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Water-based Corrosion Inhibitor for Sour Gas Production

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ABSTRACT

Production of natural gas containing >4 ppmV of hydrogen sulfide (sour gas) poses challenges for oil and gas field operators due to the high corrosion and potential downstream fouling risk to pipelines and other assets in the production operation, as well as concerns about environmental and health impacts due to the toxic nature of hydrogen sulfide. This paper discusses a specific challenge at a customer site related to the formation of substantial gunk in the downstream sour water stripper operating at atmospheric pressure and ambient temperature.

The objective of the effort was to mitigate gunk formation in the stripper without sacrificing the efficacy of the existing corrosion control program (OCI-1). This paper examines the development of a gunk test protocol that mimics the gas field conditions and the development of a fit-for-use water-based corrosion inhibitor product. The new inhibitor (WCI-2) was found to resolve the gunk issue while providing equivalent corrosion protection as compared to OCI-1 based on evaluation performed using a Rotating Cage Autoclave.

Key words: Corrosion, Water-based Corrosion Inhibitor, Gunk, RCA, Gas pipelines

INTRODUCTION

Natural gas is a mixture of several hydrocarbon gases including methane, ethane, propane, butane, and pentane associated by carbon dioxide, nitrogen, helium, and hydrogen sulfide[(1)]. Natural gas may contain significant amount of acidic gases such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2). Gas with H_2S is referred to as sour gas and is problematic for a variety of reasons: toxicity and flammability, high corrosion, potential downstream fouling risk to pipelines and other assets in the production operation, as well as concerns about environmental and health. As per the International Energy Agency, about 43% of the world's natural gas reserves are sour. In Russia, 34% of total reserves are sour gas comprised of around 25% H_2S and 15% CO_2. They are the world's largest natural gas producer [(2)]. The Middle East contains 60% sour gas reserves comprised of around 30% H_2S and 10% CO_2 [(3)]. About one-third of the natural gas produced in Canada's Alberta and British Columbia provinces is sour [(4, 5)]. In Asia, gas reserves contain up to 15% H_2S and 10% CO_2 [(5)].

Corrosion, a natural potential hazard associated with oil and gas production and its transportation, occurs due to inherent corrosivity of aqueous phase containing dissolved acidic gases. Fouling in the form of gunk can occur when sour/acidic gas reacts with production chemicals. Gunk can be defined as undesirous deposits observed in the process. Corrosion causes metal impairment whereas corrosion and fouling together can lead to complete loss of technical system operational capability. Various production chemicals including corrosion inhibitors (CI) are being used to protect the assets, but selection of appropriate chemistry and its evaluation based on mimicking field conditions is important to avoid further downstream issues.

In this paper, we will look at a specific challenge at a customer site related to the formation of substantial gunk in the downstream sour water stripper. The customer was using an oil-soluble corrosion inhibitor, but because of change in their system parameters, slight gunk formation was observed during the twice-yearly cleaning process. Request was received to mitigate gunk formation in the stripper without sacrificing the efficacy of the existing corrosion control program. The challenge was accepted and a thorough study was planned to:

1) Understand the sour gas production field conditions
2) Mimic gunk formation for different corrosion inhibitors via testing
3) Evaluate selected corrosion inhibitors using RCA
4) Evaluate 'No Harms' test for proposed corrosion inhibitor

EXPERIMENTAL PROCEDURE

1) Understand the Sour Gas Production Field Conditions

At customer site, sour gas production well head operating pressure is 30 MPa, pressure inside the station and gathering pipelines are 8-9 MPa, well head temperature ~40-60° C and after heating ~55° C. Average gas flowrates are 3-8 m/s. Liquid fraction ≤ 0.05%. Gas pipeline dimensions were 4", 6", 8", and 10".

Table 1: Production gas composition

Composition	He	H_2	N_2	CO_2	H_2S	CH_4	C_2H_6	C_3H_8
Content (mol.%)	0.04	0.01	1.25	8.65	12.45	77.54	0.03	0.03

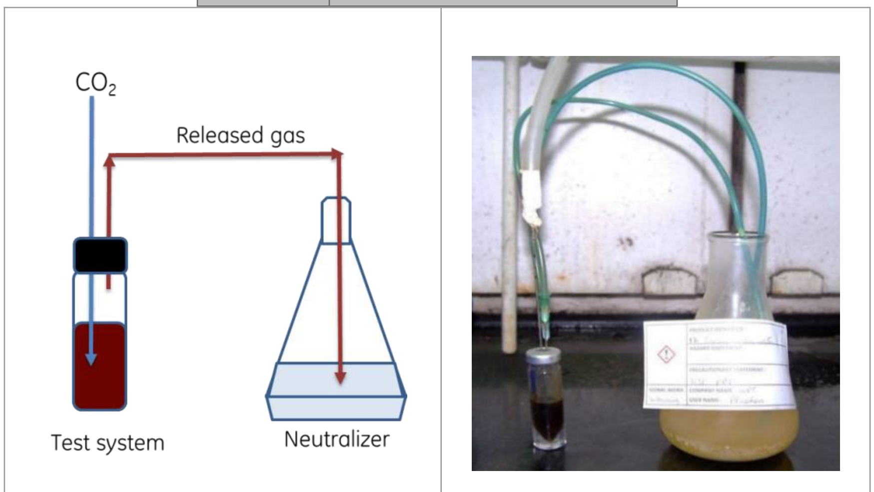
2) Mimic Gunk Formation for Different Corrosion Inhibitors via Testing

Synthetic brine was prepared as per produced water composition in Table 2. Five different CI chemistries (OCI-1, WCI-1, WCI-2, WCI-3 and WCI-4) were subjected to gunk formation testing. Test setup consisted of closed bottle with gas purging and gas exit facility. Outlet of exit gas was passed through neutralizer solution.

The gunk test was performed by using two different test systems: (1) Sodium hydrosulfide was dissolved in synthetic brine water (1:1 ratio), further mixed with an oil-based corrosion inhibitor (OCI) in 1:2 ratio and (2) Sodium hydrosulfide dissolved in water-based corrosion inhibitors (WCI) in 1:2 ratio. CO_2 gas was purged for 10 minutes in respective test systems and solutions were left overnight. Visual observations were done for gunk formation in form of settled/dispersed deposition. Figure 1 shows the test setup.

Table 2: Synthetic brine composition

Salts	Concentration (PPM)
K^+	1.15×10^3
Na^+	3.99×10^4
Ca^{2+}	2.28×10^3
Mg^{2+}	4.97×10^1
NH_4^+	1.07×10^2
Cl^-	6.64×10^4
SO_4^{2-}	8.21×10^2



(a) Diagrammatic view of lab setup **(b) Lab setup**

Figure 1: Gunk test setup

3) Evaluate Selected Corrosion Inhibitors using RCA

Rotating cage autoclave (RCA) per ASTM G170 and G184 was used to evaluate downselected CI chemistries. Test fluid was 100% brine solution (Table 2), pH of brine solution was adjusted to 4.5 using 1% HCl, test temperature was set to 30°C, stirrer speed was fixed to 1000 rpm and CO_2 pressure of 2.2 bar was maintained in autoclave. Corrosion inhibitors were evaluated using RCA under field equivalent or pipeline flow conditions. It is important to compare equivalent pipeline velocity for the same shear stress used in the experiment with the actual flow velocity [(6)]. Higher the difference indicates that CI was evaluated under harsh conditions in lab.

4) Evaluate 'No Harms' Test for Proposed Corrosion Inhibitor

(a) Foaming tendency: 1% solution of CI chemistry was prepared using synthetic brine water, stirred at 1400 rpm for one min and poured into a cylinder. Initial foam height and time required to collapse the complete foam was monitored. Figure 3 represents the foaming test setup and initial foam height for individual CI chemistries.

(b) Emulsion Tendency: 1% aqueous solution of CI chemistry and diesel was mixed in 1:1 ratio and transferred to stopper glass cylinder. Cylinder was heated to maintain the mixture temperature at 40°C. Further it was rotated in an up-down manner 200 times and monitored for phase separated at intervals of 5, 10, and 15 minutes.

RESULTS AND DISCUSSION

As shown in Figure 1, indivdual test system was purged with CO_2 and some of the them turns to yellowish in color with a rotten egg smell -- an indication for H_2S liberation and reaction with CI chemistries. Per Table 3, all five corrosion inhibitors were subjected to gunk test. Gunk in the form of deposit was observed in OCI-1, WCI-3 and WCI-4 (Figure 2a) whereas no gunk was observed in sample WCI-1 and WCI-2 (Figure 2b). It was observed that formulations containing nitrogen based compounds has resulted in gunking. WCI-1 and WCI-2 samples were stored for 180 days and no gunk was observed during storage period.

Table 3: Gunk test observations

Chemistries	Solubility	Gunk formation	
		Overnight	Six months
OCI-1	Oil	Yes	Yes
WCI-1	Water	No	No
WCI-2	Water	No	No
WCI-3	Water	Yes	Yes
WCI-4	Water	Yes	Yes

(a) Gunk in WCI-3

(b) No gunking in WCI-2

Figure 2: Visually observed gunk

OCI-1(benchmark product), WCI-1, and WCI-2 were further subjected to evaluate corrosion inhibition efficiency as per test conditions discussed in Section 3. Respective chemistries were dosed at 100 ppm on a product basis into each RCA experiment. Table 4 summarizes the obtained results. WCI-1 and WCI-2 show equivalent percentage corrosion inhibition as compared to OCI-1. Shear stress was calculated using experimental conditions and found to be 40 Pa. Equivalent pipe velocity for different pipe diameters (4”,6”,8”,10”) were calculated using above shear stress value and found to be 36-41 m/s. Calculated flow velocity are higher than the actual flow velocity, i.e. harsher test conditions were used in experiment as compared to field. It will definitely provide better pipeline corrosion inhibition in the field.

Table 4: Compilation of CI's performance

Chemistries	Solubility	Dosage (ppmP)	% inhibition
Blank	-	0	NA
OCI-1	Oil	100	78 ± 1
WCI-1	Water	100	80 ± 1
WCI-2	Water	100	81 ± 2

WCI-2 was further evaluated for no harm in comparison with OCI-1. It was observed that WCI-2 has given 80ml of initial foam height. Foam was highly unstable and collapsed within a minute, whereas no foam was observed in OCI-1 (Figure 3). Figure 4 represents observation for emulsion tendency, in both cases unstable emulsion were formed and separated into two phases within 10 minutes.

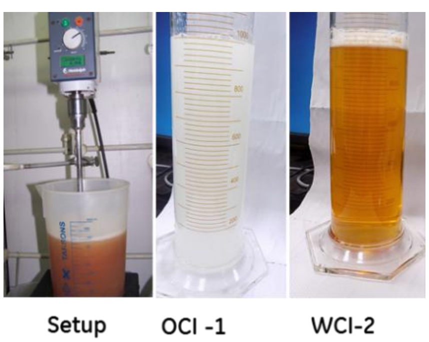


Figure 3: Foaming test setup and observations

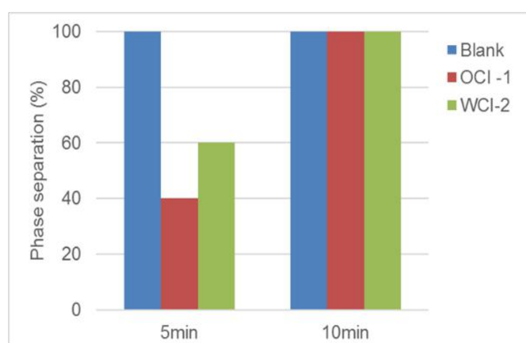


Figure 4: Observation for emulsion tendency

CONCLUSIONS

- ✓ Gunking issue was addressed through a chemical treatment solution, a recommended water based corrosion inhibitor (WCI-2)
- ✓ Basic application property of pipeline corrosion protection was retained, WCI-2 was found to be equivalent corrosion inhibitor as compared to OCI-1
- ✓ WCI-2 cleared the ‘no harms’ test: foaming and emulsion tendency
- ✓ Based on shear stress calculation, lab experimental conditions were found to be more severe than field conditions
- ✓ Fit-for-use water based corrosion inhibitor “WCI-2” was successfully deployed

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