# 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

AMERICAN PETROLEUM INSTITUTE

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

**Downstream Segment**

API TECHNICAL REPORT 939-D
SECOND EDITION, MAY 2007


Prepared under contract for API by:

Honeywell Process Systems (Parts I and II)
Dr. Russell D. Kane
Dr. David Eden
Anand Venkatesh

CC Technologies Laboratories, Inc. (Part IV)
Michael P.H. Brongers, P.E.
Dr. Arun K. Agarwal
Dr. John A. Beavers

Southwest Research Institute® (Part III)
Dr. Narasi Sridhar
Dr. Julio Maldonado
Elizabeth Trillo, Ph.D.


ADDENDUM 1, OCTOBER 2013


Prepared under contract for API by:

iCorrosion LLC (Part V)
Dr. Russell D. Kane

Honeywell Process Solutions (Parts VII and VIII)
Dr. Anand Venkatesh
Mark Yunovich

Southwest Research Institute® (Parts VI and IX)
Dr. Elizabeth Trillo



energy API®
AMERICAN PETROLEUM INSTITUTE

## Special Notes

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

Neither API nor any of API's employees, subcontractors, consultants, committees, or other assignees make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or usefulness of the information contained herein, or assume any liability or responsibility for any use, or the results of such use, of any information or process disclosed in this publication. Neither API nor any of API's employees, subcontractors, consultants, or other assignees represent that use of this publication would not infringe upon privately owned rights.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any authorities having jurisdiction with which this publication may conflict.

API publications are published to facilitate the broad availability of proven, sound engineering and operating practices. These publications are not intended to obviate the need for applying sound engineering judgment regarding when and where these publications should be utilized. The formulation and publication of API publications is not intended in any way to inhibit anyone from using any other practices.

Any manufacturer marking equipment or materials in conformance with the marking requirements of an API standard is solely responsible for complying with all the applicable requirements of that standard. API does not represent, warrant, or guarantee that such products do in fact conform to the applicable API standard.

All rights reserved. No part of this work may be reproduced, translated, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 1220 L Street, NW, Washington, DC 20005.

*Copyright © 2007, 2013 American Petroleum Institute*

## 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.

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

This document was produced under API standardization procedures that ensure appropriate notification and participation in the developmental process and is designated as an API standard. Questions concerning the interpretation of the content of this publication or comments and questions concerning the procedures under which this publication was developed should be directed in writing to the Director of Standards, American Petroleum Institute, 1220 L Street, NW, Washington, DC 20005. Requests for permission to reproduce or translate all or any part of the material published herein should also be addressed to the director.

Generally, API standards are reviewed and revised, reaffirmed, or withdrawn at least every five years. A one-time extension of up to two years may be added to this review cycle. Status of the publication can be ascertained from the API Standards Department, telephone (202) 682-8000. A catalog of API publications and materials is published annually by API, 1220 L Street, NW, Washington, DC 20005.

Suggested revisions are invited and should be submitted to the Standards Department, API, 1220 L Street, NW, Washington, DC 20005, standards@api.org.

## 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.

## 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.

## 939-D Contents


Page

Part I Literature Review and Phase I Experience Survey . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 1

Part II Phase II Experience Survey and Corrosion Field Monitoring . . . . . . . . . . . . . . . . . . . . . . 49

Part III Identification and Mitigation of Factors Causing SCC in Fuel-Grade Ethanol . . . . . . . . 115

Part IV Causes of SCC and the Influence of Contaminants in Fuel-Grade Ethanol. . . . . . . . . . 151

Part V Ethanol SCC Field Survey Update and Review of Recently Published Literature . . . . . 175

Part VI SCC of Carbon Steel in Fuel Ethanol Environments . . . . . . . . . . . . . . . . . . . . . . . . . . 207

Part VII Fracture Evaluation of Notched SSR (N-SSR) Specimens . . . . . . . . . . . . . . . . . . . . . . 233

Part VIII Ethanol SCC Research on PWHT Effects and Threshold Stress Determination . . . . . . 253

Part IX Ethanol SCC Studies—Composition, Round Robin, and Statistical Matrix SSR Testing . . 301

# Part I

# Literature Review and Phase I Experience Survey

AMERICAN PETROLEUM INSTITUTE

# Part I Contents

Page

I.1 Executive Summary . . . 1

I.2 Introduction . . . 2
I.2.1 Scope . . . 2
I.2.2 Technical Basis . . . 2
I.2.3 Technical Approach . . . 2

I.3 Background . . . 3
I.3.1 Ethanol—Description of Manufacture, Distribution, Storage, and Use . . . 3
I.3.2 Significance of SCC Problem. . . . 5
I.3.3 Potential Magnitude of Risk to Assets . . . 6

I.4 Review of Published Literature . . . 6
I.4.1 Corrosive Attack in Organic Media . . . 6
I.4.2 Corrosion and SCC in Ethanolic Environments . . . 8
I.4.3 Corrosion and SCC in Alcohol Containing Environments . . . 16
I.4.4 SCC of Steel in Other Environments. . . . 20
I.4.5 External SCC of Steel Pipelines. . . . 24

I.5 Company Reports and Experience Survey on SCC in Fuel-Grade Ethanol . . . 25
I.5.1 Materials . . . 25
I.5.2 Metallurgical and Microstructural Aspects of Cracking in Plate and Pipe . . . 25
I.5.3 Environmental Parameters. . . . 29
I.5.4 Mechanical Factors . . . 31
I.5.5 Unpublished Laboratory Studies. . . . 32
I.5.6 Other Comments . . . 35

I.6 Other Sources of Information . . . 36
I.6.1 Information from The Materials Technology Institute (MTI) of the Chemical Process Industries . . . 36
I.6.2 NACE RefinCor . . . 37
I.6.3 News Sources . . . 39

I.7 Findings and Results . . . 39
I.7.1 Summary of Important Findings . . . 39
I.7.2 Gap Analysis . . . 40

Bibliography . . . 46

Figures
I.1 Comparison of Electrode Potentials of Metals in Different Solvents: Including Water, Methanol, and Ethanol . . . 7
I.2 Corrosion Rate (icorr) of Zinc, Iron, and Nickel in Primary Alcohols Plotted Versus Carbon Number of Solvent: Methanol (C =1); Ethanol (C = 2) . . . 9
I.3 The Corrosion Rate (K, Cor) and Final Corrosion Potential ($E_{H2}$, $\gamma_{H2}$) of Steel in Ethanol/Water Solutions. . . . 10
1.4 Influence of Concentration of Inhibitors. . . . 10
I.5 The Polarization Behavior of Aluminum Alloy in Water/Ethanol Solution . . . 11
I.6 Polarization Behavior of Steel in Methanolic Solutions . . . 12
I.7 Polarization Behavior of Steel in Ethanolic Solutions . . . 12
I.8 Susceptibility to SCC in Methanol versus Water Content . . . 17
I.9a Influence of Water on SCC of Zr-alloy in Hydro-methanolic Media ($W$ = Fracture Energy; $W_o$ = Fracture Energy in Air) . . . 19