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ARE THERE SUFFICIENT NATURAL RESOURCES ON MARS TO SUSTAIN HUMAN HABITATION? METHANE AND CARBON DIOXIDE HYDRATES AS RAW MATERIALS TO SUPPORT COLONIZATION

Robert E. Pellenbarg* , Michael D. Max, and Stephen M. Clifford*****

ABSTRACT

There is a good possibility that long-term production of deep biosphere methane (CH_4) has occurred on Mars. Resultant methane would tend to rise buoyantly toward the Martian surface. This methane would have been captured over a long period of time and will now be stored in methane hydrate, which has the potential to concentrate methane and water. Both CH_4 and carbon dioxide (CO_2, a predominant gas in the Martian atmosphere) are stable as gases on the Martian surface but probably lie within the hydrate stability field as vast resource deposits in surface-parallel zones that reach close to the Martian surface.

In order for humankind to establish itself on Mars, colonies should become self-sustaining there as soon as possible. With hydrates of both CO_2, (oxidized carbon, C, at +4 oxidation state) and CH_4, (reduced C at -4 oxidation state), Mars would contain the basic elements for human habitation: fuel, potable water, and industrial feedstock in a near-surface situation suitable for controlled extraction. With the addition of nuclear- or solar-electric energy, the synthetic organic chemistry necessary to support human habitation on Mars is an exercise in miniaturized, innovative chemical engineering. Instead of transporting fuel for the return journey and all the items needed for human habitation of Mars, optimized standard industrial chemical plants would be designed for operation on Mars in order to manufacture a variety of plastic objects, such as shelter, habitats, vehicles and other apparatus, in addition to synthetic liquid high energy-density fuels.

Thus, identification and quantification of methane hydrate and carbon dioxide hydrate, or proof of their absence, must be regarded as one of the emerging questions about Mars which must be answered in order to allow for effective planning and preparation for human travel to Mars. The

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* Chemistry Division, Naval Research Laboratory, Code 6101, Washington DC 20375.
** MDS Research, Suite 302, 1211 Connecticut Ave. NW, Washington DC 20036
***Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058

actual presence of these hydrates may prove to be the key to colonization of Mars.

INTRODUCTION

The National Aeronautics and Space Administration (NASA) of the United States, along with other national and international space agencies, is planning for planetary exploration. Although this exploration is making use of information-gathering robots at present, planning for human travel to the planets is under way. Mars should be the first planet selected for direct human investigation because of its relative nearness, the possibility that it once had, and could still have, life, and because surface conditions are within a range that present technology can provide for sustainable human habitats, at least for short periods. Any attribute of Mars that could be exploited to provide for longer-term human habitation and possible planetary terraforming in the future, however, is very important to consider at this time. Better knowledge about the natural resource base of Mars is fundamental to organizing both visits and colonization, much the same as any of the historical exploration that has been carried out on Earth. Where natural resources are varied and abundant, colonization has a greater chance for success. If most supplies and materials must be transported one-way to Mars, the planet may only be an outpost rather than a colony. To become a true, viable colony, human habitation on Mars must become self-sustaining as rapidly as possible. Indeed, if long-term habitation on Mars is to be contemplated, the atmosphere and surface of Mars must be remediated and the climate made milder.

Present conditions on Mars would seem to support a Stone Age existence. That is, the raw materials on the surface of the planet would appear to allow dry masonry construction, but little else. Materials science must be brought to bear to engineer materials that will allow implementation of the technology to permit colonists to prevail. Although there may not be a wide variety of materials on Mars, what is there may provide a sufficient, but small, list of resources, present in staggering quantities. Relatively basic chemical engineering can be used to convert these natural resources into the materials to assure colonial success; if the colonists are bold and clever, and the course to human habitation of Mars has been properly mapped and implemented by Earth-based agencies, then there is a high probability for success for permanent human habitation of Mars.

METHANE ON MARS AND ITS POTENTIAL SIGNIFICANCE

If the early evolution of the Martian surface followed that of Earth, then abundant methanogenic bacteria were likely present in the aqueous environment of the young Martian surface. During the transition to the present cryogenic Martian crust, this life would probably have adapted to deep biosphere form, along with existing deep biosphere, similar to that we now recognize in the warm, deep sediments and rocks of Earth. Deep microbial biosphere on Mars would almost certainly also have been methanogenic, as it is on Earth.

Long-term production of deep biosphere methane, if it in fact occurred, has enormous implications for the potential of human travel to Mars and occupation of the planet. If no significant deep methanogenic biosphere ever produced large amounts of methane, then fuel and other basic requirements for human habitation would have to be imported. If methane is available, however, the entire situation regarding the likelihood of human habitation of Mars becomes radically more favorable.

A mechanism for the long-term concentration exists on Mars as it does on Earth (Max and Lowrie, 1996). Biogenic methane produced as a waste product tends to migrate buoyantly upward in pore water rock porosity until it reaches the Hydrate Stability Zone (HSZ), which is a temperature/pressure region in which methane hydrate is stable. One m^3 of methane hydrate contains about 164 m^3 methane (Earth STP) and 0.87 m^3 of fresh water. On Mars, the particular pressure-temperature and thermodynamic equilibrium associated with the cold Martian surface is favorable for the formation of a substantial HSZ (Max and Clifford, 2000).

Methane hydrate and water-ice form a mixed cryogenic zone in which water-ice is stable from the surface to about 0 °C at depth and hydrate is stable from some depth below the surface (depending on average surface temperature, total pressure, and geothermal gradient) to some depth below the base of the water-ice stability zone. Under current ambient conditions on Mars, methane hydrate is stable close to, but not at, the surface. Since the dominant constituent of the Martian crust appears to be basalt (or basalt-derived weathering products), the difference in lithostatic pressure at any depth between Mars and the Earth simply scales in proportion to the ratio of gravitational accelerations for the two planets (i.e., ~0.38 g). At the 200 ^oK average surface temperature of Mars, hydrate is not stable at less than about 140 kPa (data in Sloan, 1997), which corresponds to a depth of ~15 m (assuming an ice-saturated permafrost density of $2.5x10^3$ kg/ m^3). Given a reasonable estimate of the thermal properties of the crust, the base of the Martian HSZ should then extend to depths that lie from several hundred meters to as much as a kilometer below the surface of Mars. Thus, the total thickness of the HSZ on Mars is likely to vary from ~3 km at the equator, to ~8 km at the poles (Max and Clifford, JGR-Planets, in press).

If concentrated methane in the form of methane hydrate can be found in the near subsurface of Mars, then all the elements necessary for the human habitation of Mars exist there. Altering the pressure-temperature conditions of hydrate will release both abundant methane (held in a compressed form) and water simultaneously. Additional water from occluded permafrost ice will supplement the water produced from dissociation of methane hydrate, but may not be necessary.

Water, of course, is the most basic requirement for human habitation of Mars and it is likely that water (as ice) is present in the Martian cryosphere. Water will support a human-supportive biosystem for both plants and animals, under controlled conditions. But other elements are required for a self-sustaining of human habitation. Oxygen and hydrogen (fuel) can be produced by electrolysis from the water using electricity produced either from small nuclear reactors and/or solar power. Combustion of methane, however, produces both water and CO_2 either in fuel cells or by high temperature chemical reactions. This CO_2, or gas from CO_2 hydrate, would amend the atmosphere in enclosed biomes to be constructed on Mars.

In addition to its utility as a fuel, however, methane is a basic hydrocarbon building block and is a primary feedstock for the manufacture of plastics and other synthetics (including higher energy-density liquid fuels) from which virtually every object necessary for human habitation of Mars can be manufactured. Existing chemical engineering technology can be miniaturized, optimized for Martian conditions, and used to fabricate virtually everything necessary in-situ, on Mars. This fabrication potential would be the final element required for the permanent human habitation of Mars. Fuels for returning to Earth and exploring further would be produced on Mars itself. The transport requirements to support human habitation on Mars would be reduced by the ability to produce many, if not most, of the physical objects required on Mars, from Martian materials. The ability to produce pressurized habitats, clothing, vehicles, etc. with only the import of a relatively small amount of specialized equipment or materials (e.g. chemical catalysts) from Earth would greatly change the support economics and enhance the likelihood of successful long-term occupation of Mars.

The possible existence of methane hydrate in the shallow subsurface of Mars offers extraordinary potential to support and sustain the human habitation of Mars. Thus, identification and quantification of methane hydrate, or proof of its absence, must be regarded as one of the key questions about Mars that must be answered in order to allow for effective planning and preparation for human travel to Mars. Indeed, the question of availability of methane hydrate on Mars may prove to be the key to human occupation of Mars.

'MINING' HYDRATE

Mining carbon and oxygen compounds on Mars will follow techniques being developed for recovering gas and water from hydrate on Earth where the newly recognized methane hydrate resources in permafrost and oceanic environments constitute an emerging major energy resource (Max, 2000).

From the outset, recovery of methane or carbon dioxide from hydrate will require application of secondary recovery techniques because the hydrate is present in the form of solid permafrost hydrate. Methane recovery from hydrate will involve forced dissociation. In addition, knowledge about the dispostion of hydrate in the Martian cryosphere is required before recovery scenarios can be envisaged; comparison with permafrost hydrate on Earth provides only a first order estimation of hydrate disposition on Mars because of the profound differences in geological and biological attributes. On Earth, hydrate is most stable in the upper part of the HSZ and least stable near the HSZ base and recovery scenarios usually target the base of the HSZ (Max and Chandra, 1998; Max and Dillon, 1999). On Mars, where the base of the HSZ will likely occur below the water-ice cryosphere (Max and Clifford, 2000), this may be found at a considerable depth. Because drilling capability on Mars will be limited initially, shallower hydrate deposits would provide the first drilling and recovery targets.

Methane can be derived from hydrate by melting the hydrate. This melting can be accomplished in three major ways. Firstly, heat in the form of hot water or steam can be applied directly to the buried hydrate through drill holes. This technology is well known to the hydrocarbon industry and is often used with heavy oils. Secondly, hydrate can be decomposed, by altering the position of the hydrate stability phase boundary via introduction of inhibitor fluids containing suitable dissolved ionic material, which functions similarly to antifreeze and lowers the melting temperature. Thirdly, dissociation can be induced where hydrate is present close to its pressure-temperature limits of stability where free gas is in contact with the hydrate. Lowering the pressure in the gas deposit will cause hydrate in contact with the gas to dissociate, drawing heat from the environment. It is likely that commercial recovery of methane from hydrate on Earth will use a combination of the three methods, optimized for the characteristics of individual deposits, and lessons learned here can be applied on Mars. The closer the pressure-temperature position of the hydrate body is to the stabile phase boundary, the less thermal energy needs to be introduced or the less chemical inhibitor is required to cause dissociation.

Both hydrate and associated gas deposits of methane and carbon dioxide may prove to be recoverable resources on Mars. Permafrost hydrate deposits will be capable of holding considerable gas pressure because of the strength of the bounding geological rocks and regolith. Thus methane hydrate deposits on Mars are likely to be similar to conventional hydrocarbon traps on Earth, for which both natural occurrence and methods for recovery are well understood. Recovery should be possible using modified conventional drilling and recovery technology.

Little is now known about the subsurface character of the Martian geology. Virtually nothing is known about the likelihood or location of structural or stratigraphic traps, or their Martian equivalents. The sedimentary and lithic material from which the upper strata of Mars is composed is also poorly characterized. Nonetheless, the cryosphere on Earth exhibits many features that could be important to providing pathways for gas accumulation and migration, which are vital to recovery of significant volumes of gas on Earth, and provide further insight to the parallel situation on Mars. In addition to primary porosity extensive secondary porosity in the form of faults, fractures, and 'frost heaving' volume changes owing to ice and hydrate formation may produce pathways for fluid and gas migration in rocks that are otherwise too tight to allow significant internal flow. Extensive faulting has been observed in gas hydrate bearing strata in many areas, and the faults show evidence of fluid flow (Dillon et al., 1998). Where gas will not spontaneously flow, mechanical fracturing (fracking, a standard procedure used now on Earth) is also possible on Marsh, but this approach would introduce additional operational problems and requirements.

CHEMICAL OPPORTUNITIES AND CONSTRAINTS ON MARS

There is no question that the Martian atmosphere contains CO_2, (C, at +4 oxidation state) albeit at very low concentrations. It is highly likely that CO_2 hydrate also occurs on the planet. Thus, Mars possesses fixed, but oxidized, carbon. If, as seems increasingly probable, the Martian crust contains CH_4 (C at -4 oxidation state) trapped as hydrate, the planet would thus also posses fixed, reduced carbon. In addition, CO_2 and CH_4 hydrate concentrate fixed carbon and water (H_2O)

at the same place. These chemically fixed carbon species are important in that they are gases under current surface conditions on Mars.

Specifically, gases are readily moved, from source to use site, from well to chemical processing plant. With both oxidized and reduced species of carbon-bearing gases available on Mars, and with the addition of nuclear- or solar-electric power energy, the synthetic organic chemistry is merely an exercise in chemical engineering. The carbon-bearing source gases are available, and the chemical engineering technology to transform the carbon gases to useful end products currently exists. Needed only is the design, deployment and operation of fairly routine chemical processing plants on the Martian surface, factories which will yield a cornucopia of on-site organic matter of crucial value to the Martian colonists.

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

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

(1) is desirable because it converts reduced carbon (CH_4) to oxidized carbon (CO and CO_2); oxidized carbon is a necessity for further organic chemical manipulations. However, the enthalpy of the system does not favor the reaction a written. Indeed, the reaction would absorb some 80 kcal of energy to proceed, without proper manipulation. Now, the reaction could be catalyzed, and/or run in a reactor permeable to hydrogen so that the reaction is driven to the right. More than likely, 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):

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

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

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

(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 the available CH_4, even if abundant CO_2 were present on Mars. Thus, it may be useful, depending on actual feedstock gases, to consider encouraging the following reaction (4):

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

The net desired result is to obtain CO and $H_{2\,\text{as}}$ pure as possible, so that the Fischer-Tropsch Process (FTP) can be brought to bear. The FTP is a reaction of hydrogen with carbon monoxide, generically as follows (5, intentionally unbalanced):

$$H_2 + CO \text{ ----->} \; CH_3(CH_2)_nCH_3 + CH_3(CH_2)_nOH + H_2O \quad (5)$$

carried out with an appropriate catalyst, and under suitable conditions of temperature and pressure. With proper selection of these three parameters, the FTP will yield liquid hydrocarbon fuels, oils, waxes, or a variety of other organic chemicals. Catalysis based on cobalt, nickel, ruthenium and iron is widely and effectively employed.

In summary, the presumed abundant methane, carbon dioxide, and water, from hydrates on Mars, can be chemically converted to carbon monoxide (CO) and hydrogen (H_2). These gases can be easily converted to higher molecular weight organic matter using the Fischer-Tropsch Process. Thus, we have a basic process that would yield motor fuels, for example. Utilization of these on Mars will be discussed later.

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

$$C + H_2O \text{ ----------> } H_2 + CO \qquad (6)$$

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):

$$3C + CaO \text{ ----------> } CaC_2 + (CO + CO_2) \qquad (7)$$

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

$$CaC_2 + H_20 \text{ ----------> } C_2H_2 + CaO \qquad (8)$$

and acetylene and be condensed to benzene (9):

$$3C_2H_2 \text{ ---------- } C_6H_6 \qquad (9)$$

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):

$$CH_3COH \text{ -------> } C_2H_4 + H_2O \qquad (10)$$
$$C_6H_6 + C_2H_4 \text{ ----------> } C_2H_3C_6H_5 \text{ [Styr]} + H_2 \qquad (11)$$
$$n(\text{Styr}) \text{ ----------> } (\text{Styr})_n \text{ [polystyrene plastic]} \qquad (12)$$

These few examples demonstrate the concept of creating useful materials for application on Mars. Beginning with very simple, essentially inorganic forms of carbon, it is possible to engineer a variety of useful organic-based materials that can be fashioned as required to support human habitation of Mars. Please refer to any organic chemistry text book for more detail, and other potential synthetic pathways, on the discussion immediately above.

ENERGY SOURCES ON MARS

There must be an energy source to support the chemical engineering discussed above and to provide power in general. Synthetic chemistry, even on the restricted industrial scale required by the initial Martian colonies, will require power for heating, pressurizing, and irradiating chemical reaction vessels, for example. Dependable high-energy-density power sources, at first, can be provided either by a nuclear or solar installation. Once a colonial industrial capability is available, distributed power systems (e.g. small combustion engines or fuel cells based on engineered fuels and oxidizers) could become widely utilized.

Although nuclear power is attractive from the standpoint of power density and dependability, the reactor and its nuclear fuel would have to be transported from Earth. However, the reactor need not be brought to the planet's surface. It could be placed in a stable orbit around Mars, or emplaced on either Deimos or Phobos, from where power could be beamed to the surface of Mars via microwave radiation. However, nuclear power has several drawbacks. There are three prime concerns that must be dealt with. Firstly, is the cost of transporting a relatively heavy reactor from Earth-vicinity to Mars. Secondly is the possibility of a nuclear accident in the Earth's atmosphere or in the vicinity of Mars. Thirdly is the problem of what to do with the spent nuclear fuel, an issue that has yet to be dealt with satisfactorily on Earth. If the colonization of Mars is operated similar to research activities in Antarctica (a possible precedent), then nuclear power may be prohibited on the planet.

If concerns about nuclear power are overwhelming, solar energy is likely to be the initial power source for a Martian colony. A key factor in this energy equation is the fact that Mars is roughly twice as far from the sun as is Earth, and thus receives roughly one-quarter the energy per unit area as does Earth. Solar collectors on Mars would thus need to be some four times as large as they would need to be on Earth for the same energy output. This situation may at first appear to be a significant and costly transportation problem if one were contemplating bringing bulky and heavy solar panels to Mars. New technology lightweight panels may solve the weight concern, but not necessary the bulk problems of transport. However, an alternative approach would be to use light-weight plastic-film-based solar radiation collectors to boil water to give high pressure steam fed to electrical generators.

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 (external combustion) engines, however, may provide an optimal 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 internal combustion engines that require high-technology metallurgy (assuming the availability of metallic ores). On the other hand, hydrogen stripped from the methane may be used in fuel cells to provide electricity.

DISCUSSION

Here, then, is an emerging challenge for the chemical industry. In order for successful colonization of Mars to occur, potential colonies should be self-sustaining there as soon as possible. Instead of transporting all the items needed for human habitation of Mars, standard industrial chemical plant must be designed to be carried to Mars and optimized for operation on Mars itself. This apparatus would have to be relatively small and energy-efficient, as well as being able to manufacture a variety of plastics and objects, some of them complex in form. Development of this capability, involving development of nanotechnology, MEMS, and other new processes is now possible. The chemical industry should become part of the planning and development process for space research, human space travel, and extraterrestrial colonization ventures. Indeed, there has recently been reported a quantum leap in this direction. The Virtual Engineered Composites (VEC) process is discussed at length in a recent TIME magazine article. The VEC is likened to a "3 - D fax machine" in which moldable plastics are formed on-site using new technology controlled from a remote location via an electronic link. In essence, the design goes in one end of the electronic line, and a finished product pops out of the fabrication unit on the other end! One needs only supply semi-finished plastics (as discussed above) to the fabrication unit; software and the VEC unit do the rest. (Gibney, 2000)

Fuel is vital for both energy and byproduct production on the Martian surface and for fueling the return trip to Earth. If energy-dense fuel can be produced on Mars, then Mars will be a true stepping stone to exploration of the entire Solar System. Artificially produced FTP has been shown to be motor fuels. These hydrocarbon fuels, or hydrogen, which would have to be liquefied for use in a rocket vehicle, could be combusted using gaseous oxygen, from the electrolysis of water, as the oxidizer. The benefit of FTP-liquids over hydrogen is that they are naturally liquid under a wide range of pressure-temperature conditions and does not need special cryogenic handling or storage facilities, as does hydrogen.

In this paper, discussion of organic chemical engineering has been confined to producing useful organic compounds containing only carbon, hydrogen, and oxygen. There are myriad other organic materials which incorporate such atoms as chlorine, sulfur, phosphorus or nitrogen, 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 easily produced by the electrolysis of salt (NaCl). Are there salt deposits on Mars? 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., K_3PO_4), which would provide readily usable industrial feedstock. And, of course, both nitrate and phosphate are required as fertilizer for any attempts to grow plant biomass on Mars.

In the longer term, use of methane as a fuel and in other chemical processes will produce CO_2 gas. This will increase atmospheric CO_2 and will aid the greenhouse effect over time even without a planned atmospheric remediation plan, although initially there will be little impact. Increasing atmospheric density and enhancing the greenhouse effect of the atmosphere should 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. Of course, it is highly probable that enough CO_2 and other greenhouse gases would be released into enclosed space (e.g. large greenhouses) to allow the cultivation of biomass on Mars without remediating the atmosphere as a whole, at least initially. If the correct woody plants were to be cultivated, colonists would have access to wood, a superb engineering material. Further, the wood would probably be cultivated from essentially sterile cuttings or seeds, so that the importation of serious plant diseases, rot fungus, or termites, which would compromise the wood, could be precluded. Whereas it seems potentially useful to produce synthetic carbon-based chemicals and materials for short term objectives, biomass would supply a cellulose-basedbyproduct for the long-term. If methane hydrate concentrations can be located on Mars, their location may provide the determining factor in selecting habitation and colonization sites there because they will contain the basic elements necessary for human habitation: water, power, food, shelter. In addition, any locally derived materials used in the inhabited installations will not accrue the transport costs of bringing such materials from Earth. For true colonization to be contemplated, the inhabitants of Mars must be as self-sustaining as possible.

Mars beckons constantly. Since even before ancient astronomers noted a “red wanderer” among the fixed stars, Mars has beckoned. As a race, we have always been called to the planet, at first only visually, but now as a defining challenge. Now, it is time, and increasingly possible, to seize the elevating opportunity offered by the Red Planet. Technology in hand will permit us to travel to Mars, to establish beachheads, to prevail. The authors have given a brief sketch of some available technology, to be applied to Martian natural resources, which will undergird colonial success after the pioneering explorers and soon-to-follow colonists create footprints, and more, on Mars. Needed only is the will to fulfill our interplanetary destiny.

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