1.41	1.370	7.45	5.84	9.87	0.360	9.77
14X16	1.41 - 1.19	0.626	8.81	3.31	11.84	0.128	11.57
16X18	1.19 - 1.00	0.272	10.26	2.39	12.97	0.059	12.92

$$K = \frac{\text{Log}\,\dfrac{100}{\%\ \text{Penetration}}}{\text{Residence Time}}$$

Test Method: ASTM D3803 (1989)

5NU542

TABLE 2

PARAMETRIC STUDY OF PARTICLE SIZE EFFECTS ON $CH_3{}^{131}I$ PENETRATION AT 30°C, 95% RH

Impregnant: KI-Amine

Base Carbon: Coconut

		0.25 sec. Residence Time 40 FPM (20 cm/sec) velocity 2.0 inch (50 mm) bed depth		0.125 sec. Residence Time 80 FPM (40 cm/sec) velocity 2.0 inch (50 mm) bed depth		0.25 sec. Residence Time 80 FPM (40 cm/sec) velocity 4.0 inch (100 mm) bed depth	
US Sieve Mesh	Particle Size mm	Penetration %	K Value	Penetration %	K Value	Penetration %	K Value
8X10	2.38 - 2.00	1.020	7.96	5.690	9.96	0.504	9.19
10X12	2.00 - 1.68	0.380	9.68	3.960	11.22	0.165	11.13
12X14	1.68 - 1.41	0.152	11.27	1.310	15.06	0.033	13.93
14X16	1.41 - 1.19	0.057	12.98	0.930	16.25	0.009	16.18
16X18	1.19 - 1.00	0.032	13.98	0.690	17.29	0.002	18.80

$$K = \frac{\text{Log}\dfrac{100}{\%\ \text{Penetration}}}{\text{Residence Time}}$$

Test Method: ASTM D3803 (1989)

5NU542

TABLE 3

PARAMETRIC STUDY OF VELOCITY EFFECTS

ON $CH_3{}^{131}I$ PENETRATION AT 30°C, 95% RH

Adsorbent: NUSORB KITEG II

Velocity		1.0 inch (2.5 cm) Test Bed			2.0 inch (5.7 cm) Test Bed			4.0 inch (10.0 cm) Test Bed		
FPM	CM/SEC	Penetration %	Residence Time Sec.	K Value	Penetration %	Residence Time Sec.	K Value	Penetration %	Residence Time Sec.	K Value
20	10	0.93	0.250	8.13	0.0596	0.500	6.45	0.0013	1.000	4.88
30	15	2.65	0.166	9.48	0.166	0.333	8.35	0.0030	0.666	6.79
40	20	4.80	0.125	10.55	0.291	0.250	10.14	0.0093	0.500	8.06
60	30	10.03	0.084	11.88	1.13	0.166	11.73	0.0190	0.333	11.17
80	40	17.1	0.063	12.18	2.70	0.125	12.55	0.0740	0.25	12.52

$$K = \frac{\text{Log}\,\frac{100}{\%\ \text{Penetration}}}{\text{Residence Time}}$$

Test Method: ASTM D3803 (1989) except Velocity

5NU542

TABLE 4

PARAMETRIC STUDY OF TEMPERATURE EFFECTS ON $CH_3{}^{131}I$ PENETRATION AT 95% RH, 40 FPM

Adsorbent: NUSORB KITEG II

	1.0 inch (2.5 cm) Test Bed 0.125 Sec. Residence Time		2.0 inch (5.0 cm) Test Bed 0.25 Sec. Residence Time		4.0 inch (10.0 cm) Test Bed 0.5 Sec. Residence Time	
Temperature, °C	Penetration %	K Value	Penetration %	K Value	Penetration %	K Value
25	5.62	10.00	0.304	10.06	0.0105	7.95
30	4.80	10.55	0.291	10.14	0.0093	8.06
40	3.34	11.81	0.131	11.53	0.0065	8.37
60	2.55	12.75	0.125	11.61	0.0046	8.67
80	0.95	16.18	0.105	11.91	0.0043	8.73

$$K = \frac{\text{Log}\dfrac{100}{\%\ \text{Penetration}}}{\text{Residence Time}}$$

Test Method: ASTM D3803 (1989) except Temperature

5NU542

TABLE 5

PARAMETRIC STUDY OF HUMIDITY EFFECTS ON $CH_3{}^{131}I$ PENETRATION AT 30°C, 40 FPM

Adsorbent: NUSORB KITEG II

	1.0 inch (2.5 cm) Test Bed 0.125 Sec. Residence Time		2.0 inch (5.0 cm) Test Bed 0.25 Sec. Residence Time		4.0 inch (10.0 cm) Test Bed 0.5 Sec. Residence Time	
Relative Humidity %	Penetration %	K Value	Penetration %	K Value	Penetration %	K Value
70	0.747	16.96	0.027	14.27	0.0016	9.59
80	1.70	14.08	0.048	13.27	0.0022	9.32
85	2.18	13.28	0.107	11.88	0.0043	8.73
90	3.05	12.16	0.192	10.86	0.0067	8.35
95	4.80	10.56	0.291	10.14	0.0093	8.06

$$K = \frac{\text{Log} \dfrac{100}{\%\ \text{Penetration}}}{\text{Residence Time}}$$

Test Method: ASTM D3803 (1989) except %RH

5NU542

TABLE 6

PARAMETRIC STUDY ON $H^{131}I$

PENETRATION THRU KI-AMINE IMPREGNATED CARBON

Impregnant: NUSORB KITEG II

Base Carbon: Coconut

Temperature °C	RH %	Velocity FPM	1.0 inch (2.5 cm) Bed Depth Penetration %	1.0 inch (2.5 cm) Bed Depth K Value	2.0 inch (5.0 cm) Bed Depth Penetration %	2.0 inch (5.0 cm) Bed Depth K Value
30	95	40	6.7	9.4	1.25	7.6
30	95	80	16.3	12.6	3.7	11.5
30	70	40	2.7	12.5	0.9	8.2

$$K = \frac{\text{Log} \dfrac{100}{\%\ \text{Penetration}}}{\text{Residence Time}}$$

Test Method: ASTM D3803 (1989) except $H^{131}I$ challenge

5NU542

FIGURE 1

PARAMETRIC STUDY OF PARTICLE SIZE EFFECTS ON $CH_3{}^{131}I$ PENETRATION AT 30°C, 95% RH

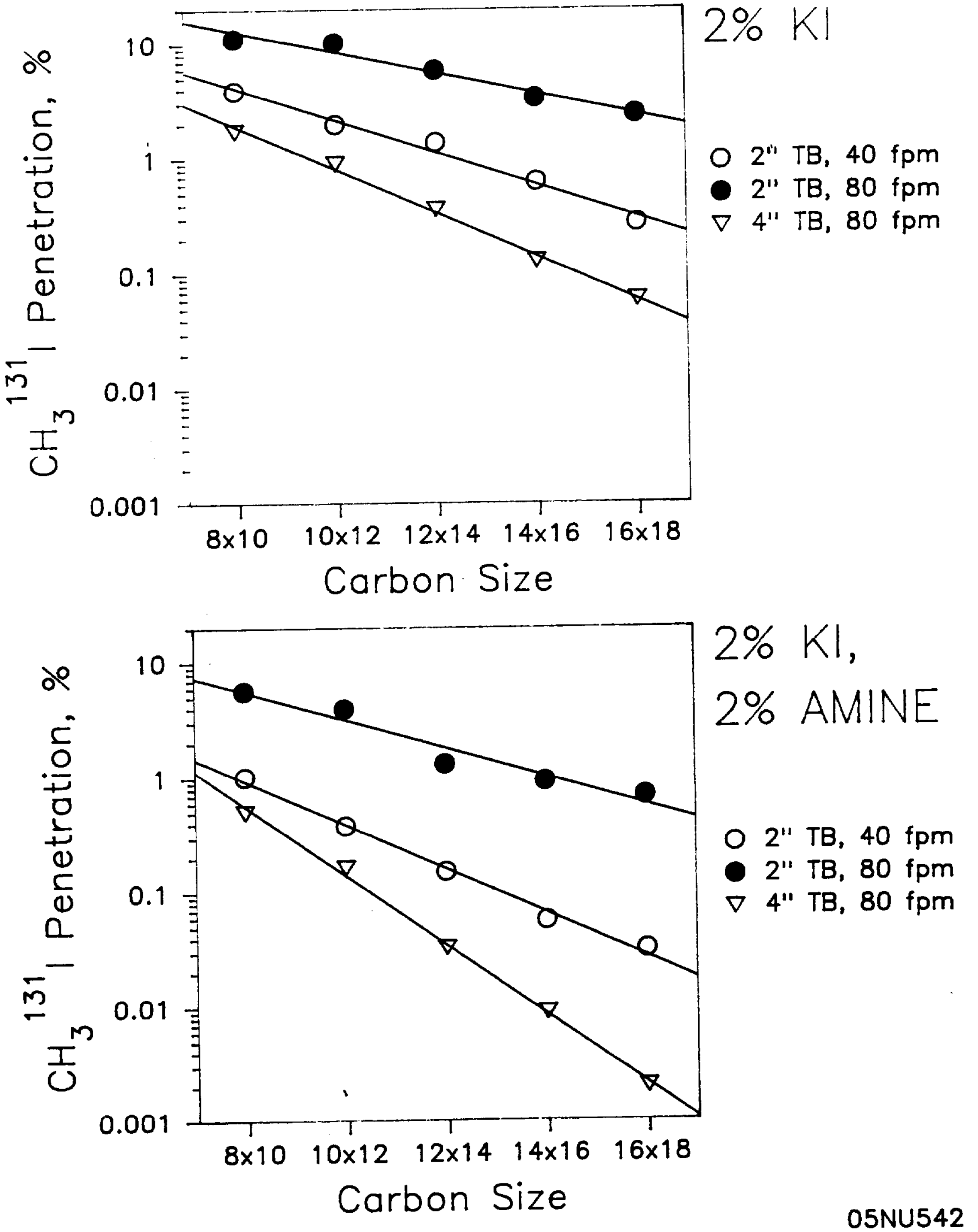

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FIGURE 2

PARAMETRIC STUDY OF VELOCITY EFFECTS ON $CH_3{}^{131}I$ PENETRATION AT 30°C, 95% RH

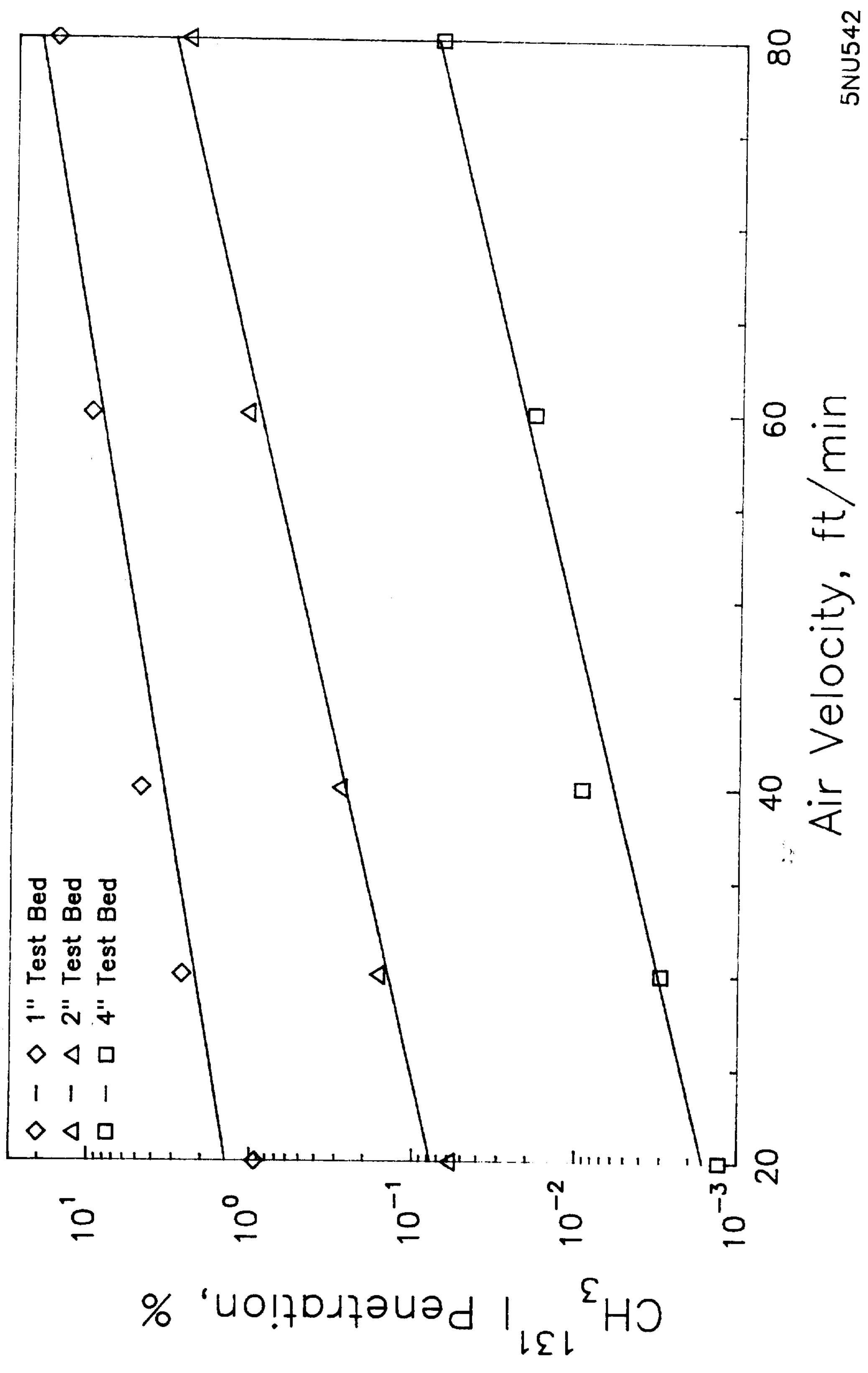


FIGURE 3

PARAMETRIC STUDY OF TEMPERATURE EFFECTS
ON $CH_3{}^{131}I$ PENETRATION AT 95%, 40 FPM

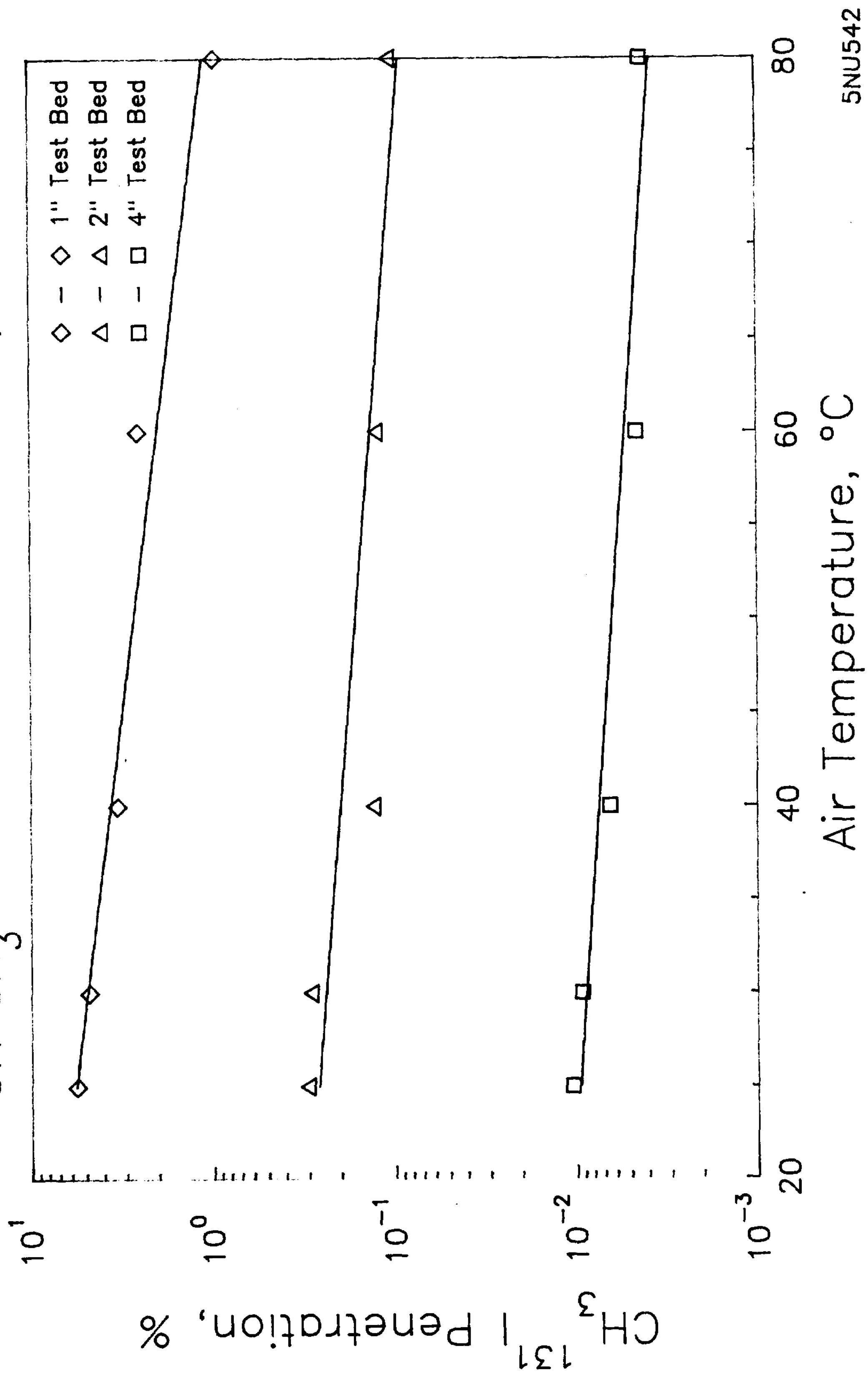
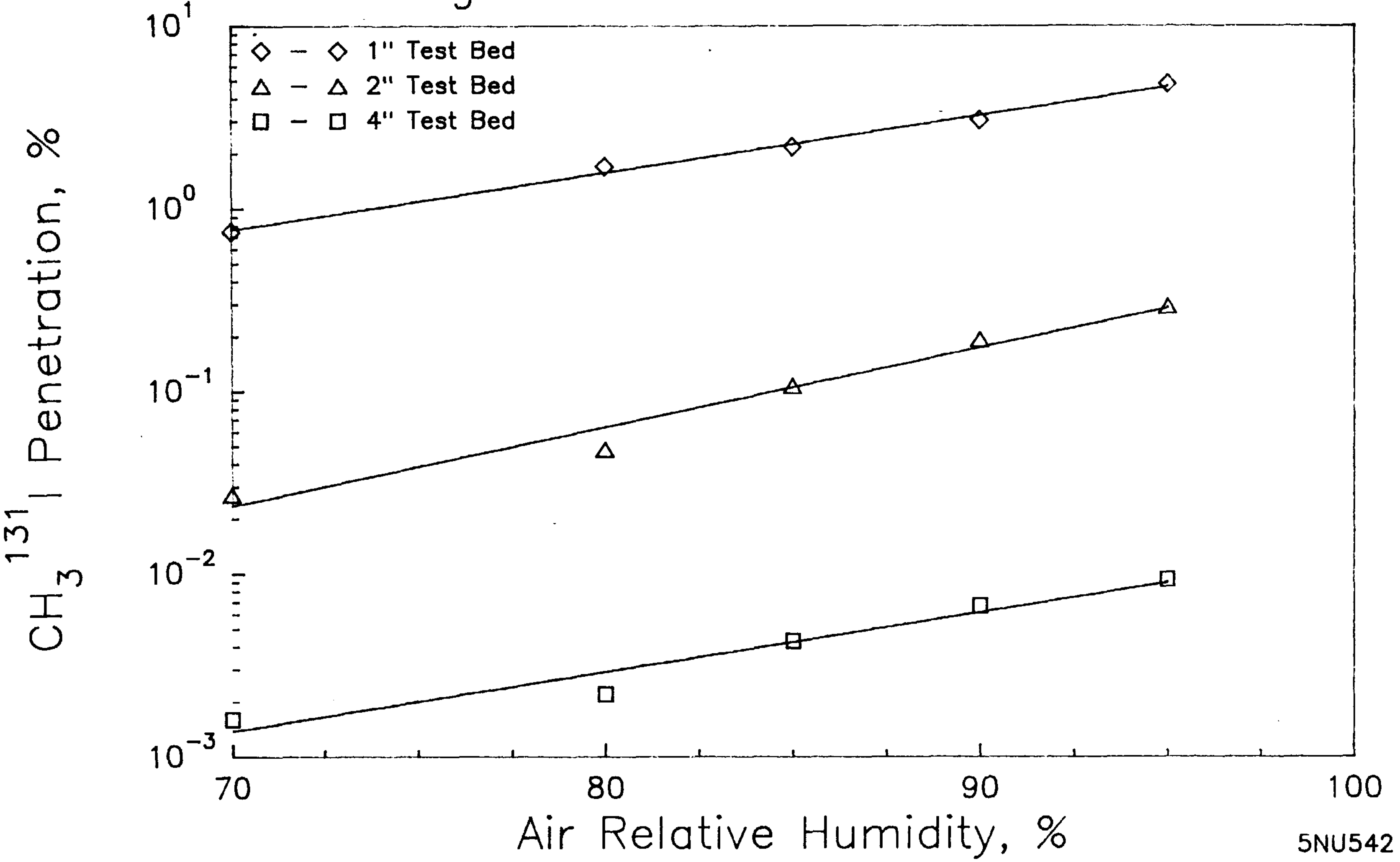


FIGURE 4

PARAMETRIC STUDY OF HUMIDITY EFFECTS ON $CH_3{}^{131}I$ PENETRATION AT 30°C, 40 FPM



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DISCUSSION

SCHOLTEN: You said, with smaller grain size and higher velocity, you get better performance, but you also get a higher delta P. Have you also looked at the correlation between performance and delta P? I think it might be the same. So, you can use a large grain size and make a deeper bed or you can get the same results by taking a shallower bed with smaller sizes.

KOVACH: That is correct. One reason why we ran the particle size effects is that very often people are comparing carbons without determining the particle size distribution of these adsorbents. It just demonstrates that it is extremely difficult to correlate results without knowing in great detail what the particle size distribution of the adsorbent is. I am not proposing that we go to finer particle size and deeper beds. I am saying that the option exists to do either, particularly for non-safety systems, because in nuclear power plants, electricity is not that expensive. They can tolerate the higher pressure drop for systems that don't have to operate off the diesels. I know that pressure drop represents a cost, but, generally, space is even more expensive. If you can put in a smaller air cleaning system that has 80 ft/min velocity in a 4 in. deep bed, and you now have HEPA filters and prefilters available which can handle 2,000 cfm in the 24 x 24 in. size, I think the cost that you save by having a smaller air cleaning system will more than pay for the slightly higher electricity cost right at the generation site.

SCHOLTEN: Also a choice.

TESTING OF ADSORBENTS USED IN NUCLEAR POWER PLANT AIR CLEANING SYSTEMS USING THE "NEW" STANDARDS

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Abstract

Ever since the publication of the NRC Information Notice No. 87-32: "Deficiencies in the Testing of Nuclear-Grade Activated Charcoal," nuclear power facilities in the U. S. have struggled in their efforts to "... review the information for applicability to their facilities and consider action, if appropriate ..." as stated in the notice. Despite the fact that the notice also states that no "specific action" is required, the encouragement of resident NRC inspectors at some nuclear power facilities has prompted a variety of responses ranging from no change at all in testing requirements to contemplated changes in plant technical specifications.

This confusion is a result of a couple factors. The first and foremost factor is the lack of a current revision to NRC Regulatory Guide 1.52. This is the basic document used in nuclear power plant technical specifications for the testing of engineered-safety feature (ESF) post accident air cleaning systems and is considered to be significantly outdated and in error in many technical areas. The second factor is the standards that have been written since the last revision of Reg. Guide 1.52 (Revision 2, 1978) which include two revisions of ANSI N509 and N510 (1980 and 1989) two revisions of RDT M16-1T (now NE M16-1T), two versions of ASTM D3803 (1979 and 1989), two versions of ASTM D4069 (1981 and 1990) and three versions of an ASME code AG-1 (1985, 1988 and 1991). These standards were ostensibly promulgated in an effort to eliminate the inconsistencies and ambiguities of the regulatory guide. However, few of the standards and codes listed above are commensurate with each other and, thus, present a nearly insolvable maze to the HVAC engineer asked to upgrade his adsorbent testing requirements following the "new" standards.

Accordingly, this paper describes our experience with a number of nuclear power facilities in their efforts to meet the requirements of the new standards for testing adsorbents from nuclear power plant air cleaning systems. Additionally, the existing standards are discussed in light of the current state of the art for adsorbent testing of adsorbent media from nuclear air treatment systems. Test results are presented showing the impact of "new" test requirements on acceptance criteria when compared to the "old" test requirements and recommendations are offered for solution of this testing problem in the future.

Introduction

Ever since the publication of the NRC Information Notice No. 87-32: "Deficiencies in the Testing of Nuclear Grade Activated Charcoal",[1] nuclear power facilities in the U.S. have struggled in the efforts to "... review the information for applicability to their facilities and consider action, if appropriate..." as stated in the notice. The information notice itself adds to the confusion that exists regarding acceptable testing standards when it states that "ASTM Standard D-3803-1979 was developed to specify the requirements for testing charcoal and was accepted by the NRC (Regulatory Guide 1.52, 1979)." There is no Regulatory Guide 1.52, 1979. Thus it comes as no surprise that the responses to this information notice have been many and various. The primary factor contributing to this confusion is a lack of a current Revision for NRC Regulatory Guide 1.52.

Regulatory Guide 1.52 (Revision 2, 1978)[2]

This is the basic document used in nuclear power plant technical specifications for the testing of engineered-safety-feature (ESF) post accident air cleaning systems and is considered to be significantly outdated and in error in many technical areas. Although few of the power plants that we provide testing services for use this document literally anymore, it is still referenced in practically all purchase orders as a requirement. However, even in its original sense, the document is confusing because of the paper trail that must be followed. As an example, shown in Table 1 is a reproduction of Table 2 from Reg. Guide 1.52 Rev. 2 which is the guide for how to test used activated carbon samples and the decontamination efficiencies that can be claimed based on the test results. Let's say we have a carbon sample removed from a stand-by gas treatment system that has no humidity control. First, the only place that tells one how often to test the carbon is a footnote in the table. Next, there's no category that specifically covers the sample (i.e. air filtration system outside containment with no humidity control). So we have to run the test at a humidity different than 70%, but what humidity should be used and what methyl iodide penetration should we look for? We turn to test 5.b. of Table 5-1 of ANSI N509-76[3] for help. Shown in Table 2 is a reproduction of Table 5-1 from ANSI N509-1976. We can assume from this table that 95% relative humidity should be used but we still do not have an acceptance criterion for the result (since that table is for new carbons). We turn to RDT-M16-IT par. 4.5.3 for guidance on performing the test (with pre- and post-loading sweep medium at 25°C).

Which RDT-M16-IT do they mean though? By process of elimination, RDT M16-IT October 1973[4] is chosen. Paragraph 4.5.3 in turn references 4.5.1 which gives a rudimentary method. There is only one utility that we provide testing services for that demands the 25°C equilibration, 80°C loading and 25°C post sweep called out by literally following this maze. Even then we still don't know what an acceptable result would be. It soon became apparent to anyone trying to use the Reg. Guide 1.52 Rev. 2 that it was confusing and subject to different interpretations at best. This lead to a proliferation of newer standards, the first which was RDT M16-IT December 1977[5].

RDT Standards

The December 1977 version of the RDT M16-IT standard was a major step forward for testing of nuclear grade adsorbents for a couple of reasons. First, it was an attempt to put all of the testing requirements into one document. And secondly, its appendix C "Standard Method for Radioiodine Testing of Nuclear Grade Gas-Phase Adsorbent" provided a prescriptive method that hopefully could be followed to obtain reproducible test results on nuclear grade adsorbents. The technical and performance requirements for adsorbents in this standard formed the basis and, in fact, are identical to those in ANSI-N509-1980 (except the RDT standard calls the 30°C 95% R.H. a qualification test and the ANSI standard calls it a batch test). The method for radioiodine testing became the basis for and is nearly identical to ASTM D3803-79, "Test Methods for Radioiodine Testing of Nuclear-Grade Gas-Phase Adsorbents."[5] This standard does a good job of describing and specifying the requirements for virgin adsorbents, but does not address the test of used (surveillance) samples. The later version of this standard, NE M16-IT October 1981[6] (now under the auspices of the DOE) changes little from the 1977 standard except to incorporate the ASTM D3803-79 test methods by reference. These standards are not often specified by commercial power plants when requesting adsorbent testing.

ASTM D3803

Originally issued in 1979, these methods are identical to the methods in the 1977 RDT standard. The same five tests are specified (methyl iodide at 30° and 95% relative humidity, 80°C and 95% relative humidity, 130°C and 95% relative humidity, elemental iodine test at 30°C and 95% relative humidity and an elemental iodine retention test at 180°C. This method does prescribe testing for used carbon samples for the 30°C, 80°C and 130°C tests by eliminating the equilibration period where the carbon is exposed to humid air. The issuance of ASTM D3803-86 was not a revision of the standard test methods but just a reapproval of the existing 1979 methods. The revision D3803-89 will be discussed later.

ASTM D4069-81

ASTM D4069[7] provides specifications for physical properties and performance requirements for virgin impregnation carbons used for radioiodine control. The specifications for the 1981 version are identical to N509-1980. The 1986 version has no changes from the 1981 version, while the 1990 revision reflects the changes made in D3803-89. Little use has been made of this specification in the industry.

ANSI N509 and N510

In response to changes in test methodology, ANSI N509 was revised and issued as ANSI N509-80. It's companion standard, ANSI N510-1975, "Testing of Nuclear Air-Cleaning Systems was also revised and issued as ANSI N510-1980[8]. N509-80's performance requirements and physical properties for new activated carbon (shown as Table 3 here) are the same as the RDT standard. It defers to ASTM D3803 for test methodology for radioiodine tests and it makes a batch test out of the 30°C, 95% relative humidity methyl iodide test and makes a lot or qualification test out of the 80°C, 95% relative humidity methyl iodide test. The ANSI N509-1980 standard does an excellent job of describing and specifying virgin adsorbents for radioiodine control, but, other than discussing how to sample installed adsorbers, no guidance for testing used adsorbents is given. The companion N510-1980 does mention that tests to samples withdrawn from adsorbers should be performed. It defers testing procedures to ASTM D3803 and test conditions to plant technical specifications.

The newest versions of N509 and N510, 1989 are really stop gap standards since CONAGT (ASME Committee on Nuclear Air and Gas Treatment) intends on replacing these standards with ASME AG-1, "Code On Nuclear Air and Gas Treatment"[9]. Thus, testing of adsorbents is deferred to AG-1-1988, Section FF for new adsorbents and plant technical specification for used adsorbents for N509-89. N510-89 is somewhat different. It does provide some guidance for when to test used carbon samples (before each leak test, after 720 hours of operation), what tests to perform (ASTM D3803-79) and what acceptance criteria to use (owner's specifications).

AG-1 Code

ASME AG-1-1985 "Code on Nuclear Air and Gas Treatment" section FF, Adsorbent Media, "provides minimum requirements for the performance, design, acceptance testing, and quality assurance for adsorbent media used in air and gas cleaning systems in nuclear facilities." It accomplishes this by specifying ASTM D3803-79 as the test method, and acceptance criteria for each test (identical to N509-80 and ASTM D4069). No guidance is given for testing used (surveillance) samples of carbon (defers to technical specifications). The 1988 revision of AG-1 as well as the 1991 revision of AG-1 are identical to the 1985 version.

ASTM D3803-1989

The NRC move to have systems outside containment tested at 30°C in the early 80's[10], created quite a stir in the industry where systems outside containment had been tested at 80°C and 95% or 70% relative humidity (depending on whether or not the system had relative humidity control). Where a 1% penetration had been the acceptance criterion for used carbon samples, plants were faced with testing at 30°C and 95% relative humidity where 3% penetration was allowed for new carbons. When the results of testing at 30°C for used carbons started circulating around the industry and when large difference in results were noticed, CONAGT decided to conduct an interlaboratory comparison of ASTM D3803-79 Method A (30°C, 95% relative humidity, methyl iodide test on new carbon). When vastly different results were obtained from testing the same carbon, the NRC contracted with the Idaho National Engineering Laboratory to investigate the problem. The result of this program published as EGG-CS-7653, "Final Technical Evaluation Report for the NRC/INEL Activated Carbon Testing Program"[11] included as an appendix a draft revision of ASTM D3803. As a result of the interlaboratory comparison following this draft revision, a validated revision of ASTM D3803 was published as D3803-89 containing only the 30°C, 95% relative humidity methyl iodide test for both new and used carbons. As a caveat to tests required at other conditions (a problem which has been brought to the attention of CONAGT[12]), annex A5 was added to give additional guidance.

Plant Technical Specifications
Problem with Testing Adsorbents

Shown in Table 4 are a sampling of typical testing requirements for "tech. spec." systems at a number of plants we service. As can be readily seen in the table, a variety or conditions are used to test the same kind of system. The problem of trying to change testing is seen when say a Palo Verde would like to change to the 30°C test of ASTM D3803-89 for their control room. The 99% efficiency that they are currently using implies an assigned decontamination efficiency of no more than 95% for their accident analysis. If they used the 30°C test and 95% efficiency, they would be allowed no more than 90% credit in the accident analysis and could thus violate their technical specifications. Other plants have had to deal with this issue and so we will use them as examples and hopefully provide some guidance for other plants that desire to upgrade their adsorbent testing to current standards.

Solutions and Recommendations

In Table 5 are presented some solutions to the problem of testing using the new standards. Perhaps the easiest solution is to take exception to the temperature requirement of 80°C for Reg. Guide 1.52, Rev. 2 and use 30°C as the Braidwood plant has done. In the case of the Calvert Cliffs plant, they have developed a program to look at the results of testing their in-place carbon using different conditions. Results of these tests are shown in Table 5 and indicate that an acceptable test at one condition does not mean that an acceptable result will be obtained using a different condition.

Two extremely important things were learned during the INEL/NRC interlaboratory comparison. First, the 30°C, 95% relative humidity, methyl iodide test is the most sensitive test for assessing the performance of new and used carbons. Secondly, the efficiencies claimed for used carbon tested at 80°C according to the Reg. Guide are not realistic when compared to results obtained at 30°C. Also presented in Table 5 are recommendations for testing new and used carbon for radioiodine control. For new carbons we recommend the 30°C and 95% relative humidity methyl iodide test and a 180°C elemental iodine retention test with the acceptance criteria the same as AG-1. If additional tests are required to satisfy technical specifications, we recommend using the procedure of ASTM D3803-89 and the conditions and acceptance criteria of the technical specifications. For used carbon testing inside containment the method of ASTM-3803-89 is recommended using conditions of 80°C and either 70% or 95% relative humidity depending on whether the system has humidity control or not (this test would be identical to the D3803-79 method B test). The same holds true for used carbons outside containment except 30°C and 70% or 95% relative humidity is used. Suggested acceptance criteria have also been offered. The 99% efficiency suggested for the 80°/70% relative humidity test is the same that has been in use for 1.52, Rev. 2. Where the other efficiencies would cause a no violation of technical specifications, perhaps two tests can be performed (as several plants have done). One test can be performed to satisfy technical specifications, while the D3803-89 test can be performed to judge the condition of the carbon. Unfortunately, without a revision to the Regulatory Guide, this may be the best we can do in the interim.

References

1. NRC Information Notice No. 87-32: "Deficiencies in the Testing of Nuclear Grade Activated Charcoal"; United States Nuclear Regulatory Commission, Office of Nuclear Reactor Regulation, Washington, DC 20555, July 10, 1987.

2. USNRC Regulatory Guide 1.52, Revision 2, March 1978; "Design, Testing and Maintenance Criteria for Post Accident Engineered-Safety Feature Atmosphere Cleanup System Air Filtration and Adsorption Units of Light-Water-Cooled Nuclear Power Plants"; USNRC, Washington, DC 20555.

3. American National Standard ANSI/ASME N509-1976, 1980, 1989; "Nuclear Power Plant Air Cleaning Units and Components", American Society of Mechanical Engineers, 345 East 47th Street, NY 10017.

4. RDT M-16-1T, "Gas-Phase Adsorbents for Trapping Radioactive Iodine and Iodine Compounds, January 1971, June 1972, October 1973, December 1977, USAEC, Division of Reactor Research and Development, Now USDOE, Office of Scientific and Technical Information, Oak Ridge, TN 37831.

5. ASTM D3803-79, 86, 89; "Standard Test Methods for Radioiodine Testing of Nuclear-Grade Gas-Phase Adsorbents", ASTM, 1916 Race Street, Philadelphia, PA 19103-1187.

6. NE M16-1T, "Gas Phase Adsorbents for Trapping Radioactive Iodine and Iodine Compounds," October 1981, USDOE, Nuclear Energy Programs. Oak Ridge, TN 37830.

7. ASTM D4069-81-86-90; "Standard Specification for Impregnated Activated Carbon Used to Remove Gaseous Radioiodines from Gas Streams", ASTM, 1916 Race Street, Philadelphia, PA 19103.

8. American National Standard ANSI/ASME N510-1975, 1980, 1989; "Testing of Nuclear Air-Cleaning Systems," American Society of Mechanical Engineers; 345 East 47th Street, New York, NY 10017.

9. ASME AG-1-1985, 1988, 1991; "Code on Nuclear Air and Gas Treatment," American Society of Mechanical Engineers, 345 East 47th Street, New York, NY 10017.

10. Letter from William Gamill, NRC Chief of Effluent Treatment Systems Branch, to Fred Leckie, NCS, September 24, 1981.

11. Scarpellino, C.D. and Sill, C.W.; "Final Technical Evaluation Report for the NRC/INEL Activated Carbon Testing Program," EGG-CS-7653 April 1987, Idaho Falls, Idaho 83415.

12. ASME/CONAGT; "White Paper on Methyl Iodide Testing," 9 March 1992, Draft 6.

Table 1
From Regulatory Guide 1.52, Rev. 2 1978
Laboratory Tests For Activated Carbon

Activated Carbon[a] Bed Depth[b]	Assigned Activated Carbon Decontamination Efficiencies		Laboratory Tests for Representative Sample[c]
2 inches. Air filtration system designed to operate inside primary containment.	Elemental iodine Organic iodide	90% 30%	Per Test 5.c[d] for a methyl iodide penetration of less than 10%.
2 inches. Air filtration system designed to operate outside the primary containment and relative humidity is controlled to 70%.	Elemental iodine Organic iodide	95% 95%	Per Test 5.b[d] at a relative humidity of 70% for a methyl iodide penetration of less than 1%.
4 inches or greater. Air filtration system designed to operate outside the primary containment and relative humidity is controlled to 70%.	Elemental iodine Organic iodide	99% 99%	Per Test 5.b[d] at a relative humidity of 70% for a methyl iodide penetration of less than 0.175%.

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[a] The activated carbon, when new, should meet the specifications of regulatory position C.3.i of this guide.

[b] Multiple beds, e.g., two 2-inch beds in series, should be treated as a single bed of aggregate depth.

[c] See regulatory position C.6.b for definition of representative sample. Testing should be performed (1) initially, (2) at least once per 18 months thereafter for systems maintained in a standby status or after 720 hours of system operation, and (3) following painting, fire, or chemical release in any ventilation zone communicating with the system.

[d] See Table 5-1 of ANSI N509-1976 (Ref. 1).

Table 2
From ANSI-N509-1976
Summary Table of New Activated Carbon Physical Properties Batch Tests
to be Performed on Finished Adsorbents

Test	Acceptable Test Method	Acceptable Results	
1. Particle Size Distribution	ASTM D2862	Retained on #6 ASTM E11 Retained on #8 ASTM E11 Maximum Through #8, retained on #12 Through #12, retained on #16 Through #16, ASTM E11 Through #18, ASTM E11	Sieve: 0.0% Sieve: 5.0% Sieve: 40% to 60% Sieve: 40% to 60% Sieve: 5.0% max Sieve: 1.0% max
2. Hardness Number	RDT M16-1T, Appendix C	95 minimum	
3. Ignition Temperature	RDT M16-1T, Appendix C	330°C minimum at 100 fpm	
4. Activity	CCL4 Activity, RDT M16-1T, Appendix C	60 minimum	Base
5. Radioiodine Removal Efficiency			
a. Methyl Iodide, 25°C and 95% Relative Humidity	RDT M16-1T, par, 4.5.3, except 95% relative humidity air is required.	99%	
b. Methyl Iodide, 80°C and 95% Relative Humidity	RDT M16-1T, par. 4.5.3, except 80°C and 95% relative humidity air is required for test (pre- and post-loading sweep medium is 25°C)	99%	
c. Methyl Iodide in Containment	RDT M16-1T, par. 4.5.4, except duration is 2 hours at 3.7 atm. pressure.	98%	
d. Elemental Iodine Retention	Savannah River Laboratory	99.9% loading 99% loading plus elution	
6. Bulk Density	ASTM D2854	0.38 gm/ml minimum	
7. Impregnant Content	State Procedure	State type (not to exceed 5% by weight)	

Table 3
From ANSI N509-1980
Performance Requirements and Physical Properties of (Unused) Activated Carbon

Test	Test Method	Acceptance Value
Performance Requirements		
Molecular Iodine, 30°C, 95% RH[1]		0.1% penetration, maximum
Molecular Iodine, 180°C	ASTM D3803	99.5% retentivity, minimum
Methyl Iodine, 30°C, 95% RH		3% penetration, maximum
Methyl Iodide, 80°C, 95% RH[1]		1% penetration, maximum
Methyl Iodide, 130°C, 95% RH[2]		2% penetration, maximum
Physical Properties		
Particle Size Distribution	ASTM D2862 using 8 x 16 U.S. Mesh	Retained on #6 Sieve: 0.1% maximum Retained on #8 Sieve: 5.0% maximum Through #8, on #12 Sieve: 60% maximum Through #12, on #16 Sieve: 40% maximum Through #16 Sieve: 5.0% maximum Through #18 Sieve: 1.0% maximum
Ball Pan Hardness	ASTM D3802	92 minimum
$C\ Cl_4$ Activity (on base)	ASTM D3467	60 minimum
Apparent Density	ASTM D2854	0.38 g/cm^3 minimum
Ash Content (on base)	ASTM D2866	state value
Ignition Temperature	ASTM D3466	330°C minimum
Moisture Content	ASTM D2867	state value
pH of Water Extract	ASTM D3838	state value

NOTES:

[1] Tests shall be performed only for qualification purposes.

[2] Test shall be performed only for qualification purposes on activated carbon to be installed in primary containment cleanup system.

Table 4
Plant Technical Specification

Plant	System	Test Method	Test Conditions	Acceptance Criterion
Palo Verde	Control Room	D3803-79B	80°C/70% R.H.	99.0%
	Fuel/Aux. Bldg.		80°C/70% R.H.	99.0%
	H_2 Purge		80°C/70% R.H.	99.0%
Prairie Island	Control Room	D3803-89	30°C/70% R.H.	95.0%
		1.52, Rev. 2	130°C/95% R.H.	92.0%
	Aux. Bldg.	D3803-89	30°C/70% R.H.	95.0%
		1.52, Rev. 2	130°C/95% R.H.	92.0%
	Shield Bldg.	D3803-89	30°C/95% R.H.	95.0%
		1.52, Rev. 2	130°C/95% R.H.	92.0%
	Spent Fuel Pool	D3803-89	30°C/70% R.H.	95.0%
		1.52, Rev. 2	130°C/95% R.H.	92.0%
Vogtle	All	INEL Protocol	30°C/70% R.H. 4" Test Bed	Various
Ginna	Control Room	N510-75	51.7°C/95% R.H.	90%
	Spent Fuel	N510-75	65.6°C/95% R.H.	90%
	Post Accident	N510-75	141.1°C/95% R.H.	90%
	All Others	N510-75	51.7°C/95% R.H.	90%
SONGS	Control Room U1	3803-79	30°C/70% R.H.	90%
	Control Room U2 & U3 Air Clean-up	1.52, Rev. 2	80°C/70% R.H.	99%
	Control Room U2 & U3 Emergency Vent	1.52, Rev. 2	80°C/95% R.H.	90%

Table 5
Solutions to Testing with New Standards

Plant	System	Test Method	Test Conditions	Acceptance Criterion
Braidwood	Fuel Handling	1.52, Rev. 2	30°C/95% R.H.	90%
	Control Room	1.52, Rev. 2	30°C/70% R.H.	99%
Calvert Cliffs	Control Room	1.52, Rev. 2	30°C/95% R.H. 30°C/70% R.H. 130°C/95% R.H.	Result: 93.56% Result: 99.50% Result: 99.83%
	ECCS Pump Room	1.52, Rev. 2	30°C/95% R.H.	Result: 58.80%
	Spent Fuel Pool	1.52, Rev. 2	30°C/95% R.H.	Result: 99.45% (new carbon)
Recommendations:	New Carbon	ASTM D3803-89	30°C/95% R.H.	97%
		ASTM D3803-86	180°C I_2 Retention	99.5%
	Any Tech. Spec. Item Not covered	Use procedure of ASTM D3803-89	Tech. Spec.	Tech. Spec.
	Used Carbon			
	Systems inside containment with humidity control	ASTM D3803-89	80°C/70% R.H.	99%
	Systems outside containment with humidity control	ASTM D3803-89	30°C/70% R.H.	95%
	Systems inside containment without humidity control	ASTM D3803-89	80°C/95% R.H.	97%
	Systems outside containment without humidity control	ASTM D3803-89	30°C/95% R.H.	92%

DISCUSSION

FREEMAN: Should your chart of recommendations have the acceptance criteria on the expected or credited efficiency of the system rather than just giving acceptance criteria?

KOVACH: I think NUCON could establish them for a lot less money than the NRC, but I don't think we are the ones to set them.

HAYES: Just a comment with respect to the criteria you have proposed for used carbon. I would say that for inside containment (and in most cases we are talking ESF systems there) it is really not applicable any more. When Revision 0 of Reg. Guide 1.52 was issued, the NRC was at the stage where sprays were not utilized nor considered as part of the fission product removal system. The major concern and emphasis, both in terms of charcoal (RDT-161T) testing and with respect to Reg. Guide 1.52, was for systems within containment. However, very early in the design cycle, containment sprays began to replace in-containment filtration systems such that today there are only 3 or 4 plants that have safety-grade charcoal systems within containment. So, I would say, unless you need an incontainment system to mitigate the consequences of, say, a fuel handling accident inside containment, you wouldn't have to address that particular item. If you did, I would say that the worse conditions are at a much lower temperature than either 80°C or 130°C. So, my recommendation would be that you should do the 30° C test for all charcoal.

The other question was; "What will be the credited accident efficiency associated with the acceptance criteria?" Depending upon the safety factor currently used by the NRC, i.e. whether you have relative humidity control, you may have a charcoal that will be credited an adsorber efficiency of only 50%. There are not a whole lot of facilities that could utilize an adsorber efficiency of 50% in their accident evaluation and still maintain their design basis doses within the NRC's acceptance criteria.

I will defer the rest of that discussion until our panel tomorrow, when we will explain the correlation between acceptance criteria for the laboratory test, the accident evaluation by the utility, and then by the NRC.

EXPERIENCE WITH ONTARIO HYDRO'S IN PLACE CARBON FILTER TESTING

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Abstract

It is now 5 years since Ontario Hydro's first use of freon to test for both integrity and carbon quality in Nuclear Generating Station carbon ventilation filters. The method has since been refined and the equipment modified and the test has now become routine. Alongside the freon test, a 24 hour methyliodide desorption test is also routinely performed on the worst (most desorbing) filters as indicated by the freon test. The method uses non-active methyliodide injection and neutron activation analysis of dual carbon sampling beds. A chemical means of iodine analysis to replace the neutron activation analysis is being pioneered to streamline the process and render it fully field applicable. So far, the method is still developmental but field testing is hoped for during 1992. In the interim, to complement the freon testing, some TEDA impregnant analysis of carbon grab samples has been carried out. Data on apparent TEDA loss from Emergency (standby) filters over a 3 year period will be presented.

I - Introduction

Ontario Hydro currently operates 18 large CANDU nuclear units with 2 more scheduled to come on stream within a year, which will give an installed capacity of approximately 12.4 GWe. Two older units have been shut down and are being decommissioned. From the earlier to the most recent nuclear generating stations, ventilation system flow rates have risen from a few thousand cfm to over 100,000 cfm (50,000 cfm per filter) for a given system (Figure 1). This has naturally created some challenges in the area of filter testing.

Development of the Freon Test

Freon-11 was first used at Ontario Hydro to test for carbon filter bypass leakage in 1987, replacing an earlier bypass leakage test which used continuous injection of inactive methyliodide and portable gas-chromatographic grab sampling. This earlier test was time-dependent and consequently unable to distinguish between bypass leakage and rapid breakthrough of the test agent. In addition, it was not suited to the higher flow systems.

Based on work performed by Taylor of the British CEGB(1) and the NUCON company of Columbus, Ohio, USA, it was decided to try using the desorption profile of the freon pulse injected in the bypass leakage test to give an indication of the carbon quality. Early results of this work were reported at the 1988 Air Cleaning Conference(2). However, it was realised at the same time that a freon desorption profile could, at best, only indicate physical characteristics of the carbon and that some measure of overall performance was needed (Figure 2). This overall performance is defined in the Ontario Hydro safety analysis as follows: methyliodide desorption shall not exceed 1% of the filter loading per 24 hour period for normal operation filters (mainly 100 mm bed depths with some 50 mm) and 0.01% per 24 hours for emergency filters (200 mm bed depths).

Replacement of the Laboratory Test

The previously used ASTM D3803 laboratory test was not able to validate this safety analysis assumption. Also, as reported at the 1988 Conference(2), an Ontario Hydro Research Project found considerable variation in airflow through various parts of the carbon bed from a commercial filter, as well as between the filter and the test canisters used to provide the D3803 sample. This led to serious questions about the sample representivity. Finally, the criticism following the international interlaboratory comparison testing caused the D3803 to be discontinued at Ontario Hydro, and the laboratory that performed the test was permanently diverted to other uses.

However, as Victor Deitz mentioned in a previous air cleaning conference, in a similar way to how the memory of TEDA that has apparently disappeared from carbon lingers on in terms of its MeI trapping ability(3), so the memory of the D3803 lingered on, at least in our regulators' minds. The test is now performed again on used emergency filter carbon by Chalk River Nuclear Laboratories, Atomic Energy of Canada Limited. Some data from these tests are presented later in this paper.

In-Place Methyliodide Desorption Test

In order to provide a more direct measure of the safety analysis criteria referred to above, an in-place 24 hour desorption test using non-active MeI was developed. A 24 hour sample of filter outlet air is drawn through carbon sampling beds for subsequent neutron activation analysis (Figure 3). The test was described and very preliminary results reported in the 1988 Air Cleaning Conference(2). Further results are reported in this paper.

II - Freon Test

The basic method of performing the freon bypass/desorption test at Ontario Hydro has not changed since we first described it at the 1988 Air Cleaning Conference. A pulse of freon is injected into the ventilation flow well upstream of the filter and the concentrations measured up and downstream of the filter. The upstream detector is then switched from the ppm to the ppb range and the equipment left running for a minimum of 20 minutes to observe the desorption profile (Figure 4). However, with the experience of using the test over the last 5 years, a number of changes have been made to the test procedure and to the NUCON test equipment used to perform it. They are as follows:

(1) What was referred as a FEDI (Freon Eleven Desorption Index) in 1988 is now called a CQI or Carbon Quality Index, although the three components of the desorption profile used to calculate it are essentially the same. They are:

   (a) Elapsed time before desorption starts to occur (time to breakthrough).

   (b) Maximum instantaneous desorption observed divided by the elapsed time.

   (c) Maximum rate of increase of desorption.

   The three factors are normalized for inlet concentration and summed in units of inverse time to give the CQI.

(2) A field check of the downstream freon detectors using a 250 ppb freon standard and of the upstream detectors using a 10 or 20 ppm standard is carried out prior to each filter bank test.

(3) The injection pulse has been shortened to 15 s. This measure was adopted to help clarify the distinction between bypass leakage and rapid desorption that was sometimes apparent from our 50 mm carbon beds that have been in service for some time (Table 1). This necessitated removal of the mixing chambers from the detectors used for the filter outlet measurement. The calibration with the standard gases similarly uses 15 s pulses.

(4) Plans to correct the CQI for different relative humidities, specially significant for RH values greater than about 50% which tend to reduce the freon hold-up time, proved to be overly ambitious. It became apparent that corrections would have to be developed for almost every variation of carbon condition and bed thickness (Table 2), leading to a very complex set of curves with limited applicability. Instead, the simpler approach of testing in the Spring and Fall to moderate relative humidity effects and changes was adopted.

(5) Instead of trying to develop the freon desorption test into a precise and definitive measure of the carbon effectiveness, replacing the ASTM D3803, it is now used as a "predictive indicator" of carbon filter performance, as well as for trending analysis. Positive indications arising from the freon desorption test are followed up by the more expensive and labour-intensive 24 hour MeI desorption test alluded to earlier. This dual approach appears to have been working generally satisfactorily and some comparative data are presented in Table 3.

A CQI calculated to be between zero (no observable desorption for the duration of the test, usually 20 minutes) and unity is taken to indicate acceptable quality carbon for the 100 mm filter beds, by far the most common bed thicknesses in use at Ontario Hydro. A CQI greater than unity will call into consideration the filter's history of test results and the relative humidity prevailing at the time of the test and may trigger a MeI desorption test. It has been found that a CQI of unity is a very conservative limit, even at low relative humidities. A 100 mm bed of carbon in near new condition shows no evidence of desorption for the duration of the test. Carbon of the same bed thickness in service for several years in the bypassed mode also appears to show no desorption.

For the 200 mm beds, which are a component of the emergency filters, the CQI limit was set at 0.1 instead of 1 (Figure 5). However, in practice, no significant desorption has been observed and none would be tolerated. Any significant desorption would result in a carbon change with a follow-up investigation.

50 mm beds, which exist at only one station, and have been in service for a considerable period now, frequently exhibit rapid breakthrough of the freon, sometimes almost indistinguishable from bypass leakage. It is these filters that currently pose the biggest challenge to our freon desorption test.

The freon test does, of course, only indicate the physical condition of the carbon. To avoid having to take carbon samples routinely from filters for TEDA analysis, with all the associated problems of representivity, we are accumulating data in an attempt to demonstrate that in-service weathering of carbon leads to physical deterioration (ie, poisoning) at a rate equal to or faster than the loss of TEDA. As reported in the 1988 Air Cleaning Conference(4), Ontario Hydro buys only 5% TEDA impregnated carbon, and all new supplies are QA checked prior to acceptance. Therefore, starting with approximately 5% TEDA, physical deterioration should be the dominating factor. Some data are presented in Table 4.

III - Methyliodide (MeI) Desorption Test

The 24 hour MeI desorption test has also been modified since we first described it in the 1988 Conference. Instead of using the 1 inch thick "off-the-shelf" impregnated carbon cartridges as sampling beds, we have now developed an integral probe and sampling bed holder that is inserted into the filter or the ductwork as appropriate. This allows the pump to be left at a convenient location and eliminates losses on long lengths of sample lines (Figure 6).

The sampling bed holder contains two beds of TEDA impregnated low background iodine carbon arranged in series and separated by a screen. These beds have been sized so that they fit in their entirety into the capsule inserted into the reactor for the neutron activation analysis, thereby avoiding having to attempt to obtain representative subsamples from the sampling beds for analysis. The purpose of having the second sampling bed is to pick up any desorption from the first bed. Table 5 shows desorptions that have been found for the sampling beds at similar flow rates over the same time periods but with different carbon mesh size.

The sensitivity of the test is limited by the availability of carbon that has low background iodine as well as being low in other elements that have a tendency to interfere with the neutron activation analysis of iodine, including Sodium, Manganese, Aluminum, Vanadium, Potassium, and Titanium. We have managed to find carbons with background iodine levels less than 1 ppm which we impregnate with TEDA in house. We have found it is important with this method to submit blank TEDA impregnated samples rather than unimpregnated blanks along with the used sampling beds for activation analysis. This is because on one occasion it was discovered that the impregnation caused the background iodine levels to jump dramatically. The reason was never fully identified although contaminated TEDA was the suspected cause.

Our procedures now call for a filter inlet sample to be collected in addition to the outlet sample. This acts as a check that the expected amount of MeI actually challenged the filter. Although the methyliodide is introduced into the ventilation flow over a period of only a few minutes, the inlet sample pump is left running for the full 24 hours, to duplicate the conditions of the filter outlet sample as far as possible. This information could be useful, for example, with respect to collection bed desorption.

MeI Desorption at Pickering Nuclear Generating Station

This technique helped explain some very perplexing results that arose from tests of the Irradiated Fuel Bay filter at our Pickering Nuclear Generating Station. This single filter is a component of the system that ventilates the air space above the water in which used fuel and such items as adjuster and cobalt rods are stored.

For the first two MeI desorption tests, conducted in the fall of 1988 and 1989, only the filter outlet was sampled. No iodines (above background levels) were detected despite the fact that the filter was known, from previous D3803 tests, freon desorption results, and length of service, to be in poor condition. When the procedure was amended to include filter inlet sampling, no iodine was found there either during tests in late 1990, despite the fact that the injection port and inlet and outlet sampling locations were those used successfully in the freon and DOP tests. Similarly, the probe and sampling beds were those used successfully at other locations. New cylinders of MeI were ordered and the tests repeated in May 1991. The results were the same; no MeI above background was collected upstream or downstream of the filter.

The fuel bay ventilation system at Pickering the same as the other stations with one exception, being the first of our commercial nuclear stations, the system was considerably smaller with only a single filter housing instead of the more common bank of four filters sharing a common inlet as at our other stations. Because of the much lower flow rate, smaller gas cylinders, from the same supplier, were used. Subsequent investigation disclosed that these smaller cylinders were made of aluminum instead of the usual steel, and that a black residue had been reported inside returned cylinders. From this information, it was theorised the MeI may have reacted with the aluminum to form an aluminum iodate compound. New steel cylinders have been ordered and the test is due to be repeated this fall.

IV - Alternate Testing Strategies

Despite the improvements and some encouraging test results from the 24 hour MeI desorption test, it still suffers from a number of drawbacks (Figure 7). These include:

(1) Handling of heavy cylinder and pumps.

(2) Difficulty of obtaining reliable supplies of low background iodine carbon.

(3) Long lead time to obtain neutron activation results.

(4) Possible future loss of local reactor facilities to perform the neutron activation analysis.

(5) Somewhat inadequate detection limit.

(6) Expense; each filter requires 4 samples for neutron activation analysis, not including blanks. A typical bank of 4 filters may require up to 20 samples.

(7) Having to load up the filters with larger than desirable quantities of MeI for each test to obtain the required sensitivity.

To overcome these problems, in conjunction with our Research Division, we have been searching for a chemical method to replace the neutron activation analysis. The first method we investigated consisted of collecting the filter outlet sample by passing the air through various proprietary reusable organic vapour collection tubes. These are marketed as part of a temperature-programmable injection system for gas-chromatographs using thermal desorption. After considerable work, the method had to be abandoned. The collection tubes, made of glass, proved not rugged enough for field use and frequently resulted in breakage. When attempting the thermal desorption process into the gas-chromatograph, it would either prove almost impossible to desorb the MeI off the sample tubes or else other organic compounds would desorb off at the same time, seriously interfering with the gas-chromatographic analysis.

The second method is still under development. Air samples are collected over a 24 hour period in stainless steel canisters whose interior walls have been electropolished by a method commonly referred to as the Summa process. This avoids the need for any collection media other than the containers themselves (Figure 8).

The 24 hour integrated air samples are returned to the laboratory for capillary gas chromatographic analysis. In order to achieve the necessary MeI detection level, the sample is first passed via a heated nickel line to a cryogenic separation trap (-150° C) where the volatile components such as oxygen and nitrogen can be vented off leaving the trace components frozen. The first cryo trap is then heated and the sample passed into a second cryo trap which retains the sample as a tight plug prior to injection onto the capillary columns. To achieve injection, the second trap is heated to 160° C over a short period of time.

Currently, flame ionisation detectors are being used, giving a detection limit of 4 ng for MeI in pure air. However, a different setup using an electron capture detector on a separate gas chromatographic system has been used to demonstrate a detection limit of 3 pg for MeI under ideal conditions.

The stability of MeI sample storage in the properly pre-treated Summa canisters has been demonstrated over as long as a 3 month period. The largest size holds 32 L, and starting with an evacuated canister, a 60 L sample of air could be obtained at the rated canister pressure of 20 psi. For field sampling, a flow controlled sampling rate could be maintained over the 24 hour period, or alternatively, some form of intermittent sampling regimen may be more suitable.

It remains to be determined to what extent moisture and normal station airborne contaminants interfere with the detection level. However, if the system proves successful, a portable field version may be developed in order to give immediate results.

V - Experience with Emergency Filters

Each of the operating CANDU stations in Ontario has a system known as an Emergency Filtered Air Discharge System or EFADS. This is a poised standby system to be operated only following a large LOCA. It is connected to the negative pressure containment system and contains duplicated demisters, heaters, particulate and 8 inch carbon bed filters. Its function is to provide for a long-term controlled and filtered venting pathway from containment, including the vacuum building, to compensate for pressure rise due to in-leakage. Obviously, the condition of the carbon beds in these filters is of critical importance, as they form the final barrier to the environment. they are subject to the very stringent requirement of no more than 0.01% desorption of methyliodide per 24 hours.

Leak testing with freon has been relatively straightforward and problem-free with only the occasional test failure (> 0.05%), contributed to by loose test canisters or fittings, which have now been removed and permanently blanked off from all the EFADS filters. However, testing the 24 hour methyliodide desorption rate has not been possible (other than attempting to infer it from the ASTM D3803) due to the inability to achieve a detection limit applicable to such a restrictive desorption figure. Even in the laboratory setting, this could be extremely problematic for the D3803, and would additionally involve the question of the representativeness of the grab sample. However, regulatory pressure was increasing to demonstrate that the systems, including the filters, could meet very stringent reliability criteria.

Published data and information presented at earlier Nuclear Air Cleaning Conferences have indicated that although TEDA desorption could become significant over the long term, weathering and poisoning are likely to be of greater significance (5,6). All new carbon purchases are QA tested, as mentioned earlier in this paper, and any that do not meet specification, including TEDA impregnant content, are rejected. The carbon is multiple grab sampled upon placement into the EFADS filter to check for aging deterioration while in storage (Table 6).

Knowing the initial TEDA content and the fact that the filters are operated only for testing for the equivalent of a few hours per week, we have made the argument that the dominant process of deterioration of carbon efficiency will be a physical one. This obviates the need for routinely opening up the system (thereby contributing to its unavailability) to take grab samples for TEDA analysis.

The routine freon leakage tests are performed every 6 months, together with the 20 minute desorption profile check. If any indications were to arise from the freon desorption (none ever have), the carbon would be changed immediately and investigations conducted on the removed carbon to determine the cause. However, assuming no indications do arise (excluding bypass leakage), we have committed to changing the carbon after 3 years in service, assuming acceptable test results in the interim (Figure 9). The removed carbon is sampled and analyzed for remaining TEDA impregnant content (it is our belief that it is only on purchase, filling, and removal that representative grab sampling can be conducted on carbon due to the good mixing opportunities afforded).

The above strategy was broadly acceptable to our regulators, who made an additional request that we have performed ASTM D3803 MeI laboratory tests on the removed carbon. This have been done on several filters and the results are included in Table 6.

VI - Anticipated Future Developments

The supply and use of freon-11, even in small quantities, is becoming restricted and we are committed to its eventual phase-out. Although there is a variety of environmentally acceptable test agents that could be used with the existing Nucon detectors to perform a bypass leakage test, the number suited to a desorption test is obviously more limited. The hold-up time on reasonable quality carbon must be long enough to avoid any overlap with bypass leakage yet still short enough so as not to unduly prolong the test (Figure 10). Other undesirable characteristics such as high melting points (R-112), carbon bleed-through at low moisture levels (R-12), low detection sensitivity (R-113) are also considerations.

Materials under consideration for investigation include other CFCs, HCFC-123, 22, etc, Sulfur Hexafluoride and non-active methyliodide. In the event methyliodide proved feasible as a leakage test agent, it may prove possible to combine it with either a short-term or a 24 hour desorption test. This could also help avoid the criticism that the freon desorption test is insensitive to the TEDA impregnant level. MeI is also less sensitive to moisture levels but has the drawback of being considerably less easy to handle as well as permanently using up part of the filter.

Investigation of selected test agents will be performed on a recently completed low-flow test rig at our Research Laboratories, known as the Aerosol Research Facility or ARF (Figure 11). This consists of a 34 ft long, 2 ft square, fully instrumented, variable flow-rate, stainless steel tunnel. Test sections are engineered to hold HEPA filters or straight carbon test beds of 1 inch and 2 inch thicknesses. The "single pass" tunnel also has mixing orifices, turbulence reducers and upstream and downstream sampling sections. At the low flows required for carbon filter work (20 cm/s), relative humidities close to 100% can be obtained by means of water spray atomizers.

So far we have only had the opportunity to perform DOP detector response tests on the ARF. We shortly hope to begin tests on carbon beds with different test agents at varying relative humidities, to compare their desorption characteristics to freon 11.

VII - Conclusions

(1) The dual approach of using the in-place freon, and where indicated, the 24 hour MeI desorption tests to assess carbon quality, represents a satisfactory compromise between test simplicity, expense, and effectiveness.

(2) Attempting to apply a correction factor to freon desorption results for varying RH does not appear to be practical unless dealing with a small number of beds of a uniform quality carbon.

(3) We have shown that for carbon in the standby mode, physical deterioration occurs at a faster rate than loss of chemisorption capability, and therefore, becomes the determining factor in assessing carbon performance. This may allow the freon desorption test to give a reliable overall assessment of carbon performance.

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TABLE 1

An apparent connection between Carbon Quality Index (CQI) and Bypass Leakage obtained for 2" beds in need of replacement. The results were obtained using a 30s injection of Freon 11, subsequently shortened to 15s.

CQI	Bypass Leakage (%)
17.6	1.4
5.7	1.2
5.0	1.2
4.5	0.7
4.0	0.2
3.1	0.2

TABLE 3

Comparison between the Carbon Quality Index (CQI) and the 24-hr Methyliodide Desorption Test Results for various 2" and 4" beds. Relative Humidities (RH) are included for completeness.

	CQI (RH%)	24-hr MeI Desorption
2" BEDS	0.8 (51)	0.7
	1.0 (51)	2.8
	>1.0 (51)*	2.2
	>1.0 (33)*	6.0
	>>1.0 (51)*	3.0 (1.5% over first 20 min)
	>>1.0 (21)*	16
	>>1.0 (??)*	20
4" BEDS	<0.1 (24)	<0.1
	<0.1 (19)	<0.1
	0.1 (19)	0.1
	0.2 (22)	0.1
	0.2 (22)	0.2
	0.3 (22)	<0.4*
	0.3 (18)	0.7
	0.4 (34)	<0.4*
	3** (45)	<0.4*

* Minimum Detectable Level for the test.

** High bypass leakage made precise calculation of a CQI problematic.

TABLE 2

The effect of relative humidity on the Carbon Quality Index (CQI). obtained for various beds at different times.

	CQI	Relative Humidity (%)
a) 2" BEDS	0.1	21
	0.1	20
	0.2	24
	0.2	21
	0.3	20
	0.3	34
	0.4	36
	0.4	10
	0.6	36
	0.7	34
	0.8	34
	0.8	36
	0.9	24
	> 1*	53
b) 4" BEDS	<0.1	41
	<0.1	19
	<0.1	40
	0.1	18
	0.1	23
	0.1	22
	0.2	22
	0.4	45
	0.5	46
	0.8	45
	2.1	48
	2.2	52
	2.4	53
	3.7	59
	> 1*	47
	>>1*	58
	>>1*	69
c) 8" BEDS	<0.1	30
	<0.1	18
	<0.1	16
	<0.1	42
	0.1	41
	0.2	44

* Various factors such as extremely rapid desorption of the freon, substantial bypass leakage, made calculation of an exact CQI problematic.

TABLE 4a

TEDA and ASTM D3803 Test Results compared with Carbon Quality Indices for various carbons.

TEST DATE	TEDA (duplicated) %	CQI (RH%)	ASTM D3803 2" Efficiency (%)
Normally Bypassed 4" Fuel Bay Bed:			
OCT 88 (old carbon- 6 years in service)	N/A	>>1	62.2 (1" - 38.7)
MAY 89 (new carbon	3.9; 3.9	0.4 (49)	>99.9
JULY 90	2.9; 3.0	1.1 (52)	N/A
JULY 91	2.5; 2.6	0.6 (51)	99.89
Continuously Operated 4" Reactor Building Bed:			
OCT 88 (old carbon- 6 years in service)	N/A	>>10*	34.2 (1" - 18.4)
MAY 89 (new carbon	3.9; 3.9	0.2 (25)	>99.9
JULY 90	1.5; 1.5	1.3 (36)	N/A
JULY 91	0.9; 0.9	1.8 (25)	74.0

* Reading off-scale high.

TABLE 4b

Carbon Quality Index and ASTM D3803 Test Results of Carbon in Service 7 - 8 yr.

ASTM D3803 Efficiency - (%)				CQI (RH%)
1/3*	mid	2/3*	Average	
82	64	81	76	56 (33)
95	72	98	88	82 (62)

* Grab samples for the ASTM D3803 were taken from one-third, middle and two-thirds the distance from one side of the filter.

TABLE 5

Methyliodide Sampling Bed Desorption

(ug MeI per g Carbon)

Sampling Bed US Mesh Size	Filter Inlet Sampling Beds		Filter Outlet Sampling Beds		Blank
	Front Bed	Back Bed	Front Bed	Back Bed	
COURSE					
6-14	578	186	2	0.86	< 1*
6-14	232	539	1.2	1.7	0.76
6-14	4070	54	<15*	<15*	<15*
6-14	4500	19	<15*	<15*	<15*
FINE					
50-200	1715	<25	350	<25	<25
50-200	6260	27	990	<25	<25

* Background Iodine Levels

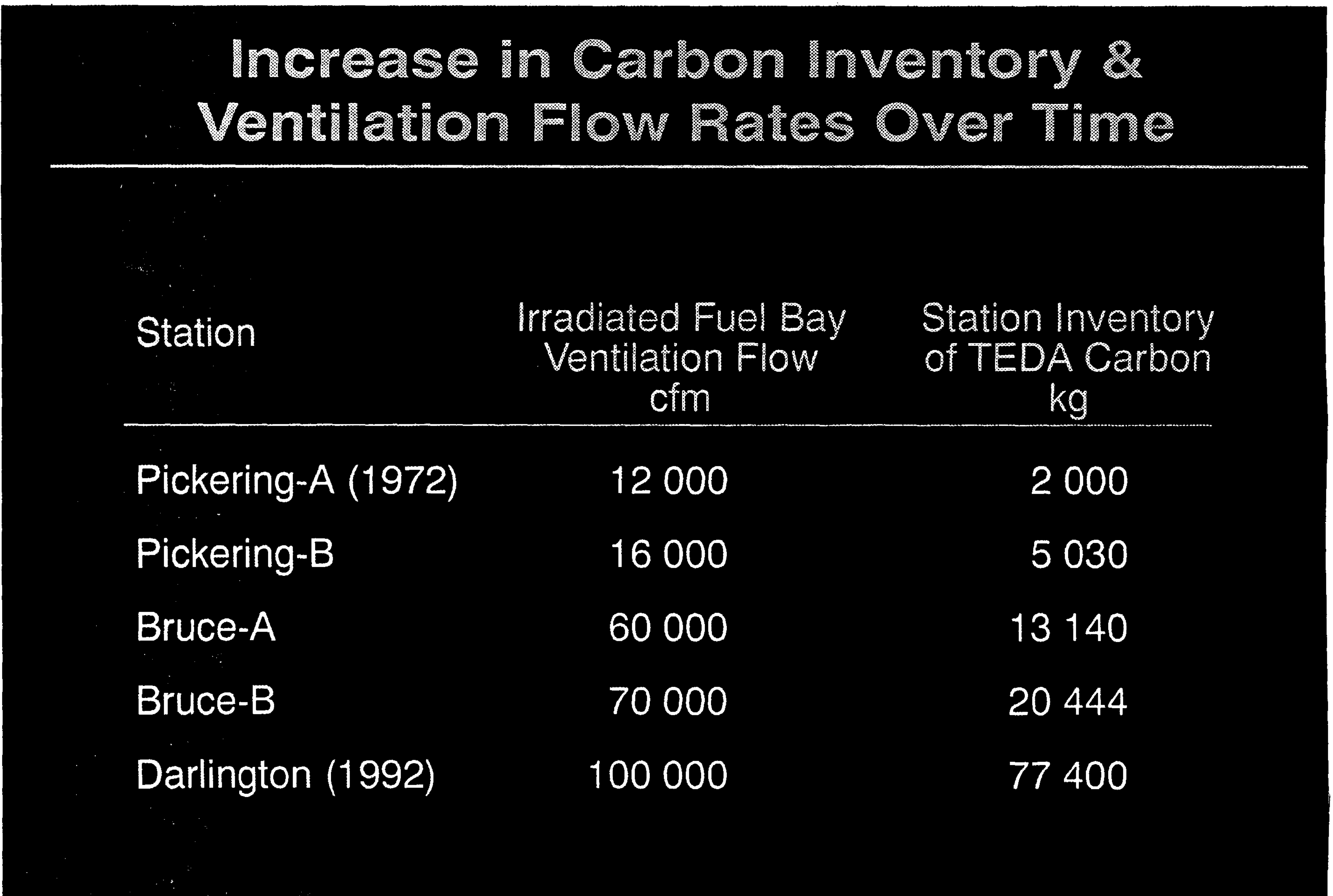
Notes: Sampling bed face velocity is approximately 40 times that of the main filter bed.

TABLE 6

Apparent TEDA loss and impact on performance as measured by the ASTM D3803 for an emergency standby filter carbon manufactured in 1985.

FILTER 1 (8" bed)	TEDA	TKN*	ASTM D3803 2" Efficiency - (%)
Installed (1988)	3.8; 3.9	4.0	99.37
After 3 yr (1991)	2.7; 2.8	---	99.97; 99.95; 99.97; 99.96
FILTER 2 (8" bed)			
Installed (1988)	3.8; 3.9	4.0	99.37
After 3 yr (1991)	3.8; 3.9	---	99.98; 99.95; 100; 99.96
FILTER 3 (8" bed - same carbon)			
New (1985)	3.5; 3.3	3.9	99.37
3yr service(1991)	2.6; 2.3	4.6; 5.0	99.89; 99.93; 99.91; 99.86

* TEDA number derived from the Total Kjeldahl Nitrogen Test.



Increase in Carbon Inventory & Ventilation Flow Rates Over Time

Station	Irradiated Fuel Bay Ventilation Flow cfm	Station Inventory of TEDA Carbon kg
Pickering-A (1972)	12 000	2 000
Pickering-B	16 000	5 030
Bruce-A	60 000	13 140
Bruce-B	70 000	20 444
Darlington (1992)	100 000	77 400

FIGURE 1

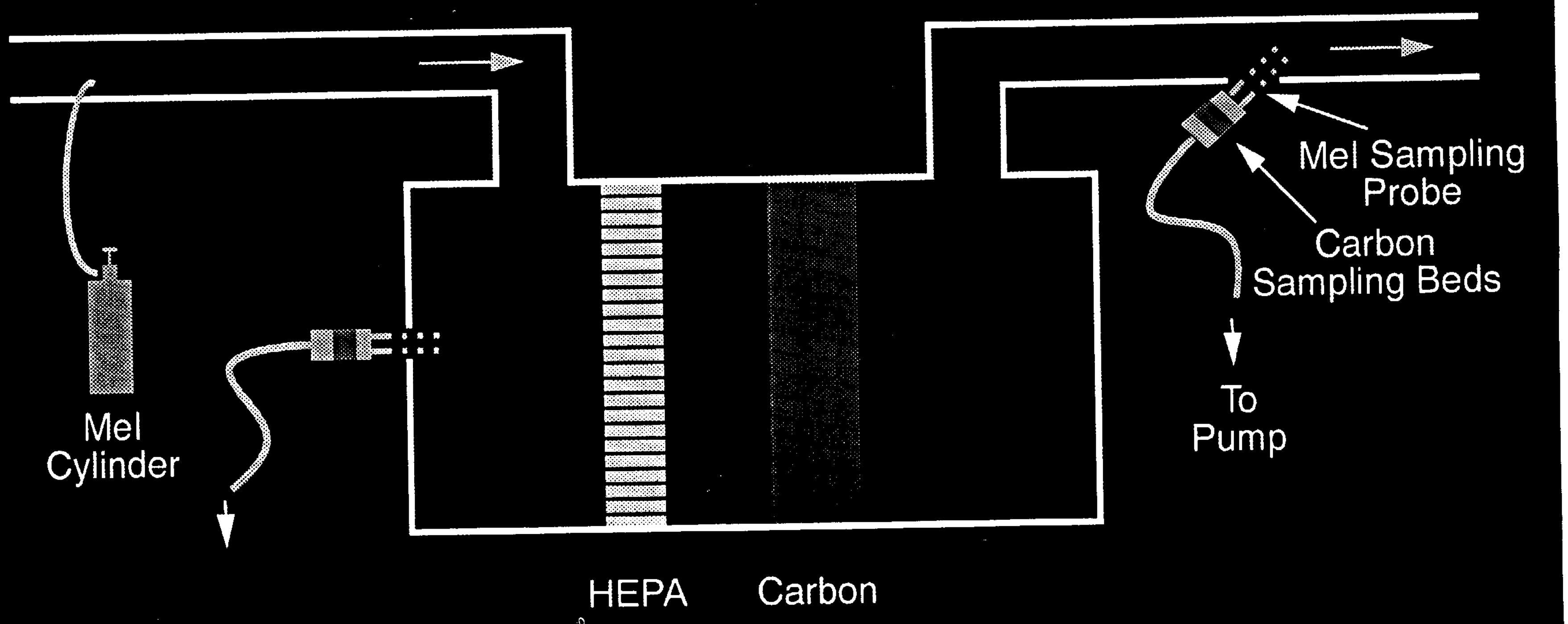
Testing Practices Currently Employed at Ontario Hydro

Testing For:	Type of Test	
Bypass Leakage	Freon	In-Place
Carbon Physical Condition	Freon Desorption	in-Place
Carbon Effectiveness	24-hr MeI Desorption (max. 1% per 24 hrs, 0.01% for emergency filters)	In-Place
Carbon 'Efficiency'	ASTM D3803 (not directly applicable to O-H safety analyses)	Laboratory*

* Now used only for emergency filters at Ontario Hydro

FIGURE 2

24 Hr Methyliodide Desorption Test



MeI Cylinder

HEPA

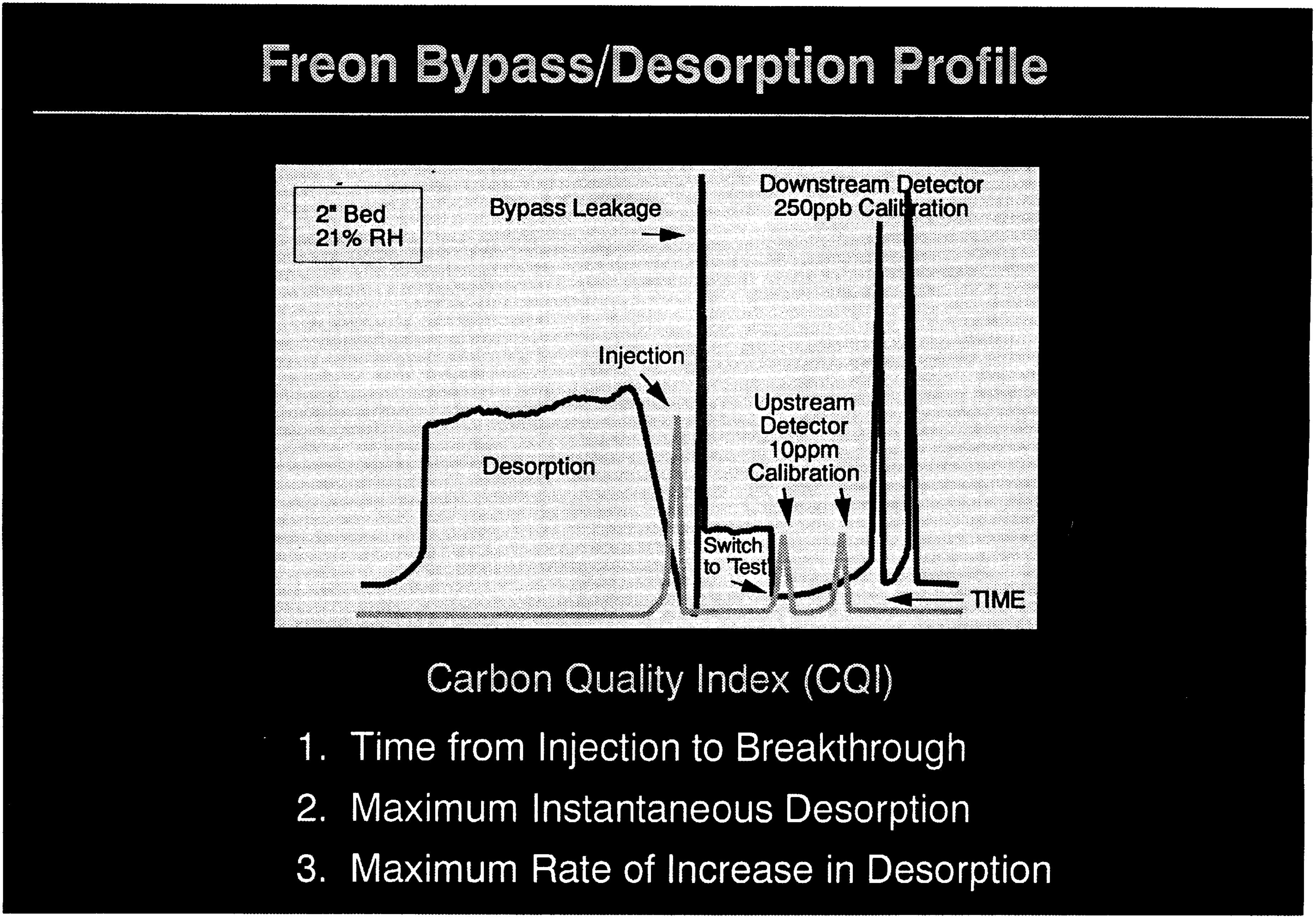
Carbon

MeI Sampling Probe

Carbon Sampling Beds

To Pump

FIGURE 3



Freon Bypass/Desorption Profile

Carbon Quality Index (CQI)

1. Time from Injection to Breakthrough
2. Maximum Instantaneous Desorption
3. Maximum Rate of Increase in Desorption

FIGURE 4

Freon Bypass/Desorption Profile

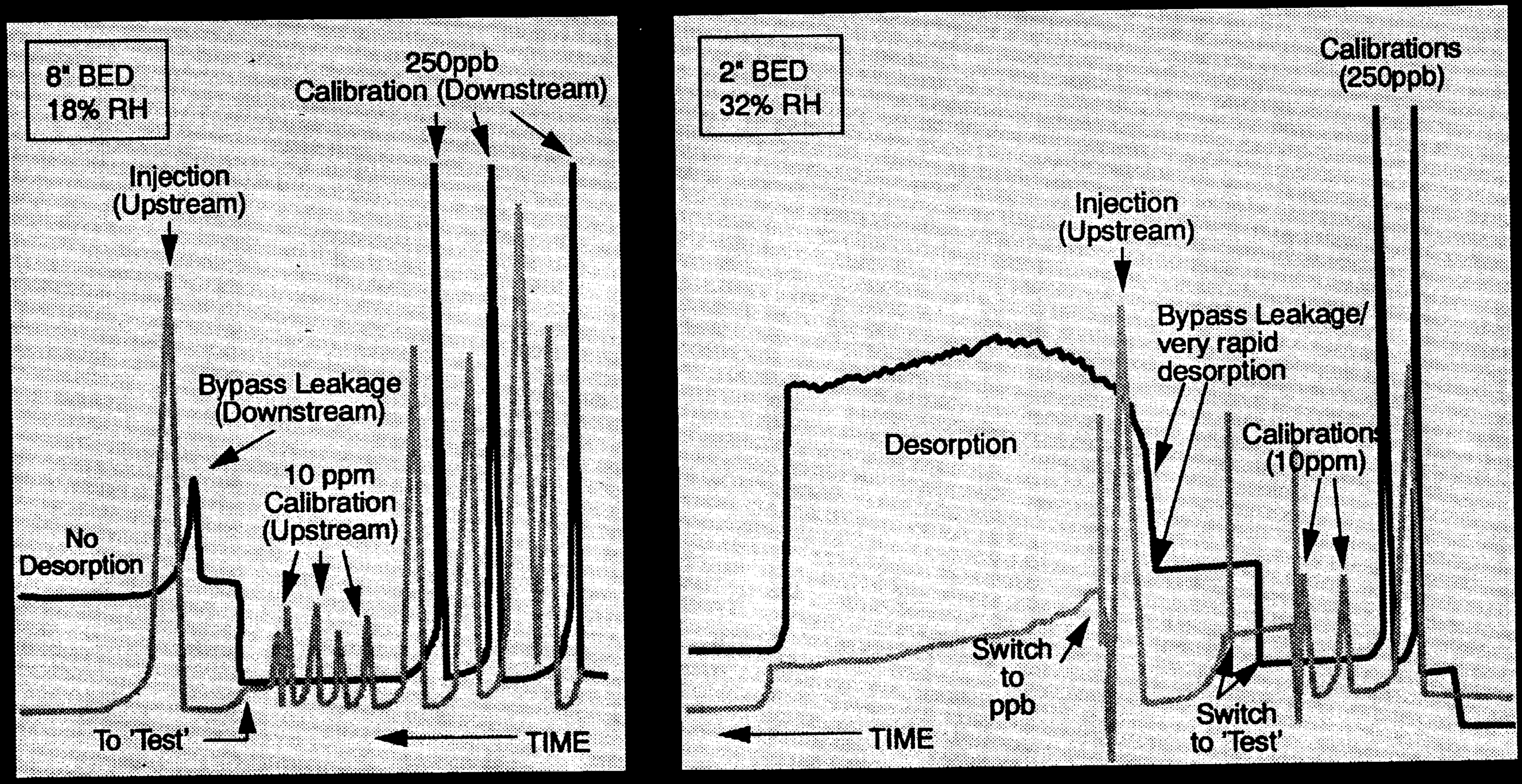


FIGURE 5

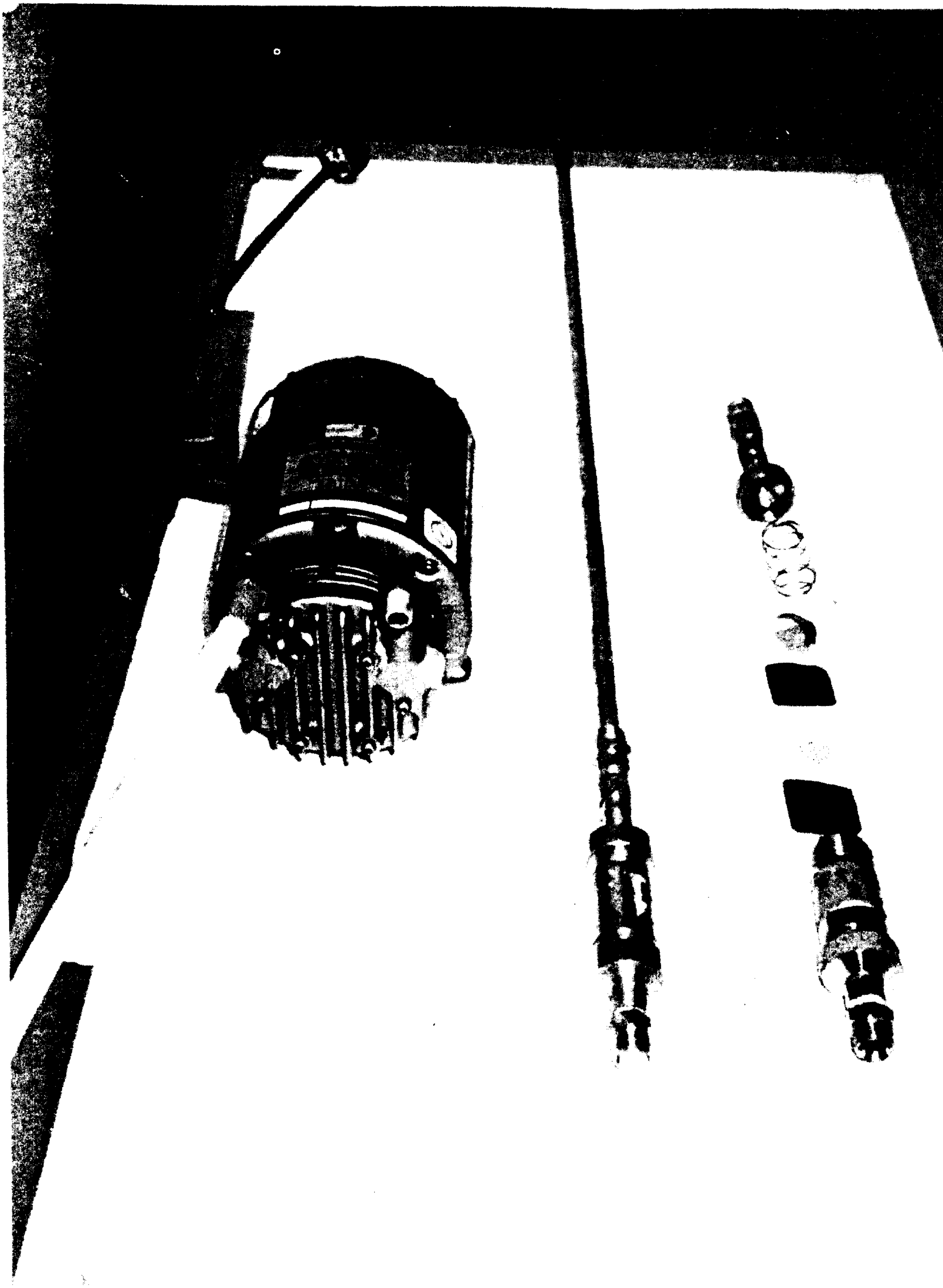
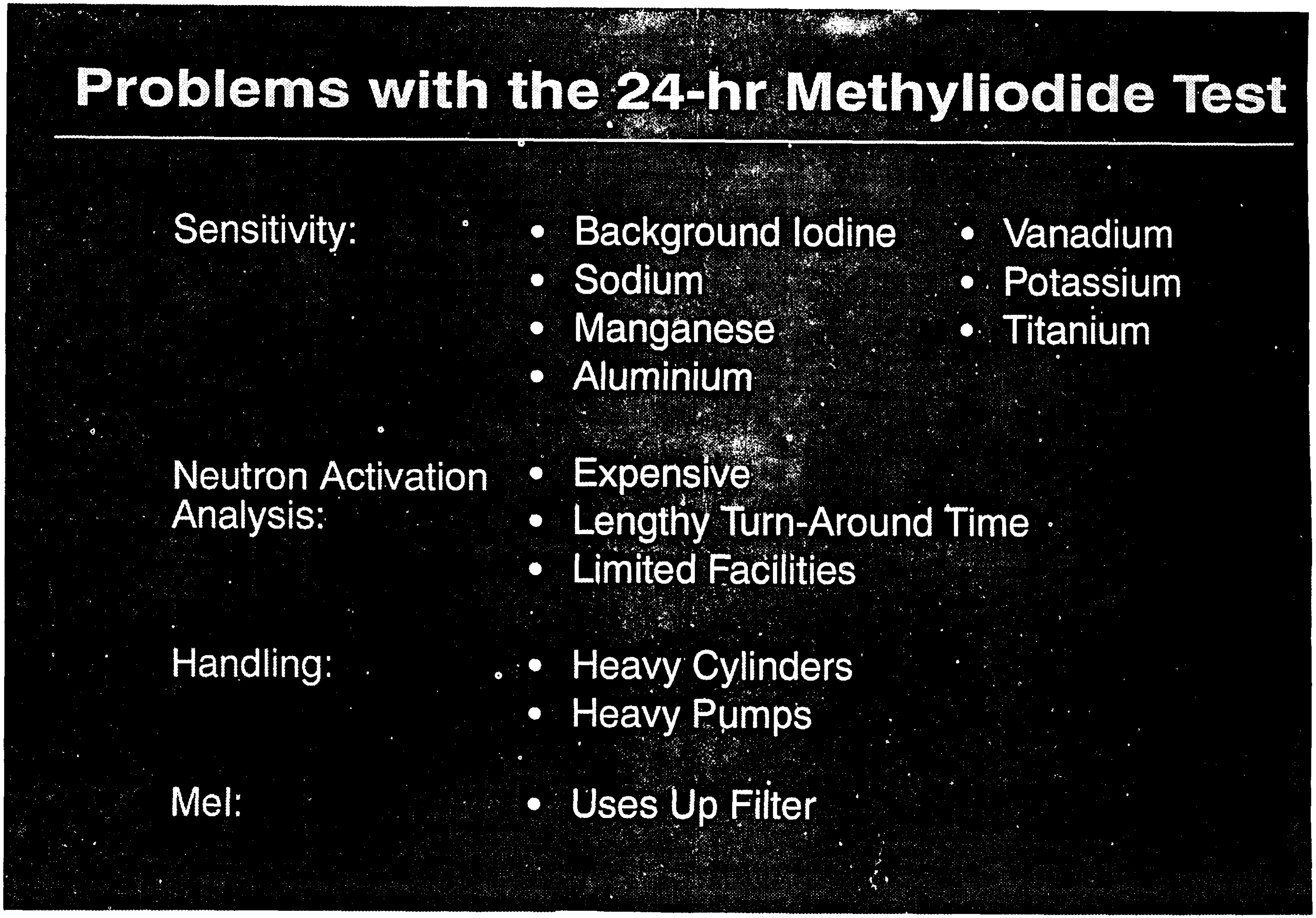


FIGURE 6



Problems with the 24-hr Methyliodide Test

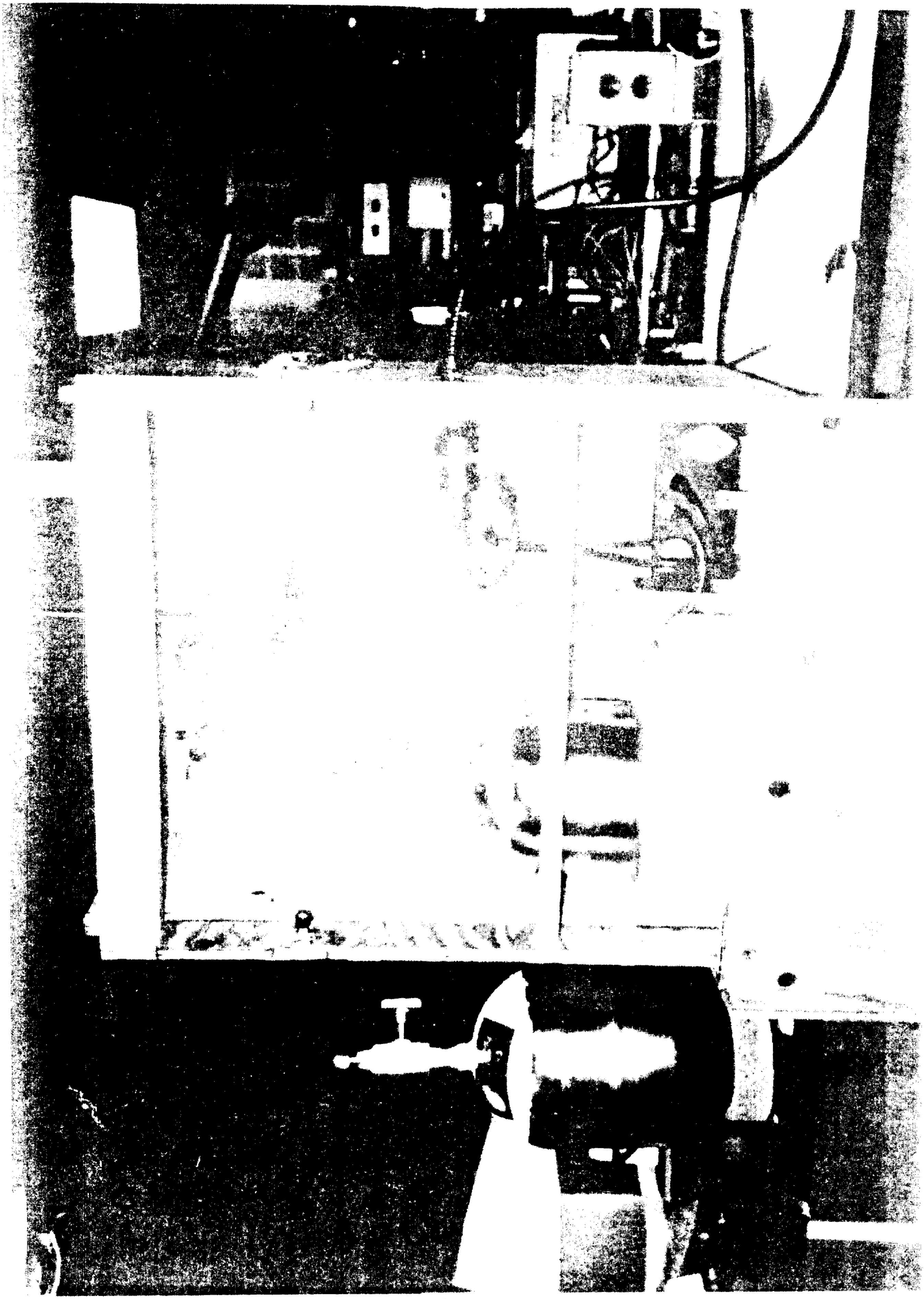
Sensitivity:
- Background Iodine
- Sodium
- Manganese
- Aluminium
- Vanadium
- Potassium
- Titanium

Neutron Activation Analysis:
- Expensive
- Lengthy Turn-Around Time
- Limited Facilities

Handling:
- Heavy Cylinders
- Heavy Pumps

MeI:
- Uses Up Filter

FIGURE 7

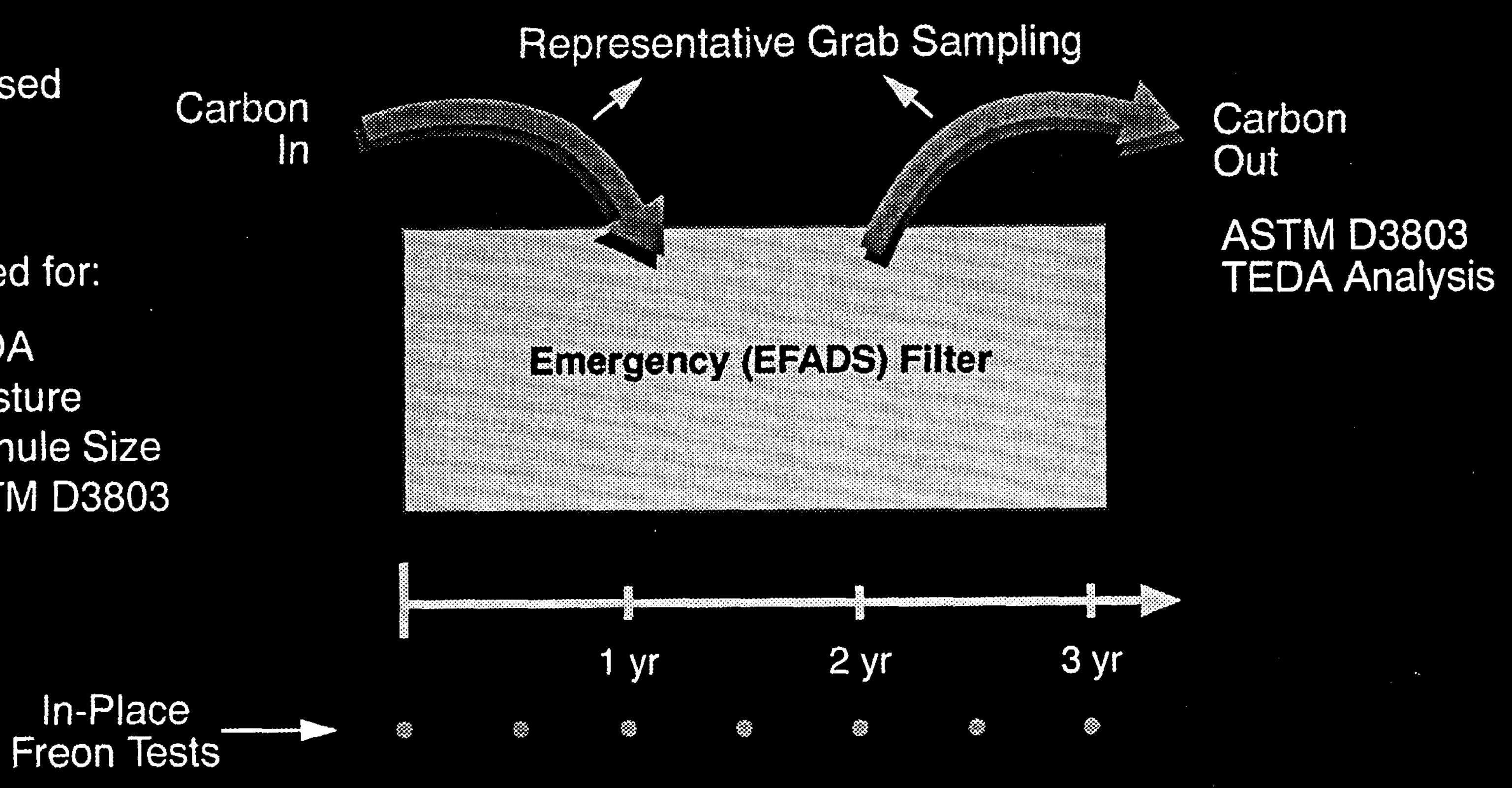


Emergency Filter Testing

Carbon
Purchased
Tested
Stored

Retested for:

1. TEDA
2. Moisture
3. Granule Size
4. ASTM D3803



ASTM D3803
TEDA Analysis

FIGURE 9

Alternatives to Freon 11 for Filter Testing

- Other Freons
- Various HFCs
- HCFCs (including HCFC 123)
- Sulfur Hexaflouride (SF6)
- Methyliodide (non-active)

1. Hold-up time on 2" beds of poor quality carbon: ≥1min
2. Hold-up time on 4" beds of poor quality carbon: <30min
3. Relatively insensitive to RH below ≈50%
4. Gaseous at ambient temperatures
5. Highly Desirable Features:
   - Easy to handle/non-toxic
   - Easy to detect

FIGURE 10

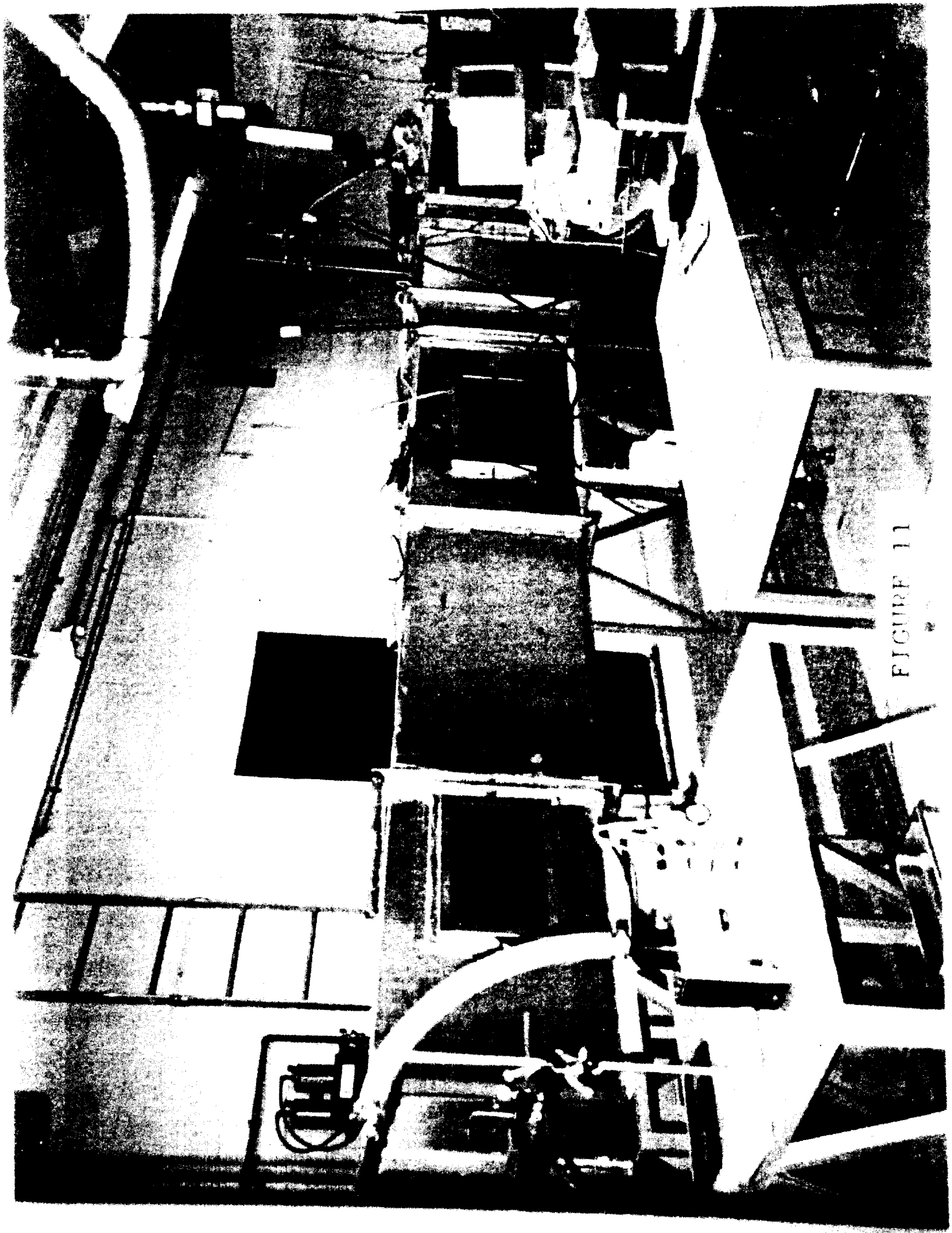


FIGURE 11

DISCUSSION

HUNT: On the Freon desorption profiles, I noticed that bypass leakage was indicated. It preceded the upstream Freon-11 injection peak. I wonder if you could explain that?

HOLTORP: That is a very good point. It appears to precede it, but it actually doesn't come before. In fact, it comes at the same time. The way it is done is, the two pins on the chart recorder are simply offset by about a minute, just for clearance, and that is why it appears that the by-pass leakage comes before the injection.

HUNT: So, they are detected at the same time, it is just a matter of the recorder setting.

REPLACEMENT TRACER AGENTS FOR THE IN-PLACE LEAK TESTING OF ADSORBERS IN NATS

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P. L. Lagus
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ABSTRACT

Refrigerant-11 and refrigerant-112 (R-11 and R-112) are currently the tracer agents recognized by ANSI/ASME N510(1) and U.S.N.R.C. Regulatory Guide 1.52(2) for the in-place leak testing of nuclear air and gas treatment systems (NATS). These agents are chlorofluorocarbons and are associated with the destruction of the ozone layer in the upper atmosphere. Federal law mandates that these materials be phased out of use by the year 2000, so suitable replacements must be found. Any replacement material must meet certain selection criteria including favorable adsorption on in-service nuclear carbons, relatively short adsorber retention, detectability in minute concentrations, ease of generation at low concentrations, ease of discrimination from other background compounds, and non- interference with the adsorption of radioiodine by nuclear grade activated carbon. Replacement tracer agents must also be non-toxic, non-flammable, and should not be commonly found in the plant environment.

Perfluorocarbons, based on field and laboratory trials, are ideally suited as substitutes for R-11 and R-112. Perfluorocarbons are environmentally benign and are easily detected by traditional electron capture chromatography. PFCs are easily handled in liquid form at room temperature and can be generated at low concentrations for in-place adsorber leak testing. Certain perfluorocarbons may be substituted for R-11 and R-112 with little or no modification to commercially available testing equipment.

INTRODUCTION

Our work on the search for a new tracer agent began over a year ago when it became clear that the use of current test gases would not be permitted under new EPA regulations. Because the family of chemicals known as the perfluorocarbons are known for their low toxicity and chemical inertness, our work in finding replacement gases was focused in their direction. The process of establishing a new tracer to be used for testing nuclear adsorber banks is a complex and time consuming problem requiring both regulatory changes and a technical development program. We proceeded on the premise that a tracer gas should be found which offers at least comparable and preferably better in-place leak testing characteristics than the currently used materials.

SELECTION CRITERIA

The following selection criteria were considered in evaluating candidate materials:

1. Toxicity
2. Effect on radioiodine efficiency of nuclear grade activated carbon
3. Detectability
4. Compatibility with current commercially available test instrumentation
5. Unique usage
6. Ozone depletion potential
7. Chemical reactivity
8. Retention on carbon
9. Commercial availability
10. Equivalency of adsorber leak test results

INITIAL SCREENING

The following materials (Table-1) were considered as potential replacements for R-11 or R-112:

TABLE-1

REPLACEMENT MATERIAL	POTENTIALLY REPLACES
Perfluorodimethylcyclobutane (PDCB)	R-11
Perfluoromethylcyclohexane (PMCH)	R-112
Perfluoropentane (PFP)	R-11
Perfluoromethylcyclopentane (PMCP)	R-11
Dichlorotrifluoroethane (HCFC-123)	R-11

Of the four perfluorocarbons initially selected, perfluoropentane was eliminated from further consideration because:

1. PFP has poor sensitivity relative to other perfluorocarbons and refrigerant-11. The estimated lower level of detectability (LLD) was 10 ppb when measured by electron capture gas chromatography.
2. The commercially available product has very low purity. Analysis of the product showed that it was composed of three distinct components, probably isomers, complicating further evaluation.

Dichlorotrifluoroethane (HCFC-123), a recommended refrigerant replacement for industrial chillers, was also eliminated because:

1. HCFC-123 has a TLV of 10 ppm for an 8 hour day. Manufacturers' reference MSDS recommends the use of respirators when working environments may exceed the 10 ppm limit. Additionally, personal monitoring is suggested when using this chemical.
2. HCFC-123 has an ozone depletion potential of 0.02. Since future use of this chemical in industry will require ozone depletion factors of zero, HCFC-123 is considered a temporary replacement.

3. Any material considered as a tracer gas replacement for R-11 should not be a chemical that is commonly used in the industrial environment. Since HCFC-123 is a recommended replacement for large commercial chillers, high background contamination levels are likely to be found in the test environment.

A thorough evaluation of PDCB was conducted using each of the criteria specified in selection criteria of this paper. PMCP and PMCH were also studied on a more limited basis. The evaluation of PMCP and PMCH is still ongoing, but some of the initial data has been included in this paper. The following are the results of these evaluations.

TOXICITY

Perfluorocarbons have been known for many years to be biologically benign(3,4). Perfluorodimethylcyclobutane has been used in the development of artificial blood substitutes. PDCB, PMCP and PMCH have been used in ventilation testing for almost ten years. Hence, the adoption of one or more of these perfluorocarbons as an in-place leak test agent should pose no health-related problems for field test personnel.

EFFECT ON THE RADIOIODINE EFFICIENCY OF NUCLEAR GRADE ACTIVATED CARBON

Tests were conducted at NCS Corporation to determine the effect PDCB might have on nuclear grade activated carbon. NCS has in-house radioiodine facilities permitting nuclear adsorbents to be evaluated for small differences in results between similar samples. NCS test chambers have the capacity to test two samples at the same time. Samples of test adsorbents are contained in the test chamber simultaneously, with all test parameters except flowrate maintained at common conditions. Temperature, humidity, pressure, adsorbate loading, and iodine^{131} content are identical for each test sample. This allows small differences between the tested samples to be determined by minimizing scatter due to differences in test apparatus.

Samples evaluated for PDCB influence were split into two portions. One half was placed in a glass bottle. One per cent (1%) by weight of PDCB was added to the bottle containing the test carbon, and the bottle was tightly capped. After thorough mixing, the sample was allowed to stand a minimum of 24 hours. The other half of the sample was used for the reference measurement of radioiodine efficiency with no PDCB added. One percent (1%) loading of PDCB is the equivalent of 200 field tests with the inlet concentration maintained at 1 ppm for a duration of 10 minutes and with the assumption that no desorption occurs between tests.

After the addition of the PDCB to the carbon, radioiodine efficiency measurements were made on each sample. In all cases, both the sample with PDCB and the sample containing no PDCB were tested at the same time in the same test chamber. Any significant difference in the measured radioiodine performance could be attributed to the presence of PDCB on the test carbon.

All radioiodine testing was conducted according to methodology specified by ASTM D3803-1989(5) using CH_3I^{131} except that temperature, pre-equilibration period, and relative humidity were varied as indicated. Tests without a pre-equilibration period (thermal), normally considered to be less severe, were also performed so that the adsorbed PDCB would be present on the carbon when the methyl iodide contacted the adsorbent.

The following are radioiodine efficiency results (Table-2) for both new and used carbon samples at various testing conditions.

TABLE-2

RADIOIODINE TESTING RESULTS

CARBON SAMPLE TYPE	TEMPERATURE DEGREES CENTIGRADE	RELATIVE HUMIDITY %	PRE-EQUILIBRATION PERIOD	METHYL IODIDE % EFFICIENCY NO PDCB	METHYL IODIDE % EFFICIENCY 1% PDCB
NEW	30	95%	18 HOURS	99.48%	99.51%
NEW	30	95%	18 HOURS	99.74%	99.73%
NEW	30	95%	16 HOURS	97.88%	97.91%
USED	30	95%	18 HOURS	88.63%	88.57%
USED	30	95%	18 HOURS	98.14%	98.23%
NEW	30	70%	18 HOURS	99.99%	99.99%
USED	30	70%	THERMAL	99.78%	99.78%
USED	30	70%	THERMAL	96.70%	96.79%
USED	51.7	95%	THERMAL	99.98%	99.97%
USED	65.6	70%	16 HOURS	99.99%	99.99%
USED	80	95%	THERMAL	99.11%	99.08%
NEW	80	95%	THERMAL	99.99%	99.99%
NEW	130	95%	2 HOURS	99.90%	99.88%
USED	130	95%	THERMAL	99.89%	99.88%
USED	130	95%	THERMAL	97.55%	97.48%

The results in Table-2 show differences in the radioiodine efficiency performance are within the precision and bias values stated in ASTM D3803-1989, Standard Test Method for Nuclear-Grade Activated Carbon and INEL EGG-CS-7643(6). PDCB appears to have no effect on the iodine removal efficiency of nuclear grade activated carbon when the carbon is exposed to many times more test agent than would be required for a standard ANSI/ASME-N510 adsorber bank leak test. Because the PDCB has no measurable effect on nuclear adsorbents, perhaps the Reg. Guide 1.52, Rev. 2 requirement of operating plant adsorber systems for a specified time following leak testing could be eliminated, if PDCB is adopted as a leak test agent.

DETECTABILITY and COMPATIBILITY

ANSI/ASME N510 requires that field test equipment be capable of detecting test agents in the presence of other background contaminants. The presence of halocarbon gases other than R-11 and R-112 in the plant air requires that the equipment must be able to detect and identify as well as measure the relative test agent concentrations. The oldest version of ANSI/ASME N510-1975(7) requires that the inlet concentration be limited to 20 ppm. Newer ANSI/ASME standards have relaxed this requirement allowing the use of less sensitive instrumentation. These standards put no maximum limits on the inlet concentration which allows any concentration to be used. This practice is wasteful and costly and accelerates the destruction of the protective ozone layer.

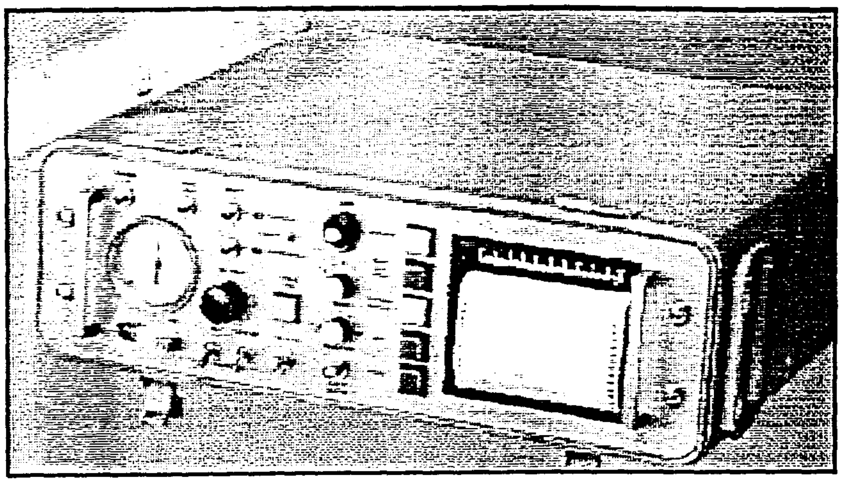
Perfluorodimethylcycyobutane (PDCB) is easily detected when analyzed by traditional electron capture gas chromatography. Gas chromatography, as it is used in field testing, is a technique used to separate, identify, and measure a gas phase component in both the upstream and the downstream air flowing through an adsorber bank satisfying the requirements of ANSI/ASME N510.

An NCS Corporation Model LMP-10 halocarbon analyzer (Figure-1) was used for detectability testing. The LMP-10 is a portable, self-contained, field-rugged, electron capture detector equipped gas chromatograph. The LMP-10 is designed for the specific task of filter testing, and is able to analyze refrigerant-11 only, with no interferences from other halocarbons. (R-12, R-22, R-114, R-13B1, R-113, trichloroethane, etc.) The selection of a replacement test gas should require little or no change in the gas chromatography, thus allowing interchangeable use of test agents with existing field instruments. PDCB has a similar column retention time as that of R-11, satisfying this requirement.

R-11 is detected at less than 15 parts per trillion (ppt) under laboratory conditions. When using an NCS Model LMP-10, PDCB concentrations of 40 ppt are easily detected in the field. The use of low concentrations of test gas is possible due to the high detection sensitivity for PDCB and the lack of common PDCB background since PDCB will not be encountered in high concentrations in the field environment.

Figure-1

NCS Corporation Model LMP-10



Sensitivities for PDCB, PMCP, and R-11 are displayed in Table-3. As indicated, the laboratory sensitivity for PDCB using an NCS Corporation Model LMP-10 is approximately 11 ppt. Typical chromatograms illustrating the sensitivity to PDCB, PMCP, and R-11 are shown in Figure-2. Field sensitivity should fall in the 30 ppt range. Because of the superior sensitivity of the electron capture detector to perfluorocarbons and R-11, inlet concentrations of 1 ppm or less may be successfully used for the testing of nuclear adsorber systems. This reduction of the inlet test agent concentration in itself will have a positive impact on our environment regardless of the tracer gas that is ultimately selected.

TABLE-3

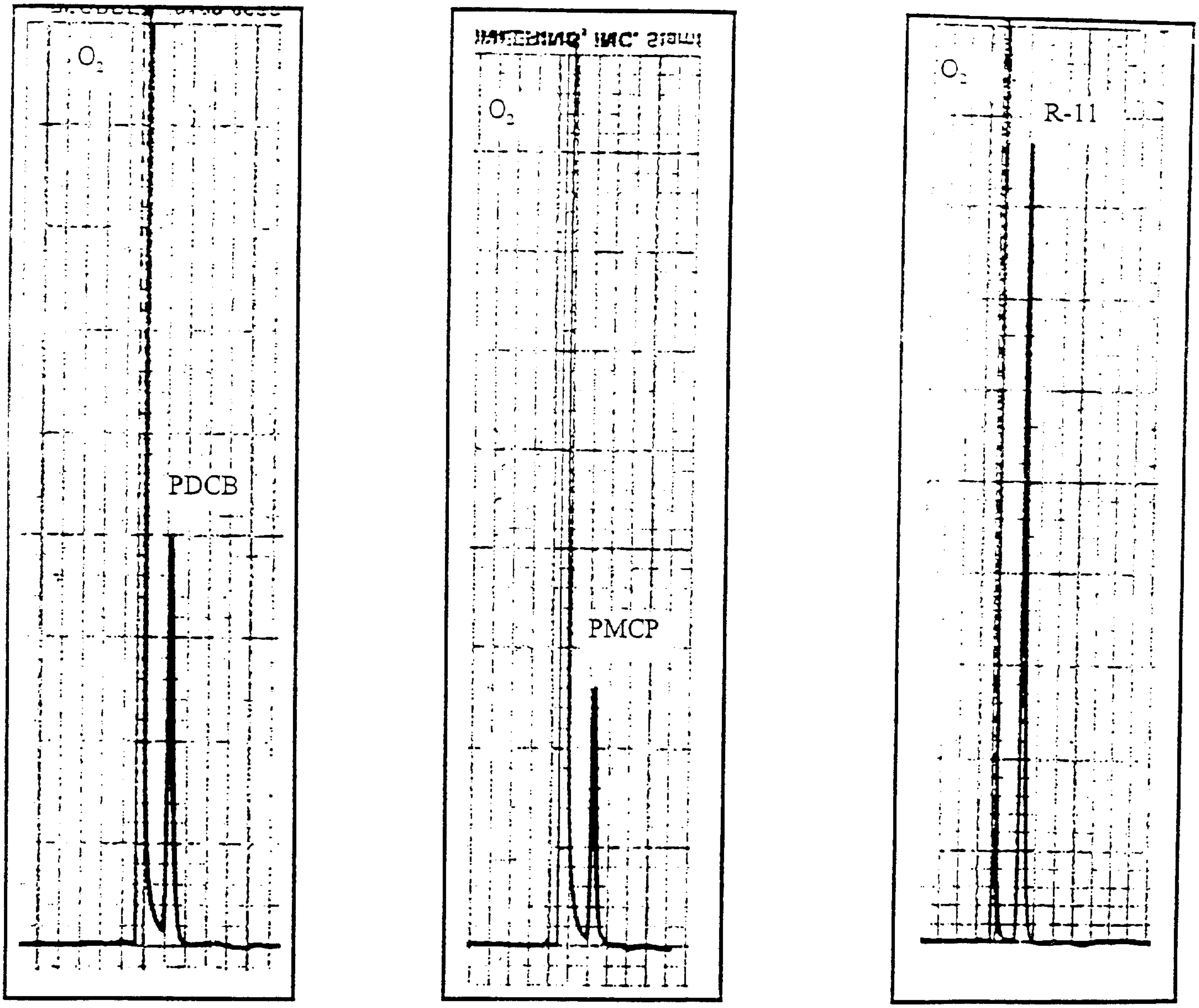
DETECTOR SENSITIVITIES

(Parts per Trillion)

TRACER AGENT	LABORATORY SENSITIVITY	FIELD SENSITIVITY
R-11	12 PPT	36 PPT
PDCB	11 PPT	33 PPT
PMCP	1.3 PPT	3.9 PPT

FIGURE-2

DETECTABILITY OF VARIOUS TRACER GASES



PDCB — 4550 PPT

PMCP — 355 PPT

R-11 — 10600 PPT

All charts recorded on attenuation X10 using an NCS Corporation Model LMP-10 Halocarbon Monitor.

UNIQUE USAGE

A new test agent to replace refrigerant-11 and R-112 should be unique in the industrial work place. R-11 has many uses in a typical nuclear plant including its use as a test agent in NATS testing. R-11 is used in industrial chillers and in degreasing and cleaning operations.

When large amounts of a chemical are routinely used in a nuclear plant, high concentrations will accumulate within the plant's interior. These high backgrounds often create ambiguous results for performing tests per ANSI/ASME-N510 with non-chromatographic instrumentation. The selection of a prospective test agent is compromised if the same material is used throughout a nuclear plant for other operations. PDCB has no known industrial uses so that any PDCB backgrounds encountered in nuclear ventilation adsorber testing would only be the result of prior testing operations. The adoption of PDCB as an in-place filter test agent would make adsorber testing easier for testing personnel who now commonly encounter high R-11 backgrounds.

OZONE DEPLETION POTENTIAL

Any new material selected as a test gas to replace R-11 and R-112 should exhibit zero ozone depletion potential. The desire to mitigate the reduction of ozone in the Earth's upper atmosphere is the primary driving force behind the move to replace chlorofluorocarbons as a test agents in nuclear air cleaning systems. The selection of a gas without zero ozone depletion potential could only be considered an interim action, with future replacement required. Perfluorocarbons such as PDCB are fully fluorinated materials having a zero ozone depletion potential because they do not contain chlorine or bromine atoms that have been associated with the destruction of the ozone layer. Thus the selection of a perfluorocarbon such as PDCB could be considered a permanent replacement for R-11.

CHEMICAL REACTIVITY

The perfluorocarbon family of chemicals are virtually inert. Because PDCB is a fully fluorinated compound, it is unlikely that any undesirable chemical reactions with either the base carbon or its impregnates can occur. PDCB has been used as a tracer gas in building ventilation studies for many years with no known incompatibilities of any kind (8,9,10).

RETENTION ON CARBON

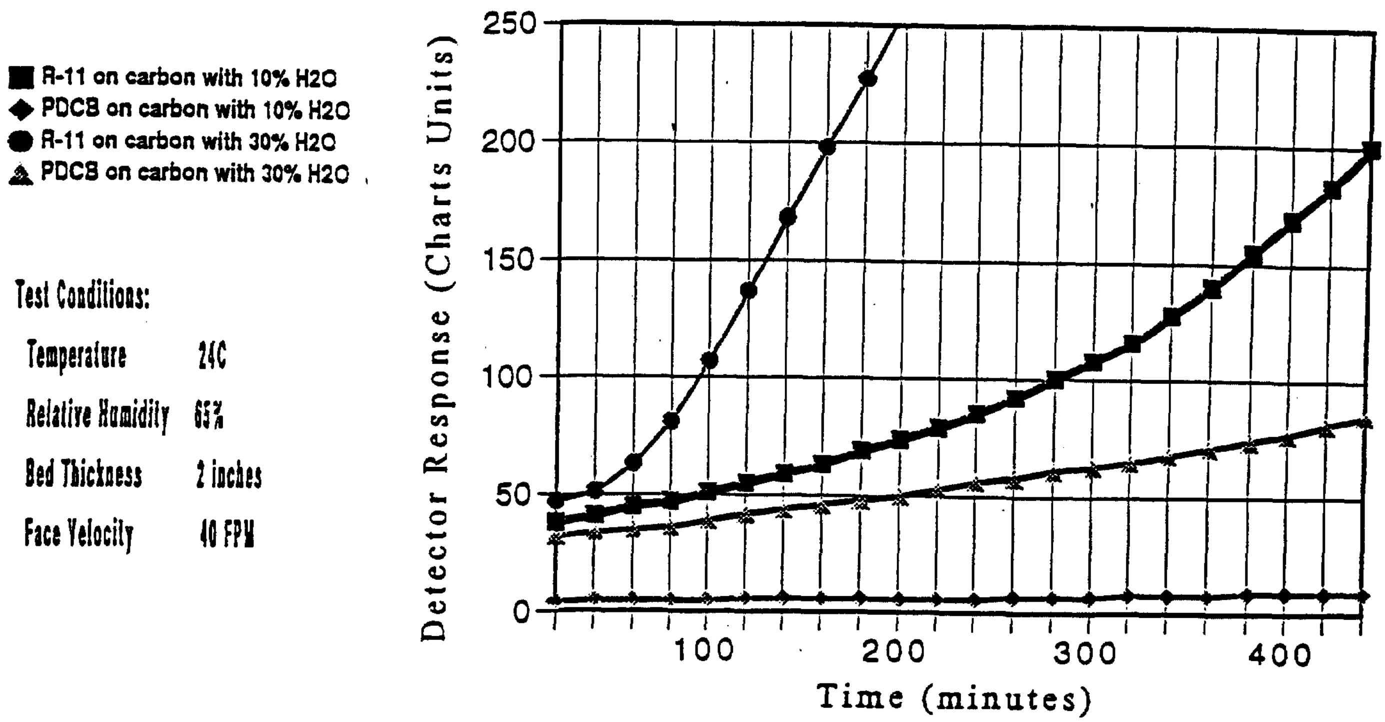
Rapid desorption of refrigerant-11 from nuclear grade carbon has been a problem for field testing personnel for many years. Adsorber systems in the nuclear plant environment collect various volatile organic compounds from sources such as paints and cleaning agents. Eventually, the carbon banks adsorb sufficient amounts of these pollutants so that R-11 adsorptive properties are reduced. Additionally, the carbon beds are at an adsorption equilibrium with the moisture content in the air. As humidities approach saturation (100%), the moisture content in the carbon bed may reach 50% by weight. With organic materials and moisture collecting in the carbon, very little internal surface area is available for the adsorption of the R-11.

Tests were performed on samples of carbon having moisture contents of 10% and 30% by weight to compare R-11 and PDCB retention characteristics. Constant concentrations of PDCB and R-11 were run simultaneously through the carbon. The inlet and outlet concentrations of both test agents were monitored over time to determine desorption profiles for each test agent (See Figure-3). PDCB is retained longer than R-11 on both high and low moisture content carbons.

Longer retention of PDCB on the carbon should facilitate the testing of nuclear adsorber banks, allowing increased testing time prior to desorption of the tracer.

DESORPTION OF PDCB & R-11 FROM CARBON

Figure-3



COMMERCIAL AVAILABILITY

Perfluorodimethylcyclobutane (PDCB) is available commercially. The cost of the chemical is approximately $90/lb. (1992 prices). The higher cost of PDCB at present is due to the limited commercial demand for it. Costs will fall if demand for the product increases. To bring costs in line with present ANSI/ASME-N510 R-11 test costs, one possible solution is to reduce the PDCB injection concentration by a factor of ten. This can be accomplished without compromising the overall ANSI/ASME-N510 sensitivity due to the high detectability of PDCB by electron capture gas chromatography. The cost of using PDCB at a 1 ppm inlet concentration for a duration of 10 minutes is $0.70/1000 CFM tested versus $0.26/1000 CFM for R-11 when using an inlet concentration of 10 ppm. The cost of R-11 will rise steadily as the government implements taxes on refrigerants to discourage the use of chlorofluorocarbons.

EQUIVALENCY OF ADSORBER LEAK TEST RESULTS

Adsorber leak tests were performed using PDCB and R-11. A small filtration system consisting of a HEPA filter and a 2" carbon adsorber incorporating a fixed mechanical leak was used for the testing evaluation. The system flow rate was 40 fpm which gives a residence time of 0.25 seconds.

An NCS Model LMP-10 was connected to the test fixture with the upstream sample probe located just upstream of the carbon adsorber bed, and the downstream sample probe located downstream of the fan to enhance mixing of the tracer with air. Because of the small size of the system, generation of the test agents was accomplished by evaporation from a container with an orifice that was placed upstream of the adsorber in the system inlet tube. While this injection method allowed the addition of small amounts of test gas, some variability in the delivery concentration was noted due to evaporative cooling.

The testing was performed on new carbon with various moisture contents as well as degraded carbon removed from a nuclear plant that had a radioiodine penetration of 26% when tested according to ASTM D3803-1989. Additionally, this carbon had a high relative moisture content (29%).

Results of this testing are illustrated in Table-4 and demonstrate the equivalency of PDCB as a replacement for R-11.

TABLE-4

RESULTS OF LEAK TESTING USING PDCB AND R-11
% MECHANICAL LEAK

SAMPLE	PDCB	R-11
NEW CARBON (<5.0% H_2O)	0.23%	0.20%
NEW CARBON (<5.0% H_2O)	0.22%	0.21%
DEGRADED CARBON	0.21%	0.21%
CARBON WITH 10% H_2O	0.24%	0.26%
CARBON WITH 30% H_2O	0.22%	0.21%

Our evaluation of perfluoromethylcyclopentane (PMCP) is underway. While no data other than detector sensitivity (see table-3) is supplied in this paper, PMCP also exhibits the desirable properties of PDCB. PMCP has a boiling point of 45 degrees Centigrade versus 41 degrees for PDCB. With its lower level of detectability (3.9 ppt), PMCP is an additional candidate for the replacement of refrigerant-11 in the testing of nuclear air and gas treatment systems.

Work is also proceeding on perfluorocyclohexane (PCMH) as a replacement for refrigerant-112. PMCH has boiling temperature of 76 degrees Centigrade and should be more retentive in the carbon of the adsorber banks. This perfluorocarbon may have application in situations where an adsorber bank being tested has a very high moisture content, high organic solvent loading, or has short residence time normally found in Type 1 nuclear filters with one inch thick carbon beds.

SUMMARY

The use of the perfluorocarbon family of chemicals appears warranted in the testing of nuclear air and gas treatment systems. PDCB meets all the selection criteria established for the replacement of refrigerant-11 in the testing of NATS. The material has low toxicity, has no apparent effect on nuclear grade activated carbon, is extremely detectable, and yields leak rates comparable to those measured using R-11. With its zero depletion potential, the use of PDCB should not damage the Earth's protective ozone layer. Because PDCB exhibits longer retention time on carbon than R-11, the in-place testing of nuclear adsorber systems should be a simpler process. Although PDCB seems to be an ideal substitute for R-11, more research is required. Our work is continuing on perfluorodimethylcyclobutane replacement for CFCs in the in-place testing of NATS. We are also testing the effectiveness of other perfluorocarbons such as the highly detectable PMCP and the heavier PMCH. Before any of the perfluorocarbons can be adopted as a new test agent for the testing of NATS, a consensus is needed in both the standards committees and regulatory agencies of our industry.

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DISCUSSION

KOVACH: I have some questions relating to the desorption curve. I think in ANSI N-510 we started out with R-112. The reason we stopped using it was because it had very similar desorption properties to those you are showing for your new proposed material. I think the reason we decided to use R-11 is because it desorbes fast enough to make it possible to find a leak when you had one. When you had no leak, it was better because it came out faster.

PEARSON: Normally, you don't keep running the material into the filter once you have identified a leak; you stop and see if you can identify the problem. When you are using PDCB, of course, you are able to go back and test it several times before desorption occurs at such a level that you need to give it some time to desorb.

KOVACH: I think the previous speaker showed that you can find a leak in about 20 seconds.

PEARSON: That is possible, but this makes that type of testing unnecessary.

KOVACH: I think that type of testing makes this type of testing unnecessary.

PEARSON: I don't agree with that. I think this test gives you much more data to look at. We are talking about running it for, perhaps, 10 minutes. We feel that this is much more valuable then a simple 20 second or 5 second pulse.

KOVACH: Do you think the mechanical leak will increase over the 10 minutes, or that it will change?

PEARSON: No, it doesn't change in 10 minutes, but I think the more time and more data you have to look at, the more precise you can be with your measurements.

KOVACH: Have you used anything else beside your own instrument?

PEARSON: As a matter of fact, the manufacturers of PDCB use regular laboratory-grade and other types of detectors, other than our own instrument. It is very, very sensitive. In fact, there are probably thousands of electron capture gas chromatographs in use throughout the United States.

KOVACH: What is the volume you are sampling?

PEARSON: We use a 1 cc sampling loop.

KOVACH: You are extrapolating from a 1 cc sample to parts per trillion levels coming out of air cleaning systems?

PEARSON: That is true, that is absolutely true. Anyone that understands gas chromatography knows that this is not a problem.

JACOX: I believe if you read all of the current laws relating to ozone depletion, you will see that R-11 is being banned as a refrigerant, but there are many exceptions for other uses. It will be a number of years, perhaps never, before it will be banned for this specific use. When it is no longer produced in large quantities for a refrigerant, the price will skyrocket. The price may be more of a driving force than an actual ban.

PEARSON: That is absolutely true. It is going to be banned as a refrigerant and manufacturers are going to quite making it. It is going to become very scarce and expensive. I don't think we are setting a good example by continuing to use refrigerant-11 if there is something available that might work better.