



DET NORSKE VERITAS

Final Report
Monitoring Conditions Leading to
SCC/Corrosion of Carbon Steel in
Fuel Grade Ethanol

Pipeline & Hazardous Materials Safety Administration
U.S. Department of Transportation



Consolidated Program for Development of Guidelines for Safe and Reliable
Pipeline Transportation of Ethanol Blends – WP#323
Report No.: 2010-9382 (86082756)
February 11, 2011



Monitoring Conditions Leading to SCC/Corrosion of Carbon Steel in Fuel Grade Ethanol For: Pipeline & Hazardous Materials Safety Administration U.S. Department of Transportation East Building, 2nd Floor 1200 New Jersey Ave., SE Washington, DC 20590 Account Ref.: DTPH56-08-T-000013	DET NORSKE VERITAS USA, INC. 5777 Frantz Road Dublin, OH 43017-1386, United States Tel: (614) 761-1214 Fax: (614) 761-1633 http://www.dnv.com
--	--

Date of First Issue:	November 6, 2010	Project No.	86082756
Report No.:	2010-9382	Organization Unit:	SRIUS915
Revision No.:	1	Subject Group:	

Summary:
 This is the draft final report of the project on field monitoring of conditions that lead to SCC in ethanol tanks and piping. The other two aspects of the consolidated program, ethanol batching and blending effects (WP#325) and source effects (WP#323) are reported separately.

Prepared by:	Narasi Sridhar	Signature 
Verified by:	Arun Agarwal	Signature 
Approved by:		Signature

- | | | |
|-------------------------------------|--|----------------|
| <input checked="" type="checkbox"/> | No distribution without permission from the client or responsible organizational unit (however, free distribution for internal use within DNV after 3 years) | Indexing Terms |
| <input type="checkbox"/> | No distribution without permission from the client or responsible organizational unit | Key Words |
| <input type="checkbox"/> | Strictly confidential | Service Area |
| <input type="checkbox"/> | Unrestricted distribution | Market Segment |

Rev. No. / Date: Reason for Issue: Prepared by: Approved by: Verified by

Executive Summary

Pipeline companies have a keen interest in assessing the feasibility of transporting fuel grade ethanol (FGE) and ethanol blends in existing pipelines. A 2003 survey of industry, reported in API Technical Report 939-D (2nd edition), indicates that stress corrosion cracking (SCC) has been observed primarily in user terminals exposed to ethanol products, but not in ethanol producer tanks, rail/tank car/shipping transportation, nor end-user systems (e.g., gas tanks). More recently, a short segment of pipeline transporting FGE in North America was reported to have suffered SCC. In contrast, Brazil, which has transported anhydrous and hydrous ethanol for many years, has not reported any SCC in their pipeline system. At present, there is an incomplete understanding of why the occurrence of SCC differs so significantly in different parts of the supply chain. Monitoring some of the factors that affect SCC, dissolved oxygen and corrosion potential, may lead to a better understanding of SCC risks. The following conclusions and recommendations can be made:

- A wireless monitoring probe to measure dissolved oxygen concentration and corrosion potential was successfully installed and demonstrated
- The data thus far suggest that the oxygen concentration is moderately high even at a site where no SCC was seen. This is consistent with other finding reported in WP#323 that chloride is another important factor in causing SCC
- The project encountered considerable time delays due to: difficulties in integrating the oxygen monitoring system with the wireless communication system and due to time required in getting site approval for installation and data acquisition.
- At the time of writing this report, sufficient data is still not available to make meaningful conclusions about operational parameters that could lead to SCC at a given location. However, monitoring probes are being installed by an ethanol producer and two other terminals. These data, when available will help shed light on field conditions.
- Other monitoring methods, for example, chloride monitoring/analysis and instrumented SCC coupons, should be explored.

Table of Contents

1.0	BACKGROUND	1
1.1	Monitoring Methods	1
1.2	Project Objectives	4
2.0	TASK1: DEVELOPMENT OF MONITORING PROBES	4
2.1	Experimental Methods	6
2.2	Results of Laboratory Tests	7
2.3	Reference electrode.....	7
2.3.1	Short term performance	7
2.3.2	Long term potential stability	9
2.3.3	Cd ²⁺ leaking rate	11
2.4	Oxygen concentration in ethanol	11
3.0	TASK 2 – PERFORM FIELD MONITORING AT A TANK FARM.....	13
3.1	Assembly of Probes and electronics	13
3.2	Site Selection	15
3.3	Data Collection	16
4.0	SUMMARY AND RECOMMENDATIONS.....	18
5.0	REFERENCES	18

List of Tables

Table 1. Gaps addressed by the projects in this consolidated program 4

Table 2: A concentration comparison of several ions in fuel grade ethanol after long
term electrode immersion 11

List of Figures

Figure 1. Conceptual approach to risk assessment using corrosion potential and dissolved oxygen monitoring data.	3
Figure 2. The potential difference between Cd/Cd(ClO ₄) ₂ reference electrode and Ag/AgCl (with 1 M LiCl in ethanol).	8
Figure 3. The changes in the OCP of a carbon steel sample in fuel grade ethanol at different aeration conditions.	9
Figure 4. The potential change of a carbon steel in fuel grade ethanol against various reference electrode as a function of time.	10
Figure 5. The appearance of the reference electrodes after four months of immersion in the fuel grade ethanol.	10
Figure 6: A comparison of the measured oxygen concentrations and the theoretical values as a function of the oxygen concentration in the purging gas.	12
Figure 7: A comparison of the oxygen partial pressure in ethanol with quiescent air, nitrogen purging, and air purging.	12
Figure 8: The partial pressure of oxygen as a function of chloride concentration in ethanol.	13
Figure 9. Overall schematic layout of the wireless monitoring system.	14
Figure 10. The Aginova and Polestar systems assembled inside an intrinsically safe storage box (open) that was then installed at a terminal site.	15
Figure 11. Installation of the probes (right hand figure) at a tank piping in Columbus, Ohio.	16
Figure 12. Web portal where the wireless data from many sites may be viewed and exported.	16
Figure 13. Capture of the monitoring data from the Columbus site on February 11, 2011. The data can be captured in real time by logging on to a password-protected web site.	17

1.0 BACKGROUND

The U.S. Energy Independence and Security Act of 2007 established a nationwide renewable fuels standard, starting from 9 billion gallons (34 billion liters) of all biofuels in 2008 to 36 billion gallons (136 billion liters) in 2022. The most recent Renewable Fuel Standards issued by the U.S. Environmental Protection Agency [1] specifies a number of alternative biofuels, including corn-based ethanol, cellulosic ethanols, biodiesels, and other advanced biofuels that may be manufactured in the future using hitherto unknown technologies. At present, biofuel is first sent to blending terminals through tanker trucks, rail cars, and barges, where they are blended with gasoline or diesel and then sent to consumer filling stations via trucks. In the U.S. 67 percent of the ethanol is transported to blending terminals via trucks, 31 percent by rail cars, and 2 percent by barges [2]. The rail, truck, and barge transport modes are more costly and less efficient than pipeline transport for long distances. It has been estimated that for long-distance transportation of fuel, pipeline is less hazardous than trucks or rail cars based on frequency of fatalities per distance transported. While the ethanol pipeline infrastructure in the U.S. is still nascent, Brazil has a well-established ethanol pipeline already and is planning to expand this infrastructure even further.

Reliable and safe transportation of ethanol is critical to the viability of pipelines as the primary transportation mode. A 2003 survey of industry, reported in API Technical Report 939-D (2nd edition), indicates that stress corrosion cracking (SCC) has been observed primarily in user terminals exposed to ethanol products, but not in ethanol producer tanks, rail/tank car/shipping transportation, nor end-user systems (e.g., gas tanks). More recently, a short segment of pipeline transporting FGE in North America was reported to have suffered SCC. In contrast, Brazil, which has transported anhydrous and hydrous ethanol for many years, has not reported any SCC in their pipeline system. At present, there is an incomplete understanding of why the occurrence of SCC differs so significantly in different parts of the supply chain.

The occurrence of SCC could be related to ethanol loading/unloading conditions (oxygen ingress), the presence of scale, or the presence of other contaminants. Lacking continuous corrosion potential data, it has not been possible to determine what changes occur in a tank during operation. A similar problem could exist for pipelines transporting ethanol. Therefore, monitoring the corrosion potential of steel and dissolved oxygen concentration is important to obtain long-term operational information. The use of the monitoring data for decision-making is equally important. For example, if the corrosion potential enters the SCC regime, the time period during which the corrosion potential is in the SCC regime (critical time period) is important in determining SCC risk. The critical time period would depend on the crack initiation time data, which will be developed in another project within the consolidated program.

1.1 Monitoring Methods

Essentially four types of monitoring methods may be used to determine whether there is a risk of SCC in ethanol. Their advantages and disadvantages are indicated below:

Direct Measurement of Dissolved Oxygen: If a dissolved oxygen measuring probe for ethanol can be developed to reliably monitor dissolved oxygen content, then the most important factor leading to SCC in ethanol can be directly monitored. Independent lab tests to correlate dissolved oxygen content vs. SCC (WP#325) have already established the limits of oxygen for different blends.

Electrochemical Noise (EN) or Multielectrode Array Measurement: Electrochemical noise measurement involves measuring small changes in galvanic current or potential on carbon steel due to disturbances of the protective film. A commercial instrument, SmartCET marketed by Honeywell, has been used to determine whether EN signals correlate to SCC. Although observations of enhanced activity of the probe have been reported and hypothesized to be due to oxygen entry or otherwise corrosion activity (API 939D, 2nd Edition), the method has some major disadvantages: (i) the high resistivity of ethanol can result in the masking of electrochemical signals or can lead to spurious signals, (ii) EN, in ethanol at least, is essentially a “black box” approach – it has no fundamentally established relationship to SCC, but attempts to fingerprint known SCC events, essentially in the lab, with EN signal anomalies, and (iii) it is essentially a “lagging indicator” i.e. EN signals, if they are believable, follow SCC events, they do not presage these events. Multielectrode array measurements may overcome some of the limitations of the EN measurements because of the small electrode sizes, but suffer most of the same limitations.

Corrosion Potential Measurement: As mentioned before, a strong correlation exists between SCC and corrosion potential. The corrosion potential is measured by connecting a high impedance voltmeter between the component of interest and a reference electrode. Thus, corrosion potential measurement constitutes direct monitoring of the actual, mechanically stressed component, not a coupon. It is also consistent with many known mechanisms of SCC in steel and thus has a strong mechanistic foundation. It is a “leading indicator” i.e. it indicates when steel is getting into SCC prone regime even prior to an actual occurrence of SCC. Lastly, it is a simple, well established technique that is easy to implement in the field. Essentially the monitoring of corrosion potential is no different than monitoring “off potential” in a CP system, except a different design of the reference electrode, specifically for ethanol, is used. The main limitation of corrosion potential monitoring is in the case of inhibitor additions which may mitigate SCC, but only affect potential slightly. Also, some ethanols, such as the sugar-cane based ethanol may not cause SCC for reasons not related to corrosion potential.

Stressed Coupons: Stressed coupons (e.g., U-bends): These have been used traditionally to monitor SCC occurrence in many process systems. In the case of ethanol SCC, unwelded, U-bend specimens have not exhibited any cracking in the laboratory even after several months of exposure. Welded coupons have exhibited SCC in approximately 45 days, provided welding is intentionally done badly. The main problem with stressed coupon approach is the simulation of actual service conditions and providing known accelerating mechanism to determine SCC

potential in a reasonable timeframe. For example, cyclic loading is known to accelerate SCC, but U-bend coupons are statically loaded. Stressed coupons are also lagging indicators and, unless instrumented, do not provide a continuous monitoring capability. EN measurements have been conducted using stressed U-bend specimens (e.g., API 939D), but these suffer from the limitations of the EN measurements mentioned above. It has been noted in slow strain rate tests, that the corrosion potential drops significantly once cracking occurs. In such a case, monitoring the potential difference between a stressed U-bend specimen and an inert electrode such as Pt may yield information on when SCC occurs.

For ease of implementation, it was agreed that corrosion potential (OCP) and dissolved oxygen monitoring will be performed as part of this project. The overall approach is to perform risk assessment by using a combination of these measurements as shown in Figure 1.

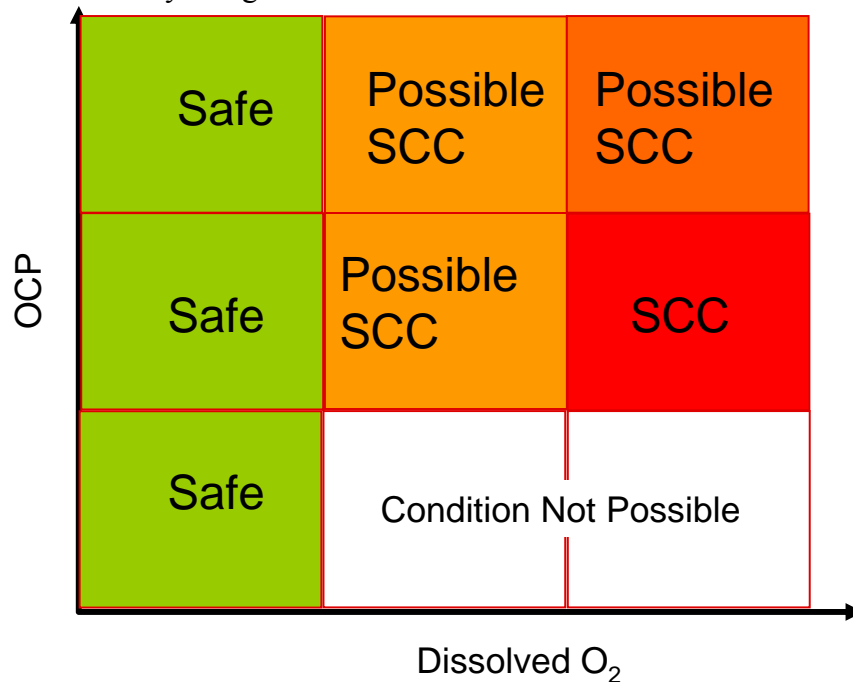


Figure 1. Conceptual approach to risk assessment using corrosion potential and dissolved oxygen monitoring data.

When the oxygen concentration is low, then no SCC is observed in any ethanol, regardless of the corrosion potential. When the oxygen concentration is moderate to high, then, some ethanol samples that show a high corrosion potential may not cause SCC and so this is a warning for further evaluation, for example through laboratory testing. For those ethanol samples that show a high oxygen and moderate corrosion potential, a significant risk of SCC exists.

1.2 Project Objectives

A Roadmap meeting, held on October 25-26, 2007, identified several gaps related to ethanol transportation in pipelines. A Consolidated Program, consisting of three projects, is being conducted to address several of these gaps:

WP#323 – Effect of ethanol source on SCC of carbon steel

WP#325 – Effect of Ethanol Blends and Batching Operations on Stress Corrosion Cracking of Carbon Steel

WP#327 – Monitoring Conditions Leading to SCC/Corrosion of Carbon Steel

The specific gaps addressed by WP#327 are shown in Table 1. Gaps addressed by the projects in this consolidated program. The red dots indicate their priority/importance

Table 1. Gaps addressed by the projects in this consolidated program

Proposed Project	Gaps Addressed
WP#327	<ul style="list-style-type: none"> • What needs to be monitored: why, where and when ●●●●●●●● • Avoiding O₂ contamination ●●●●●● • Lack appropriate commercial monitoring technologies ●●●●

The major objectives of the proposed project are to:

1. Develop a field operable monitoring system that can determine when the conditions conducive to SCC occur and for how long do those conditions prevail.
2. Install the monitoring system and conduct studies over an extended period of time
3. Develop guidelines for decision making from monitoring and other laboratory information

2.0 TASK1: DEVELOPMENT OF MONITORING PROBES

Typically, the potential of a metal in an environment of interest is measured against a reliable reference electrode. The reference electrode potential must not respond to changing redox conditions, must be pH independent, chemically resistant, must not release unwanted species into the test solution, and must be mechanically rugged. In organic solvents such as ethanol, Ag/AgCl reference electrode (with 1M LiCl dissolved in ethanol as filling solution) and some pseudo-

reference electrodes are often used for potential measurements. Although these electrodes are good for short term lab experiments, they are not the best electrodes when it comes to long term field potential monitoring programs. For example, Ag/AgCl reference electrodes (in 1M LiCl in ethanol) tend to leak electrolyte and therefore require constant maintenance, not to mention the chloride leakage from the electrode body over long period of time that could impose corrosion and SCC risk on the materials. For the pseudo-reference electrodes, the reliability of the potential data collected over a long period of time is questionable because, in many cases, the surface of these pseudo-reference electrodes can change and cause potential drifting. Therefore, a rugged, stable, reliable reference electrode is needed to monitor the corrosion potential of steel in ethanol.

The determination of the oxygen concentration in an aqueous environment is often achieved by a Clark (electrochemical) cell, which measures oxygen concentration based on the limiting current density of the oxygen reduction reaction. The Clark cell typically consists of platinum as the cathode for the oxygen reduction reaction and an Ag/AgCl wire as both the anode and reference electrode. The electrodes are usually immersed in a saturated KCl solution housed by the electrode body. An oxygen permeable membrane on the electrode tip separates the KCl solution from the environment to be measured to prevent the environment from being contaminated. The Clark cell, however, cannot be used to measure oxygen concentration in ethanol due to the following reasons: a) the membranes on the Clark cells are usually incompatible with ethanol. In other words, the life time of these membranes in ethanol is limited; b) the solubility of oxygen in ethanol differs from that in aqueous environments and needs to be calibrated with independently measured oxygen concentration in ethanol; c) even though the oxygen reduction current in an ethanol containing a supporting electrolyte (a supporting electrolyte provides sufficient ionic concentration without affecting the electrode processes) can be determined electrochemically, a membrane is necessary to separate the actual ethanol sample in which oxygen is measured from the ethanol containing the supporting electrolyte (referred to here as the measuring solution) to prevent mixing of the two solutions. Thus far, no membrane materials have been identified that have low leakage rate of the electrolyte from inside of the electrode while maintaining sufficient oxygen permeation from the test sample to the measuring solution. Thus, oxygen probes that function based on mechanisms other than electrochemical reduction of oxygen are desired to measure the concentration of oxygen in ethanol.

The first objective of this work was to develop a reference electrode that uses a solid polymer gel as the electrolyte to minimize the maintenance requirement. The performance of this reference electrode was evaluated from different aspects. The second objective of this work was to evaluate an optical oxygen probe for use in ethanol. The oxygen concentration in ethanol was measured and the sensitivity of the probe to the oxygen concentration change was investigated.

2.1 Experimental Methods

The gel electrode was based on the concept developed by Reiter and co-workers [3] but was modified to improve the reproducibility. The electrode consists of a cadmium wire ($d=1\text{mm}$) in a poly(methyl methacrylate) (PMMA)-propylene carbonate polymer electrolyte. The polymer electrolyte was formed by the polymerization of the methyl methacrylate (MMA) monomer^{*}, Superacryl®[†] that contains the polymerization initiator (dibenzoylperoxide (1%)) and 0.3 M of $\text{Cd}(\text{ClO}_4)_2$ in propylene carbonate (PC).

The mixture composition of the three components mentioned above in the work by Reiter and co-workers was 1.5 mL MMA, 1.75 g of Superacryl and 1 mL $\text{Cd}(\text{ClO}_4)_2$ in PC (0.3 M). After introducing the mixture into a glass tube, the tube was placed in a preheated oven at 90°C for 5 h. When following this procedure in the present work, however, it was found that bubbles sometimes formed in the electrolyte. When these bubbles were present at the end of the electrode, the performance of the reference electrode could be affected due to the high impedance caused by the bubbles. The formation of the bubbles could be a result of the active polymerization reaction. Because the Superacryl contains the initiator for this reaction, its amount was reduced to 1.25 g in the present work to reduce the reaction speed. The electrode body containing the mixture was left in a vacuum chamber for one hour to allow any generated bubbles to escape. Additionally, the electrode was left at room temperature to slow down the polymerization reaction. After the gel was solidified, the electrode was placed in an oven at 80°C for two hours to complete the curing process.

Once the electrode was prepared, it was kept in the PC solution for 10 days prior to use. After that, the $\text{Cd}/\text{Cd}(\text{ClO}_4)_2$ reference electrode was checked against the Ag/AgCl electrode that is commonly used in ethanol. The Ag/AgCl electrode uses 1 M LiCl dissolved in ethanol as the filling solution and has exhibited good stability in organic solvents. Additionally, the corrosion potential of a carbon steel electrode was measured against the prepared gel electrode under quiescent air and deaerated condition to investigate its sensitivity to the potential change of the carbon steel sample immersed in simulated FGE. Furthermore, to evaluate the long term performance of the gel reference electrode, the potential of a carbon steel sample in the simulated FGE was monitored against two gel electrodes with different seal material (vycor frit and ceramic tip) and a Ag/AgCl electrode (in 1M LiCl ethanol solution) for four months. All reference electrodes and a carbon steel coupon were immersed in fuel grade ethanol (approximately 350 mL) and the potential of the steel coupon was monitored periodically versus three reference electrodes. At the end of the four month exposure, the concentrations of Cd^{2+} , Cl^- and Ag^+ were analyzed to determine the approximate average leakage rates of these ions through the seal materials on the electrodes.

^{*} Sigma-Aldrich, USA

[†] Spofa-Dental, Prague, Czech Republic

The evaluated oxygen probe is based on the concept of collisional fluorescence quenching of an organometallic sensor in the presence of oxygen^{*}. The fluorescence intensity and lifetime vary inversely with the partial pressure of oxygen. From the measured partial pressure of oxygen, the concentration of oxygen in the environment of interest can be calculated provided the solubility follows Henry's law and the Henry's law constant is known. Prior to use, the oxygen probe was calibrated following the operation instruction in deaerated ethanol as well as in ethanol purged with 20% oxygen (N₂ balance). The partial pressure of oxygen was then measured in pure ethanol purged with different oxygen and nitrogen mixtures (with oxygen concentrations from 0.5% to 20%). The concentration of oxygen in ethanol was subsequently calculated using the Henry's law constant obtained in the literature and compared to the theoretical values. The oxygen concentrations in ethanol containing chloride were also measured to evaluate the chloride effect on oxygen solubility.

2.2 Results of Laboratory Tests

2.3 Reference electrode

2.3.1 Short term performance

The potential difference between the Cd/Cd(ClO₄)₂ reference electrode and the Ag/AgCl electrode in a simulated FGE is shown in Figure 2. The chemistries of the simulated FGE were reported elsewhere [4]. The potential difference initially increased and reached a fairly stable value at -290 mV (vs. Ag/AgCl). This indicates that the Cd/Cd(ClO₄)₂ reference electrode is stable in ethanol and can serve as a sound reference.

^{*} Polestar Technology, Inc., USA

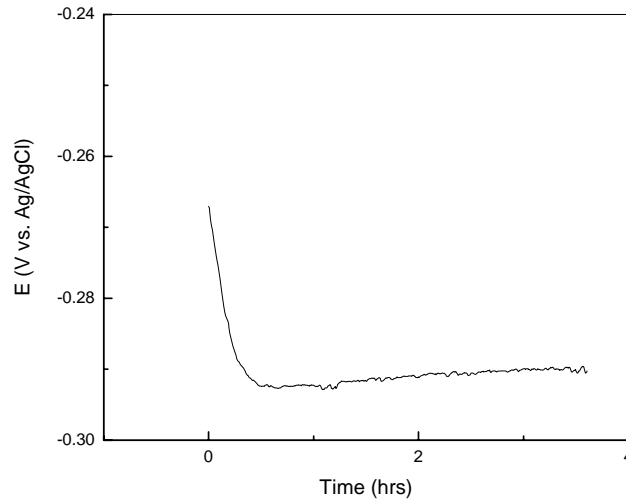


Figure 2. The potential difference between Cd/Cd(ClO₄)₂ reference electrode and Ag/AgCl (with 1 M LiCl in ethanol).

Figure 3 shows the changes in the open circuit potential (OCP) of a carbon steel sample in a simulated FGE at different aeration conditions. When changing the purging gas from nitrogen to oxygen, it is expected that the OCP of the carbon steel sample would shift towards a more positive direction. This is because the OCP is partly dictated by the oxygen reduction reaction, which has a high equilibrium potential. Both the equilibrium potential for this reaction and the reaction kinetics depend on the partial pressure of oxygen. Therefore, purging nitrogen results in a lower dissolved oxygen concentration and lower OCP. The OCP of the carbon steel would be driven to become more positive as oxygen increases and more negative as oxygen decreases. The change in the OCP was measured with the Cd/Cd(ClO₄)₂ electrode as the reference and is shown in Figure 4. When oxygen was introduced, a sharp increase in the potential was noted. This suggests that the Cd/Cd(ClO₄)₂ electrode, similar to any other standard reference electrodes, is sensitive to the change that takes place on the measured working electrode (sample).

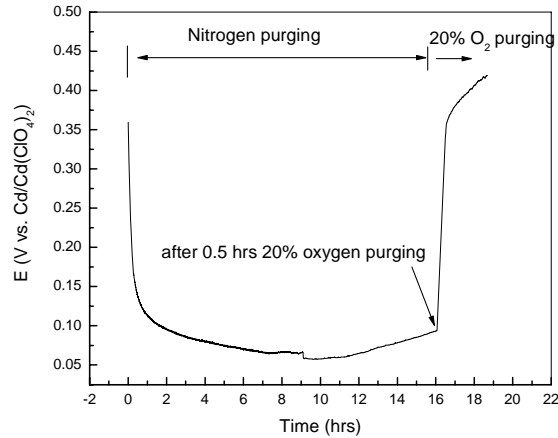


Figure 3. The changes in the OCP of a carbon steel sample in fuel grade ethanol at different aeration conditions.

2.3.2 Long term potential stability

The potential changes of the carbon steel sample in FGE against different reference electrodes as a function of time are shown in Figure 3. The OCP of the carbon steel increased in the first month of exposure and maintained a stable value throughout the entire testing period. The OCP of the carbon steel is more positive when measured against the Cd/Cd(ClO₄)₂ reference electrodes than measured against Ag/AgCl electrode. This is consistent with the observation that the potential of the Cd/Cd(ClO₄)₂ electrode vs. Ag/AgCl was -260 mV, as shown in Figure 4. There was some difference between the vycor sealed and the ceramic sealed electrodes with respect to the potentials measured. When inspecting the reference electrodes after 4 months exposure, a bubble was found in the electrode sealed with vycor at the tip of the electrode. The electrode sealed with the ceramic tip was intact and the same as prior to the long term exposure Figure 4. This suggests that the porosity of the vycor allowed a considerable amount of ethanol to penetrate into the electrode body to cause a local dissolution of the polymer gel. Although the dissolution of the gel seemed to not have a significant effect on the potential measurement, it could eventually cause sufficient volume loss in an even longer exposure and thus change the electrode performance by increasing the electrode impedance. For the Ag/AgCl electrode, the electrode body was almost empty and only had a few milliliters of solution left inside after four months of immersion. Surprisingly, the potential measured against Ag/AgCl electrode did not show any indication of reference malfunctioning. When checking the Ag/AgCl electrode, it was noted that the silver wire inside was sticking to the electrode wall. Because ethanol has excellent wettability, a conductive path may still have been maintained with the solution volume left inside the electrode and thus the potential measurement was not affected. However, since all the filling solution would have eventually leaked out, it would have needed refilling and other maintenance to assure that the Ag/AgCl electrode worked appropriately.

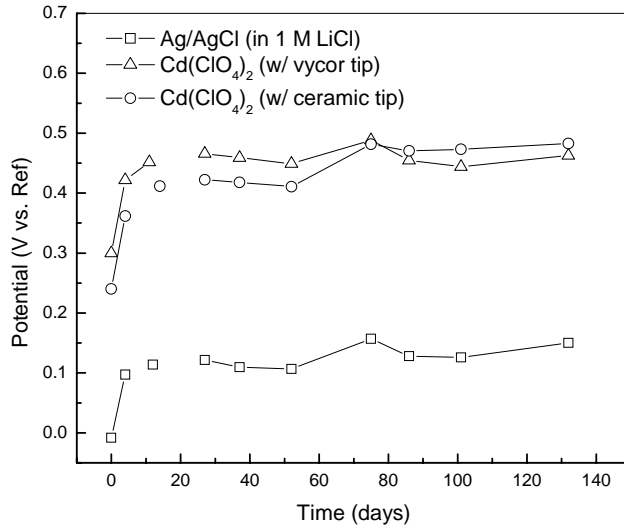


Figure 4. The potential change of a carbon steel in fuel grade ethanol against various reference electrode as a function of time.



Figure 5. The appearance of the reference electrodes after four months of immersion in the fuel grade ethanol.

2.3.3 Cd²⁺ leaking rate

Table 2 compared the concentrations of several ions in the FGE after four months of immersion with the reference electrodes. The chloride concentration was much higher than the other two ions and was primarily from the Ag/AgCl electrode. This is consistent with the observation that the Ag/AgCl electrode was almost dry after 4 months immersion. Cd²⁺ was from both the vycor sealed and the ceramic sealed Cd/Cd(ClO₄)₂ electrodes. Because a bubble was noted in the vycor sealed electrode, more Cd²⁺ probably came from the vycor sealed electrode than from the ceramic sealed electrode.

Table 2: A concentration comparison of several ions in fuel grade ethanol after long term electrode immersion

Cl ⁻ (ppm)	Li ⁻ (ppm)	Cd ²⁺ (ppm)
422	16.4	2.95

2.4 Oxygen concentration in ethanol

Figure 6 is a comparison of the measured oxygen concentration and the theoretical oxygen concentration as a function of the oxygen concentration in the purging gas. For measurements 1 and 2, the partial pressure was measured with the oxygen probe and the concentration was calculated using the equation below:

$$C(O_2) = \frac{P(O_2)}{k} \quad [1]$$

Where, C(O₂) is the oxygen concentration in the ethanol; P(O₂) is the partial pressure of oxygen in the ethanol measured by the oxygen probe; k is the Henry's constant (10320 Pa.m³/mol for oxygen in ethanol [5]). The theoretical values were calculated using the same equation but with the partial pressure calculated directly based on the oxygen concentration in the purging gas.

The oxygen concentration from the measurements showed a linear relationship with the oxygen concentration in the purging gas, similar to the theoretical values. The measured results agreed well with the theoretical values when the oxygen content in the purging gas was small. When the oxygen content in the purging gas was higher than 5%, the oxygen concentrations based on the measurement were slightly higher than the theoretical values. The reason for the discrepancy is not clear yet. Nevertheless, the measured oxygen concentration when purged with 20% oxygen-nitrogen mixture (80.2 ppm) was found to be very close to the concentration determined by Franco and Olmsted III experimentally using a photochemical method [6]. In their work, the

oxygen concentration in air-equilibrated ethanol was 78.7 ppm ($\pm 6\%$), a much higher value than the oxygen concentration in air saturated water.

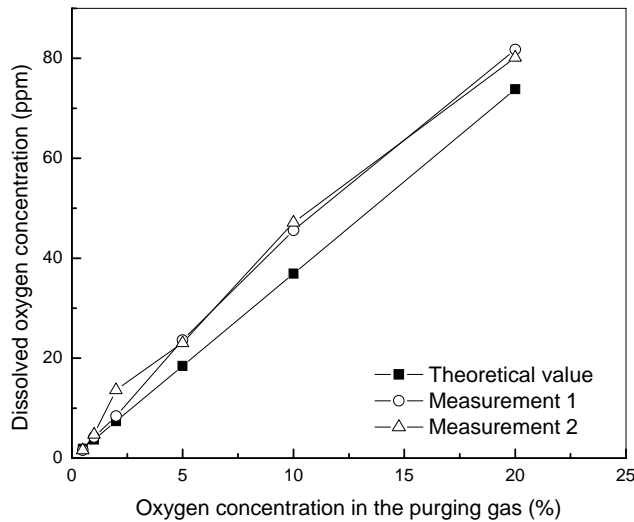


Figure 6: A comparison of the measured oxygen concentrations and the theoretical values as a function of the oxygen concentration in the purging gas.

The oxygen probe can respond to the depletion of oxygen in the ethanol solution quickly. As shown in Figure 7, immediately after nitrogen purging began, the measured partial pressure (thus the concentration of oxygen) decreased to zero.

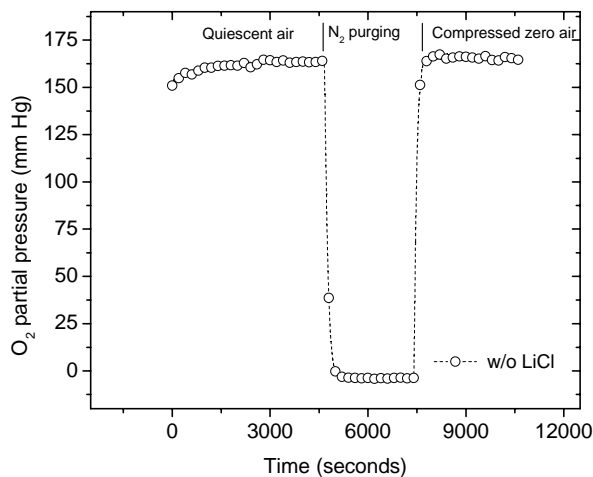


Figure 7: A comparison of the oxygen partial pressure in ethanol with quiescent air, nitrogen purging, and air purging.

Similarly, the measured partial pressure increased as soon as oxygen was introduced into ethanol by means of sparging with compressed zero air (no CO₂). This implied that the evaluated oxygen probe can precisely reflect the change in the oxygen concentration in the ethanol.

It is well known that the equilibrium oxygen concentration in aqueous solutions strongly depends on the salt content. Similarly, the salt concentration or chloride level influences oxygen solubility in ethanol. Figure 8 shows the measured oxygen partial pressure in ethanol as a function of chloride concentration. Clearly, the oxygen solubility decreased with the increase in the chloride concentration, similar to what is observed in aqueous solutions. Even though only the effect of chloride was investigated, it is expected the solubility of oxygen would decrease when the overall salt content was increased.

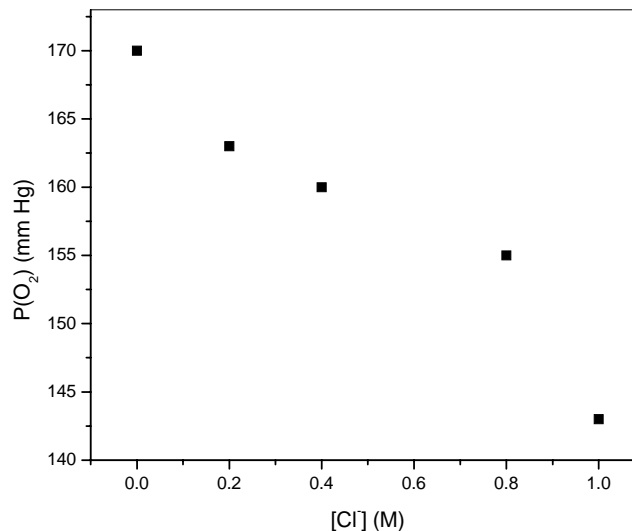


Figure 8: The partial pressure of oxygen as a function of chloride concentration in ethanol.

3.0 TASK 2 – PERFORM FIELD MONITORING AT A TANK FARM

3.1 Assembly of Probes and electronics

The corrosion potential and oxygen probes were assembled into a package consisting of the probes, data acquisition electronics, wireless communication system, and remote data acquisition system. This is schematically indicated in Figure 9.

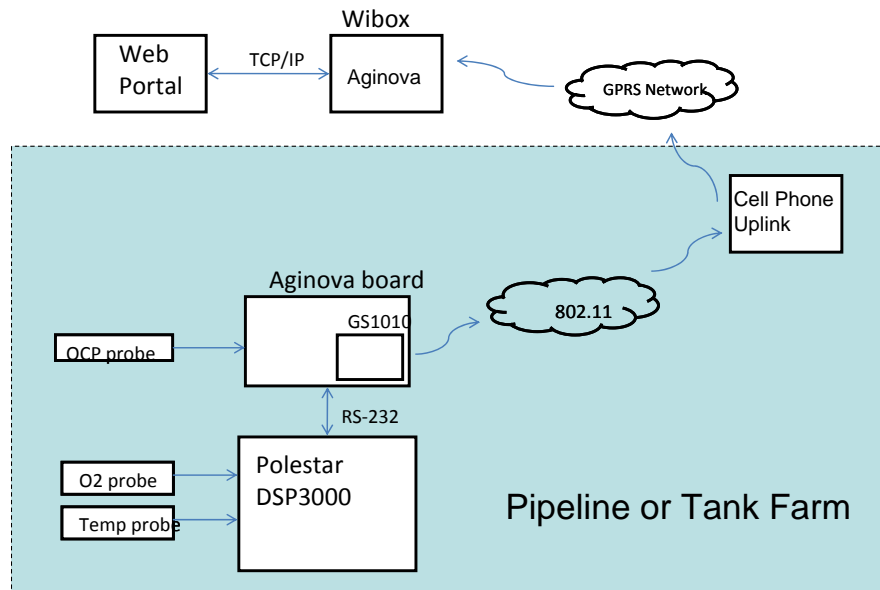


Figure 9. Overall schematic layout of the wireless monitoring system

The wireless data acquisition and communication system was manufactured by Aginova and integrated the electronics of the Polestar oxygen measurement system through a cable interconnect. The whole unit was then assembled in an intrinsically safe box for installation at site.

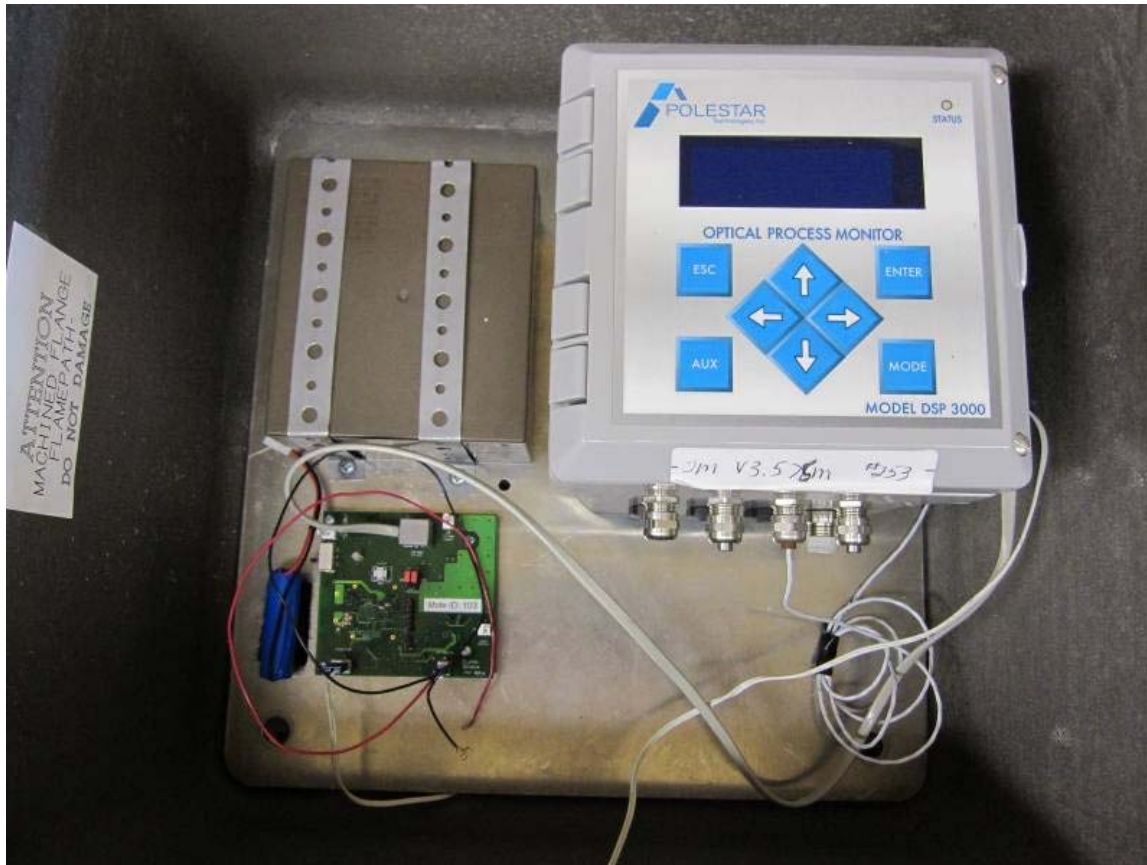


Figure 10. The Aginova and Polestar systems assembled inside an intrinsically safe storage box (open) that was then installed at a terminal site.

3.2 Site Selection

Although monitoring pipelines is the ultimate interest of this project, at present it is more convenient to monitor piping systems associated with tanks. Therefore, tank sites of two terminals and one producer were chosen. The first terminal site was at Columbus, Ohio. This site has not suffered any incidents of ethanol SCC. The second terminal site was to have been in Hawaii, where an incidence of ethanol SCC had occurred early in 2010. However, due to logistical and other reasons this site had to be abandoned. A replacement site is yet to be found. The third site is an ethanol producer site that had not seen any SCC. Probes have been installed at this location. It was the original intent to install the system at a tank. However, the terminal site was concerned about potential leaks through the probe. Therefore, it was decided to install the probe at a piping that exited the tank. This is shown in Figure 11.



Figure 11. Installation of the probes (right hand figure) at a tank piping in Columbus, Ohio.

3.3 Data Collection

The data that is acquired can be viewed in real time at a password protected web site (Figure 12).

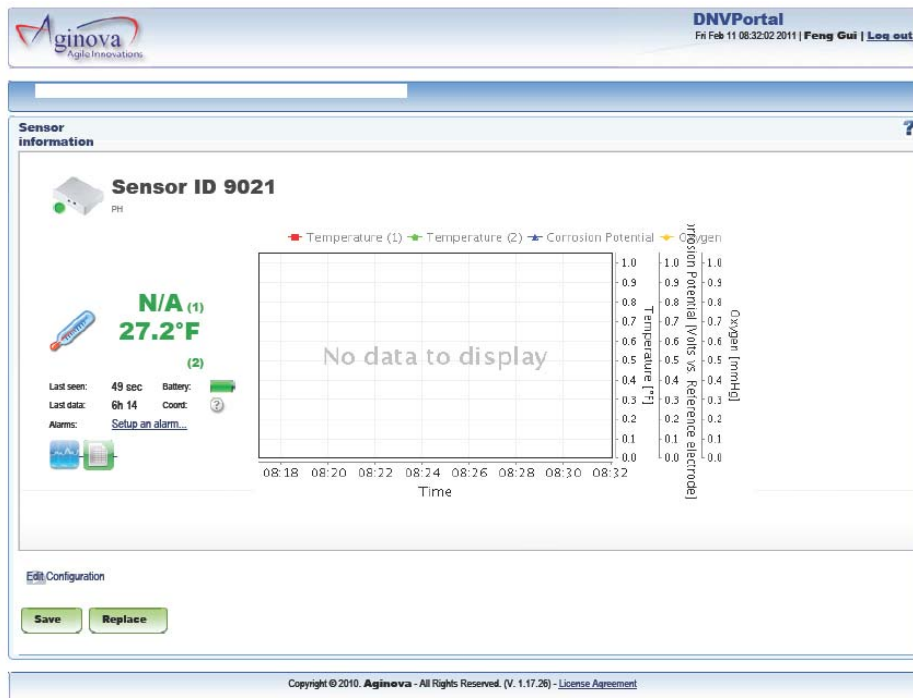


Figure 12. Web portal where the wireless data from many sites may be viewed and exported

An example of the data from the web portal is shown in Figure 13.

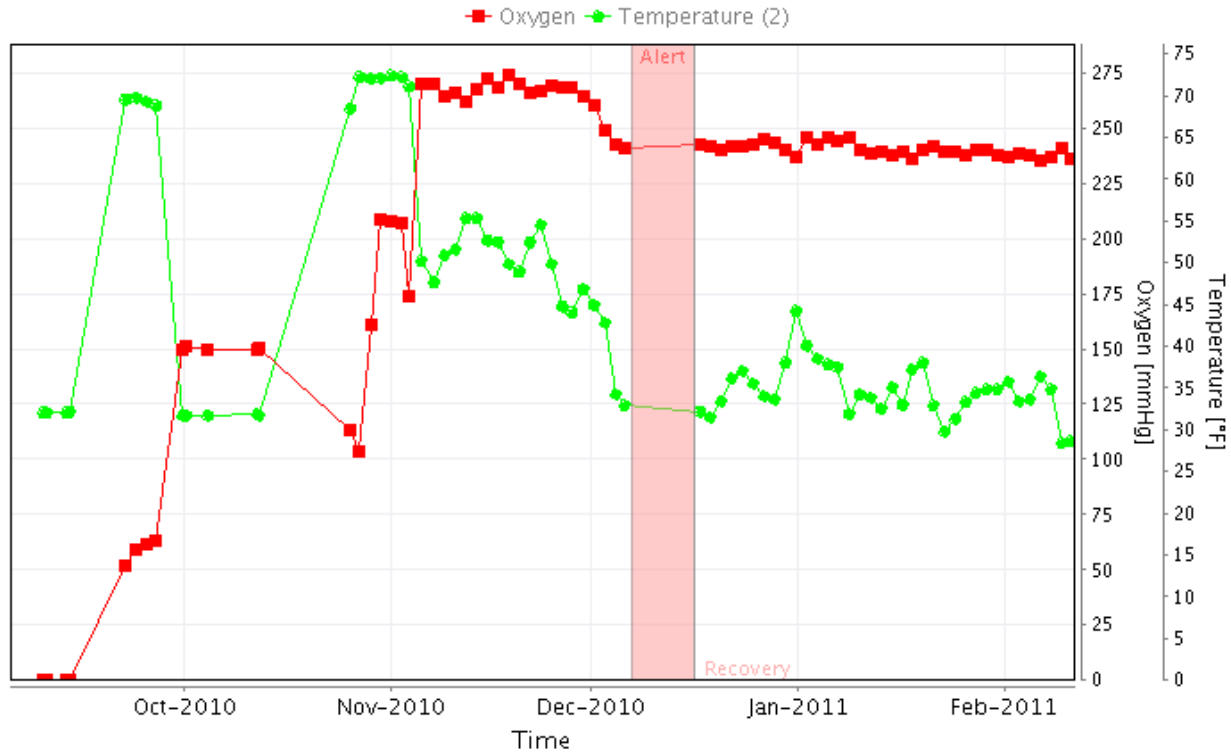


Figure 13. Capture of the monitoring data from the Columbus site on February 11, 2011. The data can be captured in real time by logging on to a password-protected web site.

Data acquisition was initiated in January of 2010, but a problem was noticed in the calibration of oxygen monitoring system at the low winter temperatures. The system had to be disassembled and sent to the manufacturer for recalibration and also reinstallation of the firmware. The acquisition of data commenced in May, but was again interrupted in mid-August due to problems with the wireless communication system. Acquisition was restarted in mid-September. The main observation from the project thus far is that the oxygen concentration and corrosion potentials are moderately high despite lack of SCC at this site (Figure 13).

A probe is being installed in an ethanol producer tank site. Although this producer collected some data on dissolved oxygen previously, the data were considered to be problematic because of electrical noise arising from the proximity of other equipment. A wireless probe is being reinstalled at this site and data will be collected in the next few months.

Two other probes will be installed in terminals of two companies. At present preliminary site planning is being done. The data from these sites will not likely be available for another few months. It is the intent of this project to continue to acquire data after the project is closed and

provide this data to industry as a means to assess field-related information and decide on appropriate monitoring and mitigation techniques.

4.0 SUMMARY AND RECOMMENDATIONS

- A remote monitoring probe to measure dissolved oxygen concentration and corrosion potential was successfully installed and demonstrated.
- The data thus far suggest that the oxygen concentration is moderately high even at a site where no SCC was seen. Therefore, other factors, such as chloride and cyclic loading, may be important.
- Additional probes are being installed at a producer site and two other terminals. At the time of writing this report, sufficient data is still not available to make meaningful conclusions about operational parameters that could lead to SCC at a given location.
- Other monitoring methods, for example, chloride monitoring and instrumented SCC coupons, should be explored.

5.0 REFERENCES

1. National Renewable Fuels Standard Program for 2010 and Beyond, Environmental Protection Agency, <http://www.epa.gov/otaq/renewablefuels/index.htm>.
2. National Commission on Energy Policy's Task Force on Biofuels Infrastructure, Bipartisan Policy Center, Washington D.C., U.S., www.energycommission.org, (2008).
3. J. Reiter, J. Vondrák and Z. Micka, Solid State Ionics, 177, 3501 (2007).
4. J.A. Beavers, F. Gui, and N. Sridhar, Effect of Ethanol Blends and Batching Operations on SCC of Carbon Steel, Draft Final Report of the Consolidated Program for Development of Guidelines for Safe and Reliable Pipeline Transportation of Ethanol Blends – WP#325, U.S. Department of Transportation, PHMSA, Report No.: 2010-9362 (86082756) October 30, 2010
5. P. Lühring and A. Schumpe, J. Chem. Eng. Data, 34 (1989).
6. C. Franco and J. Olmsted, Talanta, 37, 905 (1990).

DNV Energy

DNV Energy is a leading professional service provider in safeguarding and improving business performance, assisting energy companies along the entire value chain from concept selection through exploration, production, transportation, refining, and distribution. Our broad expertise covers Asset Risk & Operations Management, Enterprise Risk Management; IT Risk Management; Offshore Classification; Safety, Health and Environmental Risk Management; Technology Qualification; and Verification.

DNV Energy Regional Offices:

Asia and Middle East

Det Norske Veritas Sdn Bhd
24th Floor, Menara Weld
Jalan Raja Chulan
50200 Kuala Lumpur
Phone: +603 2050 2888

North America

Det Norske Veritas (USA), Inc.
1400 Ravello Drive
Katy, TX 77449
United States of America
Phone: +281-396-1000

Europe and North Africa

Det Norske Veritas Ltd
Palace House
3 Cathedral Street
London SE1 9DE
United Kingdom
Phone: +44 20 7357 6080

Offshore Class and Inspection

Det Norske Veritas AS
Veritasveien 1
N-1322 Hovik
Norway
Phone: +47 67 57 99 00

Cleaner Energy & Utilities

Det Norske Veritas AS
Veritasveien 1
N-1322 Hovik
Norway
Phone: +47 67 57 99 00

South America and West Africa

Det Norske Veritas Ltda
Rua Sete de Setembro
111/12 Floor
20050006 Rio de Janeiro Brazil
Phone: +55 21 2517 7232

Nordic and Eurasia

Det Norske Veritas AS
Veritasveien 1
N-1322 Hovik
Norway
Phone: +47 67 57 99 00

DET NORSKE VERITAS

Pipeline & Hazardous Materials Safety Administration
Monitoring conditions Leading to SCC/Corrosion of Steel in
Fuel Grade Ethanol



MANAGING RISK