National Aeronautics and Space Administration

Corrosion Control in the Aerospace Industry

NACE Colombia

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Introduction

- NASA's current plans for space exploration.
- NASA has faced corrosion since the start of the space program in 1962.
- NASA conducts its space launch and exploration operations in environments that are unique to corrosion.
- NASA launches from one of the most corrosiond natural environments in North America.
- Natural corrosion conditions on launch pads are aggravated by solid fuel rocket (SRBs) exhaust products.
- Spacecraft are subjected to very varied environments in relation to corrosion:
  - Orbits around the earth Interior areas with purified environment and controlled humidity Interior areas with uncontrolled environment
  - Launch platforms (near the ocean)
  - Environments on other planets
- NASA considers the development of corrosion control technologies as one of the areas needed to reduce cost and improve sustainability and efficiency.

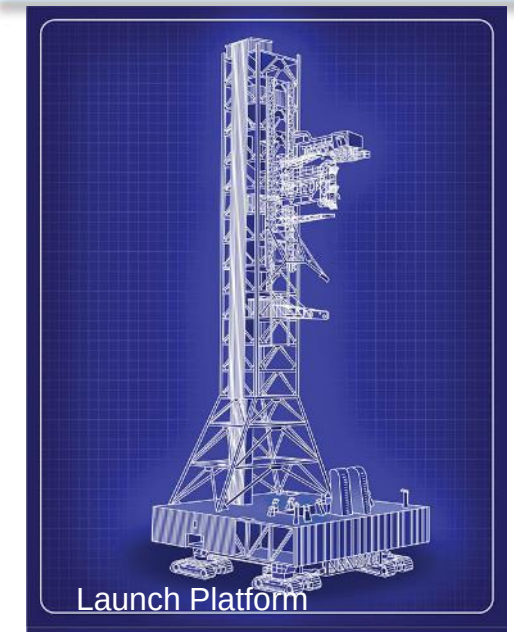
NASA's Current Plans for Space Exploration

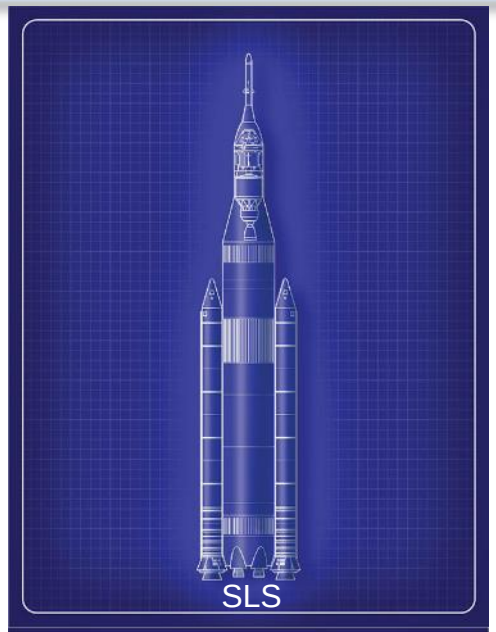
https://www.youtube.com/watch?v=vl6jn-DdafM

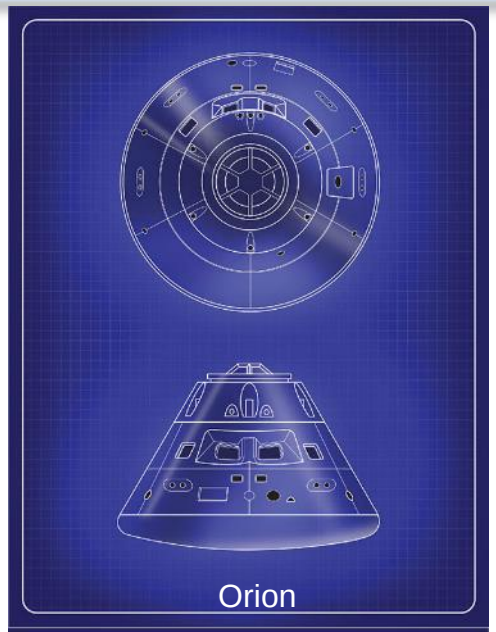
NASA's Current Plans for Space Exploration

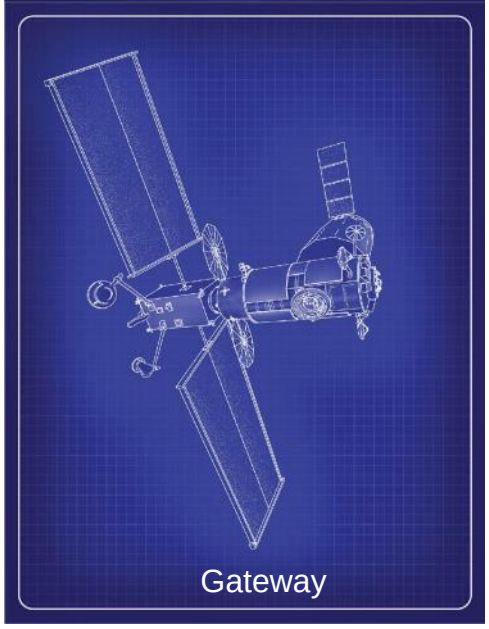
- Artemis is NASA's program with the goal of bringing the first woman and the next man to the moon's south pole in 2024.
- Artemis is the twin sister of Apollo and the goddess of the Moon in Greek mythology.
- The Space Launch System (SLS), the Orion crew module, the lunar landing module, and the Portal station (Gateway) will extend human exploration beyond the Moon.
- NASA is developing the technologies, building the hardware and engineering operations teams that will launch the vehicle that will one day take a manned ship to Mars.

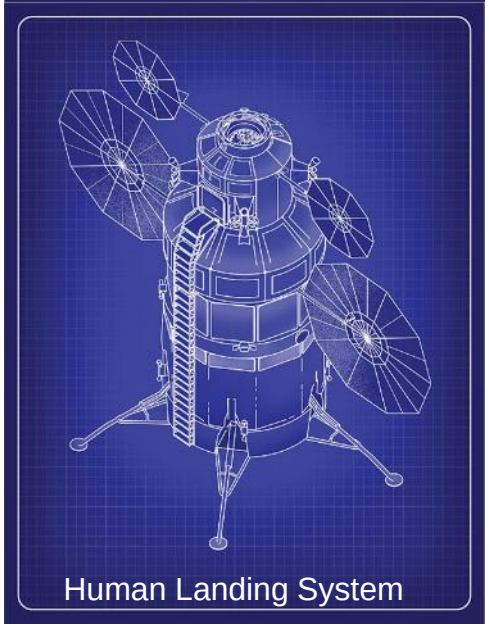
Artemis Program

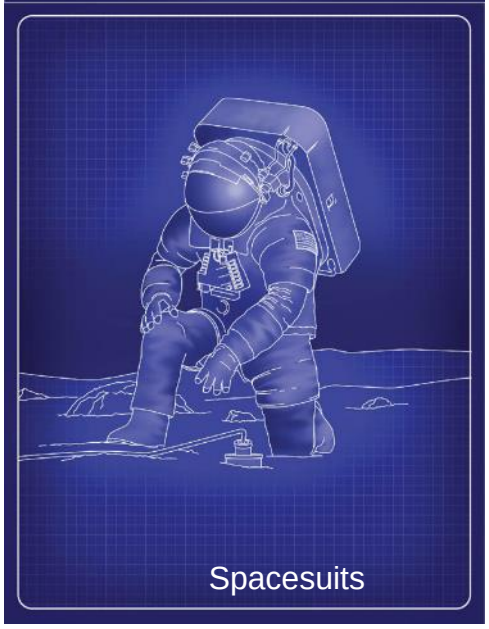

Launch Platform


SLS


Orion


Gateway


Human Landing System

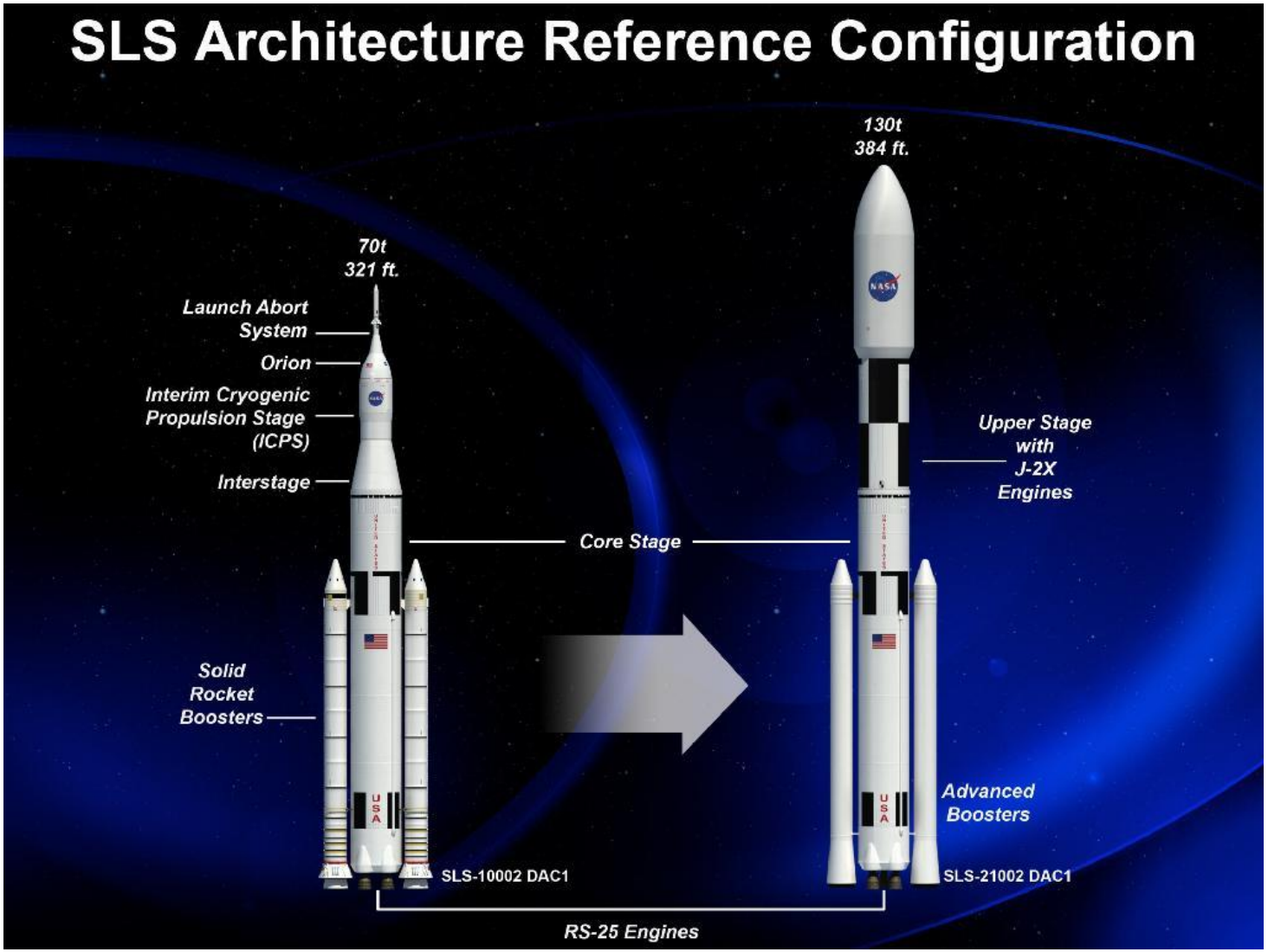

Spacesuits

Launch Pad

Space Shuttle Launch Pad (39 B)

SLS-ready 39B launch pad

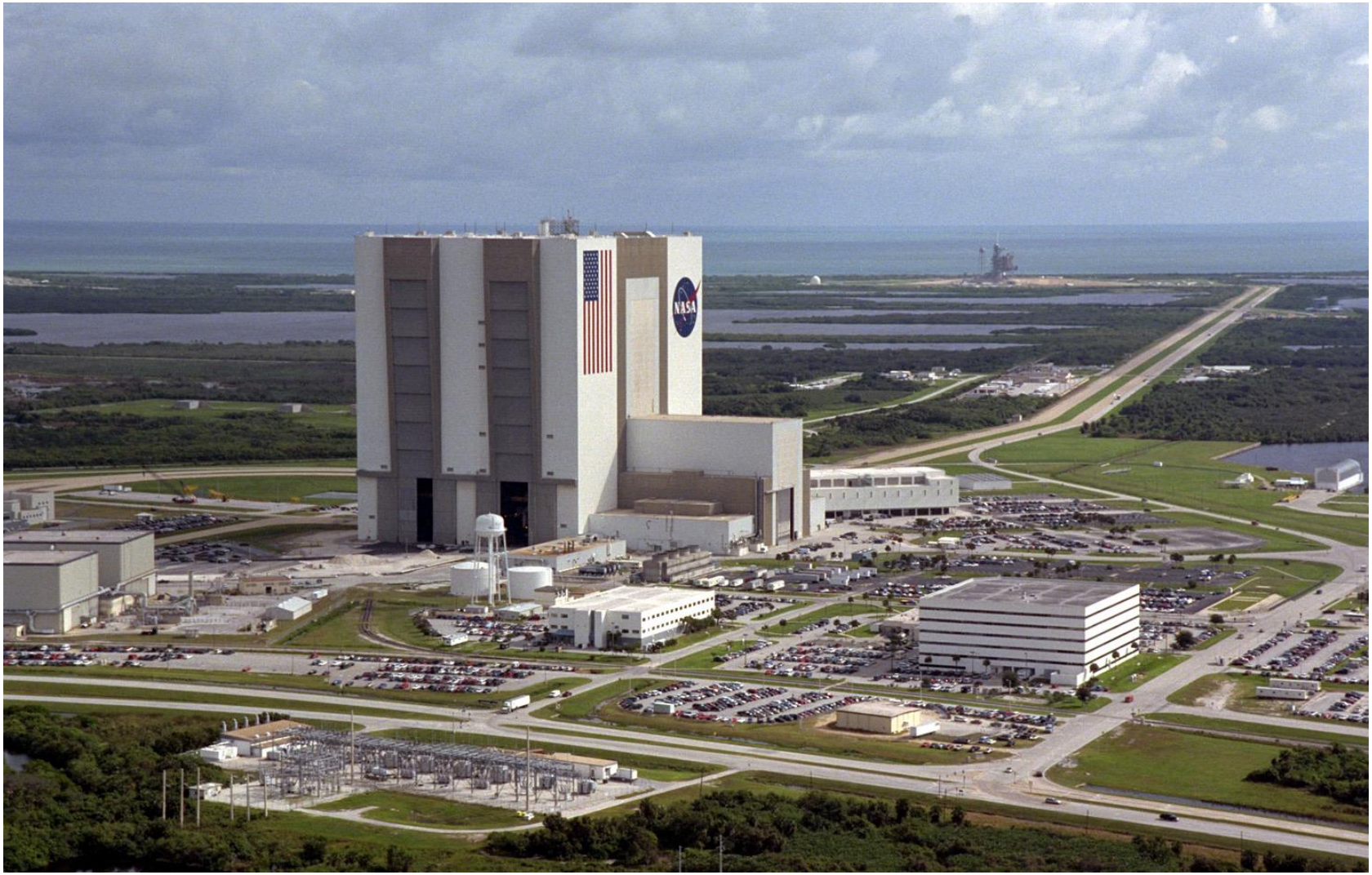
Space Launch System (SLS)



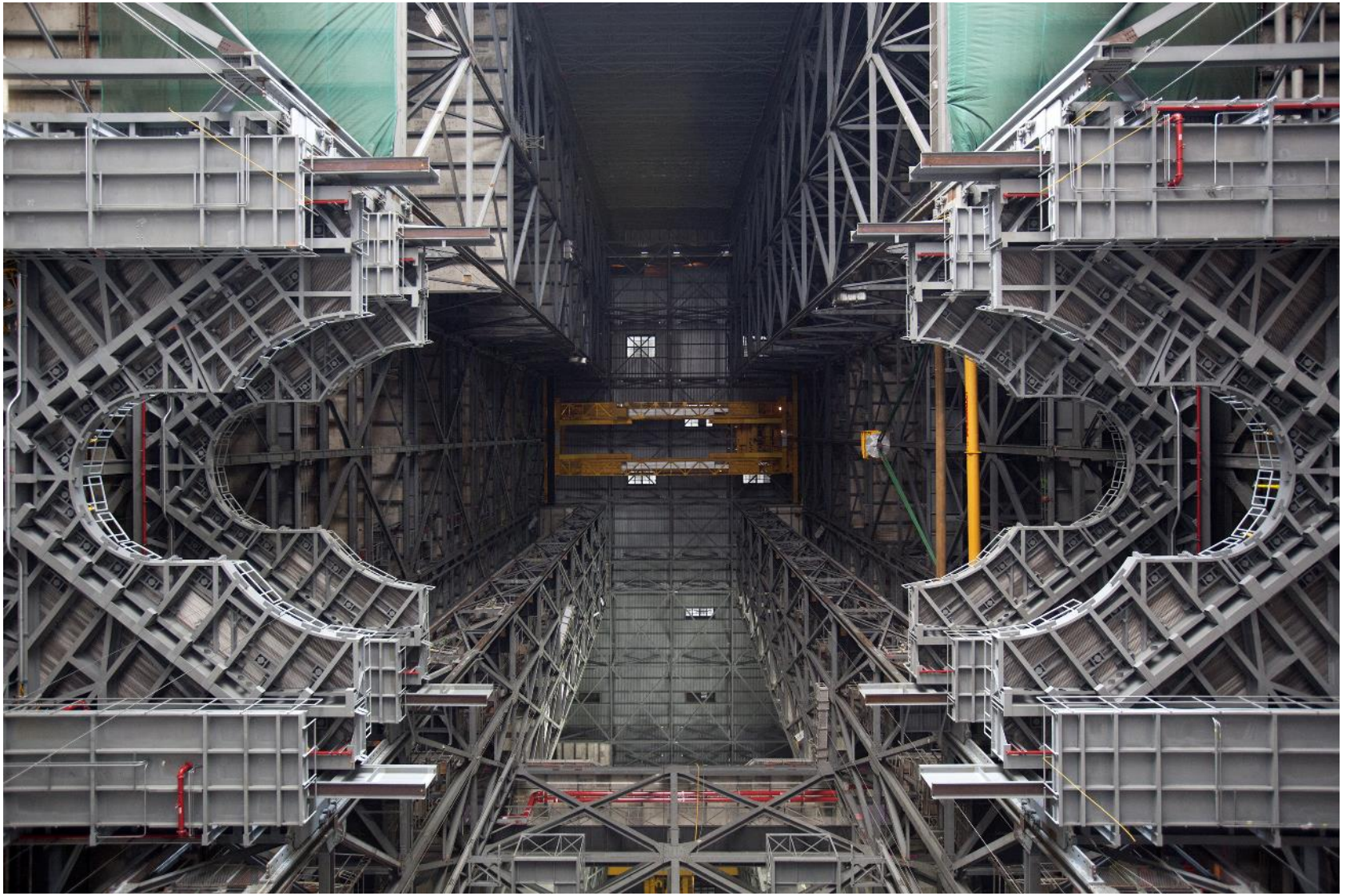
Orion

Orion/SLS combination is critical to extending human presence beyond low earth orbit

Vehicle Assembly Building (VAB)

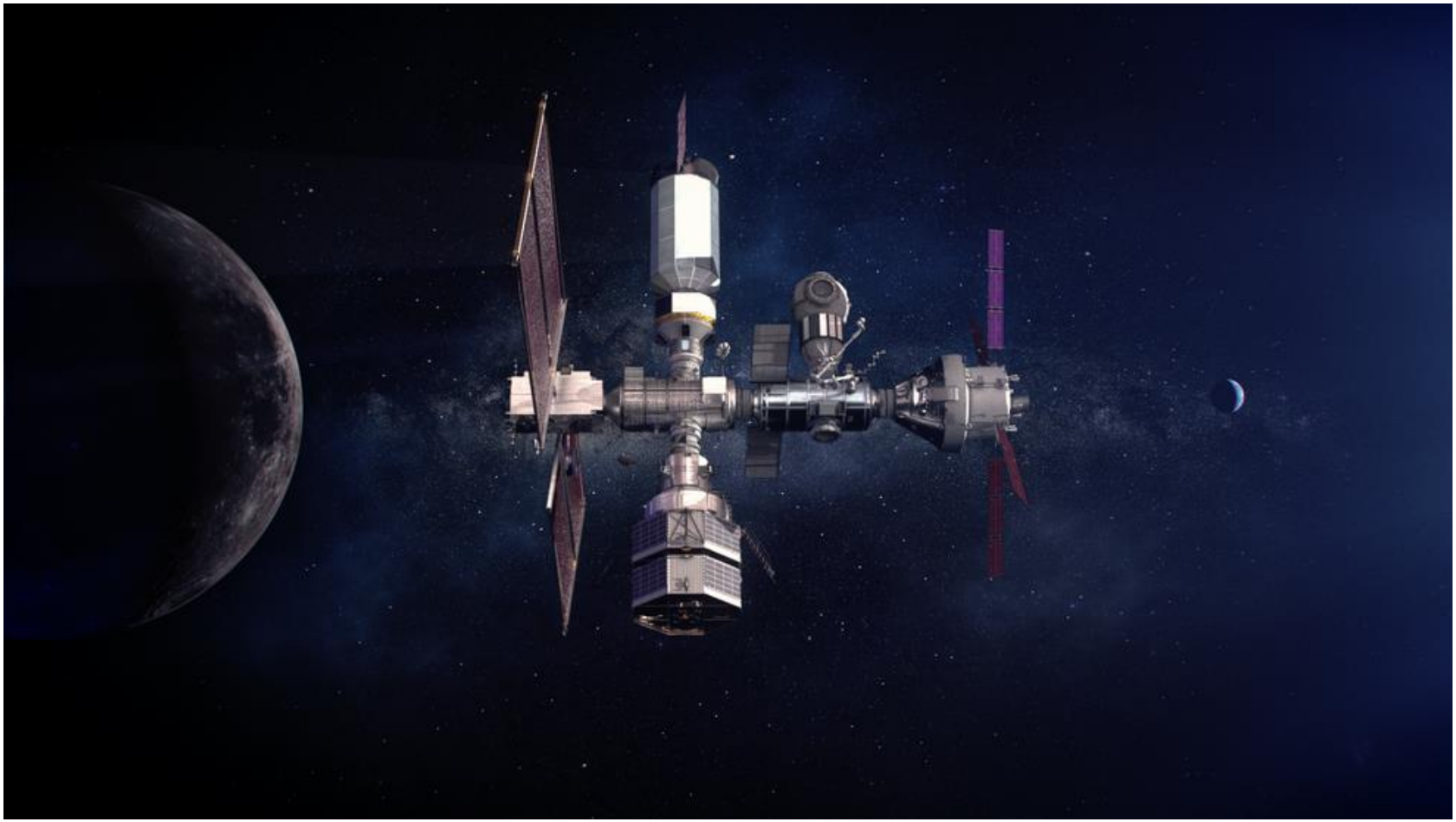


Vehicle Assembly Building (Interior)

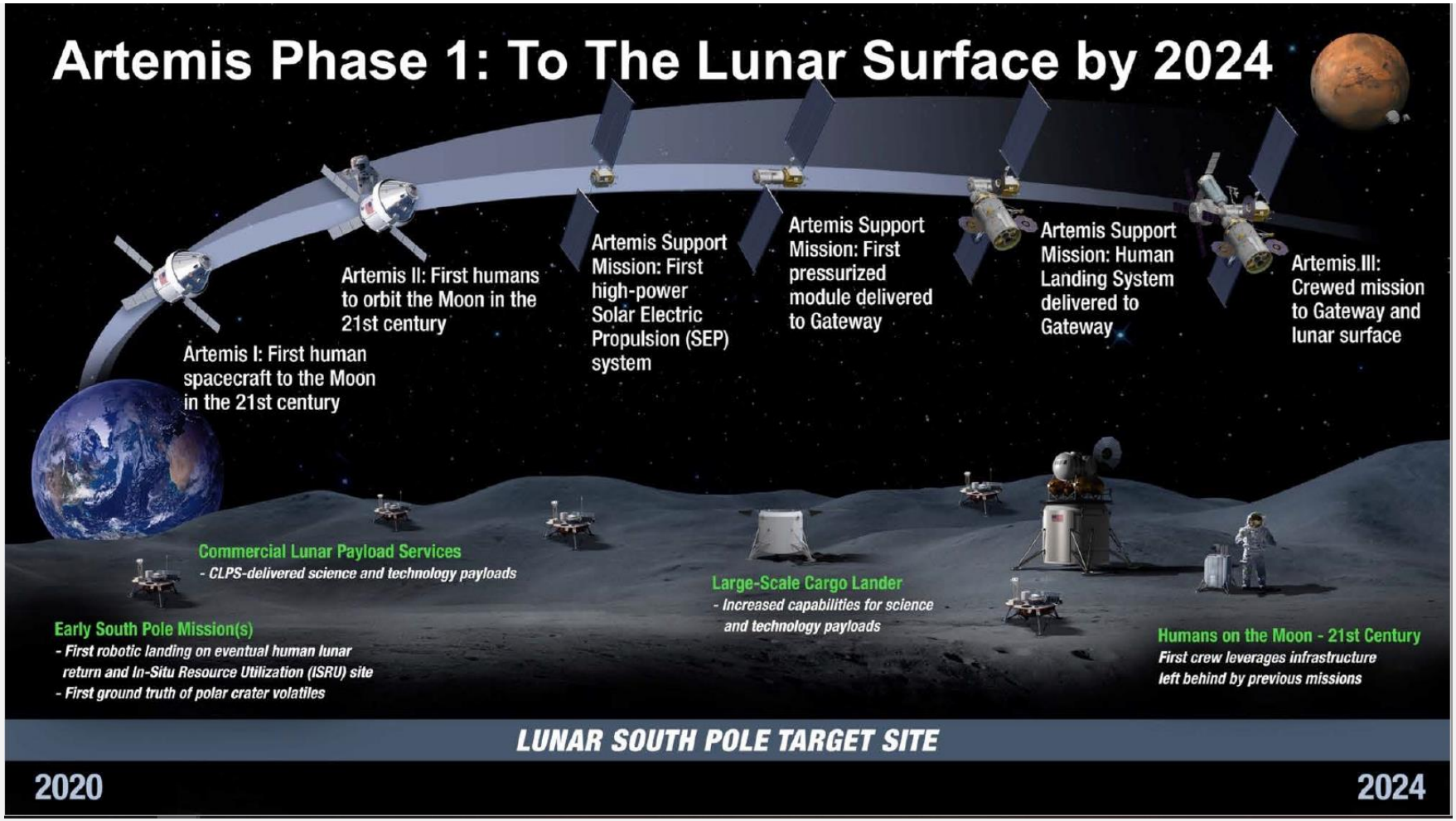


Orion/SLS are the Basis for Exploration beyond Earth Orbit

Gateway

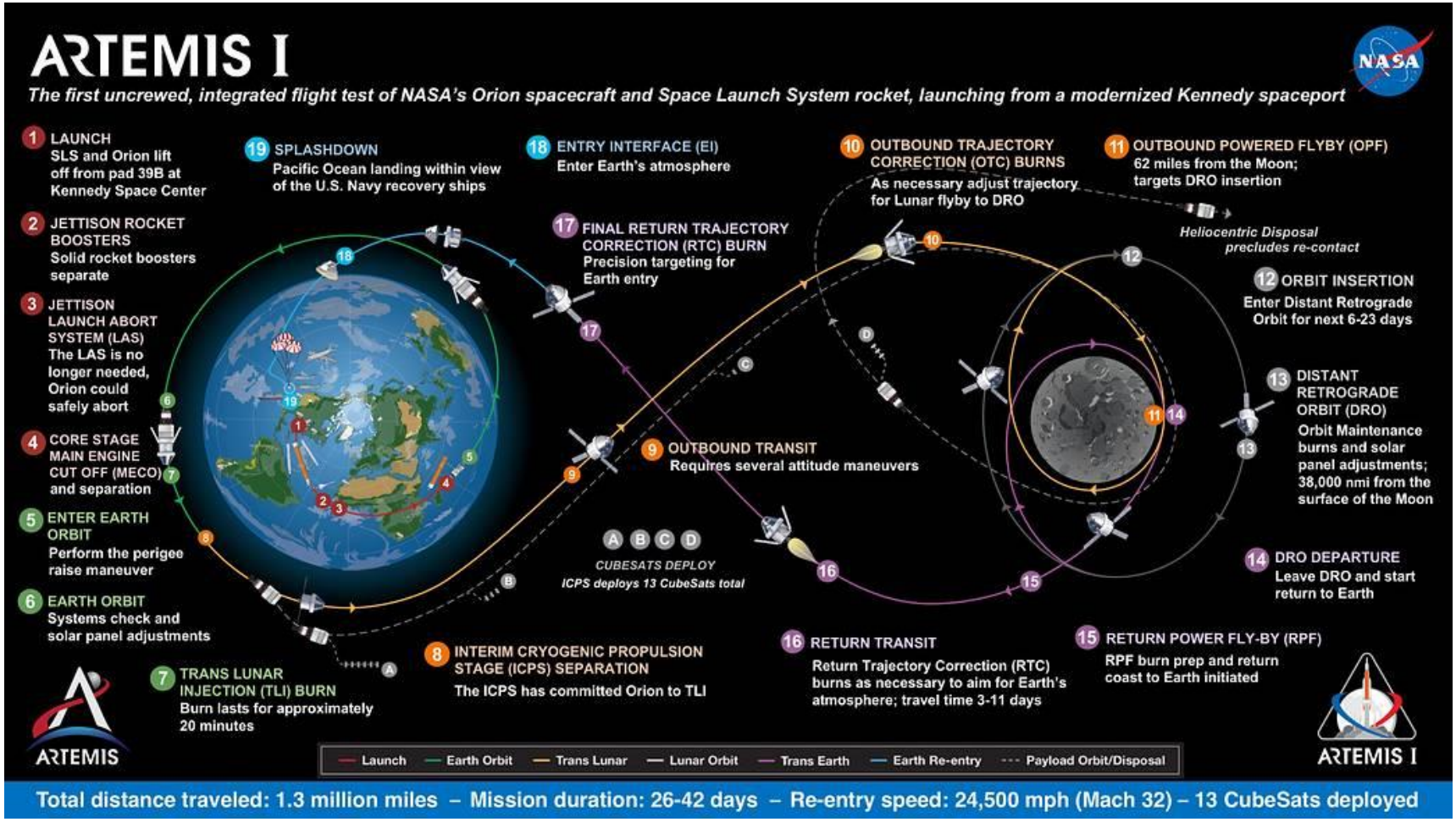


Artemis Phase 1



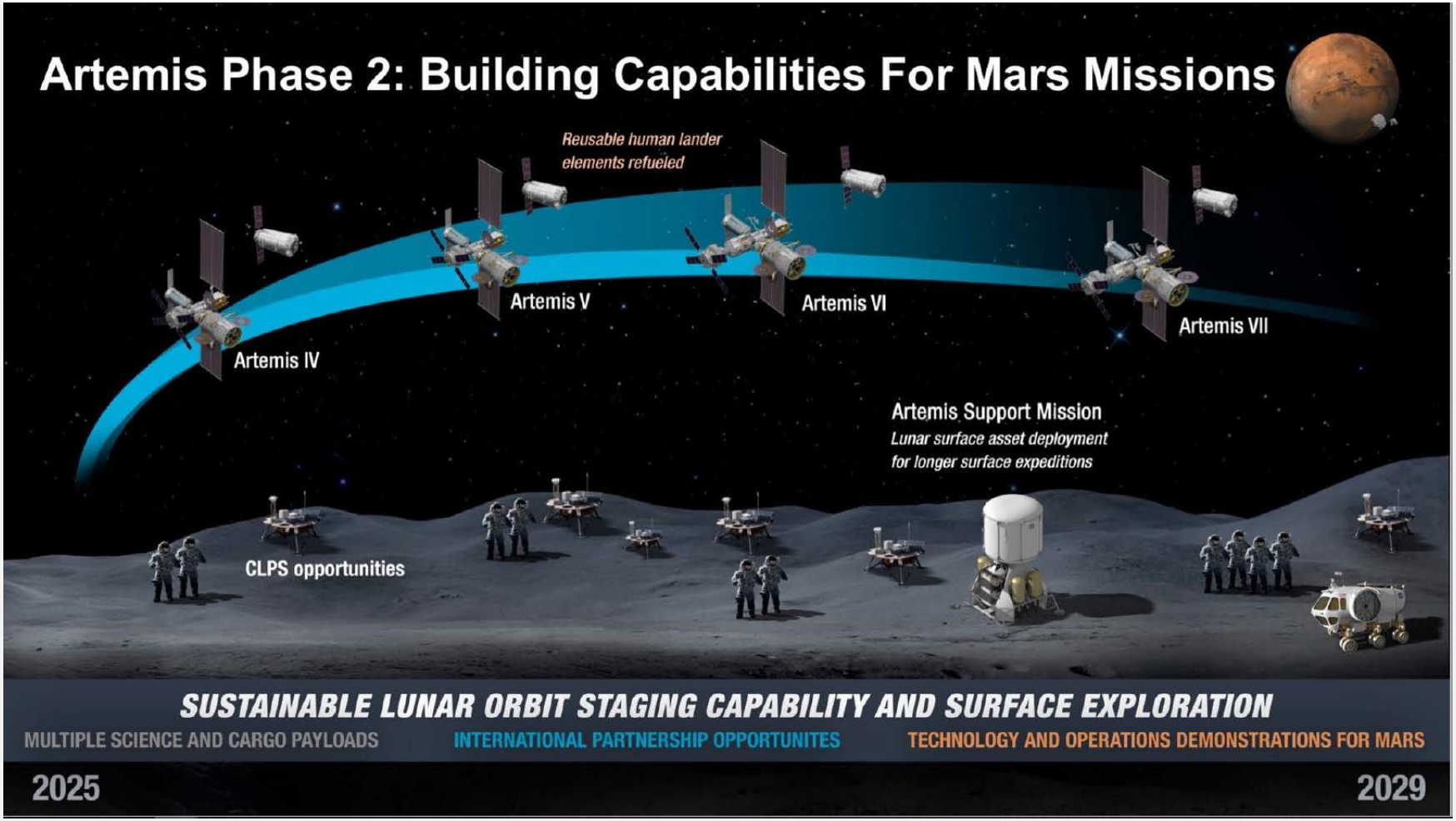
Artemis I: First test flight of the SLS and Orion rocket as an integrated
Artemis II system: First manned flight of the SLS rocket and Orion to the Moon
Artemis III: First manned mission to the surface of the Moon (2024)

Artemis I*



*Planned for November 2021

Artemis Phase 2



Artemis IV – VII Manned Flights to Gateway

Space Environment

The Space Environment is characterized by:

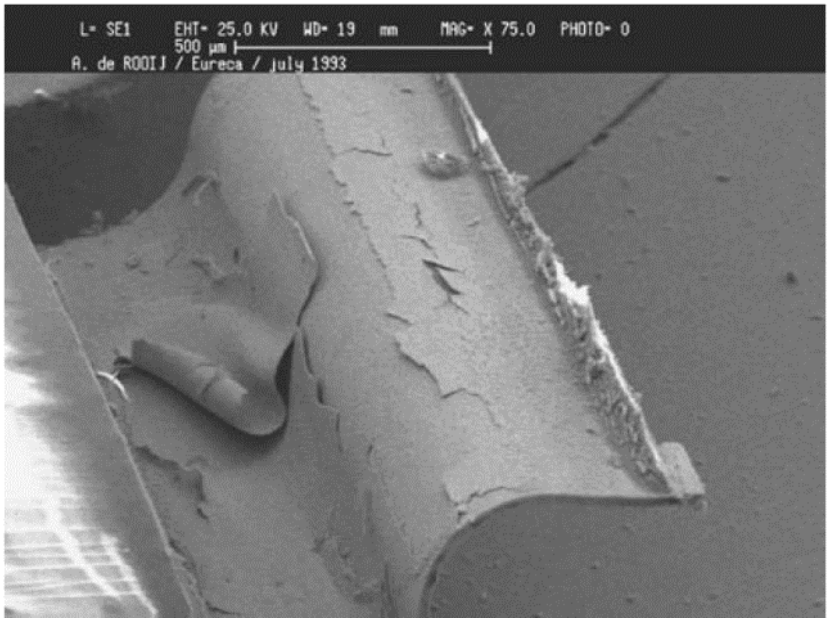
- Low pressure (vacuum)
- Atomic Oxygen (causes erosion of materials)
- Ultraviolet (UV) radiation
- Charged particles
- Temperature extremes
- Electromagnetic radiation
- Micrometeoroids
- Human-made debris

Interaction between Materials and Atomic Oxygen

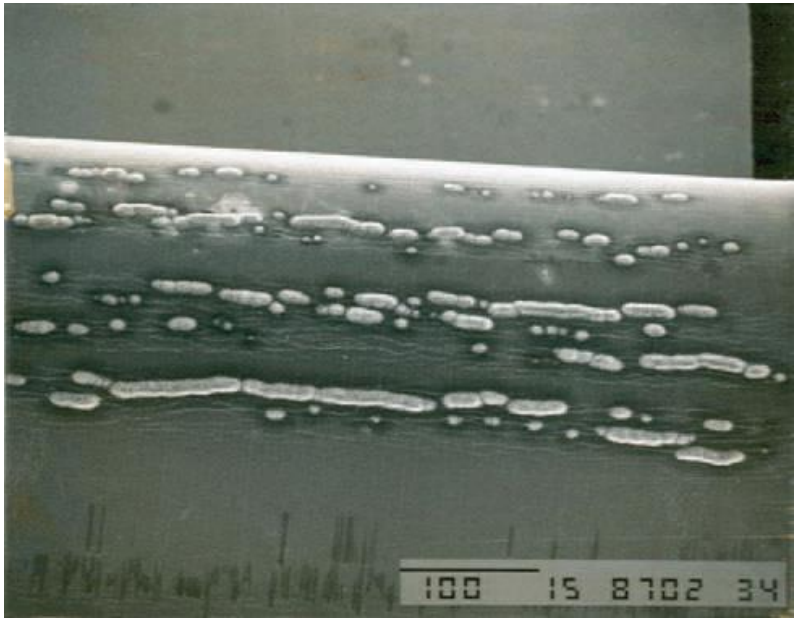
Interaction of the Space Shuttle with the upper atmosphere creates a corona seen at night (right photo), in part, due to atomic oxygen.

In the upper reaches of the atmosphere, about 200-500 miles (322-805 km), an elemental form of oxygen is created from exposure to intense solar ultraviolet light. Oxygen molecules are decomposed from O_2 into two separate oxygen atoms. This form of elemental 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.

Corrosion caused by Atomic Oxygen



Silver interconnector in a solar cell in Eureca



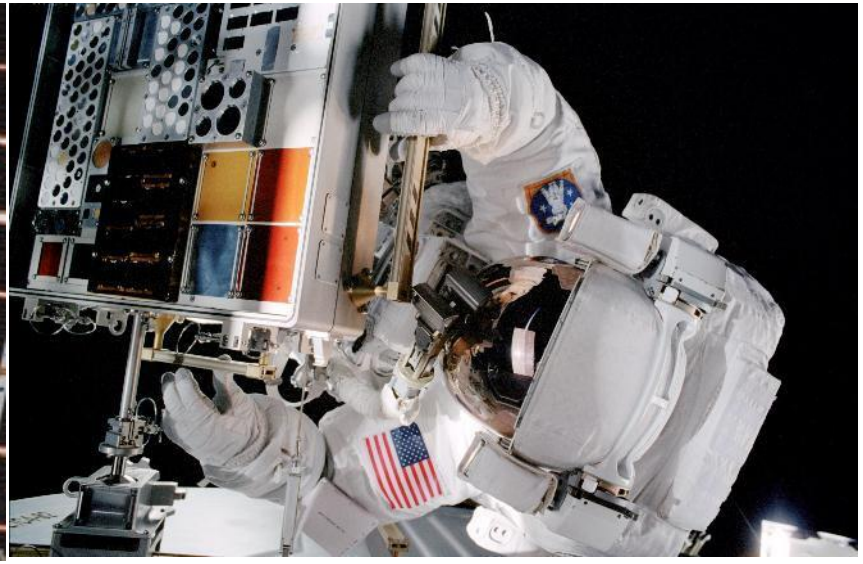
Silver covered with gold where you see the formation of silver oxide caused by atomic oxygen in coating defects

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

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.

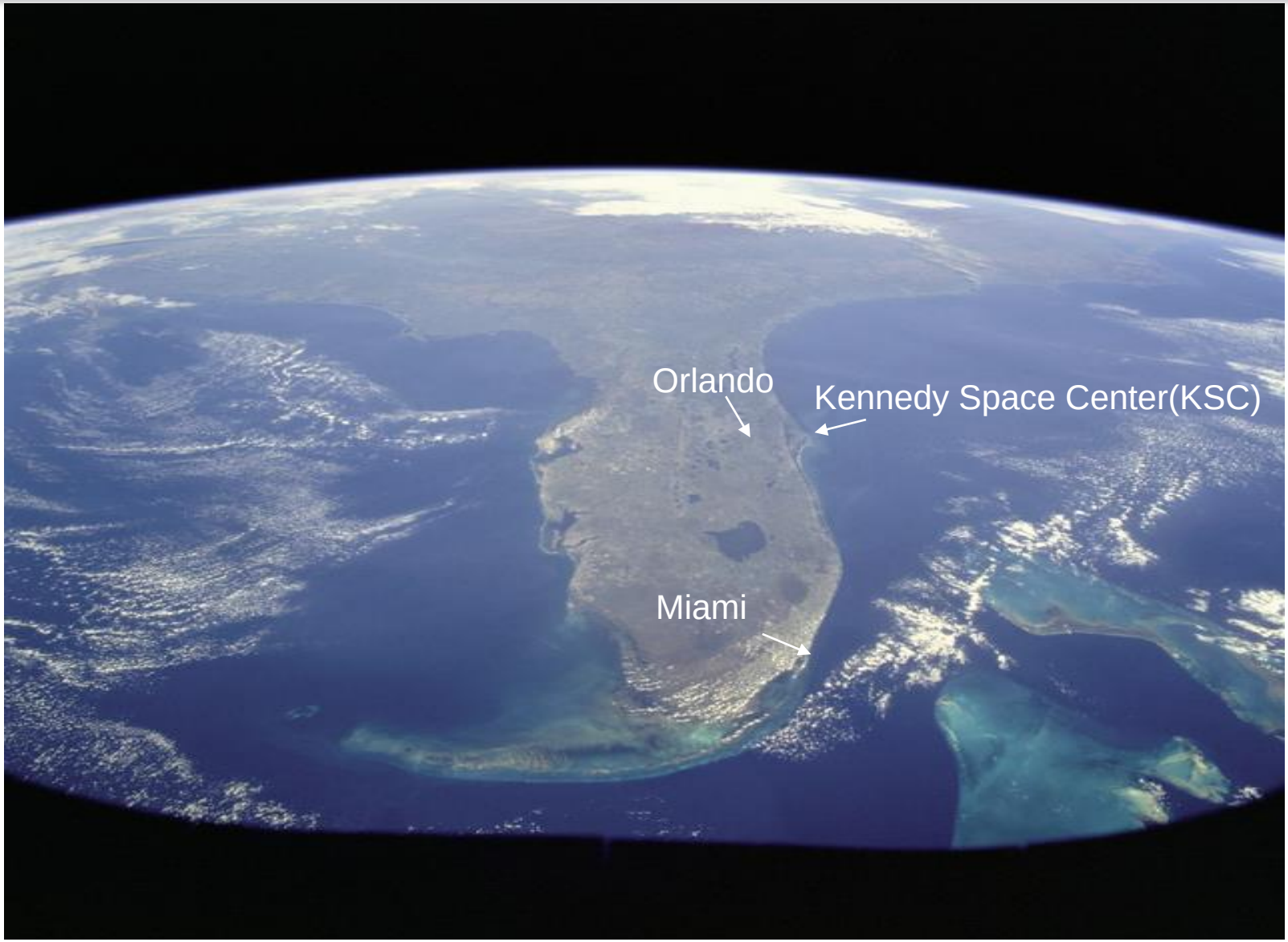
International Space Station Technology – Benefits Fine Art

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 and Space Exploration

One challenge with space exploration is that equipment must withstand radical 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.

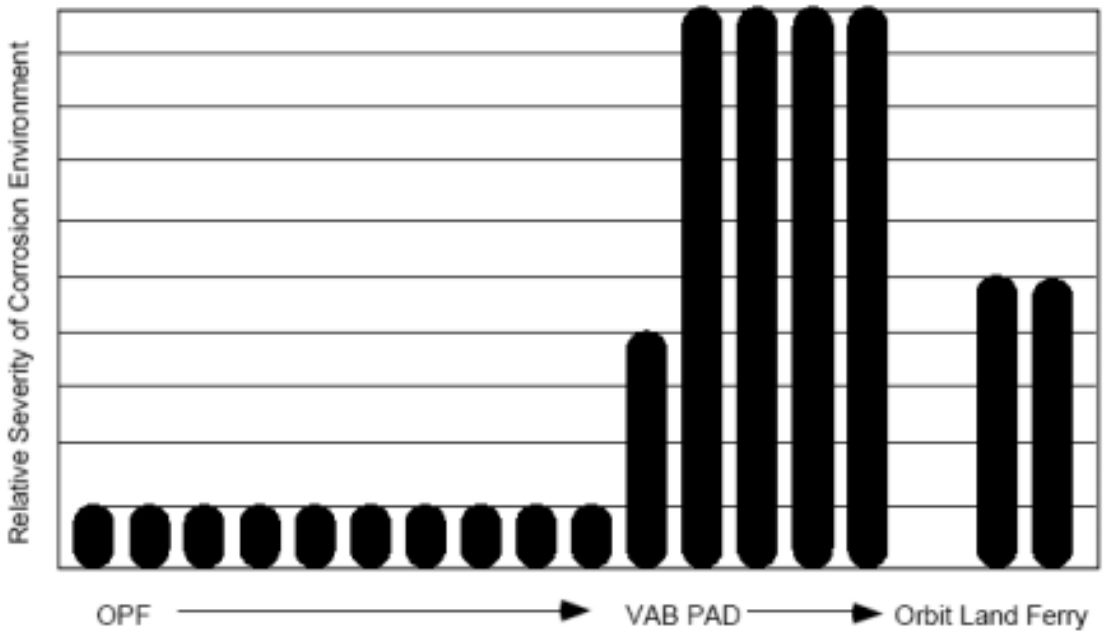
KSC Natural Launch Environment



KSC Launch Environment

Natural Salt Fog Chamber

Orbiter Environmental Conditions



FERRY

Orbiter preparation facility (OPF)

VAB

PAD

LAND

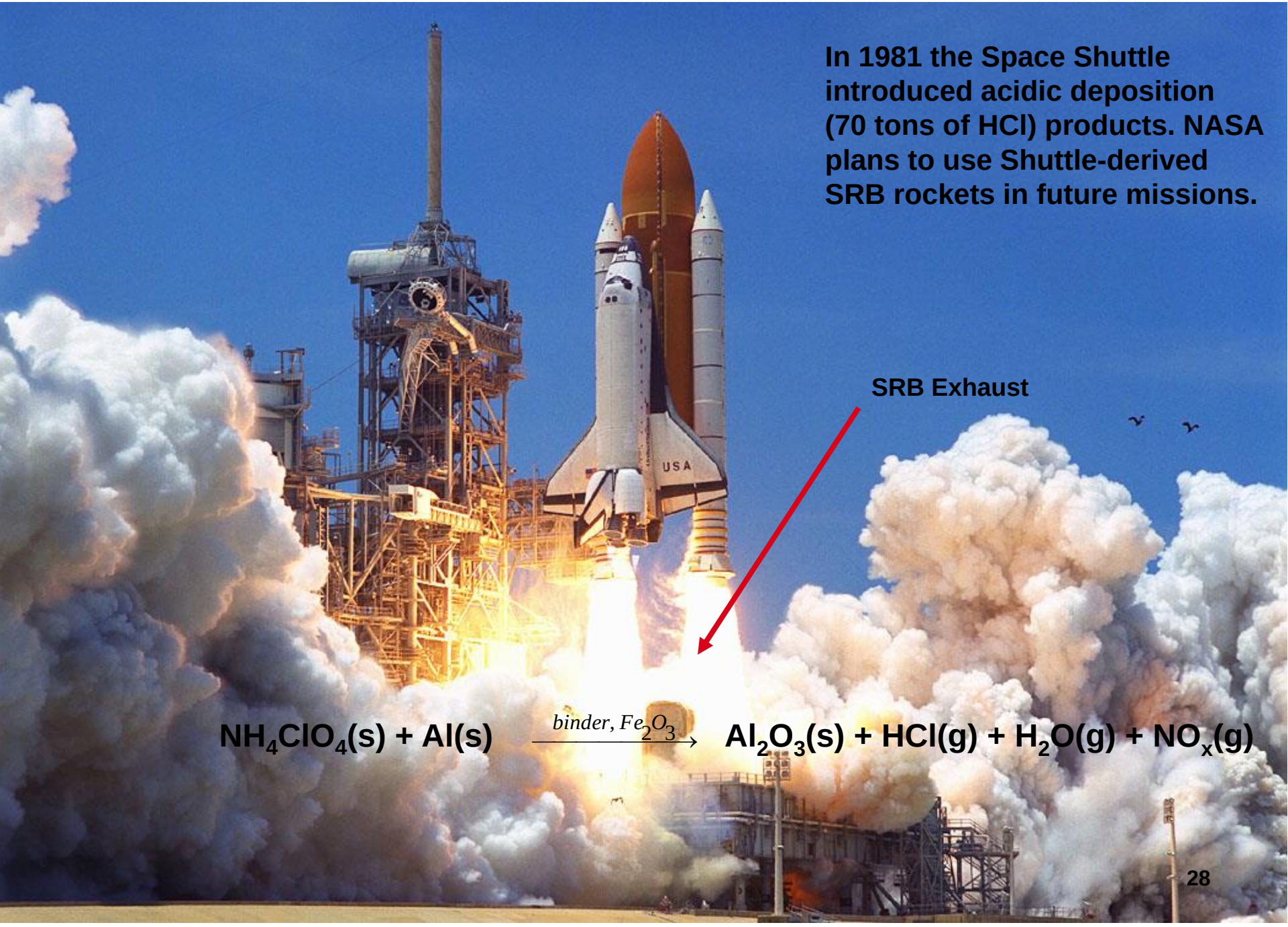
Orbiter Environmental Conditions

- Normal operating environment - temperature and humidity controlled
- Exposed to salt spray on the launch pad (30-90 days)
- In reality, flight delays usually extend. For example, Columbia spent 166 days on the launch pad before its tenth flight. High humidity led to condensation in space that would leave behind salt residues
- Post landing - exposed to external environments and fluids from de-servicing after landing
- Ferry flight - water intrusion

KSC Launch Pad Environment

The launch environment at KSC is extremely corrosive:

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

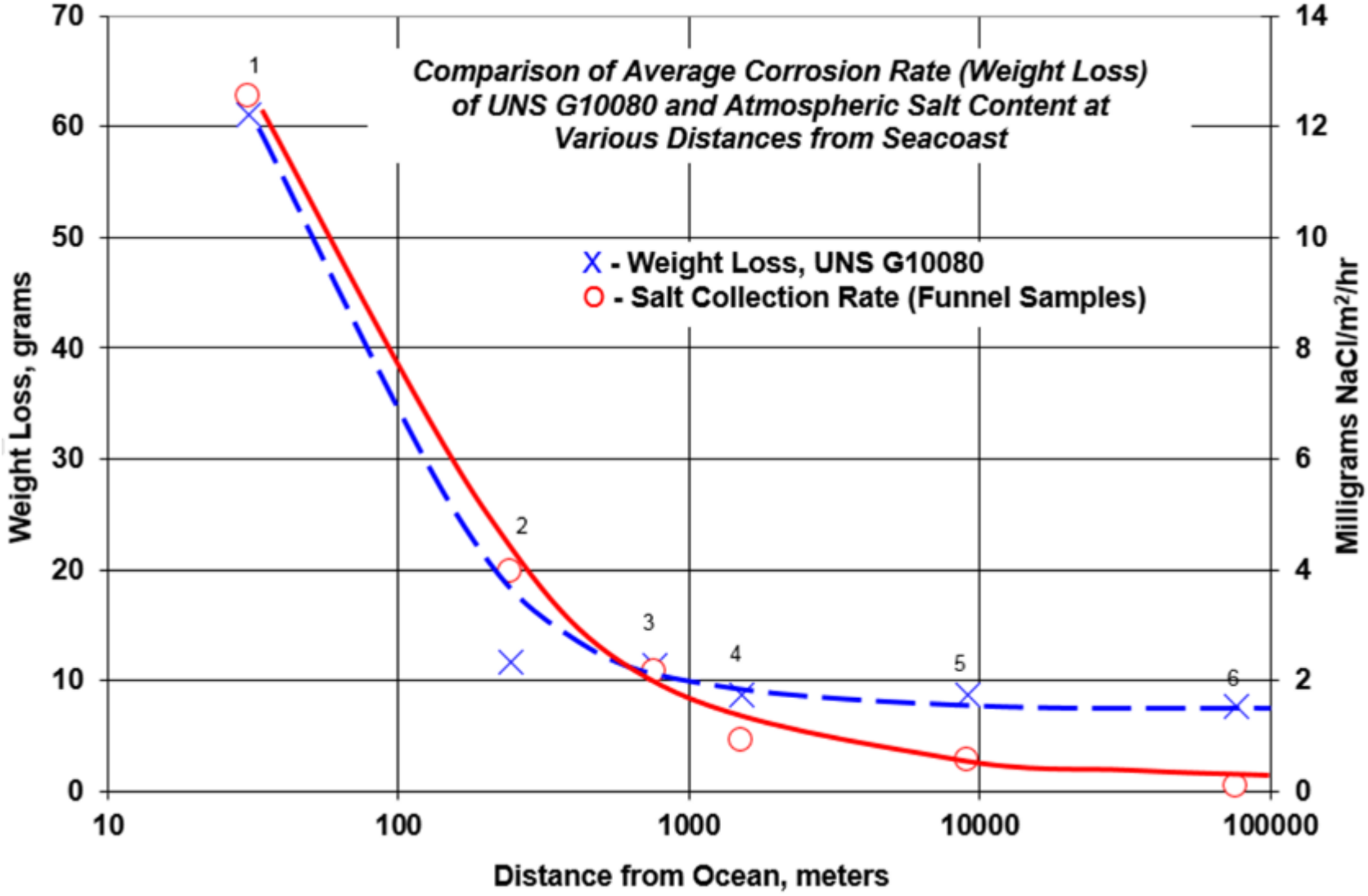


In 1981 the Space Shuttle introduced acidic deposition (70 tons of HCl) products. NASA plans to use Shuttle-derived SRB rockets in future missions.

SRB Exhaust

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

Changes in Corrosion Rate with Distance from the Ocean



Corrosion Rates of Carbon Steel

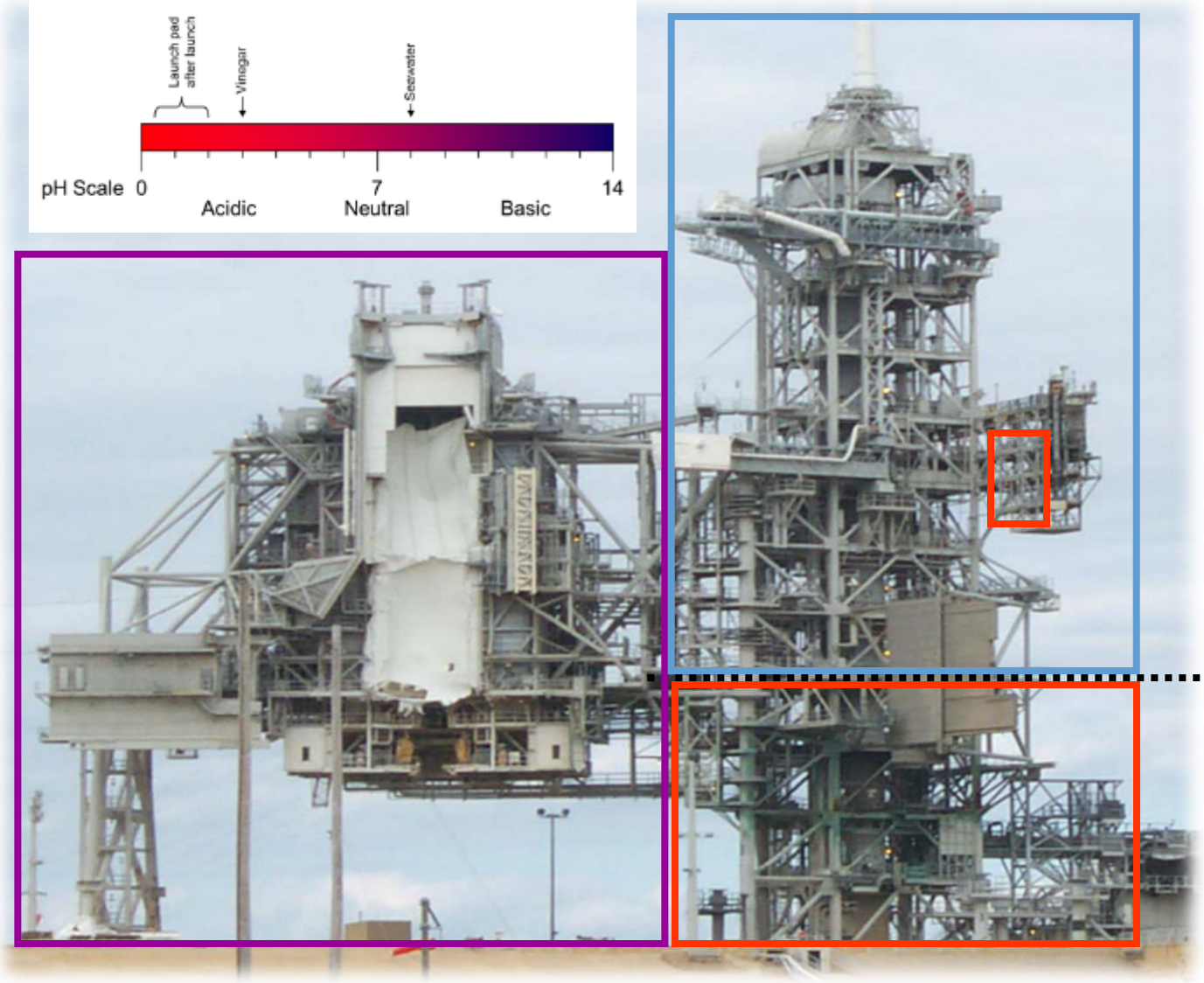
Corrosion rates of carbon steel calibrating specimens at various locations*			
Location	**Type Of Environment**	**µm/yr**	**Corrosion rate[a] mils/yr**
Esquimalt, Vancouver Island, BC, Canada	Rural marine	13	0.5
Pittsburgh, PA	Industrial	30	1.2
Cleveland, OH	Industrial	38	1.5
Limon Bay, Panama, CZ	Tropical marine	61	2.4
East Chicago, IL	Industrial	84	3.3
Brazos River, TX	Industrial marine	94	3.7
Daytona Beach, FL	Marine	295	11.6
Pont Reyes, CA	Marine	500	19.7
Kure Beach, NC (80 ft. from ocean)	Marine	533	21.0
Galeta Point Beach, Panama CZ	Marine	686	27.0
Kennedy Space Center, FL (beach)	*Marine*	*1070*	*42.0*

[a]Two-year average

* Data extracted from: S. Coburn, Atmospheric Corrosion, in Metals Handbook, 9th ed, Vol. 1, Properties and Selection, Carbon Steels, American Society for Metals, Metals Park, Ohio, 1978, p.720

A mil is one thousandth of an inch

Launch Complex 39 pH Values after a Space Shuttle Launch



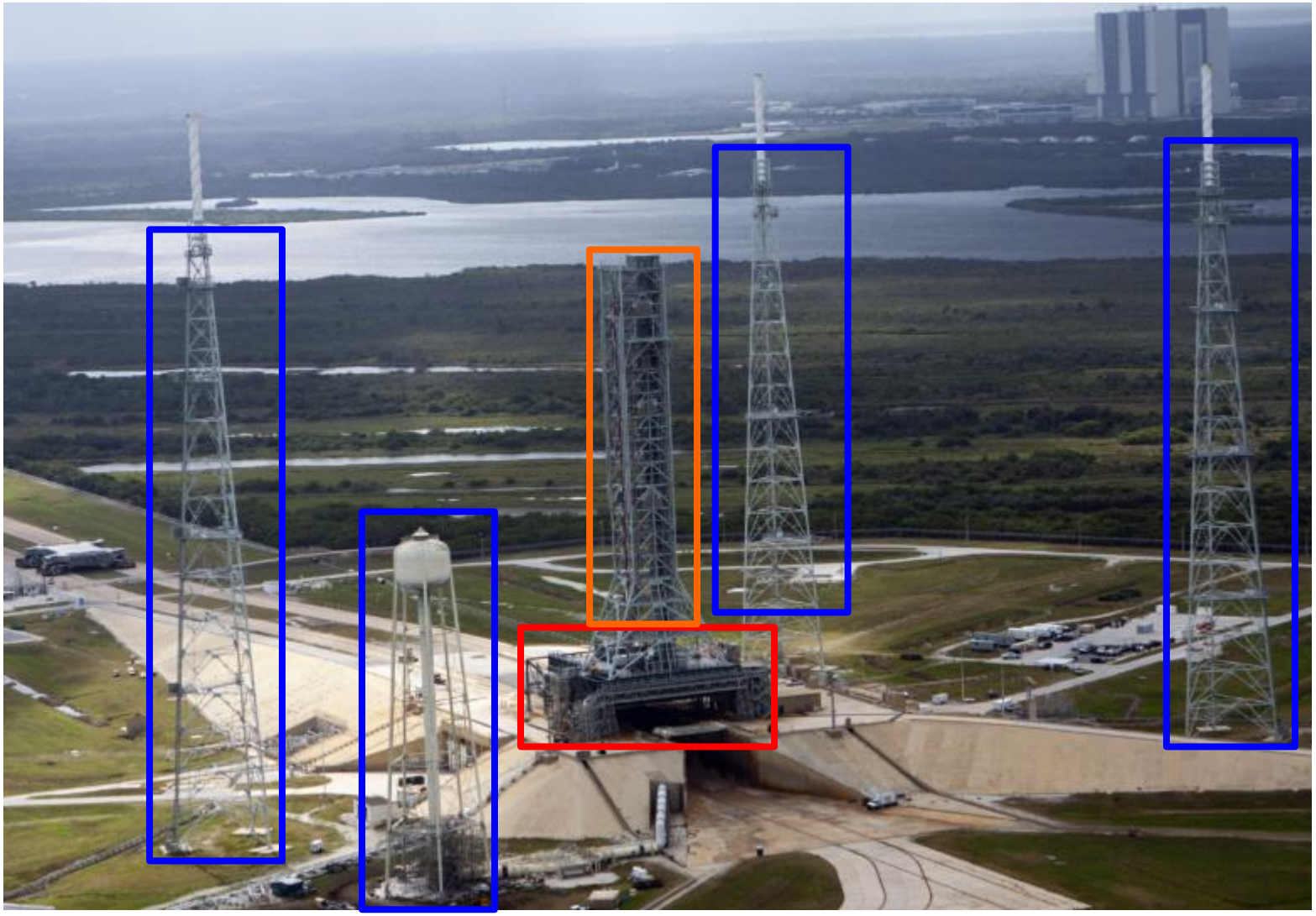
Zone 3:
pH ~2-3

Zone 2:
pH ~ 2-3

FSS 115" Level

Zone 1:
pH ~ 0-1

Exposure Zones on New Launch Complex 39B



Zone 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

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

Coatings Qualification Protocol

- Adhesion
  - Pre- and post-heating (24 hours at 400 ºC)
  - Post heat adhesion value must be greater than pre heat adhesion value, and meet the statistical requirements for repeatability
- Atmospheric Exposure Testing
  - Evaluations are performed after 18 months of exposure for initial qualification
  - Final evaluations are performed after 60 months of exposure for final approval and placement on the approved products list
  - The acidic slurry is placed on the appropriate panels every six weeks for the first 18 months of exposure.
- Photographs
  - Taken prior to exposure, and after 18 months and 60 months of exposure
- Color/Gloss (Not a pass/fail criterion)
  - Color and gloss are taken prior to, and after 18 months of atmospheric exposure
- Blistering, corrosion under paint and corrosion from the scribe evaluations (Pass/fail criterion)
  - Corrosion evaluations are performed after 18 months and 60 months of environmental exposure

Preparation of Test Panels

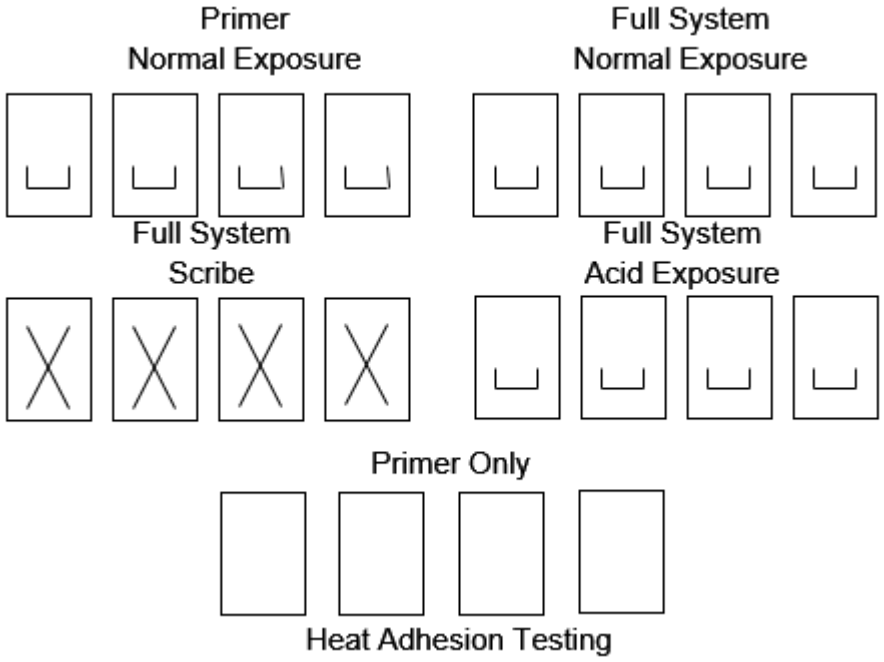
- **Standard AISI M1020 carbon steel test coupons**
  - **Two types: composite and flat panel**
- **Surface cleanliness & roughness of coupons**
  - **Inspected, measured, and documented before application of primer**

Composite Panel

Flat Panel

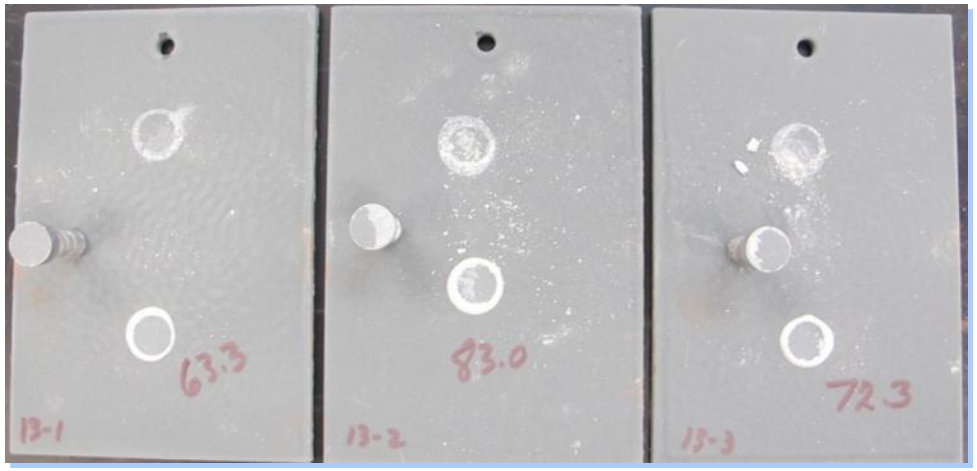
Test Matrix

- 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 into 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

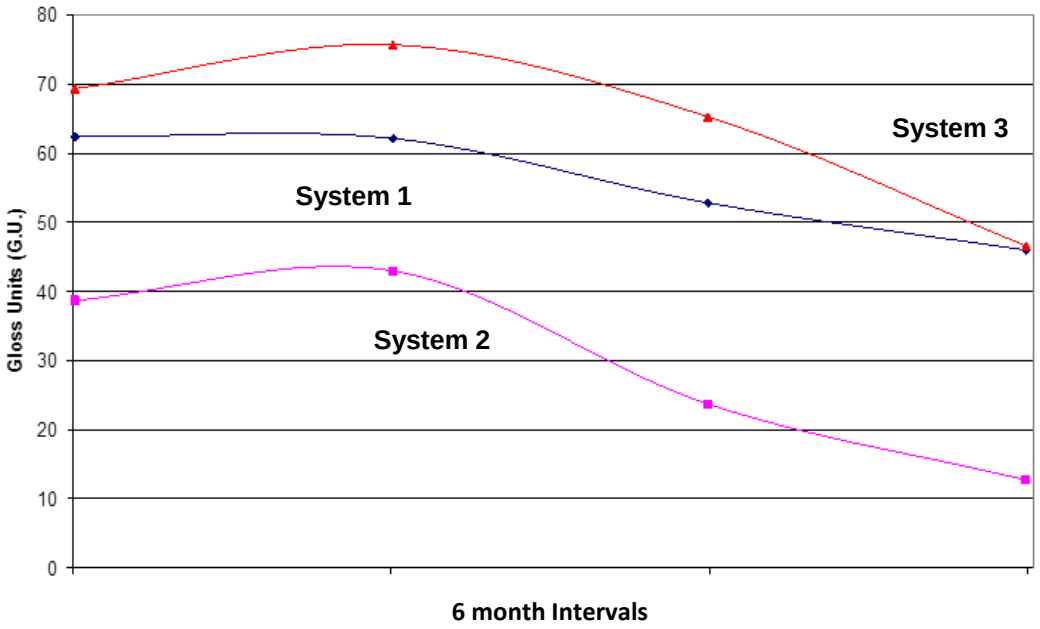
Atmospheric Exposure Testing

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

Gloss

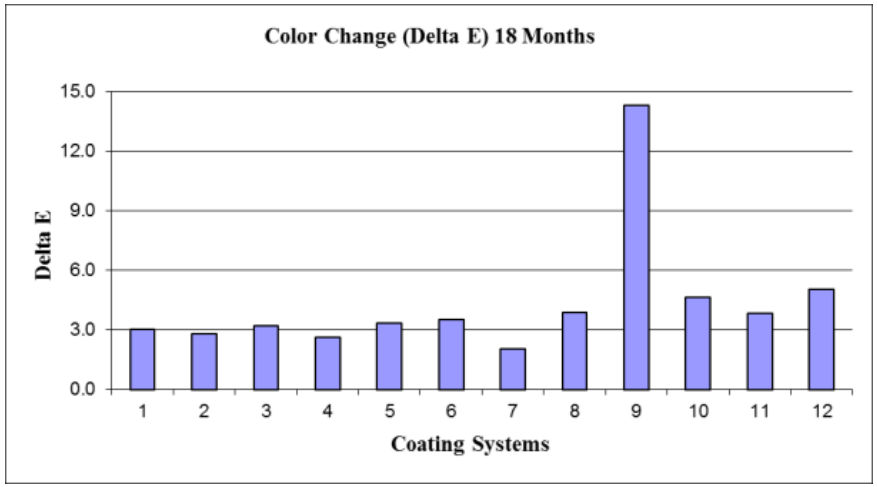
- Gloss is not a pass/fail criterion
- Gloss values are important for aesthetic qualities
- A reduction in gloss may indicate degradation to the coating
- Gloss measurements are performed with a portable gloss meter according to ASTM D523, “Standard Test Method for Specular Gloss”

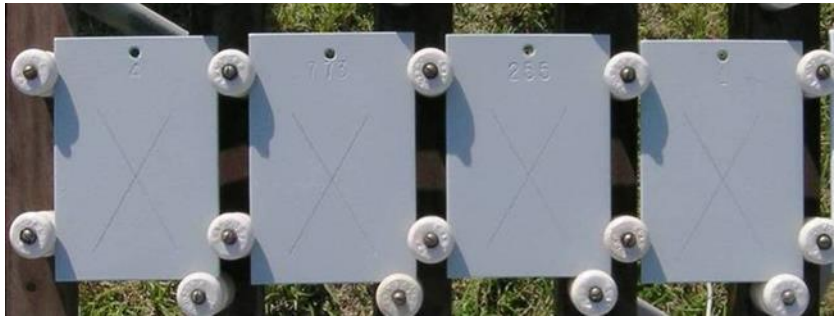
	Average Gloss*		
System	initial	18 Month	Gloss Retention
1	62	46	74%
2	39	13	33%
3	69	47	67%



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”



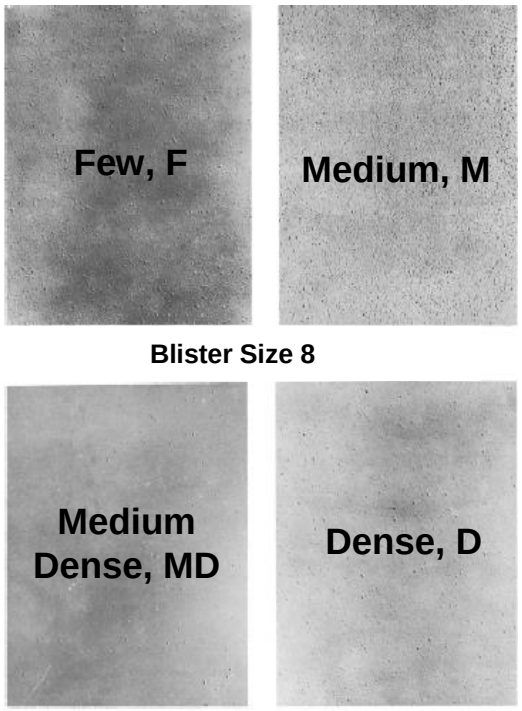


System 9 – Initial Condition

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

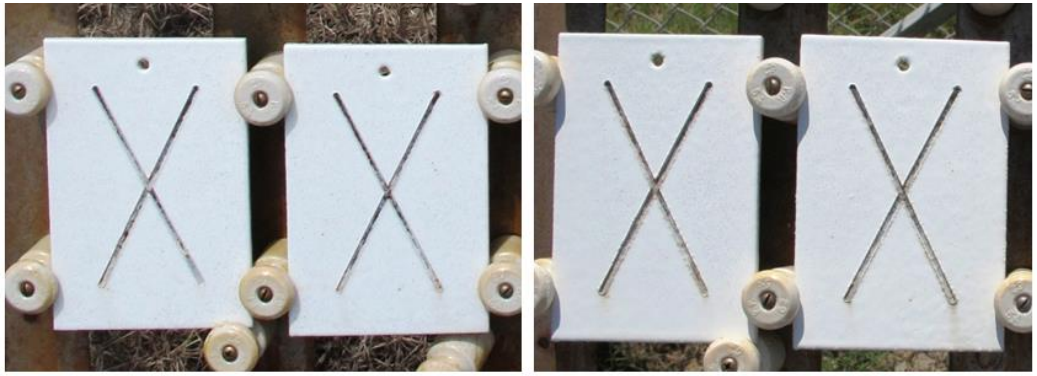
- Corrosion under paint is a pass/fail Criterion
- Acid rinsed and non acid rinsed are evaluated by this method
- Corrosion Under Paint is determined via pictorial examples in ASTM D610, “Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surface”
- According to NASA-STD-5008B, a 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

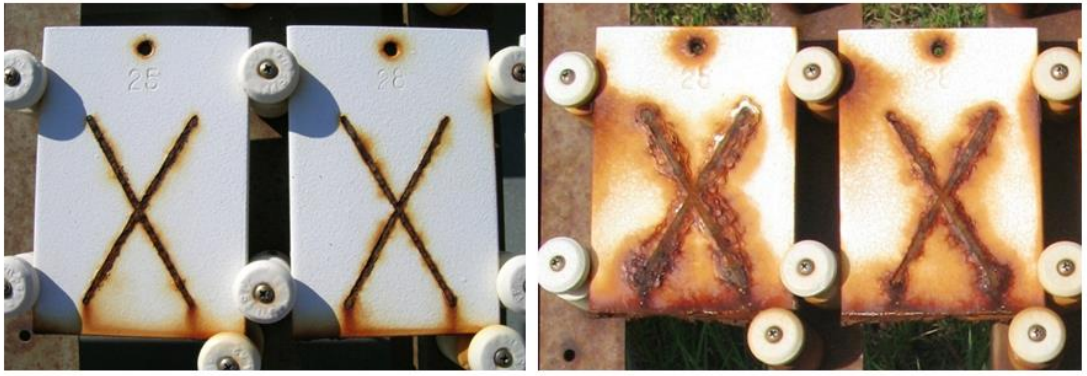
18 month and 60 month exposure – Not Approved for Use

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

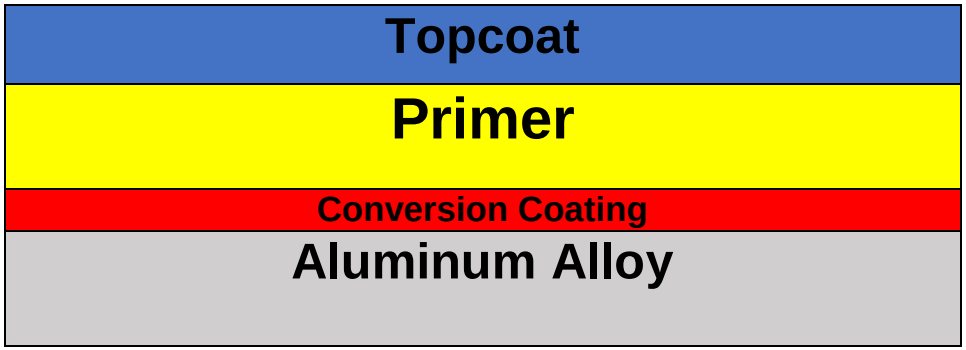


18 month and 60 month exposure – Not approved for use

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 Coatings



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

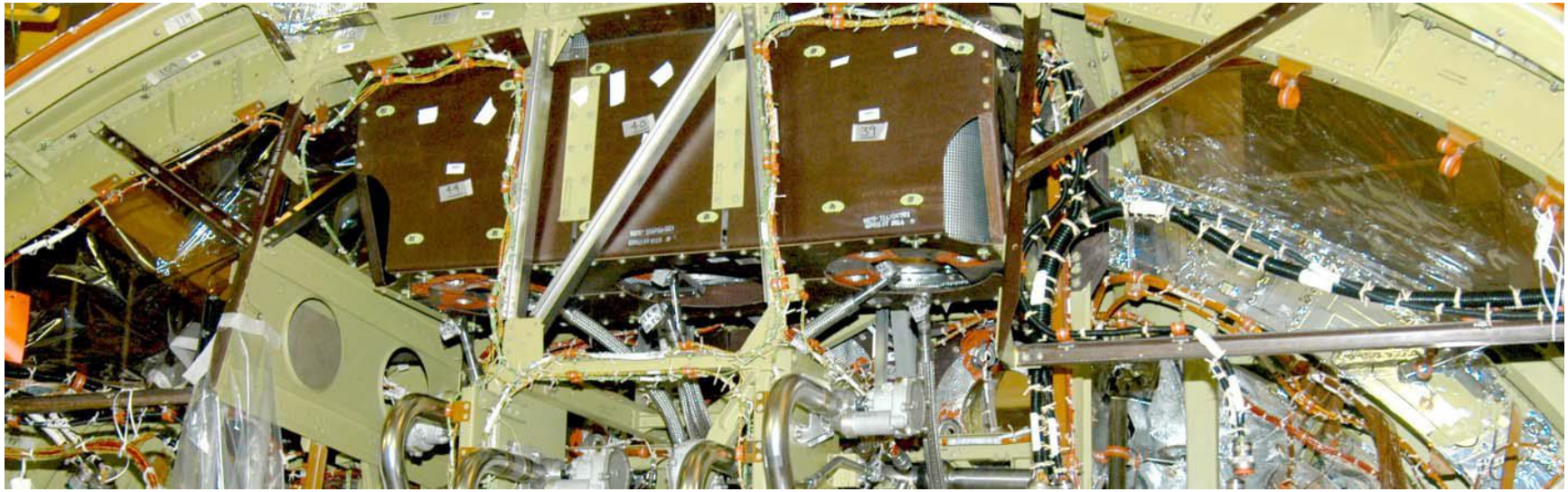
- **The conversion coating provides the first layer of corrosion protection and acts as a base for improved adhesion to the primer**
- **Chromate and chromate-phosphate-based conversion coatings have been used for this purpose for several decades, as they are effective in inhibiting the corrosion of 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
- 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



Problems with Ageing Super Koropon Primer

- **The Orbiter Program relied heavily upon the corrosion protection ability of a hexavalent chromium Cr(VI) primer (Super Koropon)**
- **The primer was used to cover most of the structure, as a bonding surface for the thermal protection system, and to protect critical components**
- **Long-term planning for the maintenance and inspection of the orbiters was not given full consideration until after the orbiters were already constructed**
- **In 2004 the Smithsonian gave permission for removal of certain components from the 30 year old Orbiter Enterprise to perform an age life prediction investigation***

Koropon coated structure on Enterprise

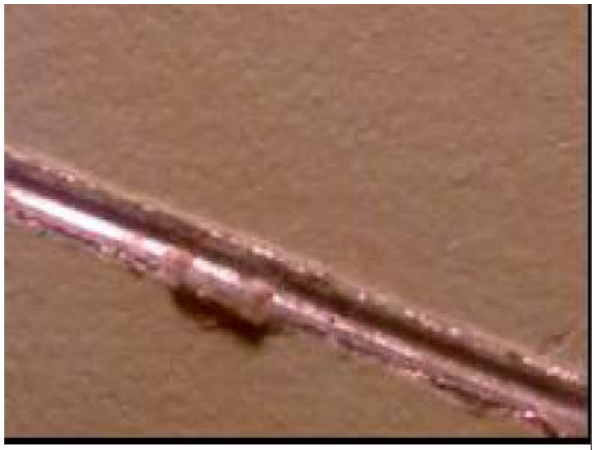
*J.K. Lomness and L.M. Calle, "Comparison of the Chromium Distribution in New Super Koropon Primer to 30 Year Old Super Koropon Using Focused Ion Beam/Scanning Electron Microscopy," http://corrosion.ksc.nasa.gov/pubs/ChromiumDistribution.pdf

Corrosion Protection Performance Study

- The performance of the 30 year old Koropon was compared to that o a newly coated panel (control)
- Both panels were scribed and salt fog tested for 1500 hours
- The Enterprise panel performed poorly compared to fresh Koropon panel
- Pitting on the scribe line appeared after 500 hours of salt fog testing
- Blisters away from the scribe appeared after 1000 hours of salt fog testing
- No corrosion was observed on the control panel

Enterprise Panel
Scribe Pitting @ 60X mag
After 500 hours

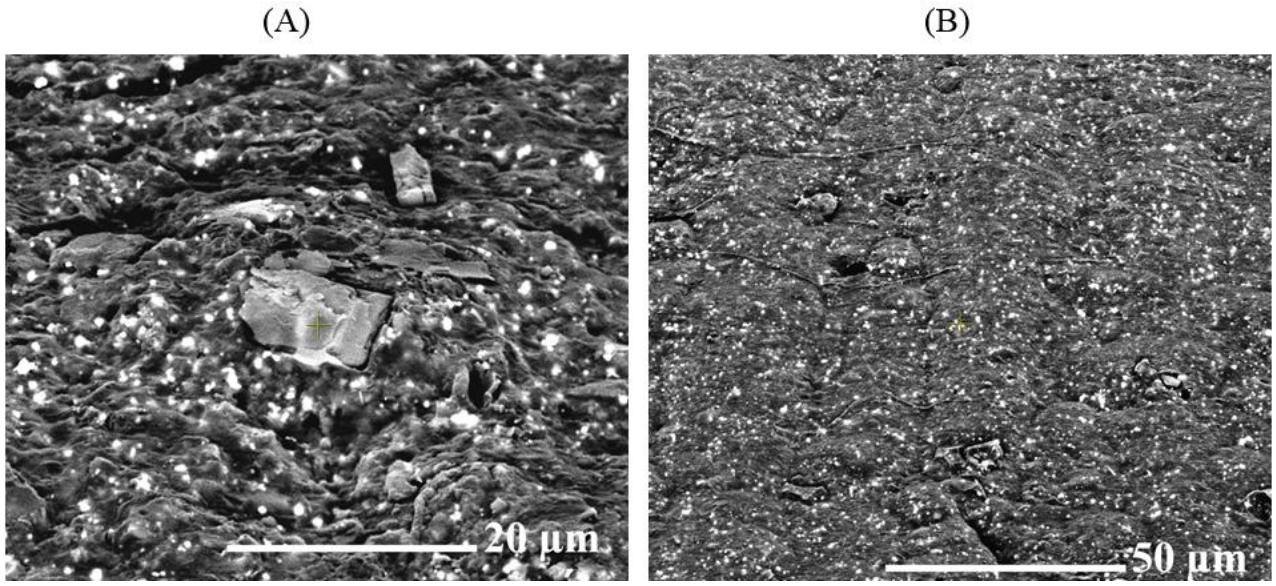
Enterprise Panel
Blister @ 60X mag
After 1000 hours



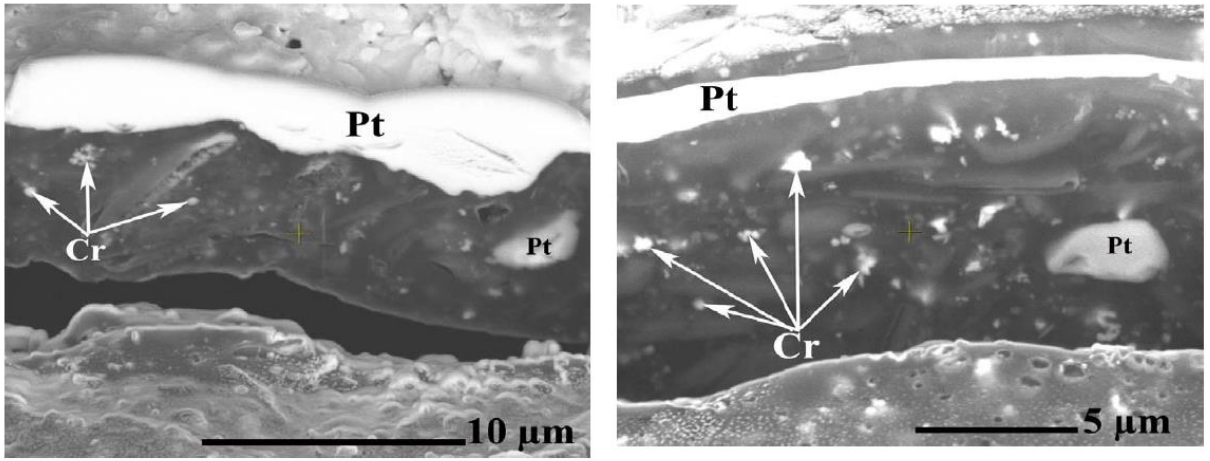
Control Panel
Scribe @ 60X mag
After 1500 hours

Corrosion Protection Performance Study

High magnification revealed a different surface morphology:
Enerprise primer (A) is rougher than the control (B)



The SEM EDS images indicated that there is less chrome in the Enterprise film (A) than in the control film (B) and that it is not distributed very well



Enterprise Cross Section

Control Cross Section

Corrosion Control Review Board (CCRB)

- Approximately after 12 years of operation, a corrosion control review board was formed
- The goals of this board included:
  - An assessment of the extent and causes of corrosion
  - Implementation of both long term and short term corrective actions
  - Generation and maintenance of a historical corrosion database
  - Development and implementation of methods for the detection of corrosion
  - Development and implementation of corrosion training and certification programs

New Materials and Coatings to Meet Changing Demands

- The evolution of aerospace and automotive materials, coatings and application processes are motivated by:
  - Environmental regulations
  - Demands for better energy efficiency and performance
  - Sustainable supply chain

- Future systems require smart coatings with corrosion protection on demand, self-healing and corrosion detection

Artistic illustration of the vehicle assembly building, NASA's space launch system, and the Orion crew module on the mobile launcher, with the 39B Launch Platform in the background.

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 ^{o}C)

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

Corrosion Preventive Compounds (CPCs)

- Corrosion preventive compounds (CPCs) are temporary coatings that can be applied to prevent new corrosion sites from forming or to suppress any corrosion that has initiated
- CPCs commonly contain corrosion inhibitors suspended in a mixture of solvents and a base oil or grease
- The base oil acts as a carrier fluid for the inhibitors and also as a protective barrier to environmental elements
- The solvent acts as a base oil and inhibitor dispersant and is intended to evaporate after application
- CPCs can be soft or hard films, and can be primarily composed of a petroleum, hydrocarbon, or fluoropolymer material depending on their end user requirements
- CPCs have been used on aircraft for many years as a relatively inexpensive method of combating corrosion

Corrosion Preventative Compounds (Orbiter)

- **After testing, three materials identified for use**
  - Fluid Film® (Lanolin Based Grease)
  - Calcium Grease (Paraffin Based Grease)
  - Dinitrol AV-30 (Waxy Hydrocarbon)

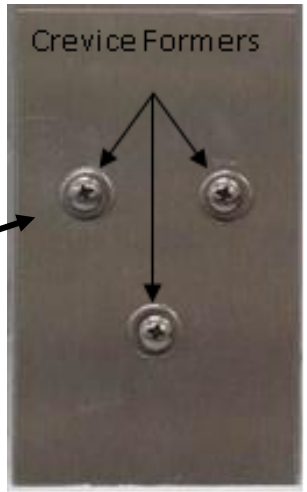
- **Areas of application**
  - Fluid Film®: Ground support equipment
  - Calcium Grease: Actuators and the Elevon Cove Primary Seal Tube
  - Dinitrol AV-30®
    - **Spray-on:** Interior cavities
    - **Brush-on:** Vent doors, door cavities, carrier panels, wing leading edge faying surfaces

Galvanic Corrosion Solutions at KSC

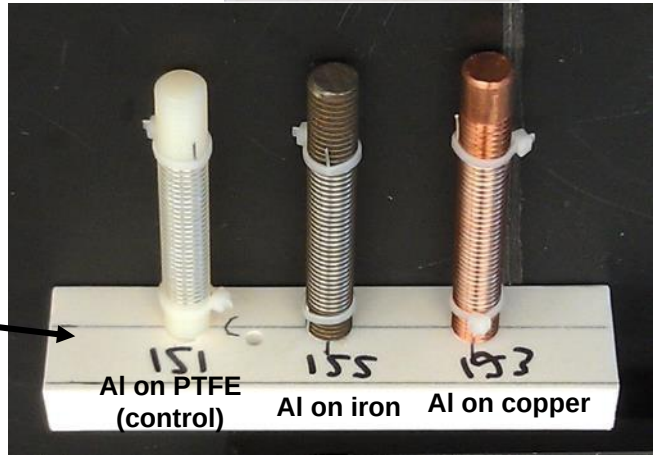
- Solutions for common galvanic corrosion issues
- Use Corrosion Preventative Compounds (CPCs): oils, greases, and non-permanent hard films with corrosion inhibitors
- Effectively penetrate into crevices, fasteners, washers, around fittings to interrupt the corrosion reactions

Galvanic corrosion testing at NASA KSC Beachside Atmospheric Test Site

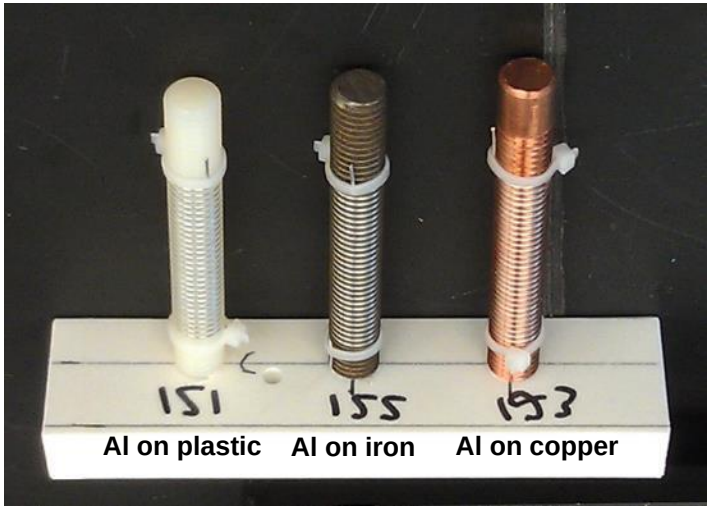
SS washer on Al and SS: galvanic and crevice corrosion



Wire on bolt testing: galvanic couples

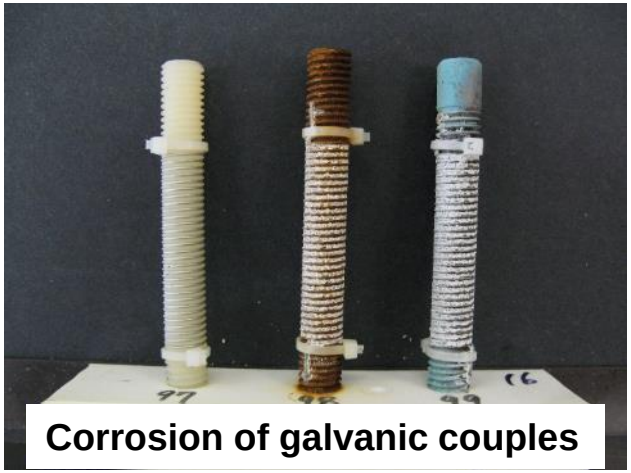


Galvanic Corrosion Mitigation with Environmentally Friendly CPCs



No corrosion control

Coated with CPCs



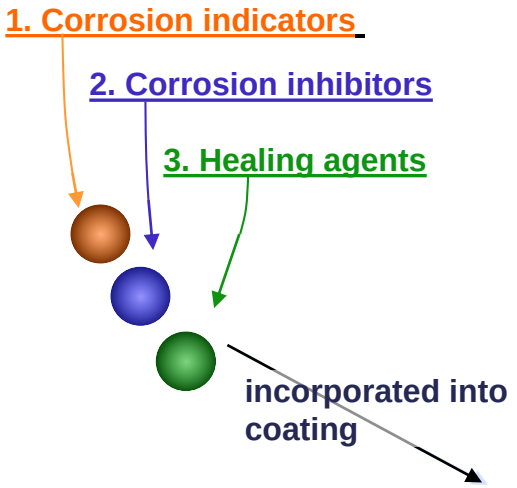
Corrosion of galvanic couples

Successful corrosion control

Smart Coatings for Corrosion Control

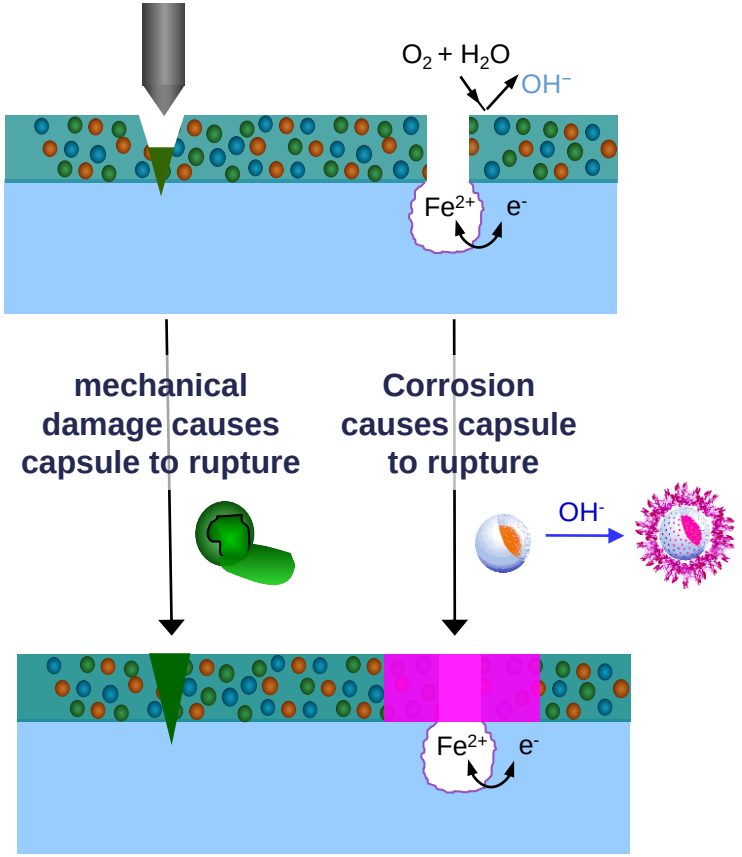
- The use of "smart coatings" for corrosion sensing and control relies on the changes that occur when a material degrades as a result of its interaction with a corrosive environment.
- Such transformations can be used for detecting and repairing corrosion damage.
- NASA's Corrosion Technology Laboratory is developing a coating that can detect and repair corrosion at an early stage.
- This coating is being developed using 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

Smart Coating for Corrosion Detection and Control



Ruptured Microcapsule:

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



Summary

- NASA has been battling corrosion since the inception of the Space Program in 1962.
- NASA launches from the most naturally corrosive environment in North America.
- NASA's Space Technology Roadmap includes corrosion control technologies as one of the areas needed to lower the cost and improve the sustainability and efficiency of its space exploration missions.
- Corrosion control in the aerospace industry is based on materials selection and coatings.
- The aerospace industry has relied on hexavalent chromium coatings for corrosion control of aluminum alloys.
- New corrosion control coatings are needed to replace hexavalent chromium coatings because of their toxicity and imminent ban.
- NASA is developing smart coatings as replacements for hexavalent chromium coatings for the aerospace industry.

Thank you

Additional Information

Where are the Orbiters Now?

- After 135 missions and 30 years the Orbiter fleet was retired in 2011
- Lessons learned from the Orbiter program have aided NASA in the design and manufacture of new spacecraft so that exploration of space can continue
- The Orbiters are proudly being displayed for all the public to see in New York City, Washington D.C., Los Angeles, and at the Kennedy Space Center in Florida.

Space Shuttle Discovery at the Smithsonian National Air and Space Museum, Washington D.C.

Endeavour on display at the California Science Center in LA

Enterprise, the prototype orbiter at the Intrepid Sea, Air, and Space Museum in New York

Atlantis Exhibit at the Kennedy Space Center

Atlantis embarked on its 33rd and final mission on 8 July 2011

Space Shuttle Atlantis exhibit at the Kennedy Space Center Visitor Center

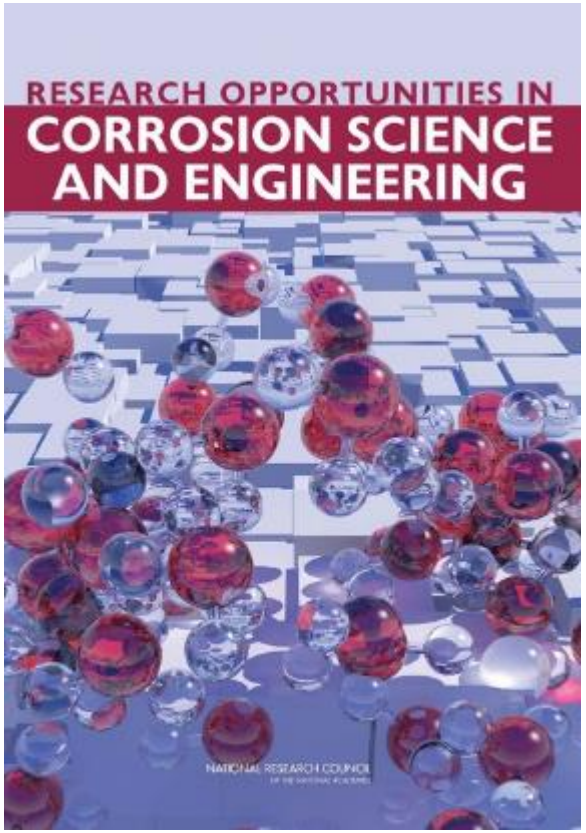
What is Corrosion?

- Corrosion is the deterioration of a material due to reaction with its environment (M.G. Fontana). It literally means to "gnaw away"
- Degradation implies deterioration of the properties of the material.
- Metal atoms in nature are present in chemical compounds (i.e. minerals).
- Metals in their uncombined state are in a high energy state. The tendency is to corrode and revert to the low energy state. Corrosion has been called metallurgy in reverse.

KSC Crawler/Transporter
Structural Steel Corrosion

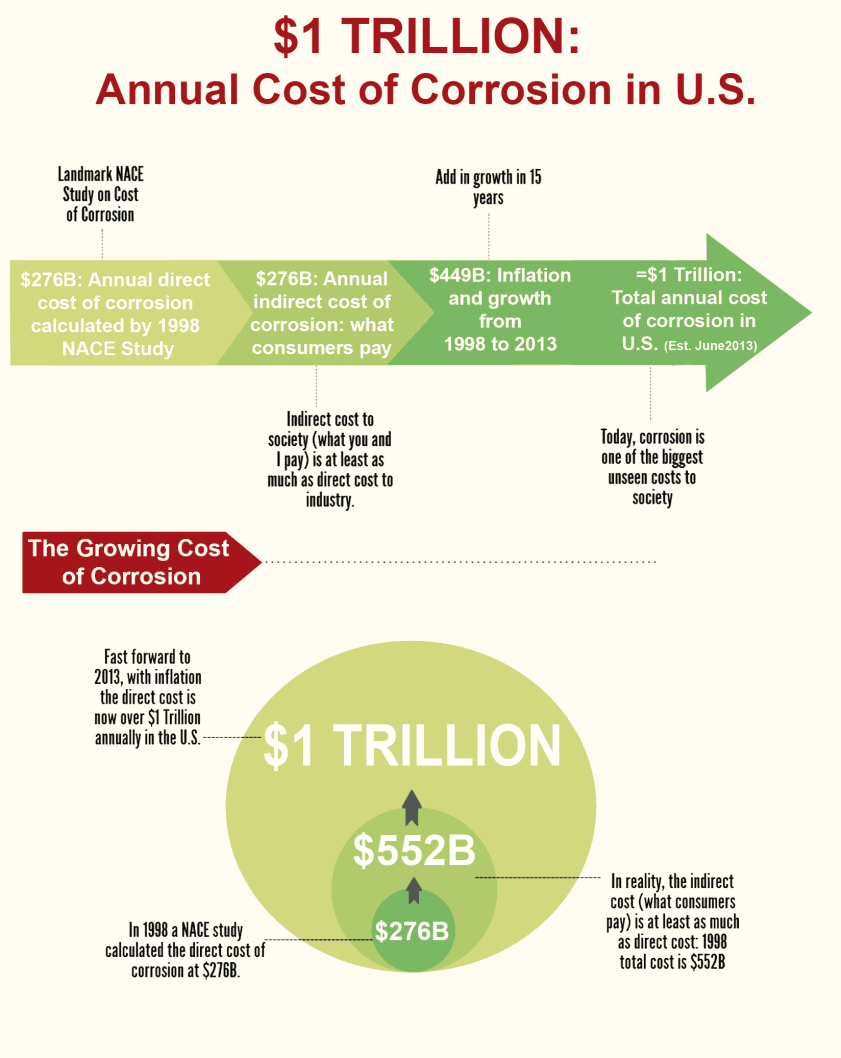
Corrosion Grand Challenges*

- **Development of cost-effective, environment-friendly, corrosion-resistant materials and coatings.**
- **High-fidelity modeling for the prediction of corrosion degradation in actual service environments.**
- **Accelerated corrosion testing under controlled laboratory conditions. Such testing would quantitatively correlate with the long-term behavior observed in service environments.**
- **Accurate forecasting of remaining service time until major repair, replacement, or overhaul becomes necessary. i.e., corrosion prognosis.**



***Research Opportunities in Corrosion Science and Engineering,** Committee on Research Opportunities in Corrosion Science and Engineering; National Research Council (2010)

Cost of Corrosion



- **At US $2.2 (1.6 €) trillion, the annual direct cost of corrosion worldwide is over 3% of the world's GDP.***
- **Direct costs do not include the environmental damage, waste of resources, loss of production, or personal injury.**

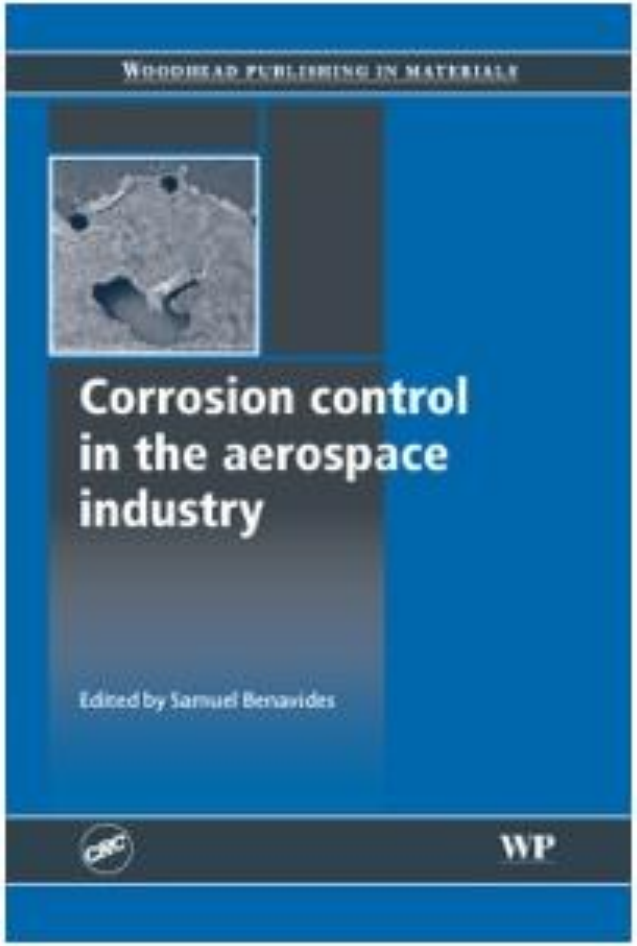
*World Corrosion Organization 2010

(1 Trillion = 10^{12} = 1 billon)

Corrosion in the Aerospace Industry

- The aerospace industry employs high strength aluminum alloys as structural materials for airplanes because of a combination of valuable mechanical properties, strength to weight ratio, good corrosion resistance, easy recyclability, and formability.
- Aluminum needs alloying with other elements in order to improve its mechanical strength.
- This alloying of aluminum with other metallic elements has a significant effect on its corrosion resistance properties.
- Reduction in corrosion resistance occurs as a result of the heterogeneous microstructure attributed to the second phase intermetallic particles of various sizes and compositions in the aluminum alloy matrix.
- The presence of these intermetallic particles in the aluminum alloy microstructure is often responsible for localized corrosion in the form of pitting, intergranular corrosion, exfoliation corrosion, etc., depending on the alloy type.
- Aluminum alloy surfaces are coated to enhance their corrosion resistance.

Reference



Chapter 9: L. M. Calle, “Corrosion control in space launch vehicles,” In Corrosion Control in the Aerospace Industry, Edited by S. Benavides, Woodhead Publishing Series in Metals and Surface Engineering, 2009.

Orion 37 days prior to 1st Test Flight