Mars Atmospheric In Situ Resource Utilization Projects
at the Kennedy Space Center

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NASA – Kennedy Space Center

Earth & Space 2016
Orlando, FL
April 12-15, 2016
Outline

• Projects and Team Members
• Martian Resources
• Mars Atmospheric Processing Module
• Mars Propellant Production with Ionic Liquids
• Self-Cleaning Boudouard Reactor for Full Oxygen Recovery
• Conclusions
Projects and Team Members

- **Mars Atmospheric Processing Module:** Paul Hintze, Anne Meier, and Jon Bayliss (KSC)
- **Ionic Liquids:** Paul Hintze, Tracy Gibson, Jan Surma (KSC), Laurel Karr, Steve Paley (MSFC), and Matt Marone (Mercer University, GA)
- **Self-Cleaning Boudouard Reactor for Full O_2 Recovery:** Paul Hintze, Anne Meier, Jon Bayliss, Tracy Gibson, James Captain, Griffin Lunn, Robert Devor, (KSC), Matt Mansell (MSFC), and Mark Berggren (Pioneer Astronautics)
Martian Resources

- **Atmosphere of Mars**
  - 95.9% CO₂
  - 2% Ar, 1.9% N₂
  - <1% pressure of Earth’s atmosphere (~7 mbar)

- **Significant Amounts of Water in the Top 1-Meter of Regolith**
  - Water ice caps at the poles
  - ~2% at least everywhere else
  - ~10% even at equatorial regions
  - **Curiosity rover ground truth:**
    - 1.5-3% water in surface regolith (SAM)
    - Average 2.9% water (DAN), up to 7% in top 60 cm of regolith in some locations-seasonal variation
    - Transient liquid water at night in the top 5 cm of regolith
MARCO POLO Project

• **ISPP: In Situ Propellant Production**
  – Demonstrate production of Mars Sample Return propellant
  – Reduce risk for human Mars missions

• **MARCO POLO - Mars Atmosphere and Regolith Collector/Processor for Lander Operations**
  – Started in 2011

• The **Atmospheric Processing Module (APM)**
  – Mars CO₂ Freezer Subsystem
  – Sabatier (Methanation) Subsystem

• Collect, purify, and pressurize CO₂

• Convert CO₂ into methane (CH₄) and water with H₂

• Other modules mine regolith, extract water from regolith, purify the water, electrolyze it to H₂ and O₂, send the H₂ to the Sabatier Subsystem, and liquefy/store the CH₄ and O₂
**Lander Design Concept**

**Atmo Processing Module:**
- CO2 capture from simulated Mars atmosphere (KSC)
- Sabatier converts H2 and CO2 into Methane and water (KSC)

**C&DH/PDU Module:** (JSC)
- Central executive S/W
- Power distribution

**Soil Processing Module:**
- Soil Hopper handles 30 kg (KSC)
- Soil dryer uses CO2 sweep gas and 500 deg C to extract water (JSC)

**Water Processing Module:** (JSC)
- Currently can process 520g/hr of water (max 694 g/hr)

**Water Cleanup Module:** (KSC)
- Cleans water prior to electrolysis
- Provides clean water storage

**Liquefaction Module:** (TBD)
- Common bulkhead tank for Methane and Oxygen liquid storage

**RASSOR 2.0:** (KSC)
- Excavator
- Provides feed to Soil Dryer

**1 KW Fuel Cell and consumable storage (JSC & GRC)**
- Using metal hydride for H2 storage due to available
- 1 KW No Flow Through FC (GRC)
- 10 KW main power FC not shown (JSC)

3m x 3m octagon lander deck
• Collect and purify 88 g CO\textsubscript{2}/h (>99%)
  – From simulated Martian atmosphere
  – 10 mbar; 95.4% CO\textsubscript{2}, 3% N\textsubscript{2}, 1.6% Ar
• Supply 88 g CO\textsubscript{2}/h at 50 psia to the Sabatier reactor
• Convert CO\textsubscript{2} to 32 g CH\textsubscript{4}/h and 72 g H\textsubscript{2}O/h
• Operate autonomously for up to 14 h/day
• Minimize mass and power
• Fit within specified area and volume
  – 9,000 cm\textsuperscript{2} pentagon
  – 10,000 cm\textsuperscript{2} rectangle for easier lab operations
  – 44 inches tall (112 cm, same as Water Processing Module)
• Support MARCO POLO production goals of 0.032 kg CH\textsubscript{4}/h and 0.128 kg O\textsubscript{2}/day (50% of O\textsubscript{2}) for a total of 2.22 kg propellant/14 h day
• Sufficient for a Mars Sample Return Mission
• ~17% of full-scale O\textsubscript{2} production goal for human Mars Missions (0.75 kg O\textsubscript{2}/h/module x 3 modules = 2.2 kg O\textsubscript{2}/h), i.e. 1/6\textsuperscript{th} scale
Atmospheric Processing Operations

88 g/h CO₂ @ 50 PSI

Sabatier Reactor (<600°C)
- 2 g/h H₂
- 72 g/h H₂O
- 32 g/h CH₄
- 2 g/h H₂

CH₄/H₂ Separator
- CH₄
- H₂O

Condenser
- Water Cleanup Module
- H₂O

CH₄ Dryer
- CH₄

CH₄ storage
- CH₄

Electrolysis Stacks
- H₂O
- H₂

Water Processing Module
- H₂O

Regolith Oven
- H₂O(g)

Ballast tank

CO₂ freezer

Mars Mix

Ballast tank

CO₂ freezer

Mars Mix

128 g/h O₂

95.4% CO₂, 3% N₂, 1.6% Ar at 10 mbar
Atmospheric Processing Module

- Sabatier Reactor
- CO₂ Storage Tanks
- Avionics
- Membrane Module
- Recycle Pump
- CO₂ Freezers
- Copper Heat Exchanger
- CO₂ Freezers and Chiller
Design of KSC Sabatier Reactor

- 30 cm long stainless steel tube with an OD of 2.54 cm and a wall thickness of 0.21 cm. Twelve tests at various flow rates overheated.
- Single-pass conversion = 90% @ 88 g CO₂/h + 3.5:1 H₂/CO₂
- Based on Pioneer Astronautics design for steam oxidation of trash to methane.
- 1.5 h integrated test with CO₂ Freezers and recycling system showed 100% conversion to pure CH₄.
Long-Duration Tests Were Successful

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabatier Run Duration</td>
<td>7.0 h</td>
<td>7.0 h</td>
<td>7.0 h</td>
</tr>
<tr>
<td>Gas Composition</td>
<td>CO₂</td>
<td>CO₂</td>
<td>Mars Gas</td>
</tr>
<tr>
<td>Average CO₂ Freezing Rate</td>
<td>102 g/h</td>
<td>100 g/h</td>
<td>102 g/h</td>
</tr>
<tr>
<td>Average Fraction of CO₂ Frozen</td>
<td>79%</td>
<td>76%</td>
<td>72%</td>
</tr>
<tr>
<td>Average Cryocooler Power</td>
<td>139 W</td>
<td>150 W</td>
<td>158 W</td>
</tr>
<tr>
<td>Average energy needed to Freeze CO₂</td>
<td>4917 J/g</td>
<td>5051 J/g</td>
<td>5655 J/g</td>
</tr>
<tr>
<td>Average CO₂ Supply Rate to Freezers</td>
<td>128 g/h</td>
<td>142 g/h</td>
<td>146 g CO₂/h</td>
</tr>
<tr>
<td>Average CH₄ Production Rate</td>
<td>32 g/h</td>
<td>32 g/h</td>
<td>32 g/h</td>
</tr>
<tr>
<td>Average CH₄ Purity</td>
<td>~99.9%</td>
<td>~99.9%</td>
<td>96.0%*</td>
</tr>
<tr>
<td>Average H₂O Produced</td>
<td>67 g/h</td>
<td>69 g/h</td>
<td>64 g/h</td>
</tr>
</tbody>
</table>

*Due to pressure losses during manual draining of Sabatier water condenser
Selected Results from Long-Duration Tests

Cryocooler Temperature and Power

CO₂ Freezer Cold Head Temperatures and Cryocooler Power Consumption during the Third Run of the 7-h Integrated Test Series

Sabatier Reactor Temperatures during the Second Run of the 7-Hour Integrated Test Series
Conclusions from the Long-Duration Tests

- **CO₂ Freezer Subsystem operates well**
  - Exceeds 88 g/h freezing and supply rate
  - Freezes ~70% of incoming CO₂
  - Provides valuable data for power to freeze CO₂ at Mars pressure
    - Averages 0.22 W/g CO₂ frozen = only 108% of theoretical
  - Contributes to Human Mars Mission ISRU system designs, e.g. 680 W lift for 3.1 kg CO₂/h

- **Sabatier Subsystem also operates well**
  - New reactor is efficient
  - Recycling system (membrane module + recycle pump) works well
  - Pure CH₄ obtained at expected rate
  - ~7% of water is missing (<1% of loss is in CH₄)
Recent Work and Current Status

• Additional integrated tests performed
  • Faster and slower production rates tested
    – 1.0-1.6 SLPM feed to CO₂ Freezers (87-71% frozen; 4800-5400 J/g)
    – Sabatier works at 0.3 to 1.2 SLPM CO₂ (0.75 SLPM nominal, 550°C max T)
    – Some CO observed in CH₄ after higher flow rates (now testing catalyst)

• Better LabVIEW automation implemented (sequences)
• Plan “virtual” integrated MARCO POLO tests with other systems at KSC and JSC in May and September – Hardware integration in FY17
• Testing is supporting Mars ISRU design studies
• Long Term Goal is to continue to refine ISRU technologies for potential robotic Mars missions using SpaceX “Red Dragon” (date TBD) and Mars Pathfinder in 2026/28
Introduction – Ionic Liquids

- Ionic Liquids (ILs) are organic salts that have melting points near room temperature.
- Certain ILs adsorb CO$_2$ at low partial pressures and provide a medium for electrolysis to useful compounds.

Typical Ionic Liquid Cations and Anions:

- Imidazoliurn
- Pyridinium
- Pyrrolidinium
- Halide
- Nitrate
- Tetrafluoroborate
- Hexafluorophosphate
- Methanesulfonate
- Tosylate
- Alkylsulfate
- Bis(trifluoromethylsulfonyl)imide
Potential Benefits for ISRU

Current Mars Propellant Production Process Diagram

Mars Propellant Production Process Diagram with IL Electrolysis

- Advantages of IL capture/electrolysis:
  - No high temperature processing of CO₂
  - One less pump and no cryocoolers
  - Four fewer major process steps
  - Estimated ~50% less mass and ~25% less power
CO₂ Uptake at Low Partial Vacuum
~50% Mole Fraction at ~10 mbar

“CO₂ absorption capacity in (a) [emim][2-CNPyr], (b) [emim][4-Triaz], (c) [emim][3-Triaz], and (d) [emim][Tetz] at 22 °C. The CO₂ solubility in [P₆₆₆₁₄]+ counterparts from ref 10 are also shown for comparison.” (Brennecke, 2014)
Technical Approach

• Select best available candidate COTS ILs and electrocatalysts (KSC)
  – Based on literature review
• Prepare new task-specific ILs (AZ Technology/MSFC)
• Determine CO₂ capture efficiency and conductivity of ILs (Mercer University and KSC)
• Measure electrochemical windows (KSC)
• Design/build electrochemical cells (KSC)
• Test electrolysis of CO₂ + H₂O to CH₄ + O₂
Results

- COTS IL candidates: [EMIM][BF$_4$], [BMIM][BF$_4$], [BMIM][TFMSI], [BMIM][PF$_6$] and [HMIM][B(CN)$_4$]
- Electrocatalysts: Copper cathode/Pt anode, TiO$_2$ cathode/Pt anode
- Several ILs have good electrochemical windows and conductivity
- Two-compartment cell w/Nafion membrane
  - Polycarbonate not suitable: CaCO$_3$ precipitate,
  - Switched to glass cell
- Three TSILs prepared: AZ-1, AZ-2, and AZ-3 (code named to protect IP)
  - High CO$_2$ sorption and conductivity
AZ-3 Shows High IL Conductivity with CO$_2$ and CO$_2$ + H$_2$O

Conductivity of AZ-1, AZ-2, AZ-3 and [P$_{66614}$][3-CF$_3$Pyra] vs. time for CO$_2$ uptake with and without 5% dissolved water
AZ-3 Shows High CO₂ Uptake (No Water Added)

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>CO₂ Uptake at ~25°C, wt%</th>
<th>CO₂ Uptake at 60°C, mol%</th>
<th>Viscosity Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ-1</td>
<td>9.0</td>
<td>NA</td>
<td>High (m.p. = 18°C)</td>
</tr>
<tr>
<td>AZ-2</td>
<td>9.6</td>
<td>9.1</td>
<td>High</td>
</tr>
<tr>
<td>AZ-3</td>
<td>15.6</td>
<td>NA</td>
<td>High</td>
</tr>
<tr>
<td>[BMIM][PF₆]</td>
<td>0.50</td>
<td>NA</td>
<td>Low</td>
</tr>
<tr>
<td>[HMIM][BF₄]</td>
<td>0.70</td>
<td>NA</td>
<td>Low</td>
</tr>
<tr>
<td>[EMIM][BF₄]</td>
<td>2.6</td>
<td>NA</td>
<td>Low</td>
</tr>
<tr>
<td>[BMIM][BF₄]</td>
<td>0.6</td>
<td>NA</td>
<td>Low</td>
</tr>
<tr>
<td>[BMIM][TFMSI]</td>
<td>0.5</td>
<td>NA</td>
<td>Low</td>
</tr>
</tbody>
</table>
## Summary

(Underlined ILs = Candidates)

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>CO₂ Capacity, wt.% (R.T., 1 atm, dry)</th>
<th>Electrochemical Window, V</th>
<th>Conductivity with CO₂ (mS/cm, 40°C)</th>
<th>Compatible with Cu</th>
<th>Other Issues</th>
<th>Tested Solubility of Water, v/v%</th>
<th>Methane Production Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM][TFSI]</td>
<td>0.46</td>
<td>2.1</td>
<td></td>
<td>No</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>[BMIM][PF₆]</td>
<td>0.50</td>
<td>2.4</td>
<td></td>
<td>Yes</td>
<td>Precipitate, Cu darkened</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>[BMIM][BF₄]</td>
<td>0.55</td>
<td>1.8</td>
<td></td>
<td>Yes</td>
<td></td>
<td>Small</td>
<td></td>
</tr>
<tr>
<td>[HMIM][B(CN)₄]</td>
<td>0.70</td>
<td>0.6</td>
<td></td>
<td>No</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>[EMIM][BF₄]</td>
<td>2.6</td>
<td>1.6</td>
<td></td>
<td>No</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>AZ-1</td>
<td>9.0</td>
<td>4.4</td>
<td>0.67</td>
<td>No</td>
<td></td>
<td>5</td>
<td>X</td>
</tr>
<tr>
<td>AZ-2</td>
<td>9.6</td>
<td>2.4</td>
<td></td>
<td>Yes</td>
<td>IL darkened</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>AZ-3</td>
<td>15.6</td>
<td>1.2</td>
<td>Slow color change</td>
<td>Precipitate</td>
<td></td>
<td>5</td>
<td>Possible CH₄ and CO (TiO₂ only)</td>
</tr>
</tbody>
</table>
Self-Cleaning Boudouard Reactor for Full O$_2$ Recovery from CO$_2$

- Initiated by NASA RFP for “GAME CHANGING DEVELOPMENT PROGRAM, ADVANCED OXYGEN RECOVERY FOR SPACECRAFT LIFE SUPPORT SYSTEMS APPENDIX NH14ZOA001N-14GCD-C2”
- Only 50% of O$_2$ can recovered from respiratory CO$_2$ on the ISS
- Sabatier reactor makes CH$_4$ and H$_2$O
- CH$_4$ is vented, losing H$_2$
- H$_2$O from cargo limits H$_2$ availability to 50% recovery
- RFP seeks at least 75% recovery
- Deep space missions (Moon, Mars moons, Mars surface, asteroids, etc.) need closer to 100% recovery
- Joint KSC/FIT/ORBITEC/Pioneer Astronautics proposal was not selected, but received encouragement from STMD GCD
- KSC funded a FY14 CIF project
- Completed in July 2015
Approach - Break Bosch Reaction into Two Parts (Demo’d by MSFC)

- Bosch Reaction: \( \text{CO}_2 + \text{H}_2 \rightarrow \text{C}_{(s)} + 2 \text{H}_2\text{O} \) (\( \rightarrow 2 \text{H}_2 + \text{O}_2 \))
- RWGS: \( \text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \) (\( \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \))
- Boudouard: \( 2 \text{CO} \rightarrow \text{C}_{(s)} + \text{CO}_2 \) (Fe catalyst, \( \text{H}_2 \) enhancer)
- Need a method to remove C from catalyst as it forms
- Several concepts developed and one tested so far with encouraging results
Self-Cleaning Boudouard Reactor

- Used CO/H₂/N₂ feed
- Tested steel wool reactor for comparison
- Tested 1” and 2” ID reactors
- Collected carbon in HEPA filter bag as it was generated
Results Are Encouraging

Parameters for Each Reactor

<table>
<thead>
<tr>
<th></th>
<th>1” REACTOR</th>
<th>2” REACTOR</th>
</tr>
</thead>
<tbody>
<tr>
<td>REACTOR VOLUME, ML</td>
<td>76</td>
<td>300</td>
</tr>
<tr>
<td>CATALYST MASS, G</td>
<td>1.31</td>
<td>11.82</td>
</tr>
<tr>
<td>H₂ FLOW, SCCM</td>
<td>232</td>
<td>909</td>
</tr>
<tr>
<td>CO FLOW, SCCM</td>
<td>232</td>
<td>909</td>
</tr>
<tr>
<td>N₂ FLOW, SCCM</td>
<td>52</td>
<td>202</td>
</tr>
</tbody>
</table>

CO₂ and CH₄ Yields for Both Reactors
Boudouard Summary

• 1” reactor ran for 12 h
  – Reached 47% conversion, collected 27% of C in bag
  – Found to be damaged upon disassembly
• 2” reactor run for 35 h
  – Reached 40% conversion, collected 60% of C in bag
  – Equivalent to ~45% of 1 crew CO₂ → O₂/day
  – Damage was similar to 1” reactor
  – Evaluating improvements to reactor design
• Lasted much longer than steel wool reactors
• Fe, Ni, & Cr seen in carbon fines (corrosion of stainless steel wall)
• Will check ability to filter contaminants from air and water
• Relevance to Mars: carbon for filters, 3D printing, radiation shielding, dry lubricant (stable in vacuum), carbothermal reduction for metals production (Fe, Al, Si), diamonds?, terraforming?
Conclusions

• KSC is developing both low and higher TRL Mars ISRU technologies

• Significant progress made on Atmospheric Processing Module for methane/oxygen production

• Initial CO$_2$/H$_2$O electrolysis using Ionic Liquids shows more work is needed
  – NASA Graduate Fellow at KSC this fall

• Very encouraging results so far for Self-Cleaning Boudouard reactor for both O$_2$ recovery from CO$_2$ and carbon production
Questions?

MARCO POLO Modules

APM (KSC) CO₂/Ar/N₂(g) WCM (KSC)

H₂O(l) H₂O(g) Soil

CH₄(g) H₂O(l) Soil

H₂(g) RASSOR (KSC)

WPM (JSC) O₂(g)

Hopper/Lander (KSC)

[FY17 - CryoCart/Thruster (JSC)]

Scanning electron microscope image of carbon collected during the 1 inch diameter reactor test

Experimental setup for testing the Pine Research Instrumentation H-cell