Mars Atmosphere Resource Recovery System (MARRS)

Final Report

NIAC/USRA Phase I Research Grant # 07600-046

Christopher England, Engineering Research Group
P.O. Box 295, Sierra Madre, CA 91025-0295
Tel: 626.355.1209 E-Mail cengland@earthlink.net

J. Dana Hrubes, Raytheon Polar Services Inc.
E-Mail hrubesda@spole.gov

July 24, 2001
# Table of Contents

Mars Atmosphere Resource Recovery System (MARRS)  
NIAC/USRA Phase I Research Grant # 07600-046

<table>
<thead>
<tr>
<th>Sec</th>
<th>Subject</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Executive Summary</td>
<td>iii</td>
</tr>
<tr>
<td>1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Design Approach of A MARRS Direct Extraction Plant</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>A Mars Surface Architecture Based on MARRS</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>Composition of the Martian Surface Atmosphere</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>Primary Compression</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>Primary Separator</td>
<td>47</td>
</tr>
<tr>
<td>7</td>
<td>Secondary Compression And Condensation</td>
<td>53</td>
</tr>
<tr>
<td>8</td>
<td>Purification And Storage Of Products</td>
<td>57</td>
</tr>
<tr>
<td>9</td>
<td>Energy And Mass Estimates</td>
<td>60</td>
</tr>
<tr>
<td>10</td>
<td>Outreach Activities</td>
<td>66</td>
</tr>
<tr>
<td>11</td>
<td>Recommendations for Further Study</td>
<td>68</td>
</tr>
<tr>
<td>12</td>
<td>Acknowledgements</td>
<td>71</td>
</tr>
<tr>
<td>13</td>
<td>Contact Information</td>
<td>71</td>
</tr>
</tbody>
</table>

---

Copyright 2001 by the Engineering Research Group, Sierra Madre, CA 91025.  
All rights reserved. This work was sponsored in part by the NASA Institute for  
Advanced Concepts.
**Executives Summary**

**Description of Project**

The Mars Atmosphere Resource Recovery System (MARRS) is a physical process that extracts oxygen, water and other valuable constituents directly from the martian atmosphere. Oxygen makes up over 0.1% of the surface atmosphere. The MARRS process efficiently removes this and other valuable constituents including water, and can produce substantial amounts of electrical power as a bonus.

Under a Phase I NIAC grant, the first conceptual design of a plant to recover minor atmospheric components on the surface of Mars was conducted. The design showed that the direct extraction of oxygen and water from the martian atmosphere is technically feasible, and, when implemented on a scale suitable for human exploration, uses less energy and requires less launch mass than other proposed resource recovery methods.

Figure ES-1 outlines how the naturally occurring oxygen and water are recovered. The thin atmospheric gases are compressed, and the dominant component, carbon dioxide (CO₂) is condensed. This simple step concentrates the remaining gases by up to 25-fold, making them easily recoverable by conventional purification methods such as air distillation.

Further compression recovers water as ice, and subsequent cooling and cryogenic separation produces pure liquid oxygen and liquid carbon monoxide (CO), the latter an important natural constituent of the martian air.

The liquefied CO₂, available in large quantities, is expanded back into the thin atmosphere to recover most of the energy needed for compression. The raw energy to drive the extraction process is supplied as heat, most likely from a nuclear or radioisotope source.

Some liquid CO₂ can be stored for use in backup power systems and any other operation that can make use of an expanding working fluid. This feature makes the MARRS process a highly flexible basis for a martian surface architecture for large robotic and human exploration missions. Liquid CO₂ is the “steam power” for Mars.
Major Findings

1. Oxygen requirements for the MRM can be met with a MARRS plant driven by a 120 kilowatt thermal heat source. This plant produces twice the liquid oxygen needed for Earth return and twice the oxygen needed for crew respiration. The plant produces 5.8 kg/hr of liquid oxygen at 16% efficiency. Evolved technology would produce correspondingly more products as efficiency increases.

2. MARRS can recover up to 1 kg/hr of pure water while producing oxygen for the MRF. The production rate, however, will be highly variable according to season, latitude and location. Landing sites could be selected based on water recovery prospects.
3. **MARRS** can produce the oxygen needed for the Mars Reference Mission (MRF) with less mass and approximately less energy than electrolysis-based methods. These benefits accrue from several factors including

(a) Efficient use of the cold martian environment to reduce energy requirements. The CO\textsubscript{2} is already near its condensation temperature, making oxygen recovery straightforward.

(b) Economies of scale obtainable in continuous materials-handling processes for fluids. These benefits are much less attainable in surface dominated processes such as electrolysis.

(c) Recovery of multiple useful products. Water and carbon monoxide are recovered with virtually no added equipment. When reacted by Fischer-Tropsch synthesis, these two components can produce efficient fuels for surface use or Earth return.

(d) The use of heat as the primary energy source. Heat can be supplied on Mars by lightweight nuclear reactors or radioisotope sources. Reactors made from stainless steel are recommended as the least expensive and most durable.

(e) The production of electrical power within the **MARRS** process. The direct extraction process provides a primary power generating capacity as well as reserve power systems based on liquid CO\textsubscript{2} expansion engines.

4. The main technical uncertainty of the **MARRS** process is the technology to compress the thin dusty Martian atmospheric gases efficiently and reliably to the needed processing conditions. A robust method was outlined to meet this need, but further studies are needed. The optimum technology will depend strongly on the size of the plant. Small plants may benefit from simple thermal-swing compression technology currently being studied by NASA. At the largest sizes, axial compression, familiar to jet engines, is the method of choice.

5. The production rate for oxygen may be substantially higher than estimated, or, correspondingly, the energy and mass lower. While the conceptual design assumes an atmosphere containing 0.13% oxygen, studies show that this value may be substantially higher (up to 0.4%). As a result, oxygen production as well as energy and mass estimates in this report are likely highly conservative.

6. Electricity can be produced within the **MARRS** process at levels up to about 200 kW\textsubscript{e}/MW\textsubscript{th}. There is a direct tradeoff between the production rates for oxygen, and for electrical and mechanical power.
When examined in the context of the NASA-JSC Mars Reference Mission, MARRS could save over 15,000 kg of launch mass, possibly as much as 30,000 kg. The reduction is related primarily from

a. the simplicity and low energy requirements of the process attributable to the efficient utilization of the martian environmental conditions,
b. the large production rates of products that reduce the transportation requirements for consumables,
c. the availability of a fuel precursor (carbon monoxide) in substantial quantities, and
d. offsets for mass needed in the MRM for air revitalization and air conserva-
tion on Mars.

More studies are required to assess these benefits.

A Martian Surface Architecture

MARRS provides the opportunity to recover oxygen, water and other products using only heat as an energy source and without the need for either high temperature operations or chemical reactions. The conventional chemical engineering design for a thermophysical process allows for a confident design based on established design principles.

Figure ES-2 shows how an atmospheric resources extraction process can be the basis of an entire surface architecture. Using heat and generating power by expansion of the extracted gases, MARRS can be configured into a highly redundant resource recovery system that includes massive amounts of power storage as liquid CO₂.

The MARRS process uses the cold martian environment to very great advantage. Its qualification as the basis of a surface architecture comes largely from taking advantage of the cold martian temperatures. Removal of the CO₂ from the oxygen and water is highly efficient at these temperatures. MARRS also makes best use of a heat source that can be made highly robust from stainless steel. Other processes fail to take advantage of the engineering advantages of the low temperature environment.

Importance of Producing Oxygen and Water on Mars

Several important studies have shown the overwhelming benefits of manufacturing propellants and consumables on the surface of Mars. The MRM, for example, assumes that propellant for Earth return flights is manufactured from Martian resources, chiefly from carbon dioxide. Without in-situ production, the masses of propellants that must be both launched from Earth and landed for subsequent Mars ascent are prohibitive. Similarly, the Mars Direct mission, proposed by Dr. Robert
Zubrin, assumes in-situ production as the only means to achieve an Earth launch mass at reasonable cost.

![Diagram of Mars Outpost Architecture](image)

**Figure ES-2. A Mars Outpost Architecture by Atmospheric Resource Recovery**

Technologies for the production of oxygen and water on Mars are enabling for human habitation, and for return of martian samples in quantity. These resources are needed to manufacture propellants for return-to-Earth voyages, and, of course, for sustaining human habitation for extended periods.

Of particular importance would be a technology that produces all the components of breathable air, and in substantial quantities. The amount of recycling of waste products can be reduced so that revitalization equipment may be correspondingly reduced. Mission improvements associated with the reduced need for resource conservation, also reduce mass. Hazards associated with biological contamination within crew quarters may also be reduced.

**Production Rates for Oxygen, Water and Other Products**

After energy recovery, the overall efficiency of MARRS is estimated as 16% using a nuclear heat source. For a 120 kWth heat source, the production rates are 5.8 kg/hr of oxygen, 0.6 kg/hr of water, and 2.9 kg/hr of carbon monoxide (corresponding to ~0.24 kg/hr of hydrogen, or ~2 kg/hr of methane). Corresponding values for the
potential electric propulsion propellants of neon, krypton and xenon are roughly 12, 6 and 3 grams per hour.

**Martian Environmental Variability**

A major finding of this study is that the Martian surface environment is very poorly understood from an engineering point of view. Only scattered surface measurements have been made of temperature, pressure and composition (the thermodynamic variables). Diurnal variations in density, expected to be as much as 30%, will dramatically affect the design of any process that utilizes the surface atmosphere. For example, an energy-poor mission might operate a compression plant only at night when the atmospheric density is relatively high.

Seasonal and multiyear variations in pressure and composition will influence design as well. Up to 30% of the atmosphere is removed at the South Pole each year, likely raising the global fraction oxygen and carbon monoxide. This increase would reduce compression energy and equipment requirements by a like amount.

**The Accuracy of Martian Surface Composition Information**

The surface composition of the atmosphere, shown in Table ES-1, is the generally accepted one. Examination of the sources for this information indicates that the values are only approximate. The surface concentration of carbon monoxide, for example, has not yet been measured. Its value reflects satellite observations that include the entire atmospheric column. Atmospheric models, however, show that the production rate of carbon monoxide and oxygen, produced by photolysis of carbon dioxide, are highest at the surface.

Table ES-1 also shows our estimate of the range of possible concentrations at a north latitude site such as the Viking 2 lander site. Oxygen may be present at concentrations of up to 0.4% by volume. If so, estimates for oxygen production rates from MARRS might be tripled, or energy reduced by 65%.

Satellite data show a wide variability in column abundance of water, both regionally and seasonally. It is expected that surface concentrations will be greatest in the Northern Hemisphere, especially during northern spring and summer. The

<table>
<thead>
<tr>
<th>Component</th>
<th>Nominal</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>95.32 v%</td>
<td>94-97</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.7 v%</td>
<td>2-3.5</td>
</tr>
<tr>
<td>Argon</td>
<td>1.6 v%</td>
<td>1-2.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.13 v%</td>
<td>0.1-0.4</td>
</tr>
<tr>
<td>CO</td>
<td>0.07 v%</td>
<td>0.02-0.14</td>
</tr>
<tr>
<td>Water</td>
<td>0.03 v%</td>
<td>0.005-0.04</td>
</tr>
<tr>
<td>Neon</td>
<td>250 ppm</td>
<td>100-400</td>
</tr>
<tr>
<td>Krypton</td>
<td>30 ppm</td>
<td>15-50</td>
</tr>
<tr>
<td>Xenon</td>
<td>8 ppm</td>
<td>3-20</td>
</tr>
<tr>
<td>Ozone</td>
<td>3 ppm</td>
<td>0.5-20</td>
</tr>
</tbody>
</table>

Table ES-1. Surface Composition of the Martian Atmosphere
atmospheric concentration of water may drive the selection of a site for a MARRS plant.

Recommendations

Detailed recommendations are included in Section 11 of this report. The primary needs are (1) to better understand the nature of the resources available in the atmosphere, and (2) to better define direct extraction processes and their advantage to human and large robotic exploration of Mars.

Summary

Under a NIAC Phase I grant, Engineering Research Group conducted a conceptual design of plant to extract valuable products from the Martian atmosphere. The Mars Atmosphere Resource Recovery System is feasible because (1) the atmosphere of Mars is mostly carbon dioxide, which can be condensed and removed, and (2) the surface environment of Mars is sufficiently cold that the energy to compress and liquefy the bulk of the atmosphere is low.

MARRS can efficiently recover oxygen, water and fuel precursors in amounts almost unimaginable by other proposed processes. It takes advantage of the economies of scale associated with continuous processing by chemical engineering means. It uses the martian environment to unique advantage by utilizing the thermodynamic and mechanical advantages of low environmental temperature and pressure.

Engineering Research Group believes that the Mars Atmosphere Resource Recovery System is an enabling concept for sustained human presence on the surface of Mars.

End of Section
1.0 INTRODUCTION

1.1 Background

MARRS is a physical process that extracts oxygen, water and other constituents directly from the Martian atmosphere. Molecular oxygen on Mars was discovered by Earth-based measurements in 1972, and later confirmed by the NASA's Viking landers in 1976. Its concentration has been characterized as “trace” by planetary scientists, and with the observation that the Martian surface atmosphere is only about 1/100th that of the Earth, direct recovery of oxygen has been considered not practical.

Table 1.1 shows the accepted surface composition that is present at an average pressure of about 750 Pascals (Pa) or 7.5 millibar. It is currently believed that oxygen and carbon monoxide are formed abiotically from the photolysis of CO₂ by solar ultraviolet radiation. Thus, if recoverable, both products are renewable martian resources.

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount, vol %</th>
<th>Amount, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>95.32</td>
<td>96.63</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.7</td>
<td>1.74</td>
</tr>
<tr>
<td>Argon</td>
<td>1.6</td>
<td>1.47</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.13</td>
<td>0.096</td>
</tr>
<tr>
<td>CO</td>
<td>0.07</td>
<td>0.045</td>
</tr>
<tr>
<td>Water</td>
<td>0.03</td>
<td>0.012</td>
</tr>
<tr>
<td>Neon</td>
<td>0.00025</td>
<td>0.000116</td>
</tr>
<tr>
<td>Krypton</td>
<td>0.00003</td>
<td>0.000058</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.000008</td>
<td>0.000024</td>
</tr>
<tr>
<td>Ozone</td>
<td>0.000003</td>
<td>0.000003</td>
</tr>
</tbody>
</table>


Table 1-1. The Composition of the Surface Atmosphere of Mars
Engineering Research Group conducted a preliminary analysis that showed that oxygen, carbon monoxide and water could, in fact, be separated efficiently from the CO\(_2\)-dominated atmosphere by taking advantage of

(1) the low Martian ambient temperature,
(2) the high condensation temperature of CO\(_2\) relative to the martian ambient

If the bulk of the atmosphere can be efficiently condensed as a liquid, separation of the lower boiling components (termed "permanent gases") should be easily achievable by conventional means such as distillation. Atmospheric water, even though higher boiling than CO\(_2\), can similarly be recovered by separation from the bulk liquid as ice.

The major issues associated with the proposed method for recovery of products are

(1) the energy requirements,
(2) the mass required to construct the separation plant on Mars.

The very low pressure at the surface of Mars, often cited as the chief barrier to utilization of the atmosphere, is not fundamentally a critical issue for MARRS. While the energy required for pressurizing the atmospheric gases may be high, much of that energy can be recovered by efficient expansion back to the very low pressure. The concept in a low-pressure adaptation is described in a U.S. patent [Eck, 1992] for an open Brayton cycle turbo-compressor and turbo-generator working in the martian atmosphere.

1.2 In-Situ Resource Utilization

Producing supplies on the body being explored can greatly reduce the burdens of planetary exploration. In-situ resource utilization (ISRU) of a planetary atmosphere is especially advantageous because the resource is delivered continuously to the utilization plant without the need for mining equipment or other collecting machinery.

The need for production of oxygen and other resources on the Martian surface has been well documented as enabling technologies for large sample return, and, of course, for human exploration. The reasons are many, and include

(1) the expense of launching propellants from Earth that are needed for the return of samples or crew,
(2) the difficulty in landing a massive propellant load on Mars, and
(3) the energy requirements to maintain cryogenic propellants on the Martian surface between return launch opportunities.

In-situ propellant production (ISPP) is widely thought to be an attractive and even necessary technology, even for substantial robotic presence on Mars.
For the case of Mars, ISPP centers on the manufacture of liquid oxygen and hydro-carbon propellants to enable a return journey to Earth. However, the previously proposed methods are complex, requiring compression of CO\textsubscript{2} and the electrolysis of water and CO\textsubscript{2} to produce oxygen. While these methods are attractive for small units and low oxygen production rates, they may be excessively complex and massive for large plants, and may not produce the economies of scale attainable by a physical resource extraction process.

1.3 Summary of the Phase I Proposal to NIAC

Engineering Research Group (ERG) responded to the NIAC CP-99-03 solicitation with a proposal to investigate the concept of direct extraction of products from the martian atmosphere. The process was termed the Mars Atmosphere Resource Recovery System, or MARRS. Central to ERG's proposal was mechanical compression of the thin atmosphere followed by liquefaction of the CO\textsubscript{2}. As shown by the relative amounts of components in Table 1-1, at least 1000 kg of CO\textsubscript{2} must be liquefied for each kilogram of oxygen recovered.

The large amount of liquid CO\textsubscript{2} available to the process suggested that open cycle operations utilizing this liquid could be widespread on the surface of Mars for power production, transportation, mining and industrial uses. Thus, MARRS can be a basis of a surface architecture for a continuous presence on the surface of Mars, whether by large robotic systems, or by human explorers. This feature fulfills a requirement of the NIAC solicitation for concepts that can be developed into whole systems or architectures.

ERG proposed a study that emphasized the physical chemistry and the chemical engineering of the direct extraction process. The focus for Phase I was to be a "fleshing out" of the concept to provide a basis for comparison with competing processes that have been the subject of analysis and development for over 20 years. MARRS was considered a sufficiently attractive alternative that these comparisons could be convincing based on the limited Phase I resources.

Figure 1-1 illustrates the major elements of direct extraction to recover oxygen. The major inputs are thermal energy and martian atmospheric gases, and the products include oxygen, carbon monoxide and nitrogen. Water is recovered as ice within the process as described later.

Dust-tolerant robust compressors provide a high-density dust-free gas to higher-performance compressors that raise the gases to pressures greater than 1300 kPa (13 bar). Intercooling recovers much of the compression heat and lowers the total compression power. Cooling then liquefies the major component, CO\textsubscript{2}, leaving behind oxygen and other valuable gases. Still more compression supplies a product-rich gas for purification and storage. Most of the compression energy is recovered by
expansion of the compressed and liquefied CO₂ back into the low-pressure martian environment.

The MARRS process is conceptually straightforward, requires only engineering development to implement, and can be designed by conventional engineering methods.

![Diagram](image)

**Figure 1-1. Major Elements of the MARRS Direct Atmospheric Extraction Process**

1.4 **Adaptations to the Phase I Proposal**

ERG proposed a conceptual design effort that focused on separation of the permanent gases from the liquefied CO₂. Calculations had shown that a simple condensation would provide up to 96% recovery of products. ERG proposed that this key step should be verified by test, and confirming experiments were intended. Subsequent process design as well as discussions with experts suggested, however, that these experiments were unnecessary.

There were two convincing arguments. First, in presentations at the Jet Propulsion Laboratory and at the Mars Society's Convention 2000, experts familiar with cryogenic separations suggested that excellent separation was an obvious consequence of the difference in condensation temperatures between CO₂ (195K) and the permanent gases (78K to 90K). Examination of ERG's calculations supported this view. More sophisticated calculations using solubility theory for non-electrolytes indicated that the initial calculations were conservative, with subsequent estimates showing improved separation.
Second, results of a process definition study showed that simple stripping of the initial liquid CO$_2$ condensate with nitrogen or argon provides very nearly 100% recovery of all the low-concentration gases including water. High purity nitrogen and argon are available in large amounts to strip valuable products including water from the liquid CO$_2$ prior to its re-expansion. This operation assures that nearly all products captured will be recovered even if the physical chemistry of the separation is poorly understood.

The primary issue that remained after public presentation and discussion of the direct extraction concept was compression of the thin atmosphere. Participants suggested difficulty because of (1) the volume of gas that must be collected and compressed, and (2) the presence of atmospheric dust that influenced the Viking and Pathfinder landers.

Partly as a result of this input, ERG focused its Phase I effort less on the physical chemistry and separations aspects of MARRS, and more on compression and environmental issues. One critical issue concerns the amount of oxygen available in the Mars atmosphere for extraction. This issue is central to MARRS and its resolution was a major activity of ERG’s effort to understand the direct extraction process.

1.5 General Approach to Estimating the Potential of the MARRS Process

The authors have attempted to take neither a highly optimistic nor a highly conservative approach to the design of the MARRS process. For example, we have assumed an overall efficiency of only 16%, a value that is believed very reasonable. Compression efficiencies were taken as about 40% where a mature technology might expect 70%. These conservative assumptions will likely be offset by yet-to-be-discovered requirements for a martian presence such as an exceptionally high robustness.

The adaptation of chemical engineering principles to human exploration of space leaves many uncertainties. Rules of thumb that represent the experience of chemical engineers for design may not always apply. For example, a process design is often based on optimization of efficiency. A process for use on Mars may be based on optimization of the Earth launch mass. In both cases, however, the design will be based on the lowest cost process that meets all mission requirements.

As discussed later in Section 4, the chief uncertainty is the character of the resource itself, the martian atmosphere. This report assumes the published values of oxygen concentration in the atmosphere at the martian surface, namely, 0.13%. This value could be as high as 0.4%, but is unlikely to be below 0.1%. On this basis, studies in this report may overestimate the energy and mass for recovering oxygen on Mars, possibly by a factor of three.
1.6 Organization of This Report

In Section 2 we describe the MARRS process to familiarize the reader with important concepts and principles that enable the efficient extraction of oxygen from the martian atmosphere. We describe the various operations that are required, and include some detail about steps of particular technical concern. The requirements for oxygen suggested by the Mars Reference Mission provide the basis for the overall energy and mass calculations.

Section 3 describes an overall architecture based on direct extraction of resources from the atmosphere within a paradigm of “plenty of energy, plenty of products.” Section 4 describes ERG’s research into the scientific community’s understanding of the atmospheric environment on Mars. This environment is uniquely variable in physical and chemical properties. Little of this variability is well understood.

Starting with Section 5, details are provided on the detailed design basis for the major units studied. The last sections summarize the study, provide recommendations for additional studies, and outline ERG’s activities in providing information on Mars to the public.

1.7 Related and Intermediate Technology

1.7.1 ELECTROLYSIS OF CARBON DIOXIDE TO PRODUCE OXYGEN

A thermophysical method for continuously producing oxygen and fuels on Mars has not previously been proposed. Prior concepts require (a) the transportation of hydrogen or other hydrogen-containing compounds from Earth followed by complex chemical and electrolytic processing, (b) electrolysis of the carbon dioxide in the atmosphere to produce oxygen, or (c) a combination of these methods. The chief source for a continuous and plentiful oxygen supply in these concepts is the high-temperature electrolysis process shown in Figure 1-2 where carbon dioxide is stripped of one of its oxygen atoms. A detailed description of the technologies and requirements are provided in Zubrin [1997].

For oxygen production, this technology is the chief alternative to the MARRS direct extraction process, and the process to which it can be compared. Energy and mass estimates for each method are shown later in this report. For the redundancy needed for human missions to Mars, electrolysis processes are likely to be a substantial part of even very large piloted projects.
1.7.2 COMPRESSION BY THERMAL SWING ADSORPTION (TSA)

To operate the CO₂ electrolyzer, the gas must be supplied at pressures above about 100 kPa (1000 mbar). Current concepts to supply CO₂ at this pressure include compression of the atmosphere by TSA on carbon or molecular sieves. This technology was successfully tested for an experiment utilizing TSA and CO₂ electrolysis for a NASA Mars surface spacecraft that was originally scheduled for launch in 2001.

When compared with mechanical methods, compression by thermal swing adsorption is believed to be inherently less efficient because of the energy and energy transfer required to heat and cool the inert adsorption medium. It is believed attractive, however, for all small systems including a small direct extraction system. This study did not attempt to determine the relative merits of non-mechanical compression systems for capture of the martian atmosphere.

1.7.3 DIRECT EXTRACTION OF ATMOSPHERIC RESOURCES ON MARS

MARRS is the first method that uses traditional chemical engineering methods for resource recovery, achieving predictable economies of scale available to non-electrolytic processes. It produces a variety of highly useful products including the critical ones associated with long-term life support and return-to-Earth. No other technology approaches the versatility and usefulness of the direct extraction process.

The process described in this report assumes a large production capacity for oxygen consistent with the Mars Reference Mission. MARRS may be adaptable to less ambitious missions, but substantial changes in the conceptual design would be in order.
1.99 References


2.0 DESIGN APPROACH OF A MARRS DIRECT EXTRACTION PLANT

This section provides a detailed description of the MARRS process, and outlines ERG’s design strategies. Details of design calculations are provided in later Sections of this report.

2.1 General Description and Assumptions

The Mars Atmosphere Resource Recovery System (MARRS) captures the Martian atmosphere, and extracts many of its valuable constituents. Table 2-1 lists the atmosphere’s approximate composition with oxygen making up over 0.1% by volume. At cold temperatures at or near those seen on the martian surface, the majority component of the atmosphere will condense, leaving behind oxygen, carbon monoxide, and other lower-boiling components as gases. After removal of residual carbon dioxide, these products are purified by conventional cryogenic fractionation methods.

![Table 2-1. Composition of the Surface Atmosphere on Mars](image)

Figure 2-1 illustrates the effects of removing CO₂ on the concentration of the remaining components. The top bar shows the amounts of components in the atmosphere under “normal” conditions with oxygen at 0.13%. The middle bar shows the amounts of components remaining if a closed container were cooled to a temperature typical of the martian poles. Oxygen is concentrated over ten-fold to 1.5%. The bottom bar illustrates that even higher concentrations of oxygen can be produced by compression, and, in addition, CO₂ occurs as a conveniently handled liquid. The MARRS process follows the compression approach in the bottom bar that can produce a gas rich in oxygen, carbon monoxide and water.

A key design principle of MARRS is that the process operates at sufficient pressure to condense carbon dioxide as a liquid. At this pressure, the triple point pressure of
CO₂, the volume of gas is reduced by a factor of about 12,000 from its volume at martian ambient pressure. The remaining gas can be processed efficiently in conventional equipment that is physically small.

A

Mars atmosphere @ 250K, 7.5 mbar
95% CO₂, 2.6% N₂, 1.3% Ar, 0.13% O₂, 0.07% CO, <0.03% H₂O
This is what’s in the ambient atmosphere

B

Residual atmosphere @ 130K, 0.66 mbar
53% CO₂, 29.5% N₂, 14.7% Ar, 1.5% O₂, 0.8% CO, <0.3% H₂O
This is what’s left if we freeze out the CO₂

C

Compressed atmosphere @ 217K, 10640 mbar
38% CO₂, 38% N₂, 19% Ar
1.9% O₂, 1.0% CO, <0.4% H₂O
And if we compress the gases and rain out the CO₂

Figure 2-1. Illustration of Gas Composition Changes Due to CO₂ Condensation

2.2 Mars Reference Mission (MRM) Requirements

2.2.1 OXYGEN

For human exploration of Mars, oxygen is needed for propellant as liquid and gaseous oxygen, for respiration as a 20% mixture with nitrogen and argon, and for a variety of biological and sanitary uses. By far the largest requirement is for liquid oxygen propellant part of a propulsion system for Mars ascent and Earth return.

Table 2-2 provides a summary of oxygen requirements that forms the basis for the MARRS design. Single redundancy is assumed for both propellant and respiratory oxygen with the assumption that water electrolysis or other technology will provide additional backup. The MARRS design is sized for recovery of 58600 kg of liquid oxygen.
2.2.2 RECOVERY OF WATER

The MRM suggests the transport of water from Earth with substantial recycling and reclaiming of waste. MARRS recovers water in amounts up to about 100 grams of water per kg of oxygen at favorable locations and times of year where the mixing ratio of water may be as high as 0.03%. Northern latitude lowlands are such locations. At these favorable locations, MARRS can recover as much as about 2,900 kg of water, assuming recovery for half of the martian year.

Water recovery by MARRS is a direct savings of Earth-transported material, and provides a substantial reduction in Earth launch mass for the MRM. An estimate of the improvement can be made if the landed mass is assumed to be about 10% of the Earth launch mass, or a savings of 29,000 kg launch mass.

2.2.3 CARBON MONOXIDE

MRM does not provide a requirement for carbon monoxide. MARRS, however, provides it at nearly just the cost of storing it. When reacted with water, the water gas shift reaction

\[ \text{CO} + \text{H}_2\text{O} \Rightarrow \text{CO}_2 + \text{H}_2 \]

produces hydrogen, the best rocket fuel for use with liquid oxygen. Further reactions of CO and H\(_2\) can produce more easily storable fuels such as hydrocarbons by Fischer-Tropsch synthesis. Methane has previously been suggested as one of these.

MRM specifies 13,000 kg of methane that can be produced by the overall reaction

\[ 4 \text{CO} + 2 \text{H}_2\text{O} \Rightarrow \text{CH}_4. + 3 \text{CO}_2 \ . \]

Studies sponsored by NASA have demonstrated the production of methane from CO and hydrogen. A MARRS process sized for the MRM oxygen requirement will
produce approximately 27,500 kg of CO₂, sufficient to produce about 3,900 kg of CH₄ without redundancy and at 100% efficiency.

2.2.4 NITROGEN AND ARGON

The MRM can greatly benefit from the large production of nitrogen and argon for mixture with oxygen as a respiratory gas. Their availability lessens the need for precision air locks and air revitalization while on the surface of Mars. An outline of MRM mass savings are given later in this report.

2.3 MARRS Process Outline

Figure 2-2 outlines the overall process by which the martian atmosphere is captured, compressed and condensed, stripped of its valuable components, and then released through turbo-expanders to produce electrical and mechanical power. A portion of the liquid carbon dioxide, available in large amounts, is stored and used as a working fluid for portable and emergency power.

![Figure 2-2. Elements of Atmospheric Resource Recovery on Mars](image)

The martian atmospheric gases are raised from a pressure of about 750 Pa (~7.5 mbar) to about 1300 kPa (13 bar). The latter is a pressure above the triple point pressure of CO₂, ensuring that CO₂, when condensed, will be a liquid. At lower pressures, it would occur as a solid and not be amenable to efficient processing.
Compression is conducted in several stages with intercooling. This method minimizes the compression energy and provides a means to recover virtually all of the compression heat. The over 1500-fold compression required coupled with the initial low density of the gases, is the major challenge for MARRS. Figure 2-3 illustrates the primary compression with intercooling and heat addition. Most of the compression power is recovered immediately by expanding the CO₂ back into the martian environment while adding thermal energy.

After the compression, the dense gases are cooled, allowing carbon dioxide to condense as a liquid. Oxygen and the other light gases are mostly retained in the gas phase. Water, still below its condensation pressure, also remains as a vapor. The 5% of light gases remaining in the liquid CO₂ are stripped from the liquid by clean waste gas to maintain nearly 100% recovery efficiency.

The enriched gas stream, about 1/12,000th of the initial volume, is further compressed to remove additional carbon dioxide as illustrated in Figure 2-4. Water is recovered as ice by centrifugation of liquid CO₂ after the second condensation. The ice is removed from the process using mechanical lock-hoppers, a robust and reliable method for continuously removing the solid from the otherwise fully fluid process.

The pressures required for both the primary and secondary compression/condensation units require a detailed analysis that includes an accurate description of the composition of the atmosphere. Section 4 of this report discusses the current poor understanding of this composition. Generally, if recovery of water were a high priority, the primary compression would be at the low range shown in Figure 2-4, and the secondary compression at the high range.
The product-rich gases are subject to conventional polishing operations and cryogenic distillation to recover oxygen, nitrogen, argon and carbon monoxide as highly purified components. The design for the cryogenic distillation can be made with very high confidence provided that the feedstocks entering the cryogenic system are free from frosts such as from CO₂, water and ozone.

The fractionation column operates with the lower regions slightly warmer than the upper regions. Nitrogen (and traces of neon) is the lowest boiling component, and exits the fractionation column at the top. The higher boiling components exit towards the bottom. With a proper column design, very high purity gases can be recovered.

Figure 2-5 shows conceptually how “frosts” can be removed by cyclic operation of adsorption beds. Product-rich gas is cleaned by one bed while another is heated to desorb the unwanted gases. A third bed acts as a reserve. The adsorption beds are essential to clean the any residual CO₂ before cryogenic fractionation.

Re-expansion of the liquid carbon dioxide recovers a substantial portion of the MARRS process energy. The CO₂ is also used as an open cycle working fluid to produce electrical power. Figure 2-6 shows the relationship of the power recovery elements. Heat is added at a number of places within the primary processing units to re-vaporize and expand the byproduct CO₂. The placement is partly determined by the need to prevent the condensation of CO₂ as “dry ice” during expansion. This need also occurs during release to the atmosphere where a buildup of solids could affect plant operation.
The joining of electrical and resource production allows the MARRS process to be the basis of an integrated Martian surface architecture for long-term human presence. The use of liquid carbon dioxide as an open cycle working fluid for local transportation expands the architecture for surface, atmospheric and spaces transportation.
2.4 Energy Requirements

In ERG’s conceptual design, energy is supplied to the extraction process primarily by heating the re-expanding waste CO\textsubscript{2}. The resulting expansion produces the mechanical and electrical power for the process. As part of a surface architecture, MARRS can be adapted to supply primary electricity for a large presence on Mars as well as oxygen and water.

Natural or nuclear heat sources are suitable energy sources provided that they can supply heat at temperatures over about 300°C. Over 80% of the needed energy is consumed in compressing and re-expanding the atmospheric gases. Purification of products has lesser impact on the process's mass and energy requirements.

Energy usage depends very strongly on environmental factors. At low Martian ambient temperatures such as found at the poles, carbon dioxide condenses naturally as a solid. It can be imagined that only negligible energy might be needed to convert CO\textsubscript{2} to a liquid after pressurization. Optimization studies are needed to determine the relative benefits of (1) cooling by heat transfer to the environment, or (2) cooling by vaporization and expansion of CO\textsubscript{2}. The lowest mass system will likely use a combination of internal and external heat transfer.

2.5 Compression Strategy

A central assumption for MARRS is that CO\textsubscript{2} and most products occur within the process as fluids. This approach allows efficient processing with low-mass equipment that can take full advantage of economies of scale. The thermodynamic properties of CO\textsubscript{2} require that its partial pressure be raised to above its triple point, or 518 kPa (5.18 bar), to condense as a liquid. Depending on the ambient surface pressure, the needed compression will be from about 500 to 2000 times.

Multistage compression with intercooling raises the pressure to about 1300 kPa (13 bar). Initial compression to the lowest pressure that is compatible with liquefaction of the majority of the CO\textsubscript{2} is assumed the most efficient option for MARRS since it minimizes the amount of gas handled. No detailed trade study was made of this approach.

The product-rich vapors, still containing mostly CO\textsubscript{2}, are further compressed to above 3000 kPa (30 bar) to condense additional CO\textsubscript{2}. Water vapor condenses as ice, which floats on the carbonic liquid and is removed mechanically. The optimum pressure for the secondary condensation must be determined by a detailed tradeoff study, not part of the current work. Additional stages that increase pressure to 10 MPa (100 bar) may be desirable to minimize issues associated with removal of CO\textsubscript{2} frosts.
2.6 Heat Source Strategy

Heat can be used to great advantage on the Martian surface where the ambient temperature can drop to below –100°C. In this environment, moderate-temperature heat sources such as geothermal and conventional nuclear energy provide as much thermodynamic work as high temperature (and correspondingly high technology) sources. Figure 2-7 illustrates the relationship between heat sink temperature to efficiency. The Carnot efficiency is about the same, for example, with a 400°C heat source on Mars (Label 1) as for a 900°C heat source on Earth (Label 2). There is little theoretical advantage to use high temperature sources.

![Figure 2-7. Theoretical Efficiencies for Source and Sink Temperatures](image)

The use of a lower temperature heat source simplifies many practical materials issues. The conceptual design of MARRS assumes a 400°C nuclear source delivering heat at 350°C through a secondary heat transfer loop. These temperatures are compatible with common alloy materials such as stainless steel. The heat transfer fluid, presumed to be argon, is returned at –20°C. A study of nuclear sources or technologies was not conducted as part of the current study.

2.7 Product Recovery Strategies

The initial compression raises the CO₂ partial pressure to above its triple point pressure, assuring that, upon condensation, the CO₂ will appear as a liquid. Over 95% of the oxygen and similar fractions of the other permanent gases will remain in
the gas phase. A simple stripping step using pure nitrogen will remove virtually all
the remaining oxygen and carbon monoxide to the gas phase. This product-rich
phase still consists primarily of CO$_2$.

2.7.1 LIQUEFIED CARBON DIOXIDE AND XENON

The liquefied CO$_2$ (LCO$_2$) is clean and nearly pure, containing only its saturation level
of the stripping gas. MARRS stores a substantial amount of LCO$_2$ that is used for
energy storage, production control, and as a clean fluid for air bearings. LCO$_2$ is
considered a major product of the MARRS process.

Xenon, an excellent propellant for electric propulsion, will remain in the LCO$_2$ in very
small concentrations. It is possible that an efficient method of recovery could be
found such as multistage distillation to recover a xenon-rich fraction. The potential
recovery of residual water from the LCO$_2$ might make such a process desirable. In
this study, no process was identified for residual water and xenon recovery.

2.7.2 RECOVERY OF WATER

Additional compression of the product-rich gases to at least 3000 kPa (30 bar) along
with cooling to –50°C removes more carbon dioxide. Water will condense as ice on
the liquid carbon dioxide if its partial pressure exceeds its vapor pressure. As a solid,
water is recovered mechanically from the secondary and higher condensers.

The current design for MARRS uses the value of 0.03% suggested by Owen [1977],
but this amount varies seasonally and globally. At 0.03%, substantial amounts of
water can be recovered. Volume percentages of 0.01% or below are common, how-
ever, at colder, higher locations in the Southern Hemisphere. The production of
water will depend heavily on where the MARRS plant is sited, with high northern
latitudes generally favored.

2.7.3 RECOVERY OF OXYGEN AND OTHER PERMANENT GASES

2.7.3.1 Final Processing of Product-Rich Stream

The permanent gases including nitrogen, argon, oxygen, CO, krypton, and neon are
recovered from the product rich stream once it is depleted of CO$_2$. Conventional
cryogenic separation by distillation recovers highly purified products. This separation
is not seen as a technical issue for MARRS. A major process issue is, however,
removal of CO$_2$ frosts that will occur as the cryogenic cooling proceeds.

MARRS assumes that CO$_2$ frosts will be removed by thermal cycling of portions of
the separation process. The current study did not evaluate the merits of duplicate
equipment to maintain production, but none may be needed. Thermal cycling along
with purging to the atmosphere will remove both CO$_2$ and an ozone frost, the latter
being an explosion danger that is well known in air separation technology.
2.7.3.2 Recovery of Nitrogen and Argon

Pure nitrogen and argon are recovered in large excess when oxygen or water are the primary products of the extraction process. Both have important uses within MARRS. Argon is used as an inert heat-transfer fluid from the heat source, which is presumed to be a nuclear source.

Nitrogen gas is used as a stripping agent for liquid CO$_2$ after condensation. Liquid nitrogen is used as a refrigerant for storage of products, particularly liquid oxygen. If light hydrocarbon fuels such as methane were produced from the CO product, LN$_2$ would help maintain them as cryogenic liquids. Excess nitrogen and argon are vented to recover the energy of compression.

2.7.3.3 Recovery of Oxygen and Carbon Monoxide

Oxygen and carbon monoxide are retained as liquids from the cryogenic distillation process. Their small amount relative to the major constituents implies a small energy impact on the overall process. Both are recovered as highly purified components.

2.7.3.4 Recovery of Krypton and Neon

Krypton, an excellent propellant for electric thrusters, may be recoverable as a heavy fraction of the cryogenic distillation. Neon may appear as a non-condensable gas. Whether either of these gases is collected will depend on their mission value and on the added mass and sophistication required of the cryogenic system.

2.8 Product Storage

Estimates were made for storage mass although this element is not considered part of the MARRS design. Low-pressure cryogenic storage of oxygen and carbon monoxide is assumed, with residual cold or liquid nitrogen being used as a refrigerant. Because CO is thermodynamically unstable by disproportionation,

\[ \text{CO} + \text{CO} \Rightarrow \text{C} + \text{CO}_2, \]

means must be established of preventing the occurrence of a catastrophic runaway reaction.

Carbon dioxide is stored above its triple point pressure, thus requiring pressurized systems of high relative mass. In a mature ground architecture utilizing MARRS-based technology, underground storage of CO$_2$ may be an attractive option.
2.9 Summary of the Basic MARRS Design

MARRS is an engineering process consisting of a number of well-established technologies. The chief uncertainty is the primary compression stage that accomplishes the primary step, that of capture of the Martian atmosphere. Technology exists for this difficult step, however, requiring only adaptation for the presence of dust and for the variable environment.

Studies preliminary to the present work demonstrated that the energy and mass required for a MARRS process is reasonable provided that the scale of operation is sufficiently large. Current studies show substantially lower energy and mass are needed when the Martian environment is utilized for heat rejection and process cooling.

2.99 References

3.0 A SURFACE ARCHITECTURE FOR HUMAN EXPLORATION

At a sufficient scale, MARRS produces from the atmosphere most of the products needed for an extended human stay on the surface of Mars. These include consumables such as oxygen and water, inerts such as nitrogen and argon, working fluids such as carbon dioxide, and power for both stationary and mobile needs. This section outlines how the products might be produced, stored and distributed at a martian outpost.

3.1 Approach for Conceptual Design

MARRS captures most of the needed resources for human exploration. Within the context of the Mars Reference Mission and its requirement for liquid oxygen propellant, the direct extraction process produces air, water, rocket propellants, and propellants for surface transportation. MARRS can supply all of these in a highly redundant and fault tolerant architecture that enables extended surface presence on Mars.

The major elements of the surface architecture include

A. The storage and use of liquid CO₂ as the basis of a backup power storage system.
B. The use of a reactor heat source operating at less than 500°C with secondary heat transfer at less than 400°C.
C. Highly redundant primary gas compression in a system that is designed for system expansion and repair or replacement of spent units.
D. Single-string thermophysical processing after primary compression.
E. Frost control utilizing cyclic operation of redundant freeze-out vessels.
F. Redundant refrigeration plants for servicing purification and storage units.
G. Redundant energy recovery from liquid CO₂ with a capability of producing power by a simple compression/expansion cycle.
H. Redundant mechanical startup capability.

Redundancy in heat sources was not considered as part of this project. A separate study on heat source options and technologies would provide the needed input. Options include radio-isotope sources, utilization of carbon monoxide, or solar and areothermal sources.
3.2 **Overall Surface Layout**

Figure 3-1 diagrams the elements of a surface architecture based on direct extraction of resources from the atmosphere. The major sections are highlighted in Figure 3-2, and include:

a. The reactor heat source with secondary heat exchange, redundant startup, and a thermal utility that supplies heat for miscellaneous plant and human activities.

b. Power generation, which is closely coupled with the heat source.

c. Primary compression, the largest part of the plant which is spread out over a large area.

d. Primary separation, consisting of compression stages for clean gas and removal of the major fraction of CO₂ from product gases.

e. Purification, refrigeration and water recovery in which the product-rich gas stream is highly compressed to recover water and remove most of the remaining CO₂.

f. Cryogenic storage, primarily for liquid oxygen to be used as propellant. Carbon monoxide may also be stored as a liquid.

g. Liquid CO₂ storage in lightweight tanks. The amount of LCO₂ storage will depend on detailed system studies, but is expected to be large because of its high value.
h. Fuels plant, which may convert carbon monoxide and hydrogen to rocket propellants or other products.

i. Backup power section that utilizes liquid CO\(_2\). A heat source is required for producing power. The heat may be derived from several options.

A detailed study is needed to estimate placement of the heat source, primary compression units and power generation units. These sections must be closely coupled to maintain a low mass and high efficiency. The primary compression section, however, must be placed away from the heat source and expansion sections to maintain the composition and thermal properties of its atmospheric feed. The power generation section must allow for an accumulation of CO\(_2\) frost.

Other sections of MARRS are physically much smaller, and their placement is more flexible. Liquid CO\(_2\) storage may be distributed widely including at crew habitats, at transport stations, and even remotely such as at mining sites and outposts.
3.3 Energy Input, Startup and Power Production

The energy source is closely coupled with its major use, the power recovery/power production section shown in Figure 3-3. Roughly 80% of the supplied energy is consumed in expansion of CO\textsubscript{2} back into the atmosphere to produce the net compression and other mechanical requirements of the plant.

![Figure 3-3. Heat Source Detail and Power Recovery Detail](image)

**MARRS** utilizes heat efficiently over a range of temperatures from about 250°C to 450°C. This range is within the temperature capability of nuclear reactors constructed primarily of stainless steel, a material resistant to martian environmental conditions. A secondary heat exchanger isolates the reactor from the power production. Further isolation by tertiary heat exchange (a thermal utility) is provided for heat needed for the remainder of the plant and for the habitat.

Argon, supplied by the process, is used as the primary reactor coolant. This flows into a secondary heat exchanger that uses carbon dioxide as the heat exchange fluid. Argon may be substituted in this step as its plentiful availability from the MARRS process is assured. The heat is supplied for power-recovery at the turbo-expanders as well as within the process where needed. Optimization of heat recovery is a critical part of assuring the lowest-mass MARRS process, and will be a major design commitment.
Startup capability is fully redundant. A small turbo-compressor/expander provides startup mechanical and electrical power. In addition, the heat source/expander combination can also operate as a low-efficiency power producer upon startup for redundancy.

The thermal utility provides additional heat to the process, to the habitat, and for miscellaneous needs such as a biological environment. Carbon dioxide is used as the heat transfer medium for safety and availability.

3.4 Primary Compression, Cooling, Separation

Primary compression is characterized by large intake plenums on the order of two meters in diameter. Figure 3-4 diagrams a design with highly redundant intakes, and extensive heat exchange between compression stages and for the final condensation. The design for MRM requires about 10 inlet compressors. The outputs of the first compression stages are combined, cooled by both internal and external heat exchange with the martian atmosphere, and further compressed. Finally, these gases are cooled to condense the bulk of the CO₂ within the primary separator.

Figure 3-4. Atmosphere Compression and Primary Processing

The primary compressors are designed to be dust tolerant and to aid in dust removal by utilizing centrifugal separation. Swirling flow and filtering prior to secondary compression further cleans their output. Secondary compression raises the gases to above the triple point pressure of CO₂ so that, when condensed, the condensate is liquid rather than solid.
The saturated vapors are condensed in a multistage column with the remaining dust being collected within the liquid. The separator is designed to strip all of the oxygen, water and carbon monoxide from the condensing CO$_2$ by injection of pure nitrogen produced later on in the process. The fully depleted liquid CO$_2$ is then used as a working fluid for power recovery and generation.

The cold martian atmosphere is used to cool the compressed gases, and provides a major asset for increasing the efficiency of the MARRS process. Expansion of high pressure CO$_2$ from subsequent processing can also be used to aid condensation, but a detailed design is required to assure that CO$_2$ always occurs within the process as a fluid.

3.5 Separation, Purification and Cryogenic Storage

The pressurized product-rich gases are subject to additional compression that, after cooling,

a. Further lowers the volume of the gases to be processed.
b. Condenses the bulk of the remaining CO$_2$.
c. Enables the recovery of water (as ice) by raising its partial pressure above its vapor pressure.

Figure 3-5 outlines the units needed to complete the recovery of atmospheric resources. The gases entering the boost compressor have about 1/12000$^{th}$ the volume rate of flow and about 1/10$^{th}$ the mass as that entering the primary compressors. As a result, the compression and subsequent processing steps are of a much smaller scale.

The amount of compression needed will be determined by (1) the requirements for water recovery, and (2) a detailed system optimization study. The detailed design of this section is highly dependent on atmospheric composition, location, and seasonal variation. For example, if the amount of oxygen is 0.2% rather than the commonly quoted value of 0.13%, oxygen recovery would be 50% higher.

Compression to 100 bar will recover most of the water (at the 0.03% level), and remove most of the remaining CO$_2$ as liquid. The water is recovered as ice that floats on this liquid and is removed by lock hoppers. The efficiency of the lock hoppers, often of concern, is not important since loss of a small amount of CO$_2$ is not critical to the process.
A separate refrigeration plant that uses nitrogen as the working fluid provides cryogenic cooling of the remaining gases. This step removes any remaining CO₂ and water as frosts. The clean gases are sent to a cryogenic distillation operation for final production of liquid oxygen, liquid carbon monoxide, and both gaseous and liquid nitrogen.

A key element of the purification element is the production and removal of the CO₂ and water frosts by cycling multiple frost-collecting units. Three or more vessels that collect the frosts are alternately opened to the atmosphere and heated to vent the unwanted solids. This step also removes ozone and any unknown trace compounds that might affect purification.

The relative amounts of products will be highly dependent on both process-related and environment-related factors. Gaseous nitrogen is used within the process as a stripping agent, and may be used as a purge gas. Argon is used for an inert heat exchange medium. Liquid nitrogen is used as a refrigerant for the other cryogens, and may also be used as a working fluid for open-cycle processes in place of LCO₂.

Adaptation of conventional chemical engineering methods can provide a reliable and predictable product recovery design.

3.6 Surface Infrastructure Utilizing Liquid Carbon Dioxide

As an open-cycle working fluid, LCO₂ resolves many of the energy storage and backup power requirements of a martian outpost. Storage tanks at peak daytime temperatures of 250K would contain pressures of less than 20 bar (less than 300 bar).
psi), well within the capability of lightweight tankage. Bladder-like storage or even underground storage are possible options.

Figure 3-6 illustrates how LCO₂ storage is stored at multiple locations, and is used for backup and reserve power. An expanding Mars outpost can expand LCO₂ storage indefinitely to provide emergency or secondary power. A gas turbine utilizing carbon monoxide and oxygen is an additional option for reserve power. Even this technology can use LCO₂ to increase power much like terrestrial power systems use steam injection for increasing mass flow.

Carbon monoxide, a poor rocket fuel, can be used to create a variety of energetic rocket fuels by well-established chemical processes. Hydrogen is needed for these processes, however, in relative amounts that may be more that can be produced by MARRS. Other sources of hydrogen such as native water or transported hydrogen may be required to operate a fuel plant.

As surface transportation fuels, both CO/O₂ and LCO₂/heat are candidates, the latter for shorter trips than the former. A LCO₂/heat engine is similar in application to a conventional steam engine, but with higher efficiency because of the ability to expand the working fluid to a low pressure. Carbon monoxide as a liquid or pressurized gas, used with liquid oxygen, can drive both surface vehicles and aircraft. MARRS provides many options for transportation and mechanical operations on Mars.

![Figure 3-6. Liquid Carbon Dioxide for Energy and Power Redundancy and Storage](image-url)
3.7 Additions to a Conceptual Architecture for MARRS

MARRS provides options for a well-defined, robust surface architecture on Mars. Additional consumable resources that are not recovered from the atmosphere are needed, however, among which is water. MARRS can recover water if its volume fraction in the atmosphere is on the order of 0.03%. These levels may be representative of summer mid-latitude levels rather than global averages. If so, then resources from the regolith may be needed for permanent habitation.

MARRS can supply the heat, other consumables, and mobile power needed to mine other resources. Redundant processes for making oxygen and other consumables may be required. The MARRS process design assumes that some oxygen for breathing air will be produced by electrolysis of water, and perhaps by electrolysis of carbon dioxide. This oxygen will provide double redundancy for human respiration.

Hydrogen may be brought from Earth and require storage. The form could be as ammonia, methane, liquid hydrogen or perhaps some other compound. These requirements fit easily into the concept of the MARRS process that provides storage, power and heat to a complex infrastructure.

3.99 References


End of Section
4.0 COMPOSITION AND VARIABILITY OF THE MARTIAN SURFACE ATMOSPHERE

4.1 Background

NASA’s Viking landers measured substantial seasonal changes in atmospheric pressure while on the Martian surface. These changes are closely correlated with the deposition of atmospheric components at high latitudes during polar winters. In particular, over 30% of the entire atmospheric mass condenses each Martian year at the South Pole. Locally, this condensation could raise the concentration of oxygen and carbon monoxide at the martian Poles by over 10-fold. To evaluate this impact, ERG undertook a study to understand how atmospheric variability would affect engineering processes, and, in particular, oxygen concentration, at the Martian surface.

A primary result of ERG’s research was a discovery that the concentrations of the minor components in the atmosphere are uncertain. Measurements on the martian surface from the Viking landers have been discarded, and the materials related to the analysis of these data are not available. Earth-based data, however, provide some confirmation of the published composition, validating the availability of resources central to the concept of direct extraction from the atmosphere.

This section discusses the impacts of on the MARRS process of

   a. compositional uncertainty, especially with respect to oxygen and water,
   and

   b. environmental variability, and how it effects thermodynamic and
      engineering processes.

4.2 Uncertain Composition of the Mars Surface Atmosphere

4.2.1 SOURCE DATA

The primary reference to the value for oxygen is a paper by T. Owen et al [1977] that evaluated composition information gathered from the Viking 1 and 2 landers in 1976. The value of 0.13% is widely accepted along with the general composition at the Martian surface given in Table 1-1 (repeated below). For example, the NASA-Ames Research Center and the University Corporation for Atmospheric Research (UCAR) websites currently duplicate these values as a primary NASA reference for the atmospheric makeup. The comprehensive reference, MARS [Kieffer et al, 1992] also references these values.
Table 1-1. The Composition of the Surface Atmosphere of Mars (repeated for convenience)

Figures 4.1 and 4.2 display elements of the technical paper from which Table 1-1 is abstracted. Noteworthy is the title of the paper in Figure 4.1 which refers to the "surface" in contrast to the caption for the table in Figure 4.2 which refers to "the lower atmosphere."

These figures are shown to support ERG's understanding that the surface composition of Mars is not well established in the context of engineering design. The variability in composition due to seasonal condensation of CO₂ at the poles has not been measured. The likely occurrence of composition changes has more recently been noted by T. Owen [in Kieffer, 1992] and by H. Kieffer [in Kieffer, 1992]

The measurement data on which Table 1-1 was based are not currently available. As part of work conducted under this grant, an effort was begun to locate the meas-
urements taken by the Gas Chromatography-Mass Spectrometer (GCMS) experiments on the Viking landers. Within about nine months it was established by officials of the NASA-Planetary Data System that

(1) The original data are not archived within NASA.
(2) Secondary analysis materials are not available from the authors of the paper detailing the surface composition.
(3) The raw data were saved privately in the form of computer printouts by a former investigator.

| Table 4-2. Table Listing Mars Atmosphere Components (from T. Owen et al [1977]) |

The senior author is currently leading an effort to recover the Viking GCMS atmospheric data for conversion to digital form and archiving within NASA. Once retrieved, these data will be re-examined from an engineering perspective to better understand the true composition of the martian surface atmosphere and its variability. There are no current plans by NASA or the European Space Agency (ESA) to measure the seasonal dependence of oxygen concentration on Mars or to measure carbon monoxide at the surface.

4.2.2 ASSESSMENT OF THE CONCENTRATION OF MOLECULAR OXYGEN

Owen et al [1976] suggests that the concentration of oxygen may range from 0.1% to 0.4%. Table 4-2 presents our estimates of the range of bulk composition that the atmospheric components may display due to uncertainties and seasonal variation. Local variations may be much greater, even dramatically greater. Local loss of CO$_2$ at the Poles during late Fall and Winter, for example, will leave behind the permanent gases, perhaps in 10-fold greater abundance at times. Conversely, in the Spring when the Polar caps are disappearing, the non-condensable gases will be highly depleted locally.
<table>
<thead>
<tr>
<th>Component</th>
<th>Nominal</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>95.32 v%</td>
<td>94-97</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.7 v%</td>
<td>2-3.5</td>
</tr>
<tr>
<td>Argon</td>
<td>1.6 v%</td>
<td>1-2.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.13 v%</td>
<td>0.1-0.4</td>
</tr>
<tr>
<td>CO</td>
<td>0.07 v%</td>
<td>0.02-0.14</td>
</tr>
<tr>
<td>Water</td>
<td>0.03 v%</td>
<td>0.005-0.04</td>
</tr>
<tr>
<td>Neon</td>
<td>250 ppm</td>
<td>100-400</td>
</tr>
<tr>
<td>Krypton</td>
<td>30 ppm</td>
<td>15-50</td>
</tr>
<tr>
<td>Xenon</td>
<td>8 ppm</td>
<td>3-20</td>
</tr>
<tr>
<td>Ozone</td>
<td>3 ppm</td>
<td>0.5-20</td>
</tr>
</tbody>
</table>

Table 4-1. Estimated Range of Composition, Mars Surface Atmosphere

The impact of inaccurate measurements or variable composition of resource gases on the MARRS process is substantial. Mass and energy for the extraction will be roughly linear with composition of oxygen. Oxygen concentrations as high as 0.4% could cut the mass and energy consumption of an extraction process by over 65% when compared with the nominal 0.13%. Such an occurrence would broaden the applicability of direct extraction processes, and change the process design.

Molecular oxygen is produced from photolysis of CO₂, and will occur at the highest rate at the surface of Mars where the concentration of CO₂ is the highest. Because oxygen concentrations may be highest at the surface, the mass and energy consumption for a MARRS process will be substantially lower than described in this report. High concentrations of oxygen and carbon monoxide are, of course, highly favorable to a direct extraction process.

4.2.3 VARIATION IN WATER VAPOR CONTENT OF THE SURFACE ATMOSPHERE

The concentration of water vapor is highly variable in the martian surface atmosphere because of variations in temperature, local pressure, altitude and, possibly, subsurface sources. At the surface, water vapor may be particularly abundant early in the day as ice-frost, accumulated overnight, evaporates from the top surfaces of the regolith. Such a variation is highly favorable to most processes that seek to capture this water.

Figure 4-3 illustrates the vapor pressure of ice at low temperature and at a surface pressure of 7.5 mbar. At surface temperatures of ~60°C, for example, the equilibrium concentration for water vapor is more than four times the value given in Table 4-1. Large increases in humidity might be expected at the first few meters of surface atmosphere, especially during the morning hours. Conversely, low humidity may be expected in the evening hours as the regolith cools and freezes out the water vapor.
Figure 4-3. Variation of the vapor pressure of ice at low temperature [Weast 1981]

Figure 4-4 indicates diagrammatically the impact that this variability can have on an extraction process. In the MARRS process, for example, concentrations of water vapor below 0.01% will be difficult to capture, but nearly all water vapor above 0.03% can be recovered. Direct extraction will provide better recovery of products displaying a composition profile shown in Figure 4-4 than if an average is used.

Figure 4-4. Illustration of Diurnal Concentration Changes Due to Sublimation of Frost
Water vapor originating from frosts may exhibit a substantial concentration gradient, even in the first few meters. Measurements, if planned, must include both time and height above the surface to provide input to surface-based extraction processes.

4.3 Environmental Variability

4.3.1 DIURNAL AND SEASONAL TEMPERATURE VARIABILITY

The day-night temperature variation at the martian surface is notably large, especially in the context of thermodynamic properties and usage. Figure 4-5 displays temperature measurements made by the Viking 2 lander over two martian years. The location was a northerly site at 48° North latitude that ERG considers an attractive position for a MARRS process that produces water. From the point of view of thermal processes, the temperature at which heat can be rejected ranges from about 150K to 250K. A Carnot efficiency calculated from

\[ \eta = 100 \frac{(T_H-T_C)}{T_H} \]

changes markedly with seasonal and diurnal variations according to Table 4-2. Similar changes occur at only a few unique sites on Earth such as the North and South Poles. The low ambient temperature, however, is highly favorable to thermodynamic processes such as MARRS.

Figure 4-5. Variation in Temperature at the Viking 2 Site
The diurnal temperature variation also has an appreciable effect on density, and therefore, on transport properties in the environment such as heat transfer. Table 4-2 shows this variation for the extremes of temperatures seen by the Viking 2 lander. Roughly speaking, heat transfer is expected to be about 30% less effective at the higher martian ambient temperatures due to density effects alone.

<table>
<thead>
<tr>
<th>Heat Source Temperature</th>
<th>Heat Sink Temperature</th>
<th>Carnot Efficiency</th>
<th>Density of Atmosphere at Sink Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>°K</td>
<td>°K</td>
<td>percent</td>
<td>kg/m³ @ 7.5 mbar</td>
</tr>
<tr>
<td>373</td>
<td>150</td>
<td>59.8</td>
<td>1.08</td>
</tr>
<tr>
<td>373</td>
<td>250</td>
<td>33.0</td>
<td>0.65</td>
</tr>
<tr>
<td>473</td>
<td>150</td>
<td>68.3</td>
<td>1.08</td>
</tr>
<tr>
<td>473</td>
<td>250</td>
<td>47.1</td>
<td>0.65</td>
</tr>
<tr>
<td>575</td>
<td>150</td>
<td>73.9</td>
<td>1.08</td>
</tr>
<tr>
<td>575</td>
<td>250</td>
<td>56.4</td>
<td>0.65</td>
</tr>
<tr>
<td>673</td>
<td>150</td>
<td>77.7</td>
<td>1.08</td>
</tr>
<tr>
<td>673</td>
<td>250</td>
<td>62.9</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 4-2. Carnot Efficiency for Several Heat Source and Sink Temperatures

4.3.2 SEASONAL PRESSURE VARIABILITY

The primary information available that describes the variability of Martian surface pressure comes from the Viking landers. Figure 4-6 shows the daily average surface pressure at the Viking 2 site over a two-year period. The surface pressure varied seasonally from about 740 Pa (7.4 mbar) and 1000 Pa (10.0 mbar) corresponding to a seasonal increase of over 35%.

Pressure variations will have a first-order effect on the energy requirements for compression for a process such as MARRS. Efficiency and productivity will be highest when the pressure is highest since the compression work will be the lowest. On Earth, there are no comparable changes because there is no major component of the atmosphere that can be removed seasonally by condensation (or added by vaporization). These variations illustrate that the environment around engineering processes such as MARRS will change, and that systems must be designed to accommodate these changes.

4.3.3 GLOBAL-SCALE TOPOGRAPHICAL VARIABILITY

The difference of atmospheric pressure between the landing sites is another variable of interest to engineering processes. The Mars Global Surveyor spacecraft (a mission still in progress) discovered that the Northern Hemisphere of Mars is substantially lower in elevation than the Southern Hemisphere. Generally speaking, the more northerly sites within the Northern Hemisphere are lower in elevation, and have
a higher surface pressure. The temperature will, on average, also be higher at comparable latitudes.

The difference in pressure between the Viking 1 and Viking 2 sites is, on average, about 10%. The surface pressure nearing the North Pole is likely to be the highest on average at constant latitude, perhaps as high as 1500 Pa (15 mbar) based on simple calculations. Adding to the advantage of a MARRS-like process is the lower environmental temperature, which favors higher practical and thermodynamic efficiencies for engineering processes.

4.4 Impact of Variability and Uncertainty on Direct Extraction Processes

The MARRS process was conceived primarily as a method to efficiently extract the 0.13% oxygen from the Mars surface atmosphere by traditional chemical engineering methods. The surface of Mars, however, is characterized by unusually large variations in thermodynamic and transport properties. Wide temperature swings, for example, will affect atmospheric density that in turn will affect heat transfer rates. This variation as well as changes in composition have a first order effect on a direct extraction process, and on any system or process that interacts appreciably with the environment.

The primary uncertainties for MARRS are the amounts of resources that can be recovered. An average oxygen concentration of 0.26%, a good possibility, would cut
the mass and energy of oxygen production by half. Diurnal variations in water
content may allow highly efficient recovery of water despite its low average concen-
tration. Measurements of composition and of the thermodynamic and transport vari-
ables are needed to establish the engineering basis for MARRS and other processes
such as heat rejection that interact with the environment.

4.99 References

Owen, T., Biemann, K., Rushneck, D. R., Biller, J. E., Howarth, D. W., and LaFleur,

Owen, T., and Biemann, K., “The Composition of the Atmosphere at the Surface of
803.

Weast, R. C., and Astle, M. A., Handbook of Chemistry and Physics 67th Ed., CRC

Kieffer, H.H., Jakosky, B. M., Snyder, C. W., and Matthews, M. S., Editors, “Mars,”
5.0 PRIMARY COMPRESSION

5.1 Primary Issues for Compression

From the Martian ambient, overall compression ratios of 500 to 2000 are needed to achieve pressures that are comfortably above the triple point pressure of CO₂, namely, about 5.2 bar. Achieving these high ratios will require technologies that can capture the thin dusty atmosphere with lightweight components. There is good precedent, however, in high altitude jet aircraft that can compress air at about the same pressure as that found on Mars.

The technology used for compression in the MARRS process, and the compressor mass and efficiency, will depend on several factors including:

a. the size (throughput) of the plant,
b. the robustness needed for the compressors,
c. mass constraints for the plant,
d. mission requirements for products, such as water.

For mechanical compression, Figure 5-1 suggests a relationship among compression technologies and plant size.

![Figure 5-1. Compression Technologies for Capture of the Martian Atmosphere](image-url)
A mix of technologies may also be an option as discussed later in this section. For this study, a plant processing about 6000 kg of atmospheric gases per hour meets the MRM oxygen goal. At this size, axial compressors are believed to be the preferred candidate for the higher compression systems although turbo-compressors may be preferred for reliability and robustness.

5.2 Thermodynamic Properties of the Carbon Dioxide

MARRS is conceived as a process that handles CO\textsubscript{2} as a fluid (gas or liquid) whenever possible. This approach maximizes the economies of scale. Figure 5-2, taken from Perry (1965), provides information on the thermodynamic space in which the design of MARRS exists. The CO\textsubscript{2} must be compressed and expanded along a temperature-pressure path so that, when it condenses, it does so as a liquid. This requirement gives a lower limit for pressure and temperature for condensation of about 5.2 bar and about –56\textdegree C.

Figure 5-2. Multi-Property Thermodynamic Diagram for Carbon Dioxide
[Perry, 1963]

5.3 Multistage Compression

Compression in several stages, with intercooling between stages, provides the most efficient method for accomplishing the 500-2000 fold pressure increase. Figure 5-3 illustrates stepwise compression of CO\textsubscript{2} from about 7.5 mbar to 13 bar using multistage compression with five intercooling units. The final cooling step is shown as heat removal by heat exchange with the environment although the actual method will
be determined by studies that include an optimization by mass (ultimately, launch mass).

The heat removal during intercooling will come from expansion of CO$_2$ on its way to power recovery and return to the environment. This gas must be heated in any case to insure that, during release to the martian environment, it doesn’t condense immediately out of the expansion engine.

![Enthalpy-Pressure Diagram for Carbon Dioxide](image)

**Figure 5-3.** Enthalpy-Pressure Diagram for Carbon Dioxide (courtesy Quest Consultants, 2000)

### 5.4 Compression Requirements for the Mars Reference Mission (MRM)

The specific compression power required to recover oxygen for the MRM is given in Table 5-2. This calculation assumes a 22-stage compression with five intercooling units cooling to 233K (–40°C).

<table>
<thead>
<tr>
<th>SPECIFIC POWER 40% efficiency</th>
<th>SPECIFIC POWER 70% efficiency</th>
<th>TOTAL MECH POWER, MRM</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/kg/hr CO$_2$ kW/kg/hr O$_2$</td>
<td>kW/kg/hr CO$_2$ kW/kg/hr O$_2$</td>
<td>kW @ 40% effic. kW @ 70% effic.</td>
</tr>
<tr>
<td>15.0</td>
<td>15.1</td>
<td>8.560</td>
</tr>
</tbody>
</table>

Basis: 22 compression stages to 13 bar, 5 intercooling stages

**Table 5-2. Compression Power Requirements for Mars Reference Mission**
Since the compression technology is uncertain, Table 5-2 provides the power requirements for both an immature (40% mechanical efficiency) and mature (70% mechanical efficiency) compression system.

5.4 Fore-Compression: A Method of Adapting to Martian Environmental Variability

The selected design approach for MARRS is to utilize a low ratio “fore-compression” stage to prepare the gases for a conventional multistage compression. Fore-compression removes martian dust, and delivers the gases to subsequent compression stages at constant conditions. This approach is followed to enable optimization of a majority of compression equipment that must operate in an otherwise highly variable environment. Diurnal variation in density, for example, may be over 35% due to temperature changes, and seasonal variation may be over 30% due to condensation at the Martian poles.

Seasonal variability in the fraction of recoverable products in the Martian atmosphere may be up to 30% reflecting the waxing and waning of carbon dioxide frost at the poles. During the South Polar winter, for example, a greater concentration of oxygen, water and carbon monoxide can be expected in the northern latitudes. The main effect on an extraction process will be changes in the rate of production of these products. The compression and cryogenic separation systems will operate relatively unchanged.

5.5 Technology Options for Compressors

The chief options for compression include positive displacement, turbo-compressors and axial compressors. These technologies are all adaptable to Martian conditions, and all have benefits and drawbacks relative to the others. The differences are primarily related to size and throughput. Piston compression favored for small sizes, and axial compression for a large installation.

An initial study of compression technologies was made in which the major issues were (1) physical dimensions and launch mass, and (2) tolerance to dust. These were the issues considered the most important to several reviewers of MARRS who, in fact, viewed the ability to accomplish the needed compression as the main barrier to its acceptance as a viable resource recovery method.

Ultimately, the concept of fore-compression was chosen since it resolves the key issues of atmospheric capture, dust control, and delivery of gases to the higher stages at nearly constant properties. Fore-compression also isolates the most difficult reliability and redundancy issues into a separate engineering element.
5.6 Fore-Compression Design Approach

5.6.1 FLOW AND EQUIPMENT CONSIDERATIONS

The initial capture of the thin Martian atmosphere will require compression devices capable of processing uniquely large volumes of gas. A “soft” assumption might be that the devices must be compatible in size to current launch vehicles, setting, for example, a characteristic size of about six meters for an inlet cowl. For diameters of this size the flow regime will range between laminar and turbulent, and unusual flow conditions are not expected.

Equipment pressurizing atmospheric gases from, for example, 750 Pa (7.5 mbar) to 2250 Pa (22.5 mbar) may not be subject to high stresses since the pressure differences experienced can be low. For example, a one-meter diameter piston compressor that achieves this 3-fold compression would see only 1180 N (400 lb) at the header. While detailed mechanical design was not included in the current study, a low stress associated with the small pressure differences allows considerable flexibility in selecting compression technologies.

5.6.2 DELIVERED PROPERTIES FROM FORE-COMPRESSION

To outline the compression requirements for MARRS, an assumed condition for gases delivered to the non-variable compression sections is needed. This condition should have sufficient margin to take into account all applicable variations in the Martian surface environment. These include, chiefly, temperature, density, and pressure.

At the Viking 2 site at 48 deg North latitude, the average daily pressure varied seasonally, exhibiting a range from about 750 Pa (7.5 mbar) to 1000 Pa (10.0 mbar). Lower values are likely to occur at lower latitudes due to variations in Martian topography. If the lowest daily pressure expected is assumed as, say, 600 Pa (6 mbar), then a three-fold increase in pressure would provide margin for input to subsequent compression elements. A delivered pressure of 1600 Pa (16 mbar) from the fore-compressor is taken as a primary design condition.

Surface density changes with temperature, the latter varying up to 35% during a sol, being highest early in the morning. The improvement in compression efficiency due to increased density has not been studied.

5.6.3 PISTON COMPRESSION

Figures 5-4 and 5-5 illustrate a simple piston-type compressor that will be highly mass-efficient, and also highly tolerant of dust. Figure 5-3 illustrates a two-cylinder linear compressor that is similar in function to a bicycle pump that pumps on both strokes. The major difference is that the MARRS fore-compressor must be large.
Reed or flapper valves are sufficient to hold the back pressure, which is less than 1000 Pa (10 mbar).

![Diagram of a Bi-Directional Piston Compressor Resistant to Dust](image)

**Figure 5-4. Diagram of a Bi-Directional Piston Compressor Resistant to Dust**

Figure 5-5 illustrates the use of reed valves around the circumference of the piston. Multiple valves are expected to reduce flow resistance and provide redundancy to blockage.

Simple lightweight piston compressors can begin the capture of the martian atmosphere, can provide primary dust control, and can provide conditioning for the more efficient compressors that raise the pressure to MARRS processing requirements.

5.7 Final Compression Options

5.7.1 FACTORS IN THE SELECTION OF THE COMPRESSION SYSTEM

Once a clean gas is available, there are many options for compression of the martian atmospheric gases to the needed pressures. The final choice will be determined by (a) the size of the MARRS plant, (b) the maturity and confidence of the design, (c) the robustness of the compressors, and (d) the mass and efficiency associated with the compression system. A combination of technologies may be preferable, with the most dust tolerant methods used at the early stages of compression.
5.7.2 Scroll Compressors

Scroll compressors, used commonly in air conditioner systems, are highly robust, capable of high compression ratios, and throttleable. Figure 5-6 illustrates the mechanism that is essentially a rotary positive displacement action. Scroll compressors are candidates for all stages of compression, but may be particularly useful with high density gases in multiphase flow (including solid CO₂). They have the disadvantage of relatively high mass per unit throughput when used with low density gases. Scroll compressors might be attractive for small, unattended air extraction plants.

5.7.3 LARGE PISTON COMPRESSORS

Conventional piston compressors were not considered applicable to MARRS because of their need for lubrication. Adaptations might be possible if liquid CO₂ can be used as a lubricant or labyrinth seal.

5.7.4 TURBOCOMPRESSORS

Turbocompressors are an interim step to axial compressors, being higher in mass but more tolerant of dust. Their use within MARRS will depend on the need for robustness and adaptability to inlet conditions.
5.7.5 AXIAL COMPRESSORS

Axial compressors offer the lowest mass but highest intolerance to dust. The design for MARRS assumes that the gases entering the axial compressors will be cleaned and conditioned to near-constant temperature and pressure. A detailed study is needed to verify that this strategy provides the lowest mass compression system.

5.8 Summary of Compression Options

Compression is the dominant process in the direct extraction of resources from the martian atmosphere. It takes a thin, difficult-to-handle feedstock and provides a dense, easily processable fluid from which production of oxygen, water, and other materials can be conducted as a matter of course. The design of the compression sections for MARRS will be a major undertaking, and require detailed knowledge of the environment in which it operates.

Heat recovery within the compression process must be extremely well integrated to reduce compression energy. Selection of compression technology must allow for frequent energy recovery units. New technology for axial compressors may be advantageous wherein heat recovery is internal to the compressor. A substantial amount of further study is needed.

5.99 References

6.0 PRIMARY SEPARATOR

6.1 Approach for Conceptual Design of Condenser/Separator

MARRS is based on the ability to condense the majority component of the martian atmosphere, leaving behind a product-rich gas. After compression sufficient to raise the CO₂ above its triple point pressure, the design focuses on (1) the most effective method of removing the heat of condensation, and (2) efficient recovery of oxygen and water.

The primary condenser receives the captured Martian atmosphere at a temperature and pressure sufficient to condense a portion of the CO₂ as a liquid. The CO₂ phase diagram dictates these conditions with the condensation temperature always being above ~216K (~-57°C). The pressure of CO₂ must be at least 518 kPa (5.18 bar), but higher partial pressures condense more CO₂.

For the MARRS design, removal of CO₂ is achieved in two compression/condensation stages. Additional studies are needed to confirm this approach for specific mission requirements such as reliability, redundancy and launch mass. For the two-stage approach, the primary condenser removes a majority of the CO₂ but none of the water. The second stage removes at least 90% of the total CO₂ and recovers water as ice.

Compressed gases enter the primary condenser at 13 bar after a series of compression and cooling steps shown in Figure 6-1. This pressure is allows a sufficiently high margin for preventing condensation of CO₂ as a solid. This pressure is a primary variable in process optimization, and should be examined when process options are better defined. Another assumption is that the gases entering the condenser are free of dust. The multiple compression stages with intercoolers should assure this clean condition.

Table 6-1 indicates changes in composition of the gas phase after the first condensation step. Water at the expected atmospheric concentrations is below its vapor pressure, and does not condense.
Figure 6-1. Route of Gases to the Primary Condenser

<table>
<thead>
<tr>
<th>Component</th>
<th>Vol % before condensation</th>
<th>Vol % after condensation</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>95.46</td>
<td>46.03</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>2.70</td>
<td>32.17</td>
<td>- compression to 13 bar</td>
</tr>
<tr>
<td>Argon</td>
<td>1.60</td>
<td>19.06</td>
<td>- condensation at 220K</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.13</td>
<td>1.55</td>
<td>- approx. ~85% of total</td>
</tr>
<tr>
<td>CO</td>
<td>0.07</td>
<td>0.83</td>
<td>compression energy</td>
</tr>
<tr>
<td>Water</td>
<td>0.03</td>
<td>0.36</td>
<td></td>
</tr>
</tbody>
</table>

Table 6-1. Gas Compositions Associated with the Primary Separator

### 6.2 Issues in Condenser Design

To maintain only fluid phases, the condenser must be operated within the restrictions of the phase diagram, shown in Figure 6-2. The minimum pressure is 518 kPa (5.18 bar), the minimum temperature is 216K (-56°C), and the maximum temperature is 304K (31°C).
There are key tradeoffs in design that will require detailed optimization, not conducted as part of the current study. Generally, operating at the lowest pressure and lowest temperature will reduce compression power, but higher pressure will remove more CO$_2$. Higher pressure and temperatures will reduce the requirements for heat transfer and its associated mass.

The current study assumes that the optimization will find the lower-pressure option the most favorable since the compression power requirement is very large. However, if the oxygen concentration in the Martian atmosphere is in the upper range of possible values, say, 0.3% to 0.4%, the reduced power requirements may argue for different condenser operating conditions. For a fully defensible design, a full MARRS plant optimization would be required.

The primary condensation step is straightforward provided only that frosts of CO$_2$ and water do not block heat transfer and fluid flow. The heat exchange requirement, however, is substantial since the entire heat of condensation for most of the CO$_2$ must be removed. Roughly speaking, the rate will be about five times that of the power of the thermal source.

Figure 6-3 illustrates diagrammatically the heat flow required. For the conceptual design, a brief optimization study was performed, and a combination of internal and external heat exchange was chosen for operating the condenser.
Expansion of spent liquid CO\textsubscript{2} can achieve high volumetric density for heat exchange, but the design must prevent occurrence of CO\textsubscript{2} solids. This restriction may limit internal energy recovery within this step.

![Diagram of CO\textsubscript{2} expansion and cooling process]

Figure 6-3. Dual Heat Exchange Train for Primary Condenser

6.3 Distribution of Components between Phases

6.3.1 SIMPLE CONDENSATION

MARRS depends on concentration of the product gases due to condensation of the bulk CO\textsubscript{2}. If these gases have high solubility in the CO\textsubscript{2}, then the process efficiency will be lowered, and full solubility would invalidate MARRS as a process for ISRU. Thermodynamic calculations indicate that 95\% or more of the permanent gases will remain in the gas phase during the initial condensation of bulk CO\textsubscript{2}. Table 6-2 shows the percentage of these gases that, at equilibrium, remain in the gas phase after condensation. The solubility increases with total pressure, a potential issue for high-pressure operations.

The calculations shown in Table 6-2 use the method of Gjaldbek [1952] to account for non-ideal solubility. Carbon dioxide is considered a simple physical solvent that does not interact chemically with the permanent gases. A similar method of calculation is not available for the water-CO\textsubscript{2} system. To provide a good estimate of water recovery, experimental measurements are required.
Percentage in gas phase (regular solution theory) | Component
---|---
| Pressure (bar) | CO₂ | O₂ | N₂ | Ar | CO | H₂O |
| 6 | 97 | 98.4 | 97.2 | 98 | n/a | |
| 13 | 93.6 | 96.5 | 94 | 95.7 | n/a | |
| 30 | 85.2 | 92.1 | 86.1 | 90.2 | n/a | |

Basis: Equilibrium at 220K

Table 6-2. Calculations for Permanent Gas Recovery from Simple Condensation

6.3.2 Stripping Process for Recovering Additional Products

Virtually all of the remaining oxygen and other minor components of the Martian atmosphere can be recovered after each condensation by a simple stripping step. Pure nitrogen or argon, produced during product purification, is blown through the liquid CO₂ to remove the remaining gases and incorporate them into the secondary product stream. Figure 6-4 illustrates the method as a multistage stripping operation, but a single stage may be sufficient.

![Figure 6-4. Illustration of Stripping the Primary MARRS Condensate](image)

Stripping resolves any uncertainty in solubility of components since it produces an additional thermodynamic driving force for separation. In particular, it resolves much of the uncertainty of water recovery by positively placing water in the secondary gas stream.
6.4 **Design Strategies for the Primary Condenser**

Figure 6-3 outlines the functional design of the primary condenser with both external and internal heat transfer. Once sufficient energy is removed, condensation will begin, and equipment will enter a two-phase or even three-phase flow regime. Part of the design strategy is to condense most of the CO$_2$ at the highest temperatures, saving the low temperature cooling sources for the remaining heat exchange. While a detailed design optimization is needed, a countercurrent design provides good efficiency while minimizing issues associated with the formation of CO$_2$ frosts in the cooling equipment.

6.5 **Direct Heat Exchange Option**

Direct injection of cold waste components into the primary condenser may allow design of a lower mass but less efficient condenser. Injection of liquid nitrogen, for example, might reduce the heat transfer area and mass sufficiently to make up for the need for additional gas processing. Injection of very cold CO$_2$ might accomplish the same end. Direct injection as well as other process options should be examined in a more detailed design study where launch mass and launch costs are included as a key part of the optimization.

Reference:

7.0 SECONDARY COMPRESSION AND CONDENSATION

7.1 Approach for Conceptual Design

The secondary processing section prepares the product-rich stream for separation and purification. This section has two primary purposes:

(1) removal of most of the remaining CO$_2$ from the product gas stream,
(2) recovery of water.

These steps are accomplished primarily by compression to above 3000 kPa (30 bar), and by cooling to the lowest practical temperature. The majority of the remaining CO$_2$ is condensed as a liquid, and water vapor, now at a partial pressure above its vapor pressure, condenses as a solid, which floats on the CO$_2$.

The optimum final pressure depends on many practical aspects of removing CO$_2$, H$_2$O and even O$_3$ frosts, and must be determined by more detailed optimization studies. The ERG design model shows benefits to the separation at pressures as high as 10 MPa (100 bar). This model looks only at physical chemistry and separation issues, however, and does not take into compression efficiencies, and mechanical and stress issues associated with very high pressure.

Table 7-1 shows the amounts of CO$_2$ remaining after condensation at high pressure when the feedstock has been concentrated at 13 bar in the primary condenser. Removal of CO$_2$ is the primary effect of pressure. A detailed optimization is required to determine the optimum pressure for secondary compression and condensation. This optimization will include the mass and energy required for final frost removal which will likely use adsorbent beds.

<table>
<thead>
<tr>
<th>Composition (percentage) of remaining gas phase</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>30</td>
<td>19.9</td>
</tr>
<tr>
<td>100</td>
<td>6.0</td>
</tr>
<tr>
<td>150</td>
<td>4.0</td>
</tr>
<tr>
<td>200</td>
<td>3.0</td>
</tr>
<tr>
<td>Basis: Equilibrium at 220K</td>
<td></td>
</tr>
</tbody>
</table>

Table 7-1. Composition of Compressed Martian Gases After Condensation of CO$_2$
7.2 Compression Method

Secondary compression raises the pressure of the product-rich stream from roughly 1300 kPa (13 bar) to over 3000 kPa (30 bar), or by at least a factor of two or three. The selected technology may depend on the scale of MARRS plant. The high pressure introduces stress issues not encountered in the primary compression section.

A final pressure of 30 bar is assumed for the conceptual design. This level offers a compromise between (1) energy, mass and process complexity, and (2) good CO₂ removal, water recovery, and requirements to remove frosts that will form as the product-rich stream enters the cryogenic separation section.

Scroll pumps may provide the most robust technology if multiphase flow is expected. Regardless of the technology, compression energy will be only a small part of the total compression load.

7.3 Water Recovery and Its Physical Chemistry in MARRS

Water can condense when its partial pressure in the compressed atmosphere exceeds its vapor pressure. At 220K, its partial pressure must be above about 0.0025 mbar. Table 7-2 shows the relationship between atmospheric concentration and partial pressure at 30 bar total pressure. Water will condense if its concentration in the atmosphere is above about 0.005%. The condensation temperature, however, must be close to the triple point of CO₂. Slightly higher temperatures will reduce the capture of water substantially.

<table>
<thead>
<tr>
<th>mixing ratio of water vapor</th>
<th>partial pressure</th>
<th>notes:</th>
</tr>
</thead>
<tbody>
<tr>
<td>percent</td>
<td>mbar</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>0.003</td>
<td>30 bar total pressure</td>
</tr>
<tr>
<td>0.01</td>
<td>0.006</td>
<td>condensation occurs when</td>
</tr>
<tr>
<td>0.02</td>
<td>0.011</td>
<td>partial pressure &gt; vapor pressure</td>
</tr>
<tr>
<td>0.03</td>
<td>0.017</td>
<td>vapor pressure = 0.0025 mbar at 220K</td>
</tr>
<tr>
<td>0.04</td>
<td>0.022</td>
<td>vapor pressure = 0.0088 mbar at 230K</td>
</tr>
</tbody>
</table>

Table 7-2. Comparison of Pressures for Condensation of Water Ice

Figure 7-1 shows the steep vapor pressure curve for ice. A key element of MARRS is its ability to operate at just the right temperature to recover the atmospheric water.
7.4 Water Recovery Concept

The recovered water will precipitate on the liquid CO₂ as illustrated in Figure 7-2. Ice, with a specific gravity of about 0.93, will float on LCO₂, which has a specific gravity of about 1.4. The amounts of water may be relatively small, amounting to about 0.6 kg/hr, which suggests a non-continuous method of removal such as lock hoppers. For comparison, liquid CO₂ is removed at a rate of 2000-3000 kg/hr. If the diurnal variations of water content in the atmosphere are large (as discussed in Section 4), water production could be much higher.

The ice crystals can be separated within the condenser by a design that causes the liquid CO₂ to swirl. The resulting centrifugation accelerates the separation. Experiments are needed to determine the most effective method of water recovery.

7.5 Summary of Secondary Condenser Unit Design

Water recovery determines much of the design of the secondary compression/condenser system. If water is a critical product, the operating pressure will be the highest attainable in order to raise the partial pressure of water vapor. If efficiency is most important, the operating pressure may be reduced and a third compression/condenser section added.
The temperature of the secondary condenser unit, however, is set at near 220K, or as close to the triple point of CO₂ as is possible. Even slightly higher temperatures will prevent recovery of much of the water. The result will be added mission costs and mass.

Figure 7-2. Illustration of Water Collection from Secondary Condenser
8.0 PURIFICATION AND STORAGE OF PRODUCTS

8.1 Conceptual Design for Purification

The MARRS process uses cryogenic distillation to separate the permanent gases as illustrated in Figure 8-1. No detailed design was conducted. The distillation plant will not be a major mass or energy cost to the MARRS. This follows because

a. The gases supplied to the plant are at pressures easily sufficient to supply the liquefaction energy,
b. The total amount of material to be processed is relatively small, and
c. Most of the gases processed exit the cryogenic plant as gases and not liquids, and their liquefaction energy is recovered internal to the plant.

![Diagram of the Purification and Cryogenic Distillation Plant]

Figure 8-1. Diagram of the Purification and Cryogenic Distillation Plant

Nitrogen and argon are produced in large amounts and are used within the plant as stripping gases, refrigerants and heat transfer fluids. Oxygen is recovered as a liquid for storage and use as a local propellant and respiratory gas. Carbon monoxide is
recovered as a gas or liquid provided that it finds a use within the MARRS architecture.

Cryogenic distillation will produce highly purified liquids or gases depending on the requirements of the mission or system architecture. Table 8-1 lists the products and some of their uses. Liquid oxygen will be a major product, a primary propellant for Mars ascent and Earth return. Water is produced at about 0.6 kg/hr when present in the martian atmosphere at 0.03%. Lower mixing ratios deteriorate the production of water sharply.

<table>
<thead>
<tr>
<th>Product</th>
<th>Recovery Rate</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen gas)</td>
<td>up to 5.8</td>
<td>respiratory agent</td>
</tr>
<tr>
<td>Oxygen (liquid)</td>
<td>up to 5.8</td>
<td>rocket propellant</td>
</tr>
<tr>
<td>Water</td>
<td>0.7</td>
<td>primary consumable, fuel precursor</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>2.7</td>
<td>rocket fuel precursor, reserve fuel</td>
</tr>
<tr>
<td>Nitrogen (gas)</td>
<td>up to 105</td>
<td>respiratory agent, stripping gas</td>
</tr>
<tr>
<td>Nitrogen (liquid)</td>
<td>up to 105</td>
<td>refrigerant, multi-use working fluid</td>
</tr>
<tr>
<td>Argon (gas)</td>
<td>88</td>
<td>propellant, heat transfer fluid, resp. agent</td>
</tr>
<tr>
<td>Rare Gases</td>
<td>0.01</td>
<td>propellant, heat transfer fluid</td>
</tr>
<tr>
<td>CO₂ (liquid)</td>
<td>high</td>
<td>multi-use working fluid</td>
</tr>
</tbody>
</table>

Table 8-1. Manifest for a MARRS Direct Extraction Process

8.2 Final Cleanup of Carbon Dioxide and Other Frosts

Some CO₂ will escape the final condensation steps and must be removed as solids prior to cryogenic processing, i.e., processing below the triple point of CO₂. Figure 8-1 diagrams triplicate packed beds that remove CO₂ as an adsorbed solid. Typical adsorbents are activated carbon and zeolites (Molecular Sieves™), each of which can adsorb as much as 20% their mass in CO₂.

In the adsorption step, the restriction of operating above the triple point of CO₂ is removed. The beds are operated at temperatures below 220K to reduce contamination of the cryogenic system to very low levels. They key option in the adsorption step is the method of desorbing CO₂ and regenerating the bed.

The two primary methods are thermal swing adsorption (TSA) and pressure swing adsorption (PSA). The choice of methods depends on a detailed process optimization. A combination of methods is likely whereby the beds are heated moderately (TSA) while exposed to the low ambient pressure.
In either method, ozone frosts or any unknown volatile contaminants will be removed along with the CO$_2$. Ozone frosts are explosive, and their removal is a necessary feature of purification operations.

8.3 Product Storage

Storage is not unique to the MARRS direct extraction concept and was not included for study. Mass requirements to store 60,000 kg of oxygen were estimated, however, at no more than 3000 kg. Active refrigeration is required, but can be supplied without extra mass by the cryogenic distillation plant.

Storage of liquid CO$_2$ may be advantageous on a very large scale, especially within a MARRS surface architecture. Carbon dioxide is liquefied at the rate of about 6000 kg/hr and is highly available. Unlike the cryogenic tankage, CO$_2$ will require vessels capable of containment pressures over 50 bar, but may not need substantial insulation in many martian locations.

8.4 Summary of Product Purification and Storage

After removal of most of the CO$_2$ from the compressed gas streams, the total mass flow of product-rich gas is less than 1/20$^{th}$ of the initial atmospheric intake, and less than 1/12000$^{th}$ of the initial volume. The final conditioning of recovered products has only a minor influence on MARRS system mass.

The cryogenic engineering is straightforward except for the variable environmental conditions on the martian surface. Because MARRS is a thermophysical process with extensive exchange of heat with the environment, it must be adaptable to rapid changes in temperature, pressure and density. There are few applicable engineering precedents.

Cryogenic distillation provides respiratory gases free of carbon monoxide. Other methods of direct extraction, if proposed, will need to address this issue for human exploration.

End of Section
9.0 ENERGY AND MASS ESTIMATES

9.1 Overall Process Energy Estimate

9.1.1 GROSS COMPRESSION POWER AND COMPARISON WITH ELECTROLYSIS

The energy requirements for MARRS are dominated by the compression of over 1000 kg of martian atmosphere to recover each kg of oxygen. For 22 stage compression with five intercooling heat exchangers and a mature technology, the gross (i.e., exclusive of power recovery) power requirement is 8.6 kW-hr/kg O₂. The values given in Section 5.0 are repeated in Table 9-1.

<table>
<thead>
<tr>
<th>SPECIFIC POWER</th>
<th>SPECIFIC POWER</th>
<th>TOTAL MECH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40% efficiency</td>
<td>70% efficiency</td>
</tr>
<tr>
<td>W/kg/hr CO₂</td>
<td>kW/kg/hr O₂</td>
<td>kW/kg/hr CO₂</td>
</tr>
<tr>
<td>15.0</td>
<td>15.1</td>
<td>8.560</td>
</tr>
</tbody>
</table>

Basis: 22 compression stages to 13 bar, 5 intercooling stages

Table 9-1. Gross Compression Power Requirements for Mars Reference Mission

For comparison, electrolysis of CO₂, an alternate method of producing oxygen on Mars, requires over 10 kW/kg O₂/hr in direct current electrical power [note 9-1]. Water electrolysis requires about 6.7 kW/kg O₂/hr [note 9-2]. On the basis of gross power and even without power recovery, MARRS is an attractive alternative to electrolysis of both CO₂ and water for producing oxygen.

9.1.2 THERMAL ENERGY REQUIREMENTS

In the MARRS process, power and energy recovery are intimately integrated with power production. This integration is advantageous primarily because of the large-scale production of a working fluid, LCO₂, as a by-product of oxygen and water recovery. When this working fluid is utilized as martian “steam,” the result can be a very high overall process efficiency.

The estimate of total process energy depends primarily on

a. the efficiency of power generation from the heat source,
b. the percentage of compression energy that can be recovered by expansion back into the atmosphere,
c. energy requirements for the balance of the plant including human habitation.
An calculation of thermal energy requirements for MARRS can be made by estimating the following factors:

a. an efficiency of power generation,

b. the gross compression power requirement,

c. efficiencies for both power and heat recovery,

d. a power requirement for balance-of-plant as a percentage of the total power.

Table 9-2 provides these values as well as an estimate of MARRS thermal energy requirements normalized to the rate of oxygen production. For a mature plant, the thermal power requirement is 110 kW to supply oxygen for the Mars Reference Mission with single redundancy of both propellant and respiratory oxygen.

<table>
<thead>
<tr>
<th>Item:</th>
<th>Notes</th>
<th>kW/kg O₂/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Generation Efficiency</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>Normalized Compression Power</td>
<td>8.63 kW/kg O₂/hr</td>
<td>8.63</td>
</tr>
<tr>
<td>Power Recovery Efficiency</td>
<td>50%</td>
<td>-4.32</td>
</tr>
<tr>
<td>Power for Balance of Plant</td>
<td>15% of Compression Power</td>
<td>1.29</td>
</tr>
<tr>
<td>Net Power Generation</td>
<td>5.61 kW/kg O₂/hr</td>
<td>5.61</td>
</tr>
<tr>
<td>Thermal Power Needed for Power Recovery</td>
<td>50% of Compression Power</td>
<td>11.22</td>
</tr>
<tr>
<td>Thermal Power Needed for Balance of Plant</td>
<td>25% of Compression Power</td>
<td>2.16</td>
</tr>
<tr>
<td>Total Thermal Power</td>
<td>kW/kg O₂/hr</td>
<td>18.99</td>
</tr>
<tr>
<td>Total Thermal Power, kW for MRM</td>
<td>for 5.8 kg O₂/hr</td>
<td>110.12</td>
</tr>
</tbody>
</table>

Table 9-2. Thermal Power Estimates for Mars Reference Mission

9.1.3 POWER REQUIREMENTS FOR A NON-THERMAL SYSTEM

The gross power consumption for MARRS (i.e., 8.63 kW-hr/kg O₂) also provides a rough estimate of the power required for a non-thermal direct extraction process. If solar photovoltaic power were available in substantial amounts, a process similar to MARRS could recover oxygen and water with the total power amounting to roughly 12 kW-hr/kg O₂, or about 70 kW.
9.2 Overall Process Mass Estimate

9.2.1 GROSS MASS ESTIMATE AND COMPARISON WITH ELECTROLYSIS

A mass estimate for a MARRS process is premature because of the uncertainties in both technology and requirements. Nonetheless, a rough estimate based on functional elements can be provided. A very large “architecture-sized” plant will benefit from scaling laws available to continuous thermophysical process such as MARRS, advantages not fully available to electrolytic processes.

Table 9-3 provides a mass list for a direct extraction plant capable of supplying oxygen to the Mars Reference Mission. This estimate does not include equipment not directly related to the MARRS plant such as product storage. Under a full architecture, many other items would be included such as cryogenic and pressurized product storage, distribution networks, backup equipment, and thermal, electrical and mechanical utilities.

<table>
<thead>
<tr>
<th>Mass, kg</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>Atmosphere capture and fore-compression</td>
</tr>
<tr>
<td>3700</td>
<td>Primary compression section with heat recovery</td>
</tr>
<tr>
<td>900</td>
<td>Primary condenser and heat exchanger</td>
</tr>
<tr>
<td>450</td>
<td>Secondary compressor and condenser (no water recovery)</td>
</tr>
<tr>
<td>400</td>
<td>Product-rich gas cleanup and frost control</td>
</tr>
<tr>
<td>200</td>
<td>Cryogenic distillation</td>
</tr>
<tr>
<td>5000</td>
<td>Nuclear reactor heat system with primary heat exchanger</td>
</tr>
<tr>
<td>200</td>
<td>Cryogenic distillation</td>
</tr>
<tr>
<td>500</td>
<td>Thermal and power utilities</td>
</tr>
<tr>
<td>1100</td>
<td>Piping and distribution</td>
</tr>
<tr>
<td>13650</td>
<td>Total Mass for MRM (excludes non-MARRS support)</td>
</tr>
</tbody>
</table>

Table 9-3. Mass Estimates of MARRS for Mars Reference Mission

The mass required for primary compression assumes extensive heat recovery using intercooling and expansion of cooled and liquefied CO$_2$. This requirement for heat transfer is a major mass and energy driver. Internal heat recovery for MRM amounts to over 530 kW$_{th}$, or almost five times the net thermal power for the process.

Prior to the conception of MARRS, ERG estimated the mass of a nuclear powered electrolysis plant of the same production rate. Table 9-4 provides these estimates based on CO$_2$ electrolysis at 10 kW/kg O$_2$ with production of pressurized CO$_2$ feed gas by thermal swing adsorption.
Table 9-4. Mass Estimate for CO₂ Electrolysis for Oxygen Production on Mars

<table>
<thead>
<tr>
<th>Mass, kg</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>Electrolyzer 2000 amp/m², 20 kg/m² active surface, 10 kg/m² structure</td>
</tr>
<tr>
<td>5000</td>
<td>Nuclear reactor with primary heat exchanger</td>
</tr>
<tr>
<td>2500</td>
<td>Power and heat system for electrolyzer</td>
</tr>
<tr>
<td>2660</td>
<td>Thermal swing compression system, 15% adsorption, 3 swings/sol, 50% utilization of CO₂</td>
</tr>
<tr>
<td>2000</td>
<td>Electrolyzer/TSA Spares</td>
</tr>
<tr>
<td>2230</td>
<td>TSA desorption power (electrical heat)</td>
</tr>
<tr>
<td>200</td>
<td>Cryogenic conditioning for storage</td>
</tr>
<tr>
<td>300</td>
<td>Thermal and power utilities</td>
</tr>
<tr>
<td>16390</td>
<td>Total mass for MRM (excludes storage)</td>
</tr>
</tbody>
</table>

A detailed comparison of methods should be conducted, but will be difficult. MARRS generates power internal to the process so that power generation is intimately related to the recovery of products. Electrolysis for oxygen production requires power generation for both electrolysis and peripheral processes such as providing a high-pressure gas to the electrolyzer.

9.3 Summary of Mass and Energy for MARRS and Electrolysis

ERG believes that both direct extraction and electrolysis will be used for human exploration of Mars. Electrolysis of water will be used on all long-term human exploration missions. Electrolysis offers advantages in both mass and energy on a small scale.

For Mars and at larger sizes, however, direct extraction will accumulate economies of scale that are universal to processes of its type. Internal heat recovery will become more efficient, water recovery will be more effective, and compression equipment will approach near theoretical efficiencies.

The by-products of water, carbon monoxide and liquid CO₂ provide more advantages to direct extraction of the atmosphere. Water can even be a primary product of MARRS if the location provides sufficient atmospheric resources. The floor of Vallis Marineris, for example, might have sufficient humidity to recover substantial amounts of water because of its sheltered location and low elevation. The best locations for water are also the best locations for oxygen, although the reverse is not necessarily true.
9.4 Mass and Energy Opportunities for the Mars Reference Mission

A large-scale plant producing oxygen and nitrogen frees the MRM from many of its mass allocations. Table 9-5 suggests a few areas where a direct extraction plant benefits a human exploration mission.

<table>
<thead>
<tr>
<th>Product</th>
<th>Recovery Rate kg/hr</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen (gas)</td>
<td>up to 5.8</td>
<td>respiratory agent</td>
</tr>
<tr>
<td>Oxygen (liquid)</td>
<td>up to 5.8</td>
<td>rocket propellant</td>
</tr>
<tr>
<td>Water</td>
<td>up to 1.6</td>
<td>primary consumable, fuel precursor</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>2.7</td>
<td>rocket fuel precursor, reserve fuel</td>
</tr>
<tr>
<td>Nitrogen (gas)</td>
<td>up to 105</td>
<td>respiratory agent, stripping gas</td>
</tr>
<tr>
<td>Nitrogen (liquid)</td>
<td>up to 105</td>
<td>refrigerant, multi-use working fluid</td>
</tr>
<tr>
<td>Argon (gas)</td>
<td>88</td>
<td>propellant, heat transfer fluid, resp. agent</td>
</tr>
<tr>
<td>Rare Gases</td>
<td>0.01</td>
<td>propellant, heat transfer fluid</td>
</tr>
<tr>
<td>CO₂ (liquid)</td>
<td>high</td>
<td>multi-use working fluid</td>
</tr>
</tbody>
</table>

Table 9-5. By-Product Manifest for MARRS Direct Atmospheric Extraction

While the chief function of ISPP in the MRM is oxygen for propellant, MARRS' by-products allow replacement of substantial mass in other portions of the mission. A major fraction of fuel can be replaced by hydrocarbons produced from reactions of carbon monoxide and water. A MARRS plant could be sized to produce adequate fuel for mission requirements while producing additional oxygen, possibly for use in larger habitats.

A key issue for MRM and MARRS is the amount of water that is available in the surface atmosphere. Section 4 discusses the possibility of recovering larger amounts than are predicted from daily or seasonal average values. Measurements are needed to determine the temporal mixing ratio of water vapor at the surface in several martian locations.

---

Note 9-1. For electrolysis of CO₂, a value of 10.1 kW O₂/kg/hr was determined from Faraday's law and an assumption of 3.0 volts per electrolysis cell as reported for YSZ cells. The theoretical voltage at cell operating temperatures of 900°C is less than 1.0 volts. The need for the higher voltages is not clear to the authors, but may be related to the requirement for high current density on the electrodes (1) to reduce mass, and (2) to lessen the impact of electronic conductivity in the YSZ electrolyte.
Note 9-2. For electrolysis of water, a value of 6.7 kW/kg O₂/hr is determined from Faraday’s law and an assumption of 2.0 volts per electrolysis cell. Lower voltages will increase electrolyzer mass due to a reduction in current density.
10.0 OUTREACH ACTIVITIES

The MARRS concept and closely related topics have been the subject of several talks before diverse audiences. Copies of most presentations are available from ERG (please contact Dr. C. England at cengland@earthlink.net).

March 24, 2000 – “Planetary Chemical Engineering,” a talk by Dr. Christopher England for the Center for In-Situ Exploration and Sample Return, Jet Propulsion Laboratory, Pasadena, CA. Issues related to conducting chemical engineering design in a non-terrestrial environment were discussed. The MARRS process, not yet named or funded, was used as an example.

June 12, 2000 – “Mars Atmosphere Resource Recovery System: MARRS,” a talk by Dr. Christopher England at the NIAC Annual Meeting, Virginia. Preliminary studies leading up to the MARRS proposal to NIAC was presented that included rough energy and mass estimates.


October 12, 2000 – “Making Air on Mars,” a talk by Dr. Christopher England to the Engineering Honor Students Society, University of Southern California, Los Angeles, CA. Planetary chemical engineering, how to make air, the science behind the design, and questioning the scientists and their science were discussed.

December 1, 2000 – “The Mars Surface Atmosphere: The Rodney Dangerfield of Mars Exploration,” a talk by Dr. Christopher England for the Center for In-Situ Exploration and Sample Return, Jet Propulsion Laboratory, Pasadena, CA. The loss of ground truth data, the uncertainty of martian atmospheric information, and the need for understanding the atmosphere and its composition were discussed.


May 14, 2001 – “Making Air on Mars,” a talk by Dr. Christopher England for the Santa Clarita Astronomy Club, Santa Clarita, CA. The MARRS process and the state of knowledge of martian environmental science was discussed.
June 1, 2001 – “Follow the Oxygen: An Approach to Mars Exploration,” a talk by Dr. Christopher England for the Center for In-Situ Exploration and Sample Return, Jet Propulsion Laboratory, Pasadena, CA. An analysis of the current exploration program was presented to provide insight into why the martian atmosphere should be elevated in importance within this program. Arguments for both scientific and engineering goals were presented.

June 6, 2001 – “Recovery of Viking GCMS Atmospheric Data,” a proposal with New Mexico State University (a Hispanic Serving Institution) to NASA for recovery of the Viking measurements. The proposed work included studies to detect variation in composition between measurements.
11.0 RECOMMENDATIONS FOR FURTHER STUDIES

11.1 Summary of the MARRS Project

Oxygen and the other components of air can be extracted from the martian atmosphere by processes that separate them from the majority component, carbon dioxide, by condensation. The cold environment aids the recovery of these components by reducing the amount of energy required to process the atmospheric gases. The current study for NIAC outlined many fundamentals of the process, and suggested methods that most efficiently extract usable components.

Recommendations for advancing the technologies for oxygen recovery are provided below. The MARRS-related items are taken from the body of this report. In additions, suggestions are made for understanding the atmosphere in a way that supports both scientific and human exploration goals. A design for resource recovery only makes sense if the resource, and the environment that holds it, is understood.

A complete design for a resource recovery system is a major undertaking. This report suggests many potential avenues for research and development. The most important need, however, is to understand the environment on Mars, and in specific locations on Mars, well enough to execute a preliminary design. A primary goal to enable human exploration of Mars must be to accumulate the scientific knowledge that enables this understanding.

11.2 Recommendations for Scientific Study of Mars to Support Human Exploration

1. **DETERMINE THE EXTENT OF THE RESOURCE.** Determine the composition, and variability of composition, of the martian surface atmosphere. The mixing ratio of molecular oxygen should be determined at several locations with an error of less than about 7%. It is currently +/- 100%, perhaps more. Obtaining values for oxygen at this accuracy will provide much of the scientific and engineering background needed for understanding the atmosphere and its relationship with the regolith. Of course, the values are primary inputs to any process of resource extraction from the atmosphere.

2. **DETERMINE THE VARIABILITY OF THE RESOURCE.** Determine the pressure-volume-temperature-wind-dust dataset for at least several locations on Mars. These parameters must be understood to design equipment of any size that interacts with the environment. Current rovers are overdesigned for heat transfer because of uncertainties in air movement and other environmental factors. These values are also primary inputs for atmospheric resource extraction.
11.3  Recommendations for Further Studies of Direct Extraction Processes Based on the MARRS Concept

The following recommendations represent the author’s prioritization of tasks that support better characterization of compression-based direct extraction processes on Mars.

1. DEMONSTRATE THE CONCENTRATION OF OXYGEN BY COMPRESSION AND CONDENSATION. Before ERG proposed the MARRS process to NIAC, the amount of oxygen in the martian atmosphere was considered “trace” by scientists. A simple condensation experiment can demonstrate that a product with up to 2% of oxygen can be manufactured from the martian atmospheric gases by simple and understandable means. Refining of this gas to make air can then be seen as a matter of course. The goal is to quickly familiarize the technical community that air-on-Mars can be a technical reality.

2. DEMONSTRATE THE RECOVERY OF WATER FROM CONDENSATE OF CARBON DIOXIDE. The physical chemistry of water recovery in the MARRS process dictates a narrow range of recovery pressure and temperature. These same restrictions apply to other methods such as direct condensation during martian night. Water is a key resource for human exploration, and its potential for recovery may accelerate development of MARRS or a similar process. A demonstration of water recovery would illuminate issues associated with diurnal variations in water due to sublimation of frost.

3. DETERMINE THE MASS IMPACT OF DIRECT EXTRACTION OF RESOURCES ON THE MARS REFERENCE MISSION. The savings provided by the MARRS process in landed mass, launch mass, costs and schedule to the MRM mass will be substantial. Studies should be conducted to assess the benefits of, in addition to oxygen, recovering water and carbon monoxide. The studies should be extended to account for a reduced need for air revitalization and consumables recycling on Mars if both are available from an atmospheric resource recovery process.

4. INVESTIGATE THE IMPACT OF THE MARS ENVIRONMENT ON COMPRESSION REQUIREMENTS, TECHNOLOGIES AND OPTIONS. Variability of the environment and its resources is a unique aspect of Mars exploration. The power for compression of the martian atmosphere will vary markedly with both diurnal and seasonal changes. A major study is required to assess how best compression should be accomplished. Parameters needed include whether water recovery is a primary function (may determine the final pressure), and the location. Studies should include several locations including polar, equatorial (perhaps Vallis Marinaris) and mid-latitude regions.
5. INVESTIGATE OPTIONS FOR MULTISTAGE PRIMARY COMPRESSION. Capturing the martian atmospheric resources is a prime factor in the mass and power requirements for MARRS. Multiple stages of compression with substantial intercooling can reduce the power but at the expense of added equipment. A detailed understanding of these tradeoffs is needed to accurately scale the power requirements for a MARRS process. These studies should accommodate actual martian atmospheric gases rather than a simple model based on carbon dioxide.

6. INVESTIGATE TWO-STAGE APPROACH TO REMOVAL OF CARBON DIOXIDE. Carbon dioxide is separated from more valuable products by compression and condensation. This report suggests a two-stage removal step as a way to minimize the amount of compression power needed. A detailed analysis of this approach is needed including options of more stages and higher pressure. Studies should include optimization of all CO₂ removal systems including the final adsorption “polishing” operation.

7. INVESTIGATE TECHNOLOGIES FOR REMOVING FROSTS. A key uncertainty for MARRS is the reliability of a frost-removal system prior to production of liquid oxygen. This system must operate at high efficiency. MARRS assumes an adsorption-based system, but how the adsorbent is regenerated should be examined. If exposure to martian ambient pressure will regenerate the adsorbent, this method might be preferred over thermal swing adsorption. Heating the adsorbent, however, may provide a more reliable frost-removal system. Studies are needed that concentrate on how resources are supplied to the cryogenic system.

8. EXPLORE AND COMPARE OTHER ATMOSPHERIC RESOURCE RECOVERY OPTIONS INCLUDING ELECTROLYSIS AND ADSORPTION-BASED METHODS. ERG believes that the MARRS process outlined in this report is the best overall option for a large-scale martian surface presence. Other methods of manufacturing needed resources from the atmosphere may be attractive at smaller scales. These include variations of MARRS, chemical processes, and electrochemical processes such as electrolysis. Comparison of processes is difficult, and merits extensive studies to evaluate options for both human and large robotic exploration.

9. DEVELOP GUIDELINES FOR REDUNDANCY OF SUPPORT TECHNOLOGIES FOR HUMAN EXPLORATION. The concept of redundancy for human exploration of Mars may require both redundant production of consumables, and redundant technologies, i.e., different technologies that produce the same products. While MARRS is envisioned as a process that uses conventional technology, the environment in which it will work is not conventional. Other methods of oxygen production such as water electrolysis (and water recovery) might be needed even if MARRS proves an overwhelm-
ingly advantageous technology. Guidelines will be required before a detailed technology plan for human exploration of Mars can be established.

10. DEVELOP GUIDELINES FOR REDUNDANCY AND PRODUCTION MARGINS OF CONSUMABLES. While extra consumables seem generally desirable for human exploration of Mars, the amounts needed for backup, contingencies, and unforeseen needs are not clear. This report assumes single redundancy for the application of MARRS to the Mars Reference Mission, i.e., it makes twice the oxygen needed. Less redundancy would reduce launch mass for the production plant somewhat, and possibly change the detailed design.

11. DEVELOP EARLY GUIDELINES FOR A LAYOUT FOR A MARRS PLANT WITH EMPHASIS ON THE HEAT SOURCE. The mass of a resource extraction plant will include hardware such as piping and shielding associated with the heat source. A layout that includes heat source options (e.g., reactor vs. radioisotope sources) is needed to assess the mass impacts of the source, and of transport of heat to the extraction process. A reactor will need more shielding while an isotope source would be less controllable.

12. INVESTIGATE A LOW-POWER OPTION FOR MARRS WITH COMPRESSION ONLY AT NIGHT. The substantially higher density of the martian surface atmosphere at night may reduce power requirements a significant amount. The colder temperature may also reduce the cost and mass of heat transfer substantially. A study is needed that scales the potential advantages of smaller-scale plants with limited available power.
12.0 ACKNOWLEDGMENTS

The authors wish to thank the NASA Institute for Advanced Concepts and its organizers for supporting this work. Their insight into the benefit of incorporating new ideas into NASA’s exploration programs encourages the incorporation of independent thinking into the science and engineering of space research.

Thanks are also due to the many whom have encouraged our efforts, and helped us overcome substantial skepticism and even ridicule. Among these supporters are Mr. Hartwell Long of the Jet Propulsion Laboratory who suggested the proposal to NASA, Dr. Jose Chirivella of Ergo-Tech Systems Co. who helped us understand several engineering aspects of the atmospheric environment, and Dr. Donald Rapp of the Jet Propulsion Laboratory who supplied us with comprehensive introductory material on ISPP.

13.0 CONTACT INFORMATION

Christopher England, Ph.D., P.E.
Engineering Research Group
P.O. Box 295
Sierra Madre, CA  91025-0295
Tel:  626.355.1209  Fax: 626.355.1209
Email: cengland@earthlink.net

J. Dana Hrubes, P. E.
Raytheon Polar Services, Inc.
Amundsen-Scott South Pole Station
Antarctica
Email: hrubesda@spole.gov
Email: jdh@fortress.com (after 11-15-01)