A Multifunctional Coating for Autonomous Corrosion Control

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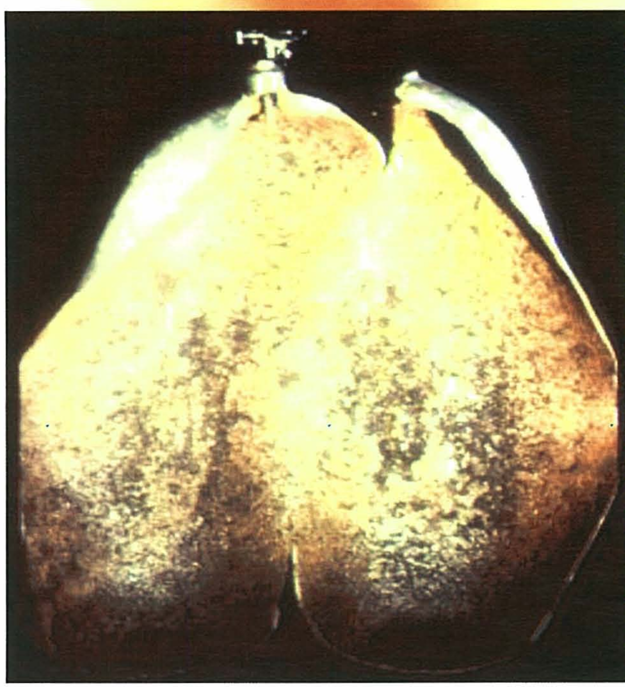
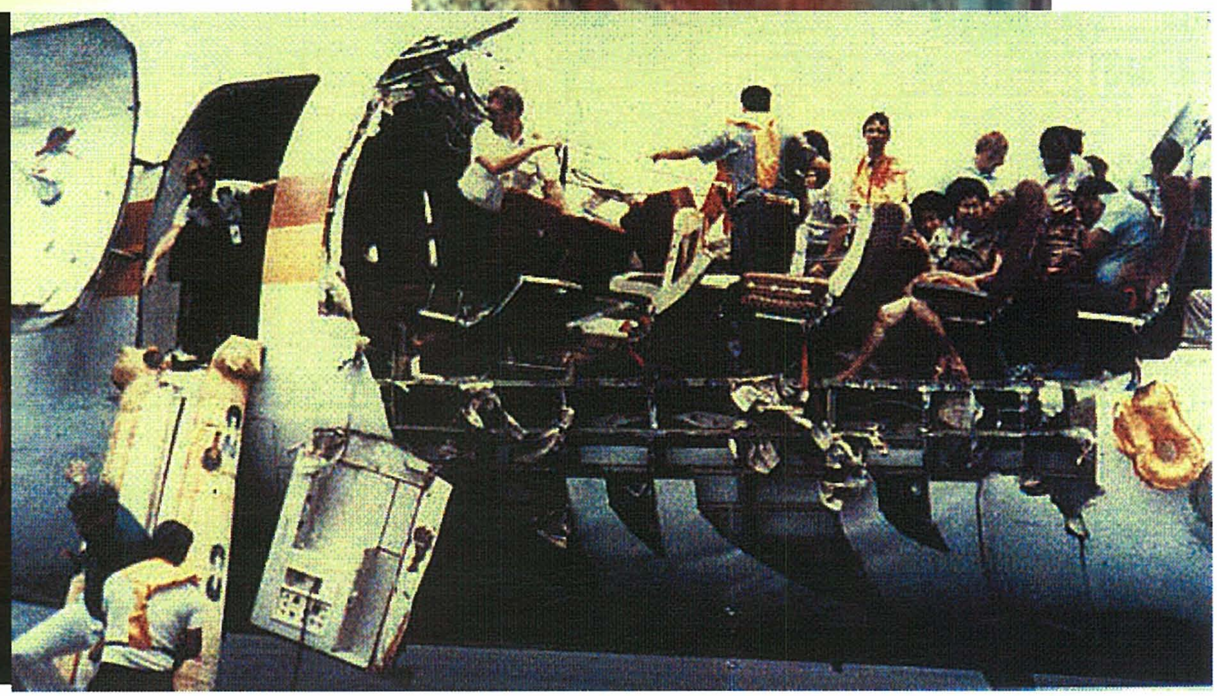
Effects of Corrosion



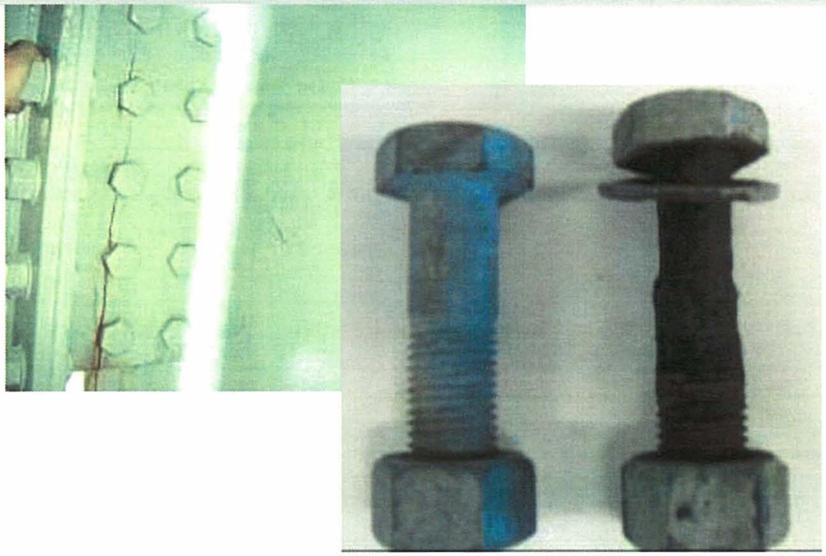


What is Corrosion?

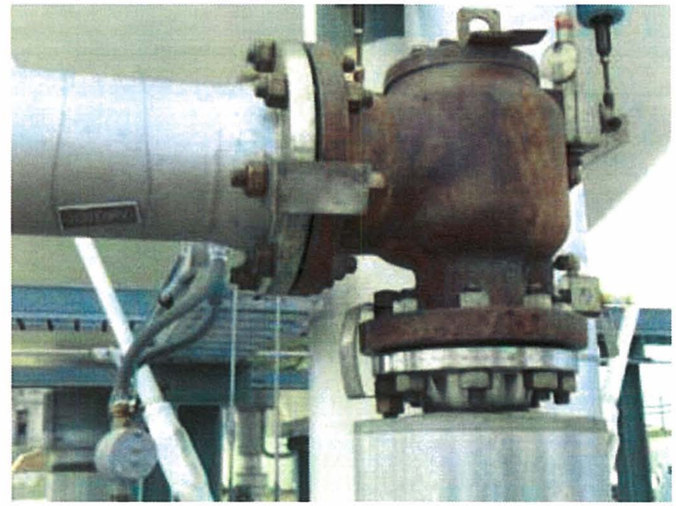
- "Corrosion is the environmentally induced degradation of a material that involves a chemical reaction.
- Degradation implies deterioration of the structural properties of the material.

KSC Crawler/Transporter
Structural Steel Corrosion

Examples of Launch Pad Corrosion

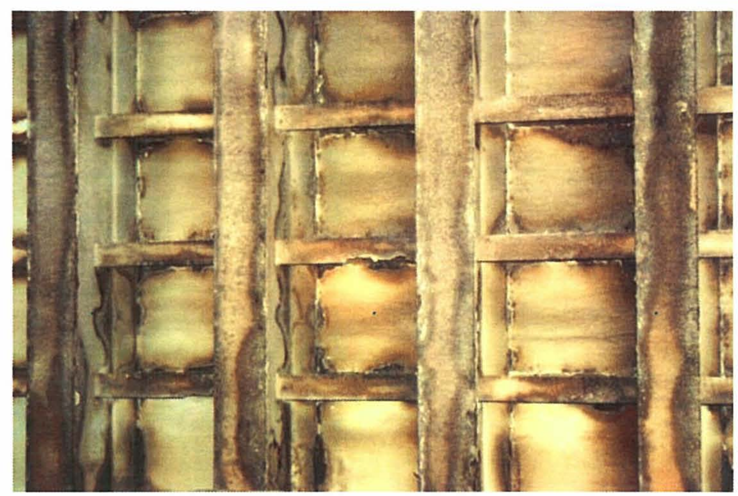


Enclosed / Inaccessible Areas



Dissimilar Metals

KSC Launch tower structural steel corrosion

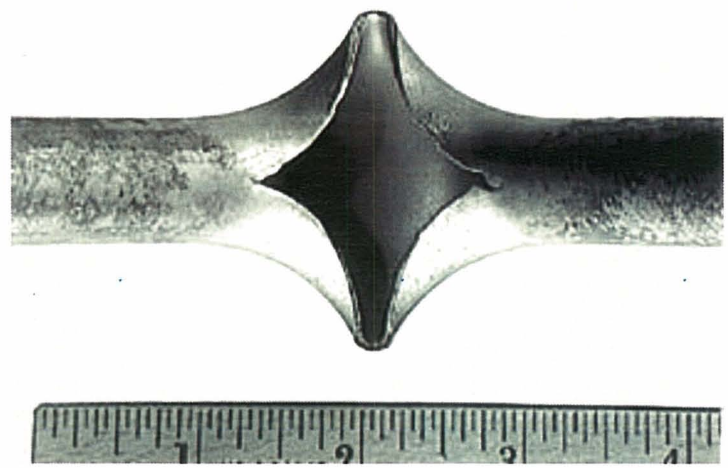


Under the LC 39B Flame Trench

Examples of Launch Pad Corrosion (cont.)

Pitting of SS 317L Tubing

Micrograph (100X) of pit in SS 304 tubing



SS 304 tubing split caused by pitting

Cost of Corrosion

- **Overall direct cost of metallic corrosion in the U.S.: $276B/year (3.1% GDP).[1] $578B (4.2% GDP in 2007)**
- **Cost of corrosion control at KSC Launch Pads estimated as $1.6M/year[2]**
- **Estimated 20 year lifecycle savings from smart coating technology: $132M**

[1]Corrosion Costs and Preventive Strategies in the United States, Report FHWA-RD-01-156, September 30, 2001
[2] Estimate based on corrosion control cost of launch pads (39A and 39B) and the 3 MLPs in 2001

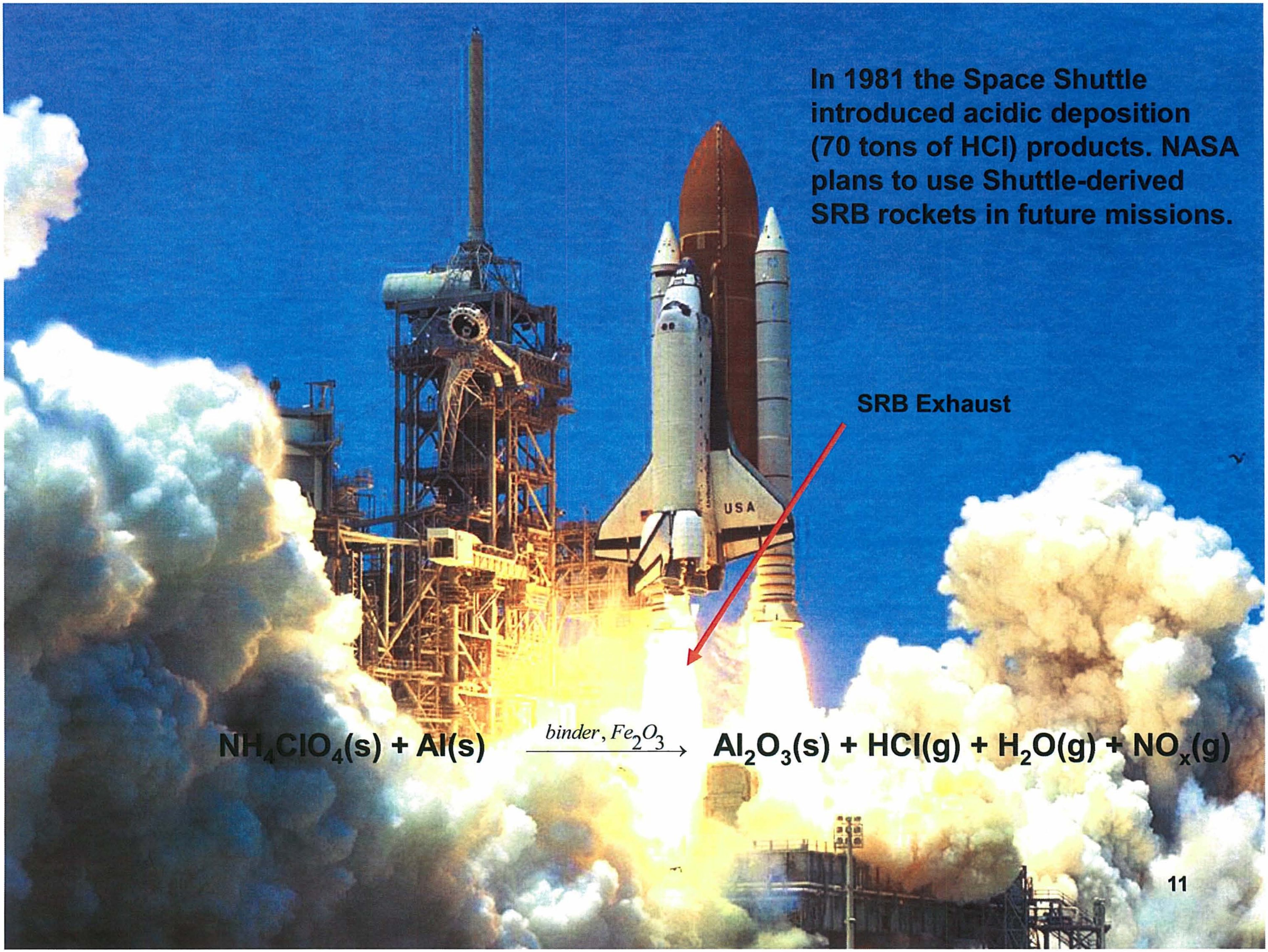
KSC Natural Environment

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


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
USA
$NH_4ClO_4(s) + Al(s) \xrightarrow{binder,\ Fe_2O_3} Al_2O_3(s) + HCl(g) + H_2O(g) + NO_x(g)$
11

Corrosion Rates of Carbon Steel

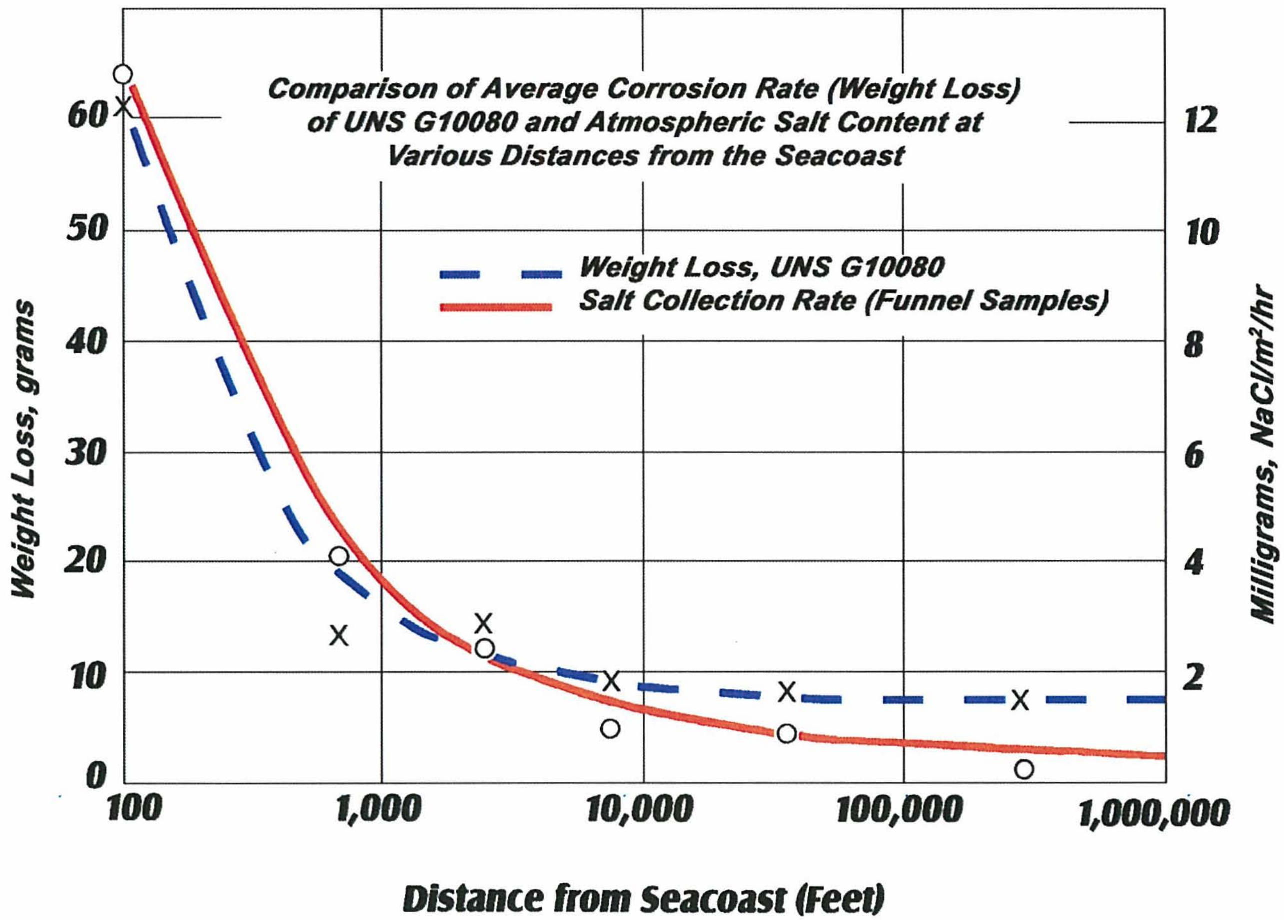
Corrosion rates of carbon steel calibrating specimens at various locations*			
Location	Type Of Environment	µm/yr	Corrosion rate[a] mils/yr
Esquimalt, Vancouver Island, BC, Canada	Rural marine	13	0.5
Pittsburgh, PA	Industrial	30	1.2
Cleveland, OH	Industrial	38	1.5
Limon Bay, Panama, CZ	Tropical marine	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

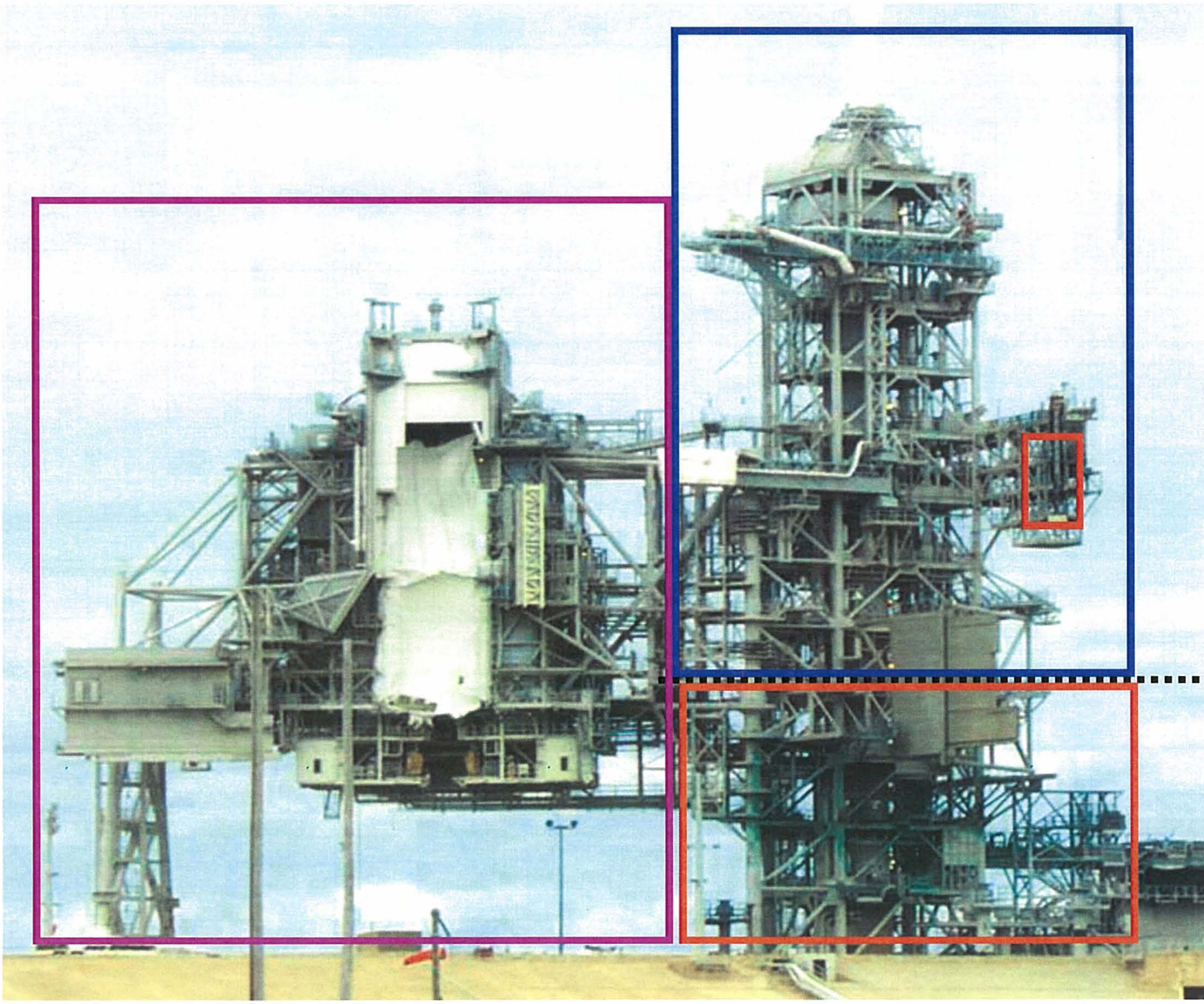
* Data extracted from: S. Coburn, Atmospheric Corrosion, in Metals Handbook, 9th ed, Vol. 1, Properties and Selection, Carbon Steels, American Society for Metals, Metals Park, Ohio, 1978, p.720

A mil is one thousandth of an inch

Changes in Corrosion Rate with Distance from the Ocean



Launch Complex 39 Zones of Exposure



Zone 3: Surfaces, other than those located in Zones 1 or 2, that receive acid deposition from solid rocket booster exhaust products.

Zone 2: Surfaces that receive elevated temperatures and acid deposition from solid rocket booster exhaust with no exhaust impingement.

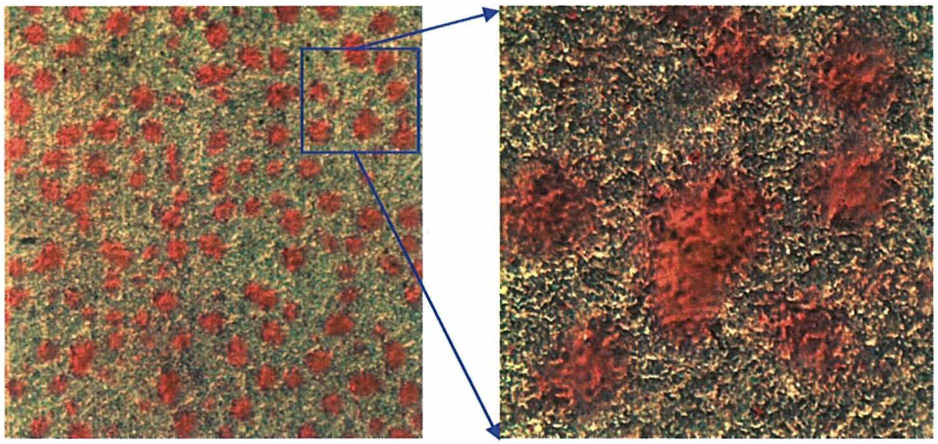
FSS 115" Level

Zone 1: Surfaces that receive direct rocket engine exhaust Impingement and ET/IT Attachment point

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

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.



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 microcapsules 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.

Electrochemical Nature of Corrosion

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

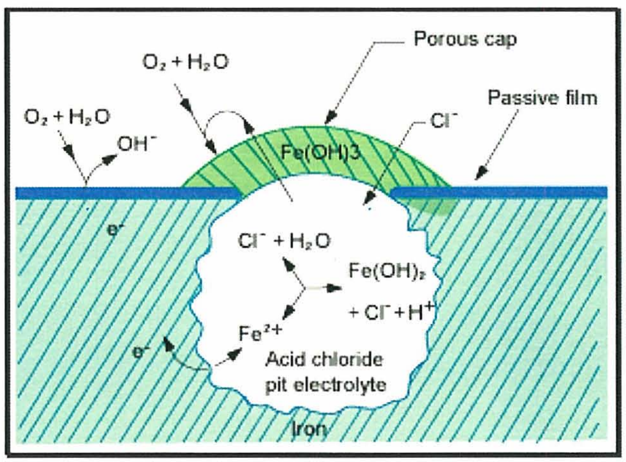
Overall Reaction:

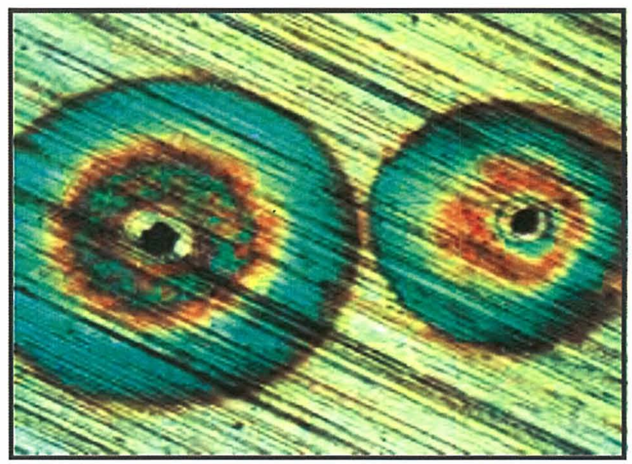
$$2H_2O + O_2 + 2Fe \rightarrow 2Fe^{2+} + 4OH^-$$

Anodic: $Fe \rightarrow Fe^{2+} + 2e^-$

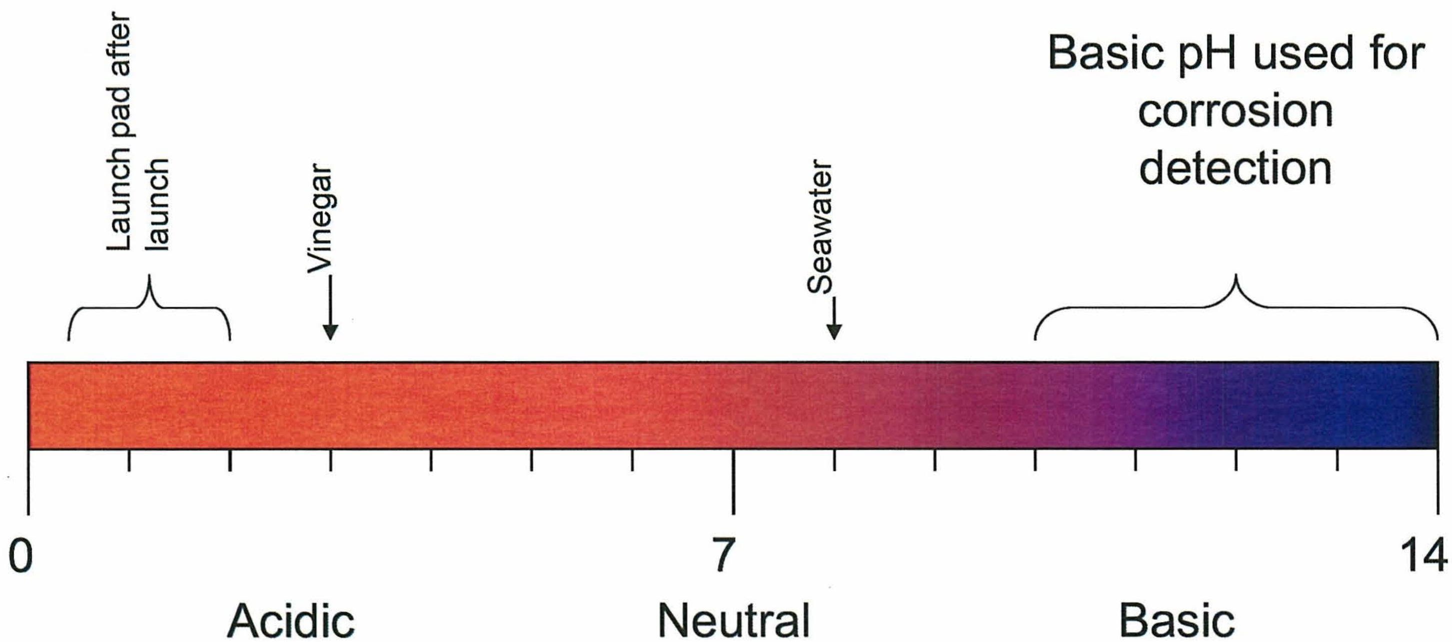
Cathodic:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$





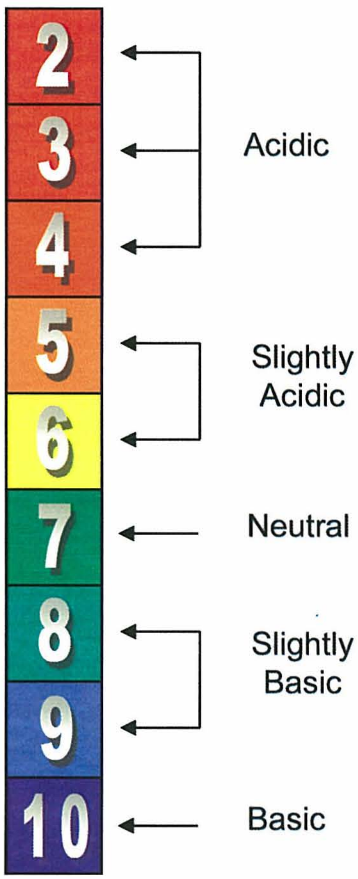
Corrosion and pH

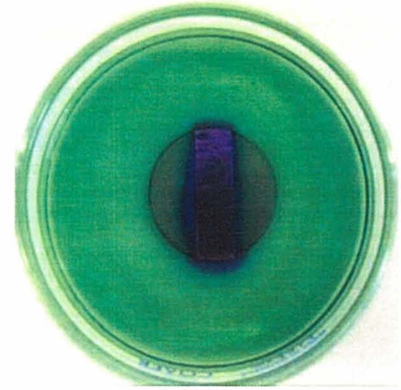


pH Scale

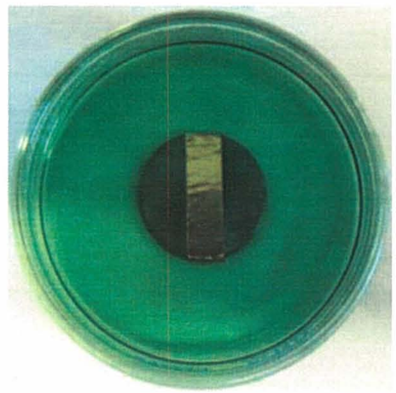
Corrosion Indication

pH changes that occur during corrosion of a metal

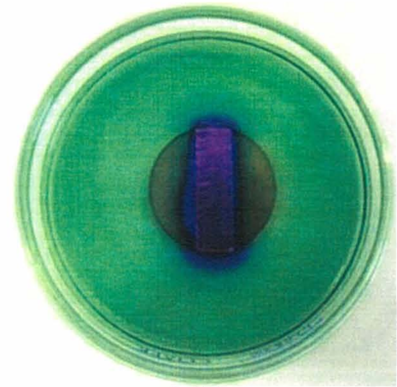




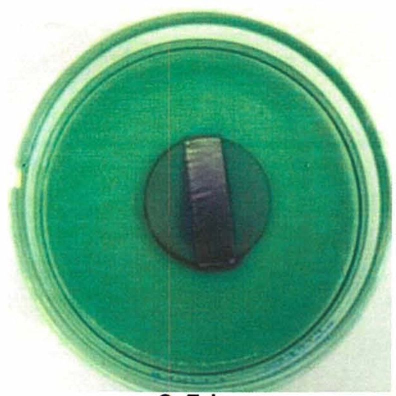
1.5 hours



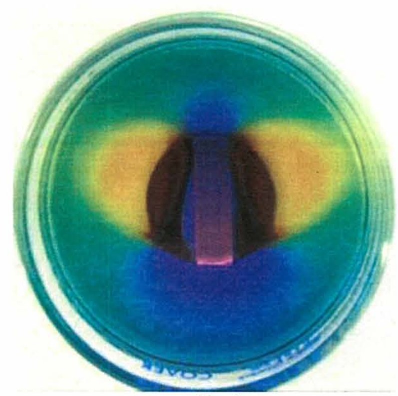
Elapsed Time: 0 hours



4.5 hours



0.5 hours



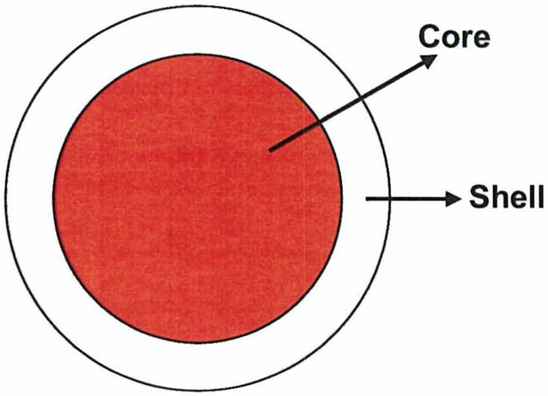
3 days

Smart Coating "Brain"

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

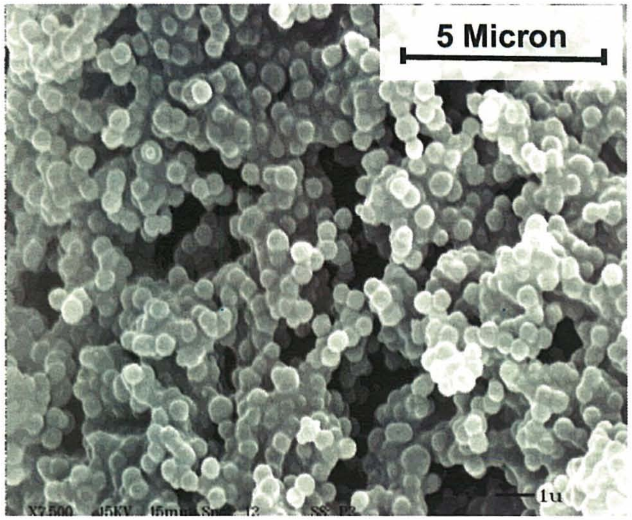
What are microcapsules?

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



Why microencapsulate a material?

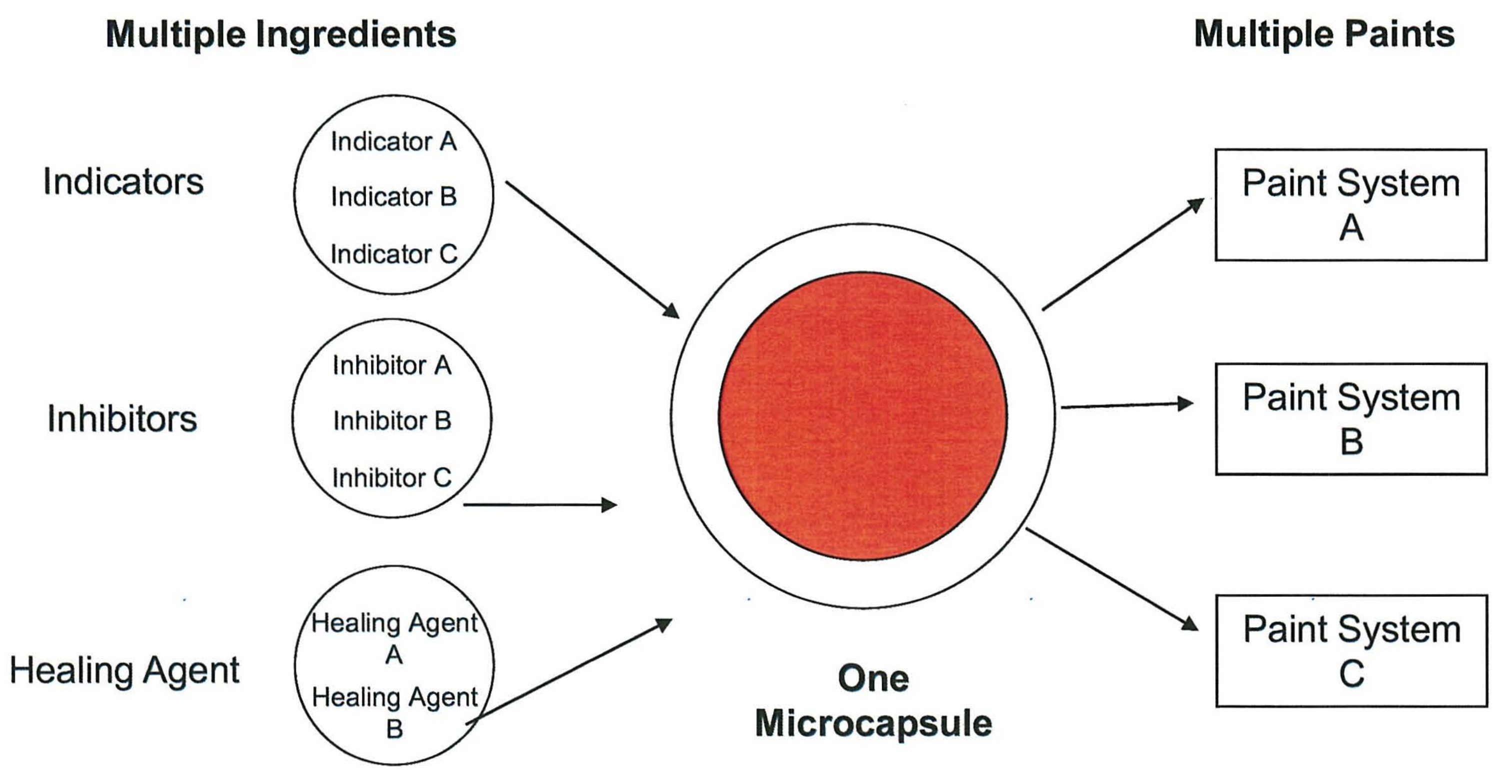
- To achieve controlled-release.
- Make active materials easier/safer to handle.
- Compartmentalize multiple component systems.
- Protect sensitive materials from their environment.
- Versatility



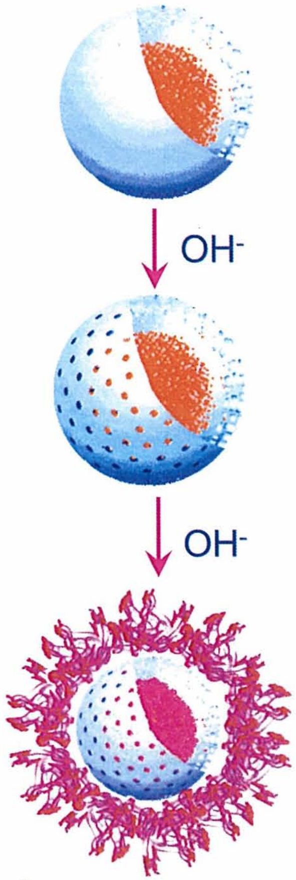
Microcapsules developed at KSC

Microencapsulation Versatility

- **Versatility: Microcapsules can deliver multiple types of contents into different paint systems shortening the time to a new coating formulation when one of the components becomes unavailable.**



pH Sensitive Microcapsules for Corrosion Sensing

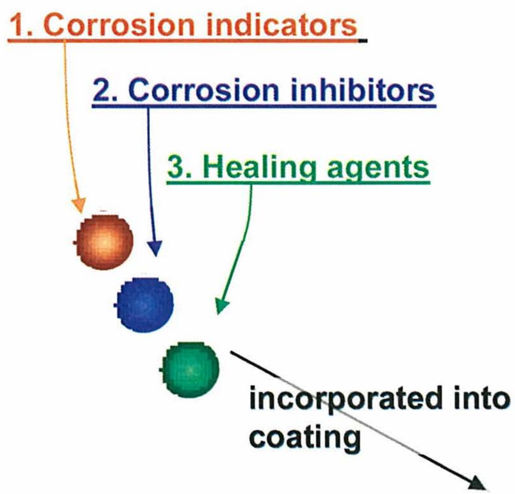


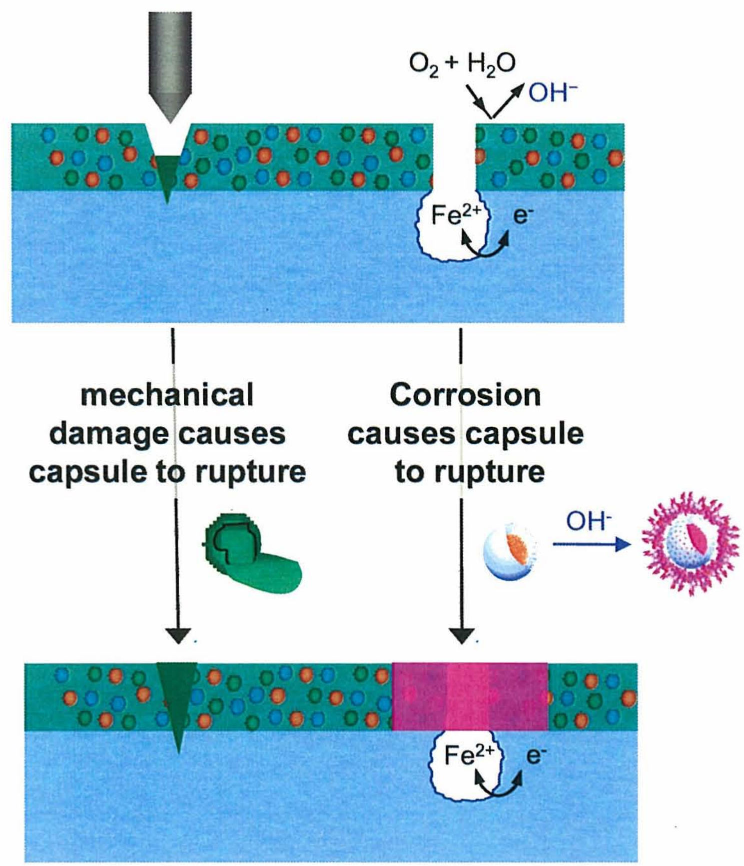
Microcapsule containing pH indicator (inhibitor, self healing agents)

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

Smart Coating Response to Corrosion

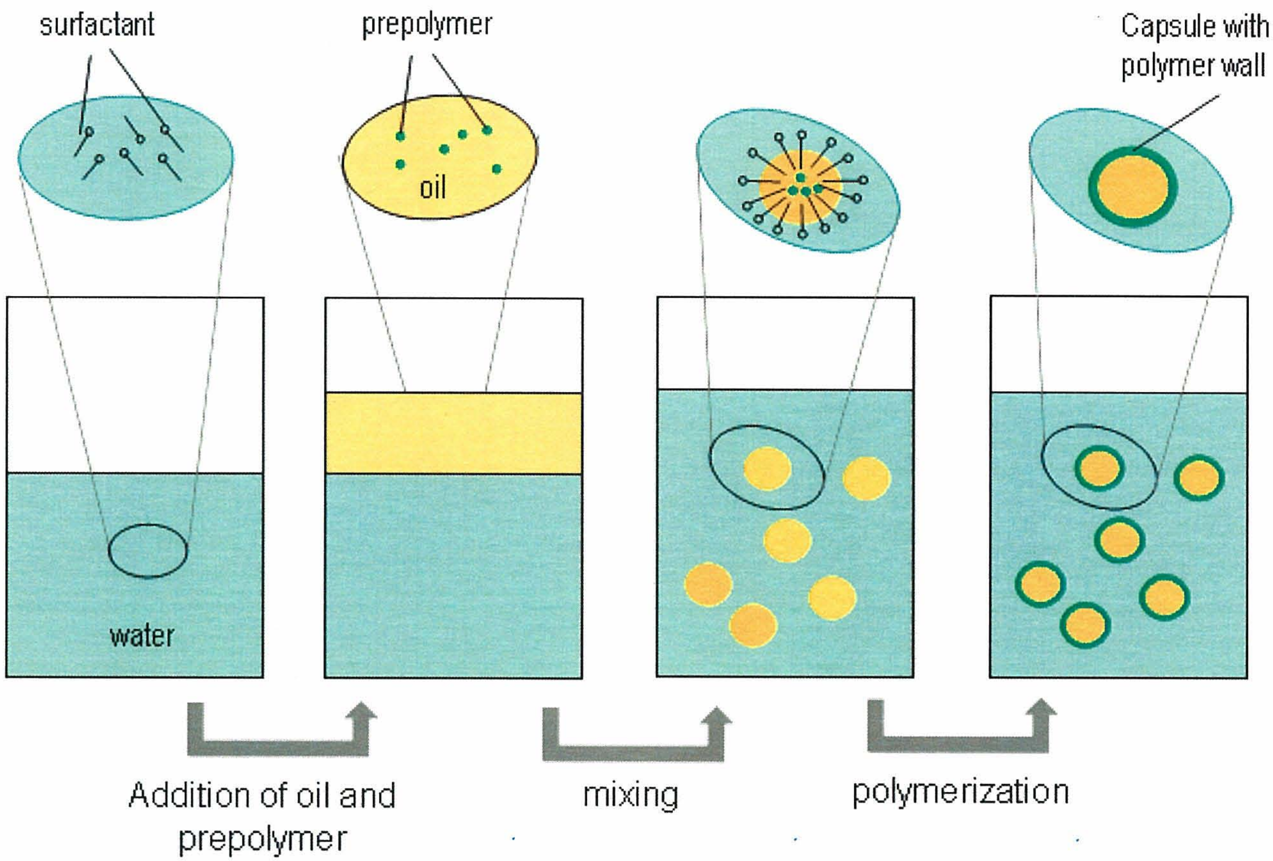




Ruptured Microcapsule:

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

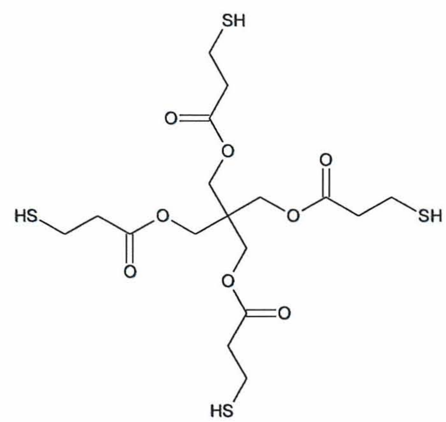
Hydrophobic Core Microcapsules



Interfacial polymerization of oil-in-water microemulsion process for making hydrophobic-core microcapsules. Oil is shown in yellow and water in blue.

Chemistry of pH-sensitive Microcapsules

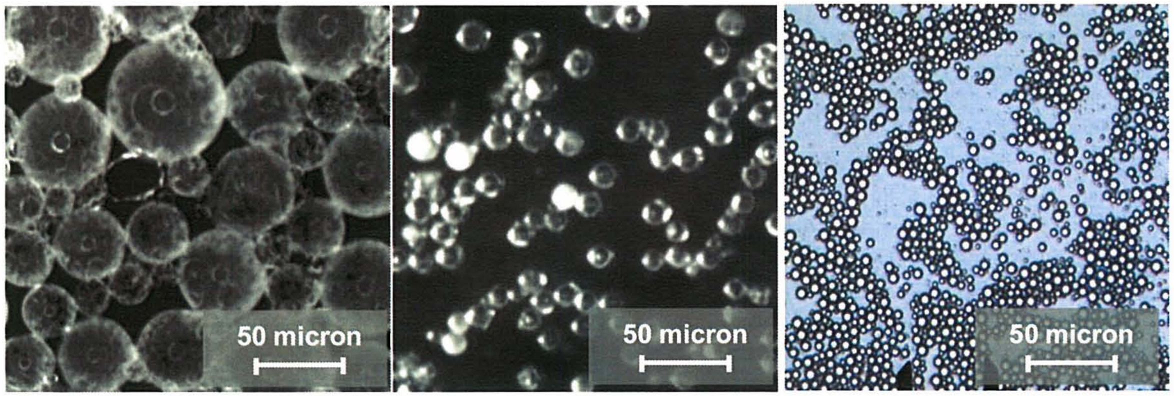
- Polymeric wall formation involves using a cross-linking agent that has one or more ester and mercapto groups such as pentaerythritol tetrakis (3-mercaptopropionate) (PTT):



- Film-forming monomers and pre-polymers such urea formaldehyde and melamine formaldehyde are used to provide structural integrity to the wall

- Wall break down occurs by base-catalyzed ester hydrolysis

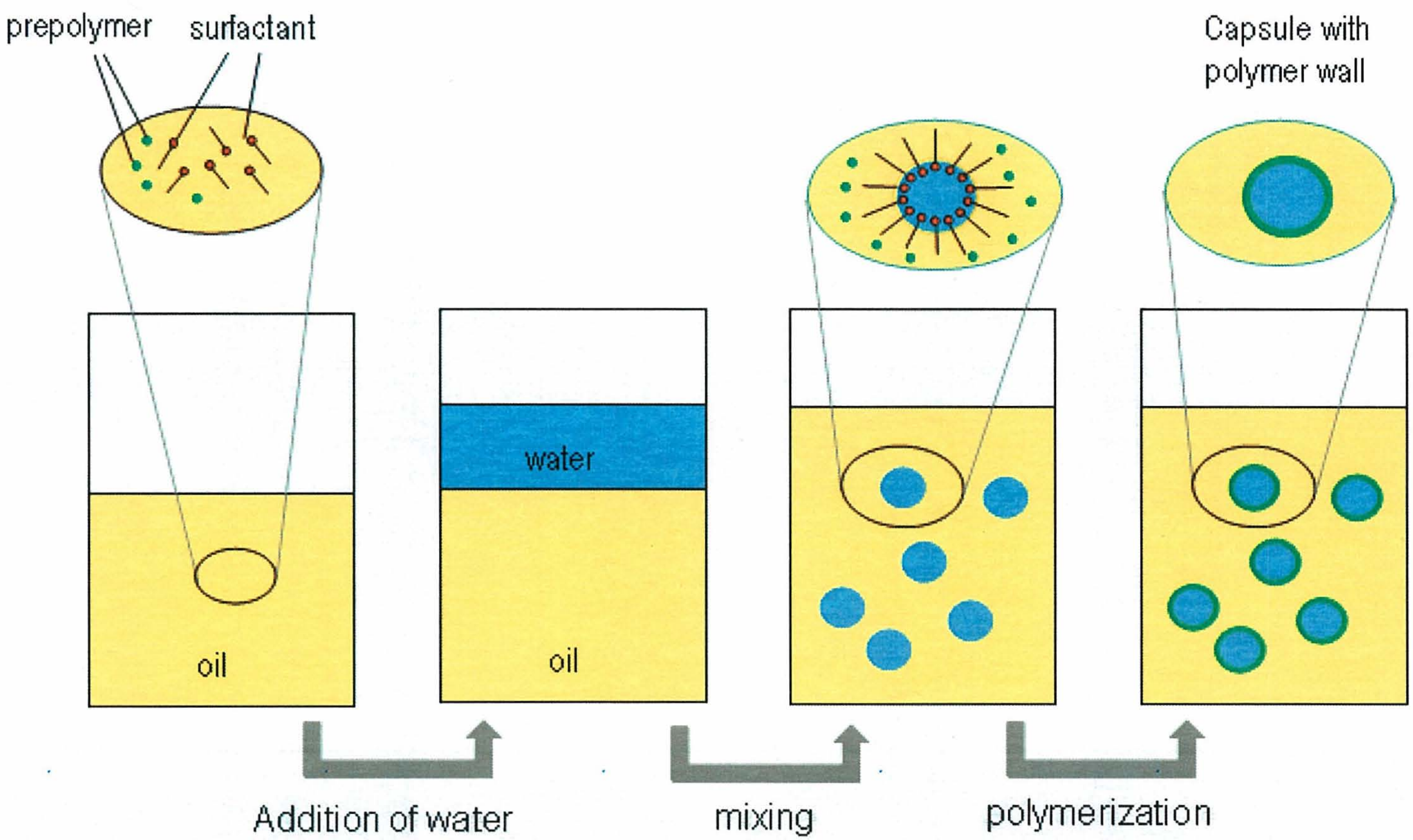
Hydrophobic-core Microcapsules



Optical microscopy images of Hydrophobic-core microcapsules of different sizes

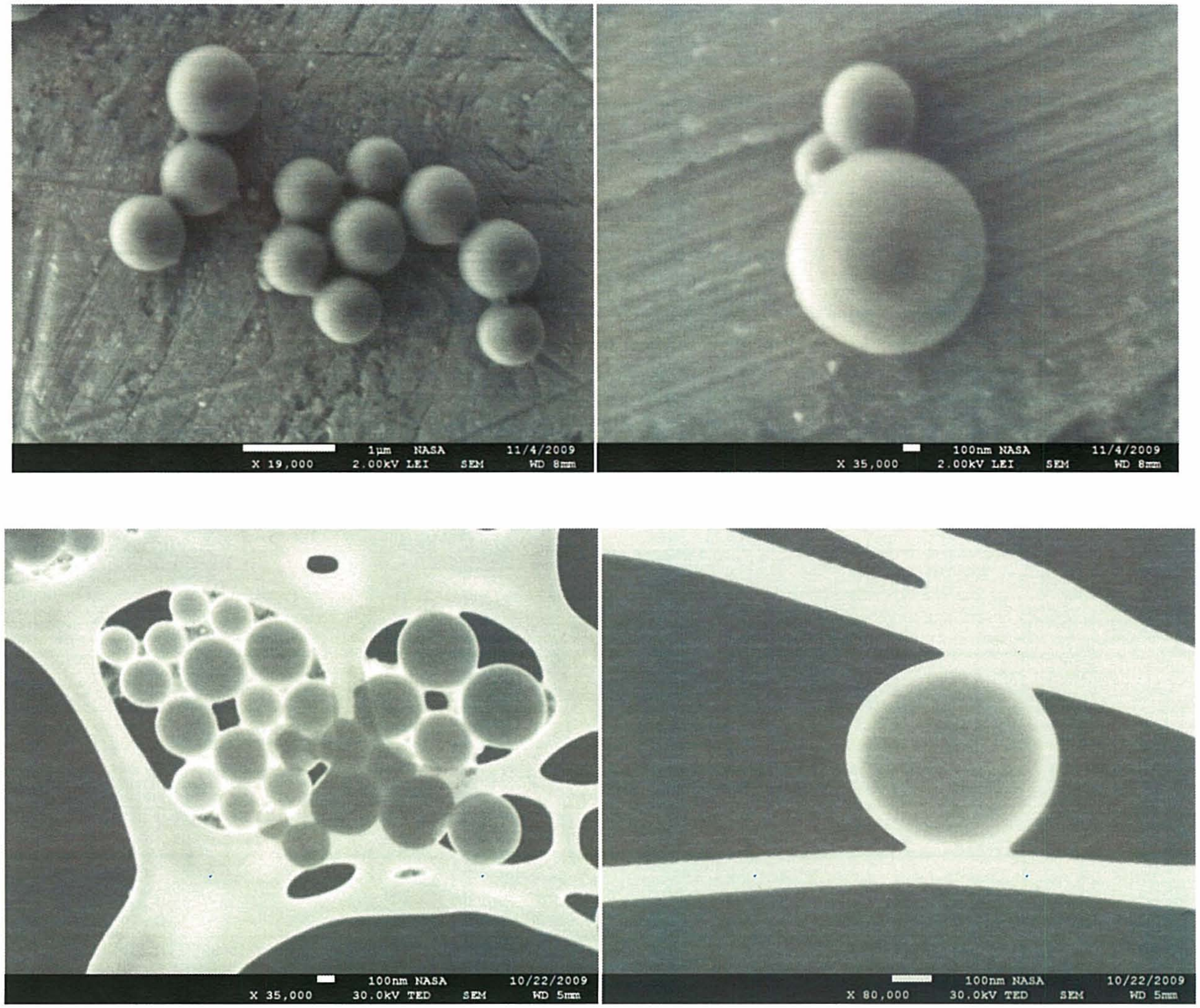
Free flowing powder samples of hydrophobic-core microcapsules. The core contents of these microcapsules are Rhodamine B (on the left), Phenolphthalein (in the middle), and a universal pH indicator (on the right).

Hydrophilic Core Microcapsules



Interfacial polymerization of water in oil microemulsion process for hydrophilic-core microcapsules. Oil is shown in yellow and water in blue.

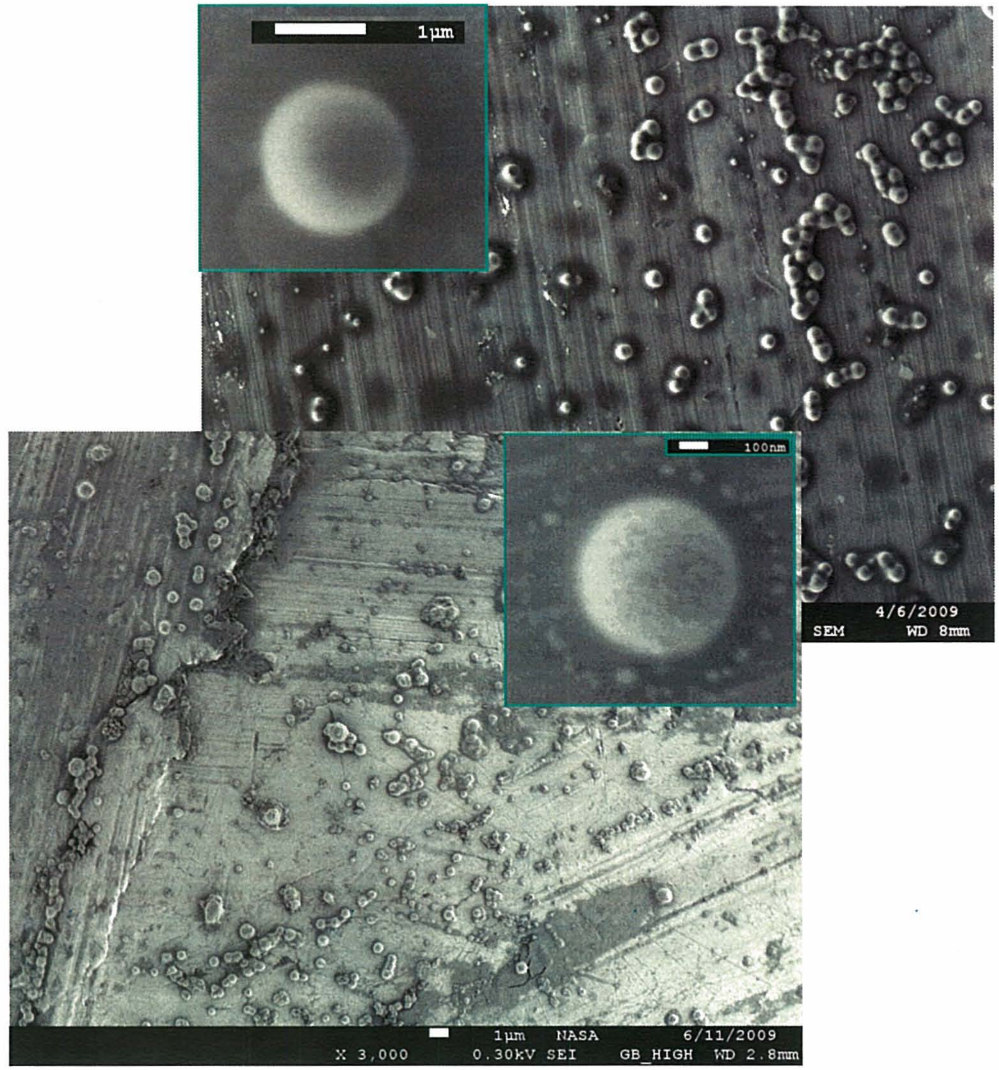
Hydrophilic-core Microcapsules



SEM images of the hydrophilic-core microcapsules

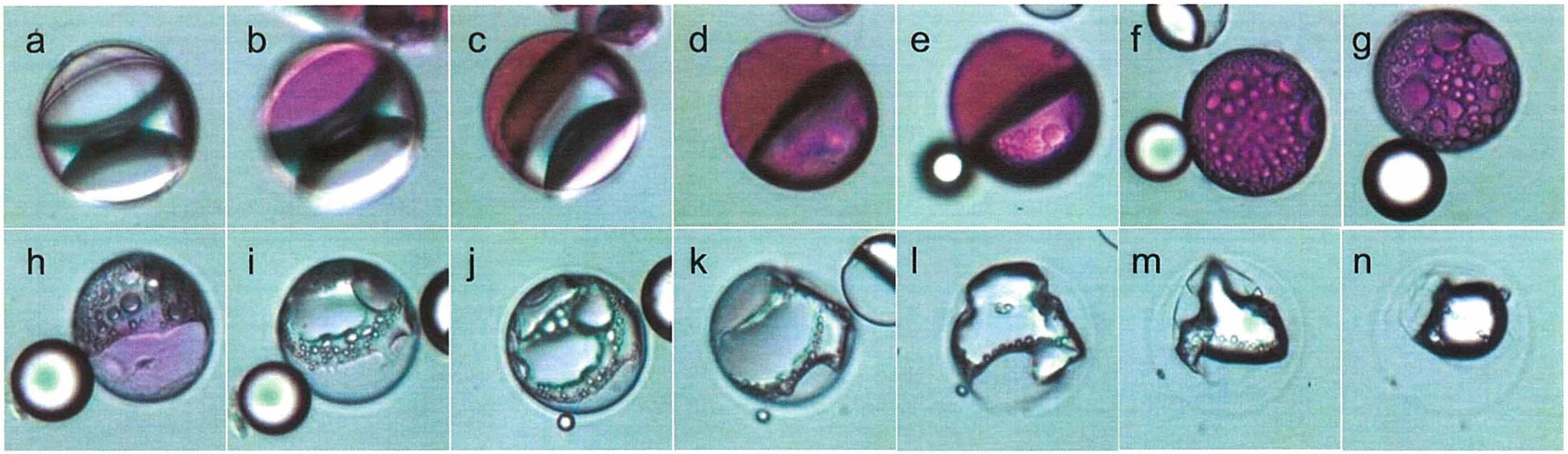
Microcapsules for Corrosion Indication and Inhibition

When corrosion begins, the microcapsule will release the contents of the core (indicator, inhibitor, and self healing agent) in close proximity to the corrosion.



SEM images of microcapsules with corrosion indicator (top) and inhibitor (bottom).

Microcapsule Response to pH Increase

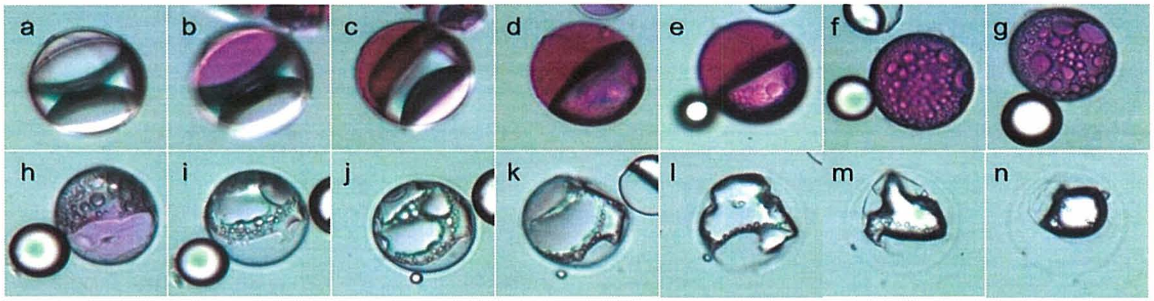


Capsule wall breakdown and indicator color change under basic conditions: NaOH, (pH of 12)

- Frames **a-d**: the basic solution starts to penetrate the microcapsule wall and the indicator inside changes color
- Frame **e**: the microcapsule begins to slowly release its contents (as evidenced by the small droplet that begins to form on the bottom left quadrant of the frame).
- Frames **f-h**: oil droplets are observed as the aqueous solution penetrates the hydrophobic microcapsule core
- Frame **i**: The content continues to be released until it dissipates into the solution.
- Frames **j-n**: The microcapsule wall eventually breaks down completely.

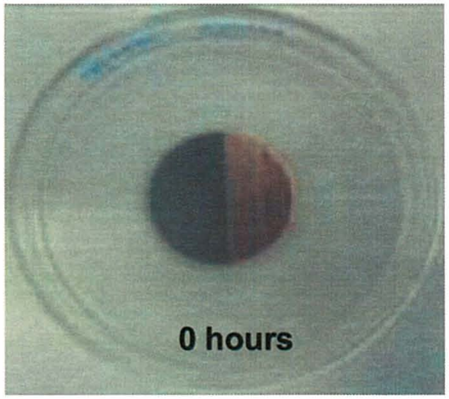
Microcapsules for Corrosion Indication

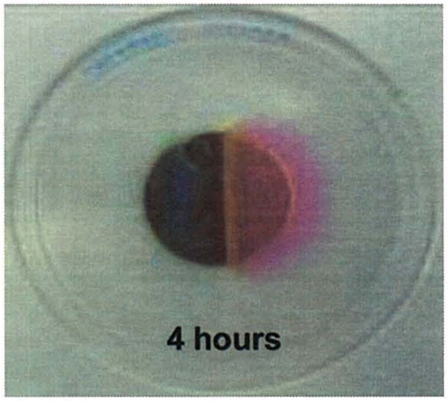
pH sensitive microcapsules with corrosion indicator for corrosion detection



Time lapse pictures of a microcapsule with indicator breaking down under basic pH conditions.

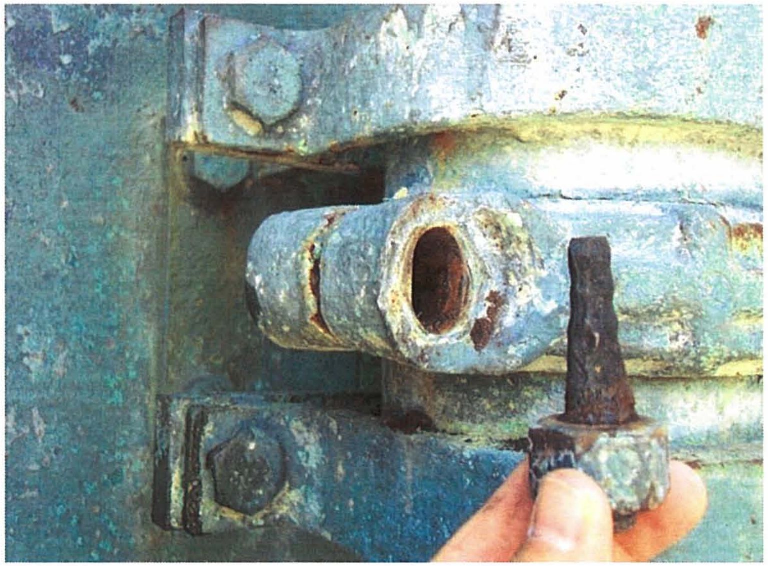
Significance:
Damage responsive coatings provide visual indication of corrosion in hard to maintain/inaccessible areas (on towers) prior to failure of structural elements.



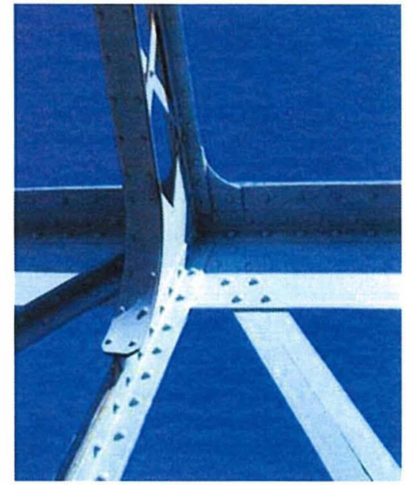


A galvanic corrosion test cell consisting of a carbon steel disc in contact with copper tape was immersed in gel with microcapsules containing a corrosion indicator. As the carbon steel corrodes, the encapsulated corrosion indicator is released and its color change to purple shows the initiation and progress of corrosion

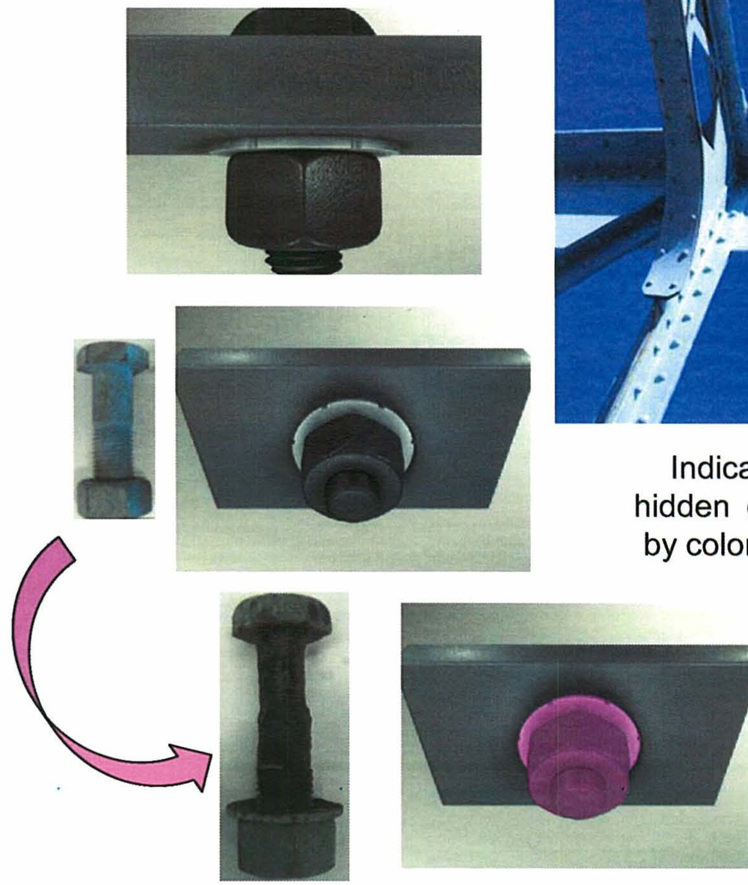
Indication of Hidden Corrosion



Pad 39B MLP-1: Bolt from Victaulic joint on center upper shield



Indication of hidden corrosion by color change



Conceptual illustration of corrosion indication in structural bolts at the launch pad

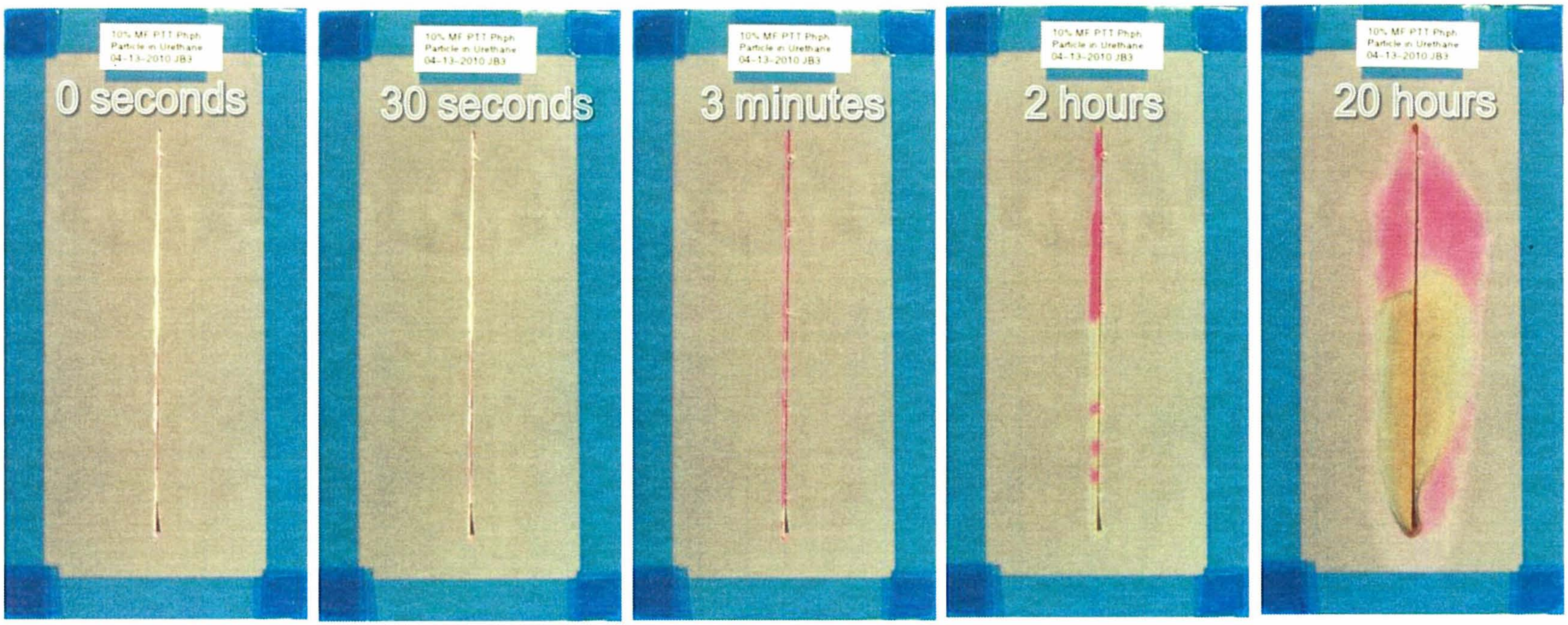
Hidden Corrosion Indication

System label	Metal Substrate	Coating systems
1	Zinc galvanized nut and bolt	Clear urethane coating containing 10% phenolphthalein (phph) microcapsules.
2	Zinc galvanized nut and bolt	First coated with epoxy, then top coated with clear urethane containing 10% phph microcapsules.
3	Sand blasted nut and bolt.	The ends of the nut and bolt were coated with inorganic zinc coating; the entire nut and bolt was coated with urethane containing 10% phph microcapsules.
4	Sand blasted nut and bolt	The ends of the nut and bolt were coated with inorganic zinc coating. The entire nut and bolt was coated with epoxy and then top coated with a clear urethane containing 10% phph microcapsules.
5	Zinc galvanized nut and bolt	The ends of the nut and bolt were coated with urethane containing 10% phph microcapsules.
6	Zinc galvanized nut and bolt.	The ends of the nut and bolt were coated with epoxy and then top coated with urethane containing 10% phph microcapsules.

Coating systems used for hidden corrosion indication testing.

Nut and bolt set up for crevice corrosion testing. The pictures show results after 600 hour of salt fog exposure

Experimental Corrosion Indicating Coating



Salt fog test[1] results of panels coated with a clear polyurethane coating loaded with 20% oil core microcapsules with corrosion indicator in their core. The coating detects corrosion in the scribed area at a very early stage (0 seconds) before the appearance of rust is visible.

[1]ASTM B 117-97, Standard Practice for Operating Salt Spray (Fog) Apparatus, ASTM International, 1997

Summary

- KSC is developing a smart coating, based on pH-sensitive microcapsules and particles, for early corrosion detection, corrosion inhibition, and self-healing
- The corrosion indicating function has been demonstrated by incorporating an encapsulated corrosion indicator into a clear polyurethane coating. Salt fog test results showed that the coating detects corrosion at a very early stage before the appearance of rust is visible.
- Salt fog test results showed the effectiveness of the encapsulated corrosion indicator in detecting hidden corrosion in an epoxy coating with urethane as a top coat.

Acknowledgements

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PROJECT MANAGEMENT AND SUPPORT

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