Series-Bosch Technology For Oxygen Recovery During Lunar or Martian Surface Missions

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Long-duration surface missions to the Moon or Mars will require life support systems that maximize resource recovery to minimize resupply from Earth. To address this need, NASA previously proposed a Series-Bosch (S-Bosch) oxygen recovery system, based on the Bosch process, which can theoretically recover 100% of the oxygen from metabolic carbon dioxide. Bosch processes have the added benefits of the potential to recover oxygen from atmospheric carbon dioxide and the use of regolith materials as catalysts, thereby eliminating the need for catalyst resupply from Earth. In 2012, NASA completed an initial design for an S-Bosch development test stand that incorporates two catalytic reactors in series including a Reverse Water-Gas Shift (RWGS) Reactor and a Carbon Formation Reactor (CFR). In 2013, fabrication of system components, with the exception of a CFR, and assembly of the test stand was initiated. Stand-alone testing of the RWGS reactor was completed to compare performance with design models. Continued testing of Lunar and Martian regolith simulants provided sufficient data to design a CFR intended to utilize these materials as catalysts. Finally, a study was conducted to explore the possibility of producing bricks from spent regolith catalysts. The results of initial demonstration testing of the RWGS reactor, results of continued catalyst performance testing of regolith simulants, and results of brick material properties testing are reported. Additionally, design considerations for a regolith-based CFR are discussed.

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Nomenclature

CDEA	=	Carbon Dioxide Extraction Assembly
CFR	=	Carbon Formation Reactor
CFRA	=	Carbon Formation Reactor Assembly
CM	=	Crew Member
FAA	=	Fluid Analysis Assembly
FFCA	=	Fluid Feed Control Assembly
FRVA	=	Fluid Recycle and Vent Assembly
GSA	=	Gas Supply Assembly
HEA	=	Hydrogen Extraction Assembly
HT	=	Heater
MBR	=	Moving Bed Reactor
MSFC	=	Marshall Space Flight Center
RFMBR	=	Radial Flow Moving Bed Reactor
RHXR	=	Regenerative Heat Exchanger
RWGS	=	Reverse Water-Gas Shift
RWGSRA	=	Reverse Water-Gas Shift Assembly
S-Bosch	=	Series-Bosch
SLPM	=	Standard Liters per Minute
TRL	=	Technology Readiness Level
WSA	=	Water Separation Assembly

I. Introduction

AT the end of 2013, NASA released the Space Technology Roadmaps[1], the culmination of a three year effort in which fourteen technology areas were identified, assessed for key challenges, and evaluated for impact to space and terrestrial missions. The roadmaps provide a universally available reference for future planning and technology development for NASA. One of the major challenges identified for Atmosphere Revitalization in the roadmap for the area of Human Health, Life Support, and Habitation Systems (TA06), is that of increased oxygen recovery from metabolic carbon dioxide. The roadmap specifies two milestones with respect to advancing O_2 recovery by physico-chemical methods to a Technology Readiness Level (TRL) of 6 as described in NASA NPR 7123.1B.[2] Specifically, 75% O_2 recovery capability is targeted by the end of 2014 and 100% O_2 recovery is targeted by the end of 2019. For this reason, NASA continues to explore the Bosch process as a method of maximizing oxygen recovery.

The Bosch process has been described in detail previously.[3-6] Briefly, in the first step, the Reverse Water-Gas Shift (RWGS) reaction converts carbon dioxide and hydrogen to carbon monoxide and water (Eq. 1). In the second step, two carbon formation reactions proceed in parallel to convert the carbon monoxide to solid carbon, water, and some byproduct carbon dioxide (Eqs. 2 and 3). Previous testing has shown that during carbon formation the Boudouard reaction is the primary reaction occurring. Very small quantities of H_2 maintain a well-reduced surface allowing the CO to react. Thus, very little water is actually formed during this step. The overall Bosch process is shown in Eq. (4).

<u>Step 1:</u>

RWGS $$CO_2 + H_2 \leftrightarrow H_2O + CO \quad (1)$$

<u>Step 2:</u>

CO Hydrogenation $$CO + H_2 \leftrightarrow H_2O + C(s) \quad (2)$$

Boudouard $$2CO \leftrightarrow CO_2 + C(s) \quad (3)$$

<u>Overall:</u>

Bosch Process $$CO_2 + 2H_2 \leftrightarrow 2H_2O + C(s) \quad (4)$$

Historically, the Bosch process has been conducted over iron, nickel or cobalt catalysts. However, the carbon product eventually fills the reactor, leaving the catalyst thinly dispersed as micro- or nano-scale particles, and

catalyst replacement is generally required. For long-duration space missions, this catalyst has always been assumed to be resupplied from Earth, resulting in significant resupply cost.

In recent years, development at Marshall Space Flight Center (MSFC) has focused on a Series-Bosch (S-Bosch) approach, outlined in Figure 1, in which each step in the chemical process occurs in a dedicated reactor at

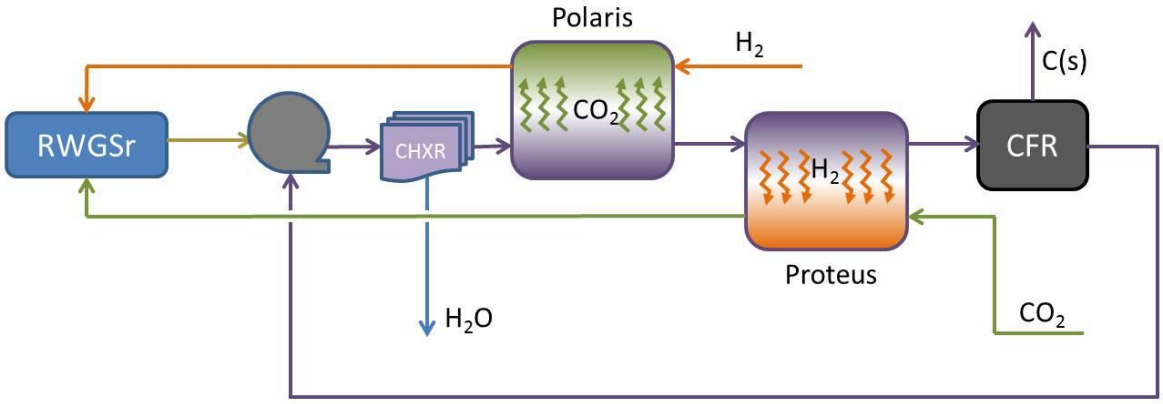

Figure 1. Series-Bosch Approach for Oxygen Recovery.

optimized temperatures and pressures and with unique catalysts. The integrated system will include an RWGS reactor, a modular membrane assembly for CO_2 separation (Polaris), a modular membrane assembly for H_2 separation (Proteus), a carbon formation reactor, a compressor, and a water separation system. The entire system will be operated at sub-ambient pressures to protect the crew from potential leaks of CO.

In the first (RWGS) step of the process, no carbon is produced, and the catalyst life span is sufficiently long that it is not considered a consumable. With this in mind, a nickel foam catalyst was selected based on CO_2 conversion efficiency and resistance to carbon fouling, and an RWGS reactor was fabricated in 2012.[6] This RWGS reactor is intended to operate between 3 and 8 psia.

When integrated with the greater Atmosphere Revitalization architecture, CO_2 will be provided from the Carbon Dioxide Management System (CO_2 compressor combined with CO_2 holding tanks as used on the *International Space Station*). As seen in Figure 1, prior to entering the RWGS reactor, the CO_2 will be used as a sweep gas for the H_2 separation membrane. H_2 will be provided directly from the Oxygen Generation System (when available) and will be analogously used as a sweep gas for the CO_2 separation membrane before entering the RWGS reactor. The sweep-sides of both membrane assemblies are intended to operate at 3-8 psia (shown in Figure 1 as the green and orange lines), while the retentate sides of the membranes, along with the carbon formation reactor, are intended to operate at 8-13 psia (shown in Figure 1 as purple lines). This will provide both concentration and pressure gradients across the membranes, along with effective dilution and removal of the permeate species from the sweep side of the membranes, in order to drive the separations.

Downstream of the membrane assemblies, the sweep gas streams are combined and fed to the RWGS reactor. The product gases from the RWGS reactor mix with a carbon dioxide-rich recycle stream from the CFR, then pass through a compressor, increasing the pressure by approximately 4 psi. Water is condensed out of the gas stream in a water separation assembly, and the dry gas is then passed through both of the membrane assemblies described above – where CO_2 and H_2 are separated out of the stream – before flowing into the carbon formation reactor. The gas exiting the carbon formation reactor is recycled back to the compressor inlet, where it mixes with the RWGS reactor effluent, and another cycle begins. Because no H_2 storage is currently available in the SOA architecture, membrane sweep gases will only be used when H_2 is available. When the OGS is not operating, the membranes will have only a pressure differential to separate CO_2 and H_2. The effect of this on system operation has yet to be characterized. However, testing is currently scheduled for this purpose (results not provided here).

As mentioned previously, by the end of 2012 the S-Bosch test stand had been designed, the RWGS reactor had been fabricated, and the modular membrane assemblies had been purchased and were awaiting integration. Because the carbon formation catalyst had not yet been selected, CFR design and manufacture were not completed at that time. Additionally, several commercial entities had previously completed Phase I Small Business Innovative Research projects involving Bosch technology. These efforts resulted in various concepts for carbon formation

reactors. Therefore, the interfaces to the CFR were designed to accommodate integrated testing of any number of carbon formation reactor approaches, including NASA's regolith-based approach.

At the same time S-Bosch design was proceeding, MSFC was testing Martian and Lunar regolith simulants as possible catalysts for carbon formation reactors. Once initial testing of these materials proved the feasibility of the concept, it was determined that one of these materials would be selected for an initial carbon formation reactor design. For reasons described in Section IV, Martian regolith simulant was chosen as the baseline catalyst. Additionally, because a crew of four will produce approximately 1.1 kg C/day (2.4 lbs C/day), disposal of the solid product material poses a real design and logistics challenge, as well as an opportunity to utilize the considerable carbon mass. Thus, it was proposed that the solid regolith-and-carbon mixture produced by the CFR might be repurposed in the production of bricks for surface construction.

This paper provides the current status of the S-Bosch test stand assembly, the initial results from RWGS reactor testing, discussion of design considerations for a regolith-based carbon formation reactor, and the results of regolith brick testing.

II. Series-Bosch Test Stand Hardware Description

In 2012, a process design for an S-Bosch test stand was produced. The design effort was discussed previously.[6] The test stand was designed based on a modular approach to allow flexibility in testing individual components and sub-assemblies. This design incorporated nine sub-assemblies, including a Gas Supply Assembly (GSA), a Fluid Flow Control Assembly (FFCA), an RWGS Reactor Assembly (RWGSRA), a Fluid Recycle and Vent Assembly (FRVA), a Water Separation Assembly (WSA), a Carbon Dioxide Extraction Assembly (CDEA), a Hydrogen Extraction Assembly (HEA), a Carbon Formation Reactor Assembly (CFRA), and a Fluid Analysis Assembly (FAA). With the exception of the CFRA, a test development unit for each of these sub-systems was fabricated and assembled.

Figure 2. Gas Supply Assembly for S-Bosch.

Figure 3. S-Bosch Test Stand. *As assembled, the test stand includes the FFCA, RWGSRA, FRVA, WSA, and FAA.*

The GSA, shown in Figure 2, was ultimately built to provide gas supply to multiple test stands. The GSA provides compressed He, Ar, N_2, CO_2, CO, H_2, and CH_4. Two cylinders of each compressed gas are installed, and a valve is used to switch between the two supply cylinders whenever one becomes empty. This enables continuous supply for long-duration testing.

The FFCA, the RWGSRA, the FRVA, the WSA, and the FAA were assembled and integrated, as shown in Figure 3, for initial RWGS Reactor testing (discussed below). The RWGS Reactor insulation was custom prepared by Promat, Inc. (Mayville, TN) using Microtherm Super G insulation. Unifrax Fiberfrax blankets were layered across the insulated reactor to limit losses through insulation couplings.

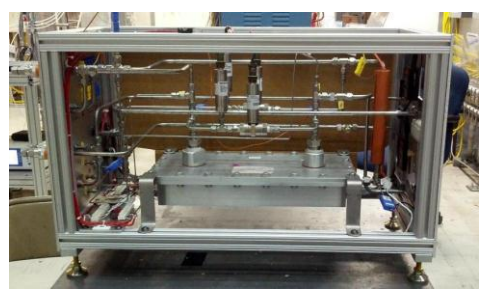

Figure 4. Carbon Dioxide Extraction Assembly. *CDEA and HEA are physically identical with the exception of the membrane material.*

The CDEA, shown in Figure 4, and HEA are physically identical with the exception of the specific membrane used in each and the arrangement of heaters and insulation on the membrane

packages' surfaces – due to different expected operating temperatures. (The heaters and insulation had not been installed at the time of submission.) Both were assembled but remain separate from the integrated test stand. These sub-assemblies will be integrated into the test stand following stand-alone testing.

While a CFRA has yet to be designed or assembled, the modularity of the S-Bosch test stand enables any CFRA with appropriate interfaces to be integrated. As a result of the modular design approach, the CFRA may be easily integrated directly to the FFCA for stand-alone testing, or to several combinations of the other sub-assemblies for partially-integrated testing. Additionally, connections are also available to the FAA to enable gas analysis during testing.

III. RWGS Reactor Stand-Alone Testing

Once the S-Bosch test stand, as shown in Figure 3, was fully assembled and shake-down testing complete, two tests were planned to evaluate the performance of the RWGS reactor. The first test, the Thermal Profile Test, was designed to characterize the thermal profile of the reactor at various combinations of temperature and flow rate. The second test, the RWGS Stand-Alone Performance Test, was designed to evaluate the reaction performance of the reactor at various inlet feed ratios, temperatures, and pressures. Details of this testing are described below.

A. RWGS Reactor Stand-Alone Testing Materials and Methods

The S-Bosch test stand was used to test the the RWGS reactor for both the Thermal Profile Test and the RWGS Stand-Alone Performance Test. The RWGS reactor was equipped with three band heaters evenly spaced axially along the reactor. These heaters can be independently controlled with set points between 25-850°C.

Initially, gas pre-heating was intended to be performed using a regenerative heat exchanger (RHXR). However, during shake-down testing it became clear that the lengthy tubing sections between the RWGS reactor and RHXR could not be sufficiently insulated to provide significant pre-heating of the RWGS reactor inlet. Thus, a rope heater (set-point temperatures 25-400°C) was installed on the inlet tube and insulated. Heat input from this pre-heater simulates the presence of an effective RHXR. It is assumed that future modifications to the assembly design will enable regenerative heating, thereby eliminating the long-term need for the heater wrap. Required efficiency factors for a future RHXR design can be determined from pre-heater temperature data.

The RWGS reactor catalyst bed is five inches in diameter, eight inches in length, and was equipped with nine thermocouples to monitor temperatures within the catalyst bed during testing. The approximate location for each thermocouple is shown in Figure 5. Each thermocouple is identified first by its axial location and second by its radial location (e.g. Outlet Mid).

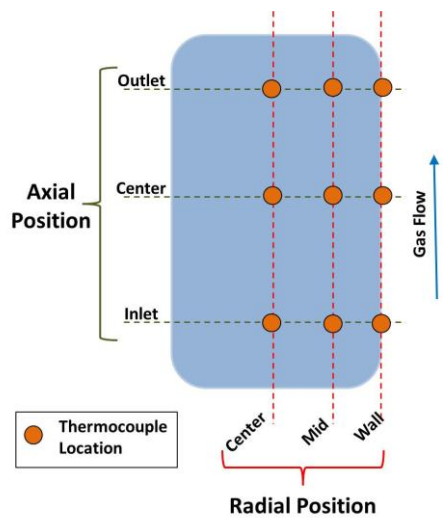

Figure 5. Thermocouple placement in the RWGS reactor. *Reactor shown as blue rectangle, thermocouple locations indicated with orange circles.*

1. *Thermal Profile Testing*

The Thermal Profile Test was completed in two parts. In Part I, the goal of testing was to observe the thermal profile of the reactor at various wall temperature setpoints (controlled by the three external heaters). The reactor was maintained at 8 psia and fed 1, 5, or 10 SLPM of pure nitrogen. Hydrogen and CO_2 were not used for this testing due to concerns with H2 safety in a test stand that had not been thermally tested. The RWGS band heaters (HT1, HT2, and H3) were independently set at temperatures ranging from 25-800°C. The pre-heater was not used for this testing, so reactor inlet gas was at room temperature. The setpoints for each run were maintained until steady state was reached before recording each data point.

For Part II, the goal of testing was to characterize the thermal profile within the reactor under more realistic operating conditions, in which the reactor inlet gas was above room temperature. The reactor was again maintained at 8 psia, but fed 5 or 10 SLPM of pure nitrogen. Again, the RWGS band heaters were independently set at various temperatures. The pre-heater was initially set at 50°C and varied until the center inlet thermocouple was within 15°C of the inlet wall temperature. The pre-heater was then varied until the center inlet thermocouple was within 10°C of

the inlet wall temperature. Pre-heater set-points and the inlet temperatures achieved by these set-points were documented for later data analysis.

2. RWGS Reactor Stand-Alone Performance Testing

The purpose of the RWGS Reactor Stand-Alone Performance Test was to evaluate the performance of the reactor when fed various quantities and ratios of CO_2 and H_2 at various temperatures and pressures. For each test point, using results from the Thermal Profile Test, the reactor heaters and pre-heater were held at temperatures which would provide the most uniform catalyst bed temperature distribution as possible, with target temperatures of 650°C, 700°C, and 750°C. The reactor was maintained at pressures of 3psia, 5psia, 8psia, or 14.7 psia. CO_2 was fed to the reactor at 1-crew member (CM), 2-CM, or 4-CM flow rates. The H_2:CO_2 molar feed ratio was set at 4:1, 3:1, or 1:1. For each setpoint, the run parameters were maintained until steady state was reached.

B. RWGS Reactor Stand-Alone Testing Results and Discussion

The RWGS Reactor Thermal Profile Testing was completed as planned. Details are provided below. RWGS Reactor Stand-Alone Performance Testing has been delayed due to H_2 safety concerns. Testing will commence as soon as a Test Readiness Review has been completed.

1. Thermal Profile Testing Part I

As stated previously, the purpose of Part I of the Thermal Profile Test was to observe the thermal profile of the reactor at various wall temperatures and gas flow rates. Figure 6 shows a contour plot of the measured temperatures at each thermocouple in the reactor for all flow rates when the heaters were set to 700°C. Note that the plot shows one half of the reactor cross-section. The plots were made by interpolating between points using cubic spline in MATLAB. A similar profile was observed for all temperatures tested. The effect on temperature distribution of increasing gas flow rate can more clearly be seen in Figure 7. The maximum radial temperature difference for a given flow rate, axial position, and heater temperature was calculated by taking the heater temperature and subtracting the lowest observed temperature at the same axial position. The displayed "average maximum" radial temperature difference values were obtained by taking the mean of the maximum values at every heater temperature for each axial position. Error bars indicate standard deviation. As can be seen, when flow

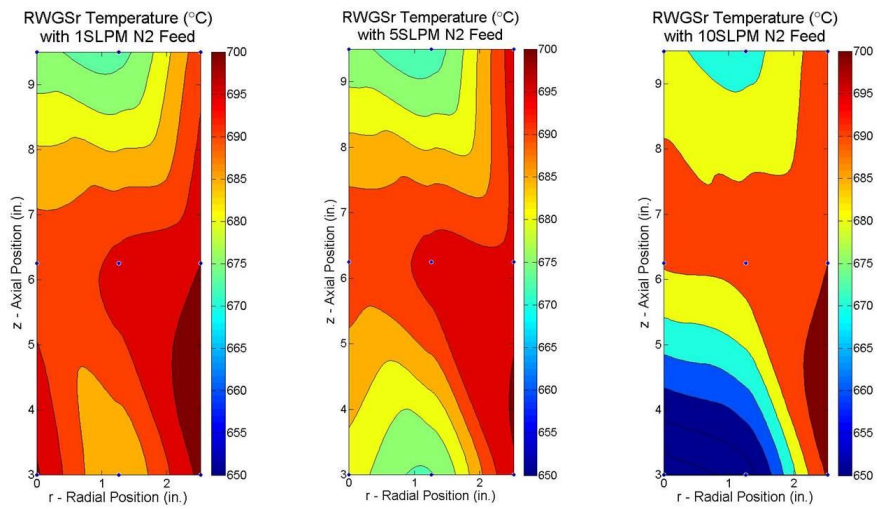

Figure 6. Effect of Gas Flow Rate on Temperature Distribution in RWGS Reactor with no Pre-Heater. *All reactor heaters set to 700°C.*

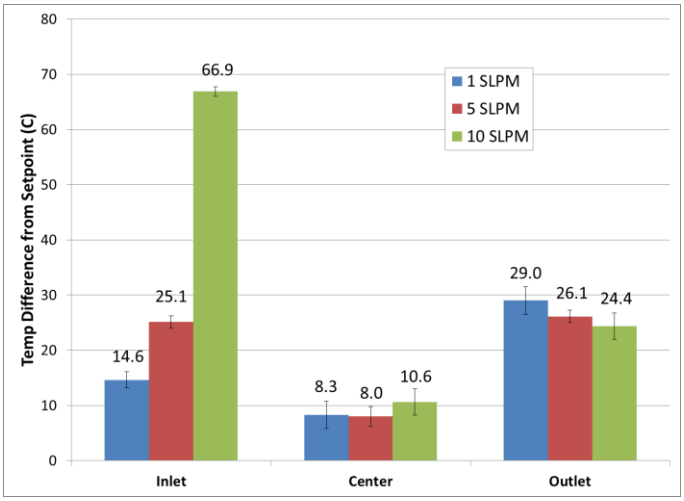

Figure 7. Average maximum radial temperature difference observed at Inlet, Center, and Outlet axial locations in the RWGS reactor. *Error bars indicate standard deviation (n=5). No statistical difference was observed at the Center and Outlet for the three flow rates tested (p>0.05). Values observed at the Inlet were statistically different (p<<0.05).*

rates were sufficiently low, conduction dominated the thermal transfer within the reactor as demonstrated by relatively low radial thermal gradients in the reactor. When flow rates were increased, convective thermal transfer was more dominant as demonstrated by the increasing radial thermal gradients at the reactor inlet. It is important to understand thermal gradients within the reactor, as temperature plays an important role in determining the rates and equilibrium points of the RWGS and side reactions, and thus the operating temperature profile will be considered in optimizing the reactor performance. The RWGS reaction is mildly endothermic (dH_{rxn} = 41 kJ/mol) so will likely only affect the thermal profile slightly. Additionally, since the kinetics and thermodynamics of the RWGS reaction are enhanced by higher temperatures (dG<0 at temperatures > 828°C), it will likely be desirable to operate the reactor at the highest achievable temperatures. Cooler areas near the inlet will represent under-utilized catalyst bed volume. Thus, it is expected that pre-heating the inlet gas will lead to higher temperatures at the inlet mid and center points, thereby improved bed volume utilization.

Data from testing also demonstrated cooler temperatures at the bed outlet mid and outlet center points. It is believed that this phenomenon is due to a particularity of this reactor design. The reactor is sealed at the outlet by a large end cap, and we expect that this feature acts as a significant heat sink. Future iterations of the RWGS reactor will consider alternative design approaches to limit the cooling near the reactor outlet.

As shown in Figure 8, gas exiting the reactor is hotter at higher flow rates. This is expected since higher flow rates would require proportionally higher heat rejection to achieve the same temperature decreases. Any future effort at RHXR design will need to include this effect as part of the analysis.

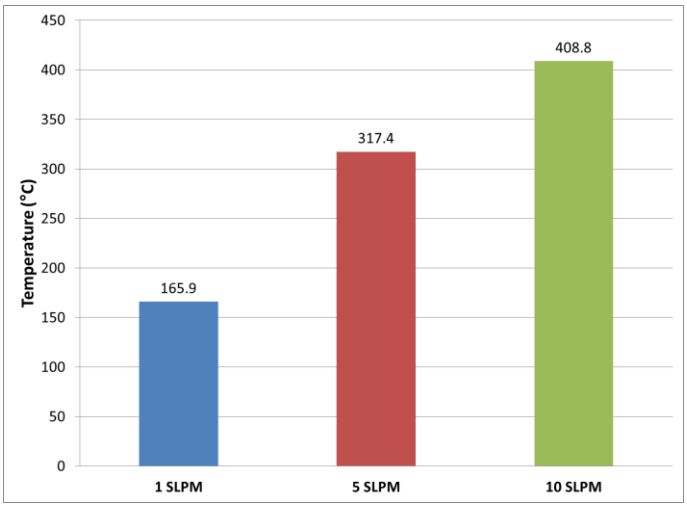

Figure 8. Temperature downstream of RWGS reactor at various gas flow rates. *Reactor heaters set at 700°C.*

2. Thermal Profile Testing Part II

Based on the data collected in Part I testing, it was clear that regenerative heating of the RWGS reactor influent is desirable. However, due to the challenges associated with the existing RHXR, it was decided that near-term testing would include a gas pre-heater to simulate an RHXR. As stated above, the pre-heating temperature was recorded and can be readily correlated to input requirements for an equivalent regenerative heating design. A heater wrap was installed on the inlet gas tube to the RWGS reactor for this purpose. Thus, the goal of Part II testing was to characterize the effect of inlet temperature on temperature distribution within the reactor.

The effect of the addition of the pre-heater was observed for 5 SLPM and 10 SLPM of nitrogen flow. Expected realistic conditions for the system will be approximately 5-10 SLPM total gas feed. Thus, 1 SLPM was omitted from this final testing. As before, the maximum radial temperature difference at each axial position was calculated by taking the heater temperature and subtracting the lowest observed temperature at that axial location. The pre-heater provided sufficient heat to decrease the observed radial variations in the reactor for both flow rates. Figure 9 shows the effect of pre-heating the inlet gas to ~250°C on the radial temperature differences at the inlet,

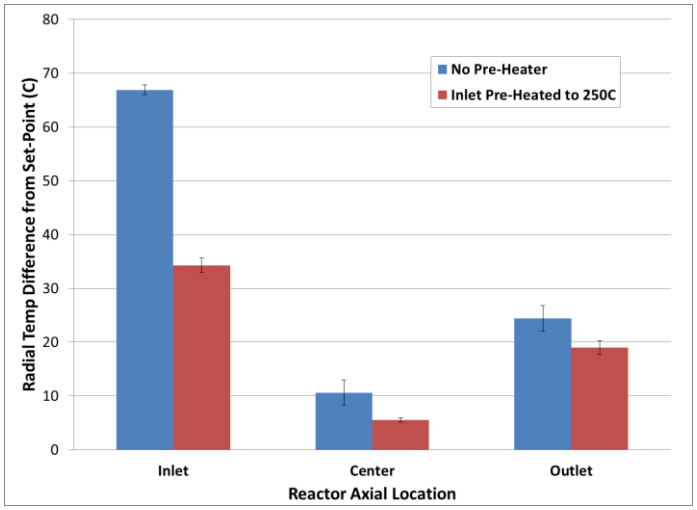

Figure 9. Effect of Incoming Gas Pre-Heated to 250°C on the Maximum Radial Temperature Differences observed in the RWGS reactor. *Nitrogen fed to the reactor at 10 SLPM.*

center, and outlet of the reactor at 10 SLPM nitrogen flow. Although less pronounced, a similar effect was observed for the 5 SLPM nitrogen flow test. This may be more easily understood by examining the contour plots shown in Figure 10. These plots compare the effect of a pre-heater on the modeled thermal profile of the reactor when gas flow is 10 SLPM, reactor heaters are set to 700°C, and the incoming gas is not pre-heated, is preheated to ~200°C, or is preheated to ~250°C. A clear concern from this test is the fact that an increase in gas temperature of 250°C only reduced the measurable variation in temperature at the inlet by about 33°C. This lends additional support to the hypothesis that there are significant cold regions between the inlet of the reactor and the first thermocouples. As mentioned previously, these colder regions are effectively unutilized, or underutilized regions of the reactor and will result in a corresponding reduction in the chemical efficiency when the reactor is used for CO_2 conversion to CO. Due to design limitations, the incoming gas cannot be heated to temperatures greater than 250°C at the 10 SLPM flow rate. Thus, only extrapolations can be made to predict the incoming gas temperature required to achieve higher catalyst bed inlet temperatures, as well as greater theoretical chemical conversions when CO_2 and H_2 are introduced. Ultimately, there were two key outcomes from the pre-heater test. First, data was gathered that will enable us to better understand the thermal characteristics of the reactor and system and enhance the thermal model fidelity. Secondly, the operational testing limits of the reactor inlet temperature for the current design have been identified. The next step will be to determine if this capability adequately represents what can reasonably be achieved from a RHXR.

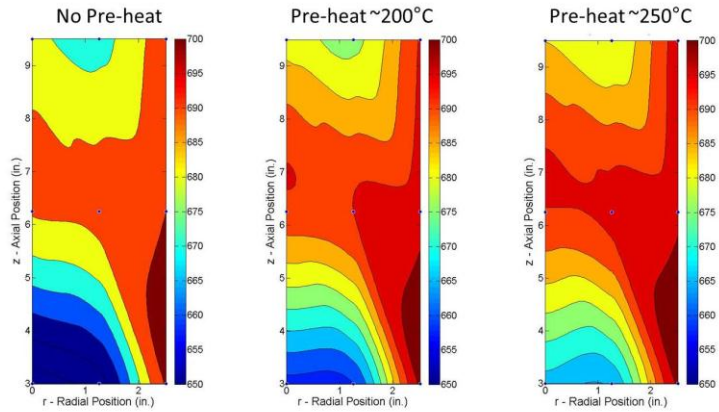

Figure 10. Effect of inlet gas temperature on thermal profile of RWGS reactor. *Wall heaters set to 700°C.*

IV. Regolith-Based Carbon Formation Reactor

Based on the data gathered in 2012 for Lunar and Martian regolith simulants, it was determined that a regolith-based carbon formation reactor was feasible in a surface Bosch system. Thus efforts began to design a ¼ -CM sized reactor. Several considerations have been taken into account for the design:

1. Regolith Specifications:

While Lunar and Martian regolith simulants were both tested, Martian regolith was chosen as the baseline catalyst for the reactor. This was done for several reasons. First, of the mapped regions of the Martian surface, the minimum observed iron concentration is ~10 wt%. The observed range is 10-20 wt%.[7] Comparatively, while some areas of the Lunar surface contain as much as 20wt% iron, the majority of the Lunar surface contains <5 wt%.[8] Thus, a regolith-based carbon formation reactor for a Martian surface mission would be possible regardless of landing location, while only certain regions of the Lunar surface would permit the use of regolith as a catalyst. Second, a Martian surface mission is still an acknowledged long-term goal of NASA. Finally, while this approach could be made to work for certain Lunar missions, the availability of atmospheric CO_2 on the Martian surface makes the Bosch process a much more attractive approach for life support oxygen recovery.

In addition to type of regolith, it was important to select a size range of regolith to be used in the reactor. Martian regolith, like Earth's soil can vary dramatically in size. To limit pressure drop across the reactor while still maximizing surface area, a particle range of 355um to 1mm was chosen.

2. Gravity Dependence:

Existing oxygen recovery technology is designed to operate independent of gravity for the *ISS* application where only microgravity effects the hardware. However, for surface missions, it will be

possible to take advantage of available gravity. Because the CFR application discussed here uses a planetary regolith as catalyst, it is possible that gravity may be influencing the reactor. Thus, for the carbon formation reactor, it was assumed that gravity is influencing the reactor when regolith is used as a catalyst, though no distinction was made between Earth and Martian gravity. For transit missions, regolith is not anticipated to be the catalyst of choice. Thus, microgravity is assumed for non-regolith catalyst materials.

3. Reactor Approach:

Martian regolith simulant is very similar to Lunar regolith simulant in texture. While no data is available for the flowability of Martian regolith simulant, Lunar regolith simulant has been more thoroughly studied. Thus, it was assumed that Martian regolith, like Lunar regolith, is cohesionless/free-flowing (ff_c>10).[9] With this in mind, several reactor approaches were considered including a packed bed reactor, a fluidized bed reactor, a moving bed reactor (MBR), and a radial-flow moving bed reactor (RFMBR).

The packed bed reactor approach was immediately eliminated due to the observed pressure drop across the Martian regolith simulant at the particle sizes chosen for this application. In sub-scale testing, significant pressure drop (>5 psid) was observed at Reynold's numbers as low as 5 with only 3-4 inches of catalyst. Because the system is intended to be operated at sub-ambient pressure to protect the crew from any leaks, significant pressure drops make the approach unviable.

A fluidized bed reactor approach was also considered but rejected for two reasons. First, in sub-scale testing, it was determined that the velocities required to achieve fluidization were unachievable with the operational quantities of gas available unless very small quantities of the simulant were used. Second, if the system was designed to use very small quantities of catalyst, the high frequency of catalyst change-out required would demand an unrealistic quantity of crew time and attention.

The third approach considered was that of a MBR. Moving bed reactors are set-up as a packed bed reactor would be, but the solid catalyst is constantly added and removed such that the catalyst is continuously, or nearly continuously replaced. The gas flow can either be co-current or counter-current to the catalyst flow.[10] This approach, like the packed bed reactor approach, was eliminated due to pressure drop concerns.

The final approach considered was that of a RFMBR. In this approach, the reactor is built of three concentric cylinders as depicted in Figure 11. The center-most and outer-most cylinders are for gas flow into and out of the reactor. The intermediate cylinder is used to hold the catalyst material. The catalyst can then be continuously (or nearly continuously) added and removed from the system. This approach eliminates the concern with pressure drop because the catalyst volume perpendicualar to the gas flow is significantly lower than it would be in a traditional MBR design.[10-14] Realistic volumes of gas may be used with this approach and because catalyst material may be pressure fed into the heated portion of the reactor, automation of the system will limit the required crew time.Thus, a RFMBR was chosen as the baseline design approach for the regolith-based carbon formation reactor.

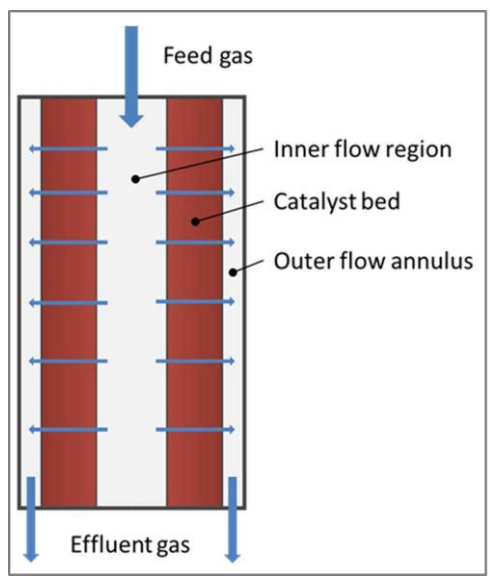

Figure 11. General design for a Radial-Flow Moving Bed Reactor.

4. Heating Method:

Based on the assumption that the carbon formation reactor would be modeled after a RFMBR design, three approaches to heating were considered: external band heaters, an internal core heater, or a combination of both. Thermal modeling is required to determine the best approach. All three are still under consideration.

Mechanical design of the Martian regolith simulant-based carbon formation reactor is still ongoing. This design will be based on the above mentioned assumptions, data from sub-scale regolith testing, COMSOL modeling, and thermal modeling. The resulting design will be fabricated and tested in the S-Bosch test stand.

It should be noted that other design considerations must be identified including the method of introducing catalyst, the method of removing the catalyst material, where to put the spent catalyst until it can be disposed of or reused. Other logistical challenges must also be considered including regolith collection and sieving on the Martian surface. With time, all of these will be addressed and considered as the approach is more fully developed.

V. Regolith Brick Testing

Because Bosch technology produces considerable quantities of solid carbon as a byproduct, there is an opportunity to repurpose the carbon into a useful product. One potential product is regolith bricks for surface construction. A study was undertaken for two purposes: to determine the best method of producing bricks from regolith containing carbon, and to determine the effect of the carbon material on brick mechanical properties. Details of this study are provided below.

A. Regolith Brick Testing Materials and Methods

Regolith Brick Testing was conducted in two parts: Brick Preparation Evaluation and Brick Mechanical Properties Evaluation. The Materials and Methods for each are provided below.

1. Brick Preparation Evaluation Materials and Methods

Three methods of producing Martian regolith bricks were explored. The first method was based on sintering,[14] the second used sulfur as a binder,[15] and the last used polyethylene as a binder.[16]

All methods used stainless steel 304 brick forms produced in-house at MSFC. The walls were made of 1/16" thick flat stock that was subsequently welded together to produce 1"W x 3"L x 1"H forms. SS 304 was chosen due to a low sensitivity to sulfur. JSC Mars-1AC Martain regolith simulant was purchased from Orbitec and sieved to include particles from 355µm to 1mm. Two furnaces were used to prepare the bricks. A Blue M Electric Company M-25A-1A standard furnace was used for non-vacuum applications. For vacuum applications, a Thermolyne 59300 High Temperature Tube Furnace equipped with a Varian SD-300 mechanical vacuum pump was used.

For the sintering method, Martian regolith simulant was placed into the brick forms and vibrated to settle the material. The forms were then placed in a high temperature furnace for two hours at 500°C at ambient pressure. After two hours of baking, the furnace was evacuated and heated to 1100°C. After two hours at the higher temperature, the furnace was powered off and allowed to cool at the natural cooling rate of the furnace. Bricks were removed when the furnace temperature reached <45°C.

For efforts using sulfur as the binder, a mixture of 80 wt% regolith simulant and 20 wt% sulfur (purchased from Sigma Aldrich) was pre-mixed and placed in the brick forms. The forms were placed in the standard furnace at 160C for 30 minutes and allowed to cool at the natural cooling rate of the furnace. Bricks were removed when the furnace temperature reached <45°C.

For efforts using polyethylene as a binder, the brick forms were lined with parchment paper to facilitate removal of the completed bricks. 70 wt% regolith simulant and 30 wt% polyethylene (purchased from Sigma Aldrich), was pre-mixed and placed in the brick forms. The forms were placed in the standard furnace, slowly heated to 150°C, and maintained at temperature for four hours. The bricks were allowed to cool at the natural cooling rate of the furnace and removed when the temperature reached <45°C.

2. Brick Mechanical Properties Evaluation Materials and Methods

Based on the results (discussed below) of the Brick Production Evaluation, only the polyethylene-based regolith simulant bricks were tested for mechanical properties. Mechanical tests included compression testing, tensile strength testing, modulus of elasticity testing using the 3-point bending test, and freeze-thaw cycling.

Compression, tension, and bending tests were completed using an Instron 5960 Dual Column Tabletop Universal Testing Systems. Freeze-thaw testing was attempted using a Pulser/Receiver Olympus Model 5077 instrument . This strategy used an ultrasonic 'sonometer-type' analytical method with the following evaluation conditions:

- Output - 400 Volts
- PRF (Hz) – 100
- Frequency Setting – 0.5MHz

• Gain – 50 dB (40 dB from pre-amp)
• Panametric probes (V101 0.5 MHz/1.0”’ & A101R 0.5MHz/1.0’’)

Probes were set up in a through-transmission arrangement, and an additional Perspex stepped-cylinder delay line was used as known reference.

B. Regolith Brick Testing Results and Discussion

Three methods of producing bricks were explored. Once a best method was identified for preparing the bricks, four mechanical properties tests were conducted to determine the effect of carbon contained in regolith bricks. The results and a discussion of this testing are provided below.

1. Regolith Brick Preparation Testing Results and Discussion

The three regolith brick preparation methods explored were a sintering method, a sulfur-binding method, and a polyethylene-binding method.

The sintering method, which requires relatively high teperatures, and correspondingly high power, was eliminated first as a possibility for a Martian surface mission. The tested samples were either too heated or not heated enough, as seen in Figure 12, even within the same experiment due to variations in temperature inside the furnace. Because high quality bricks were difficult to achieve repeatedly, and given the large power requirements necessary to prepare the sintered bricks, the sintering approach was eliminated from consideration.

Figure 12. Sintered regolith simulant bricks. *Variations in sintering observed as a result of position in high temperature furnace.*

Sulfur was considered for martian simulant because it is readily available on the martian surface. Sulfur has a relatively limited working temperature and pressure range and sublimation easily occurs. Despite all attempts to control and monitor the temperature in the furnace, most of the sulfur sublimated before melting to form the bricks. Additionally, as seen in Figure 13, the products of the sulfur experiments were very brittle (friable). Thus, a sulfur-binding method was eliminated from consideration.

Figure 13. Sulfur-bound regolith simulant bricks. *Rapid sublimation of the sulfur resulted in brittlenses of the brick products.*

Polyethylene-binding was ultimately chosen as the preferred method for brickmaking. Polyethylene was considered originally for its radiation shielding properties, its relatively low melting temperature, and its abundant availability in flight due to packaging that can be repurposed. Although temperature variations in the furnace resulted in uneven heating, as evidenced in Figure 14 by uneven discoloration, the resulting bricks were consistent in external texture and size, but were not homogenous as observed when bricks were broken in half. Additionally, shrinkage of the bricks was universally observed and due to the nature of the mechanical testing equipment,

Figure 14. Polyethylene-bound regolith simulant bricks. *Uneven discoloration indicates uneven temperature distribution in the furnace.*

required additional processing. Specifically, after formation in the furnace, the edges of the bricks were not parallel. The edges of the bricks were shaved using a rotary mechanical cutting bit. Figure 15 provides images of the bricks before and after shaving. Future preparation of the bricks will use larger forms so that unparallel sides may be cut or shaved to produce a geometrically preferable brick shape in the desirable dimensions.

Once the polyethylene-binding method was chosen, four bricks were produced using Martian regolith simulant containing no carbon material as controls. Martian regolith simulant containing carbon was produced via the Bosch process as described previously for 1 hour, 4 hours, or 16 hours.[6] Four bricks were made from the product of each testing duration. The mechanical properties of these bricks were then evaluated and compared to the control.

Figure 15. Martian regolith simulant brick before (left) and after (right) edge shaving.

2. Brick Mechanical Properties Evaluation Results and Discussion

Compressive strength, modulus of elasticity, tensile strength tests, and freeze-thaw testing were planned for bricks containing regolith simulant only (control) and regolith simulant containing carbon from 1-hr, 4-hrs, and 16-hrs of reaction. The results of this testing are provided below.

Compressive and Tensile Strength Evaluation

For the compressive strength evaluation, two control bricks were tested and three bricks each of the 1-hr, 4-hr, and 16-hr samples. For the tensile strength evaluation, only one control brick was tested and two each of the 1-hr, 4-hr, and 16-hr samples. Figure 16 shows the results of that testing. Each point represents the average of the tested bricks and error bars indicate standard devation. Due to high variation between samples, there was no significant difference observed for compressive strength between any of the samples tested. For tensile strength testing, the control brick showed much higher strength; however, a lack of duplicates makes it it impossible to draw statistically significant conclusions. Thus, at this time, it cannot be shown that the presence of carbon in the regolith simulant improved the mechanical properties of the resulting bricks. However, it is possible that any positive effect of the carbon material was overshadowed by the non-homogeneity of the samples. Future testing may improve upon polyethylene/regolith simulant mixing thus providing more accurate results.

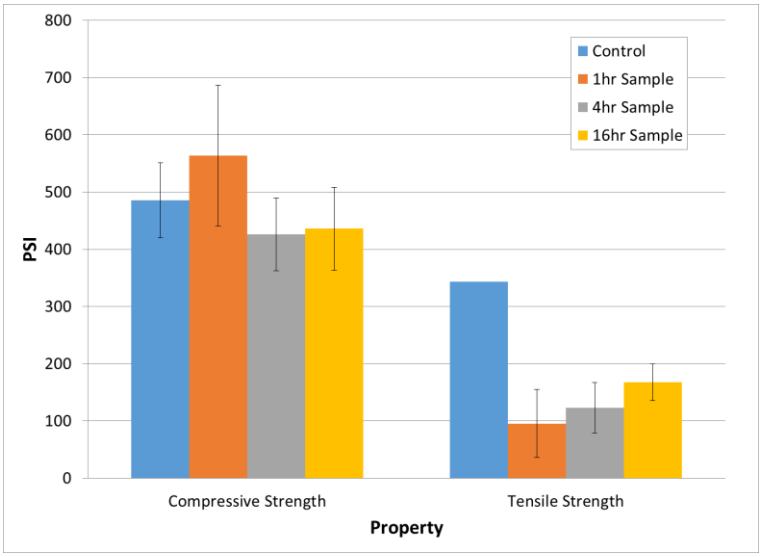

Figure 16. Compressive and tensile strength testing results for unreacted Martian regolith simulant (control) and samples containing carbon from 1-hr, 4-hr, and 16-hr Bosch processing.

Another consideration for the use of regolith bricks is that of suitability for structures. On Earth, most large structure masonry is completed using concrete. The required compressive strength of concrete in structures is

dependent on several factors including the type of mortar used, the climate, the design of the structure itself, etc. At a minimum, concrete must demonstrate a compressive strength of 1,900 psi to be used in the building of structures.[17] Cold climates, such as those anticipated on the surface of Mars, may increase that minimum to 4,800 psi. Clearly the polymer bricks produced in this study would not provide the necessary strength for an Earth application. However, because polymers have been shown to provide radiation shielding properties, strength may be less of a concern on the Martian surface. Design of structures will ultimately need to take this into consideration and to make the necessary concessions.

Modulus of Elasticity Evaluation

For the modulus of elasticity testing, one control brick was tested and two bricks each of the 1-hr, 4-hr, and 16-hr samples. Like the results from the compression and tensile strength test, there was significant variation between samples. As mentioned previously, this was likely due to the non-homogeneity of the brick samples. Thus, no conclusions could be made regarding the effect of carbon on the modulus of elasticity.

Freeze-Thaw Cycle Evalaution

Several attempts were made to conduct the freeze-thaw cycle testing. However, while running the tests, the results routinely showed significant levels of both signal attenuation (e.g., 500kHz leaving the transmitter, and less than 100kHz at the receiver) as well as signal variability tied to end-to-end positioning within each sample. This is believed to be due to the plastic-rich nature of these samples, and their apparently high non-homogenous morphology. Thus, the samples were unsuited to using this test for quantitative purposes and freeze-thaw data was not obtained.

VI. Future Work

The considerable progress made in desiging, fabricating, and assemblying the S-Bosch test stand has enabled the capability to test various carbon formation reactors. It is anticipated that testing of the regolith-based carbon formation reactor will be completed by the end of FY14. While catalytic activity of the regolith has been demonstrated, further analysis of the material to determine specific properties (e.g. iron surface area, iron distribution, specific carbon capacity, etc) will be useful for comparison with traditional catalysts and is expected to be completed in follow-on work. Additionally, regolith as a catalyst assumes a surface system. However, for Martian transit missions, a more traditional catalyst will be necessary. The reactor design discussed here may also accommodate iron beads, thus future testing will be conducted to explore performance including carbon handling.

Based on results from FY14 testing, a redesign and upscaling of the reactor may be pursued in the future. Additionally, testing of commercially produced carbon formation reactors may be attempted given available timing and personnel support. Finally, based on the lessons learned from the regolith brick mechanical testing, this effort may be repeated with an improved method and materials.

Acknowledgments

The authors would like to acknowledge the support of MSFC ES62 ECLSS Development Branch technical support from Kenny Bodkins, Bob Jones, Paul Carothers, Tony Mahathey, Dan Donovan, and John Thomas for test stand design, fabrication, assembly, and upkeep, and Tom Williams for software development. The authors would also like to thank Mr. Mike Ryschkewitsch, the Presidential Early Career Award for Scientists and Engineers, MSFC's Technical Innovation Program, and the Next Generation Life Support Project for funding this effort. Finally, the authors would like to thank Monsi Roman, Melanie Holloway, and Scott Jones for project management and contracting support.

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