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A New MIC Control Strategy in Low Velocity Gas Gathering Pipelines

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ABSTRACT

Internal corrosion related failures in oil and gas gathering systems are increasing, especially in conditions categorized as “low risk” by computer modeling. Such systems usually exhibit, low pressure, low temperature sweet gas production, and relatively low total dissolved solid content waters. The failure rate is commonly influenced by two major factors; 1) undiagnosed microbiologically influenced corrosion (MIC) mechanisms, and 2) the unappreciated impact of corrosive chemical biocides used to treat sessile and planktonic bacteria. Low velocity gas gathering systems are particularly difficult to treat for MIC as a result of pigging challenges and the tendency for corrosive biocides to concentrate in the water phase over time. Here we report a new water soluble quaternary ammonium compound, didecyldimethylammonium bicarbonate/carbonate (DDABC), that acts as an MIC corrosion control agent against common oilfield bacteria. At the proper dilution, DDABC also acts as a thin film forming anodic inhibitor on steel. Supporting lab and field tests indicate this inhibitor is effective in competitive evaluations against glutaraldehyde, THPS, and quaternary ammonium chloride based agents. In a field trial reported herein, DDABC reduced the failure rate of a 1,653 km low velocity gas gathering field to approximately one-sixth the original rate in a 20 month field trial.

Keywords: MIC, gas gathering, quaternary ammonium, anodic inhibitor, low velocity, DDABC

INTRODUCTION

Background

The North American petrochemical pipeline system represents a key infrastructure asset valued at approximately $541 billion dollar replacement cost.[1] Comprised of approximately 483,900 miles of transmission pipe including some 300,000 miles dedicated to natural gas in the lower 48 states, the system also connects approximately 425,000 gas producing wells via an individual gathering pipeline infrastructure. Corrosion related transmission pipeline cost estimates convey annual expenditures of $5.4 to $8.6 billion distributed among the cost of failures (10%), capital (38%), and operations and maintenance (52%).

Several recent high-profile pipeline failures (both liquid and natural gas) have brought renewed interest to various internal pipeline corrosion mechanisms.[1] Internal corrosion problems (underground storage and associated pipelines) were historically thought to be due to H_2S (hydrogen sulfide), O_2 (oxygen), and CO_2 (carbon dioxide) with microbiologically influenced corrosion being largely ignored. Better investigative techniques have recently shown a number of pipeline failures related to MIC and some recent estimates suggest MIC may contribute to as many as 20 to 30 percent of pipeline corrosion failures. Additionally, because water is needed for microbial growth, conventional thinking holds that low water systems such as crude oil transport lines could not support significant MIC. A large number of pipeline failures are now known to be associated with low water production facilities. The oil and gas industry is quickly recognizing this problem's scope in both gathering and transportation systems prompting attention from both oilfield microbiologists and from asset integrity teams.

A commonly misunderstood process, MIC is defined as corrosion influenced by the presence or activities of microorganisms including bacteria and fungi. Individual bacteria can attach to a pipe surface and grow into a biofilm. Thus, bacteria occur as both free floating (also referred to as planktonic) and as attached biofilm (sessile populations). Bacteria can proliferate and form multilayer colonies on pipes under natural deposits such as mineral scale, wax or asphaltene. In these complex colonies, more benign film forming bacteria can form a protective layer over bacteria such as Acid Producing Bacteria (APB) and Sulfate Reducing bacteria (SRB). It is important to note that microorganisms located at the metal surface do not directly attack the metal or cause a unique form of corrosion. Instead, byproducts associated with an organism's metabolic activity promote known forms of corrosion, including pitting, crevice, and under-deposit corrosion. Typically, the products of a growing microbiological colony accelerate the corrosion process by either: (1) preventing natural film-forming characteristics of metallic corrosion products that would otherwise redeposit and inhibit further corrosion or, (2) providing an additional reduction reaction that accelerates the corrosion process.

MIC Field Management Considerations

Both the research and industrial communities recognize the impact of biofilms in various aquatic industrial applications.[2,3,4] Discussions on the strategies of biofilm control in various applications are leading towards the conclusion that complete biofilm kill is not a realistic target. In practice, regrowth of biofilm cells that survive biocidal treatment may be slow but inevitable.[5] Most of the current biocides were developed for microorganism control in the pre-biofilm phase.

MIC causing bacteria easily proliferate under conditions that commonly exist in oil and gas gathering and transportation pipelines. For example, topography changes often result in pipeline low spots and concomitant areas of low flow, where water stagnates. These low spots comprise essentially stagnant aqueous conditions which can lead to the deposition of both organic and inorganic matter. Particularly in cases of insufficient flow turbulence or inefficient pigging, these areas provide ideal growth situations for various MIC related bacteria. Chemical service companies have long monitored wells, gathering pipeline, facilities, tanks and sales lines for bacteria and attest that low bacterial counts at a source location can lead to extremely high levels of bacteria at downstream locations where stagnant, high growth conditions occur. Pipeline facility operators know that stagnant conditions indeed exist at numerous inaccessible points in their systems. Often in pipelines deemed “low water” systems, stagnant points have gone unrecognized as locations of concern.

MIC has always been associated with oil and gas systems that produce or contain significant or “high” quantities of water. Oil and gas systems including transmission and low-pressure gathering systems have historically been considered to contain “low” water volumes since pipeline water specifications for crude oil are typically between 0.4 – 0.5%. The potential for water to phase separate and remain in the pipe is quite high when total oil volumes are considered. These systems are still considered to be “low” volume water systems because over great distances the water percent by line volume is taken as being insignificant. The field observation is that water does indeed collect in low spots where bacteria then proliferate.

Common internal pipeline corrosion mitigation strategies include dewatering, cleaning (pigging), chemical inhibition, and internal pipeline coatings. Dewatering strategies attempt to remove corrosive fluids prior to pipeline introduction via engineering control components typically located at pipeline compressor and pump stations. In other cases, specific low points are selected along the pipeline right-of-way for the installation of “drips” which serves to remove condensed water. Cleaning or pigging is typically accomplished with a cleaning or scraping pig and can also make use of various cleaning media, including solvents, biocides, acids, and detergents to aid in cleaning effectiveness. As the pig passes through the line, it pushes and/or scrapes fluids, waxes, and debris including bacterial colonies from the line. Sessile bacteria populations are difficult to clean in this manner and may soon replicate under environmentally favorable growing conditions. If for operational reasons, the corrosion cells containing aggressive bacteria cannot be disrupted via pigging, then the other option is to use a chemical means to penetrate and kill the bacteria within the corrosion cell. A biocide’s ability to reliably penetrate the scale, wax, asphaltene or hydrophobic slime layer is chemistry and formulation dependent. Surfactant containing biocide products have the best penetration ability because of their dual hydrophilic / hydrophobic characteristics. However, biocides and biocide formulations can themselves be very corrosive.

In many cases, asset integrity engineers also rely on computer-based corrosion prediction models to help determine if corrosive factors such as temperature, pressure, flow regime, or gas and fluid chemistries pose a significant corrosion failure probability.(1) Although these corrosive models are based on sound engineering principles and do well to address various physical pipeline factors, they are less accurate when it comes to MIC related threats. Additionally, some software programs provide no predictive method for the corrosive action of the chemistry package selected to address MIC-related corrosion.

Low Pressure Gas Gathering Systems

MIC control strategies for low pressure pipeline gathering systems pose a specific problem where pigging facilities are not available or where pigging will cause operational challenges such as production loss. Due to historical design practice, many of the aging oil and gas producing fields across North America lack adequate pig launch/retrieval sites. Quite frequently these aging fields are also losing pressure and thus operate with minimal backpressure for optimal production flow. For these reasons, many older fields lack adequate MIC control means via pigging and it is no surprise that low-pressure gathering systems have been experiencing numerous documented failures associated with MIC.[6]

In an effort to remedy this situation, pipeline operators have tried to apply biocide and/or corrosion inhibitor programs to low pressure gathering pipeline systems. Chemical introduction into such systems presents several issues. First, it is impossible to batch treat these systems in a traditional way since there are no pigging facilities, often times due to cost factors. Continuous injection can result in chemical phase separation; with the biocide settling at the bottom of the pipe. Even in cases where injection atomizers are utilized, an inherently low gas velocity affords insufficient turbulence for the injectors to be useful. Despite highly variable results, both types of chemical application have been used since no better alternative existed. In pipeline systems where pigging is difficult or non-existent, industry has been searching for new techniques to address MIC control problems.

This paper reports progress from our recent investigation regarding the inherent corrosivity of a chosen biocide treatment in low velocity gas gathering pipelines. A DDABC based system is described, which simultaneously exhibits broad spectrum biocidal efficacy while providing corrosion inhibition characteristics.

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[1] Software such as those available from entities such as Honeywell, Broadsword Corrosion Engineering, InterCorr and other are based upon calculations from the DeWaard and Milliams equation or the Norsok M506 prediction program.

EXPERIMENTAL PROCEDURE

Biocide Evaluations

The first evaluation step was to determine the efficiency of the various chemistries with respect to their ability to effectively prevent bacteria proliferation. Specific biocidal products were selected for study due to their known efficacy in both high and low total dissolved solids content waters. Although various formulations for active ingredients exist, only commercially relevant formulations were tested. Commercial biocide formulations (See Table 1) were used as received with the following active concentration levels: glutaraldehyde (50%); tetrakis (hydroxymethyl) phosphonium sulphate (THPS) (30%); n-alkyl (C_{12}, C_{14}, C_{16}) dimethylbenzylammonium chloride (ADBAC) (50%); didecyldimethylammonium bicarbonate/carbonate (DDABC) (50%); oxydiethylene bis(alkyldimethylammonium chloride) (DDAC) (32%). Laboratory screening was used to determine relative use rates required for equivalent biocidal performance.

Table 1
Summary of Biocide Actives Evaluated

Biocide	Active Ingredient	Active Concentration as received	50% brine field dilution concentration
A	n-Alkyl (C_{12}, C_{14}, C_{16})Dimethyl Benzyl Ammonium Chloride (ADBAC)	50%	25%
B	Didecyl Dimethyl Ammonium Bicarbonate/carbonate (DDABC)	50%	25%
C	Glutaraldehyde	50%	25%
D	Oxydiethylene Bis(Alkyl Dimethyl Ammonium Chloride) (DDAC)	32%	16%
E	Tetrakis (hydroxymethyl) phosphonium Sulphate (THPS)	30%	15%

Produced water from the actual operating gas gathering system was used for experimentation. Samples were prepared the same day from freshly obtained field water supply and blank samples indicated 10^5 cfu /mL APB, SRB and anaerobic bacteria. Field water composition is provided in Table 2. Planktonic biocidal activity screening evaluations were performed in duplicate via standard API RP38 serial dilution methods in 10mL sterile nutrient / indicator bottles.(2) Experimental bottles were inoculated with the experimental biocidal chemical products at a rate of 100 ppm (formulated, as received) prior to incubation for 21 days at room temperature under static conditions.

Corrosion Testing

To approximate relevant field application conditions, various experimental compositions were screened for corrosivity in the concentrated form and at a 50% field water (compositions given in Table 2) dilution. Corrosion screening was conducted according to a modified ASTM

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[2] American Petroleum Institute serial dilution method RP38 with Dalwyn sterile nutrient bottles employed

Table 2
Produced Water Composition Used

Ion	Na^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	Ba^{2+}	HCO_3^-	Cl^-
ppm	4390	52.4	5	4.4	6.8	718	6650

Table 3
Autoclave Test Conditions

Total Pressure (psi)	100
CO_2 (psi)	3
N_2 (psi)	97
Temperature (°C)	Room Temp.
Coupon Material	CS 1018
Coupon Finish	Oxide
Length of Test	72hrs
Static or Dynamic Testing	Static

G1-90 procedure. Samples were placed into a high pressure, high temperature (HTHP) autoclave (autoclave testing conditions used shown in Table 3), which contained 1018 carbon steel coupons in intimate contact with the chemical-brine mixture.

Field Evaluation Conditions

The test location consisted of a traditional shallow gas and oil, low pressure 15-20 psi field with largely passive extraction. The field provides “sweet” gas and oil with almost no hydrogen sulfide concerns. The gas evolved is low in water content (<0.5%) and there is no need for secondary water injection methods. Water which collects in pipes is typically low in solids content, with low to moderate salinity (Table 1), and has long residence time (months) with laminar flow characteristics. The field consists of approximately 1,500 wellheads typically 700-900M deep spread over an area of about 10 x 25 miles and is interconnected by an irregular spider web network of 3” gathering pipes. Standard 3” gathering lines connect to main trunk [gathering] lines 6” and bring materials to centralized separation equipment for both gas/water (2-phase) and gas/oil/water (3-phase) separation. The total gathering pipe length was estimated at 1,653km. Internal leaks are typically seen at 4 and 8 o’clock on the pipe cross section at the water / gas interface.

The DDABC test formulation was applied quarterly via either pig slug injection or gravity feed slug injection at each wellhead. The target concentration was 1250 ppm, but this was highly variable due to actual water hold up in specific gathering pipes. The DDABC based product exited the process at the water separator in the water layer which was ultimately subjected to deep well disposal. Periodic monitoring of this water layer during the quarterly treatment program revealed the presence of DDABC at levels ranging from 200-800 ppm.

DDABC Corrosion Inhibition Mechanism Evaluation

DDABC Material. Fifty percent concentrate produced according to the commercial process was used as received.(3) DDABC is a 50wt% aqueous concentrate consisting of a nominal 50wt% DDABC, 40wt% water, and 10wt% propylene glycol. The bicarbonate to carbonate ratio is proprietary and an approximate molecular weight of 380 is employed in stoichiometric calculations. All amounts reported here are as percent active ingredient. Thus, a 0.10% active DDABC solution was prepared by dissolving 0.20 wt% DDABC in the following water samples at room temperature with stirring; i) deionized water ii) tap water (Allendale, NJ) or iii) 5% Salt (NaCl) Water.

Electrochemical tests. Steel (ASTM A366, 0.037% C, 0.19% Mn, 0.18% Cr,) and (black, 0.030%C, 0.31% Mn, <0.10% Cr), aluminum (6061-T6, 0.6% Si, 0.3% Cu, 1.0% Mg, 0.2% Cr) were tested in 3.5% NaCl (salt content equivalent to seawater), and deionized water. Samples were approximately 2.5 cm x 10 cm in size. The surfaces of the test samples were first dry sanded using 400-grit SiC, with the exception of the galvanized steel, which was tested in the as-received condition. Glass O-ring joints (20 mm ID) were clamped to the sanded surface with the O-rings lightly coated with vacuum grease. The glass joints were filled with 25 mL of the test solution. The open circuit potential (OCP) was measured immediately after the solution was poured in the tube using a saturated calomel electrode (SCE). The samples were covered and then allowed to equilibrate overnight, and tested the next day using the three-electrode method and the standard electrochemical methods described below.

Electrochemical Impedance Spectroscopy (EIS). Impedance was measured at the OCP using a 5 mV root mean square sine wave, with frequencies starting at 100 kHz, ending at 0.01 Hz. The EIS tests were conducted with an EG&G 263A Galvanostat/Potentiostat and an EG&G 5210 Lock-in Amplifier, using EG&G 298 impedance software.

Linear Polarization (LP). LP was used to estimate the corrosion rate of a metal. A potential is applied to the sample at 20 mV negative of the OCP. The potential is then ramped at 0.167 mV/sec to 20 mV above the OCP. The result is typically a straight line with a slope equal to the polarization resistance, Rp. The larger the resistance, the more effective the inhibitor. The LP tests were conducted also with an EG&G 263A using EG&G 352 corrosion software. Both the EIS and LP are considered nondestructive tests.

Potentiodynamic Polarization (PDP). PDP is similar to the linear polarization; however, the potential is ramped from 250 mV below the OCP to several hundred millivolts above the OCP, a much larger range, at a faster scan rate of 1 mV/sec. The PDP can measure the cathodic and anodic rates and the passive current density. The PDP tests were also conducted with an EG&G 263A using EG&G 352 corrosion software.

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[3] Carboquat MW50 material from Lonza Inc. was employed. Lonza does not have specific US - FIFRA biocidal claims for AP or APB bacterium. At the time of this publication, registrations are pending.

RESULTS

Laboratory and Field Trial Results

The field from which the water samples were taken historically also experienced numerous gathering system MIC corrosion related failures, Figure 1. Failures have been attributed to various mechanisms including internal MIC, external, mechanical, and unknown causes.

The corrosion related failures in this field are not localized to a particular operator but are in fact a problem that affects the entire area. All area fields produce from shallow gas reservoirs that make very little water which varies in composition from essentially 100 ppm chlorides to 10,000 ppm chlorides. This type of production results in small pockets of fluid that remain stagnant in the lines and allow for bacteria proliferation under nearly ideal conditions. The specific water composition employed in this study appears in Table 1. The corrosion trend highlighted in Figure 1 is not unique to low pressure gas gathering systems. Pipelines used in other fluid transport applications can also exhibit a propensity for water hold-up and may exhibit similar corrosion failures. This model field was chosen as a vehicle to demonstrate that proper biocide selection is a crucial decision

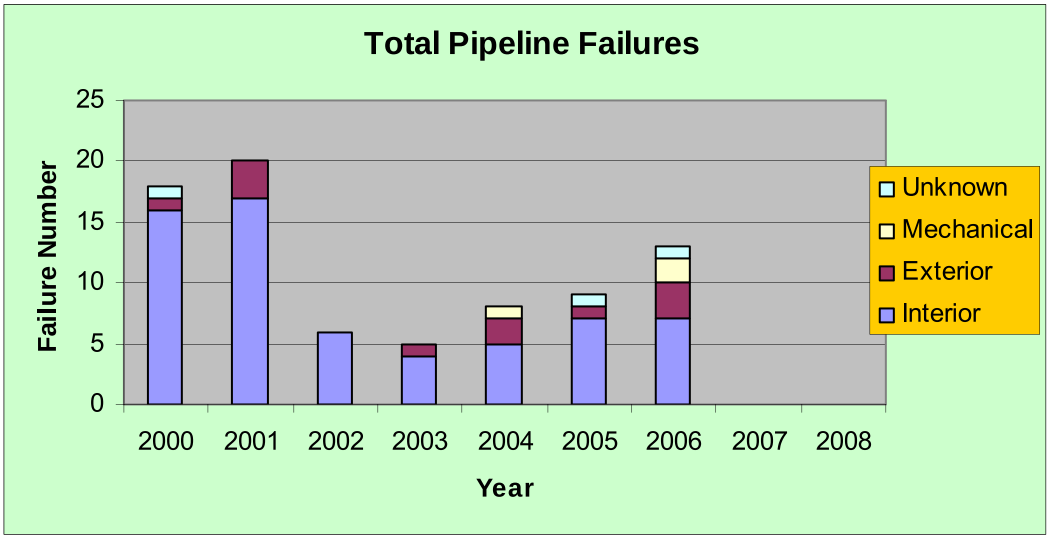

Figure 1 - Field Pipeline Failure History

Laboratory results which demonstrate the relative planktonic efficacies of various biocide candidates at a constant practical dosage of 100 ppm (as received) are shown in Figure 2. This data inidicates that DDABC affords biocidal performance comparable to all other biocide candidates including THPS. However, corrosivity data presented in Figure 3 and Figure 4 show that for a given biocide concentration, much higher levels of corrosivity are incurred for all of the other biocides versus DDABC. Thus, a much higher level of corrosivity is incurred to reach an equivalent biocide performance level with non-DDABC formulations. We also noted that the corrosion rates of the oxydiethylene bis(alkyl dimethylammonium chloride) (DDAC) were of the same order of magnitude as other members of the alkyldimethylammonium chloride family.

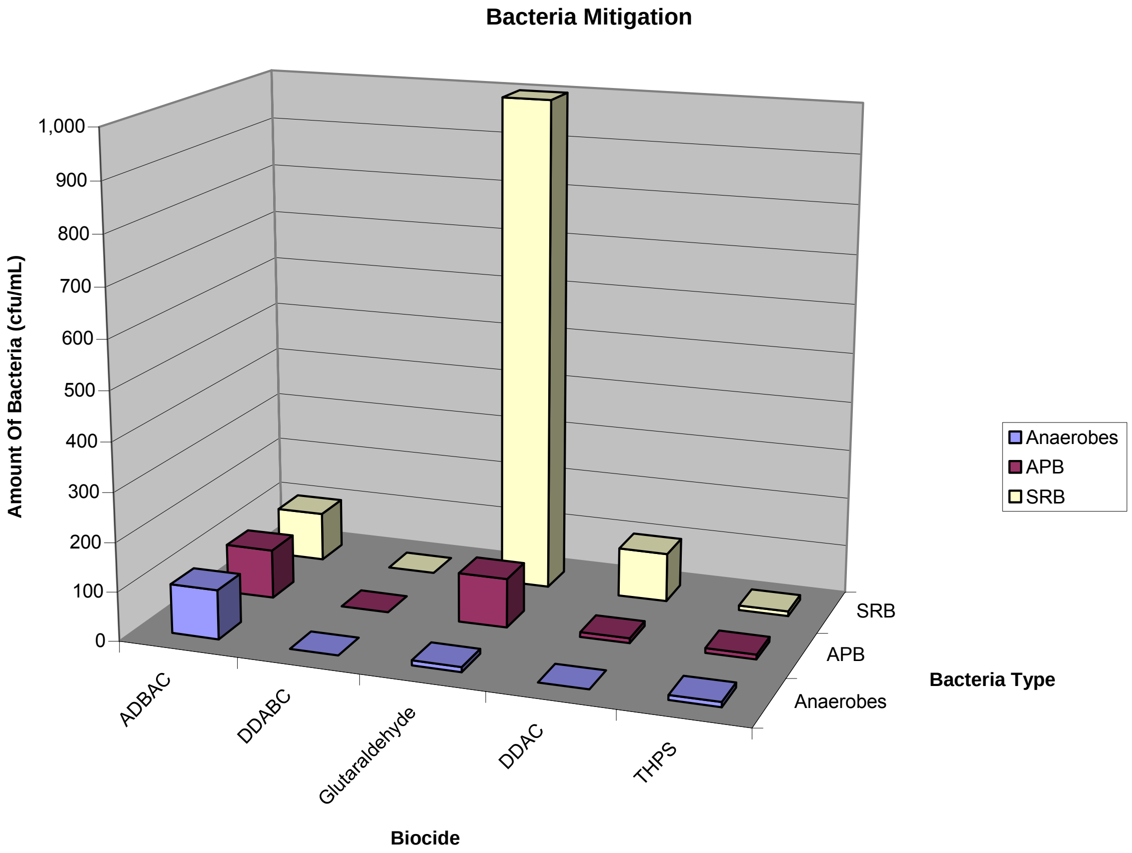

Figure 2 - Biocidal activity of tested products. *Note : Blank Sample Showed 10^5 cfu /mL APB, SRB & Anaerobes

Table 4
Autoclave Corrosion Results using Commercial Biocides with a 50% dilution

Product Tested (50% In Field Brine)		Average Corrosion Rate (mpy)	Corrosion Rate Normalized to DDABC rate	Coupon Observations (Visual)
A	n-Alkyl (C12, C14, C16) Dimethyl Benzyl Ammonium Chloride (ADBAC)	1.76	4.4 X	uniform
B	Didecyl Dimethyl Ammonium Bicarbonate/carbonate (DDABC)	0.40	1.0 X	uniform
C	Glutaraldehyde	3.50	8.8 X	uniform
D	Oxydiethylene Bis(Alkyl Dimethyl Ammonium Chloride) (DDAC)	5.06	12.7 X	uniform
E	Tetrakis (hydroxymethyl) phosphonium Sulphate (THPS)	25.78	64.5 X	uniform

Table 5
Autoclave Corrosion Results For Neat Products.

Product Tested (100% In Field Brine)		Average Corrosion Rate (mpy)	Corrosion Rate Normalized to DDABC	Coupon Observations (Visual)
A	n-Alkyl (C12, C14, C16)Dimethyl Benzyl Ammonium Chloride (ADBAC)	2.46	3.6 X	uniform
B	Didecyl Dimethyl Ammonium Bicarbonate/carbonate (DDABC)	0.68	1.0 X	uniform
C	Glutaraldehyde	12.80	18.8 X	uniform
D	Oxydiethylene Bis(Alkyl Dimethyl Ammonium Chloride) (DDAC)	5.16	7.6 X	uniform
E	Tetrakis (hydroxymethyl) phosphonium Sulphate (THPS)	36.80	54.1 X	uniform

a) ADBAC b) DDABC c) Glutaraldehyde d) DDAC e) THPS

Figure 3 - Autoclave Test Coupons from result reported in Table 4

After consideration of the laboratory efficacy and corrosion results, a field campaign was initiated at the end of 2006 with a commercial DDABC active prototype formulation. This field trial was necessary in order to validate simple laboratory test observations which addressed planktonic activity on actual sessile conditions in the field. Prior to this the field had tried a number of different biocidal chemistries including n-alkyl (C_{12}, C_{14}, C_{16} blend) dimethylbenzylammonium chloride (ADBAC), oxydiethylene bis(alkyl dimethyl ammonium chloride) (DDAC), and tetrakis (hydroxymethyl) phosphonium sulphate (THPS). No other significant changes were made during this time such as pigging practice, water flow rates or field gas pressure. Data trends from Figure 5 after 20 months DDABC field treatment demonstrate a continuous and marked reduction in observed pipeline failures. Indeed, failure rates in 2005 and 2006 of six internal failures were reduced to a rate of one in each of 2007 and 2008, respectively.

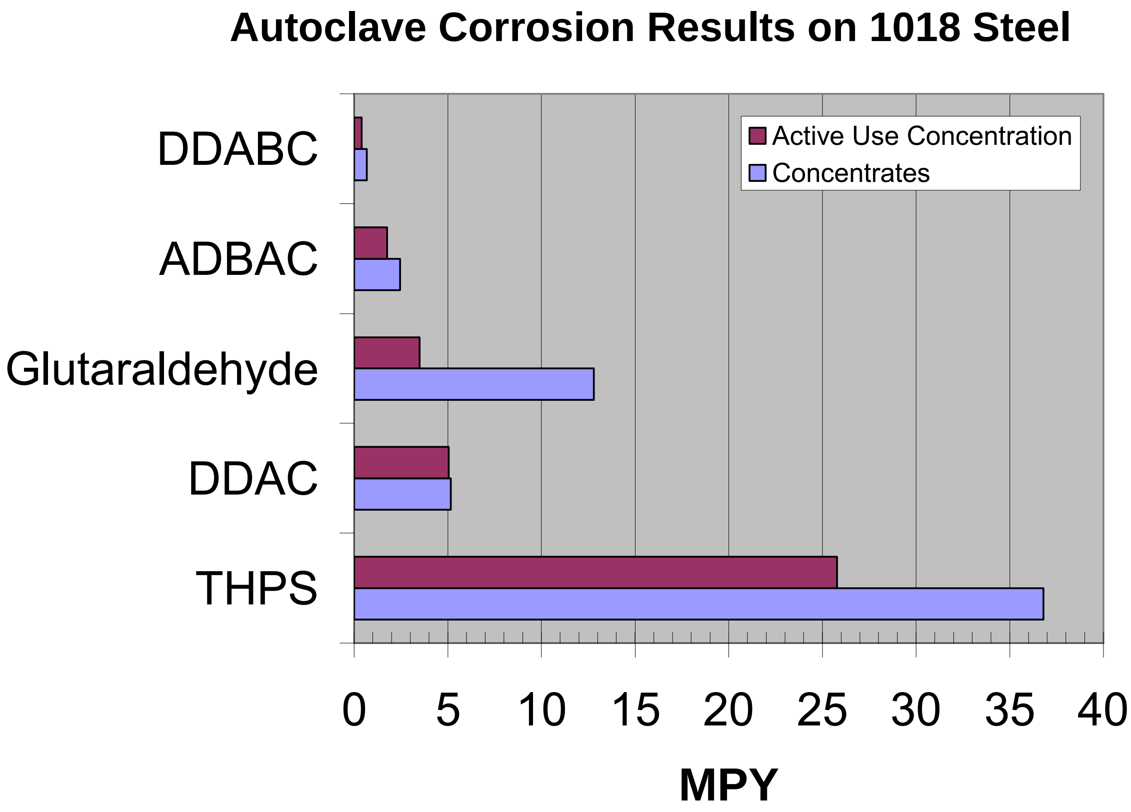

Figure 4 - Summary of autoclave derived corrosion data on both active use dilutions and concentrate treatment formulations obtained via modified ASTM G1-90 procedure.

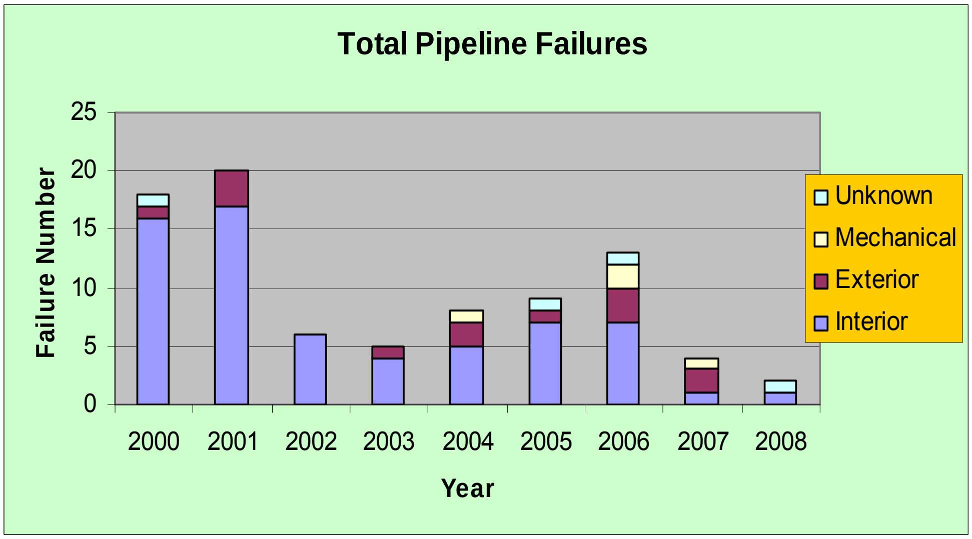

Figure 5 - Field Pipeline Failure History through August 2008

DDABC Corrosion Inhibition Mechanism

DDABC has also been evaluated as a corrosion inhibitor via standard electrochemical tests on a variety of commercially significant metals including steel, aluminum, copper, and zinc galvanized steel and shown to be highly effective. At the proper dilution, the inhibitor migrates to the metal/solution interface and forms a mono-molecular film on the anodic sites.

Concentration Effects on Thin Film Formation. The film-forming tendencies of neat DDABC at two levels were tested on 1010 steel in deionized water using electrochemical impedance spectroscopy (EIS). The observed data in Figure 6 indicates a significant difference in behavior between the high and low DDABC concentrations.

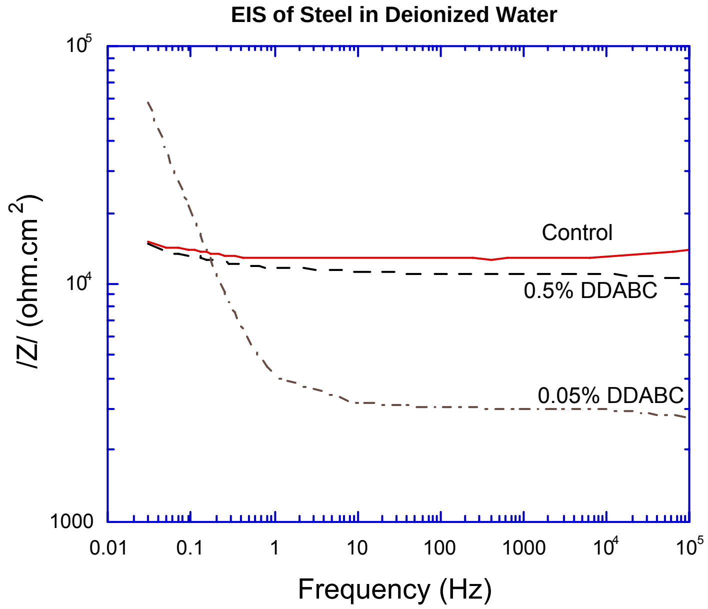

Figure 6 - EIS measurements of DDABC at various concentrations in DI water on steel

The low 0.05% DDABC level showed a measurable capacitive effect at the low frequencies (left side of Figure 6) indicative of a barrier film. If the film is approximated as a parallel plate capacitor, then the thickness of the film may be estimated.7 All estimates show that the film is only 0.5 nm in thickness (assuming a dielectric constant of water, ε = 80), and in the present case, this correlates to an absorbed film of approximately one monolayer thick.(4) However, the higher 0.5% DDABC level clearly exhibits no such measurable thin film and behaves in fashion similar to the water control. Significantly, DDABC also exhibits an interesting concentration dependent behavior with respect to polarization resistance (Rp) measurements in the same concentration region. As shown in Figure 7, both dilute and concentrated DDABC solutions exhibit very low Rp, but at an optimal level of ca. 0.05% exhibits extremely high resistance. Polarization resistance correlates directly with corrosion resistance, and taken together these observations indicate a thin film capable of imparting high resistance at optimal

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[4] Note the dielectric constant of this molecule is not currently unknown. Using the dielectric constant of a polymer, e=3, gives unrealistic subatomic dimensions for the monolayer.

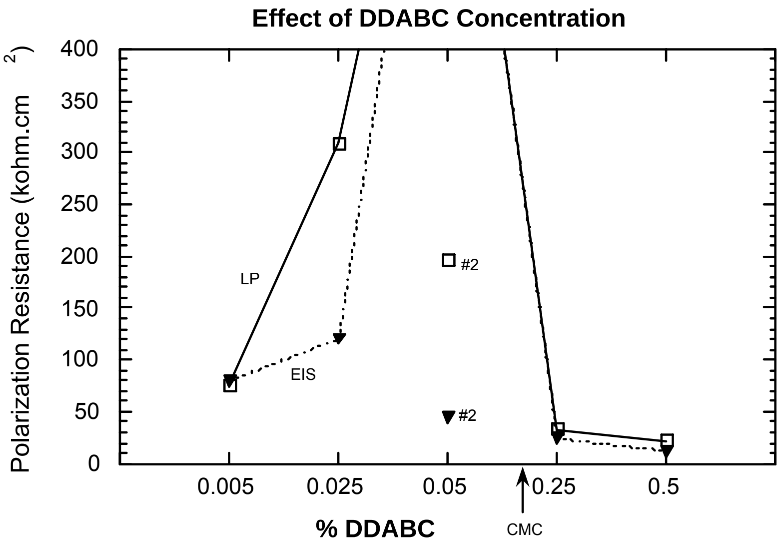

Figure 7 - Polarization resistance as measured by EIS and LP as a function of DDABC concentration in DI water on steel

concentrations. However, at either low or high concentrations no such thin film results. It is also noteworthy that this film can be destroyed or damaged by polarizing the metal either −20 mV or +20 mV. Indeed, the Rp for 0.05% DDABC is off-scale for the first measurement, but the test disturbed the surface film and the second Rp measurement resulted in the lower value plotted at point #2.

Figure 6 also suggests a potential explanation for this concentration dependent behavior. The solution resistance range (the high frequency impedance on the right side, Figure 6) shows a minimum (3,000 ohm) for 0.05% DDABC. This indicates that at 0.05% DDABC, sufficient carbonate anions and quaternary cations remain in solution, increasing its conductivity. However, the 0.5% DDABC only shows three times higher resistance (10,000 ohm) despite the fact it is ten times more concentrated. DDABC molecules which are clustered in micelles at high concentrations provide one potential rationale for this discrepancy. The critical micelle concentration (CMC) was determined by measuring the surface tension and was estimated to be 0.10% DDABC.[8] However, a recent report demonstrates a more complicated equilibrium behavior in solution with at least three distinct micelle and aggregate structures present.[9] Figure 8 provides the relevant pictorial explanation that at high concentrations DDABC forms micelles which aggregate the majority of the inhibitor molecules into a rod shaped aggregate. In this form, DDABC is not energetically available to adsorb onto the metal surface. However at low and moderate concentrations, trimeric aggregates exist in kinetic equilibrium with spherical micelles in solution which are able to interact with the metal surface. As long as sufficient concentration exists to afford an effective, continuous, thin film, corrosion inhibition will result. Thus the observed DDABC concentration dependence on corrosion performance can be understood in terms of both solution micelle behavior and sufficient thin film formation.

Linear Polarization (LP) Results. Linear polarizations for steel in DI water are shown in Figure 9 where circuit potential versus current density is plotted. Note that a direct relationship between the line's slope and corrosion resistance exists and high positive slope indicates

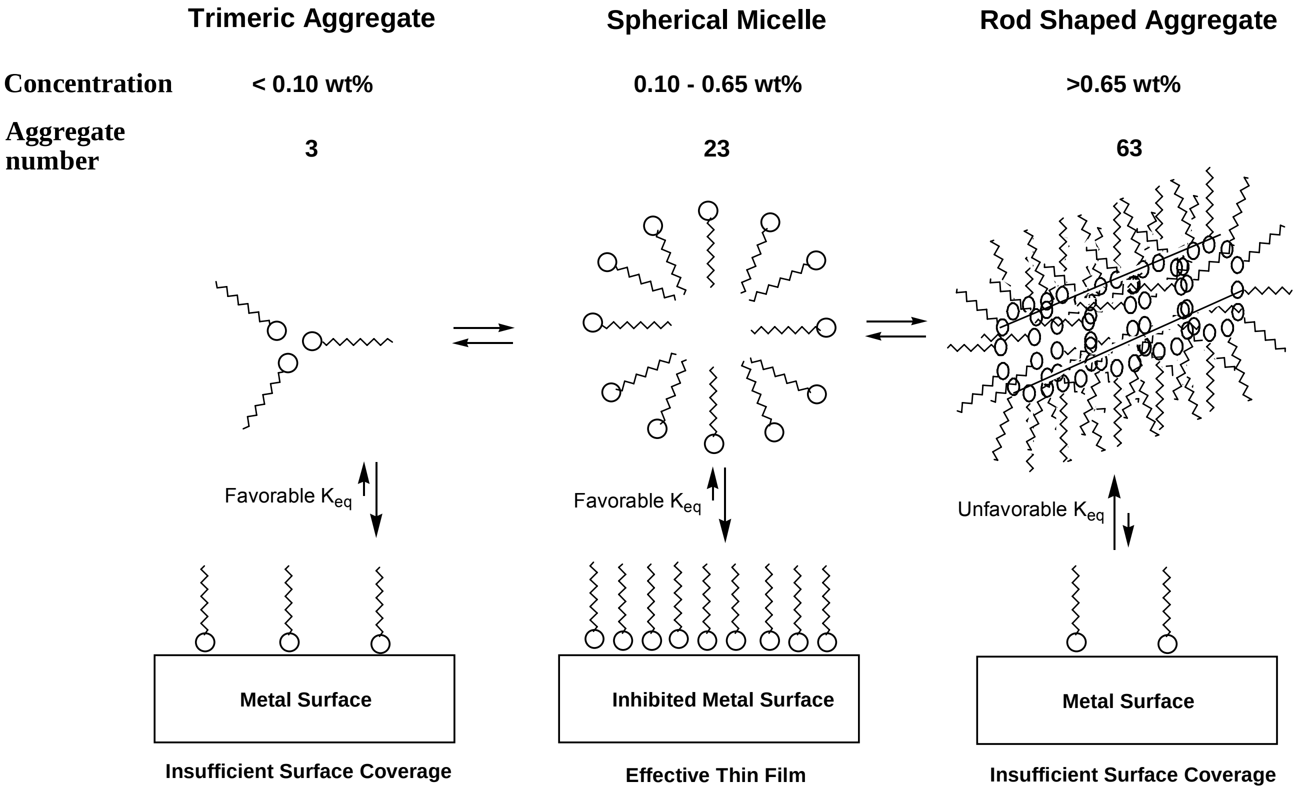

Figure 8 - Schematic revealing complex DDABC aggregation and micelle behavior changes as a function of concentration

greater corrosion resistance. The data reinforces information from the EIS plots in that low slopes (low corrosion resistance) are observed for high DDABC concentration of 0.5% in the same region where a thin film was not observed. However, the slope's magnitude increases with decreasing DDABC concentration for a maximum at 0.05% in the region where a thin film is expected. The slope then drops again predictably at lower than optimal concentrations of 0.025 and 0.005% presumably due to insufficient thin film surface coverage.

One abnormality in the LP results was noted which is related to the response the thin film to applied voltage. In the first test at 0.05% DDABC, the curve was vertical, or even perhaps negative. In the second test run a few minutes later on the same sample, the curve has a more linear slope, although steeper than the other concentrations. This abnormal response indicates an adsorbed film which was blocking the anodic and cathodic sites, which is then damaged during the polarization. This effect is the same for 0.05% DDABC whether the LP is run in the positive or negative directions. While linear polarization is generally considered a non-destructive, reproducible technique, this appears not to be the case for the 0.05% DDABC. Noteworthy, LP indicates the amount of current passed in 0.05% DDABC (#1) is approximately one electron charge per square nanometer, which would be the magnitude for one adsorbed quaternary ammonium cation per square nanometer.

Potentiodynamic Polarization Potentials. The PDP tests for steel in DI water are shown in Figure 10. Consistent with other results, we see that concentrated 0.5% DDABC is almost the same as the uninhibited DI water. However, the 0.05% DDABC has a ten times lower passive current. In this system, the DDABC acts as an anodic inhibitor, lowering the anodic current by ten times.

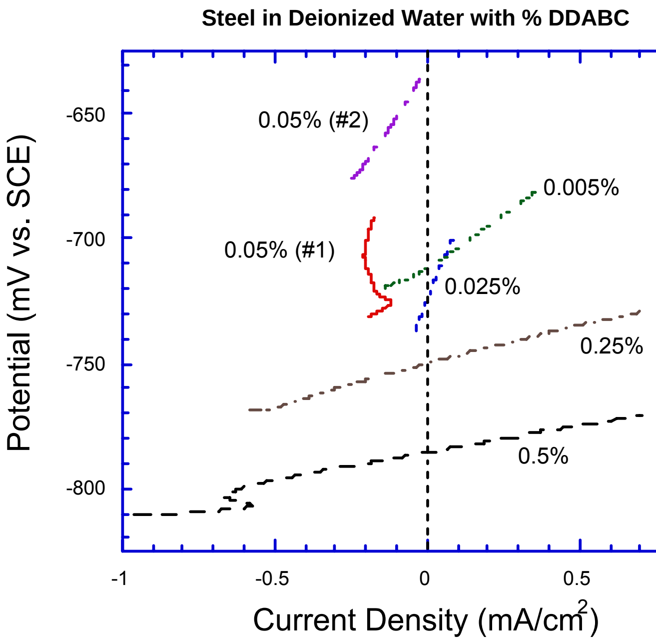

Figure 9 - Linear polarization measurements on steel at various DDABC concentrations in DI water

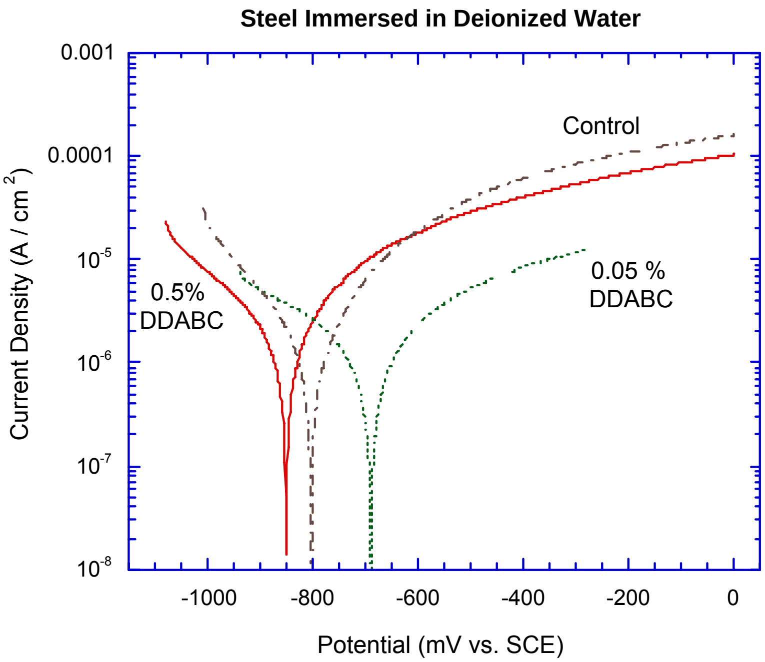

Figure 10 - Potentiodynamic polarization measurements on steel at various DDABC concentrations in DI water showing passivation

CONCLUSIONS

The ability of DDABC to reduce internal corrosion failures in the test field is attributed not only to its efficacy as a biocide, but also to its ability to act as a thin film forming anodic inhibitor. The material demonstrates an ability to leave a thin corrosion inhibitor film on the walls of the pipe thus reducing the risk of the concentrated product causing corrosion of the pipeline via an electrochemical corrosion mechanism.

The appropriate biocide chemistry choice for the treatment of MIC relevant bacteria in oil and gas pipelines represents a very important component in the overall system corrosion performance. Particularly in MIC prone situations where mechanical pigging is either unavailable or ineffective, chemical biocide treatments can accumulate in the line resulting in high, corrosive material concentrations. The biocide treatment itself thus represents an additional source of corrosivity which has previously gone unaddressed.

Laboratory evaluations demonstrate the DDABC material performs efficiently as both a biocide and a corrosion inhibitor when compared to commonly employed treatments including glutaraldehyde, THPS, ADBAC, and DDAC quaternaries. The DDABC system displayed advantages as an MIC corrosion control agent at equivalent use levels and this data was sufficient to support an extended field trial.

Under field test conditions where biocide concentrations were expected to accumulate in gathering pipes for extended durations, DDABC effectively reduced corrosion related failures by a factor of approximately six fold over previous MIC control programs. This observed reduction can be attributed to both potent biocidal efficacy and thin film forming tendencies of DDABC to act as an anodic inhibitor.

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