# **Corrosion Resistance of Materials in the Mars Environment**

Luz M. Calle,<sup>1</sup> Michael R. Johansen,<sup>2</sup> Jerry W. Buhrow<sup>3</sup> and Carlos I. Calle<sup>4</sup> NASA, Kennedy Space Center, FL, 32899

and

Wenyan Li<sup>5</sup> Aecom Management Services, Inc., Kennedy Space Center, FL, 32899

This paper presents the results of a literature search of available data relevant to corrosion resistance of materials in the Mars environment, as a background for future experimental work. Corrosion resistance is one of the most important properties in selecting materials for landed spacecraft and structures that will support surface operations for the human exploration of Mars. Currently, the selection of materials is done by assuming that the corrosion behavior of a material on Mars will be the same as that on Earth. This is understandable since there is no data available on the corrosion resistance of materials in the Mars environment. However, given that corrosion is defined as the degradation of a metal that results from its chemical interaction with the environment, it cannot be assumed that corrosion is going to be the same in both environments, since they are significantly different. This theoretical study was motivated by the suggestion, by a team of researchers, that some of the structural degradation observed on Curiosity's wheels may have been caused by corrosive interactions with the transient liquid brines, reported to be present on Mars, while the most significant damage was attributed to mechanical damage. An extensive literature search, on data relevant to corrosion on Mars, confirmed the need to investigate the interaction between materials, used for spacecraft and structures designed to support long-term surface operations on Mars, and the Mars environment. Experimental studies are needed to investigate the corrosion behavior of materials in relevant components of the Mars environment such as: the Mars atmosphere, the presence of brines, the interaction between these brines and materials, the effect of radiation on these interactions, and the possible catalytic effects of the clays present in the Martian regolith. The findings from this theoretical study provide strong justification to conduct experimental work to investigate the interaction between spacecraft materials with simulated Martian environments to reduce Mars exploration costs.

# Nomenclature

DAN	=	Dynamic Albedo of Neutrons
GRS	=	Gamma Ray Spectrometer
MAHLI	=	Mars Hand Lens Imager
MER	=	Mars Exploration Rover
MSL	=	Mars Science Laboratory
RSL	=	Recurring Slope Lineae
SAM	=	Sample Analysis at Mars
SOA	=	state of the art

<sup>&</sup>lt;sup>1</sup> Senior Research Scientist, Exploration Systems and Development Office, Mailcode: UB-E, Kennedy Space Center, FL, 32899.

<sup>&</sup>lt;sup>2</sup> Research Engineer, Spaceport Technologies Office, Mailcode: UB-G, Kennedy Space Center, FL, 32899.

<sup>&</sup>lt;sup>3</sup> Laboratory Manager, Materials Laboratory Branch, Mailcode: NE-L7, Kennedy Space Center, FL, 32899.

<sup>&</sup>lt;sup>4</sup> Senior Research Scientist, Spaceport Technologies Office, Mailcode: UB-G, Kennedy Space Center, FL, 32899.

<sup>&</sup>lt;sup>5</sup> Research Scientist, URS Services, Inc., Mailcode: LASSO-001, Kennedy Space Center, FL, 32899.

# I. Introduction

THE need to investigate the corrosion behavior of materials, relevant to Mars exploration, was first suggested on a report from a workshop, sponsored by NASA Human Exploration and Operations Mission Directorate and by NASA Planetary Protection Office, on "Planetary Protection Knowledge Gaps for Human Extraterrestrial Missions," conducted at NASA Ames Research Center, March 24-26, 2015, Moffett Field, CA. The report cites, as other areas of critical research: "those that include environment characterization and definition (properties of dust and dirt, dust storms, etc.) as well as efforts to develop suitable Mars simulants based on scientific understanding of regolith conditions (even if there is no Mars sample return in advance of a human mission). Attention should also focus on the use of additives to trace possible backward contamination, as well as chemical additives to understand materials degradation due to toxicity and corrosion."<sup>1</sup> The need to investigate the corrosion behavior of materials, relevant to Mars exploration, was also suggested, as a low priority objective, by the Mars Exploration Program Analysis Group (MEPAG) as Investigation B7.1: "Analyze regolith and surface aeolian fines (dust), with a priority placed on the characterization of the electrical and thermal conductivity, triboelectric and photoemission properties, and chemistry (especially chemistry of relevance to predicting corrosion effects), of samples of regolith from a depth as large as might be affected by human surface operations."<sup>2</sup>

The current state of the art (SOA), regarding the selection of materials for landed spacecraft for human surface operations on Mars, is to assume that their corrosion behavior on Mars will be the same as that on Earth. The goal of this project was to investigate the effect of the Mars environment on spacecraft materials, by conducting a literature search of available data relevant to corrosion in the Mars environment.

#### **II. Background**

Mars is often called the red planet. The reddish color of the Martian surface is due to the high iron oxide  $(Fe_2O_3)$ , also known as iron(III) oxide or hematite, content in its regolith. Iron(III) oxide (rust) is formed when iron metal becomes oxidized in the presence of oxygen  $(O_2)$ . This process is also known as corrosion. Metal corrosion is the deterioration of a metal or its properties caused by a reaction with its environment. Corrosion occurs mainly through electrochemical reactions. These are chemical reactions that take place when electrons are transferred from one chemical species to another in the presence of an electrolyte.

Corrosion of a metal requires the following components and characteristics:

- Anode: Where metal is lost and electrons are produced (oxidation).
- Cathode: Where electrons are consumed (reduction).
- Metal: Provides the path for current to flow when electrons move from the anode to the cathode.

• Electrolyte: An aqueous solution in which the electrical current is carried by ions. Negative ions (anions) flow toward the anode and positive ions (cations) flow towards the cathode.

A metal can be protected from corrosion by covering it with a coating that isolates it from the environment, thus preventing its reaction with it. The metal will be protected for as long as the coating remains intact. The coating can be an applied paint or an oxide layer. When  $O_2$  is present in the environment, such as the Earth's atmosphere, metals react with it to form an oxide layer on the surface that may act as a coating to protect them from corrosion. Aluminum spontaneously forms a thin but effective protective oxide layer, on contact with air, which prevents further oxidation. This oxide, unlike the oxide layers on many other metals, adheres strongly to the base metal. If damaged mechanically, the aluminum oxide layer repairs itself immediately. This layer is stable in the general pH range between 4 and  $9.^{3, 4, 5}$  However, this oxide layer can breakdown in the presence of aggressive anions, such as chloride (Cl<sup>-</sup>) and perchlorate (ClO<sub>4</sub><sup>-</sup>), resulting in the pitting corrosion of the aluminum.

Space-age aluminum alloys are lightweight, durable, extraordinarily strong, and their corrosion resistance is very good in most terrestrial environments. However, it is not known how aluminum and its alloys interact with the Martian environment. The Curiosity mission is just the latest example of aluminum's vital role in the development of modern aviation and humankind's exploration of space. Chosen for its lightweight and ability to withstand the stresses that occur during ground and launch operations, aluminum has been used on Apollo spacecraft, the Sky-lab, the Space Shuttles, and the International Space Station. Aluminum alloys consistently outperform other metals in areas such as mechanical stability, thermal management, and reduced weight. One example is the aluminum alloy AA7075-T7351, which is used to make the thin-walled rigid wheels on the Mars Science Laboratory (MSL). Figure 1**Error! Reference source not found.** shows one of the six flight wheels of Curiosity.<sup>6, 7</sup> The wheel is hard anodized, a process used to increase the thickness of the natural oxide layer on the surface of the metal, for greater strength and improved corrosion resistance in terrestrial environments. The Mars mission scheduled to launch in 2020 will use the same type of corrosion protection. This is understandable, given that one of the most important

factors in the design of the wheels is the mechanical strength required to transport heavy instruments across the rugged surface of Mars. Since the publication of the first evidence of liquid water on present-day Mars by Martin-Torres et al.,<sup>8</sup> according to Curiosity data, and the report of the presence of brines by Ojha et al.,<sup>9</sup> a new frontier of scientific challenges has emerged, such as the corrosive interaction between brines (electrolytes) and spacecraft materials in the Mars environment.<sup>10</sup> The hydrated salts present in the brines would lower the freezing point, just as salt on roads here on Earth causes ice and snow to melt more rapidly. The hydrated salts, most consistent with the chemical signatures analyzed by Ojha et al.,<sup>9</sup> are likely a mixture of magnesium perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub>), magnesium chlorate (Mg(ClO<sub>3</sub>)<sub>2</sub>), and sodium perchlorate (NaClO<sub>4</sub>). Some perchlorates have been shown to keep liquids from freezing, even when conditions are as cold as minus 70°C (203K).

Perchlorates have previously been seen on Mars: NASA's Phoenix lander and Curiosity rover both found them in the planet's soil, and some scientists believe that the Viking missions in the 1970s measured signatures of these salts. However, the study of recurring slope lineae (RSL) detected perchlorates, now in hydrated



Figure 1. Curiosity's wheel made from a single piece of machined aluminum alloy AA7075-T7351. The main rim is 1.9 cm thick (0.75-inches). NASA / JPL / Emily Lakdawalla.

form, in areas different from those explored by the landers. This also is the first time that perchlorates have been identified from orbit. It should be mentioned that other researchers<sup>11</sup> have suggested that a dry avalanche process can explain the formation of the RSL on Mars, without requiring liquid water or  $CO_2$  frost activity. On Earth, naturally produced perchlorates are concentrated in desserts, and some types of perchlorates are used as rocket propellant.

Despite the overwhelming evidence that oxidation of materials is unavoidable on Mars, corrosion of materials has not been a major concern for Mars Missions, due to its arid atmosphere and the lack of evidence of liquid water. The recent discovery of perchlorates is indicative of their widespread presence on the surface of Mars.<sup>12</sup> Perchlorate and chlorate (ClO<sub>3</sub><sup>-</sup>) species have also been found in a Martian meteorite.<sup>13</sup> Their role in lowering the freezing temperature of water in the Martian soil supports the presence of transient liquid water on Mars.<sup>9</sup> This new found evidence of liquid brines coincided with the surprisingly significant damage observed on Curiosity's wheels (Figure 2 and Figure 3). Soon after its landing, disturbing cracks started to appear on some of them. This was surprising, given that the design was similar to that of the Mars Exploration Rovers (MERs), Spirit and Opportunity, which never showed such a wear and tear when experiencing the same mean pressure (i.e. platform weight over wheel area in contact with a flat terrain). It has been hypothesized that, the daily contact of the anodized aluminum, making it more susceptible to damage against sharp rocks. Rover engineers concluded that the damage was caused exclusively by mechanical forces. Although the large cracks in the wheel are likely caused by mechanical damage,



**Figure 2.** Curiosity's wheels showing signs of severe damage after almost 10 km of traverse.

there is a pattern of distributed sub-millimeter sized blisters, in the vertical wall of the T-print of the wheels, that cannot be attributed to rock scratching. This pattern resembles aluminum alloy pitting corrosion, as shown on the image taken by the ChemCam remote microscopic-imager on sol 502 (Figure 3). A team of researchers<sup>8</sup> has suggested that, given the strong oxidizing character of perchlorate anions and their byproducts, the damage that cannot be attributed to rock scratching may be caused by corrosive interactions of brines with the aluminum alloy wheel.14 Any Martian surface Cl--containing deliquescent brine would be expected to be very corrosive. In particular, for the Martian deliquescent brines, the Cl<sup>-</sup> concentration in the Ca- and Mgperchlorate eutectic mixtures are factors of 420 and 246 greater, respectively than a diluted copper(II) chloride (CuCl<sub>2</sub>) solution (10 mM), which has been

reported to cause 10-50 µm-sized blisters, with copper (Cu) deposits, produced after aluminum pitting corrosion, similar to those circled in red in Figure 3, within 10 minutes.<sup>5</sup> The anodizing process increases the thickness of the natural oxide layer on the aluminum wheels, but the abrasion can wear out the external protecting layer and expose the bare aluminum metal to corrosion. The presence of chloride and perchlorate anions in brines may add stress to the aluminum wheels through pitting corrosion. Thus, it can be hypothesized that the presence of corrosive chloridecontaining brines on Mars should have implications on spacecraft design for human surface operations in support of long duration exploration missions. Considering that the overall environment of Mars is more oxidizing than that of Earth, the potential challenge of metal corrosion and materials degradation should not be ignored.

The quest to find life on Mars, by searching for water and organic compounds, the building blocks of life on Earth, and microbial life in the regolith, has generated a great deal of data relevant to corrosion on Mars.



Figure 3. Curiosity's ChemCam images of a damaged area of the rover's middle right-wheel. The image shows not only a large crack in the wheel (area inside blue rectangle on left image) but some sub-millimeter-sized blisters in the vertical wall of the T-print of the wheels (circled in red on the middle and right images) which cannot be attributed to rock scratching. It has been suggested that the blisters are caused by the corrosive interaction between transient brines and the aluminum alloy.

#### A. Available Data Relevant to Corrosion on Mars

Results from experiments designed to look for life have indicated that Mars' surface is lifeless and depleted of organics at the parts-per-billion levels. These results have been explained by the presence of oxidizing agents on the surface of Mars. These oxidizing agents also can cause corrosion of materials on Mars. One of the most significant recent findings, that is relevant to corrosion, is the existence of transient liquid water and water activity at Gale crater on Mars (the exploration zone of NASA's Curiosity rover), reported by a team lead by F. Martin-Torres.<sup>8</sup> Their observations support the formation of night-time transient liquid brines in the uppermost 5 centimeters of the subsurface that then evaporates after sunrise. There is an active exchange of water at the atmosphere/soil interface which is the area that would come in contact with landed spacecraft and structures built to support surface operations on Mars. The research team expects that liquid brines are abundant beyond equatorial regions where atmospheric humidity is higher and temperatures are lower. As it was suggested in a recent publication,<sup>10</sup> the presence of transient liquid brines has significant implications for spacecraft design and surface operations, given the potential for corrosive interactions between the brines and spacecraft materials.

Sample Analysis at Mars (SAM),<sup>15</sup> and Dynamic Albedo of Neutrons (DAN)<sup>16</sup> instruments, over the course of a full Martian year (1.88 Earth years), have provided the largest environmental data set ever recorded *in-situ* on Mars. This data is relevant to study the interaction between spacecraft materials and the Mars environment.

#### **B.** Brines on Mars

Brines on Mars are produced under specific environmental conditions in the daily capture (and release) of atmospheric water vapor by deliquescent salts that exist at the surface of Mars, such as chlorides and perchlorates.<sup>17</sup> The perchlorates found in situ are likely calcium perchlorate (Ca(ClO<sub>4</sub>)<sub>2</sub>), as detected by Curiosity at Gale,<sup>18</sup> and magnesium (Mg(ClO<sub>4</sub>)<sub>2</sub>) or sodium (NaClO<sub>4</sub>), perchlorates as observed at the Phoenix polar landing site.<sup>19</sup> Reanalysis of Viking data suggested that perchlorates could have been present there as well.<sup>20, 21</sup> Chloride is distributed globally on Mars as detected by the Mars Odyssey Gamma Ray Spectrometer (GRS).<sup>22, 23</sup> Oxygen was

one of the most abundant gases released during thermal analysis of materials at Curiosity's Rocknest site. Its release was correlated with the release of chlorinated hydrocarbons.<sup>24</sup> This  $O_2/Cl$  correlation makes a strong case for the presence of chlorine in the form of perchlorates. The suggestion that the presence of chloride and perchlorate anions in brines may cause pitting corrosion on Curiosity's wheels and future Martian exploration platforms<sup>8</sup> is worth of further investigation.

# C. Perchlorates and Martian Conditions

Since the detection of perchlorates on Mars, several studies have been aimed at understanding their effects on the habitability of the planet. The recent work of J. Wadsworth and C.S. Cockell<sup>25</sup> showed the significant bactericidal effects of UV-irradiated perchlorate on life at ambient temperatures and under Martian conditions. This finding is relevant to corrosion since it showed that, when irradiated with a simulated Martian UV-flux, perchlorate is more reactive at ambient temperatures and ambient conditions. The study also showed that two other components of the Martian surface, iron oxides and hydrogen peroxide, act in synergy with perchlorates to cause a 10.8-fold increase in cell death when compared to cells exposed to UV radiation after 60 seconds of exposure. The mechanism of perchlorate action on cells is likely to be its degradation to deleterious reactive oxygen species, such as hypochlorite (CIO<sup>-</sup>), commonly known as chlorine bleach, and chlorite (CIO<sub>2</sub><sup>-</sup>). Similar photoproducts have been previously observed in perchlorate irradiated with ionizing radiation.<sup>26, 27</sup> C.D. Georgiou et al.<sup>28</sup> reported that  $\gamma$  -radiolyzed perchlorate-containing Mars soil salt analogues (in a CO<sub>2</sub> atmosphere) generate, upon H<sub>2</sub>O wetting, the superoxide radical (O<sub>2</sub><sup>-\*</sup>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and hydroxyl radicals (OH<sup>+</sup>). This study also validated that analogue radiolysis forms oxychlorine species that, in turn, can UV-photolyze to OH<sup>+</sup> upon UV photolysis. Additionally, UV photolysis of the perchlorate  $\gamma$ -radiolysis product, chlorite, generated the oxychlorine products trihalide (Clo<sup>-</sup>), chlorine dioxide free radical (Clo<sup>-</sup>), and hypochlorite, with the formation of OH<sup>+</sup> by UV photolysis of ClO<sup>-</sup>.

A resent review paper by Lasne et al.<sup>29</sup> provides an excellent summary of the oxidants detected or proposed to be present at the surface of Mars in light of recent exploration results. These findings suggest the importance of conducting experiments to investigate the combined effects of Martian soil simulant, activated by surface photochemistry, as well as the influence of clays as catalysts, on materials relevant to long-duration surface operations on Mars.

#### **III.** Materials Behavior in the Mars Environment

Although the current rover on Mars, Curiosity, does not have electrochemical sensors, it has captured images that can provide a visual indication of the interaction between materials and the Mars environment. A relevant example is shown in Figure 4.<sup>30</sup> The photo shows the Lincoln cent that is attached to a calibration target used by the rover's camera known as the Mars Hand Lens Imager, or MAHLI. Figure 5 shows an image of elongated crystal shapes taken on the surface of Mars by the Curiosity rover. An inset on the picture shows the 1909 VDB Lincoln cent.<sup>31</sup> Curiosity was launched on November 26, 2011 to search areas of Mars for past or present conditions favorable for life, and conditions capable of preserving a record of life. The rover landed on the planet on August 6, 2012. It has been surveying a small portion of the planet ever since. This is the first time that a coin has been subjected to the conditions of another planet while being monitored. Figure 6 shows four different photos of the Lincoln cent taken on Earth and on Mars. The only change that can be visually observed on the pictures is the accumulation of Martian dust, which is interesting because the coin is mounted on a vertical position. The Lincoln cent appear to show no visual signs of corrosion of copper.

Figure 7 shows a set of U.S. pennies, selected at random from a household coin jar, to show signs of corrosion. The pennies at the bottom (dated from 1999 to 2017) show very little or no visible signs of corrosion. The pennies at the top are dull and covered by corrosion products. Although the cause of corrosion is unknown, because the pennies were not subjected to a controlled experiment, it can be hypothesized that the pennies at the top were exposed to more corrosive environments than those at the bottom. When copper is exposed to air, its shiny copper color will transition to dull brown. At a later stage, the formation of copper sulfate, carbonate, and chloride salts, in varying concentrations will turn the surface green (as seen on some of the pennies on the top row). This process is influenced by many factors such as: moisture, temperature, and the environment to which the metal has been exposed to. The penny shown on Figure 6 shows no sign of corrosion. This is not surprising given that the penny has been exposed to the Martian atmosphere which contains only minor amounts of water (210 ppm).<sup>32</sup>



Figure 4. NASA's Mars rover Curiosity with and inset showing the calibration targets, including a 1909 Lincoln penny, at the end of its robotic arm. Image credit: NASA/JPL-Caltech.



Figure 5. Image of elongated crystal shapes taken on the surface of Mars by the Curiosity rover on the 809th Martian day, or sol, of Curiosity's work on Mars on November 15, 2014. An inset on the picture shows the 1909 VDB Lincoln cent that is attached to a calibration target used by the rover's camera known as the Mars Hand Lens Imager, or MAHLI. Image Credit: NASA, JPL-Caltech, MSSS.

International Conference on Environmental Systems



**Figure 6.** Four different photos of the 1909 VDB Lincoln Cent on Mars rover Curiosity. VDB are the initials of Victor David Brenner who designed the coin. The first photo was taken on Earth in August 2011. Subsequent photos were taken on Mars on September 9, 2012, October 2nd, 2013, and on November 15, 2013. Image credit: NASA, JPL-Caltech, MSSS.



**Figure 7.** U.S. pennies selected at random from a household jar of coins to show different states of corrosion: the pennies at the bottom (left to right) date from 1999, 2005, 2006, 2011, 2014, 2015, and 2017; the pennies at the top are corroded and only the second penny from the left has a visible date (1984).

# **IV.** Chemical Weathering Rate Derived from Meteorites

Meteorites can be used to obtain information about their environment. Some meteorites are mostly iron like the "Egg Rock" meteorite found by Curiosity (Figure 8).<sup>33</sup> The study of iron meteorites found by spacecraft exploring Mars, such as the MERs Spirit and Opportunity, as well as the MSL or Curiosity rover, can provide information on how the exposure to the Martian environment has affected them. Iron meteorites, like the one shown in Figure 8, will weather or oxidize as a result of their interaction with the environment. Scientists have used chemical analysis results gathered by the rovers to obtain an estimate for the rate of oxidation of the iron. C. Schroder et al.<sup>34</sup> used the oxidation of iron in stony meteorites, investigated by the MER Opportunity at Meridiani Planum, to estimate the chemical rate of oxidation and concluded that the chemical weathering rates were about 1 to 4 orders of magnitude slower than that of similar meteorites found in Antarctica, where the slowest rates are observed on Earth. The authors of the study suggest that the extremely slow weathering of meteorites, which contain metallic iron as a phase very sensitive towards chemical alteration or corrosion, is not a threat over the lifetime of a spacecraft and that the Opportunity rover is testament to that, showing no signs of corrosion after more than 12 years of operating on Mars (April 2016), in contrast to the concern expressed by Martin Torres et al. about the corrosive effects of chlorine-containing brines on spacecraft.<sup>10</sup>



**Figure 8.** The dark, golf-ball-size object in this composite, colorized view from the ChemCam instrument on NASA's Curiosity Mars rover is a nickel-iron meteorite, as confirmed by analysis using laser pulses from ChemCam on Oct. 30, 2016. The grid of bright spots on the rock resulted from the laser pulses. Credit: NASA/JPL.

# V. Electrochemical Corrosion of Minerals in Martian Rocks

In 2018,<sup>35</sup> the Curiosity rover (Figure 9) found evidence for abundant organic compounds in the ancient mudstone rocks in Gale Crater on Mars. These carbon molecules ranged from simple to fairly complex, but their actual origin was still unknown. They could be created by abiotic processes (without life). Or they could be the molecular remains of once-living organisms. A new study<sup>36</sup> has shown one possible way that these or similar organics might have been created on Mars (Figure 10).<sup>37</sup> The researchers studied organics found in three Martian meteorites – Tissint, Nakhla, and NWA 1950 – and compared them to the organics discovered by Curiosity. They found that both sets of organic carbon were quite similar, suggesting a possible similar origin and hypothesized that the meteorites' organic compounds were likely created by electrochemical corrosion of minerals in Martian rocks by a surrounding salty liquid brine.



**Figure 9.** NASA's Curiosity rover found organic carbon compounds in ancient mudstones, similar to ones previously discovered in Martian meteorites. Credit: NASA/GSFC.



**Figure 10.** A high-resolution transmission electron micrograph (scale 50nm), from a transmission electron microscope, of a grain from the Martian meteorite Nakhla. The organic carbon layers are found between the intact "tines." This texture is created when the volcanic minerals of the Martian rock interact with a salty brine and become the anode and cathode of a naturally occurring galvanic cell in a corrosion reaction. This reaction would then have enough energy – under certain conditions – to synthesize organic carbon. Image courtesy of Andrew Steele/Carnegie Science.

The discovery that natural systems can essentially form a small galvanic cell that drives electrochemical reactions between minerals and surrounding liquid brine has implications that need to be considered when selecting materials, relevant to surface operations on Mars. Like minerals, metallic materials, such as aluminum alloys, can react with the brines and degrade (corrode) in the process.

#### VI. Summary

Our extensive literature search on the available data relevant to Mars corrosion, or the lack thereof, confirmed the need for further investigation of the interaction between materials, used for spacecraft and structures to support long-term surface operations on Mars, and the Mars environment, as it was first suggested by F.J. Martin-Torres et al. and recommended in the "Mars Science Goals, Objectives, Investigations, and Priorities: 2015 Version," prepared by the Mars Exploration Program Analysis Group (MEPAG) Goals Committee.

The quest for life on Mars has been to "follow the water." Water is critical for life as we know it and it is also critical for corrosion, given that an aqueous electrolyte solution is one of the requirements for corrosion to occur. It is important to note that a great deal of the data relevant to corrosion on Mars is available from investigations aimed at explaining the results obtained from experiments that were designed to look for evidence of life on Mars. Oxidants were hypothesized as being responsible for the lack of organics found by the Viking mission which reached Mars in 1976. The presence of perchlorates in Mars regolith was identified by NASA's Phoenix Lander in 2009, and demonstrated as a component of transient liquid brines on September 2015. These findings are relevant to corrosion since oxidants can corrode materials and transient liquid brines can serve as the electrolyte solution that supports corrosion. Furthermore, the finding by J. Wadsworth and C. S. Cockell in 2017 that perchlorates become more bactericidal when irradiated with simulated Martian UV flux, and that other components of the Martian surface act in synergy with the irradiated perchlorates, has implications for the corrosive interaction between materials and the brines that are worth of investigation. It is well known that perchlorates here on Earth are powerful oxidants at high temperatures but stable at room and lower temperatures. However, it is not known how perchlorates interact with materials when they are activated by high energy radiation as it exists on Mars.

Our simple preliminary experiments,<sup>38</sup> designed to look at the interaction between spacecraft AA7075-T73 aluminum alloy and the gases present in the Mars atmosphere, at 20°C and a pressure of 700 Pa, showed that there is an interaction between the small amount of oxygen present in the Mars gas and the aluminum alloy. Further studies are needed to consider other important components and conditions of the Mars environment that can affect this interaction such as: the presence of brines that can act as an electrolyte, the effect of radiation on the oxidizing properties of perchlorates, the possible catalytic effects of the clays present in the Martian regolith, as well as the temperature and pressure conditions.

To understand the corrosion mechanisms on Mars, the interaction between materials and the Martian environment should be studied under simulated Martians conditions that include: Martian atmospheric conditions, soil chemistry, radiation, and exposure to brine water.

The goal of the recommended work would be:

(1) To gain a further understanding of the corrosion behavior of spacecraft materials on Mars by investigating the effect of each Martian environment parameter (individually and in combination) on their corrosion-relevant properties.

(2) Evaluate the corrosion behavior of selected candidate materials, with different surface corrosion protection treatments, from several candidate aerospace alloys under simulated Martian conditions. These materials should include aluminum alloys, stainless steels, and titanium.

(3) Make recommendations on corrosion resistant materials and surface treatments to enable long-term surface operations in support of human exploration missions in the Martian environment.

#### Acknowledgments

The authors would like to thank the NASA Kennedy Space Center Innovation Fund for funding this work.

# References

<sup>&</sup>lt;sup>1</sup> "Planetary Protection Knowledge Gaps for Human Extraterrestrial Missions," Workshop Report, DAA-TN36403, NASA Ames Research Center, Moffett Field, CA, March 24-26, 2015, <u>https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20160012793.pdf</u> [cited 5 February 2020].

<sup>4</sup> Deltombe, E. Vanleugenhaghe, C., M., and Pourbaix, M., Atlas of Electrochemical Equilibria in Aqueous Solution, Pergamon Press, Oxford, 1966.

<sup>6</sup> Whitwam, R., "NASA Reports Two New Breaks in Curiosity Rover's Wheels," https://www.extremetech.com/extreme/246398nasa-reports-two-new-breaks-curiosity-rovers-wheel [cited 5 February 2020].

<sup>7</sup> "Curiosity Mars Rover Wheel Damage: The Problem and Solutions," https://forums.spacebattles.com/threads/curiosity-marsrover-wheel-damage-the-problem-and-solutions.309527/ [cited 5 February, 2020].

<sup>8</sup> Martin-Torres, F. et al., "Transient Liquid Water and Water Activity at Gale Crater on Mars," *Nature Geoscience*, Vol. 8, 2015, pp. 357-361.

<sup>9</sup>Ojha, L. et al., "Spectral Evidence for Hydrated Salts in Recurring Slope Lineae on Mars," *Nature Geoscience*, Vol. 8, 2015, pp. 829-832.

<sup>10</sup> Martin-Torres, F. and Zorzano, M.P., "Should we Invest in Martian Brine Research to Reduce Mars Exploration Costs?" Astrobiology, Vol 17, No. 1, 2017, pp. 3-7.

<sup>11</sup> Schmidt, F., Andrieu, F., Costard, F., Kocifaj, M., and Meresescu, A.G., "Formation of Recurring Slope Lineae on Mars by Rarefied Gas-Triggered Granular Flows," *Nature Geoscience*, Vol. 10, 2017, pp. 270-273.

<sup>12</sup> Kerr, R. A., "Pesky Perchlorates all over Mars," Science, Vol. 340, Issue 6129, p.138 (2013).

<sup>13</sup> Kounaves, S., Carrier, B. L., O'Neil, G. D., Stroble, S. T., and Claire, M.W., "Evidence of Martian Perchlorate, Chlorate, and Nitrate in Mars Meteorite EETA79001: Implications for Oxidants and Organics," Icarus, Vol. 229, pp. 206-213, (2014).

<sup>14</sup> "Curiosity's Wheel Damage," <u>http://www.leonarddavid.com/curiositys-wheel-damage-effects-of-corrosion/</u> [cited 11 February 20201.

<sup>15</sup> SAM: Sample Analysis at Mars on the Rover Curiosity, https://ssed.gsfc.nasa.gov/sam/ [cited 5 February 2020].

<sup>16</sup> MSL: DAN (Dynamic Albedo of Neutrons), <u>https://pds-geosciences.wustl.edu/missions/msl/dan.htm</u> [cited 5 February 2020].

<sup>17</sup> Zorzano, M. P., Mateo-Marti, E., Prieto-Ballesteros, O., E. Osuna, S., and Renno, N., "Stability of Liquid Saline Water on Present Day Mars," Geophys. Res. Lett., Vol. 36, Issue 20, 2009, pp. 1-4.

<sup>18</sup> Leshin, L. et al., "MSL Science Team, Volatile, Isotope and Organic Analysis of Martian Fines with the Mars Curiosity Rover," Science, Vol. 341, 2013, pp. 1-9.

<sup>19</sup> Hecht, M.H. et al., "Detection of Perchlorate and the Soluble Chemistry of Martian Soil at The Phoenix Lander Site," Science, Vol. 325, 2009, pp. 64-67.

<sup>20</sup> Navarro-Gonzalez, R., Vargas, E. de la Rosa, J., Raga, A.C., and McKay, C.P., "Reanalysis of the Viking Results Suggests Perchlorate and Organics at Midlatitudes on Mars," J Geophys Res., Vol. 115, 2010, pp. 1-11.

<sup>21</sup> Navarro-Gonzalez, R., Vargas, E. de la Rosa, J., Raga, A.C., and McKay, C.P., "Correction to Reanalysis of the Viking Results Suggests Perchlorate and Organics at Midlatitudes on Mars," J Geophys Res., Vol. 116, 2011, pp. 1-2.

<sup>22</sup> Keller, J.M. et al., "Equatorial and Midlatitude Distribution of Chlorine Measured by Mars Odyssey GRS," J Geophys. Res., Vol. 111, Issue E3, 2006, pp. 1-18.

<sup>23</sup> Feldman, W.C. et al., "Global Distribution of Near-Surface Hydrogen on Mars," J Geophys. Res., Vol. 109, Issue E9, 2004, pp. 1-13

<sup>24</sup> Archer, P.D. et al., "Abundances and Implications of Volatile-Bearing Species from Evolved Gas Analysis of the Rocknest Aeolian Deposit, Gale Crater, Mars," J. Geophys. Res.: Planets, Vol. 119, 2014, pp. 237-254.

<sup>25</sup> Wadsworth, J. and Cockell, C. S., "Perchlorates on Mars Enhance the Bactericidal Effects of UV Light," Scientific Reports, Vol 7, published online July 7, 2017, https://www.nature.com/articles/s41598-017-04910-3 [cited 4 February 2020].

<sup>26</sup> Quinn, R. C., Martucci, H. F. H., Miler, S. R., Bryson, C. E., Grunthaner, F. J., and Grunthaner, P. J., "Perchlorate Radiolysis on Mars and the Origin of Martian Soil Reactivity," Astrobiology, Vol. 13, No. 6, 2013, pp. 515-520.

<sup>27</sup> Martucci, H.F.H., "Characterization of Perchlorate Photostability under Simulated Martian Conditions," Proceedings of the. National Conference on Undergraduate Research (NCUR), 2012, pp. 1359-1363.

<sup>28</sup> Georgiou, C.D., Zisimopoulos, D., Kalaitzopoulou, E., and Quinn, R.C., "Radiation-Driven Formation of Reactive Oxygen Species in Oxychlorine-Containing Mars Surface Analogues," Astrobiology, Vol. 17, No. 4, 2017, pp. 319-336.

<sup>29</sup> Lasne, J. et al., "Oxidants at the Surface of Mars: A Review in Light of Recent Exploration Results," Astrobiology, Volume 16, Number 12, 2016, pp. 977-996.

<sup>30</sup>Mars-Bound NASA Rover Carries Coin for Camera Checkup https://www.nasa.gov/mission pages/msl/news/msl20120207.html [cited 6 February 2020].

<sup>31</sup> "1909 Lincoln Cent on Mars in NASA Astronomy Pic of the Day," http://www.coinnews.net/2014/12/12/1909-lincoln-centon-mars-in-nasa-astronomy-pic-of-the-day/ [citeded 5 February 2020].

<sup>32</sup> "Mars Fact Sheet," https://nssdc.gsfc.nasa.gov/planetary/factsheet/marsfact.html, [cited 5 February 2020].

<sup>33</sup> "Curiosity Mars Rover Checks Odd-looking Iron Meteorite." https://www.ipl.nasa.gov/news/news.php?feature=6667 [cited 5 February 20201.

11

International Conference on Environmental Systems

<sup>&</sup>lt;sup>2</sup> "Mars Science Goals, Objectives, Investigations, and Priorities: 2015 Version, Mars Exploration Program Analysis Group (MEPAG), Finalized and Published online: June 19, 2015, Prepared by the MEPAG Goals Committee,

https://mepag.jpl.nasa.gov/reports/MEPAG%20Goals Document 2015\_v18 FINAL.pdf [cited 5 February 2020]. <sup>3</sup> Pourbaix, M., Atlas d'Equilibres Electrochimiques, Gauthier-Villars & Cie, Paris, 1963, p. 171.

<sup>&</sup>lt;sup>5</sup> Vargel, V., *Corrosion of Aluminum*, 1<sup>st</sup> ed., Elsevier, Oxford, 2004.

<sup>36</sup> Steele, A., , "Organic Synthesis on Mars by Electrochemical Reduction of CO<sub>2</sub>," Sci. Adv. Vol 4, No. 10, eaat5118, (2018).
<sup>37</sup> Steele, A. et al., "Naturally Occurring "Batteries" Fueled Organic Carbon Synthesis on Mars," https://carnegiescience.edu/news/naturally-occurring-batteries-fueled-organic-carbon-synthesis-mars [cited 4 February 2020].

<sup>38</sup> Calle, L. M., Li, W., Johansen, M. R., Buhrow, J. W., and Calle, C. I., "Corrosion on Mars: An Investigation under Relevant Simulated Martian Environments," NASA/Technical Publication, 2017-219743, 2017.

<sup>&</sup>lt;sup>34</sup> Schroder, C., Bland, P. A., Golombek, M. P., Ashley, J. W., Warner, N. H., and Grant, J. A., "Amazonian Chemical Weathering Rate Derived from Stony Meteorite Finds at Meridiani Planum on Mars," *Nature Communications*,

<sup>&</sup>lt;sup>35</sup> "NASA Finds Ancient Organic Material, Mysterious Methane on Mars,' https://www.nasa.gov/press-release/nasa-finds-ancient-organic-material-mysterious-methane-on-mars [cited 5 February 2020].