Water to Breathe?
A new technology may make it possible...
Oxygen From Water

Group 7

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May 2, 2003
New Technology

• A recently discovered technology uses the compound
\[ \text{H}_2\text{O(terpy)Mn(O)}_2\text{Mn(terpy)OH}_2\text{](NO}_3\text{)}_3 \]
(oxygen evolving complex OEC) to catalyze the evolution of oxygen from water.
Project Objective

• To develop and design a profitable process that uses the OEC to produce oxygen from water.
Proposal

• We propose a process that will use the OEC with a series of multifunction reactors, a hydrogen oxygen separator and solar power to provide life-supporting oxygen on manned space exploration missions.

• As a basis for comparison we examine oxygen production to support a five man crew.
Space Exploration

- Currently, water electrolysis provides oxygen for the International Space Station and Mir.
- Also electrolysis is proposed for Mars exploration.
- Our task is to see if we can offer advantages over electrolysis.
Presentation Outline

• How the Chemistry Works
• Process Design / Technical Details
• Mars Logistics
• Economic Justification
• Conclusion
Chemistry

- Process utilizes 2 sets of reactions.
  - Oxygen Production/Catalyst Regeneration
  - Sulfuric Acid Regeneration/O₂ Recovery
- 2 reactors involved
  - 1 CSTR and 1 PFTR
    - After several revisions to original design
Main Catalyst

- $C_{30}H_{22}Mn_2N_6O_2$
- In the process, the hydrated form is used.
- $C_{30}H_{26}Mn_2N_6O_4$
- This has an additional water molecule attached to the Mn atom.
Overview of Chemistry

• Oxygen Production/Catalyst Regeneration
  \[17\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow 17\text{H}_2 + 8\text{O}_2 + \text{H}_2\text{SO}_5\]

• Sulfuric Acid Regeneration/O₂ Recovery
  \[\text{H}_2\text{SO}_5 \rightarrow \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2\]

• Overall
  – \[17\text{H}_2\text{O} \rightarrow 17\text{H}_2 + 8.5\text{O}_2\]
  – Daily: \[2400\text{H}_2\text{O} \rightarrow 2400\text{H}_2 + 1200\text{O}_2\]
Chemistry: In the Beginning

- Original Design was based on a direct scale up from the chemistry
  - Everything added to a beaker was poured into a batch reactor
  - Very Complicated Design
Problems: In the Beginning

• $\text{H}_2\text{SO}_4$ regenerated NO/NO$_2$ reaction
  – Air contamination
• Many reactors
  – Complicated PFD
The Beginning... ugly
The Middle Ages

• We get wiser, eliminate NO/NO₂
  – Equipment Eliminated
    • 1 Reactor
    • 1 Separator
    • 2 Pumps
  – Healthier solution regenerates with MnO₂ catalyst
    • No new chemicals added
Still in the Dark

- Problem: Perpetual Acid Dilution
- Still complicated PFD
Not so Bright PFD

[Diagram of a process flow diagram with labeled components R1, R2, R3, S1, and P1, showing flow streams labeled with H2O, O2, and H2SO4.]

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[The diagram depicts a process flow involving multiple reactors (R1, R2, R3) and a separator (S1). The flow streams include water (H2O), oxygen (O2), and sulfuric acid (H2SO4).]
Chemistry Conquered: Bright Ideas

• Realize catalyst regeneration and $O_2$ production can occur simultaneously
  – Allows for continuous process

• Possible because
  – Catalyst not affected by pH
  – $O_2$ production is the Rate Limiting Step
PFD a Chemical Engineer can be Proud Of
Individual Reactions

• Oxygen Production/Catalyst Regeneration

\[
2C_{30}H_{26}Mn_2N_6O_4 + 16H_2O \rightarrow 4C_{15}H_{11}N_3 + 2MnO_4^- + 2Mn^{3+} + 8O_2 + 40H^+ + 44e^- \\
2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O \\
7H_2SO_4 + 7H_2O \rightarrow 7H_2SO_5 + 14H^+ + 14e^- \\
34H^+ + 34e^- \rightarrow 17H_2 \\
2Mn^{2+} + 2Mn^{3+} + 4C_{15}H_{11}N_3 + 6H_2SO_5 + 2H_2O + 4H^+ + 14e^- \rightarrow 2C_{30}H_{26}Mn_2N_6O_4 + 6H_2SO_4
\]

\[
17H_2O + H_2SO_4 \rightarrow 17H_2 + 8O_2 + H_2SO_5
\]

• Sulfuric Acid Regeneration/O_2 Recovery

\[
H_2SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2 \text{ (in the presence of MnO}_2\text{ catalyst)} \\
H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \text{ (in the presence of MnO}_2\text{ catalyst)} \\
H_2SO_5 \rightarrow H_2SO_4 + \frac{1}{2}O_2
\]
Theoretical Thermodynamics

- Reaction requires 285.8 kJ/mole H\textsubscript{2}O
- Need 2400 moles H\textsubscript{2}O per day
  - 685.920 MJ per day
  - 7.94 kW per day
  - Actual numbers are higher due to pumping, heat loss, etc...
Continuous System

• Advantages:
  – Simple operations
  – Smaller space occupied
  – Less catalyst required
  – Low equipment cost
  – Heat integration
  – Low operating cost
  – Keep the $O_2$ concentration constant
Continuous System (cont.)

- Require two reactors
- Total reactor volume 30 L
- Reactor costs $15,500 (Including heat exchanger)
Continuous System (cont.)

- CSTR:
  - Produce $O_2$
  - Regenerate catalyst
  - Condition:
    - Pressure: 9 atm
    - Temperature: 25°C
Experimental Reaction Rate

\[ y = -0.0007x^2 + 0.127x \]

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Moles O₂/Mole Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
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<td>1</td>
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<td>4</td>
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<td>5</td>
<td>5</td>
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</table>

Experimental Data

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Mol O₂/Mol cat.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
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<tr>
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<tr>
<td>6</td>
<td>0.6</td>
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</tbody>
</table>
Continuous System (cont.)

• CSTR:
  – Volume: 20L
  – Energy required: 8.4kW
  – Catalyst used: 10.1 moles
  – Feed water flow rate: 2.8L/hr
  – Sulfuric acid 0.57M, flow rate: 111L/hr
Continuous System (cont.)

• PFTR
  – Regenerate sulfuric acid
  – Enthalpy change: -0.27 kW
  – Catalyst: MnO$_2$
  – Condition:
    • Pressure: 9 atm
    • Temperature: between 50 and 100$^\circ$C
Continuous System (cont.)

• PFTR:
  – Volume: 10L
  – ID = 15cm
  – Length 56cm
  – Feed flow rate: 111L/hr
  – Catalyst lined reactor tubes
Hydrogen Oxygen Separation

Definition of the problem
   Design a particular process that can meet the requirements.

   Feed flowrate = 1200 mol O₂/day
   Purity = 100%
<table>
<thead>
<tr>
<th>Separation Process</th>
<th>Favorable Flowrates</th>
<th>Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryogenically distillation</td>
<td>High</td>
<td>Compressor Heat exchanger Expander</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Expander Distillation Column Condenser</td>
</tr>
<tr>
<td>PSA (Pressure Swing Adsorption)</td>
<td>Medium</td>
<td>Two adsorbers Compressor</td>
</tr>
<tr>
<td>Membrane</td>
<td>Low</td>
<td>Compressor Membrane</td>
</tr>
</tbody>
</table>

**Less is more**
Membrane

Goal: Maximum recovery of Oxygen

Topological Optimization

Several different flowsheets were considered

Optimization includes: Feed/permeate pressure ratio, Number of membrane units and recovery of hydrogen.
Excel Based Program
<table>
<thead>
<tr>
<th>Variables for YOU to SPECIFY:</th>
<th>Length</th>
<th>0</th>
<th>t1</th>
<th>t2</th>
<th>r_{H_2}</th>
<th>r_{O_2}</th>
<th>Hydrogen</th>
<th>Oxygen</th>
<th>Actual Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desired mols Hydrogen in Oxygen stream (yr)</td>
<td>0.02</td>
<td>0</td>
<td>1.6698472</td>
<td>0.1450177</td>
<td>0.0169865</td>
<td>0.0114017</td>
<td>0.8830105</td>
<td>0.9865383</td>
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<tr>
<td>Feed/Permeate Ratio (PR)</td>
<td>9</td>
<td>0.02</td>
<td>1.6688555</td>
<td>0.14750713</td>
<td>0.0333085</td>
<td>0.0029324</td>
<td>0.9666815</td>
<td>0.9870647</td>
<td>0.9970647</td>
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<tr>
<td>mols of Hydrogen in Feed (yr)</td>
<td>0.88686667</td>
<td>0.03</td>
<td>1.5186871</td>
<td>0.1940261</td>
<td>0.04882719</td>
<td>0.0044454</td>
<td>0.96017281</td>
<td>0.9657464</td>
<td>0.9657464</td>
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<tr>
<td>Selectivity (S)</td>
<td>12</td>
<td>1.62763155</td>
<td>0.15065113</td>
<td>0.0625551</td>
<td>0.0053167</td>
<td>0.93376848</td>
<td>0.9406893</td>
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<tr>
<td>Desired Feed Flow Rate (SCFH)</td>
<td>200</td>
<td>25</td>
<td>1.62324141</td>
<td>0.15212685</td>
<td>0.08258952</td>
<td>0.0074533</td>
<td>0.91741408</td>
<td>0.9254767</td>
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<tr>
<td>Number of Membranes you want to use</td>
<td>1</td>
<td>0.05</td>
<td>1.62389557</td>
<td>0.15371712</td>
<td>0.09582289</td>
<td>0.0086995</td>
<td>0.90117712</td>
<td>0.910105</td>
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<table>
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<tr>
<td>Area Factor (G) (maybe 0.31)</td>
<td>0.21218053</td>
<td>0.08</td>
<td>1.60412632</td>
<td>0.15987071</td>
<td>0.13104805</td>
<td>0.2112664</td>
<td>0.86395958</td>
<td>0.8703728</td>
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<tr>
<td>Recovery of Hydrogen (r_1) (maybe 0.98)</td>
<td>0.93333272</td>
<td>0.09</td>
<td>1.59408565</td>
<td>0.15956204</td>
<td>0.14696592</td>
<td>0.1363914</td>
<td>0.85994968</td>
<td>0.8630086</td>
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<td>Recovery of Oxygen (r_2)</td>
<td>0.65210089</td>
<td>0.11</td>
<td>1.58390113</td>
<td>0.16034953</td>
<td>0.16278403</td>
<td>0.1530263</td>
<td>0.83721597</td>
<td>0.8409873</td>
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<table>
<thead>
<tr>
<th>RESULTS:</th>
<th></th>
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<tr>
<td>mols of Hydrogen in permeate (yn)**</td>
<td>0.15528037</td>
<td>0.13</td>
<td>1.5522873</td>
<td>0.1586159</td>
<td>0.20697225</td>
<td>0.2021792</td>
<td>0.79302775</td>
<td>0.9797208</td>
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<tr>
<td>F1</td>
<td>7.0707E-09</td>
<td>0.14</td>
<td>1.5413381</td>
<td>0.1674337</td>
<td>0.22508623</td>
<td>0.2189225</td>
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<td>0.9710077</td>
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<tr>
<td>F2</td>
<td>-1.3973E-09</td>
<td>0.15</td>
<td>1.5302362</td>
<td>0.16927652</td>
<td>0.24399952</td>
<td>0.2356504</td>
<td>0.75610404</td>
<td>0.9624149</td>
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<tr>
<td>t3</td>
<td>1.7801E-08</td>
<td>0.16</td>
<td>1.51906769</td>
<td>0.17115359</td>
<td>0.25580293</td>
<td>0.2529567</td>
<td>0.74415371</td>
<td>0.9674034</td>
<td>0.9674034</td>
</tr>
<tr>
<td>Final Area Factor (G)</td>
<td>0.2122</td>
<td>0.17</td>
<td>1.5073941</td>
<td>0.1730982</td>
<td>0.27058669</td>
<td>0.2702717</td>
<td>0.7394321</td>
<td>0.9728273</td>
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</tr>
<tr>
<td>Recovery of Hydrogen (r_1)</td>
<td>0.9534</td>
<td>0.18</td>
<td>1.49016141</td>
<td>0.17489736</td>
<td>0.26361803</td>
<td>0.2677714</td>
<td>0.71343371</td>
<td>0.9172206</td>
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<tr>
<td>Recovery of Oxygen (r_2)</td>
<td>0.6521</td>
<td>0.19</td>
<td>1.48139446</td>
<td>0.17896684</td>
<td>0.30490881</td>
<td>0.2964881</td>
<td>0.89334119</td>
<td>0.9649531</td>
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<tr>
<td>Area of the All of the Membranes (ft²)</td>
<td>181.0972</td>
<td>0.20</td>
<td>1.45996141</td>
<td>0.18100203</td>
<td>0.32159075</td>
<td>0.3144651</td>
<td>0.6721943</td>
<td>0.8695349</td>
<td>0.8695349</td>
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<tr>
<td>Area of Each Membrane (ft²)</td>
<td>181.0972</td>
<td>0.22</td>
<td>1.44776847</td>
<td>0.1830891</td>
<td>0.34325642</td>
<td>0.3099772</td>
<td>0.6572548</td>
<td>0.9046028</td>
<td>0.9046028</td>
</tr>
<tr>
<td>square meters</td>
<td>16.82</td>
<td>0.23</td>
<td>1.43483069</td>
<td>0.1851087</td>
<td>0.36862626</td>
<td>0.3523889</td>
<td>0.6438374</td>
<td>0.9621711</td>
<td>0.9621711</td>
</tr>
</tbody>
</table>

| square meters | 16.82 | 0.24 | 1.42210112 | 0.18730287 | 0.37282907 | 0.3937192 | 0.6221793 | 0.982908 | 0.982908 |
| O₂ purity | 0.97999988 | 0.25 | 1.40971459 | 0.18947062 | 0.38691982 | 0.4163863 | 0.6100692 | 0.9840337 | 0.9840337 |
| recovery | 0.84559445 | 0.26 | 1.3982247 | 0.19167234 | 0.40879944 | 0.4353331 | 0.59812056 | 0.9584856 | 0.9584856 |
| UO₂ Cost | 516.920 | 0.27 | 1.3891457 | 0.19390921 | 0.41470407 | 0.4545245 | 0.65825613 | 0.9544755 | 0.9544755 |
| Permeate | 179.59 | 0.28 | 1.3891457 | 0.19510589 | 0.42393402 | 0.4741325 | 0.7160583 | 0.9588575 | 0.9588575 |
| Retentate | 51.18 | 0.29 | 1.3590748 | 0.19460697 | 0.4414479 | 0.4933912 | 0.6650522 | 0.9590080 | 0.9590080 |
| 0.3 | 1.34102679 | 0.20 | 0.20006289 | 0.45352505 | 0.5514744 | 0.54649459 | 0.94859259 | 0.94859259 |
Optimization Equations

Pressure Ratio = \( PR = \frac{P_{\text{Feed}}}{P_{\text{Permeate}}} \)

Recovery of Hydrogen = \( r_1 = \frac{Q \cdot (y_r \cdot PR - y_p)}{y_f} \)

Recovery of Oxygen = \( r_2 = \frac{Q \cdot (PR \cdot (1 - y_r) \cdot (1 - y_p))}{S \cdot (1 - y_f)} \)

\( y_r = \frac{(1 - r_1)}{[(1 - r_1) + (1 - y_f) / y_p \cdot (1 - r_2)]} \)

\( y_p = \frac{R_{1G} - r_1}{(R_{1G} - r_1) + ((1 - y_f) / y_p \cdot R_{2G} - r_2)} \)
### Engineering Ideas

#### Optimized Flowsheets

<table>
<thead>
<tr>
<th></th>
<th>Without Reactor</th>
<th>Featuring a Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Concentration</td>
<td>98%</td>
<td>100%</td>
</tr>
<tr>
<td>Recovery of Oxygen</td>
<td>62%</td>
<td>64%</td>
</tr>
<tr>
<td>Membrane Units</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>
Results

**Oxygen Profile Across Membrane**

**Recoveries vs Length**
Optimized Membrane

- Recovery of Oxygen: 65%
- Pressure Ratio: 9
- PRISM® hollow fiber membrane
- Membrane Area: 17 m²
- Estimated cost: $17,000
Reactor 3

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]

- Complete purification of Oxygen
- Catalyst: a fixed-bed 0.5\% Platinum
- Volume: 0.5 L
- Estimated cost: $700
Reactor 4

2H₂ + O₂ → 2H₂O

- Complete purification of Hydrogen
- Catalyst: a fixed-bed 0.5% Platinum
- Volume: 2.7 L
- Estimated cost based on Pt cost: $3800
## Cost Breakdown

Table 1: Price Breakdown 1200 mole per Day Ex.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Quantity</th>
<th>Price / Unit</th>
<th>Total Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor 1</td>
<td>1</td>
<td>$10,100</td>
<td>$10,100</td>
</tr>
<tr>
<td>Reactor 2</td>
<td>1</td>
<td>$3,800</td>
<td>$3,800</td>
</tr>
<tr>
<td>Heat exchanger</td>
<td>1</td>
<td>$500</td>
<td>$500</td>
</tr>
<tr>
<td>Reactor 3</td>
<td>1</td>
<td>$700</td>
<td>$700</td>
</tr>
<tr>
<td>Reactor 4</td>
<td>1</td>
<td>$3,700</td>
<td>$3,700</td>
</tr>
<tr>
<td>H₂-O₂ Separator</td>
<td>1</td>
<td>$17,000</td>
<td>$17,000</td>
</tr>
<tr>
<td>Water Pump</td>
<td>1</td>
<td>$3,600</td>
<td>$3,600</td>
</tr>
<tr>
<td>Liquid Pumps</td>
<td>3</td>
<td>$160</td>
<td>$480</td>
</tr>
<tr>
<td>Catalyst</td>
<td>10.1 mol</td>
<td>$25,200 / mol</td>
<td>$254,500</td>
</tr>
<tr>
<td><strong>Total Unit Cost</strong></td>
<td>****</td>
<td>**</td>
<td><strong>$294,220</strong></td>
</tr>
</tbody>
</table>
Water in Mars

• Where can we find water in Mars?
  - North pole: 75% of top 3 ft of soil is ice
  - Subsurface as liquid

• How much water is on Mars?
  - 0.03% of mars weight
What to do with $H_2$ produced?

• Vent $H_2$ gas to the Martian atmosphere

• Future Options:
  – Produce more water from $CO_2$
    \[ 4H_2 + CO_2 \leftrightarrow 2H_2O + CH_4 \]
  – Methane can be liquefied and used for space vehicle propulsion
Power Supply

- Total system energy requirements 9.2 kW
- Mars may receive 44% less solar radiation than Earth
- Solar panel area needed: 1880 ft²
- 139 panels cost $83,400
Battery Power Supply

- Rechargeable batteries ensure constant power supply.
- Design for emergency 1 day power supply
Battery

• Characteristic:
  – 12 V/ 446 AH at 100 hr rate
  – Weight: 272 grams
  – Operating conditions: -40 C to 60 C
  – Cost is $813 per battery
  – Each battery delivers 53.5 Watts
Power Requirements

• The system requires 9.2 kW

• We will need 172 batteries to provide 9.2 kW

• Total cost of $140,000
Establishing an Atmosphere in Tent on Mars

- Tent Size
- Tent Volume = 25,000 ft³
- 79% N₂ & 21% O₂ needed
- CO₂ & H₂O vapor removed
Establishing an Atmosphere in Tent on Mars

- $O_2$ Produced by unit per day
- Amount of $O_2$ 5 men need per day
- Air Needed in Tent = 25,000 ft$^3$ = 19,750 ft$^3$ N$_2$ & 5,250 ft$^3$ O$_2$
- Time Needed to Fill Tent with $O_2$ = 5.5 days
Establishing an Atmosphere in Tent on Mars

- \( \text{N}_2 \) needed
  - 2 x 800 L Liquid \( \text{N}_2 \)
- \( \text{CO}_2 \) & \( \text{H}_2\text{O} \) removed
  - 1 person = 234 moles / day
  - 5 man team = 27,000 L of each / day
- Silica gel - Molecular Sieve System
Establishing an Atmosphere in Tent on Mars

- Two Systems Used
  - 1 Adsorbing & 1 Desorbing
- Columns will regenerate 4 Times / day
- Regenerate by Heating Columns to 300 °C
Establishing an Atmosphere in Tent on Mars

- **H₂O Vapor Removed**
  - Want 30% Humidity
  - Need 7,500 ft³
  - If 27,000 ft³ H₂O removed, Air should stay at 30% Humidity
  - Silica Gel Adsorbs 6,750 L H₂O / time
  - 0.481 L / Column
  - Need 4 L Silica Gel
  - Column = 1 ft high & 1.8 in diameter
  - Silica Gel cost = $643.
Establishing an Atmosphere in Tent on Mars

- CO₂ Removed
  - 27,000 ft³ / day
  - Molecular Sieve 13X Adsorbs 6,750 L CO₂ / cycle
  - 65.3 L / column
  - 262 L Molecular Sieve 13X
  - Column = 4 ft high & 10.3 in diameter
  - 13X Cost = $70,100
Economics

• Identified Possible Applications for the Process
  – Steel-making Industry
  – Paper Manufacturing
  – Sewage Treatment
  – Medical Use
  – Life Support Applications
Economics

• Industrial Scale Applications
  – Typical Plant produces 2000 tons O₂ per day
  – For Our Process:
    \[(56 \text{ mil. mol O}_2 / \text{ day})(1 \text{ mol cat. / 182.4 mol O}_2 \text{ day})\]
    \[= 307,000 \text{ mol cat.}\]
    
    At catalyst cost of $25,200 / mol cat.
    Total catalyst cost would be $7.7 billion!
    Compared to less than $200 million for a
    Cryogenic Plant
Economics

• Small Scale Applications
  – Laboratory
  – Home Medical Use
  – Space Station
  – Mars Exploration
On Earth

• For laboratory or home use, compressed oxygen costs less than $0.30 per 100 scf.

• Comparable Oxygen from Water unit = no less than $50,000

• Not worthwhile when maintenance and energy costs are included.
In Space

- To provide a 5 man crew with oxygen:
  - Electrolysis requires 12.7 kW
  - OFW only needs 9.2 kW
Comparison

• Thermodynamic Efficiency: \( \frac{\Delta H_{RXN \ H_2O}}{\text{Energy Required}} \)

• \( \Delta H_{RXN \ H_2O} = 686 \text{ MJ} \)

• TE electrolysis = 686 MJ / 1080 MJ = 63.5 %

• TE OFW = 686 MJ / 795 MJ = 86 %
Comparison

• Electrolysis total cost $1,275,000
  – Electrolysis equipment cost approx. $720,000
  – Additional cost for power supply $555,000
  – Power supply is 44% total cost

• OFW total cost $689,000
  – OFW unit cost $295,000
  – Power supply costs $394,000
  – Power supply is 57% total cost
Comparison

• Advantages of OFW over electrolysis:
  – For electrolysis, 38% more energy means 38% more solar panel area required
  – Potentially much less than 1/2 of the cost of electrolysis
Uncertainties

• Experimentation to test catalyst useful life

• Continuous reaction efficiency

• Reactor scale-up
Conclusions

• Water can be used for $O_2$ production
• Eventually plants will be used
• Waste $H_2$ stream has many possibilities
• Infinite space exploration potential
• Nifty thinking on our part