

# EVALUATION OF CORROSION INHIBITORS EFFECTIVENESS IN OILFIELD PRODUCTION OPERATIONS

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**ABSTRACT:** It is known that corrosion is a natural process and is impossible to prevent completely. Thus we only try to control corrosion. Even though coatings and cathodic protection are often more effective, chemical inhibitors are also widely used to reduce corrosion particularly in gas wells producing CO<sub>2</sub>, H<sub>2</sub>S and water. The effectiveness of the inhibitor and compatibility with produced fluids must be tested in the laboratory. Inhibitor film efficiency depends on the inhibitor concentration and contact time with the metal surface. A compact and relatively inexpensive system called High Speed Autoclave Test (HSAT) was used with corrosive gases, such as H<sub>2</sub>S and CO<sub>2</sub>. Using this system, the effectiveness of inhibitor was evaluated and all the variables that influences corrosion rate were easily controlled in the laboratory, in order to predict field corrosion rates. Several inhibitors were evaluated, active ingredients of those inhibitors include long chain amines, amides, and imidazoline est inhibitors were tested at the concentration range of 500-10000ppm in a mixture of brine/hydrocarbon in the presence of H<sub>2</sub>S and CO<sub>2</sub>. In the experimental investigation, results showed that inhibitor D (imidazoline surfactant) was the most efficient (92%) at 1000ppm.

**KEYWORD:** Corrosion Inhibitors, Concentration, Experimental Investigation, Inhibitor efficiency.

## 1 INTRODUCTION

Oil and gas production operations utilize a tremendous amount of iron and steel materials. These materials are in form of pipes, tubing, casing, pumps, valves and other accessories which are susceptible to corrosion depending on the composition and characteristics of the produced fluids. The produced fluids either in two-phase or three-phase are transported through a net-work of pipelines from various sizes of tubings to central gathering stations where separation and emulsion treatment are being carried out. However, in transportation, the internal parts of the pipelines are in constant contact with fluids and other impurities such as hydrogen-sulphide, carbondioxide and others that propagates corrosion under the operating temperature and pressure conditions.

One of the major ways of protecting the internal production pipelines in the field of operations against corrosion is by applying corrosion inhibitors. The corrosion inhibitors are evaluated in order to determine if the corrosion preventive measures applied are necessary and to know if the required life-time can be achieved with an inhibitor as effective life of corrosion inhibitors varies with the quantity of water intrusion. The purpose of the paper is to evaluate the effectiveness of commercially available corrosion inhibitors under different temperature and pressure conditions with different well effluents. A greater number of scientific studies have been devoted to corrosion inhibitors. However, most of what is known to have grown from trial and error experiment, both in the laboratories and in the field. Rules, equations, and theories to guide inhibitor development or use are very limited. By definition, a corrosion inhibitor is a chemical compound or substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of an inhibitor can be expressed by a measure of this improvement:

$$\text{Inhibitor efficiency (\%)} = 100 \frac{(\text{CR uninhibited} - \text{CR inhibited})}{\text{CR uninhibited}}$$

Where;

CR uninhibited = Corrosion rate of uninhibited

CR inhibited = Corrosion rate of inhibited

In general, the efficiency of an inhibitor increases with an increase in inhibitors concentration (e.g. a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%). Also, the reliability of assessment of the effectiveness of gas flow lines protection by inhibition depends on the method employed. Assessment based on results received by several methods make it possible to find a set of inhibitors that rate the most effective for each specific field and to develop the most optimal technology for their application. As a matter of fact, the effectiveness, or corrosion inhibitor efficiency, of a corrosion inhibitor is a function of many factors like: fluid composition, flow regime, temperature, partial pressure of CO<sub>2</sub> and H<sub>2</sub>S. If the correct inhibitor and

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quantity is selected, then it is possible to achieve high, 90-99% efficiency. Some mechanism of its effect are function of a passivation layer (a thin film on the surface of the material that stops access of the corrosive substance to the metal), inhibiting either the oxidation or reduction part of the redox corrosion system (anodic and cathodic inhibitors), or scavenging the dissolved oxygen.

## 2. EFFECT OF INHIBITORS

Gopal and Jepson (1995), defined inhibitor as a substance, that when added in small concentrations decrease the effect of corrosion rate. Inhibitors fall into four general categories, based on mechanism and composition, these categories are;

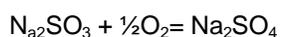
- i. Barrier Inhibitors
- ii. Neutralizing Inhibitors
- iii. Scavenging Inhibitors

**2.1. BARRIER INHIBITORS:** Barrier inhibitors form a layer on the corroding metal surface, modifying the surface to reduce the apparent corrosion rate. They represent the largest class of inhibitive substance. Adsorption type inhibitors are the most common barrier layer inhibitors. In general these organic compounds are adsorbed and form a stable bond with the metal surface. The apparent corrosion rate decreases as surface adsorption is completed. Vapour phase corrosion inhibitor (VPCI) is adsorption type corrosion inhibitors with high passivation properties. These inhibitors form a stable bond with the metallic surface. Generally, they have a high vapour pressure that allows the material to migrate to distant metallic surface. Therefore, VPCI, require no direct contact with the metal surface to be protected. Conversion inhibitors also form barrier layers. They passivate the metallic surface by developing and insoluble metal oxide on the surface. Typical examples of this type of inhibitor are organic phosphates and chromates (Margarita Kharshan, 1998).

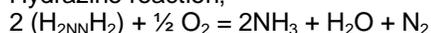
**2.2. NEUTRALIZING INHIBITORS:** Neutralizing inhibitors reduce the hydrogen ions in the environment. Typical neutralizing inhibitors are amines, ammonia (NH<sub>3</sub>), and morpholine. These inhibitors are particularly effective in boiler water treatment and weak acid solutions but have been widely used on flow lines (Margarita Kharshan, 1998).

**2.3. SCAVENGE INHIBITORS:** Scavenging inhibitors remove corrosive ions from solution. Well known scavenging inhibitors include hydrazine and sodium sulphite. These two inhibitors remove dissolved oxygen from treated boiler water (McMahon et al, 2005).

Sodium sulphite reaction;



Hydrazine reaction;



## 2.4. DEMANDS OF INHIBITORS

**2.4.1. POUR POINT:** Because inhibitors are usually stored and used outdoors, they must remain liquid at low temperature. A pour point of -30°C (-20°F) is usually required. Some areas of the world may have an even lower

pour point requirement (-40-to-45°C) or (-40-to-50°F). The required pour point often restates the activity and solvent systems of particular inhibitors (Hamby, 1981)

**2.4.2 SOLUBILITY:** It is dictated by the intended uses. By their way nature, inhibitors cannot be truly soluble in either hydrocarbon or water; degree of dispensability is more descriptive ( Jones et al, 1996)

**2.4.3 PERFORMANCE:** The end user of corrosion inhibitors will often specify a laboratory test that the inhibitor must go before a field trial or purchase will be considered. The wheel test is commonly used in the oil and gas producing industry. Therefore, many inhibitors are formulated to pass the wheel test. But in this project HSAT is used as our reference point (Hamby, 1981).

**2.4.4 EMULSION TENDENCIES:** The application of the inhibitors must not cause secondary problem. Batch treatment has often caused emulsions of the hydrocarbons and water that, relatively to normal operations, are externally difficult to break. In some cases, the emulsions resulting from batch treatment were so severe that the surface separation equipment was literally stopped by the emulsion formed by the presence of high inhibitor concentration. Therefore, inhibitors are specifically formulated to be non-emulsifying. Alternatively emulsion-breakers (chemical) are added to formulations in small amounts to prevent emulsions (Hamby 1981).

## 3. EXPERIMENTAL PROCEDURE

Corrosion test was performed in a modified HSAT test. The HSAT tests uses an open cage spindle containing flat coupons and are rotated at different speeds, in order to generate high local shear stresses on the leading edge of the coupons. This test has been extensively used in developing corrosion inhibitors for applications where ultra-high shear conditions caused severe localized corrosion in gas pipelines. The test has often been called a rotating cage test. In the normal procedure, a mixture of brine/hydrocarbon is added to the autoclave. After purging/evaluation to remove oxygen, inhibitor is added at a specific concentration. The stirrer is then turned in and the pressure and temperature are adjusted to test conditions. At completion of the test, the apparatus are allowed to cool. Coupons are then removed, inspected, and re-weighed. A corrosion rate is calculated for a specific test time and weight loss. In this work, corrosion test are reported for experiment at 188°C (370°F), 10.3Mpa (500psi) and 232°C (450°F), 2.88Mpa (420psi), and open cage spindle containing flat coupons are used. Each coupon is used in the spindle. Each coupon has a surface area of 11.3cm<sup>2</sup>. The ratio of volume of liquids surface of the coupons is 133cm. At 200ppm, the linear velocity of the coupon in the cage is 6.65m/sec (21.82ft/sec). Brine was added to the autoclaves, after purging/evacuation to remove O<sub>2</sub>, inhibitor was added at specific concentration, the stirrer was turned on, and the pressure was adjusted to 2.884mpa (420psi). The partial pressure of CO<sub>2</sub> in the test was 2.88mpa (420pisa). The concentration of the H<sub>2</sub>S used in the test was 12ppm. After reaching the test temperature of 232°C (450°F), the test was contained for 18hrs. After this time, the system was allowed to cool and the coupons were removed, inspected and re-weighed after cleaning. A

corrosion rate was calculated for the specific test concentrations. Inhibitors performance was assessed on the basis of corrosion rate relative to the blank-corrosion efficiency. The brine composition used in our test at 188°C (370°F), 10.3mpa (1500psi) is shown in Table 2. An 80/20 mixture of brine/condensate was used as the test fluid. Testing was conducted using 10.3Mpa (1500psi) of CO<sub>2</sub>, 0.021 Mpa (3psi) H<sub>2</sub>S, and temperature of 188°C (370°F). Testing was performed at both 2000 and 500rpm to stimulate high flow rate and low flow rate condition, respectively. Testing was done on the high speed autoclave test (HSAT) described earlier. The linear velocity at 500rpm is 1.66m/sec (5.45ft/sec). The inhibitors used in the experiment were oil soluble corrosion inhibitors. Corrosion inhibitors A was a cyclic amine based corrosion inhibitor. Corrosion inhibitors B was amido-imidazoline based corrosion inhibitors. Corrosion inhibitors C was amine imidazoline based corrosion inhibitor. Corrosion inhibitors D was an imidazoline surfactant based corrosion inhibitors.

### 3.1 DISCUSSION AND ANALYSIS OF RESULTS

The results of test using different concentration in high speed autoclave test at 2000ppm, 232°C (450°F), 2.88mpa (420psi) CO<sub>2</sub>, and 12ppm H<sub>2</sub>S are shown in figures 1. The corrosion rate without corrosion inhibitors is 4.01mm/yr. Over 90% protection is obtained using 1000ppm of corrosion inhibitor A. The amount of corrosion inhibitors needed to achieve this amount of protection is large. This is characteristic of high temperature gas flow line situation where blank corrosion rate are lower due to the formation of an Iron carbonate scale but the concentrations of inhibitors needed to treat for corrosion are higher. The results of experiment on corrosion inhibitors performance with high speed autoclave testing under a pressure of 10.3mpa (1500psi) CO<sub>2</sub>, 0.021mpa (3psi) H<sub>2</sub>S with a rotating cage of 2000rpm in an 80/20 mixture of brine and condensate at 188°C (370°F) are shown in figures 2. The test duration is 18hrs. The uninhibited rate in the test is 5.08mm/yr (200mpy). Corrosion inhibitors A, an oil soluble water dispersible corrosion inhibitors that has performed well in laboratory test at 232°C (450°F), 2.88mpa (420psi) CO<sub>2</sub>, and 12p, H<sub>2</sub>S did not do well in this test. Corrosion inhibitor B also did not do well. At high concentration using 1000ppm, corrosion inhibitors C provided above 87% protection. A new formulation corrosion inhibitors D, gave the best protection under these severe conditions. Corrosion inhibitor of above 92% using a dosage of 1000ppm was obtained in our laboratory test. Longer duration test may give lower corrosion rates, due to resistance developed by the gas. In order to mimic low shear conditions, high speed autoclave test at 500rpm were conducted at carbon dioxide partial pressures of 10.3mpa (1000psi), 0.02mpa (3psi) hydrogen sulfide in a 80/20 mixture of brine and condensate at 180°C (370°F). The results of test with corrosion inhibitor C and corrosion inhibitors D are shown in figure 3. The uninhibited rate is higher (13.77mm/yr.) then in systems under higher shear (5,08mm/yr). This is sometime seen in corrosion tests involving hydrogen sulphide. A 90% corrosion inhibitor protection is achieved using corrosion inhibitors C at a dosage of 1000ppm. Higher corrosion inhibitors efficiency of above 96% can be

obtained using the new corrosion inhibitors D at a dosage of 500ppm.

**Table 1:** Brine used in testing at 232°C (450°F) and a partial pressure 2.884Mpa (420Psi) carbon dioxide.

Component	Concentration (mg/L)
Nacl	5100
CaCl <sub>2</sub> .2H <sub>2</sub> O	600
MgCl <sub>2</sub> . 6H <sub>2</sub> O	70

**Table 2:** Composition of Brine used in testing at (370°F) 10.3Mpa (1500Psi).

Component	Concentration (mg/L)
Nacl	144810
CaCl <sub>2</sub> .2H <sub>2</sub> O	18510

#### Experiment 1 : Results

Inhibitor A

Concentration	Corrosion Rate	Remarks
0	4	
500	1.3	
1000	0.4	
2000	0.2	

#### Experiment 2 at 188°C : Results

Inhibitor A

Concentration	Corrosion Rate	Remarks
0	10	
500	7	
1000	0.4	
2000	0.2	

**Inhibitor B**

Concentration	Corrosion Rate	Remarks
0	4.5	
500	3.8	
1000	3.3	
2000	3.25	

**Inhibitor C**

Concentration	Corrosion Rate	Remarks
0	4.5	
500	3.28	
1000	3.10	
2000	2.8	
5000	0.8	
10,000	0.5	

**Inhibitor D**

Concentration	Corrosion Rate	Remarks
0	4.5	
500	0.23	
1000	0.21	
2000	0.20	
5000	0.19	
10,000	0.88	

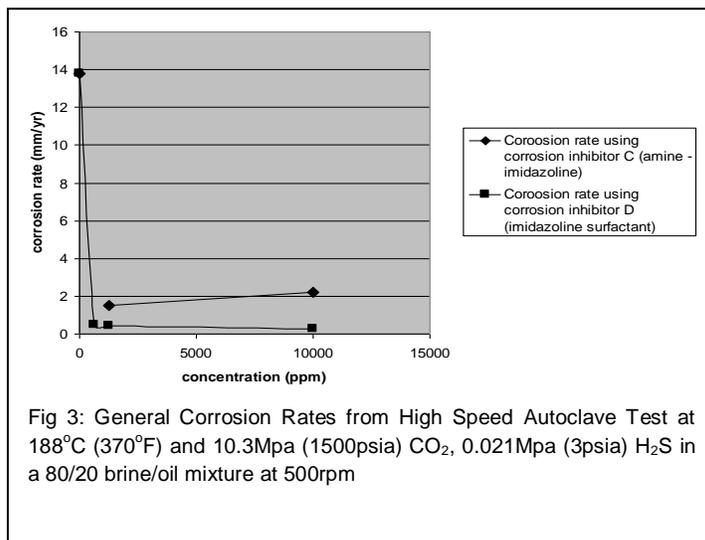


Fig 3: General Corrosion Rates from High Speed Autoclave Test at 188°C (370°F) and 10.3Mpa (1500psia) CO<sub>2</sub>, 0.021Mpa (3psia) H<sub>2</sub>S in a 80/20 brine/oil mixture at 500rpm

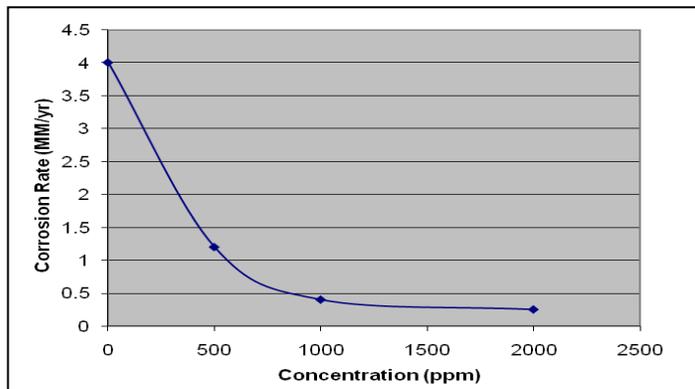


Fig 1: A plot of corrosion rate vs Concentration (ppm); Results of Corrosion Test at 232°C (450°F), 2000rpm with a partial pressure of 2.884Mpa (420Psia) CO<sub>2</sub> and 12ppm concentration of H<sub>2</sub>S at

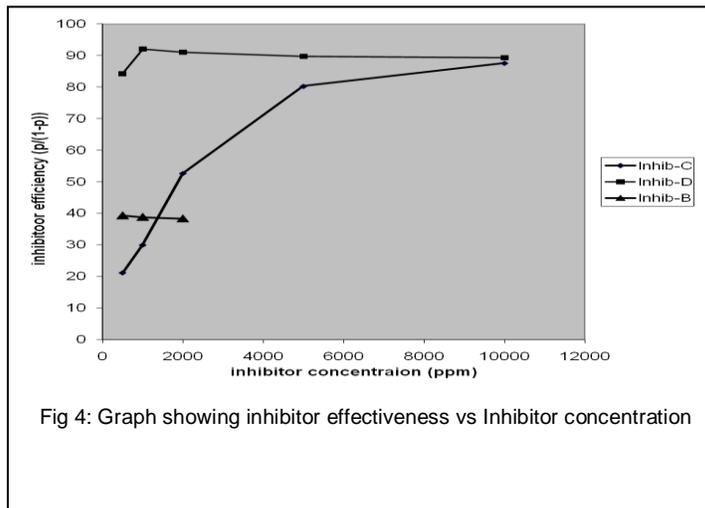


Fig 4: Graph showing inhibitor effectiveness vs Inhibitor concentration

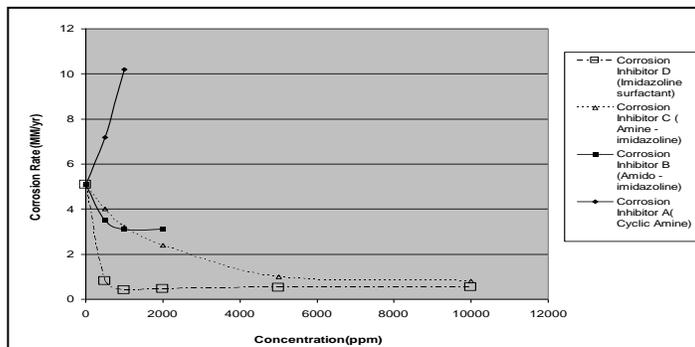


Fig 2: General Corrosion Rate from High Speed Autoclave Test at 188°C (370°F) and 10.3Mpa (1500psia) CO<sub>2</sub>, 3psia H<sub>2</sub>S in a 80/20 brine/oil mixture at 2000rpm

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## Appendix

Table 3: Molecular composition of a typical Nigeria Reservoir fluid

<u>Components</u>	
Nitrogen	0.21
Carbondioxide	2.34
Methane	40.66
Ethane	2.16
Propane	0.14
Iso Butane	0.57
Normal Butane	0.05
Iso Pentane	0.33
Normal Pentane	0.01
Hexanes	0.98
Heptanes +	52.55
Total	100.00%
Molecular Weight	149.03
Heptanes +	
Molecular Weight	265.00

## CORROSION RATE CALCULATION:

The corrosion rate is calculated by the following formula:

$$\text{Corrosion rate (mpy)} = \frac{\text{Coupon weight loss (g)} \times 2.23 \times 10^4}{\text{Total exposed area of coupon (in}^2\text{)} \times \text{Exposure time (days)} \times \text{metal density}}$$

Corrosion Rate in mpy

Low	< 1.0
Moderate	1.0 – 4.9
High	5.0 – 10
Severe	> 10

## PITTING RATE CALCULATION

The pitting rate can be calculated by the following formula.

$$\text{Pitting rate in mils per year (mpy)} = \frac{\text{Pitting depth (mils)} \times 365}{\text{Exposure time (days)}}$$

## Mole (%)

In addition, this crude is waxy.

Table 4: Typical Analysis of condensate water

Content	A Field from Niger (ppm)	Delta Field (ppm)
Sodium Chloride	304	254
Sodium Bicarbonate	138	161
Calcium Sulphate	26	30
Calcium Chloride	19	7
Magnesium Chloride	20	21
Iron	220	255
Organic acids as acetic acid	480	450