Corrosion Technical Series

NACE Education Presents:

Corrosion Control for Spacecraft

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NACE INTERNATIONAL

Overview

Introduction

- NASA's current plans for space exploration
- What is corrosion
- Requirements for corrosion to occur
- Corrosion control

Spacecraft and aerospace assets unique environments

- Ground
- Space
- Other destinations (Moon and Mars)

Materials Selection

- Materials testing
- Coatings testing, qualification, and development

Summary

Introduction

NASA's Current Plans for Space Exploration
What is Corrosion?
Requirements for Corrosion to Occur
Corrosion Control

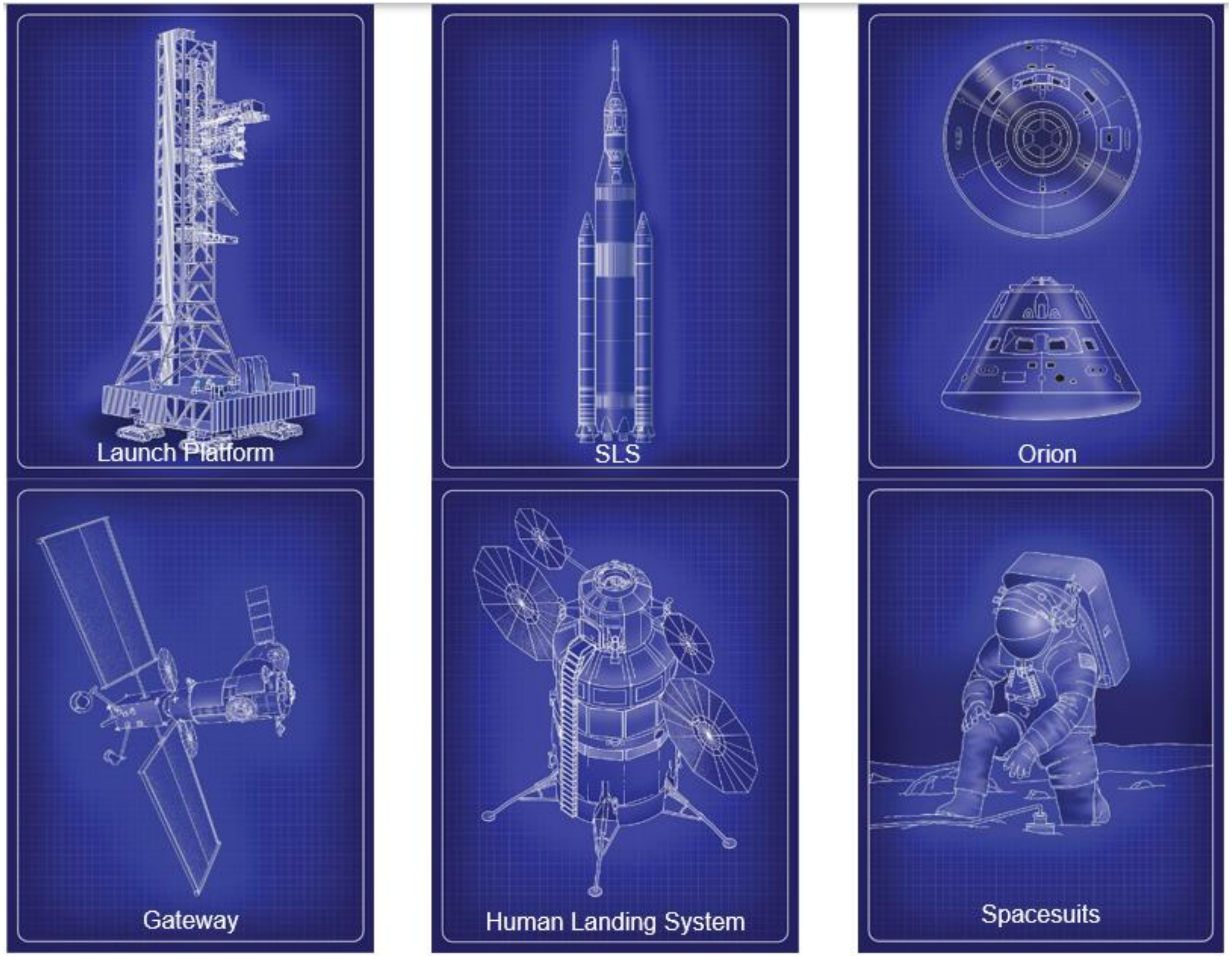
NASA's Current Plans for Space Exploration

https://www.youtube.com/watch?v=vl6jn-DdafM

NASA's Current Plans for Space Exploration

- Artemis is NASA's program with the goal of bringing the first woman and the next man to the moon's south pole in 2024.
- Artemis is the twin sister of Apollo and the goddess of the Moon in Greek mythology.
- NASA is developing the technologies, building the hardware and engineering operations teams that will launch the vehicle that will one day take a crewed ship to Mars.
- The Space Launch System (SLS), the Orion crew module, the lunar landing module, and the Gateway will extend human exploration beyond the Moon.
- All of these vehicular components must be thoroughly tested and qualified to ensure they can withstand their environment.

Artemis Program



What is Corrosion?

The deterioration of a material, usually a metal, or its properties because of reaction with its environment.

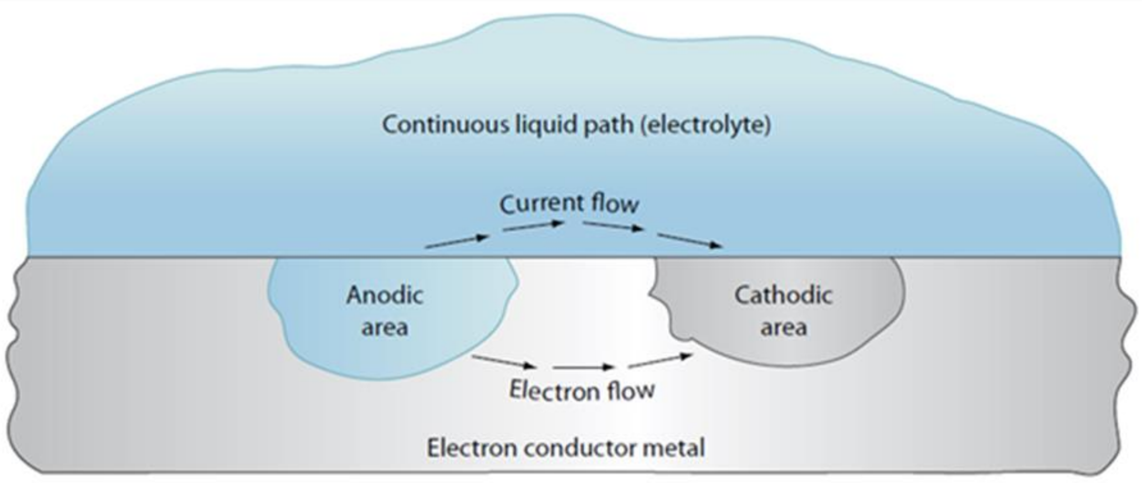


Illustration of the components required for corrosion to take place.[1]

[1] *Aviation Maintenance Technician Handbook (FAA-H-8083-30A), 2018.*

Requirements for Corrosion to Occur

- **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.

Corrosion Control

- Material selection
- Environment
- Coatings
- Design

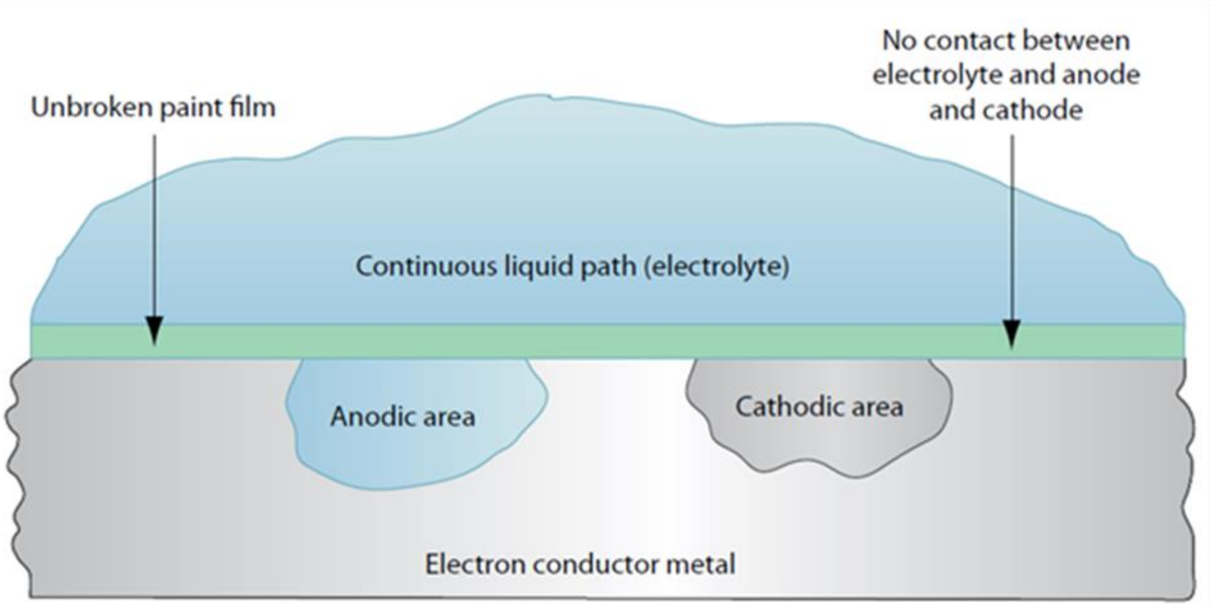


Illustration of a metal covered with a coating for corrosion protection.[1]

Spacecraft Environments

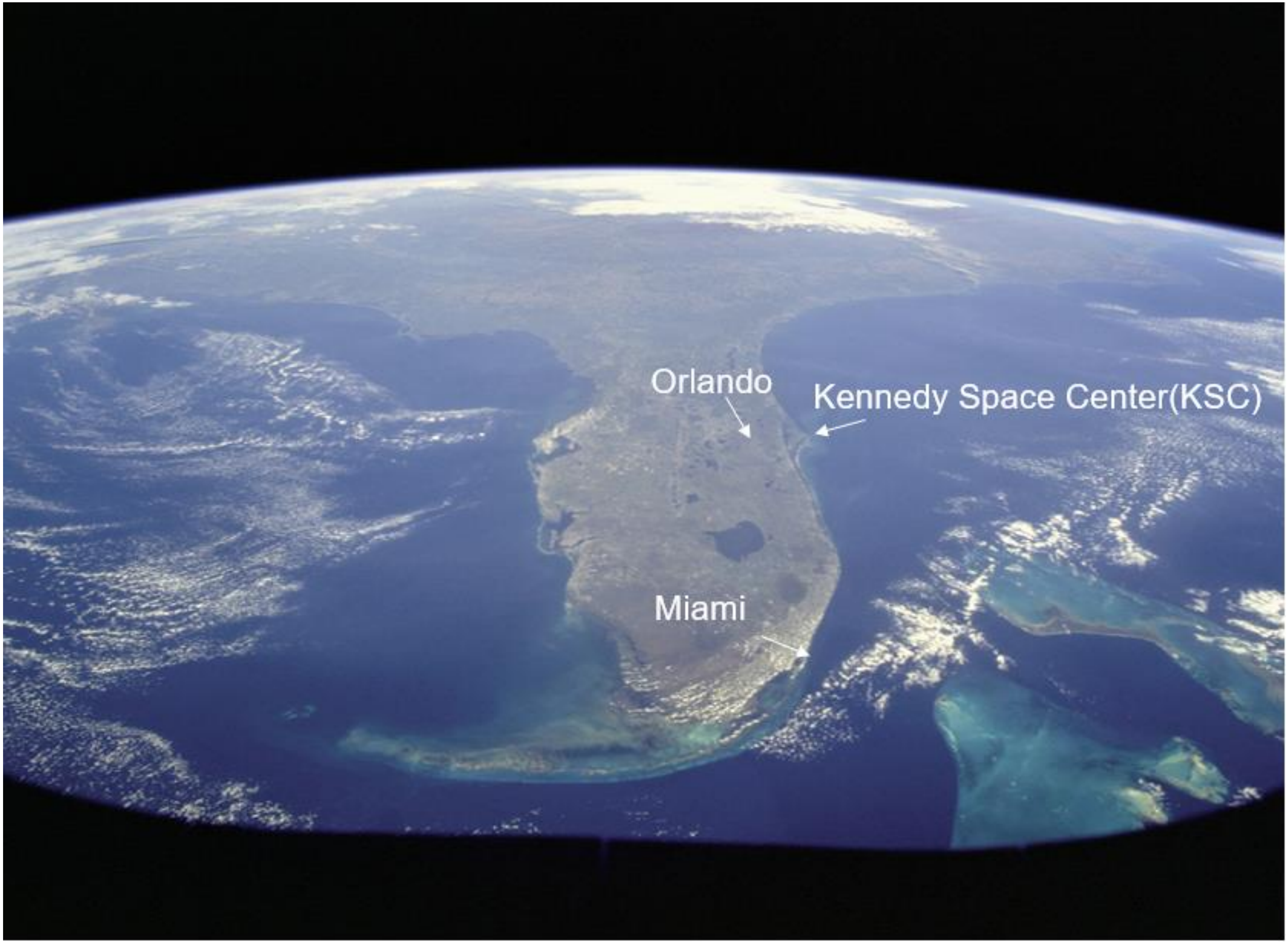
- Earth
- Space
- Other destinations (Moon and Mars)

Spacecraft Corrosive Environments: Earth[2]

- **Class 1**: Exposure to seawater (immersion) environments.
- **Class 2**: Exposure to seacoast (atmospheric) environments.
- **Class 3**: Exposure to inland (≥50 miles from seacoast), outdoor environments.
- **Class 4**: Exposure to potentially corrosive chemical systems or microbial induced corrosion.
- **Class 5**: Exposure to indoor/uncontrolled humidity environments.
- **Class 6**: Continuous and exclusive exposure to temperature- and humidity-controlled (non-condensing) environments, such as clean room, dry air, and nitrogen-purged environments (maximum humidity 65 percent).

[2]*NASA-STD-6012, Corrosion Protection For Space Flight Hardware, 03/08/2012.*

KSC Natural Launch Environment



Space Shuttle Launch Pad (39 B)

SLS-ready 39B launch pad

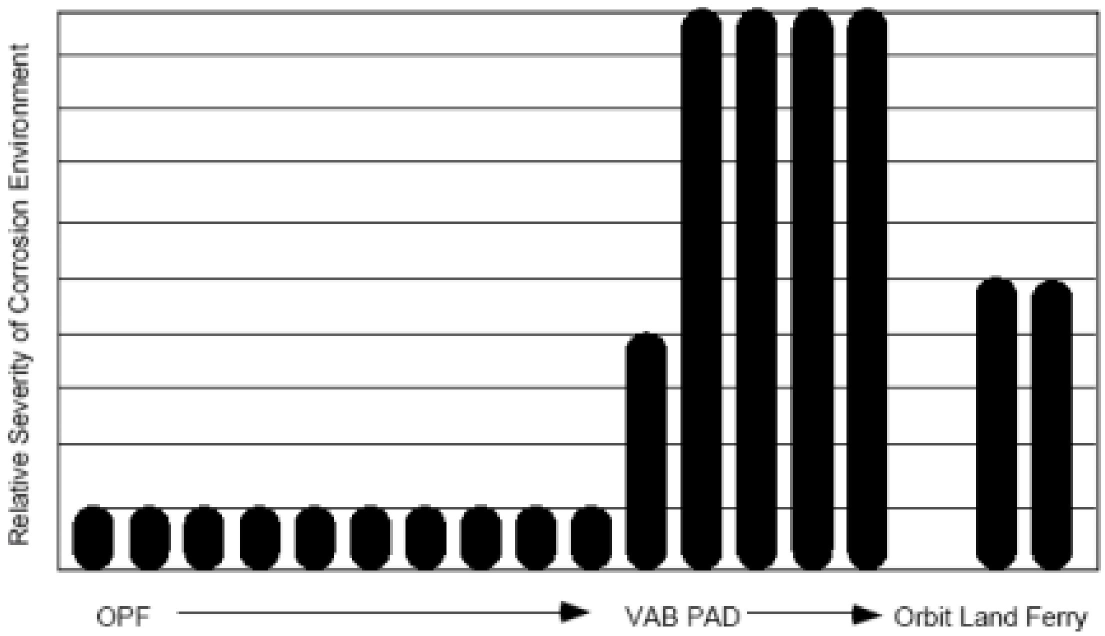
Orbiter Environmental Conditions

- Normal operating environment - temperature and humidity controlled
- Exposed to salt spray at the launch pad (30-90 days)

In reality, flight delays usually extend. For example, Columbia spent 166 days at the launch pad before its tenth flight. High humidity led to condensation that would leave behind salt residues.

- Post landing - exposed to external environments and fluids from de-servicing after landing
- Ferry flight - water intrusion

Orbiter Environmental Conditions



FERRY

Orbiter preparation facility (OPF)

Vehicle Assembly Building (VAB)

PAD

LAND

One of the challenges for space exploration is that equipment must withstand drastic conditions, from the heat of rocket exhaust to extreme cold in space. Surprisingly, one of the most destructive forces is the corrosive effect of saltwater-laden ocean spray and fog. It rusts launch structures and equipment at the Kennedy Space Center.

Natural Salt Fog Chamber

KSC Launch Pad Environment

The launch environment at KSC is extremely corrosive:

- Ocean salt spray
- Heat
- Humidity
- Sunlight
- Acidic exhaust from SRBs

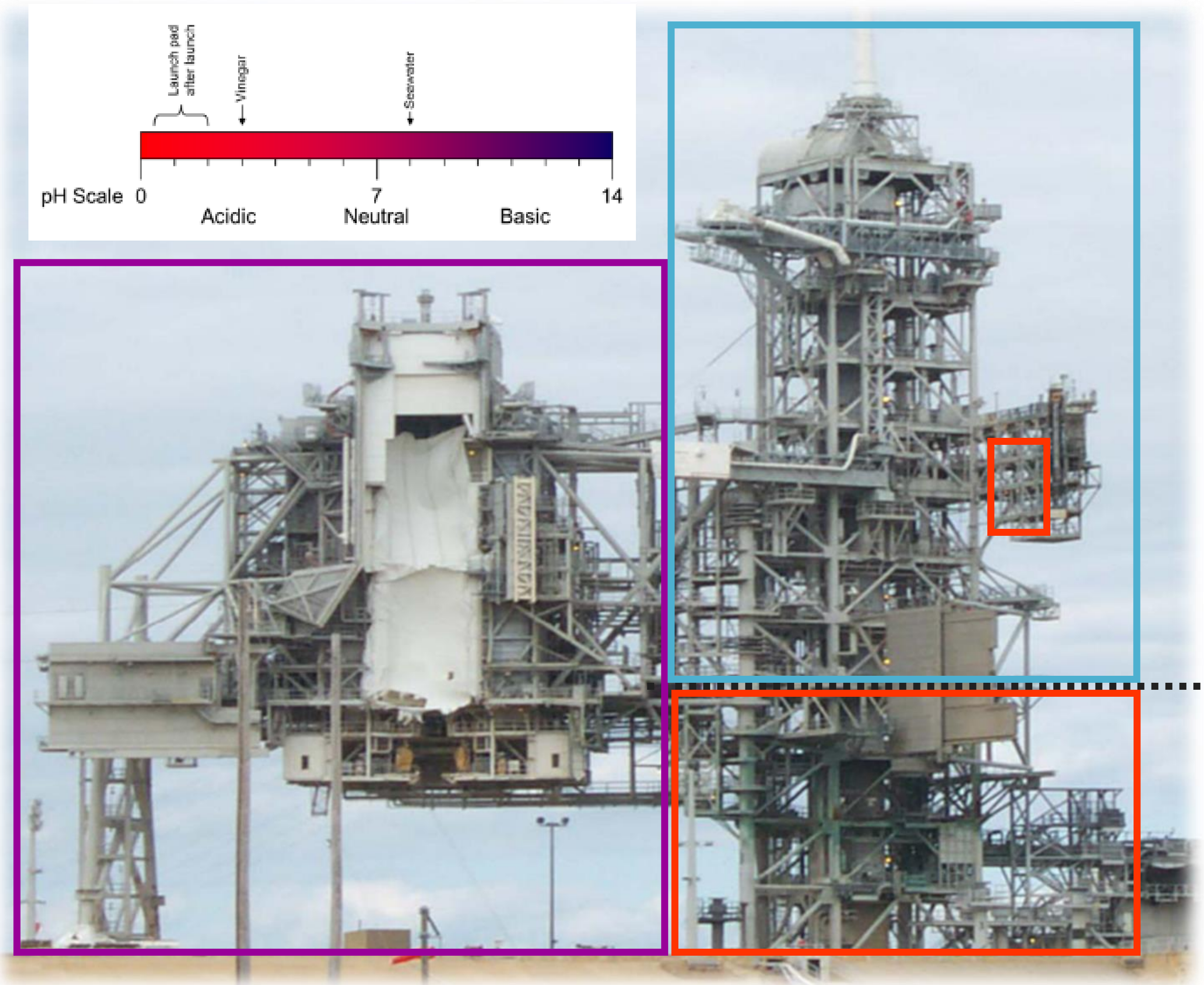
Space Shuttle Launch Environment

In 1981 the Space Shuttle introduced acidic deposition (70 tons of HCl) products. NASA plans to use Shuttle-derived SRB rockets in future missions.

SRB Exhaust

$$NH_4ClO_4(s) + Al(s) \xrightarrow{binder,\ Fe_2O_3} Al_2O_3(s) + HCl(g) + H_2O(g) + NO_x(g)$$

Launch Complex 39 pH Values after a Space Shuttle Launch



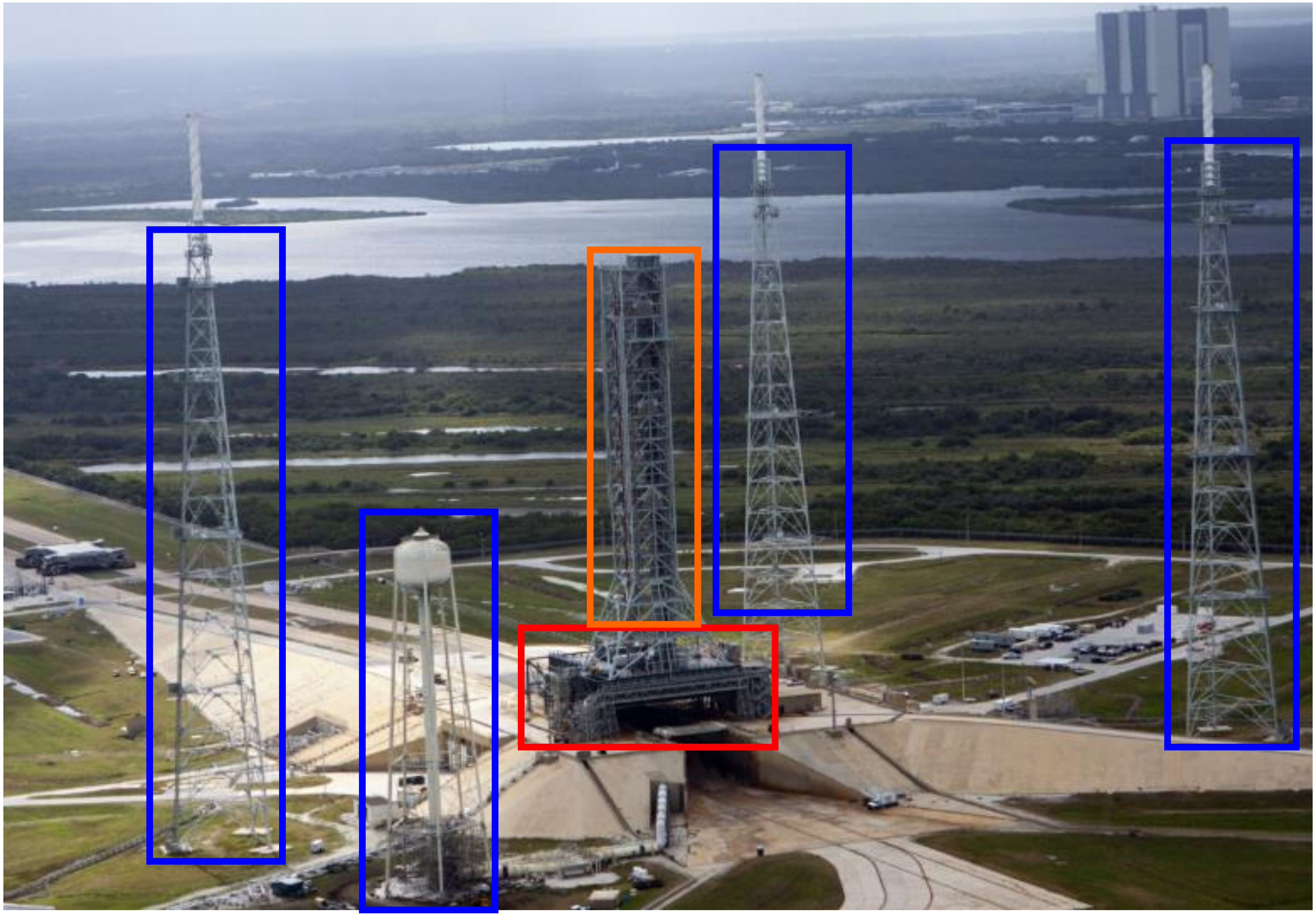
Zone 3: pH ~2-3

Zone 2: pH ~ 2-3

FSS 115" Level

Zone 1: pH ~ 0-1

Exposure Zones on New Launch Complex 39B



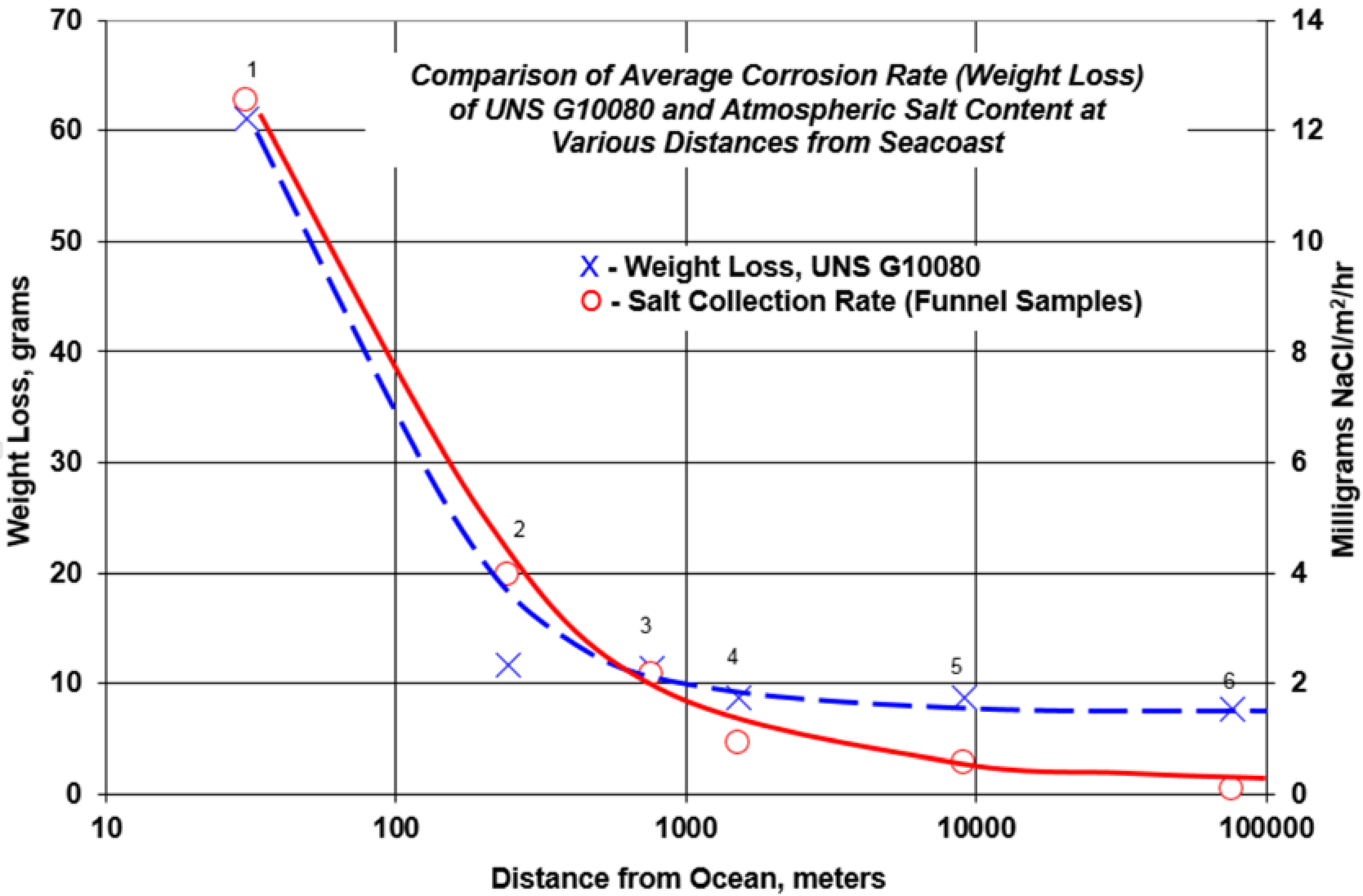
ZONE 3
pH-2-3

ZONE 2
pH 2-3

ZONE 1
pH 0-1

Zone 1: Direct or indirect impingement by SRB exhaust; Zone 2: Elevated temperatures and acid deposition; Zone 3: Acid exposure or other types of chemical contamination

Changes in Corrosion Rate with Distance from the Ocean



Coatings

Coating Systems at KSC
Coatings Testing and Qualification
- NASA's Protective Coatings Standard
- NASA-STD-5008B

Coating Systems at KSC

- **Inorganic zinc is the primary coating used to protect carbon steel at the Kennedy Space Center.**
  - **Hot Dipped Galvanizing (HDG)**
  - **Thermal Spray (TSC)**
  - **Zinc-rich Coating**
- **Ordinarily, inorganic zinc is not top-coated, but there are exceptions:**
  - **Areas that are exposed to highly acidic effluent**
  - **Specialized systems such as cryogenic tanks**

NASA's Protective Coatings Standard NASA-STD-5008B

Purpose

- To establish uniform engineering practices across NASA programs
- To provide a design standard for the development of specifications and requirements for
  - Safety
  - Materials
  - Equipment
  - Procedures
  - Quality assurance inspections
  - Provide and maintain a qualified products list

Preparation of Test Panels

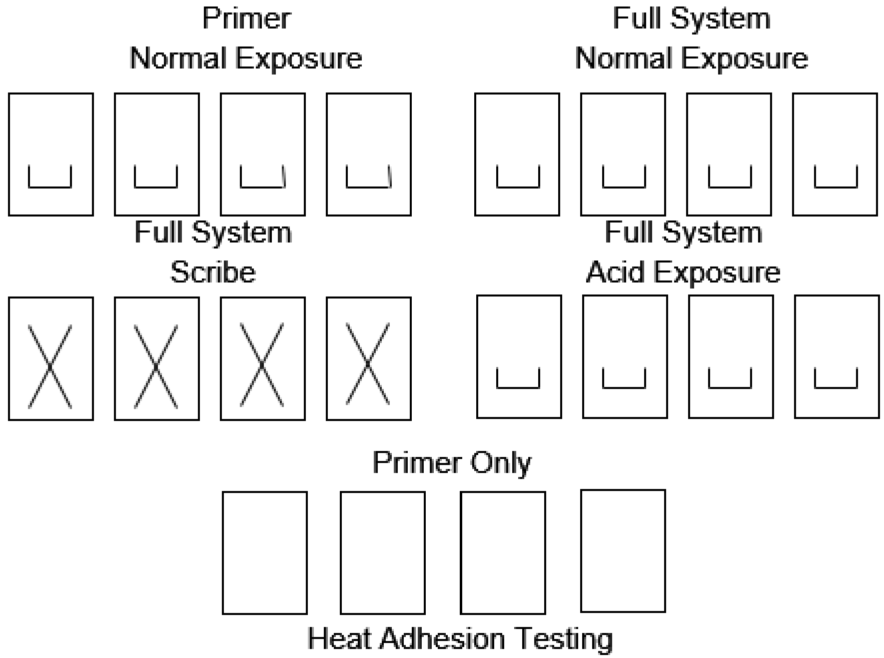
- Standard AISI M1020 carbon steel test coupons
  - Two types: composite and flat panel
- Surface cleanliness & roughness of coupons
  - Inspected, measured, and documented before application of primer

Composite Panel

Flat Panel

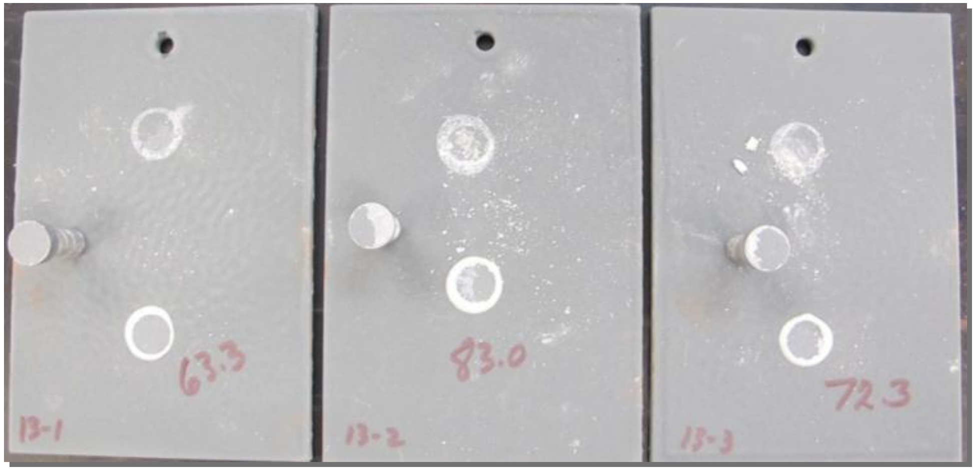
Test Matrix

- 4 composite primer only (normal conditions)
- 4 composite top coated (normal conditions)
- 4 composite top coated (acid conditions)
- 4 flat top coated (scribe test – normal conditions)
- 4 flat primer only (to measure heat resistance/adhesion)



Adhesion

- Adhesion is a pass/fail criterion
- Tensile adhesion testing is performed via ASTM D 4541, "Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers"
- Tensile adhesion values are determined for cured panels. The panels are placed in an oven at 400 °C for 24 hours and retested
  - ➢ Any deterioration such as charring or burning is a means for disqualification
  - ➢ Loss of adhesion after heating is a means for disqualification



Coating system qualified for use

Atmospheric Exposure Testing

KSC Atmospheric Exposure Test Site

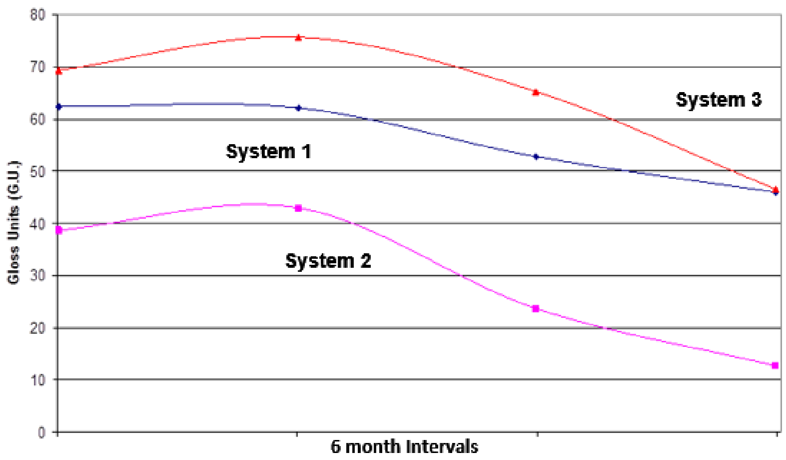
Atmospheric Exposure Testing

Atmospheric exposure testing at the beach and near the launch pads at NASA's Kennedy Space Center

Gloss

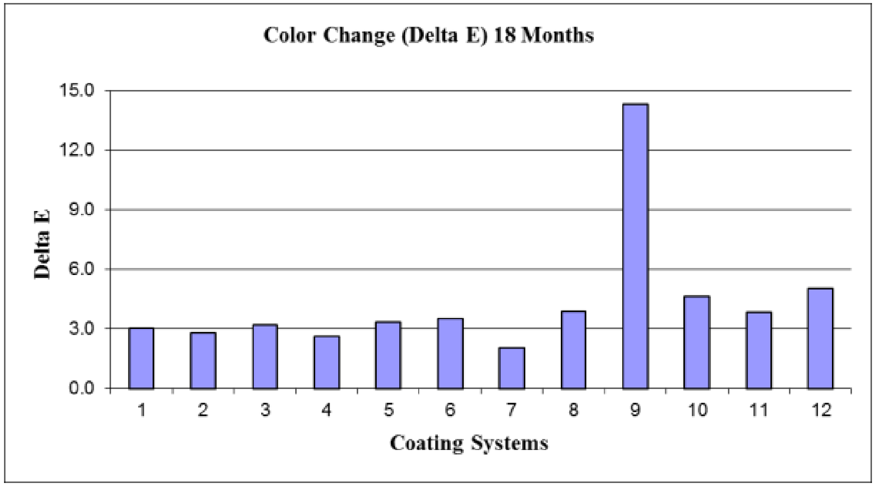
- Gloss is not a pass/fail criterion
- Gloss values are important for aesthetic qualities
- A reduction in gloss may indicate degradation to the coating
- Gloss measurements are performed with a portable gloss meter according to ASTM D523, "Standard Test Method for Specular Gloss"

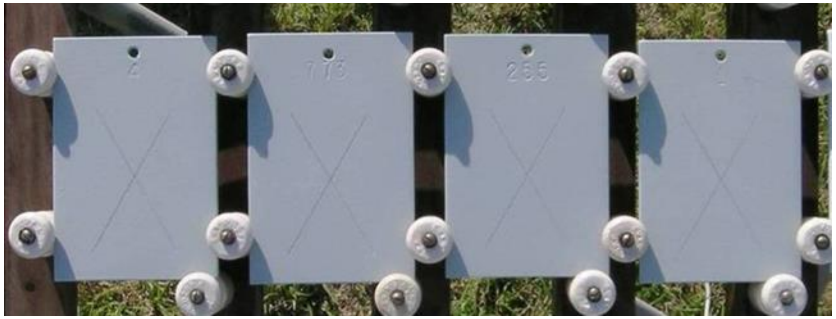
Average Gloss			
System	Initial	18 Month	Gloss Retention
1	62	46	74%
2	39	13	33%
3	69	47	67%



Color

- Color is not a pass/fail criterion
- Color can be important for aesthetic and safety qualities
- A change in color may indicate degradation to the coating
- Change in color is calculated via ASTM E308, “Standard Practice for Computing Colors of Objects by Using the CIE System”



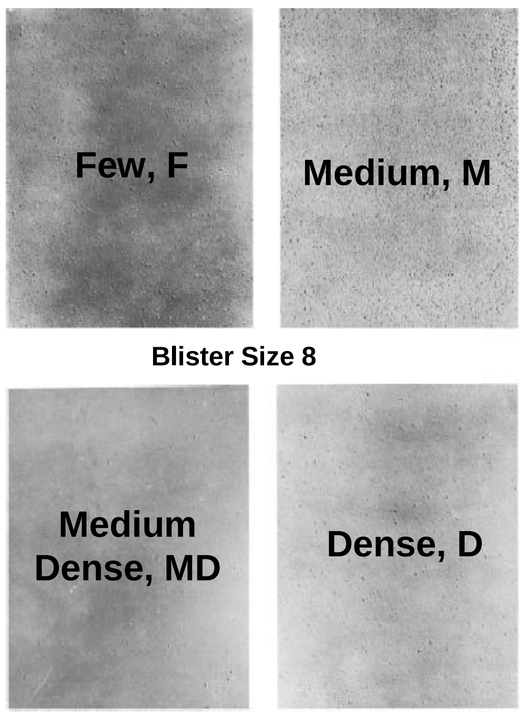


System 9 – Initial Condition

System 9 – 18 Month Condition

Blistering

- Blistering is a pass/fail Criterion
- Blistering is determined via pictorial examples in ASTM D714, “Standard Test Method for Evaluating Degree of Blistering of Paints”
- According to NASA-STD-5008B, a rating of 9F is required to gain acceptance and final approval.

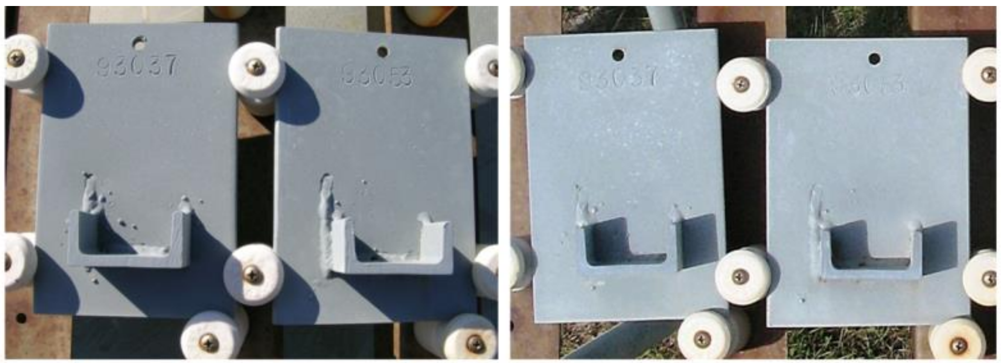


ASTM D714 Pictorial Example for Size 8 Blisters

Blistering of Acrylic Topcoat over Inorganic Zinc

Corrosion under Paint

- Corrosion under paint is a pass/fail Criterion
- Acid rinsed and non acid rinsed are evaluated by this method
- Corrosion Under Paint is determined via pictorial examples in ASTM D610, “Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surface”
- According to NASA-STD-5008B, a rating of 8 (>0.03% to 0.1% rusted for aliphatic polyurethane, water reducible, and polysiloxane topcoats) or 9 (>0.01% to 0.03% rusted for inorganic zinc).

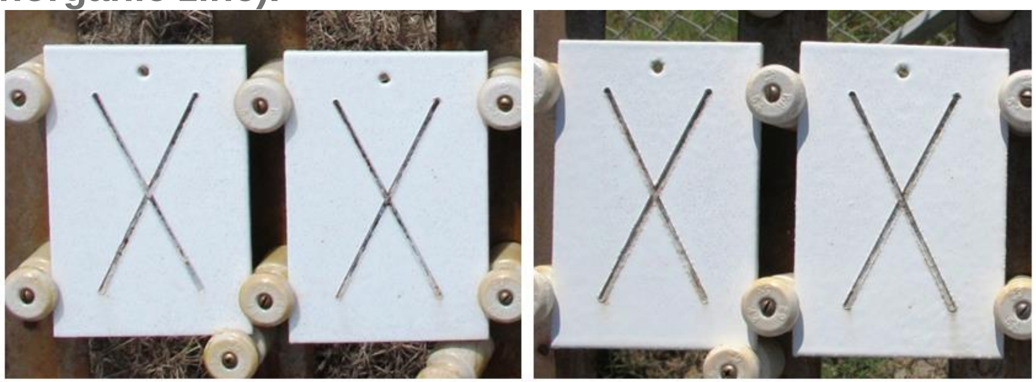


18 month and 60 month exposure – Approved for Use

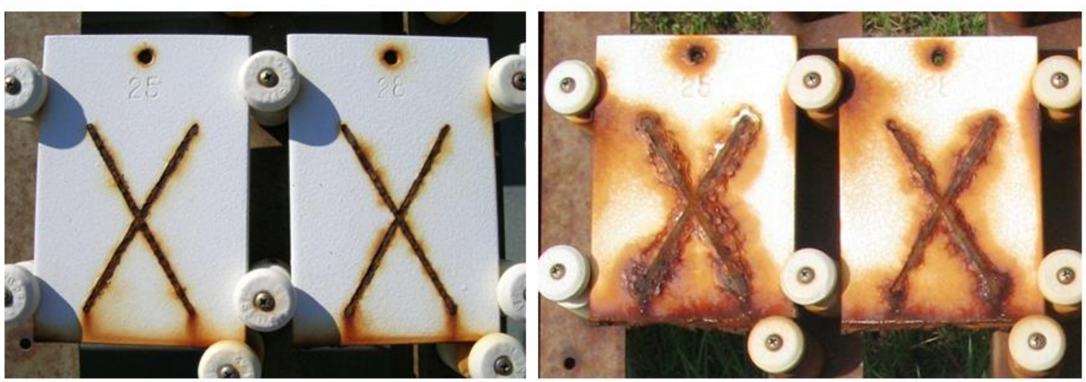
18 month and 60 month exposure – Not Approved for Use

Corrosion from the Scribe

- Corrosion from the Scribe is a pass fail criterion
- These panels are not acid rinsed
- Corrosion from the Scribe is determined via measurements of creep from the scribed region according to ASTM D1654, “Standard Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments”
- According to NASA-STD-5008B, a rating of 8 (mean creep > 0.5 mm to 1.0 mm for aliphatic polyurethane, water reducible, and polysiloxane topcoats) or 9 (mean creep > 0.0 mm to 0.05 mm for inorganic zinc).



18 month and 60 month exposure – Approved for use



18 month and 60 month exposure – Not approved for use

Summary

NASA conducts its space launch and exploration operations in environments that are unique in terms of corrosion.

The methodology used to test and qualify coatings for ground operations is based on NASA-STD-5008B standard:

- **Adhesion before and after heating (Criterion for passing or failing)**
- **Color after atmospheric testing (Not a criterion for passing or failing)**
- **Gloss after atmospheric testing(Not a criterion for passing or failing)**
- **Blistering (Criterion for passing or failing)**
- **Corrosion under the coating (Criterion for passing or failing)**
- **Corrosion from the scribe (Criterion for passing or failing)**
- **Examples of coating failures and successes according to the requirements were shown**

Aerospace Materials and Coatings

Space environment
Corrosion in space
Materials testing for space

Space Environment

The Space Environment is characterized by:

- Low pressure (vacuum)
- Atomic oxygen (causes erosion of materials)
- Ultraviolet (UV) radiation
- Charged particles
- Temperature extremes
- Electromagnetic radiation
- Micrometeoroids
- Human-made debris

Interaction between Materials and Atomic Oxygen

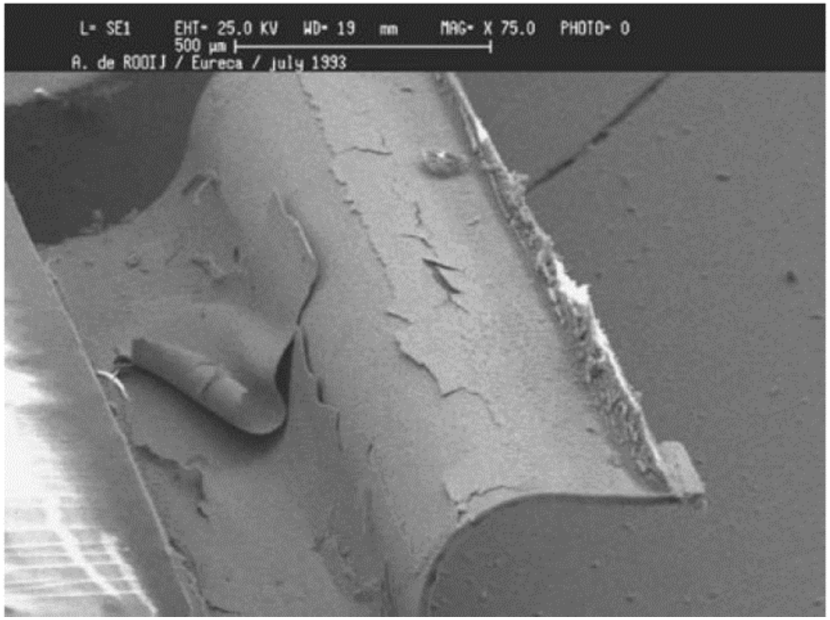
Interaction of the Space Shuttle with the upper atmosphere creates a corona seen at night (right photo), in part, due to atomic oxygen.

In the upper reaches of the atmosphere, about 200-500 miles (322-805 km), oxygen molecules are decomposed from O_2 into two separate oxygen atoms. This form of elemental oxygen (atomic oxygen) is highly reactive and exposes a spacecraft to corrosion that shortens its life. While developing methods to prevent damage from atomic oxygen, it was discovered that it could also remove layers of soot or other organic material from a surface. Atomic oxygen will not react with oxides, so most paint pigments will not be affected by the reaction.

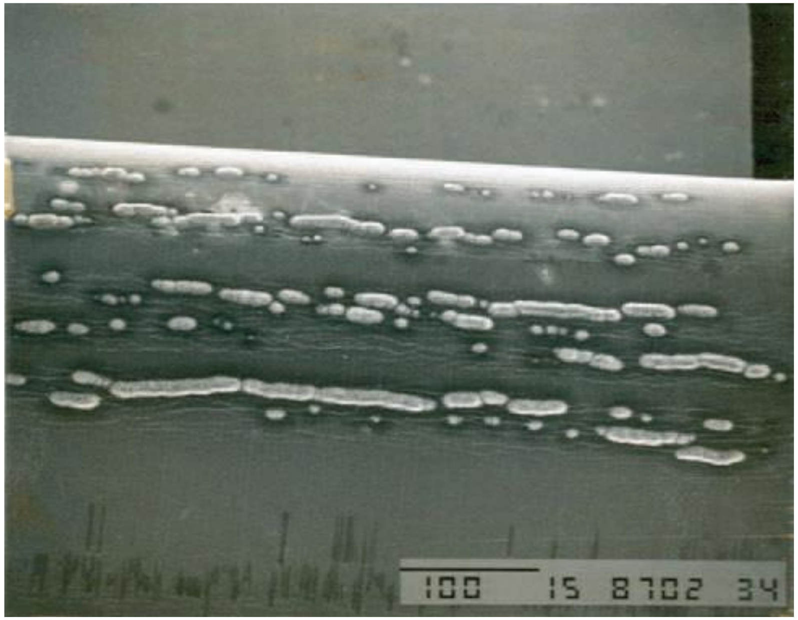
International Space Station Technology – Benefits Fine Art

The left photo was taken after the Cleveland Museum of Art's staff attempted to clean and restore it using acetone and methylene chloride. The right photo is after cleaning by the atomic oxygen technique.

Corrosion Caused by Atomic Oxygen

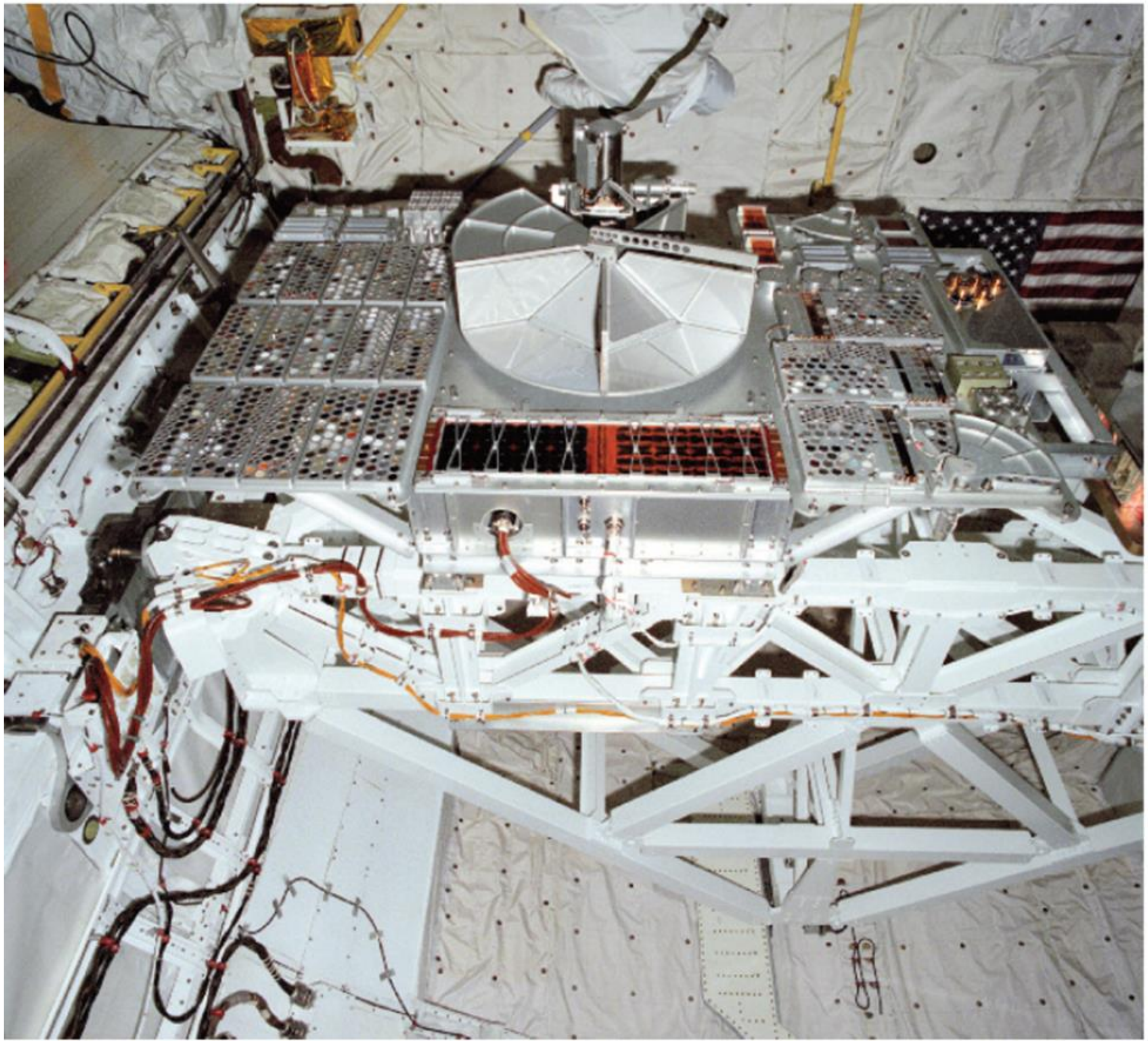


Silver interconnector in a solar cell in Eureca



Silver covered with gold where you see the formation of silver oxide caused by atomic oxygen in coating defects

EURECA was a mission of ESA (August 1992 - July 1993). Its main objective was the study of environmental effects on the spacecraft. Image credit: ESA

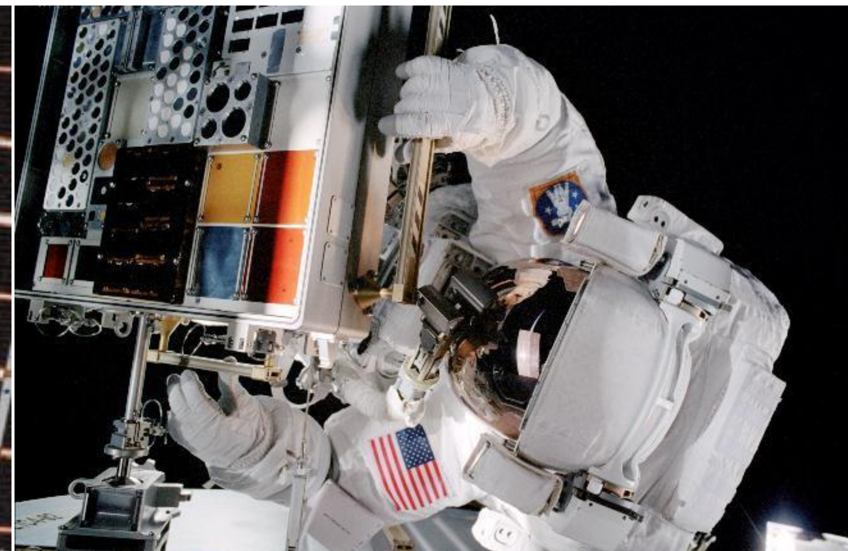


Evaluation of atomic oxygen interaction with Materials III flight experiment in the Orbiter payload bay of STS-46 (1992). Material exposure samples are located on both sides of the mass spectrometer gas evolution measurement assembly in the center.

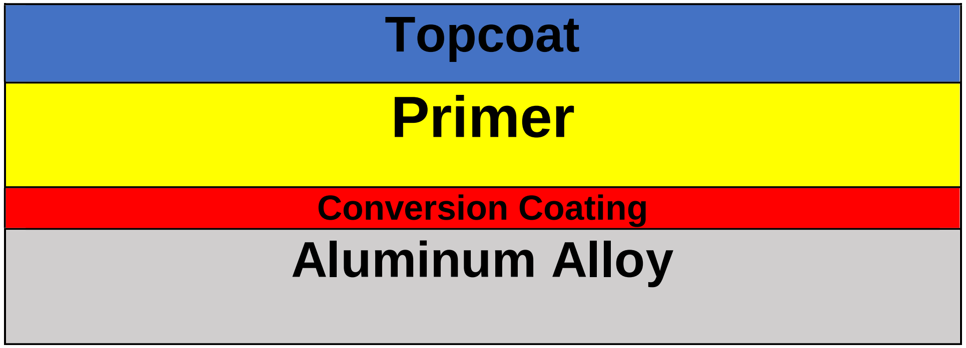
Materials Testing for Space

Materials are tested on the exterior of the International Space Station. The payload container is mounted so one side faces the Earth and the other faces space. The experiments provide a better understanding of material durability, from coatings to electronic sensors, which could be applied to future spacecraft designs.

NASA astronaut Patrick G. Forrester installs exposure experiments designed to collect information on how different materials weather in the environment of space



NASA astronaut Andrew Feustel retrieves long duration materials exposure experiments before installing others during a spacewalk on May 20, 2011.



Schematic of a typical multi-coating system used to protect aluminum

- The conversion coating provides the first layer of corrosion protection and acts as a base for improved adhesion to the primer
- Chromate and chromate-phosphate-based conversion coatings have been used for this purpose for several decades, as they are effective in inhibiting the corrosion of aluminum alloys
- However, the use of chromium-containing chemicals has been limited because of harmful carcinogenic effects, and intense research efforts are in progress to find alternatives

Environmental Regulations Influence Coating Development

- Environmental regulations are progressively stricter and are motivating the coating industry to remove many corrosion-protective coatings that are harmful to humans and the environment.
- These regulations also motivate the development of new technologies for corrosion protection.

Examples:

- Smart coatings
- Water-based coatings
- Coatings with a reduced content of volatile organic compounds (VOCs)

Design Considerations (Materials)

- Most of the orbiter structure is aluminum
- Corrosion protection was based on having no failures due to corrosion with a 10-year or 100-mission life (actually, 30 years and 135 missions)
- All materials were tested for corrosion resistance using methods available at the time
- In general, all aluminum used in structural applications was required to be conversion coated or anodized and coated with a chromated epoxy primer (Koropon)
- The use of galvanic couples (dissimilar metals in contact with one another) was avoided unless suitably protected against corrosion
- All fasteners had to be installed with wet epoxy. The epoxy of choice was a hexavalent chromium primer under the brand name Super Koropon

Coatings on Orion Spacecraft

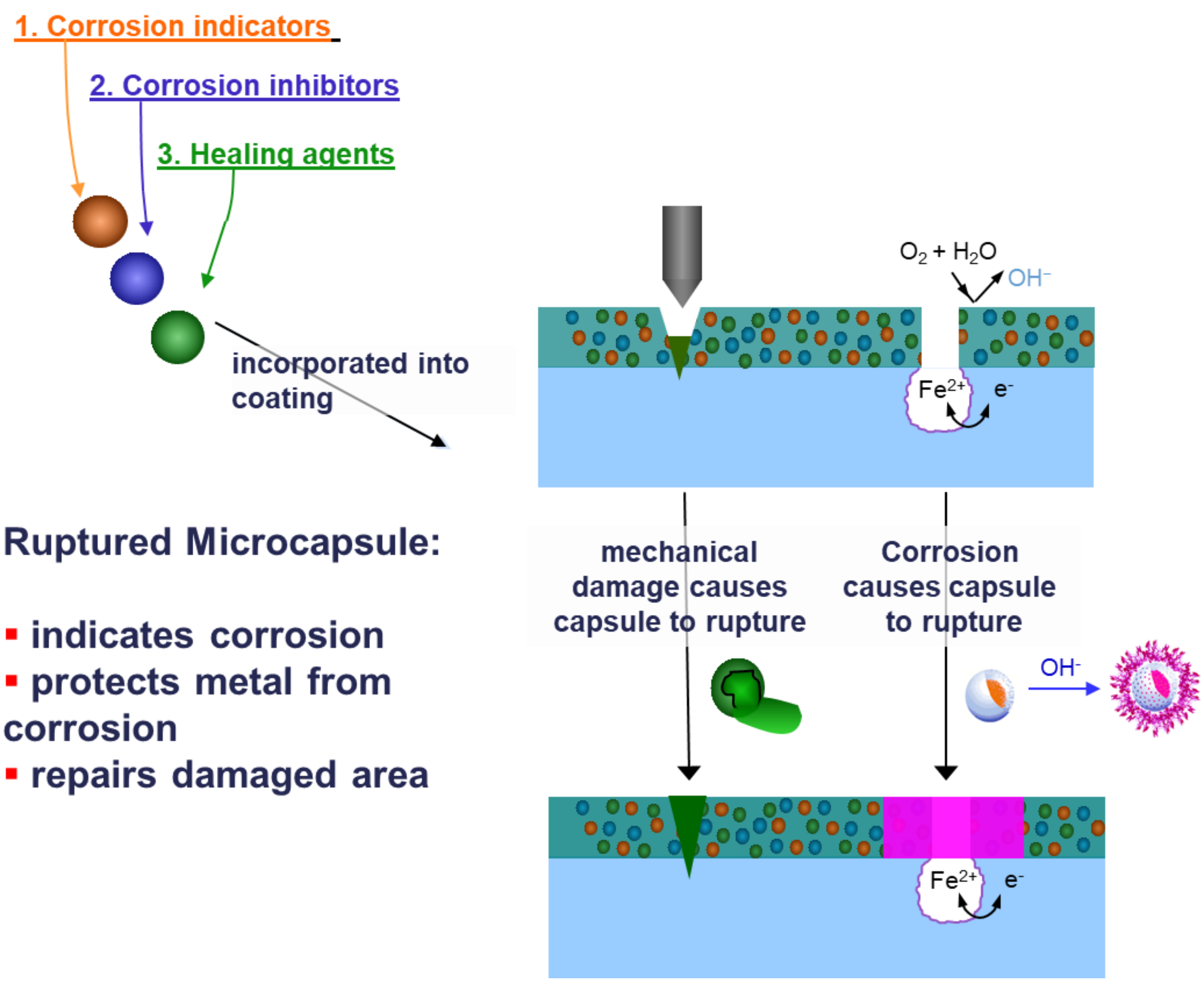
Corrosion protection coating on aluminum lithium alloy (left) and heat shield (right). The heat shield protects the spacecraft from temperatures reaching 4000 degrees Fahrenheit (2204 ºC)

Orion Heat Shield

Textron technicians apply the Avcoat material by “gunning” the material into each of the 330,000 individual cells of the honeycomb structure

Smart Coatings for Corrosion Control

- The use of "smart coatings" for corrosion sensing and control relies on the changes that occur when a material degrades as a result of its interaction with a corrosive environment.
- Such transformations can be used for detecting and repairing corrosion damage.
- We developed a smart coating technology that can detect and repair corrosion at an early stage.
- This technology is based on pH-sensitive microcontainers that deliver the contents of their core when corrosion starts to:
  - Detect and indicate the corrosion location
  - Deliver environmentally friendly corrosion inhibitors
  - Deliver healing agents to repair mechanical coating damage



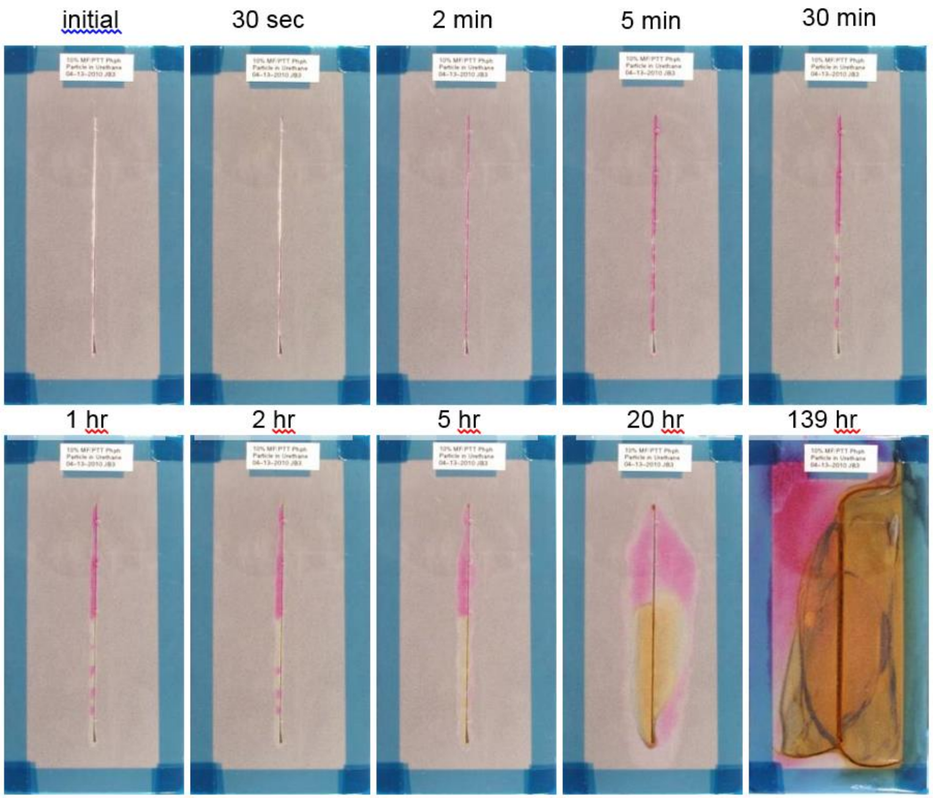
Ruptured Microcapsule:

- indicates corrosion
- protects metal from corrosion
- repairs damaged area

Corrosion and pH

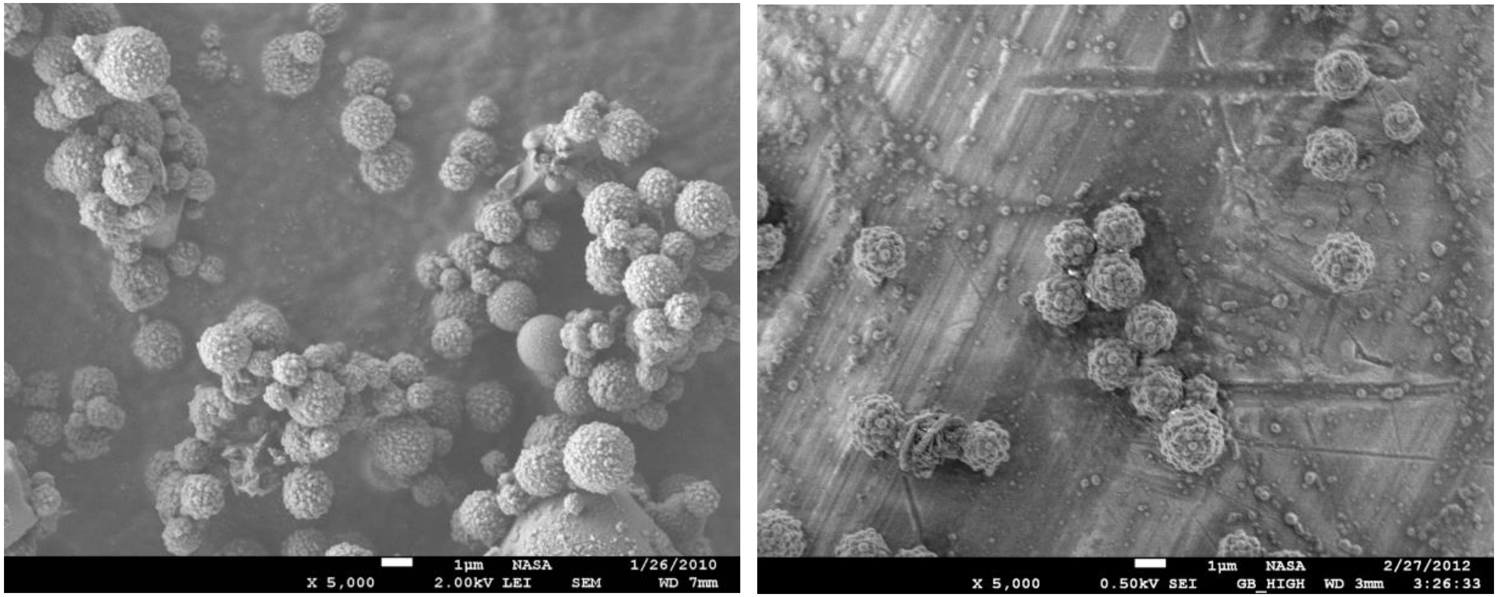
Corrosion Indication Test Results

- Results from a salt immersion test of steel panels coated with a clear urethane coating blended with 10 wt% of phenolphthalein encapsulated into micro-particles.
- The panels were scribed and observed visually to detect the color changes associated with the onset of corrosion on the scribe versus exposure time.
- The onset of corrosion was visible in the scribe in less than 30 seconds after immersion, which is considerably earlier than the 2 hours it takes for the typical color of rust to appear.



Corrosion indication test results

Micro-particles for Corrosion Indication



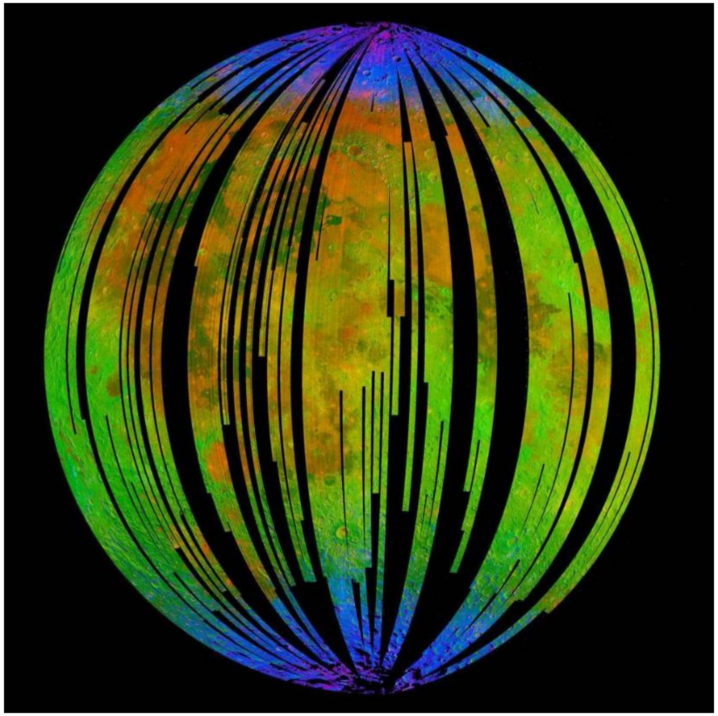
SEM image of indicator micro-particles with color changing indicator phenolphthalein (left) and with fluorescent indicator fluorescein (right)

Corrosion at other Destinations

Corrosion on the Moon?
Corrosion on Mars

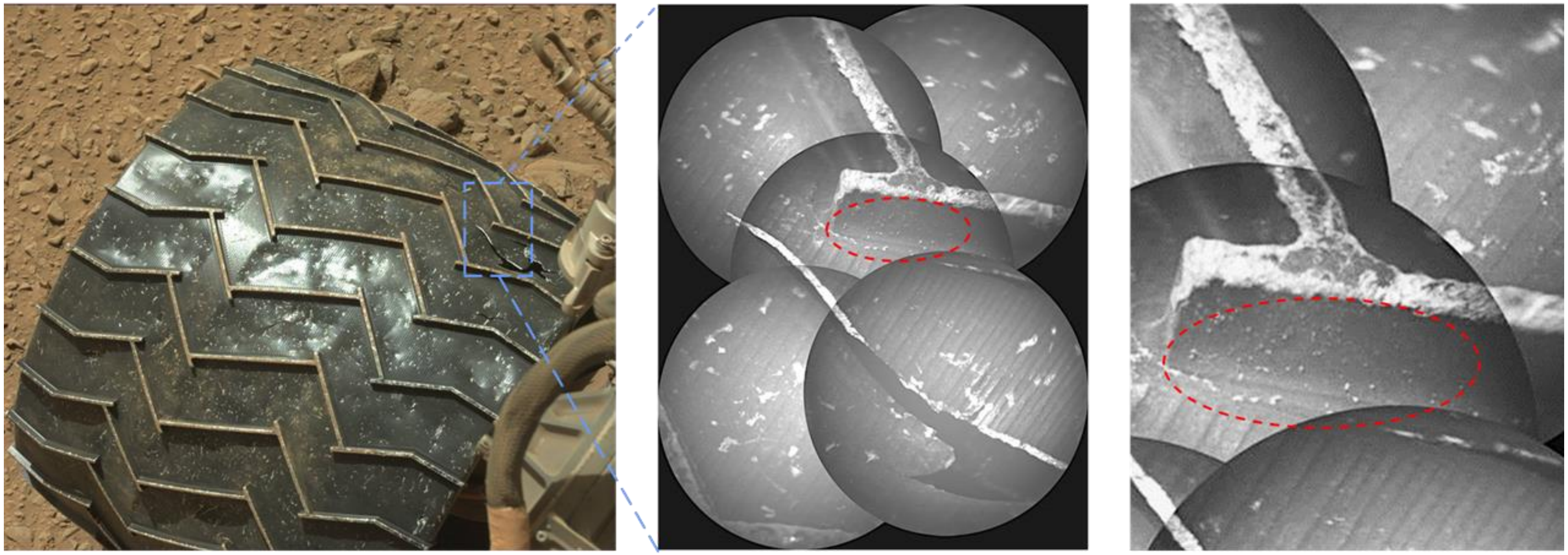
Corrosion on the Moon?

- The blue areas in this composite image from the Moon Mineralogy Mapper (M3) aboard the Indian Space Research Organization's Chandrayaan-1 orbiter show water concentrated at the Moon's poles. Homing in on the spectra of rocks there, researchers found signs of hematite (Fe_2O_3), a form of rust.
- So far there is no explanation for the presence of hematite on the Moon since there is no oxygen on the Moon.
- It has been hypothesized that trace amounts of oxygen from the Earth reach the Moon.



Credits: ISRO/NASA/JPL-Caltech/Brown University/USGS

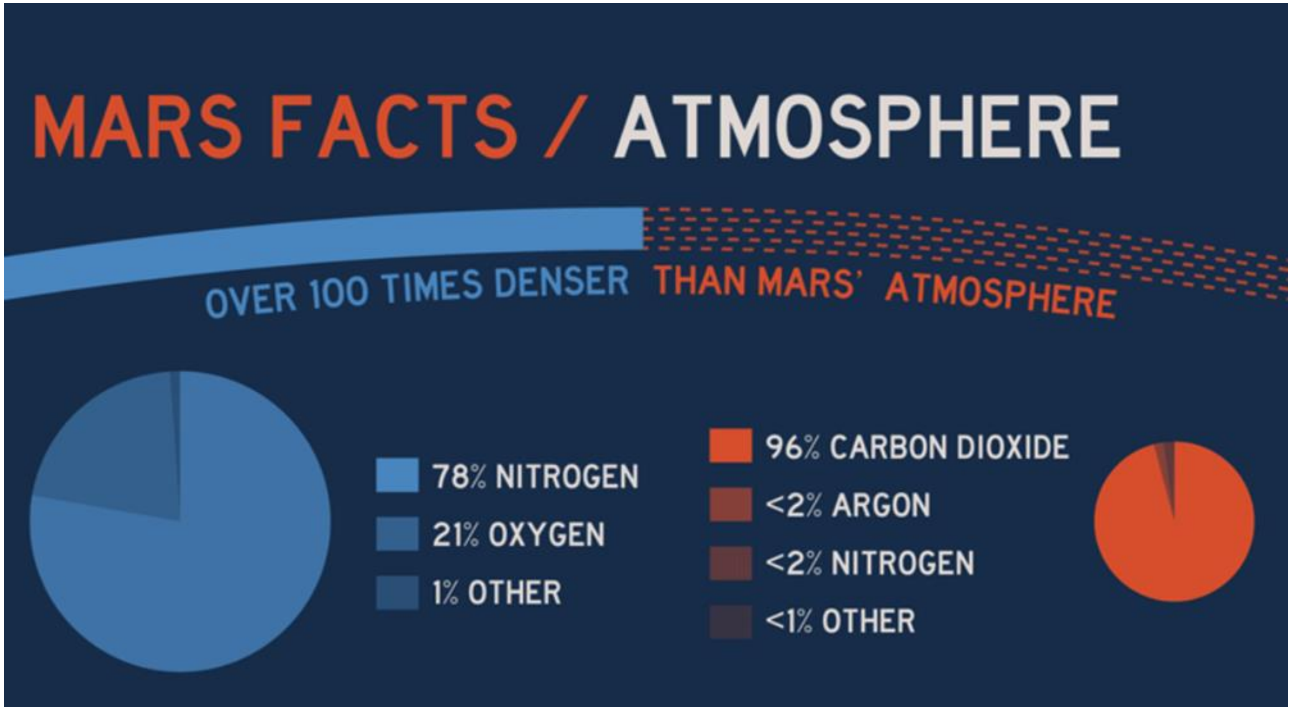
Corrosion on Mars?



Curiosity's ChemCam images of the rover’s middle right-wheel. The image shows a large crack attributed to rock scratching, and some sub-millimeter-sized blisters in the vertical wall of the T-print that can not be explained in terms of mechanical damage. It has been suggested that it’s due to the corrosive interaction between transient brines and the aluminum alloy.[3]

[3]*F. J. Martin-Torres, et al., Transient liquid water and water activity at Gale crater on Mars, Nature Geoscience 8, 357-361 (May 2015).*

Mars Atmosphere

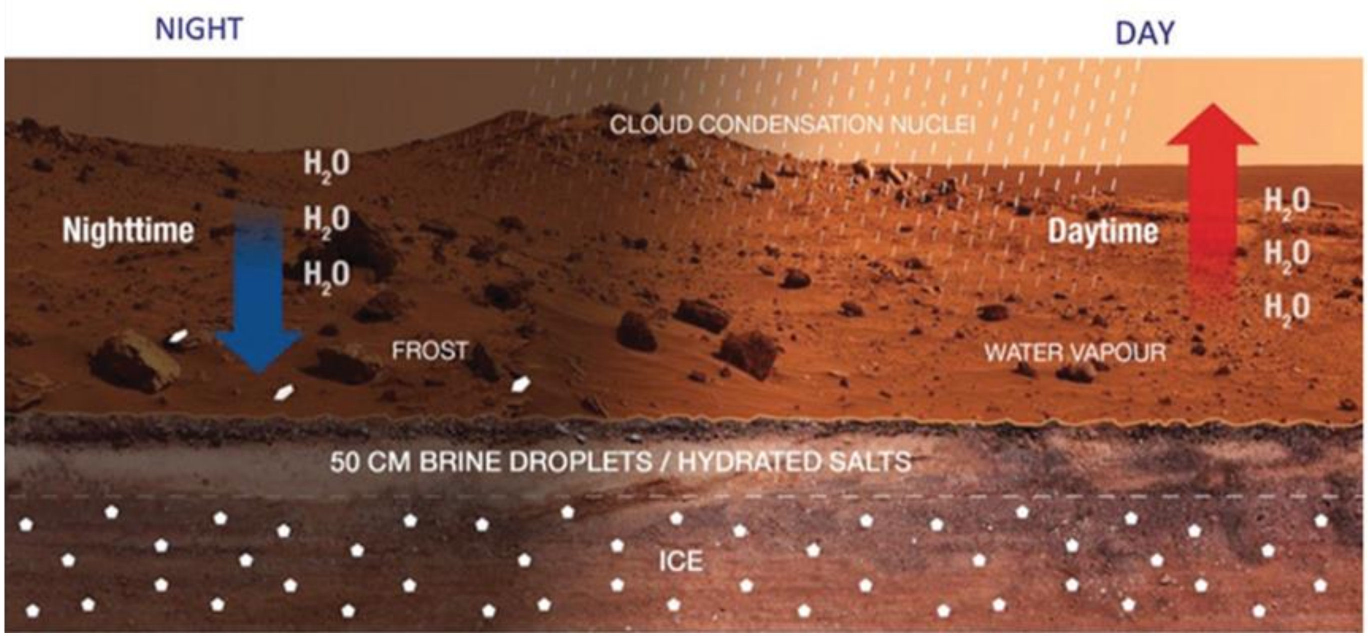


Earth's atmosphere (blue) in comparison with that of Mars (red)

The Mars Environment:

- Particle and radiation environment
- Chemical composition of atmosphere
- Chemical composition of dust/Soil
- Water in the subsurface

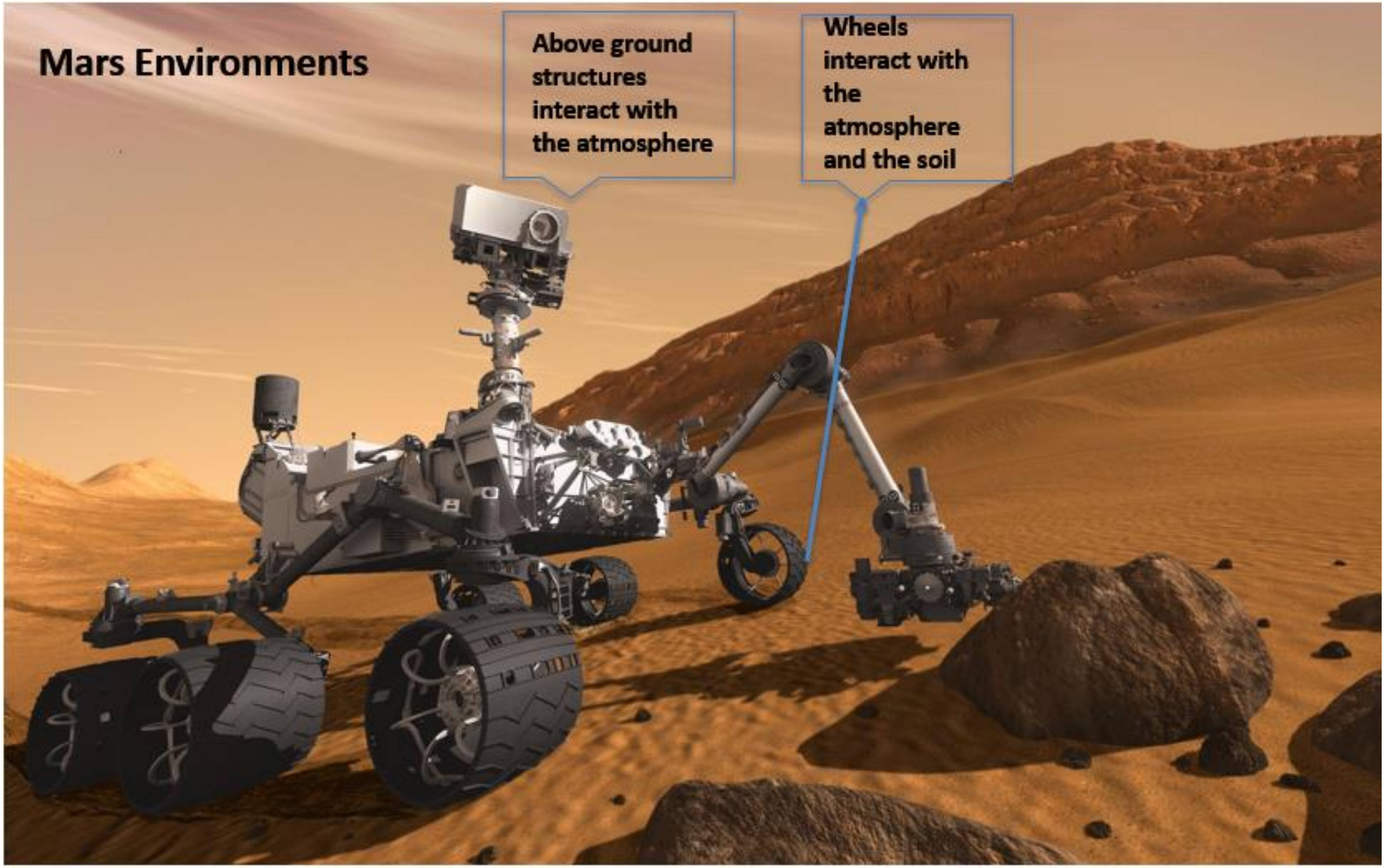
Water on Mars



The water cycle on Mars. The diurnal cycle is represented for a low-latitude region.[4]

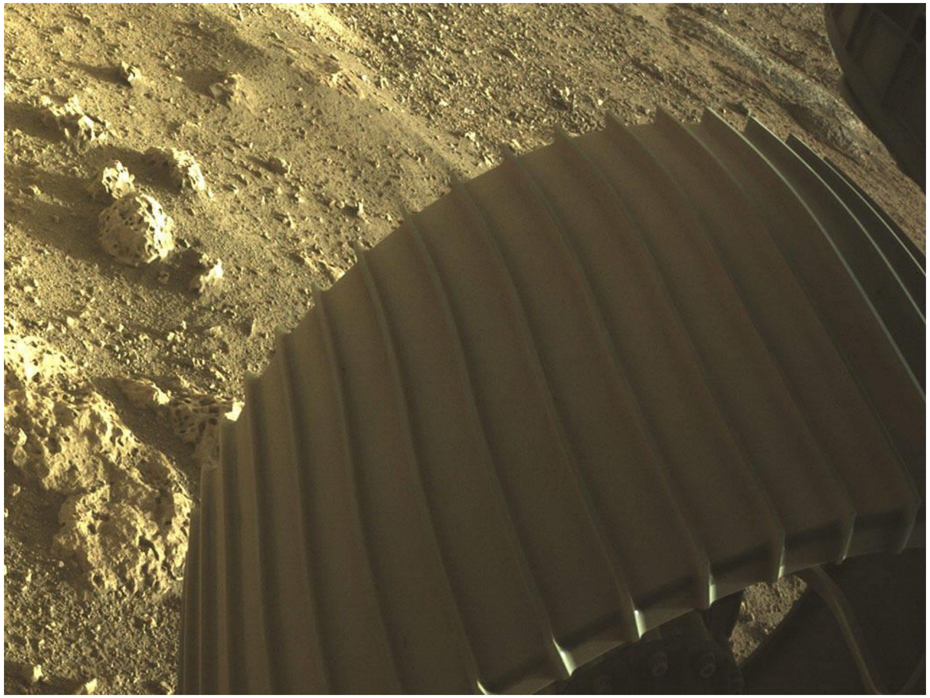
[4]Martin-Torres F. J., and Zorzano M.P., "Should We Invest in Martian Brine Research to Reduce Mars Exploration Costs?," Astrobiology, Vol. 17, No. 1, 2017, pp. 3-7

Mars Environments



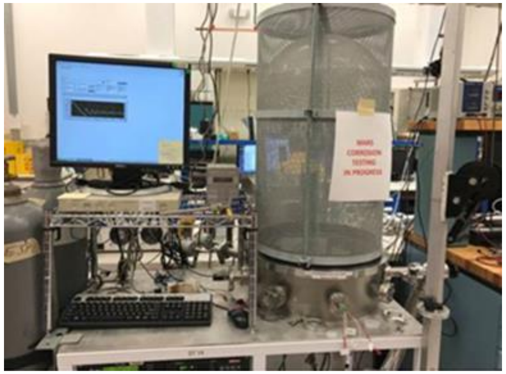
NASA’s Rovers Wheels

Curiosity rover’s wheel, March 19, 2017 (16 km since August 2012)

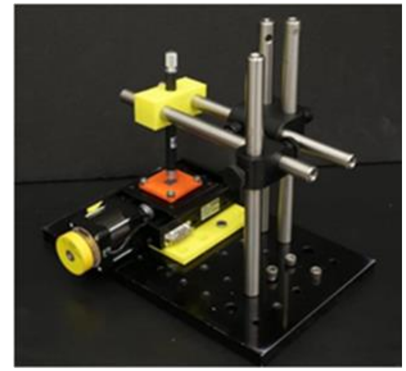


Aluminum wheels of NASA's Curiosity (left) and Perseverance (right). Perseverance’s wheels are slightly larger in diameter and narrower, have twice as many treads, and are gently curved instead of chevron patterned.

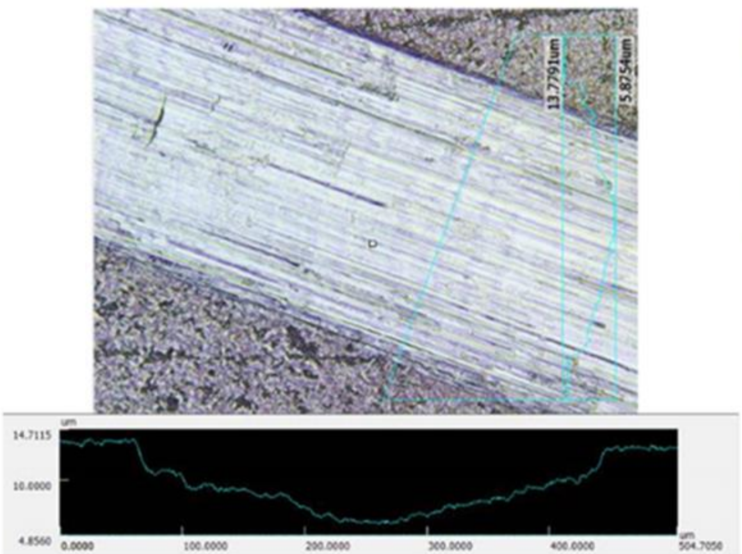
Experimental Results (Simulated Mars Atmosphere)

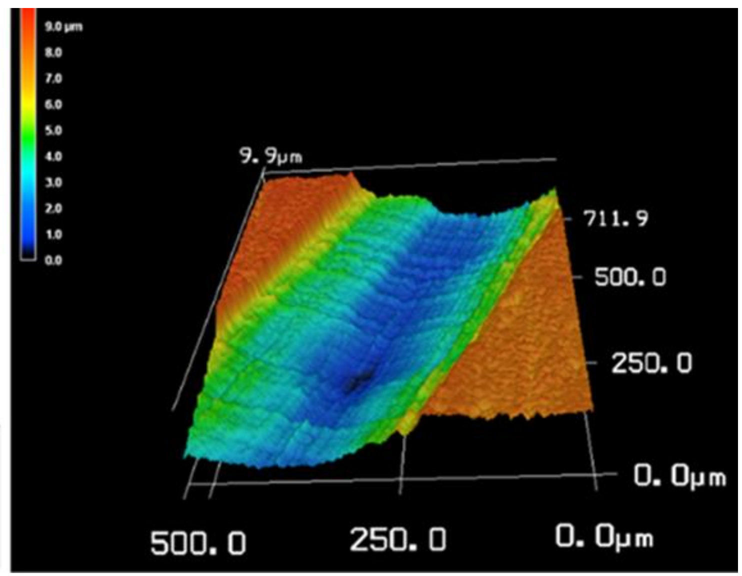


Mars chamber at KSC



3D printed sample holder with scribing tool

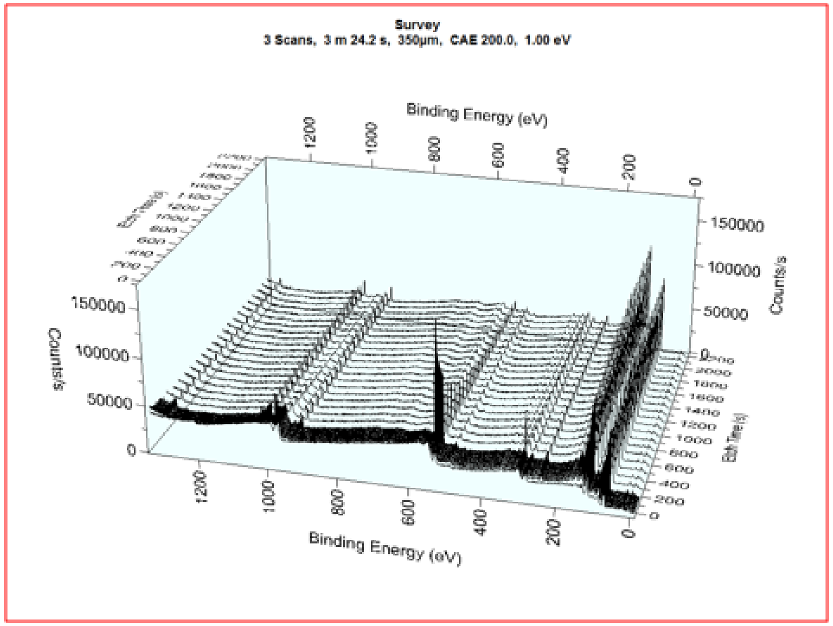


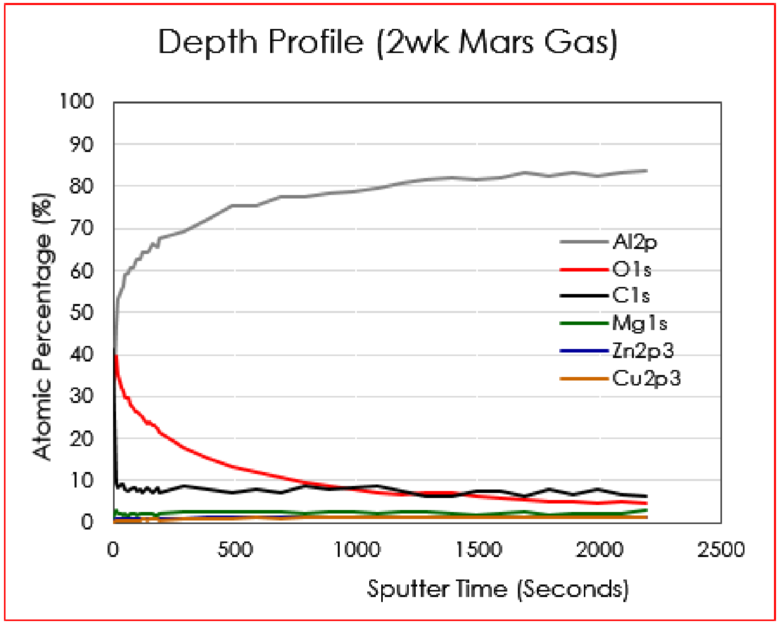


Cylindrical carbide scribe profile imaged using laser confocal microscopy

XPS Analysis

2 Weeks Exposure to Simulated Mars Gas

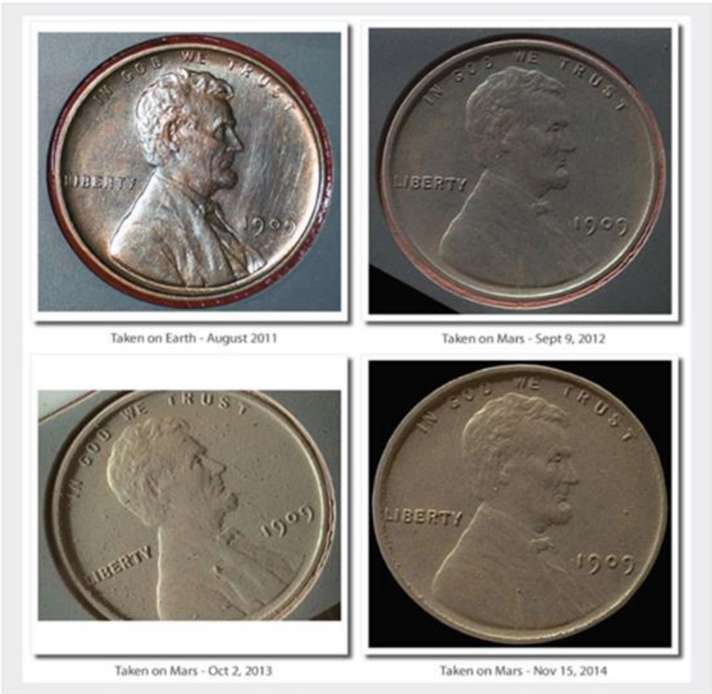




The quick drop of carbon content below the sample surface and the appearance of oxygen and aluminum peaks indicated the formation of an oxide layer.

Visual Data from Images

Curiosity with an inset showing the calibration targets known as the Mars Hand Lens Imager, including a 1909 Lincoln penny, at the end of its robotic arm.



The first photo was taken on Earth in August 2011. Subsequent photos were taken on Mars on 09/09/2012, 10/02/2013, and 11/15/2013. The only visible change is the accumulation of Martian dust.

Conclusions

- Corrosion on the Moon is not a concern.
- Exposure to the Mars atmosphere is not a concern for materials corrosion.
- The presence of brines in the Martian soil (regolith) is a concern for corrosion of materials that will be in close interaction with the soil.
- Further investigation is needed to understand how materials, relevant to long-term surface operations on Mars, interact with the Mars environment (atmospheric and soil/regolith).

Summary

Corrosion and coatings for spacecraft and assets in unique environments

Summary

- NASA has been solving corrosion-related problems since the inception of the Space Program.
- NASA spacecraft and assets operate in unique environments: Indoors (with and without climate control), coastal launch pads, space, Moon, and Mars.
- **Materials selection is based on testing under conditions that are as close as possible to the actual service conditions.**
- As NASA prepares for the exploration of Mars, it is important to investigate material behavior in the Mars environment.

Questions?

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