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# Efficiency of film-forming corrosion inhibitors in strong hydrochloric acid under laminar and turbulent flow conditions

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ABSTRACT

The effect of fluid velocity on the corrosion rate of low carbon steel in inhibited 4 M HCl at 80 °C has been examined. When the inhibitor film fully covers the metal surface, the corrosion rate slightly increases with increasing flow velocity which can be attributed to a partial erosion of the inhibitor film. When the inhibitor film coverage is in the lower range, the corrosion takes place at the diffusion limit and an increase in flow velocity results in a strong decrease in corrosion rate due to an increased rate of mass transport of the corrosion inhibitor to the metal surface.

## 1. Introduction

Acidizing treatments of oil and gas wells are commonly used to create artificial flow channels in carbonate formations and to increase permeability by dissolving clays and other pore plugging materials near the wellbore [1]. Either organic acids such as acetic acid or mineral acids such as HCl or HCl/HF mixtures are injected into the reservoir via the wellbore.

For this application, corrosion inhibitors are enabling because uninhibited acidizing treatment fluids would induce severe corrosion of both downhole casing completions and coiled tubing strings. Basically, the inhibitor films protect the bare metal from corrosion by providing a "barrier" between the aggressive acid solution and the metal surface. A broad range of organic film-forming corrosion inhibitors have been developed to retard the acid corrosion of downhole equipment and coiled tubing strings [2]. Commercially available acid corrosion inhibitor formulations are complex mixtures containing of film-forming inhibitor molecules (e.g. various nitrogen heterocycles, quinoline-based quaternary ammonium compounds and polymerizable acetylenic alcohols), an oily phase, and a solvent package. Often surfactants are included to aid dispersion of the inhibitor in the acid. For high temperature applications, critical components in the inhibitor cocktail are polymerizable inhibitors. Acetylenic alcohols, $\alpha$-alkenylphenones and $\alpha,\beta$-unsaturated aldehydes are typical polymerizable inhibitors [3–6].

Coiled tubing is used to inject highly corrosive acidizing fluids directly into the target zones/formations bypassing most of the client's casing and completion hardware. Coiled tubing can be defined as any continuously-milled tubular product manufactured in lengths that require spooling onto a take-up reel during the primary manufacturing process [7]. The tube is straightened prior to being inserted into the wellbore and is recoiled for spooling back onto the reel. Tubing internal diameters normally range from 0.75 in. to 4 in. and single reel tubing lengths in excess of 9 km are available commercially.

In coiled tubing acidizing, a variety of fluids are pumped through coiled tubing into the producing formations. Since the acidic fluids are pumped at fairly high rates, flow velocity may influence the corrosion and inhibition process. In this paper, the effect of fluid velocity on the corrosion rate of low carbon steel in 4 M hydrochloric acid at 80 °C in the presence of a commercially available inhibitor formulation has been examined.

## 2. Experimental

### 2.1. Material

All electrodes for electrochemical testing were prepared from field grade tubular goods. Tenaris coiled tubing HS80 low carbon steel was used. The composition of this steel is 0.1–0.15% C, 0.6–0.9% Mn, <0.03% P, <0.005% S, 0.3–0.5% Si, 0.45–0.7% Cr, <0.4 Cu% and <0.25% Ni; iron makes up the remainder. This material has a ferrite/pearlite microstructure and ferrite grain sizes are in the range of 5–10 μm. The pearlite phase is composed of alternating ferrite–cementite layers.

Analytical reagent grade 4 M HCl was supplied from Sigma–Aldrich. The following physico-chemical parameters of 4 M HCl

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at 80 °C were used to calculate the flow velocity parameters: dynamic viscosity ($4.8 \times 10^{-4}$ kg m$^{-1}$ s$^{-1}$), density (1020 kg m$^{-3}$), and diffusion coefficient ($5.25 \times 10^{-9}$ m$^2$ s$^{-1}$).

In all experiments varying concentrations of the corrosion inhibitor formulation were used. The proprietary inhibitor mixture contains polymerizable molecules (alkenylphenones), a quaternary salt of a nitrogen-containing heterocyclic aromatic compound (quinolinium salt), nonionic surfactants and a solvent package (alcohols) [4].

### 2.2. Surface finish

Immediately before placing the electrode into the test solution, the surface of specimen was ground with P1200 grit SiC emery paper, washed in tap water, ultrasonicated in DI water for 5 min in order to remove any residual SiC grains, rinsed again with DI water, degreased in acetone, rinsed with DI water and dried with an air drier. The average surface roughness parameter, $R_a$ was determined to be 0.14 ± 0.01 μm.

### 2.3. Electrochemical equipment

All the electrochemical measurements were carried out in the potentiostatic mode using a three-electrode cell arrangement. An Autolab PGSTAT 302 N Potentiostat was used. The setup comprises a 0.5 L glass container with a thermostatic water-jacket and a glass top designed to be fitted with a Ag/AgCl (3 M KCl) reference electrode, a graphite counter electrode, a thermometer and a gas two-way purge tube. A fine Luggin capillary was placed close to the working electrode to minimize ohmic resistance effects. The experiments were carried out under dynamic flow conditions in de-aerated solutions saturated with nitrogen. The temperature was maintained at 80 ± 1 °C. Nitrogen saturation was initiated 30 min prior to the tests and was continued throughout the experiment.

Corrosion tests were performed with HS80 rotating cylinder electrodes (RCE) (1.5 cm diameter and 0.3 cm height). The RCE effective area was 1.41 cm$^2$ and this value has been used throughout for corrosion rate calculations. Each working electrode is mounted on a polyether ether ketone sleeve, attached to a Pine Research Instrumentation Company modulated speed rotator (model AFMSRCE) fitted with an RCE electrode holder system. Experiments were performed in the RCE rotation range from 5 to 6000 rpm. No crevice corrosion was observed under the rubber washers used to mount the RCE in the holder. The rotation speed is usually maintained for 3 h. At the end of the test period the working electrodes were cleaned and examined under a high magnification optical microscope.

### 2.4. Electrochemical measurements

Corrosion experiments were carried out in deaerated 4 M HCl at 80 °C in the presence of various concentrations of the corrosion inhibitor, 0.0065–0.2 wt.%, under laminar (5 rpm, 0.004 m s$^{-1}$) and fully developed turbulent (6000 rpm, 4.7 m s$^{-1}$) flow conditions. The standard testing period was 3 h. Experiments were started by monitoring the corrosion potential (every 30–180 s) at a specific rotational speed and measuring the polarization resistance every 20–30 min. Finally the cathodic potentiodynamic sweep was recorded. This procedure was repeated for a variety of flow velocities and for different corrosion inhibitor concentrations.

### 2.5. Linear polarization studies

Linear polarization resistance (LPR) measurements were carried out in a potential range ±10 mV with respect to the open circuit potential (OCP or $E_{corr}$) at a scan rate of 0.2 mV s$^{-1}$. The polarization resistance ($R_p$) was determined from the slope of the potential vs. the current. The Tafel slope determined from the potentiodynamic polarization tests and the polarization resistance was used to calculate the corrosion current using the Stern–Geary equation:

$$i_{corr} = \frac{B}{R_p} = \frac{b_a b_c}{2.303(b_c - b_a)} \frac{1}{R_p}, \qquad (1)$$

where $b_a$ and $b_c$ are measured or estimated. Knowledge of $R_p$, $b_c$ and $i_{corr}$, enables direct determination of the corrosion rate at any instant in time using Eq. (1). Faraday's Law was used to calculate the corrosion rate in terms of a penetration rate:

$$\text{Corrosion Rate}\,(\text{mm year}^{-1}) = \frac{M}{nF\rho} i_{corr} = K\ i_{corr}, \qquad (2)$$

where $M$ is the atomic weight of the metal, $\rho$ is the density, $n$ is the charge number which indicates the number of electrons exchanged in the dissolution reaction, $F$ is the Faraday constant, $i_{corr}$ is current density (mA cm$^{-2}$) and $K$ is constant ($K = 11.527$).

### 2.6. Potentiodynamic polarization

Potentiodynamic polarization tests were carried out after LPR experiments and served to determine the corrosion current ($i_{corr}$), OCP, and Tafel slopes of the cathodic ($b_c$) curve. These cathodic Tafel curves were obtained by changing the electrode potential automatically from OCP to −200 mV at a potential sweep rate of 1 mV s$^{-1}$. They were corrected for the ohmic drop, previously determined by electrochemical impedance measurements. The cathodic corrosion current was conventionally determined by extrapolation of the cathodic Tafel slope to the OCP.

### 2.7. Chronoamperometry

Chronoamperometry tests were carried out by applying a constant potential to the electrode and recording the current density as a function of time, for periods from 1 s to 300 min. A constant potential, typically −0.65 V vs. Ag/AgCl, was applied to the working electrode which was rotated at speeds of 5 and 6000 rpm.

## 3. Results and discussion

### 3.1. Oilfield and laboratory testing conditions

The majority of matrix acidizing jobs are pumped at a rate of two barrels per minute, which corresponds to a linear flow velocity of 5.34 m/s, a wall shear stress of 49.44 Pa and a Reynolds number of 403,000 for a standard coiled tube with inner diameter 1.4 in. (Table 1). The flow in pipe is transitionally turbulent at $Re \cong 2000$ and is fully turbulent at $Re \cong 100{,}000$ [8].

It is critical to choose a suitable laboratory method to match or mimic the corrosive and flow conditions found in the field environment. A number of experimental techniques are available to investigate flow effects under laboratory conditions [9,10]. Pipe flow loops, rotating electrochemical probes and jet impingement experiments are established methods to simulate a variety of flow conditions and to cover a broad temperature range. Corrosion testing in strong inorganic acids like hydrochloric acid at elevated temperature is usually associated with rapid reaction rates and safety concerns.

In this study, the effect of flow velocity on the inhibition of low carbon steel in hot hydrochloric acid was assessed using a rotating cylinder electrode. A critical issue when attempting to use the RCE to simulate realistic flow conditions is to choose the correct electrode rotation speeds at which to perform electrochemical mea-