CO_2 Corrosion Inhibitor Assessment Using Various Measurement Techniques in oilfield

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ABSTRACT

Tests and evaluation studies were conducted to select the best performance and treating rich carbon dioxide fluid composition associated with crude oil are produced. The experiments include standard electrical resistance probe for direct corrosion monitoring technique, and inspection by using an ultrasonic test to assess corrosion inhibitor.

The improvement process for chemical treatments development requires an effective strategy. The effective process for field testing inhibitor required twenty-four days to determine inhibitor performance and verifying minimum effective concentration. The standard electrical resistance probe with changeable dosage test was utilized. Ultrasonic testing one of the most widely used non-intrusive techniques is applied to measure of localized corrosion. Measurement apparatuses are adequate systems for monitoring of treatment efficiency.

Keywords: corrosion monitoring, CO_2 corrosion inhibitor, standard electrical resistance.

1 Introduction

Corrosion inhibitors are applied to decrease the rate of internal corrosion in pipelines carrying oil and gas from wells to oilfields and processing plants; even so, no single inhibitor claims all situations. The efficiency of an inhibitor is determined not only by the characteristics of the gas, crude oil and associated water of the pipeline and by the characteristics of the inhibitor itself, but the operating conditions of the oilfield (temperature, pressure, and flow rate) [1].

Because of the complication involved in evaluating corrosion inhibitors, the variety of measurement techniques to evaluate inhibitors, the costs coupled with assessing and utilizing corrosion inhibitors to decrease the rate of internal corrosion of pipelines, and the widespread utilizes of inhibitors, it is important to assess inhibitor performance and verifying minimum effective concentration that are measuring quality and quantity of inhibitors.

Knowledge of the inhibitor performance by measurement techniques has historically been used to control whether a system is protected. This requires confidence in the correlation between measurement techniques results and oilfield conditions. If the amount of corrosion inhibitors present in the oilfield is established at minimum effective concentration, then the system is considered protected and economic. As water chemistry changes, such tests need to be repeated to ensure their relevance to current oilfield conditions.

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The study has been executed to identify dosage injected of corrosion inhibitor into the crude oil well. The well has been injected in the annulus where it should provide corrosion protection for the tubing. This well is high CO_2 producing and as such have a history of CO_2 induced pitting corrosion on the tubing found during work over. The corrosion inhibitor being injected downhole into the casing to ensure the protection of both the tubing and the flow lines of this well.

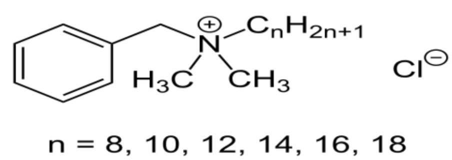
An inhibitor with an efficiency of 90% would be expected to reduce a baseline corrosion rate of 100 mpy down to 10 mpy, which may still not be acceptable based on the corrosion allowance life of oilfield infrastructures. For many conditions inhibitor efficiencies greater than 90% is achievable and desirable, but under certain severe conditions (e.g. highly turbulent flow or slug flow) an efficiency of no better than 70% may be the best attainable. Inhibition efficiency higher than 90% was achieved which is in line with the standard in oilfield [2].

2 Chemical Composition and Functionality of Corrosion Inhibitor

Corrosion inhibitions are chemical treatments that prevent a metallic surface interact with corrosive fluids. This surface is covered to give the surface a certain level of protection. Corrosion inhibitors usually build a film of the adsorbate on the metallic surface of the adsorbent, protecting the metallic surface by creating a film. The life of the film depends on many factors, including the type of inhibitor, dissolved acidic gases, temperature, velocity, water cut, all the latter affecting the corrosive of the system. Continuous treatment is generally the preferred treatment since the concentration of inhibitor can be varied at any given time. A higher concentration of inhibitor can be applied until a film is established, and then the concentration of inhibitor can be reduced to a level enough to maintain the inhibitor film [3]. Several Corrosion inhibitors are available to prevent occurring corrosion, but the effective corrosion inhibitor used in the well is 25% of alkyl dimethyl benzyl ammonium chloride with 25% mixture of aliphatic polyamines in water solution. alkyl dimethyl benzyl ammonium chloride is a corrosion inhibitor designed for use in oil field. The product provides excellent corrosion inhibition in a wide range of environments, including hydrogen sulfide, carbon dioxide and in the presence of trace quantities of oxygen. The product is also effective in the control of bacterially induced corrosion. Physical and chemical properties have been summarized in the Table 1 [4].

Polyamine refers to a compound that consists of at least two amino groups. It is a highly charged, low molecular weight aliphatic polycation. One of the largest groups of organic corrosion inhibitors is the organic amine group. Aliphatic amines, mono-, di-, or polyamines and their salts, are all used as corrosion inhibitors. Aliphatic amines adsorb by the surface-active $-NH_2$ groups which forms a chemisorption bond with the metal surface. The hydrocarbon tails orient away from the metal surface toward the solution. Further protection is provided by the formation of a hydrophobic network which excludes water and aggressive ions from the metal surface. Since a lot of metal corrosion is caused by acidic compounds, the basic organic amines can also react with the acidic compound to form an amine salt which then forms a coating on the metal thereby preventing further corrosion of the metal from occurring [5].

Table 1: *Physical and chemical properties of alkyl dimethyl benzyl ammonium chloride*

CAS Number	8001-54-5
Chemical name (CA)	Alkyl dimethyl benzyl ammonium chloride; Quaternary ammonium compounds
Other names	*N*-Alkyl-*N*-benzyl-*N*,*N*-dimethylammonium chloride; Benzalkonium chloride; ADBAC; BC50.
Molecular formula	$C_9 H_{13} N Cl C_n H_{2n+1}$ where n =8, 10, 12, 14, 16, 18
Structural formula	
Molecular weight (g/mol)	Avg. = 359.6 g/mol
Appearance	100% is white or yellow powder; gelatinous lumps; Solution BC50 (50%) is colourless to pale yellow solutions
Density	0.98 g/cm^3
Solubility in water (% weight)	100%
Flash point	250 °C (482 °F; 523 K) (if solvent based)

The effectiveness of inhibitors depends on the chemical composition, molecular structure, and their attractions with the metal surface. Because film creation is an adsorption process, the operating conditions such as temperature and pressure are important factors for creating the film. Organic corrosion inhibitors will be attracted according to the ionic charge of the inhibitor and the ionic charge on the metallic surface [6].

3 Corrosion Rate Measurements

ER probe is generally used for the monitoring and optimization of the chemical treatment efficiency. The locations and positions where ER probes are installed is not always representative of the pipe surface. The flow conditions around probes are different from those on the pipe surface because of the geometry of these elements. The corrosion rates are generally measured on surface filmed by a corrosion inhibitor. the rate of uniform corrosion is generally low and most of the failures are caused by localized corrosion.

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3.1 Corrosion Rate and Inhibition Efficiency Calculation

When measuring the ER probe, the instrument produces a linearized signal (S) that is proportional to the exposed element's total metal loss (M). The true numerical value being a function of the element thickness and geometry. In calculating metal loss (M), these geometric and dimensional factors are incorporated into the probe life (P), and the metal loss is given by [7]:

$$M = (S \times P)/1000 \tag{1}$$

Metal loss is conventionally expressed in mils (0.001 inches), as is element thickness.
Corrosion rate (C) is derived by [7]:

$$C = \frac{P \times 365\,(S_2 - S_1)}{\Delta T \times 1000} \tag{2}$$

ΔT being the elapsed time in days between instrument readings S_1 and S_2.

Efficiency of a corrosion inhibitor is to reduce corrosion rate down to an acceptable level determined by design and operational considerations. The inhibition efficiency was obtained from the corrosion rate (CR) at different concentrations of inhibitor. The efficiency of that inhibitor is thus expressed by a measure of this improvement [8]:

$$\text{Inhibitor Efficiency (\%)} = 100\times(CR_{uninhibited} - CR_{inhibited})/\ CR_{uninhibited} \tag{3}$$

where: CRuninhibited = corrosion rate of the uninhibited system
CRinhibited = corrosion rate of the inhibited system

3.2 Evaluating of Corrosion Inhibitor by Electrical Resistance Probe

Corrosion monitoring is a critical part of any oilfield corrosion control program. It should be integrated with other programs designed to optimize the process conditions, chemical injection and inspection to recognize the full potential to successfully manage oilfield operations.

Crude oil transmission pipeline system was operating between a crude oil wellhead terminal and a manifold receiving terminal over several ten miles. Pipeline system crude oil had the water cut 35 % and rich carbon dioxide. An electrical resistance probe was supported before manifold receiving terminal. A corrosion monitoring program was developed to determine if internal corrosion was a problem in the pipeline.

This field evaluation requires approximately 24 days. Figure 1 shows the experimental procedure to estimate minimum effective concentration. the performance is determined using standard electrical resistance probes. This detailed process is designed to qualify an inhibitor formulation for field application. The inhibitor field testing protocol utilizing electrical resistance probes required 12 days to complete an incumbent baseline, 12 days to complete the test using the candidate dosage, for a total of 24 days [9]. Significant information on this technique can be found in ASTM G96 for corrosion monitoring and in NACE Publication 3D170-84.

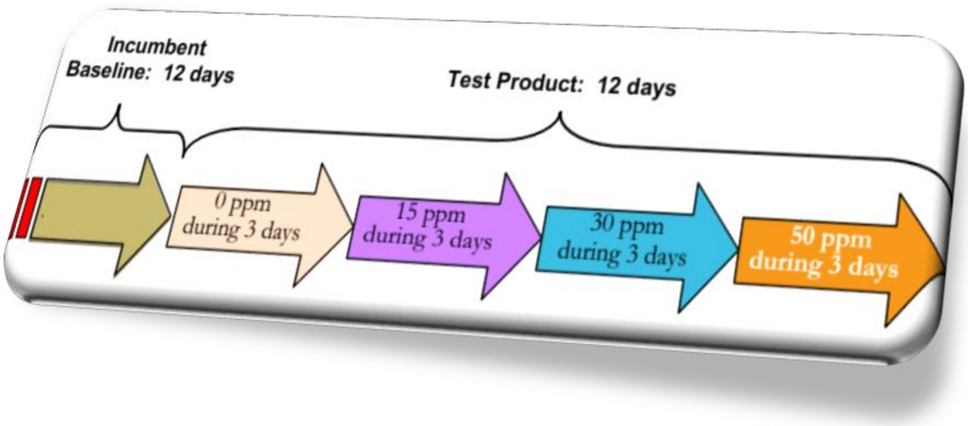

Figure 1: The experiment procedure

3.3 Ultrasonic Inspection Test

The limitations of the ER technique are that they provide representative data for general corrosion. They do not have the ability to accurately detect localized attack. The local attack rate can be over ten times the general corrosion rate. Such differences are important when trying to assess the relevance of inspection techniques such as ultrasonic tests of remaining section thickness.

Ultrasonic inspection or ultrasonic testing is applied to measure a variety of material characteristics and conditions. An ultrasonic examination is performed utilizing a device that generates an ultrasonic wave with a piezoelectric crystal at a frequency between 0.1 and 25 MHz into the piece being examined and analyses the return signal. Ultrasonic inspection has been used for decades to measure the thickness of solid objects.

Corrosion Inhibitor has been injected in annuals for approximately two years to protect the inner and outer surface of a tubing string, the flow line and the inner surface of the casing from corrosion. When the pump failed, and a workover was performed. Two lengths of the pipes were brought; both ends of the pipes were cut-out in different lengths and cut-out in half as samples.

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4 Results and Discussion

4.1 The inhibitor performance and inhibition efficiency

Figures 2 present the data collected from the pipeline of the well. The slope of the metal loss data provides the corrosion rate. uninhibited segment followed by inflexion points or changes in metal loss data. This allows a better analysis of the data, especially at the lower concentrations, leading to an improved understanding of the inhibitor performance at different concentrations.

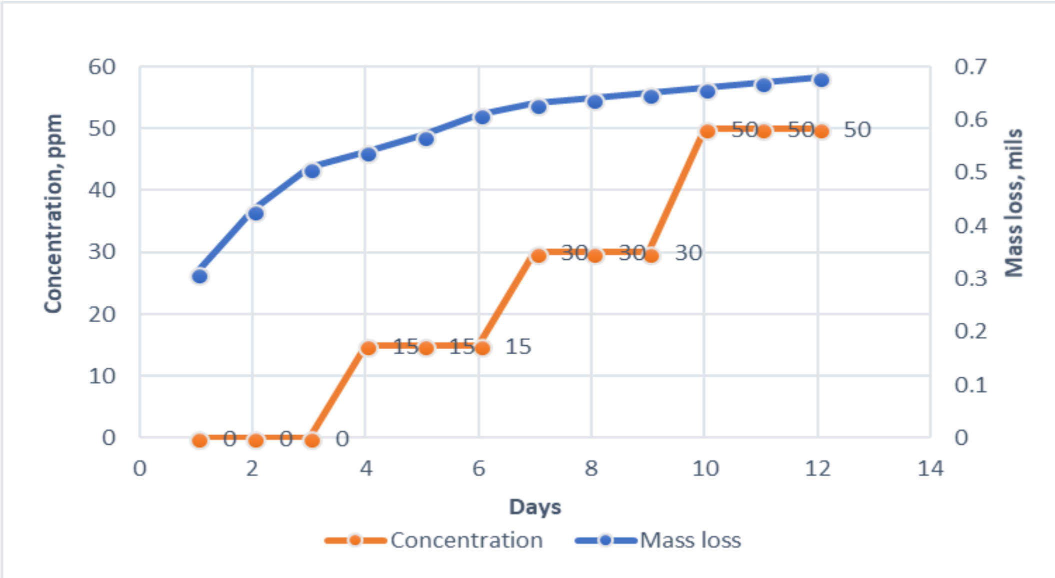

Figure 2: Metal Loss and dosage data by using electrical resistance probe

Figures 3 shows corrosion inhibitor reduced the corrosion rate considerably and the rate decreases with increase in the inhibitor concentration. The uninhibited reading at the rate of 51.1 mpy while 30 ppm concentration reduced the corrosion rates to 3.65 mpy. if the process is prone to rapid changes in corrosivity, ER probes typically may not provide accurate and reliable corrosion rate data. In some cases, namely where H_2S is present, they can be prone to error due to the presence of conductive sulfide corrosion products on the sensing element which may lead to non-conservative results. While ER data may not give reliable indications of the absolute corrosion rate, they can yield useful indications of trends and changes in corrosion activity [10].

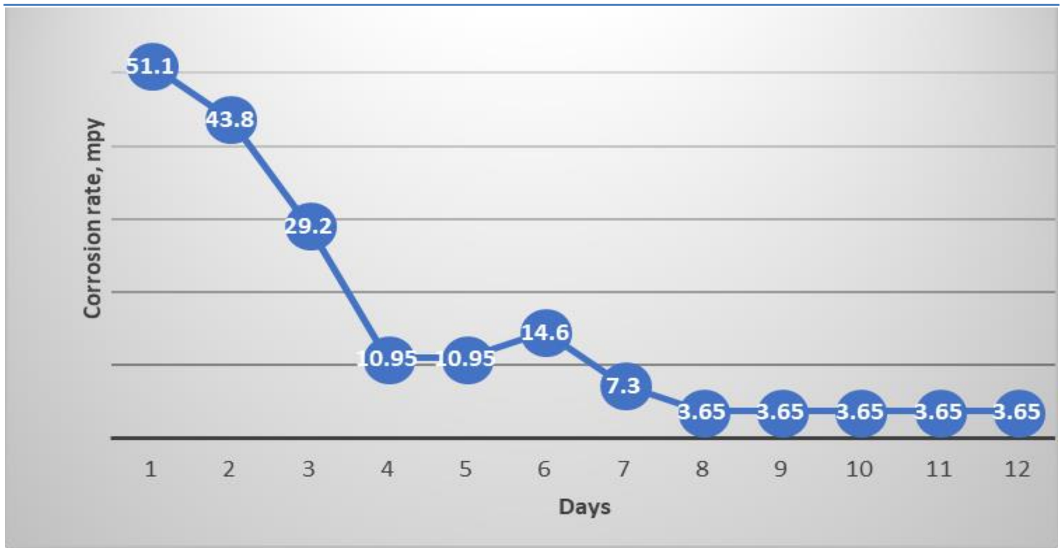

Figure 3: Corrosion rate versus time

Figure 4 shows inhibition efficiency of 93 % was observed at 30 ppm dosage. Moreover, as the concentration increases to 50 ppm, the corrosion performance was constant at the same inhibition efficiency.

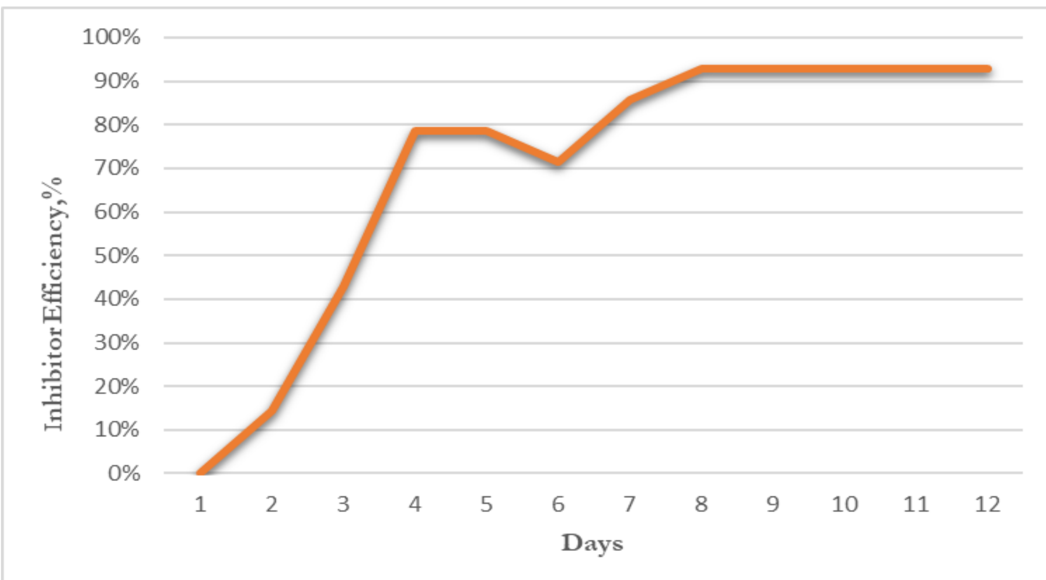

Figure 4: Inhibition efficiency versus time

4.2 localized corrosion Inspection

From the visual inspection performed on the external surface, the pipes appear to be in good condition aside from a thin layer of iron oxide scales were observed, and no signs of any

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external corrosion were noted at the time of inspection. The internal surfaces of the pipes were in good condition, although the internal surfaces of the pipes were covered with a thin layer of scales. The material was made of carbon steel. All the samples a total in all 8 pieces of the pipes were ultrasonically tested and the normal wall thickness of the pipe is 6.35 mm. The results have been briefly in Table 2.

Table 2: *Summary of the ultrasonic inspection test*

The samples	Minimum Thickness, mm	Maximum Thickness, mm	Findings
Sample No. 1	6.7	7.3	A thin layer of scales
Sample No. 2	6.1	7.5	Minor internal erosion corrosion was observed
Sample No. 3	6.2	7.2	Minor internal erosion corrosion was observed
Sample No. 4	6.5	7.2	A thin layer of scales
Sample No. 5	6.6	7.5	A thin layer of scales
Sample No. 6	6.4	7.5	A thin layer of scales
Sample No. 7	6.2	8.2	Minor internal erosion corrosion was observed
Sample No. 8	6.1	7.3	Minor internal erosion corrosion was observed

5 Conclusions

The chemicals of alkyl dimethyl benzyl ammonium chloride and aliphatic polyamines have been found to be good corrosion inhibitor for the protection of the inner and outer surface of a tubing string, the flow line and the inner surface of the casing from corrosion. The corrosion inhibitor is suitable to protect oilfield infrastructures, where a three-phase and CO_2 - rich fluid combination are present.

The inspection results show that the inspected tubing samples are in good conditions. Thus, local corrosion of carbon steel is effectively decreased by corrosion inhibitor.

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