Personal Statement, Relevant Background, and Future Goals

When I was three years old and living in Cuba, my dad and eleven of his mechanic shop friends set sail for the United States on a wooden boat constructed with scrap wood they had scavenged for months. It was not his first attempt to free our family from poverty and dictatorship. Only this time, his dream was realized when, off the Floridian coast, Dad and his friends were rescued by a cruise ship and brought to the US. Today, due to foreign policy changes, this same scenario would have resulted in a different outcome. Therefore, I recognize how fortunate I am to now live in a country where my father's hard work and determination has provided a better life for our family.

Although my mom, sister, and I received mail from Dad shortly after his safe passage, none of us realized we would not be reunited for five long years. My mom embraced the roles of both mother and father in a country laden with poverty. She cared for my younger sister and me while maintaining our farm, which was our main source of food and income. Furthermore, my mom ensured I attended school each day by pedaling her bicycle across farm towns with me on the back, instilling in me the importance of an education. As I reflect upon those years, the fortitude I learned from her is a characteristic I rely upon during my current journey towards a Ph.D.

When I finally arrived in the United States, I learned that my dad had started his own machine shop business and saved his profits to reunite our family. I acclimated to the US school system relatively well, albeit the language barrier proved to be somewhat overwhelming. However, some subjects such as math and science leveled the playing field when I compared myself to my peers, for I understood this material well and excelled. Early on, I noticed the difference between the resources readily available in the US, where clean water is the norm, and in Cuba, where clean water is not readily available. As I made friends with schoolmates who had also emigrated from developing regions, I shared the commonality of feeling guilt over the pleasure of having safe drinking water on a daily basis when I knew others were not as fortunate. As I grew closer to high school graduation, this guilt transformed into a sense of responsibility. Thus, I chose to pursue a career in environmental engineering with the personal goal of making a difference worldwide.

Attending the University of Florida and enrolling in the Environmental Engineering program was the first step toward attaining my goal. As I progressed in my academic experience, it became apparent that undergraduate research was the next critical step in my development. During my sophomore year, I connected with Dr. David Mazyck through his water and wastewater treatment course. I soon realized his research aligned with my interests, so I worked hard to join his research group. Dr. Mazyck's main research at UF includes the synthesis of various sorbents for removing mercury from water and air, an important global problem. My initial foray into the lab started with methods intended to better acquaint me with the laboratory environment, statistical analyses, and safety practices; however, when I was introduced to the concept of activated carbon, my interest was immediately aroused. I became fascinated with the fact that a material could be manipulated with respect to its physical (e.g., surface area) and chemical (e.g., oxygen functional groups) attributes to enhance its performance. Activated carbon, although viewed as a mature technology by some, still has numerous unknowns, and its use across a myriad of applications provides a link to making a global impact.

For approximately six months, several graduate students, including past NSF Graduate Research Fellows, mentored me. After excelling in my tasks, I was entrusted with independent research endeavors focusing on powdered activated carbon (PAC) for the removal of mercury (Hg) from coal-fired power plant flue gas. With this new research topic, I began to investigate the background of Hg and learned it is a controversial toxin that may cause ADD and/or ADHD in adults and developing children. Moreover, it is widely known that pregnant women should not ingest Hg during pregnancy to prevent potential birth defects. In an effort to increase safety, today there are apps available for download to your mobile device that can tell you the respective mercury concentration in any fish that can be consumed. Therefore, my research was and would continue to be of critical global importance for the benefit of our current and future generations.

Hg is captured from flue gas by injecting PAC before an Electrostatic Precipitator (ESP) or a Fabric Filter (FF), one of which is installed in all coal-fired power plants to avoid particulate matter from being emitted out of the stack. As I worked to familiarize myself with this system, I learned that flow rates through these ducts are particularly fast and therefore the residence time of the PAC to remove mercury is short (i.e., typically less than 1 second). I grew to understand there are 3 steps required for Hg removal by PAC. The first step is by bulk diffusion (whereby the contaminant and the PAC must contact). The second involves intraparticle diffusion and the third, actual adsorption by the PAC. Intraparticle diffusion is controlled by the pore size of the activated carbon in such a manner that as pore size increases, intraparticle diffusion increases. My undergraduate research focused on optimizing pore size for Hg capture, a necessary first step for my Ph.D. research.

When I first attempted to confirm improved Hg capture by increased pore sizes, I struggled to create the necessary conditions for the experiments. Initially, I constructed a test stand with a source of Hg, a means for heating, and other facets to simulate flue gas and verify the hypothesis that larger pore sizes are beneficial. As often occurs with research I encountered some obstacles, the greatest being how to create a consistent Hg influent concentration. Undeterred, I created air-phase Hg by passing air through a flask containing elemental Hg. The flow rate, humidity, and temperature of this gas dictated the Hg concentration. After months of trials and erratic data, including careful statistical analysis to verify replicates, I succeed in confirming improved Hg removal when I increased the pore sizes of the activated carbons I synthesized in the lab. While these outcomes are not too surprising, they are a necessary foundation for my Ph.D. work, discussed later, focusing on the identification of oxygen functional group(s) that promote Hg oxidation.

One year prior to graduation, Dr. Mazyck offered me an internship at Carbonxt, a start-up small business enterprise of which he is CEO. At Carbonxt I had an opportunity to supervise lab personnel and integrate with senior management gaining experience about balance sheets, profit and loss statements, and the frenetic pace of a small business where everyone assumes multiple responsibilities. Part of my duties included mentoring three (3) undergraduate students who were behind me in their studies. Their responsibilities included characterization of activated carbons, competitor analysis, and the compilation and organization of results from full-scale tests. As their supervisor, I was charged with teaching them how to operate the necessary analytical equipment and ensuring lab productivity. As their mentor, I quickly learned the delicate balance between instilling confidence, constructively pointing out areas of needed improvement and challenging them to develop.

My most memorable experience from this internship included fieldwork at a coal-fired power plant where I conducted particulate and mercury sampling across the electrostatic precipitator and at the stack during activated carbon injections. This 10-day experience focused on testing innovative activated carbon injection lances designed to enhance PAC distribution in the flue duct to help facilitate bulk diffusion. I was solely responsible for critical measurements that enabled the team to evaluate the difference between the four lances tested during that trial period. Indeed, all of the lances showed improvements, with one in particular increasing Hg removal by approximately 20%; this was quite a significant improvement in this environment. By using this lance, less sorbent and therefore lower costs, could be used to meet the EPA regulations. My time at the power plant allowed me to put various concepts into perspective regarding air pollution control devices and the efforts behind burning cleaner fuels. Through this experience I saw no limitations on where I would be able to make a difference with my research, intensifying my original goal to create a positive impact as an environmental engineer.

This past summer, after graduation, I continued working with the company, serving as a representative at the Air Pollution Control and Air Quality Conferences. These conferences exposed me to leaders of the activated carbon industry, equipment manufacturers, and utilities from across the country. Networking with researchers about the issues the power industry faces due to new regulations and monitoring concerns motivated me to become more involved. At several technical sessions, I learned about new methods the community has been using to treat various pollutants and the extent of the methods' success in the field. My enthusiasm grew given the possibilities to participate in the strategy the industry was taking by getting involved in the research, thus becoming part of the solution.

As a first year graduate student this semester, I have begun tackling the major research tasks associated with my activated carbon research project including preliminary titration studies (used to identify surface functional groups on carbon surface) and an extensive literature review. Within the graduate program, I took on the responsibility of mentoring a McNair undergraduate fellow, Jewel Cumberbach, with a research interest in the environmental field. Meeting with my mentee on a biweekly basis gives me the opportunity to guide her and discuss new findings in the field of mercury and activated carbon. As a result of our collaboration, she successfully presented our data and research at the UMBC McNair Conference 2014 in Atlanta, GA.

Overall my experiences in research and in the field have led me to a clear path focused on the exploration of specific mechanisms responsible for the binding of Hg to carbon surfaces in the presence of other flue gas constituents. My doctoral work will serve as a catalyst to initiate my career as a professor where I plan to continue mentoring by enthusiastically helping other students realize their academic and professional goals. Naturally I am drawn to helping women, but having grown up in an impoverished country, I clearly understand the importance of mentoring students from all over the world as my area of research, Hg, is a global pollutant. Tenure and promotion will require great attention, and once attained, my new goal would be to start small business enterprises to create technical, high paying jobs for others. At that stage of my career, I will have graduated at least one Ph.D. student who could potentially serve as the first member/employee. Dr. Mazyck will be a valuable mentor for me through this process. My witness to the opportunities he has created through his businesses, particularly for minorities and women, has instilled within me a passion to accomplish similar heights. I chose to pursue my Ph.D. at the University of Florida due to its high caliber of research, the unique Entrepreneurship and Leadership Certificate program, and the mentoring of small business development available to students, all of which combine to forge a superb foundation upon which to build my professional career. My track record is proof of my drive and eagerness to succeed; thus, I am confident that through my research endeavors I will make a global difference and bring honor to the NSF as a Graduate Research Fellow.

# Enhancement of Activated Carbon Oxygen Functional Groups for Enhanced Mercury Capture from Coal-Fired Power Plant Flue Gas

*Key Words: activated carbon, surface chemistry, mercury.*

Background: With the signing at the Minamata Convention on Mercury by over 92 countries last October, the environmental and health risks associated with anthropogenic mercury emissions became evident at a global stage. The United States, through the Environmental Protection Agency's Mercury and Air Toxics Standards (MATS), will be mandating the removal of about 90% of mercury from coal-fired power plant emissions starting April 2015. The technology most often employed is the injection of powdered activated carbon (PAC) impregnated with bromide/bromine (B-PAC), whereby bromide/bromine is added to enhance Hg oxidation and subsequent adsorption by the carbon (i.e., oxidized Hg is adsorbed much more readily than elemental Hg and both exist in flue gas depending on coal rank and coal halogen content). However, the Electric Power Research Institute (EPRI) recently presented at the Air Quality IX Conference (October 2013), and confirmed my assumption that the bromide/bromine within B-PAC can desorb and corrode essential power plant components. Although PAC is the best available control technology, improvements in its ability to remove Hg are warranted to reduce sorbent costs for compliance. For example, coal-fired power plants are expected to spend about $0.5 B annually on PAC [1]. Reduced compliance costs for the US utilities are important, and even more critical for developing nations so their global economic impact can be strengthened without the costly hindrance from environmental policies.

Hypothesis: It was proposed by Olson et al. (2003) that activated carbon has a specific site on its surface (carbene site, where the carbene is a carbon molecule with two binding sites, see Figure 1c) and they specifically state in their work that oxygen functional groups may not be primarily responsible for Hg removal from flue gas [2]. I am not aware of any research that attempts to resolve this controversy, and my hypothesis is that activated carbon's surface can be engineered to enhance the presence of oxygen functional groups (namely carboxylic, lactonic and carbonyls) to enhance Hg capture. These functional groups will be developed through controlling the temperature and oxygen content of the process gas as a post treatment during activated carbon manufacturing. The premise is these particular oxygen functional groups could accept an electron from Hg and serve as chemisorption sites for this now oxidized Hg. The illustration in Figure 1 depicts, from left to right, an activated carbon granule. Image B enlarges to a pore whereby it is hypothesized that elemental Hg is oxidized by specific functional groups on the carbon surface. Finally, image C enlarges the pore to depict the surface of the carbon with oxygen functional groups.

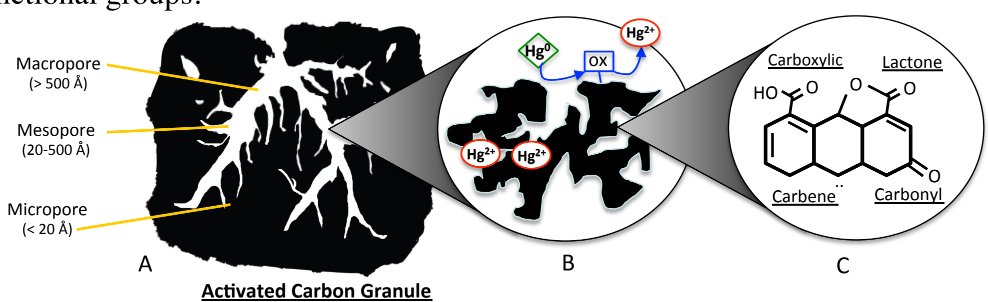


**Figure 1: A. Cross-sectional area of an activated carbon granule. B. Mercury oxidation and adsorption sites on the carbon surface. C. Surface functional groups on activated carbon.**

Research Objectives: The objectives of this research are to (1) enhance the carboxylic, lactonic and carbonyl oxygen functional groups on activated carbon (AC) through heat treatments, (2) characterize these ACs (e.g., surface area and quantity and type of oxygen functional groups), (3) compare these ACs in a simulated flue gas consisting of elemental Hg to assess Hg removal in comparison to the concentration of the functional groups, and (4) disseminate the results in journals (e.g., Environmental Science & Technology), conferences (e.g., Air & Waste Management Association), and possibly to the United Nations, for my advisor is one of 5 selected by the World Coal Association to assist the UN with the preparation of the Global Treaty for Hg.

Methodology: My previous research responsibilities included the construction of a Hg test stand in which modified ACs can be compared for the removal of Hg. Activated carbon synthesis will begin with lignite coal (chosen because it's the most popular base material for PAC manufacturing used in Hg capture), activated with steam at 850 deg. C to create porosity based on my previous research, followed by exposing the carbon to different ratios of oxygen and $N_2$ to create various oxygen functional groups, while the carbon is cooling from 850 deg. C to ambient (more specifically between 450 and 350 deg. C) The resulting surface area of these carbons will be similar, thus permitting evaluation solely on the impact from the oxygen functional groups. ACs will then be characterized via Boehm titration and Fourier Transform Infrared (FTIR).

My research is premised on Olson et al. (2003) having an incorrect hypothesis. Note, their work is purely theoretical, for they do not measure these carbene sites, nor I am aware how this could be accomplished [3]. In the event my hypothesis is incorrect, my research will still contribute to science because (1) at this time it is not well understood how to create the desired oxygen functional groups on activated carbon and (2) comparisons can be made regarding Hg capture and the concentration of functional groups on the carbon surface. Indeed, linear trends may not exist regardless of the hypothesis, and therefore, a multi-linear regression analysis will be used to assess the variables that have the biggest impact on Hg removal.

Intellectual Merit and Broader Impacts: Activated carbon surface chemistry is not well understood and less likely investigated as a plausible means to enhance carbon's removal of constituents (i.e., the AC industry turned to halogens). This research will not only provide a clearer understanding of Hg oxidation and adsorption onto AC, but could also pave the way for optimizing ACs for a myriad of other applications. Hg is a global concern and most nations have yet to address its removal from coal-fired power plant flue gas. Coal is presently about 35% responsible for electricity production in the US and more so for other developing nations. Hg emissions can remain airborne for up to one year, and therefore, research understanding its removal is critical. Throughout this work, mentoring undergraduate students is essential to provide them the same opportunities I experienced. I am particularly interested in mentoring minorities and women and will mentor them through the process of publishing (including them as co-authors), conference presentations (e.g., Air Quality), and through the development of a 4 part lecture to be presented in Dr. Mazyck's Activated Carbon Environmental Design course. Assisting with the next steps of the UN Global Treaty regarding Hg control technologies was a significant factor in pursuing my doctoral degree at the University of Florida.

**Literature Citations: 1)** ICAC, Air Pollution Control Technology Market Approaches Key Compliance Deadlines in 2015-2017. **2)** Olson, E.S. et al. Catalytic effects of carbon sorbents for mercury capture. Journal of Hazardous Materials, 2000. Vol.74, p 61-79. **3)** Olson, E.S. et al. The multiple site model for flue gas Mercury interactions on activated carbons: The Basic Site. Fuel Chemistry Division Preprints 2003. Vol. 48

# Intellectual Merit Criterion

### Overall Assessment of Intellectual Merit
Very Good

### Explanation to Applicant
This proposal seeks to improve the surface characteristics of the ativated carbon to increase the oxygen functional groups whcih appears to be a novel feature. The proposal is well written to certain level but more details on the underlying science would have been better.

# Broader Impacts Criterion

### Overall Assessment of Broader Impacts
Good

### Explanation to Applicant
This research has potential to contribute in the scientific field. The braoder impacts include training of the women engineers and presnrations at the conferences.

# Summary Comments
The intellectual merits and broader impacts could have been improved with further details.

# Intellectual Merit Criterion

### Overall Assessment of Intellectual Merit
Excellent

### Explanation to Applicant
The applicant has had excellent prior research experiences, both as an undergraduate researcher, and as an employee at a start-up Carbonxt. Her undergraduate GPA was 3.78/4.0 at the University of Florida, and she is currently enrolled in a phD program at University of Florida. Her proposed research to promote Hg oxidation by modification of activated carbon binding sites was very well written and well references. She included specific objectives and hypotheses. The applicant does not have any prior publications from her work as an undergraduate researcher.

# Broader Impacts Criterion

### Overall Assessment of Broader Impacts
Excellent

### Explanation to Applicant
The broader impacts of this application are also excellent. The applicant is female, and emigrated to the US from Cuba at age 8. In her first semester as a PhD student, she has engaged in mentoring, and she demonstrates a passion for mentoring females and underrepresented minorities.

# Summary Comments
Overall, I found this to be an excellent applicant with strong promise for an academic career.

# Intellectual Merit Criterion

## Overall Assessment of Intellectual Merit

Excellent

## Explanation to Applicant

The academic background of the candidate is strong, and the focus and determination exhibited is impressive. The work experience gained at a start-up company is both valuable (because it directly relates to the applicant's intended area of study) and also reflective, because it demonstrates the applicant has the characteristics required to be successful in research.

# Broader Impacts Criterion

## Overall Assessment of Broader Impacts

Excellent

## Explanation to Applicant

The research statement (related to mercury capture using activated carbon) is well-written and specific, and is supported by the applicant's previous experience as an undergraduate research assistant and employee at a company that works in the field.

# Summary Comments

This application clearly demonstrates a well-prepared applicant who has the academic foundation, focus, and determination required for success. The applicant has a very specific and well-articulated plan of study, as well as a detailed plan for how graduate study will be leveraged into career success.