Stress Corrosion Cracking of Carbon Steel in Fuel-Grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing

API TECHNICAL REPORT 939-D
SECOND EDITION, MAY 2007

ADDENDUM 1, OCTOBER 2013

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Stress Corrosion Cracking of Carbon Steel in Fuel-Grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing

Downstream Segment

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SECOND EDITION, MAY 2007

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Foreword

Stress corrosion cracking (SCC) of steel in contact with fuel ethanol has been observed, for the most part, in user terminals, specifically storage tanks and loading/unloading racks prior to blending fuel ethanol with gasoline to produce gasoline grade E10. SCC has not been observed in storage tanks used by ethanol producers or in equipment after blending ethanol with fuel. These observations prompted API and the Renewable Fuels Association (RFA) to fund a multi-year research effort to examine the factors that could lead to SCC of steel in fuel ethanol and to gain greater understanding of the extent of SCC in field equipment. The original research program was conducted concurrently by Southwest Research Institute® (SwRI®), CC Technologies, Honeywell Process Systems and iCorrosion LLC. Separate reports of the results from these studies were provided in Parts I - IV of API Technical Report 939-D 2nd Edition, dated May 2007.

Since that time further API-funded fuel ethanol research, field surveying and other activities have continued by the aforementioned organizations and the results of these tasks are found in Parts V - VIII of this addendum to the API Technical Report 939-D. It includes new findings that corroborate many of the conclusions found in the previous 939-D report. These new findings also provide new insights into other possible locations for SCC failures in field operations handling ethanol including ethanol-carrying pipelines and the SCC potential of exposure to other ethanol-gasoline blends with ethanol contents greater than E10 up to E85. Other factors examined are the influence of ethanol sources, the impact of post weld heat treatment, use of potential and dissolved oxygen monitoring for identification of conditions likely to support SCC, and the effects of deaeration and inhibitors specifically designed to reduce susceptibility to SCC.

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Executive Summary

The effect of various impurities in fuel ethanol on stress corrosion cracking of steel was studied with the goals of: (i) determining if the existing fuel ethanol specification needs to be modified to mitigate SCC, (ii) recommending modifications in operating practice to mitigate SCC, and (iii) identifying monitoring methods and quality control practices. The current ASTM D4806 fuel ethanol specification places maximum limits on the concentration of water (1 volume percent), total acidity expressed as acetic acid (56 mg/l), chloride (32 mg/l—in 2009 decreased to 8 mg/l), methanol (0.5 volume percent), and denaturant (4.76 volume percent), and specifies a range for pHe (6.5 to 9.0). The study, funded jointly by API and Renewable Fuels Association (RFA), found that:

— SCC of steel can occur in fuel ethanol meeting the ASTM D4806 specification.

— Within the specification limits, none of the constituents in ethanol appear to have an adverse effect on SCC. Acetic acid and pHe over a wide range have no effect on SCC susceptibility. Chloride and methanol appear to increase SCC susceptibility, but are not essential for SCC. Water within the range of water contents studied does not affect SCC susceptibility of steel. However, complete removal of water was not attempted, therefore, it can only be speculated that completely anhydrous ethanol would not cause SCC. The inhibitor Octel DCI-11 lowers the corrosion rate of steel in ethanol, but has no effect on SCC. Therefore, narrowing the current fuel ethanol specification does not appear to be a viable solution to mitigate SCC.

— In addition to water, which was present in all the samples studied, the most statistically important factor that caused SCC in fuel ethanol appears to be dissolved oxygen. When dissolved oxygen was minimized through nitrogen purging, no SCC occurred in the presence of all other species at their maximum levels. When oxygen, in the proportion present in ambient air, was purged into ethanol, SCC occurred in the absence of all other species. Thus, SCC of steel in fuel ethanol can be mitigated by strictly limiting access to oxygen.

— Galvanic contact with pre-corroded steel appeared to exacerbate SCC. However, the present study indicated that galvanic coupling to rusted steel is not essential in causing SCC.

— SCC can be either intergranular or transgranular. SCC appeared to be intergranular in low-chloride ethanol (both laboratory and field samples), whereas in high chloride or methanol-containing ethanol it was transgranular.

— These observations may signify that a narrow range of potential is necessary for SCC to occur. The steel exposed to the user ethanol with access to air attained corrosion potential within the SCC-prone regime. On the other hand, in the one sample of producer ethanol from RFA, the steel exhibited a much higher corrosion potential that may have placed it outside the cracking potential regime. Since only one sample each of producer and user ethanol was studied, the variability in the corrosion potential of steel in ethanol obtained from the field cannot be quantified at this time. Further testing is needed to validate these conclusions.

— Corrosion potential is a simple method to monitor the potential for SCC of steel exposed to ethanol. In all cases where SCC was observed, the corrosion potential was above about 0V with respect to Ag/AgCl EtOH reference electrode. When the potential was below this value, no SCC occurred regardless of the concentrations of various species in ethanol. Statistical analysis indicated that oxygen was the most significant factor that increased the corrosion potential. The rust present on iron also increased the corrosion potential, but at a statistically lower significance level. Presence of methanol increased the corrosion potential, whereas acetic acid and chloride decreased the corrosion potential. But these effects were at a statistically lower significance level than that of oxygen.

— The cyclic potentiodynamic polarization curve may be another indicator of the susceptibility of steel to SCC in a particular ethanol. In SCC-prone environments, significant hysteresis was observed. However, further tests are needed before this can be used as a quality control tool.

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Recommendations

1) The effect of certain impurity levels beyond those specified in ASTM D4806 needs to be examined. It is well known that a small concentration of water is sufficient to prevent SCC in anhydrous ammonia. Although the present study found that water up to 1 volume percent had no influence on SCC in ethanol, it is not known whether additional water would mitigate SCC. Further investigation of the effect of water beyond the ASTM limit on SCC should be undertaken, provided such water additions are acceptable commercially.

2) A method to monitor the dissolved oxygen level in ethanol should be developed and tested in the field. Corrosion potential can be used as a measure of oxygen content, assuming no other oxidants are present in the ethanol. The Ag/AgCl/EtOH reference electrode is quite suitable for measuring the corrosion potential, but needs to be ruggedized for field use.

3) Additional samples of user and producer ethanol should be acquired and the variability in the corrosion potential of steel in these ethanol samples should be measured. Furthermore, the cyclic potentiodynamic polarization behavior of steel in these ethanol samples should be determined.

4) Since slightly anodic potentials and rust appears to exacerbate SCC, mitigation methods may include grit blasting steel surfaces on new tanks prior to filling with ethanol, minimizing exposure of steel to air/moisture, or cathodic protection using sacrificial anodes/coatings. Impressed current systems will not be effective because of the low conductivity of ethanol. The galvanic protection of steel bottoms needs to be demonstrated through laboratory tests.

5) Although the study of the effect of stress level on SCC was not a goal of this project, it is well known that a threshold stress or stress intensity factor exists for SCC of steel. Fracture mechanics type testing (using variable loading to simulate loading/unloading of tanks) may help establish threshold stress intensity factor and crack growth parameters for evaluating the risk of tank failure. Slow strain rate tests provide rapid means to determine SCC, but do not provide the appropriate parameters for estimating risk of SCC from known defects.

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Part I

Literature Review and Phase I Experience Survey

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Part I

Stress Corrosion Cracking of Carbon Steel in Fuel-Grade Ethanol: Review and Survey (Phase I)

I.1 Executive Summary

An extensive survey of published literature, service experience and previously unpublished studies on stress corrosion cracking (SCC) of carbon steel in fuel-grade ethanol and related topics was conducted by Honeywell Process Systems (Houston, Texas) for The American Petroleum Institute and a consortium which also includes the Renewable Fuels Association.

The present study was the first part of a multi-part plan to address the needs of industry regarding potential problems associated with SCC of carbon steel in fuel ethanol. The initial direction taken was that a white paper needed to be developed expeditiously to provide a concise and accurate review of the currently available information on SCC in fuel-grade ethanol, documentation of the experience from companies involved in fuel ethanol supply, mid-stream distribution and refinery use, and an initial assessment of the potential economic impact of this problem to the refining industry. The technical basis of the white paper originates from the information presented and identified at an API workshop on SCC in fuel-grade ethanol held on January 14 – 15, 2003. Members of the Renewable Fuels Association (RFA) and its staff also attended this meeting and provided insight into ethanol production, and became active members of the technical resource group guiding the planned future work. Since (as indicated above) the project period for the initial review and survey development was limited, the main portion of this effort involved an endeavor to gather the data identified and/or discussed in the January workshop and to search for and capture additional information from readily available sources as time allowed.

This study has found that experiences related to the use, handling and storage of fuel-grade ethanol and recent unpublished studies indicate real concerns regarding the phenomenon of SCC of steel tanks, vessels, piping and associated equipment in fuel ethanol service. It appears that this situation has already had an impact on commercial operations. Even though only limited references to SCC of steel in ethanol have been found in the published literature, documented failures of equipment in user's storage and transportation facilities have dated back to the early 1990s. The literature provides information on the influence of various parameters on ethanol corrosivity. The major factors identified from this survey include: water content, pHe, sulfate and chloride concentration, temperature, electrochemical potential, and use of inhibitors.

A review of the literature on SCC of steel in methanol and SCC of steel in other environments (e.g., caustic, carbonate-bicarbonate, amine, etc.) show that SCC in ethanol is likely to occur over a limited range of environmental conditions, possibly within the range given in the ASTM standard for fuel ethanol. Particular attention should be given to those conditions that are on the borderline between passivity and active (general) corrosion. Such conditions typically involve the development of small, local anodic sites on the metal surface that act as initiation sites for SCC under the influence of stress. The results of published and previously unpublished studies on ethanol corrosion and SCC have identified conditions that produce localize corrosion related to normal impurities and the use of inhibitors. These conditions appear to include some that may be within the range of the ASTM standard for fuel ethanol. Furthermore, there is preliminary data that also indicates that SCC may not be related to additions of denaturants and inhibitors to fuel-grade ethanol. SCC was observed in laboratory tests in an ethanol sample that, by analysis, was found not to contain such additives.

Metallurgical and mechanical factors were also identified that appear to relate to conditions that promote SCC in fuel-grade ethanol. These include increased susceptibility in the region of the base metal adjacent to the weld heat affected zone. In one regard, the increased susceptibility of this region in service appears related to locally high tensile residual stresses around non-post weld heat treated weldments. However, when specimens are machined from this region (despite some relieving of residual stresses in the process), the material in this near-weld region has been shown to have a higher susceptibility to cracking than the base metal remote from the weld. Therefore, microstructural effects may also be important. Mechanical factors that have been associated with promoting SCC in fuel-grade ethanol have been high mechanical loads, stress concentration and flexural loading (dynamic stressing/straining). This is consistent with several other mechanisms of SCC in steels. Laboratory methods that have successfully reproduced SCC in fuel-grade ethanol in steels have likely involved severe plastic straining as found in u-bend and slow strain rates tests.

Through 2003, approximately a dozen failures produced by SCC of carbon steel in fuel-grade ethanol were identified, with several more possible but unconfirmed cases. These included plate steels and roof springs used in aboveground storage tanks, along with associated piping. Cracks produced by SCC are tight and oxide filled, making them hard to identify by visual examination and conventional magnetic particle testing. Wet fluorescent magnetic particle testing appears to have the sensitivity to find these cracks.

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Remedial actions have included weld repairs, and replacement and use of internal tank coatings/linings on the bottom, lower sides, roof areas, and fixtures. Coatings used in this service must have chemical resistance to fuel-grade ethanol.

A gap analysis was conducted that identified items that need to be addressed to better minimize service problems associated with SCC in fuel-grade ethanol. These gaps include the need for better definition of the environmental variables that promote and/or control SCC in fuel-grade ethanol, and the role of metallurgical and mechanical variables, which have not been quantitatively addressed. There is also a need to study whether it is possible to have SCC in fuel-grade ethanol that meets the current industry standards. Additionally, the relationship between laboratory tests (u-bends and slow strain rate tests) and service experience has not been well established.

I.2 Introduction

I.2.1 SCOPE

The API Refining Subcommittee on Corrosion and Materials (SCCM) contracted the development of this white paper document on SCC in fuel-grade ethanol to Honeywell Process Systems. A broad cross-section of companies have a high interest in this problem and have actively participated in this effort to review and survey the industry experience. This group includes users, ethanol producers, research organizations and API and RFA representatives. This was the first part of a multi-part plan to address the needs of the industry regarding this SCC problem. The initial focus was that the white paper needed to be developed expeditiously to provide a concise and accurate review of the currently available information on SCC in fuel-grade ethanol, documentation of the experience from companies involved in fuel ethanol supply, mid-stream distribution and refinery use, and an initial assessment of the potential economic impact of this problem to the refining industry.

The SCCM plan was for the white paper to precede an effort involving detailed individual interviews to supplement the survey data, and applied research and testing to specifically investigate SCC in fuel-grade ethanol as it applies to refinery operations. This proposal covers only the white paper development phase of the API sponsored effort. However, it does try to identify gaps in information and technology that might be addressed in the subsequent work.

I.2.2 TECHNICAL BASIS

The technical basis of the white paper originates from the information presented and identified at the workshop held on January 14 – 15, 2003. This meeting was well attended by representatives from a broad cross-section of companies that have a high interest in this problem. Based on the API request for proposal (dated January 30, 2003), it was of utmost importance to develop this white paper in a short time frame so that subsequent actions could be more completely formulated and activities initiated quickly to meet the industry need for this information.

I.2.3 TECHNICAL APPROACH

Since (as indicated above) the project period for the proposed white paper development was limited, the main portion of this effort involved an endeavor to gather the data identified and/or discussed in the API workshop on SCC in fuel-grade ethanol (January 2003) and to search and capture additional information from readily available sources as time allowed. Sources of additional information were obtained through literature search (see Appendix I.A for a listing of literature obtained that was not cited in the reference section of this report), computer database surveys and an email canvass of technical contacts in the refining industry, ethanol production and distribution, and chemical processing. This information was analyzed for specific trends and important relationships needed to better understand the operational hazards and risks in the storage and handling of fuel ethanols. The specific intent of this work was to produce an analysis of the existing experience on corrosion in ethanol and alcohols, and SCC to serve as an improved technical basis for operational guidelines as well as a guide for future studies in this area.

I.3 Background

I.3.1 ETHANOL—DESCRIPTION OF MANUFACTURE, DISTRIBUTION, STORAGE AND USE

I.3.1.1 Description

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 grape and apple. While grain and synthetic alcohols are technically the same (the molecule is identical), there are differences in the amounts of contaminants (sec-butanol, acetone and methanol) in each. High resolution gas chromatography (HRGC) can detect the differences by looking at the contaminants in the ppm range. Fuel ethanol is not sold with zero water con-

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tent, ethanol with no water content is referred to as "anhydrous ethanol." Denatured alcohol typically contains up to 1% water and other constituents. Denatured ethanol with less than 0.5% water content is considered "anhydrous ethanol." Ethanol with higher water content is usually referred to as "hydrated ethanol." Such hydrated ethanol is uncommon in the United States but is used widely in fuel in Brazil.

I.3.1.2 Standards

There are several standards that govern the properties, analyses, and use of fuel-grade alcohol and ethanol-containing fuels. These include the following standards available through ASTM:

a. D 4814 *A Standard Specification for Automotive Spark Ignition Engine Fuel*

b. D 4806 *Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel*

c. D 5798 *Standard Specification for Fuel Ethanol (Ed75 – Ed85) for Automotive Spark-Ignition Engines*

d. D 6423 *Standard Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75 – Ed85)*

A recommended practice for fuel ethanol is available through the RFA, titled *Fuel Ethanol—Industry Guidelines, Specifications and Procedures*—RFA Publication #960501. This document provides a basis for understanding the process of ethanol production, and the compositional analysis and variability of the final product. This document references many of the ASTM standards given above, as well as other standards that may be more restrictive than ASTM.

I.3.1.3 Manufacture

Modern production of ethanol from starch or sugar-based feedstocks is similar to processes that have been used for centuries. However, the process has been considerably refined in recent years. There are two production processes: wet milling and dry milling. The main difference between the two is in the initial treatment of the grain.

In the dry milling process, the entire corn kernel or other starchy grain is first ground into flour (meal) and processed without separating out the various component parts of the grain. The meal is slurried with water to form a "mash" and enzymes are added to convert the starch to simple sugar. Ammonia or another nitrogen source is added as a nutrient to the yeast and may be used for pH control. The mash is cooked, cooled and transferred to fermenters where yeast is added and the conversion of sugar to ethanol and carbon dioxide (CO_2) begins. After fermentation, the resulting mixture is transferred to distillation columns where the ethanol is separated. The ethanol is concentrated to 190 proof using conventional distillation and then is dehydrated to approximately 200 proof in a molecular sieve system. The anhydrous ethanol is then blended with up to 5% denaturant to render it undrinkable prior to shipment. It is then ready for shipment to gasoline terminals. However, for foreign shipments, it may not be necessary to add denaturants until it enters the United States.

In the wet milling process, the grain is soaked in water with dilute sulfurous acid. This steeping facilitates the separation of the grain into its many component parts. The corn slurry is then processed through a series of grinders to separate the corn germ. The remaining fiber, gluten and starch components are further segregated using a centrifugal screen and separators. The steeping liquor is then concentrated in an evaporator. This concentrated product is co-dried with the fiber component and is then sold for other uses. The starch and any remaining water from the mash can then be fermented into ethanol. The fermentation process for ethanol is very similar to the dry mill process previously described.

The final product is governed by ASTM D 4806, which gives the compositional and physical limits for fuel ethanol. These are shown in Table I.1.

A parameter that is used in evaluation of ethanolic environments is the pHe as defined by ASTM D 6423. The pHe value is a measure of the acid strength of high ethanol content fuels. These include ethanol, denatured fuel ethanol, and fuel ethanol. It is applicable to fuels containing nominally 70 volume percent ethanol, or higher. pHe is similar to the pH parameter used in aqueous solutions. However, it is important to realize that neutral in aqueous solutions is at a pH value of 7. In ethanolic solutions, neutrality is near a pHe value of 9. Therefore, the pHe value for alcohol solutions is not directly comparable to pH values of water solutions. Additionally, the value of pHe will depend to a certain degree on the fuel blend and other factors that are given in the ASTM standard.

In the United States, denaturants are added to fuel alcohol in accordance with the Bureau of Alcohol, Tobacco and Firearms (BATF). According to Federal Regulation Title 27 Parts 19, 20 and 21 (including *CFR* 19.1005, 27 *CFR* 21.124 and C.D.A. 20),

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Table I.1—Quality Specification for Fuel Ethanol Per ASTM D 4806

Property	Units	Specification	ASTM Designation
Ethanol	%v min	92.1	D 5501
Methanol	%v max	0.5	—
Solvent-washed Gum	mg/100 ml max	5.0	D 381
Water Content	%v max	1.0	E 203
Denaturant Content	%v min %v max	1.96 4.76	D 4806
Inorganic Chloride Content	ppm (mg/L) max	40 (32)	E 512
Copper Content	mg/kg max	0.1	D 1688
Acidity as Acetic Acid	%m (mg/L)	0.007 (56)	D 1613
pHe	—	6.5 – 9.0	D 6423
Appearance	Visibly free of suspended or precipitated contaminants (e.g., clear and bright).		

denaturant is to be added to alcohol in order to make it unfit for beverage or internal human medical use. These include the following listed substances:

a. kerosene;

b. deodorized kerosene;

c. rubber hydrocarbon solvent;

d. methyl isobutyl ketone;

e. mixed isomers of nitropropane;

f. heptane; or,

g. any combination of the above;

h. 1/8 ounce of denatonium benzoate N.F. (Bitrex) in 2 gallons of isopropyl alcohol.

ASTM D 4806 further restricts denaturants to include natural gasoline, gasoline components, or unleaded gasoline with an end boiling range less than 225°C. Additionally, it lists specifically prohibited denaturants that include:

- methanol that does not meet ASTM D 1152,
- pyrroles,
- turpentine,
- ketones,
- tars (high molecular weight pyrolysis products of fossil fuels or non-fossil vegetable matter).

Through an Internet search on the word “denaturant,” other references giving substances for denaturant use included natural gasoline, conventional unleaded gasoline, kerosene or raffinate. Raffinate is a product derived after extracting aromatics from refinery reformates, hydrogenated pyrolysis gasolines from ethylene plants, and by-product streams from paraxylene isomerization plants. It is a complex mixture of mostly C6–C9 saturated hydrocarbons with up to 5% aromatics and 4% olefinic compounds. Apparently, those that contain the latter compounds would not be acceptable for addition to fuel ethanol.

BATF CDA 20 also requires a minimum of 2 gallons of denaturant be added to every 100 gallons of ethanol. However, ASTM also specifies a minimum of 2 parts per 100 parts ethanol which allows up to 4.96% denaturant to be used in fuel ethanol. Some ethanol producers add close to the maximum allowable amount.

Regulators in California have been active since the late 1990s to further regulate fuel ethanol. These standards became effective December 31, 2003. These standards will place additional restrictions on denatured ethanol that will limit sulfur (10 ppm max.), benzene, olefins, and aromatics that are more restrictive than the ASTM standard.

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I.3.2 SIGNIFICANCE OF SCC PROBLEM

During the course of this study (March – September 2003), a review of the literature was conducted. While the published literature mentions susceptibility to stress corrosion cracking (SCC) in ethanolic environments, most of the literature focuses on the phenomena of general corrosion and localized corrosion (pitting) of steel in fuel ethanol, hydrated ethanol and ethanol/gasoline blends that contain water and certain levels of impurities. Only limited reference to SCC of carbon steel in ethanolic environments was identified in the published literature. There is extensive literature that shows that methanol can be a SCC agent for steel and it can be influenced by various impurities, temperature and metallurgical condition of the steel.

This study has also found that experiences in the refining industry related to the use, handling and storage of ethanol fuel and recent unpublished studies indicate real concerns regarding the phenomenon of SCC of steel tanks, vessels and piping in fuel ethanol service. It appears that this situation has already had an impact on commercial operations. Documented failures of ethanol process equipment have dated back to the early 1990s.

A workshop was held in January 14 – 15, 2003 in Richmond, California. This meeting brought together representatives from many business sectors to discuss service experiences, evaluate the results of recent engineering and research studies and discuss recommended mitigation practices. The initial findings of this workshop indicated that information was available from multiple sources on the various aspects of this problem. However, there was only limited understanding of the scope of the problem.

Furthermore, at this forum, there was no real consensus of the role of the various possible factors contributing to SCC in refinery equipment. One of the major inconsistencies identified in the workshop discussions was the apparent absence of experience with SCC of steel components in the ethanol manufacturing and transportation sectors, and a number of terminal facilities. It appears that this problem has been primarily observed in tanks, vessels and piping in refinery service where the denatured fuel alcohol is stored prior to being blended with gasoline. Another factor discussed was the multiple sources of fuel ethanol that may have contributed different chemical species in the form of water, inhibitors, denaturants and impurities (e.g., metals, inorganic salts, acids, and other organic species). This aspect is complicated since ethanol has been generally considered a “commodity” with minimum concern for batch-to-batch and source-to-source variations. The multiple sources of fuel ethanol also include various feedstocks from which the ethanol is derived. These include corn and other grains, grapes and grape by-products, sugar cane, sugar beets and other types of biomass. It also involves sources domestic to the United States, Canada and from international manufacturers. Other issues highlighted in this meeting as being of concern include operational practices such as filling and storage procedures, sparging (agitation) techniques, transportation and residence time.

I.3.3 POTENTIAL MAGNITUDE OF RISK TO ASSETS

The initial review by ethanol users has indicated that repair costs to individual tanks and service lines associated with the SCC are not inconsequential. Since some instances of SCC are not well documented and the specific causes are unknown, it is impossible to accurately assess the magnitude of the risk to assets. Nevertheless, ethanol has been stored in more than 3000 tanks throughout the country in the last twenty years without a reported case of SCC at a manufacturing site. Furthermore, users are adding hundreds of additional tanks for ethanol storage over the next several years. Due to the large number of current and future tanks dedicated to ethanol storage and the many pipelines and other storage facilities that are used in petroleum transport, the potential of repair associated with this or any issue affecting petroleum and ethanol storage cannot be dismissed.

I.4 Review of Published Literature

I.4.1 CORROSIVE ATTACK IN ORGANIC MEDIA

In general, most practitioners of corrosion engineering and science are much more familiar with the basic principals of corrosion processes in aqueous solutions than they are with non-aqueous media such as organic solvents. However, based on a review of the applicable literature, many of these principals are common. This section will present a discussion of important similarities and differences between aqueous and organic systems as applicable to understanding corrosion of metallic materials in ethanol.

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For the most part, the similarities between organic and aqueous media dominate. Figure I.1 shows the relationship between the electrode potentials of various materials in water and selected organic solvents, including methanol and ethanol [1]. While less data is available for ethanol, it appears that the trend is basically the same where the potential for the hydrogen electrode is similar for water, methanol and ethanol. For the most part, the behavior of the common metals Cu, Pb, Ti, Cd, Zn and Al are similar among these systems, and for methanol in particular. It is primarily in the region of Hg and Ag, which have a very high electrode potential in water, where a significant reduction of the electrode potential is observed. Water, methanol and ethanol are all protic media capable of sustaining electron transfer and ionization of the hydrogen atom. In most cases, corrosion processes and galvanic interactions would be expected to be thermodynamically similar in water, methanol and ethanol with the following electrode potential ordering maintained: $E^o_{Zn} < E^o_{Fe} < E^o_{Ni} < E^o_{Cu}$.

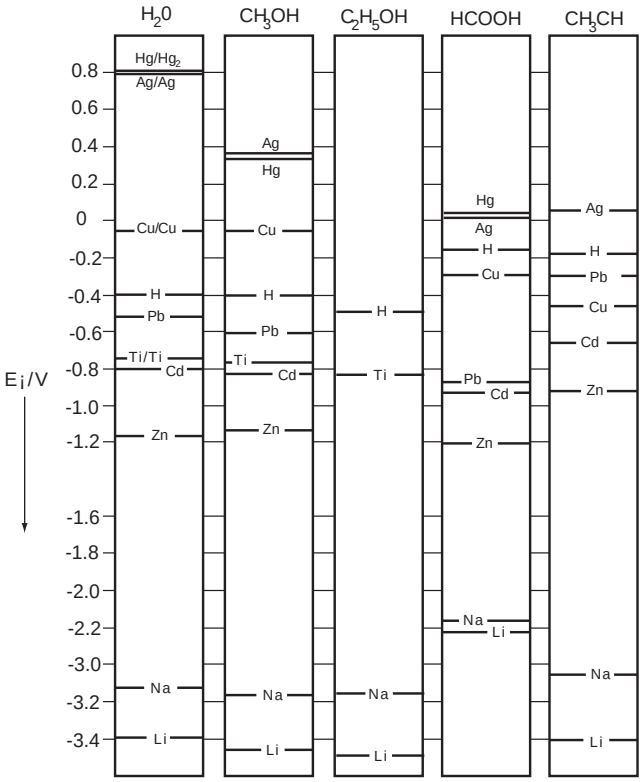


Figure I.1—Comparison of Electrode Potentials of Metals in Different Solvents: Including Water, Methanol and Ethanol

There are also differences in the physical properties of water, methanol, ethanol and other organic solvents that may contribute to differences in corrosion behavior. Table I.2 shows a comparison of these properties [1].

Ethanolic solutions have lower conductivity than either methanol or water and higher pH values at neutrality. The later point is extremely important in judging the acidity of ethanolic environments. Whereas pH 7 is considered neutral for aqueous solutions, pH 9.55 is the neutral point for ethanol. Therefore, environments that have a pH of 6 in aqueous solutions may be considered only mildly acidic, whereas in ethanol pH 6 represents a solution of significantly higher acidity (as defined by the magnitude of depression from the neutral pH value). Oxygen solubility is also a major departure point as well. Oxygen solubility values in methanol and ethanol are similar; however, they are both an order of magnitude higher than that of water. Therefore, the availability of oxygen for participation in the corrosion reaction is expected to be generally greater in ethanol and its solutions as well.

Table I.2—Physical Properties of Selected Environment

Environment	Dielectric Constant @ 25°C	pH Value at Neutralization	Oxygen Solubility –cm^3 @1 atm/25°C	Specific Conductibity $Ohm^{-1}cm^{-1}$
Water	78.5	7.00	0.0227	5.6×10^{-1}
Methanol	32.6	8.35	0.227	1.6×10^{-1}
Ethanol	24.3	9.55	0.221	4.3×10^{-2}
Formic Acid	48.0	3.1	0.047	2.8×10^{-2}
Acetic Acid	6.4	7.7	~0.18	2.8×10^{-3}

Another important aspect of ethanol with potential relevance to its corrosivity is its hygroscopic nature relative to other fuels (see Table I.3). It shows a large increase in water content of ethanol, as measured by the Karl Fischer method [2], after a thirty day exposure to a humid environment. This increase in ethanol is much greater than that observed for either gasoline or E10 (gasohol). Additional information discussed later in this report indicates that water pick-up can occur even in a controlled laboratory environment. Therefore, open exposure to the atmosphere during transportation or storage tends to increase water content and likely impacts corrosion reactions.

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Table I.3—Hygroscopic Tendencies of Selected Fuels and Constituents

Fuel Type	Before Exposure (Vol%)	After 30 days @ 20°C and 100% Relative Humidity (Vol%)
Gasoline	0.02	0.10
Gasohol(E10)	0.03	0.72
Fuel Ethanol	0.21	51.75

For the specific concerns of this study (the corrosion behavior of steel), the comparison of the electrode potential of iron in water, methanol and ethanol with ionic impurities is perhaps the most useful. This reveals that the electrode potentials for iron decrease in the following order: E^o H_20 > E^o methanol > E^o ethanol [1]. This generally indicates that the oxidizing power of the medium is decreasing in the same order. Therefore, it is expected that on first glance, the corrosivity would also decrease in the same order, thus making ethanolic solutions potentially less corrosive than either those of methanol or water. But, corrosion studies conducted in many alcohol containing environments show that the relationship is a little more complex. Figure I.2 shows corrosivity of zinc, iron and nickel in water and in alcohols versus their chain length (for $C_1 – C_8$) [1]. The relationship displayed indicates that there is an increase in aggressivity going from water to methanol (C_1), which then decreases with increasing carbon number. This relationship leaves ethanol with approximately the same general corrosivity as water. The reason for the increase in corrosivity going from water to methanol is generally considered to be the effect of the increased oxygen solubility in methanol. Since it has been shown that the oxygen solubility of methanol and ethanol is similar (both higher than that of water), the decrease in corrosion rate from $C_1 – C_8$ is likely to be the result of the increased chain length and, in turn, its impact on molecular or ionic mobility in the media.

I.4.2 CORROSION AND SCC IN ETHANOLIC ENVIRONMENTS

A major finding of this study was that there was very limited documented data on SCC of ethanol of steel obtained from the published literature through September 2003 [3, 4]. The first of the two references cited indicate that SCC of steel may be possible in ethanolic solutions as evidenced by examination of surface features of slow strain rate (SSR) test specimens exposed to ethanol with additions of LiCl and H_2SO_4. The cracking in ethanol appeared qualitatively to be less severe than found for methanol but ductility loss data (elongation or reduction in area versus air properties) were not presented.The cracking of steel in methanolic and ethanolic environments was compared to SCC of steel in liquid ammonia where susceptibility can be affected by minor impurities of water. The second reference describes the SSR testing of steel in ethanolic solutions with formic and acetic acids, and water at 60°C. Additions of 0.10% – 25% formic and 0.10% water in ethanol did not produce SCC. However, steel bend specimens produced SCC in a solution of 0.01% acetic acid and 0.10% water that was less severe than found in methanolic solutions. Cracking was less than 0.01 mm in depth.

Despite the limited data on SCC of steel in ethanolic solutions, there was, in fact, substantial information found on the general and pitting corrosion behavior of steel in ethanol and ethanolic solutions that were relevant to the present concerns for corrosion of steel tanks and piping in fuel ethanol. Since SCC of steel likely involves corrosion to a certain degree and, in particular, the initiation of local anodic sites, it was felt that this review should attempt to characterize corrosion in ethanolic solutions.

In overview, the literature is consistent in the representation that ethanol solutions are generally less aggressive than those of methanol. However, perhaps more importantly, it also teaches that ethanol containing certain impurities can produce corrosion of carbon steel and other materials. Furthermore, these impurities can quite commonly promote tendencies toward localized corrosion. The particular situation noted from the published literature was that the trend for steel is for passive or very low corrosion rate (pseudo-passive) conditions to exist in very mild environments (e.g., pure ethanol). With increasing aggressivity of the environment, there is an initiation of local anodic attack, followed by general corrosion at still higher levels of solution aggressivity.

There has been extensive literature on corrosion of materials commonly found in automobile fuel systems exposed to ethanolic environments such as fuel ethanol and alcohol/gasoline blends with certain levels of naturally occurring impurities. While this work is not specifically aimed at the storage, distribution and handling of fuel ethanol in steel equipment and piping, it does provide a meaningful basis for understanding the potential for corrosion (and its nature) in these systems.

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I.4.2.1 Influence of Water

The corrosion rate and final corrosion potential of aluminum, steel, and copper alloy in ethanol/water solutions covering the complete range from 100% water to 100% ethanol are provided in Figure I.3 [5]. Figure I.3 depicts the average corrosion rate for 15 days (Curves 1, 2, and 3) and the final corrosion potential (Curves 1´, 2´, and 3´) vs. water content of ethyl alcohol. Figure I.4 depicts the influence of concentration of inhibitors, with Plot A showing the effect of inhibitor G-2 on the corrosion rate of aluminum alloy in relation to water content of alcohol, and Plot B showing the effect of inhibitor G-4 on corrosion rate and potential of aluminum alloy in pure alcohol. Admittedly, this does not focus specifically on the typical water contents in fuel ethanol (0.1% – 1%), however, it does show that the expected corrosion rates in pure ethanol and pure water are similar, as mentioned previously herein. It also indicates that maximum corrosivity in this system is reached in the range of about a 50:50 blend of water and ethanol. However, the final potential of steel following prolonged exposure in pure water tends to be much more electronegative than that in ethanol (–400 mV compared to 90 mV, respectively versus E_{H2}).

The polarization behavior of aluminum in water/ethanol solutions (shown in Figure I.5) without intentionally added impurities shows substantial regions of passivity particularly in the region between 0% – 75% ethanol [5]. The extent of the passive region and the passive current show complex variations over this range. For pure water, the corrosion potential of steel is marginally within the lower portion of the passive region. For 75% ethanol and 25% water, the corrosion potential is in the passive to active transition range. This is one region in other metal-environment systems where localized corrosion and SCC have been shown to occur.

The electrochemical behavior of iron in methanol and ethanol was reported as a function of water content (at 25°C) and 0.1M $LiClO_4$ used to increase solution conductivity and will also increase the oxidizing nature of the solution. Of particular interest is the influence of additions in the lower range from 0% – 2% water (see Figures I.6 and I.7) [6].

This study indicated that in anhydrous methanol, the passive region for steel was essentially non-existent. With the addition of 0.5% water, the polarization curve was unchanged except for a shift in the electronegative (more active) direction and an increase in current density. The addition of 1% water, however, resulted in formation of a broad passive region extending from the open circuit corrosion potential (approximately –600 mV SCE) and +800 mV SCE. Further addition of water to 2% left the passivity more or less unchanged except for slightly increased passive current densities. Similar evaluation of iron in ethanolic solutions over the same range of water content show a large passive region in the anhydrous ethanol ranging from the open circuit potential

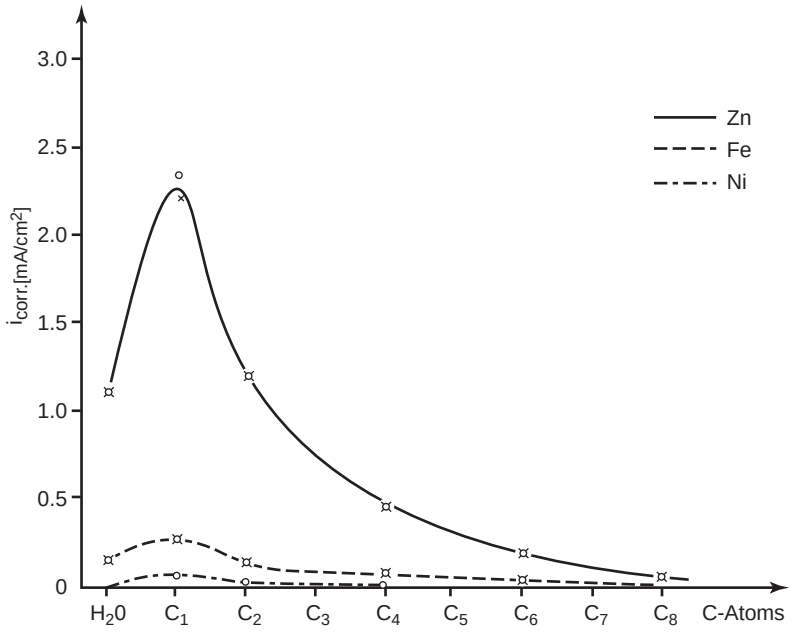


Figure I.2—Corrosion Rate (i_{corr}) of Zinc, Iron and Nickel in Primary Alcohols Plotted Versus Carbon Number of Solvent: Methanol (C =1); Ethanol (C = 2)

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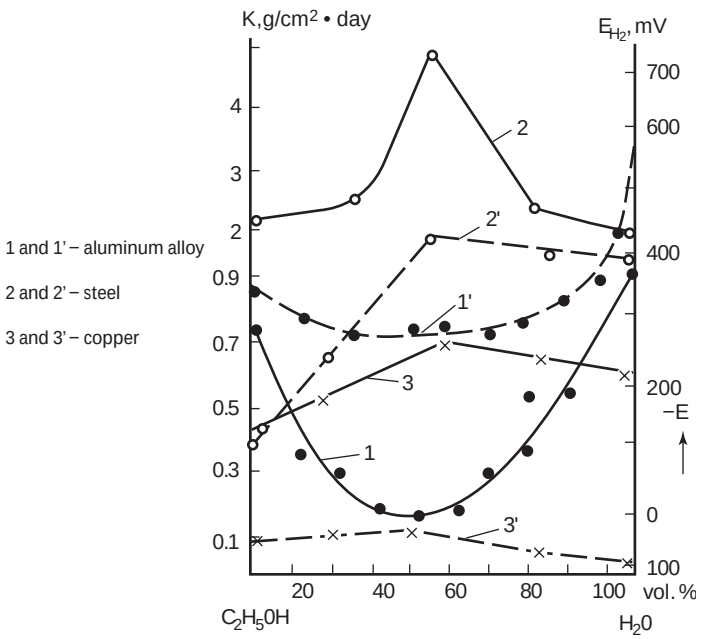


Figure I.3—The Corrosion Rate (K, Cor) and Final Corrosion Potential (E_{H2}, γ_{H2}) of Steel in Ethanol/Water Solutions

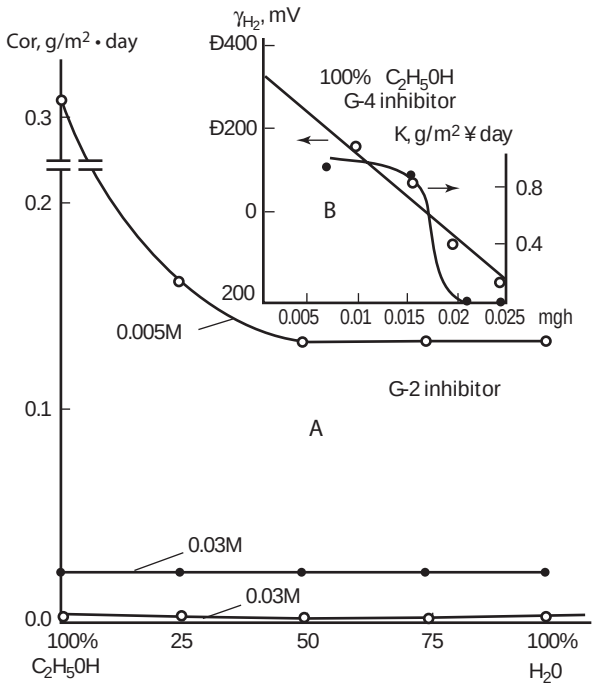


Figure 1.4—Influence of Concentration of Inhibitors

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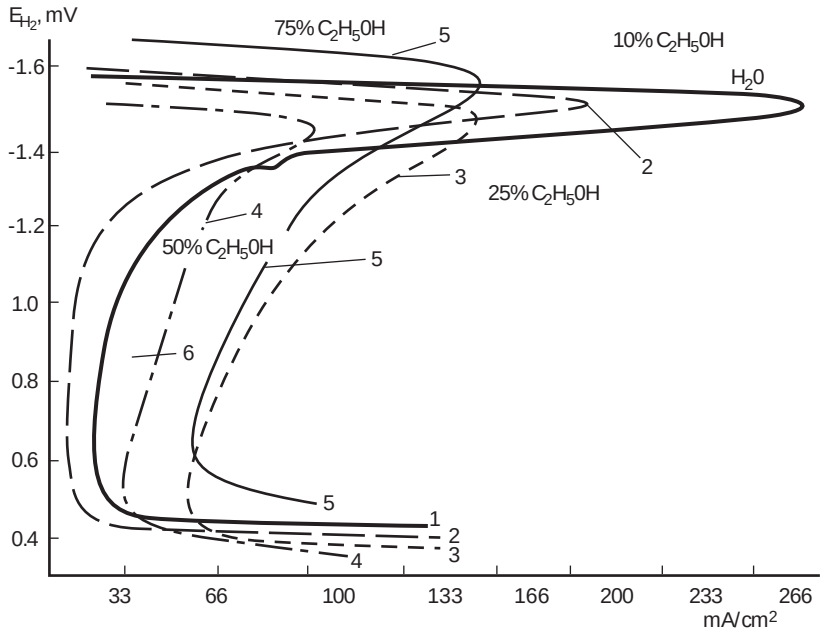


Figure I.5—The Polarization Behavior of Aluminum Alloy in Water/Ethanol Solution

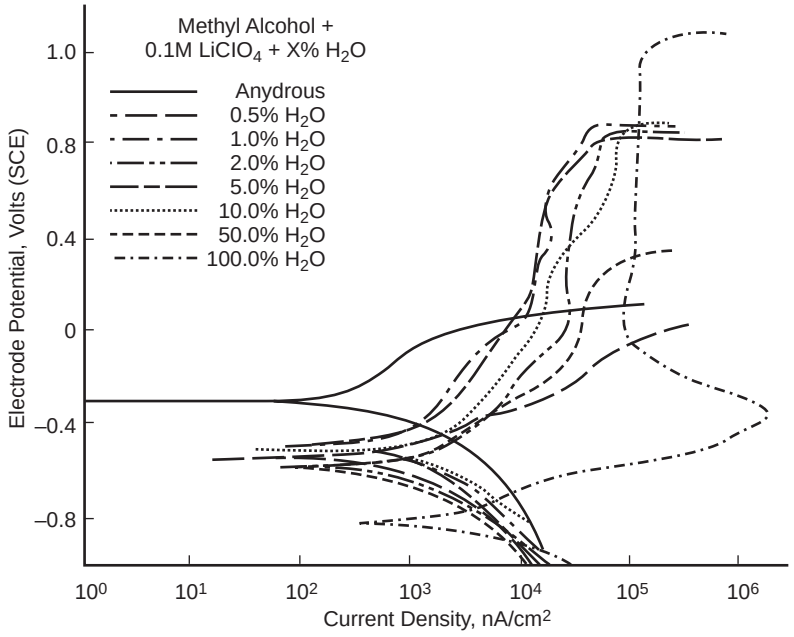


Figure I.6—Polarization Behavior of Steel in Methanolic Solutions

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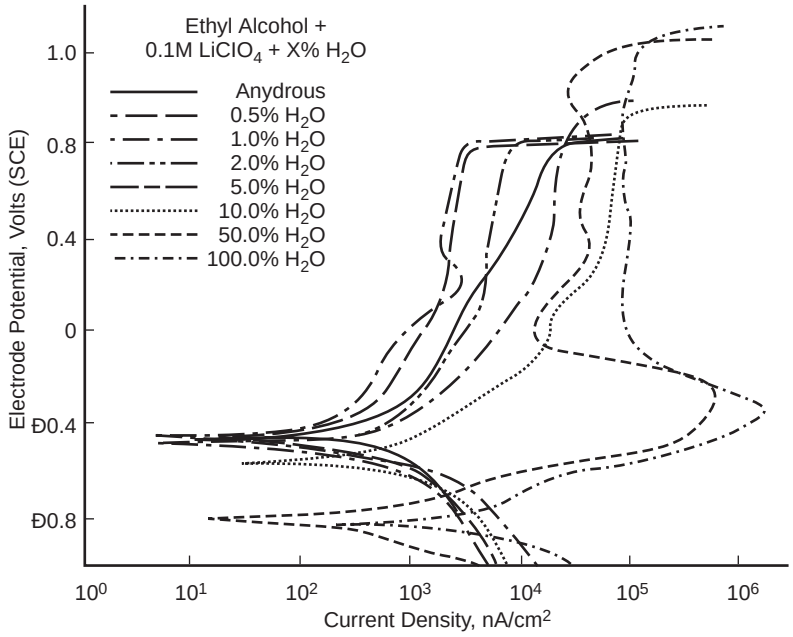


Figure I.7—Polarization Behavior of Steel in Ethanolic Solutions

(approximately 400 mV SCE) up to about 800 mV SCE. The addition of 0.5% water maintained the same passive region as for the anhydrous ethanol except that the passive current densities were reduced and with a further reduction with the addition of 1% water to ethanol. Starting at 2%, higher levels of water in ethanol show a return to increasing passive current densities and movement of the open circuit corrosion potential to more electronegative (active) potentials.

Examination of the polarization curves for steel in methanolic solutions (see Figures I.6 and I.7) indicate the conditions likely to produce localized corrosion and/or SCC as well as the ranges of potential where these phenomena might occur. In Figure I.6 it shows that pure (anhydrous) methanol exhibits only active behavior in the anodic region of its polarization curve for steel. This condition is not likely to promote local anodic corrosion processes as would be the case if active-passive behavior would be observed in the anodic portion of the polarization curve. At 0.5% water, only a very small inflection in the active curve can be found. However, between 1% and 10% water in methanol, active passive behavior is observed as indicated by the near vertical portion of the E-log I plot and the abrupt break to the horizontal transpassive region at about 800 mV SCE. A well developed active-passive behavior can be seen in the polarization curve conducted in water. Local anodic behavior is commonly exhibited when the potential is in the active-passive transition or transpassive portions of the anodic polarization curve.

By comparison, the polarization curves for steel in ethanol-water (see Figure I.7) show active behavior in the anodic region which almost approximates a passive condition, but still shows increases in current with increasing applied potential. Increasing concentrations of 0.5% – 1% water reduce the current in the “passive” region with a near vertical segment (passive) followed by a transpassive horizontal portion of the curve. It also produces an additional undulation in this region at about 200 mV SCE in the polarization curve for the 1% water condition. Increasing the water content yields substantial increases in the passive current and decreases the slope of the E-log vs. I plot. Higher percentages of water in ethanol in the range of 50% – 100% support the development of full active-passive behavior. Based on the review of the polarization curves for steel in ethanol with between 0.5% and 1% water, it appears that the most likely region for localized pitting or SCC attack would be under oxidizing conditions in a potential range of between 200 and 800 mV SCE.

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In a Brazilian study involving additions of a 20% HCl solution to ethanol, the corrosion rate and morphology were found to change according to Table I.4 [8, 9].This data indicates the change in corrosion rate from high to low to high and corrosion morphology from uniform to pitting back to uniform over the range of 1% – 80% water content. This illustrates the complex relationship of acidic water in ethanol. At low concentrations, it leads to a dramatic reduction in the general corrosion and the onset of pitting at around 4% water in ethanol. However, the trend is reversed with supplementary additions of acidic water.

Table I.4—Impact of Additions of 20% HCl to Ethanol on Corrosion Rate

Water (%)	Duration (hrs)	Corrosion Rate (mmpy)	Corrosion Morphology
0	44	4.5	Uniform
1	300	2.5	Uniform
4	300	0.53	Pitting
6	300	0.01	Slight Pitting
32	140	0.01	Uniform
64	140	2.5	Uniform
80	140	2.8	Uniform

The generally observed corrosion products of iron or steel in ethanol/water solutions have been investigated. In anhydrous ethanol, they have been found to be primarily α FeO (OH) and some γ Fe_2O_3 [7]. In 80% ethanol/20% water solutions, the corrosion products were largely γ Fe_2O_3 and γ Fe_3O_4.

I.4.2.2 Influence of Impurities and Inhibitors

Studies have looked at the influence of common impurities found in fuel ethanol and fuel ethanol/gasoline blends on corrosion behavior of steel. Most of these studies were focused on the impact of these effects on fuel system components such as carburetors, fuel injection and combustion systems. One of the types of impurities identified in alcohol fuels are organic acids [2]. Formic acid is an impurity and combustion byproduct of methanol. Similarly, acetic acid is an impurity and combustion byproduct of ethanol. The presence of acetic acid in ethanol tends to increase the general aggressivity of the ethanol with respect to corrosion of steel and other materials. Other acid components found in ethanols made from biomass (grain, corn, sugar, grapes, etc.) include sulfuric acid. Sulfur dioxide is used resulting in the formation of sulfuric acid which is commonly used in the wet milling process prior to fermentation and may contribute low (ppm) level impurities to the final product [10]. This acidity would tend to increase the total acidity and possibly lead to the occurrence of additional corrosion reactions. In studies with stainless steels, the addition of sulfuric acid to ethanol resulted in an increase in corrosion potential with time, which tended to reinforce the passivity of the stainless steel in the environment [11 – 13].

It appears that impurities in the system increase corrosion of ethanol solutions containing low levels of water contamination. There is also evidence that impurities can impose a change in corrosion morphology to that of localized pitting corrosion. Additionally, in studies of AISI 1005 steel exposed to 94% ethanol with 6 volume percent water in combination with 50 mg/L acetic acid, 3 mg/L NaCl, 2.5 mg/L H_2SO_4 and 2.5 mg/L Na_2SO_4 with an ethanolamine inhibitor indicated that the rate of corrosion was reduced but the nature of the corrosion changed markedly to localized corrosion. This pitting was specifically mentioned as an effect that limited the use of the electrochemical impedance technique for evaluation of this system [14].

Studies were conducted on the corrosion in Brazilian fuel-grade ethanol with the impurity levels shown in Table I.5 [8].

Corrosion rates and pitting tendencies were measured in both this material as well as pure ethanol. The results are shown in Table I.6. This table indicates that the corrosion rates in fuel ethanol are generally greater than those found in pure ethanol. Additionally, the corrosion is more likely to be localized in nature. However, in all cases, the corrosion rates were low being up to 1.9 mpy in pits and only 0.006 mpy – 0.36 mpy when generalized.

Table I.5—Characteristics of Brazilian Ethanol Fuel (AEHC)

Characteristics	Result
Specific Gravity at 20°C	0.8093 ± 0.0017
Alcohol (%)	93.6 ± 0.6
Total Acid (mg/100 ml), max.	3.0
Aldehyde (mg/100 ml), max.	6.0
Esters (mg/100 ml), max.	8.0
Higher alcohols (mg/100 ml), max.	6.0

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There is also information in the published literature from another Brazilian study [15] that indicates that the corrosion of steel in fuel ethanol varies with the concentration of water and various impurities that may be inherent to certain ethanol producing processes. A parametric study was performed on hydrated ethanol in support to its automotive uses as fuel. The variables investigated included the following:

a. water content,

b. sulfate concentration,

c. chloride concentration,

d. pH.

Table I.6—Corrosion in Brazilian Fuel Ethanol

	Fuel Ethanol		Ethanol	
Test	Morphology	Corrosion	Morphology	Corrosion
1	Pitting	Density—35 pits/in.^{2} Rate—1.9 mpy	General	0.006 mpy
2	General	Rate—0.36 mpy	General	0.009 mpy
3	Pitting	Rate—0.09 mpy		

The focus of the study was the influence of these variables on the corrosion of mild steel. The test conducted involved ninety days of immersion exposure. The greatest effect noted was the influence of pH on increasing corrosion. Interactions were also identified between the parameters such as water content in the alcohol, sulfate concentration and chloride ion concentration. A summary of the results of this study are provided in Table I.7.

The results in Table I.7 were sorted in descending order based on the extent of mass loss corrosion during the exposure. Most notable is the influence of pH. All of the environments in the top half of the listing that are characterized as the most corrosive were run at pH 4. These environments have approximately an order of magnitude higher mass loss than those at pH 8.5. The next most important factor in producing high corrosivity appears to be high sulfate level as evidenced by the position in the top two slots at the top of the list. It was somewhat surprising that the three most corrosive environments (at the top of the list) were those with the lower amount of water. Additionally, high chloride concentrations existed in all but one of the top five most corrosive environments.

One shortcoming of the study was that it did not measure susceptibility to localized pitting attack on the steel coupons. As mentioned previously, pitting of steel in ethanolic solutions might produce sites for SCC as observed in other SCC systems described in this report. Therefore, the most corrosive environment in Table I.7 does not necessarily pose the greatest risk for SCC of mild steel. It is important to realize that the range of water in the Brazilian studies presented herein were higher than that of interest for fuel ethanol in the present study (up to 1%). However, this information shows a substantial range of variation for the corrosion rate of steel in ethanolic environments containing water and some of the possible effects of impurities. It may also indicate why no SCC experience has been found in Brazil. It may actually be in a range outside that for SCC where the predominant mode of attack is general corrosion.

A more in-depth study of both general corrosion and pitting tendencies in hydrated ethanolic solutions with 4.8% – 10% water was conducted [16]. This work shows that pitting corrosion was the predominant mode of corrosion in the presence of impurities of sulfate under certain conditions. Conditions that promoted pitting attack were those with pHe in the range 5.6 – 7.9, acidity from acetic acid in the range 0.61 – 1.10 mg/100 ml of solution, and sulfate ion concentrations between 0.5 mg/L – 2 mg/L.

Further information can be gleaned from studies in Brazil [17]. This includes a major evaluation program studying the influence of inhibitors on the corrosion of AISI 1020 steel when freely corroding and when separately coupled to zinc and brass. These data are shown in Table I.8.

The ethanol used in this study was between 93.5% – 94.1% with the balance being water (hydrated ethanol) with other impurities at levels that are higher than found in fuel ethanol made under current specifications. The specific gravity was 0.8068–0.8084. Impurities included the following: H_2SO_4, 1.7 ppm – 2.0 ppm, chloride, 3.74 ppm – 5.81 ppm, and total acidity, 1.3 – 1.5 mg/100 ml. The results in Table I.8 indicate that all but three inhibitors reduced corrosion rate inhibitor efficiencies greater than 98%. However, one

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inhibitor formulation actually had a worsening influence on corrosion rate shown by a negative inhibitor efficiency. The effect of a galvanic couple of zinc and brass to steel reduced corrosion rates in all cases. Therefore, inhibited corrosion rates for all but three inhibitors reduced the corrosion rate by about two orders of magnitude. For the Zn-steel couples, it appears that the corrosion rate of steel, when inhibited, exhibited about the same galvanic corrosion as when not inhibited. In the case of the coupling of steel to brass, inhibition had a beneficial effect on the extent of corrosion in all cases when compared to the non-inhibited case. However, the inhibitors with inhibitor efficiencies less than 83% were noticeably less effective in reducing galvanic corrosion in this case.

Table I.7—Parametric Study of Selected Variables on Corrosion in Hydrated Ethanol

Solution	Variables				Mass Loss	
	Ethanol (%)	SO_4^{-2} (mg/L)	Cl^- (mg/L)	pH	(g/m^2)	(g/m^2)
ABCD	92.6	4	2	4	13.600	12.500
ABD	92.6	4	0.5	4	11.000	11.300
ACD	92.6	1	2	4	10.200	8.000
BCD	93.8	4	2	4	9.710	11.200
CD	93.8	1	2	4	9.010	9.530
BD	93.8	4	0.5	4	8.750	9.200
AD	92.6	1	0.5	4	5.800	4.120
D	93.8	1	0.5	4	5.130	4.580
ABC	92.6	4	2	8.5	1.470	1.270
B	93.8	4	0.5	8.5	1.010	0.958
A	92.6	1	0.5	8.5	0.955	1.000
AB	92.6	4	0.5	8.5	0.950	1.110
BC	93.8	4	2	8.5	0.928	0.960
Base	93.8	1	0.5	8.5	0.885	0.744
C	93.8	1	2	8.5	0.870	0.900
AC	92.6	1	2	8.5	0.724	1.090

I.4.3 CORROSION AND SCC IN ALCOHOL CONTAINING ENVIRONMENTS

While it has been shown that only limited information is available on SCC of steel in ethanolic solutions, there is substantial information on the corrosion and SCC of steel, Ti and Zr alloys in methanolic solutions. A summary of this work is present as it provides insights into corrosion mechanisms operating in alcohol-water solutions in the presence of various impurities which may assist in the understanding of steel in ethanol. Such effects include the role and critical ranges of water content, temperature and strain rate effects, and the impact of material processing on susceptibility to SCC.

I.4.3.1 Steel

In solutions of methanol and water in the range of 200 ppm – 460 ppm, the natural (air-formed) oxide film on the surface is not stable and partially dissolves leading to the following reaction in the protic medium [18]:

$$2\ MeOH \Rightarrow MeOH_2^+ + MeO^-$$

The oxide free areas on the steel surface will rapidly dissolve according to the following reaction:

$$Fe^{2+} + H_20 \Rightarrow FeOH^+ + H^+$$

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Table I.8—Influence of Inhibitors and Galvanic Coupling on Corrosion of Steel in Brazilian Fuel Ethanol

Inhibitor	Freely Corroding		Coupled to Zinc	Coupled to Brass
	Electrochemical Corrosion Rate (10^{-3} mm/yr)	Inhibitor Efficiency (%)	Deviation from Mean Corrosion During Test (g/m^2)	Deviation from Mean Corrosion During Test (g/m^2)
No Inhibitor	399.862	0	–1.98	–8.21
Promax 8027	3.008	100	–1.24	–1.79
Treatolite	3.144	99	–0.83	–1.00
AAM-32/VW03	4.054	99	–0.94	–1.20
Viscoal	3.112	99	–0.95	–2.07
AAM-32	3.144	99	–0.98	–1.18
Alco Lub	3.876	99	–1.03	–1.15
Aditol	4.532	99	–1.26	–2.44
Torq	6.850	98	–0.85	–1.26
Promax Proal	6.056	98	–1.80	–1.90
A.I.C.A.	68.570	83	–1.02	–1.16
Super Q	383.422	4	–1.20	–3.87
Molysil Sprit	2478.216	−519	–1.05	–6.51

Note: Values in Columns 4 and 5 indicate change in corrosion rate from value given in Column 2 on each row.

In aerated conditions, the corrosion of steel in methanol is given by the following equation:

$$Fe^{2+} + MeOH => FeOMe^{+} + H^{+}$$

This leads to local anodic attack under aerated conditions which, in turn, sets up the conditions required for SCC. If sufficient corrosive causing agents are added to the system, the anodic attack changes to a more generalized form over the complete surface where pitting and/or SCC would not be expected to occur.

The role of acidity in partially hydrated methanolic environments has also been evaluated in terms of its role in the corrosion mechanism. The presence of H^+ in methanol contributes to destruction of the normally protective oxide film. An anodic Tafel slope of 30 – 35 mV per current decade has been measured. At higher currents, loss of linearity in the potential versus log current relationship was also observed as a result of diffusion controlled transport of the Fe^{2+} ions. At still higher anodic potentials, adsorbed oxygen is formed and the growth of a passive oxide layer takes place as:

$$Fe + H_2O \text{ (ads)} => Fe\text{-}O_{ads} + 2H+ = 2e–$$

$$n\ Fe\text{-}O_{ads} => \text{iron oxide}$$

(Fe_2O_3 or Fe_3O_4; corrosion product layer)

The region of potential that corresponds to this transition from active (anodic) to passive behaviors is precisely where pitting and SCC can occur. However, these processes depend on the level of acidity and water content in the environment through specific (and possibly competitive) adsorption on the metal surface. Therefore, there may be differences in the exact behavior of water and acidic species in other alcohols such as ethanol. Chloride ions also have a distinct destabilizing effect which is very evident in methanol with only 10^{-3} M required to promote the complete activation of the steel.

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Studies have been conducted to evaluate the phenomenon of SCC of steel in methanolic environments [4, 19, 20]. Typically, these studies have included the use of plastically deformed and/or dynamically strained tests such as found in u-bend (ASTM G 30) and slow strain rate (ASTM G 129) specimens. In aerated solutions at 20°C, it has been shown that there is a critical amount of water that produces SCC in steel that ranges from somewhere above 0 but less than 0.05 volume percent to just below 1% water by volume, based on reported trends in multiple tests (see Figure I.8). The highest probability of failure by SCC was reported to be around 0.20% water in methanol.

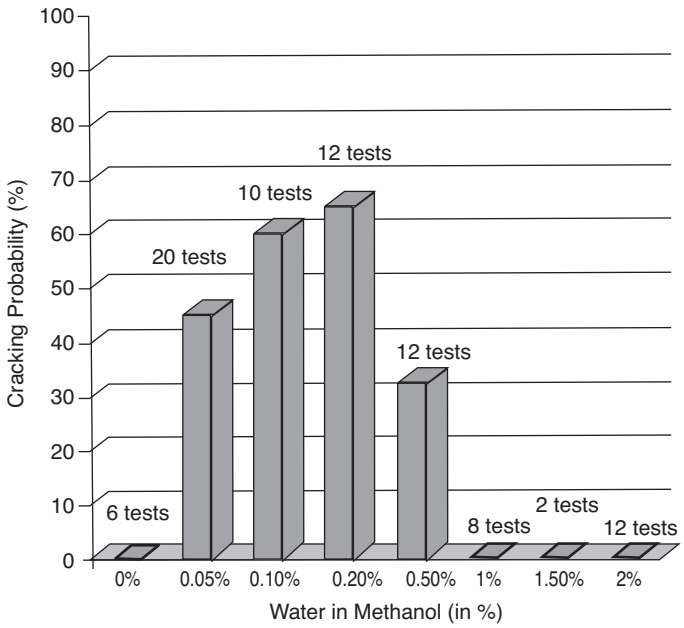


Figure I.8—Susceptibility to SCC in Methanol versus Water Content

Another key variable for SCC of steel in methanol were additions of formic acid and chloride into the environment. Additions of formic acid in the range of 0 ppm – 300 ppm were shown to increase susceptibility to cracking. Additions of 50 ppm also increased cracking severity in solutions already containing 300 ppm formic acid and 0.3% water. Deaerated conditions with 63 ppb dissolved oxygen produced much less susceptibility to cracking than did the fully aerated environment with 77 ppm dissolved oxygen. In all cases, cracking was characterized as being primarily intergranular SCC with multiple crack initiations. Crack initiation sites were located in areas of local anodic activity in the highly stressed region of the test specimens.

Several types of hot rolled, pressure vessel steels and high strength low alloy steels (which ranged in yield strength from 480 to over 700 MPa) were examined [4]. These steels ranged in composition from 0.1% – 0.2% carbon, 0.9% – 2% Mn and between 0.010% and 0.025% sulfur (max.). Conclusions were that steel composition and strength did not have an effect on cracking susceptibility. Additionally, neither the electrochemical potential of the steel nor the temperature of the environment (up to 60°C) appear to have affected the cracking tendencies of the steel. However, another research study on SCC of steel in methanol using slow strain rate testing, indicated that the time to failure decreased with increasing environment temperature and there was no SCC at the lowest temperature tested (30°C). SCC failures were limited to a broad range of anodic potential in a methanol solution with vinyl resin, whereas cathodic potentials did not produce SCC.

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Studies of iron and a low alloy steel (Fe-0.94Cr-0.98Ni-0.16Mo) with a yield strength of 932 MPa, [20] showed that conditions of slow oxide growth were observed in methanolic solutions containing impurities in the following range: acidity (0 to 10^{-3} M with formic acid), chlorides (10^{-4} – 10^{-3} M) and water (0.01% – 0.5%) when the potential was held between –200 and +100 mV SCE. By comparison, SCC of steel was observed in the more controlled range of conditions indicated as follows:

a. 10^{-4} M formic acid

b. 10^{-4} – 10^{-3} M chloride

c. 10.1% – 0.5% water

d. –100 – 0 mV SCE applied potential

The absence of dissolved oxygen in the environment decreased the potential of the metal to less than –100mV, thus eliminating SCC failure.

The influence of other variables on methanol SCC was also evaluated. The concentration of formic acid in methanol between 0.005 and 0.04 wt. percent produced SCC in steel with a minimum time to failure occurring between 0.01 and 0.02 wt. percent at a solution water content of 0.1% at 60°C. It was shown that hot rolled steels exhibited higher susceptibility than some cold rolled steels or pure iron. However, some cold rolled steels were found to have susceptibilities to SCC that were similar to the hot rolled steels. Increasing chromium content in steel over the range 0.01 – 0.10 increased time to failure, whereas increased rolling temperature tended to decrease failure time. Heat treatment of the steel in the range 200°C – 600°C following cooling increased time to failure as did increased cooling rate (water spray or air cooling versus oil quenching). The extension rate used in the slow strain rate test was also observed to influence the results of SCC tests. Susceptibility to cracking in one hot rolled steel increased with decreasing initial strain rate starting in the range 10^{-4} – 10^{-5}/sec Initial strain rates outside of this range did not produce SCC in steel. Additionally, levels of strain in static bent specimens required to produce SCC was estimated to be about 4% based on analysis of the results from steels with strain values in the range 7% – 15%.

I.4.3.2 Ti-Alloys

There has been documentation of SCC in methanolic environments primarily supported by work conducted on titanium alloys. [21 – 22] Much of the early work related to Ti and Ti-alloys in anhydrous or near-anhydrous methanol. Intergranular SCC was reported in commercially pure (α) Ti and in β Ti alloys. Susceptibility to this form of SCC was found to:

a. increase in severity with increasing halide (chloride, bromide) concentration, and

b. decrease in severity when water additions exceeded a critical level.

Higher halide concentrations also increased the critical level of water for maximum susceptibility. Typically, anodic polarization tends to increase cracking susceptibility while cathodic polarization decreases it. Potentials below –250 mV (Ag/AgCl) have been shown to prevent SCC in these systems. This behavior is common for SCC where local anodic processes (rather than hydrogen embrittlement) govern the initiation and propagation of cracks. Some highly alloyed Ti materials can also exhibit a transition from intergranular SCC to transgranular SCC by cleavage in the phase as the stress intensity is increased.

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I.4.3.3 Zr Alloys

SCC has been reported in Zr and Zr-alloys exposed to hydrated methanolic media containing various amounts of HCl solutions [22 – 24]. Cracking has been reported in the range of lower water content less than 20% and also in a range of higher water content from 40% – 90% water (see Figure I.9a). In the lower range of water content, SCC was observed over a wide range of potential above –100 mV SCE as shown in Figure I.9b. The range of applied potential where SCC was observed was above the repassivation potential in the environment. Sites for SCC were observed to be areas of local anodic attack with intergranular features on surrounding metal surfaces that exhibited passive behavior. SCC was characterized as transgranular cleavage.

Additional work was performed on Zr and Zr-alloys in methanol, ethanol and other alcohols with increasing carbon number to octanol containing iodine using slow strain rate testing techniques at an initial strain rate of 4.7×10^{-6} sec^{-1}. No indication of water content was provided, but it was expected to be low since analytical grade chemicals were used. SCC tendencies indicated that the cracking was intergranular in nature and crack growth rates decreased with increasing chain size (C number equal 1 – 8) from about 10^{-7} – 10^{-5} m/sec The decrease in crack growth rates with increasing carbon number was related to a decrease in surface mobility with increasing carbon number.

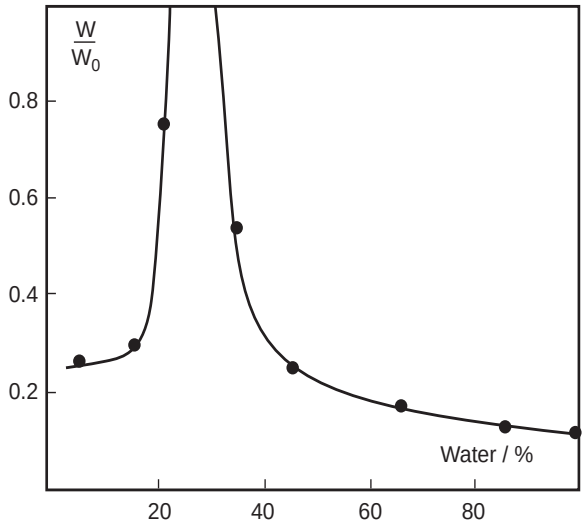


Figure I.9a—Influence of Water on SCC of Zr-alloy in Hydro-methanolic Media (W = Fracture Energy; W_o = Fracture Energy in Air)

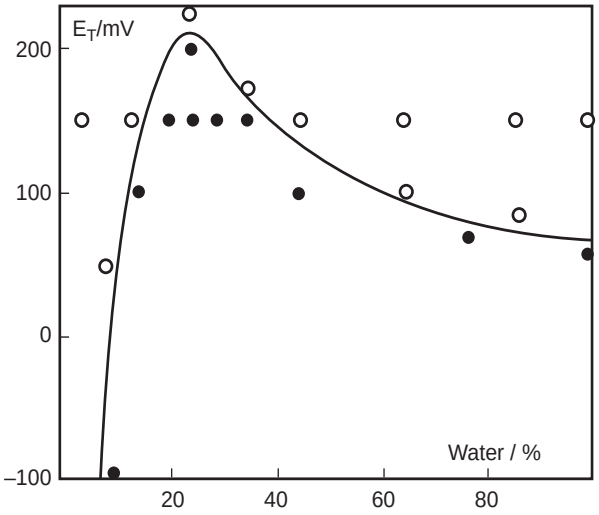


Figure I.9b—Influence of Water on Corrosion Potential of Zr-alloy in Hydro-methanolic Media (E_T versus SCE)

I.4.3.4 Stainless Steel

Electrochemical studies of AISI 321 stainless steel in ethanol, propanol and butanol solutions with H_2SO_4 revealed that increasing concentrations of acid increased the development of active-passive behavior in the anodic region of the polarization curves [11]. This was characterized by:

a. an increase in the current at the active-passive transition;

b. a decrease in passive current density; and

c. an increase in the current in the transpassive range.

The main differences between this electrochemical behavior and that observed in isopropanol and butanol was the lack of a distinct transpassive transition in the latter two environments. Pitting was extensive in the ethanol solutions while pitting was not observed in either the isopropanol or butanol solutions. These results confirm that ethanol has particular tendencies toward pitting corrosion in stainless steels as was shown for steel in ethanol-water solutions containing impurities.

I.4.4 SCC OF STEEL IN OTHER ENVIRONMENTS

There is experience with corrosion and SCC in various steel-environment systems that may further shed light on the processes applicable in alcohol containing solutions. The environments of interest include those containing anhydrous ammonia, caustic, CO-CO_2, carbonate-bicarbonate, and monoethanolamine. The SCC of steel in these environments is described in the following sections and compared/contrasted to what is currently known for ethanol and methanol.

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I.4.4.1 Ammonia SCC

This chemical is of major commercial importance and one where carbon steel is commonly used. SCC of steel was first observed in ammonia storage vessels in the early 1950s. In most cases, cracks were detected through inspection prior to the onset of leakage or failure. However, there were major ruptures of a tanker in 1968 and a storage tank in 1973 [25 – 26].

In most cases, SCC failures in ammonia have occurred at ambient temperature and have been characterized as transgranular, progressing at slower rates relative to other SCC phenomena. This is contrasted to observations of SCC of steel in alcoholic media which has tended to be intergranular in nature or mixed mode (both intergranular and transgranular cracking).

Studies have shown that aeration promotes ammonia SCC of steel whereas the presence of water in amounts greater than 0.1% inhibits cracking (see Figures I.10 and I.11).

Levels of oxygen greater than 5 ppm are required to sustain cracking of carbon steel unless carbon dioxide is also present, which lowers the threshold to only 1 ppm. Other studies using slow strain testing procedures have shown SCC with as little as 0.01 ppm oxygen in the environment and inhibition of cracking at 0.08% water. It has also been reported that some compounds such as hydrazine, ammonium carbonate and ammonium bicarbonate may act as inhibitors for SCC in this system.

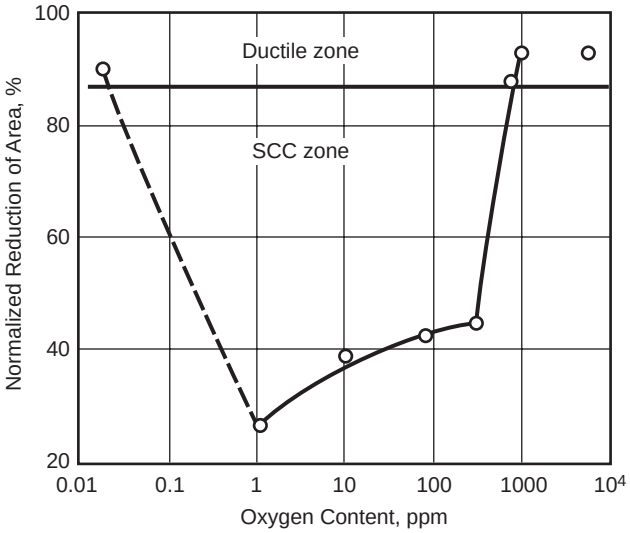


Figure I.10—Influence of Aeration on the Susceptibility of Steel to Ammonia SCC

Other variables identified that play a role in ammonia SCC of steel include the presence of high mechanical stresses, and cracking increases with strength or hardness of the material [25]. Thermal stress relief has been shown to reduce susceptibility to SCC. Ammonia SCC of steel has been reported to occur over a wide range of potential from –500 mV to over +1000 mV SCE.

Field experiences with SCC of steel in ammonia show that water was not always an effective inhibitor for SCC particularly after the development of cracks in the material. Additionally, even if water is contained in the liquid ammonia, SCC can still occur in the vapor phase where ammonia is condensing. In designing for resistance to ammonia SCC, it has been recommended that low strength steels be used (up to UTS of 483 MPa max.—70 grade steels). Weld hardness should be specified to be less than HB 225 with post weld heat treatment (PWHT) at 595°C min be applied.

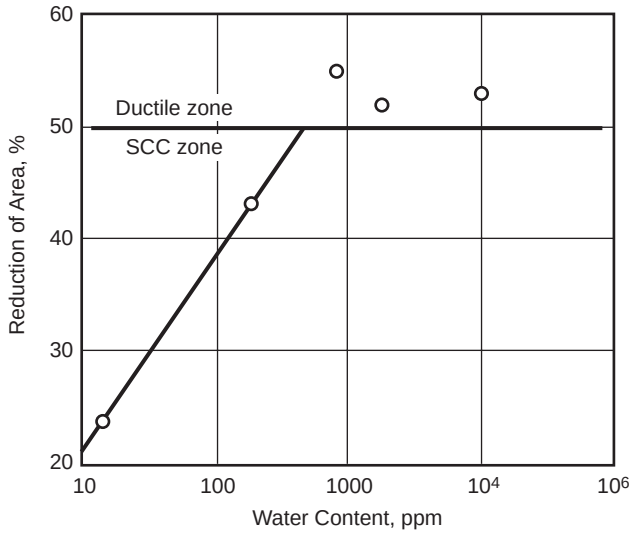


Figure I.11—Influence of Water Content on the Susceptibility of Steel to Ammonia SCC

I.4.4.2 Caustic SCC

Most of the published information on SCC in caustics involves aqueous solutions of NaOH. Experience with caustic SCC is summarized in the NACE caustic soda service chart and data in MTI and other publications. These have been superimposed in Figure I.12 [27]. This data presentation shows that cracking of steel in caustic is primarily an elevated temperature phenomenon that occurs over a broad range of NaOH compositions. More recently, additional data has been obtained for other caustic salts such as KOH which indicates that SCC of steel in these cases may be more selective in terms of conditions that promote cracking [28]. Temperature and corrosion potential (as varied by additions to the environment) were critical differences in defining conditions for SCC in KOH.

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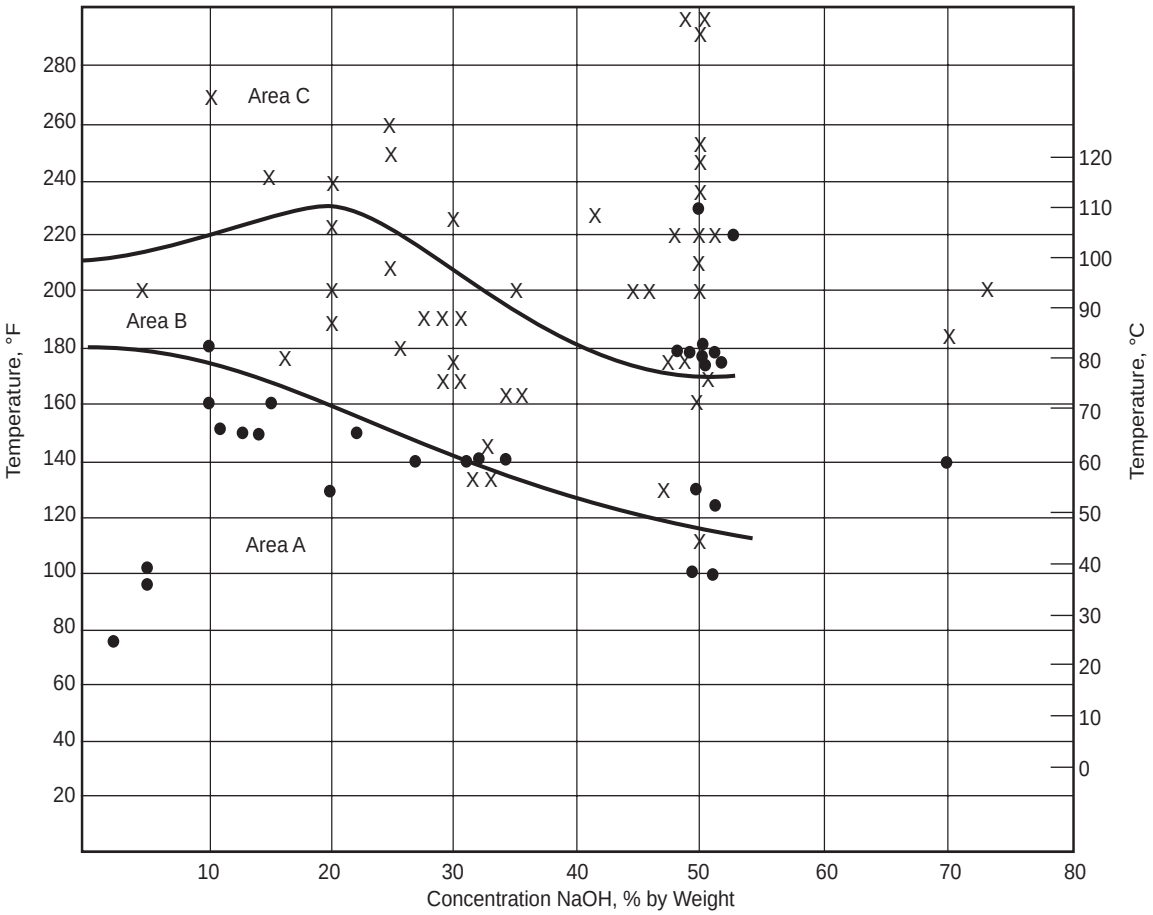
Cracking in NaOH has been reported to be primarily intergranular in nature and occur over a relatively narrow range of applied potential around 400 – 500 mV SCE. It has also been observed in a second range of potential at more electronegative conditions. This second region of potential is between –700 mV to –1000 mV SCE.

SCC of steel by caustic is promoted by high stress. Depending on the temperature and concentration range, application of PWHT to steel weldments and bends is one method used to reduce susceptibility to caustic cracking. Usually at low temperatures, PWHT is not required. However, at higher temperatures (40°C to about 110°C depending on the concentration of NaOH) PWHT is normally specified to minimize the occurrence of SCC in steel equipment. At still higher temperatures SCC has been reported to occur in both weldments and base metal, and alternative high alloy materials are needed to prevent SCC [29].

I.4.4.3 CO-CO_2 SCC

In the late 1960s and early 1970s several incidents were reported of SCC of steel components handling reformed or coal gas [30 – 31]. In all cases, there was evidence of an acidic, aqueous environment due to the presence of between 10% – 20% CO_2 in the gas phase. Unlike the reports for cracking of steel in methanol and initial reports for ethanol, the morphology of the cracks produced by CO-CO_2 SCC were transgranular. Additionally, intergranular SCC was reported in steel at higher pH in FCC overhead applications with environments containing NH_3-H_2S-CO_2 believed to be associated with carbonate cracking [32].

The cracking in CO-CO_2 environments mentioned above [30 – 31] was reproduced in the laboratory under controlled conditions and found to occur specifically as a result of the presence of CO in addition to the CO_2 when tested in and around 20°C. The environments were mildly acidic (around pH 5.5 – 6.0). The higher the concentration of CO the shorter the time to failure observed in



Note: Region A—Carbon steel with no-PWHT except for steam trace lines; Region B—Carbon steel, stress relief of welds and bends
Region C—Nickel alloys to be considered. (●) no SCC failure of steel; (X) failure of steel by SCC.

Figure I.12—NACE Caustic Soda Service Chart and Data in MTI and Other Publications

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the laboratory tests. Furthermore, SCC was found to occur in the narrow range of potential around 200 mV SCE. Application of cathodic polarization prevents cracking initiation and also stops cracks that have already initiated. This effect has also been used as evidence that CO-CO_2 cracking is caused by anodic SCC processes.

The critical role of CO has been shown to be the result of its inhibitive action in acidic solution through selective adsorption on the metal surface. Through this inhibitive action, CO effectively reduces the general corrosion rate and over a narrow range of composition produces the correct potential and surface condition to promote the onset of localized corrosion forming pits that act as the initiation points for anodic SCC. There may be similarities with this type of cracking behavior and that in methanol (and possibly in ethanol) where the range of SCC is limited by regions of passivity and active corrosion where SCC occurs in the transition between these modes of corrosion.

Later this mechanism for SCC was also identified to occur in aqueous solutions produced in combustion gases containing CO and CO_2 used in oilfield miscible flooding reported in 1997 [33]. In this case, the composition of the gas was such that there was 3.7% mole CO_2 and 0.28% mole CO. In both cases, SCC was observed in piping and in highly strained laboratory specimens using u-bend and slow strain rate testing techniques. Increasing the corrosivity of the environment to induce a condition of general corrosion was successful in mitigating this form of SCC. However, SCC could be re-initiated through application of partially effective corrosion inhibitor rendering an environment where localized corrosion could take place. A similar concern exists for steel in inhibited alcohols; partial inhibition could drive a condition of general corrosion into a mode of corrosion dominated by local anodic attack.

I.4.4.4 Amine SCC

There has been a large degree of concern for SCC in amine systems over the past twenty years. This concern has developed in scrubbing systems used in both gas processing units and in refinery applications. Much of the interest in this problem was magnified by the failure of a sour gas absorber column, which killed seventeen people in the 1980s. However, it was later found that the cause of this failure was not due to amine SCC but rather the result of wet H_2S cracking in the lower part of the unit [34].

Another factor in the increased concern over amine SCC is improvement in inspection capabilities which have been developed, such as the use of wet fluorescent magnetic particle testing (WFMPT). Amine SCC, similar to cracking in other caustic environments, tends to be characterized as having many small, tight cracks that are difficult to view with conventional magnetic particle testing. They are further characterized as tight, intergranular cracks filled with oxide. This description is exactly the same as that used in describing cracks in steel produced by SCC in fuel-grade ethanol.

Amine cracking has been found to occur almost exclusively in non-PWHT steel equipment. The cracking is very localized in and around the weld HAZ and/or associated base metal driven by the residual tensile stress associated with the non-PWHT weldments. Historically, amine SCC problems were found to be limited to equipment operated at temperatures above 80°C. However, in recent years, the limiting temperature for SCC has decreased to temperatures in the range of 40°C – 60°C. Experience has also shown that the onset temperatures for amine SCC can vary with the type of amine. This limiting temperature must be carefully considered since it is commonly based on maximum operating temperature. In some cases, it appears that cracking originally associated with particularly low operating temperatures may, in fact, have occurred because of excess ambient temperature during shut-in or during high temperature steam treatments.

The most important aspects of amine SCC to be recently identified are the effects of impurities in the amine and their role in crack initiation [35]. Many laboratory studies have tried to simulate SCC in amine systems using reagent grade chemicals without success. It appears that corrosion film stability is very important in the initiation of SCC and that impurities can have a major role in determining film stability. Furthermore, it is now realized that SCC occurs only during conditions of film instability. If the conditions are benign and steel passivity is exhibited through formation of a protective corrosion film on the steel surface, then the corrosion is uniform and occurring at a low rate. Under these conditions no cracking appears to occur. If the conditions are severe and active corrosion occurs, then no SCC will be exhibited either. However, excessive hydrogen charging of the steel may occur leading to hydrogen cracking mechanisms such as sulfide stress cracking, hydrogen induced cracking and stress oriented hydrogen induced cracking. Only in the limited region of transition from passive to active corrosion behavior will amine SCC occur.

In amine systems, impurities that appear to be involved in the disruption of surface corrosion films and SCC are sulfide, carbon dioxide, chloride, and cyanide [9]. At alkaline pHs, carbonate films will tend to passivate steel leading to low corrosion rates and resistance to SCC. In systems with hydrogen sulfide in addition to carbon dioxide, the carbonate film can be disrupted and replaced with a sulfide, which is not passive in nature leading to active corrosion of steel. Most importantly, when weak sulfiding

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agents such as thiosulfate and thiocyanide species are present in combination with carbonates and bicarbonates, local disruption of the carbonate film occurs leading to localized corrosion that aids in the initiation of amine SCC. Presumably chlorides also can assist in this process. Table I.9 shows a summary of conditions where amine SCC has been observed.

Amine systems have been found to be the most aggressive from the standpoint of SCC along with lean rather than rich amine systems. Typically, cracking occurs most readily at high temperatures (> 80°C), but can occur at lower temperatures (< 80°C) if the correct conditions for SCC are present.

Table I.9—Amine Concentration and Temperature Dependence of Fissuring in MEA Solvents Under Carbon Dioxide Atmosphere

		Characteristics of Fissures in Slow Strain Rate Specimens with and without Additives in Environment		
MEA Conc. (%)	Temperature (F)	No Additives	Carbonate/Bicarbonate Added	Contaminant Package Added
15	160	None	Light	None
	240		Medium	Slight
25	160	Medium	None	Slight
	240		Medium	Severe
50	160	(General	None	Slight
	240	Corrosion Only)	Corrosion in Slight Fissures	Slight

I.4.5 EXTERNAL SCC OF STEEL PIPELINES

Pipelines are typically buried and installed with external protection that includes coatings and cathodic protection. However, they can be subjected to external coating damage, and subsequent disbondment. Pipelines also involve a combination of hoop and tensile loading and fluctuating stresses particularly down stream of compressor stations. At locations of coating damage and disbondment, an environment can form that can produce SCC of steel [36 – 38].

For example, one environment is a high pH solution resulting from the cathodic processes on the cathodically protected pipe. The principle components of this electrolyte are carbonate and bicarbonate ions typically producing a pH in the 9 – 13 range. In a narrow band of applied potential between –600 mV and –750 mV versus $Cu/CuSO_4$ this environment has been found to promote SCC. For this form of external SCC of steel pipelines to occur, tensile stress is an important parameter. In particular, a tensile mean stress combined with cyclic loading is a very important factor as it provides an added driving force to disturb corrosion films on the metal surface and thus sustain the cracking process. Additionally, mildly elevated temperatures conditions (also prevalent down stream of compressor stations) tend to promote cracking as well. This tends to increase the range of potential where SCC of steel can occur. In service, temperatures in excess of 40°C are usually required for high-pH SCC to occur.

Cracking by this mechanism is commonly observed to be intergranular in nature producing oxide filled cracks. This description is again similar to that given for cracking of steel in methanol and ethanol. Secondly, the role of high tensile stress and cyclic loading (as described later in this report) also is the same as found for SCC of steel in alcoholic environments.

It is now recognized that there are now two types of external SCC that have been identified in steel pipelines. These are referred to as high pH SCC (as discussed above) and the more recently identified near-neutral pH SCC that can occur in the range of pH 5 – 7. In contrast to high pH SCC of pipelines and SCC of steel in alcohols, near-neutral pH SCC is manifested as transgranular cracking in an environment composed of diluted groundwater containing dissolved CO_2. However, the pH range for this new type of SCC of steel pipelines is similar to that which may be expected in fuel ethanol environments (pH 7 is neutral for aqueous solution where as neutral is closer to 9 on the pHe scale).

The CO_2 originates from the decay of organic matter. Cracking is further exacerbated by the presence of sulfate reducing bacteria. As with high-pH SCC, disbonded coating shields the cathodic protection current and creates a micro-environment where the potential is in the proper range and SCC can be sustained. A cyclic loading is important for crack initiation and growth of near-neutral SCC as it is for the more classical high pH SCC. There is some evidence that hydrogen may play a role in this near-neutral SCC mechanism.

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I.5 Company Reports and Experience Survey on SCC in Fuel-Grade Ethanol

Evidence has been provided from multiple fuel ethanol users showing occurrences of SCC of steel components (e.g., tanks, piping, roof hanger springs) exposed to fuel ethanol in user storage and transportation equipment. In some cases, the failed equipment had seen prior non-ethanol service. A summary of documented SCC in fuel-grade ethanol and SCC-free service experience found by this study is given in Table II.D-1 of Part II. This table summarizes the results of reports and related documents and correspondences which include plant experiences, metallurgical and chemical analyses, and laboratory corrosion studies. Most of these results were presented in a forum that was held in Richmond, California in January 2003. A short one page survey form (see Appendix II.A of Part II) was developed that was easily transmitted and completed, in an attempt to obtain any further information that may be available. Additionally, telephone interviews were also conducted in an effort to obtain further information related to SCC in fuel-grade ethanol. Where applicable, the results of the survey and telephone interviews have been included in the summary table or included in the discussion presented in this section.

The following discussion aims to highlight specific areas where experience has been gained on materials, environmental or mechanical effects that may help to further the understanding of SCC in fuel-grade ethanol, minimize its occurrence and help scope future studies of this area.

In general, it should be noted that all SCC failure in fuel-grade ethanol failures were experienced by users of fuel ethanol. No ethanol manufacturers have reported leaks from SCC. Furthermore, a major inspection program of tanks located at a particular manufacturing facility has not found evidence of SCC in reported inspections. However, some end users have not experienced any SCC in fuel-grade ethanol. Most of the experience received for this report has come from end users that have experienced failures.

I.5.1 MATERIALS

All cases of SCC failures from the field have occurred in carbon steel constructional materials. The grades include the following: ASTM A 36, A 53 and A 516 Grade 70. These are hot rolled plate and pipe products used in the fabrication of storage tanks, vessels and piping. Additionally, highly cold worked steel springs (of unspecified grade) used in roof hanger assemblies have also shown susceptibility to SCC. No reports were obtained that indicated that the SCC was the result of materials being out of specification.

I.5.2 METALLURGICAL AND MICROSTRUCTURAL ASPECTS OF CRACKING IN PLATE AND PIPE

With the exception of cases involving roof springs, failures from SCC in fuel ethanol have mainly occurred in plate steels, in locations near, but not in, welds. The reports indicate that the cracking can be either transverse or longitudinal with respect to the weld orientation. These cracking regions are located in the base metal adjacent to welds. Multiple reports indicate that the cracking was located generally in a region between the weld heat affected zone (HAZ) to about 1 in. into the base metal (see Figures I.13 – I.15).

Cracking was primarily intergranular in nature with some isolated descriptions of transgranular or mixed mode cracking. Typical cracking morphologies associated with SCC in fuel-grade ethanol are shown in Figures I.16 – I.18.

The microstructures reported were mainly ferrite or ferrite and pearlite which are typical in hot rolled steel products. No mention was found of anomalous microstructures or microstructures associated with transformation products such as bainite and martensite commonly associated with areas of high hardness.

In one well documented case, microhardness measurements (converted to HRB values) for the tank bottom failures were made away from the cracked location and near the cracks. These results indicate that the hardness in the area of cracking was 73 HRB whereas the hardness remote from the cracking was somewhat less at 68 HRB. All readings were much lower than the equivalent HRC 22, commonly recognized as the threshold hardness for sulfide stress cracking (a hydrogen embrittlement phenomenon occurring in H_2S-containing environments). The microstructure was typically ferrite or a ferrite/pearlite mix with no mention of anomalous microstructures.

In another case, the hardness adjacent to the cracking was measured to be HRB 85 – 89, whereas the hardness away from the cracked region was HRB 83 – 84. In both cases, the hardness in the region exhibiting SCC was slightly higher than that in the remote areas in the base metal. However, all readings were normal for hot rolled plate and pipe products.

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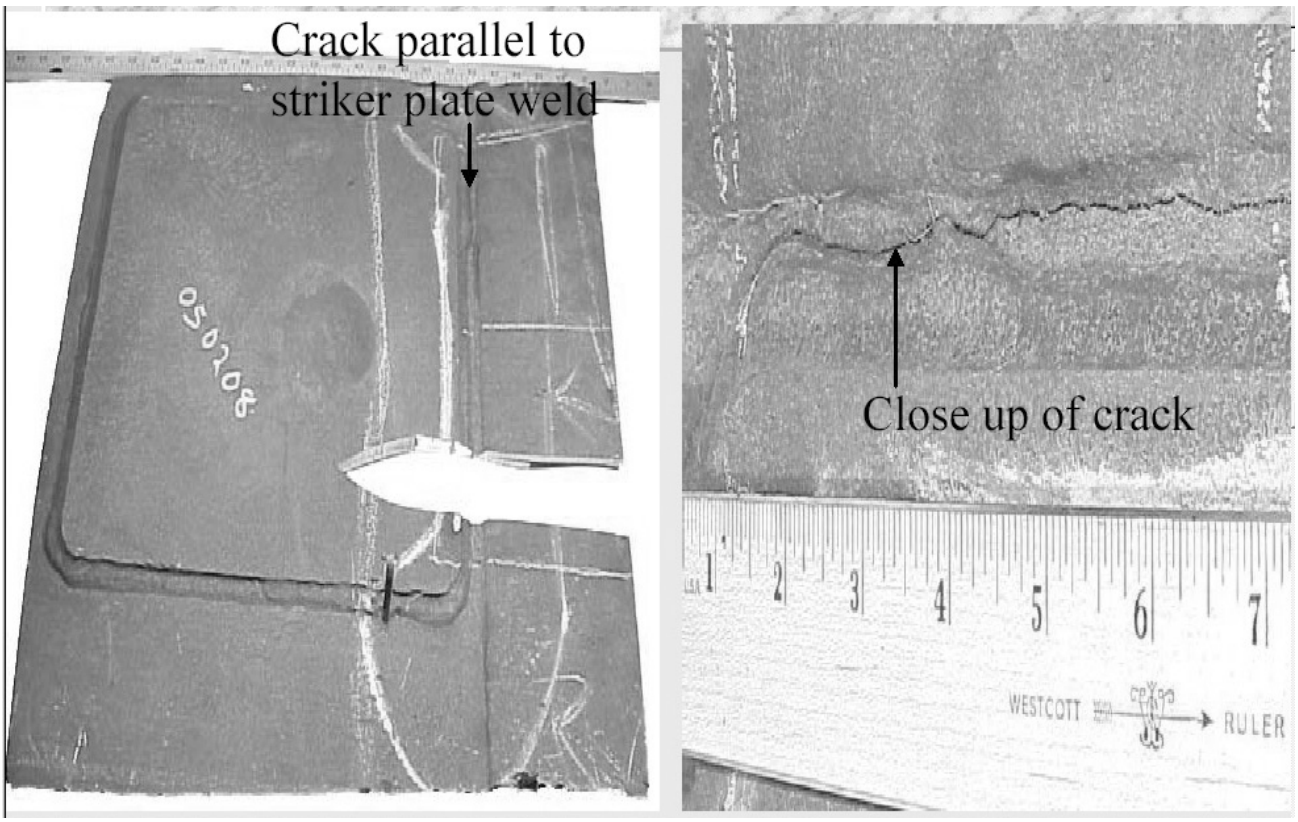
I.5.3 ENVIRONMENTAL PARAMETERS

The information obtained from users of fuel ethanol noted that the sources of the ethanol being handled in the tanks varied considerably from location to location and even at the same location. Several tanks experiencing failures commingled ethanol from many sources. However, failures were also observed in equipment that reportedly handled ethanol only from a single domestic source. Still others reported failure shortly following receipt of cargos from Europe and South America. Furthermore, the physical locations of the equipment experiencing SCC in fuel-grade ethanol range from U.S. West Coast to Mid-Continent to Great Lakes locations.

In one case, tank product analyses made over a period of about three months indicated the results given in Table I.10. This abbreviated analysis indicates that the water content was fairly constant at about 0.7% and purity varied from 94.9% – 95.7%. The major variable in these analyses was the value of pH in the ethanol (pHe) which varied from 3 – 7.7.

In another case, a brown solid or sludge was reported on the bottom of an ethanol storage tank consisting mostly of sodium sulfate (both polymorphs III and V), combined with rust, and a small amount of dirt. This was the only case of an actual sludge on the tank bottom being reported as of September 2003. The analysis of this deposit is given below:

50 wt%	Na_2SO_4-III
26 wt%	thenardite, Na_2SO_4-V
4 wt%	magnetite, Fe_3O_4
7 wt%	lepidocrocite, γ-FeOOH
11 wt%	goethite,α-FeOOH
1 wt%	quartz, SiO_2
0.7 wt%	calcite, $CaCO_3$
0.8 wt%	dolomite, $CaMg(CO_3)_2$



Note: Crack running parallel to fillet weld in striker plate.

Figure I.13—SCC in Steel Tank Bottom

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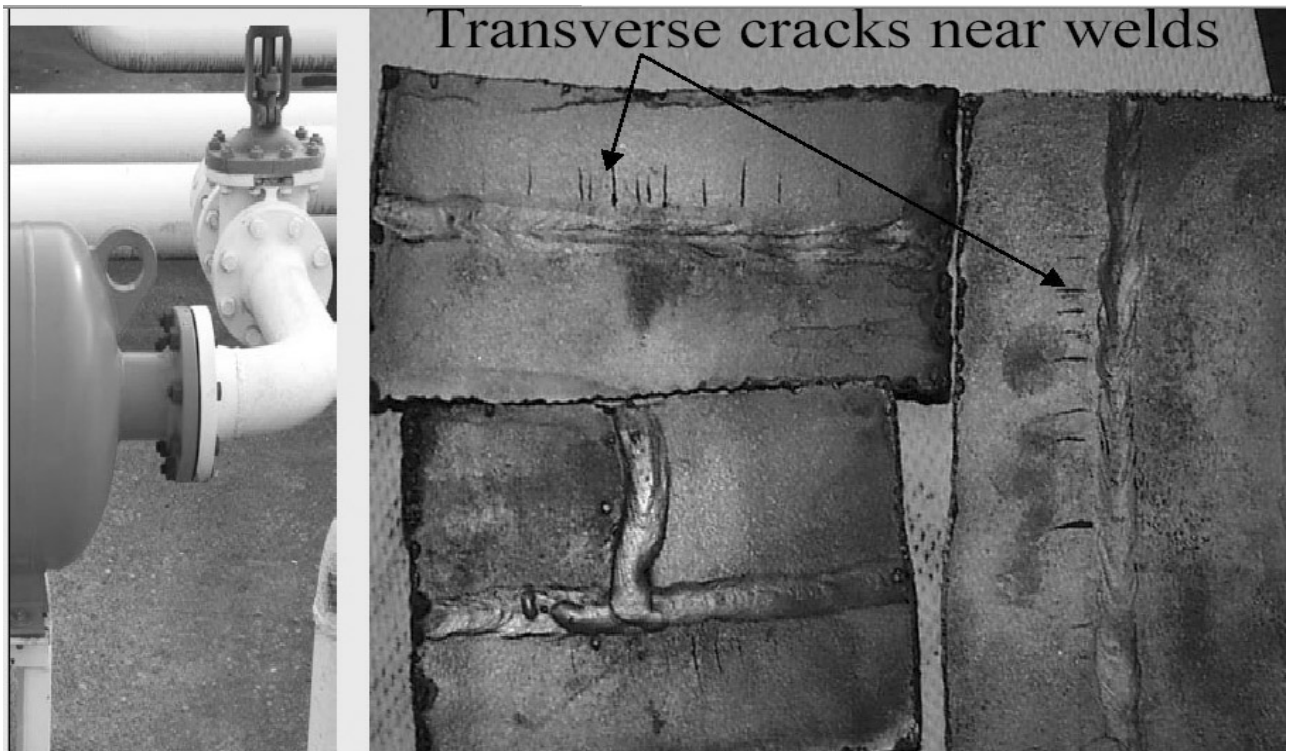


Figure I.14—SCC in Steel Air Eliminator Vessel

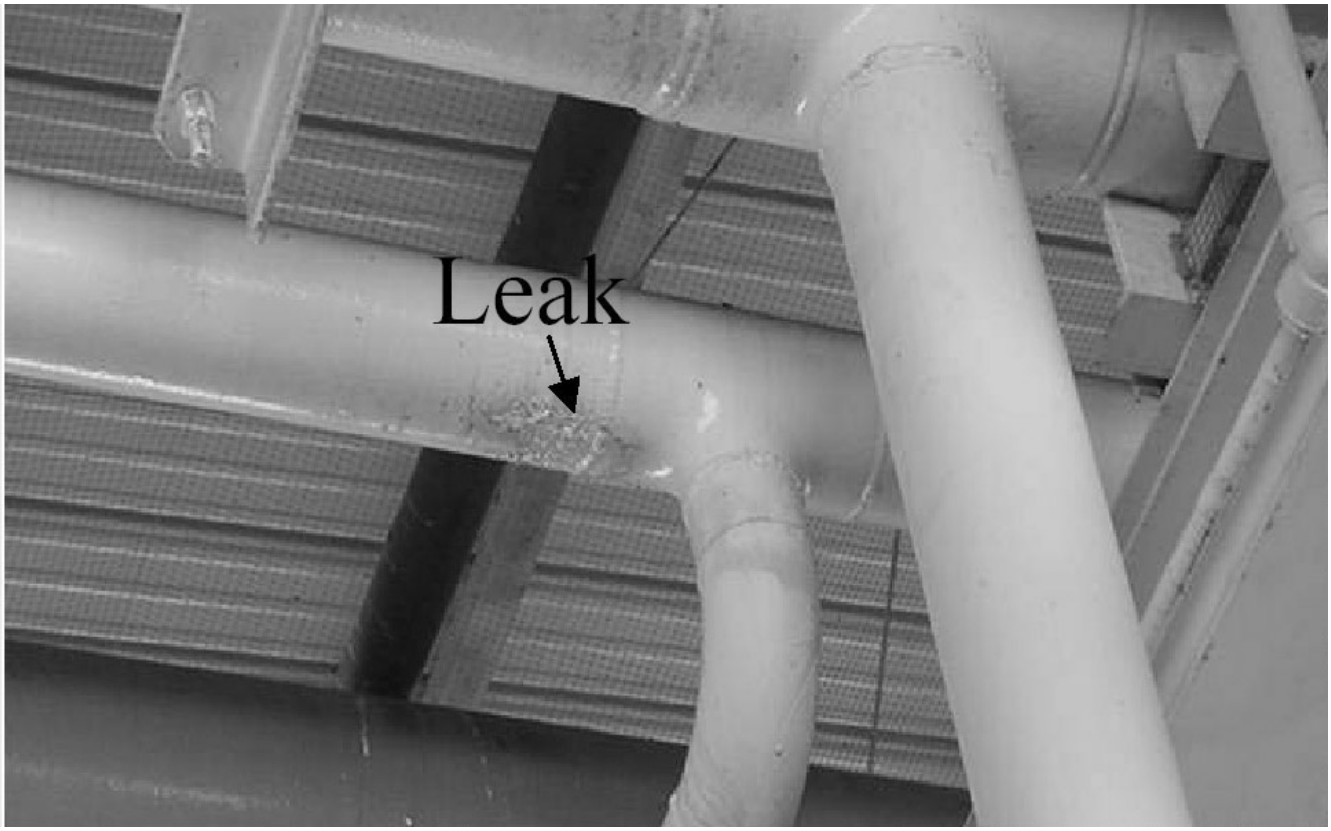


Figure I.15—Leak in Piping Resulting from a Crack Adjacent to the Weld

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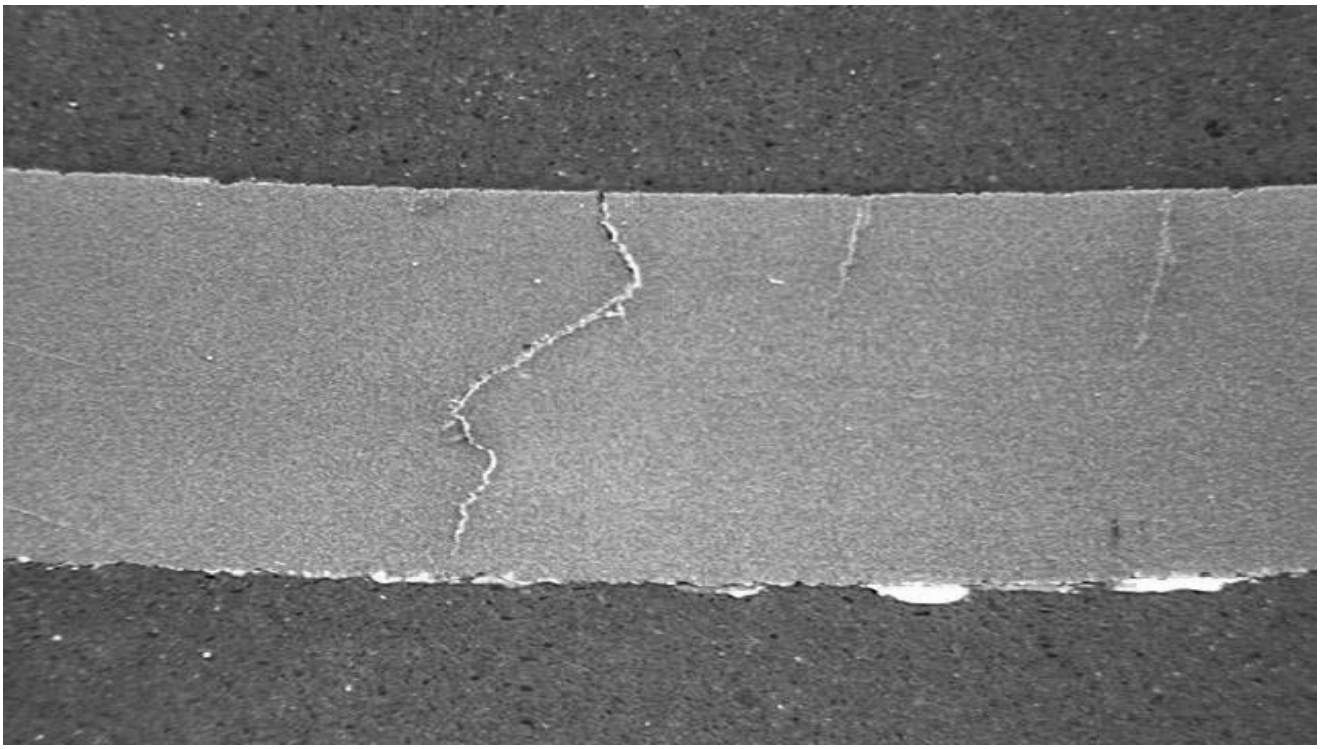


Figure I.16—Characteristics of SCC in Steel Exposed to Fuel Ethanol, Showing Multiple Crack Initiations and Through-Thickness Propagation in Piping

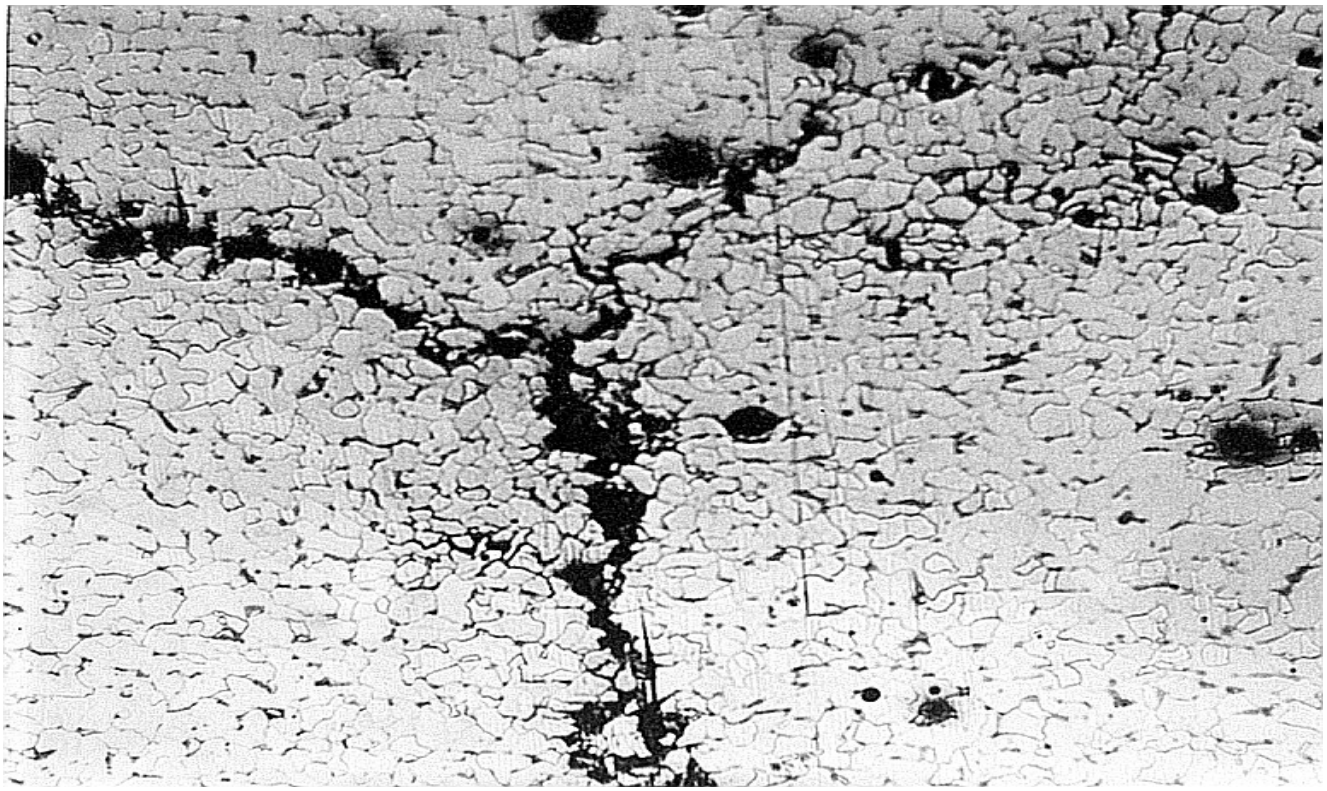


Figure I.17—CC in Steel Tank Bottom Showing Highly Branched, Intergranular Cracks at 100X

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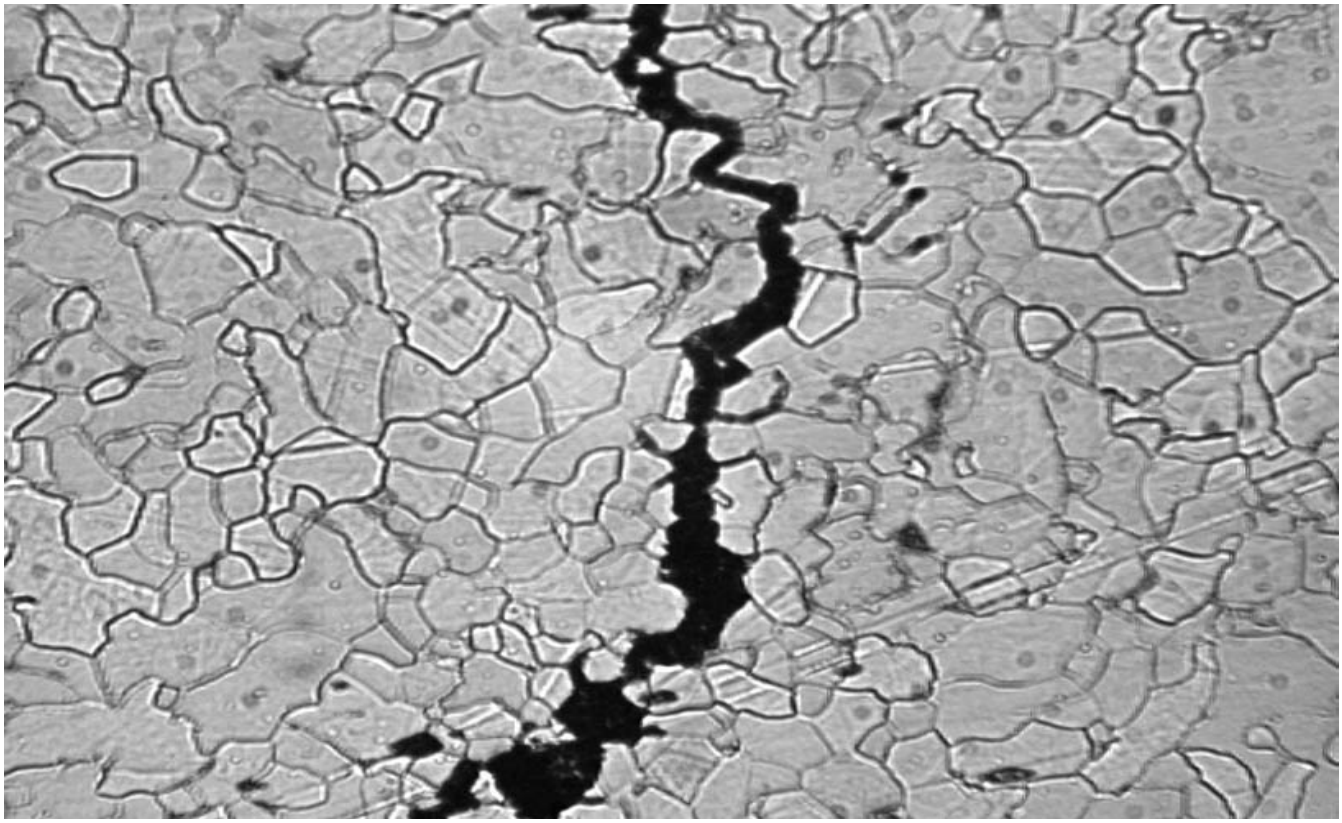


Figure I.18—SCC in Steel Metallographically Prepared with Grain Boundary Etch at 500x

Table I-10—Ethanol Product Analysis

Date	Location	API	Purity	H2O	pHe
31-May	Great Lakes	47.7	95.6	0.6728	7.5
16-Jun	Great Lakes	47.6	95.7	0.7662	7.1
1-Jul	Great Lakes	47.6	96.0	0.7489	7.7
16-Jul	Great Lakes	47.6	95.2	0.7869	4.5
4-Aug	Great Lakes	47.4	95.5	0.7614	3.0
15-Aug	Great Lakes	47.2	94.9	0.7466	7.5

Some additional reports from other locations included comments indicating that the source of ethanol for some West Coast locations included ethanol from Russia or Italy. It also referred to sulfur in the ethanol in trace quantities, in the form of organic sulfides that may be linked to cracking. There are also some unconfirmed suspicions that SCC tends to occur only when water content is less than 0.5%. This suspicion does not agree with the results presented in Table I.10 and cited elsewhere herein, which have indicated that the water content in fuel-grade ethanol is widely considered to be above 0.5%. However, this information when taken in total does suggest that water may be an important factor in SCC which has not, as yet, been properly assessed.

Additionally, another report indicated that the water content at the bottom of the ethanol storage tank was actually higher than in the upper portion of the tank. The values indicated were 1.21% on the bottom of the tank versus 0.62% in the middle to top, both of which were above 0.5%. Since SCC in fuel-grade ethanol was observed in both the lower and upper portions of the tank (bottoms and roof hanger springs), water may not be the critical variable. It is also possible that several variables may work in combi-

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nation to produce an environment capable of causing SCC susceptibility in steel components. Based on the previous summary of other SCC mechanisms in steel, the condition that produces cracking is likely to be one that results in a low corrosion rate with some tendencies for local anodic attack.

A broader sampling of ethanol analyses was obtained by one end user on the West Coast. The results of the analyses of these samples are given in Appendix I.B (see Table I.B-1). This study investigated nine samples of ethanol from various sources including one sample of reagent grade ethanol. The results of these analyses show substantial variation in several parameters. These parameters include total sulfur (0.93 ppm – 106 ppm), water (0.11% – 0.81%), and pHe (3.49 – 8.78). Acidity as acetic acid varied from 19.2 ppm – 38.6 ppm. The highest sulfur levels were found in ethanol derived from wine/sugarcane and the lowest came from corn and sugarcane. One sample of ethanol derived from wine and sugarcane was one to two orders of magnitude higher in total sulfur than any of the other samples. The highest water content was in inhibited ethanol from corn and the lowest water content was in ethanol also derived from corn. The pHe value was one of the parameters with the greatest variability in the samples used in the study. Since pH is a logarithmic scale a change from 3.5 to almost 9 is a change of five orders of magnitude in hydrogen ion concentration.

The results from other users of fuel-grade ethanol, presented in Tables I.B-1 and II.D-1, were compared with the ASTM standard for fuel ethanol given in Table 1. It can be seen that in most respects, the ethanols analyzed in all of the above mentioned studies were within the ASTM standards. All but one ethanol sample (the wine/sugarcane derived product) would be considered acceptable under the 10 ppm sulfur limit. All were less than 1% water content. All samples were well under the 70 ppm maximum in acetic acid and the 40 ppm for inorganic chloride. Only one sample of ethanol (the corn derived, non-inhibited product) was not within the specified range of pHe from 6.5 – 9.0. If these analyses are considered along with those mentioned previously herein, concerns for fuel ethanol purity and adherence to ASTM standard at the user's facilities may need to be raised. As mentioned previously, one tank had a sulfate-rich deposit on the bottom, which certainly would exceed the total sulfur limit on the bottom of the tank. Additionally, the lot of ethanol with a pHe value of 3 also falls outside the current specifications. In the cases identified, the potential sources of fuel ethanol contamination were not clearly identified and closer attention to product purity issues is definitely warranted.

Due to the importance of environmental variables on SCC phenomena and the apparent variability of fuel ethanol composition as assessed through the above mentioned studies, further information was requested on chemical composition. Additional analyses were obtained from one West Coast user of ethanol. Transfer and tank analyses are shown in Tables I.11 and I.12.

These tables indicate variable water content in the transfer analyses ranging from 0.53% – 1.28%. Two of the analyses indicated cloudy and hazy with water contents of approximately 1%. In the more complete tank analyses, sulfur varied from less than 2 ppm – 55 ppm with most of the analyses in the range of 4 ppm – 12 ppm. For the analyses where pHe was measured, the pHe values were between 7 and 8. The acidity (as acetic acid) ranged from 30 ppm – 40 ppm in most cases; however, readings of 50 ppm – 110 ppm were also observed. In the one case where the ethanol was found to be cloudy and hazy the sulfur was high (55 ppm) and chloride was measured and found to be 1200 ppm. This later reading was far in excess of the ASTM standard limits of 40 ppm, indicating gross contamination of the fuel ethanol.

I.5.4 MECHANICAL FACTORS

Based on a review of the case studies provided in this work, high stress/strain and flexural loading appears to be, at least qualitatively related to the presence of SCC in steel equipment. All failures of steel tanks and piping examined thus far have involved non-PWHT welds. Therefore, the area around the weldments would be expected to have high levels of residual tensile stress that could extend into the base metal.

Tank bottom welds exhibiting SCC in fuel-grade ethanol have been predominantly fillet welds between overlapped plates or between striker plates and the steel plates used to fabricate the tanks. These weld configurations are likely to provide stress concentration particularly in the regions adjacent to the weld. An additional factor that may increase cracking susceptibility is the flexing that occurs in tank bottoms as they are emptied and filled. This produces a condition of dynamic straining that has been shown to play a role in other SCC mechanisms in steel and other materials. This is particularly similar to the reported conditions that promote carbonate-bicarbonate SCC found to occur externally on coated pipelines. Also suspect are attachment welds and high mechanical loads that may induce high stresses and provide additional stress concentration in associated piping systems. The one case of SCC also involved cracking in a formed steel head on an air eliminator vessel also brings to light the possible impact of residual stresses from forming as well.

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I.5.5 UNPUBLISHED LABORATORY STUDIES

Several limited studies were conducted by various investigators to evaluate corrosion and SCC of steel in ethanol environments. The results of these investigations have not as yet been published. Due to the importance of this cracking phenomenon, these results are presented herein to further define the nature of SCC in fuel-grade ethanol and help guide future studies that may be funded by API or other parties.

I.5.5.1 Study #1

A study [39] was conducted using coupons (per ASTM G 31) and potentiodynamic methods defined in ASTM G 5 and G 59 as adapted to a rotating cylinder apparatus using rotational speeds from static to 12 ft/sec The mass loss corrosion rates for various ethanol environments were very low (see Appendix I.B). Excess water additions had only a minor influence on the corrosion rate which was still very low. The uninhibited ethanol derived from corn (with the lowest value of pHe) was the most corrosive with a corrosion rate of 0.0041 mpy. The rotating cylinder experiments did not show an increase in corrosivity with rotational speed. There was no report of corrosion morphology and therefore assumed that the corrosion was general in nature.

An additional part of this investigation included the exposure of u-bend SCC specimens per ASTM G 30 machined from AISI 1010 carbon steel. Additional u-bend specimens were included of welded AISI 4130 steel at HRC 30 and 55. The environment was an ethanol that reportedly had produced SCC in the field (indicated as West Coast Stock in Table I.B-1. The test temperature was initially room temperature, which was raised after one month to 100°F for two weeks, 120°F for two weeks and 130°F for one week. Evidence of failure was made by visual examination. No SCC was observed in these tests. Additional SCC tests were conducted with 100 ppm and 1000 ppm acetic acid and with additions of sulfate that were 50%, 100% and 150% of the total sulfur by weight. Again, no SCC was observed.

I.5.5.2 Study #2

Welded u-bend SCC specimens of a carbon steel were placed in an ethanol sample that had produced SCC in a user's steel equipment [40]. This sample of ethanol was reported to be wine derived and was tested with and without an inhibitor. All u-bend specimens cracked at room temperature (uncontrolled). The failures occurred in an exposure period of between five to six months from initiation.

Table I.11—Transfer Analyses for a West Coast Terminal

Date	Clarity	Sulfur (ppm)	pHe	Acidity (ppm)	KF Water %
7/8/2002	C & B				0.53
6/23/2002	C & B				0.53
5/17/2002	C & B				0.47
5/1/2002	C & B				0.61
7/14/2001	C & B				0.71
1/17/2001	C & B				0.55
12/2/2000	C & H				1.01
12/1/2000	C & H				1.01
11/21/2000	C & B				0.85
11/10/2000					1.28
11/7/2000					0.61

Note: C & B = Clear and Bright, C & H = Cloudy and Hazy

Table I.12—Tank Analyses for a West Coast Terminal

Date	Appearance	Sulfur (ppm)	pHe	Acidity (ppm)	KF Water%
7/29/2002	C & B	4			
7/16/2002	C & B		7.4	40	
7/9/2002	C & B	5	7.3	30	
5/6/2002	C & B	5	7.3	40	
11/18/2001	C & B	6	7.4	40	
10/10/2001	C & B	5			
2/21/2001	C & B	12	7.0	110	
1/2/2001	C & B	3	7.8	40	
11/28/2000	C & H	55			Chloride—1200 ppm
11/24/2000	C & B	< 2	8.0	50	0.9

Note: C & B = Clear and Bright, C & H = Cloudy and Hazy

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I.5.5.3 Study #3

A sample of fuel ethanol was provided for slow strain rate testing per ASTM G 129 at room temperature [41]. The sample was reported to be denatured but non-inhibited ethanol derived from corn. The tests were conducted on carbon steel at an initial strain rate of 1×10^{-6} sec^{-1}. The specimens were taken from the base metal adjacent to the weld, oriented with their axis parallel to the weld. The specimen showed extensive cracking throughout the gage section (see Figure I.19). A metallographic section was made of the failure region and is shown is Figure I.20.

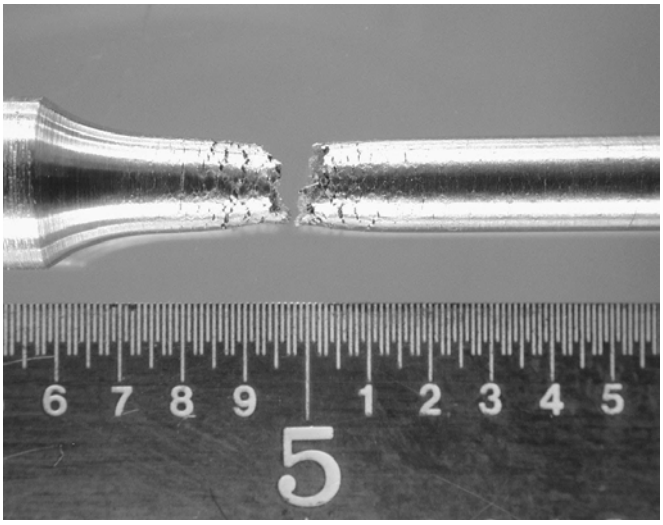
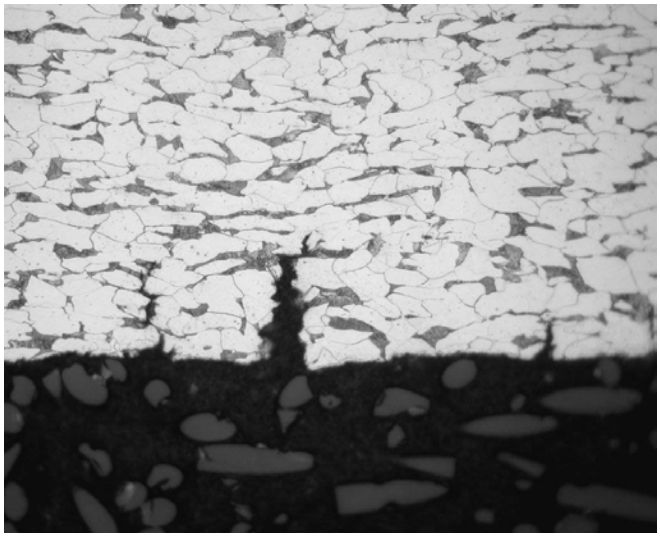


Figure I.19—SCC Produced on Welded Carbon Steel in Fuel Ethanol

Both Figures I.20 and I.21, show the failures produced by SCC in fuel-grade ethanol under laboratory conditions to be predominantly intergranular cracking with areas of mixed mode or transgranular failure. Elongation and reduction in area ratios for this condition were 0.89 and 0.78 (versus air properties), respectively. Tests were also conducted with inhibitor added that produced similar susceptibility to SCC with elongation and reduction in area ratios of 0.73% and 0.81%, respectively. Tests in the same environment as the initial tests with water added to 1.5 weight percent showed much reduced cracking susceptibility with the ductility ratios in the range of 0.87 – 0.93.

In the above mentioned tests, the water content was not measured at the time of the initial test that produced SCC. The second test (with water added) was conducted about a month later and the water content was measured to be 0.447% before the addition was made. About five months later the ethanol was tested again and was found to be 0.659% which was an increase of about 50%. When the ethanol was re-tested at this time, no cracking was observed.



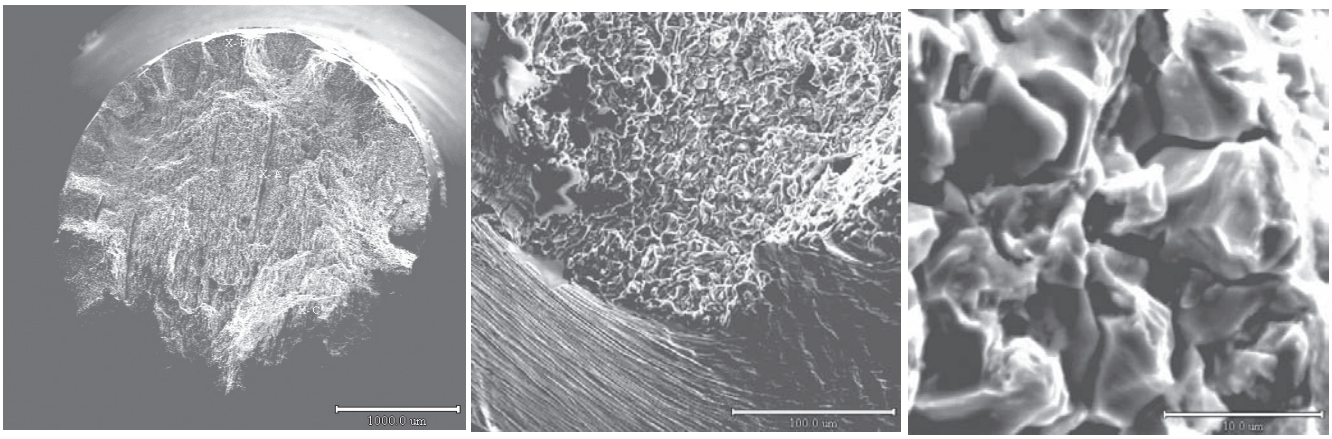
Note: Cracking was a mixture of intergranular and transgranular features.

Figure I.20—Close-Up of SCC from Figure I.18

SSR tests were also conducted in a fuel ethanol sample reportedly derived from wine obtained from a Caribbean source. The water content of this sample was 0.749%. Substantial secondary cracking and susceptibility to SCC was observed in this sample. This sample was also found not to contain denaturants or inhibitors.

The results presented are from a small lot of ethanol samples and limited number of SSR tests. In most cases, only limited product analyses were conducted at the time of testing. However, the SSR tests appear to indicate that susceptibility to SCC in these environments may involve multiple variables and is not limited to the influence of water content. Limited tests have also shown reduced susceptibility to SCC when the steel specimen was machined from the base metal away from the near-weld region and when the strain rate was increased to 4×10^{-6} sec^{-1}.

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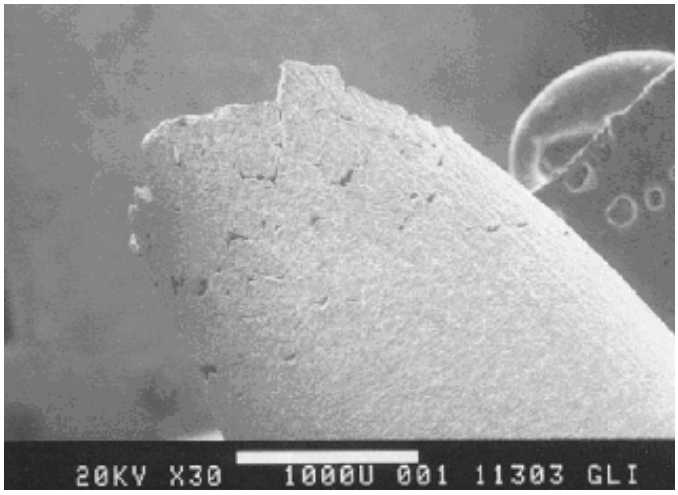


Note: Produced by SCC in laboratory environment.

Figure I.21—Close-Up SEM Photomicrographs of Fracture Surface

I.5.5.4 Study #4

A limited program was conducted that included a combination of electrochemical and SSR testing [42]. These tests were performed using synthetically prepared ethanolic environments with additions of 5% methanol and 1% water, and in a simulated fuel-grade ethanol based on the specifications of ASTM D 4806. These tests were conducted on specimens machined from API X 46 line pipe steel at room temperature at an initial strain rate of 1×10^{-6} sec^{-1}. No evidence of SCC was observed in 100% ethanol or when 5% methanol or 5% methanol plus 0.5% water was added. When a simulated fuel-grade ethanol was used as the test environment fissuring was obtained in the highly strained necked region as shown in Figure I.22.



Note: Fissures in necked region of specimen.

Figure I.22—SEM Photomicrograph of SSR Specimen Tested in a Simulated Fuel-Grade Ethanol Environment

Electrochemical cyclic polarization tests were also conducted on specimens of AISI 1018 carbon steel in the same environments used for the SSR tests. The results of these tests are given in Figure I.23. Based on the observations made from these tests, it was concluded that the shapes of the polarization curves were not characteristic of other environments where steels exhibit SCC which commonly have a well defined active-passive transition. The corrosivity of the simulated fuel-grade ethanol increased with increasing water content. The simulated fuel-grade ethanol environments (with and without water) were the only environments found to exhibit pitting and the formation of a dark film after polarization.

I.5.6 OTHER COMMENTS

I.5.6.1 Nature of Ethanol

Based on telephone interviews it became apparent that there are many theories and proposed mechanisms for SCC in fuel-grade ethanol. Particularly of interest was the fact that the manufacturers of fuel ethanol have not experienced SCC problems whereas several (but not all) users of fuel ethanol have experienced SCC. Therefore, many people believe that this may be caused by changes in the product through shipment and handling from the time the product leaves the manufacturing facilities to the time it arrives at the end user's facilities and is blended with gasoline.

The basic understanding of the nature of ethanol found in these discussions is that it is a polar molecule that can attract water, carbon dioxide and oxygen from the surrounding environment through contact with air, seawater and other fluids. This relates

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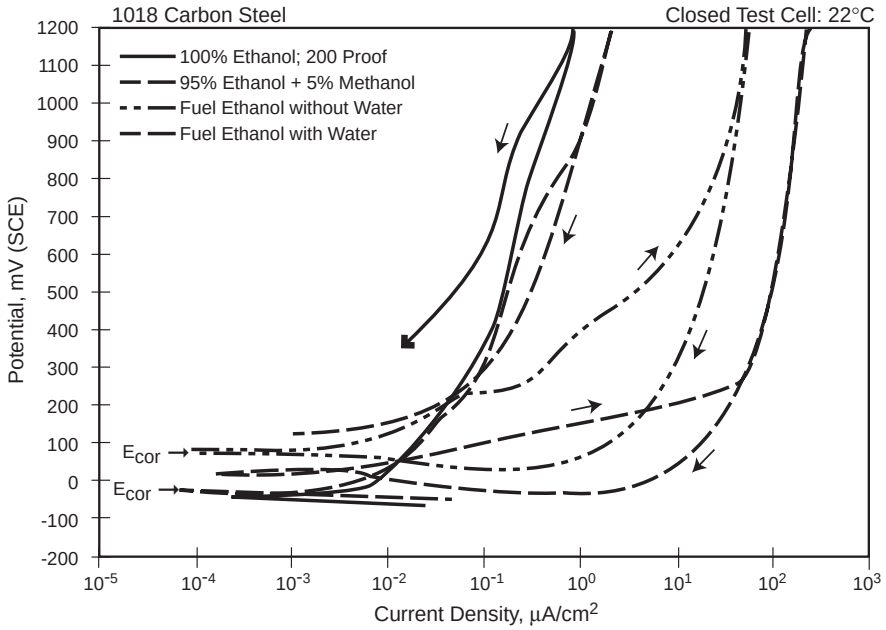


Figure I.23—Cyclic Polarization Curves for Carbon Steel in Ethanolic Environments

directly to some of the laboratory studies described herein that indicated that the water content increased even in a controlled laboratory setting. One end user who has not experienced SCC in fuel-grade ethanol problems indicated that they take efforts to make sure the equipment is clean and dry prior to the introduction of ethanol service. Once the ethanol is placed in storage tanks, it needs to be monitored so that the ASTM specifications are maintained.

Additionally, nearly all domestic manufacturers of fuel ethanol use inhibitors and many use Octel DC11. Another inhibitor mentioned was Baker Petrolite Tolad 3224. The attributes of the inhibitor usually include some degree of corrosion protection along with pH elevation. Inhibitor constituents were reported to be a dimer acid or fatty acid base amine added as a pH modifier and stabilizers (free radical scavenger). Some users have recognized that some inhibitors work better than others particularly in the ability to handle the pH adjustment and maintain it over time.

Most manufacturers add denaturants and inhibitors but many add these chemicals immediately prior to shipment. Therefore, one of the major differences in the service environment between end users and many manufacturers of fuel ethanol is the lack of additives, when the product is at the manufacturer's facilities.

Another common concern was for conversion of sulfur dioxide and water to form sulfuric acid. Several reports of decreases in pHe over time were reported.

I.5.6.2 Experiences with Ethanol

Many of the interviewees believed that SCC of steel equipment was basically a "West Coast" problem related to the use of foreign sources of ethanol that may be derived from wine (Europe) or sugarcane (South America). The survey and company reports presented herein confirmed that SCC in fuel-grade ethanol is not restricted to only West Coast operations. Cases of SCC were reported from nearly all parts of the United States including: Northwest, Southwest, Mid-Continent and Great Lakes regions. Furthermore, reports of SCC were found for end user operations that reported using foreign, foreign and domestic, and only domestic sources of ethanol.

Another difference between the practices used by manufactures and end users of ethanol reported in the survey was related to storage. Many manufacturers use internal circulation in ethanol storage tanks. None of the end users participating in this survey or telephone discussions reported using this technique. The circulation is designed to minimize variations in the tank. In contrast, it was noted that one end user report indicated that sulfate sludge was present on the bottom of the ethanol tank. Another end user reported higher water content in the ethanol on the bottom of the tank than found in the middle or upper portions of the tank.

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I.5.6.3 Design and Stresses

The presence of SCC in highly stressed or flexural locations was also confirmed in the survey. The survey and the follow-up telephone interview revealed that in one of the first reported incidents of SCC in the early 1990s, the influence of stress condition was confirmed. Four new tanks were installed and were identified to have a non-standard weld configuration and also had an inclusion line at the point of failure. The three remaining tanks with the same weld configuration in ethanol service were modified to a lower stress weld geometry and the failed tank was repaired in a like manner. No further evidence of SCC in fuel-grade ethanol has been found.

Several respondents cited qualitative experience that indicated that in addition to high tensile stresses, stress concentration and flexural loading may also be key aspects in SCC in fuel-grade ethanol initiation and growth. High turnover rates (loading and unloading of the tanks) lead to repeated flexing of the tanks. One unconfirmed report was made that inland barges may also have experienced SCC as a result of the flexural loading common to this mode of transportation.

I.6 Other Sources of Information

I.6.1 INFORMATION FROM THE MATERIALS TECHNOLOGY INSTITUTE (MTI) OF THE CHEMICAL PROCESS INDUSTRIES

MTI Publication 15, *Guidelines for Preventing SCC in the CPI*, is a major reference for the chemical process industry documenting the occurrences of SCC in chemical process environments. It was authored by Dale McIntyre and Paul Dillon and includes over 50 years of experience with SCC in various process environments. Under "Miscellaneous Environments" for steels, this publication lists the following as causative agents for SCC in steel:

a. carbonates,
b. H_2O-CO-CO_2,
c. cyanide,
d. amine,
e. fluoride, and
f. phosphates.

Prior to the use of fermentation/distillation processes to produce ethanol, industrial experience had included the production of ethanol by two processes. Initially, the process was via ethyl sulfate hydrolysis after absorption of ethylene in concentrated sulfuric acid. Later developed was a process of direct hydration of ethylene to make the ethanol.

From one major manufacturer, commercial ethanol included the "pure" product (200 proof) along with 43 different denatured grades. In general, these have been handled in carbon steel. The only exception was if the tank had a large area-to-volume ratio and problems of iron contamination of product were involved. There has been no documented experience of SCC in carbon steel by any mechanism.

A selection of MTI members were polled on a confidential basis for their experience with ethanol and associated SCC of carbon steel. One member stated that it has many years of failure-free experience with absolute alcohol made by hydrogenation of ethylene. Another manufacturer has made 200-proof ethanol from ethylene and has not seen any evidence of SCC. It was the belief from these discussions that the current series of SCC is associated with "biological" alcohol, distilled from grain, sugar, grapes, etc., and thus may contain low levels of contaminants. However, the exact nature of the contamination was not conclusively known.

It was further mentioned that there could be critical ranges of water content and acid in the alcohol derived from fermentation and distillation, which promote SCC. The main SCC agents being suspected are trace amounts of formic acid and/or acetic acid. It was also suspected that some denaturants might have an effect and were thus worth investigating. Additional suspicions were that SCC in fuel-grade ethanol could be induced in a relatively narrow range of pH and water content. Recommendations included checking the incoming alcohol for acetaldehyde, which is easily oxidized to acetic acid.

It was related that there were MTI forum notes from past years, which are posted on the MTI web site, that addressed this issue and are available to member company representatives. One company noted that they had seen SCC in fuel-grade ethanol from a South American source (probably ethanol distilled from sugar fermentation) that they attributed to contamination by organic acids and carbon disulfides.

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I.6.2 NACE REFINCOR

A review was conducted of RefinCor, which contains the minutes of the information exchanges from the NACE STG 34 committee on refinery corrosion and its precursor NACE Committee T-8. This source references open discussions back to the 1980s. The version searched was RefinCor 5.0 which includes the minutes through 2000. The review was based on a keyword search using the word "ethanol". All but a few references were to SCC in fuel-grade ethanol of steel tanks and piping. These are summarized below.

1980. During a review of NACE RefinCor software, the first reference to fuel ethanol was found in 1980 (80C13.1-01) indicating severe pitting in an aluminum truck trailer carrying 100% ethanol for mixing into gasohol with 5% water. Aluminum is evidently acceptable when the ethanol contains low amounts of water, but above 0.03% water, pitting can be a problem. The following discussion (80C13.1-02) indicated a similar effect of water in ammonia, where 0.2% water is required to inhibit SCC in carbon and low-alloy steel tanks or truck trailers.

1995. In a marketing facility, two tanks used for storing ethanol for blending were reported to exhibit intergranular SCC in the CS tank floors (95C5.2-01). It was limited to areas between two fillet welds about 2.5 cm (1 in.) apart resulting in a high-restraint area, but acceptable per API 650. One tank was double bottomed and was only in ethanol service. The ethanol product was from Europe; however, it was processed further in South America, ultimately being delivered in Washington state. The ethanol was reported to have a relatively low water content, but no specifics were given.

The following discussion (95C5.2-02) indicated that ethanol produced in the states is normally enzyme dried and distilled. An important note was also made that, this was why fresh ethanol for gasoline can pass a rusting test when fresh, but after several weeks, it may not because of free sulfuric acid.

1998. Another operator described an intergranular SCC in an ethylene evaporator vessel (98C5.14-09) that was part of a liquid ethylene storage facility related to a lube unit. This was one of four vessels. There was a possibility of a steam leak into the vessel about ten years prior to this cracking incident which could have resulted in a 10% ethanol/water mixture.

1999. Two intergranular SCC failures of ethanol storage tanks were described where cracking was observed in or around the heat affected zone (99C5.15-010). Laboratory work confirmed that addition of water of 1% could inhibit SCC of steel; however this was not desirable for fuel ethanol. The plan was to replace the bottom of the tanks and coat them. Further investigations of related piping revealed SCC. All of these cases, SCC was observed with ethanol purchased from overseas sources and not with domestic ethanol.

There was further discussion in 1999 (99F5.14-01) by the same presenter. It was indicated that one reason for the present concern about SCC in fuel-grade ethanol was because MTBE was being replaced with ethanol as a fuel oxygenate. There were suspicions that the source of ethanol may be contributing to SCC or that it may be possibly due to contaminants in the ethanol. The cracking was described as looking like classic intergranular carbonate cracking at weld heat-affected zones. Remedial measures being used included coating welds in tanks and post weld heat treatment of repairs in piping. There were no other contributions to the discussion at that time.

2000. The same presenter from 1999, indicated that they had become aware of more instances of SCC in ethanol service (2000C5.14-01). They had since started some laboratory testing to try to identify the specific species in the ethanol that might be responsible and what additions to ethanol would prevent this. This is potentially a big problem since there was to be a lot of piping and tanks in ethanol service in California in the near future. They had also coated several tanks by this point and that, as with anhydrous ammonia, water additions were very effective in preventing the SCC mechanism in the steel-ethanol system. However, the exact amount of water required for inhibition was not determined. Laboratory testing was planned, but there were concerns that with excessive water rusting and product contamination issues could arise.

Further discussion was presented by a second end user (2000C5.14-02) indicating that reportedly a tank had cracked after going into ethanol service in Washington state. There was also another case reported in a terminal in the eastern part of the United States. Another operator in Philadelphia was reported to have experienced leaks in three tanks and piping associated with the tanks in ethanol service. A pipeline operator has a procedure to immediately flush lines with gasoline after it has been in ethanol service and to not leave ethanol in segments of piping. However, these most recent cases were presented as second-hand information but they supported the fact that there is an issue. Getting first-hand information from ethanol service at terminals was difficult.

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Another presenter indicated that there is a major problem with ethanol, and in ASTM they have found that ethanol can contribute to gums and other problems in gasoline (2000C5.14-03). At that time, there were apparently three major producers of ethanol and several small private producers such as farm cooperatives. Cargill, Staley, and ADM were the three main producers at that time. Most major manufacturers stopped using facilities made from copper and have changed to stainless steel systems. One commonly observed phenomenon is that the fresh ethanol will usually pass a rust test. Because fuel ethanol is around 198 – 200 proof, it contains some water and over time it can form some sulfuric acid from the combination of sulfur dioxide and water. It was indicated that some reformulated gasoline will tend to corrode the brass in carburetors because of sulfuric acid corrosion.

In follow-up discussions, it was related that the ethanol being handled on the West Coast has not produced corrosion (2000C5.14-04). There was no measurable metal loss and the corrosion rates are essentially nil. The SCC experienced thus far had no accompanying corrosion. The cracking experienced was in tanks only. This user heard of SCC occurring in pipelines and was still investigating at the time of the presentation.

In further discussions (2000C5.15-06), a third presenter replied that they had problems in light-refined products, and ethanol. However, no mention of the nature of the ethanol problems were given.

Further discussions were presented later the same year where problems were reported in ethanol storage where they had two recent failures (2000C5.15-06). One was a pipe failure, the other was a strainer failure. SCC was suspected in both. It was related that grain-based ethanol may have a rust inhibitor which may also inhibit SCC of carbon steel. It may be possible that wine-based fermented product may not have this inhibitor. A failure analysis was pending.

Another user commented that they have marketed ethanol made from ethylene for many years. They never added inhibitor and never had SCC in ethanol tanks or service (2000F5.15-03). No comments were made from this user on the use of ethanol derived from corn, grain or other biomass.

2002. A presentation was made regarding a field SCC failure. It involved an ethanol storage tank in the Pacific Northwest. It was constructed in 1949 and a new floor was installed in 1991. It was predominantly a denatured ethanol service. It has been in that service since 1991 with one exception. For a short period it was used to store gasoline. A floor leak was observed in 2001. The tank was cleaned but the leak could not be found by vacuum box testing. WFMT was performed around the welds and numerous longitudinal cracks were found in the higher stressed areas. They were near the HAZ but about 0.25 in. – 0.375 in. into the base metal. In addition, every floating roof-seal spring failed.

All the cracks were intergranular. The microstructure of the steel was a mixture of ferrite-pearlite as would be expected. Because the cracks were intergranular, SCC was suspected. The floating roof-seal springs also showed intergranular crack morphology. The ethanol supply history could not be tracked and there was no information concerning contaminants in the ethanol.

Previously, there were lengthy discussions about corn-based (fermented) versus non-fermentation process ethanols. However, a determination of the cause of SCC could not be made. They did look into and found additional failures that had the same characteristics as SCC were found. All of the ethanol comes in by barge or ship on the Pacific and they buy ethanol from many different sources.

The cracks could not be seen visually. It took WFMPT to find them. It was surmised that internal coatings would be one mitigation technique and were wondering if inhibition might be used to minimize SCC susceptibility. The pHe was adjusted because of the updated ASTM standard for denatured ethanol requires a more limited range of pHe. The major ethanol suppliers already inhibit their ethanol.

I.6.3 NEWS SOURCES

A keyword search was conducted on LexisNexis™ at www.LexisNexis.com. This service provides access to legal, news, public records and business information; including tax and regulatory publications. The keywords used included “ethanol,” “ethyl alcohol,” “SCC,” “stress corrosion cracking,” “tanks,” and “storage tanks.” However, no relevant information was found relating this problem.

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I.7 Findings and Results

I.7.1 SUMMARY OF IMPORTANT FINDINGS

Based on the overall findings presented herein, several major findings were obtained. These include:

I.7.1.1 *SCC in fuel-grade ethanol is not just a "West Coast" problem limited to a few users that deal with foreign sources of ethanol*. This study has shown that SCC has been observed in equipment used to handle and store fuel ethanol and that it is not specific to any particular source, supplier, and geographic location.

I.7.1.2 *End users should not consider fuel-grade ethanol a "commodity." Fuel ethanol varies widely in composition.* However, there is presently no clear understanding of the influence of compositional variables that can occur in commercially available fuel ethanol.

I.7.1.3 SCC in fuel-grade ethanol does not take years to develop. *In some cases, failures occuring in less than one year have been reported.*

I.7.1.4 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.*

I.7.1.5 *Based on preliminary laboratory studies, the factors that increase corrosivity of fuel ethanol appear to be increased water content and decreased pHe.* Based on previous studies other potential factors may include sulfur, sulfate and chloride concentration.

I.7.1.6 *Based on existing information on other SCC phenomena in steels and other materials, it is not expected that parameters that increase corrosivity of the fuel ethanol will necessarily produce increased susceptibility to SCC.* When reviewing the conditions that produce SCC in other systems, the most severe susceptibility to cracking usually occurs under a defined set of conditions between regions of passivity and active general corrosion. Under these conditions (that also include electrochemical potential), cracking commonly occurs where local anodic attack can prevail and promote initiation of cracking.

I.7.1.7 *Based on preliminary laboratory studies, SCC has been produced in a sample of fuel ethanol that apparently does not contain denaturants or inhibitors.* This type of sample could serve as a basis for future studies to better understand the role of parametric effects on SCC in fuel-grade ethanol.

I.7.1.8 *SCC in fuel-grade ethanol has been reproduced in laboratory tests in fuel ethanol samples obtained from the field.* U-bend specimens and slow strain rate (SSR) tensile specimens have been used to evaluate specific stocks for SCC. These specimens provide for high levels of plastic strain and/or dynamic straining that appear to promote cracking.

I.7.1.9 *Evidence of out of specification ethanol has been reported*. Data shows that excessively low pHe, high sulfur and varying water contents can occur. However, the relationship (if any) of these parameters to SCC is not clear at this time.

I.7.1.10 *Some evidence has been generated based on laboratory results, which indicates that material from the near weld region in the base metal may have a greater susceptibility to SCC than base metal.* This region has been shown to have greater susceptibility in laboratory tests than base metal specimens from the same plate.

I.7.1.11 *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-CO_2-water and carbonate-bicarbonate SCC.

I.7.1.12 *The economic impact of SCC in fuel-grade ethanol service in end user facilities has been well over $1 million in direct costs in the last few years. Ethanol usage and facilities will increase substantially within the coming few years leading to increased risk of SCC in fuel-grade ethanol and its associated direct costs.*

I.7.1.13 *A variety of remedial actions are being used to mitigate SCC of steel equipment in ethanol service.* Remedial actions include use of coatings and selective use of PWHT and stress relief.

I.7.2 GAP ANALYSIS

Based on the findings of this study the following gaps are recognized that should be addressed in future research studies:

I.7.2.1 *Some end users have misconceptions about SCC in fuel-grade ethanol, thinking that it is a "West Coast" problem, ethanol is a "commodity" and cracking only occurs after 6 – 8 years.* The findings of this study indicate that SCC failures have

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