SORPTION OF CESIUM BY GRAPHITES
AS A FUNCTION OF STRONTIUM AND BARIUM
CONCENTRATION AT HIGH TEMPERATURES

Progress Report

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ABSTRACT

Three apparatus with associated furnace and monitoring systems for the study of the sorption of cesium by graphite at high temperatures as a function of the concentration of strontium and barium have been constructed, tested and are now operating satisfactorily.

A sorption experiment is underway with H-327 (HTGR) graphite and a satisfactory cesium isotherm has been obtained at $1092 \pm 5^{\circ}\text{C}$. Another sorption experiment is underway with unimpregnated H-451 ("isotropic") graphite and an experiment with H-451 impregnated with Sr-85 tagged strontium ($\sim 200 \mu\text{g/gm}$) is about to begin. Earlier sorption runs were not completed because of experimental difficulties such as faulty seals and equipment failure.

A 50 KVA graphite-tube (King) furnace, for impregnation runs at 1200 to 2000°C , and associated equipment was assembled, debugged and used. Impregnation techniques were developed and the distribution of strontium (and cesium) were roughly determined after diffusion anneals.

To obtain insight into the nature of metal-graphite sorption, microscopic studies were begun. This included graphite surface characterization using a JSM-2 scanning electron microscope. Also studies of the micro-distribution of cesium, strontium and barium are underway or planned using (1) an energy-dispersive X-ray analyzer (EDAX), (2) X-ray micro-radiography, and (3) auto-radiography.

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I. INTRODUCTION

The purpose of this research is to quantitatively determine the equilibrium vapor pressures of cesium as a function of its concentration and the graphite sample temperature for various mixtures of cesium, strontium, and barium sorbed by two typical nuclear grade graphites, the "near isotropic" (Great Lakes H-451) and the needle coke (Great Lakes H-327), and a well characterized high purity spectroscopic grade of graphite powder (Union Carbide SP-1C). Cesium sorption isotherms will be obtained for concentrations of strontium and barium ranging from that corresponding to approximately mono-layer coverage to zero concentration for the particular graphite sample over the sample temperature range of 700°C to 1100°C with cesium equilibrium vapor pressures ranging from approximately 10^{-9} atm to 10^{-4} atm. The experimental information obtained will be analyzed to obtain a model by which the vapor pressures of cesium for mixtures of sorbed fission products may be predicted from single component sorption data.

II. SUMMARY OF PROGRESS AND RESULTS

Three sorption apparatus furnace and monitoring systems have been constructed and are operating satisfactorily from 25°C to 200°C ($\pm 2^\circ\text{C}$) at the source end and 100°C to 1125°C ($\pm 5^\circ\text{C}$) at the sample end. Their in-place arrangement is shown in Figure 1A. One calibrated single channel analyzer system capable of automatically accepting a scintillation detector (NaI) input from each sorption apparatus system in sequence has been constructed and is operating satisfactorily. This system permits the monitoring of the time-dependent sorption (or release)

behavior of the graphite sample. Equilibrium data point spectra are obtained from one of two multi-channel analyzers (ND-2200 or ND-3300) for more precise concentration analyses. Figure 1D illustrates the arrangement of the sorption apparatus with distillation side-tube on the vacuum bench. Not shown are the cold traps at the top and bottom of the source tube.

One sorption isotherm at $1092^{\circ}\text{C} \pm 5^{\circ}$ has been obtained from cesium on H-327 at sample vapor pressures ranging from 3×10^{-9} to 1×10^{-6} atm of cesium (see Figure 4 and Table 1). Another sorption experiment is in progress for cesium on H-451 and another is being prepared for cesium on H-451 impregnated with approximately 200 $\mu\text{g/gm}$ of strontium with SR-85 tracer). Three other sorption runs were previously attempted; however, they had to be terminated at varying stages because of erratic heater controller behavior, detection system malfunction, and possible oxygen contamination.

Assembly of a water-cooled, safety regulated, graphite tube furnace (King furnace) controlled via a 440 VAC, 50 KVA saturable reactor with a 54 KVA step down transformer (12 to 18 VAC taps) has been completed. This unit is capable of being used for diffusion anneals at temperatures of between 1200°C and 2000°C ($\pm 10^{\circ}\text{C}$) in purified inert gas atmospheres. A photograph of the King furnace with associated support systems is shown in Figure 3A. For sample sectioning and profiling, a toolmaker's lathe with a graphite shaving collection device has been set up in a radiological containment facility.

Preliminary diffusion anneals were conducted using the King furnace to assess and refine our experimental technique for homogeneously impregnating the graphite sample rods with strontium. We have concluded

that approximately 95% of the impregnant metal can be homogeneously diffused throughout the graphite sample by evaporating a dilute solution of acetone and metal nitrate onto the sample, outgassing the sample at or below 400°C prior to placing it in a molybdenum container (protected by tantalum foil) whose lid is held securely shut by an outer screw-topped graphite canister, and annealing the sample-container arrangement in a purified, inert gas atmosphere for 2 to 6 hours at 1400°C to 1500°C. If need be, the outer sample surface may be machined off under an inert atmosphere prior to loading the sample in the sorption apparatus.

Surface characterization using a JSM-2 scanning electron microscope is presently being investigated on the pre-exposed samples of graphite. Preliminary studies are planned to examine the sensitivity of the energy-dispersive X-ray analyzer (EDAX) unit to barium, cesium and strontium in order to qualitatively identify possible major metal accumulation areas on the graphite samples. Localization of these areas by this method may then permit a more in-depth quantitative scan by micro-probe analysis.

Also, a combined X-ray and auto-micro-radiography technique is under investigation using X-ray diffractometer equipment on wafered graphite samples. Some difficulty is being experienced in preparing graphite wafers of less than 0.3 mm in thickness so that satisfactory resolution may be obtained.

III. DISCUSSION

Although all of the necessary experimental equipment has been assembled and is operating, several re-occurring problems have been

experienced. Some of these problems, notably temperature controller malfunctions, can be attributed to the age of the equipment in use and to the rather severe demands placed upon it - primarily the requirement of continuous reliable operation at set temperature $\pm 2^{\circ}\text{C}$ for periods of 2 to 3 months. However, continuing efforts are underway to repair and modify existing components to obtain optimum performance and reliability. Troublesome units will be replaced with available funds when it is deemed that they can no longer be made serviceable.

For increased protection of each of the three Lindberg sorption furnaces, an independent thermocouple over-temperature sensing safety circuit is being constructed locally to shut these furnaces down at 1140°C . Thus, our experimental isotherms will be limited to temperatures below 1120°C rather than the originally proposed 1200°C . It should be noted that this limitation is required, both because of the maximum design operating temperature of the Lindberg furnace (1200°C) and the oxidation temperature of the Inconel 600 sample tube (1177°C in air) of the sorption apparatus.

During the period of this contract, a multi-channel analyzer was not available for several months due to component failure and servicing problems. The problems, however, appear to have been corrected and one of the two available multi-channel analyzers should be operational at all times in the future.

The continuing research effort will be directed towards obtaining cesium sorption isotherms in strontium impregnated graphites in the priority order H-451, H-327, and SP-1C graphite at concentrations of about $300\text{ }\mu\text{gm/gm}$ and below in the temperature range of 700 to 1100°C .

These will be followed by similar experiments using barium impregnated graphites and barium-strontium co-impregnated samples, to an extent determined by time and equipment availability. Also, if further preliminary investigations prove fruitful, graphite sample characterization and the study of metallic element micro-distribution will be continued using micro-radiography, electron microscopy and micro-probe analysis as discussed above.

IV. CONTACTS WITH OTHER LABORATORIES

Contacts have been made and are continuing with laboratories interested in this research work. These include Brookhaven National Laboratory (Dr. Don Schweitzer), Oak Ridge National Laboratory (Dr. H. J. de Nordwall - until his departure and now Dr. A. P. Malinauskas), Los Alamos National Laboratory (Dr. Fred Schilling and Dr. Brad Holian) and General Atomic Company (Dr. Wayne Bell). Although experimental sorption studies similar to ours are not presently being done at these laboratories, all of these parties have an interest in the results which we expect to have forthcoming in the next several months. These interests are, in general, in connection with the analysis of HTGR safeguards.

V. PERSONNEL

Students who are working or have worked on this project do so in connection with graduate research thesis requirements. In two cases funds for student support came from sources other than the contract.

Mr. Joe R. Bryce - working for M.S. Degree; diffusion of strontium in graphite. Worked on King furnace cooling and gas purification systems and impregnation and analysis of Sr in graphite. On leave to serve in U. S. Army (unsupported).

Mr. Nai Chueh "Carl" Wang - worked on King furnace control system and graphite sectioning techniques. Decided to take professional degree (unsupported).

Mr. Paul T. Williams - first year graduate student. Strontium impregnation and diffusion experiments (supported).

Mr. Timothy D. Pyecha - working on a Ph.D.; on all aspects of the research (supported).

Of the Department faculty, besides the Principal Investigator, Professor Thomas S. Elleman has given technical advice and administrative support which is greatly appreciated.

Figure 1A. Photograph of Sorption Apparatus Furnace and Monitoring Systems, Detection System and Vacuum Bench Arrangement.

Figure 1D. Photograph of Sorption Apparatus on Vacuum Bench.

Figure 3A. Photograph of Graphite Tube Furnace (King Furnace) with Associated Support Systems.

H-327 Sample Weight: 3.826 gm.

BET Surface Area: 0.26 m²/gm.

Run Number	Time At Temperature (Hours)	Source Temperature (+ 2.0°K)	Sample Temperature (+ 5.0°K)	Cesium Source Vapor Pressure (Atm)	Cesium Sample Vapor Pressure (Atm)	Equilibrium Cesium Concentration		
						$\frac{\mu\text{gm Cs Sorbed}}{\text{gm Graphite}}$	$\frac{\mu\text{Mole Cs Sorbed}}{\text{gm Graphite}}$	$\frac{\mu\text{Mole Cs Sorbed}}{\text{m}^2 \text{ BET}}$
RO2	100	297	1070	*1.576(-9)	2.991(-9)	70.58	0.531	2.043
RO9	161	297	1168	1.576(-9)	3.125(-9)	63.35	0.477	1.833
RO1	208	297	1271	1.576(-9)	3.259(-9)	102.25	0.769	2.959
R12	217	302	1366	2.595(-9)	5.517(-9)	58.73	0.442	1.700
R13	103	323	1363	1.772(-8)	3.637(-8)	68.63	0.516	1.986
R14	135	348	1363	1.280(-7)	2.522(-7)	92.75	0.698	2.684
R15	121	373	1368	7.048(-7)	1.319(-6)	151.27	1.138	4.378

* Read as 1.576×10^{-9}

Table 1: Cesium Sorption by H-327 Graphite

Figure 4. Cesium Sorption by H-327 Graphite at 1365° K .