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CESIUM SORPTION IN MATERIALS FOR THERMIONIC CONVERTERS, II

by

M. K. Yates and G. O. Fitzpatrick

Prepared under
Contract AT(04-3)-167
Project Agreement No. 14
for the
San Francisco Operations Office
U. S. Atomic Energy Commission

April 1970

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SUMMARY

This report covers work done from January 1968 to June 1969 under AEC Contract Number AT (04-3)-167 on cesium sorption in materials which serve as high-temperature cesium reservoirs in thermionic converters.

Cesium vapor pressure/sample temperature/sample loading characteristics were measured for two different types of graphite and one sample of porous tungsten. When the data on the graphite samples were compared to some earlier data, it was found that the isotherms for different types of graphite were similar; but the transition between two cesium graphite equilibrium states was better defined in some samples than in others. Hysteresis effects were present in most of the graphite samples but appear to pose no particular problems to the thermionic converter. The data concerning the cesium loading in the porous tungsten sample were obscured by soluble cesium compounds present on the inner oven surfaces. It was determined, however, that the primary sorption mechanism was surface adsorption.

Long-term isostere stability tests were run on two graphite samples and one carbon sample. All samples were operated $\sim 800^{\circ}\text{C}$ at a cesium vapor pressure of ~ 10 torr. Periodically cesium pressure/sample temperature curves were taken. Stability testing of one graphite sample using a radioactive technique for cesium pressure determination was discontinued after 3360 hours because of high background radiation levels. No changes in either heat of reaction or cesium pressure larger than the experimental error of $\pm 20\%$ were observed. Stability testing of the carbon sample, also using the radioactive technique of cesium pressure determination was discontinued after 2000 hours for the same reason. The variations observed in the carbon's heat of reaction were not larger than the experimental error of $\pm 30\%$. During the initial 1200 hours a 20-35% cesium pressure decrease

was observed, an amount corresponding to that expected from observed cesium accumulation in the counting volume.

The second graphite sample was tested in an apparatus where the cesium vapor pressure was determined by measuring the cesium condensation temperature of an insulator. This sample was tested for 1225 hours, and no significant change was detected in the sampled temperature-cesium pressure isostere. The insulator technique proved capable of a cesium condensation temperature determination within $\pm 10^{\circ}\text{C}$, with relative determinations accurate to $\pm 2^{\circ}\text{C}$.

Finally, the required temperature control accuracy for some sorption reservoirs is shown to be approximately one-half that required for a liquid cesium reservoir, and tolerable cesium losses in sorption reservoirs are given for a cesium vapor pressure change.

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INTRODUCTION

This report is a continuation of work on cesium sorption in materials for thermionic converters.¹ The cesium sorption testing of various samples is discussed, where the primary characterization involves the measurement of cesium pressure/cesium loading isotherms. The design of long-term thermal test apparatus is also discussed, and results of the tests are given. Finally some aspects of the incorporation of sorption reservoirs into thermionic converters are considered, namely, tolerable cesium losses and required temperature control for various materials used as sorption reservoirs.

PRESSURE-TEMPERATURE-LOADING TESTS

The design of the apparatus used in most of these tests has been described before.¹ It has been modified slightly (as shown in Fig. 1) in order to better outgas the sample and to eliminate any possibility that cesium might collect on the reference side of the capacitance manometer.

Basically, the apparatus consists of a liquid-cesium reservoir (with ~ 2 grams of cesium having a specific Cs¹³⁴ activity of 250 μ curies/gm), the manometer, and the sample. The sample's cesium loading is determined by counting the radioactive cesium present. The cesium vapor pressure is determined by measuring the temperature of the liquid reservoir and using the P-T curve recommended by Nottingham and Breitwieser as that giving the best fit to experimental vapor pressure data.² The capacitance manometer is calibrated against the liquid reservoir.

The cesium sorption characteristics of two graphite samples and one porous tungsten sample have been measured. Table 1 lists the physical characteristics of these samples as well as those of two other graphite samples that were tested earlier. Table 2 lists the impurities for these samples.

Fig. 1 Plan View of Pressure - Temperature Loading Apparatus

GRAPHITE PRESSURE-TEMPERATURE-LOADING TEST

The reproducibility of sorption characteristics in nominally identical types of graphite was of interest, as well as comparisons between samples of different types. As shown in Table 1, samples of annealed pyrolytic, molded, and a layered graphite cloth were tested.

The annealed pyrolytic graphite was produced by vapor deposition followed by a high-temperature heat treatment (3000°C). The result was a dense graphite that is highly oriented with almost all of its carbon layers parallel to the substrate surface. As a result, its physical properties vary greatly with the axis chosen, i.e., it is very anisotropic.

The molded graphite was made from particles less than 0.003 inch in diameter compacted under high pressure. It is less dense and much more isotropic than the pyrolytic graphite.

The last sample type tested was CARB-I-TEX, a unique structure made up of layered graphite cloth impregnated with a graphite binder. We have found its expansion properties to be anisotropic, expanding much more in a direction perpendicular to the cloth layer planes than in the other two when loaded with cesium. This type of graphite is the least dense of those tested, due primarily to imperfect binder impregnation. Two samples of the same nominal type, but from different batches were tested. The presence in the sample of two forms of graphite, the cloth and the binder, makes it very difficult to get meaningful x-ray data on layer spacing and crystallite size.

The pressure-temperature-loading characteristics of the samples are shown in Figures 2 through 5. Data have been taken over a cesium pressure range of 0.1 to 30 torr and sample temperatures from 600° to 1100°C . Loadings up to 1.2 grams cesium/gram graphite have been obtained. Also shown in Figures 2 through 5 is the 700°C isotherm based on Salzano and Aronson's work on the cesium-graphite lamellar compounds.³

Table 1

Physical Characteristics

Sample No.	Type	Source	Density gm/cm ³	N ₂ BET Area m ² /cm m ² /cm ³		X-Ray Data ¹ (Å)					
						Axis 1		Axis 2		Powder	
						L _c	C _O	L _c	C _O	L _c	C _O
1	Annealed Pyrolytic Graphite	Gulf General Atomic	2.08	0.8	1.7	1150	6.734	675	6.729	675	6.719
2	Molded Graphite 3499S	Speer Carbon Products	1.62	2.28	3.69	350	6.750	370	6.713	540	6.724
3 } 4 }	Flat Layered Graphite Cloth bonded with Graphite, CARB-I-TEX 700	Carborundum Co.	1.35	0.39	0.56	No meaningful data obtained No meaningful data obtained					
	1.48		0.75	1.11							
5	Porous Tungsten W-2 w/oB	Electro- Optical- Systems	11.81	Avg. pore diameter=1.92μ Pore cross sectional density = 3.87 x 10 ⁶ pores/cm ²							

¹Axis 1 and Axis 2 are perpendicular axis, one chosen to correspond approximately to the sample's natural axis determined by anisotropy. The powder tested was obtained from sample scrappings and should represent a sample average.

C₀ represents an average layer spacing determined from the angle of reflection of X-ray peak.

L_c represents an average crystallite size, determined from the X-ray peaks half-width. A crystallite is a three-dimensional atomically ordered structure bounded by micropores or highly angled carbon layers.

Fig. 2 Pressure - Loading Isotherms Sample No. 1
GGA Annealed Pyrolytic Graphite

Fig. 3 Pressure - Loading Isotherm Sample No. 2
Speer Carbon Products Molded Graphite 34995

Fig. 4 Pressure-Loading Isotherms Carborundum CARB-I-TEX 700

Fig. 5 Pressure-Loading Isotherm Sample No. 4 CARB-I-TEX 700

Evidence of the transitions between the various cesium-graphite compounds appeared in all of the samples. In particular, the beginning of the transition between CsC_{24} and CsC_{10} was well defined in all samples and occurred at nearly identical sample temperatures and cesium vapor pressures. However, the constant pressure regime where the CsC_{24} and CsC_{10} compounds in equilibrium was narrow and poorly defined in the CARB-I-TEX samples and very wide and sharply delineated in the annealed pyrolytic sample. The molded graphite sample fell between these two extremes in this respect. Of the other transitions, only the one between CsC_{24} and CsC_{36} was well defined and that only in the annealed pyrolytic and molded graphite samples. In general, cesium loadings were less than that expected if complete formation of a particular compound had taken place. The two CARB-I-TEX samples differed in cesium loading by 25%.

In an attempt to explain the difference in the graphite isotherms, various physical characteristics of the samples were measured. These characteristics (Tables 1 and 2) include density, BET surface area, and purity. Also included are the average layer spacing and crystallite size determined for two perpendicular axes and for a sample average. One measured parameter that seems to correlate with "compound definition" in the sample's cesium sorption characteristics is sample density. Higher densities correlate well with more distinctly defined compound states. Larger crystallite size also correlated with better plateau definition.

In order to study the cesium sorption characteristics of graphite further, a group of samples was prepared by G. Engle of Gulf General Atomic Incorporated that covered a very wide range of possible physical properties. Three groups of samples were prepared, each by a separate technique, and the samples in each group heat treated at a variety of temperatures.

The first group consisted of five low-temperature pyrolytic carbon samples deposited on graphite disks at 1450°C from propane in a fluid bed. Their carbon structure is turbostratic in nature, and their crystallite orientation is nearly isotropic. They have a density near 1.67 g/cm^3 . Heat treatment to 3100°C improves the crystallinity of the carbon structure only slowly.

Table 2
SAMPLE IMPURITIES (ppm)

Sample No.	Al	B	Mg	Fe	Ca	Cu	V	Si	Ti
1	< 1	< 0.5	< 0.5	< 1	< 20	< 1	< 0.5	< 10	< 1
2	< 1	1	1	1	< 20	0.5	20	40	40
3	2	0.5	1	8	40	5	< 0.5	10	1
4	8	2	8	10	< 20	< 1	10	< 10	10

The second group consisted of five samples of massive pyrolytic carbon, a commercial product probably deposited on a graphite substrate from methane at 2000°C to 2200°C. Their density is $\sim 2.2 \text{ g/cm}^3$. Their carbon layer planes are highly aligned parallel to the substrate, but still are of a turbostratic nature in the as-deposited state. With heat treatment they quickly become more crystalline.

The third group consisted of seven samples of artificial graphite made from calcined petroleum coke commercially produced and outgassed at 1300°C, and bonded at GGA with carbon from the pyrolysis of a coal-tar pitch. The final product is quite porous, with a density of $\sim 1.7 \text{ g/cm}^3$. Further heat treatment greatly increases its crystallinity.

Table 3 lists the samples, their heat treatment, and x-ray parameters. No cesium sorption tests have been run on these samples.

HYSTERESIS EFFECTS IN GRAPHITE

Hysteresis effects were observed in almost all of the graphite isotherms. The first item of interest was whether a transition would occur from one branch of the curve to the other if the cesium loading was held constant and a pressure-temperature curve taken. In order to study this effect, the capacitance manometer was used with one sample (No. 4) to take pressure-temperature data. The data were taken with the valve to the liquid reservoir closed. The results are shown in Fig. 6. Two curves taken at the same loading are of particular interest; one was taken on an adsorption branch, one on a desorption branch after unloading from 30 torr. Both curves indicated that a transition from one hysteresis branch to the other would not occur when changing sample temperature if the cesium loading remained constant. Because of the volume of the measuring system, actual loadings dropped by approximately 1% when going from 0 to 30 torr.

In order to further investigate the hysteresis characteristics of the pressure-temperature curves, small sorption-desorption loops were traversed around one operating point, $\sim 800^\circ\text{C}/10 \text{ torr}$. The results of the

Table 3
Graphite Sample Characteristics

Sample Type	Heat Treatment		X-Ray Parameters	
	Temp (°C)	Time (hr)	C ₀	L _c
Massive Pyrolytic Carbon	2100	1	6.850	225
Massive Pyrolytic Carbon	2650	1	6.715	213
Massive Pyrolytic Carbon	2900	1	6.726	465
Massive Pyrolytic Carbon	3000	1	6.726	1350
Massive Pyrolytic Carbon	3100	1	6.726	505*
Low Temperature Pyrolytic Carbon	2100	1	6.910	49
Low Temperature Pyrolytic Carbon	2650	1	6.861	80
Low Temperature Pyrolytic Carbon	2900	1	6.826	112
Low Temperature Pyrolytic Carbon	3000	1	6.816	119
Low Temperature Pyrolytic Carbon	3100	1	6.726	505
Artificial Graphite	2100	1	6.850	290
Artificial Graphite	2200	1	6.826	350
Artificial Graphite	2300	1	6.784	460
Artificial Graphite	2650	1	6.736	810
Artificial Graphite	2900	1	6.726	1000
Artificial Graphite	3000	1	6.724	1150
Artificial Graphite	3100	1	6.720	1350

* The L_c of this sample is anomolous and is being remeasured.

Fig. 6 Sample No. 4 CARB-I-TEX 700 Constant Cesium Loading Isosteres Carborundum CARB-I-TEX Sample No. 4

data taken are shown in Figs. 7 and 8. When starting from a sorption point and unloading the sample, the initial point could always be reproduced. However, the initial point could not be returned to when starting from a point on the desorption branch and unloading the sample. From these data it appears that it is desirable for a reservoir in a thermionic converter to be operating on the sorption branch of the curve to prevent changes in its equilibrium cesium pressure characteristics due to reservoir unloading.

POROUS TUNGSTEN SAMPLE PRESSURE-TEMPERATURE LOADING TEST

During testing of the W-2w/oB sample, very long equilibrium times (over a week) and low cesium loadings (2 mg maximum) were found. Postoperational analysis indicated that over 90% of the cesium present during the highest observed loadings existed in the form of soluble cesium compounds present on the oven inner surfaces. Only 0.12 mg of cesium were found in the W-2B sample itself.

Based on the samples calculated surface area of $0.8 \text{ m}^2/\text{cm}^3$ and a cesium cross sectional area of $28\text{\AA}^2$, this corresponds to a cesium coverage of $2/3$ monolayer. This result agrees with cesium sorption seen on previously tested porous tungsten samples and indicates that the primary cesium sorption mechanism was surface adsorption.¹

LONG-TERM THERMAL STABILITY TESTING OF CESIUM LOADED SAMPLES

Long-term testing was intended to demonstrate the stability of the cesium-substrate system in a realistic temperature environment. Two slightly different approaches were used, varying only in their methods of cesium vapor pressure measurement. In the first approach, pressure was measured by determination of the quantity of radioactive cesium vapor present in a calibrated volume. In the second approach, pressure was measured by determining the condensation temperature of an insulator exposed to the cesium vapor over the sample.

Fig. 7 Isotherm Hysteresis Sorption
Branch Carborundum CARB-I-TEX
Sample No. 4

Fig. 8 Isotherm Hysteresis on Desorption
Branch Carborundum CARB-I-TEX
700 Sample No. 4

RADIOACTIVE TECHNIQUE

The design of the test vehicle used with the radioactive technique is shown in Fig. 9. The sample was held in a 1/4 in. -diameter, 0.030 in. wall tube by crimps at the top and bottom. On the top is a 10 cm³ volume. The sample holder was made entirely of niobium with two weld joints and one pinch off (or cold weld).

After placing the sample inside the niobium tube, the assembly was mounted on the pressure-temperature loading apparatus and the sample out-gassed. Then sufficient P-T-L data were taken to insure that the sample's sorption characteristics were stable. Finally the sample was equilibrated at $\sim 800^{\circ}\text{C}$ and 10 torr cesium pressure and separated from the liquid reservoir by closing the valve. After cooling, the samples were pinched off, instrumented, and mounted in a separate vacuum system. Pressure-temperature curves were taken by counting the radioactive cesium in the volume at the top of the sample holder. The sample temperatures were held constant and the pressure-temperature curve periodically remeasured.

Three tests were run using this technique: A liquid cesium sample which served as a control; a sample of CARB-I-TEX 700; and a sample of Pure Carbon FC-50.¹ The liquid reservoir test was terminated after 3175 hours of operation. The liquid cesium had been held at a temperature of approximately 366°C (10 torr) and the volume at approximately 500°C during the test. The results of the test are shown in Fig. 10. No detectable change ($\pm 12\%$) was observed in the slope of the volume count rate/cesium pressure line during the test.

The CARB-I-TEX 700 sample test was terminated after 8226 hours at temperature, but data on the sample's sorption characteristics were taken only in the first 3360 hours of operation. The graphite pressure-temperature curves are completely characterized by the sample's heat of reaction, and the cesium pressure at a given sample temperature. These parameters

Fig. 9 Long-Term Stability Test Station

are plotted in Figs. 11 and 12. No detectable changes were noted in either parameter, both of which are considered accurate to $\pm 20\%$.

The Pure Carbon sample was operated at temperature for a total time of 4900 hours, but sorption data were taken only in the first 1200 hours of operation. The results of this test are shown in Figs. 13 and 14. No change was detected in the carbon heat of reaction, which is considered accurate to $\pm 15-35\%$. A drop in cesium pressure was observed which correlates well with that expected due to observed cesium losses to the counting volume. The carbon-cesium isotherms, reported in Ref. 1, were used to determine the pressure drop expected with the lower cesium loadings.

The termination of testing of these three samples was due to an increase in the radiation background observed in the 10cm^3 volume above the sample. At the conclusion of the testing, the amount of cesium in the volume was determined by counting techniques. Thirteen, 17 and 16 mg of cesium were found in the volumes over the carbon, graphite and liquid samples, respectively. Scans were made across the carbon and liquid volumes and are shown in Fig. 15. The residual cesium found correlates well with the area of inner oven surface exposed to cesium. The volume over the graphite sample was cleaned with water, removing all but 0.05 mg of the cesium present, thus ruling out the possibility of cesium diffusion into the niobium as a source of cesium buildup. The most likely cause of buildup is a cesium reaction with oxides or other impurities on the inner volume surfaces.

INSULATOR TECHNIQUE

The design of the sample holder for the insulator technique of cesium pressure determination^{4,5} is shown in Fig. 16. It is fabricated of niobium and has a Lucalox insulator Cu-Ni brazed in on one end. The sample is placed in the other end. After outgassing and cesium loading, the sample holder is sealed by pinching off the niobium tube.

Fig. 10 Long-Term Stability Test - Liquid Sample

Fig. 11 Long-Term Stability Test - Carborundum CARB-I-TEX 700

Fig. 12 Long-Term Stability Test - Carborundum CARB-I-TEX 700

Fig. 13 Long-Term Stability Test - Pure Carbon FC-50

Fig. 14 Long-Term Stability Test - Pure Carbon FC-50

Carbon Long Term Stability Test Oven
Total Cesium Inventory = 12.7 mg

Liquid Long Term Stability Test Oven
Total Cesium Inventory = 16.0 mg

Fig. 15 Background Cesium Concentration Profiles in Long-Term Stability Test Ovens

Fig. 16 PT Test Insulator Assembly

During this reporting period one sample, CARB-I-TEX 700, was tested using this technique. It was tested in the same apparatus used for the other long-term stability tests (Fig. 9). The sample's isostere was determined by measuring the insulator resistance-temperature curve at a fixed sample temperature. The ascending branch of the hysteresis curve has proved to be most reproducible, and the insulator temperature giving a resistance of $1000\ \Omega$ on the ascending branch has been used as the cesium condensation temperature. A typical insulator resistance-temperature curve is shown in Fig. 17. The hysteresis in the insulator resistance - temperature curve combined with temperature profiles in the sample and insulator areas limits the absolute determination of the cesium dewpoint to $\pm 10^{\circ}\text{C}$. The relative accuracies of pressure determination correspond to liquid cesium temperature errors of $\pm 2^{\circ}\text{C}$. Data taken on the CARB-I-TEX sample initially and after 1225 hours of operation at a temperature of 775°C indicated that no significant change in the sample isostere had occurred (Fig. 18).

Future tests are planned in a test assembly designed to hold six of these sample holders (Fig. 19). This assembly was designed to be used either in the laboratory or in the GGA TRIGA Mark III reactor. A common heat sink is used on each end, each with redundant heaters. The lower heat sink is designed to operate around 800°C and will contain all of the samples. The upper heat sink will operate $\sim 350^{\circ}\text{C}$ and will provide a uniform thermal environment for the insulator seals.

APPLICATION TO THERMIONICS

Two questions which have often come up during discussions of the applications of a sorption reservoir to a thermionic converter have been: What accuracy of reservoir temperature control is required for optimum cesium pressure operation, and what are the tolerable cesium losses for reservoir materials?

Table 4 lists the slope of the sample temperature/cesium vapor pressure curves for various materials (taken from Ref. 1) at a typical operating

Fig. 17 Insulator Temperature - Resistance
Curve Long-Term Stability Test -
Carborundum CARB-I-TEX 700

Fig. 18 Cesium Condensation Temperature - Sample
Temperature Data Carborundum CARB-I-TEX 700

Fig. 19 Six Sample Long-Term Cesium Pressure-Sample Temperature Test Assembly

TABLE 4

Slope of P-T
Curve at 10 torr
For Various Materials

<u>Material</u>	<u>Cesium Loading mg/Cs/g</u>	<u>Temperature at 10 torr</u>		<u>Slope of P-T curve at 10 torr °C/torr</u>
		<u>°C</u>	<u>°K</u>	
Liquid Cesium		366	639	4.7
Pure Carbon FC-50	350	1031	1304	11.0
	450	866	1139	8.0
	550	758	1031	6.4
	650	686	959	6.0
Graphite ⁽¹⁾	150	1053	1326	11.0
	250	960	1233	8.7
	350	942	1215	9.6
	475	795	1068	8.3
Tungsten ⁽¹⁾	~ 1	856	1129	11.1

point, 10 torr. The values range from $\sim 5^{\circ}\text{C}/\text{torr}$ for a liquid reservoir to $\sim 11^{\circ}\text{C}/\text{torr}$ for carbon loaded to 350 mg Cs/g, graphite loaded to 150 mg Cs/g or a porous tungsten reservoir loaded to ~ 1 mg Cs/g. In both carbon and graphite the cesium pressure becomes more sensitive to temperature as the cesium loading increases.

The question of cesium losses to converter components, residual gases, or leakage becomes very important when one contemplates placing material with a cesium reserve of 10's or 100's of milligrams inside the converter envelope. One would prefer a sorption reservoir material which could tolerate the loss of a large fraction of its reserve cesium before the vapor pressure dropped much below the operating value.

Using data reported in Ref. 1, the tolerable cesium losses in a variety of materials were compared. Choosing a point at 10 torr, the amounts of cesium that could be lost before the vapor pressure dropped by 20% were calculated. The results are plotted in Fig. 20 as milligrams cesium loss per cm^3 as a function of sample temperature.

The carbon and graphite samples can tolerate the highest loss, 10 to 900 mg/cm^3 . On the other hand, the tungsten and alumina samples can lose only 0.02 to 0.2 mg/cm^3 before the pressure drops 20%. The losses tolerable in the W-10 Ta sample range down from 12 mg/cm^3 depending upon sample temperature.

Tolerable loading losses are not too sensitive to operating temperature except in the two graphite samples, where peaks occur when the transition from one two-phase equilibrium to another occurs. These transitions are sharply defined in the annealed pyrolytic graphite sample and less well defined in the CARB-I-TEX 700 sample.

Two methods of loading the reservoir materials with cesium are available. These are:

1. Provision of a cesium excess, the desired loading being achieved by equilibrating the reservoir material in cesium vapor at the desired reservoir temperature and cesium pressure.

Fig. 20 Tolerable Cesium Losses as a Function of Sample Loading Temperature

2. Provision of the precise amounts of cesium and reservoir material necessary to achieve the desired loading.

The first method has the advantage of providing operation with one point on the reservoirs cesium pressure-reservoir temperature curve well known, regardless of variations in reservoir sorption characteristics. It also does not require an actual knowledge of reservoir material or cesium quantities used. However, if operation at a cesium loading allowing the largest tolerable cesium loss is desired with a graphite reservoir, the first technique becomes much less attractive since the allowable sample temperature errors during the loading of a pyrolytic graphite reservoir are only $\pm 10^{\circ}\text{C}$ (Fig. 20). Outside of that band the tolerable cesium losses quickly reach their lowest values. Thus for graphite samples, a loading using the second method would insure operation at the highest available tolerable loss levels.

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