Considerations for Capturing and Converting Martian CO_2 with Room Temperature Ionic Liquid-Based ISRU Systems

Michael A. Lotto[1], Jordan B. Holquist[2], David M. Klaus[3], and James A. Nabity[4]
University of Colorado, Boulder, CO 80309, United States

Room temperature ionic liquids (RTILs) are an emerging option for capturing carbon dioxide (CO_2) at ambient pressures on the surface of Mars due to their negligible vapor pressures and affinity for CO_2. Some RTILs also promote the efficient and selective electrochemical reduction of CO_2 to useful products, such as carbon monoxide (CO) or methane (CH_4). An in-situ resource utilization (ISRU) system may be able to utilize these properties to both capture CO_2 from the Mars atmosphere and facilitate the subsequent reduction process. Several RTIL-based ISRU architectures are introduced and characterized. A discussion regarding the operational environment is also included.

Nomenclature

Ar	=	argon
CH_4	=	methane
CO	=	carbon monoxide
CO_2	=	carbon dioxide
g	=	gram
H_2O	=	water
ISRU	=	in-situ resource utilization
K	=	kelvin
kg	=	kilogram
MOXIE	=	Mars Oxygen ISRU Experiment
N_2	=	nitrogen
O_2	=	oxygen
Pa	=	pascal
RTIL	=	room temperature ionic liquid
SOE	=	solid oxide electrolysis
SILM	=	supported ionic liquid membrane

I. Introduction

A crew of four astronauts will require 6,978 kilogram (kg) of methane (CH_4), 24,634 kg of oxygen (O_2), and 24,179 kg of water (H_2O) for Mars surface operations over a 500 day mission and the subsequent launch of an ascent vehicle needed to begin the journey back to Earth.[1] Assuming a gear ratio of 11.3 kg in Low Earth Orbit for every kg delivered to the surface of Mars,[2] a single Block II Space Launch System will be able to deliver ~11,500 kg to the planet. As such, nearly five Block II Space Launch Systems will be needed to deliver just these three consumables from Earth. In-situ resource utilization (ISRU) technologies, instead, can be employed to generate them from local resources on the surface of Mars.[2] The atmosphere is comprised of 95.7% carbon dioxide (CO_2), 2.03%

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[1] Ph.D. Candidate, Aerospace Engineering Sciences, University of Colorado Boulder, Engineering Center, Room ECAE 171, Boulder, CO, 80309; michael.lotto@colorado.edu, (425)802-3073

[2] Ph.D. Candidate, Aerospace Engineering Sciences, University of Colorado Boulder, Engineering Center, Room ECAE 171, Boulder, CO, 80309; jordan.holquist@colorado.edu, (217)341-8015

[3] Professor, Aerospace Engineering Sciences, University of Colorado Boulder, Engineering Center, Room ECAE 107, Boulder, CO, 80309; klaus@colorado.edu; (303)492-3525

[4] Associate Professor, Aerospace Engineering Sciences, University of Colorado Boulder, Engineering Center, Room ECAE 105, Boulder, CO, 80309; james.nabity@colorado.edu; (303)492-3243

nitrogen (N_2), 2.07% argon (Ar), and additional minor constituents at an average pressure of 610 pascals (Pa).[3,4] The surface, meanwhile, contains water in various forms, including hydrated minerals and ice.[5-7] Depending on the technologies that are implemented, these resources can be converted into consumables, such as oxygen, hydrogen, and methane, needed for life support and propulsion purposes.[2] Nitrogen and argon can also be separated from the atmosphere for use as make-up buffer gas in a habitat.

CO_2 capture can be achieved with various room temperature ionic liquids (RTILs) that exhibit a variety of advantageous properties, including preferential absorption of CO_2 at low partial pressures, relatively high uptake capacities and rates, and the ability to be regenerated for additional capture cycles.[8,9] RTIL-based systems are already being developed for spacecraft cabin and extravehicular activity applications.[9-12] Furthermore, with vapor pressures on the order of 10^{-10} Pascal at room temperatures,[13] they are also well-suited for CO_2 capture at the surface of Mars ($\sim$610 Pa[4]) since they will not evaporate or volatilize when exposed to the open atmosphere. Some even possess a co-catalytic effect with the concurrent conversion of CO_2 into reduced products, such as carbon monoxide (CO) and CH_4,[14,15] with various cathodes, and such reactors can also generate oxygen via water oxidation in the same process vessel.

This paper discusses options for RTIL-based Mars ISRU systems, as well as the resulting architectures for CO_2 capture and processing, while also qualitatively identifying advantages and disadvantages of each configuration. Implications of operating a liquid-based capture stage at the surface of Mars are also addressed.

II. Implications of the Operational Environment on CO_2 Capture and Processing with RTILs

The operational environment of Mars introduces numerous design challenges for incorporating an RTIL-based ISRU system, including particulate contaminants, relatively low temperatures and pressures, and atmospheric contaminants. Particulate contamination brings a potential risk of clogging and unwanted side reactions occurring within the process, so dust should be filtered or otherwise prevented from entering the gas stream prior to CO_2 capture. For context, Phillips III et al. estimated an average of 8.5 dust particles/cm^3 in the atmosphere near the surface on a clear day.[16] The Mars Oxygen ISRU Experiment (MOXIE) to be carried on the Mars 2020 rover has been designed to handle approximately 3 dust particles/cm^3 for a total of 5×10^8 particles or $\sim$0.15 g of material over 25 hours of operation.[17] Since MOXIE is a 1% scale ISRU payload, by extrapolation, a full-scale solid oxide electrolysis (SOE) reactor may have to filter out $\sim$4.8 kg of particles over 330 days of operation.[18] Using the volumetric density from Phillips III et al.,[16] this dust mass loading may be as high as 13.5 kg. Rapp et al. also note that these estimates do not include contributions from saltation of heavy grains, dust devils, or storm activity, so these values may be conservative.[17] Although the exact specifications of an RTIL capture system will be different from MOXIE, these values can serve as order of magnitude estimates during initial development of a dust filtration subsystem.

Local surface temperatures depend on position, season, and time of day, but to provide some examples, the Mars Science Laboratory (latitude 4.5°S) and Viking 2 Lander (latitude 47.9°N) measured temperatures between 180-280 Kelvin (K) and 160-220 K over a Martian year, respectively.[19,20] Although phase diagrams for RTILs can be relatively complex,[21] freezing points are typically greater than 200 K, while melting temperatures can be notably higher (e.g., 50 K higher than the freezing temperature).[22] Therefore, given the typical operating temperatures at the surface of Mars, an RTIL-based ISRU system will require temperature control in order to prevent freezing. The freezing and melting points of RTILs also depend non-linearly on water content,[23,21] so these relationships should be characterized for any aqueous RTIL that is a candidate for ISRU.

The relationship between viscosity and temperature will depend on the selection of the cation and anion, but to provide examples, performance data show the viscosity of 1-butyl-3-methylimidazolium hexafluorophosphate increased from $\sim$50 cP to $\sim$280 cP when its temperature was decreased from 333.15 K to 298.15 K.[24] Similarly, Seo et al. showed that the viscosity of RTILs with the trihexyl(tetradecyl)phosphonium cation and various anions increased from $\sim$100-300 cP to $\sim$1000-4000 cP when their temperatures were decreased from 323.15 K to 283.15 K.[8] As a result, the viscosity of the RTIL must also be accounted for in the design of the supporting thermal control system. The viscosity of some RTILs can also change with CO_2 uptake;[8] this is further complicated by an inverse relationship between viscosity and diffusivity since increases in the former can slow CO_2 uptake rates.[10]

CO_2 uptake also decreases as temperature increases.[25] As an example, Jacquemin et al. reported that CO_2 solubility in 1-butyl-3-methylimidazolium hexafluorophosphate decreased by a factor of about 3 when temperature was increased from 283.15 K to 343.15 K.[26] Meanwhile, Seo et al. showed that small amounts of water (e.g., 4.5 weight percent) improved CO_2 uptake for trihexyl(tetradecyl)phosphonium 2-cyano-pyrrolide, particularly at low partial pressures;[8] however, it should be noted that excess water will reduce the uptake capacity of a solution due to dilution of the RTIL. Lastly, the viscosity of water/RTIL mixtures decreases as water content increases.[27]

The uptake capacity of an RTIL depends on CO_2 partial pressure, particularly at relatively low pressures.[28] RTILs with high solubility at low partial pressures, however, will be inherently sensitive to small changes in partial pressure. As an example, the CO_2 uptake of trihexyl(tetradecyl)phosphonium 2-cyano-pyrrolide with a water content of 4.5 weight percent increases from 1.5 to 6.4 weight percent when CO_2 partial pressure is increased from 600 Pa to 3,300 Pa.[8] However, the uptake capacity of this RTIL is only 7.2 weight percent at a CO_2 partial pressure of 92,000 Pa. In other words, CO_2 uptake is readily enhanced with small increases in partial pressures near zero, but improvements in uptake slow with higher partial pressures. For context, the average atmospheric pressure of Mars is 610 Pa,[4] while the lowest topographic location on the planet has a pressure around 1,155 Pa.[29] In light of this, the uptake capacity of an RTIL on Mars will probably be sensitive to ambient CO_2 partial pressures and enhanced uptake rates may be achieved with small artificial increases in pressure.

Temperature can also play a significant role in the solubility selectivity of an RTIL. For various ionic liquids between 25°C and 70°C, Finotello et al. observed higher selectivities for CO_2 over N_2, CH_4, and H_2 at lower temperatures; however, the slopes of these trends varied with each RTIL.[30] As an example, the CO_2:N_2 selectivity of 1,3-Dimethylimidazolium methyl sulfate decreased from almost 120 to about 10 over 25°C to 70°C, while the CO_2:N_2 selectivity of 1-n-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide decreased from about 30 to 10 over the same temperature range. So, the design of the thermal control system should also account for this relationship. Ultimately, some undesired gases (N_2, Ar, CO, and O_2) will probably be captured as well, so the impact from the cumulative long-term buildup of minor constituents may also need to be assessed for an architecture.

Time is another important parameter in the capture and desorption stages of any RTIL-based loop, and the CO_2 absorption/desorption curve will probably be non-linear.[9,10] In short, the RTIL will probably exhibit higher uptake rates at the start of the CO_2 capture phase, but absorption will then slow as the RTIL nears its saturation point. Conversely, initial desorption rates will probably be high near the saturation point and then slow as the absorbed mass of CO_2 approaches zero. As a result, CO_2 capture, desorption, and processing rates must be well-characterized with respect to time so that they can be reliably controlled.

A single-loop architecture with a room temperature reactor (Figure 4, as discussed later) further confounds the selection of operational conditions since an optimal catholyte will probably be different from a desirable capture liquid. The solution in the room temperature reactor will also likely require elevated water content in order to achieve sufficiently low viscosity and facilitate high ionic conductivity and mass transfer.[27,31,32] Typically, ionic conductivity also increases with temperature,[33] while it is inversely proportional to viscosity.[34] Conversely, the addition of water introduces a concern regarding the hydrolytic stability of the RTIL; hexafluorophosphate and tetrafluoroborate, which are common anions in literature, hydrolyze and generate hydrofluoric acid and other byproducts in the presence of water, thereby introducing a risk to downstream systems.[35-37] So, the hydrolytic stability of candidate RTILs must also be considered if they are to be used in an aqueous solution. Data also suggest that the electrochemical window of the RTIL decreases with elevated temperatures and the addition of water.[38] As an aside, it should also be noted that the presence of water in the cathode compartment can decrease the faradaic efficiency of the reactor due to the competing hydrogen evolution reaction, which typically proceeds at a lower overpotential.[39] Since the electrochemical window and product selectivity are critical parameters for the performance of the electrochemical reactor, they should be well characterized and controlled for a desired water concentration.

Figure 1 summarizes the relationships between relevant independent variables (temperature, CO_2 partial pressure, time, and water content) and the primary dependent properties of a given RTIL that are affected by each of them.
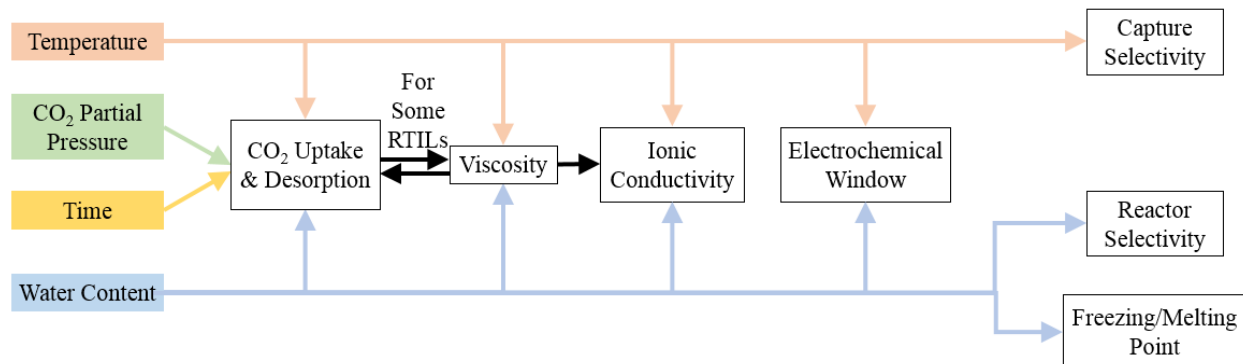

Figure 1. Independent Variables (Temperature, CO_2 Partial Pressure, Time, and Water Content) and Important Dependent RTIL Properties that are affected by them

The viability of a given RTIL will largely be dictated by the dependent properties shown above, so the cation and anion must be carefully selected in order to create an RTIL that possesses desirable traits for CO_2 capture and/or reduction (e.g., high CO_2 uptake/desorption, high CO_2 capture selectivity, low viscosity, high ionic conductivity, wide electrochemical window, sufficiently low freezing/melting points). As an example, the choice of anion strongly controls the resulting CO_2 solubility;[40] this is particularly evident when comparing anions that physically capture CO_2 (relatively low uptakes at low partial pressures) against those that form a chemical complex with it (relatively high uptakes at low partial pressures).[41,8] RTILs can be further tuned by appending functional groups to the cation or anion; Bates et al. demonstrated the tunability of RTILs by incorporating an amine group into the structure of an imidazolium cation, thereby enhancing the CO_2 solubility of the resulting RTIL,[42] while Gurkan et al. showed that amine-functionalized anions can yield even larger CO_2 solubilities.[43] Since then, Seo et al. reported that aprotic heterocylic anions possess high CO_2 solubilities but avoid the significant increases in viscosity seen with amine-functionalized options after CO_2 capture.[8,34] For additional information on functionalization for CO_2 capture, the reader is directed to a comprehensive review by Cui et al.[44] Meanwhile, longer alkyl chains of the cation can also be utilized to improve CO_2 solubility, albeit to a lesser extent than the selection of the anion.[40] Conversely, longer alkyl chains have been shown to increase the viscosity and decrease the electrical conductivity of an RTIL.[45,46] Additional properties that may need to be considered beyond those in Figure 1 include density, pH, surface tension, heat capacity, thermal conductivity, and thermal stability.

Research and development should collect sufficient data to quantify the relevant dependencies shown in Figure 1 for a candidate RTIL in a given ISRU architecture. However, the systematic evaluation of multiple independent variables across numerous RTILs can rapidly become impractical, so pathfinding experiments are critical to down-selecting to initial RTIL candidates and operational envelopes. Computational modeling of the performance of a given cation/anion pair would also aid this selection process.[47,48]

III.   Options for Handling CO_2 with Room Temperature Ionic Liquids on Mars

A. Capture

An RTIL system can be utilized to capture CO_2 from the Martian atmosphere for use as feedstock in a downstream reactor. Since the RTIL will preferentially absorb CO_2 and allow N_2 and Ar to pass through the system, an RTIL-based CO_2 capture stage may also be utilized as a first step in buffer gas generation in order to offset the 130-1,300 kg that will be lost from airlock operations and habitat leakage during a crewed mission.[18,49] As an aside, an entirely different RTIL that preferentially absorbs N_2 or Ar may be employed in a separate capture system. However, there are relatively little data on Ar and N_2 solubility, and existing measurements show that typical solubilities for these gases are low.[50,51] Novel RTILs need to be identified to improve the viability of this latter concept.

There are a variety of plausible contactors that may be used as an interface between the RTIL loop and atmosphere, including those notionally depicted in Figure 2 and further described below.

Flat Plate Contactor

With the Flat Plate Contactor (Fig. 2a), the RTIL flows through a channel that is directly exposed to the Martian atmosphere, and gravity keeps the liquid within the channel. After preferentially absorbing CO_2 from the atmosphere, the CO_2-rich RTIL is pumped to a desorption stage or a reactor. The advantage of this configuration is in the simplicity of the atmosphere/RTIL interface. However, the exposed surface area of the RTIL is low for a given system volume, which is undesirable for a Mars ISRU system where mass and volume must be minimized. Dust contamination also presents a particular concern for this open interface.

Flat Plate Contactor w/ Membrane

A variation of the Flat Plate Contactor employs a CO_2-permeable polymeric membrane to separate the atmosphere and RTIL, as denoted by the dashed line in Fig. 2b. The membrane mitigates particulate contamination of the liquid and ensures that the RTIL remains in the system (i.e., Martian wind cannot blow the RTIL out of the channel) at the expense of slower CO_2 uptake rates.[9] However, the risk of dust clogging individual pores in the membrane, as well as accumulating on top of the membrane, must be considered in the selection of the membrane, particularly if upstream filters are not utilized. Similar designs (e.g., flat sheet contactors) have been utilized in the biotech and biopharmaceutical industries,[52] but unfortunately, this configuration still suffers from a low surface area to volume ratio, which in turn, leads to low capture rates for a given volume. As a result, these Flat Plate Contactor configurations (Fig. 2a. and 2b.) may be the simplest, most reliable options, but at the expense of elevated mass and volume requirements.
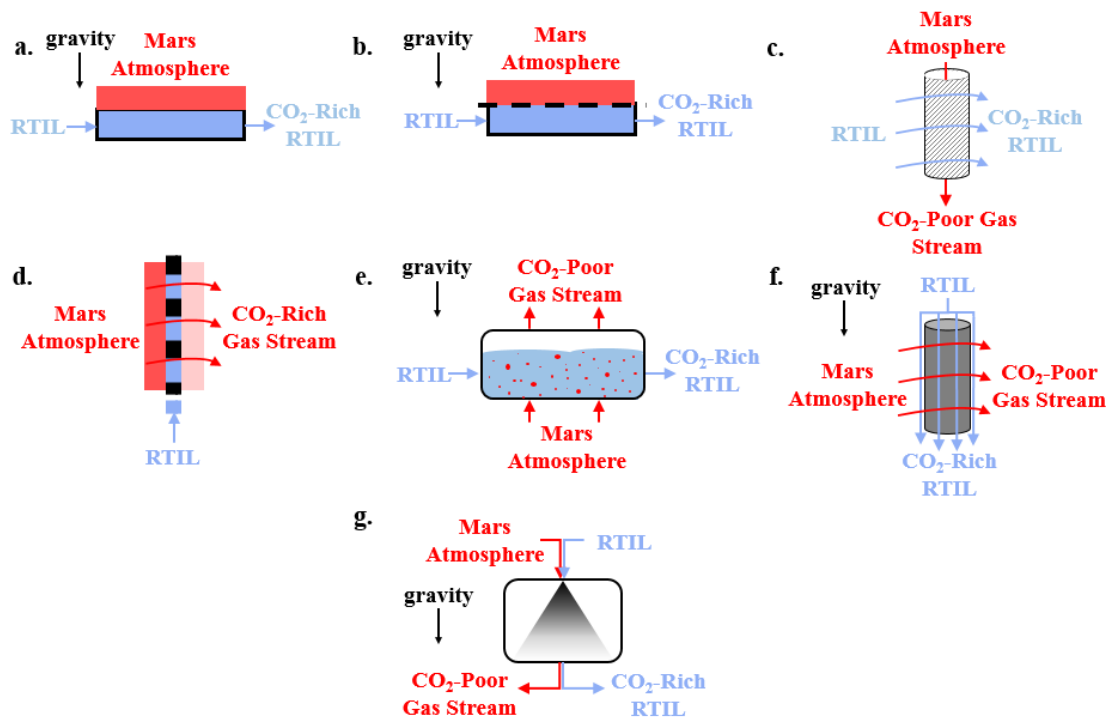
Figure 2. Schematics of RTIL-based CO₂ Capture Designs. (a) Flat Plate Contactor (cross-sectional view). (b) Flat Plate Contactor with Membrane (cross-sectional view). (c) Hollow Fiber Contactor. (d) Supported Ionic Liquid Membrane. (e) Sparge System. (f) Solid Pin Contactor. (g) Aerosol Mist System.

Hollow Fiber Contactor

In the Hollow Fiber Contactor (Fig. 2c), gas is pumped through a manifold of hollow fibers with diameters on the order of a millimeter or less, while the RTIL is pumped across their exterior surfaces.[9] This contactor is the same as the configuration in Fig. 2b; however, this design achieves higher surface area to volume ratios.[11] The fibers can also be oriented in any direction with respect to gravity, as this design relies on the RTIL being actively pumped. In addition, this configuration benefits from previous development efforts for terrestrial applications, such as blood oxygenation, bioremediation, and wastewater treatment.[53] Compared to the flat plate contactor, however, this design requires an additional pump or compressor to overcome the pressure differential inherent to the hollow fibers and to drive gas through the system. These fibers may also be prone to clogging from particulate contamination, given their small diameters. An alternative option is to flow the RTIL through the interior of the hollow fibers and the gas stream across their exteriors.

Supported Ionic Liquid Membrane

Another option is to use a supported ionic liquid membrane (SILM) (Fig. 2d), which immobilizes the RTIL in the pores of the material. This technology is being developed for zero-g applications,[11,12] as well as terrestrial CO₂ sequestration.[54] Wickham et al. have developed numerous SILM modules using hollow fiber geometries, given their high surface area to volume ratios.[11,12] For Mars applications, RTIL-impregnated membranes can be used to preferentially separate CO₂ from the atmosphere; the gas can then be desorbed on the downstream side of the membranes to create a CO₂-rich gas stream. Physical transport through the membrane is facilitated by its relative thinness, as it is only microns thick, and yet, the structure of the SILM still retains the liquid.[55-58] Additionally, transport through the membrane can be facilitated if the CO₂ chemically reacts with the liquid membrane,[59,60,54] particularly if the RTIL is augmented with redox carriers that are electrochemically pumped with a potential difference across the membrane.[61-63] A disadvantage with SILMs is that a concentration differential is required to drive CO₂ transport across the membrane, so incoming CO₂ must be compressed.[11] In addition, the low-pressure side of the membrane must be designed such that it mitigates the risk of liquid being driven out of the pores by the pressure differential.[11]

Sparge System

Sparging (Fig. 2e) offers another feasible configuration where the Martian atmosphere is bubbled through a reservoir of ionic liquid that preferentially absorbs CO_2. The entire volume of ionic liquid can be exposed since buoyancy drives the bubbles upwards and facilitates mixing. As the diameter of the bubbles decreases, higher contact surface areas can be achieved within a given system volume, and to control their behavior, the density, viscosity, and surface tension of the ionic liquid must be well characterized.[64] However, this configuration requires an additional compressor or pump in order to flow gas through the capture vessel. Future research opportunities for this contactor include the modeling of bubble dynamics in RTILs at Martian gravity and the optimization of the gas diffuser required for bubble formation. Fortunately, this gas/liquid contactor (frequently referred to as a bubble column) has been employed for numerous terrestrial uses, including chemical, petrochemical, wastewater treatment, and metallurgical applications.[65]

Solid Pin Contactor

With the Solid Pin Contactor, the RTIL is pumped into a reservoir at the top of the system, which distributes the liquid over a manifold of circular openings. Beneath each circular opening, there is a cylindrical post with a diameter on the order of a few millimeters or less.[66] Gravity then drives the RTIL downwards along the exterior surfaces of these solid pins, allowing the RTIL free-surface contact with the CO_2-rich gas stream (Fig. 2f). Similar to the Hollow Fiber Contactor, the density of the solid pins can be increased within a given module volume by decreasing their diameters, thereby creating a higher surface area to volume ratio. Alternative, but similar, concepts include the use of corrugated wedge walls instead of cylindrical posts, as well as hollow tubes as described by Graf et al.[66] This general concept (also known as falling films) has been employed for terrestrial industries, such as sulfonation and chlorination reactions, as well as CO_2 absorption with alkaline solutions.[67] However, a pump or compressor may be required to evenly distribute fresh gas across all of the solid pins. The annular gap between each circular opening and solid pin may also be prone to clogging if particulates are introduced.

Aerosol Mist System

Aerosol misting (Fig. 2g) with an RTIL was developed by Yates et al. for zero-gravity applications, but it may be adapted for use in a Mars ISRU architecture.[10] Yates et al. sprayed various mixtures of water and 1-butyl-3-methylimidazolium acetate in high concentrations of droplets on the order of 100 to 1000 nm using a TOPAS ATM-210 aerosol generator, thereby achieving high surface area to volume ratios.[10] It should be noted that the viscosity of the solution must be controlled with the selection of a suitable cation and anion, water content and operating temperature since this property drives the distribution of droplet sizes,[10] which in turn, affects the contact surface area and capture rate. This technology (also referred to as a spray tower) has been developed for various terrestrial industries, such as the removal of sulfur oxides from the flue gas of coal-fired power plants, scrubbing of acid gases released by furnaces and incinerators, and terrestrial CO_2 sequestration applications.[68] Unfortunately, aerosol generators typically require elevated pressure to create the aerosol droplets (e.g., 3 bar in the study by Yates et al.[10]); however, the exact specifications will vary across units. In addition, any coalescence of droplets during operation rapidly decreases contact surface area, slowing uptake rates as a result.[68]

B. Desorption to Concentrate or Transfer

Reduced partial pressure and elevated temperature can be used to desorb gases and regenerate the RTIL. Yates et al. utilized a pure N_2 gas stream at a temperature of 30°C to regenerate 1-butyl-3-methylimidazolium acetate, which chemically complexes with CO_2.[10] Meanwhile, Seo et al. demonstrated that trihexyl(tetradecyl)phosphonium 2-cyano-pyrrolide, which also forms a chemical complex with CO_2, can be desorbed with a nitrogen gas stream at 80°C.[8] They also showed that this RTIL remains stable over three absorption/desorption cycles while using this desorption temperature. However, unless a feedstock of nitrogen can be provided for the Mars ISRU architecture, a reduction in CO_2 partial pressure will probably be achieved by vacuum desorption of CO_2 from the non-volatile RTIL.[11]

Interestingly, the relatively low atmospheric temperatures on Mars can be leveraged to take advantage of the inverse relationship between temperature and gas solubility. An RTIL at typical Mars temperatures will possess a notably higher CO_2 uptake capacity than when it is at room or elevated temperatures, so if gas uptake is performed at Mars temperatures, adequate desorption rates might then be attained exclusively with elevated temperatures, thereby avoiding the need for different pressures at the capture and desorption steps. This general concept is highlighted in data collected by Gurkan et al., albeit for a higher temperature regime.[25]

C. Processing

A variety of reactions can be utilized to process the captured CO_2, depending on the desired products. For *methane* production, the leading technology is the Sabatier reaction,[69,70] but less mature options include high and room temperature electrochemical reactors,[71,32] as well as photocatalytic processes.[72] Options for *oxygen* generation include the Bosch reaction with water electrolysis,[73] SOE,[17] the reverse water gas shift reaction with water electrolysis,[74] room temperature electrochemical reactions,[75] and photocatalytic reactions.[76] On the other hand, captured CO_2 can also be utilized as feedstock for bioregenerative life support systems.[77] With the exception of O_2 generation via certain electrochemical and photocatalytic processes, it should be noted that these technologies also consume water or hydrogen during their respective reactions. For electrochemical systems, continuous-flow reactors have numerous advantages over those that operate in batch mode, such as improved mixing and mass transfer;[78] continuous flow also avoids any warm-up period that may be associated with batch processing for high temperature reactors.

IV. Potential ISRU Architectures with Room Temperature Ionic Liquids

A. CO₂ Capture for Alternative (non-RTIL) Reactor Processes

A room temperature ionic liquid can be employed to capture CO_2 upstream of a reactor that relies on other reactions (e.g., high temperature, photocatalytic, or bioregenerative reactors). A notional depiction of this configuration is shown in Figure 3.

The capture stage first exposes an ionic liquid to the Martian atmosphere, allowing the RTIL to preferentially absorb CO_2. The CO_2-loaded RTIL is then pumped to a desorption step in order to release the captured CO_2. The released gas is then stored in tanks for

Figure 3. Notional Stages of an RTIL-Based CO₂ Capture System and Downstream Reactor

eventual use as feedstock in a downstream reactor, while the CO_2-poor RTIL is pumped back to the capture stage for additional cycles.

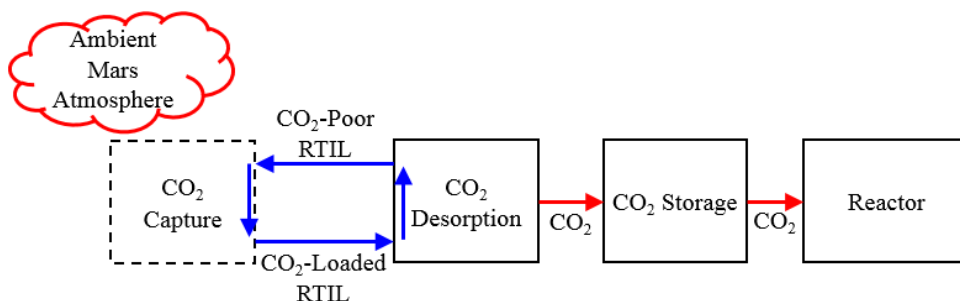Since RTILs remain stable at ambient Mars pressures, the capture stage can be operated at or near atmospheric pressure, assuming an RTIL with sufficient CO_2 solubility is utilized. To provide some examples, Seo et al. reported that 1-ethyl-3-methylimidazolium 2-cyano-pyrrolide possesses a CO_2 uptake capacity of approximately 6.9 weight percent at a CO_2 partial pressure of 800 Pascals and 295.15 K, while 1-ethyl-3-methylimidazolium 3-triazolide possesses an uptake capacity of 3.7 weight percent at a CO_2 partial pressure of 550 pascals and 295.15 K.[34] Another notable advantage with the configuration in Figure 3 is the lack of cryocoolers, which are required for CO_2 freezers and are relatively mass and power intensive.[69]

B. CO₂ Capture for a Room Temperature Electrochemical Reactor

As seen in Figure 4, the RTIL-based capture stage can also be integrated with a room temperature electrochemical reactor, which uses the same ionic liquid as the solvent, electrolyte, and co-catalyst for the reduction reaction.[15, 79-81] After capturing CO_2, the RTIL is pumped into an adjacent reactor, delivering the CO_2 to a catalytically active electrode, which electrochemically converts it into a desired product when a reducing potential is applied. The CO_2-poor RTIL is then circulated back to the capture stage, allowing the process to repeat.

Since the ionic liquid delivers CO_2 directly to the room temperature reactor, the vacuum and thermal systems for the

Figure 4. Notional Configuration for CO₂ Capture and Processing with one RTIL

desorption and storage steps in Figure 3 are not required, avoiding associated power and thermal requirements. The high temperatures and elevated pressures of leading reactors (SOE and Sabatier) can also be avoided.[17,82] For a
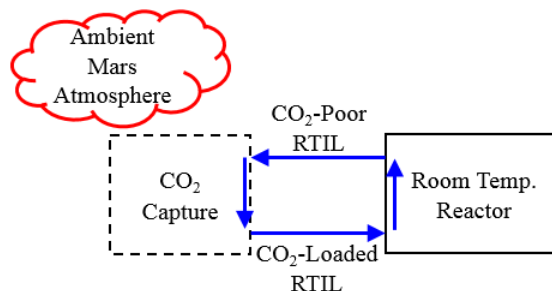
methane-production system, water can also be electrolyzed in the same process vessel, thereby avoiding the standalone water electrolysis unit required in a Sabatier architecture.[83] On the other hand, this configuration introduces an additional risk of delivering dust directly to the reactor, so dust accumulation in the capture stage must be well-characterized and mitigated to maintain nominal reactor operations. Such a system would also probably require a downstream purifier (e.g., electrochemical or membrane separator[69]) to generate pure rocket propellant, unless ~100% selectivity can be sustained at the cathode.

The development of viable cathodes for CO_2 reduction is still on-going since current designs provide insufficient selectivities, reaction rates, energetic efficiencies, and stabilities.[84] Over the years, many cathode/electrolyte pairs have been shown to generate CO with and without ionic liquids, such as silver with 1-ethyl-3-methylimidazolium tetrafluoroborate,[14] a bismuth-based catalyst with 1-ethyl-3-methylimidazolium hexafluorophosphate,[85] a molybdenum disulphide catalyst with 1-ethyl-3-methylimidazoilum tetrafluoroborate,[86] tungsten diselenide with 1-ethyl-3-methylimdazolium tetrafluoroborate,[87] and nanoporous silver with sodium bicarbonate.[88] Such processes could be utilized for oxygen production on Mars since O_2 is generated as a byproduct. Examples of cathode/electrolyte pairs that generate methane include nitrogen-doped graphene-like materials with 1-butyl-3-methylimidazolium tetrafluoroborate,[32] metal-organic frameworks with 1-butyl-3-methylimidazolium tetrafluoroborate,[15] as well as copper sulfide nanosheets with potassium bicarbonate.[89]

Unfortunately, the architecture in Figure 4 requires dynamic control of the electrolyte compositions in the electrochemical cell, introducing additional complexity to the system. More specifically, water content in the anolyte must be controlled in order to maintain adequate acidity and to replace water consumed during the oxidation process. Water will also be generated at the cathode as a byproduct of the CO_2 reduction reaction, and if it is not removed, excess water will dilute the ionic liquid solution over time, thereby negatively affecting the solution's CO_2 solubility and catalytic effects. Water content in the cathode compartment must also be controlled in order to maintain an appropriate pH, ionic conductivity, and viscosity for the catholyte.

An aqueous RTIL also complicates the operation of a CO_2 capture stage at low pressures since water may boil or rapidly evaporate. For context, the vapor pressure of water at 293.15 K is 2,339 Pascals.[90] Loss rates, however, will vary with the design of the system—a contactor that directly exposes the solution to the atmosphere (e.g., Solid Pin Contactor) will probably lose water at a different rate than a membrane-based unit (e.g., Hollow Fiber Contactor). Potential mitigation strategies include elevated pressure in the capture stage or appropriately-sized water extraction systems that offset this loss.

C. Dual-RTIL Loop for CO_2 Capture and Conversion

A dual-RTIL system is another potential configuration for an ISRU architecture, as depicted in Figure 5. This configuration utilizes one ionic liquid to separate CO_2 from the
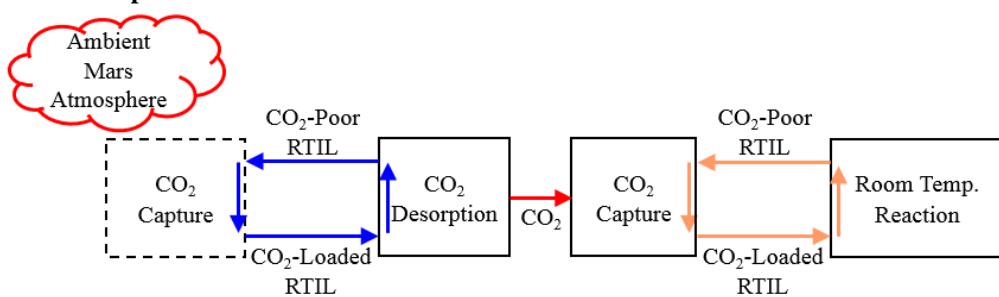

Figure 5. Notional Configuration for Dual-Liquid Capture and Processing

atmosphere, and after this step, the CO_2 can be transferred to a second RTIL, which delivers the gas to a room temperature electrochemical reactor and facilitates the reduction reaction.

The primary advantage of this configuration is that each RTIL can be optimized for their respective functions. More specifically, an ionic liquid that possesses high CO_2 solubility at Mars pressures can be employed for the first step. In addition, the sole function of this RTIL is to capture CO_2, so it may not need to be mixed with water, potentially avoiding the challenge of using an aqueous solution for CO_2 capture at low pressures (Figure 4). But, an optimal RTIL for CO_2 capture may bind the molecule too strongly and slow its rate of adsorption onto the reactor catalyst. So, the reactor may benefit from the use of a different RTIL that is better suited for this process and the subsequent reduction reaction, leading to the second RTIL loop as illustrated in Figure 5.

Another significant advantage of this architecture is in the opportunity to develop the CO_2 capture stage independently of the room temperature reactor, similar to the option described above for non-RTIL processing (Figure 3). Since there are still numerous challenges associated with the room temperature electrochemical reduction of CO_2 into desired products, including slow reaction rates, inadequate selectivities, and high overpotentials,[84] on-going research and development efforts are targeting novel cathodes that will resolve these issues. As a result, though, a

flight-ready cathode has yet to be established. Ultimately, the cathode's interaction with the RTIL will depend on its eventual properties, such as material composition, morphology, and particle size,[91] so the reactor RTIL cannot be finalized until candidate cathodes are mature. In light of this challenge, the dual-RTIL scheme provides the opportunity to develop the capture stage independently of the reactor, which is not necessarily plausible for the integrated, single-loop configuration shown in Figure 4.

The primary disadvantage of this architecture compared to the single-loop configuration, however, is the need for a desorption step and a second capture stage. In addition to introducing additional mass, power, and volume, these steps may also slow the delivery of CO_2 to the reactor. And while the use of separate loops introduces the option of operating the atmospheric CO_2 capture stage and reactor at significantly different pressures, an additional challenge may be created if the capture, desorption, or reaction stages induce a pressure differential across one of the loops. In such a scenario, the system will need to be designed to retain the liquid (e.g., ensure the liquid does not seep through a membrane due to the pressure differential).

Meanwhile, the relative immaturity of current room temperature electrochemical reactors is the primary disadvantage of this architecture compared to the scheme in Figure 3, which can be designed around a mature CO_2 reduction technology. Unless future cathodes approach ~100% selectivity for a desired product, a separator will also probably be needed downstream of the configuration in Figure 5. In addition, compared to the capture RTIL, a larger volume of reactor RTIL will probably be required to transfer and react CO_2 at the same rate that it is separated from the atmosphere, assuming the reactor RTIL has lower solubility.

V. Summary

Various gas/liquid contactors have been developed for terrestrial and spaceflight applications, and when coupled with room temperature ionic liquids, which have negligible vapor pressures, such devices may be suitable for CO_2 capture at the low pressures found on the surface of Mars. RTILs can also serve as the solvent, electrolyte, and co-catalyst in a room temperature reactor, introducing several plausible configurations for establishing RTIL-based ISRU architectures. These include:

- RTIL-based capture and desorption stages that generate CO_2 feedstock for a high temperature, photocatalytic, or bioregenerative reactor
- A single RTIL that captures CO_2 and delivers it to a room temperature electrochemical reactor for processing
- A dual-RTIL loop, where one half is optimized for CO_2 capture and the other is designed for CO_2 processing in a room temperature electrochemical reactor

There are numerous relationships between important operational parameters (temperature, CO_2 partial pressure, time, and water content) and dependent properties (CO_2 uptake, viscosity, electrochemical window, ionic conductivity, gas selectivity, and freezing/melting point) that vary significantly with each RTIL. These relationships must be well characterized before a given RTIL can be utilized for Mars ISRU.

Beyond the fundamental research needed to thoroughly characterize the various RTIL properties, the performance of integrated systems at representative scales with relevant inputs and operational conditions has not yet been demonstrated at steady state for long durations. Although existing cathode/RTIL combinations are probably still inadequate for Mars ISRU, system-level experiments with existing options can be employed to identify unknown challenges and advance the technology in parallel with reactor maturation. Theoretical system-level analyses of full-scale RTIL-based ISRU applications can also be used to quantify potential advantages and disadvantages of the proposed architectures. Equivalent system mass analyses, in particular, would provide valuable trade space insight and could help guide down-selections from the configurations presented above.

In short, RTIL-based ISRU technologies are well-positioned to serve as dissimilar, redundant systems for oxygen, methane, and buffer gas generation on Mars, but in addition to fundamental research on RTIL properties and cathodes, systems-level analyses are required to advance the technology readiness level of this novel approach.

Acknowledgments

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