



# Advanced once-through flow cell methodology for evaluation of a new staged inhibition concept to mitigate corrosion of carbon steel in high-strength hydrochloric acid flow

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## ABSTRACT

A new staged acid corrosion inhibition (ACI) concept, utilising polymerisable ACIs, has been developed to minimise the corrosion of coiled tubing and wellbore casing materials during matrix acidizing operations. The concept has been evaluated using a customised once-through flow cell and 4 molar hydrochloric acid at 80 °C. A high quality, protective inhibitor film is established using an elevated ACI concentration during the test period 0–1 h (Stage 1), followed by a significantly reduced ACI concentration during the period 1–4 h (Stage 2). This approach is able to maintain good film persistency and acceptably low corrosion rates.

## 1. Introduction

In the oil and gas industry, matrix acidizing treatments are implemented to increase the rate of hydrocarbon production from carbonate and sandstone reservoirs. Many of these treatments involve the injection of high strength hydrochloric acid (HCl) into target zones within the reservoir in order to increase permeability via the partial dissolution of reservoir rock (carbonate formations) and/or the dissolution of particles introduced into the near wellbore region during drilling [1]. It is essential to add acid corrosion inhibitors (ACIs) to high strength HCl formulations in order to minimise the corrosion of coiled tubing (CT) and wellbore casing materials; CT is often used to deliver the acidizing fluid to target zones within the reservoir [1]. In the absence of ACIs, high strength HCl fluids would result in *uninhibited* corrosion rates up to 1000 mm/yr for carbon steel [2–4]. Therefore, highly efficient ACIs are essential for safe, effective and sustainable matrix acidizing operations. ACI molecules adsorb to exposed steel surfaces (CT and wellbore casing) to provide effective protection from acid corrosion at temperatures up to 150 °C [5,6]. The most effective ACI formulations contain *polymerisable* film-forming molecules, which function by adsorbing on the exposed steel surfaces before polymerising to create a thicker and more robust barrier to corrosive attack [7–9]. Acetylenic alcohols, such as propargyl alcohol and its derivatives, are examples of polymerisable ACIs and have been shown to be very effective across a broad range of high-strength

acidic environments [2,3,6,8].

Two distinct inhibition processes, typically termed adsorption-polymerisation, occur at the metal-solution interface when acetylenic alcohol ACIs are employed in high strength HCl solutions to minimise the corrosion of carbon steel [3]. Firstly, the ACI molecules adsorb to the steel surface, establishing a film at the steel-solution interface [10]. Several different adsorption pathways have been proposed, including chemisorption, electrostatic adsorption and hydrogen bonding between the ACI molecules and the steel surface [3]. Adsorption is followed by polymerisation reactions, whereby the adsorbed ACI molecules are polymerised producing a robust and protective polymeric film on the steel surface. Polymerisation of adsorbed acetylenic alcohol molecules may occur directly or via the polymerisation of by-products formed as a result of the hydrogenation and hydration of acetylenic alcohol molecules; such polymerisation reactions are catalysed by the metal surface [3]. It has been suggested that the presence of iron ions (Fe<sup>2+</sup>) near the metal surface acts as a catalyst for propargyl alcohol polymerisation [11]. Inhibition mechanisms of ACIs have recently been discussed in detail by Barmatov et al. [3] in a separate study.

Current field practices employ a fixed concentration of ACI in all the acid injected during a matrix acidizing treatment. Such a fixed concentration of ACI may not be optimal in terms of the overall efficiency of corrosion protection [12]. Accordingly, a staged acid corrosion inhibition concept has been proposed [12]; this involves using a higher ACI

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concentration during Stage 1 to establish a persistent inhibitor film followed by a significantly lower ACI concentration during Stage 2 to maintain the Stage 1 film and its low corrosion rate. Typically, the Stage 1 ACI dosage would be implemented in a low volume of acid sufficient to establish the persistent film on all exposed steel surfaces, as compared to the main volume of acid pumped during Stage 2. The staged acid corrosion inhibition concept relies on the *persistence* of inhibitor films formed by *polymerisable* ACI chemistries and mixtures [12]. Several staged ACI inhibitor chemistries and formulations are described in three granted U.S. patents [13–15].

The performance of staged ACI treatments has been extensively evaluated in the laboratory by electrochemical testing using rotating cylinder electrodes (RCEs) at 80 °C and by weight loss coupon testing at temperatures in the range of 77–121 °C [12]; these investigations compared the persistence of Stage 1 films formed on the low carbon steel HS80™ (Tenaris coiled tubing) and the medium carbon steel N80 (wellbore casing material). However, the electrochemical (RCE) methodology employed by Barmatov et al. [12] has limitations. For example, having established the Stage 1 film on the RCE, the film is exposed to air when it is transferred to the vessel containing the Stage 2 test solution; this transfer procedure could influence the properties and persistence of the film. In addition, both the electrochemical RCE tests and the weight loss coupon tests described in reference [12] are performed in ‘closed’ environments, i.e. the HCl and ACI components of the test solutions can be somewhat consumed during the experiment and, therefore, the solution chemistry can change during the Stage 1 and Stage 2 exposure periods.

In order to address the above-mentioned limitations, the objective of this study was to evaluate the performance of staged ACI treatments (4 M HCl, 80 °C) in a customised once-through flow cell. The once-through flow cell, originally designed by Barker et al. [16,17] to simulate acid flow-back after matrix acid injection, was adapted for the evaluation of staged ACI treatments investigated in this study. The once-through flow cell offers the advantage of a continuous flow and fresh supply of HCl and ACI; this is more realistic relative to matrix acidizing field operations. In addition, the flow cell set-up enables the ACI concentration to be changed seamlessly without interrupting the flow and without exposing the steel coupon to air and/or any potential contaminants.

In order to evaluate the performance of the staged ACI approach using the once-through flow cell, three main aspects were investigated. Firstly, having established the Stage 1 film, the ACI concentration in Stage 2 was varied to determine and understand how the Stage 2 dosage influences the persistency of the Stage 1 film. Secondly, the effect of the carbon steel type and properties was investigated using typical coiled tubing and wellbore casing materials. Finally, the influence of a pre-corrosion step was evaluated in order to assess the performance of staged ACI treatments applied on steel surfaces whose roughness is more realistic relative to the steel surfaces encountered in the field application.

## 2. Experimental procedure

### 2.1. Materials

Two carbon steel grades were compared for all experimental conditions: HS80™ (Tenaris) low carbon steel (CT) and N80 medium carbon steel (wellbore casing). The elemental composition of these materials is shown in Table 1. HS80™ has a ferrite-pearlite microstructure whilst N80 is a quenched carbon steel and has a ferrite-martensite

microstructure. The microstructure of both steels is shown in the scanning electron microscopy (SEM) images given in Fig. 1; the images were taken after chemical etching of the metal surfaces in a 2% Nital solution. All the flow cell experiments used 4 M HCl solution, purchased from Fisher Scientific. The ACI evaluated in this study is a commercial acetylenic alcohol-based polymerisable corrosion inhibitor.

### 2.2. Once-through flow cell experiments

The flow cell designed by Barker et al. [16] for electrochemical investigation of carbon steel in HCl flow was modified for the evaluation of staged ACI treatments. The flow cell assembly and experimental setup is shown in Fig. 2. A detailed description of the flow cell design and methodology for its application in HCl flow experiments has been reported by the authors previously [16]. A more concise description is given here. The flow cell consisted of three layers: a bottom and top layer, manufactured from a highly chemical-resistant polyethylene, and a 3 mm thick, laser-cut Viton gasket to seal the flow cell during flow. A 10 × 10 mm, 5 mm thick carbon steel coupon was mounted and sealed in the centre of the bottom flow cell layer using an acid-resistant, non-conductive resin with strong edge retention to minimise crevice corrosion around the sides of the coupon. A copper wire was soldered to the reverse side of the coupon, prior to mounting in resin, to enable electrical connection to a potentiostat for the purpose of conducting electrochemical measurements. Once the resin had dried, the layer was wet-ground using 120, 600, 800 and 1200 grit silicon carbide (SiC) grinding paper successively, to produce a uniform surface texture across the entire coupon area and to ensure the coupon was flush with the surface of the flow cell layer to prevent any disturbance to the flow. To improve the flow cell function for the study of the staged inhibition approach, a more effective acid resistant resin was utilised along with a redesign of boltholes to improve the compression seal. A new methodology (detailed later in Section 2.3) was established to enable seamless transition to low ACI concentrations.

A combination electrode (Thermo Scientific), consisting of a silver/silver chloride (Ag/AgCl) reference electrode and platinum (Pt) counter electrode disc (located on the bottom surface of the combination electrode exposed to the flow), was mounted in the top layer for electrochemical measurements. The electrode was fixed in position using an M20×1.5 cable gland and sealed with acid-resistant, non-conductive resin. The combination electrode was positioned directly opposite the carbon steel coupon to minimise solution resistance in electrochemical measurements.

To seal the flow cell and channel flow over the carbon steel coupon, a Viton gasket was designed. The gasket was positioned between the bottom and top layers and compression-sealed using eight M5 bolts. Before assembling the flow cell, all layers were washed with deionised water and dried. Once sealed, the flow cell was integrated into the experimental set-up and immersed in a water bath, to maintain a temperature of 80 °C inside the flow cell throughout the tests. Experiments were performed over 4 h, equivalent to the duration of a matrix acidizing procedure in the industrial application. Experiments beyond this period have been completed in other studies to assess ‘flowback’, whereby the acid strength is diluted by production fluids once flow from the reservoir restarts after the matrix acidizing procedure is finished [16, 17]. Temperature measurements were taken using a thermocouple integrated within the flow cell [16]. A water bath temperature of 85 °C was required to maintain a temperature of 80 °C within the flow cell. The flow of HCl into the cell was controlled by a peristaltic pump

**Table 1**  
Composition (wt%) of HS80™ and N80 carbon steels.

Steel	C	Mn	P	S	Si	Cr	Cu	Ni	Mo	Fe
HS80™	0.10	0.60	< 0.03	< 0.005	0.30	0.45	< 0.40	< 0.25	–	≥ 97.0
N80	0.24	1.19	0.011	0.013	0.22	0.036	–	–	0.018	98.3

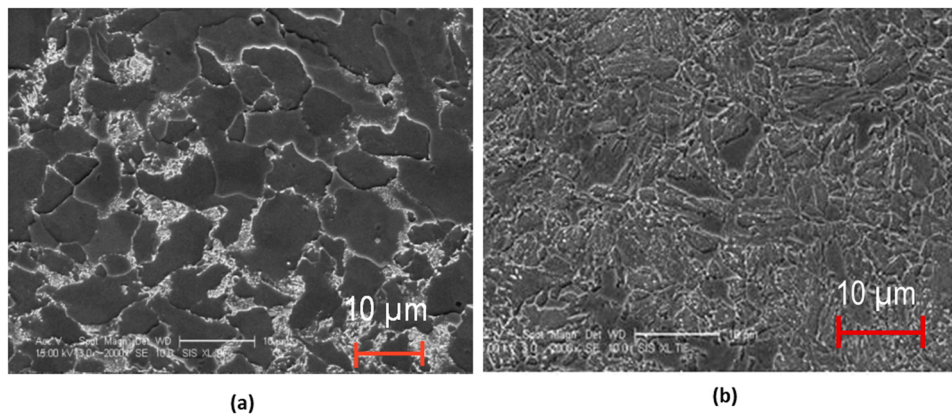


Fig. 1. SEM images of (a) HS80™ and (b) N80 carbon steels after chemical etching in a 2% Nital solution.

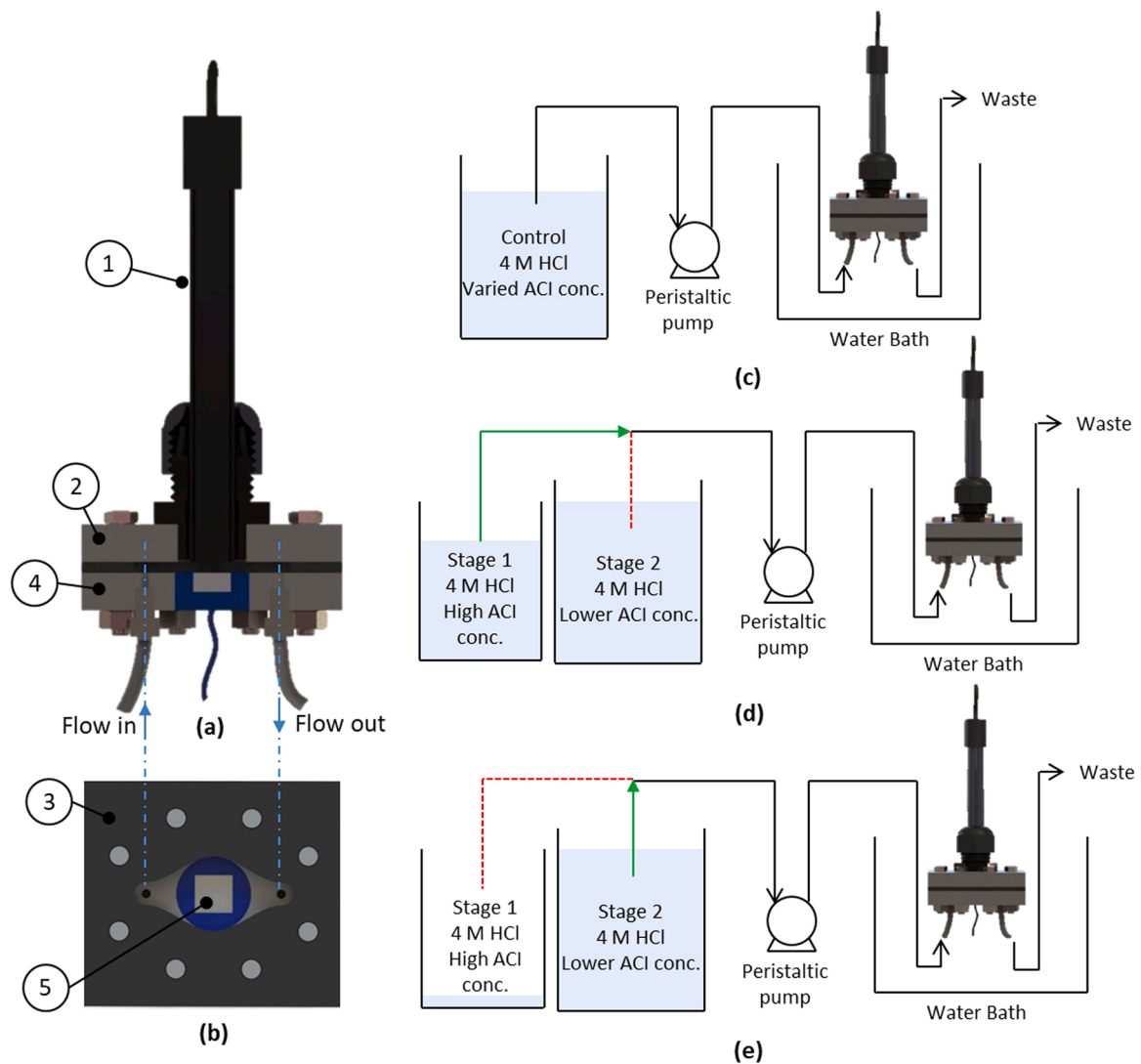


Fig. 2. Once-through flow cell and experimental apparatus for HCl flow corrosion experiments, showing (a) cross-section of the flow cell assembly consisting of (1) combination reference and counter electrode, (2) top layer, (3) gasket and (4) bottom layer containing (5) carbon steel coupon; (b) top view of flow cell gasket, showing the flow path across the coupon; (c) 'Control' experimental setup consisting of one glass beaker containing 4 M HCl and ACI and (d, e) Staged experimental setup consisting of two glass beakers containing 4 M HCl and a high and low dosage of ACI, showing (d) Stage 1 operation and (e) Stage 2 operation. A peristaltic pump, chemical-resistant tubing and a water bath completed the experimental apparatus.

(Ismatec). The acid solution was transported at a flow rate of 5 mL/min from one of two glass beakers each containing 4 M HCl, each maintained at ambient temperature and each containing different concentrations of the ACI (corresponding to Stages 1 and 2 of the test, as discussed later).

The eye shape gasket design has been established as an effective design for preventing undesirable flow effects, such as recirculation of fluid, in flow cells [18,19]. Computational fluid dynamics simulations of the gasket design confirmed that no undesirable flow effects would be observed, below a flow rate of 15 mL/min, and that it was appropriate for use in once-through HCl flow experiments, ensuring uniform conditions over the entire exposed surface of the carbon steel coupon [16]. Flow velocities across the sample have been predicted to be approximately 8 mm/s and 20 mm/s, at flow rates of 1 and 10 mL/min respectively for this gasket design [5,20]. Chemical-resistant PharMed® tubing (supplied by Saint-Gobain Performance Plastics) with an inner diameter of 1.6 mm was used to transport the acid solutions and this tubing was mounted in the flow cell using a barbed flangeless nut. To ensure that the acid solutions had sufficient time to heat to 80 °C, prior to entering the flow cell, approximately 1.5 m of this tubing was submerged in the water bath.

### 2.3. Staged ACI methodology

Two main types of ACI experiment were completed, defined as 'control' and 'staged' experiments in the following sections. Four different concentrations of the ACI were compared for all conditions: 0.2 wt%, 0.1 wt%, 0.02 wt% and 0.005 wt%.

#### 2.3.1. Control experiments

Control experiments were performed to determine the inhibition efficiency of the ACI when used in a fixed concentration throughout the 4 h test period. The ACI was added into 1450 mL of 4 M HCl (at ambient temperature), 15 min prior to the start of the test; this solution was stirred using a magnetic stirrer at 100 rpm throughout the experiment to maintain a homogenous distribution of ACI in the HCl solution. The tubing was positioned in the beaker to allow for the HCl and ACI solution to be pumped into the flow cell at a fixed flow rate of 5 mL/min throughout the 4 h test. The flow cell temperature was maintained at 80 °C throughout. Barmatov et al. [12] demonstrated that the same acetylenic alcohol-based polymerisable ACI (applied in the same concentrations as this study) was not significantly affected by flow rate, to mitigate corrosion of HS80™ carbon steel in 4 M HCl at 80 °C in RCE experiments under laminar and turbulent flow conditions.

#### 2.3.2. 'Staged' experiments

In staged ACI experiments, after Stage 1 (typically, 1 h), the concentration of the ACI was reduced (Stage 2) for the remainder of the 4 h experiment. The two stages were categorised as follows:

- Stage 1 – film formation stage (0–1 h): an ACI concentration of 0.2 wt% was added into 350 mL of 4 M HCl, 15 min prior to the start of the test and stirred using a magnetic stirrer at 100 rpm.
- Stage 2 – film maintenance stage (1–4 h): a lower concentration of ACI was added to 1150 mL of 4 M HCl 15 min prior to the start of this stage and stirred using a magnetic stirrer at 100 rpm. The ACI concentration in Stage 2 was either 0.02 wt%, 0.01 wt% or 0.005 wt% for the remaining 3 h; the objective was to assess which Stage 2 ACI concentrations could maintain acceptable corrosion protection during the 1–4 h test period.

The setup used two glass beakers as demonstrated in Fig. 2. The tubing was positioned in the Stage 1 solution and pumped into the flow cell at a flow rate of 5 mL/min for 1 h before the peristaltic pump was briefly stopped whilst the tubing was removed, cleaned using deionised water and dried to ensure no inhibitor remained on the tubing, before transferring it to the Stage 2 solution. The pump was then restarted,

having been stopped for < 20 s, to re-establish the 5 mL/min flow rate. Throughout both stages the flow cell temperature was maintained at 80 °C. To confirm that the tubing transfer method did not influence the results, an experiment was performed with equal ACI dosages (0.2 wt%) in Stage 1 and Stage 2; the results of this experiment proved that a constant corrosion rate was achieved, equivalent to that measured in the control experiment using 0.2 wt% ACI.

### 2.4. Influence of pre-corrosion

The surface texture of carbon steel coupons is known to have a significant influence on uninhibited corrosion rates and corrosion inhibitor performance [2,4,20,21]. The majority of published corrosion inhibitor studies are performed using 'smooth' surfaces, where the test coupon has been wet ground to a very low surface roughness. However, surfaces encountered in the field application are often significantly rougher as a result of manufacturing processes and/or the effects of repeated usage and pre-corrosion. Therefore, in order to evaluate the performance of the staged ACI approach under more realistic conditions and to provide data for comparisons with smoother (wet ground) surfaces, the carbon steel coupons located in the flow cell were pre-corroded by flowing *uninhibited* 4 M HCl for a fixed time period before initiating the staged ACI treatments.

To establish an appropriate pre-corrosion period, uninhibited corrosion experiments were completed initially in 4 M HCl flow at 80 °C using the flow cell for periods of 10 min and 20 min on both HS80™ and N80 carbon steel. Short pre-corrosion periods were chosen as it was undesirable to induce excessive corrosion which could potentially influence the flow characteristics through the flow cell by significantly decreasing the thickness of the material and creating the potential for flow recirculation over the test coupon.

Prior to their pre-corrosion, coupons were prepared using the same methodology as for the control and staged tests (i.e. they were mounted in the flow cell and wet ground using SiC paper up to 1200 grit). The surface properties of the pre-corroded coupons were analysed using a Bruker NPFLEX white light interferometer, by removing the coupon from the flow cell, cleaning with deionised water and drying with compressed air before analysis. A pre-corrosion period of 10 min was subsequently chosen after this analysis (results presented later) and integrated into the methodology for the staged ACI experiments. During the pre-corrosion followed by staged ACI tests, a flow of uninhibited 4 M HCl was pumped at 5 mL/min through the flow cell before the pump was stopped. The pump and the tubing were then moved to the glass container filled with 4 M HCl and 0.2 wt% ACI prior to restarting the pump and continuing the test according to the staged experiment methodology (Section 2.3.2). As described later, additional staged ACI experiments were completed on pre-corroded N80 carbon steel using a Stage 1 ACI concentration of 0.5 wt%.

### 2.5. In situ electrochemical measurements

Electrochemical measurements were performed in situ to measure how the ACI concentration influenced corrosion rates of the carbon steel coupons during the 4 h exposure period. The same electrochemical procedure was employed for measurements in both the control and staged ACI experiments. A standard three electrode cell was used, consisting of a working electrode (the carbon steel coupon) and a combination Ag/AgCl reference and Pt counter electrode. Electrodes were connected to an Ivium CompactStat™ potentiostat. Linear polarisation resistance (LPR) measurements were performed by polarising the carbon steel coupons from – 5 mV to + 5 mV, relative to the open circuit potential (OCP), at a scan rate of 0.25 mV/s. LPR measurements were undertaken every 15 min, giving a total of 16 measurements during the 4 h test period, with the OCP being monitored in between each LPR measurement. LPR measurements have demonstrated a very good agreement with mass loss results to evaluate the corrosion rates of

carbon steel in 4 M HCl environments at 80 °C when ACIs are applied [16]. In pre-corrosion experiments, the OCP of the coupon was measured during the pre-corrosion period but no LPR measurements were performed due to the high uninhibited corrosion rate and therefore the high corrosion current density expected when polarising the coupon. Results were reported as  $1/R_p$ , the reciprocal of the polarisation resistance obtained from LPR measurements; this parameter is directly proportional to the corrosion rate. The determination of accurate Tafel constants to calculate corrosion rates can be challenging in environments with high currents, as observed in 4 M HCl corrosion experiments, creating ambiguity in corrosion rates. In addition, it is likely that Tafel constants would vary during staged ACI experiments leading to inaccurate calculations of corrosion rate. These electrochemical procedures have been shown to be acceptable for measurements in HCl environments without inducing any undesirable effects on the surface or the ACI film as a result of excessive polarisation [16].

### 3. Results and discussion

#### 3.1. Control experiments

Control experiments were performed to determine the corrosion behaviour of the HS80™ and N80 carbon steels during a 4 h test period in the presence of a series of fixed concentrations of the ACI in 4 M HCl flow at a flow rate of 5 mL/min and temperature of 80 °C. Results are presented in terms of average values of  $1/R_p$  and OCP versus time in Fig. 3. Each average value of  $1/R_p$  and OCP is determined by duplicate

experiments performed for each fixed ACI dosage; error bars show the maximum and minimum values. For comparison, Barmatov et al. [7] reported a corrosion rate of 565 mm/year ( $R_p = 0.57 \Omega\text{-cm}^2$  and  $1/R_p = 1.74 \Omega^{-1}\text{-cm}^{-2}$ ) for HS80™ (RCE rotating at 6000 rpm) after 3 h exposure at 80 °C to 4 M HCl containing 0.003 wt% of the same inhibitor; this corrosion rate was calculated by assuming a Stern-Geary coefficient of 23.3 mV. Similarly, when the ACI concentration was increased to 0.2 wt%, Barmatov et al. [7] reported a corrosion rate of 2.75 mm/year ( $R_p = 94 \Omega\text{-cm}^2$  and  $1/R_p = 0.01 \Omega^{-1}\text{-cm}^{-2}$ ).

As expected, at any given a exposure period, an increase in the ACI concentration results in lower average values of  $1/R_p$  (Fig. 3). When the ACI concentration is 0.2 wt%, a highly protective and stable inhibitor film is formed on both the HS80™ and N80 carbon steels. In the case of HS80™, when the ACI concentration is 0.2 wt%, the average value of  $1/R_p$  is  $0.004 \Omega^{-1}\text{-cm}^{-2}$  after 3 h exposure (Fig. 3(a)). These data are in good agreement with  $1/R_p$  values reported by Barmatov et al. [7] for equivalent materials and testing conditions, viz.  $1/R_p = 0.01 \Omega^{-1}\text{-cm}^{-2}$  for turbulent flow conditions (RCE rotating at 6000 rpm) and  $1/R_p = 0.001 \Omega^{-1}\text{-cm}^{-2}$  for laminar flow conditions (RCE rotating at 5 rpm).

For all ACI concentrations, measured values of  $1/R_p$  were lower on HS80™ than on N80 (Fig. 3). For ACI concentrations 0.01 wt% and 0.02 wt%, the films formed on HS80™ were more stable than those formed on N80. The OCP measurements were relatively constant during the 4 h exposure periods for the films on HS80™ but, by comparison, more variable and less repeatable OCP measurements were observed for the films on N80. There is a correlation between the OCP and  $1/R_p$  measurements for the films formed on HS80™ but a similar correlation

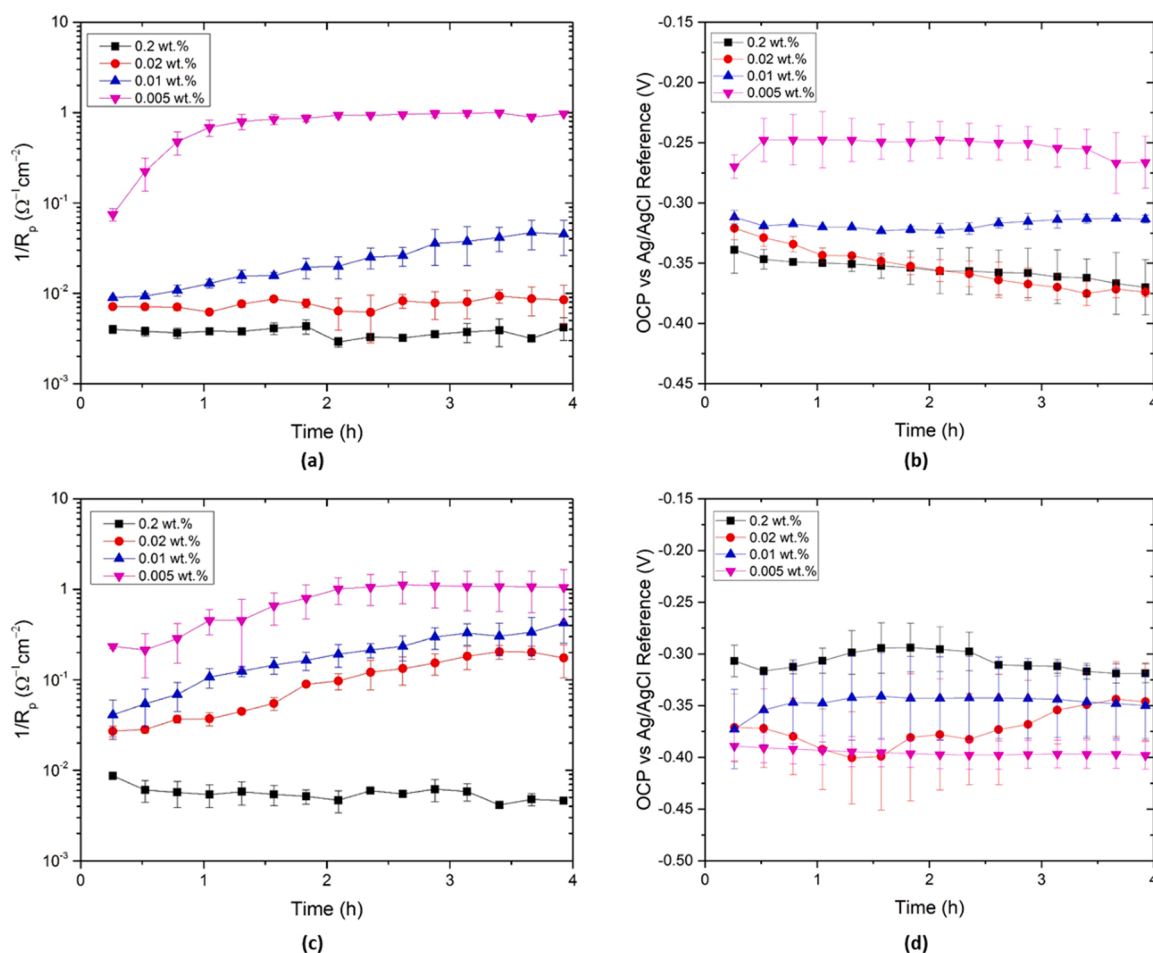


Fig. 3. Control experiments using a fixed concentration of ACI over 4 h and plotted as  $1/R_p$ , obtained from in situ LPR (a,c) and OCP (b, d) measurements of (a, b) HS80™ and (c, d) N80 carbon steel coupons, mounted in a once-through flow cell and exposed to 4 M HCl flow at a temperature of 80 °C and a flow rate of 5 mL/min.

is not observed for the films on N80.

In the presence of the lowest ACI concentration 0.005 wt%, relatively inefficient inhibitor films were formed on both carbon steels. Within the time period 1–2 h, values of  $1/R_p$  for these films increased dramatically, suggesting initial inhibitor adsorption to the surface followed by poor inhibitor film persistence during the polymerisation stage. Values of  $1/R_p$  became more constant towards the end of these tests but it should be noted that the sensitivity of these measurements would have been influenced by the significance of the solution resistance relative to the value of  $R_p$  being measured. In a previous study, the solution resistance was measured to be  $0.6 - 1.3 \Omega\text{-cm}^2$  (by electrochemical impedance spectroscopy) using the same flow cell and experimental materials and conditions (HS80™, 4 M HCl and 80 °C). In addition, it should be noted that the high corrosion rate in the presence of 0.005 wt% ACI would result in significant quantities of material removal, potentially influencing the HCl flow path within the flow cell as the experiment progressed.

The influence of ACI concentration on the measured  $1/R_p$  is compared for HS80™ and N80 in Fig. 4. The  $1/R_p$  results are averages of all values measured across a minimum of two 4 h tests. Error bars represent the standard deviation of all data points across the two tests. In general, for all inhibitor concentrations, higher values of  $1/R_p$  are observed for N80 as compared to HS80™. As described later, this conclusion is significant with regard to the evaluation of inhibitor film persistency in staged ACI treatments.

### 3.2. Staged experiments

Staged ACI experiments were performed by maintaining a fixed ACI concentration (0.2 wt%) for an initial 1 h period to establish a protective inhibitor film (Stage 1) followed by reducing the ACI concentration for the remaining 3 h (Stage 2). The ACI concentration 0.2 wt% was chosen for Stage 1 on the basis of the results of the control experiments shown in Figs. 3 and 4. The effect of the staged approach on OCP measurements, taken every 1 s throughout the 4 h period (in between LPR measurements), was assessed by comparing the HS80™ control experiment (0.2 wt% ACI for 4 h) and the staged experiment (0.2 wt% ACI for 1 h followed by 0.005 wt% for 3 h). In previous HS80™ RCE experiments [12], a short-lived but significant increase in OCP was observed after the RCE was transferred from the Stage 1 to the Stage 2 solution. In the present study, using the once-through flow cell, only a slight increase in OCP was observed after the ACI concentration was changed from 0.2 wt

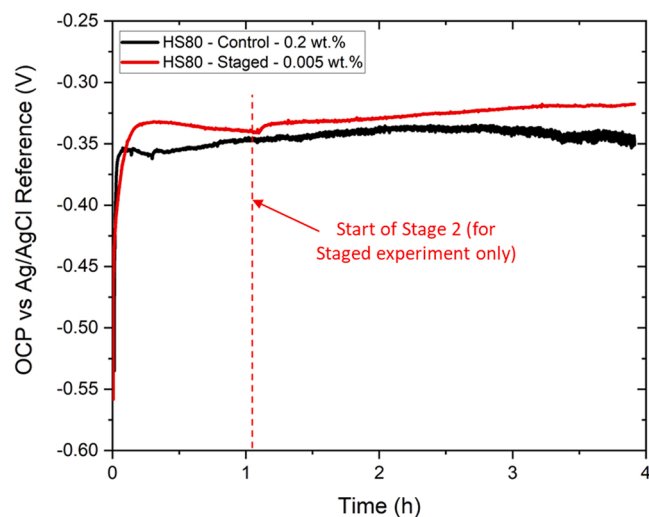


Fig. 5. Comparison of OCP measurements during control experiment (0.2 wt% ACI for 4 h) and staged experiment (0.2 wt% ACI for 1 h followed by 0.005 wt% for 3 h). HS80™ carbon steel coupons mounted in a once-through flow cell. 4 M HCl flow at a temperature of 80 °C and a flow rate of 5 mL/min.

% to 0.005 wt% (Fig. 5). This increase was likely caused by the change in conditions associated with the lower ACI concentration, as opposed to being caused by the transfer between different stages. This demonstrates the advantage of using the once-through flow cell technique for enhanced experimental control relative to the RCE transfer method.

The results of the staged ACI experiments are shown in Fig. 6. The performance of Stage 2 ACI concentrations 0.02 wt%, 0.01 wt% and 0.005 wt% was compared. Stages 1 and 2 are identified on the plots to define the point at which the fluid composition was switched to the lower ACI concentration. The  $1/R_p$  results shown in Fig. 6 were obtained from LPR measurements taken from a minimum of two experiments for each of the material and staged fluid conditions; error bars represent the maximum and minimum values determined.

The results shown in Fig. 6(a) indicate that the Stage 1 inhibitor film formed in 1 h on HS80™ using an ACI concentration of 0.2 wt% can be maintained for 3 h by Stage 2 solutions containing 0.01–0.02 wt% ACI. The results obtained for the Stage 2 solution containing 0.005 wt% ACI indicate some significant degradation of the film during the time period 3–4 h. By comparison, Stage 1 films formed on N80 using 0.2 wt% ACI were less persistent, particularly when the Stage 2 solution contained 0.005 wt% ACI (Fig. 6(b)). For Stage 2 ACI concentrations in the range 0.01–0.02 wt%, on both steel types, only a minor increase in  $1/R_p$  was observed during the time period 3–4 h. Overall, these results indicate that a low corrosion rate can be achieved by pumping 4 M HCl containing 0.2 wt% ACI for 1 h followed by 4 M HCl containing only 0.01–0.02 wt% for the next 3 h. This suggests that the staged ACI approach can deliver significant benefits in terms of reducing the overall usage of inhibitor as compared to pumping 4 M HCl containing 0.2 wt% for the full 4 h period.

Several different environmental conditions are known to destabilise inhibitor films resulting in low film persistency. Prevailing flow conditions may cause mechanical removal of the inhibitor film, e.g. due to high shear stresses and turbulent flow [7]. Another important factor influencing film stability and persistence is the availability of ‘fresh’ inhibitor molecules in the fluid near the surface of the film [22]. In the present study, a fluid flow rate of 5 mL/min through the once-through flow cell creates a laminar flow condition such that any mechanical removal of the inhibitor film is highly unlikely [23]. Therefore, it is reasonable to conclude that it is the low concentration of ACI molecules in the maintenance fluid, near to the inhibitor film surface, that is mainly responsible for instability of the Stage 1 film (increase in  $1/R_p$ ),

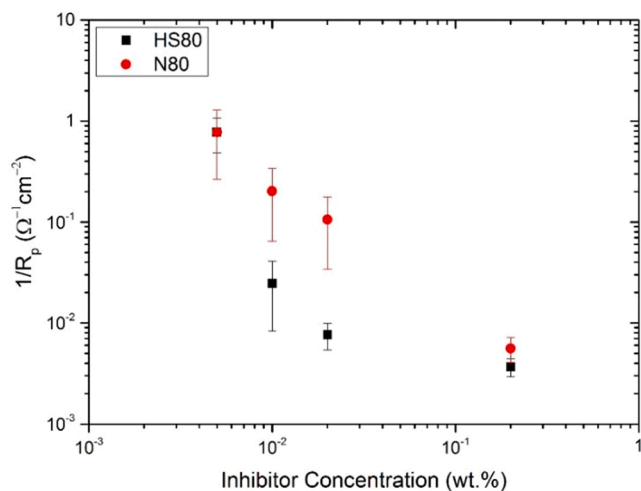
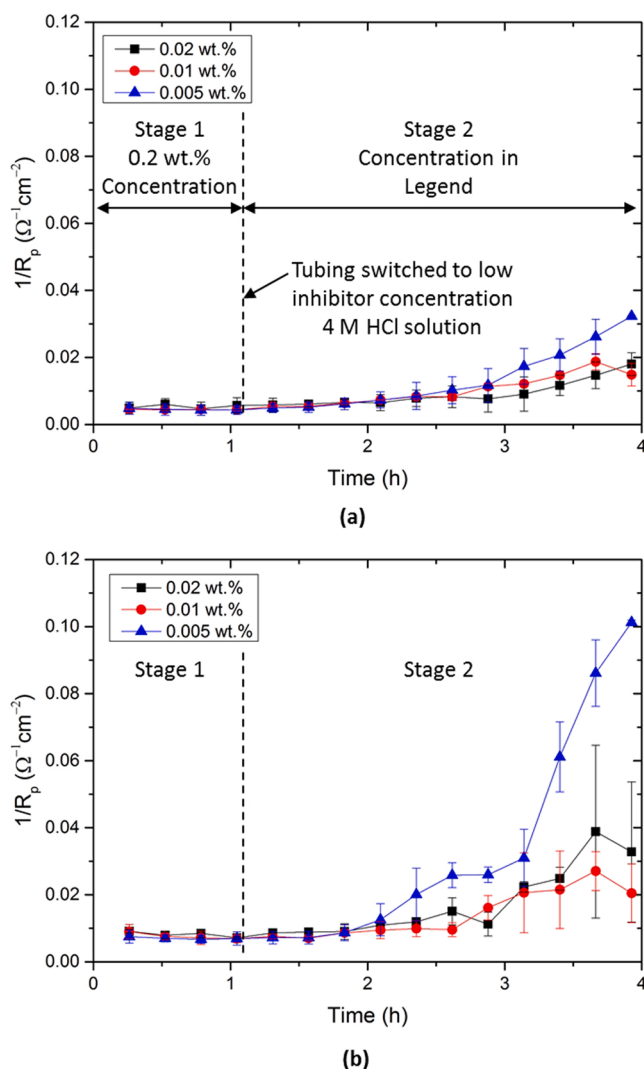


Fig. 4. Comparison of average  $1/R_p$  for ACI films formed on HS80™ and N80 carbon steel as a function of ACI concentration. Measurements acquired using once-through flow cell during 4 h exposure in 4 M HCl flow at 80 °C and a flow rate of 5 mL/min.



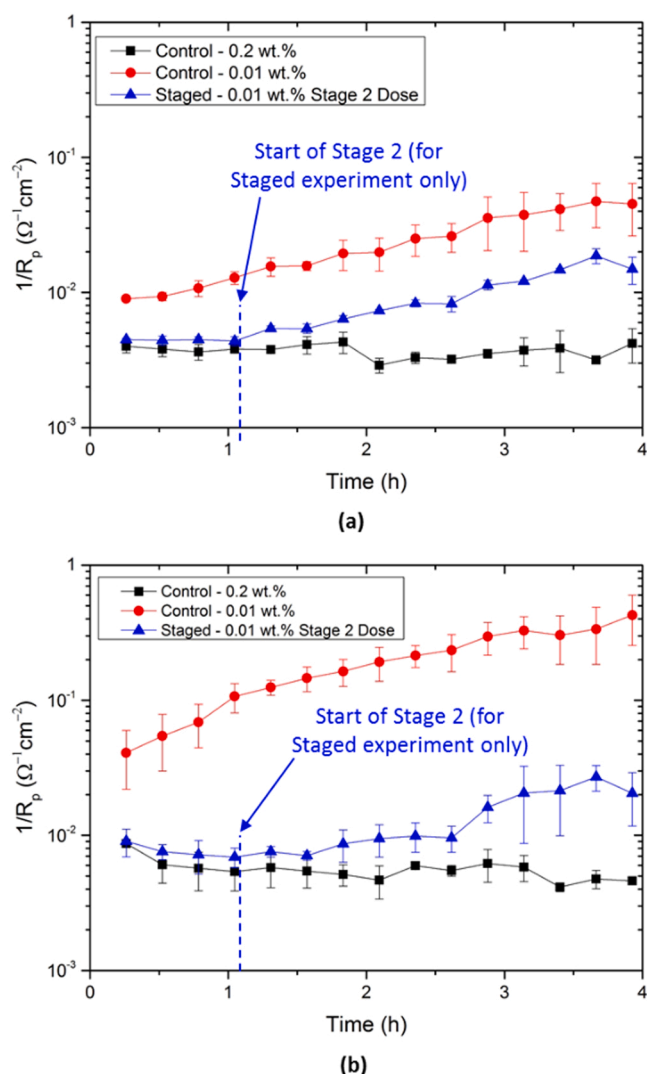
**Fig. 6.** Staged experiments consisting of a 0.2 wt% ACI film-forming stage (Stage 1) followed by a lower fixed ACI concentration for 3 h (Stage 2, ACI concentration given in legend) and plotted as  $1/R_p$ , obtained from in situ LPR measurements of (a) HS80™ and (b) N80 carbon steel coupons, mounted in a once-through flow cell, in 4 M HCl flow at a temperature of 80 °C and a flow rate of 5 mL/min.

for example, when the Stage 1 film on N80 is exposed to the Stage 2 solution containing 0.005 wt% ACI. It has been proposed that a *critical concentration* of ACI molecules near to the film surface is required to maintain the polymerisation process and that the presence of sub-critical ACI concentration in this region has a significant detrimental effect on the protection efficiency of the film [22]. For N80 (Fig. 6(b)), Stage 2 ACI concentrations in the range 0.01–0.02 wt% are sufficient to maintain the persistency of the Stage 1 film. However, the Stage 2 ACI concentration 0.005 wt% is sub-critical meaning that the persistency of the film formed in Stage 1 is not maintained due to an insufficient concentration of “fresh” ACI molecules (i.e. provided by inflow into the flow cell) required to support the polymerisation process. Interestingly, when the Stage 2 ACI concentration is sub-critical, there appears to be a time delay before the protection efficiency of the film begins to decrease. The Stage 1 film remains protective for a significant period of time, despite the sub-critical ACI concentration in stage 2, before beginning to lose its persistency; thus, we do not observe instantaneous failure of the film. As described later, the Stage 1 ACI concentration can be increased to enhance film persistence in the presence of a low ACI concentration in Stage 2.

In contrast to equivalent experiments on HS80™, the Stage 2 ACI concentration 0.005 wt% was not sufficient to maintain good film persistency on N80 (compare Fig. 5(a) and 5(b)). Staged experiments performed using a Stage 1 ACI concentration of 0.2 wt% and a Stage 2 ACI concentration of 0.01 wt% are compared with control experiments using a fixed ACI concentration of 0.01 wt% and 0.2 wt% for both carbon steels in Fig. 7. Significantly lower values of  $1/R_p$  were observed in Stage 2 (0.01 wt% ACI) of the staged experiments relative to the control experiments (0.01 wt% ACI). This demonstrates the clear benefit of establishing a persistent film (Stage 1) in the staged experiments. When the  $1/R_p$  results shown in Fig. 7 are averaged over the full 4 h test period, the average  $1/R_p$  was 65% lower during the staged experiment than the control experiment for HS80™ and 94% lower for N80. Interestingly, low values of  $1/R_p \approx 10^{-2} \Omega^{-1} \cdot \text{cm}^{-2}$ , were *maintained* using the staged ACI approach using a significantly lower total quantity of inhibitor as compared to the control (0.2 wt% ACI for 4 h).

### 3.3. Pre-corrosion experiments

The experiments described up to this point were performed using ‘smooth’ carbon steel surfaces created by wet grinding using 1200 grit



**Fig. 7.** Comparison of staged experiments (Stage 1 (0.2 wt% ACI for 1 h) followed by Stage 2 (0.01 wt% ACI for 3 h)) with control experiments (ACI concentrations fixed at 0.01 wt% or 0.2 wt% for 4 h) for (a) HS80™ and (b) N80 carbon steel coupons mounted in a once-through flow cell. 4 M HCl flow at a temperature of 80 °C and a flow rate of 5 mL/min.

SiC paper. Such smooth, uniform and controllable surface textures with low surface roughness are ideal for controlled and reproducible laboratory flow experiments that are not affected by localised mass transport effects induced by the surface texture [24]. Surface roughness has been reported to influence how corrosive species are transported to/from the metal surface, affecting corrosion rates and corrosion inhibition efficiency [4,25,26]. However, in the field application, it is likely that the exposed steel surfaces have a rougher surface texture due to manufacturing processes, repeated exposure and pre-corrosion. It is known that inhibitor performance can be strongly influenced by the condition of the surface onto which the inhibitor molecules adsorb [20, 21]. Therefore, to simulate conditions more typical of the field, pre-corrosion experiments were performed to create steel surfaces which are more realistic in terms of those encountered during matrix acidizing operations.

HS80™ and N80 carbon steel surfaces were characterised after exposure to *uninhibited* 4 M HCl flow at 80 °C in the once-through flow cell in order to establish an appropriate pre-corrosion time period and to make comparisons with the wet ground surfaces used in the experiments described earlier. The surfaces were analysed using white light interferometry. The condition of HS80™ and N80 steel surfaces (3 × 3 mm central region) after 10 min and 20 min exposure to uninhibited 4 M HCl flow at 80 °C is shown in Fig. 8. Corrosion appeared to be uniform on HS80™ and cementite layers were revealed on the surface after

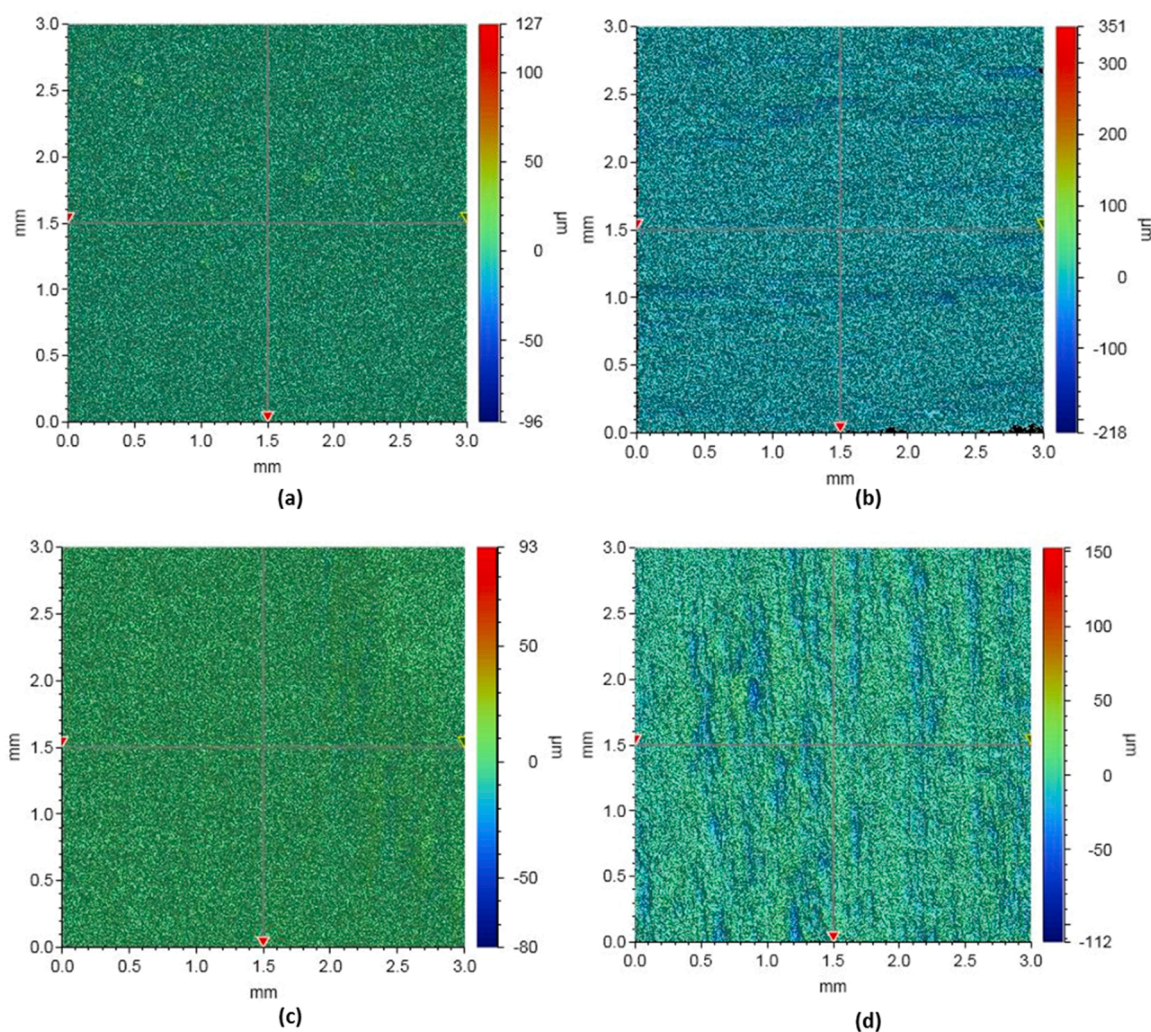
10 min and 20 min of pre-corrosion. The presence of cementite layers on the surface is known to influence inhibitor performance due to differences in inhibitor adsorption on cementite relative to ferrite [20]. More severe and localised corrosion was evident on N80 which is consistent with the generally higher values of  $1/R_p$  measured on N80 relative to HS80 and with the observation that the ACI was less effective on N80, particularly at low ACI concentrations. Relative to HS80™, it is likely that corrosion of the N80 surface leads to a more significant increase in surface area as a result of localised corrosion; this would lead to a requirement for higher ACI concentrations to maintain sufficient inhibitor coverage of the surface.

Table 2 shows the average surface roughness of HS80™ and N80 without any pre-corrosion (wet ground using 1200 grit silicon carbide

**Table 2**

Comparison of the surface roughness,  $S_a$ , of HS80™ and N80 carbon steels after 10 min and 20 min of uninhibited 4 M HCl flow through flow cell at a rate of 5 mL/min and temperature of 80 °C, compared with ‘smooth’ surfaces (i.e. 0 min), wet ground using SiC paper up to 1200 grit.

Steel	$S_a$ ( $\mu\text{m}$ )		
	0 min	10 min	20 min
HS80™	$0.11 \pm 0.01$	$1.23 \pm 0.22$	$1.09 \pm 0.24$
N80	$0.11 \pm 0.01$	$3.04 \pm 0.67$	$4.14 \pm 0.87$



**Fig. 8.** Surface profiles of (a) HS80™ after 10 min, (b) N80 after 10 min, (c) HS80™ after 20 min and (d) N80 after 20 min pre-corrosion in uninhibited 4 M HCl flow through the once-through flow cell at a flow rate of 5 mL/min and temperature 80 °C (note: the same colour range is used in the legend despite greater differences in the scale of heights, measured in  $\mu\text{m}$ , to enable better comparison of surface roughness).

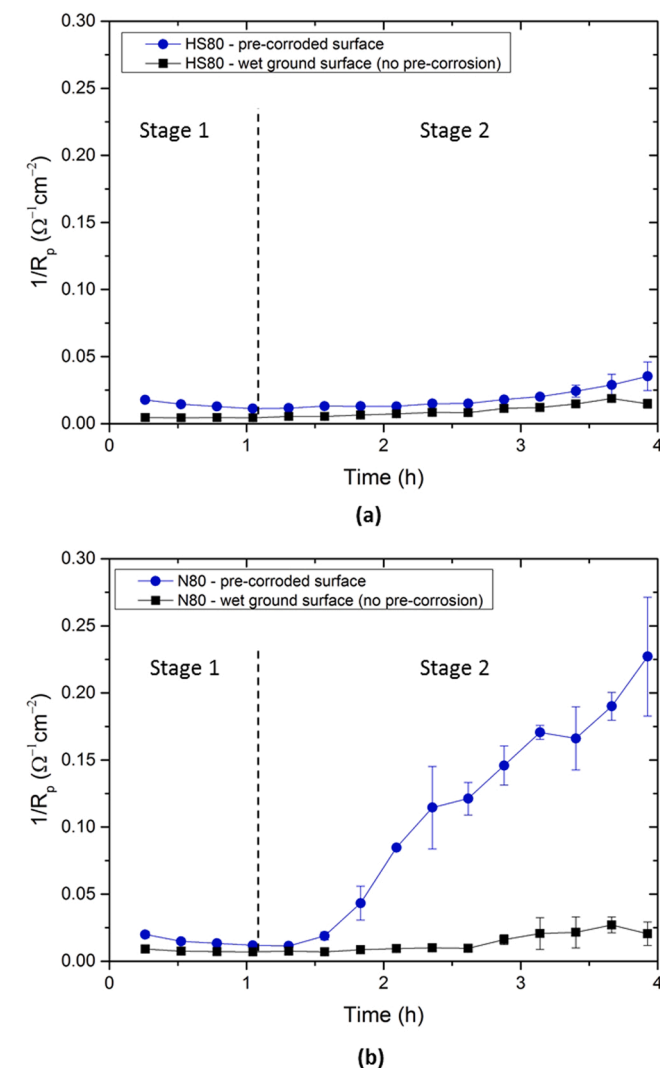


paper) and after 10 min and 20 min pre-corrosion in uninhibited 4 M HCl flow through the flow cell. The area surface roughness parameter,  $S_a$ , was obtained by applying a Gaussian cut off filter of 0.25 mm and calculated over the analysed surface area using Eq. (1).

$$S_a = \frac{1}{A} \iint_A |Z(x, y)| dx dy \quad (1)$$

where A is the surface area, Z is the measured height of the surface at positions x and y.

The average surface roughness was determined from four measurements (two repeat experiments for each treatment condition and measurements in two different  $3 \times 3$  mm locations on each coupon); the error value represents the standard deviation of the four measurements. The HS80™ results indicate a tenfold increase in  $S_a$  from  $0.11 \pm 0.01 \mu\text{m}$  for the wet ground coupons to  $1.2 \pm 0.2 \mu\text{m}$  and  $1.1 \pm 0.2 \mu\text{m}$  after 10 min and 20 min pre-corrosion, respectively. Equivalent pre-corrosion treatments on N80 resulted in larger increases in  $S_a$ ; 10 min pre-corrosion increased  $S_a$  by a factor of 30 and 20 min pre-corrosion increased  $S_a$  by a factor of 40. In view of the results given in Table 2



**Fig. 9.** Influence of a 10 min pre-corrosion period on staged ACI experiments consisting of a constant 0.2 wt% ACI concentration film-forming stage (Stage 1) followed by a lower constant ACI concentration of 0.01 wt% for 3 h (Stage 2), plotted as  $1/R_p$  versus time obtained from in situ LPR measurements for (a) HS80™ and (b) N80 carbon steel coupons, mounted in a once-through flow cell, in 4 M HCl flow at a temperature of 80 °C and a flow rate of 5 mL/min.

and in order to avoid excessive degradation of the test coupons, it was decided that a 10 min pre-corrosion period would be used in a further evaluation of the performance of staged ACI treatments as described below.

A 10 min pre-corrosion period was integrated into the staged ACI experimental methodology. Fig. 9 compares  $1/R_p$  versus time data for staged ACI treatments on HS80™ and N80, with and without 10 min pre-corrosion; all these staged ACI treatments involved the use of 0.2 wt% ACI to establish a persistent inhibitor film (Stage 1) and 0.01 wt% ACI to maintain the film (Stage 2) during a 3 h monitoring period.

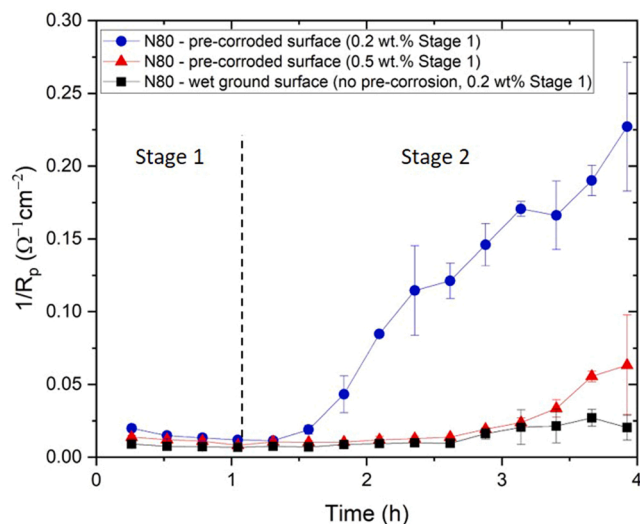
The results for HS80™ indicate a subtle effect of introducing the pre-corrosion step (Fig. 9(a)). However, following 10 min pre-corrosion of HS80™, all the  $1/R_p$  measurements during Stage 1 and Stage 2 are significantly higher than those taken in the equivalent staged experiment without pre-corrosion. In Stage 1, it is evident that the formation of a persistent film is slower on the pre-corroded rougher surface (approximately  $0.012 \Omega^{-1}\cdot\text{cm}^{-2}$  after 1 h) than on the wet ground smoother surface (approximately  $0.007 \Omega^{-1}\cdot\text{cm}^{-2}$  after 1 h). In Stage 2, both Stage 1 films (i.e. formed with and without a pre-corrosion period) are efficiently maintained but there is evidence that the Stage 1 film established on the pre-corroded surface becomes slightly less persistent during the 3.5–4 h time period.

In contrast, the results for N80 indicate a strong effect of introducing the pre-corrosion step (Fig. 9(b)). As observed for HS80™, in Stage 1, it is evident that the formation of a persistent film is slower on the pre-corroded rougher N80 surface than on the wet ground smoother surface. In Stage 2, the Stage 1 film established on the pre-corroded rougher N80 surface loses its persistency during the time period 1.5–4 h; indeed, during this period,  $1/R_p$  increases near linearly from  $0.02 \pm 0.005 \Omega^{-1}\cdot\text{cm}^{-2}$  to  $0.23 \pm 0.04 \Omega^{-1}\cdot\text{cm}^{-2}$ . However, in sharp contrast, the Stage 1 film established on the wet ground smoother N80 surface is persistent during Stage 2 from 1 to 4 h.

The results shown in Fig. 9 indicate that surface roughness is a key parameter determining the efficiency of staged ACI treatments. For HS80™, 10 min pre-corrosion increases surface roughness from  $S_a 0.11 \pm 0.01 \mu\text{m}$  to  $1.23 \pm 0.22 \mu\text{m}$  (Table 1). This increase in surface roughness (and the corresponding increase in surface area) results in a slower rate of formation of the Stage 1 film and a subtle decrease in film persistency during Stage 2. Previous publications have reported a similar effect of surface roughness on ACI film formation kinetics [27] and corrosion in CO<sub>2</sub> environments [25,26]. However, concomitant with the observed increase in HS80™ surface roughness after 10 min pre-corrosion is a significant increase in the ratio of cementite to ferrite on the surface. This change in surface composition is also likely to influence the rate of inhibitor adsorption, the distribution of inhibitor on the surface and the rate of film polymerisation and maturation. Thus, both surface roughness and surface composition influence the efficiency of staged ACI treatments.

For N80, 10 min pre-corrosion increases surface roughness from  $S_a 0.11 \pm 0.01 \mu\text{m}$  to  $3.04 \pm 0.67 \mu\text{m}$  (Table 1). It is likely that this larger change in surface roughness (relative to HS80™) was accompanied by a significant change in surface composition. For N80, the 10 min pre-corrosion step resulted in a strong decrease in the efficiency of subsequent staged ACI treatments (Fig. 9(b)). In view of this observation, additional staged ACI experiments were performed on pre-corroded N80 using an increased ACI concentration (0.5 wt%) in Stage 1 and the same ACI concentration (0.01 wt%) in Stage 2. As shown in Fig. 10, this increase in the Stage 1 ACI concentration from 0.2 to 0.5 wt% had a strong beneficial effect on the efficiency of the staged ACI treatment. A slight increase in  $1/R_p$  was observed in the time period 3.5–4 h but an acceptable level of persistency was maintained throughout the 4 h period.

These results demonstrate the importance of optimising ACI concentrations, both in Stage 1 and Stage 2, in order to design efficient staged ACI treatments. Such optimization requires careful consideration of a number of variables including steel type and properties, surface



**Fig. 10.** Comparison of two different Stage 1 ACI concentrations implemented after a 10 min pre-corrosion period and followed by a lower constant ACI concentration of 0.01 wt% for 3 h (Stage 2), plotted as  $1/R_p$  versus time, obtained from in situ LPR measurements for N80 carbon steel coupons, mounted in a once-through flow cell, in 4 M HCl flow at a temperature of 80 °C and a flow rate of 5 mL/min.

roughness and surface composition. In the field application, additional variables need to be considered in designing efficient staged ACI treatments which are significantly more cost-effective than current field practices employing a fixed concentration of ACI in all the acid injected. Notably, the design of staged ACI treatments for field implementation needs to consider and optimise the duration (and volume) of Stages 1 and 2 in order to ensure that a high quality persistent film forms on all the exposed surfaces of the coiled tubing and wellbore casing. It is essential that this film and its associated inhibition efficiency be maintained until the end of acid injection.

#### 4. Conclusions

A customised once-through flow cell has been used to evaluate the performance of a new staged acid corrosion inhibition concept [12] designed to minimise the corrosion of coiled tubing and wellbore casing materials during matrix acidizing operations. Compared to conventional electrochemical and weight loss testing methods, the once-through flow cell enables a continuous flow and fresh supply of HCl and ACI throughout the exposure period. In addition, the flow cell set-up enables the ACI concentration to be changed seamlessly without interrupting the flow and without exposing the steel coupon to air and/or any potential contaminants. The flow cell evaluation of the performance of staged ACI treatments in 4 M HCl at 80 °C led to the following conclusions:

- Having established a high quality inhibitor film by pumping 4 M HCl containing a higher ACI concentration during the test period 0–1 h (Stage 1, 0.2 wt% ACI concentration), the ACI concentration in the acid can be significantly reduced during the period 1–4 h (Stage 2, 0.01 wt% ACI concentration) whilst still maintaining an acceptably low corrosion rates of HS80™ and N80 carbon steels. This behaviour relies on the use of polymerisable ACI chemistry to form a persistent inhibitor film during Stage 1.
- A Stage 2 ACI concentration of 0.005 wt% was not sufficient to protect the N80 carbon steel, demonstrating that a critical ACI concentration in Stage 2 is required to maintain the persistence of the Stage 1 film and that this critical concentration depends on the carbon steel type and properties.

- The effect of a pre-corrosion step on the performance of staged ACI treatments was evaluated. For HS80™, 10 min pre-corrosion in uninhibited 4 M HCl increased surface roughness from  $S_a = 0.11 \pm 0.01 \mu\text{m}$  (for a wet ground surface) to  $S_a = 1.23 \pm 0.22 \mu\text{m}$ . This increase in surface roughness and the corresponding increase in surface area resulted in a slower rate of formation of the Stage 1 film but only a subtle decrease in film persistency during Stage 2. For N80, 10 min pre-corrosion in uninhibited 4 M HCl increased surface roughness from  $S_a = 0.11 \pm 0.01 \mu\text{m}$  to  $S_a = 3.04 \pm 0.67 \mu\text{m}$ . This larger increase in surface roughness resulted in a strong decrease in the efficiency of subsequent staged ACI treatments. In view of this result, additional staged ACI treatments were performed on pre-corroded N80; an increase in the Stage 1 ACI concentration from 0.2 wt% to 0.5 wt% had a strong beneficial effect resulting in an acceptable level of film persistency during the test period 1–4 h.
- In the field application, additional variables need to be considered in designing efficient staged ACI treatments. Notably, the design needs to consider and optimize the duration (and volume) of Stages 1 and 2 to ensure that a high quality persistent film forms on all the exposed coiled tubing and wellbore casing surfaces and that this film and its associated inhibition efficiency is maintained until the end of acid injection.

#### CRediT authorship contribution statement

**Joshua Owen:** Conceptualisation, Methodology, Investigation, Formal analysis, Writing – original draft. **Anne Neville:** Methodology, Supervision. **Evgeny Barmatov:** Supervision, Methodology, Conceptualisation, Resources, Writing – review & editing. **Trevor Hughes:** Supervision, Methodology, Conceptualisation, Resources, Writing – review & editing. **Richard Barker:** Supervision, Conceptualisation, Methodology, Writing – review & editing, Funding acquisition.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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