Bosch Carbon Catalyst Regeneration in Water I: Bosch Carbon Removal from Reacted Beads Utilizing Mechanical Agitation

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The ability to recover oxygen from metabolic carbon dioxide is crucial for crewed long duration missions in which the atmosphere must be recycled. Two physiochemical methods are primarily employed for this purpose: the Bosch process and the Sabatier reaction. This paper focuses on the Bosch process. It utilizes hydrogen in the presence of a catalyst to form water and solid carbon out of metabolic carbon dioxide. The solid carbon product deposits onto the catalyst and eventually causes reactor over pressurization issues. Multiple methods are currently being investigated to regenerate the catalyst's surface and break up the pressure causing carbon clogs. This paper explores whether water and mechanical abrasion would work to remove Bosch carbon by testing multiple washing conditions. The different washing conditions involved agitation intensity, heating, duration, and volume of water. It was found that it is possible to break up the clumps of carbon formed in the reactor through agitation with room temperature water in one hour and shows promise for completely cleaning the carbon off the beads' surface.

Nomenclature

AR	=	Air Revitalization
BSE	=	Backscatter Electron
CFR	=	Carbon Formation Reactor
CHX	=	Condensing Heat Exchanger
COR-CaTS	=	Carbon Dioxide Reduction Catalyst Test Stand
DI	=	Deionized
ECLSS	=	Environmental Controls and Life Support Systems
EDS	=	Energy Dispersive X-Ray Spectroscopy
ISRU	=	In-Situ Resource Utilization
ISS	=	International Space Station
LEO	=	Lower Earth Orbit
OGA	=	Oxygen Generation Assembly
PIG	=	Pipeline Inspection Gage
RWGS	=	Reverse Water Gas Shift
RWGSR	=	Reverse Water Gas Shift Reactor
S-Bosch	=	Series Bosch
SE	=	Secondary Electron
SEM	=	Scanning Electron Microscope
WPA	=	Water Processing Assembly
α	=	average mass reduction

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I. Introduction

THE Atmosphere Revitalization (AR) system on board the International Space Station (ISS) has a variety of functions. These functions include trace containment control, carbon dioxide removal, and oxygen regeneration. The technology that has been demonstrated on orbit for oxygen regeneration is the Sabatier reactor. The Sabatier reactor employs hydrogen to turn metabolic carbon dioxide into water and methane. The water is then sent to the Water Processing Assembly (WPA), and the methane is vented overboard. The water is cycled through the closed water loop until it is sent to the Oxygen Generation Assembly (OGA) which uses electrolysis to split the water into oxygen, which is sent to the cabin for the crew, and hydrogen that is returned to the Sabatier reactor to sustain the reaction [1]. Methane venting leads to an open loop Environmental Controls and Life Support System (ECLSS) system through the loss of hydrogen since it is essential to the Sabatier reaction and a main element of water. This open loop ECLSS system needs to be resupplied with water, which is currently sustainable while space travel is limited to Lower Earth Orbit (LEO), but this system would not be sustainable as space travel progresses. Methods are currently being tested to capture the hydrogen back from the methane and purify it for reuse, but a method has yet to be selected for a flight demonstration on the ISS [2], [3], [4].

The competing technology for oxygen regeneration that could close the AR loop without further post processing is the Bosch process. The Bosch process also utilizes metabolic carbon dioxide and hydrogen but instead produces water and solid carbon deposits. The water is then sent to the OGA to generate oxygen and hydrogen as it was with the Sabatier reactor. However, by creating solid carbon deposits instead of methane, the Bosch process conserves the hydrogen and thus closes the loop. It also opens a path for future In-Situ Resource Utilization (ISRU) efforts involving carbon which are currently being researched [5], [6], [7].

The Bosch process consists of three different reactions: Reverse Water Gas Shift (RWGS) shown in Equation 1, CO Hydrogenation shown in Equation 2, and Boudouard shown in Equation 3. Due to the reactions having different kinetics, prior work separated the Bosch process into a series of reactors and filtering membranes to make the reactions more efficient [5]. The series of reactors is depicted in Figure 1 and is commonly referred to as Series Bosch (S-Bosch). It consists of a Reverse Water Gas Shift Reactor (RWGSR), a Carbon Formation Reactor (CFR), the Polaris membrane (depicted in orange) to recycle carbon dioxide into the RWGSR, the Proteus membrane (depicted in green) to recycle hydrogen back into the RWGSR, and a Condensing Heat Exchanger (CHX) to capture the water for it to be sent to WPA. The lowest fidelity S-Bosch component is the CFR [8].

$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad (1)$$

$$CO + H_2 \rightleftarrows C + H_2O \quad (2)$$

$$2CO \rightleftarrows C + CO_2 \quad (3)$$

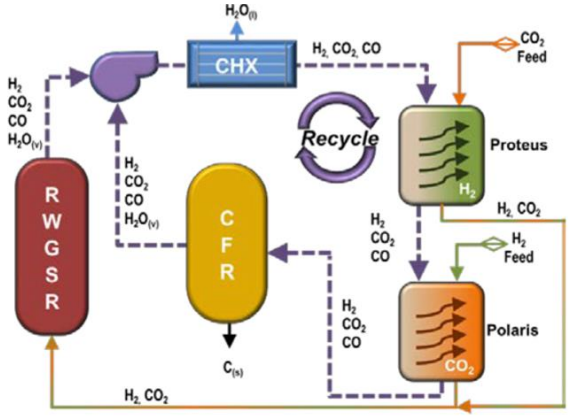


Figure 1. Series Bosch. *A schematic of the S-Bosch test stand consisting of a Reverse Water Gas Shift Reactor (RWGSR), a Carbon Formation Reactor (CFR), the Polaris membrane (depicted in orange), the Proteus membrane (depicted in green), and a Condensing Heat Exchanger (CHX) [9]. The purple symbol in the top left is a pump.*

Through previous work, a leading catalyst and reactor design combination for the CFR was determined to be small steel beads in a packed bed reactor [9]. This design was used in the testing detailed in this paper. Multiple CFRs have been designed and tested over the years, but none have been selected yet for flight demonstrations on the ISS [5], [9], [10], [11], [12]. Most reactors encountered problems due to over pressurization and catalyst degradation [5], [9], [10], [11], [12]. The over pressurization issues are caused by carbon building up inside the reactor as the reaction progresses causing clogs to form. Multiple ways of either cleaning the catalyst, preventing the carbon from adhering to the catalysts, or creating a removable catalyst have been tried [5], [9], [10], [11], [12], [13].

In prior unpublished work, removal of carbon from the catalyst was attempted through tumbling reacted steel catalyst beads. This tumbling was done without any liquid and showed reduction in the size of carbon clumps but never produced visibly clean beads. This technique is used in this work but with the addition of water to decrease the risk of combustible dust and act as a medium to capture the removed carbon. In the petroleum industry, steam thermally shocks coke deposits seen in pipes and is followed by the use of a Pipeline Inspection Gage (PIG) to mechanically remove buildup [14]. Due to coke's similarity to Bosch carbon and the petroleum industry's utilization of steam and mechanical abrasion, water with mechanical agitation was selected to serve as a preliminary study for thermal shock testing and as a continuation of the tumbling work. In the other papers in this series, catalyst degradation from this process is explored and the addition of thermal shock is investigated for its impact on experiment durations [15], [16].

II. Methods

Testing was comprised of four separate processes: carbon formation, bead washing, initial post washing analysis, and off-centered washing. These methods are discussed in detail below. All processes below took place with Amasteel S660 Cast Steel Shot that was between 1.40 mm and 2.36 mm, also referred to as "beads" due to their spherical shape.

A. Carbon Formation

The beads were processed in the Carbon Dioxide Reduction Catalyst Test Stand (COR-CaTS) in 5 batches. The beads were first placed in a 2-inch diameter quartz tube with three Fiberfrax S insulation disks on both ends and then loaded into the test stand with a bead weight of approximately 440 g. The quartz tube loaded with the catalyst was then purged with nitrogen before the heater was turned on. The heater was set to between 500 °C and 550 °C and the gas flow composition was 75% carbon monoxide, 15% hydrogen, and 10% nitrogen to run the CO Hydrogenation and Boudouard reactions that take place in a CFR. Initial system pressure was set to 15 psia. Once the pressure threshold of 16.5 psia was reached, the carbon formation reaction was stopped, and the heater was allowed to cool before the quartz tube was removed. The contents of the quartz tube were then placed in sealed bags and labeled.

B. Bead Washing

The experiments were performed inside of a Pure Lab HE 2GB glovebox. All materials passed into the box went through a vacuum chamber that was pumped down and repressurized with nitrogen three times before the materials were removed from the chamber and placed inside the box. In each experiment, samples from the resultant mixture of carbon and catalyst beads from the previously discussed carbon formation were measured out to 10 g. Samples were washed in a 400 mL beaker using deionized (DI) water. Experimental temperature was controlled manually by using a Thermoscientific SP131325 hotplate and digital thermometer for monitoring. Agitation was controlled using a stir bar and the spin speed setting controls on the hotplate, which correspond to estimated stirring speeds of 60 rpm (2), 125 rpm (4), 350 rpm (6), 700 rpm (8), 1100 rpm (10), and 1200 rpm (12) [17]. For the purposes of this paper, indicated speed settings will refer to the numerical speed dial settings on the hotplate. A filter for the samples was made from a sheet of wire mesh that was molded to fit inside of a metal funnel. The wire diameter of the mesh wire was 0.016 in. and the mesh size was 20x20 in accordance with ASTM E2016. This setup can be seen in Figure 2.



Figure 2. Experimental Setup of the Carbon Removal Tests.

Four parameters for optimal washing of the material samples were observed. As experiments were conducted, one set of

parameters would change while the rest remained constant to observe which changes hindered and which aided the removal of material from the catalyst beads. After testing each set of parameters, the experiments that followed would be set at the optimal parameter value that was found. The first parameter was temperature. Experiments were performed at 10 °C, room temperature, 40 °C, 60 °C, 80 °C, and 95 °C. The second parameter was duration of testing. Experiments were performed at 15 min, 30 min, 45 min, 1 hr, 2 hr, 5 hr, and overnight (18 hr) intervals. The third parameter was agitation. Experiments were performed without and with agitation at speed settings of 2, 4, 6, 8, 10, and 12 on the hot plate. The last parameter was water volume for the wash. Experiments were performed using 25 mL, 50 mL, 75 mL, 100 mL, 150 mL, and 200 mL of water.

1. Bead Washing Experiments without Post-Filtration Rinsing

In each experiment, both the material sample mass and washing volume of water were measured into the appropriate beakers. The water was heated to the desired temperature on the hotplate and then added to the material sample along with the stir bar. The hot plate was then set to the desired spin setting, and the heat was maintained manually by observation of the digital thermometer readings and adjusting the temperature settings accordingly. Then, the samples were washed for the time specified in the test matrix. Afterwards, the catalyst bead and water mixture was poured over the mesh filter into a waste collection beaker. The filter and funnel were tapped against the waste beaker to shake off any residual water, and then the beads were poured back into the experiment beaker. The hotplate was used to dry out the beads for 10 to 15 min before weighing the sample, and the weight of the beads was recorded. The beads in the sample were then counted by hand and the number was recorded.

2. Bead Washing Experiments with Post-Filtration Rinsing

During later testing, a post-filtration rinse of the beaker and beads was implemented. The experimental process remained largely the same as in Section B.1 with the exception that while the washed beads remained in the mesh filter, 25 mL of DI water was measured and poured into the experiment beaker to remove any material residue. The water used to rinse the beaker was then poured over the beads in the mesh filter to remove any residual loose carbon. After tapping the filter and funnel against the waste beaker to shake off any excess water, the beads were then poured back into the experiment beaker. The sample was then dried out using the hot plate for 10 to 15 min. Once dry, the beaker was allowed to cool before the sample was weighed and the measurement recorded. The beads in each sample were counted by hand and the resulting number was recorded.

C. Post Washing Bead Analysis

The beads were analyzed at multiple steps in the process by looking at physical and visual indicators, imaging under a Scanning Electron Microscope (SEM) for surface texture, and imaging under a SEM to determine the elemental make-up of the bead's surface.

1. Physical and Visual Analysis

Twenty-five unreacted catalyst beads and twenty-five catalyst beads that had been washed for 18 hr and then washed repeatedly until minimal coating removal was seen in the washing water were individually weighed on a benchtop laboratory scale. This was done to confirm the accuracy of the average mass of the catalyst beads, as reported by the manufacturer, and to compare the two sets of beads. The standard deviation was determined using the formula for sample standard deviation and the two sets of data were then filtered for outliers using two standard deviations from the mean of the sample. The following equations were used to calculate the average catalyst bead mass, using the bead density and sieve opening size information from Amasteel, and to normalize graphical data, respectively. With regards to Equation 4, 'm' is average bead mass, 'V' is the volume of one bead, 'ρ' is bead density, and 'D' is the bead diameter.

$$m = V\rho = \frac{4}{3}\pi\left(\frac{D}{2}\right)^3 * \rho \quad (4)$$

$$\alpha = Average\ mass\ reduction, \% = \frac{mass\ of\ material\ removed}{initial\ sample\ mass - (number\ of\ beads) * average\ bead\ mass} * 100\% \quad (5)$$

2. SEM Bead Surface Analysis

Several samples of beads were taken from various points in the process to be examined under a Hitachi S-3700N SEM. The samples were attached to the SEM's sample holder via carbon tape to minimize local charging and hold

the samples in place. The surface was then imaged in both variable pressure and high vacuum modes, depending on the amount of oxide and charging present on the surface of the material. Both backscatter electron (BSE) and secondary electron (SE) imaging were used to highlight surface texture or underlying material variation as needed, both at an accelerating voltage of 8 kV.

3. SEM Bead Surface Analysis

With the same microscope, a Hitachi S-3700N SEM, and the same sample preparation as in Section C.2, Energy-Dispersive X-ray Spectroscopy (EDS) was employed to determine relative composition of the materials to generate false-color mapping with an accelerating voltage of 15 kV.

D. Bead Washing Experiments with an Off-Centered Beaker

At the end of testing, the position of the beaker on the hotplate during experimentation was changed to increase turbulence in the beaker. This was the only change made to the experimental process described in Section B.2. For all previous testing, the experiment beaker was placed directly on the center of the hotplate. The beaker was moved approximately 2" back from the center of the hotplate, with the front being the dial control panel of the hotplate, and was stabilized in place with a weighed-down ring stand and a clamp attachment. The approximate off-center positioning was marked on the hotplate with a piece of tape.

III. Experimental Results and Discussion

Since the steel beads were processed utilizing four distinct methods, the results are presented here in the same manner. The results from each method are discussed in detail below.

A. Carbon Formation

The five batches of the carbon formation the catalysts beads underwent are detailed in Table 1. These results show that each batch performed similarly, thus enabling comparison between the batches in the bead washing results.

Table 1. Carbon Formation Results

Batch	1	2	3	4	5
Bead Mass (g)	440	440.5	428.61	437.48	439.83
Mass after Formation(g)	647.19	647.78	635.4	642.07	655.73
Carbon Mass (g)	207.19	207.28	206.79	204.59	215.9
Reaction Time (hr)	26.125	26.5	26.5	26.06	27.49
Carbon Formation Rate (g/hr)	7.93	7.82	7.80	7.85	7.85

B. Bead Washing

The reported results of the bead washing experiments are divided into sections based on changes implemented in the experimental process. The change made to the experimentation process initially was the addition of a post-filtration rinse of the beads, as described in the methods section of this paper. All graphs with y-axis 'α' represent the percent average mass reduction of each sample as defined in Equation 5.

1. Bead Washing Experiments without Post-Filtration Rinsing

The first set of tests were performed to verify the hypothesis that agitating the catalyst bead samples, rather than not agitating them, would result in a greater removal of material. Experiments in this set were performed using the same volume of water and duration. Tests that included agitation were conducted at the same spin setting. Temperature was the only other parameter that changed. As testing progressed, the experiments that included agitation performed substantially better than experiments without agitation in removing material from the beads. Additionally, it was observed that at higher temperature settings, less material was removed from the catalyst beads than experiments performed at cooler temperatures. Further testing was performed to confirm observations made about the effects of temperature on the removal of material from the catalyst beads and is discussed later in this paper. After the experiments concluded, it was determined that all proceeding experiments would be conducted with agitation. The results from this set of experiments are displayed in Figure 3.

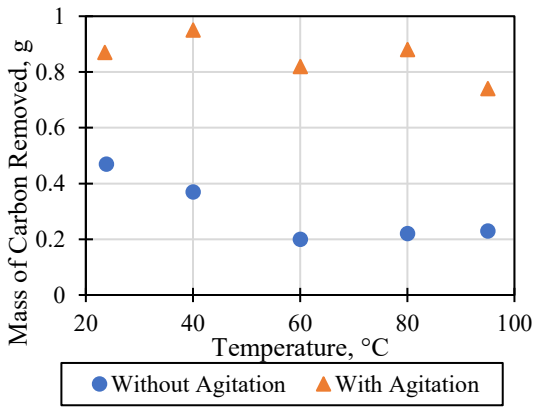


Figure 3. Material Removed from Agitation Vs. Non-Agitation. *In all experiments represented, all beads were washed with 25 mL of DI water. When agitated, a spin setting of 6 was used on a hot plate. Experiment duration was 15 min.*

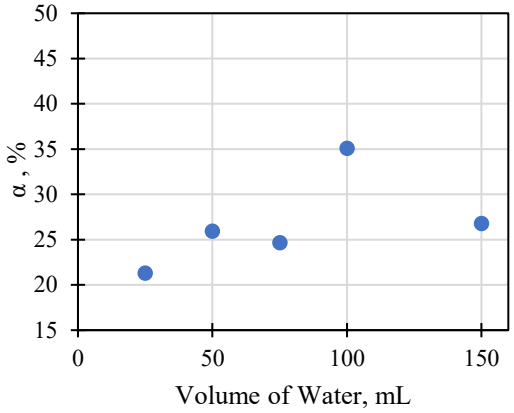


Figure 4. Material Removed from Volume of Water. *In all experiments represented, all beads were washed at room temperature and at a spin setting of 6 on a hot plate. Experiment duration was 15 min.*

A second set of tests were performed to determine what volume of water was ideal for removing the most carbon dust from the beads. Experiments in this set were performed at the same duration, temperature, and spin setting. As the volume of water increased, a maximum viable volume was observed. The percentage of material removed increased with the volume of water up until a volume of 100 mL was used. Afterwards, the increase in water volume resulted in a decrease of material removed. Since using a volume of 100 mL resulted in the greatest percentage of material removed, it was determined that all proceeding experiments would be conducted using 100 mL of water. The results from this set of experiments are displayed in Figure 4.

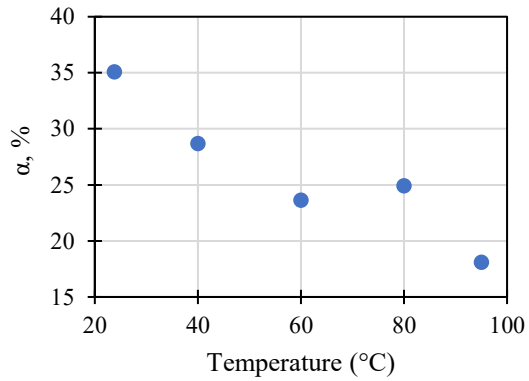


Figure 5. Material Removal from Temperature. *In all experiments represented, all beads were washed with 100 mL of DI water at a spin setting of 6 on a hot plate. Experiment duration was 15 min.*

A third set of tests was performed to establish the optimal temperature for removing carbon dust from the catalyst beads. Experiments in this set were performed at the same volume of water, duration, and spin setting. As testing progressed, experiments would perform worse as the temperature was increased. The heat would cause the carbon to form thick clumps that would cling to the beads during filtration, resulting in higher carbon dust accumulation inside the test beaker. Unexpectedly, it was observed that at higher temperatures a small amount of loose carbon in the water was carried by the emitted steam and deposited on the watch glass resting on top of the beaker. Using room temperature water resulted in the highest removal of carbon and no clumping was observed in the experiment. It was determined that moving forward, all proceeding tests would be performed using room temperature water. Results from this set of experiments are displayed in Figure 5.

2. Bead Washing Experiments with Post-Filtration Rinsing

An observation was made that during the filtration process, some of the carbon that was removed from the beads would adhere to the walls of the beaker, adding to the remaining mass of carbon during the post experimentation weighing process. A test was performed to verify whether implementing a post-filtration rinse of the test beaker and beads using DI water would aid in washing out the residual carbon. Experiments were performed at the same water volume, duration, temperature, and spin setting. 25 mL of DI water was used for the post-filtration rinse. Implementing the rinse worked exceedingly well to remove the carbon dust that remained adhered to the walls of the test beaker. It was then decided that all proceeding experiments would include a post-filtration rinse of the test beaker and beads. Results from this set of experiments are displayed in Table 2.

Table 2. Average Mass Reduction Normalized to Approximate Bead Mass from Post-Filtration Rinse

With Rinse	48.9%
Without Rinse	35.1%

A fourth set of tests was performed to determine the ideal spin speed setting for the stir bar in the test beaker. Experiments in this set were performed at the same water volume, duration, temperature, and the same volume of water for post-filtration rinsing. As the spin speed setting was increased, more material was removed from the beads. From this observation it was determined that all proceeding tests would be performed using a spin setting of 12 for the stir bar. Results from this set of experiments are displayed in Figure 6.

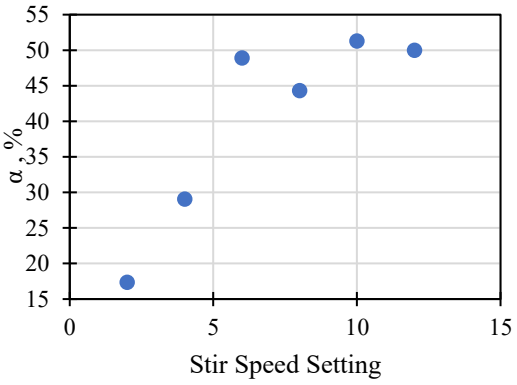


Figure 6. Material Removal from Spin Setting. *In all experiments represented, all beads were washed with 100 mL of DI water at ambient temperature. Experiment duration was 15 min, and 25 mL of DI water was used in a post-filtration rinse of the beads.*

One more temperature experiment was conducted after determining the optimal spin speed setting and implementing the post-filtration rinse. Since experiments performed well at ambient temperature it was hypothesized that sub-ambient temperatures would also aid in removing carbon dust. An experiment was performed at 10 °C and compared to another performed at room temperature. Both experiments had the same parameters for water volume, duration, spin setting, and volume of water for post-filtration rinse. The experiment at sub-ambient temperatures did perform better than the experiment at ambient temperature, however, it was determined that attempting to perform proceeding experiments at sub-ambient temperatures would not be efficient. Therefore, proceeding experiments continued at room temperature. The results from this experiment are displayed in Table 3.

Table 3. Average Mass Reduction Normalized to Approximately Bead Mass from Cold Water

10 °C	53.5%
Ambient Temp	50.0%

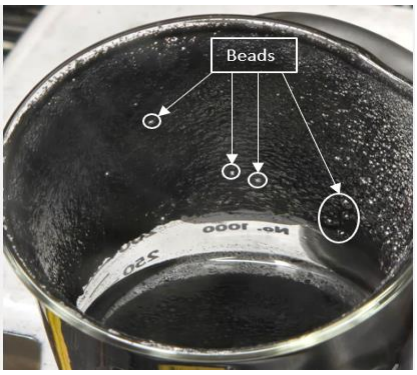


Figure 7. Coating Sludge Formation during 18 hr Duration Test. *Coating sludge formed on the walls of the beaker. Catalyst beads were embedded in the sludge. The beads were washed with 100 mL of DI water at a spin setting of 12. Experimental temperature was ambient, and 25 mL of DI water was used in a post-filtration rinse of the beads.*

Another set of tests was conducted to determine the optimal washing duration for fully cleaned or almost fully cleaned beads. Experiments in this set were conducted using the same volume of water, temperature and spin speed setting, and the same volume of water for the post filtration rinse. As experimental duration increased, more material was removed from the beads. The material and water formed a thick sludge that coated the walls of the beaker and the watch glass cover at longer durations as seen in Figure 7. Some of the beads became embedded in the sludge on the walls of the beaker. Despite this, the sludge was easily removed during the post-filtration rinse process. The results from this experiment are displayed in Figure 11 in Section D and represented by the blue dot data points.

Table 4. Mass Removed from Repeated Washing

Wash Number	1 hr	30 min
1	0.02 g	-
2	-	0.02 g
3	-	0.01 g
4	-	0.00 g

The set of beads from the 18 hr duration experiment were selected for continued washing. They were first washed again for a duration of 1 hr and then washed an additional three times over 30 min intervals. More material was removed from the beads with each wash. At the end of the third 30 min wash, no substantial amount of material was removed from the beads that could be reported on the measuring scale. Visually, there was material coming off the beads into the water. The beads continued to be washed in 30 min intervals until there was a minimal amount of visible material in the wash water. The results from this experiment are displayed in Table 4.

C. Washing Bead Analysis

The beads after washing were examined to discern whether the bulk of surface carbon was removed and thus the beads could be readily re-reacted. The cleaned beads were compared to unreacted beads to discern physical differences, reacted beads were compared to cleaned beads to inspect for signs of catalyst activity, samples of beads at multiple stages in the process were examined by SEM for surface characteristics, and then those same samples were examined with EDS to ascertain elements present on the surface of the beads.

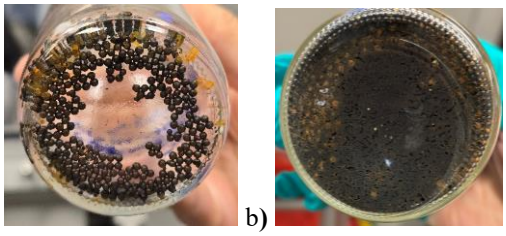


Figure 8. Oxide Formation. *a) Oxide formation on reacted washed catalyst beads, b) Oxide formation on reacted unwashed catalyst beads.*

1. *Physical and Visual Analysis*

The average mass of unreacted catalyst beads and catalyst beads that had been formed with carbon then washed for 18 hr and then washed repeatedly until minimal coating removal was seen in the washing water were compared to understand physical differences in the beads after cleaning. The average mass of the catalyst bead samples before reacting was 27.6 g with a standard deviation of 2.9 g, and the average mass of the catalyst beads after cleaning was 24.9 g with a standard deviation of 2.0 g. The high standard deviations make it difficult to draw any conclusions about mass loss or carbon removal by the mass data alone, even though it appears that the mass after washing is slightly less than before. However, later SEM analysis revealed that only a thin layer of carbon resides on the surface of the beads, thus supporting the statement that most of the carbon is removed in the cleaning process. Since the mass of individual beads has such a high standard deviation, it was determined that the calculated value of average bead mass using information from Amasteel would be used to normalize graphical data.

Another physical observation was made when the beads were placed into a container that had recently been washed and not fully allowed to dry. The beads in this container had visible signs of oxidation on their surfaces within a day as seen in Figure 8a. When those beads were exposed to DI water in open air they visibly oxidized within seconds. This is indicative of the accessibility of activation sites for further carbon formation on the catalyst. To validate oxidation as a sign of catalyst reactivation, uncleaned reacted catalyst was placed in DI water and left open to air to see if it would produce signs of visible oxidation. It also oxidized as seen in Figure 8b, but it did so in the order of hours. This proves that the catalyst surface had more available activation sites after cleaning but also that before cleaning activation sites were available. Due to this observation, a rigorous cleaning process to remove all carbon might not be necessary and focus was shifted to removing the carbon clumps.

2. *SEM Bead Surface Analysis*

Bead samples were taken from: unreacted beads; beads after the carbon formation reaction; and beads formed with carbon then washed for 18 hr and then washed repeatedly until minimal coating removal was seen in the washing water. The SEM images in Figure 9 show how the different processes affect the beads surface texture. Figure 9a is an image of a bead before any processing. The surface of the bead appears smooth and uniform with surface discolorations. The surface discolorations are due to a build-up of oxidation (rust) on the beads which can be better identified in Figure 10a. The coated bead from after reacting in COR-CaTS (Figure 9b) shows a relatively uniform coating of carbon on the bead. Although the carbon may seem to be evenly coating the bead in Figure 9b, Figure 9c of a bead post-washing shows a crack in the bead's surface. The crack shown in Figure 9c was expected because the Bosch process removes catalyst material during the reaction due to the Boudouard reaction as discussed in depth in a later paper in this series on catalyst degradation [15].

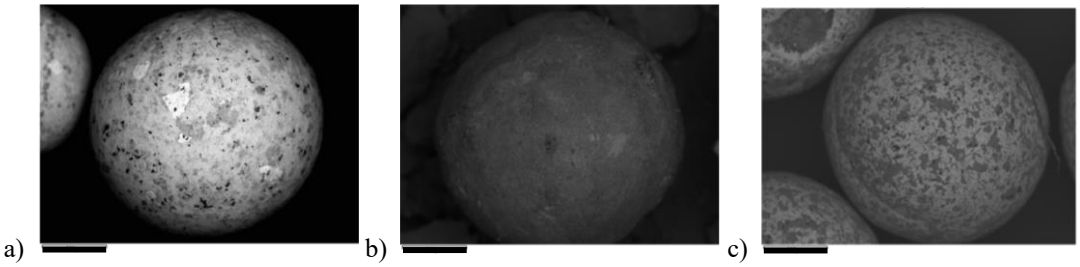


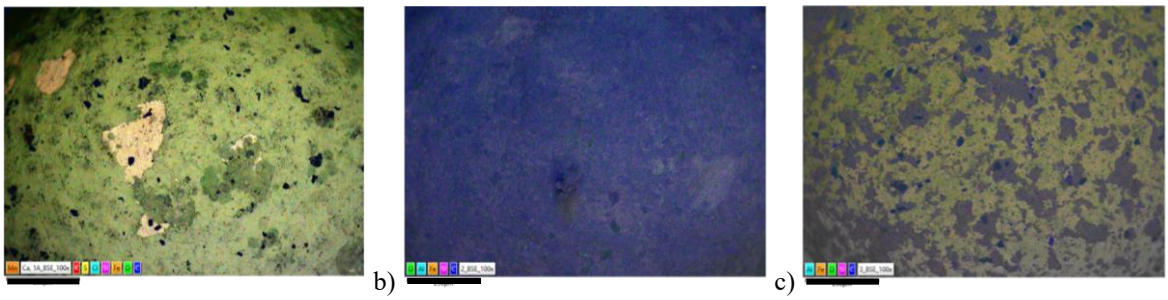
Figure 9. Bead Surface Texture Images. *All images were taken at a magnification of 50x in BSE and have a 500 µm scale bar. a) Beads before experiments. b) A bead after the carbon formation reaction. c) Beads formed with carbon then washed for 18 hr and then washed repeatedly until minimal coating removal was seen in the water.*

3. SEM Bead Composition Analysis

The same bead samples that were analyzed in Section C.2 were analyzed in this section with those samples being: unreacted beads; beads after the carbon formation reaction; and beads formed with carbon then washed for 18 hr and then washed repeatedly until minimal coating removal was seen in the washing water. Figure 10a depicts the surface composition of a bead before being reacted in COR-CaTS. The majority of the composition is oxygen and iron since beads are typically rusted when placed into COR-CaTS. Carbon, silicon, sulfur, and manganese are expected as well since they are part of the bead additives shown by Table 5. The bead depicted in Figure 10a also shows trace amounts of potassium and chlorine, which is likely due to environmental contamination. The bead that has undergone the Bosch process, Figure 10b, shows a relatively uniform distribution of carbon with trace amounts of oxygen, iron, silicon, and aluminum. These trace elements likely come from viewing the surface of the bead through the carbon layer due to the penetrative nature of EDS imaging. The final image, Figure 10c, depicts the beads after washing until the water seemed minimally saturated with material removed from the beads surface. This result shows that much of the catalyst surface has been regenerated during the washing process and thus can be re-reacted. Though earlier it was revealed through testing that regeneration of activation sites wasn't strictly necessary as the reacted but uncleaned beads could oxidize, more activation sites became readily available with more agitation time. Further testing will be needed to determine if the extra time to reveal more of the surface is beneficial to a regeneration process from a time perspective.

Table 5. Bead Alloy Composition

Element	Percentage
Carbon	0.8-1.2
Manganese	0.6-1.2
Silicon	0.4 min
Sulfur	0.05 max
Phosphorous	0.05 max



a) b) c)

Figure 10. Bead Surface Composition Images. *All images were taken at a magnification of 100x and have a 250 µm scale bar. In the images, green is oxygen, light orange is iron, dark blue is carbon, and pink is silicon. a) The image is of a bead before experiments with dark orange being manganese, red being potassium, yellow being sulfur, and cyan being chlorine. b) The image is of a bead after the carbon formation reaction with cyan being aluminum. c) The image is of a bead formed with carbon then washed for 18 hr and then washed repeatedly until minimal coating removal was seen in the washing water with cyan being aluminum.*

D. Off Centered Beaker Experiments

Washing duration experiments were repeated at shorter durations to determine the minimum agitation duration needed to break up the solid masses of carbon material within the samples. One additional change was made to the setup of the experiment. The position of the beaker on the hotplate during experimentation was off-centered and stabilized in that position to generate more turbulent mixing. This change was made due to the observation of material accumulating in dead-spaces on the edges of the beaker while centered on the hotplate. The cause of these dead-spaces could be due to the size of the beaker, the strength of the vortex, or the consistent position of the vortex. All of the experiments in these sets were conducted at the same volume of water, temperature, spin setting, and volume of water for the post-filtration wash. Experiment samples initially contained carbon-coated catalyst beads as well as solid masses of material. With the change in beaker position, the amount of material removed significantly increased at shorter duration times. However, there is not a graphically determined trend associated with duration changes as is seen with the previous duration experiments represented by the blue dots in Figure 11. Instead, visual observation of the washed beads was used to confirm the remaining presence of lingering solid masses of carbon material. Bead samples that contained no or fewer solid masses of carbon material after washing were deemed optimal for indicating

the minimum amount of agitation time needed in a reactor in order to remove pressure-causing carbon masses. The beads were counted afterwards, and the data for the shorter duration experiments with an off-centered beaker is displayed in Figure 11 and represented by the orange triangle data points. Images of the remaining carbon masses in samples after washing are displayed in Figure A1 in the Appendix.

Visual observation of the beads showed that agitating the samples at durations of 1 hr and 1.5 hr was enough to break up any solid carbon masses. Samples washed at shorter durations had remaining solid carbon masses. Tests were then repeated at durations of 1 hr and 45 min to confirm the repeatability of results. These experiments were all conducted at the same volume of water, spin setting, temperature, post-filtration rinse volume, and off-centered beaker position. Visual observation was used to confirm the absence of solid carbon masses. Images of the beads from the 1 hr and 45 min repeatability tests are displayed in Figure A1cd and A2, and Figure A1ef and A3 respectively which are located in the Appendix.

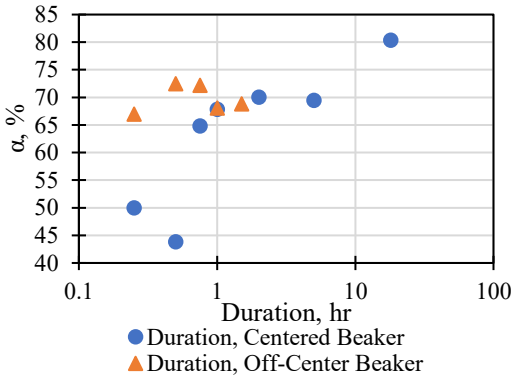


Figure 11. Material Removal from Duration. *In all experiments represented, all beads were washed with 100 mL of DI water at a spin setting of 12 on a hot plate. Experiments were conducted at ambient temperature, and 25 mL of DI water was used in a post-filtration rinse of the beads.*

IV. Conclusion and Future Work

The technique explored in this paper yielded results with great potential and opened a path forward for Bosch to become a viable technology for future applications. These results showed that in a benchtop testing environment, mechanically agitating reacted beads off-center in room temperature water at the top speed of the hot plate for 1 hr broke up all pressure causing clogs. Additionally, mechanically agitating reacted beads centered on the hot plate with the same conditions for 18 hr and then repeatedly agitating until minimal coating removal was seen in the washing water significantly increased the available activation sites of the beads. The availability of the beads' activation sites was established based on the beads' quick reaction with water to produce rust and SEM imaging of the beads' surface showing large patches of iron. Despite the many questions answered in this paper, some questions remain and are answered by later papers in this series or are planned to be answered by upcoming testing.

The questions answered in the later papers in this series are what happens to the beads internally as they are reacted and cleaned, and would thermally shocking the beads aid in reducing the cleaning time as seen in the petroleum and automotive industries? The paper in this series on thermal shock found that it would be helpful as it reduced the time necessary for agitation of the beads by half and the paper in this series on what happens to the beads throughout the process revealed that degradation, though present, was minimal [15], [16]. Current testing is underway to create lab scale devices that could be sized up and put into a reactor to test the techniques discussed in this first paper. The two most pressing devices are a carbon-water separator and an agitation mechanism.

The investigation into a carbon-water separation device will be the first step towards purifying the water used in cleaning the carbon-coated beads and measuring the quality of the water after purification. After the separation process, the water can then be either added back into the water stream or cycled back through the process depending on the purification seen after the carbon-water separation device. The agitation mechanism will help create more frequent collisions and thus more standard results. It will hopefully decrease the required agitation time even more. All these findings will then be used to inform the design of a reactor that will be capable of mechanically agitating the beads. Prototypes will be developed based on the findings from the benchtop testing and then evaluated and down selected. The selected prototype will then be refined for potential flight applications. Though more proof-of-concept work is necessary, this technique of using water to assist in the mechanical removal of Bosch carbon buildup through agitation has proven itself a good candidate for future work and has a realistic path forward towards becoming a viable reactor technology.

Appendix

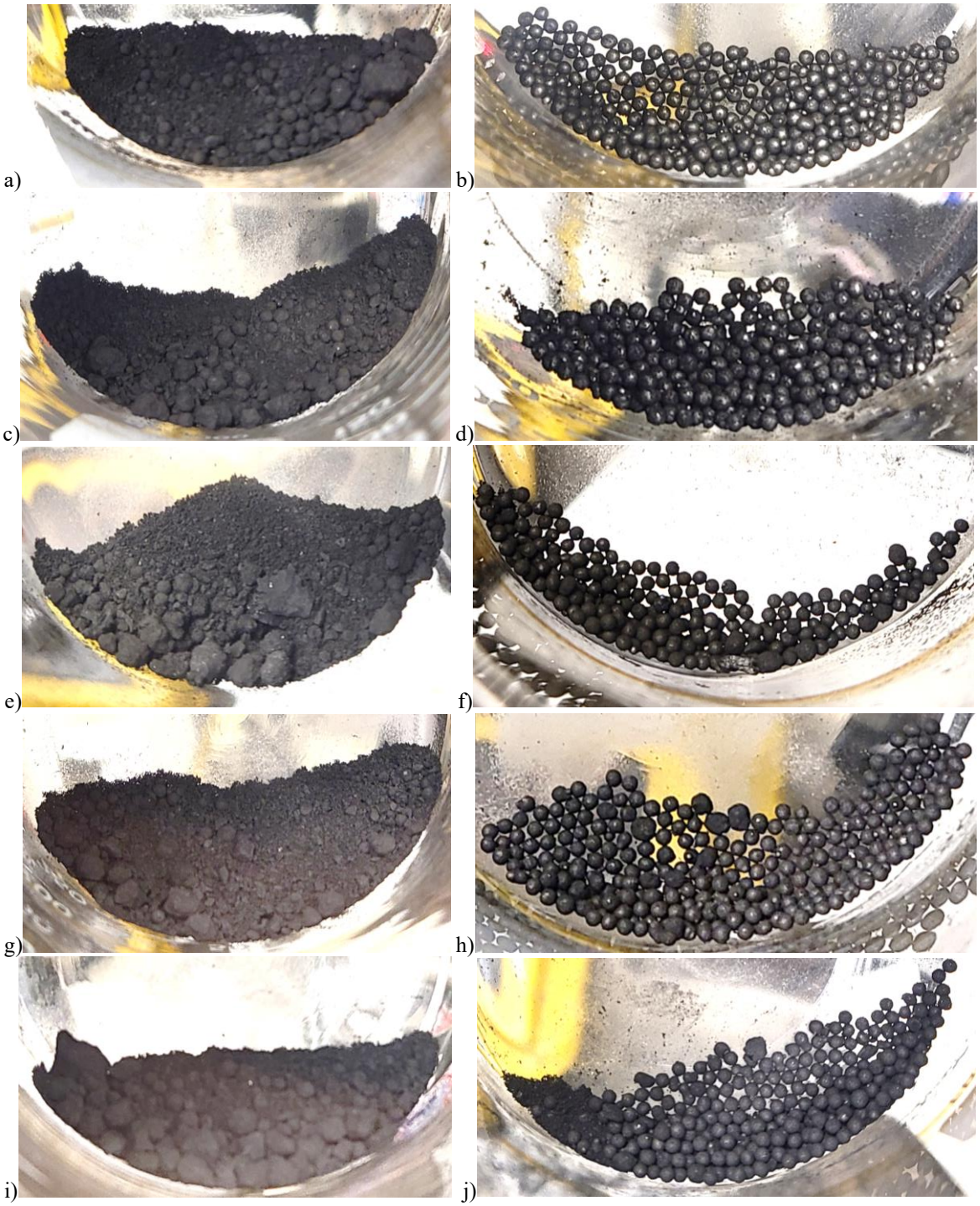


Figure A1. Material Removal from Duration with Off-Center Beaker. *All images brightened by 30%. a)-b) A before and after image of a catalyst/carbon sample washed for 1.5 hr with the beaker off-centered. c)-d) A before and after image of a catalyst/carbon sample washed for 1 hr with the beaker off-centered. e)-f) A before and after image of a catalyst/carbon sample washed for 45 min with the beaker off-centered. g)-h) A before and after image of a catalyst/carbon sample washed for 30 min with the beaker off-centered. i)-j) A before and after image of a catalyst/carbon sample washed for 15 min with the beaker off-centered.*

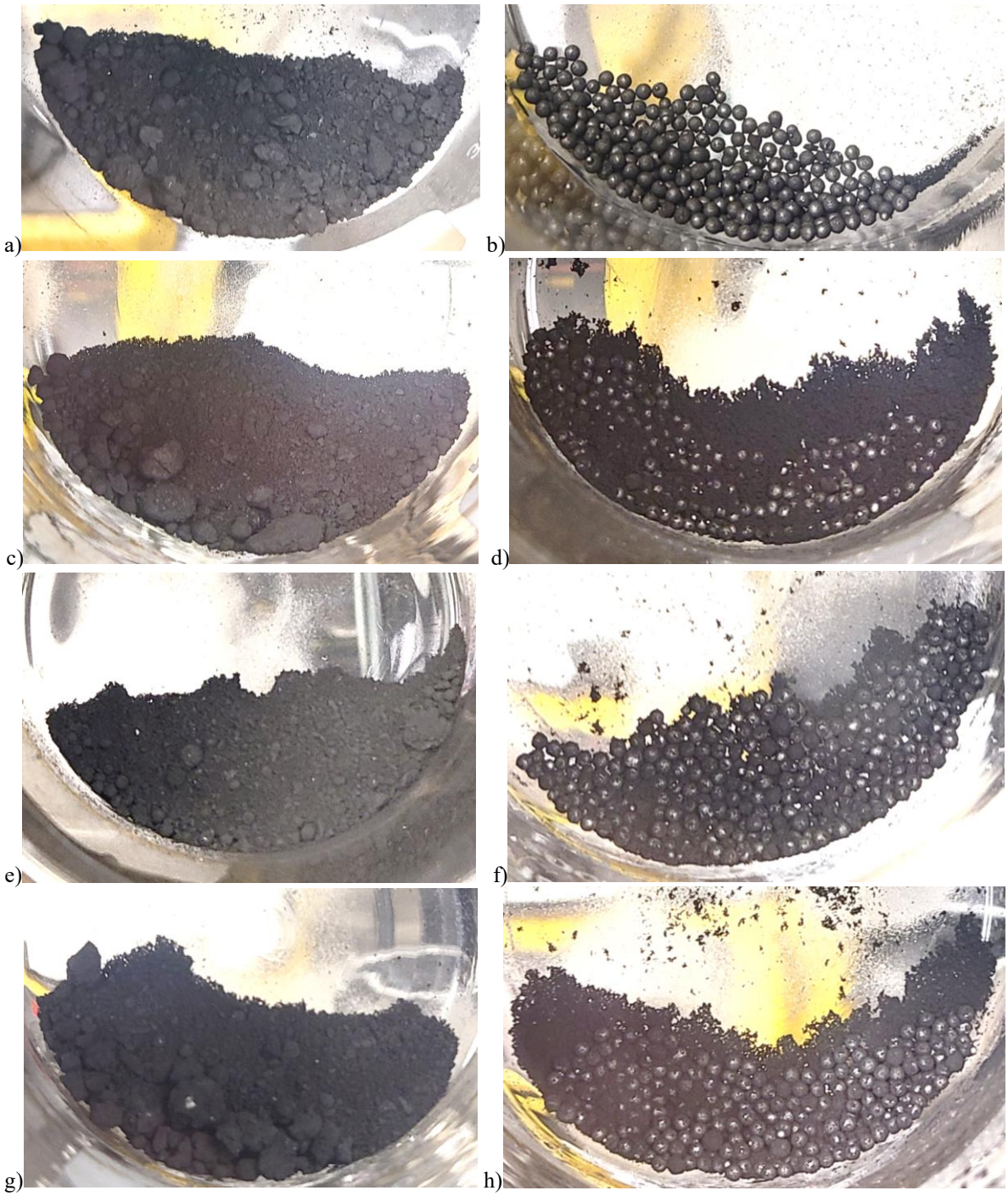


Figure A2. Material Removal from 1 hr Duration Repeatability Experiments with Off-Center Beaker. *All images brightened by 30%. a)-b), c)-d), e)-f), g)-h) Before and after images of a catalyst/carbon sample washed for 1 hr with the beaker off-centered. In all experiments represented, all beads were washed with 100 mL of DI water at a spin setting of 12 on a hot plate. Experiments were conducted at ambient temperature, and 25 mL of DI water was used in a post-filtration rinse of the beads.*

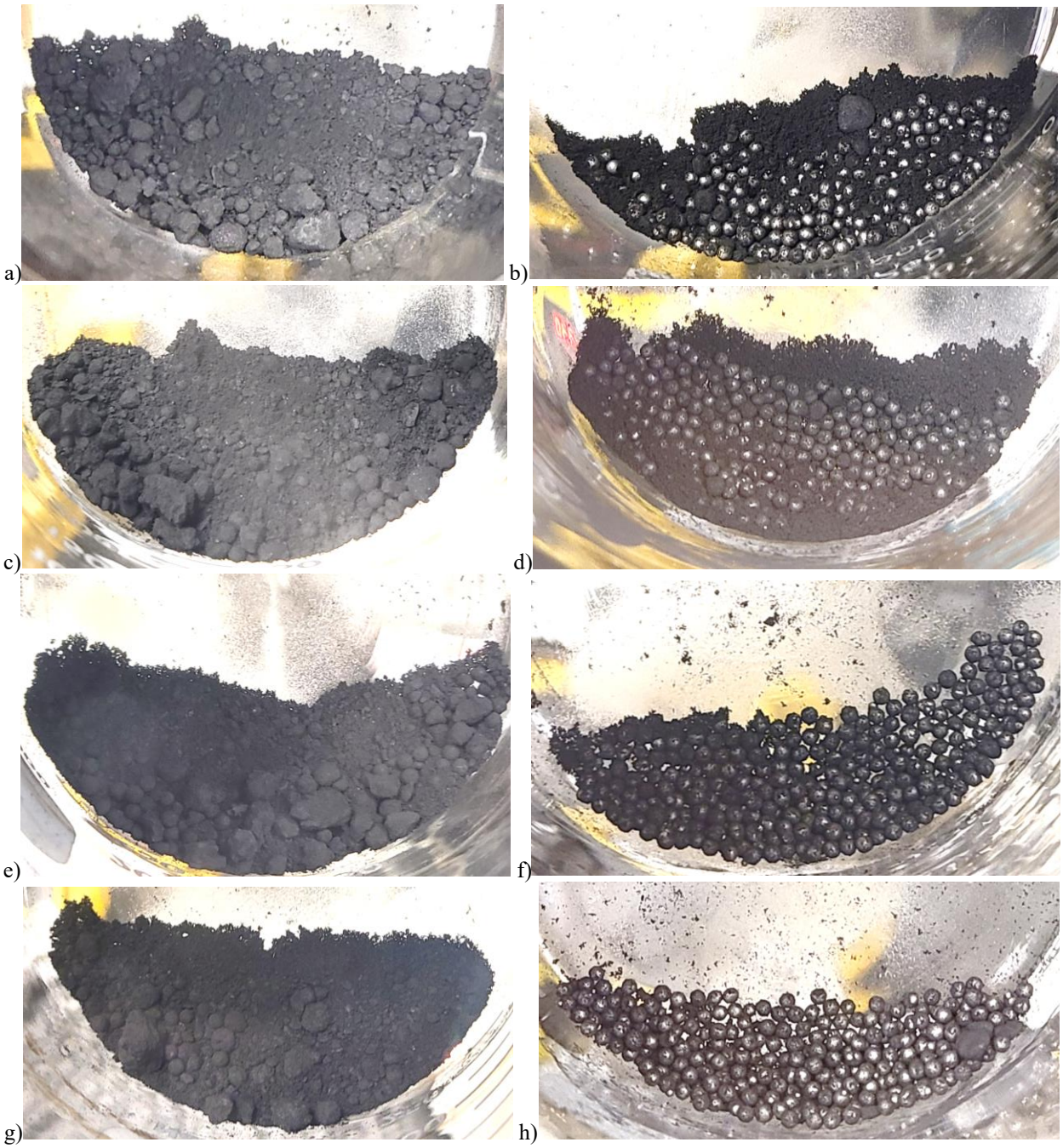


Figure A3. Material Removal from 45 min Duration Repeatability Experiments with Off-Center Beaker. *All images brightened by 30%. a)-b), c)-d), e)-f), g)-h), Before and after images of a catalyst/carbon sample washed for 45 min with the beaker off-centered. In all experiments represented, all beads were washed with 100 mL of DI water at a spin setting of 12 on a hot plate. Experiments were conducted at ambient temperature, and 25 mL of DI water was used in a post-filtration rinse of the beads.*

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