

Fission Product Sorptivity in Graphite

Reactor Concepts

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Final Report

Title: **Fission Product Sorptivity in Graphite**
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Project Overview

Both adsorption and absorption (sorption) of fission product (FP) gases on/into graphite are issues of interest in very high temperature reactors (VHTRs). In the original proposal, we proposed to use packed beds of graphite particles to measure sorption at a variety of temperatures and to use an electrodynamic balance (EDB) to measure sorption onto single graphite particles (a few μm in diameter) at room temperature. The use of packed beds at elevated temperature is not an issue. However, the TPOC requested revision of this initial proposal to included single particle measurements at elevated temperatures up to 1100 °C. To accommodate the desire of NEUP to extend the single particle EDB measurements to elevated temperatures it was necessary to significantly revise the plan and the budget. These revisions were approved. In the EDB method, we levitate a single graphite particle (the size, surface characteristics, morphology, purity, and composition of the particle can be varied) or agglomerate in the balance and measure the sorption of species by observing the changes in mass. This process involves the use of an electron stepping technique to measure the total charge on a particle which, in conjunction with the measured suspension voltages for the particle, allows for determinations of mass and, hence, of mass changes which then correspond to measurements of sorption. Accommodating elevated temperatures with this type of system required a significant system redesign and required additional time that ultimately was not available. These constraints also meant that the grant had to focus on fewer species as a result. Overall, the extension of the original proposed single particle work to elevated temperatures added greatly to the complexity of the proposed project and added greatly to the time that would eventually be required as well. This means that the bulk of the experimental progress was made using the packed bed sorption systems. Only being able to recruit one graduate student meant that data acquisition with the packed bed systems ended up competing for the graduate student's available time with the electrodynamic balance redesign and assembly portions of the project.

This competition for available time was eventually mitigated to some extent by the later recruitment of an undergraduate student to help with data collection using the packed bed system. It was only the recruitment of the second student that allowed the single particle balance design and construction efforts to proceed as far as they did during the project period. It should be added that some significant time was also spent by the graduate student cataloging previous work involving graphite. This eventually resulted in a review paper being submitted and accepted (“Adsorption of Iodine on Graphite in High Temperature Gas-Cooled Reactor Systems: A Review,” Kyle L. Walton, Tushar K. Ghosh, Dabir S. Viswanath, Sudarshan K. Loyalka, Robert V. Tompson).

Our specific revised objectives in this project were as follows:

- Experimentally obtain isotherms of Iodine for reactor grade IG-110 samples of graphite particles over a range of temperatures and pressures using an EDB and a temperature controlled EDB.
- Experimentally obtain isotherms of Iodine for reactor grade IG-110 samples of graphite particles over a range of temperatures and pressures using a packed column bed apparatus.
- Explore the effect that charge has on the adsorption isotherms of iodine by varying the charges on and the voltages used to suspend the microscopic particles in the EDB.
- To interpret these results in terms of the existing models (Langmuir, BET, Freundlich, and others) which we will modify as necessary to include charge related effects.

In pursuit of these objectives, five tasks were identified. The final outcomes of these five tasks (some with subtasks) are described below.

Task A: Selection of Students

Task Status

Eventually, two students were recruited who worked on this grant. Kyle Walton, a graduate student, was recruited right from the beginning of the grant as soon as the funding was in place and Robert Haffner, an undergraduate student, was recruited later in the grant.

Issues / Concerns

Initial funding of the grant was significantly delayed which delayed getting the students recruited. The initial proposal anticipated recruiting multiple graduate students but this did not occur even after the project objectives were modified.

Task B: Obtaining Equipment/Calibration

Task Status

Eventually all of the equipment identified for the project was obtained and assembled. This included the equipment for the packed bed sorption experiments as well as the oven and the furnace for the single particle experiments at elevated temperatures. Electrodynamic balances for the elevated temperature systems were constructed. This involved a lot of detailed custom design and shop work. The packed bed sorption experiments were the most straightforward to assemble and work began with packed beds well before the end of the project. One packed bed system was designated for iodine sorption on graphite studies and a second was assembled to

look at water sorption on graphite. Working with water vapor complemented the efforts underway with iodine. Water sorption on the same graphite powders was obtained with breakthrough curves being generated by taking the ratio of relative humidities at the inlet and outlet of the system. These studies helped us understand if a single packed bed sample could be regenerated so as to allow multiple adsorption measurements. The construction of the electrodynamic balances for elevated temperature measurements lagged significantly, however, and the systems were only assembled by the end of the project. Single particle data was not taken although the equipment assembly reached the point that some particles were eventually suspended. The characterization and calibration of these electrodynamic balances was the point that the project had reached when the end of the funding period was reached. Also, at the end of the project period work was in progress to calibrate an iodine fluorescence cell for use in determining iodine concentrations in the flows to the various test systems.

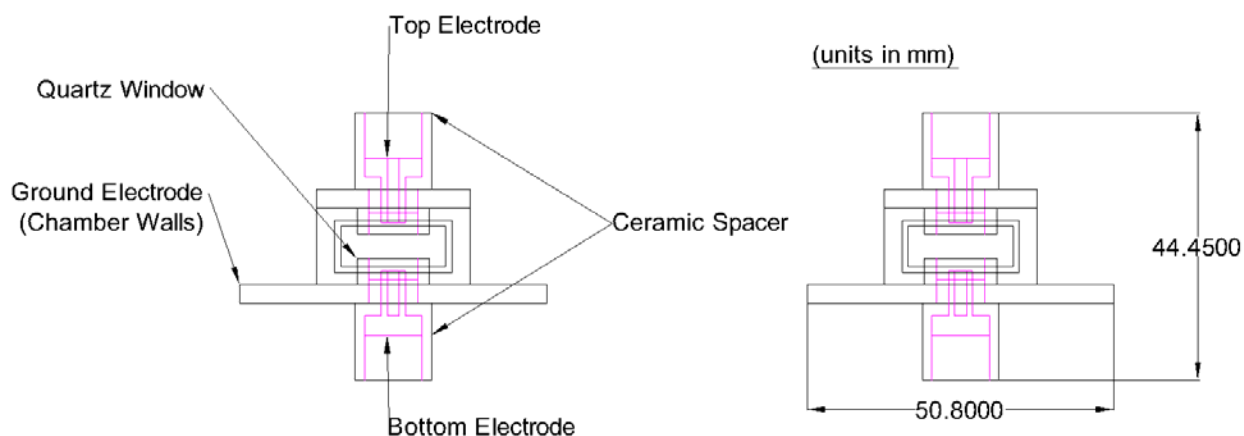
Issues / Concerns

Orders for many items experienced significant unexpected delivery delays from the various manufacturers. Custom shop work could not really begin until the ordered pieces of equipment were in and the custom designs could be finalized. A number of the ordered pieces of equipment had to be modified from their 'as received' condition in order to accommodate the inclusion of electrodynamic balances. The custom shop work took much longer than expected as well. This resulted in the construction of the electrodynamic balance systems for elevated temperatures not being completed until the end of the project which meant that no single particle data was generated. Not having an adequate iodine measurement system until right at the end of the project period may have contributed to high levels of uncertainty in the packed bed data that was acquired. Whatever the reason, there was significant difficulty in the interpretation of the sorption data from the packed bed experiments. Particle suspension with the new balance designs proved to be more difficult than with the previous room temperature balance design.

Task C: Modifications

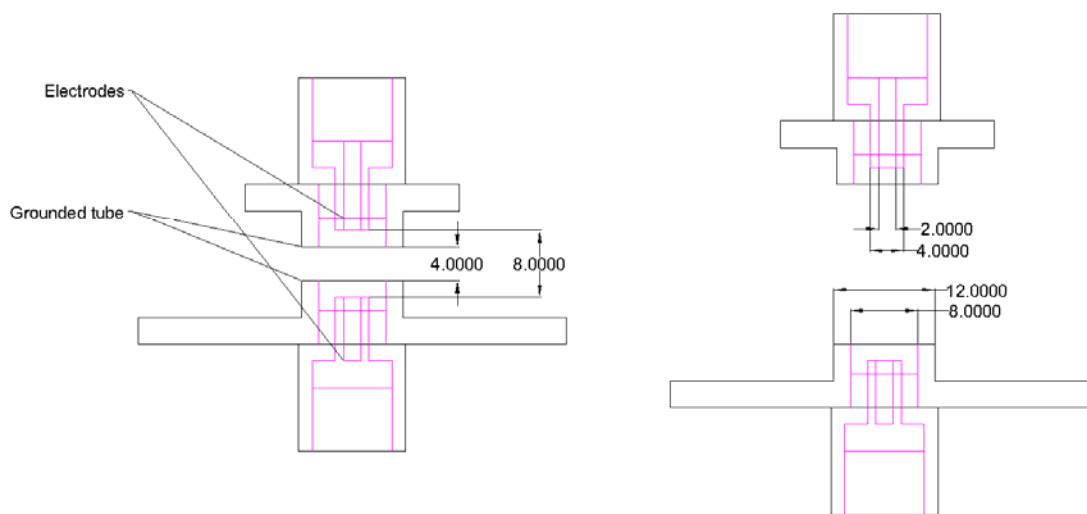
Task Status

The modifications to our original electrodynamic balance design (which also had to be rebuilt) were eventually completed taking into account the elevated temperatures that were expected and the materials that would be studied (specifically iodine). The newly designed electrodynamic balances, while similar to our original room temperature design, did incorporate some significant differences; especially with respect to the ring shapes and geometries. This required that the new balance designs be both characterized (an electric field/particle stability modeling problem) and calibrated. Details and photographs of the various systems at different stages of assembly are shown in the following figures.



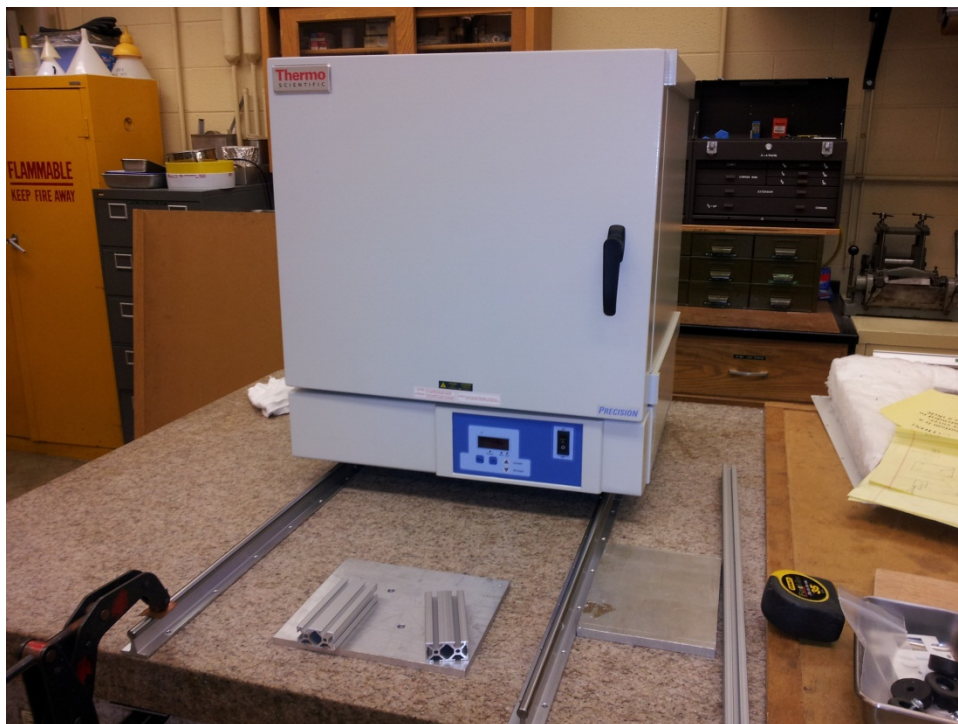
Schematic of the revised electrodynamic balance.

Electrode Spacing (units in mm):



Electrode design replicated from Heinsich et al. 2009*.

*Christian Heinisch, Jon B. Wills, Jonathan P. Reid, Theo Tschudia, and Cameron Tropeac, "Temperature measurement of single evaporating water droplets in a nitrogen flow using spontaneous Raman scattering," *Phys. Chem. Chem. Phys.* **11**, 9720–9728 (2009). DOI: 10.1039/b908555f



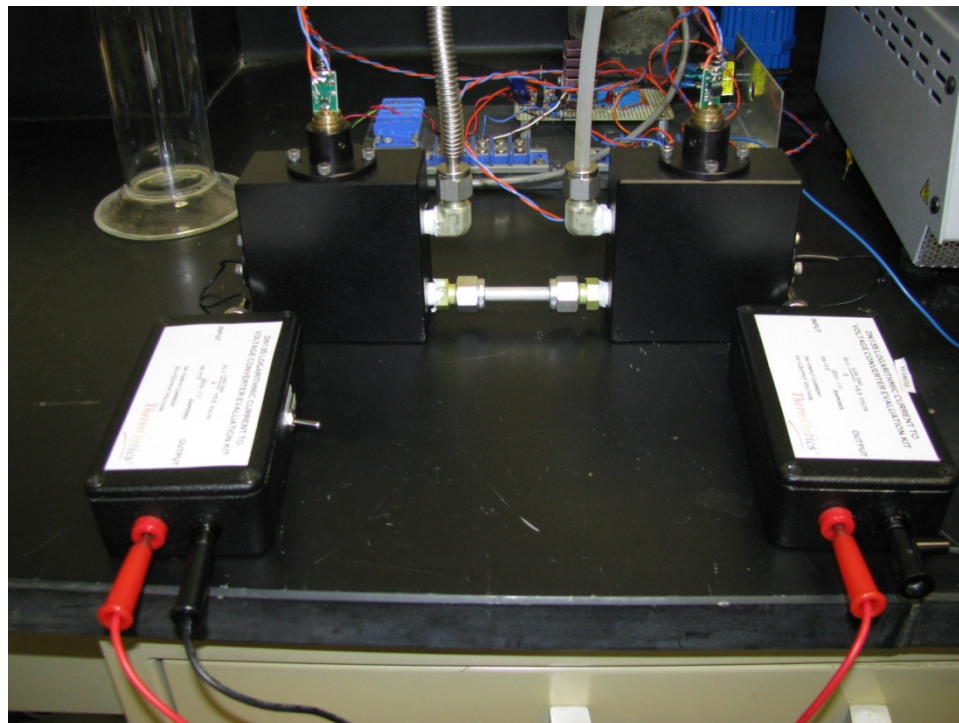
Low temperature furnace mounted on linear ball-bearing rails. With the modifications complete, the door is removable and permanently fixed to a support and the EDB in the balance chamber is mounted to the door so that the furnace can be physically withdrawn for access and particle suspension purposes and then repositioned to close the furnace for data acquisition. Gas, optical and electrical connections are permanently made through the door to the fixed balance chamber. Here, the furnace is shown located in the shop where necessary modifications are about to begin.



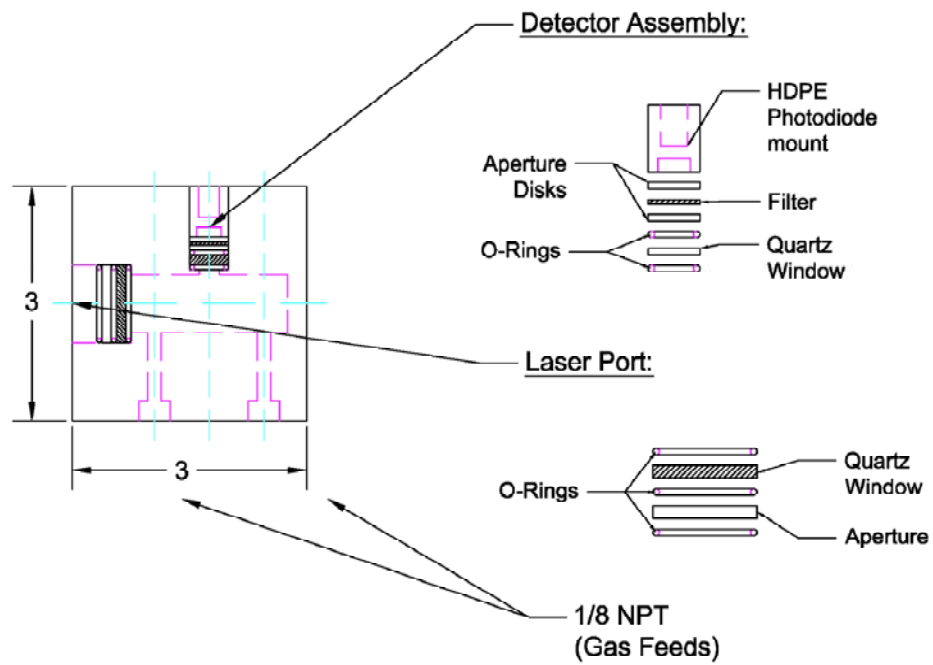
Close up of linear-ball bearing rails.



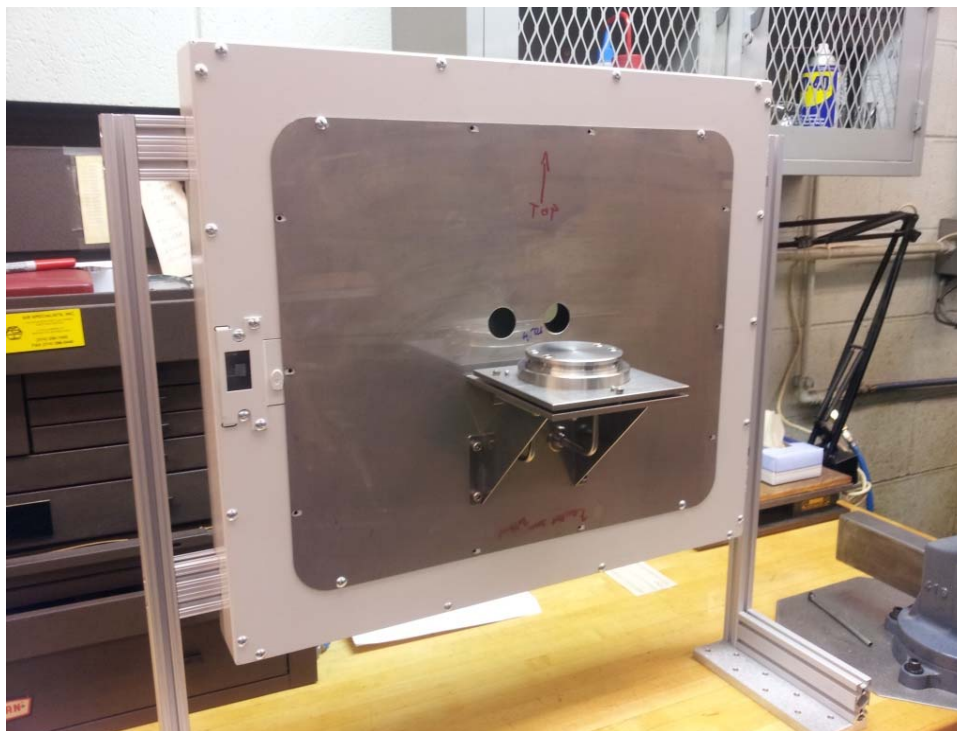
Haynes 230 top and bottom end caps for low-temperature EDB.



LIF Cells (Middle) in tandem for evaluation and calibration. Current to voltage converters (front) and laser power circuit (back) also pictured



Internal view of an LIF Cell with a diagram for photodiode and laser ports.



Modified door for the 300 °C EDB with bottom end cap and optical feedthroughs.



Modified door for the 300 °C EDB showing electrical and gas feedthroughs.



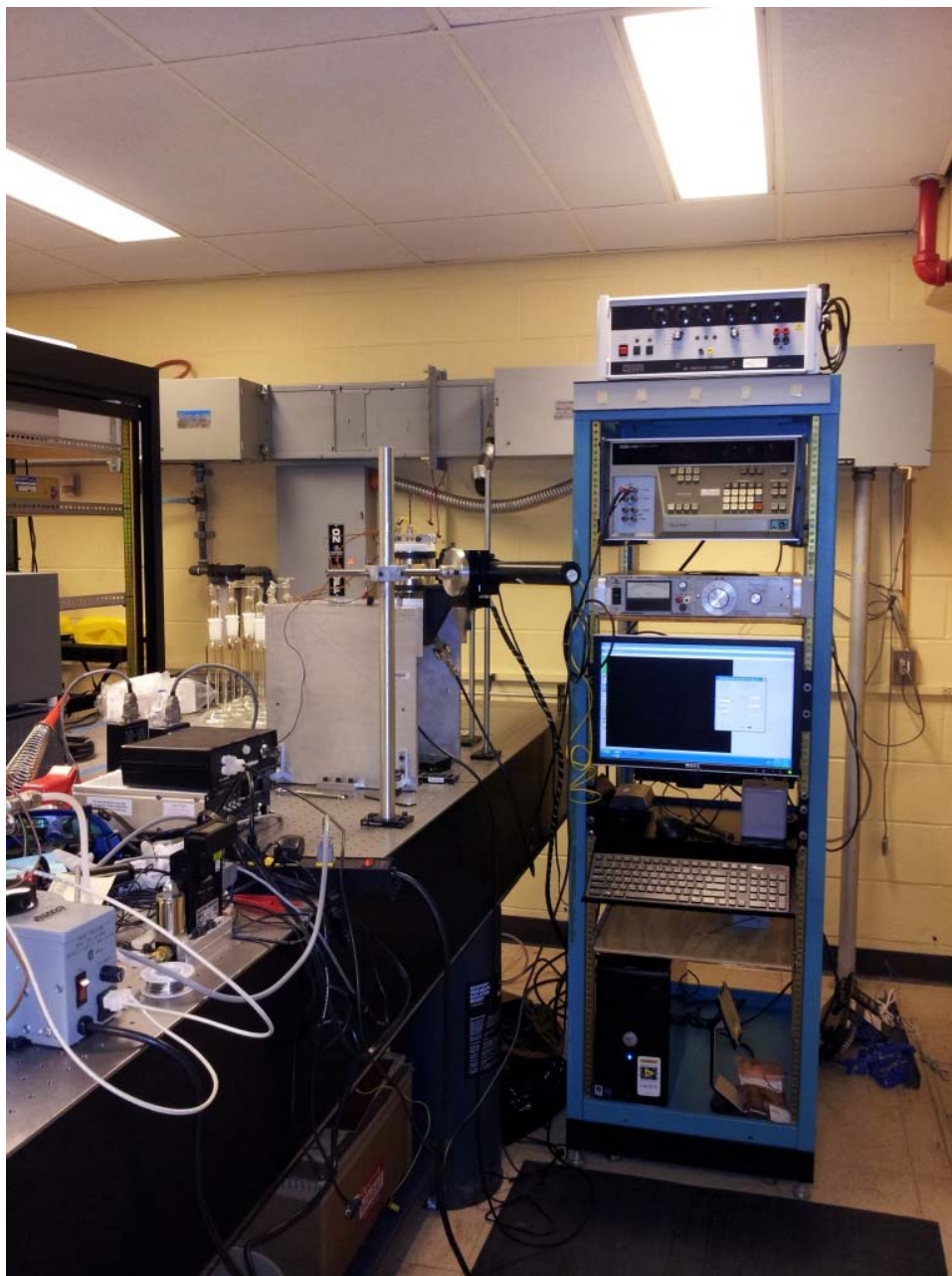
The arrangement of EDB systems for iodine adsorption measurements.



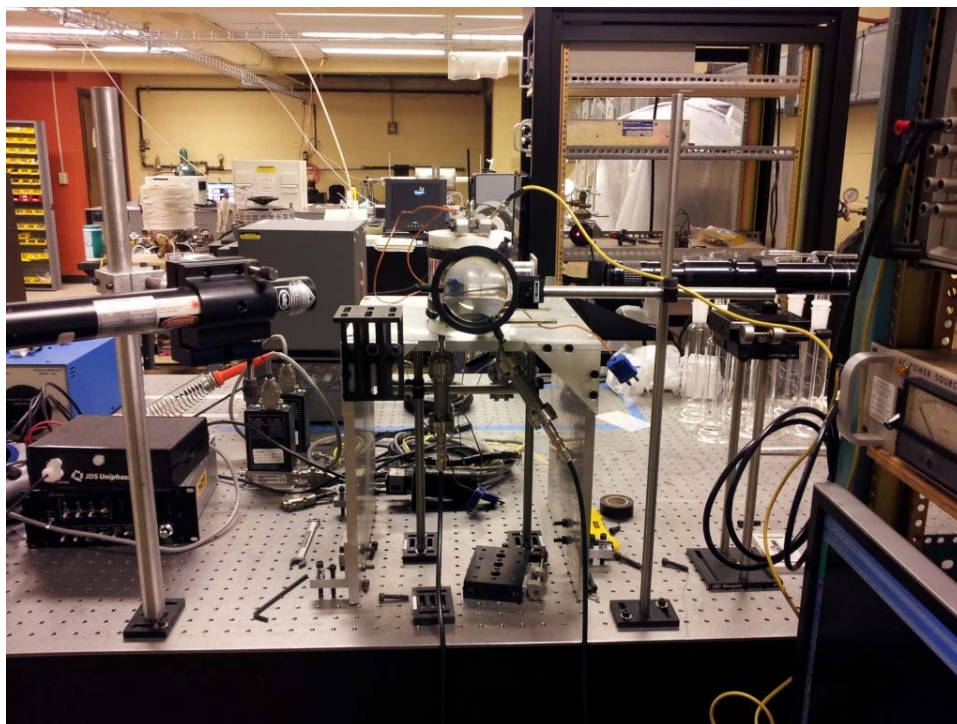
Data acquisition and levitation electronics for the very high temperature EDB. The high temperature furnace in 'as received' condition is shown at right before the door was removed and EDB modifications were made.



Data acquisition and levitation electronics for the high temperature EDB system.



Room temperature EDB and its equipment.



Redesigned room temperature EDB system.



Water vapor packed bed adsorption system.

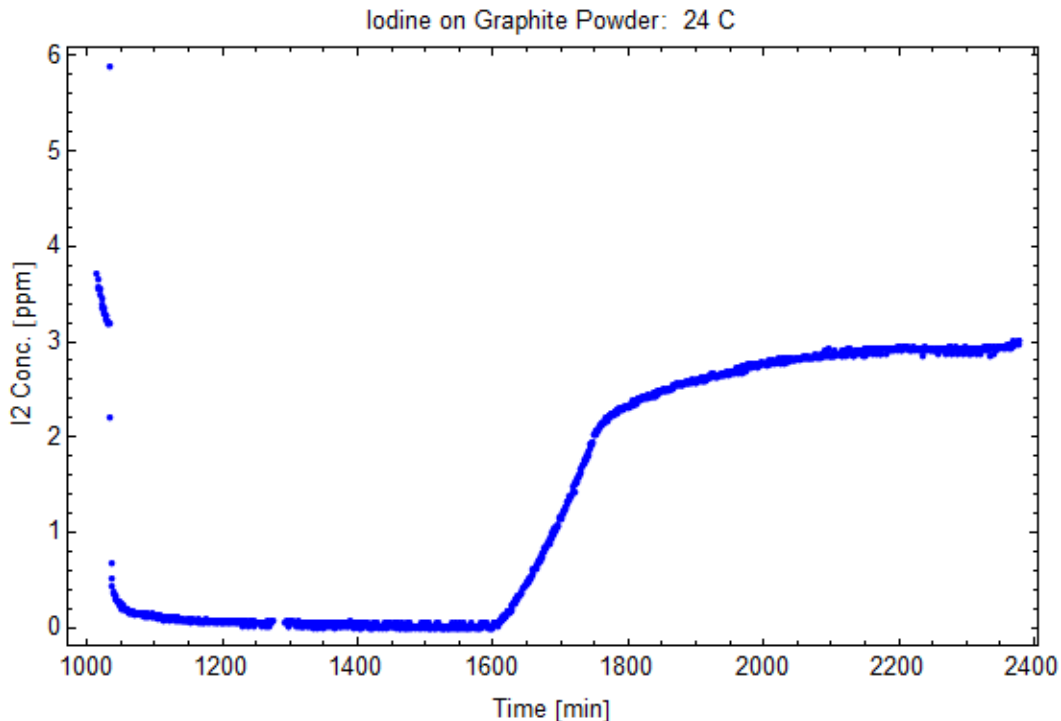
Issues / Concerns

The main issues here ended up being the delays experienced in the initial start of the project and in the delivery of ordered equipment, the extensive custom shop work that was needed which required significant time and experienced frequent delays as well, and that the project simply ran out of time.

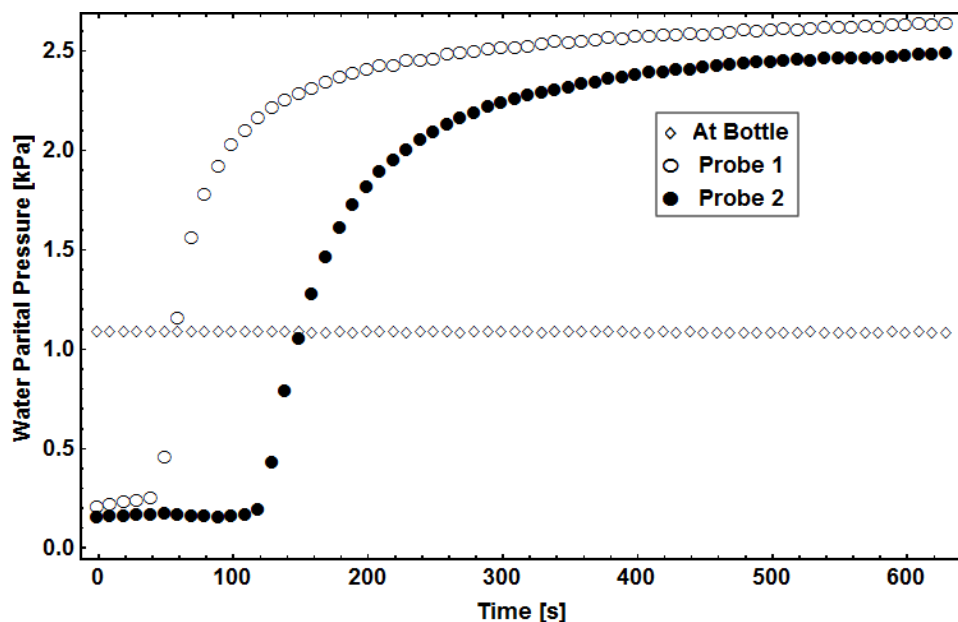
Task D: Data Acquisition

Task Status

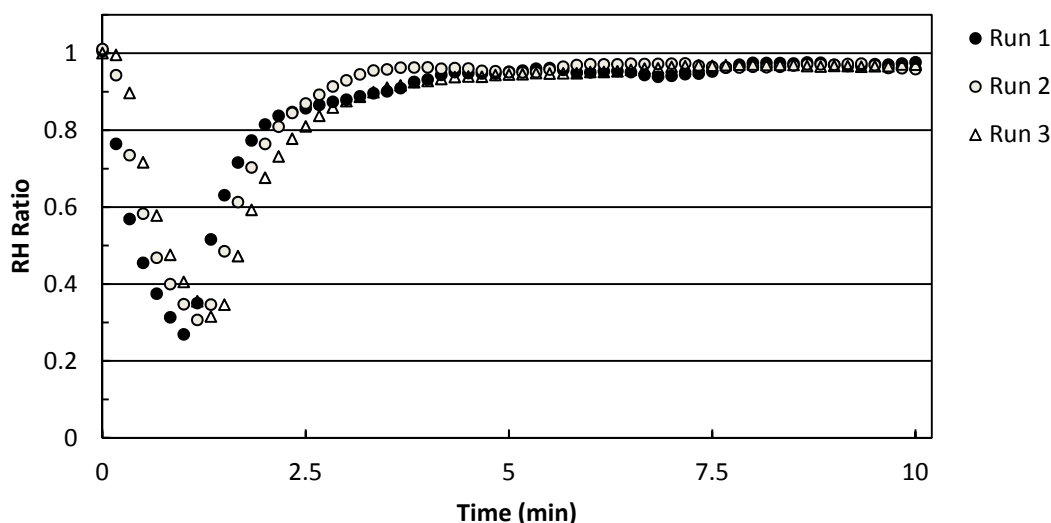
Much data was acquired with the packed bed sorption systems. The project period ended before any data could be obtained with the modified electrodynamic balance systems at elevated temperatures. Iodine adsorption at room temperature and at 100 °C with 10 ppm iodine on 99.99% graphite powder from Sigma-Aldrich was done at various times of 2, 3, 4, 6, 8, and 12 hours. The samples were analyzed by neutron activation analysis. These runs allowed an estimate to be made for the time until the graphite bed is saturated with iodine. This estimated time was needed for use in later adsorption measurements employing the LIF cell following its calibration. Concurrent measurements were made with a second system looking at water vapor sorption on graphites of interest to complement the iodine studies. Some typical data are shown below for iodine and water vapor.



A sample iodine breakthrough curve at room temperature.



Water partial pressures for an empty column bed.



Water vapor breakthrough curves on graphite at 100 °C.

Issues / Concerns

The main concern that persisted throughout the packed bed experiments was a high variability and lack of repeatability in the packed bed adsorption data. This was not as pronounced in measurements with water vapor but ended up being a major problem with respect to iodine measurements.

Task E: Data Analysis

Task Status

It proved impractical to apply any normal models for sorption to the iodine data because of the variability of the data and its lack of reproducibility. The end of the project did not leave time to explore any other modeling possibilities.

Issues / Concerns

Since no modeling and analyses were completed there were no concerns about them beyond the variability of the data that seemed to make the subject of analysis moot.

Overall Project Concerns

The greatest concern that became obvious in this work only after the end of the project period was that the change in the project objectives at the very start of the project resulted in a new project scope that was likely over-ambitious and did not leave enough time to meet all of the competing needs of the project. It is likely that a significantly higher degree of success would have been realized if the initial scope of the project had been retained. This might have been improved upon even further if that initial scope had been even more tightly focused by concentrating on only a single investigative modality such as focusing only the packed bed studies or only on the room temperature EDB studies, or on only one of the elevated temperature EDB studies. Trying to perform in all of these studies at once was very problematic; particularly given the delays in starting the project, the delays in getting the equipment that needed to be ordered, the delays in getting the custom work done on the balance systems, and the difficulty in recruiting sufficient numbers of students to tackle so many objectives at one time.

Overall Project Successes

The two greatest successes of this project were the completion of a comprehensive review of the literature on iodine sorption on graphite which resulted in a review paper on the subject being prepared, submitted and accepted and the actual construction of the modified EDB systems. Work will certainly continue using these systems as the importance of the problem of fission product sorption on graphite will certainly remain as long as interest in next generation very high temperature reactors continues.