

Performance of Corrosion Inhibitors Under High CO₂ Partial Pressures

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ABSTRACT

Corrosion inhibitors are widely used to protect carbon steel facilities in the oil and gas production industry. However, field conditions can vary significantly and become more challenging with field maturation. One of the challenges is to mitigate corrosion at high CO₂ partial pressure. Laboratory experiments were performed in a high pressure and high temperature autoclave to study the influence of CO₂ partial pressures between 1 and 10 bar on the corrosion rate of unalloyed carbon steel. Various experimental parameters were taken into account, such as water chemistry, temperature and CO₂ partial pressure. Weight loss coupons and electrochemical techniques were used to evaluate the corrosion rate. Corrosion inhibitors were tested and showed good performance in the most corrosive conditions. This lead to a better understanding of corrosion mechanisms under different CO₂ partial pressures and the selection of the best chemistries for corrosion mitigation.

Key words: CO₂ corrosion, Partial Pressures, Scale formation, Inhibition mechanism

INTRODUCTION

Carbon steel is widely used in the oil and gas industry despite its low corrosion resistance to inherently contained carbon dioxide (CO₂) and hydrogen sulfide (H₂S) in produced fluids.

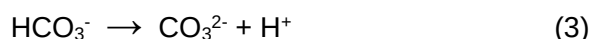
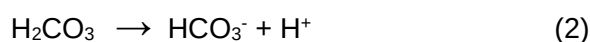
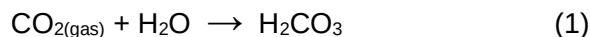
The use of corrosion inhibitors (CI) to protect carbon steel equipment is often more cost-efficient compared to the use of corrosion resistant alloys (CRA). Hence, the selection of the most effective corrosion inhibitor is an important step to preserve equipment integrity.

Laboratory equipment and test parameters have to be adapted to simulate real field conditions. Often, little monitoring tools are available in the field for performance evaluation of a corrosion inhibitor. Also, accurate techniques like inspection or intelligent pigging cannot be undertaken as frequently as one would wish. Hence, laboratory testing has to be as exhaustive as possible and take into account

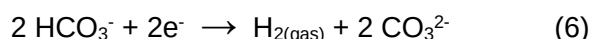
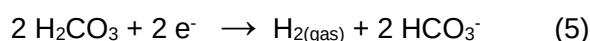
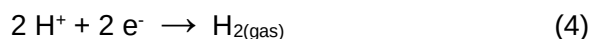
various field parameters that impact corrosion inhibitor performance. Moreover, the understanding of the corrosion mechanism and the correct choice of tests and parameters relative to the field application are the key points of the success of corrosion inhibitor selection and the entire corrosion inhibition program.

The mechanism of aqueous CO₂ corrosion is complex and has generated a large number of studies and publications¹⁻³. It involves the carbon steel dissolution in acidic environment containing the dissolved CO₂ (H₂CO₃) and the formation of low solubility iron carbonate layer known as siderite (FeCO₃) that will bring some protection depending on temperature, and decrease the apparent corrosion rate. The following reactions summarize the CO₂ corrosion mechanism.

Dissolution of CO₂ in water :



The electrochemical processes that give the CO₂ corrosion involve 3 cathodic reactions:



And the anodic reaction:



The corrosion products are iron carbonate:



Other corrosion products can be iron oxides at high temperature (160-240°C)⁴. These two phenomena, one corrosive and the other protective will compete to give an overall apparent corrosion rate. For example, temperature will increase acidic iron dissolution but will promote protective carbonate layer formation.

Hence, all the parameters that will influence either of the two phenomena have to be considered. Most studies will agree on the following effective factors influencing CO₂ corrosion rate.^{1,5}

- Influence of surface films: Corrosion products of iron in CO₂ environment can form protective iron carbonate and iron oxides films, yet decreasing the corrosion rate. These are pH and temperature dependent.
- Temperature: At below 60°C iron carbonate solubility is high avoiding protective layer formation. Corrosion rate increases with temperature. Above 60°C, iron carbonate can form at the steel surface leading to a decrease of the corrosion rate. At T>110°C magnetite can also form.
- CO₂ partial pressure: higher partial pressures will increase the corrosion rate in film-free conditions. However, at higher pH, higher partial pressures increases HCO₃⁻ and CO₃²⁻ ions concentrations which will promote protective iron carbonate formation.
- Effect of pH: Lower pH values enhance the reduction of H⁺ ions and increase the anodic dissolution rate of iron. Higher pH values, will enhance the formation of iron carbonate film and decrease the corrosion rate.
- Brine composition: In addition to Fe²⁺ ion concentration that contributes to supersaturation and protective-iron-carbonate film formation, Ca²⁺ and Mg²⁺ can also form carbonates at the metal surface depending on pH and temperature. Calcium and magnesium carbonates films on the steel surface reduce the corrosion rate, but are less protective than iron carbonate.

- Effect of acetic acid: Acetic acid would influence the corrosion process in two ways, first as a proton provider, and secondly as a reduced species at the metal surface. Acetic acid will also reduce the protectiveness of iron carbonate films, which leads to a higher corrosion rate.
- Effect of flow rate: Flow rate can enhance the corrosion rate by increasing the H^+ transportation to the bare steel surface. At the same time, the flow may remove the Fe^{2+} ions from the steel surface avoiding supersaturation and protective iron carbonate formation.
- Microstructure and heat treatment: in the case of ferritic-pearlitic steels, the cementite form Fe_3C will act cathodically and will enhance the corrosion of ferrite galvanically. Besides, lamellar pearlite, seem to provide better grip for protective scales due to cementite.
- Alloy composition.
- Presence of O_2 and H_2S .

Models can successfully predict the CO_2 corrosion rate taking into account the above parameters based on experimental data.^{6,7} However, when it comes to corrosion inhibitor selection, laboratory testing is needed.

In the present study, the following parameters were varied: pH, temperature, and CO_2 partial pressure. Flow regime was constant and Fe^{2+} concentration was generated by iron dissolution. Oxygen ingress was not taken into account. The main objective is to identify the most aggressive environments and then screen corrosion inhibitors to select the most effective ones. The performance of the inhibitors under various conditions will reveal interactions between the corrosion inhibitors and the carbonate scale layers on the metal surface.

EXPERIMENTAL PROCEDURE

Materials and chemicals

All carbon steel coupons are made of AISI 1018 Carbon steel (UNS G10180). It has a ferritic-pearlitic microstructure. Pearlite is constituted of ferrite (Iron) and cementite (Fe_3C).

Before they are introduced in the bubble test or autoclave, they are polished to 1200 grit finish, washed with deionized water, degreased with acetone and dried.

The Synthetic Water (SW) was prepared using analytical grade salts in deionized water (Table 1). NaCl, KBr, KCl are always added. $MgCl_2$, $CaCl_2 \cdot 2H_2O$, Na_2SO_4 , $NaHCO_3$ and CH_3COONa are added when indicated in the experimental conditions.

Table 1: Synthetic Water composition

Salt	mg/L	Ions	mg/L
NaCl	165 180	Na^+	64 979
KBr	690	K^+	652
KCl	810	Ca^{2+}	10 141
$MgCl_2 \cdot 6H_2O$	18 850	Mg^{2+}	1 895
$CaCl_2 \cdot 2H_2O$	37 202	Cl^-	121 166
Na_2SO_4	2 218	Br^-	461
$NaHCO_3$	689	SO_4^{2-}	1 500
CH_3COONa	1 112	HCO_3^-	500

For low pH experiments pH 4, no $NaHCO_3$ was added. However, in higher pH experiments, $NaHCO_3$ was added to reach pH 5 at $25^\circ C$, measured by a pH meter. The pH values given in Tables 1 and 2 are

calculated taking in account the CO₂ partial pressures and the temperatures, using the Scale 2000® software developed by BRGM (France).

Commercial corrosion inhibitors are used. They are referenced CI1, CI2 and CI3.

Corrosion assessment by LPR in bubble test

Corrosion inhibitor performance was tested using the bubble test apparatus. It consists of a double wall vessel with a total volume of 900 mL. 700 mL of synthetic water are introduced and deoxygenated with Nitrogen bubbling for 1h. When dissolved oxygen concentration in solution is less than 10 ppb (measured by an oximeter), continuous CO₂ bubbling is applied. The corrosion rate is measured by Linear Polarization Resistance (LPR) using a conventional three electrodes system (1018 carbon steel cylinder as working electrode 3.5 cm², Platinum counter electrode and saturated calomel reference electrode SCE). The potential scanning range is ±10 mV and the scan rate is 1 mV/s. The temperature is adjusted to 40 or 90°C ± 2°C by water circulating in the double wall. Continuous stirring is brought by a magnetic stirrer rotating at 300 rpm. Once the required temperature is reached, the carbon steel electrode is inserted and the LPR monitoring is started. The initial corrosion rate is recorded within 15 min maximum from the electrode insertion. In addition, a weight loss coupons are plates of 40x20x1 mm representing 17.2 cm² is inserted also in the bubble test. It is totally immersed in the liquid phase and maintained with a PTFE thread. During the coupon insertion, oxygen ingress is believed to be negligible due to continuous CO₂ sparging. Corrosion inhibitors are added 1.5 hours after potential stabilization, which represents the pre-corrosion step. The reported LPR measurements correspond to 1h and 24h after corrosion inhibitor injection. After, 24h immersion, the coupons are washed with deionized water, dried and conserved in closed bottles under nitrogen atmosphere.

Corrosion assessment by weight loss coupons in HPHT autoclave

The corrosion inhibitor evaluation is performed in a 2 L autoclave made of Alloy C-276 (UNS N10276). The weight loss coupons are 4 plates of 40x20x1 mm representing each 17.2 cm² (Total exposed area = 68.8 cm²). They are positioned on a central fixed Teflon® rack (PTFE). The autoclave is filled with 1800 mL of solution sparged 1 h with nitrogen then 1 h with CO₂. Oxygen content is controlled by an oximeter to below 10 ppb. Temperature is adjusted to 40 or 90°C ±2°C. The gas phase is composed by applying a total pressure with pure CO₂ from 1 to 10 bar. The test duration is 72 hours. When used, the corrosion inhibitors are contained in the water before coupon immersion, meaning that there is no pre-corrosion step. The autoclave is stirred at 500 rpm. After 72 h immersion, coupons are cleaned with an inhibited 15% HCl solution. The results given are an average of the corrosion rate of the coupons.

CR (mm/y) = 87.6 x (W / d x A x t) where:

W = weight loss in milligrams.

d = metal density in g/cm³ (7.86 g/cm³ for AISI 1018 carbon steel).

A = area of the sample in cm².

t = time of exposure of the metal sample in hours

X-ray diffraction analysis (XRD)

Diffraction is helpful in providing characterization of crystalline compounds by their diffraction patterns in specimens. XRD was performed directly on the metal coupons after cleaning with deionized water and drying taking care of minimizing the time between extraction and analysis. The coupons are put on standard DX supports. The XRD pattern is recorded on a D8 Advance X-ray powder diffractometer (Bruker® AXS).

Qualitative analysis is performed by repositioning of the diffractogram peak using the iron pattern (ICDD database: sheets Iron n°04-013-5208.) as a reference (2θ position at 44.65°). Experimental XRD data

are compared to reference patterns to determine what phases are present. The reference patterns are represented by sticks.

Semi-quantitative analysis was performed by reference intensity ratio method (RIR). The RIR is a general, instrument-independent constant for use in quantitative phase analysis by the X-ray powder diffraction internal standard method (standard is corundum). It is a semi-quantitative method for many minerals using the I/I corundum values from the ICDD database (can be done in EVA Bruker program). The results are semi-quantitative of crystallized phases content with 100% normalization.

Scale Modelling

A scale prediction study was performed with the reported water analysis and process conditions using the SCALE 2000® software. It is developed by BRGM (Orléans, France) and is specifically designed to predict the scale deposits in brines under sweet and sour conditions up to 250°C and 1000 bar. The activity calculation is based on the extended Pitzer model. This software is used also to calculate the pH and precipitable masses of different scales at the required pressures and temperatures based on pH and water composition at atmospheric conditions.

Microscopic observations

A Kayence® digital microscope was used for microscopic observation of coupons and surface profilometry.

RESULTS AND DISCUSSION

Bubble test experiments, blanks without corrosion inhibitors

The interpretation of corrosion results in different operating conditions are made on the following results:

- The XRD analysis giving the crystallized species on the coupons.
- The corrosion rate (CR) determined by LPR.

Experiments at 40°C

At 40°C, independently of the pH and the water composition, the only detected deposit on the metal surface is iron carbide Fe_3C (cementite) (Table 2). As a consequence of acidic CO_2 corrosion, ferrite (iron) dissolves leaving the chemically inert but conductive cementite to accumulate at the metal surface. The magnetic stirring conditions in the bubble test do not allow a sufficient flow velocity to remove this cementite. Di Bonaventura *et al.*⁸ found that high fluid velocities such as 12 m/s on the metal surface removed the cementite, and avoids FeCO_3 precipitation within the Fe_3C network. The higher the corrosion rate, the higher the cementite proportion compared to iron. This is consistent with higher iron dissolution and accumulation of cementite at the metal surface. The highest CR after 24h is 1.93 mm/y for BT3 where 10% cementite is detected, as opposed to BT2 with the lowest CR after 24h of 0.82 mm/y with 4% cementite.

The CR of SW (BT3) is stable over the 24h experiment at around 1.9 mm/y. The addition of HCO_3^- (BT4) leads to a reduction of the corrosion rate, which stabilizes at 1.37 mm/y. This is due to the addition of HCO_3^- that increases the pH. The presence of Ca^{2+} Mg^{2+} in SW (BT1) did not change the corrosion rate which was stable over the experiment duration (1.8 mm/y). However, the simultaneous presence of Ca^{2+} Mg^{2+} and HCO_3^- (BT4) leads to a gradual decrease of the corrosion rate from 1.72 to 0.82 mm/y. This is probably due to protective carbonate layer formation but it was not detected by XRD, which in this case, might not be sensitive enough.