METHANE AND CARBON DIOXIDE HYDRATES ON MARS: ARE THERE SUFFICIENT NATURAL RESOURCES ON MARS TO SUSTAIN HUMAN HABITATION?

Robert E. Pellenbarg, MDS Research, Suite 461, 1120 Connecticut Ave. NW, Washington DC 20036, <rep15@hotmail.com>; **Michael D. Max**, also at MDS Research, <xeres@erols.com>; **Stephen M. Clifford**, Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058, <clifford@lpi.nasa.gov>.

Introduction: The crust of Mars has been stable for enough time for methane formed by magmatic processes and/or as a byproduct of anaerobic deep biosphere activity to have risen toward the planet's surface. This methane would have been captured and stored as methane hydrate [1,2], which concentrates methane and water. Both CH_4 and carbon dioxide (CO_2, the predominant gas in the Martian atmosphere) are stable as gases on the Martian surface but could collect within the hydrate stability field in surface-parallel zones that reach close to the Martian surface.

In order for humankind to establish itself on Mars, colonies should be self-sustaining there as soon as possible. With hydrates of both carbon dioxide (CO_2,) and methane (CH_4), Mars would contain the basic elements for human habitation: fuel, potable water, and industrial feedstock in a near-surface situation suitable for controlled extraction by drilling. The presence of methane hydrate may prove to be the key to human habitation of Mars.

Instead of transporting to Mars the return-journey-fuel and all the items needed for human habitation of the planet, optimized standard industrial chemical plants can be designed for operation on Mars in order to manufacture a variety of plastic objects, such as shelter, ecohabitats, vehicles and other apparatus, in addition to synthetic liquid high-energy-density fuels.

The Formation of Hydrate Concentrates Gas and Water: A mechanism for the long-term concentration of methane exists on Mars as it does on Earth [3]. Methane produced in the subsurface migrates buoyantly upward in porosity until it reaches the Hydrate Stability Zone (HSZ), which is a region in which methane hydrate is stable. One m^3 of methane hydrate contains about 160 m^3 methane (Earth STP) and some 0.9 m^3 of fresh water. On Mars, the particular pressure-temperature and thermodynamic equilibrium associated with the cold Martian surface is favorable for the stabilization of a substantial HSZ [4].

Mining the carbon and oxygen compounds on Mars will follow techniques being developed for recovering gas and water from hydrate on Earth, where the newly discovered methane hydrate resources in permafrost and oceanic environments constitute an emerging major energy resource [1]. Techniques and equipment now being developed for commercial recovery of methane from terrestrial permafrost hydrate can be applied on Mars, especially for anticipated shallow Martian hydrate deposits.

Chemical Opportunities and Constraints on Mars: CO_2 is the principal Martian atmospheric constituent, albeit occurring at very low concentrations. Thus, Mars possesses fixed, oxidized, carbon. If, as seems increasingly likely, the Martian crust contains methane trapped as hydrate, the planet would thus also possesses fixed, reduced carbon. Importantly, CO_2 and CH_4 hydrates concentrate fixed carbon and water (H_2O) at the same location.

Consider reaction (1) below, which uses the constituents of methane hydrate as starting materials:

$$3CH_4 + 3H_2O \text{ --------->} \ 2CO + CO_2 + 9H_2 \quad (1)$$

(1) is desirable because it converts reduced carbon (CH_4) to oxidized carbon ([especially]CO and CO_2); oxidized carbon is a necessity for further organic chemical manipulations. However, the enthalpy of the system (+80 kcal) does not favor the reaction as written. Now, the reaction could be catalyzed, or run in a reactor permeable to hydrogen so that the reaction is driven to the right, or the reaction would be run under high temperature and pressure, requiring power. Alternatively, the water from methane hydrate could be electrolyzed, again requiring power, as in (2):

$$2H_2O \text{ ----------->} \ 2H_2 + O_2 \quad (2)$$

The resultant oxygen (O_2) could be reacted with the methane from the hydrate, as in (3):

$$2CH_4 + 3O_2 \text{ ---------->} \ 2CO + 4H_2O \quad (3)$$

(3) is energetically favorable, IF oxygen is available. The net desirable result of reactions (1) and (3) is to produce carbon monoxide. Keep in mind that carbon dioxide could be available on Mars directly from CO_2 hydrate, but it is desirable to have the chemical technology to convert/utilize CH_4, even if abundant CO_2 were available. Thus, it may be useful, depending on actual feedstock gases, to consider affecting the following reaction (4):

$$CH_4 + CO_2 \text{ ---------->} \ 2CO + 2H_2 \quad (4)$$

The net desired result is to obtain CO and H_2 as pure as possible, so that the Fischer Topisch Process (FTP) can be brought to bear. The FTP is a reaction of hydrogen with carbon monoxide, generically as follows (5, intentionally unbalanced):

H_2 + CO -----> $CH_3(CH_2)_nCH_3$ + $CH_3(CH_2)_nOH$ + H_2O (5)

carried out with an appropriate catalyst (e.g. Co, Ni, Fe, or Ru), and under suitable conditions of temperature and pressure. With proper selection of these three parameters, the FTP will yield liquid hydrocarbon fuels, oils, waxes, and a variety of organic chemicals.

For the purposes of colonization of Mars, access to a synthetic structural material, such as a plastic, will be critical. Consider the case of synthesizing polystyrene as a structural plastic. The "water-gas" reaction (6) is useful in this context:

C + H_2O ----------> H_2 + CO (6)

Note that hydrogen and carbon monoxide (obtained as outlined earlier) can be reacted in the reverse of (6) to give elemental carbon. Carbon will react with calcium oxide in an electric furnace to give calcium carbide (7):

3C + CaO ----------> CaC_2 + (CO + CO_2) (7)

and calcium carbide will react with water to give acetylene (8):

CaC_2 + H_20 ----------> C_2H_2 + CaO (8)

Acetylene can be condensed to benzene (9):

$3C_2H_2$ --------> C_6H_6 (9)

which will react with ethylene (from dehydration of ethyl alcohol [10] from the FTP) to give styrene (11). Styrene can be polymerized to a rigid plastic (12):

CH_3COH -------> C_2H_4 +H_2O (10)

C6H6 + C_2H_4 ---> $C_2H_3C_6H_5$ [Styr] + H_2 (11)

n(Styr) ----------> $(Styr)_n$ (12)

These few examples demonstrate the concept of creating useful materials for application on Mars. Beginning with very simple, essentially inorganic forms of carbon and water, it is possible to engineer a variety of useful organic-based materials that can be fashioned as required to support human habitation of Mars.

If abundant methane hydrate occurs in suitable proximity to the planet's surface, then synthetic FTP fuels can be manufactured. These fuels could be used to drive conventional turbine or reciprocating engines. Stirling engines, however, may provide a best solution for Mars because they operate under very low stress, and could be constructed from indigenous materials (e. g. plastic and ceramic materials, as opposed to combustion engines that require high technology metallurgy (assuming the availability of metallic ores). Alternatively, hydrogen stripped from the methane may be used in fuel cells to provide electricity.

Discussion: We have confined discussion of organic chemical engineering to producing useful organic compounds containing only carbon, hydrogen, and oxygen. However, there are many other organic materials which incorporate such atoms as Cl, S, P, or N, for instance, which would allow for very sophisticated materials to be manufactured. Martian colonists may wish to engineer polyvinyl chloride (PVC) as a structural material. For PVC, the colonists would need a source of chlorine, which is produced by the electrolysis of salt (NaCl). Are there salt deposits on Mars? Probably! If there was standing water on Mars there may well be salt deposits related to ocean evaporation. Such deposits could also contain nitrate (e.g., $NaNO_3$) or phosphate (e.g., Na_3PO_4), that would provide readily usable industrial feedstock, as well as fertilizer for growing plant biomass (giving food and cellulose, e.g. wood).

In the longer term, use of methane as a fuel and in other chemical processes will increase atmospheric CO_2 and will augment the greenhouse effect over time even without a planned atmospheric remediation plan. Increasing atmospheric density and enhancing the greenhouse effect of the atmosphere could render Mars more amenable to habitation in the longer term. Both methane and carbon dioxide are strong greenhouse gases, and if released in sufficient quantities, could lead to marked warming on the planet. Indeed, spills of methane into the Martian atmosphere are therefore, in theory, to be encouraged.

If methane and carbon dioxide hydrate deposits can be located on Mars, their location may provide the determining factor in selecting habitation and colonization sites. Specifically, gases and water from these hydrates will provide the basic elements necessary for human habitation: water, power, food, shelter and, most, if not all, of the industrial feed stocks required for sustained human habitation on Mars. Locally derived materials used in the inhabited installations will minimize the transport requirements of bringing such materials from Earth. For true colonization to be contemplated, the inhabitants of Mars must be as self-sustaining as possible.

References

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