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**In Situ Resource Utilization (ISRU) Experiments for
Mars Exploration**

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Introduction

In situ resource utilization can best be described as living off the land. In our case the “land” is the planet Mars. ISRU is based on the idea that some fraction of the consumables, life support and propellant materials do not have to be flown from earth. Rather, they can be manufactured or extracted from resources already present on Mars. The primary resources on Mars are the atmosphere, polar caps and regolith. The atmosphere of Mars is mostly carbon dioxide as shown in the table below. The proportion of oxygen on the other hand is quite small. Still, there is quite a bit of oxygen in the Martian atmosphere, but it is unfortunately tied up with carbon. Thus, one of the goals of ISRU is the separation of breathable oxygen from the carbon dioxide. Several means of separation have been proposed. We have begun experiments on another approach for production of oxygen with carbon monoxide as a useful by product. Our work on a CO₂ separator is described later in this report.

Gas	Proportion (%)
CO ₂	95.3
N ₂	2.7
Ar	1.6
O ₂	0.15
H ₂ O	0.03

Table 1: Approximate composition of Mars’ atmosphere at the surface

Regolith melting is another means of obtaining materials. Two materials of interest are iron and silicon. Iron oxide is plentiful on Mars and is of obvious importance for structural components. Silicon is the foundation of solid state devices. Power generation on Mars may be accomplished using silicon solar cells. There is discussion of the feasibility of in situ production of solar cells. This would require a means of extracting silicon from the regolith. We have conducted several experiments concerning melting and glassification of the Mars soil simulant. Other summer faculty fellows have tried various means of processing the stimulant material. These include furnace melting, microwave melting and laser ablation. We have conducted several furnace melting experiments in both air and carbon dioxide environments. We have also carried out experiments to test spark melting in a carbon dioxide atmosphere. These experiments suggest the possibility of using arc melting in a reducing atmosphere. It is important to keep in mind that we are working with a soil stimulant. Any simulant, no matter how chemically similar it is to Martian regolith, may differ in mineralogy. The underlying assumption in this work is that once a glass is formed, any differences between simulant and regolith are unimportant. The exact means of forming the glass do, however, depend on the mineralogy of the regolith. A sample return mission is required to help answer these questions.

Experiments

Melting experiments were carried out using JSC MARS-1 simulant. This material has been well characterized [1]. JSC MARS-1 is widely accepted among the scientific community. The simulant is derived from the weathered volcanic ash of the Pu'u Nene cinder cone on the Island of Hawaii. The composition of the simulant is known to be richer in Al_2O_3 , TiO_2 and water compared to the compositions determined by the Viking landers and the Mars Pathfinder.

In order to conduct melting experiments the simulant was first vacuum dried and then milled. Simulant was vacuum dried at 120°C for several days and then milled. Small particle size and proper mixing help to form a uniform glass and influence melting point of the material. JSC Mars-1 simulant is very coarse grained and one can clearly see different colored grains. A device for milling the simulant was constructed. An agate vial (Spex #8014) with two agate balls is used. The vial is agitated using a modified paint shaker (Tornado II 51000). The vial is held in place by two wooden end caps that were machined to fit into the shaker frame. The wooden end caps are held together with "missile tape". Tape on the wooden end caps keeps the ends of the vial under compression prevents material from being lost while handling. The loaded paint shaker/mill is shown below.

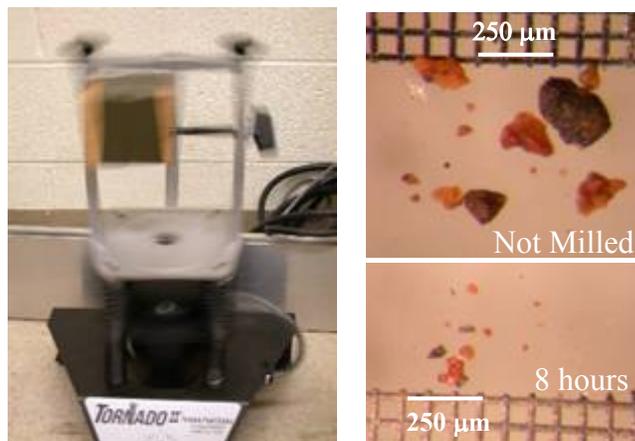


Figure 1: Milling apparatus

Eight hours of dry milling produces a very fine powder as show in figure 1. The particles shown in these photographs were dispersed by mixing simulant with methanol and spraying the mixture onto glass slides. The maximum particle size was limited by the orifice. Particles in the $500\mu\text{m}$ - $1000\mu\text{m}$ range can be found in the simulant, but they do not pass through the atomizer.

Vacuum dried and milled powders were pressed into pellets using a hydraulic press. The pellets were 1inch in diameter and had a typical thickness of about 1/8 inch. A pressure of 10Kpsi was applied to the pellet. Smaller disks and fragments were prepared by

drilling the pellets with a stainless steel core drill. All melting experiments were carried out in HBC high grade boron nitride crucibles that were machined in our furnace shop. Melted simulant has been found to stick to alumina and so boron nitride was used. Table 2 shows a summary of all melted samples produced. In each run the temperature was ramped up at a rate of 10°C/min and then held at a constant dwell temperature for 60 minutes. The temperature was ramped down at 5°C/min to a level of 500°C. Below 500°C, the sample was allowed to furnace cool by reducing the setpoint below room temperature. Samples processed in CO₂ had a pressure of 5-7mbar at the dwell temperature and about 1.3mbar at room temperature. This is comparable to the atmospheric pressure on Mars. Carbon percentages are by weight of initial simulant not total weight. The carbon source is an arc lamp rod made of spectroscopic grade carbon (Ultra Carbon type C7314) that was shaved with a knife blade.

Samples Melted in Air

A Sample melted in air at 1200°C is shown below in figure 2. Figure 2a shows the surface which is full of bubbles. This surface is a thin crust with a large cavity below. The sample in figure 2b shows a translucent glass like material that was formed inside a cavity beneath the surface of the melted sample. There are obvious inclusions in this material. We interpret this result as an indication that some of the material in the simulant did not melt. The unmelted material may have been surrounded by other phases that did melt. Electron microprobe analysis shows the presence of some FeTi oxides.



Figure 2: 1200°C Air (a) Surface, (b) Glass in cavity

Since there appeared to be some unmelted phases, we increased the processing temperature to 1300°C. We also added a cap to some of the crucibles to see if it would prevent loss of volatile materials. All of the samples processed at 1300°C were vesicular as shown in figure 3. The addition of carbon to the simulant did not reduce iron to the metallic state. Unlike samples that were laser melted or microwave melted, there does not seem to be any plagioclase or other silicates.



Figure 3: Typical sample is vesicular

Samples Melted in CO₂

Processing samples in air will not be very likely on Mars. Since the atmosphere on Mars is approximately 95% CO₂, we decided to process our samples in a furnace filled with CO₂. The Engineering Directorate (ED12) allowed us to use a high temperature tube furnace they have in building 4475. A vacuum system is connected to the furnace which is shown below in figure 4.



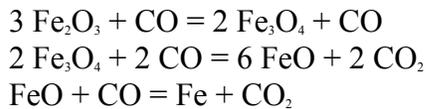
Figure 4: High temperature furnace and vacuum system

Prior to heating the sample, the furnace was pumped out with a roughing pump and then back filled with CO₂. In order to remove as much air as possible, the furnace was pumped and back filled several times. Room temperature pressure was adjusted to about 1.3mbar. At 1300°C the pressure would then be in the 5-7mbar range, typical of the Martian atmosphere. Unfortunately, the furnace malfunctioned on our first run. The temperature shown on the controller fluctuated. An auxiliary thermocouple indicated that the temperature was 1310°C. The temperature controller actually showed a decrease in temperature with full heater power applied. The furnace was shut down and allowed to cool. We doubt that the sample went much higher than 1310°C but we do not know how long it was at the maximum temperature. The cooling rate is also unknown but it appeared to be much faster than the programmed value (5°C/min.). When the furnace was turned off, the auxiliary thermocouple showed a drop of several degrees in a second. This faster cooling rate and possibly shorter time at the maximum temperature may account for the differences observed in the two sets of samples melted in CO₂.

Some of the samples melted in CO₂ contained magnetically separated simulant and were pressed into a rod rather than a disk shape. Since one of the desired results is the production of iron from regolith, we decided to use a permanent magnet to do some post processing. Magnetic separation was accomplished by placing a rare earth magnet on top of a Petri dish containing milled simulant. Shaking the dish caused some of the magnetic

material to be attracted to the magnet. The magnet produced a field of about 2.5kG. Sliding the magnet across the top of the dish helped to remove nonmagnetic dust that simply adhered to the magnetic material. This technique separated out about 5-6% of the mass of the original simulant. The magnetically depleted simulant showed only a few weakly magnetic grains remaining. This magnetically separated material was mixed with a small amount of methanol and pressed into a rod. Pressing was accomplished by pouring the material into a glass tube and tamping with a tight fitting solid rod.

The JSC MARS-1 simulant is known to contain Ti-magnetite [1] and our microprobe results show FeTi oxides, possibly ilmenite (FeTiO_3). JSC-Mars-1 simulant is derived from volcanic ash. Varying ratios of Ti-magnetite and ilmenite are found in volcanic ash. Ti-magnetite is a solid solution that lies between magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$ and Ulvospinel $\text{Fe}^{2+}_2\text{TiO}_4$. Hemitite (Fe_2O_3) can easily be reduced to metallic iron (Fe) by carbon monoxide (CO). Several reduction reactions are shown below.



Many of our samples were prepared with carbon. We thought that the carbon might help to reduce the iron oxide. In fact, many of the ISRU papers published state that the iron in Martian regolith can easily be extracted by this simple process. However, if the iron is in a more complex oxide the simple CO reduction process might not work.

Two of the samples melted in CO_2 were reagent grade iron oxides. Red Fe_2O_3 and black Fe_3O_4 were pressed into rod shapes and heated in CO_2 . The heating and cooling rates were the same as those used for melting all our other samples. The red Fe_2O_3 is not magnetic and the black Fe_3O_4 is very strongly magnetic. After melting, neither oxide retained its original color. Both samples became gray and the Fe_2O_3 became magnetic. Both Oxides are so strongly magnetic that they can support the weight of the crucible. This experiment seems to indicate that processing in CO_2 caused the iron oxide reagent to experience a change in its oxidation state.

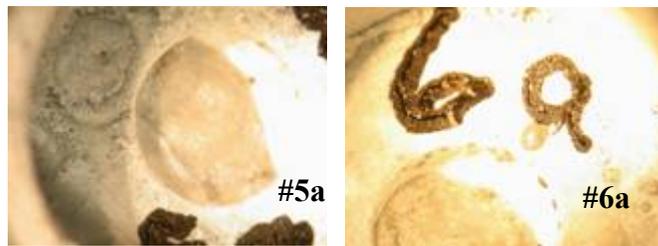


Figure 5: Iron oxides processed in CO_2 (#5a) Fe_3O_4 , (#6a) Fe_2O_3

As mentioned previously, there was a furnace malfunction during the first CO_2 run. We know, from our measurements with the auxiliary thermocouple, that the cooling rate was much faster than the programmed rate. What is not known is the maximum temperature the samples reached or how long they were at this temperature. The samples have not yet undergone microprobe analysis. We can only compare the physical characteristics of the

two batches of samples processed in CO₂. There are however some very striking difference which are outlined below. Samples identified with only a number are in the first run in which the malfunction occurred. Samples with a number and then a letter (i.e. #1a) indicate that the sample was prepared in the second CO₂ run. Samples in the second run underwent the same heating and cooling rates as those samples processed in air. Table 2 shows a summary of all samples processed in either CO₂ or air.

Figure 6 shows an example of the dramatically different results obtained in these experiments. Both samples are made from magnetically separated simulant. Sample #1 was produced when the furnace malfunctioned and sample #1a was produced with the programmed heating and cooling rates. The magnetic properties of these two samples is as difference as their appearance. Sample #1 is magnetic while sample #1a is not magnetic. Perhaps the faster cooling rate enabled sample #1 to form a glass like ball. No gas bubble can be seen in this sample unlike the structure of sample #1a. Sample #1 may have reached a high enough temperature to thoroughly out gas and then quickly cool to form the glass.

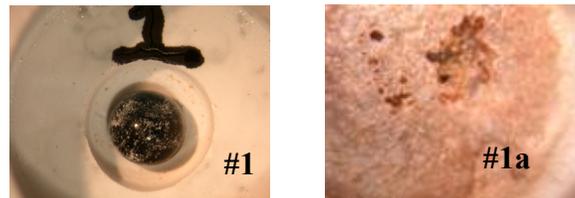


Figure 6: Magnetically separated simulant (#1) magnetic ball of glass, (#1a) not magnetic

Figure 7 shows what happened when carbon was added to the simulant. Again the sample that was formed when the furnace malfunctioned has a glassy appearance to it and the sample for which the material that was cooled slowly has a crust. Both #1a and #2a are similar in appearance and have reduced magnetic properties when compared to samples #1 and #1a. The black glassy part of sample #2 is more strongly magnetic than the glass produced in sample #1.



Figure 7: Magnetically separated simulant with 10%C added (#2) magnetic glass, (#2a) few chips slightly magnetic

Figure 8 show the results for two disks of simulant that has not been magnetically separated. Both samples are similar in appearance. Their surface is full of bubbles. The interior is composed of a vesicular material that has black and dark honey colored regions. Both of these samples contain chips of material that are slightly magnetic. Since these are not made from magnetically separated material they contain all the components of the simulant. This in turn means that there is more material to out gas and contribute to the formation of bubbles and voids.

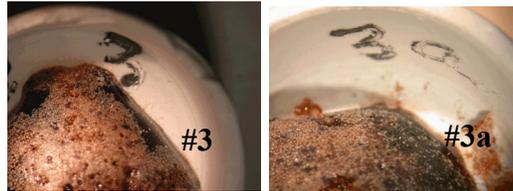


Figure 8: Simulant disks without carbon (#3) and (#3a) contain some magnetic chips

The samples shown in figure 9 are both made from simulant with 10% carbon added. Compared to samples #3 and #3a, both of these samples show enhanced magnetic properties. Again, they have a crusty surface and show considerable bubbles. Sample #4 contains a strongly magnetic chunk that appears to contain some black glassy areas. Sample #4a is magnetic, but not as strong as #4. The magnetic chunk in sample #4 will stick to a magnet and support its own weight.



Figure 9: Simulant disks with 10% carbon added (#4) has a strongly magnetic chunk, (#4a) not as strongly magnetic

These results do seem to show a pattern. In terms of their magnetic properties, samples that contain carbon (#2, 2a, 4, 4a) do seem to be more strongly magnetic than those that do not contain carbon. The samples that were heated in the furnace that malfunctioned (#2, 4) are more glass like and have stronger magnetic properties compared to those that were cooled slowly.

Oxygen Separation

The Martian atmosphere contains quite a bit of oxygen that is, unfortunately, tied up with carbon. As part of our ISRU we have considered the problem of oxygen separation. Oxygen is important for both life support and propellant. Solid Oxide electrolysis has been suggested by Sridhar as a method for oxygen production [2]. This technique relies on oxygen ion conduction in yttria-stabilized zirconia (YSZ). The YSC cell is a ceramic

material. Oxygen separation is accomplished by ionic conduction that occurs in the 750°C-900°C range. It is well known that silver oxide dissociates and produces atomic oxygen at about 285°C. Thin silver foils have been used in the production of atomic oxygen from molecular oxygen. Collisions between atoms of oxygen can then cause the atomic oxygen to be converted back to molecular oxygen. In order to produce oxygen from the Martian atmosphere, one needs to dissociate the carbon dioxide into carbon monoxide and free oxygen. The free oxygen can then be separated from the carbon monoxide by allowing it to diffuse through a thin silver film. Something similar has been tried by Vuskovic *et al.* [3], in which an RF discharge was used to dissociate the CO₂. However, the RF technique needs a low pressure to establish the discharge. An RF power source is also required. We envision a device, which would use a UV lamp or a spark source to dissociate the CO₂. UV light of wavelength $\lambda < 170\text{nm}$ has sufficient energy to break the carbon-oxygen bond. This would produce carbon monoxide and oxygen. The carbon monoxide exhaust would be used for the reduction of iron from the Martian regolith. Oxygen would diffuse through the silver film and can be used for life support and propellant. We have begun building a prototype of this apparatus as shown in figure 10. In our device, the silver film is heated by an electric heater. Since the temperature is rather low, we may be able to use a solar furnace to replace or supplement the electric heating element.



Figure 10: Prototype of O₂ production device

Spark Melting

Our final ISRU experiments were based on the idea of arc or spark melting. Furnace melting experiments showed that we were able to convert non-magnetic iron oxide (Fe₂O₃) into a magnetic state. Instead of using a furnace to melt regolith, one might be able to use an arc melter. Arc melting provides a high temperature with very rapid heating and cooling. Our spark melting experiments were conducted in a CO₂ atmosphere. The energy of the spark, no doubt produced some CO, providing a reducing atmosphere. These experiments were conducted in a resealable zipper bag that was purged with CO₂. A carbon arc lamp rod was mounted inside the bag and held in place with a Cajon type fitting. The high voltage source was a Tesla coil that was attached to the fitting. Iron oxide was mixed with methanol to produce thick slurry. This slurry was then coated onto a carbon disk. A sheet of copper was connected to a water pipe with a heavy gauge wire. The copper sheet provided a ground plane in the bag. Between the carbon disk and the ground plane, we placed a rare earth magnet. Sparks from the carbon

electrode produced holes in the iron oxide coating. When observed with a microscope, these holes show melted edges and glassy reflections. Adjacent to many of the holes are small bits of magnetic material. Sparking is a very violent process and material can be ejected from the surface. The magnet placed under the disk helped to retain any magnetic grains that were produced. Sparks striking the disk and the resulting surface features are shown in figure 12. Observation of the surface after sparking revealed magnetic grains standing up from the surface. If a magnet is passed over the surface, these small magnetic grains can be seen moving in response to the magnetic field. No such movement can be observed before spark melting. .

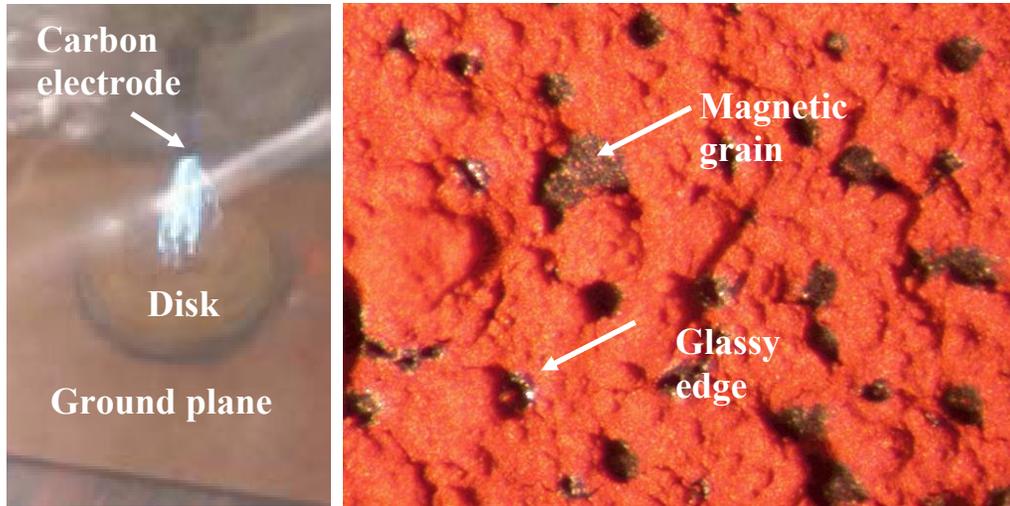


Figure 12: Spark melting Fe_2O_3

From these observations, we can conclude that the process is reducing some of the iron in the oxide. We have not yet conducted this experiment with simulant. We plan to try spark melting raw simulant as well as magnetically separated and magnetically depleted simulant. These experiments suggest the possibility of processing regolith in an arc melter equipped with a magnet trap to catch the reduced iron.

DwellTemp. (°C)	Crucible ID	Crucible Type	Atm.	Comp.	Comments
1200	M4, 1	BN No cap	Air	M4 sim.	Simulant disk, 8hr grind, 0%C
1300	M4,2 NC NCP	BN No Cap	Air	M4 sim	Simulant disk, 8 hr grind, 0%C
1300	M4,2 WC Cap	BN Cap	Air	M4 sim	Simulant disk, 8 hr grind, 30%C
1300	M4,2 NC Cap	BN Cap	Air	M4 sim	Simulant disk, 8 hr grind, 0%C
1300 (?)	1	BN No cap	CO ₂	M4 Mag Sep.	Furnace Malfunction max temp near 1300°C uncertain time. Furnace cool. Magnetically separated from M4 powder, 8hr grind. Pressed rod
1300 (?)	2	BN No cap	CO ₂	M4 Mag sep +10%C	Furnace Malfunction max temp near 1300°C uncertain time. Furnace cool. Magnetically separated from M4 powder, 8hr grind +10%C. pressed rod
1300 (?)	3	BN No cap	CO ₂	M4 sim	Furnace Malfunction max temp near 1300°C uncertain time. Furnace cool. Simulant disk, 8 hr grind
1300 (?)	4	BN No cap	CO ₂	M4 sim. +10%C	Furnace Malfunction max temp near 1300°C uncertain time. Furnace cool. Simulant disk, 8 hr grind +10% C
1300	1a	BN No cap	CO ₂	M5 Mag Sep.	Magnetically separated from M5 powder, 8hr grind. Pressed rod
1300	2a	BN No cap	CO ₂	M5 Mag Sep.	Magnetically separated from M5 powder, 8hr grind + 10% C. Pressed rod
1300	3a	BN No cap	CO ₂	M4 sim.	Simulant disk, 8 hr grind
1300	4a	BN No cap	CO ₂	M4 sim. +10%C	Simulant disk, 8 hr grind +10% C
1300	5a	BN No cap	CO ₂	Fe ₃ O ₄ Black	Pressed rod, strongly magnetic
1300	6a	BN No cap	CO ₂	Fe ₂ O ₃ Red	Pressed rod, not magnetic

Table 2: Summary of Samples Produced

Future Research

Our work has raised a number of questions that need to be answered. JSC MARS-1 simulant is chemically different than the composition suggested by Viking and Path Finder data. Reformulation of this material seems to be necessary. However, the most recent Mars Exploration Rover (MER) data has not yet been released. Once this data becomes available the simulant should be reformulated. Sample return missions are about a decade in the future. Only then will we have the ability to know the mineralogy of Martian regolith. The question of reducing iron from TiFe oxides should be dealt with in the near term. It seems reasonable to think that Martian volcanism should mirror that on Earth. If not TiFe oxide, then perhaps some other complex oxides exist in the regolith. Terrestrial soil undergoes weathering which appears to be largely absent on Mars.

Experiments conducted in CO₂ yielded very different results. We would like to experiment with cooling rates, processing time and temperature. Whatever occurred when the furnace malfunctioned produced dramatically different results and this needs to be investigated further. Electron microprobe analysis needs to be conducted so that we can understand the chemistry of the materials produced. Melting experiments need to be conducted under different atmospheric conditions. Melting in a CO atmosphere would be the next step.

There are two experiments that can be continued at Mercer University. Our oxygen separation experiments require much less expensive equipment. There are many questions to be answered about the design of our prototype device. Film thickness, substrates, operating temperature and yield all need to be explored and optimized. We also need to experiment with different dissociation mechanisms and determine which approach will make the most efficient use of electrical power. These experiments will provide excellent student research projects. Experiments with spark/arc melting also need to be continued. Again, students can conduct these experiments.

Conclusions

Transformation of iron oxides indicates reduction but, comparable results were not achieved with simulant. This suggests that more complex TiFe oxides will be difficult to reduce or will require a different method. It is difficult to draw any conclusions from our spark melting experiments. They do suggest that arc melting in a magnetic field could be an alternative to furnace melting. This is certainly worth exploring.

Acknowledgements

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Engineering Directorate (ED12) provided access to the equipment that made our CO₂ furnace melting experiments possible.

References

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[2] L. Vuskovic et al., *Oxygen Production and Separation for Martian Atmosphere by the Radio Frequency Discharge*, Proceedings of Lunar and Planetary Science ISRU II 28th Meeting 1997.

[3] Sridhar, K. R., Finn, J. E., and Kliss, M. H., *In-Situ Resource Utilization Technologies For Mars Life Support Systems*, Adv. Space Res., Vol. 25, No.2, pp. 249-255, 2000