Oxygen Extraction from Minerals

Presented by Dr. Tony Muscatello
NASA Applied Chemistry Laboratory
Kennedy Space Center
February 6, 2017
Outline

- Introduction
- Hydrogen or Carbon Monoxide Reduction of Ilmenite (FeTiO$_3$)
- Carbothermal Reduction of Metal Oxides and Silicates w/Methane
- Molten Regolith Electrolysis (MRE)
- Combined CO/Carbothermal Reduction of Metal Oxides and Silicates
- Water Extraction from Regolith
- Recent Development and Field Demonstrations
- Challenges
- Future Directions
Introduction

- Lunar regolith contains reducible oxides:

<table>
<thead>
<tr>
<th>Oxide</th>
<th>JSC-1 Lunar Simulant (wt%)</th>
<th>Lunar Sample 14163 (wt%)</th>
<th>Lunar Sample 62230 (wt%)</th>
<th>Lunar Sample 10002 (wt%)</th>
<th>Lunar Sample 12001 (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42.55</td>
<td>47.3</td>
<td>46.6</td>
<td>42.2</td>
<td>46.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>7.71</td>
<td>1.6</td>
<td>-</td>
<td>7.75</td>
<td>2.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>13.47</td>
<td>17.8</td>
<td>26.5</td>
<td>13.6</td>
<td>12.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>15.16</td>
<td>10.5</td>
<td>5.60</td>
<td>15.3</td>
<td>17.2</td>
</tr>
<tr>
<td>MgO</td>
<td>7.98</td>
<td>9.6</td>
<td>6.40</td>
<td>7.76</td>
<td>10.4</td>
</tr>
<tr>
<td>CaO</td>
<td>11.99</td>
<td>11.4</td>
<td>14.5</td>
<td>11.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.45</td>
<td>0.7</td>
<td>0.44</td>
<td>0.47</td>
<td>0.48</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.15</td>
<td>0.6</td>
<td>-</td>
<td>0.16</td>
<td>0.26</td>
</tr>
<tr>
<td>MnO</td>
<td>0.21</td>
<td>0.1</td>
<td>-</td>
<td>0.20</td>
<td>0.22</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>0.30</td>
<td>0.41</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.14</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
</tr>
</tbody>
</table>

- But they are very stable and require lots of work!
Each Apollo mission utilized Earth-derived propellants (Saturn V liftoff mass = 2,962 tons).

What if lunar lander was refueled on the Moon’s surface?
73% of Apollo mass (2,160 tons)

Assume refueling at L1 and on Moon: 34% of mass (1,004 tons)

Assume refueling at LEO, L1 and on Moon: 12% of mass (355 tons)

+Reusable lander (268 tons)

+Reusable upper stage & lander (119 tons)

Propellant from the Moon will revolutionize our current space transportation approach.

Courtesy of Brad Blair, Colorado School of Mines
Hydrogen or Carbon Monoxide Reduction of Ilmenite (FeTiO$_3$) and Pyroclastic Glass-Chemistry

- Lunar regolith and regolith at other locations (asteroids and Mars) contain a variety of metal oxides in the form of oxides, silicates, and aluminates.
- Lunar regolith contains ilmenite (FeTiO$_3$) at 0.4-12.8 vol% depending on location, with lunar mare being higher than the highlands.
- H$_2$ Reduction:  
  \[ \text{H}_2 + \text{FeTiO}_3 \rightarrow \text{H}_2\text{O} + \text{Fe}^0 + \text{TiO}_2 \ (T = 900^\circ \text{C}) \]  
  \[ \text{H}_2\text{O} + 2 \text{ e}^- \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]  
  O$_2$ Yield = ~1-2 wt% - depending on location
- CO Reduction:  
  \[ \text{CO} + \text{FeTiO}_3 \rightarrow \text{CO}_2 + \text{Fe}^0 + \text{TiO}_2 \ (T = 900^\circ \text{C}) \]  
  \[ \text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO} \ \text{(RWGS Reaction)} \]  
  \[ \text{H}_2\text{O} + 2 \text{ e}^- \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]  
  O$_2$ Yield = ~1-2 wt% - depending on location
2008 ISRU Field Test Infrastructure and Test Layout – Mauna Kea

- Varied Terrain, Slopes, & Rock Distribution for Resource Prospecting/ Mobility Demo
- Outpost Oxygen Production Field Test Location
- RESOLVE/Scarab Field Test Location
- Main Camp Area
- Main Access Road to Test Area
- Access Road to ISRU Areas
- Lodging Infrastructure
- Staging/Unpacking Area
- Flat, Open Area for Oxygen Extraction Demo
- Bad road here Cannot negotiate much
- This Road will be graded

Image © 2009 DigitalGlobe
PILOT Field Test Hardware

Rotating H\textsubscript{2} Reduction Reactor - 17 kg/batch

Lift System and Auger Loading

Dump Chute

Bucket Drum Excavator (IR&D)

Hydrogen Storage

Product Processor

Oxygen Liquefier/ Storage (IR&D)

Salt Extraction Collector and Second Stage Filter

Water Condenser

Lander Simulator (IR&D)

PILOT – Precursor ISRU Lunar Oxygen Testbed

(Lockheed Martin Astronautics – Denver)
ROxygen Field Test Hardware

Two Fluidized H₂ Reduction Reactors - 10 kg/batch each

- Water Electrolysis Units (2)
- Gaseous O₂ Storage
- Water Freezeer
- Water Tanks (2)
- Regolith hopper/auger lift system (2)
- Cratos Excavator
- Ramp to allow Cratos operations (or other small vehicle)
- Regolith reactor exhaust

NASA ROxygen H₂ Reduction System
(JSC, KSC, and GRC)
ROxygen & PILOT Tasks

- Demonstrate excavation and material delivery to plant and removal of spent regolith;
  - Increase distance and terrain complexity between plant and excavation site each day

- Demonstrate regolith processing to extract oxygen
  - Min. of 4 h on one day; nominal 8 h per day
  - Max. of 8 h/day for 5 days

- Demonstrate oxygen separation and storage
  - Liquefaction and cryogenic storage
  - Moderate pressure gaseous oxygen

- Opportunistic Demos
  - Demonstrate alternative oxygen liquefaction and storage
  - Hot fire a LO$_2$/LCH$_4$ RCS 25 lbf thruster igniter
  - Mossbauer spectrometer on Cratos to measure iron before and after processing
ROxygen Setup
PILOT
2008 Field Test Results

- **PILOT** (1000 kg O₂ per year design scale)
  - System integrated with mini rover equipped with bucket drum excavator bringing soil to the reactor. Integrated system was tested during field tests in Hawaii.
  - Processing capacity of ~15 kg of regolith per batch yielding 150 g of O₂.
  - Produced oxygen yields of 1 wt% of processed regolith.
- **ROxygen** (~667 kg O₂ per year design scale)
  - Two large-scale reactors were tested in 2008 at the first ISRU technology field tests.
  - Tests in large reactor provided oxygen yields in the range 0.2% – 0.5% by mass of regolith. The low yields are attributed to the operational limits of a contaminant scrubber.
  - Recirculation of hydrogen was achieved with removal of hydrogen halide contaminants from the produced water.
Water From Rocks!

Purity Goal…

More info at: https://isru.nasa.gov/Hydrogen-Reduction-of-Regolith.html
Concentric Hydrogen Reduction Reactor

• Technology features
  – Concentric cylindrical chambers allow the exchange of heat from the hot regolith being processed to fresh regolith waiting to be introduced.
  – Maintains regolith in fluid and loose state (fluidization) by hydrogen flow and/or vibration of the reactor – compares efficiencies.

• Results and Performance
  – Vibrofluidization and gas fluidization with Helium gas are near equally efficient in heat recuperation. Fluidization with hydrogen is not as effective.
  – Tests in large reactor provided oxygen yields in the range 0.2% – 0.5% by mass of regolith. The low yields are attributed to the operational limits of a contaminant scrubber.
  – Added mass and complexity of a dual chamber reactor is also counterproductive for ISRU usage.

Dual Chamber H₂ reduction reactor mounted on flex stand (Credit: Glenn Research Center)

Hardware schematic for dual chamber H₂ reduction reactor with thermocouple locations (credit: Glenn Research Center).
Carbothermal Reduction of Metal Oxides and Silicates - Chemistry

• Methane Decomposition and Carbon Deposition:
  \[ \text{CH}_4 \rightarrow \text{C(s)} + 2 \text{H}_2 \ (T = \text{>1600}\,^\circ\text{C}) \]

• Carbothermal Reduction:
  \[ \text{C}(\text{s}) + (\text{Fe, Ti, Si})\text{O}_x \rightarrow x \text{CO} + \text{Fe}^0 + \text{Ti}^0 + \text{Si}^0 \]

• Methane Regeneration (Sabatier Rxn):
  \[ \text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \ (T = \text{~400}\,^\circ\text{C}) \]

• Water Electrolysis:
  \[ \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]
  \[ \text{O}_2 \text{ Yield} = <15 \text{ wt\% with acceptable carbon losses} \]
Carbothermal Reduction of Silicates – Reaction Summary

Step 1
- Lunar Silicates
- CH₄
- Metal Oxide Reduction
- Clag
- H₂

Step 2
- Metals Silicon
- CO
- Carbon Oxide Reduction
- By-products
- H₂O

Step 3
- Water Reduction
- O₂
- Oxygen Liquifier
- Lunar LO₂
- CH₄
- H₂

More info at: https://isru.nasa.gov/Carbothermal.html
Carbothermal Reduction of Silicates – Practical Limitations and Solution

Typical crucible after a single carbothermal reduction processing batch in a traditional hot-wall furnace.

Direct energy processing approach where the regolith becomes its own processing container.

Lunar regolith has a very low thermal conductivity of 0.0172 - 0.0295 W/m-K.
Lunar regolith has a very low thermal conductivity of $0.0172 - 0.0295 \text{ W/m-K}$.

Regions of molten JSC-1A lunar regolith simulant produced during a 40-minute heating test.
Carbothermal Regolith Reduction Module (ORBITEC)
ORBITEC developed the Carbothermal Regolith Reduction Module to demonstrate remote, semi-autonomous extraction of oxygen from lunar regolith simulant using solar energy:

- Automated filling of the regolith hopper and transfer to carbothermal reduction reactor
- Automated gas handling system, including gas clean-up beds and methanation reactor
- Automated removal of processed regolith
- Ability to operate remotely through an http:// interface

Hardware is sized to support oxygen production at a rate 1 MT O₂ per year.
Solar Energy Collection and Delivery Module

- Physical Sciences Inc. built a Solar Energy Collection and Delivery Module that provides concentrated solar energy to the Carbothermal Regolith Reduction Module.
- Seven solar concentrators are mounted on an array with two-axis tracking of the sun.
- The solar energy from each concentrator is delivered to the carbothermal reactor via a fiber optic cable.
- Each fiber optic cable delivers 86 to 100 W (total of 600 to 700 W) of concentrated solar energy.
Carbothermal Reduction with Solar Energy

- Oxygen yields up to 10.3%wt with processing times up to 80 minutes have been demonstrated (JSC-1A lunar regolith simulant and tephra)
- The carbothermal reduction process produces silica fume as an intermediate product, so keeping the end of the quartz rod clean has been a challenge
- ORBITEC has built and successfully tested a gas nozzle that keeps the end of the quartz rod clean during processing (aerodynamic window)
Solar Concentrator/Carbothermal Reduction of Regolith for Lunar Oxygen Production – 2010 Field Demo on Mauna Kea
NASA/PSI/ORBITEC
Carbothermal Reduction with Solar Energy – Field Test Results

• The carbothermal plant
  – Performed 17 tephra melts (12 for O₂ production)
  – over 7 days
  – Produced 31.5 g of water from the tephra
• Equivalent to 28 g of oxygen
  – 9.7% oxygen yield by mass

Carbothermal Regolith Reduction Module, Solar Energy Module and Pneumatic Regolith Transfer Unit during the 2010 ISRU Analog Test.
Molten Regolith Electrolysis - Chemistry

- Molten Oxide Electrolysis:
  \[ O^{2-} \rightarrow 2 \, e^- \, (\text{cathode}) + \frac{1}{2} \, O_2 \, (\text{gas}) \, (T = >1600^\circ \text{C}) \]
  \[ \text{Fe}^{2+} \, (\text{electrolyte}) + 2 \, e^- \, (\text{cathode}) \rightarrow \text{Fe}^0 \, (\text{liquid}) \]
  \[ \text{Si}^{4+} \, (\text{electrolyte}) + 4 \, e^- \, (\text{cathode}) \rightarrow \text{Si}^0 \, (\text{liquid}) \]

- \( O_2 \) Yield = 15-37 wt% depending on scale of operation and feed (mare vs. highlands)

- Metals: [Will be covered by Laurent Sibille]

More info at [https://isru.nasa.gov/Molten_Regolith_Electrolysis.html](https://isru.nasa.gov/Molten_Regolith_Electrolysis.html)
Schematic of electrolytic cell configuration to investigate electrochemical behaviors of various anode materials in molten oxides (left) and furnace containing the cell in operation at 1600ºC (right) (MIT)

Thermal model of Joule heating in a Molten Regolith Electrolysis reactor in which the regolith itself contains a centered pool of electrolyte heated by the electrolytic current. (Image credit: NASA Kennedy Space Center)

Schematic of counter gravity Molten Material Withdrawal device (Ohio State U.)

Small casting of molten ferrosilicon (lower layer) and molten oxide of lunar composition (top layer) withdrawn by counter-gravity suction at 1600ºC from reactor furnace (Image credit: Ohio State U./KSC)
Combined CO/Carbothermal Reduction of Metal Oxides and Silicates – Chemistry (Pioneer Astronautics)

• Carbon Monoxide Silicate Reduction System (COSRS):
  - Iron oxide reduction ($T = 800\text{-}850^\circ C$):
    \[ \text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2 \quad \Delta H = -15.7 \text{ kJ} \]
  - Carbon deposition (carbon monoxide disproportionation) ($T = 600^\circ C$):
    \[ 2 \text{ CO} = \text{C} + \text{CO}_2 \quad \Delta H = -18.7 \text{ kJ} \]
  - Carbothermal reduction ($T = \text{up to } 1600^\circ C$):
    \[ \text{FeO} + \text{C} = \text{Fe} + \text{CO} \quad \Delta H = 156.7 \text{ kJ} \]
    \[ \text{SiO}_2 + 2 \text{ C} = \text{Si} + 2 \text{ CO} \quad \Delta H = 689.8 \text{ kJ} \]

More info at
http://www.lpi.usra.edu/meetings/leag2005/presentations/wed_am/04_berggren.pdf
Combined CO/Carbothermal Reduction of Metal Oxides and Silicates – Chemistry (Cont.)

- Carbon Monoxide Silicate Reduction System (COSRS):
  - Reverse water gas shift reaction (T = 400ºC):
    \[ \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}(l) \quad \Delta H = -2.9 \text{ kJ} \]
  - Electrolysis:
    \[ \text{H}_2\text{O}(l) = \text{H}_2 + \text{O}_2 \quad \Delta H = 571.7 \text{ kJ} \]

  \[ \text{O}_2 \text{ Yield} = \sim 15-20 \text{ wt\%} \]

  - Byproducts: SiO (up to 5 wt\%) can be reduced to nearly pure Si metal
    - Ferrosilicon alloy – up to 25 wt\%
Combined CO/Carbothermal Reduction of Metal Oxides and Silicates

Recoverable Oxygen in JSC-1 Lunar Simulant

<table>
<thead>
<tr>
<th>Compound</th>
<th>kg Compound per 100 kg Soil</th>
<th>Compound Molecular Weight</th>
<th>kg Oxygen per 100 kg Soil</th>
<th>Cumulative kg Oxygen per 100 kg</th>
<th>kg Carbon per 100 kg Soil</th>
<th>Cumulative kg Carbon per 100 kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>3.44</td>
<td>159.70</td>
<td>1.03</td>
<td>1.03</td>
<td>0.78</td>
<td>0.78</td>
</tr>
<tr>
<td>FeO</td>
<td>7.35</td>
<td>71.85</td>
<td>1.64</td>
<td>2.67</td>
<td>1.23</td>
<td>2.00</td>
</tr>
<tr>
<td>P₂O₃</td>
<td>0.66</td>
<td>110.00</td>
<td>0.29</td>
<td>2.96</td>
<td>0.22</td>
<td>2.22</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.04</td>
<td>152.00</td>
<td>0.01</td>
<td>2.97</td>
<td>0.01</td>
<td>2.23</td>
</tr>
<tr>
<td>MnO</td>
<td>0.18</td>
<td>71.00</td>
<td>0.04</td>
<td>3.01</td>
<td>0.03</td>
<td>2.26</td>
</tr>
<tr>
<td>SiO₂</td>
<td>47.71</td>
<td>60.00</td>
<td>25.45</td>
<td>28.46</td>
<td>19.08</td>
<td>21.34</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.59</td>
<td>79.88</td>
<td>0.64</td>
<td>29.09</td>
<td>0.48</td>
<td>21.82</td>
</tr>
</tbody>
</table>

Iron Oxide Reduction - Carbon Deposition Reactor (81 g JSC-1)

COSRS Process Description  Carbothermal Reduction Furnace
Combined CO/Carbothermal Reduction of Metal Oxides and Silicates – (Berggren 2005)

- “Identified conditions leading to maximum leverage (= O\textsubscript{2} recovered/C lost).
  - Carbon losses are mostly as silicon carbide.
  - Carbon losses can be mitigated by reacting silicon carbide with fresh silica in the lunar soil as follows.
    \[ \text{SiO}_2 + 2 \text{SiC} = 3 \text{Si} + 2\text{CO} \quad \Delta H = 833.6 \text{ kJ} \]
- Similarly, silicon carbide can be reacted with fresh ferrous oxide in the lunar soil as follows.
  \[ \text{FeO} + \text{SiC} = \text{Si} + \text{Fe} + \text{CO} \quad \Delta H = 228.6 \text{ kJ} \]
- The above reactions suggest that adding less than the theoretical, or stoichiometric, amount of carbon to reduce all of the silicon oxide might also reduce carbide formation.”
- Additional work has not been published yet.
Water Extraction from Regolith

Gases released from heated Rocknest aliquots

Volatile, Isotope, and Organic Analysis of Martian Fines with the Mars Curiosity Rover
L. A. Leshin et al.
Science 341, (2013); DOI: 10.1126/science.1238937
Challenges

• **H₂ Reduction**
  – Removal of H₂S and HF from water
  – Scale-up
  – Reactor seals

• **Carbothermal Reduction**
  – Carbon losses
  – Mass of solar concentrator and dust accumulation
  – Silica fume control

• **Molten Regolith Electrolysis**
  – Electrode consumption

• **COSRS**
  – Scale-up and development

• **Funding**
  – Moon vs. Mars vs. Asteroids
  – All of the above?
NASA has restarted its ISRU Project

NASA should fully embrace ISRU

Integrated human exploration of the inner solar system

Moon, asteroids, Mars moons, Mars

Commercial development of key technologies in partnership w/NASA to reduce costs

– i.e. shared funding

– Habitats, ISRU, spacecraft, launch vehicles, etc.

– Asteroid mining

Pick an architecture and stick with it for >8 years