DP-950

AEC RESEARCH AND DEVELOPMENT REPORT

NONDESTRUCTIVE TEST OF CARBON BEDS FOR REACTOR CONTAINMENT APPLICATIONS

PROGRESS REPORT
JULY - SEPTEMBER 1964

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NONDESTRUCTIVE TEST OF CARBON BEDS FOR REACTOR CONTAINMENT APPLICATIONS

PROGRESS REPORT: JULY-SEPTEMBER 1964

by

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ABSTRACT

A standardized nondestructive and generally applicable test for installed carbon beds in reactor containment facilities is being developed by the Savannah River Laboratory. Continuing tests show that the permissible ranges of air velocity and H_2O content of the carbon can be extended to encompass the desired test conditions for installed beds of new carbon. The major improvement reported is that of substituting "F-112" or "F-113" for "F-12" - a more volatile "Freon" used in an earlier testing method.

CONTENTS

	Page
Introduction	4
Summary	5
Discussion	7
Test Results	7
"Freon-114B2"	7
"Freon-112"	8
"Freon-113"	10
Test Development Facility for Full-Size Iodine Adsorbers	11
Conclusions	11
Program	14
References	15

LIST OF TABLES AND FIGURES

Table

I	Freon Adsorption Test Limitations for New Carbon	12

Figure

1	"Freon-112" Adsorption Efficiency of New Carbon	8
2	"Freon-112" Calibration of Electron Capture Detector	9
3	"Freon-113" Adsorption Efficiency of New Carbon	10
4	"Freon-113" Calibration of Electron Capture Detector	11

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INTRODUCTION

Halogen vapors (principally ^{131}I) that might be released accidentally into the buildings of Savannah River Plant (SRP) reactors are removed by passing exhaust ventilating air through carbon beds. New carbon beds are tested for absence of leak paths by a nondestructive technique in which "Freon-12"* is used as a stand-in for radioactive iodine vapor. Development of this technique by the Savannah River Laboratory (SRL) is discussed in progress report DP-870. The "F-12" technique is limited to testing new carbon beds before field installation with air at a maximum velocity of 20 ft/min, and with the carbon containing no more than 5% sorbed H_2O. In plant installations, velocities to 70 ft/min and relative humidities to 75% (~25% H_2O content of carbon at equilibrium) are encountered. Leaks amounting to 0.1% of the total flow are difficult to detect, because over 0.1% of sorbed "F-12" desorbs from the carbon in about 1 minute when exposed at these maximum plant conditions. About 5 minutes is required to evaluate the performance of installed carbon beds.

Because of these limitations, work was undertaken to develop a standardized nondestructive test that is generally applicable for installed carbon beds. The limitations imposed on air velocity and sorbed H_2O were reduced significantly by the use of halogenated hydrocarbons, which are less volatile than "F-12" (CCl_2F_2). This report discusses the progress and results of work in the indicated period. Future reports on the continuing work will not be restricted to quarterly periods as have been the previous three[1,2,3] and the present one, but will be issued as significant phases of the work are completed.

* "Freon" and combinations of "Freon-" or "F-" with numerals are Du Pont's registered trademarks for its fluorinated hydrocarbons.

SUMMARY

The adsorption characteristics of "F-112" (CCl_2F-CCl_2F, b.p. 92.8°C) on activated carbon were superior to all previously tested "Freons". New carbon containing up to 27% sorbed H_2O gave acceptable results when exposed to air flowing at 70 ft/min at 30°C.

"F-114B2" ($CBrF_2$-$CBrF_2$, b.p. 47.3°C) was unsatisfactory in a repeat test of a carbon bed containing >5% sorbed H_2O, probably because of decomposition of the light sensitive "F-114B2". Previous work with "F-114B2" (DP-920) showed that the first test was good with carbon containing up to ~20% sorbed H_2O.

The adsorption characteristics of "F-113" (CCl_2F-$CClF_2$, b.p. 47.6°C) were better than expected. The adsorption characteristics were expected to be about the same as those for "F-114B2" because of similar boiling points. Acceptable "F-113" tests were obtained with new carbon containing ~25% sorbed H_2O. The "F-113" adsorption efficiency was only slightly lower in a repeat test of a carbon bed, the decrease presumably being caused by the previously adsorbed "Freon".

The efficiency of carbon beds for adsorbing elemental iodine vapor is not reduced significantly below 99.99% when the beds are loaded with ~1 mg "F-112" or "F-114B2" per gram of carbon.

The first phase of the development program has been completed; it involved screening test of numerous "Freons" with small-scale carbon beds. The following relationships were established from these tests for adsorption of "Freons" on new activated carbon:

- The permissible ranges of air velocity and H_2O content of carbon increase with increasing boiling point of the "Freon".
- Iodine tests of carbon containing any of the "Freons" showed no appreciable loss in the iodine adsorption efficiency, nor significant loss in the capacity of the carbon for iodine, in the loading range of interest.
- Desorption occurs more slowly as the boiling points of the "Freons" increase.
- The limitations on the test variables (air velocity, H_2O content of carbon, and air temperature) for a given "Freon" are related and interdependent; any one limit can be extended if one or both of the other limits are decreased.

- The sensitivity of the electron capture detector generally increases with increasing number and increasing atomic weight of the substituting halogen atoms in the compound.

"F-112" has been selected as the primary tracer in the development of test procedures for installed, full-size carbon beds. Tests of "F-113" will be continued as a backup to "F-112". In the next phase of the program, standardized procedures for testing used, full-size carbon beds will be developed first. Equipment and techniques will then be developed for in-place testing of complete banks of carbon beds. The goal of this phase of the program is to demonstrate the test and technique in SRP containment facilities. Tests of small-scale beds will also be continued to establish the effects of bed parameters and type of carbon on the adsorption and desorption characteristics of "F-112", and to develop a correlation between "Freon" and iodine penetration of carbon beds.

DISCUSSION

TEST RESULTS

Adsorption tests of "Freon" compounds less volatile than "F-12" (b.p.-29.8°C) were continued in the small-scale apparatus described in DP-910. New activated carbon beds (3 inches in diameter and 1 inch thick) containing up to ~31% sorbed H_2O were exposed to air velocities to 70 ft/min and temperatures to 34°C. All test beds were prepared in a similar manner to eliminate the bed characteristics as a variable. Results are discussed below for "F-114B2" ($CBrF_2$-$CBrF_2$, b.p. 47.3°C), "F-112" (CCl_2F-CCl_2F, b.p. 92.8°C), and "F-113" (CCl_2F-$CClF_2$, b.p. 47.6°C).

Repeat tests or retests are successive "Freon" tests of carbon previously subjected to the "Freon" test. These tests are of value in estimating the effect of "Freon" loading on the adsorption characteristics of carbon beds. This report covers work with new carbon. Future reports will discuss work with used carbon (carbon with several months service in reactor ventilation systems).

"Freon-114B2"

Previous tests with "F-114B2" showed acceptable results with new carbon containing up to ~20% sorbed H_2O at 30°C. Recent work showed that repeat tests of carbon previously exposed to "F-114B2" were acceptable only when the carbon contained <5% sorbed H_2O. The repeat tests were performed on carbon in which over 90% of the previously sorbed "F-114B2" was desorbed by exposure to ambient air flow (70 ft/min, ~55% R.H., and ~25°C) for ~200 hr. Analysis of the effluent air stream with the electron capture detector showed that three other unidentified substances were on the carbon and were not completely desorbed prior to the repeat tests. The test results indicated that these substances interfered with adsorption of "F-114B2" in repeat tests of beds containing >5% sorbed H_2O. The unidentified substances were probably decomposition products of "F-114B2", which is light sensitive and decomposes to free bromine.

"F-114B2" sorbed on a carbon bed did not reduce the efficiency of the bed for adsorbing elemental iodine vapor. A small-scale carbon bed was loaded with 1.0 mg of "F-114B2" per gram of carbon by exposure to normal air flow containing 5 ppm "F-114B2" for 17 minutes. The bed was then tested for adsorption of iodine from dry air; the iodine adsorption efficiency was 99.99+%.

No further work is planned with "F-114B2" since a satisfactory repeat test could not be attained with >5% sorbed H_2O.

"Freon-112"

The adsorption characteristics of "F-112" on activated carbon are superior to all previously tested "Freons". Two small-scale carbon beds were tested, and the resulting "F-112" efficiency curves are shown in Figure 1. Curve B shows that velocities to 70 ft/min, sorbed H_2O to ~27% and air temperatures to ~30°C are acceptable test conditions for adsorption of "F-112" on new carbon. The previous maximum moisture content for an acceptable test was ~20% with "F-114B2" as a tracer. The anticipated maximum sorbed H_2O of installed carbon beds is ~25%.

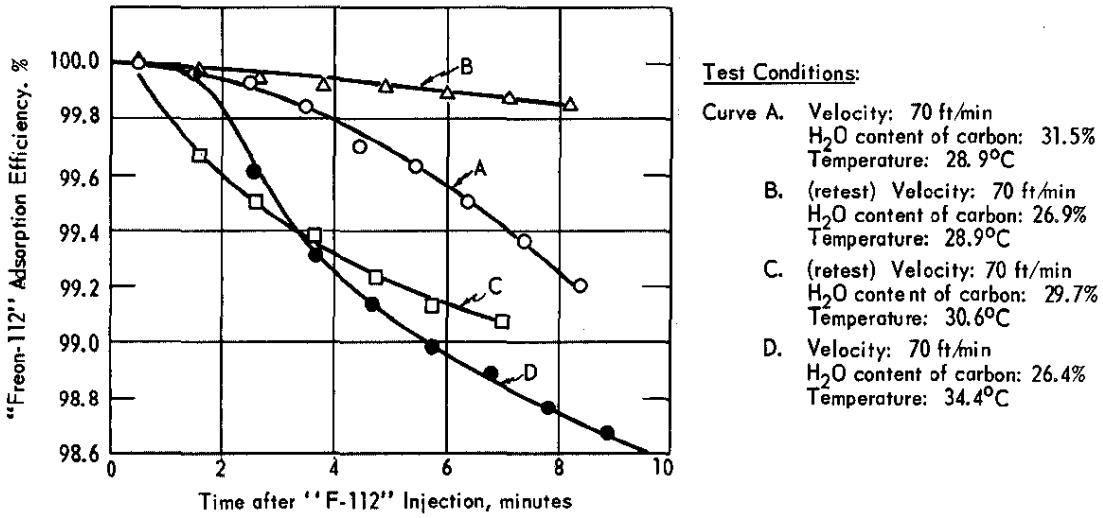

FIG. 1 "FREON-112" ADSORPTION EFFICIENCY OF NEW CARBON

Water contents >27% and air temperatures >30°C caused more rapid "F-112" penetration of the carbon bed as shown by Curves A and D, Figure 1. A comparison of Curves A and C shows that "F-112" sorbed on the carbon from the previous test causes a further reduction in the adsorption efficiency when the bed contained ~30% sorbed H_2O.

The time between any of the repeat tests was not a significant factor, because the "F-112" desorbed slowly. Preliminary measurements indicate that nearly all of the "F-112" can be desorbed by exposure of the carbon bed to normal ambient air flow for 2 to 3 weeks.

Figure 2 shows the "F-112" calibration of the electron capture detector. The minimum detectable "F-112" concentration was 0.001 ppm. A different chromatograph column was used to separate the "F-112" from

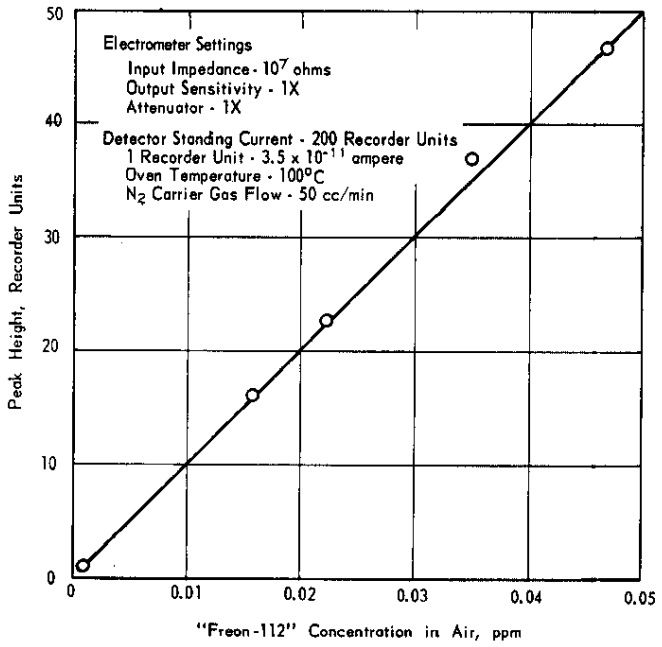

FIG. 2 "FREON-112" CALIBRATION OF ELECTRON CAPTURE DETECTOR

the O_2 for detection by the electron capture cell. All previous test work utilized a column consisting of stainless steel tubing, 10 ft long x 3/32-in ID, packed with 30% SF-96 on 45/60 "Chromosorb"*P. The new chromatograph column consisted of stainless steel tubing, 5 ft long x 3/32-in ID, that was originally packed with 30% SF-96 on 45/60 "Chromosorb" P. The column was modified by baking in an oven at 350°C for 16 hours. While being baked, the column was purged with ~50 cc/min N_2 to remove most of the stationary phase (SF-96) from the "Chromosorb". The modified column permitted the strongly adsorbing "F-112" to elude the column more quickly and with sharper peaks.

The "F-112" tests were made with an inlet "F-112" concentration of 3 ppm; hence, efficiencies >99.97% could not be determined. "F-112" tests at higher inlet concentrations are in progress.

The efficiency of carbon beds for adsorbing elemental iodine vapor was not reduced significantly below 99.99% when the beds were loaded with up to 0.88 mg "F-112" per gram of carbon. The two carbon beds previously described were tested with I_2 after exposure to the "F-112". The first carbon bed was exposed to 3 ppm "F-112" in air for ~24

* "Chromosorb" is a registered trademark of Johns-Manville Company.

minutes but was desorbed of essentially all the "Freon" before the iodine test. The bed was tested with an iodine-steam-air mixture at 70°C (as described in DP-778[4]), and the iodine loading was 0.59 mg I_2 per gram of carbon. The I_2 adsorption efficiency was 99.999 ±0.005%. The second carbon bed contained 0.88 mg "F-112" per gram of carbon (equivalent to seven "F-112" tests of 5 minutes duration each) and was tested with an iodine-air mixture at 30°C. The iodine loading was 0.82 mg I_2 per gram of carbon, and the efficiency was 99.986 ±0.005%. The test indicated some minor loss in iodine efficiency with a relatively high loading of "F-112" and I_2.

"Freon-113"

Satisfactory tests were obtained with "F-113" at an air velocity of 70 ft/min and with new carbon containing up to ~25% sorbed H_2O. The adsorption efficiency of "F-113" was higher than expected. The adsorption characteristics were expected to be about the same as that for "F-114B2" because of similar boiling points ("F-113" b.p. 47.6°C, "F-114B2" b.p. 47.3°C). The maximum sorbed H_2O content of new carbon in a satisfactory test with "F-114B2" is ~20%.

Figure 3 shows the results of two tests with "F-113". Curve A represents the results of new carbon with a H_2O content of ~25% tested at 70 ft/min and at 25.5°C. The efficiency was 99.9+% in 5 minutes. After this test, the carbon bed was exposed to filtered air at 70 ft/min, 55% R.H., and ~25°C for ~60 hours in an attempt to desorb the previously adsorbed "F-113". No significant desorption of the "F-113" occurred. In a second test of the bed (Curve B, Figure 3), the "F-113" adsorption efficiency was only slightly lower than in the first test. The upstream "F-113" concentration in the tests was 5 ppm.

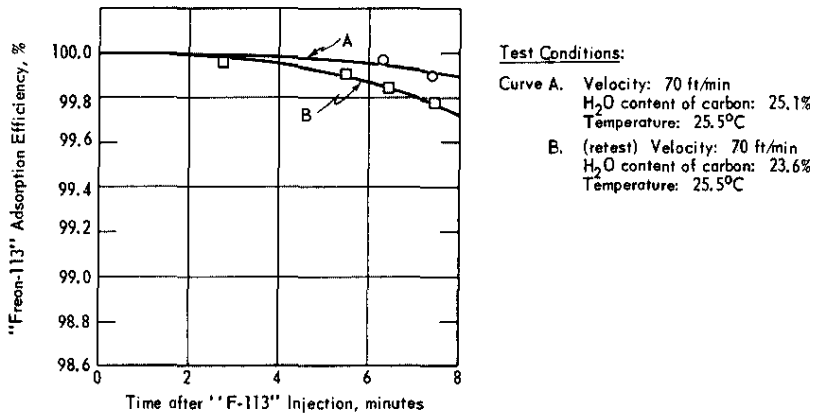

FIG. 3 "FREON-113" ADSORPTION EFFICIENCY OF NEW CARBON

Figure 4 shows the "F-113" calibration of electron capture detector. The minimum detectable "F-113" concentration in an air sample was 0.005 ppm. The chromatograph column used to separate "F-113" and O_2 in an air sample consisted of a stainless steel tubing, 5 ft long x 3/32-in ID packed with 30% SF-96 on 60/80 mesh "Chromosorb" W.

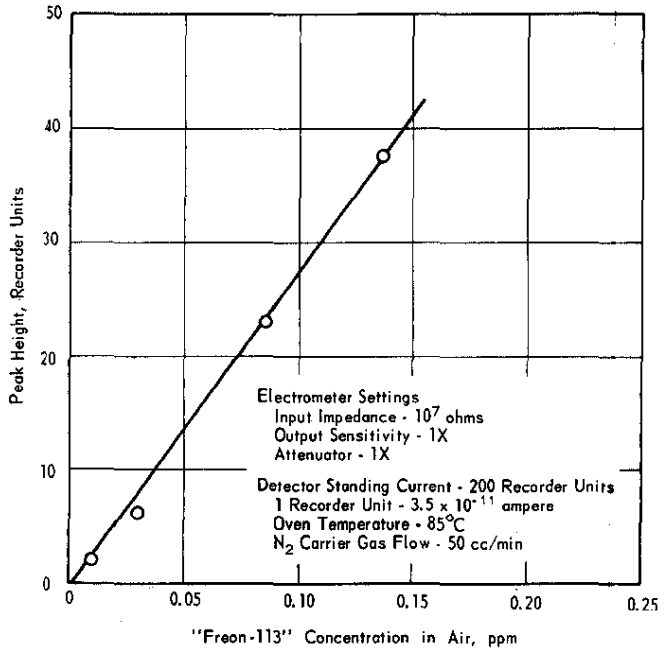

FIG. 4 "FREON-113" CALIBRATION OF ELECTRON CAPTURE DETECTOR

TEST DEVELOPMENT FACILITY FOR FULL-SIZE IODINE ADSORBERS

Construction of the facility to develop a standardized nondestructive test for full-size iodine adsorbers was about 95% complete as of September 30, 1964. The facility is described in detail in DP-910.

CONCLUSIONS

The first phase of the development program, which involved screening tests of several "Freons" by small-scale carbon beds, has been completed. The screening tests revealed several characteristics common to all "Freons" studied. These characteristics are applicable only for the adsorption of "Freons" on coconut shell charcoal of the type described in DP-778[4] but are probably similar for other type

carbons. Physical properties of the selected "Freons" are given in Table I, DP-910[2]. The conclusions drawn from the study are as follows:

TABLE I

"Freon" Adsorption Test Limitations for New Carbon

"Freon"	Boiling Point, °C	Minimum Detectable Concentration in Air, ppm by volume	Test Limitations, Max.(a) Velocity ft/min	Temp, °C	Sorbed H_2O, %
"F-12" (CCl_2F)	-29.8	0.03	20	30	5
"F-11" (CCl_3F)	23.8	0.0003	70	30	12.5
"F-114B2" ($CBrF_2$-$CBrF_2$)	47.3	0.0005	70	30	20
"F-113" (CCl_2F-$CClF_2$)	47.6	0.005	70	30	25
"F-112" (CCl_2F-CCl_2F)	92.8	0.001	70	30	27

(a) The maximum expected field test conditions are 70 ft/min face velocity, ~30°C temperature, and ~25% sorbed H_2O. These maximum field test conditions can be met by "F-112" and perhaps "F-113" on new carbon.

1. The "Freon" adsorption characteristics improve with increasing boiling point (decreased volatility) of the "Freon". This is an expected result because in physical adsorption and liquefaction of gases, the driving force is the same (Van der Waal's forces). Thus the adsorptive capacity of a surface would be expected to vary more or less in parallel with the ease of condensation of the adsorbate. The improved adsorption characteristics resulted in reducing the limitations (extending the range) on air velocity and per cent sorbed H_2O for an acceptable test. No other parameter was found to have such a marked effect on the test limitations as did the "Freon" boiling point. The limits on the test parameters are summarized in Table I for adsorption of the "Freons" studied on new carbon.

2. Iodine tests of carbon containing any of the "Freons" showed no appreciable loss in the iodine adsorption efficiency, nor significant loss in the capacity of the carbon for iodine in the loading range of interest (0.5 to 1.0 mg I_2 per gram of carbon). Apparently, I_2 (which is chemically adsorbed on carbon) displaces physically adsorbed "Freon" molecules to claim sorption sites. Only carbon containing 0.88 mg "F-112" per gram of carbon showed a measurable but insignificant loss in the iodine adsorption efficiency.

3. Desorption of "Freon" becomes more difficult with increasing boiling point (decreased volatility). "Freon" sorbed on carbon causes some loss in adsorption efficiency in repeat tests, but in

practical applications the effect will probably be minor due to the relatively low "Freon" loading of the carbon and the long desorption periods (up to 1 year in most installations). Poorer desorption of higher boiling point "Freons" may also be due to greater attractive forces between the "Freon" molecule and the active carbon site.

4. The test limits of temperature, face velocity, and carbon H_2O content are related and interdependent. Any one of the limits for a given "Freon" can be extended if one or both of the other limits are decreased. This principle was demonstrated for "F-11" in DP-910 and for "F-114B2" in DP-920.

5. The sensitivity of the electron capture detector generally increases with increasing number and increasing atomic weight of the substituting halogen atoms in the compound. (This conclusion is more applicable within classes of compounds rather than between classes as shown by the methane and ethane derivatives of "Freons", see Table I.) The more complex molecules with more halogen atoms provide an advantage as a tracer, because the greater sensitivity for detection permits lower upstream "Freon" concentrations to detect a given leak path. Thus the "Freon" loading on the carbon bed is reduced. Less "Freon" in a carbon bed results in quicker desorption. The best sensitivity of detection (0.0003 ppm) occurred for "F-11" which has 3 chlorine atoms per molecule.

6. A sharp break point occurs for sorbed H_2O and a moderate break point occurs for temperature beyond which the adsorption efficiency rapidly deteriorates. These points were demonstrated with "F-114B2" (at 70 ft/min only) as shown by Figures 2 and 4 of DP-920[5]. In this report, "F-112" was also shown to be sensitive to air temperature (Figure 1, curves B and D). The mechanisms that cause such a sharp break point are probably (1) adsorption sites are depleted by the adsorption of H_2O; and (2) the average energy (speed) of a molecule increases with temperature. Thus it can be postulated that with increased amounts of adsorbed H_2O and at higher temperatures, the adsorbate molecule has fewer sites on which to adsorb and is harder to capture and retain because of its greater energy. The break points imposed a definite limit to the parameters for an acceptable "Freon" test. However, for "F-112" and "F-113", these break points are beyond the ranges of temperature and sorbed H_2O expected in actual plant installations and therefore will not interfere with the "Freon" test.

PROGRAM

The screening tests revealed that the best adsorption characteristics were possessed by "F-112". Future work will concentrate on the development of a standardized test with "F-112". Tests of "F-113" will also be continued as a backup to "F-112". The projected program is as follows:

- Establish quantitative adsorption-desorption characteristics for "F-112" as a function of test variables and condition of carbon (new or used).
- Develop standard procedure and technique in full-size facility.
- Develop injection apparatus for "Freons" and sampling system for in-place testing of SRP carbon beds.
- Demonstrate test in SRP reactor containment facility.
- Establish effect of bed variables, condition of carbon, and type of carbon on the "Freon" adsorption-desorption characteristics.
- Develop correlation that predicts effects of parameters on "Freon" test for new carbon and on used carbon if practical.
- Develop correlation between "Freon" and iodine vapor penetration of carbon beds.

REFERENCES

1. A. H. Peters and D. R. Muhlbaier. Nondestructive Test of Carbon Beds for Reactor Containment Applications. Progress Report - June 1962 - December 1963. USAEC Report DP-870, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1964).

2. D. R. Muhlbaier. Nondestructive Test of Carbon Beds for Reactor Containment Applications. Progress Report - January-March 1964. USAEC Report DP-910, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1964).

3. D. R. Muhlbaier. Nondestructive Test of Carbon Beds for Reactor Containment Applications. Progress Report - April-June 1964. USAEC Report DP-920, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1964).

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