Gulf General Atomic Incorporated

P.O. Box 608, San Diego, California 92112

MASTER

AEC RESEARCH AND
DEVELOPMENT REPORT

GA-8083

HIGH-TEMPERATURE ADSORPTION STUDIES FOR THE PSC REACTOR DEVELOPMENT PROGRAM

by

D. R. Lofing and R. D. Burnette

Prepared under
Contract AT(04-3)-633
San Francisco Operations Office
U. S. Atomic Energy Commission

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

General Atomic Project 901

November 30, 1967

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
129

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTENTS

ABSTRACT	1
INTRODUCTION	2
EXPERIMENTAL APPARATUS.	6
EXPERIMENTAL PROCEDURE	8
Experiment No. 1	8
Experiment No. 2	11
Experiment No. 3	13
SUMMARY AND CONCLUSIONS	17
REFERENCES	18

FIGURES

1. Sorption of cesium on Barnebey-Cheney activated carbon (AC-4, 6-10X)	4
2. Freundlich isotherms for sorption of barium on graphites	5
3. High-temperature filter-adsorber unit.	7
4. Distribution of Ba ¹³³ -tagged carbon dust in carbon bed after various running times (<u>in situ</u> Aerosol experiment)	10
5. Dust concentration (Sr ⁸⁵ activity) profiles in activated carbon bed as a function of distance and run times	12
6. Penetration of carbon dust through activated carbon trap as a function of elapsed time	14
7. Dynamic iodine adsorption (I ¹³¹ activity) profiles in high- temperature activated carbon bed after various running times . . .	16

TABLES

1. Activity detected on Millipore filter at outlet of experimental trap .	11
2. Transport of iodine through activated carbon bed	15

ABSTRACT

Experimental work related to the high-temperature filter-adsorber unit for the Public Service Company of Colorado (PSC) reactor is described. Specific tests included measurements of dust or aerosol penetration as well as dynamic iodine adsorption under simulated reactor conditions of pressure, temperature, and gas velocity.

The results of the tests showed the following:

1. Normal gas flow and pressure cycling are not sufficient to cause appreciable dusting by particle degradation in a packed carbon bed.
2. For low loadings, the PSC high-temperature filter-adsorber unit is expected to be greater than 90% efficient in removing entrained dust from a process stream.
3. Iodine is essentially irreversibly adsorbed on carbon at 400°C. Reaction with impurities to form metal iodides is deemed likely.

INTRODUCTION

The purification system for the PSC reactor consists of a high-temperature filter-adsorber unit followed by a low-temperature trapping system. The high-temperature unit includes a large bed of activated carbon which operates at the temperature of the helium coolant, 750° to 800°F. Its purpose is to remove by adsorption condensable fission products such as iodine, tellurium, and cesium. The bed is also expected to be somewhat effective in filtration of dust or aerosols entrained in the process stream, in particular carbon dust which may be laden with adsorbed fission product metals.

The various fission products expected to enter the high-temperature filter-adsorber unit are those that are somewhat volatile at 800°F. These include, in order of volatility, krypton, xenon, iodine, tellurium, rubidium, cesium, strontium, and barium. In addition, less volatile species may be carried to the carbon bed by association with dust particles.

All of the above species (excluding the rare gases) will experience reduced volatility due to compound formation or because of strong adsorption on the carbon.

Iodine and tellurium are expected to exist partially as the iodide or telluride due to reaction with the abundant fission product Cs. The vapor pressure of CsI at 800°F is 1.9×10^{-7} atm, but the actual vapor pressure will be much lower due to strong adsorption on the hot activated carbon. Moreover, the dynamic adsorption of CsI on activated carbon at 400°C (752°F) has been measured, and movement of this species through a carbon bed under reactor conditions is deemed negligible. ⁽¹⁾

If cesium and rubidium vapor should enter the hot carbon bed, subsequent gas phase movement therein will be greatly retarded. This is because

of strong chemisorption on the activated carbon, resulting in extremely low vapor pressures. Figure 1 shows adsorption isotherms for Cs on carbon at 400°, 500°, 700°, 900°, and 1000°C. ⁽¹⁾ Extrapolation to the more reasonable cesium loadings expected in the reactor high-temperature filter-adsorber unit (< 0.1 mg Cs/g C) would result in extremely low vapor pressures. Substantial movement of Cs or Rb atoms through the carbon column is therefore quite improbable.

Barium and strontium will exist in the reactor system largely as the oxides BaO and SrO. This is due to the reaction

From thermodynamic considerations, 10^{-4} atm CO will maintain Ba or Sr largely as the oxide at 800°F. The resultant Ba vapor pressure in such a system has been calculated to be less than 10^{-8} atm, which will be greatly reduced due to strong adsorption on the carbon or by formation of the carbide BaC₂.

Recent measurements have confirmed that Ba and Sr are quite strongly adsorbed on graphite. ^(2, 3, 4) Figure 2 shows Ba isotherms on graphite powders at temperatures from 1000° to 2500°K. At the lowest temperature of the measurement, 1000°K (1521°F), a Ba loading of 1 $\mu\text{mole}/\text{m}^2$ (equal to 0.7 mg Ba/g C) resulted in an equilibrium vapor pressure of 3×10^{-13} atm. Extrapolating to more reasonable metal/carbon loadings (for example, 0.1 mg metal/g C) and to 800°F and considering that activated carbon, because of its relatively high surface area, is vastly superior to graphite as an adsorbent, vapor pressures several orders of magnitude lower must prevail.

It is thus concluded that the only species that can move through the column by vapor phase transport are the electronegative elements, typified by I₂. The vapor pressures of all the other candidate fission products (i. e., Ba, Sr, Cs, and Rb) will be sufficiently low to preclude vapor phase transport. However, these fission products might be adsorbed on entrained dust particles and thereby be transported through the column.

Fig. 1. Sorption of cesium on Barnebey-Cheney activated carbon (AC-4, 6-10X)

Fig. 2. Freundlich isotherms for sorption of barium on graphites

Dust particles laden with fission products might enter the filter-adsorber unit from the process stream, or they may be generated in situ by abrasion of the carbon granules due to pressure and temperature cycling or due to vibration. Accordingly, the following three experiments were performed in the test apparatus:

1. Measurement of the penetration and distribution of in situ generated dust particles
2. Measurement of the penetration and distribution of externally generated dust particles
3. Measurement of the penetration and distribution of I_2 vapor

EXPERIMENTAL APPARATUS

In order to obviate a large-scale research program, it was decided to study the behavior of the high-temperature sorbent bed at conditions similar to those expected in the reactor unit. Thus, a small helium loop was devised in which reactor conditions of pressure, temperature, and gas velocity could be simulated.

The apparatus, designated HITPOT (the filter-adsorber unit was formerly referred to as the high-temperature plateout trap), is shown schematically in Fig. 3. The apparatus consisted of an upright stainless steel test trap, 7/8-in. inside diameter and 39 in. long. The trap was heated with two clamshell furnaces. A preheated coil of 1/8-in. tubing at the trap inlet ensured uniform axial temperatures, and a water-cooled section at the outlet of the column precluded excessive heating of downstream components. A high-pressure millipore filter unit (0.22- μ pore size) was located below the test trap to collect any particulates that penetrated the column. The rest of the circuit included a circulator, flowmeter, bypass cleanup system, and assorted valves and fittings.

Fig. 3. High-temperature filter-adsorber unit

EXPERIMENTAL PROCEDURE

The experimental procedure in general was to fill the test trap with activated carbon, introduce the tagged adsorbate (specific details of each experiment are discussed in sections which follow), and charge with helium. During warmup to temperature, the liquid-nitrogen-cooled cleanup system was valved in to ensure removal of excessive gaseous impurities. The loop was then run at the desired gas flow rate for a predetermined period. Movement of adsorbate through the packed bed was monitored by axially scanning the column through a 1/4-in. slit, using a 3-in. NaI(Tl) scintillation crystal and a 400-channel pulse height analyzer. Finally, radioassay of the millipore filter discs yielded information on dust penetration.

Experiment No. 1

The initial experiment was to determine the amount of in situ generated carbon dust (aerosols) transported through a carbon bed. Dust laden with fission products may be generated in situ in the PSC filter-adsorber unit by abrasion due to vibration and gas flow.

A small amount (0.446 g) of activated carbon (6-10 mesh) was tagged with 1 to 2 mC of 7.5-y Ba^{133} activity by adding a nitrate solution of the activity to the activated carbon and allowing the solution to evaporate. The dry barium-activated carbon mixture was then placed in a closed graphite crucible and heated to 1000°C under vacuum for 3 days. This operation reduced the barium nitrate to the metal which, during the heating, was uniformly distributed throughout the activated carbon. After the heating operation, the specific activity of the tagged carbon was checked and found to be quite uniform.

The steel test trap (see Fig. 3) was inverted and filled to a depth of 3 cm with 5.7 g of activated carbon (6-10 mesh). This was followed by the Ba^{133} -tagged carbon, which was loaded through a heavy-wall plastic

tube that was inserted to the level of the previously loaded carbon. In this manner, the tagged carbon was not allowed to come in contact with the walls of the test trap. After the tagged carbon was loaded into the test trap, the plastic loading tube was carefully removed and later checked for contamination. No contamination was detected.

The tagged carbon was followed by 185.9 g of activated carbon (Barnebey-Cheney 107, 6-10 mesh), which was held in place by a tack-welded support screen. The end cap was then screwed on and seal-welded. The test trap was thereafter held in an upright position.

Before placing the test trap in the loop system, a Ba^{133} activity distribution scan was taken. Subsequent activity distribution measurements were compared with this initial scan.

After placing the test trap in the loop, the system was pressurized with helium and the liquid-nitrogen-cooled charcoal cleanup trap was used to remove any excessive gaseous impurities. The apparatus was then operated at 800°F and at 560 psig He pressure with a flow rate of 52 std liters/min. The bed was scanned prior to the start of gas flow and after various running times: 9, 45, 46 (following strong vibration), 56, and 213 days accumulated running times (Fig. 4). The test trap was vibrated violently on the 46th day of running by administering 300 sharp raps with a hammer. Very little change from the initial activity distribution was noted in the activity profile after the various running times. The greatest change was noted after the vibration test. The vibration on the 46th day caused the activated carbon to settle, as was noted by a 2-cm shift in the source activity peak. An increased amount of Ba^{133} activity (as well as carbon dust) was detected on the millipore filter following the vibration test (Table 1).

In general, the conclusions from this test are that gas flow alone is not sufficient to cause attrition of the carbon granules. The combination of gas flow and vibration, however, will cause some dusting of the carbon and, therefore, some transport of fission products out of the trap via aerosols or dust particles.

Fig. 4. Distribution of Ba¹³³-tagged carbon dust in carbon bed after various running times (in situ Aerosol experiment)

TABLE 1
ACTIVITY DETECTED ON MILLIPORE FILTER AT OUTLET OF
EXPERIMENTAL TRAP

Elapsed Time (days)	Collection Time (days)	Amount Ba ¹³³ -Tagged Carbon (μg)	Percent of Loading	Penetration (%/day)
9	9	0.13	$\sim 3 \times 10^{-5}$	3×10^{-6}
45	36	0.03	$\sim 7 \times 10^{-6}$	2×10^{-7}
46	1(a)	15.1	$\sim 3.4 \times 10^{-3}$	3.4×10^{-3}
56	10	Not detected (<0.15) ^(b)	--	--
213	89	6.4	1.3×10^{-3}	1.5×10^{-5}

(a) After vibration.

(b) After Experiment No. 2, the presence of Sr⁸⁵ raised the limit of detection for Ba¹³³.

Experiment No. 2

The second test was made to study the distribution or penetration of externally generated dust. A sample of 64-day Sr⁸⁵-tagged dust was prepared by soaking carbon black in a Sr(NO₃)₂ solution, drying, and finally heating in vacuum at 800°C for 15 hr. The dust was then injected into the inlet of the filter-adsorber apparatus while full pressure, flow, and temperature were maintained. The apparatus was shut down and gamma-scanned after 5, 34, and 66 days of operation. An additional scan was taken 2 days (63 days running time) after violent vibration (300 sharp raps with a hammer) during full-flow operation. A final scan was taken after a prolonged run for a total operation time of 157 days.

Figure 5 shows the activity profiles after the various running times. It can be seen that little change from the initial activity distribution occurred, except for the vibration test, which resulted in a broadening of the peak to cover approximately half the distance of the trap.

Fig. 5. Dust concentration (Sr^{85} activity) profiles in activated carbon bed as a function of distance and run times

It was found that approximately 41 mg of carbon black were initially distributed exponentially throughout the bed and that 0.532 mg or $\sim 1.3\%$ of the dust penetrated the trap during the first 5 days of the experiment. Millipore filter samples collected at the trap outlet during the subsequent runs showed the following amounts of carbon penetration: 6.2×10^{-3} mg during the period 5 to 34 days, 5.8×10^{-3} mg during the period 35 to 66 days, 1.0×10^{-3} mg during the period 66 to 68 days, and 5.8×10^{-3} mg during the period 68 to 157 days. These data are plotted in Fig. 6. It appears that 1.3% of the carbon penetrated the bed soon after injection and that an additional $5 \times 10^{-4} \%$ /day penetrated the bed with continued running. This penetration rate was reduced even further during the final 89-day run to $1.6 \times 10^{-4} \%$ /day.

These results indicate that the filter-adsorber unit does not act as an absolute filter for externally generated carbon aerosols, but it does appear to have some effectiveness. A conservative estimate for dust penetration for the reactor unit might be set at 10% or less.

Experiment No. 3

Although considerable work on the dynamic adsorption of I_2 on carbon had been done at General Atomic⁽⁵⁾ and elsewhere,⁽⁶⁾ most of the measurements were for small bench-scale systems and for many of the tests, less than a gram of activated carbon was used. Because extrapolation of data from bench-scale tests to the reactor situation is often tenuous, it was decided to perform a dynamic I_2 test in the filter-adsorber apparatus to obviate difficulties in interpretation of results from previous work.

In this experiment, 50 mg of 8-day I^{131} -tagged elemental iodine was sorbed on 2 g of activated carbon at room temperature. This tagged carbon was loaded into the filter-adsorber apparatus following 10 g of activated carbon. The tagged carbon was followed by 156 g of activated carbon. The overall length of the carbon bed was 100 cm.

Fig. 6. Penetration of carbon dust through activated carbon trap as a function of elapsed time

The filter-adsorber apparatus was then run at 800°F, a total pressure of 560 psig, and a flow rate of 25 std liters/min.

Figure 7 is a plot of I^{131} -activity profiles (gamma scans) after various times. Comparison of the scan taken before startup and that taken 7 days later shows the iodine moved about 2 cm. This movement was probably due only to settling of the carbon bed, as other scans taken after 32 and 64 days of running time showed very little, if any, movement of the peak. Radiation background problems were encountered in performing the 64-day scan.

In two final tests, 2.5% and 50% water vapor in helium (simulating a reactor major steam leak accident) were injected into the hot carbon bed for 15.5 hr. These tests were performed at 1 atm pressure and at equivalent gas velocities. No effect of the water vapor on the position of the iodine peak was noted.

Throughout the run a small amount of I^{131} activity was observed to penetrate the trap. This activity was probably associated with a small amount of carbon dust which was observed on the millipore filter downstream of the test trap. The filters were periodically removed for I^{131} analyses, the results of which are given in Table 2.

TABLE 2
TRANSPORT OF IODINE THROUGH ACTIVATED CARBON BED

Duration of Run (days)	Amount of Iodine on Filter (mg)	I_2 Transported to Filter (%/days)
0-7	4.89×10^{-4}	1.4×10^{-6}
7-32	1.23×10^{-3}	9.8×10^{-7}
32-64	8.19×10^{-4}	5.1×10^{-7}
64-65(2.5% steam)	2.23×10^{-4}	4.5×10^{-6}
65-66(50% steam)	Not detected ($<10^{-4}$)	--

Fig. 7. Dynamic iodine adsorption (I^{131} activity) profiles in high-temperature activated carbon bed after various running times

These results show that iodine does penetrate the hot carbon bed; however, the quantity suggests a dust mechanism, perhaps due to abrasion of the particles. For instance, the amount of iodine collected on the filter is in the 10^{-6} %/day range, which is quite similar to that observed for the in situ dust generation experiment (see Experiment No. 1). The bulk of the iodine, however, remains fixed at the bed inlet, exactly where it was placed.

A reasonable speculation is that iodine is held on hot carbon by reaction with alkali metal impurities to form stable iodides, as suggested by Lingjaerde and Podo.⁽⁵⁾ The amount of sodium and potassium in coconut-shell carbons varies from 0.1 to 1%. Assuming 0.1% potassium, 300 lb of carbon will contain 0.3 lb of potassium, which will react with and therefore hold up about 1 lb of iodine. This is well in excess of the expected release of long-lived iodine from the PSC fuel ($\sim 8 \times 10^{-3}$ lb/yr). Moreover, other metal impurities in typical coconut-shell carbons, such as Fe, Mg, Na, Ba, and Ca, will total in excess of 0.2% and will also be effective in iodine holdup.

SUMMARY AND CONCLUSIONS

The results of the tests with the filter-adsorber apparatus showed the following:

1. Dust generation from abrasion of coconut charcoal in a packed bed is minimal, unless severe vibration is encountered.
2. The PSC high-temperature carbon bed will act as a filter for entrained dust particles. A filtration efficiency of 90% is believed to be conservative.
3. Iodine and other electronegative elements will be held up in the high-temperature carbon bed as alkali metal salts. These elements at their expected low release rate will react with the high sodium and potassium impurities normally found in activated carbons.

REFERENCES

1. "HTGR Base Program Quarterly Progress Report for the Period Ending August 31, 1965," USAEC Report GA-6671, General Dynamics, General Atomic Division, September 30, 1965.
2. "Public Service Company of Colorado 330-MW(e) High-Temperature Gas-Cooled Reactor Research and Development Program, Quarterly Progress Report for the Period Ending March 31, 1966," USAEC Report GA-7086, General Dynamics, General Atomic Division, May 11, 1966.
3. "Public Service Company of Colorado 330-MW(e) High-Temperature Gas-Cooled Reactor Research and Development Program, Quarterly Progress Report for the Period Ending June 30, 1966," USAEC Report GA-7314, General Dynamics, General Atomic Division, September 30, 1966.
4. "Public Service Company of Colorado 330-MW(e) High-Temperature Gas-Cooled Reactor Research and Development Program, Quarterly Progress Report for the Period Ending September 30, 1966," USAEC Report GA-7453, General Dynamics, General Atomic Division, February 7, 1967.
5. Watkins, R. M., D. D. Busch, and L. R. Zumwalt, "High-Temperature Fission Product Trap Study for Gas-Cooled Reactors," USAEC Report GA-1990, General Dynamics, General Atomic Division, June 1961.
[Also (condensed) "Trapping Fission Products in the HTGR," Nucl. Eng. 6, 427, 1961].
6. Lingjaerde, R. O., and L. Podo, "A Study on the Trapping of Iodine at High Temperatures on Activated Charcoal," Dragon Project Report D. P. 213, OECD High Temperature Reactor Project, September 1963.