



Control de la Corrosion en la Industria Aeroespacial

Rumbo a los 50 Años
Universidad Autónoma del Carmen
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- **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. Corrosion conditions at the launch pads are even more severe due to solid rocket booster (SRB) exhaust products.**
- **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 ground operations in support of future launch activities.**
- **NASA has developed microencapsulation technology specifically designed for corrosion control applications (U.S. Patents No. 7,790,225, 2010 and 20130017612, 2013).**
- **Micro containers are being used to develop a smart multifunctional coating for autonomous corrosion detection, control, and self-healing.**
- **This presentation provides an overview of the background and progress made to date in the development of a smart multifunctional coating to indicate corrosion at an early stage and in hidden areas, to deliver corrosion inhibitors on demand, and to self-heal mechanical damage, such as a scratch.**



NASA's Current Plans for Space Exploration

"NASA's Space Launch System (SLS) and Orion will allow human exploration to continue beyond the moon in ways that were once a glimmer in our minds eye. Now we are building the hardware and developing the engineering operations teams that will launch the vehicle that will one day take people to Mars"

Space Launch System



Orion

America's new spacecraft for human exploration



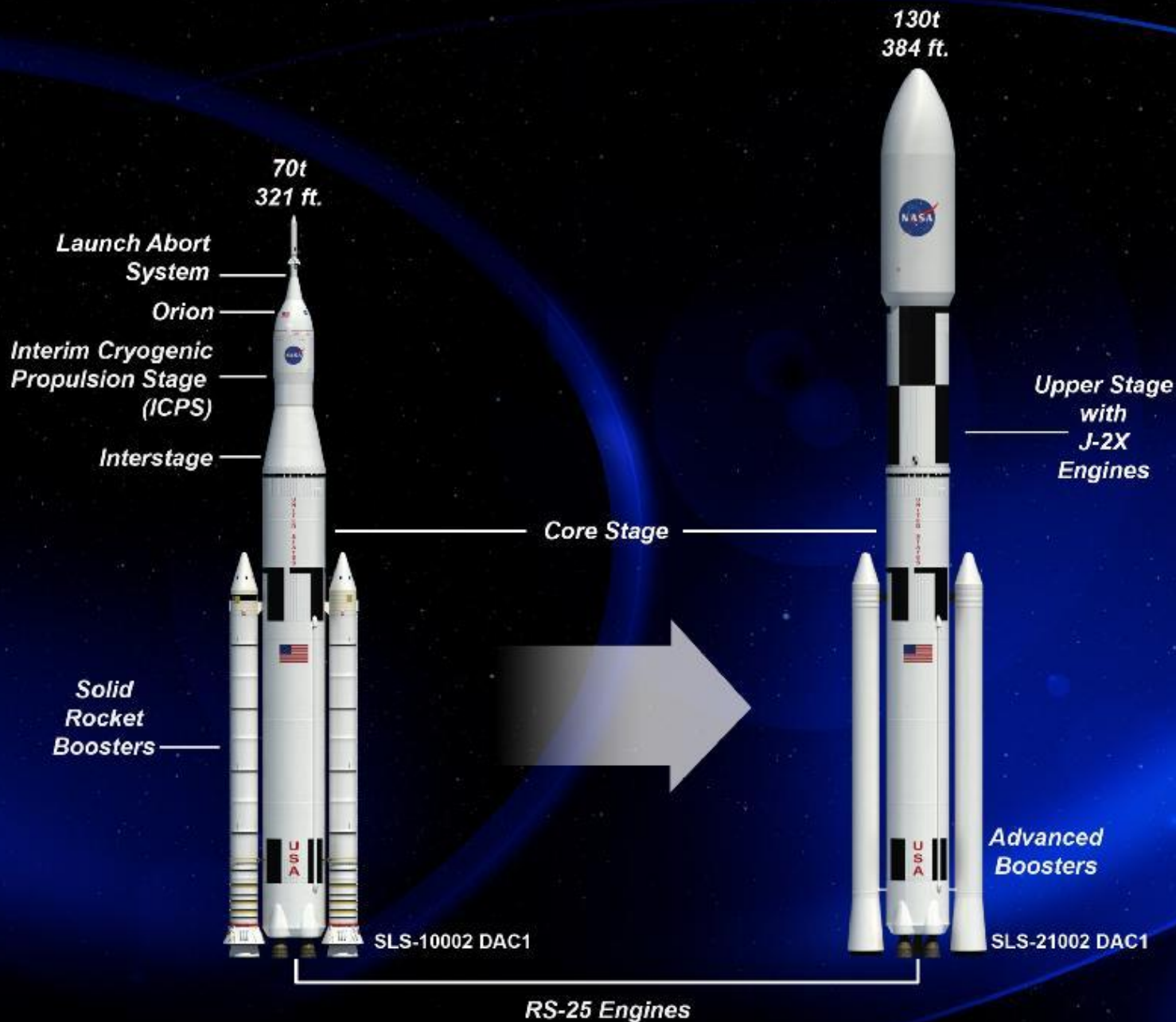
Orion



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



SLS Architecture Reference Configuration



Exploration Mission Timeline



**2010
PA-1**



**2014
EFT-1**



**2017
EM-1**



**2018
AA2**



**2021
EM-2**

Orion/SLS are the Basis for Exploration beyond Earth Orbit



HUMAN EXPLORATION

NASA's Journey to Mars



EARTH RELIANT

MISSION: 6 TO 12 MONTHS
RETURN TO EARTH: HOURS



Mastering fundamentals aboard the International Space Station

U.S. companies provide access to low-Earth orbit

PROVING GROUND

MISSION: 1 TO 12 MONTHS
RETURN TO EARTH: DAYS



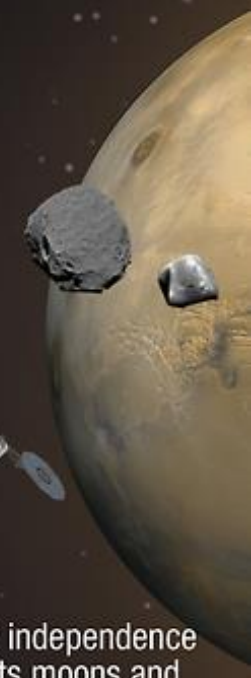
Expanding capabilities by visiting an asteroid redirected to a lunar distant retrograde orbit

The next step: traveling beyond low-Earth orbit with the Space Launch System rocket and Orion spacecraft



MARS READY

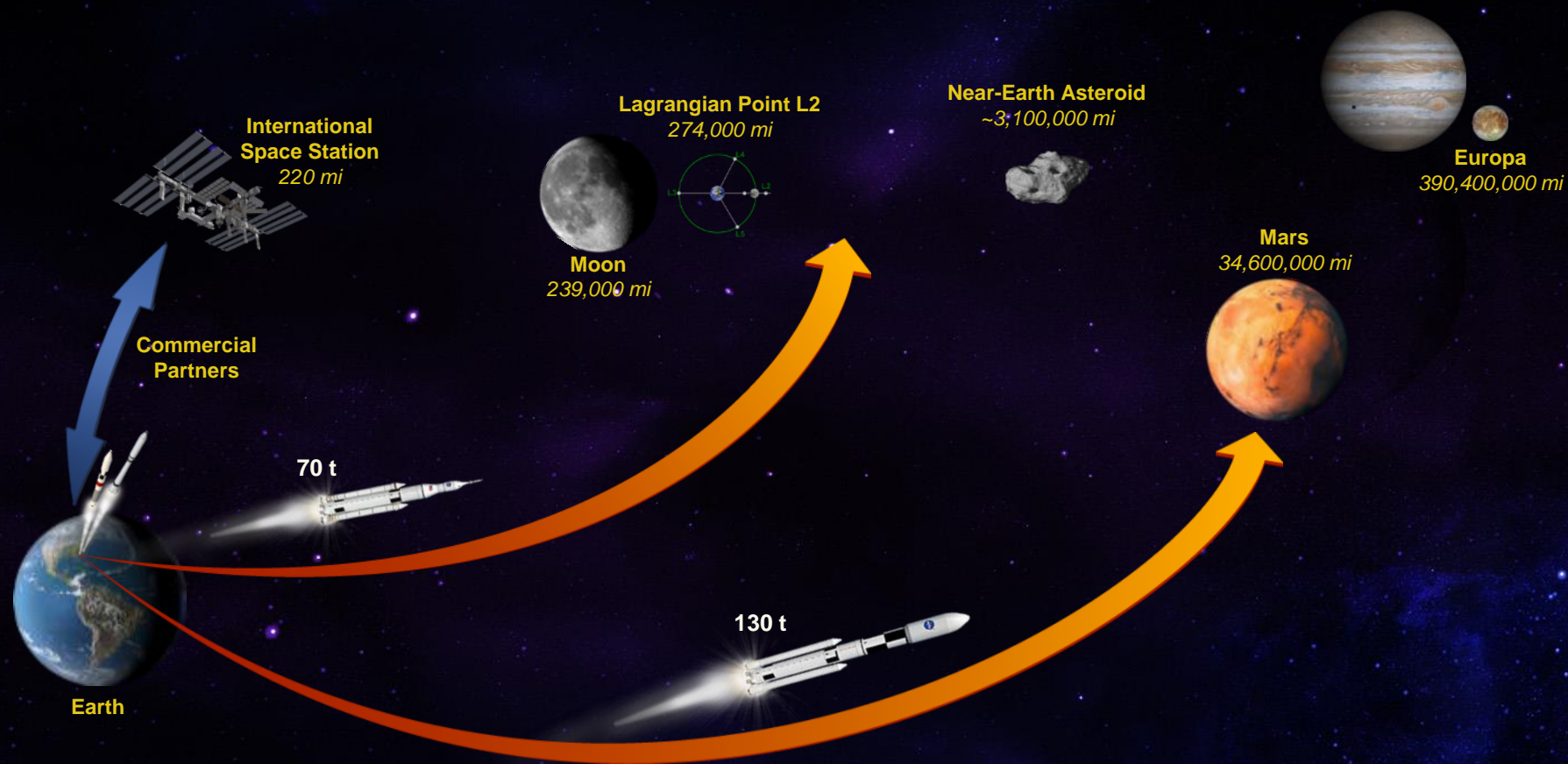
MISSION: 2 TO 3 YEARS
RETURN TO EARTH: MONTHS



Developing planetary independence by exploring Mars, its moons and other deep space destinations

www.nasa.gov

The future of exploration



Space Launch System and Orion enable solar system exploration

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.

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.**

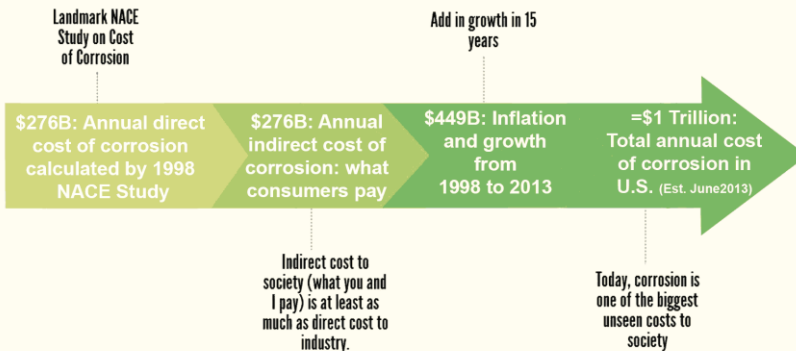


Impact of Corrosion

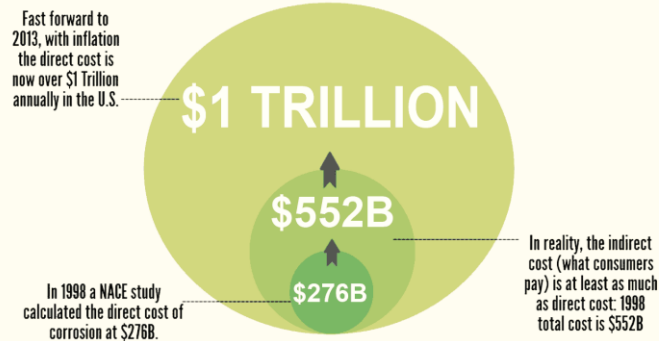


Repairs will cost about \$60 million USD and take about 2 years

\$1 TRILLION: Annual Cost of Corrosion in U.S.



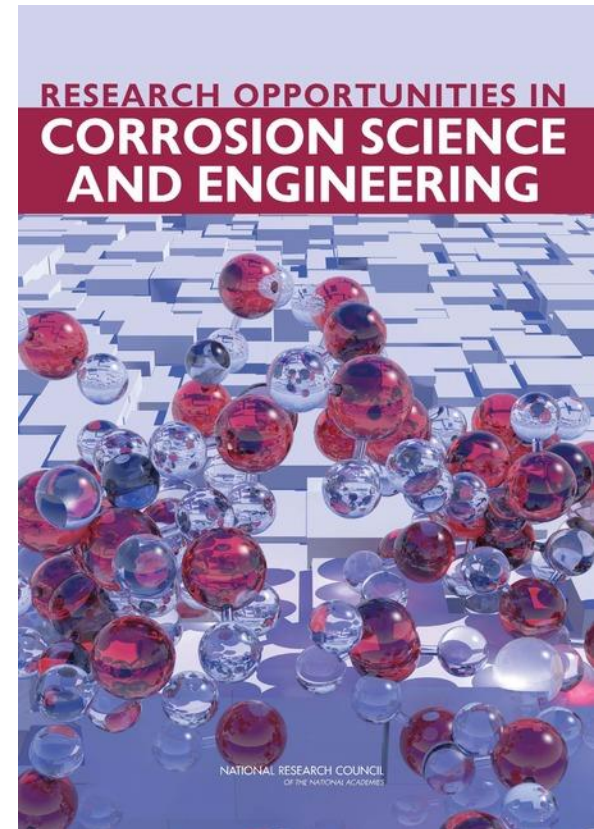
The Growing Cost of Corrosion



- 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.

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.**



- 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.



Aloha Airlines Accident, 1988



Associated Press library photo • April 28, 1988 (<http://the.honoluluadvertiser.com/2001/Jan/18/118localnews1.html>)

This picture of Aloha Airlines Flight 243, was taken after one-third of the roof flew off of the aircraft while cruising at 24,000 feet. A series of small cracks, caused by corrosion, had grown simultaneously at many nearby rivet holes, the devastating results of which can be seen in this picture. This is an extreme example of the damage that corrosion can cause, and an indication of why the protection of aluminum against corrosion is so important in the aerospace industry.

Since this mishap, the aviation community has struggled to accurately predict the onset of corrosion or the extent of structural damage it induces.

Despite advances in corrosion algorithms, computation material research, simulation, reliability and maintenance data analysis, a reliable model for prediction corrosion on aging aircraft has yet to be produced.

This incident established US civil and military programs for ageing aircraft of which corrosion was a principal area of focus.

Historically, corrosion prevention has not been appreciably designed into an aircraft.

NASA's Technology Roadmap



TA 1		LAUNCH PROPULSION SYSTEMS	TA 9		ENTRY, DESCENT, AND LANDING SYSTEMS
TA 2		IN-SPACE PROPULSION TECHNOLOGIES	TA 10		NANOTECHNOLOGY
TA 3		SPACE POWER AND ENERGY STORAGE	TA 11		MODELING, SIMULATION, INFORMATION TECHNOLOGY, AND PROCESSING
TA 4		ROBOTICS AND AUTONOMOUS SYSTEMS	TA 12		MATERIALS, STRUCTURES, MECHANICAL SYSTEMS, AND MANUFACTURING
TA 5		COMMUNICATIONS, NAVIGATION, AND ORBITAL DEBRIS TRACKING AND CHARACTERIZATION SYSTEMS	TA 13		GROUND AND LAUNCH SYSTEMS
TA 6		HUMAN HEALTH, LIFE SUPPORT, AND HABITATION SYSTEMS	TA 14		THERMAL MANAGEMENT SYSTEMS
TA 7		HUMAN EXPLORATION DESTINATION SYSTEMS	TA 15		AERONAUTICS
TA 8		SCIENCE INSTRUMENTS, OBSERVATORIES, AND SENSOR SYSTEMS			

Corrosion Control Technologies



NASA Space Technology Roadmap

America is beginning an exciting new chapter in space exploration. To enable the future, NASA has developed a set of roadmaps to define the key new technologies required for our human and robotic explorers to safely venture into deep space, to better understand how our own solar system evolved, and to unravel the mysteries of our universe.

The map you see here is a graphical representation of the NASA Space Technology Roadmaps, serving as a portal to the various technologies that NASA is developing. Let this technology portal serve as a starting point for your adventures beyond the bounds of Earth...

To learn more visit
www.nasa.gov/oct

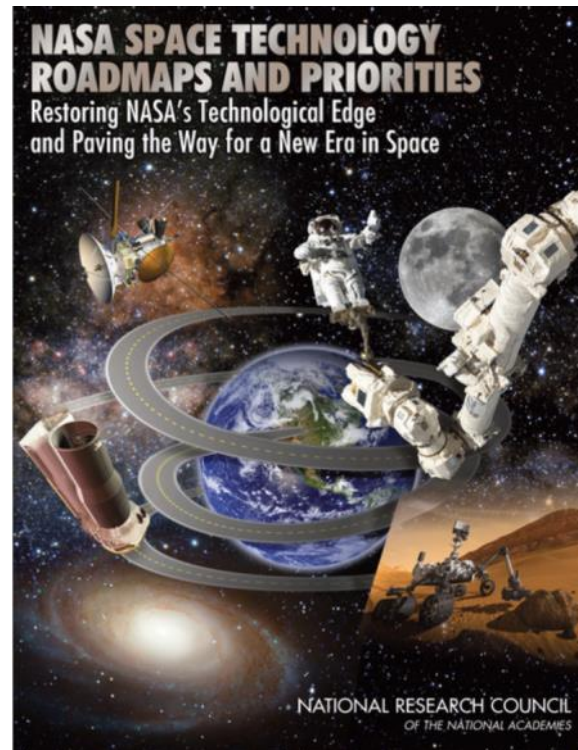


13.2.1 Corrosion Prevention, Detection and Mitigation

NASA Technology Benefits the Public



Since its inception in 1958, NASA has accomplished many great scientific and technological feats in air and space. NASA technology also has been adapted for many non-aerospace uses by the private sector. NASA remains a leading force in scientific research and in stimulating public interest in aerospace exploration, as well as science and technology in general.



13.2
Environmental and
Green
Technologies

13.2.1 Corrosion
Prevention, Detection
and Mitigation

13.2.2 Environmental
Remediation and Site
Restoration

13.2.3 Preservation of
Natural Ecosystems

13.2.4 Alternate Energy
Prototypes

New Materials and Coatings to Meet Changing Demands



- Evolution of aerospace and automotive materials, coatings, and applications processes motivated by:
 - Changing environmental regulations
 - Demands for better energy efficiency and performance
 - Sustainable supply chain
- Future systems require smart coatings with on-demand corrosion protection, healing, and corrosion sensing.
- Future aerospace and automotive platforms will utilize composites, new alloys and coatings with multifunctional capabilities

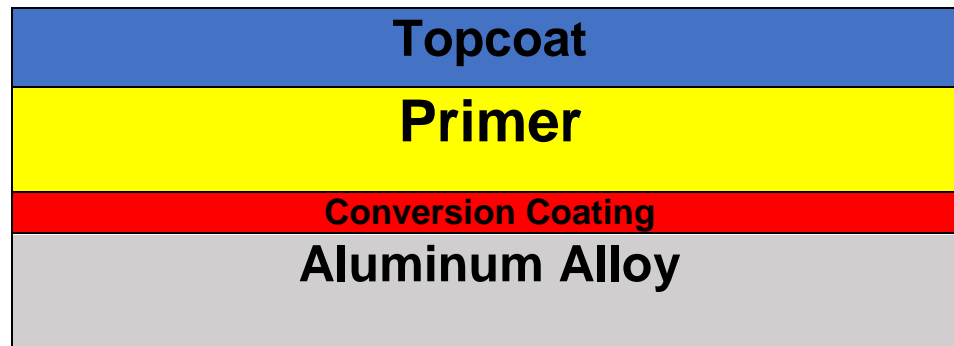


An artist illustration of the Vehicle Assembly Building and NASA's Space Launch System and Orion crew module on the mobile launcher, with Launch Pad 39B in the background.

Corrosion Protective Coatings



- **Barrier (passive).**
- **Barrier plus active corrosion inhibiting components:**
 - **Sacrificial (zinc-rich primers)**
 - **Corrosion inhibitors (can have detrimental effects on the coating properties and the environment; most expensive additive; subject to progressively stricter environmental regulations)**
- **Smart/Active/Functional/Self-healing**



Schematic of a typical multi-coating system used to protect aluminum alloys from corrosion. 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 for finding alternatives.

Coatings for the 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
- Man-made debris

Coatings on Orion Spacecraft



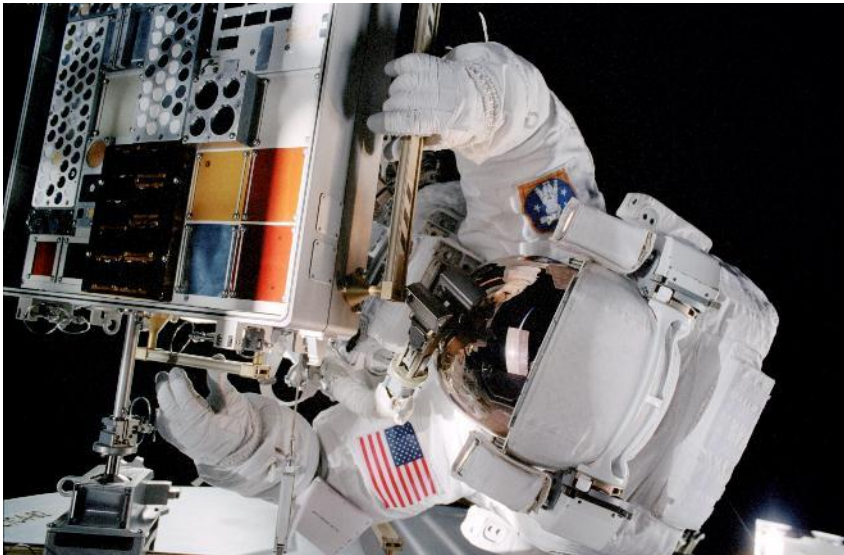
Corrosion protection coating on aluminum lithium alloy (left) and heat shield (right). The heat shield protects the spacecraft from temperatures reaching 4000 degrees Fahrenheit (2204 °C)

Orion 37 days prior to 1st Test Flight



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.

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

Atomic Oxygen Restoration



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

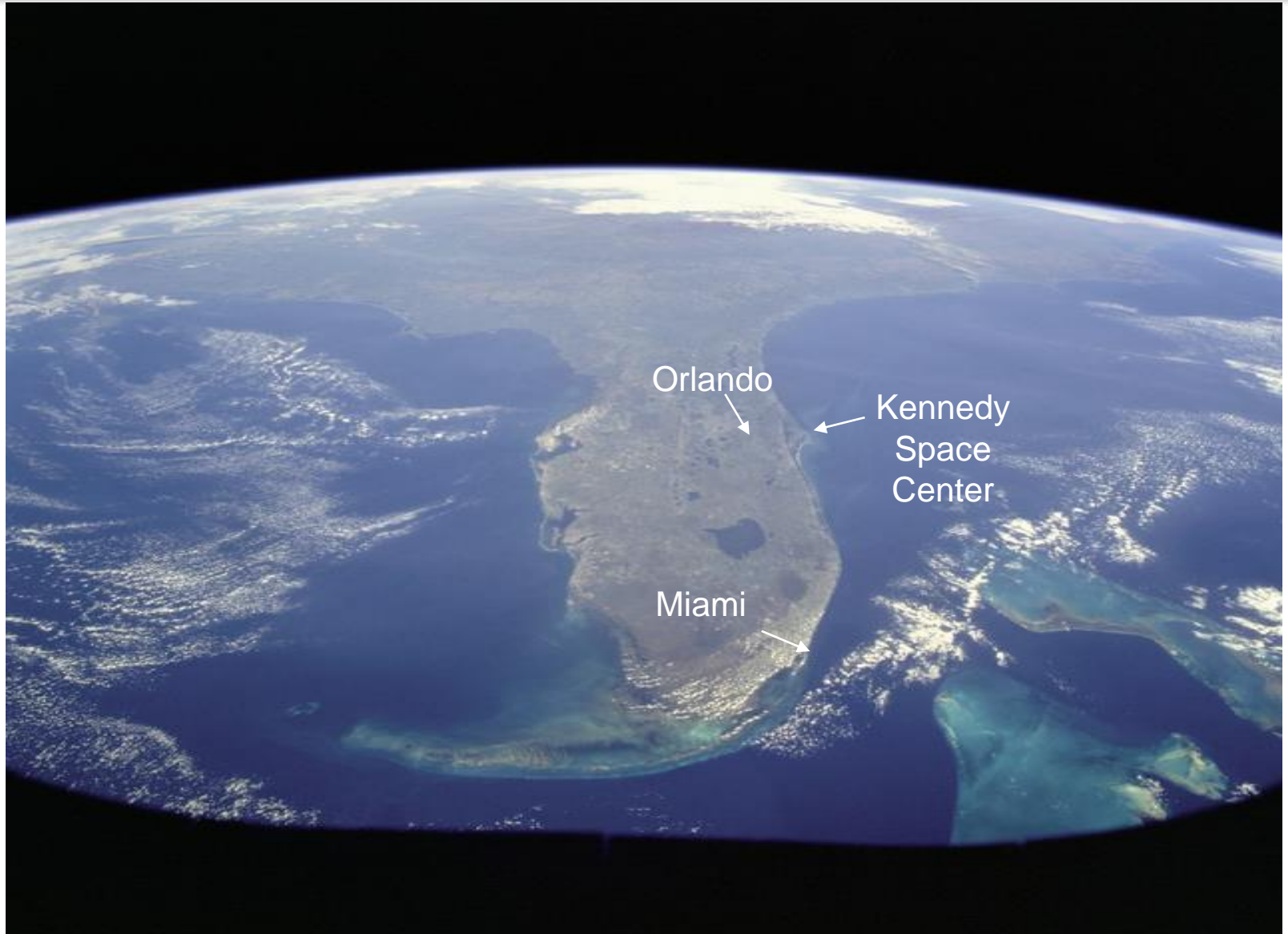
In the upper reaches of the atmosphere, about 200-500 miles, an elemental form of oxygen is created from exposure to intense solar ultraviolet light. Oxygen molecules are decomposed from O_2 into two separate oxygen atoms. This form of elemental oxygen is highly reactive and exposes a spacecraft to corrosion 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. ²⁸

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.

Coatings for NASA's Launch Environment



The Kennedy Space Center in Florida, USA, is a special place where we launch rockets from a wild life refuge in one of the most corrosive areas in the world



KSC Natural Environment



KSC Launch Environment



Corrosion Technology Laboratory at KSC Timeline



Space Program starts
Corrosion failures begin



Atmospheric exposure testing begins near the launch pads



Space Shuttle introduces acid deposition products that make corrosion worse



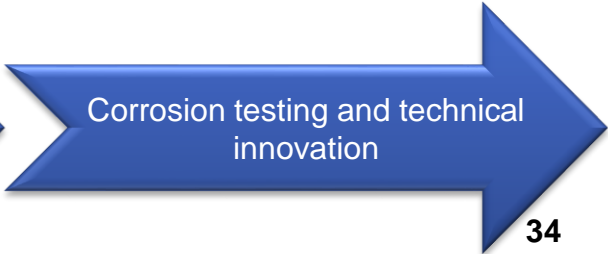
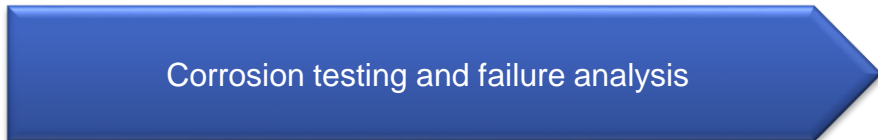
Accelerated corrosion testing (salt fog and electrochemical) begins



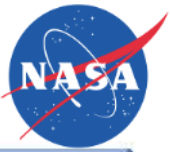
Corrosion Technology Laboratory is created



The Corrosion Technology Laboratory starts developing smart coatings



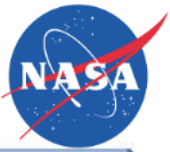
Atmospheric Exposure Testing



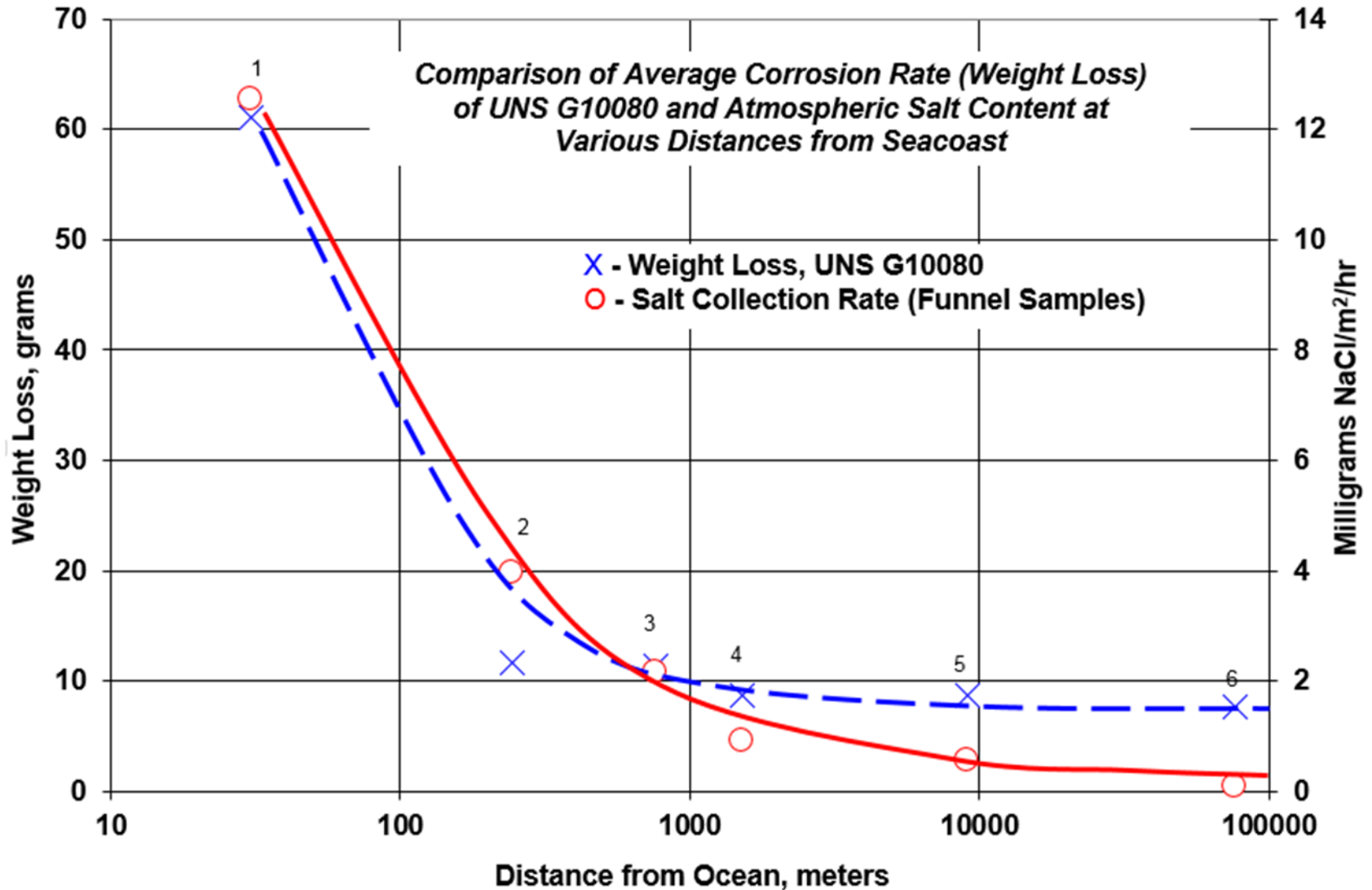
Beachside
atmospheric exposure
testing



KSC Natural Environment



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	$\mu\text{m}/\text{yr}$	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

^aTwo-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

KSC Launch Pad Environment



The launch environment at KSC is extremely corrosive:

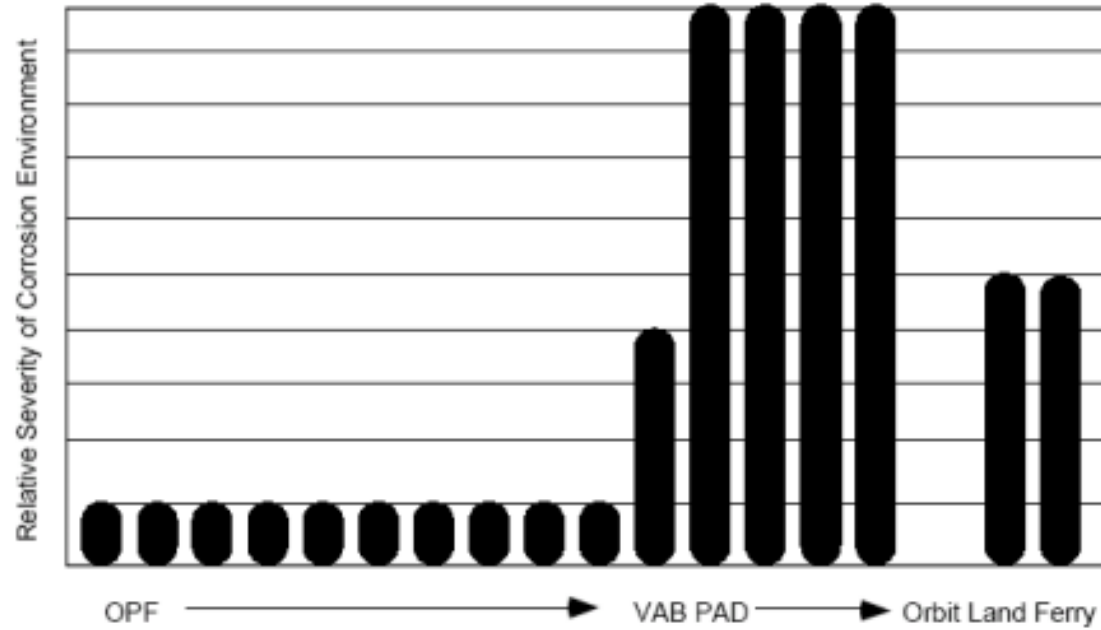
- Ocean salt spray
- Heat
- Humidity
- Sunlight
- Acidic exhaust from SRBs




Natural Salt Fog Chamber



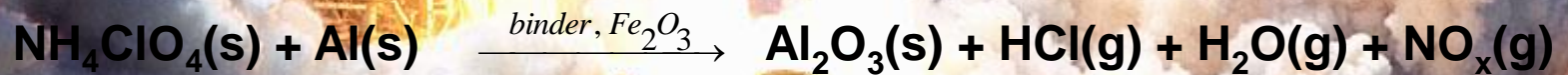
Orbiter Flight and Ground Environment



A photograph of a Space Shuttle launching from a launch pad. The shuttle is oriented vertically, with its external tank and boosters. A large plume of white smoke and fire is visible at the base of the boosters. A red arrow points from the text 'SRB Exhaust' to the base of the boosters. The background is a clear blue sky with some clouds. The text 'USA' is visible on the side of the orbiter. The chemical equation is overlaid at the bottom of the image.

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

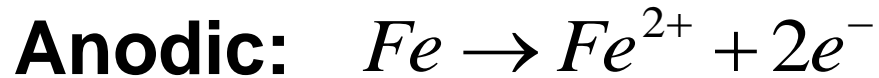
SRB Exhaust



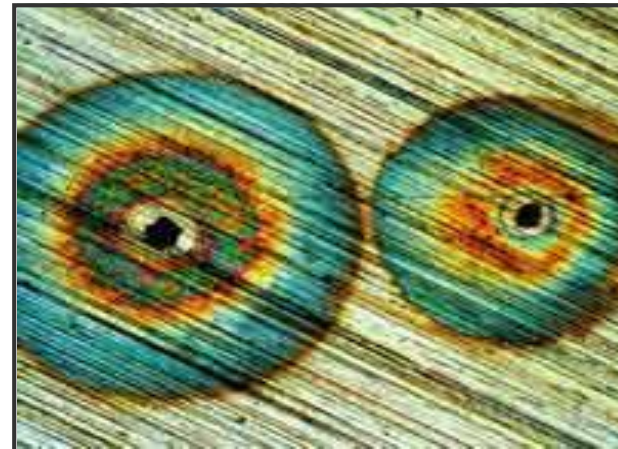
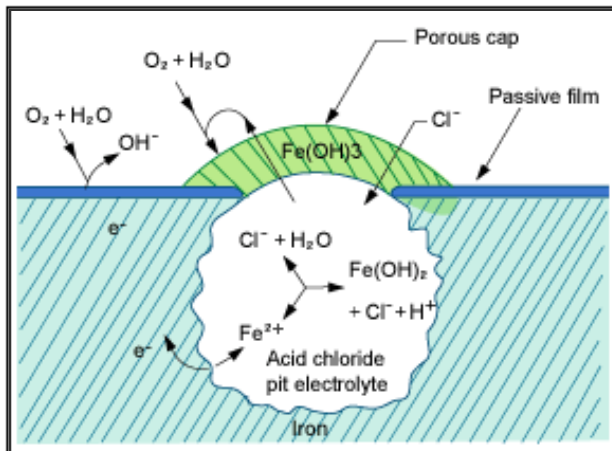
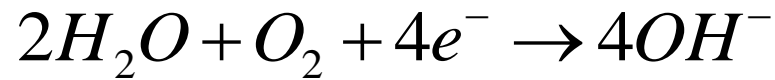
Electrochemical Nature of Corrosion

Metal is oxidized (anodic reaction); something else is reduced (cathodic reaction)

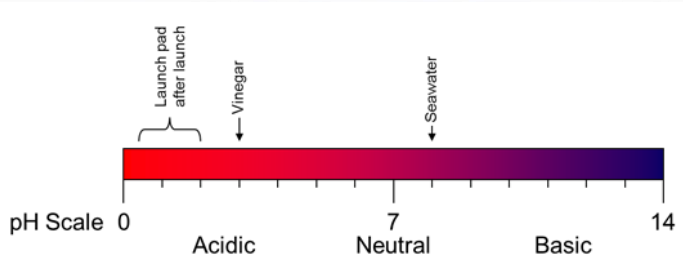
Overall Reaction:



Cathodic:



Launch Complex 39 pH Values after a Space Shuttle Launch



Zone 3:
pH ~2-3

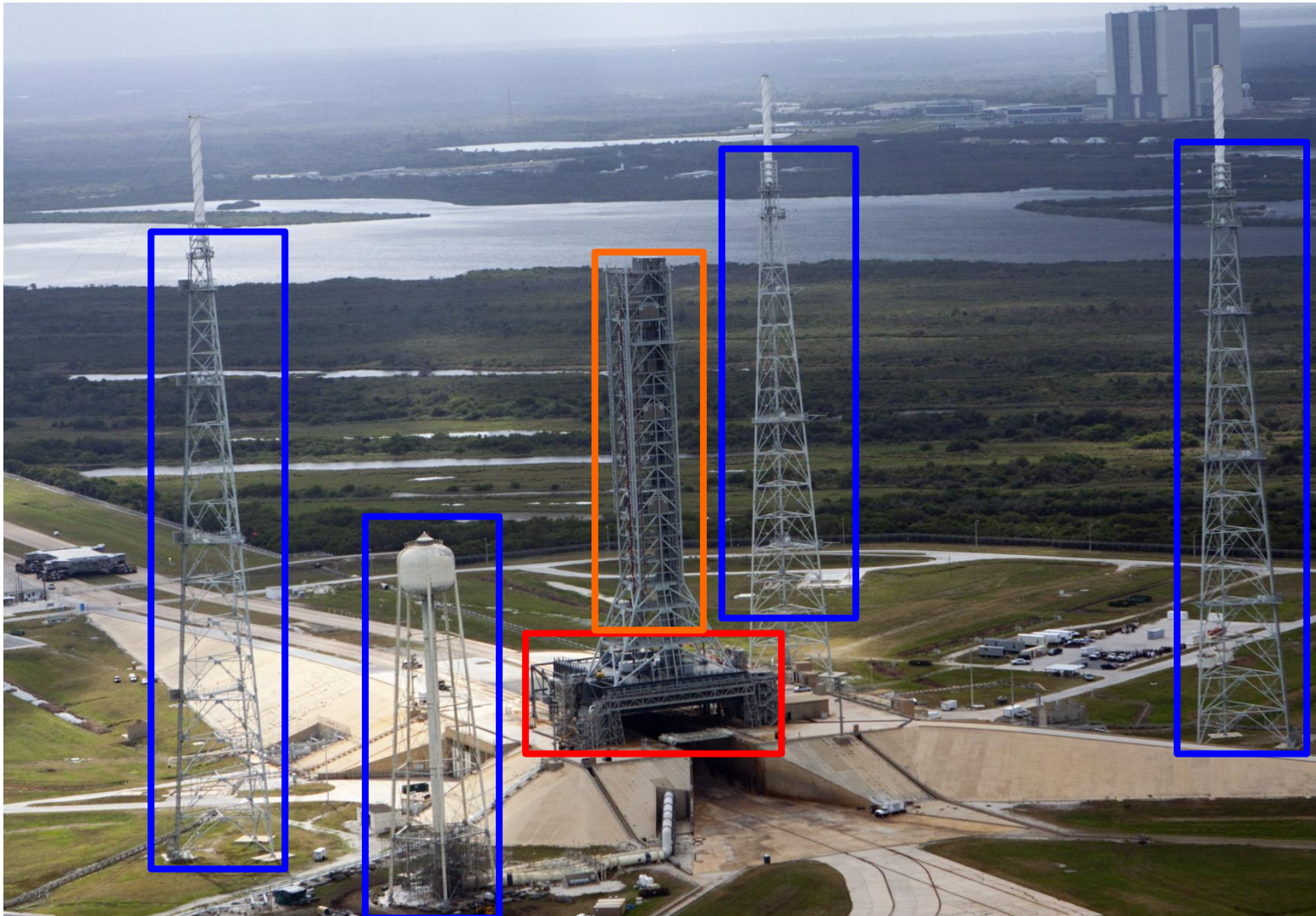
Zone 2:
pH ~ 2-3

FSS 115" Level

Zone 1:
pH ~ 0-1



New Launch Complex 39B



ZONE 3
pH-2-3

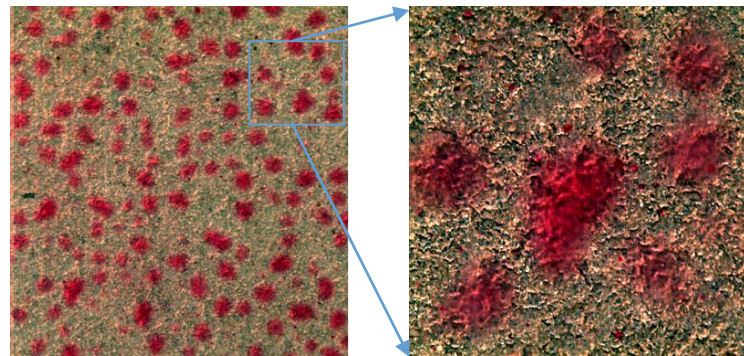
ZONE 2
pH 2-3

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

- **Barrier (passive).**
- **Barrier plus active corrosion inhibiting components:**
 - **Sacrificial (zinc-rich primers)**
 - **Corrosion inhibitors (can have detrimental effects on the coating properties and the environment; most expensive additive; subject to progressively stricter environmental regulations)**
- **Smart (Intelligent, self-healing, active or feedback active)**

A smart coating detects and responds actively to changes in its environment in a functional and predictable manner and is capable of adapting its properties dynamically. These coatings are also referred to in the literature as intelligent, self-healing, and active or feedback active, to distinguish them from barrier or passive coatings.



Smart coating responding to changing pH conditions

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.**

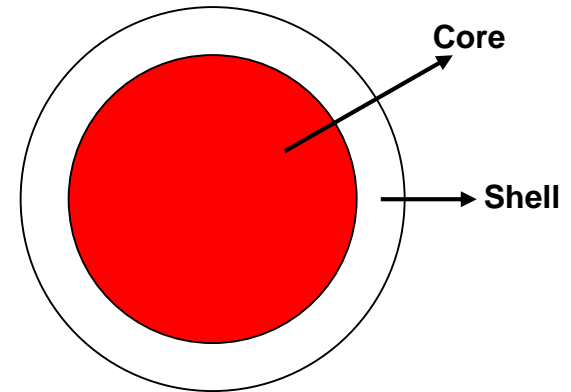
Corrosion indication, detection, and healing of mechanical damage can be achieved using microencapsulation technology

What are microcontainers?

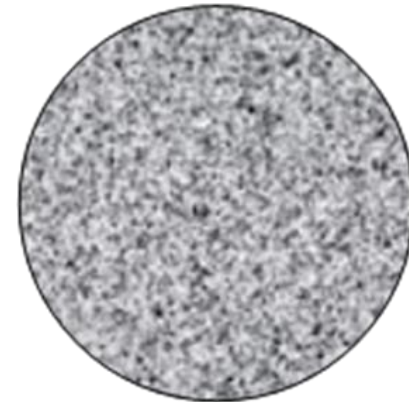
Particles or liquid drops coated in polymers. These microcontainers can carry any material that needs protection or controlled release.

Why microencapsulate a material?

- Incorporate active materials while maintaining coating integrity
- Achieve controlled-release
- Make active materials easier/safer to handle.
- Incorporate multiple component systems.
- Prevent undesired leaching
- Versatility



Microcapsules



Microparticles

Types of Feedback-Active Micro Containers for Corrosion Detection and Control

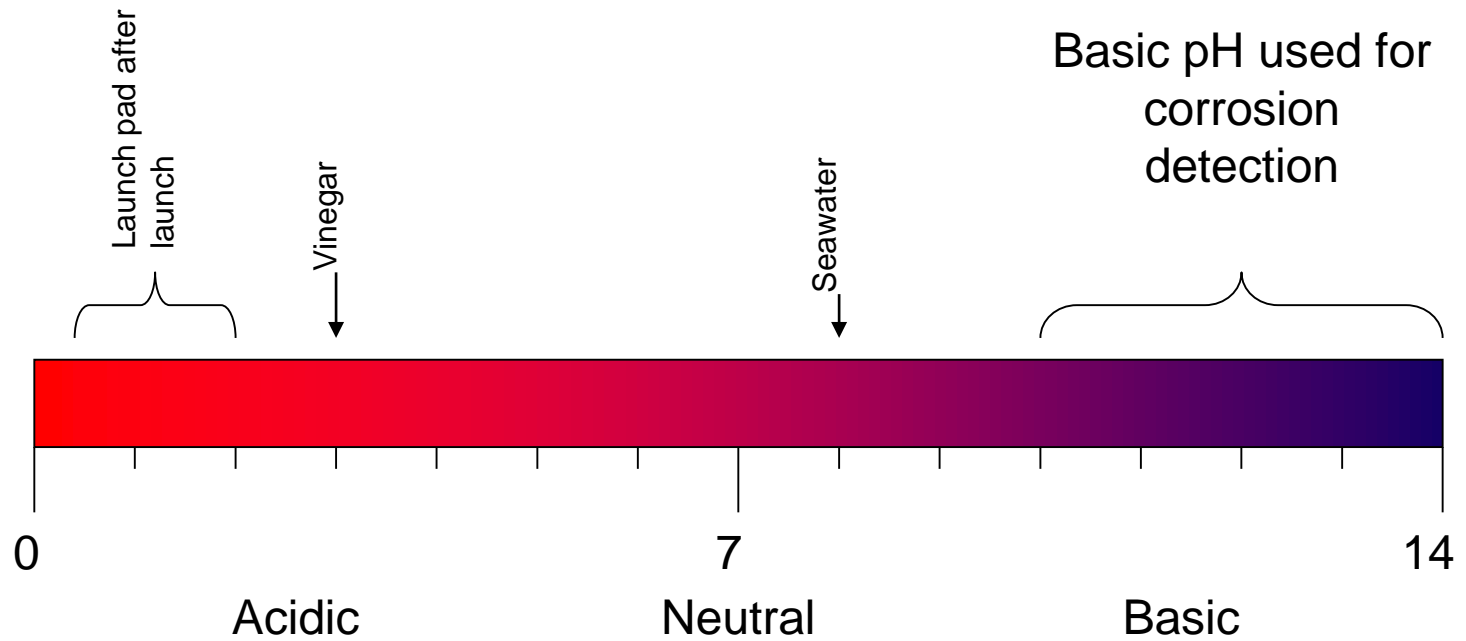


- Containers with an active ingredient-rich core and stimuli-responsive shell (microcapsules)
- Containers with an active ingredient incorporated into a stimuli-responsive matrix (micro particles)
- Containers with a porous ceramic core impregnated by inhibitor and enveloped by a stimuli-responsive polyelectrolyte (PE) shell*



*D. Grigoriev, D. Akcakayiran, M. Schenderlein, and D. Shcukin, Corrosion, 70 (2014): p.446-463.

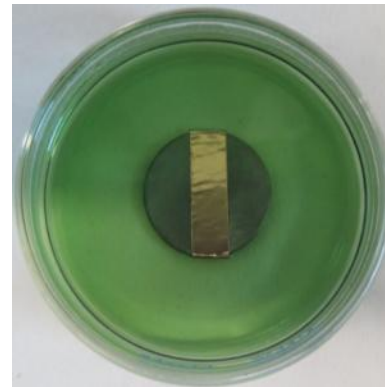
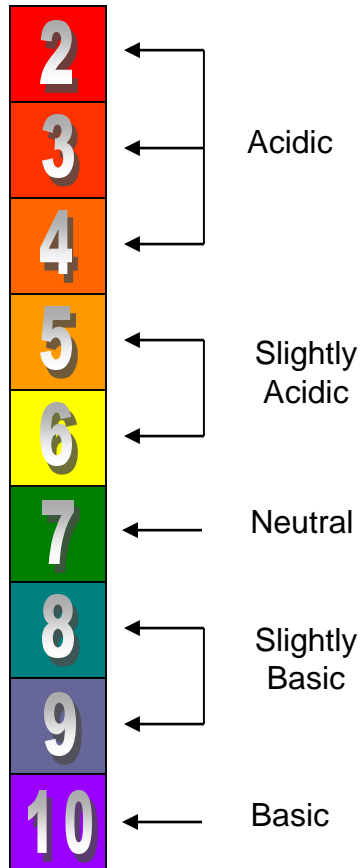
Corrosion and pH



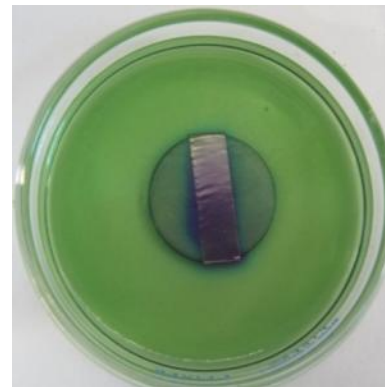
pH Scale

Corrosion Indication

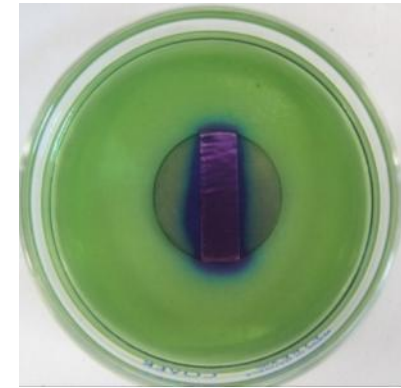
pH changes that occur during corrosion of a metal



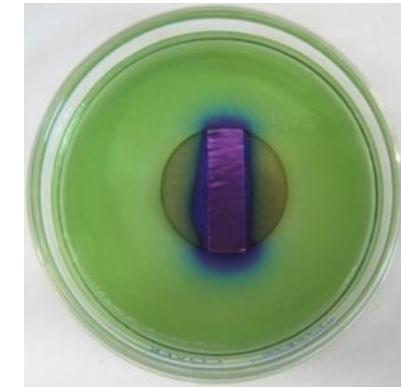
Elapsed Time: 0 hours



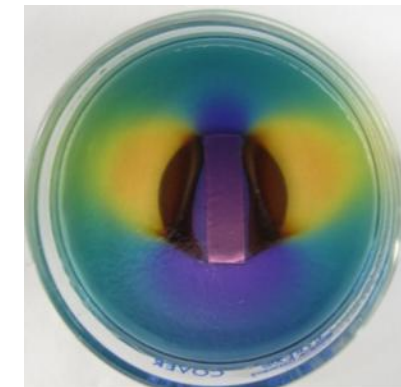
0.5 hours



1.5 hours

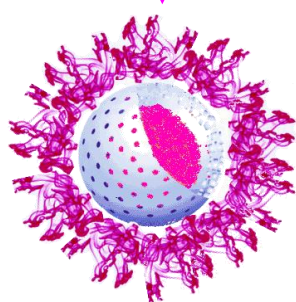
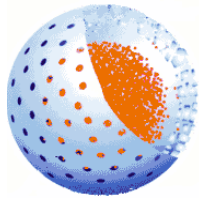
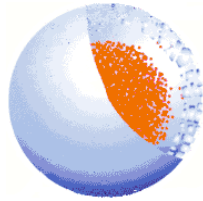
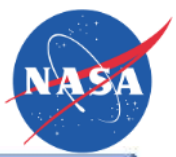


4.5 hours



3 days

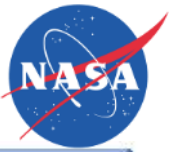
pH Sensitive Microcapsules for Corrosion Indication



Microcapsule containing pH indicator (inhibitor, self healing agents)

The shell of the microcapsule breaks down under basic pH (corrosion) conditions

pH indicator changes color and is released from the microcapsule when corrosion starts



Benefits from corrosion sensing coatings:

- Overcoming solubility limit of indicators in solvents
- Protecting indicator from coating constituents
- Easy incorporation into different paint systems

Benefits from corrosion-controlled inhibitor release:

■ Smart:

- Corrosion-controlled release on demand at tailorable rate.
- Minimization of inhibitor loss by leaching or diffusion if desired.
- Inhibitor release can be maximized when corrosion occurs.
- Inhibitor delivery when and where needed.

■ Green:

- Reduction of the detrimental impact of inhibitors on the environment.

■ Enabling:

- Inhibitor isolation avoids incompatibility with other coating components.
- Allows incorporation of water-soluble inhibitor into paint formulation without blistering.

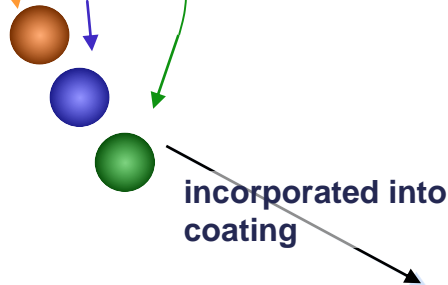
Smart Coating for Corrosion Detection and Control



1. Corrosion indicators

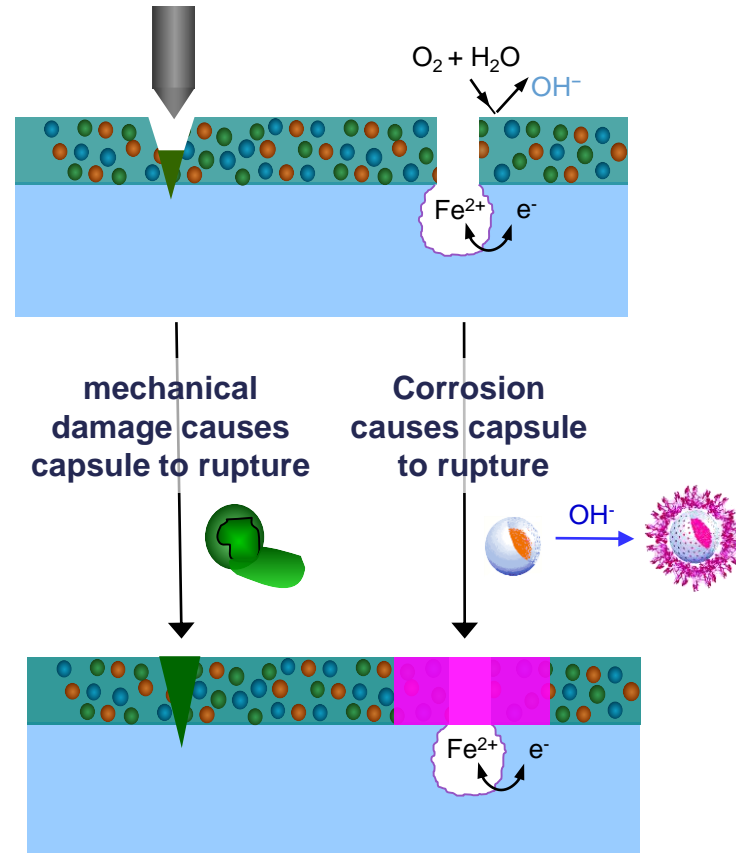
2. Corrosion inhibitors

3. Healing agents



Ruptured Microcapsule:

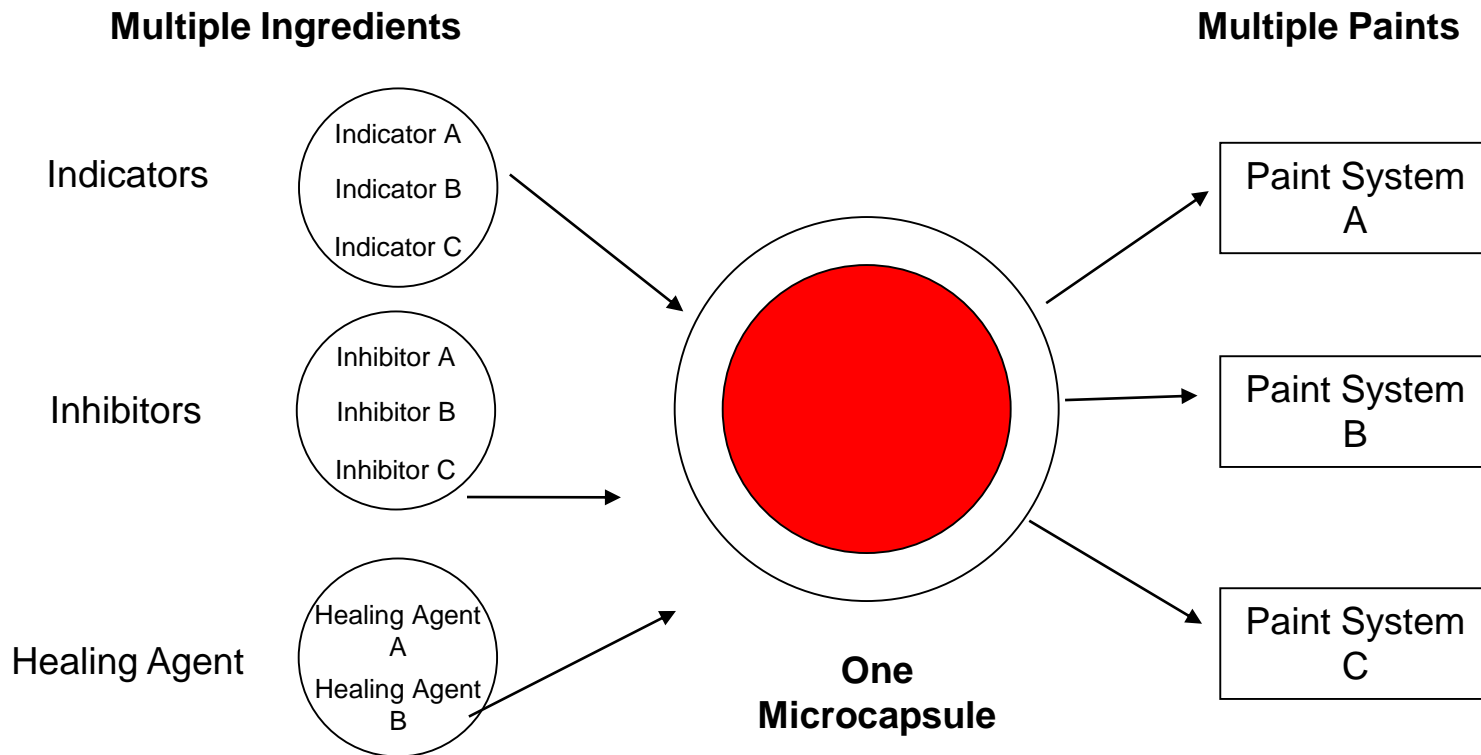
- indicates corrosion
- protects metal from corrosion
- repairs damaged area



Microencapsulation Versatility



Versatility: Microcapsules can deliver multiple types of contents into different paint systems. The microcapsule wall can be modified to deliver the contents at different rates.



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.**

Acknowledgements

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