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STRESS CORROSION CRACKING IN FUEL ETHANOL

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Abstract

The U. S. Government, through the Department of Energy (DOE), has had an ongoing program to expand the use of alternatives to gasoline and diesel fuels. Legal alternatives under the Environmental Protection Agency (EPA) include compressed natural gas (CNG), ethanol, methanol, electricity, and liquefied petroleum gas. Denatured ethanol (ethyl alcohol) is of particular interest because of its increasing use as a fuel additive to fight air pollution from internal combustion motor vehicles and as a renewable fuel source. Fuel ethanol in the U.S. is governed by the standard ASTM D 4806. It is an oxygenate intended to improve fuel combustion and reduce emissions by aiding the reduction of carbon monoxide (CO), volatile organic compounds, toxics, and fine-particulate emissions that pose a potential health threat. This paper discusses the current experience in the U.S. with respect to the problem of stress corrosion cracking (SCC) of steel equipment in the distribution chain handling fuel ethanol. Failures reported in a survey conducted by the American Petroleum Institute study have included tanks and piping downstream from the ethanol production source prior to blending with conventional grades of gasoline (E10). However, reportedly there have been no reported failures due to ethanol SCC in Brasil. Additional research is in progress to identify causative agents and to develop guidelines for identification, repair and mitigation of ethanol SCC.

Key words: ethanol, biofuel, stress corrosion cracking, guidelines, research, failure

Introduction

Ethanol has been used in automobile fuels for more than 25 years including substantial experience in Brasil. In the early 1990's the U.S. Congress passed the Clean Air Act that required oxygenate be used in the gasoline supply in specific regions of the country. Oxygenates used in the U.S. include MTBE and ethanol. Recently, MTBE has been found as a contaminant in groundwater and many states have banned its use. The U.S. government has passed new energy legislation that among other things, phases out the use of MTBE, eliminates some oxygenate requirements and phase in an increasing requirement to use renewable fuels like ethanol and biodiesel. Consequently, the use of ethanol as an additive/extender to gasoline is increasing dramatically in the fuel sector (See Figure 1).[1] The present study was part of a multi-part development effort by the American Petroleum Institute (API) Refining Committee, Subcommittee on Corrosion and Materials, to address the needs of industry regarding potential problems associated with Stress Corrosion Cracking (SCC) of carbon steel in fuel ethanol service. SCC is initiation and propagation of brittle cracks in a susceptible metal/alloy induced

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from the combined action of tensile stress (applied and/or residual) and a corrosive environment. In the case of SCC in fuel ethanol, the corrosion reaction does not produce high corrosion rates of even macroscopic localized attack. However, there were a growing number of experiences with cracking failures of steel equipment in fuel ethanol service that needed to be examined and critically reviewed.

Work Body

The initial direction taken was to expeditiously develop a white paper to provide a concise and accurate review of the currently available information on experience with SCC in fuel grade ethanol and relate it to experience with SCC in other environments in the downstream petroleum sector. This work also included documentation of the experience from companies involved in fuel ethanol supply, transportation, storage and distribution, and an initial assessment of the potential economic impact of this problem to the petroleum industry.

Ethanol is an alcohol that can be produced from a variety of sources. In the United States the most common source is from corn and grain. However, ethanol can also be produced naturally (fermented) from any carbohydrate source, such as wheat, cane, beet and fruits like grapes and apples. In Brasil, the most common source is from sugar cane. While bio- and synthetic alcohols are technically the same (the ethanol molecule is identical), there are differences in the amounts of other minor constituents such as butanol, acetone, methanol, organic acids to name only a few.

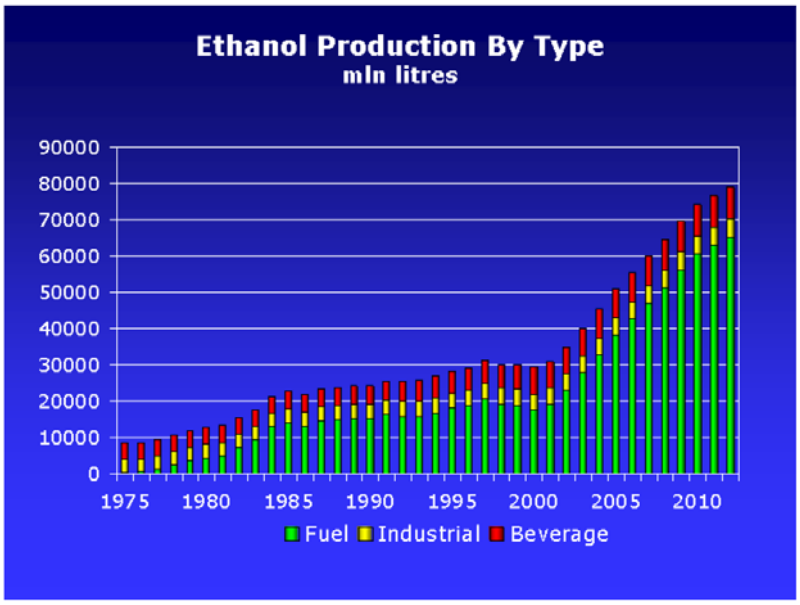

Figure 1 – Current and projected worldwide production capacity for ethanol.

It should also be kept in mind that fuel ethanol is not sold with zero water content (<0.5 percent), where it would be referred to as “anhydrous ethanol”. The ethanol used in the U.S. and many countries for automobile fuel typically contains up to 1 percent water. Ethanol with higher water contents (in the range of 4 to 6 percent) is referred to as “hydrated ethanol”. Such hydrated ethanol is uncommon in the United States but is used in fuel in Brasil. Brasil also produces ethanol to international standards (1 percent max. water content) for international export.

In the United States, denaturants are also added to fuel alcohol in accordance with the Bureau of Alcohol, Tobacco and Firearms. According to Federal Regulation Title 27 Parts 19, 20 and 21 (including CFR 19.1005, 27CFR 21.24 and C.D.A. 20), a denaturant is to be added to alcohol in order to make it unfit for beverage or internal human medical use, and to avoid government taxation.

In the U.S., there are several standards that govern fuel grade alcohol, related analyses and its use as a fuel. The primary specifications for U.S. fuel ethanol can be found in ASTM D4806 – Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel – which gives the compositional and physical limits for fuel ethanol.[2] These limits are summarized in Table 1.

A common parameter that is used in evaluation of fuel ethanol is the pHe value as defined by ASTM D6423.3 It normally ranges from 6.5 to 9.0 and is controlled by additives (referred to as inhibitors). The pHe value is a measure of the acid strength of high ethanol content fuels. It is applicable to fuels containing nominally 70 volume percent or more ethanol, or higher. pHe is similar to the pH parameter used in aqueous solutions. An extremely important point is that pH 7 is considered neutral for aqueous solutions, whereas a pHe value of 9.55 is the neutralization point for ethanol. Therefore, environments that have a pH of 6 in aqueous solutions may be considered only mildly acidic, whereas in ethanol pHe 6 represents a solution of significantly higher acidity (as defined as the magnitude of the reduction from the neutralization value).

Table 1 – Quality Specification for Fuel Ethanol per ASTM D4806

Property	Units	Specification	ASTM Designation
Ethanol	%v min	92.1	D5501
Methanol	%v max	0.5	--
Solvent-Washed Gum	mg/100 ml max	5.0	D381
Water Content	%v max	1.0	E203
Denaturant Content	%v min	1.96	D4806
	%v max	4.76	
Inorganic Chloride Content	ppm (mg/L) max	40 (32)	E512
Copper Content	mg/kg max	0.1	D1688
Acidity as acetic acid	%m (mg/L)	0.007 (56)	D1613
pHe	--	6.5-9.0	D6423
Appearance	Visibly free of suspended or precipitated contaminants (e.g. clear & bright)		

American Petroleum Institute Study

The initial API experience survey was contracted to Honeywell Process Solutions (formerly InterCorr International) in April 2003. A “white paper” based on this initial study was published by API as Technical Report 939-D in September 2003.[4] The effort also included participation by the Renewable Fuels Association (RFA) for support and guidance. It revealed that documented failures of steel equipment in fuel ethanol were conclusively associated with SCC and that these failures appeared to occur in only a portion of the distribution system for fuel ethanol. However, the causative agent (ethanol itself or one of its constituents) was not readily apparent.

Upon completion of the initial report, the API embarked on a more substantial undertaking to further understand the phenomenon of SCC of steel equipment in fuel ethanol. Three contractors were utilized to conduct this study, each with a specific scope of work. The

complete results of these studies have been published in a recent revision to the API 939D report (May 2007)[5] and in separate journal articles.[6-7] The salient findings are summarized briefly herein.

Follow-Up Experience Survey and Field Corrosion Monitoring

In the follow-on study, Honeywell continued the survey portion of the initial program with ancillary activities including updating the list of SSC failures that was published in the initial report. In addition, they conducted a new task on monitoring of corrosion and SCC in fuel ethanol systems using "passive" offline techniques involving stressed U-bend specimens, and "active" online monitoring using electrochemical techniques (SmartCET®)[8] at selected field locations.

Combined with the original study, over 20 cases of SCC in operating equipment were identified and documented in API 939D. Most cases of SCC have been in end-user storage and blending facilities (steel tanks, rack piping and components) with some failures in mid-stream, fuel ethanol distribution storage tanks. Additionally, one informal description (not included in the reported cases) was received of SCC in a steel pipeline segment exposed to fuel ethanol. An example of a field failure from ethanol SCC is shown in Figure 1. No cases of SCC were reported in fuel ethanol manufacturer facilities, tanker trucks, railroad tanker cars or barges, or following blending of the fuel ethanol with conventional (E10) gasoline blends.

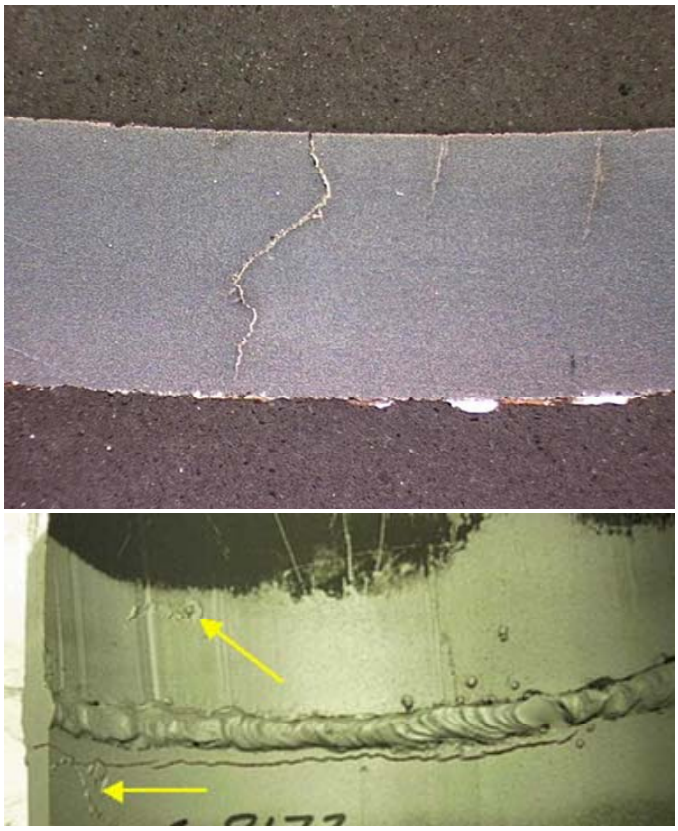

Figure 1 – SCC failure and leak area resulting from ethanol SCC in steel equipment.
Top – Through Thickness; Bottom – Internal surface with cracking adjacent to weld.

Passive monitoring using statically stressed U-bend specimens did not identify SCC when exposed to many service environments. This suggests that an important variable in the SCC

process may be dynamic or flexural tensile stresses. Additionally, these specimens did not contain a mill scaled surfaces or the protrusion of the weld bead from the surface, which was removed by machining prior to testing. Corrosion monitoring data showed that the corrosion rate of steel in fuel ethanol is in most cases low (<0.03 mm/y). But, real-time corrosion data indicated that increases in the corrosion rate and mode correlated with changes in environmental conditions. The results of the active (electrochemical) monitoring in field locations (tanks and loading rack piping) indicated increases in both corrosion rate and pitting activity with conditions of aeration and agitation – See Figure 2.

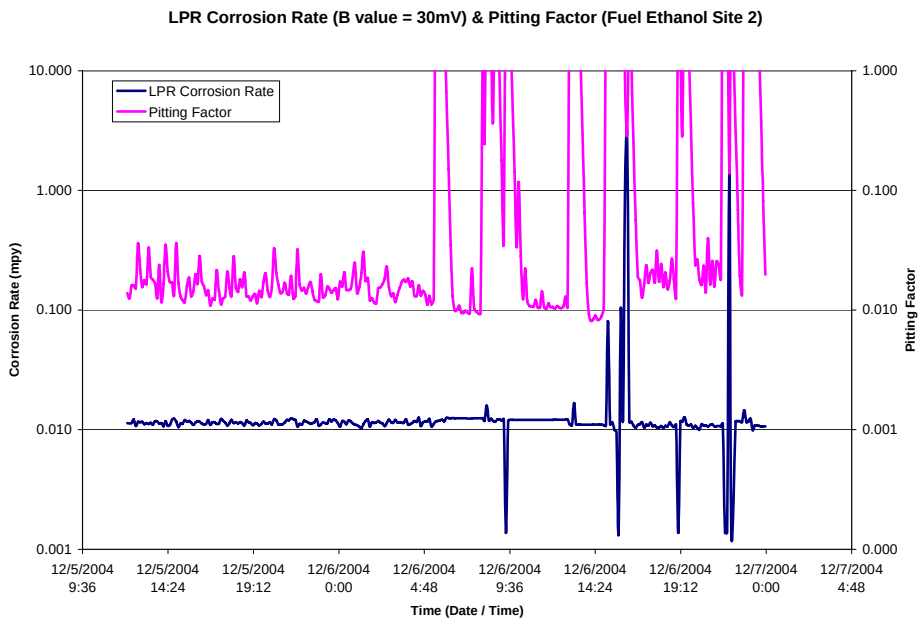

Figure 2 – Corrosion monitoring results showing increased corrosion rate and pitting tendencies in fuel ethanol at a loading rack location resulting from agitation and aeration associated with loading process.

A summary of findings from this portion of the API effort are given below:

1. Stress is an important factor in SCC in fuel grade ethanol. SCC has been reported in non-PWHT welds, areas of stress concentration (fillet welds at lap seams) and other highly stressed components (roof springs). Flexural loading common in tank bottoms, roof springs and potentially other locations appear to also promote SCC. Tank loading and/or unloading events may impart dynamic stresses that increase the likelihood of SCC.

2. While some out-of-specification ethanol was found, SCC has occurred in fuel ethanol that conformed to the ASTM D4806 standard.

3. SCC failures were in the fuel ethanol distribution system were limited to mid-stream storage facilities, and at end-user ethanol/gasoline storage and blending locations used for E10 blends, and not at manufacture sites or after the ethanol is blended with gasoline (E10).

4. SCC in fuel grade ethanol potentially has many aspects (including crack morphology) that are common to SCC produced in steel by other environments. These environments include methanol, ammonia, CO-CO2-water and carbonate-bicarbonate SCC.

A variety of remedial actions are being used to resist SCC of steel equipment in ethanol service, which include ethanol resistant coatings in storage tanks and use of PWHT and stress relief in piping systems.

Laboratory Research

Laboratory studies[5] were performed in parallel by two research organizations. Southwest Research Institute (SWRI) conducted a statistically designed study involving slow strain rate (SSR) tests on notched specimens cut from an ASTM A-36 steel plate commonly used in service. CC Technologies investigated the primary factors for a solution composition within the range defined by the ASTM standard that results in significant SCC, and verified the solution potency. The results of these study along with the follow-up experience survey and corrosion monitoring were recently published the recently revised API Technical Report 939-D.[6]

The statistically designed laboratory study involved notched slow strain rate tests and also included monitoring of corrosion potential of the test specimens during testing. The ethanol used for the statistical matrix tests was pure ethanol (200-proof) with selected additions generally within the range of constituents in the ASTM D4806 standard including of water, acetic acid, corrosion inhibitor (Octel DCI-11), dissolved oxygen, chloride, methanol, denaturant (unleaded gasoline), and galvanic contact with a steel showing prior corrosion products. Additionally, tests were conducted in ethanol obtained from a producer site and from a storage tank where SCC had occurred.

The statistical analysis of the test results from the SSR tests showed that only oxygen and galvanic contact with corroded steel couple were significant factors affecting SCC in these ethanolic environments derived from reagent chemicals. Chloride concentration was the third highest significant factor, followed by methanol, but these factors were not necessarily required to produce SCC. Other parameters, such as, denaturant, sulfate, acetic acid (pHe), and corrosion inhibitor did not have a significant effect in these laboratory tests. The aeration effect on SCC (increasing SCC susceptibility with aeration) was related to the measured corrosion potential as shown in Figure 3. The corrosion potential is primary variable affected by oxygen concentration with the presence of oxygen increasing the corrosion potential leading to SCC.

Slow strain rate tests also showed significant SCC in the ethanol obtained from an end-user, whereas no SCC was found in an ethanol sample obtained from a producer. The specimen tested in the user ethanol showed intergranular SCC, whereas the producer ethanol only resulted in ductile failure mode. The intergranular SCC was also observed in laboratory ethanol that did not contain any chloride. Analysis of the producer and user ethanol for species in Table 1 did not yield any significant difference in chemical composition. However, the corrosion potential of steel in the user ethanol was in the range where SCC was observed in laboratory ethanol mixtures, whereas the corrosion potential of steel in producer ethanol was at least 200 mV higher. The significance and cause of these differences need to be further investigated.

The important findings from this research effort are summarized below:

1. SCC occurred in slow strain rate tests in ethanol that met the ASTM D4806 specifications.
2. Aeration increases the SCC susceptibility significantly. Presence of rust deposits further increases SCC susceptibility. This latter point may help explain the absence of SCC in passive U-bend specimens with machined surfaces.
3. SCC occurs above a potential of 0 V vs. AgCl/EtOH in the presence of chloride and methanol and above 100 mV in their absence.

4. The Ecorr of user ethanol was above about 100 mV, whereas the Ecorr in producer ethanol was about 400 mV higher. Since no SCC was observed in the latter, there must be a critical potential regime for SCC in the range of 0 mV to +200 mV Ag/AgCl/EtOH. See Figure 4
5. Monitoring the corrosion potential of steel may be a useful method to identify SCC-causing conditions and alert operators. Tests to verify this are currently in progress.

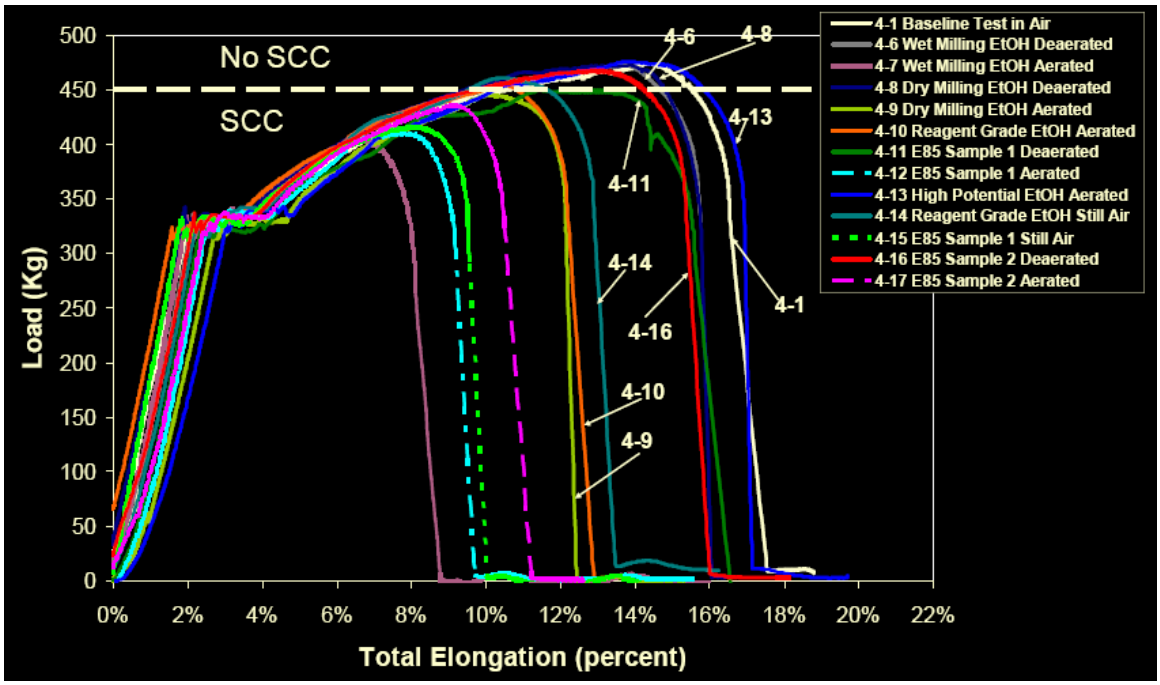

Figure 3 – Summary of results of laboratory SSR ethanol SSC tests.[7] Curves to left show greater SCC susceptibility.

Additional laboratory tests showed that an ethanolic solution that reproduced SCC in carbon steel used for tanks was within the specifications of allowable impurity concentrations as defined by ASTM D4806 (Table 1). This solution, made with 200-proof ethanol was aerated and contained ~3.7% gasoline (denaturant), 1 vol.% water, 0.5 vol.% methanol, 40 ppm chloride ions, and 0.007 vol.% acetic acid. The significant factors in this solution were found to be aeration, water, and chloride ions. SCC of steel did not occur without aeration.

Status of API Effort and Path Forward

Based on the laboratory studies and field investigations conducted to date, the data support that SCC of steel equipment is a real phenomenon and occurs even in ethanol meeting the ASTM D4806 specifications for fuel ethanol. Its impact may yet become more apparent as storage capacity for fuel ethanol is increasing annually (See Figure 4).

Various options are currently being examined to reduce operational risk due to SCC. These include modifications to the ASTM specifications for fuel ethanol along with modification to handling procedures to reduce aeration, improvement to piping and tank designs to reduce sources of excessive mechanical stress and flexural loading, selective use of PWHT, and ethanol resistant coatings.

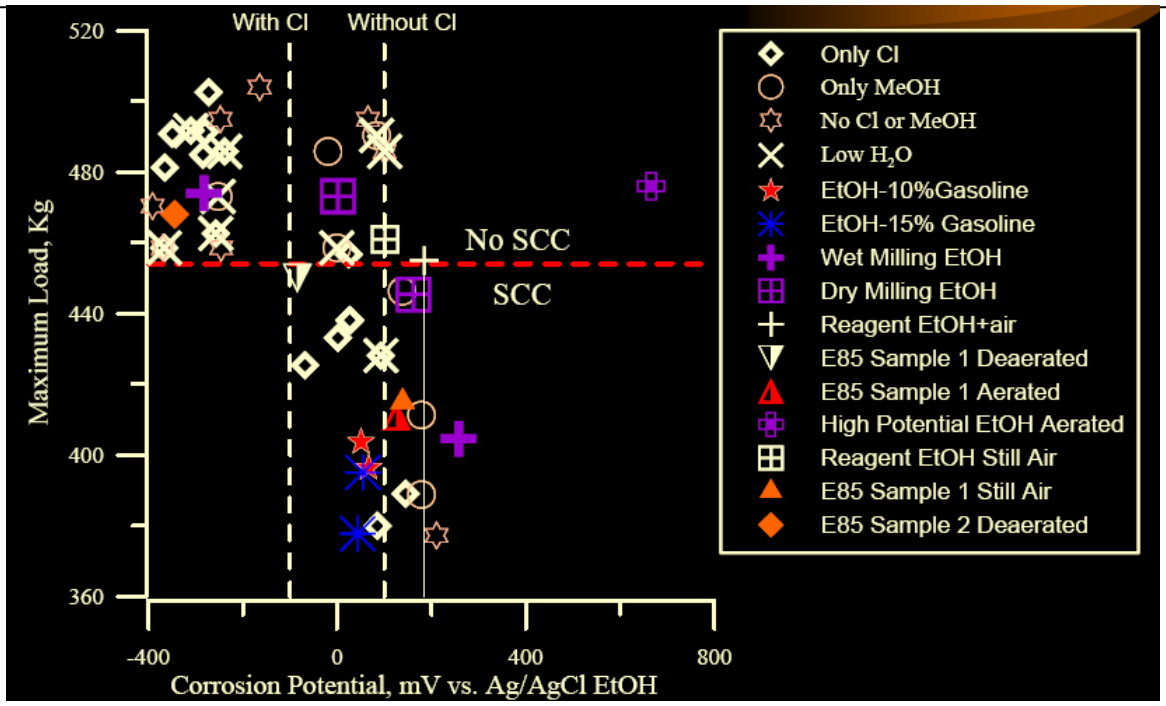

Figure 4 – Relationship between susceptibility to SCC and ethanol type and measured corrosion potential.[7]

Due to extent of the learning developed in this program thus far, it was expanded to include several new tasks with the aim of developing a more complete understanding of SCC in ethanolic environments and to provide improved guidelines to improve the serviceability of steel equipment in fuel ethanol service. The following is a summary of the work in progress from this study.

1. Honeywell is currently under contract by API working on a guidelines document for detection and mitigation of SCC in steel equipment in fuel ethanol service. A draft document has been developed that includes lessons learned from the field survey and laboratory tests along with practical experience from other situations where SCC of carbon steel is a consideration. The draft document is presently under ballot with the API Refining Committee.[8]

2. Monitoring of corrosion potential of steel components in fuel ethanol handling systems. In the laboratory study, SWRI has developed a Ag/AgCl(Ethanol) reference electrode and they identified a relationship between the corrosion potential and susceptibility to SCC. The current effort is soliciting field test sites for monitoring the actual corrosion potential of steel component.

3. Laboratory SCC tests are continuing at SWRI. This effort is aimed to evaluate ethanol from a greater range of sources including wet and dry milled ethanol derived from corn, ethanol manufactured from sugar cane and other biological sources (including hydrated ethanol), and examination of ethanol/gasoline blends such as E85.

4. The U.S. Department of Transportation has prepared a Broad Are Announcement for pipeline research that includes research on ethanol including microbiological corrosion and SCC. As the market demand for fuel ethanol appears to be

increasing, increased demands on the distribution system are anticipated. This will increase use of pipeline transportation versus existing methods (e.g. barge, rail car and tanker truck). Major issues to be address include: Oxygen contamination in pipeline transportation, mixing ethanol from various sources (blending), SCC prevention strategies, pipeline integrity (environment, repair, safety), and prioritization and methods of inspection for ethanol SCC.

Conclusions

Based on the experience and studies cited herein, it has been shown that ethanol SCC is a newly recognized corrosion phenomenon that has been around since at least the early 1990's. It has affected tanks and piping downstream of the point of manufacture until the ethanol is blended into conventional E10 grades of gasoline. New questions are being posed around changes from conventional distribution methods in the U.S. from barge, tanker truck and rail car delivery to pipelines that will be required for higher market demands in the future. Research is being conducted through several organizations on mechanisms of ethanol SCC and factors that can be used to control it. Practical guidelines for the inspection, repair and mitigation of ethanol SCC are also being developed.

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