

Iron sulphide formation and interaction with corrosion inhibitor in H₂S-containing environments

Frederick Pessu¹, Richard Barker¹, Fakuen Chang², Tao Chen² and Anne Neville¹

¹ Institute of Functional Surfaces (iFS), School of Mechanical Engineering, University of Leeds. Leeds. United Kingdom. LS2 9JT.

² Exploration and Petroleum Engineering Advanced Research Centre (EXPEC ARC) Saudi Aramco

Corresponding author: Dr Frederick Pessu

School of Mechanical Engineering, University of Leeds, Woodhouse lane, Leeds, United Kingdom. LS2 9JT.

Email address: f.o.pessu@leeds.ac.uk.

ABSTRACT

Corrosion of carbon steel in H₂S-containing environments poses serious challenges to operations in oilfield and geothermal applications. Carbon steels exposed to H₂S-containing environments are often susceptible to pitting and uniform corrosion, and linked to the properties of iron sulphide (FeS) layers that forms at the corroding interface. This paper investigates the corrosion characteristics of carbon steel in H₂S-containing environments focussing on the early stage kinetics of FeS formation and its interaction with corrosion inhibitors (CI). Experiments were conducted in 3.5 and 5.8 wt% NaCl solution at 80°C in 10% H₂S-90% CO₂-containing environments. *In-situ* electrochemical responses were measured using the linear polarisation resistance (LPR) technique. This was combined with post-experiment surface analysis; scanning electron microscopy (SEM) and X-ray diffraction (XRD) to investigate the nature and morphology of formed FeS. 3D surface profilometry was used to investigate the pitting corrosion characteristics of carbon steel caused by FeS interaction with CI. The results show a fast kinetics of FeS formation by direct reduction of H₂S_(aq) with a distinct and easily identifiable morphology, and evidence of minimum level of ferrite dissolution. The early stages of FeS formation and its interaction with CI have a strong influence on the overall corrosion characteristics of carbon steel. A dose of 30 ppm of a commercial corrosion inhibitor (CI); salts of nitrogenous molecules with a fatty acid group, at the corrosion interface induced a competition for surface absorption between CI and emerging FeS. Over the 48 h duration of this test, the FeS formation process was delayed and the mechanisms of its formation quickly became the main driver of pitting corrosion. The amount of CI dosed in this study was not able to prevent FeS-induced pitting corrosion attack on the surface.

Keywords: Iron sulphide, carbon steel, pitting corrosion, uniform corrosion and corrosion inhibitor

1. Introduction

The complex electrochemical processes that precedes and directs iron sulphide (FeS) corrosion product formation and evolution^[1-3], significantly influence H₂S-induced corrosion of carbon steel. Uniform and pitting corrosion of carbon steel materials used in H₂S-containing environments is related to a combination of complex electrochemical processes occurring at the corrosion interface^[3, 4]. H₂S-induced corrosion and FeS formation is believed to be driven by two reaction mechanisms; direct reduction of dissolved H₂S (H₂S_(aq)) and/or bisulphide ions (HS_(aq)⁻) at the material interface and aqueous corrosion reactions between ferrous species (Fe²⁺) from the corroding surface and dissolved ionic species^[1, 5-7]. The direct reduction reaction mechanism often leads to the formation of mackinawite as a thin chemisorbed corrosion product layer on the surface, while the latter drives the precipitation of crystalline FeS on the surface after saturation levels have been attained^[3, 8]. The true kinetics of FeS formation by direct reduction has not been fully investigated. The nature of chemisorbed FeS is still subject to debate.

Several researchers^[6, 8, 9] have consistently shown that uniform corrosion rate can become lower as quickly as mackinawite is initially formed. This was observed in short duration (typically 2-3 hrs) experiments at low concentrations of H₂S gas (100-500 ppm) at 30°C^[8], and in ~908 ppm of H₂S gas saturated solution at 22°C^[9]. In these studies, the aqueous corrosion reactions pathways are not fully accounted for in the corrosion rate measurements and hence limits the value in their conclusions. In the model developed by Zheng et al.^[8], for predicting uniform corrosion rate of carbon steel in H₂S-CO₂ corrosion environments, the earliest kinetics of FeS formation was assumed to be non-existent within 2 hrs of the experiment. While this may be true from a thermodynamics standpoint, the true kinetics of FeS formation still remain unclear; particularly in the early

1 stages, thus making it difficult to model. Dissolution reactions can either occur between the initially formed FeS
2 and other intermediate specie at the corroding interface, and the dissolved H₂S species^[10, 11] and/or ferrite ions
3 from corroding surface and dissolved H₂S species. The latter often leads to deposition of different morphology
4 of FeS; usually fluffy in nature, as an outer layer^[3]. The transition between both reaction mechanisms is could
5 cause the instability of mackinawite layers, leading to its breakdown and loss of protective properties^[4, 11].
6 Mackinawite is also known to easily transition to other forms of FeS such as pyrrhotite, pyrite, gregite, etc.,
7 depending on other process parameters such as pH, temperature, H₂S partial pressure and time, especially for
8 a closed system^[4]. Therefore, the protective and/or semi-protective properties of FeS (commonly mackinawite)
9 could be influenced by such transitions to other forms of FeS. The apparent complexities associated with the
10 mechanisms and progression of H₂S-induced corrosion processes is therefore important for the evolution of
11 uniform and pitting corrosion, especially as mackinawite and other forms of FeS could easily act as cathodes^[10].

12 The efficiencies of several mixed-type and anodic-type corrosion inhibitors against corrosion of carbon steel in
13 mixed H₂S-CO₂ environment were recently investigated by Zhang et al^[12]. The results showed improvement in
14 inhibitor efficiencies as a result of the fast adsorption process of cationic compounds promoted by dissolved HS⁻
15 . This observation, the fast kinetics of FeS formation and the potential for FeS to metamorphose into other forms
16 of FeS could also influence how a commercially available corrosion inhibitor (CI) will interact across the corrosion
17 interface to mitigate both uniform and pitting corrosion components of material degradation. This aspect of FeS
18 – CI interaction during H₂S corrosion is still not clearly understood and needs to be investigated.

19 This research investigates the kinetics of FeS formation and interaction with a single dose of corrosion inhibitor
20 (CI) (salts of nitrogenous molecules with a fatty acid group) in H₂S-containing environments. The uniform and
21 pitting corrosion behaviour of carbon steel were also investigated in this study. *In situ* electrochemical responses
22 are correlated with FeS formation and interaction with CI. The experiment methodologies also include the
23 correlation of FeS formation and FeS-CI interaction at corrosion interface with corrosion damage mechanisms;
24 uniform and pitting corrosion mechanism. These results will help to improve on current understanding of the
25 process and consequences of FeS formation and interaction with CI at a corroding interface.

26 **2. Materials and Experimental Procedure**

27 The work presented in this paper is based on two separate experiments, both conducted at 80°C:

- 28 1. Investigation of the initial stages of H₂S corrosion/FeS formation kinetics over 4.5 h. This was conducted
29 initially in 100% CO₂ gas for 2 hrs and then 10% H₂S – Bal. CO₂ (written as 10% H₂S-CO₂ for the rest of the
30 paper) for another 2.5hrs at 80°C. This experiment was conducted in a 3.5 wt% NaCl and referenced to
31 experiments in 100 % CO₂ and 10% H₂S-CO₂ separately. The focus of this experiment is to access how quickly
32 FeS forms and influences the uniform corrosion behaviour of carbon steel in H₂S-containing environments.
33
- 34 2. Investigation of FeS – CI interaction for 48 h at 80°C and its effect on the corrosion damage mechanisms of
35 carbon steel in 10% H₂S-CO₂-containing environment. In this experiment, *in-situ* electrochemical
36 measurement is combined with post experiment analysis of FeS corrosion products formed and
37 characterisation of pitting corrosion damage. This experiment was conducted in a 1M NaCl solution.

38 Although the brine NaCl concentration in both experiment 1 and 2 are different, it is important to note that
39 experiment 1 and 2 have not been conducted for direct comparison of research outcomes, but to correlate the
40 underpinning mechanisms of FeS formation kinetics and influence on its interaction with CI.

41 **2.1 General information on corrosion inhibitor**

42 The corrosion inhibitor used in this study is based on the products of reaction of an ethoxylated amine and a
43 dicarboxylic ester^[13] and is generally described as salts of nitrogenous bases^[14]. This class of CI was developed
44 mainly for corrosion environment dominated by CO₂ corrosion mechanisms where a significant amount of
45 ferrous ions is required to be available at the corrosion interface for effective corrosion inhibition^[13]. Corrosion
46 inhibitor film of iron carboxylate is expected to form through the reaction of the ferrous ions with the
47 inhibitor^[13]. This preferred method of CI activity makes it a suitable candidate for investigating its interaction
48 with FeS formation. A fixed amount (30 ppm) of CI was used in this study. Details of the experimental matrix in
49 this study is provided in
50

1 Table 1.

2

3 **Table 1: Experimental conditions for investigating corrosion of carbon steel in H₂S-containing corrosion environments**

S/N	Scope	Temperature (°C)	NaCl Brine (wt%)	Gas system	Duration (hrs)	pH at start of test	pH at end of test
Exp. 1	FeS Formation Kinetics	80	3.5	100% CO ₂	7	3.8±0.2	4.7±0.1
				10% H ₂ S-CO ₂	7	4.30±0.1	4.5±0.3
				100% CO ₂ (2 hrs), then 10% H ₂ S-CO ₂ (2.5 hrs)	4.5	3.8±0.2	4.20±0.2
Exp. 2	FeS-Cl interaction	80	5.8	10% H ₂ S-CO ₂	48	N/A	N/A

4

5 **2.2 Materials**

6 X65 carbon steel samples were used as the working electrodes as part of a three-electrode cell in each
7 experiment. The steel is composed of a ferritic/pearlitic microstructure. The nominal composition of X65 steel
8 is provided in Table 2.

9

Table 2: X65 carbon steel composition (wt%)

C	Si	P	S	Mo	Mn	Ni	Nb	V	Fe
0.15	0.22	0.023	0.002	0.17	1.42	0.09	0.05	0.06	97.81

10 Each carbon steel test specimen used was sectioned into 10 mm x 10 mm x 5 mm sections. Wires were soldered
11 to the back of each test specimen and then embedded in a non-conducting resin. In each of the test setups, a
12 total of 5 samples (equivalent to a total of 5 cm² of exposed surface area) per litre of test solution is maintained
13 in this study. Details of test setup are described in the next section. Prior to mounting the test samples into the
14 test vessels, the samples were wet-ground up to 1200 silicon carbide grit paper, degreased with acetone, rinsed
15 with distilled water and dried with compressed air before being assembled within the test setup.

16 **2.3 Experiment setup**

17 All experiments described in this section were performed in a 1 litre vessel at atmospheric pressure and 80°C,
18 and repeated for a minimum of 3 times. The pH of each test solution was measured at the start of each tests for
19 each condition after saturation with H₂S-CO₂ gas mixture.

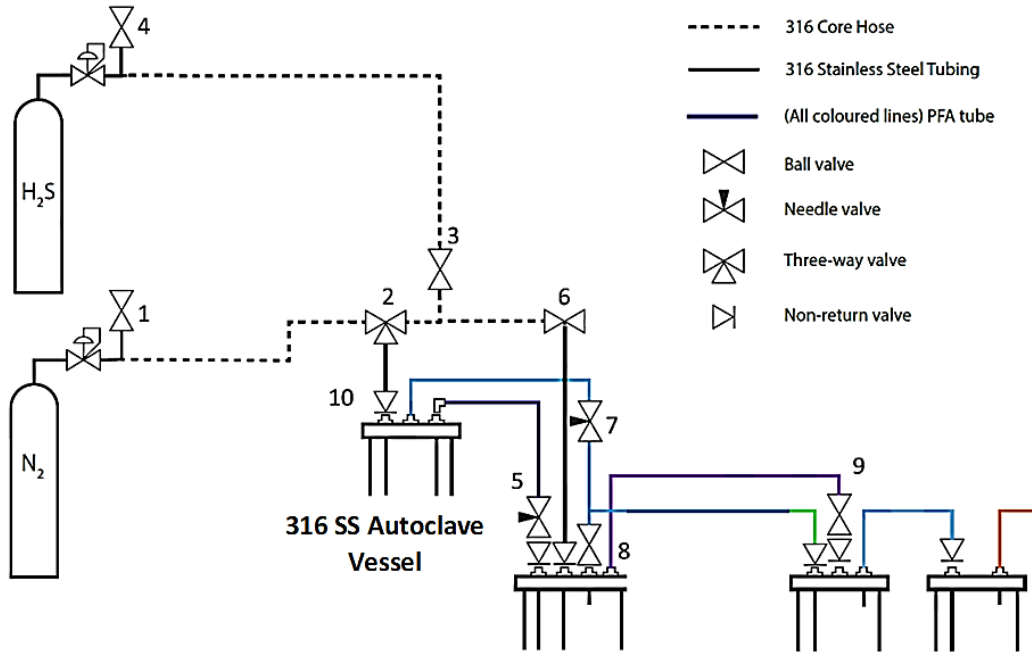
20 **2.3.1 Experiment – 1**

21 The test solutions were deaerated and saturated with CO₂ for a minimum of 12 h and heated up to 60°C. 5
22 samples were assembled in a 3 electrode cell set up each of which has an exposed surface area equal to 1 cm².
23 The test vessels are leaked-tested with 100% CO₂ before heating up to 80°C. Electrochemical measurements are
24 implemented for 2 h before a premixed 10% H₂S-CO₂ gas is introduced into the test vessels for 2.5 h. This
25 approach was implemented to monitor the electrochemical responses associated with early stages of H₂S
26 corrosion and FeS formation. In the control experiments, CO₂ was also used to deaerate the solution for up to
27 12 h for test in 100% CO₂ for 7 h, while N₂ was used to deaerate the solution for up to 12 hrs for test in 10% H₂S-
28 CO₂ for 7 hrs. The fluctuations in corrosion potential to either more anodic or cathodic values was used to
29 monitor the moment at which H₂S gas being introduced into the test vessel comes in contact with the samples
30 already immersed in a CO₂ or N₂ saturated solution for the first time. The pH was measured at the start and end
31 of each experiments under experiment – 1 as shown in

32 Table 1.

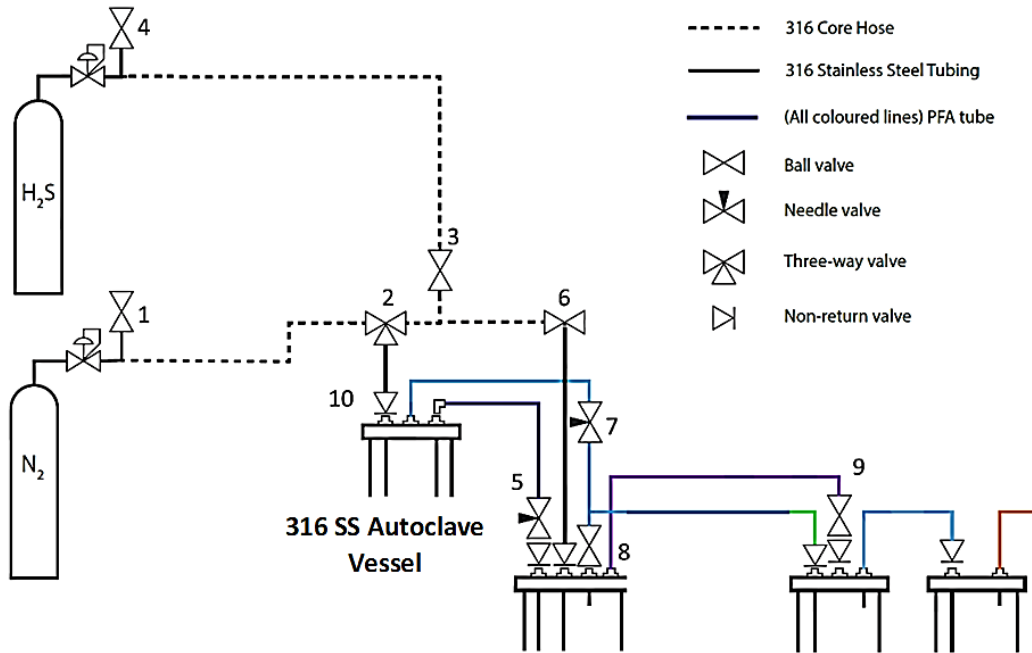
1 **2.3.2 Experiment – 2**

2 This experiment was conducted in a 1 litre autoclave shown in



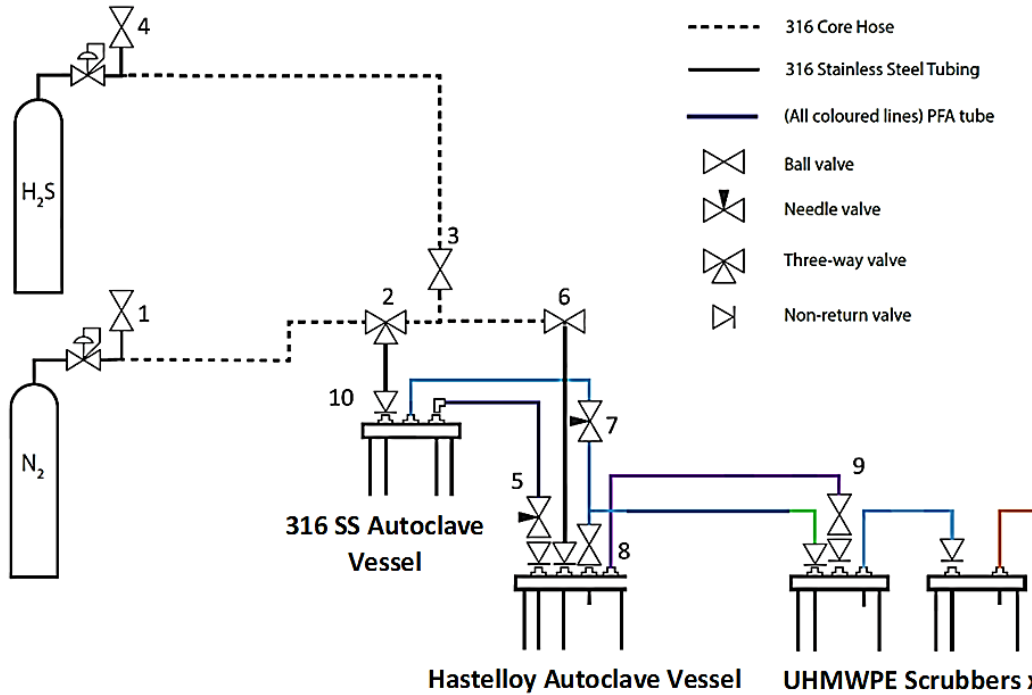
3 **Hastelloy Autoclave Vessel UHMWPE Scrubbers x 2**

4 Figure 1. The test solution was deaerated for a minimum of 12 h using N₂ in a 316 SS vessel before it is carefully
 5 introduced into an already deaerated 1 litre capacity test vessel containing 5 samples (each with a surface area
 6 of 1 cm²) safely embedded in resin and with wires attached to 3 of the 5 samples for electrochemical
 7 measurements. 10 % H₂S-CO₂ gas mixture is introduced into the test solution using valves 4, 3 and 6 (see



8 **Hastelloy Autoclave Vessel UHMWPE Scrubbers x 2**

1 Figure 1) while valves 1 and 2 (in same



2
3 Figure 1) are shut after removal of oxygen. Prior to the transfer of the deaerated solution into the test vessel,
4 the solution was heated to $80^\circ C$ in the 316 SS vessel. The exit line of the test vessel was channelled into a 2L 316
5 SS autoclaves with a PTFE liner containing 10 wt% NaOH and three other polymer vessels containing Jasorb G-
6 15 scrubbing pellets. The corrosion potential is used to monitor the moment at which H_2S gas being introduced
7 into the test vessel comes in contact with the samples already immersed in a N_2 saturated solution for the first
8 time. Corrosion rate measurements start once the H_2S gas supply was turned on.

9
10 In experiment – 2, tests with and without Cl was performed. Test without Cl was used as a reference The Cl was
11 introduced into the deaerated solution before being transferred into the test autoclave. This means that the Cl
12 is already establishing contact with the material surface before the premixed 10% H_2S-CO_2 gas is introduced. The
13 purpose of this methodology is to investigate the potential competition for the corrosion interface between the
14 Cl and FeS and its impact. This is tracked via *in-situ* measurements of electrochemical response over 48 h in
15 combination with post-experiment surface analysis after 48 h. The blank test and test with 30 ppm of Cl were
16 repeated three or more times along with *in-situ* electrochemical measurements. Only two repeats were used
17 for post the experiment surface analysis.

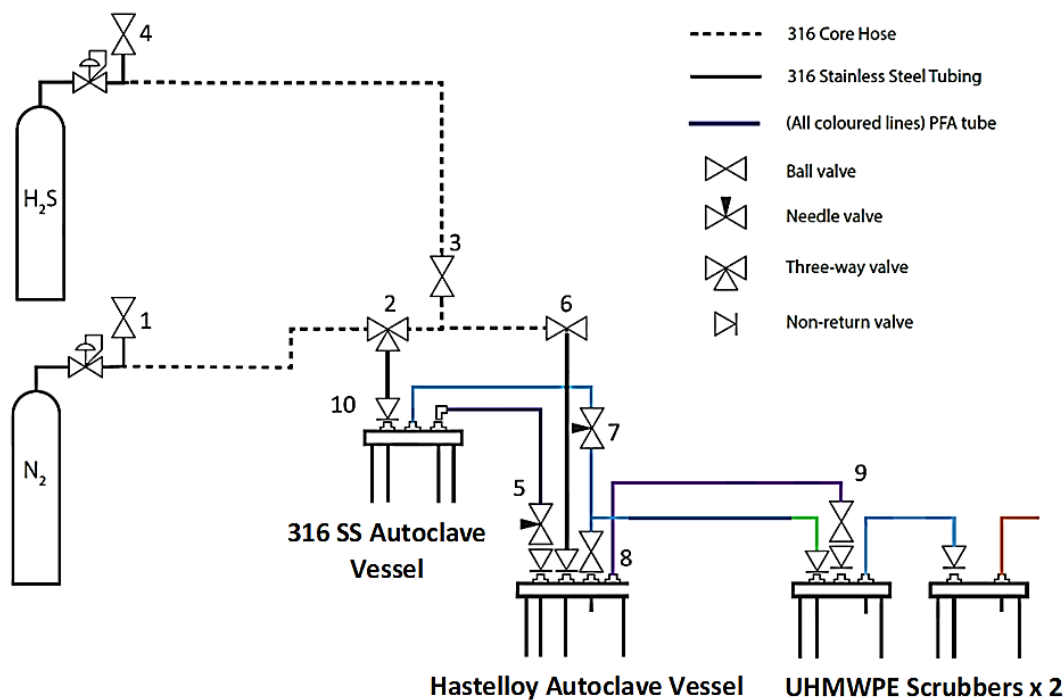


Figure 1: Schematic illustration of H₂S experimental setup used for experiment -2.

2.3.3 Post – experiment sample handling and preparation

In both experiments – 1 and 2, samples were removed for corrosion product characterisation and identification using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Pitting corrosion assessment was carried out only for samples from Experiment – 2. The samples used for pitting corrosion assessment were cleaned with Clarke’s solution to remove all traces of corrosion product before using surface profilometry to determine the extent of pitting corrosion on the steel surface. Clarke’s solution used consist of 20g of antimony trioxide, 50g of stannous chloride and 1000ml of 37% hydrochloric acid, and prepared in accordance with ASTM¹ Standard G1-03. The sample surface were wiped with a cotton pad soaked in Clarke’s solution, washed, air dried, and carefully stored in a de-aerated chamber to avoid oxidation prior to surface analysis. Pitting corrosion analysis was carried out using the NPFLEX 3D² interferometer.

2.3.4 In-situ electrochemical measurements

Electrochemical measurements were conducted on one sample per test vessel in all experiments in a three-electrode cell setup. The three-electrode cell comprises of an Ag/AgCl reference electrode and a platinum counter electrode. Electrochemical measurements were made each time the tests were repeated. All electrochemical measurements were conducted using a Gill ACM potentiostat. Linear polarisation resistance (LPR) measurements were performed by polarising each sample every 15 minutes \pm 15 mV below and above the open circuit potential (OCP) at a scan rate of 0.25 mV/s to determine the polarisation resistance (R_p). Tafel polarisation measurements were made on test samples from Experiment 1 at the end of each test; after 4.5 and 7 h. Anodic and cathodic sweeps of the Tafel polarisation curves were performed on two different samples in the same test cell, and for conditions in Experiment – 1. Tafel polarisation measurements were used to gain fundamental insights into the kinetics of FeS formation and validate the trend in corrosion rate measurements from the LPR method. Anodic and cathodic sweeps were performed up to \pm 250 mV about the OCP at a scan rate of 0.25 mV/s. Tafel constants (β_a and β_c) of 120 mV/decade were used in conjunction with R_p and Faraday’s Law to determine the *in situ* corrosion rates as a function of time for all experiments in this study.

¹ Trade name

² Trade name

1 2.3.5 Corrosion product identification

2 XRD patterns were collected using a Bruker D8³ equipped with a LynxEye⁴ detector, using a 90 position auto
3 sampler and employing Cu K α radiation with an active area of 1cm² programmable divergence slits. Scans were
4 performed over a range 2 θ = 10 to 70° at a step size of 0.033 per second and a total scan time of ~ 50 minutes.
5 The results were analyzed using X'Pert⁵ HighScore software and compared with individual crystal standards from
6 in-house database.

7 2.3.6 Characterisation of pitting corrosion damage

8 Surface profilometry was deployed in this study to assess pitting corrosion attack for Experiment – 2. Pit depth
9 measurements were conducted in alignment with ASTM G46-94⁶[15]. A 3D interferometer was used for obtaining
10 the discrete geometry of pits on over 81% of the steel surface (the remaining 19% represents the edges of the
11 sample). Pits were identified based on carefully chosen thresholds. The thresholds were chosen with reference
12 to the surface roughness of uniformly corroded areas surrounding the pits. This enabled pits with distinct pit
13 diameters, depths, shapes, and areas to be identified and quantified. ASTM G46-94⁶[15] stipulates that an average
14 of the 10 deepest pits and size of deepest pit (relative pit depth measurement after removal of corrosion
15 products) should be used for characterising pitting corrosion damage.

16 3. Results and Discussion

17 3.1 H₂S – corrosion; fast iron sulphide formation

18 Figure 2 to Figure 5 present the results from Experiment – 1 investigating the fast kinetics of FeS formation and
19 its effect on the corrosion interface. The results discussed in this section is referenced to 100% CO₂ and 10% H₂S
20 – CO₂ – containing corrosion environments for the duration of experiments. This experiment was designed to
21 help understand and elucidate the early stage kinetics of H₂S corrosion/FeS formation and the characteristic
22 behaviour of the corrosion interface.

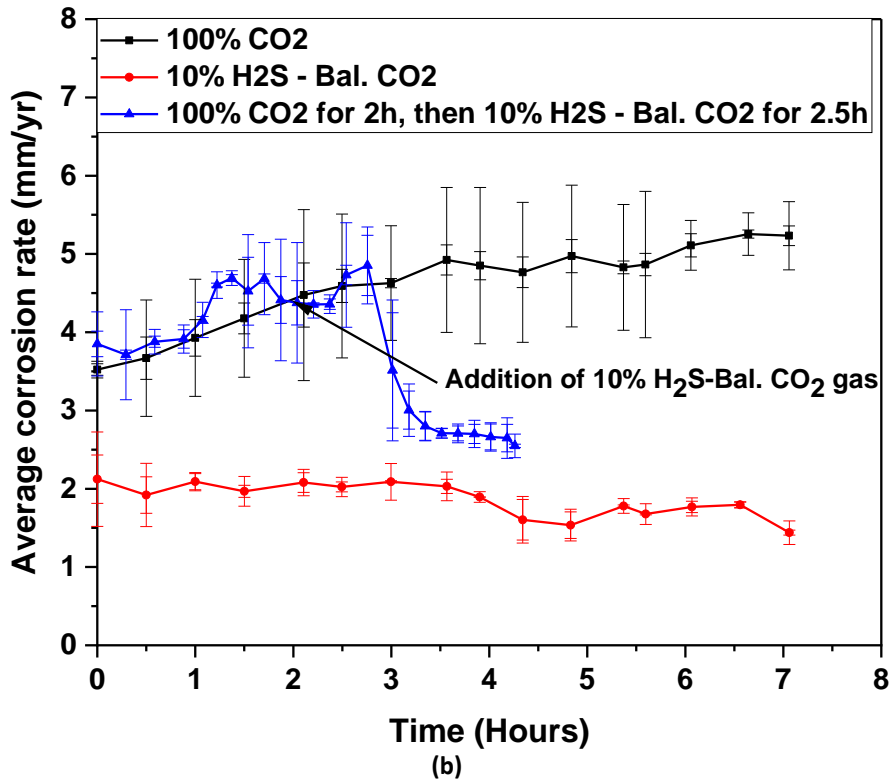
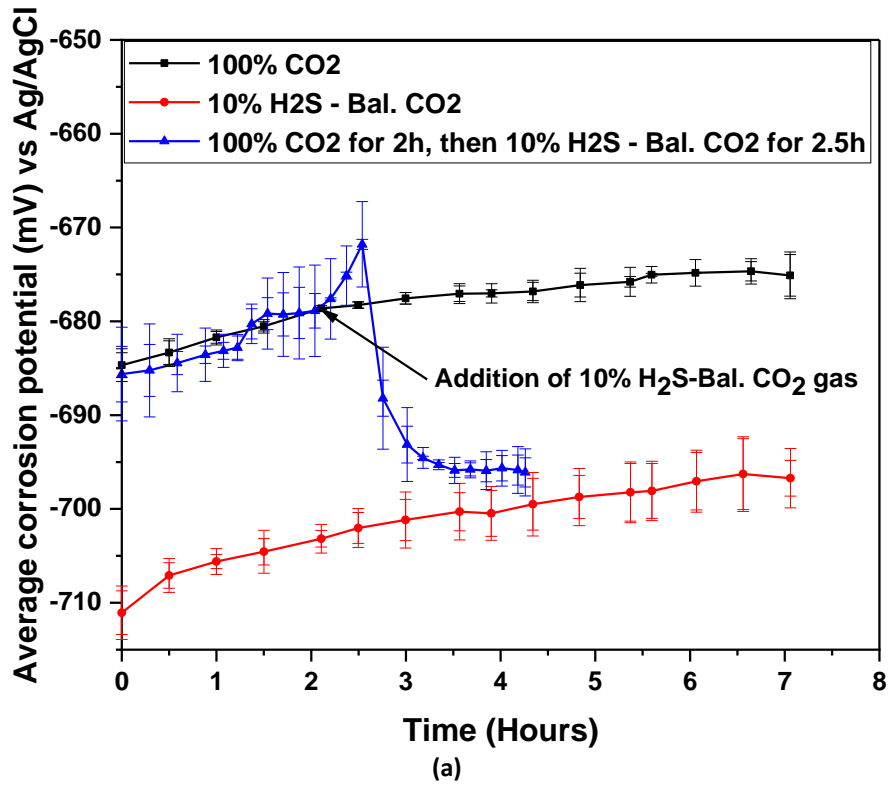
23 Referring to Figure 2(a) and (b) for corrosion potential and corrosion rate respectively, there is a rapid change
24 in corrosion characteristics with changes in the gas phase composition from 100% CO₂ to 10% H₂S – CO₂ gas
25 mixtures in real time over 4.5 h. The changes in corrosion potential (Figure 2(a)) in 100% CO₂ saturated system
26 over 2 h (before the introduction of 10% H₂S – CO₂ gas mixtures) is similar to the changes within the first 2 h of
27 test in 100% CO₂ system (from 0 – 7 hrs). The corrosion potential starts at ~ -686 and -685 mV respectively and
28 gradually increases in the positive direction to ~ - 680 mV after 2 h for both systems. This stage of a typical
29 corrosion process in 100% CO₂ corrosion systems is usually characterised by the dissolution of ferrite and the
30 establishment of empty cementite layers and results in an increase in corrosion potential^[16]. It is well
31 documented that the in 100% CO₂ saturated corrosion environments, ferrite dissolution process at the corroding
32 interface is usually fully established prior to the formation of FeCO₃ corrosion products^[16, 17]. This usually results
33 in the establishment of corroding surfaces with clearly defined anodic and cathodic microsites that influence the
34 formation of FeCO₃ corrosion products^[18, 19]. Figure 2(a) and (b) shows that the introduction of 10% H₂S – CO₂
35 gas mixtures after 2 h in 100% CO₂ corrosion systems completely transformed the mechanism of interaction
36 between an already electrochemically charged corrosion interface and dissolved sulphide species. It can be
37 observed that as soon as the 10% H₂S – CO₂ gas mixtures is introduced into the corrosion environment, the
38 corrosion rate starts dropping within 0.5 h and decreases from ~4.5 mm/yr to ~2.5 mm/yr within the last 2 h of
39 the experiment. This also correlates with the time at which the corrosion potential starts dropping towards more
40 negative potentials (from ~-677 mV to ~-700 mV) over the same time interval. The observed changes in corrosion
41 potential and reduction in corrosion rate confirm an increasing electrochemical interaction between carbon
42 steel and sulphide species^[20]. The corrosion rate after 4.5 h (~2.5 mm/yr) closely approaches the average
43 corrosion rate of tests in 10% H₂S – CO₂ gas mixtures for 7 hrs, after 4.5 h (~2 mm/yr) as shown in Figure 2(b). The
44 observed rapid reduction in corrosion potential and corrosion rate in test with 10% H₂S – CO₂ gas after 2 hrs in
45 100% CO₂ is consistent with results showing a reduction of corrosion rate within 5 minutes in H₂S environment
46 by Ma *et al.* ^[9] and potentiodynamic polarisation results published by Choi *et al.* ^[21].

³ Trade name

⁴ Trade name

⁵ Trade name

⁶ Trade name



1 Figure 2: Plot of (a) corrosion potential and (b) corrosion rate for experiments in 3.5 wt% NaCl solution saturated with
 2 100% CO₂, 10% H₂S – CO₂ over 7 h and test in 100% CO₂ for 2 h and then in 10% H₂S – CO₂ for another 2.5 h at 80°C.

3 A combination of “direct reduction” of sulphide species at the corrosion interface^[1, 22] and the very low solubility
 4 limit for FeS formation when compared to that of FeCO₃ formation^[23, 24] is known to favour the kinetics of FeS
 5 formation. The evidence of changes in the redox activities with introduction of 10% H₂S – CO₂ gas mixtures is
 6 provided in the potentiodynamic polarisation curves for the three test systems in Figure 3. The cathodic reaction
 7 curves are different in shapes to show the influence of 10% H₂S – CO₂ gas mixtures on the cathodic reaction
 8 mechanisms at the corrosion interface. The shape of the cathodic reaction line for test initially in 100% CO₂ for

1 2 h and then 10% H₂S – CO₂ gas mixtures for 2.5 h is distinct from that of test in 10% H₂S – CO₂ gas mixtures for
2 7 h. This can be described as the “double waves” profile that describes the corrosion mechanisms influenced by
3 both direct reduction of H₂S at the corrosion interface and H⁺ reduction at more negative cathodic potential [8].
4 The “first wave” occurs at more positive cathodic potential (between OCP and ~ -850 mV); representing direct
5 reduction of H₂S, while the “second wave” starts at a more negative cathodic potential (from ~ -850 mV) to
6 represent the H⁺ reduction line.

7 In 100% CO₂ systems after 7 h, the cathodic reaction is controlled by the reduction of H⁺ provided by carbonic
8 acid. Similarly, in 10% H₂S – CO₂ gas systems for 7 h, the cathodic reaction is mainly by the H⁺ reduction
9 particularly at lower pH^[25]. This is why the shape of the cathodic reaction curves are similar for both gas systems
10 after 7 h. The only difference is the suppression of the corrosion current in the 10% H₂S – CO₂ gas systems after
11 7 h. This is can be related to the fact that FeS has already been formed by direct reduction reaction at earlier
12 times than 7 h during the experiment and as such direct reduction reaction process is no longer dominant. The
13 dominance of H⁺ reduction at this stage of the corrosion process is evident in SEM images shown in Figure 4(a)
14 and (b) for tests in 100% CO₂ and 10% H₂S – CO₂ gas systems respectively for 7 h. In Figure 4(a), there is evidence
15 of the evolution of the Fe₃C layer left behind because of ferrite dissolution. In Figure 4(b), Fe₃C is now an inner
16 layer; underneath sparse deposits of FeS layer. This observation shows the competition between ferrite
17 dissolution and FeS formation that has been discussed in a previous publication^[2] as an indication of the synergy
18 of CO₂ and H₂S driven corrosion mechanisms in mixed H₂S-CO₂ environments. In this case, the direct reduction
19 of H₂S is likely to have let to the initial formation of FeS. Over the 7 h test duration, the corrosion process became
20 increasingly controlled by H⁺ reduction as direct reduction reaction mechanism is suppressed^[25]. Thus, as shown
21 in Figure 3, the shape of the cathodic reaction curve for test in 10% H₂S – CO₂ gas systems is of similar shape to
22 that of test in 100 % CO₂ gas systems after 7 h to confirm that both cathodic reaction is strongly influenced by
23 H⁺ reduction.

24 Referring to Figure 3 for test initially in 100% CO₂ for 2 h followed by 10% H₂S – CO₂ gas for 2.5 h, it is evident
25 that the level of suppression of corrosion current is closely approaching that of the test environment with 10%
26 H₂S – CO₂ gas after 7 h. Referring to the cathodic reaction line in Figure 3 and the SEM image in Figure 4(c), there
27 is evidence that the earliest kinetics of FeS formation from tests initially in 100% CO₂ for 2 h and then 10% H₂S –
28 CO₂ gas for 2.5 h is controlled by direct reduction of H₂S at the corrosion surface and not the dissolution of
29 ferrous ions. The cathodic reaction shows a prominent “first wave” at more positive cathodic potential (between
30 OCP and ~ -850 mV) for direct reduction of H₂S^[8] and a less prominent “second wave” at more negative cathodic
31 potential (from ~ -850mV) for H⁺ reduction. The SEM image in Figure 4(c) shows the presence of FeS rich areas
32 adjacent to areas with little or no FeS but also with minimum revelation of empty Fe₃C. The distribution of FeS
33 across the carbon steel surface can be observed to follow a similar pattern to the distribution of microstructural
34 phases within the steel surface (Figure 4(c)) when compared to the distribution of FeS in Figure 4(b) for test in
35 10 % H₂S – CO₂ gas mixture after 7 h. This is an indication of minimum ferrite dissolution when compared with
36 the level of exposure of Fe₃C in both 100 % CO₂ and 10% H₂S – CO₂ systems after 7 h. Therefore, the shape of
37 the cathodic reaction line in Figure 3 represents redox activity mainly controlled by direct reduction of H₂S at
38 the steel surface and the corresponding FeS formed is not driven by the saturation of the corrosion interface
39 with ferrous ion (Fe²⁺) and dissolved sulphide species.

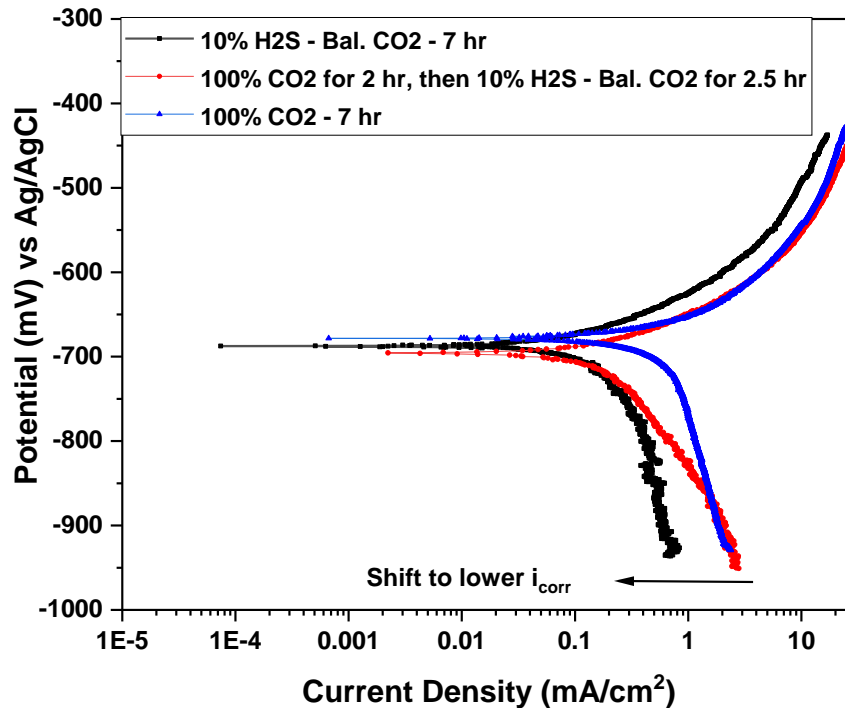
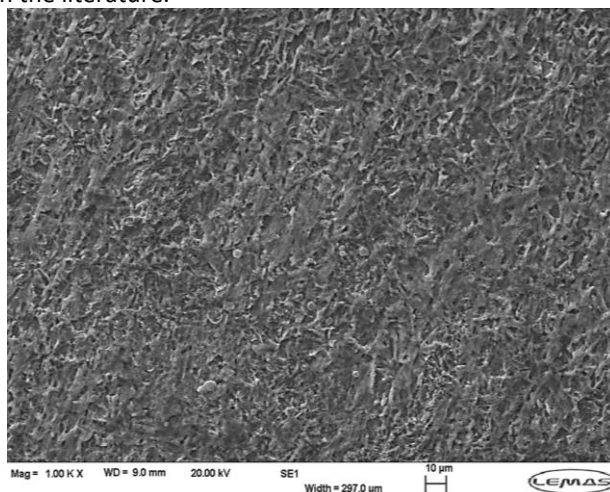
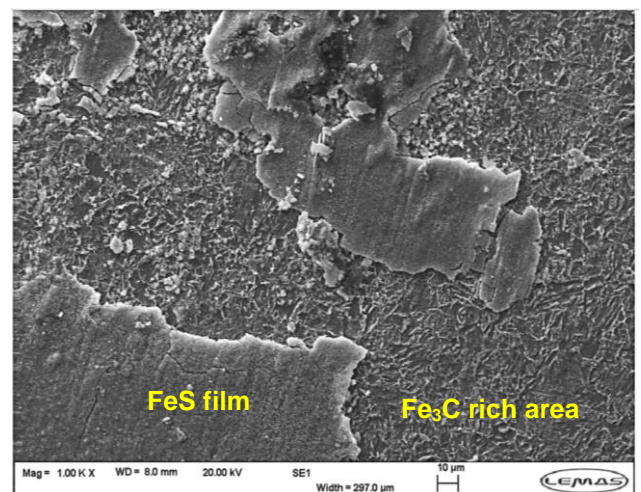


Figure 3: Potentiodynamic curves for experiment in 100% CO₂ for 7 h, 100% CO₂ for 2h and then with 10% H₂S – CO₂ for another 2.5 h, and 10% H₂S – CO₂ for 7 h.

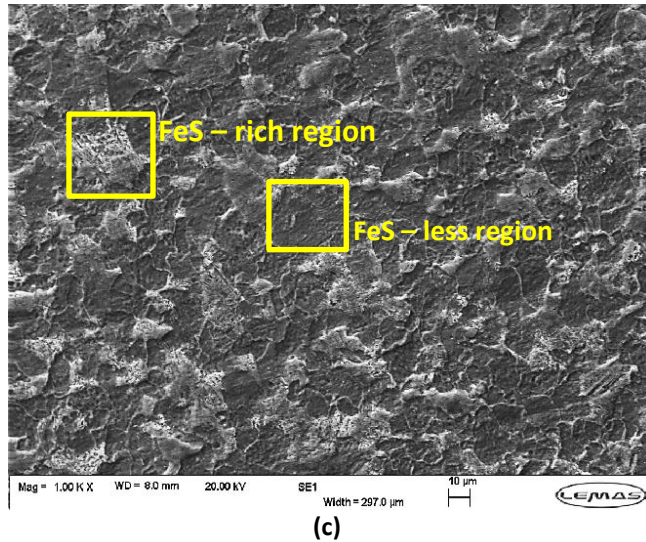
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 4 The SEM images in Figure 4(b) and (c) for tests in 10% H₂S – CO₂ gas after 7 h and initially in 100 % CO₂ for 2 h
 5 and then 10% H₂S – CO₂ gas for 2.5 h, respectively, also show different physical and morphological features of
 6 FeS formed. This correlates well with the dominating cathodic reaction mechanisms in both systems. FeS formed
 7 mainly by direct reduction of H₂S at the corroding surface emerges as a chemisorbed (amorphous –like) layer^[10]
 8 as shown in Figure 4(c) for tests initially in 100 % CO₂ for 2 h and then 10% H₂S – CO₂ gas 2.5 h. With increasing
 9 experimental time and competition between direct reduction and an increasingly dominant H⁺ reduction
 10 reaction, FeS formed is likely to become more crystalline^[2, 3]. This is confirmed by the XRD patterns in Figure 5.
 11 The XRD pattern shows a weak peak for FeS at 17.92°, 30.33° and 39.20 2° for Bragg diffraction angles of
 12 mackinawite in test initially in 100 % CO₂ for 2 h and then 10% H₂S – CO₂ gas for 2.5 h when compared to the
 13 XRD pattern for FeS formed in only 10 % H₂S – CO₂ gas mixture from 0 – 7 hrs; showing strong peaks for
 14 mackinawite at 17.92°, 30.33° and 39.20 2°. These results therefore provides new and important insights into
 15 the mechanism driving the earliest stages of H₂S corrosion and FeS formation beyond what is currently available
 16 in the literature.



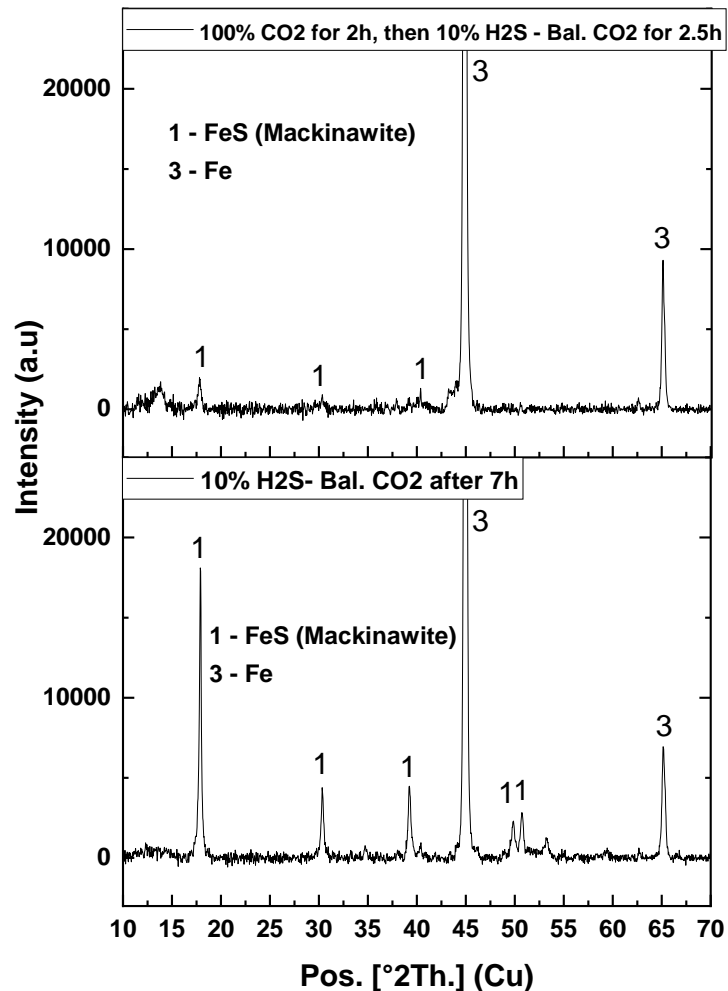
(a)



(b)



1 Figure 4: SEM Images of FeS corrosion products deposited on carbon steel after immersion in 3.5 wt. % NaCl solution
 2 saturated with (a) 100% CO₂ after 7 h (b) 100% CO₂ for 2 h and then in 10% H₂S – CO₂ for another 2.5 h and (b) 10% H₂S –
 3 CO₂ after 7 h.

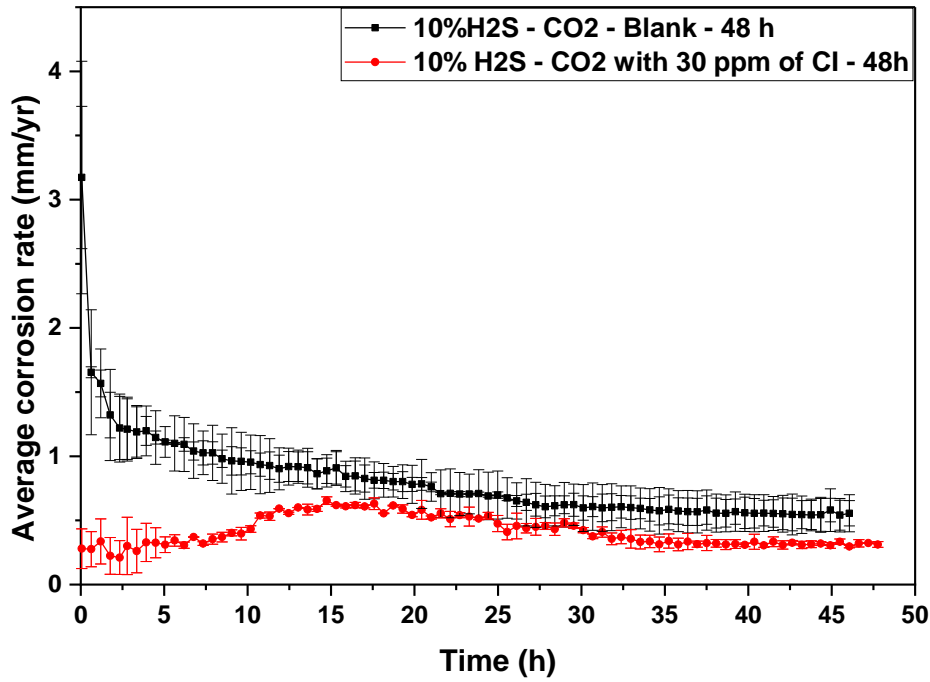


4 Figure 5: XRD pattern showing the type of FeS deposited on carbon steel after immersion in 3.5 wt% NaCl solution
 5 saturated with 100% CO₂ for 2 h and then with 10% H₂S – CO₂ for another 2.5 h, and 10% H₂S – CO₂ for 7 h.
 6
 7

8 **3.2 H₂S – corrosion; iron sulphide formation and Iron sulphide – corrosion inhibitor (CI) interaction**

9 This section investigates the interaction of a fixed concentration (30 ppm) of corrosion inhibitor (CI); made from
 10 reaction of an ethoxylated amine and a dicarboxylic ester, with H₂S corrosion and FeS formation process of
 11 carbon steel in 10% H₂S – CO₂-containing environment over 48 h. The results discussed in this section are

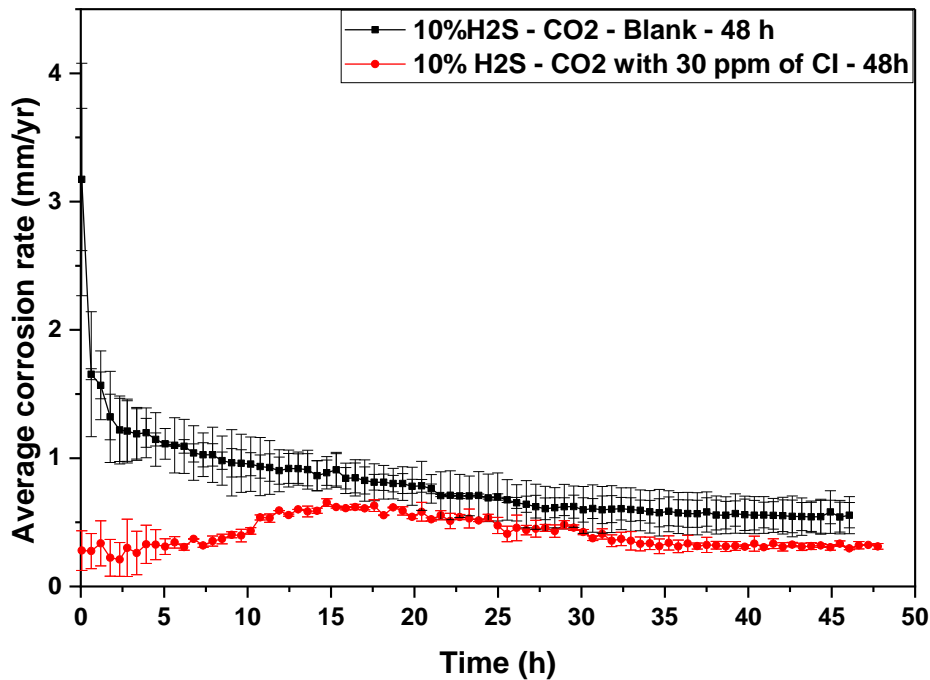
- 1 referenced to a blank test; in 10% H₂S – CO₂-containing environment without Cl. The corrosion rate and corrosion
- 2 potential for tests with and without (Cl) is presented in



(b)

- 3 Figure 6(a) and (b), respectively.

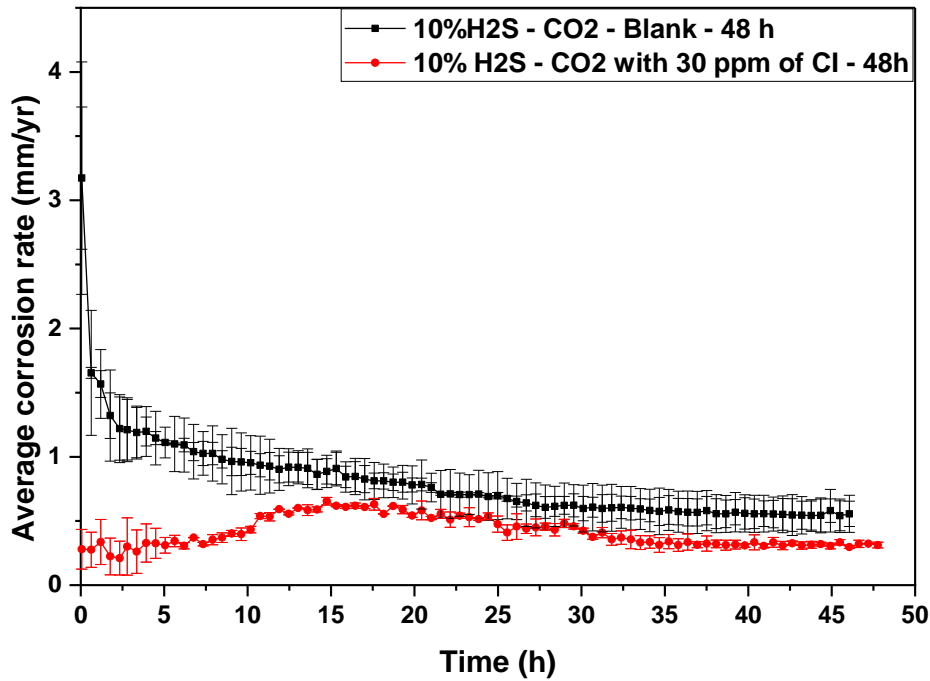
- 4 Referring to



(b)

- 5 Figure 6(a), the corrosion potential starts at a more positive value (~ -620mV) for test with Cl from the start of
- 6 tests than the blank test at ~ -670 mV due to the establishment of initial Cl film on the surface ^[12, 26]. This process
- 7 precedes the introduction of 10% H₂S – CO₂ gas mixture into the corrosion environment (see section on details

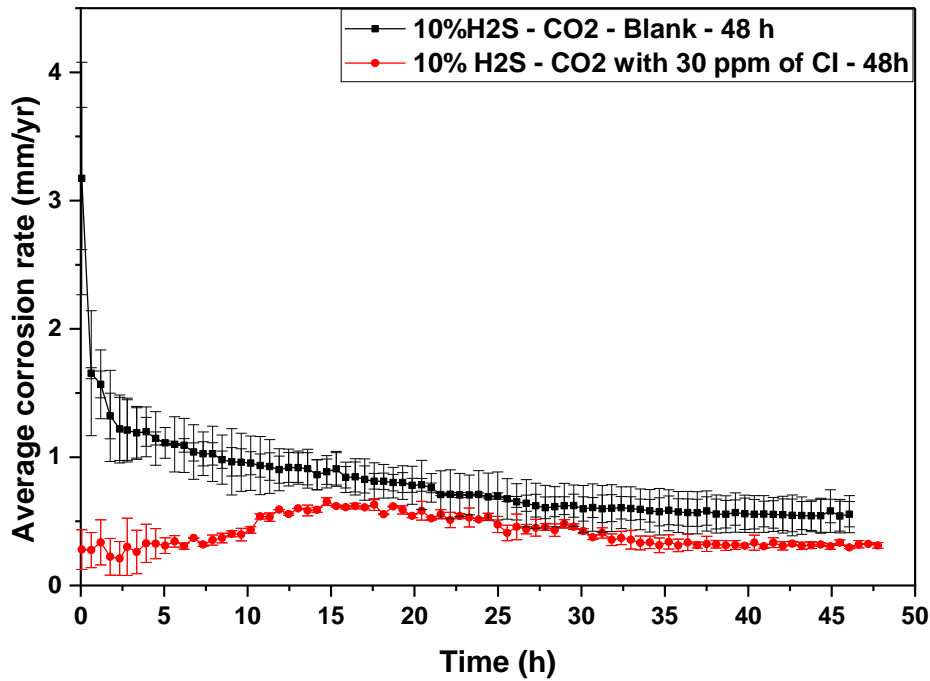
1 of experiment – 2). A further increase in corrosion potential from ~ -620 mV to ~ -600 mV was also observed
2 between 0 – 5 hrs. This correlates with periods of lower corrosion rates (at ~ 0.25 mm/yr) than in the blank tests
3 (at ~ 1.25 mm/yr) (see



(b)

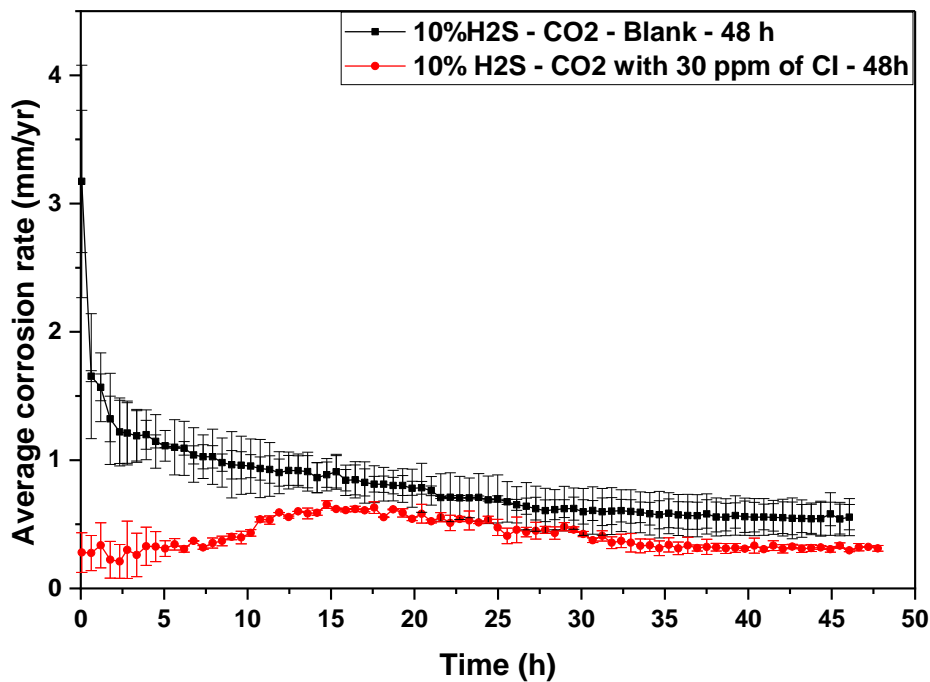
4 Figure 6(b) caused by the introduction of Cl in N_2 -saturated solution before making contact with the sample
5 surface and prior to introduction of H_2S -containing gas mixtures. This methodology was used in this study
6 because the chosen Cl inhibits corrosion through the formation of an iron carboxylate film by reacting with
7 ferrous ions ^[13]. This will require substantial availability of ferrous ions at the corrosion interface from a
8 preceding ferrite dissolution process. Referring to the results from experiment – 1 in this study, the earliest
9 kinetics of FeS formation will require minimum ferrite dissolution and hence minimum corrosion of the metal
10 surface prior to Cl interaction. This scenario therefore presents the ideal case for understanding how Cl and the
11 fast kinetics of FeS formation competes for the corrosion interface.

12 Referring to



(b)

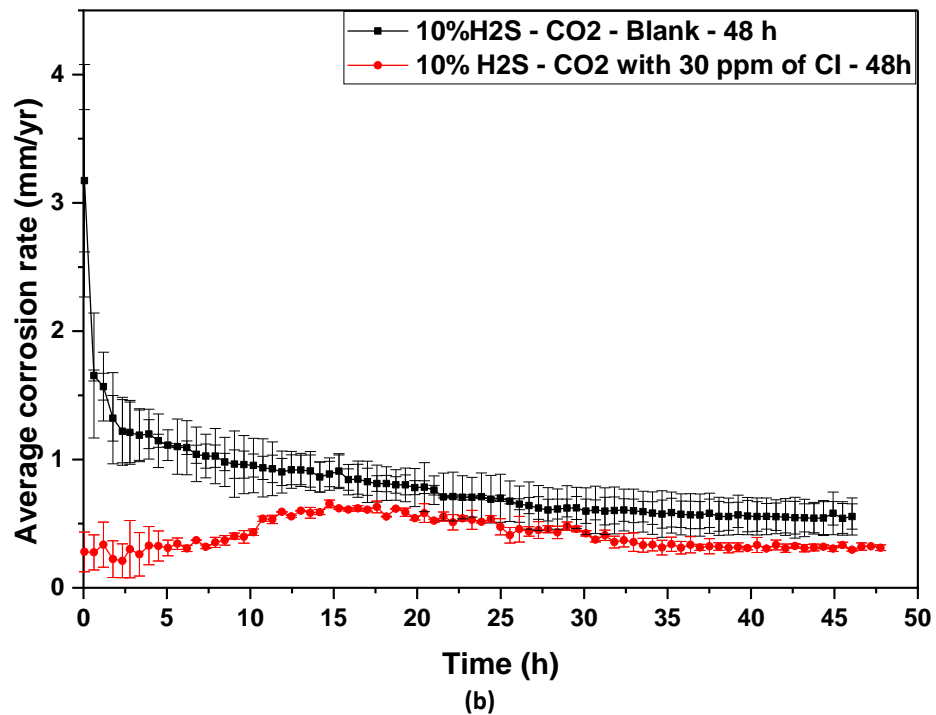
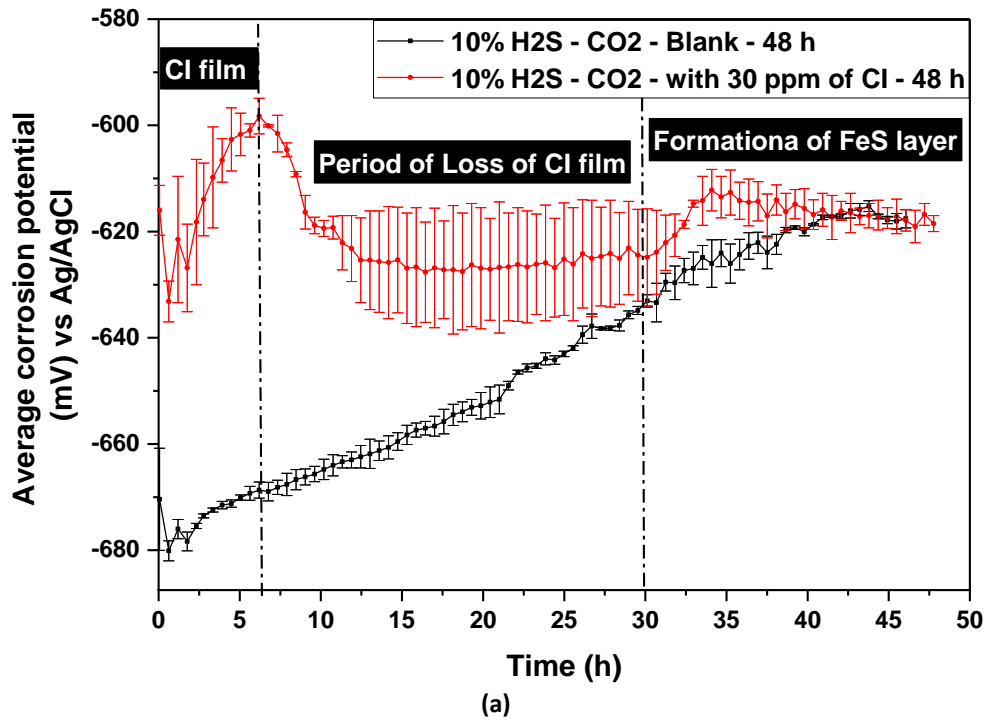
- 1 Figure 6 (a) and (b), the results of increase corrosion potential in the more anodic direction and lower corrosion
- 2 rate for test with Cl than in the blank test from this study is consistent with the results showing the effect of the
- 3 activity of anodic inhibitors used in combined H₂S-CO₂ corrosion from potentiodynamic measurements at
- 4 60°C^[12].



(b)

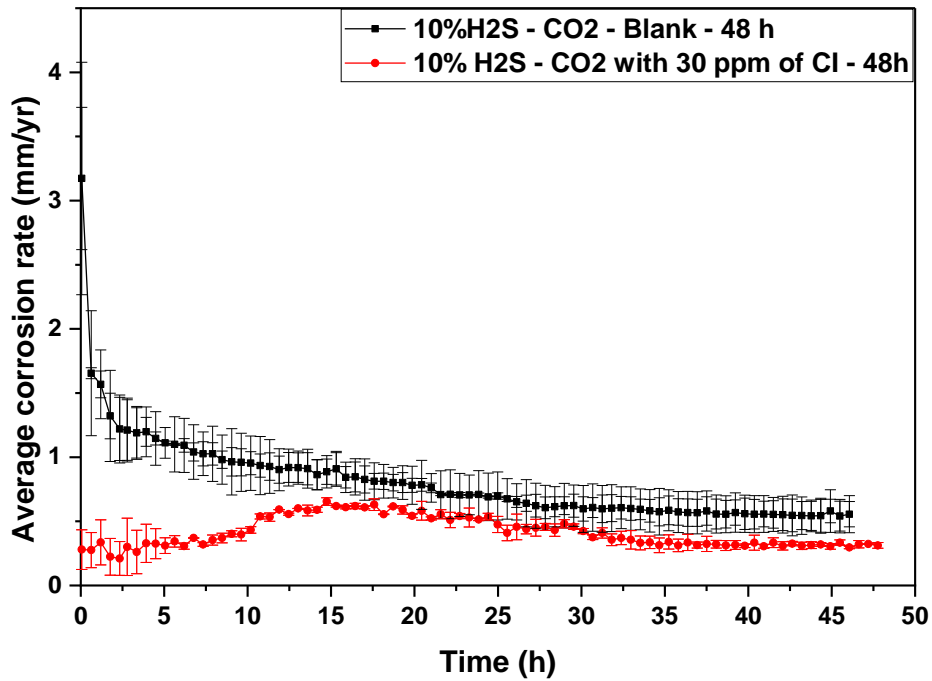
- 5 Figure 6(b) shows a ~58% reduction in corrosion rate (from ~3 mm/yr to ~1.25 mm/yr) between 0 – 5 hrs in
- 6 the blank test to highlight the inhibitive capacity from established FeS layer on the steel surface. The kinetics
- 7 and impact on corrosion characteristics of carbon steel in this case is similar to the fast kinetics of FeS formation
- 8 already established in this paper. This trend of reduction in corrosion rate in the blank test continued slowly
- 9 until after 30 h when the corrosion rate remained constant at ~0.6 mm/yr until the end of the test. During this
- 10 process, the corrosion potential of the blank test showed a steady increase towards positive potential as

1 evidence of the gradual and continuous build-up of FeS layer on the corrosion interface shown by the SEM image
 2 in Figure 7(a) and (b) for repeated tests. Although the SEM images appeared to be loosely held and at times
 3 “fluffy” from the top view, it is clearly able to suppress the uniform corrosion rate by up to 80% within 48 h by
 4 creating some interfacial barrier between the corroding steel and the environment.



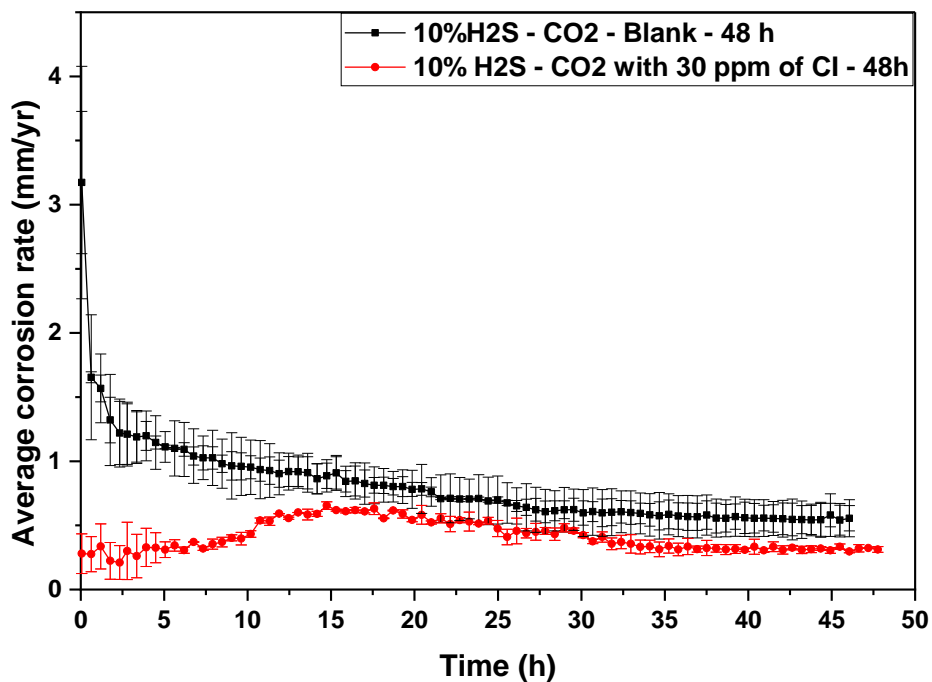
5 Figure 6: Plot of (a) corrosion potential and (b) corrosion rate for experiments in 10% H₂S – CO₂ over 48 h with 0 ppm
 6 (blank) and 30 ppm of Cl.

7 With respect to tests with 30 ppm of Cl, the corrosion potential starts decreasing between 5 and 15 h towards
 8 more negative potential values (see



(b)

1 Figure 6(a)) just as the corrosion rate in

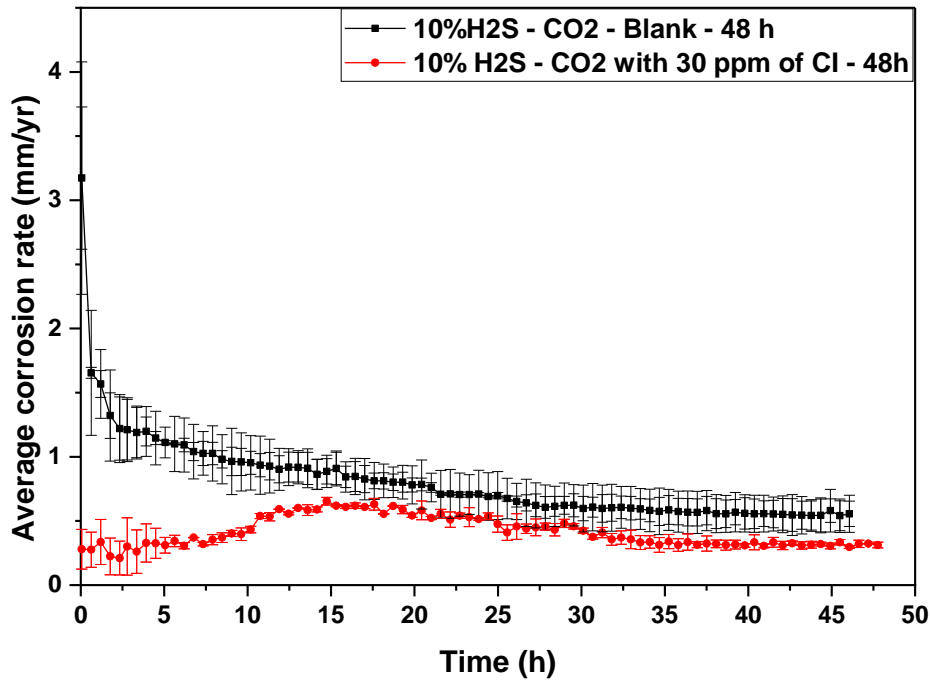


(b)

2 Figure 6(b) increases threefold to ~ 0.75 mm/yr. The corrosion potential and corrosion rate remained largely
 3 constant from 15 to 30 h before a new slight increase in corrosion potential and a corresponding slightly lower
 4 but stable corrosion rate; at ~ 0.5 mm/yr, is achieved at the end of the test. The reduction in corrosion potential
 5 and corresponding increase in corrosion rate between 5 and 15 h is caused by the deterioration of initially
 6 formed Cl film. This can create opportunities for dissolved sulphide species to interact with the corroding surface
 7 for the first time and kick-start the first stage of FeS formation process. Referring to the preferred mechanism
 8 of Cl interaction, the fast kinetics of FeS formation has prevented the formation of a more resilient iron
 9 carboxylate film by suppressing ferrite dissolution and reducing the availability of ferrous ions. It has been

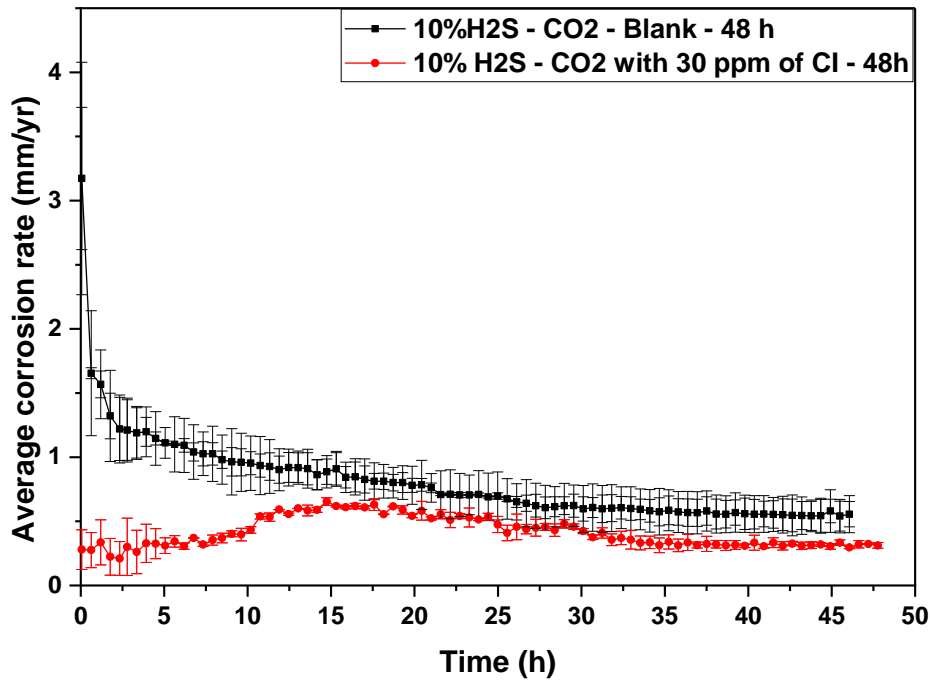
1 proposed^[13] for this particular CI that CI film coverage could also become non-uniform if substantial corrosion
2 of the interface is not allowed prior to its interaction with the CI. In other studies, it was also observed that
3 initially formed CI film can also become weakened by the interaction of active components of CI film with HS⁻
4 ^[12].

5 The FeS corrosion product observed in test with CI after 48 h is largely amorphous/non-crystalline as shown in
6 the SEM image in Figure 7(c) and (d). This morphology of FeS is usually associated with the earliest stages of FeS
7 formation kinetics. This is confirmed by the similar morphology of FeS formed in 10% H₂S – containing systems
8 previously shown in this paper after 4.5 and 7 h in Figure 4(a) and (b) respectively. It is important to note that it
9 is still unclear from this study the exact time the corroding interface makes its first contact with dissolved
10 sulphide specie in the presence of CI layer. The results from electrochemical responses (



(b)

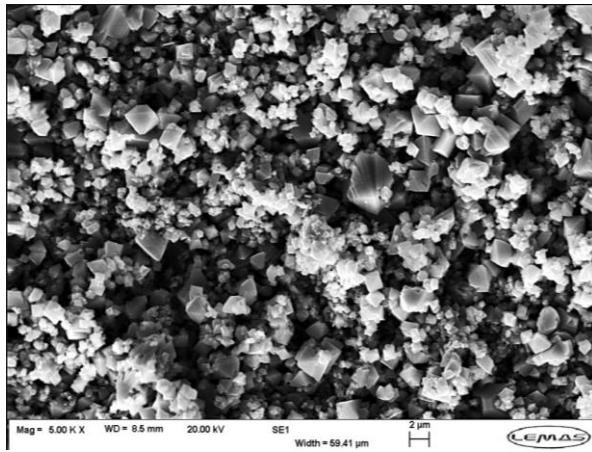
11 Figure 6(a) and (b) and SEM images (Figure 7(c) and (d)) strongly suggests that the interaction of the corroding
12 interface and dissolved sulphide species is at its earliest stages after a prior establishment of CI film. This has led
13 to the formation of an amorphous FeS film with evidence of polishing marks from the sample still imprinted and
14 retained on the FeS layer. This morphology of FeS is characteristic of FeS formed by direct reduction of H₂S at
15 the steel surface as already shown in this study. In this instance, the use of CI before the introduction of 10%
16 H₂S – CO₂ gas mixture is observed to have inhibited and delayed the initial formation of FeS, and restrict the
17 morphology of FeS to an amorphous layer when compared to the expected FeS morphology observed from the
18 blank test in Figure 7(a) and (b). The fast kinetics of FeS formation once the dissolved sulphide species makes
19 contact with steel sample also prevents the availability of ferrous ions at the corrosion interface to ensure the
20 development of a more adherent CI film. Once CI layer is successfully displaced from the corrosion interface
21 (between 5 – 15 h), FeS formation kinetics start dominating the interfacial activities, as depicted by the corrosion
22 rate and corrosion potential profiles in



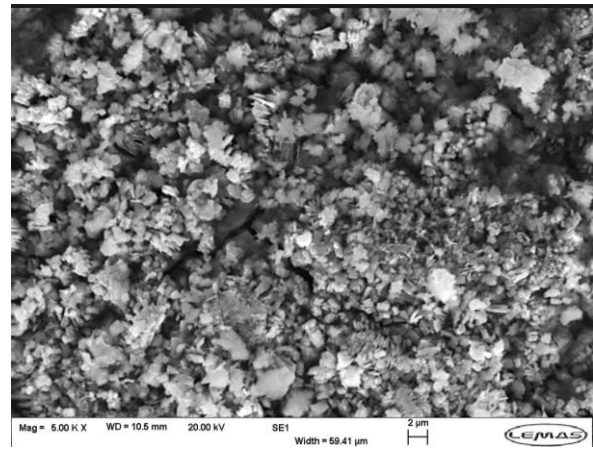
(b)

1 Figure 6(a) and (b). It is important to note that the *in situ* transition from Cl controlled corrosion interface to
 2 FeS controlled corrosion interface in a single experiment has also had the overall impact of suppressing
 3 cumulative material loss from uniform corrosion of the carbon steel sample over 48 h. This is supported by the
 4 evidence in Figure 2 and Figure 3 that shows how FeS corrosion products can influence the corrosion
 5 characteristics of the corroding surface.

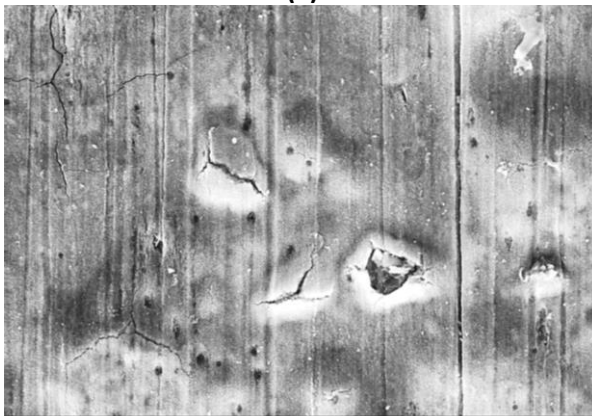
6 The influence of Cl interaction and competition for the corroding steel surface with FeS is also supported by the
 7 weak peaks for amorphous FeS formed in test with Cl (mackinawite) on the XRD pattern in Figure 8 in comparison
 8 to the strong peaks for largely crystalline FeS (mackinawite) formed in the blank test. The intensity of XRD peaks
 9 for FeS formed in test with Cl (Figure 8) is in the same range as the XRD peaks for test initially in 100% CO₂ for 2
 10 h and then 10% H₂S – CO₂ for another 2.5 h (Figure 5). There is also an observed protuberance within the FeS
 11 film in Figure 7(c) and (d) for test with Cl. Some of the regions with protuberance showed features that indicate
 12 the occurrence of either FeS film rupture and/or collapse (Figure 7(c) and (d)) under some form of internal
 13 pressure. These kind of protuberances can be linked to internal epitaxial stresses built-up as a result of the
 14 particular mechanism of mackinawite formation at this stage of the corrosion process. Mackinawite scales are
 15 known to be of larger volumes than the volume of Fe²⁺ consumed for its formation. It is believed that a larger
 16 volume fraction of mackinawite is being formed from a smaller volume fraction of consumed Fe²⁺ to introduce
 17 such internal stress effects. The ratio of these volume fractions is usually described as the Pilling-Bedworth (P-
 18 B) ratio^[27]. These observation highlight the complex interaction between Cl and FeS corrosion product layer that
 19 is still not clearly understood and will still require significant research attention and a robust research program
 20 to build on the understanding developed in this study.



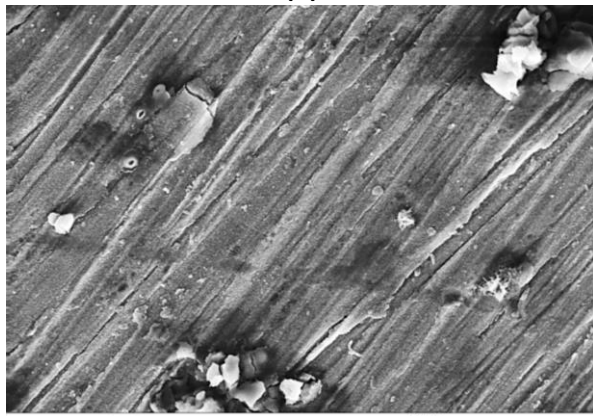
(a)



(b)



(c)



(d)

1 Figure 7: SEM Images of FeS corrosion products deposited on carbon steel in 10% H₂S – CO₂ after 48 h (a) blank (b) blank
2 - repeat (c) with 30 ppm of Cl and (d) with 30 ppm of Cl – repeat.

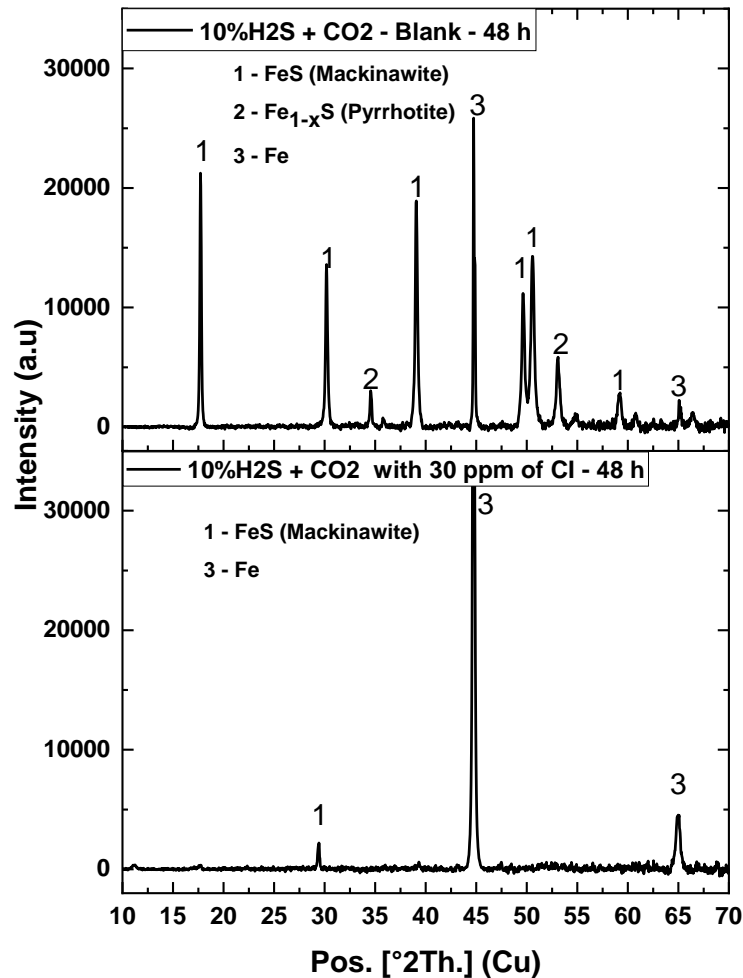


Figure 8: XRD pattern showing the type of FeS deposited on carbon steel in 10% H₂S – CO₂ after 48 h.

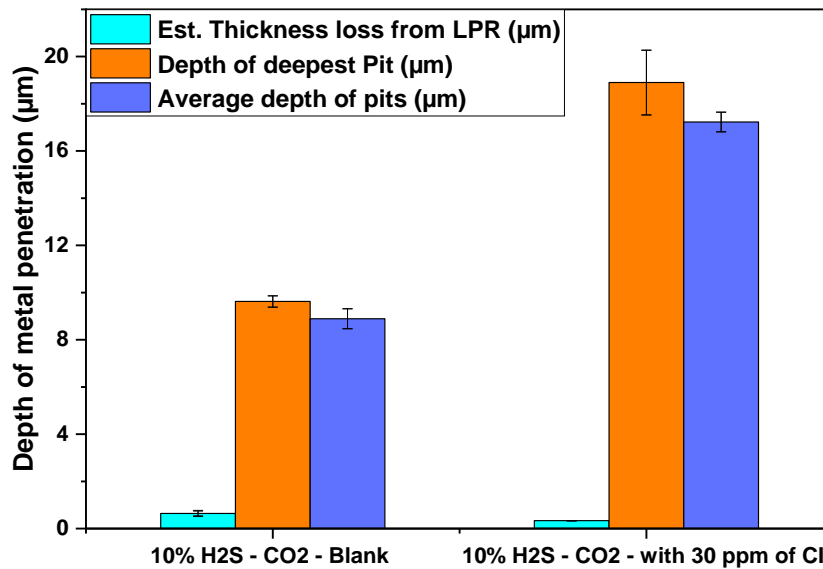
3.3 Pitting corrosion; the effect of corrosion inhibitor (CI) – iron sulphide interactions

Figure 9 presents the estimated thickness loss linked to uniform corrosion, depth of deepest pit and average of 10 deepest pits from tests conducted in 10% H₂S – CO₂-containing environment over 48 h, with and without 30 ppm of Cl. Data on thickness loss estimated from uniform corrosion is based on the assumption that the localised redox reactions within these pits over 48 h are relatively insignificant when compared to the rate of material loss from the rest of the corrosion interface captured in the electrochemical responses. It is also believed that most ferrous ions linked to the uniform corrosion rate are captured in the build-up of FeS.

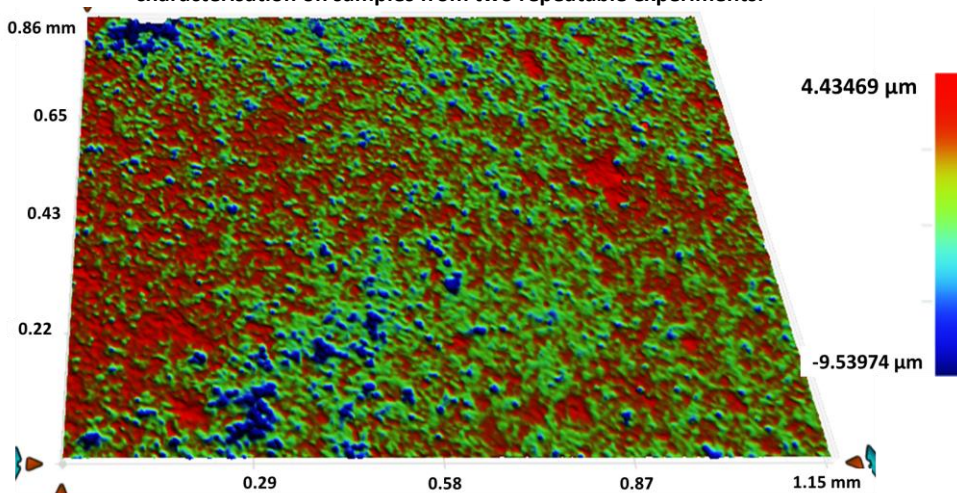
Referring to Figure 9, the depth of the deepest pit and the average pit depth is twice as high in test with Cl as the blank test while the estimated uniform corrosion contribution is half as much as the blank test. As discussed earlier, the competition for persistency of Cl film and H₂S related redox activity for the corrosion interface led to a weakened Cl layer and the formation of a semi protective and non-crystalline FeS layer. The SEM images shown in Figure 7(c) and (d) clearly show that the mechanism of formation of the resulting FeS is susceptible to rupture and/or failure, leading to the loss of film integrity when compared to the FeS formed in the blank test (Figure 7(a) and (b)). The loss or partial loss of Cl layer is known to be a prolific precursor for pitting initiation^[28]. However, when such loss of Cl occurs (typically when Cl is dosed below the optimum concentration), and precedes the formation of a FeS layer prone to rupturing, it creates the necessary conditions for pit corrosion damage to dominate the material loss mechanism. Visual evidence of pitting corrosion damage (which focuses on the identified deepest pit on an entire exposed surface) is presented for the blank test in Figure 10(a) and for tests with 30 ppm of Cl in Figure 10(b) and (c).

Referring to Figure 10(a) to (c), the areas surrounding the pits for test with Cl appear to be well protected compared to the blank test. This is due to the combined effect of partial loss of initial Cl film and the emerging

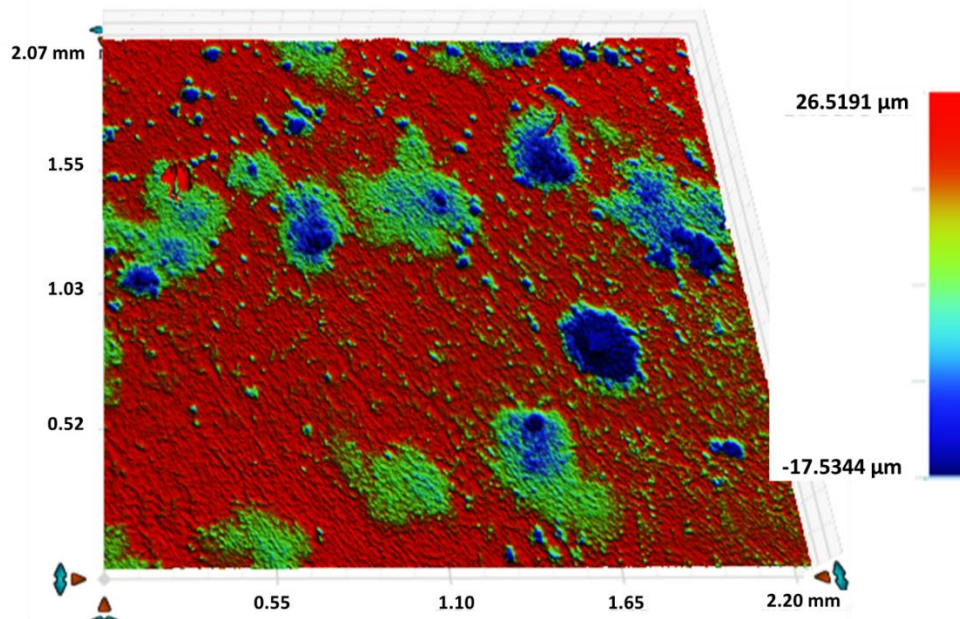
1 FeS layer. The level of protection of surfaces surrounding the pits suggest that the transition from a weak Cl film
 2 to a semi – protective FeS layer still ensures substantial suppression of uniform corrosion in areas on the steel
 3 surface where either the Cl film was initially adherent and/or the FeS layer has not been ruptured. It also shows
 4 that the rate of deterioration of initial Cl film and the formation of FeS layer were not occurring at the same rate
 5 across the entire corrosion interface. This is a recipe for the emergence of local galvanic cells, which is enhanced
 6 by the electrochemically active nature and electronic properties of FeS corrosion products [10, 29] to support
 7 pitting corrosion^[30]. Lower depth of pits were observed in the blank test because of the porous nature of the
 8 FeS corrosion product. This also implies that the migration of precipitable sulphide species can continue to
 9 interact with the base steel to drive ferrous dissolution and recede the reference surface underneath the
 10 corrosion product layer. One of the consequences of increased ferrite dissolution is the increased build-up of
 11 FeS corrosion products on the surface as shown in Figure 7(a) and (b) and supported by evidence of evenly
 12 spread areas on the steel surface with only micro-pits and uniform corrosion. It is likely that subsequent
 13 depositions to the FeS layer will continue to suppress the ferrous dissolution process and potentially support the
 14 growth of these micro-pits with time. These conclusions are supported by the pit count and pitting factor
 15 presented in Figure 11(a) and (b), respectively. Pit count data is based on a pit depth threshold of 6 μm and
 16 shows a higher number of pits in test with Cl than in the blank. The pitting factor is higher for test with Cl than
 17 the blank test to corroborate the trend in high pit penetration depth and pit count for tests in wit Cl than the
 18 blank test. This highlights the significant impact of the competitive redox activity between Cl and FeS at the
 19 corrosion interface on the mechanisms of material loss in H_2S – containing corrosion systems.



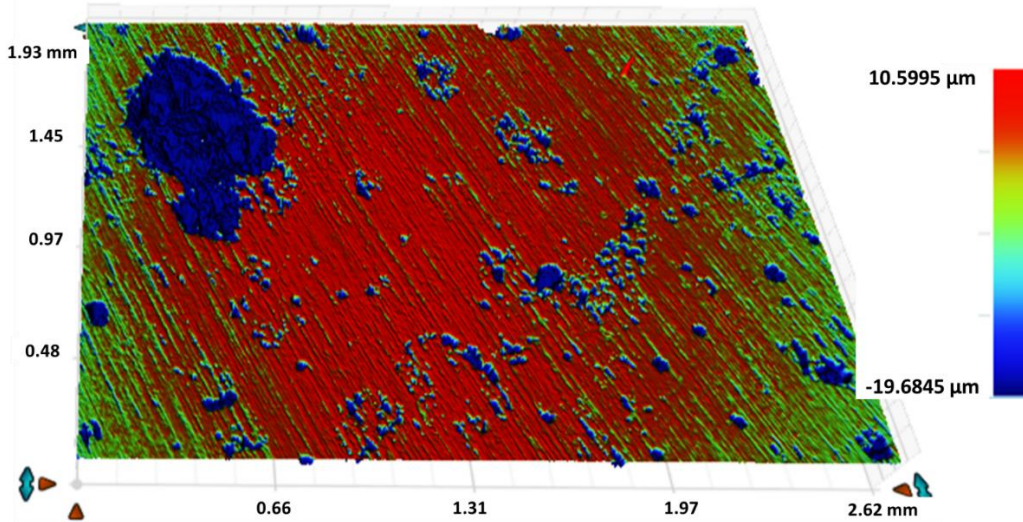
20
 21 Figure 9: Graph of the thickness loss to general corrosion, the size of deepest pit and the average of the 10 deepest pits
 22 on carbon steel in 10% H_2S – CO_2 with 0 and 30 ppm of Cl after 48 h. Error bars on pit size data are based on two (2)
 23 pit characterisation on samples from two repeatable experiments.



(a)



(b)



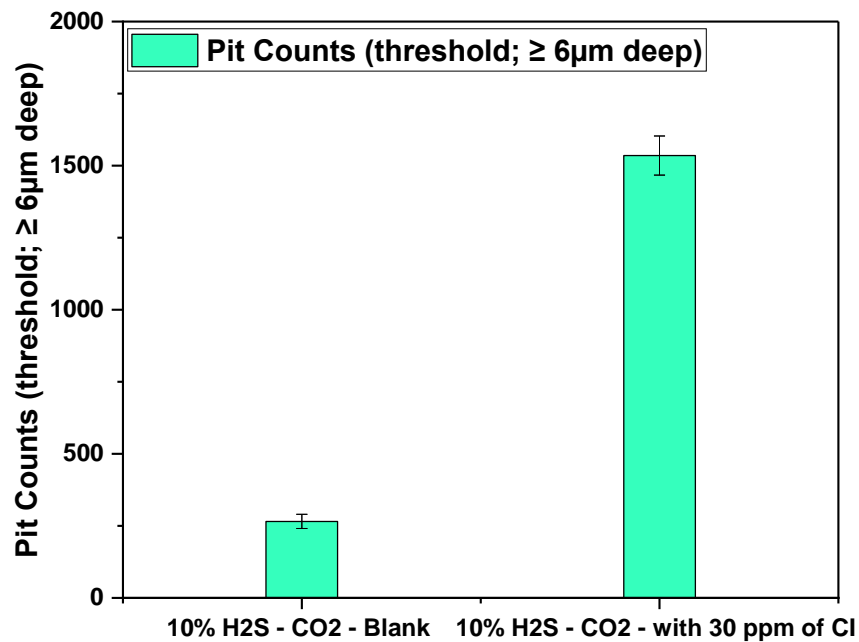
(c)

1 Figure 10: 3D image of the deepest pit on carbon steel in 10% H₂S - CO₂ after 48 h (a) 0 ppm (Blank), (b) with 30 ppm of Cl
 2 and (c) repeated test with 30 ppm of Cl.

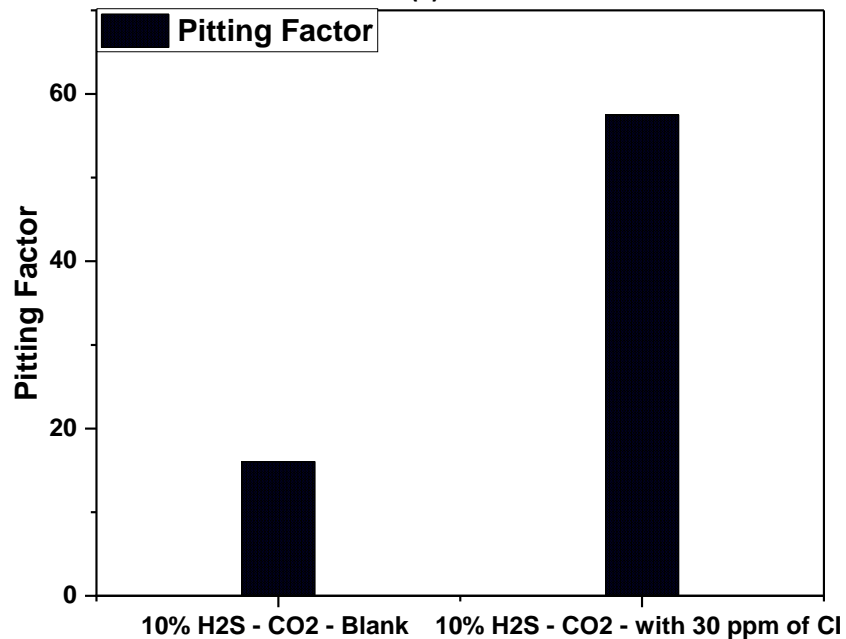
3 **The pitting factor (P_f):** is used to reflect the relative contribution of corrosion damage mechanisms; pitting
 4 and uniform corrosion to metal loss and defined in ASTM standard G46-94^[31] as:

Pitting Factor;
$$P_f = \left(\frac{P_d}{P_u} \right) \quad \text{Equation 1}$$

5 Where P_d is the total material penetration (μm) for the exposed surface area (sum of depth of deepest pit (d_{max}),
 6 (after removal of corrosion products) plus the estimated thickness loss (μm) from uniform corrosion rate
 7 measurement (termed P_u), i.e., P_d = P_u + d_{max}. A pitting factor of 1 represents general corrosion; i.e., P_d = P_u, and
 8 d_{max} = 0. The greater the (d_{max}), the greater the pitting factor.



(a)



(b)

Figure 11: A graph of (a) pit density and (b) pitting factor showing the relative contribution of uniform and pitting corrosion to metal penetration of carbon steel in 10% H₂S - CO₂ after 48 h with 0 and 30 ppm of Cl.

4. Conclusions

This paper investigates the corrosion kinetics and behaviour of carbon steel in H₂S-containing corrosion environments with emphasis on FeS formation kinetics, interaction with corrosion inhibitor and corrosion damage mechanisms. Some of the key conclusions are highlighted below.

1. FeS (Mackinawite) formation kinetics have been shown to occur quickly without the requirement of significant availability of ferrous ions. This has been shown to occur within the first 0.5 – 1 h of interaction with dissolved H₂S gas due to the direct reduction of H₂S at the steel surface.
2. The fast kinetics of FeS formation led to an incompletely covered corrosion surface by FeS, with coverage almost replicating the distribution of ferrite – pearlite phases within the steel microstructure.

1 This has an impact of substantial reduction of uniform corrosion rate due to the blocking of active
2 anodic sites by FeS formed.

3
4 3. FeS (macknowite) corrosion products quickly undergo a time-dependent morphological transformation
5 with increasing exposure time, particularly in closed test systems. The main morphological form of FeS
6 in the initial stages is amorphous.

7
8 4. The use of 30 ppm of Cl (based on the reaction of an ethoxylated amine and a dicarboxylic ester)
9 resulted in complex mechanisms of interaction of Cl, FeS and the corrosion interface. The use of Cl
10 caused a delay in the FeS formation kinetics at the corrosion interface and restricts morphology to
11 amorphous FeS. The fast kinetics of FeS formation prevented the availability of ferrous ions needed by
12 the by the Cl to form an effective corrosion barrier at the corrosion interface. This led to the
13 establishment of a weak Cl film which is easily displaced by the emerging FeS layer.

14
15 5. The competition between the Cl layer and the FeS for interaction with the corroding interface acts to
16 undermine the integrity of both Cl film and FeS layer, leading to increased severity of pitting corrosion
17 attack.

18 **Data availability**

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

21 **Credit authorship contribution statement**

22 **Frederick Pessu:** Conceptualization, Methodology, Formal analysis, Investigation, Resources, Writing
23 - original draft. **Richard Barker:** Writing - review & editing **Fakuen Chang:** Review & editing. **Tao**
24 **Chen:** Writing - review & editing. . **Anne Neville:** Writing - review & editing and supervision

25 **Declaration of Competing Interest**

26 The authors declare that there is no conflict of interest.

27 **Acknowledgement**

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