

NASA's Corrosion Technology Laboratory at the Kennedy Space Center: Anticipating, Managing, and Preventing Corrosion

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ABSTRACT

The marine environment at NASA's Kennedy Space Center (KSC) has been documented by ASM International (formerly American Society for Metals) as the most corrosive in North America. With the introduction of the Space Shuttle in 1981, the already highly corrosive conditions at the launch pads were rendered even more severe by the highly corrosive hydrochloric acid (HCl) generated by the solid rocket boosters (SRBs). Numerous failures at the launch pads are caused by corrosion. The structural integrity of ground infrastructure and flight hardware is critical to the success, safety, cost, and sustainability of space missions. NASA has over fifty years of experience dealing with unexpected failures caused by corrosion and has developed expertise in corrosion control in the launch and other environments. The Corrosion Technology Laboratory at KSC evolved, from what started as an atmospheric exposure test site near NASA's launch pads, into a capability that provides technical innovations and engineering services in all areas of corrosion for NASA, external partners, and customers.

This paper provides a chronological overview of NASA's role in anticipating, managing, and preventing corrosion in highly corrosive environments. One important challenge in managing and preventing corrosion involves the detrimental impact on humans and the environment of what have been very effective corrosion control strategies. This challenge has motivated the development of new corrosion control technologies that are more effective and environmentally friendly. Strategies for improved corrosion protection and durability can have a huge impact on the economic sustainability of human spaceflight operations.

Key words: Corrosion, launch environment, corrosion control technology, environmentally friendly, smart coatings

INTRODUCTION

The Kennedy Space Center is located on the east-central area of Florida (Figure 1). NASA has been dealing with failures caused by corrosion since the inception of the Space Program in 1962 because it launches from the most naturally corrosive environment in North America, as reported by the American Society of Materials (ASM).¹ Numerous corrosion failures of materials and coatings during the early days of the Space Program lead to the establishment of a beachside atmospheric exposure test site near the launch pads in the 1960s, during the Gemini Program, to test materials, coatings, and maintenance procedures (Figure 2).



Figure 1: Florida from space showing the location of KSC (left) and map of KSC (right). Photos courtesy of NASA.



Figure 2: KSC Beachside Corrosion Test Site: Original (left) and current (right). Photos courtesy of NASA.

During the early days of NASA's Space Program, liquid fuel rockets, like the Saturn V, were used to launch unmanned and manned missions. In 1981, corrosion conditions at the launch pads became even more severe by the presence of hydrochloric acid in the exhaust of the solid rocket boosters (SRBs) used to launch the Space Shuttle. The severity of these new corrosion conditions at the launch environment created new challenges in corrosion control for NASA.

In 1985, the Failure Analysis Laboratory at KSC introduced salt fog and electrochemical accelerated corrosion testing, as additional techniques to be used in testing and evaluating metal alloys and

corrosion protective coatings. In 2000, The Corrosion Technology Laboratory was created to achieve KSC's new goal of increased participation in research and development. During the same year, a computerized corrosion data management system was implemented to manage corrosion protective coatings at KSC.² In 2001, NASA's Technical Standard NASA-STD-5008 for Protective Coatings of Carbon Steel, Stainless Steel, and Aluminum on Launch Structures, Facilities, and Ground Support Equipment³ was approved. This standard provides uniform engineering and technical requirements for processes, procedures, practices, and methods that have been endorsed as standard for NASA programs and projects, including requirements for selection, application, and design criteria of an item. The standard includes approved product lists for inorganic zinc coatings, topcoat systems, and metallized thermal spray coatings (TSC) systems. The standard describes the minimum requirements a coating shall meet to be included in the approved list. As a result of progressively stricter environmental regulations, many of the coatings that had been approved were removed from the market. This created the need to find and qualify new coatings for inclusion in the approved products lists. Along with this testing and evaluation effort, the Corrosion Technology Laboratory started developing smart coatings, based on microencapsulation technology, specifically designed for corrosion control applications in 2004 (3 patents and several pending).⁴⁻¹⁶ In 2014, NASA's Space Technology Roadmap¹⁷ included 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. What follows is a Chronological overview highlighting NASA's efforts in anticipating, managing, and controlling corrosion. Figure 3 shows the time line of corrosion control at KSC throughout the Space Program.

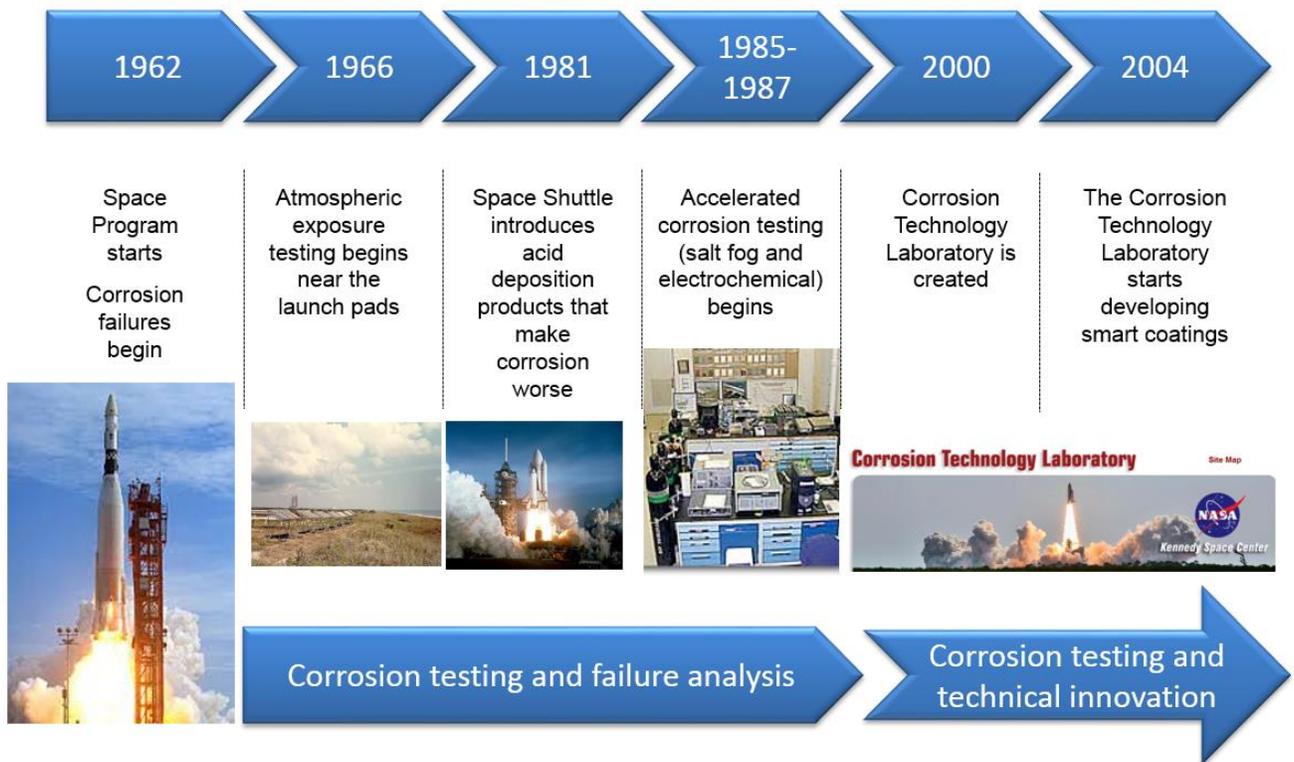


Figure 3: Corrosion control at KSC timeline

COATINGS EVALUATION AT KSC

The evaluation of protective coatings for carbon steel, stainless steel, and aluminum has been an ongoing effort for many years at KSC. In 1969, a study was initiated to identify coatings for the long-term protection of carbon steel exposed to the seacoast launch environment.¹⁸ Both organic and inorganic zinc-rich coatings were applied to test panels and exposed at the Beachside Corrosion Test

Site (BCTS). These panels were evaluated for corrosion after 18 months, 3 years, 5 years, and 10 years. The results of that study were that inorganic zinc-rich primers (ZRPs) were the best choice to provide long-term corrosion protection of launch structures and ground support equipment. The inorganic ZRPs outperformed organic zinc in the KSC seacoast environment. In general, organic topcoats were found to be detrimental to their long-term performance (Figure 4).

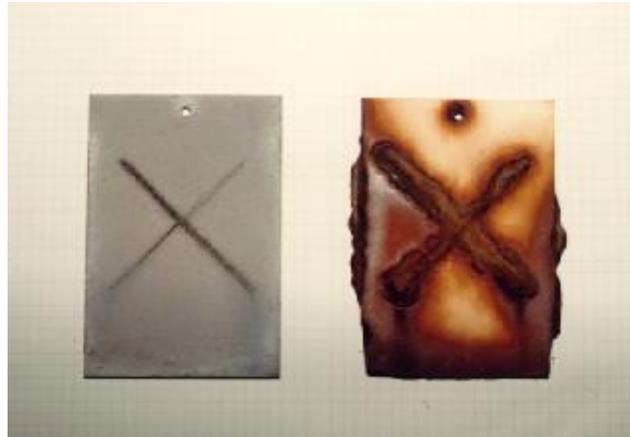


FIGURE 4: Inorganic ZRP without a top coat (left steel panel) and inorganic ZRP top coated with epoxy and urethane (right steel panel) after 8 years of atmospheric exposure at the BCTS.

Inorganic ZRPs without a top coat were used for many years at KSC for the long-term corrosion protection of carbon steel.¹⁹ Several of the original panels exposed in 1969, painted with a single coat of ZRP without a topcoat, are still showing complete corrosion protection of the carbon steel at the BCTS.

Exhaust from the Space Shuttle's SRBs deposited small particles of alumina (Al_2O_3) with hydrochloric acid (HCl) on the launch pad structures. It was estimated that 70 tons of HCl were generated during a Space Shuttle launch (Figure 5). The impingement of this exhaust resulted in the failure of the carbon steel corrosion protection provided by the unprotected inorganic ZRPs, despite the fact that a high pressure wash down of the launch pad structures was carried out as soon as possible after a launch. In response to the SRB exhaust problem, a study of new coatings to resist this new, more aggressive environment was undertaken. This study was conducted in 1982 and 1986 to identify topcoat materials to enhance the chemical resistance of the coating systems in use at KSC's launch pad structures. The 1982 study determined that 2-component coatings were far superior to single-component types, that epoxy/urethane topcoats provided some degree of protection to the ZRPs, despite the fact that the top coats decreased the effectiveness of the corrosion protective properties of the inorganic ZRPs, and that repair techniques, other than abrasive blasting, were ineffective in the launch environment.²⁰ The 1986 study focused on higher-built topcoat products to improve chemical resistance. As a result of this study, 10 topcoat systems were approved for use in the Space Shuttle launch environment.²¹

The coating systems selected as a result of the aforementioned studies were all solvent-based. In general, the topcoat systems that were successful in the 1986 study were epoxy mid-coats followed by polyurethane topcoats. The results of these test programs provided valuable data and resulted in the selection of appropriate coatings for the protection of KSC structures and ground support equipment in their uniquely aggressive marine and launch environment. However, Clean Air legislation and environmental regulations began to restrict the use of solvents in paints and coatings. These regulatory developments indicated that all solvent-based coating systems approved for use at KSC would eventually become unavailable for use.

To address this challenge, studies were undertaken in 1990, and continue to this day, to identify inorganic ZRPs and topcoat systems that can provide superior corrosion protection while complying with the anticipated strengthening of environmental quality standards.^{22, 23} Many of the coating systems tested started with water-based inorganic ZRPs followed by water-based acrylic topcoats that could result in protective coating systems with essentially zero volatile organic compound (VOC). This prospect would not only allow compliance with air quality regulations, but would also significantly reduce the use of flammable solvents and associated hazardous waste. In addition to liquid applied coatings, several powder-coating materials were evaluated for their corrosion protection performance.



FIGURE 5: Space Shuttle launch. Photo courtesy of NASA.

In an effort to reduce the time spent refurbishing facilities between launches, sprayable silicone ablative coatings were investigated as a replacement for ceramic-filled epoxy coatings. A 1994 study determined that sprayable silicone ablative coatings provided excellent heat and blast protection for launch structures.²⁴ Previous ablative materials were ceramic-filled epoxies developed in the 1960s for the manned space flight programs. The sprayable silicone ablative coatings were developed in response to concerns about damage to the protective tiles used on the Space Shuttle. The potential for damage resulted from the tendency of the ceramic-filled epoxy ablatives to spall when subjected to the thermal, impact, and pressure stresses involved in the exhaust plume of SRBs. In addition to their performance characteristics, sprayable silicone ablatives could be applied by plural component spray over an inorganic ZRP. This results in a significantly higher production rate than possible with the ceramic-filled epoxies. Ceramic-filled epoxy application requires labor-intensive mixing of a three-component system and manual application to a substrate primed with the epoxy components (without the ceramic filler). The use of sprayable silicone ablative coatings decreased the time required to refurbish the umbilical tower and other affected areas in preparation for follow up launches.

In the mid-1980s, researchers at KSC became interested in polyanilines (PANs) as protective coatings for metallic surfaces. As it was mentioned earlier, during the previous 20 years, extensive coating testing at KSC had led to the conclusion that inorganic ZRPs significantly outperformed organic zinc-rich type primers in the marine atmosphere of Florida. This was partially attributed to the better conductivity of the inorganic ZRP coating film. The materials typically used to produce the organic zinc-rich films (e.g., epoxies, vinyls, etc.) caused an undesirable insulating effect on the zinc particles. This effect resulted in decreased galvanic activity of the zinc particles for protection of the carbon steel substrate. On the other hand, the organic zinc-rich primers had one advantage in that they allowed for

less-than-perfect surface preparation on steel to achieve performance. The organic polymers provided better adhesion to marginally prepared substrates than the inorganic materials. This property, led researchers at KSC to consider the use of conductive organic materials to formulate new zinc coatings to get the high corrosion protection performance of the inorganic ZRPs without the labor intensive surface preparation requirements of the inorganic ZRPs. It was hypothesized that the conductive organic vehicle would provide both: the increased conductivity needed for superior galvanic protection of the steel substrate and better adhesion, with less-than-perfect surface preparation. Hence, the work on conductive organic polymers and the search for materials that would allow the development of a new generation of protective coatings, based on this technology, began. A study conducted in 1995 to evaluate doped polyaniline as a carbon steel protective coating, using electrochemical impedance spectroscopy (EIS),²⁵ showed that further development of the coatings would be needed in order to achieve the expected corrosion protection performance.

The Department of Energy's Los Alamos National Laboratory (LANL) awarded the 1997 Distinguished Patent Award to a team that included two KSC chemists. The patent (U.S. Patent 5,658,649), entitled Corrosion Resistant Coating,²⁶ was selected as the top patent from the 41 patents issued at LANL in 1997. The formula for the coating features PAN as its active ingredient. A collaboration between NASA/KSC and the University of Arkansas resulted in further development of the coating. As a result of this collaboration, a water and solvent soluble conductive coating was developed and commercialized under an exclusive NASA license.

NASA'S CORROSION TECHNOLOGY LABORATORY

In 2000, recognition that corrosion control was an emerging area of research at KSC, led to the creation of the Corrosion Technology Laboratory to achieve KSC's goal of increased participation in research and development in the area of corrosion control (Figure 3). The Corrosion Technology Laboratory at NASA's KSC is a unique combination of people, equipment, and facilities that provides technical innovations and engineering services in all areas of corrosion for NASA and external customers. The facilities include, in addition to the BCTS, several laboratories equipped to perform coatings application, accelerated corrosion testing, and corrosion control technology development work.²⁷

DATABASE-DRIVEN COATINGS MANAGEMENT

In 2000, a computerized corrosion data management system was implemented to store information in a database that includes the location of the structure, the type of structure, the surface area of the structure, the substrate material, and the current condition of the coating system. Photos visually document condition ratings. Once an asset is initially entered into the KSC computerized corrosion management program's database, assessment surveys provide subsequent data regarding the condition of the structures. The computerized corrosion management program supplies a set of parameters to follow when gauging the condition of the structures, which guarantees that all existing and new assets will be evaluated consistently and objectively, even when examined by different inspectors. Coating inspectors, certified by NACE International®, assess the structures and assign them a coatings appearance and performance classification based on factors such as surface cracking, pitting, heavy deposits, broken welds, loss of coating system, pancaking rust (rust buildup that indicates heavy corrosion), and loss of metal. They then enter all the data for each structure into the computerized database. The majority of the critical components are on a one-year inspection cycle. One important feature of the program is its ability to store and compare condition photos of assets that are taken over a period of time. As the inspectors assess the structures, they take photos, always from the same angle, to document the written description of the surface conditions. A comparison of photos taken over several years provides an illustration of how corrosion in a particular area has progressed over time.

The computerized corrosion maintenance program also generates reports based on queries. For instance, one report could assemble an inventory of assets rated with a particular coatings classification that will require coatings maintenance within a certain time frame. It would list the total amount of square feet of the assets' surface area and the type of coating systems currently on the surfaces, and calculate a cost estimate to recoat the assets. Another report might generate the same information for areas considered to be corrosion "hot spots" – areas experiencing severe corrosion – that need immediate attention. If a particular asset kept appearing in reports more often than it should, the corrosion control team would become aware that a potential problem existed and analyze the coating system on that asset to determine why the structure was not following its normal refurbishment cycle. By tracking areas that historically have problems, the team is able to develop long-term solutions involving either a coatings system change or design change.²⁸

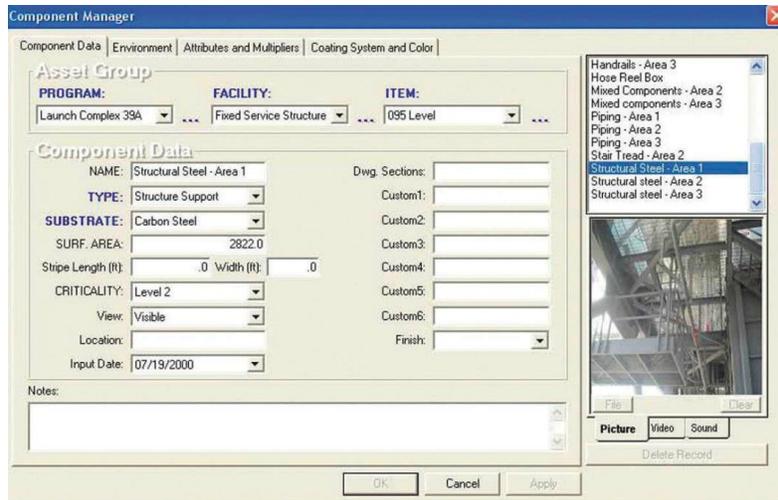


FIGURE 6: Screen Shot of Database for a Launch Pad Structural Area. Photo courtesy of NASA.

NASA TECHNICAL STANDARD NASA-STD-5008 FOR PROTECTIVE COATINGS

In 2001, NASA Technical Standard NASA-STD-5008 for Protective Coatings of Carbon Steel, Stainless Steel, and Aluminum on Launch Structures, Facilities, and Ground Support Equipment was approved. The standard was developed to establish uniform engineering practices and methods to ensure the inclusion of essential criteria in the coating of ground support equipment (GSE) and facilities used by or for NASA. The testing requirements are applicable to GSE and facilities that support space vehicle or payload programs or projects and to critical facilities at all NASA locations worldwide. The requirements were designed for non-flight hardware used to support the operations of receiving, transportation, handling, assembly, inspection, test, checkout, service, and launch of space vehicles and payloads at NASA launch, landing, or retrieval sites. The criteria and practices are used for items employed at the manufacturing, development, and test sites upstream of the launch, landing, or retrieval sites.

In order for a coating system to be used at NASA, it must be listed on the NASA-STD-5008 Approved Products List. Coating systems on this list are qualified according to the requirements of NASA-STD-5008B by the KSC Corrosion Technology Laboratory.²⁹ Typical protocol requires laboratory adhesion tests, color measurements, gloss measurements, and corrosion evaluations on the coatings exposed at the NASA BCTS. An initial evaluation of the coating system is performed after 18 months of environmental exposure. If the coating passes the adhesion testing and 18-month exposure requirements, it is initially accepted into the qualified products list. The coatings remain at the test site for a total exposure duration of 60 months. If the coating system qualifies according to the requirements of NASA-STD-5008B, final acceptance of the product is approved and the product remains on the

qualified products list. If the system does not meet the requirements, it is removed from the qualified products list altogether.

Coupon Materials and Coating Systems

Test panels are prepared for beachside exposure testing in the KSC Corrosion Technology Laboratory using standard commercially available 4-inch-by-6-inch (10.2 cm by 15.2 cm) carbon steel test panels. Two types of panels are used: a flat panel and a composite panel with a 1-inch C-channel welded onto its surface (Figure 7). The composite panel mimics features that are normally present in a carbon steel structure such as welded areas, sharp corners, and places where water can accumulate.



Figure 7: Typical Coated Flat and Composite Panels.

In preparation for the atmospheric field exposure testing, a matrix of 16 panels per coating system is prepared. Four different conditions are used:

- (1) Four primer-only composite panels exposed to normal conditions.
- (2) Four full system composite panels exposed to normal conditions.
- (3) Four full system composite panels exposed to normal conditions plus aluminum oxide (Al_2O_3) and HCl acid-slurry applications (to simulate SRB exhaust).
- (4) Four full system flat panels with a scribe exposed to normal conditions.

In preparation for laboratory adhesion testing, an additional set of four “primer only” coated test panels are included into the test matrix. Consequently, 20 test panels are required to test a single coating system for use at KSC.

In 2011, the standard was revised and updated to address environmental stewardship by including the following:

- Environmental, health, and safety impacts of processes and materials shall be taken into account when employing protective coating methods and techniques.
- Alternative, environmentally friendly materials that do not contain hexavalent chromium, lead, cadmium, or hazardous air pollutants (HAPs), such as methyl ethyl ketone, toluene, and xylene, shall be considered when determining the correct coating method/technique for each protective coating application.

Coating testing and evaluation for inclusion in the NASA coatings standards is an ongoing process driven in part by the requirement to comply with environmental regulations. Over the years, many projects have been carried out to qualify low volatile organic compound (VOC), isocyanate free, and hexavalent chromium free coatings.

SMART MULTIFUNCTIONAL COATINGS FOR CORROSION DETECTION AND CONTROL

In 2004, researchers at NASA's Corrosion Technology Laboratory started the development of a multifunctional, smart coating for the autonomous indication and control of corrosion. The original idea was to develop a coating with the inherent ability to detect the chemical changes associated with the onset of corrosion and respond autonomously to indicate it and control it. The multi-functionality of the coating would be based on micro-encapsulation technology, specifically designed for corrosion control applications. This design has, in addition to all the advantages of other existing microcapsule designs, the corrosion-controlled release function that allows the delivery of corrosion indicators and inhibitors on demand only when and where needed.

Since corrosion is mostly an electrochemical process, pH and other chemical changes are often associated with it, so it is expected that materials that are pH or otherwise electrochemically responsive can be used to detect and control corrosion. The initial step in developing the multifunctional coating involved the synthesis of pH-sensitive microcapsules suitable to incorporate corrosion indicators and inhibitors into a coating. The wall of the microcapsule was designed to break down and release the encapsulated contents in response to the pH increase at the cathodic site. As shown in Figure 8, the pH-sensitive microcapsule wall breaks down and delivers its contents when the pH increases (basic conditions). The illustration shows the delivery of an encapsulated color changing pH indicator that would indicate the presence of corrosion. In the same manner, the microcapsules can deliver fluorescent corrosion indicators, corrosion inhibitors (organic and inorganic) and self-healing agents when incorporated into a coating.

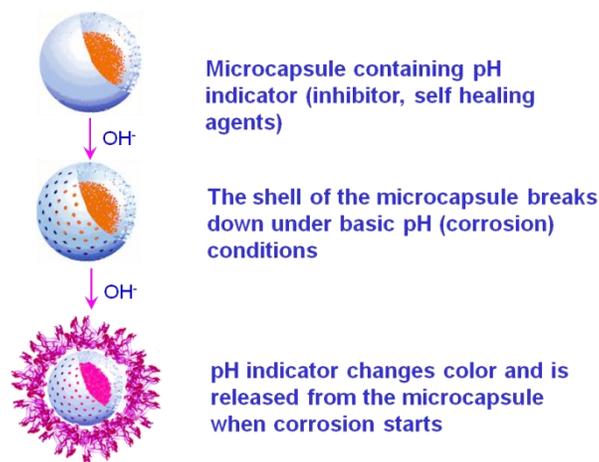


Figure 8: Conceptual illustration of a pH-sensitive microcapsule delivering a color-changing corrosion indicator as pH increases.

For corrosion applications, various compounds, such as corrosion indicators, inhibitors, self-healing agents, and dyes can be encapsulated. These microcapsules can be incorporated into various coating systems for corrosion detection, protection and self-repair of mechanical coating damage (Figure 9). The microcapsules allow the incorporation of one or multiple functions into the coating. Figure 9 shows the incorporation of three functions simultaneously. Encapsulation also allows the incorporation of different corrosion inhibitors (singly or in combinations) into the same coating. The incorporation of

microcapsule with different rates of delivery for short-term (immediate) and long-term corrosion protection is also possible. The versatility of the design is of special interest in corrosion inhibition applications. Almost all corrosion inhibitors are chemically active reagents. Very often, the reactivity that makes them effective corrosion inhibitors also causes them to be environmentally unfriendly, such as in the case of chromates. Because of this, research for new and environmentally friendly corrosion inhibitors is an ongoing effort in the corrosion protection industry. Although several organic and inorganic environmentally friendly corrosion inhibitors have been proven to be effective in laboratory testing, their incorporation into coatings often renders them ineffective due to undesired interactions between the inhibitor and the coating. These problems can be avoided by using a corrosion-triggered delivery system, such as the pH-sensitive microcapsules, to incorporate the inhibitor into the coating.

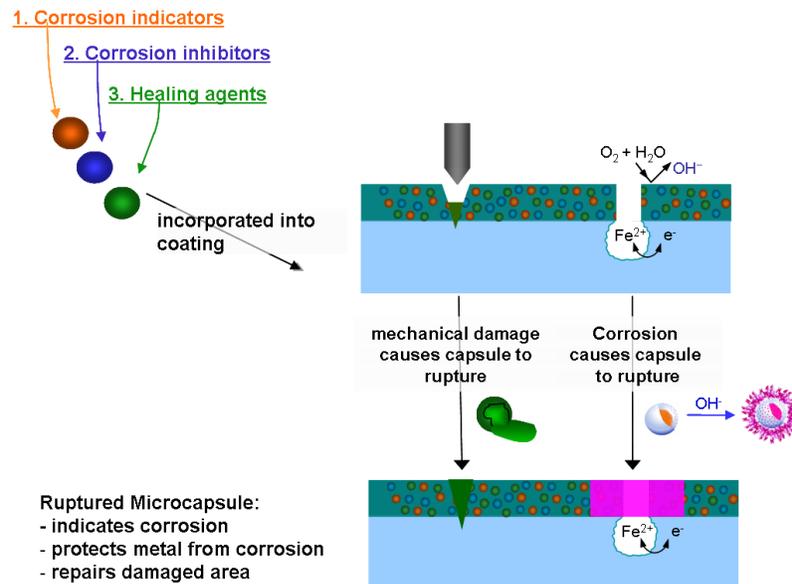


Figure 9: Conceptual illustration of a smart coating with pH sensitive microcapsules for corrosion detection and protection.

While the initial smart coating concept was based on pH sensitive microcapsules, a portfolio of different corrosion-controlled delivery systems has been developed over the years to accommodate a wide range of active ingredients and coating systems. Figure 10 shows some examples of these delivery systems that include: pH sensitive microcapsules, pH sensitive microparticles, and inorganic microcontainers. The end products of these delivery systems are pigment-grade materials with good coating compatibility that can be obtained in free flowing powder form.

Early corrosion indication and detection of hidden corrosion are highly desirable properties in a corrosion protective coating. These functions can lower operational costs and avoid downtime due to extensive repairs, as well as improve safety by avoiding structural failures. Hidden corrosion detection is needed for the protection of critical assets. Figure 11 shows an image of a corroded bolt that can only be detected by removing the bolt (left photograph) and a conceptual illustration (right) of how a corrosion detecting coating can be used to indicate the corrosion by a change in color on the head of the bolt that is visible during a corrosion inspection.

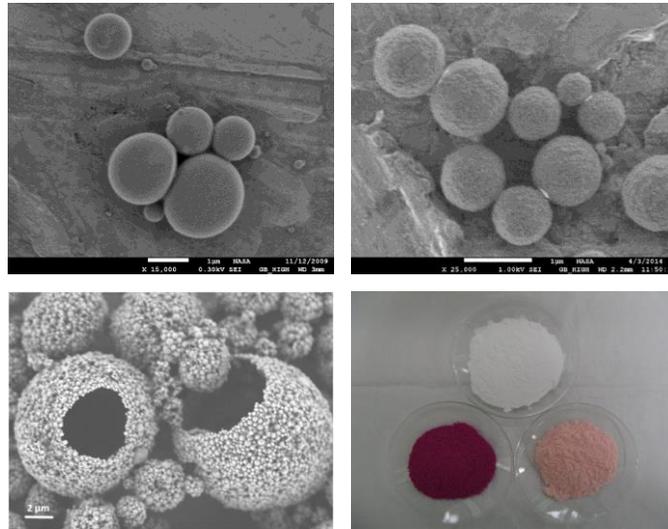


Figure 10: Microscopy images of microcapsules (top left), microparticles (top right), microcontainers (bottom left), and picture of microcapsules in free-flowing powder form.



Figure 11: Hidden corrosion at NASA's launch pad (left) and conceptual illustration of a smart coating being used to detect hidden corrosion (right).

CONCLUSIONS

NASA's has been dealing with corrosion challenges since the inception of the Space Program in 1962 due to the fact that it launches its missions from a highly corrosive marine environment. In addition, the exhaust from the solid fuel rockets makes the corrosive conditions at the launch pads even more corrosive. What started as an atmospheric exposure test site near the launch pads to evaluate coatings, materials, and maintenance procedures in the 1960s, has evolved over the years into what is now the Corrosion Technology Laboratory at the Kennedy Space Center. This lab is a network of capabilities – people, equipment, and facilities -that provides technical innovations and engineering services in all areas of corrosion for NASA and external customers.

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