ETHANOL AND STRESS CORROSION CRACKING IN PETROLEUM STORAGE TANKS AND PIPELINES

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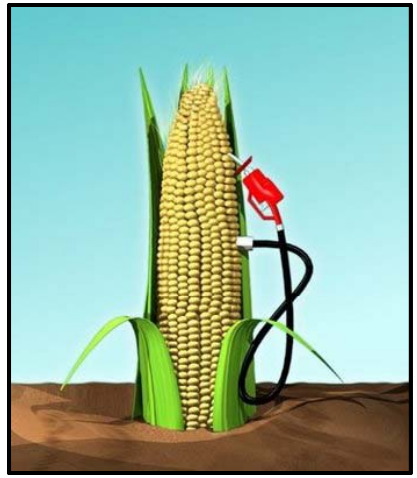
Acknowledgements

- Contributors to the API Ethanol SCC Effort and Information in this Presentation:
  - Honeywell Process Solutions
    - Experience surveys, technical oversight, lab & field testing/monitoring, guidelines development
  - Southwest Research Institute
    - R&D on parametric effects in ethanolic environments and evaluation of samples retrieved from the field
  - CC Technologies (DNV)
    - Identification of key testing variables, role of steel grades and confirmational tests
  - API Committee Leadership
    - Leigh Klein (BP) and Jim Edmondson (Shell)

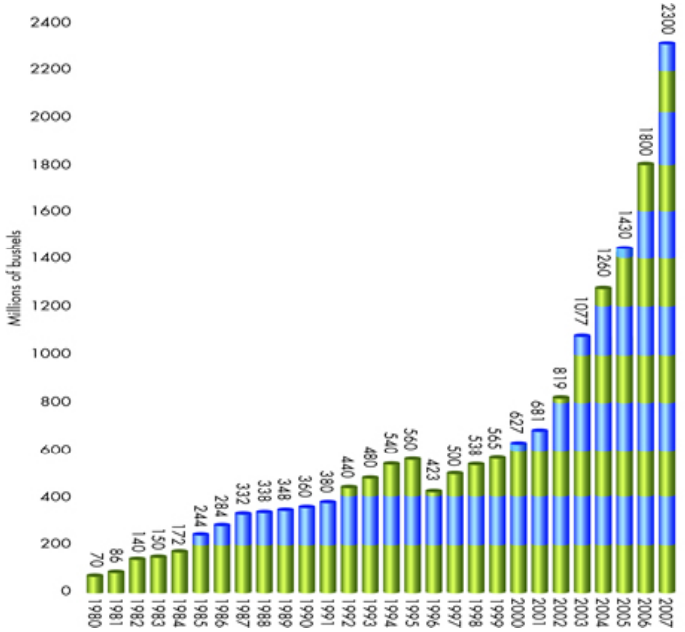


Organization

- Background
  - Production/Demand for Fuel Ethanol; What is SCC?
- Review of API 939D Research Report
  - Major conclusions
- Summary of subsequent R&D work:
  - Conclusions…. Correlations…. Impact
  - Source/production methods
- Update on 939E Technical Bulletin
  - Guidelines for protecting infrastructure
- Future/subsequent R&D work

U.S. Fuel Ethanol Production / Demand

- U.S. production has been growing since 1980's, especially since 2000
- Increased demand for ethanol as fuel oxygenate, extender, and U.S. government policies
- Future will require increases due to US government mandates for 2012 and 2020.



U.S. Distribution System for Fuel Ethanol

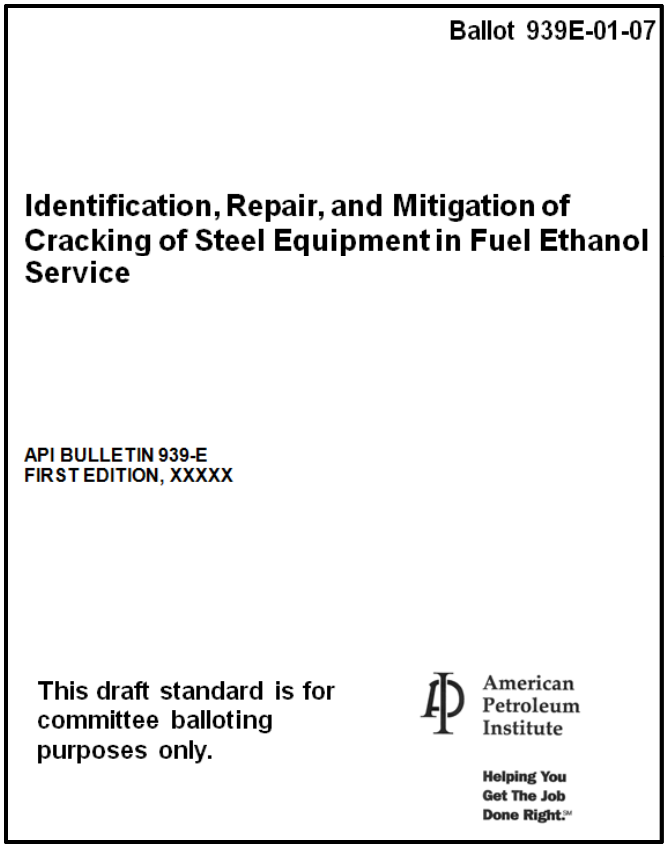
- Fuel ethanol has been delivered mainly by batch movements to oil company blending facilities for conventional (E10) blends involving:
  - Barge
  - Tank truck
  - Rail tanker car
  - Hold up at intermediate liquids terminals
  - Sometimes short dedicated pipeline segments
  - Blending facility tanks and loading/blending rack piping to produce E10 gasoline blends.
- E85 blends are not widely transported.
  - Usually, blended during final transport to consumer distribution point.
- As volumes for fuel ethanol increase, pipelines are a natural means of transport – new in the U.S.

API Effort on SCC in Fuel Ethanol

- Started in 2003 – API Refining Committee (Subcommittee on Corrosion & Materials) started with an experience survey and white paper – API 939D (1st Edition - 2003)
  - Included ethanol users, producers and mid-stream distribution
  - Performed with assistance by the Renewable Fuels Association
  - Focus was to determine the extent of existing SCC problem & better explain its basis
- Followed by additional survey, lab research and testing and field monitoring – results in API 939D (2nd Edition – 2007)
  - Develop a better explanation for SCC occurrences and process variables that might be used for control

API Effort on SCC in Fuel Ethanol - 2

- While the API research effort continued, the emphasis was augmented to include the dissemination and use of program information thru development of 939E – Technical Bulletin
- Guidelines for identification, mitigation and repair of ethanol SCC.
- API 939E has completed second balloting
  - Final version to be published by API within the next 60 days.



Ballot 939E-01-07

Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service

API BULLETIN 939-E
FIRST EDITION, XXXXX

This draft standard is for committee balloting purposes only.

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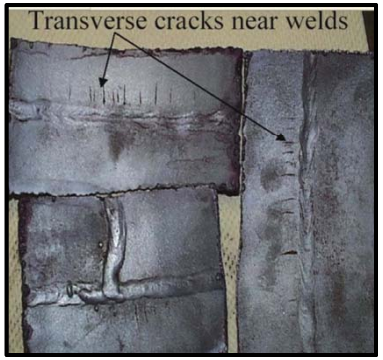
API 939D – What We Know - 1

- Over 20 field cases of SCC were identified in the survey & documented in API 939-D:
  - No cases of SCC were reported in manufacturer facilities, tanker trucks, railroad tanker cars or barges
  - SCC in mid-stream fuel ethanol distribution storage tanks, oil company storage and blending facilities (steel tanks, rack piping and components); one short pipeline segment.
  - No cases of SCC following blending of fuel ethanol into conventional E10 gasoline.

API 939D – What We Know - 2

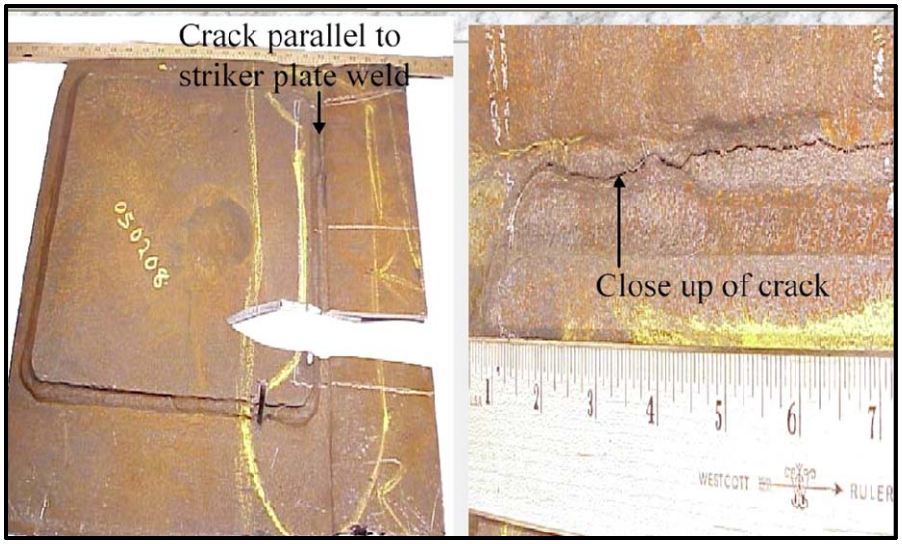
- Locations of SCC failures/leaks
  - Tank bottoms, lower shell and floating roofs
  - Loading rack piping (butt and tack welds)
  - In-line equipment (air eliminator head)
- Important aspects of SCC
  - High/variable stress locations
  - Normally near but not in welds
  - Within D4806 specification, in domestic production, & coast-to-coast
  - More often in aerated or turbulent conditions
  - Many steel grades
  - Coatings & PWHT are preventives



API 939D – Other Cases of SCC

Rack Piping

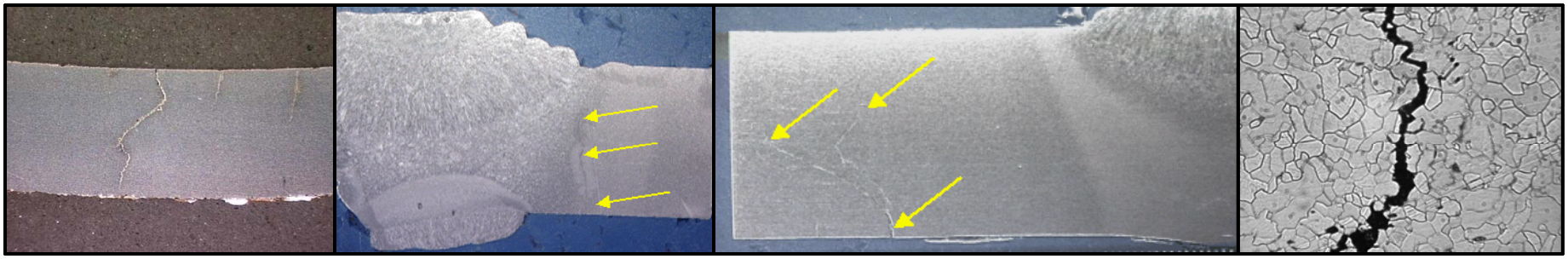
Tanks



High stress locations

Near but not in welds

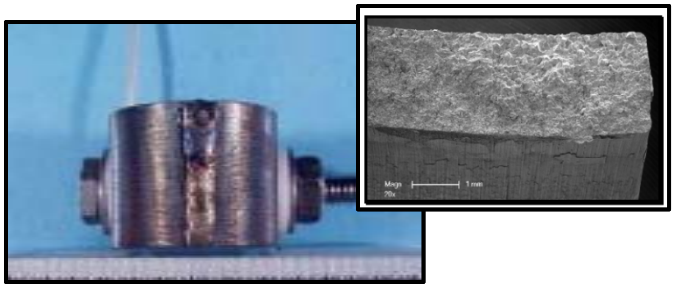
Mostly intergranular SCC

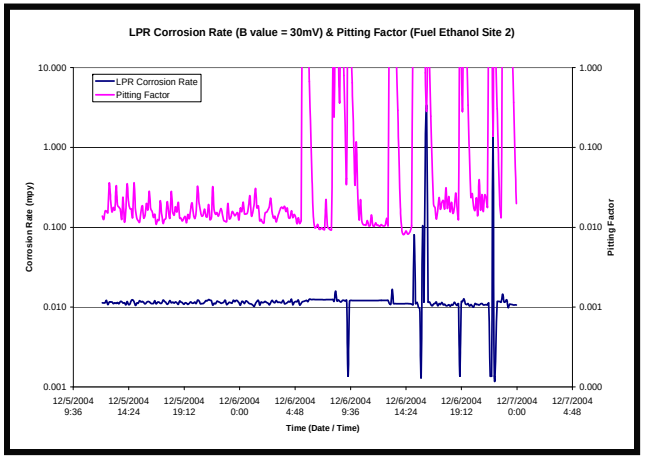


" No SCC in some locations, but more than one episode of cracking at a facility was reported in several cases"

API 939D – Conventional Monitoring

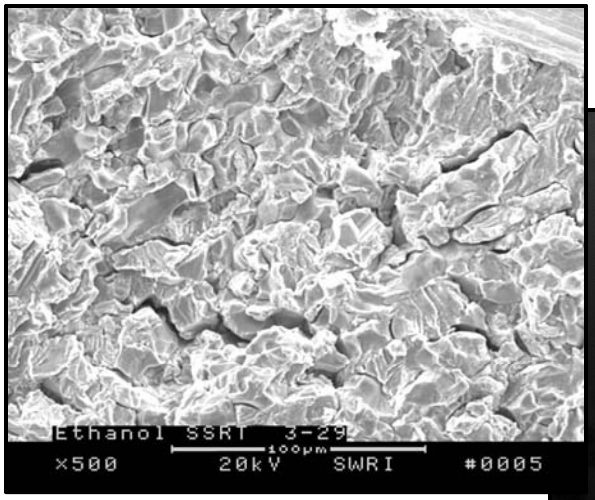
- Conducted two types of monitoring:
  - "Passive" monitoring – U-bend SCC specimens
    - No cracking – over 12 months
    - Did not successfully re-create weld profile, stress concentration, and mill scaled/clean surfaces
    - Eventually overcome
  - "Active" monitoring using electrochemical techniques
    - High corrosion rate & pitting associated with aeration & turbulence.

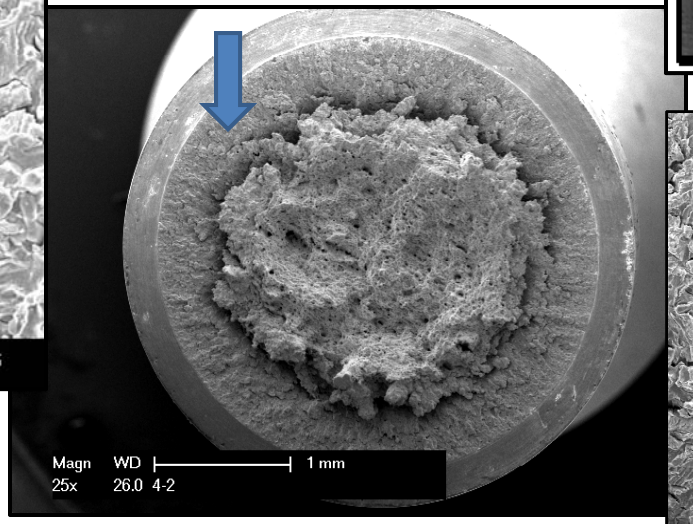


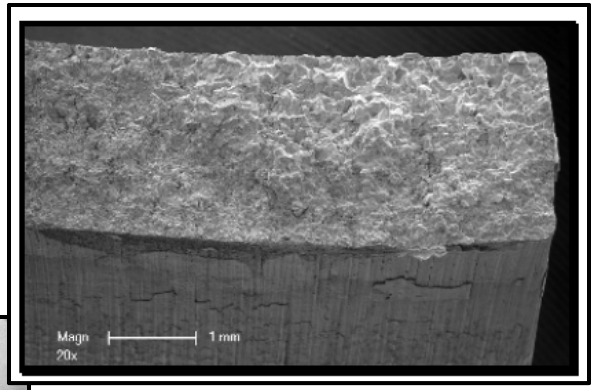


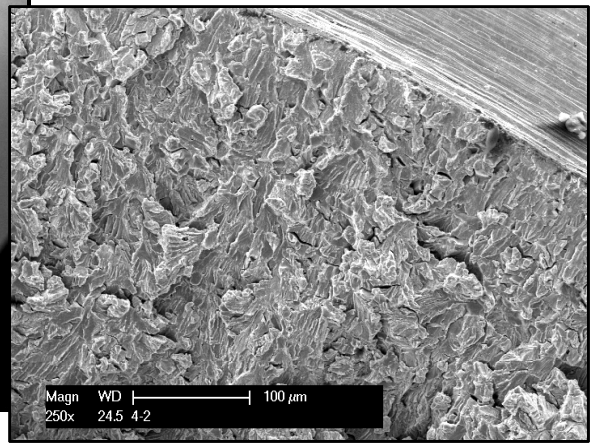
API 939D – From Research

- Lab ethanol SCC tests produced similar cracking modes to field ethanol SCC failures.

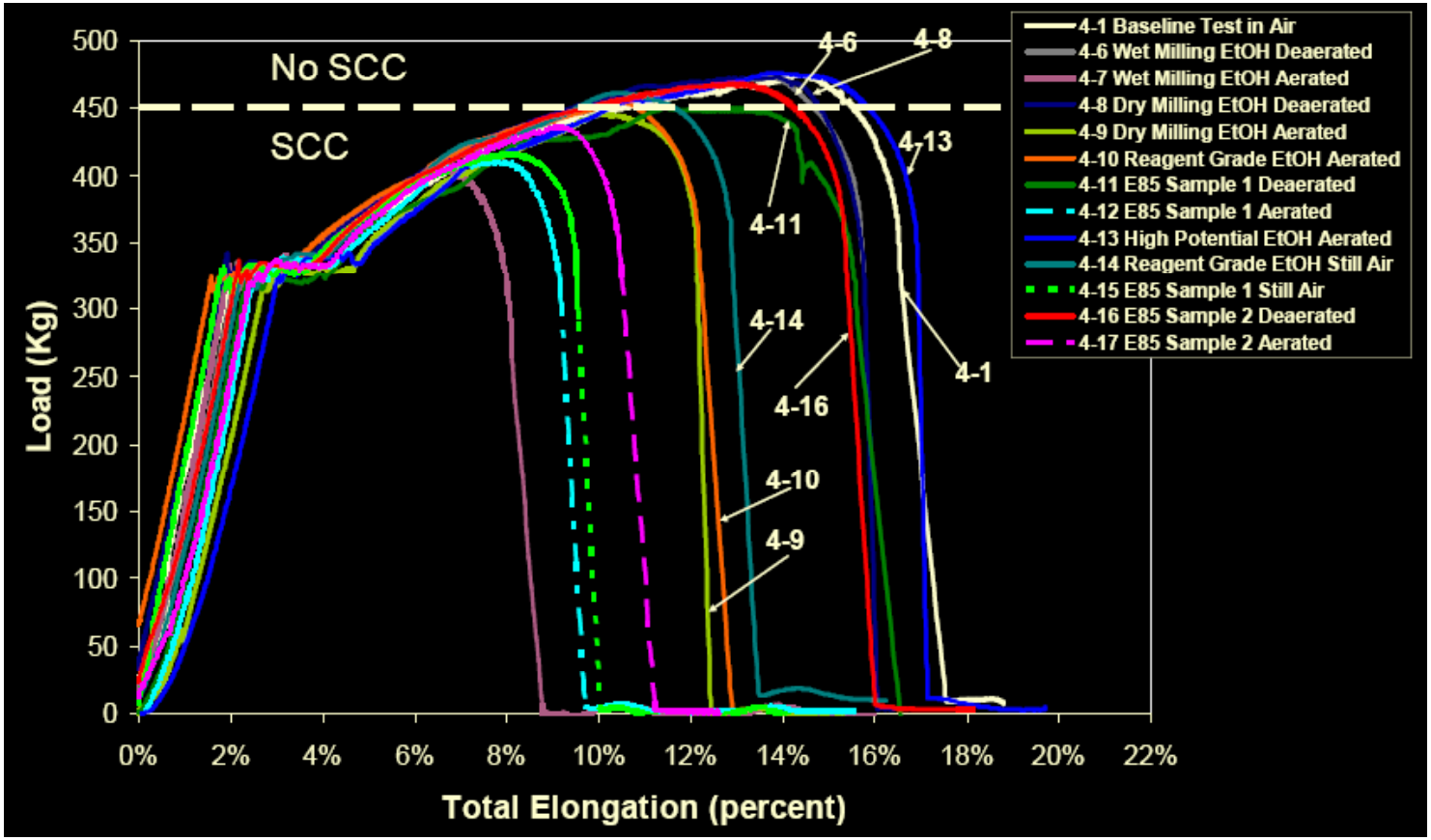






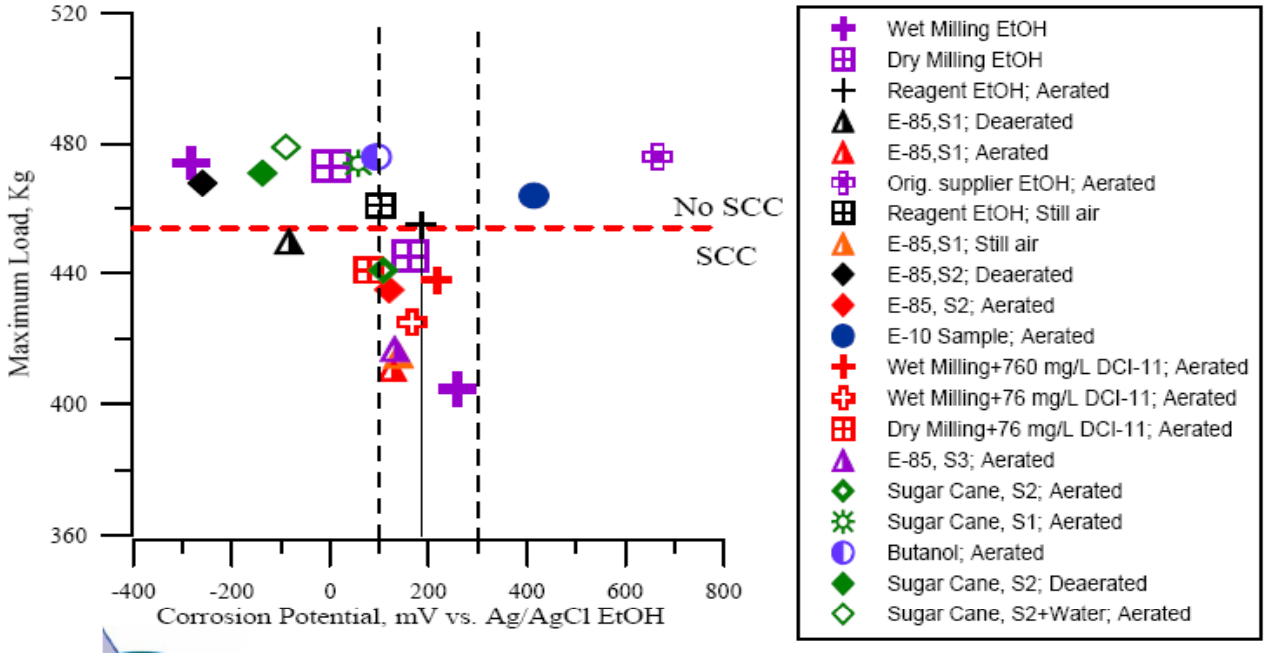


Ongoing API Research



- Based on a simple lab evaluation, a range of SCC susceptibility was identified in field ethanol samples and in E-85 fuel.

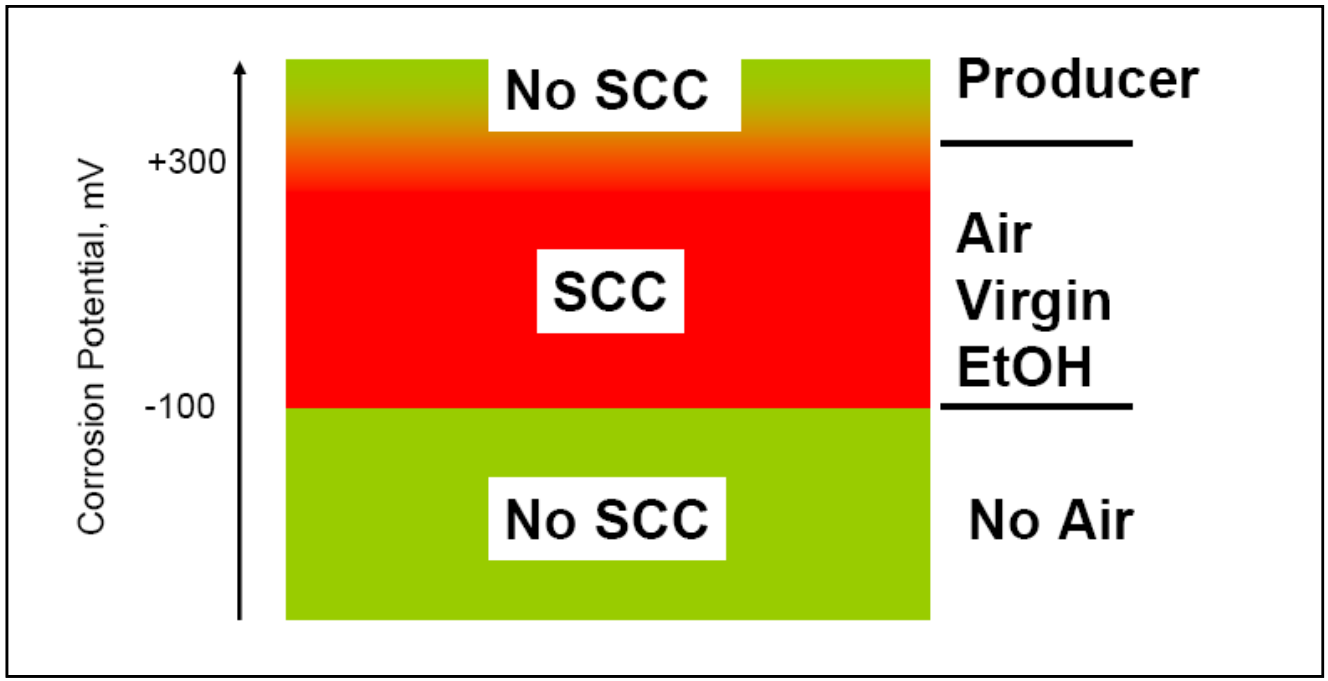
Evaluation Criteria for SCC Failures



- Ethanol processing methods (wet vs. dry milling), ethanol source (corn vs. sugarcane), aeration and water content can affect SCC susceptibility.

From Ongoing API Research

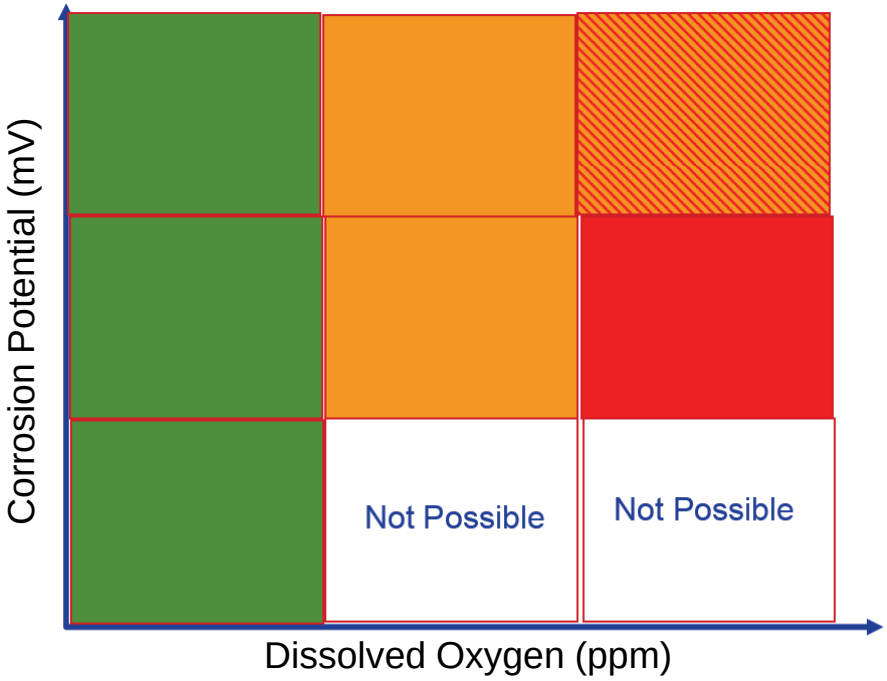
- In lab testing, cracking in fuel ethanol samples occurs over a limited range of electrochemical potential
  - Approx. -100 mV to +300 mV with chlorides per ASTM D4806
  - Approx. +100 mV to +300 mV without chlorides



Potential vs. Ag/AgCl(EtOH) reference electrode

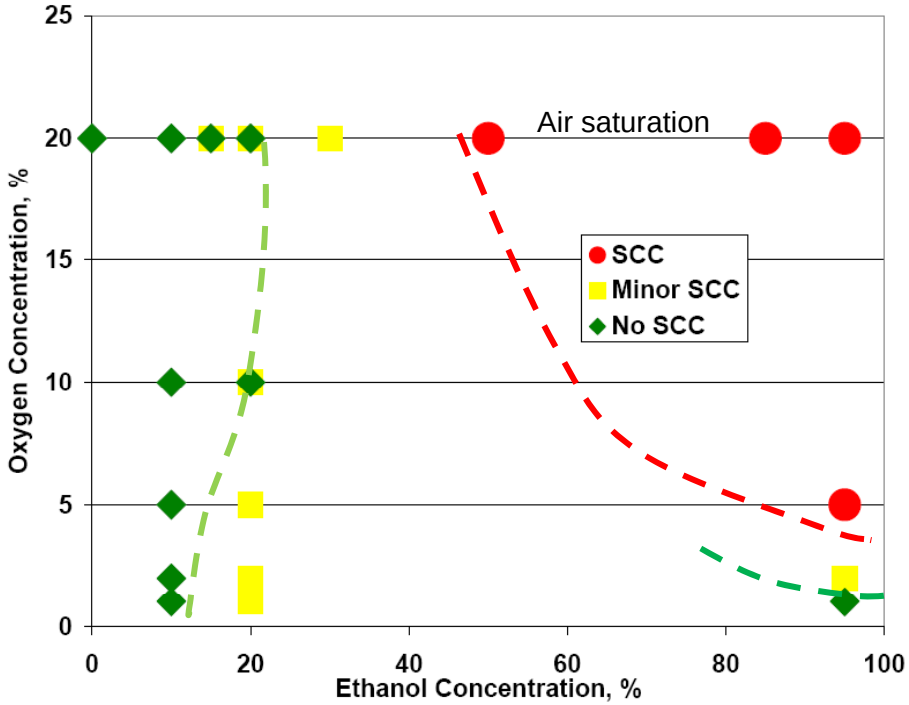
API 939D – New Monitoring Efforts

- SCC can occur in ethanolic environments with the ASTM D4806 specification!
  - Oxygen from aeration is the most significant promoter
  - Chloride and methanol increase SCC susceptibility, but were not essential for SCC to occur.
  - Galvanic contact of the SCC specimens with pre-corroded steel also exacerbated SCC.
  - Corrosion potential and dissolved oxygen may be an indicators of susceptibility to SCC in fuel ethanol. API to start a tank monitoring task.



From Other Research Programs

- Pipeliners are particularly interested in the effects of aeration and transmixtures common for batch pipeline transport with other hydrocarbon fuels
- Data indicates prevention of SCC can be obtained at 5 -10 percent of air saturation levels and in ≤20% ethanol blends.
- More data is needed to complete this picture.



API 939E – Ethanol SCC Guidelines

- This effort is based on “lessons learned” from API survey and research in a form more accessible and usable for field personnel.
- The focus of this document is on:
  - Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service
  - It is based on current engineering practices involving other forms of SCC in carbon steel equipment and insights from the API research effort.

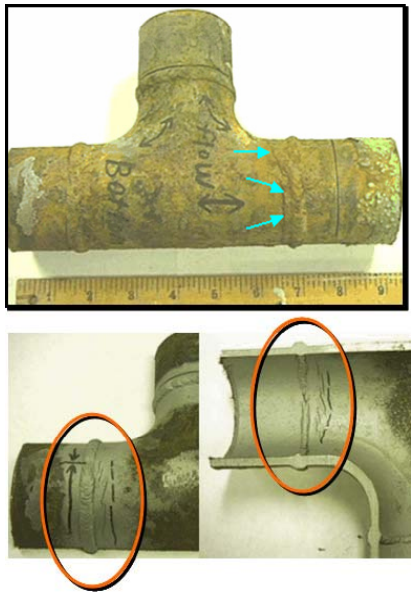
API 939E – Ethanol SCC Guidelines

Important

- Older equipment may not conform exactly to API 939E, but this does not imply that such equipment is being operated in an unsafe or unreliable manner
- It is recognized that facilities may vary and may need to be modified depending on specific operating conditions, inspection and maintenance experience
- Each user company is ultimately responsible for its own safe and reliable operations.

API 939E – Major Components

- Ethanol background, definitions & specifications
- Citing of SCC examples
  - Failure listing from 939D; also mention a short terminal-refinery pipeline segment that failed by SCC
- Summary of likely SCC locations and conditions
- Guidelines for new construction & fabrication
  - Minimize the use of lap seam welds
  - Minimize cold working and plastic deformation
  - Use of PWHT – mainly piping welds
  - Use of ethanol immersion coatings for tanks
  - Use adequate foundations and pipe supports to reduce tensile stresses and flexural loading.



API 939E – Major Components - 2

- Inspection of existing equipment
  - References to API 653, API 574, API 510 and API 570 as relevant to specific equipment
  - Inspection for SCC is complicated – cracks are tight and can not be easily seen; leakage
  - Inspection intervals versus risk – cases of SCC have been observed in less than 12 months
  - Prioritization based on severity of service, location, prior cracking experience
  - Inspection methods include:
    - Visual, WFMT, SW-UT, EM-ACFM, eddy current
    - Destructive sampling & testing (ethanol SCC confirmation is recommended) where possible.

API 939E – Major Components - 3

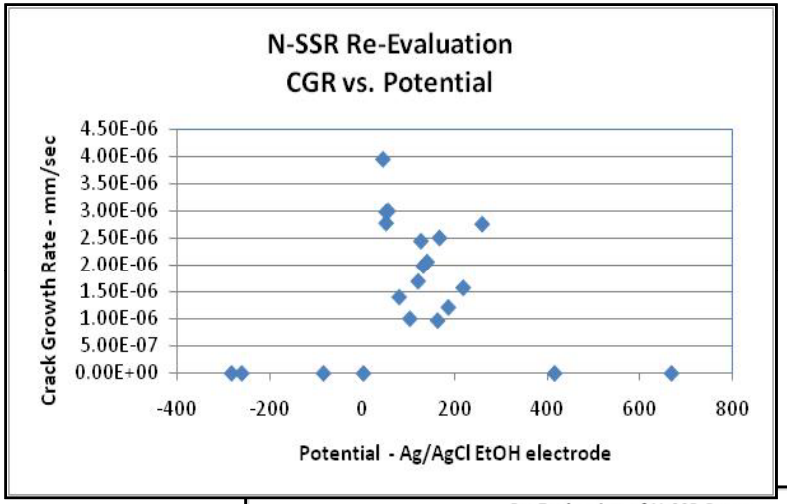
- Assessment & Repair of SCC Damaged Equipment
  - Assessment of fitness-for-service and risk – Methods of API 579 applicable. Similar to other forms of SCC in steel.
  - Temporary patches and permanent repairs (PWHT &/or coatings)
  - With and without SCC mitigation
  - Repairs by grinding, flame or arc gouging/cutting, welding
- Monitoring
  - Sampling of ethanol per ASTM D4806 – has limitations
  - Monitoring corrosion, SCC, corrosion potential, dissolved oxygen.

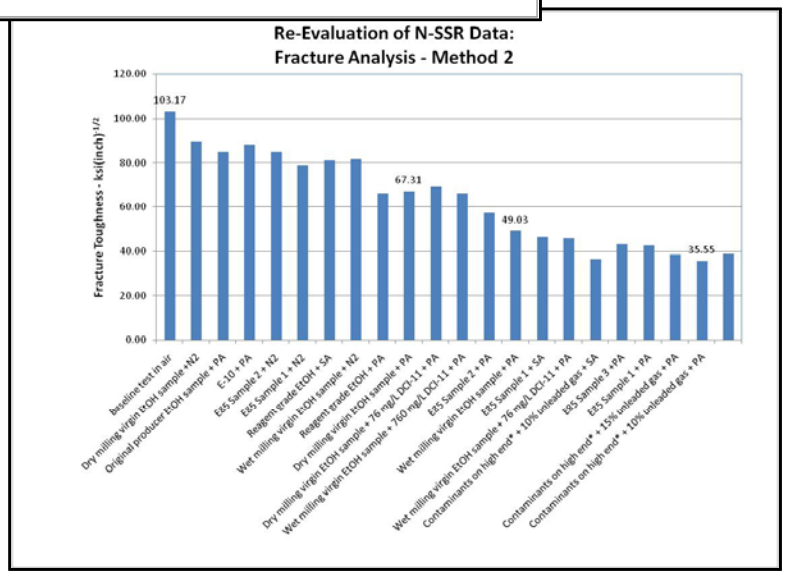
Topics of Interest for API Research

- Fuel ethanol source and composition
  - Differences in source & manufacturing method (e.g. corn, sugarcane, other ethanol feedstocks)
  - Are there natural inhibition or promoter compounds?
- Field monitoring of corrosion potential & dissolved oxygen as indicator of SCC conditions
- Threshold stresses for SCC vs. specification of PWHT (time/temperatures)
- SCC crack growth rates & driving forces
- Standardized test method(s) for SCC

Crack Growth & Fracture Mechanics

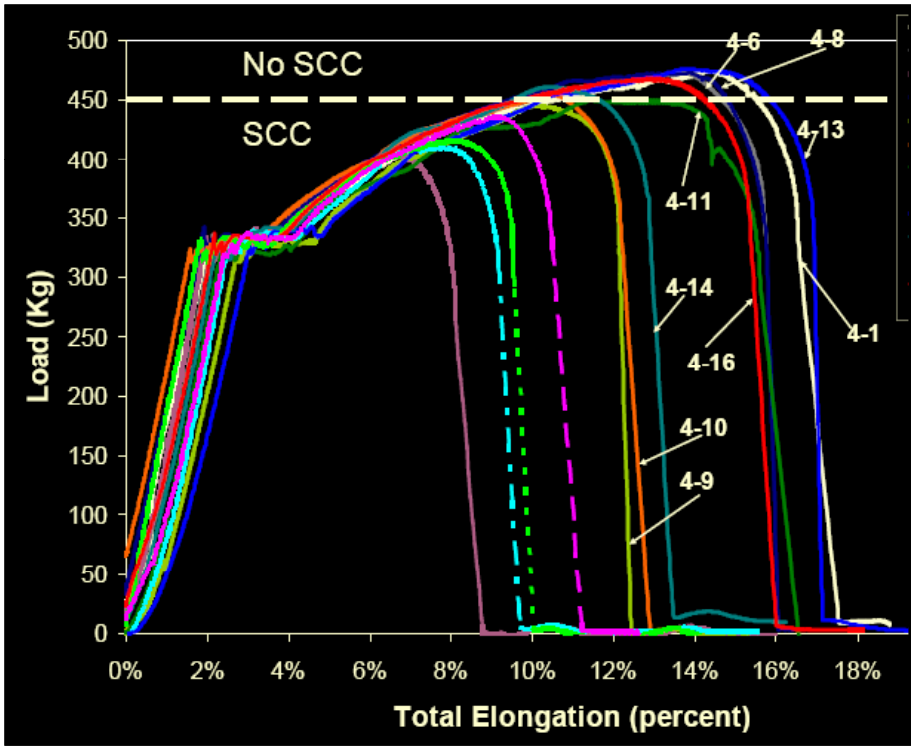
- Recent crack growth rate tests suggest time to leak/failure from ethanol SCC is months not years for susceptible conditions
- Fracture studies indicate stresses to initiate SCC are higher versus other SCC mechanisms
- PWHT or coatings are the current best practices.





Standard Test for Ethanol SCC

- Efforts have been initiated for a standard SCC test method
- This procedure will allow for rapid evaluation of ethanol samples for severity of SCC on standard materials of construction
- Can be used to evaluate sources of supply, mitigation methods (chemical treatments – inhibitors, oxygen scavengers, etc.).



Conclusions: Take Aways

- Ethanol SCC occurs at high stress and variable stress locations
- SCC observed in lab tests in fuel ethanol & blends
- Aeration is a major factor in ethanol SCC
- Fuel ethanol is not a commodity
  - Differences in SCC have been identified related to source and manufacturing method - Need more data
- Field failures only in a particular portion of the fuel ethanol distribution system
- PWHT and ethanol immersion coatings have been useful in mitigating SCC.