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Research report

The effect of alcohols and kinetic hydrate inhibitors in gas pipelines on the risk of microbial-influenced corrosion (MIC)

RESEARCH REPORT

THE EFFECT OF ALCOHOLS AND KINETIC HYDRATE INHIBITORS IN GAS PIPELINES ON THE RISK OF MICROBIAL-INFLUENCED CORROSION (MIC)

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FOREWORD

The most important group of microorganisms associated with microbial-influenced corrosion (MIC) in petroleum production facilities and pipelines are sulfate-reducing bacteria (SRB); the vast majority of MIC failures are related to their activities. One of the recurring unknowns about MIC is the likelihood of its occurrence in wet gas pipelines. A suspected reason why harmful bacteria are rarely found in these lines is that they often contain glycols, methanol or kinetic gas hydrate inhibitors, all of which are added to prevent formation of gas hydrates.

Alcohols, such as glycols and methanol, under the right conditions, can be lethal to microorganisms because of their ability to denature proteins (including enzymes) and to solubilise lipids. Conversely, at low concentrations, alcohols can actually be stimulatory to bacteria, which may use them for growth and energy production. Kinetic hydrate inhibitors provide an alternative to alcohols. These may contain solvents such as monoethylene glycol (MEG) and/or n-butyl glycidyl ether, the latter being a known toxin to higher organisms and both constituting possible bacterial nutrients at low concentrations.

Petroleum company engineers frequently ask for consultant input into corrosion risk assessments for gas pipelines. Unfortunately, the predictive model that is widely in use does not address the issue of methanol or glycol or kinetic hydrate inhibitor dosing to gas lines. As a result, risk assessments often give very high and unrealistic predictive rates for MIC in gas lines.

A small scale laboratory test programme was undertaken to ascertain the biocidal and/or bacteriostatic effects of various concentrations of common alcohols and kinetic hydrate inhibitors used in gas pipelines, using conventional culture test methods for SRB and a range of representative mixed cultures of bacteria originating from petroleum production water systems.

This research report presents the results of the laboratory study and concludes that the risk of MIC is low to moderate in wet gas lines at typical levels of alcohols or kinetic hydrate inhibitors. Current corrosion risk assessment models and protocols should be modified to take account of these corrective findings.

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1 INTRODUCTION

1.1 TECHNICAL BACKGROUND

The most important group of microorganisms associated with microbial-influenced corrosion (MIC) in petroleum production facilities and pipelines are sulfate-reducing bacteria (SRB); the vast majority of MIC failures are related to their activities. SRB live in oxygen free environments, where they obtain their required carbon from organic nutrients and their energy from the reduction of sulfate ions to sulfide. Sulfide appears as dissolved or gaseous hydrogen sulfide (H_2S), hydrogen sulfide ion (HS-), sulfide ion (S^{2-}) or metal sulfides, or a combination of those substances, according to conditions. Sulfides are highly corrosive to many metals, including carbon steel, Stott (2010).

Though by far the most attention has focused on SRB activity with respect to MIC in petroleum production systems and SRB are the subject of this study, the possible role of other microorganisms in the MIC process in wet gas pipelines should not be overlooked; in particular, high populations of methanogens are reported to be present in such environments and may have a role in MIC, Larsen (2010). There is evidence that direct electron uptake by SRB and methanogens occurs and that sulphide acts as an accelerating compound, Dinh et al. (2004).

One of the recurring unknowns about MIC is the likelihood of its occurrence in wet gas pipelines. Viable SRB have rarely been detected from import and export gas pipelines in the Southern North Sea (for example), despite many of these platforms pumping their open and closed drains fluids typically highly infested with SRB into these lines in order to meet environmental restrictions on releasing fluids to sea. A question that arises is 'what is the resultant risk of MIC?'

A suspected reason why harmful bacteria are rarely found in these lines is that they often contain glycols, methanol or kinetic gas hydrate inhibitors, all of which are added to prevent formation of gas hydrates. Gas hydrates (or clathrate hydrates) are ice-like crystalline molecular complexes, formed from mixtures of water and suitably sized 'guest' gas molecules, Sloan (1998). The concentration of the alcohols varies enormously, being anything from 10 to 80 % in produced liquids depending on the process and the specific requirements for gas hydrate inhibition; therefore, it is not possible to be more specific about 'typical' dosages of these chemical additives.

Petroleum company engineers frequently ask for consultant input into corrosion risk assessments for gas pipelines. Unfortunately, the predictive model that is widely in use does not address the issue of methanol or glycol or kinetic hydrate inhibitor dosing to gas lines, see Pots (2002). As a result, risk assessments often give very high and unrealistic predictive rates for MIC in gas lines.

1.2 TYPES OF CHEMICALS DOSED INTO GAS PIPELINES AND THEIR EFFECTS

Alcohols, such as glycols and methanol, under the right conditions, can be lethal to microorganisms because of their ability to denature proteins (including enzymes) and to solubilise lipids. Methanol can also cause translational errors in protein synthesis. Additionally, the straightforward effect of reduction in water activity may be very important in bactericidal and/or bacteriostatic effects of the alcohols. As a general rule, the anti-microbial activity of alcohols increases with molecular weight and chain length up to about C10; whilst methanol is generally considered to be a poor anti-microbial agent, ethanol exerts maximum activity at 60 to 90 % (v/v) in water mixtures. Limited information is available on monoethylene glycol (MEG), triethylene glycol (TEG) and polyethylene glycol (PEG) biodegradation rates and bacterial inhibition by methanol, MEG, TEG and PEG; such information as is available is not specific to SRB, Verschueren (2001).

Conversely, at low concentrations, alcohols can actually be stimulatory to bacteria, which may use them for growth and energy production. In fact bioreactors are frequently used in industrial systems to remove these alcoholic contaminants from waters prior to disposal.

As an alternative to alcohols, kinetic hydrate inhibitors delay gas hydrate crystal nucleation and disrupt hydrate crystal growth by becoming incorporated into the growing hydrate crystals. They are used at lower concentrations than alcohols, typically a maximum of 2-5 % of commercial product in produced fluids. Nevertheless, kinetic hydrate inhibitors do contain solvents such as MEG and/or n-butyl glycidyl ether, the latter being a known toxin to higher organisms and both constituting possible bacterial nutrients at low concentrations.

Examples of kinetic hydrate inhibitors include poly(N-methylacrylamide), poly(N, N-dimethylacrylamide), poly(N-ethylacrylamide), poly(N, N-diethylacrylamide), poly(N-methyl-N-vinylacetamide), poly(2-ethyloxazoline), poly(N-vinylpyrrolidone), and poly(N-vinylcaprolactam).

Unlike the kinetic hydrate inhibitors, anti-agglomerate hydrate inhibitors are effective only in the presence of an oil phase; they are of little interest with respect to gas pipelines and, for that reason, they were not included in the study.