35 YEARS OF CORROSION PROTECTION AT THE KENNEDY SPACE CENTER

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ABSTRACT

NASA began corrosion studies at the Kennedy Space Center (KSC) in 1966 during the Gemini/Apollo Programs with the evaluation of long-term protective coatings for the atmospheric protection of carbon steel. KSC's Beach Corrosion Test Site (BCTS), which has been documented by the American Society of Materials (ASM) as one of the most corrosive, naturally occurring, environments in the world, was established at that time.

With the introduction of the Space Shuttle in 1981, the already highly corrosive conditions at the launch pad were rendered even more severe by the acidic exhaust from the solid rocket boosters. In the years that followed, numerous studies have identified materials, coatings, and maintenance procedures for launch hardware and equipment exposed to the highly corrosive environment at the launch pad.

This paper presents a historical perspective highlighting the lessons learned in over thirty-five years of corrosion research, materials evaluation, and development work aimed at protecting and enhancing the safety and reliability of the nation's launch infrastructure and hardware.

Keywords: corrosion, carbon steel, spacecraft launch environment, atmospheric corrosion, marine atmosphere, zinc-rich primers, UNS S30400, UNS S31703, UNS S31603, UNS S31803, UNS N10276, UNS N06625, UNS N06022, UNS S31254, UNS N06200, UNS N08367, UNS S44735, UNS S32750, UNS S30403, UNS G10080.

INTRODUCTION

The Kennedy Space Center (KSC) is located on the east-central area of Florida (Figure 1). The launch environment at KSC is extremely corrosive due to the combination of ocean salt spray, heat, humidity, and sunlight. With the introduction of the Space Shuttle in 1981 (Figure 2), the already highly corrosive conditions at the launch pad were rendered even more severe by the acidic exhaust from the solid rocket boosters. Currently, KSC has to maintain about $2 billion worth of unique equipment and facilities, not including the four orbiters, valued at about $8 billion. Among the items: two launch complexes, two crawler transporters, three mobile launch platforms, and specialized testing equipment.

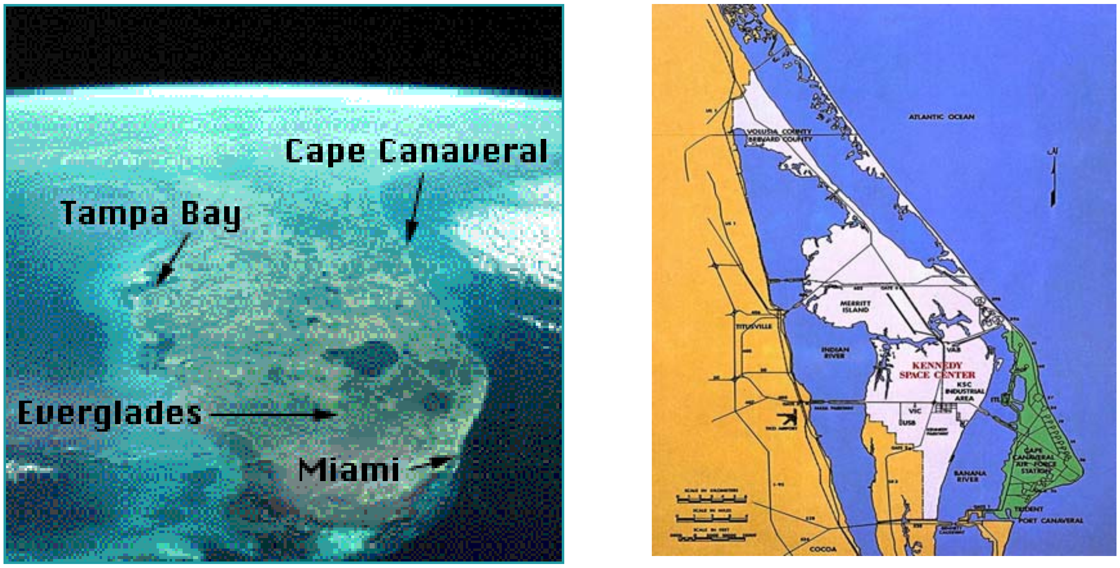

FIGURE 1. Aerial photograph of Florida showing the location of KSC (left) and map of KSC (right). Photos courtesy of NASA.

FIGURE 2. Space Shuttle Launch. Photo courtesy of NASA.

Corrosion studies began at KSC in 1966 during the Gemini/Apollo Programs with the evaluation of long-term protective coatings for the atmospheric protection of carbon steel. NASA's KSC Beach Corrosion Test Site (BCTS) was established at that time (Figure 3). In the years that followed, numerous studies at the site have identified materials, coatings, and maintenance procedures for launch hardware and equipment exposed to the highly corrosive environment at the launch pad. Results from these evaluations have helped KSC find new materials and processes that increase the safety and reliability of launch structures and ground support equipment.

FIGURE 3. KCS's Beach Corrosion Test Site. Photo Courtesy of NASA.

The BCTS has been documented as having the highest corrosivity of any long-term exposure site in North America and one of the highest in the world.[1] Table 1 compares the corrosivity of the BCTS location with other test sites. Figure 4 shows the rapid decrease in corrosion rates as distance from the BCTS increases.

TABLE 1
COMPARISON OF CORROSION RATES OF CARBON STEEL AT VARIOUS TEST LOCATIONS[1]

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
Galeta Point Beach, Panama CZ	Marine	686	27
Kennedy Space Center, FL (beach)	Marine	1070	42

(a) Two-year average

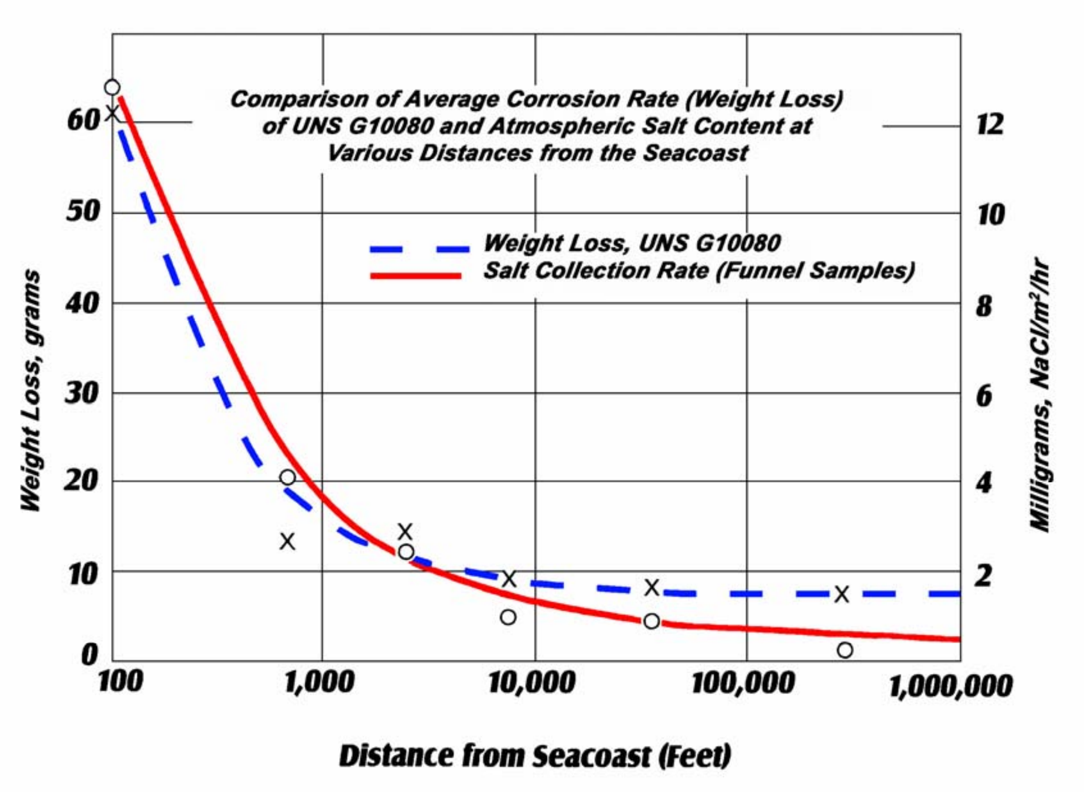

FIGURE 4. Changes of corrosion rate with distance from the ocean.[2]

The BCTS is located at approximately 1 mile (2 km) south from launch complex 39A and is approximately 100 feet (30 m) from the high tide line directly on the Atlantic Ocean. As part of the facility, a fully instrumented weather station is enclosed within the site and provides continuous information on air temperature, humidity, wind direction and speed, rainfall, total incident solar radiation, and incident ultraviolet B radiation levels. The site has approximately 600 feet (183 m) of front row exposure for atmospheric corrosion specimens. Many types of test samples can be accommodated, including standard size test coupons 4"x6" (10.2 cm x15.2 cm), stress corrosion cracking specimens, and full-scale test articles. These experiments can be performed in either a boldly exposed or sheltered configuration. Both power and data connections are available within the site to power test articles and record onboard data instrumentation outputs. The site has recently been outfitted with network connectivity for data acquisition through the Internet. The site has provided over 35 years of technical information on the long-term performance of many materials and continues to be upgraded with state-of-the-art capabilities to meet the current and future needs for corrosion protection of NASA, other government agencies, and industry.

HISTORY OF COATING EVALUATION AND DEVELOPMENT AT KSC

The evaluation of protective coatings for carbon steel, stainless steel, and aluminum has been an ongoing process 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.[3] Both organic and inorganic zinc-rich coatings were applied to test panels and exposed at the 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 protection of launch equipment and ground support structures. 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 5).

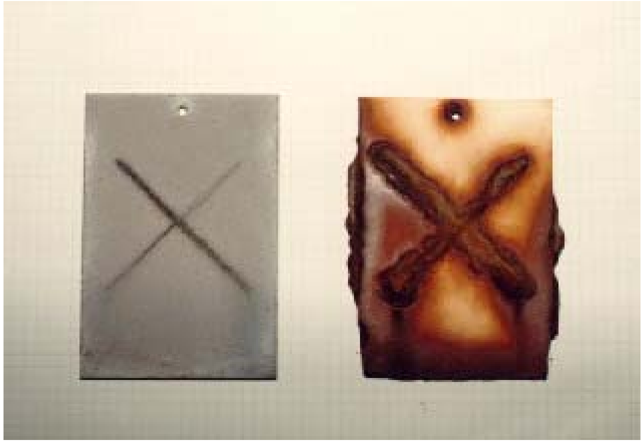

FIGURE 5. Untopcoated inorganic ZRP (left steel panel) and epoxy and urethane topcoated inorganic ZRP (right steel panel) after 8 years of atmospheric exposure at the BCTS.[5]

Untopcoated inorganic ZRPs were used for many years at KSC for the long-term protection of carbon steel.[4] Several of the original panels exposed in 1969 that were painted with a single coat of ZRP without a topcoat are still showing complete corrosion protection of the carbon steel at the BCTS.

In 1981, the Space Shuttle introduced a more aggressive environment to the launch pads at KSC. Exhaust from the solid rocket boosters (SRBs) resulted in deposited small particles of alumina (Al_2O_3) with hydrochloric acid (HCl) adsorbed onto their surface. It is estimated that 17 tons of hydrochloric acid are generated during a Space Shuttle launch. The impingement of this exhaust resulted in the failure of the carbon steel corrosion protection provided by the unprotected ZRPs despite the fact that a pressure wash down was carried out as soon as possible after a launch. In response to the SRB exhaust problem, KSC launched a study of new coatings to resist this new, more aggressive environment.

Tests were conducted in 1982 and 1986 to identify topcoat materials to enhance the chemical resistance of the coating systems in use at KSC. The 1982 study determined that 2-component coatings were far superior to single-component types, epoxy/urethane topcoats provided some protection to the ZRPs, and that repair techniques, other than abrasive blasting, were ineffective in the launch environment.[5] 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.[6]

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

To address this challenge, studies were undertaken in 1990, and are being continued to this day, to identify inorganic ZRPs and topcoat systems that would provide superior protection while complying with the anticipated strengthening of environmental quality standards.[7, 8] 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 corrosion protection performance.

In an investigation carried out in 1993 and 1994, electrochemical impedance spectroscopy (EIS) was used in combination with atmospheric exposure as a short-term method for analyzing the performance of twenty-one commercially available zinc-rich primers.[9-11] Impedance measurements were obtained for each coating before and after each week of atmospheric exposure at the BCTS for up to four weeks. Subsequent measurements were collected after 8 weeks and after one year of atmospheric exposure. The impedance data was analyzed to identify parameters that would predict the long-term performance of ZRPs. The results showed a correlation between several parameters obtained from EIS measurements in combination with atmospheric exposure and the long-term performance of ZRPs.

An evaluation program was initiated in 1994 to identify alternative inorganic topcoat coating materials for use at KSC and to study the performance of a new high-gloss polysiloxane topcoat for inorganic zinc-rich primers. Evaluation at the 18-month exposure period provided information for the revision of approved coating systems at KSC. This revision approved the use of several inorganic topcoat systems for general use with ZRPs at KSC's launch pads.

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.[12] 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. The Shuttle Contractor installed the ablative material at Launch Complex 39B (LC39B) in 1994 on the entire 95' (29 m) level and on camera and communication boxes. A project is currently underway to apply these materials to the Mobil Launch Platforms (MLPs) to reduce launch damage. Development work shows that hold down post blast shields are candidates for silicone protection.

Recent protective coatings research has concentrated on the development and evaluation of conductive polymer coatings,[13] polysiloxane coatings,[14] silicone coatings for blast and heat protection of launch structures,[15] and molybdate conversion coatings[16] as possible replacement for chromium conversion coatings.

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 lead 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 increased conductivity of the inorganic ZRP coating film. The materials typically used to produce the organic zinc-rich films (e.g., epoxies, vinyls, etc.) produced 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 result, led researchers at KSC to consider the use of conductive organic materials to formulate these zinc coatings to get the best of both types of ZRPs. The idea being that the conductive organic vehicle would provide both: the increased conductivity needed for superior galvanic protection of the steel substrate, and would allow better adhesion with less than perfect surface preparation. Hence the work on conductive organic polymers and the search for materials that would allow the production of a new generation of protective coatings based on this technology began.

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, 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 has resulted in further development of the coating. As a result of this collaboration, a water and solvent soluble conductive coating was developed. The Ligno Sulfonic Acid Doped Polyaniline (Ligno-Pani) is being commercialized under a NASA license. The technology offers several advantages, including the use of inexpensive materials, such as aniline and lignin. Lignin is a paper and pulp manufacturing waste product. Unlike existing coatings and systems used for corrosion prevention, Ligno-Pani does not utilize VOCs or heavy metals that pollute the water supply.[17]

Thin gauge stainless steel and aluminum structures such as protective bellows around drive mechanisms flex repeatedly and thus require highly flexible and adherent coatings. The aerospace industry has traditionally used paints having high VOC content for protecting vehicles and support structures. Flexible paints employ highly solvated rubber binder resins, which render the products highly volatile and difficult to apply by spraying. Silicone-based paints are formulated to yield temperature- and weather-resistant coatings that prevent corrosion by forming effective electrolyte barriers. However, silicones are normally delivered from organic solvents and exhibit poor adhesion to unprimed metals.

An industry partner for NASA/KSC developed experimental VOC-compliant primerless silicone coatings for corrosion control under a Small Business Innovation Research (SBIR) contract. The ultimate goal in developing the coatings is to provide an effective, environmentally sound method for protecting the surfaces of aluminum and stainless steel without introducing additional pretreatment and priming steps. The waterborne elastomeric anticorrosion coatings are being developed for the corrosion protection of metals such as aluminum and stainless steel in corrosive environments. These coatings consist of aqueous dispersions of silicone resins, stabilized with polymeric surfactants and pigmented with non-toxic anticorrosive additives. The latter silicone-modified polymers yield emulsions that adhere the coating to metal surfaces. By forming a topcoat-bound primer layer *in situ*, low VOC-coatings having simple application properties can be formulated.

Open circuit potential as well as impedance measurements and visual observations indicated that the newly developed primerless silicone coating was effective at the corrosion protection of stainless steel UNS S31600 but it failed on aluminum 2024-T3 and on cold-rolled steel. The failure was greater in the case of the cold-rolled steel.[18]

An environmentally friendly molybdate-based conversion coating for aluminum and aluminum alloys resulted from a collaboration between an industry partner and NASA under a SBIR contract. This innovation is important because it contains molybdate instead of chromate. The molybdate conversion coating does not contain chemicals that are harmful to the environment or to humans and it was developed as a possible substitute for chromium conversion coatings. Chromate conversion coatings have been used for the protection of aluminum alloys for over 70 years. Although their efficiency in minimizing corrosion attack is excellent, there are health and safety concerns over their use due to their toxicity and carcinogenic nature. NASA/KSC has used chromate-based coatings on many of its spacecraft and desires to replace them with safer coatings. Despite an extensive research effort over the past decade, a completely satisfactory replacement for chromate conversions coatings has yet to be identified. Preliminary tests demonstrated an exceptional corrosion protection by the new coating. These results established a sound technical feasibility for this new molybdate conversion coating.[19]

CORROSION PERFORMANCE OF ALLOYS IN THE SPACE SHUTTLE LAUNCH ENVIRONMENT

KSC's Materials Science Laboratories have conducted testing and evaluation of the corrosion behavior and corrosion protective properties of different materials in the Space Shuttle Launch Environment since 1968. The Corrosion Laboratory was established in 1985 and was outfitted with state-of-the-art electrochemistry equipment to conduct research and materials characterization in many different corrosive environments.

In 1987, a study was began to find a replacement alloy for UNS S30400 stainless steel in the metal flex hoses used in various supply lines that service the Orbiter at the launch pad. These convoluted flexible hoses, which were originally made out of UNS S30403 stainless steel, had failed by pitting. In the case of vacuum jacketed cryogenic lines, pinhole leaks caused by failure of the flex hose produced a loss of vacuum and subsequent loss of insulation. 19 alloys were investigated and evaluated using a variety of techniques that included exposure at the BCTS, electrochemical characterizations, salt fog chamber exposure, and ferric chloride immersion. As a result of that investigation, a nickel-chromium-molybdenum- tungsten substitute alloy for UNS S30400 stainless steel was identified. Flex hoses of this alloy (UNS N06022) are now performing without failures at the launch pad.[20-23]

A current investigation is underway to study the corrosion behavior of eleven corrosion resistant alloys to replace the UNS S30403 stainless steel tubing at the Space Shuttle launch sites.[24, 25] The eleven alloys include UNS S31703, UNS S31603, UNS S31803, UNS N10276, UNS N06625, UNS S31254, UNS N06200, UNS N08367, UNS S44735, UNS S32750, and UNS S30403 (included as a control). The first five were part of the previous investigation. UNS S30400 stainless steel tubing is susceptible to pitting corrosion (Figure 6) and Stress Corrosion Cracking (SCC). Use of corrosion resistant tubing will greatly reduce the probability of future corrosion failures (Figure 7). Improved safety and less maintenance cost will result from using the more corrosion resistant alloys.

FIGURE 6. Micrograph (100x magnification) of pit from KSC's launch pad tubing.[26]

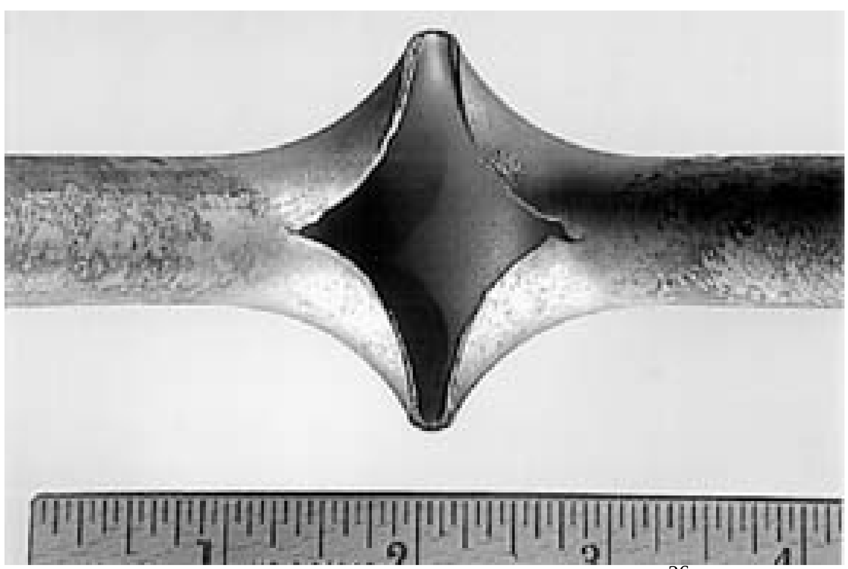

FIGURE 7. Tubing split caused by pitting.[26]

CONCLUSIONS

The Kennedy Space Center is a major source of worldwide corrosion expertise with over 35 years of technical information on the long-term corrosion performance of many materials in its highly corrosive environment. This knowledge, which was not available when the launch pads were constructed, is critical for the design of spaceports that can be operated more safely and require less maintenance between lunches.

Results from coating evaluation studies at KSC have shown that: inorganic ZRPs outperform organic ZRPs in the KSC seacoast environment; inorganic ZRPs are the best choice to provide long-term protection of launch equipment and ground support structures; in general, organic topcoats are detrimental to the long-term performance of inorganic ZRPs; inorganic topcoats perform well when used with inorganic ZRPs.

Results from investigations including atmospheric exposure at KSC's BCTS and electrochemical evaluation have shown that the nickel-based alloys, such as UNS N06022 and the higher molybdenum containing stainless steels such as UNS N08367, have consistently outperformed the 300 series stainless steels in the launch environment at KSC. These materials are the best choices to prevent pitting failures in thin-walled bellows and tubing.

The use of electrochemical techniques predicted the behavior that has been confirmed with atmospheric exposure testing. Since atmospheric exposure testing typically takes a long time (1-2 years), the use of electrochemical techniques is recommended to narrow down the number of materials to be evaluated in long-term atmospheric exposure testing.

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