

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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Downstream Segment

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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). This 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.

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 potential dynamic 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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