QUARTERLY PROGRESS REPORT

September 2016 – November 2016

PROJECT TITLE: Development and Evaluation of Contaminant Removal Technologies for Landfill Gas Processing

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PROJECT WEBSITE: http://www.eng.usf.edu/~jnkuhn/Hinkley2015.html

Work accomplished during this reporting period:

For the period outlined in this fifth report, the poisoned and fresh catalysts have been visualized under scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS). This allows to view the catalyst under very high magnification (>2500X) and to determine all present chemical species in the catalyst system. The catalysts visualized were 1.34wt% Ni 1.00wt%Mg doped with 0.16wt%Pt on a $(Ce_{0.6}Zr_{0.4})O_2$ support (0.16Pt). Fourier transform infrared spectroscopy (FT-IR) was also done on all the catalyst samples including both the low temperature reforming catalyst (0.16Pt) and the high temperature catalyst which contains all elements except the platinum (1.34wt% Ni-1.00wt%Mg/$CeZrO_2$ referred to from now on as NiMg).

Figure 1 shows the images obtained for the 0.16Pt catalyst, it can be clearly seen that the catalyst surface changes when silica is present. Figure 1(a) shows the fresh catalyst, the surface is grainy and dark. Whereas Figure 1(b) shows the 1-month poisoned catalyst, silica is visible on the catalyst surface (white regions) and the particles seem bigger. Figure 1(c) shows the 6-month poisoned catalyst where the surface is almost completely covered in silica.

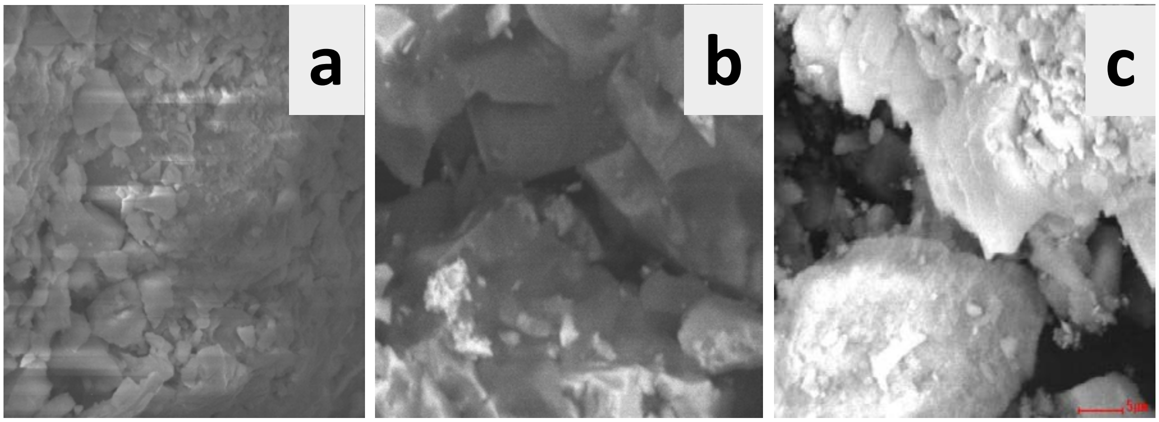
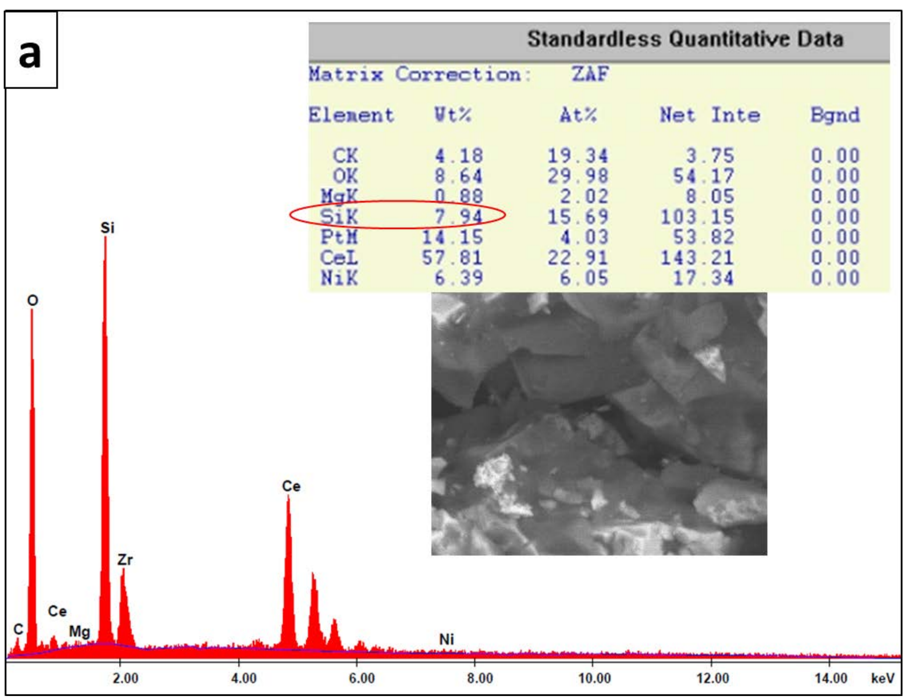


Figure 1: SEM images of 0.16Pt catalyst: (a) fresh catalyst, (b)1-month poisoned, (c) 6-month poisoned

Figure 2 shows the energy dispersive spectroscopy (EDS) results of both the 1-month poisoned and the 6-month poisoned 0.16Pt catalyst. Highlighted in red is the amount of silica detected in each sample. It can be seen that for the 1-month poisoned sample, the amount of silica detected was just under 8% by weight as seen in Figure 2(a). The 6-month poisoned sample shows the percent silica much higher at 39.89% by weight as expected as shown in Figure 2(b). This indicates that longer exposure to the uncleaned gas causes more deposition of silica on the catalyst.



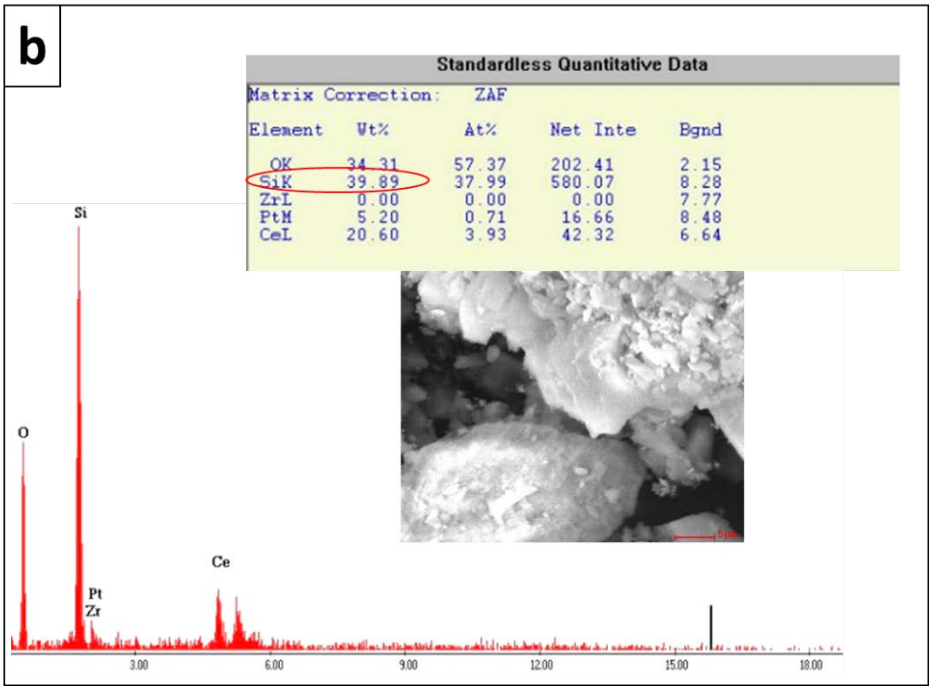


Figure 2: (a) SEM/EDS of 1-month poisoned 0.16Pt catalyst. (b) SEM/EDS of 6-month poisoned 0.16Pt catalyst.

Fourier Transform Infrared Spectroscopy (FT-IR) was done on all the catalysts both fresh and poisoned, to determine if there are any peak shifts or additions as shown in Figure 3. The presence of silica was evident by strong absorbance peaks in the 700-1200cm^{-1} range as indicated by the doted lines in the poisoned catalysts. This indicates that silica remained on the catalyst for the poisoned samples whereas the fresh samples did not display any silica peaks.

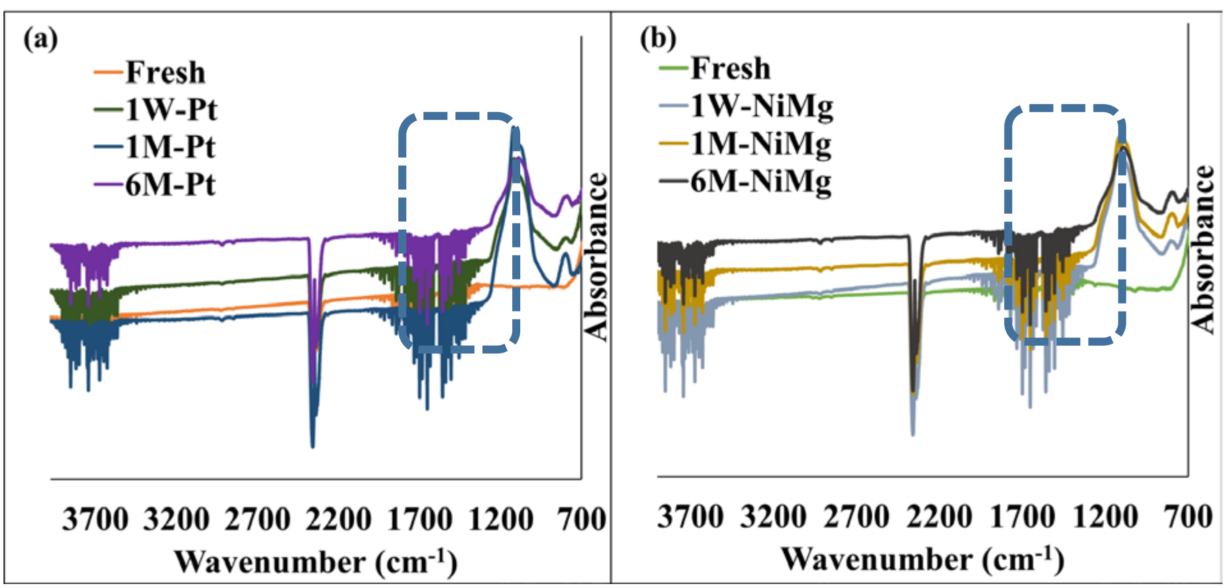


Figure 3: Fourier Transform Infrared Spectroscopy (FT-IR): (a) Fresh and poisoned 0.16Pt catalysts, (b) Fresh and poisoned NiMg only catalysts.

Furthermore, we have begun working on a simulation model using COMSOL® Multiphysics to model a variety of scenarios for flow and removal of siloxanes. This will help with developing a cost analysis and narrowing down the most efficient as well as economical removal technology and conditions.

The initial variables chosen to vary for the simulation model include two different adsorbents, three different bed heights, different relative humidity values as well as different inlet siloxane concentrations. Figure 4 shows some preliminary results using the two chosen adsorbents, activated carbon and silica gel. From the figure, it is evident that activated carbon has better performance and overall takes much longer to reach breakthrough compared to silica. Hence in the next phases of the simulation, activated carbon will be focused on as the adsorbent of choice.

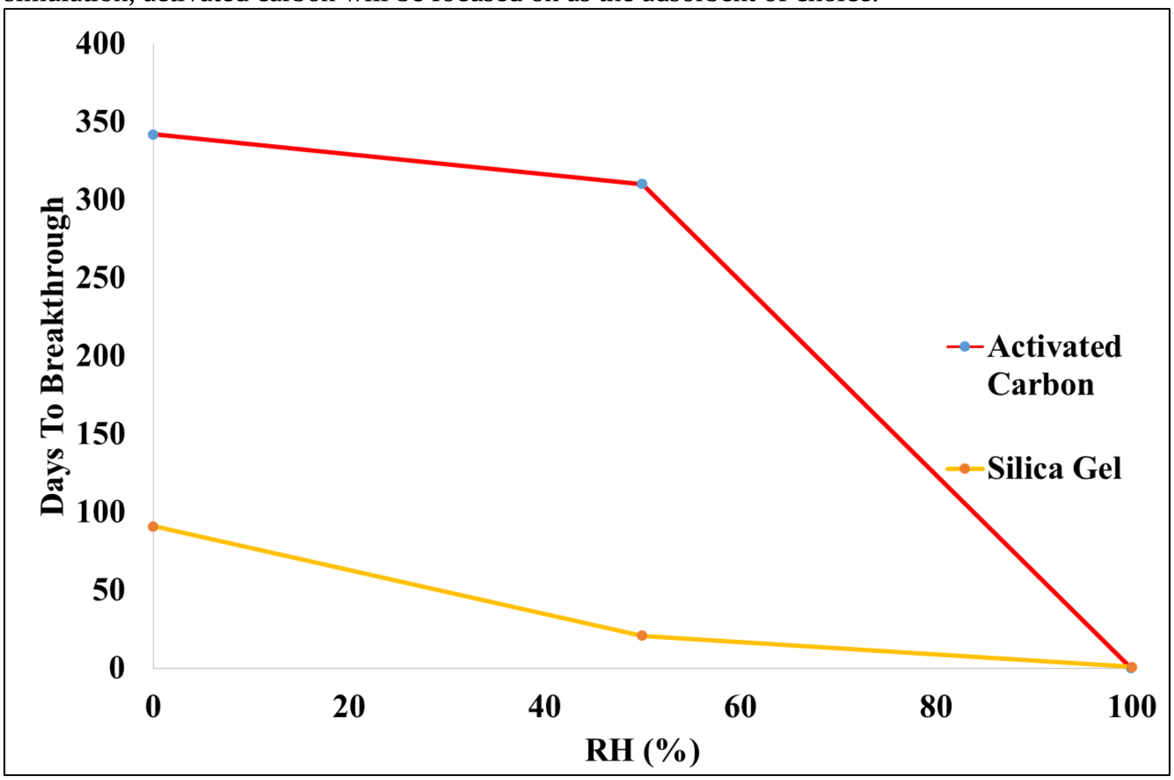


Figure 4: Effect of relative humidity on activated carbon and silica gel.

Future Tasks: The future direction would be to do reaction studies with the poisoned catalysts to determine the effect of the poisoning on the catalyst. The reactant conversion as well as product ratio will be calculated. The modeling will continue and various adsorbents and conditions will be studied before a detailed economic analysis can be done.

TAG Meetings:

A TAG meeting was held on November 9, 2016. Both the video and audio are at the link provided below.

Link: http://www.eng.usf.edu/~jnkuhn/Hinkley2015.html

This table identified the TAG member attendees at the meeting.

Name	Position	Affiliation	Email
Tim Vinson	Research Coordinator	Hinkley Center	tvinson@ufl.edu
Kelsi Oswald	Director	Pinellas County Department of Solid Waste	koswald@co.pinellas.fl.us
Canan "Janan" Balaban	Asst. Director	Florida Energy Systems Consortium	cbalaban@ufl.edu
Devin Walker	Process Engineer	BASF	dmwalker@mail.usf.edu
Matt Yung	Researcher	Nat. Renewable Energy Lab	Matthew.Yung@nrel.gov
Tim Roberge	CFO	T2C-Energy	tim@t2ce.com
Yolanda Daza	Process Engineer	Intel	yolanda.daza@intel.com

Tim Vinson, John Schert, Ralph Hirshberg, and Berrin Tansel were not able to attend.

Metrics:

1. List research publications resulting from **THIS** Hinkley Center project.

   None. Two publications are in review / revisions with peer-reviewed journals.

2. List research presentations resulting from (or about) **THIS** Hinkley Center project.

   - A poster at the USF COE Research Day (see bottom picture).
   - A poster at the Graduate Research Colloquium.
   - A poster at the USF Undergraduate Research and Arts Colloquium
   - A poster at the AICHE annual meeting in San Francisco.
   - A poster at the Engineering Research Day.

3. List who has referenced or cited your publications from this project.

   None

4. How have the research results from **THIS** Hinkley Center project been leveraged to secure additional research funding? What additional sources of funding are you seeking or have you sought?

   PI: Ergas, co-PIs: Kuhn, Joseph and Zhang. "Sustainable Bioenergy Production from the Organic Fraction of Municipal Solid Waste" Preproposal submitted to EREF. Submitted January 2016. $300,000 requested.

PI: Kuhn, co-PIs: Ergas, Joseph and Zhang. "Flexible Process for Thermochemical Conversion of Biogas to Fuels and Chemicals" Concept paper invited for full submission to DOE EERE. Submitted February 2016. $2,000,000 requested.

PI: Kuhn, co-PIs: Ergas, Joseph and Zhang. "Flexible Process for Thermochemical Conversion of Biogas to Fuels and Chemicals" Full proposal submitted to DOE EERE. $1,812,319 (total project cost with costshare = $2,026,429) requested.

Subcontract PIs: Joseph and Kuhn. Very large team grant for Department of Energy, "Modular Chemical Process Intensification Institute for Clean Energy Manufacturing". Pending.

5. What new collaborations were initiated based on **THIS** Hinkley Center project?

   No change.

6. How have the results from **THIS** Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders?

   None

Pictures:

The primary student researcher on this project is Nada Elsayed (4th year PhD student). Anthony Elwell is an undergraduate (senior) researcher also assisting with this research. The below pictures are of the team.