

Exploring CO₂ annular corrosion in flexible pipes at different pressures

Maria Eleni Mitzithra
TWI Ltd
Granta Park, Great Abington
CB21 6AL, Cambridgeshire
United Kingdom

John Rothwell
TWI Ltd
Granta Park, Great Abington
CB21 6AL, Cambridgeshire
United Kingdom

Shiladitya Paul
TWI Ltd
Granta Park, Great Abington
CB21 6AL, Cambridgeshire
United Kingdom

Fabricio Pinheiro dos Santos
Petrobras SA
Avenue Horácio Macedo 950, Ilha do Fundão
22041, Rio de Janeiro
Brazil

ABSTRACT

This paper presents in situ pH and corrosion rate results obtained from the tests carried out at 20bar CO₂, for flexible wire material, in 3.5% NaCl, at 30°C, 40°C and 60°C with a CO₂ gas flow rate of 0.001ml/min/cm², a V/S ratio of 1ml/cm² and a duration of 2 months. These are compared with tests at 40 barg CO₂, presented in previously published work, and tests at 1barg CO₂, 5barg CO₂ and 10barg CO₂ for similar annular test conditions. In general, the pH and corrosion behaviour were related to dissolved iron concentration, precipitation kinetics and scale formation on the surface of the specimens. The lowest corrosion rate was recorded for the test with the lowest V/S and CO₂ flux which featured a thin and compact iron carbonate layer. For a given V/A ratio and CO₂ flux, changes in the long term in-situ pH and corrosion rates were found to become less significant as CO₂ increases beyond 20barg and temperatures increase beyond 40°C. Different carbonated morphologies were apparent and related to the test conditions.

Key words: annular corrosion, flexible pipes, high CO₂ partial pressure, in situ pH, corrosion rate

INTRODUCTION

Flexible pipes, widely used in the offshore oil and gas industry, are structures composed of several concentric layers of high strength steel armour wires and polymeric material. The steel provides resistance to the operational loads, i.e. tensile armour wires provide resistance to axial tensile loads and pressure armour wires withstand pressure loads. The inner and outer polymeric sheaths prevent direct contact of the steel with production fluids and seawater respectively¹⁻². The steel wires reside within the annulus defined by the two polymeric sheaths. Field experience and a number of studies³⁻⁸, on flexible pipes have shown that the conditions within the annulus can evolve during service as water

and gases, such as CO₂, H₂S and CH₄, permeate from the production fluid of the bore through the inner sheath into the annular space. It follows that corrosive conditions can potentially arise in the annulus causing metallic degradation. The process being controlled by permeation means that the establishment of corrosive conditions is time dependent and can be difficult to predict accurately, not only because it requires diffusion modelling, but also because of reactions with materials within the annulus.

The corrosion rate of amou wires will be dependent on various parameters within the annulus, i.e. temperature, gas pressure and flux, and the presence of water. The low corrosion rates reported by industry (<0.01mm/year⁹⁻¹¹) are understood to be largely attributed to the degree of occlusion, i.e. the ratio of solution volume to steel surface (V/S), and the low partial pressures of acid gases present in most cases (typically <1bara). The V/S can be as low as 0.02ml/cm² and is linked with the establishment of super-saturated conditions (high concentration of dissolved iron from amou wires in the solution), which serve to moderate the pH and allow the formation of protective iron carbonate products on the wire surfaces^{2,5}. The partial pressures of gases present are controlled by their permeability through the polymeric sheaths, and their reaction rates with materials within the annulus.

Although the annulus environment is generally considered to be of low corrosivity for the majority of cases, there are situations where the annulus environment may become more aggressive than anticipated. Deep water developments in fields that are very rich in CO₂ could produce fluxes and partial pressures beyond current experience. Abrupt changes during service e.g., sudden rupture of the outer sheath leading to ingress of seawater, and the souring of fields, could further aggravate matters.

In order to be able to assess the integrity of flexible pipes subject to the most extreme service conditions, reliable prediction of corrosion rates of the steel wire material beyond conditions already reported is required.

Previous work¹² presented results for an annulus environment of 40barg CO₂ brine at different temperatures (30°C, 40°C, 60°C). Two sets of experiments were designed, where two V/S ratios (~1ml/cm² and 0.3ml/cm²) and two test durations (2 and 4 months) were employed. It was shown that an increased confinement and reduced gas flux resulted in lower corrosion rates. This in turn was related to the pH, dissolved iron concentration, and the characteristics of the iron carbonate scales formed.

This paper presents results obtained from tests carried out at 20bar CO₂, for same flexible wire material, brine, temperature range, CO₂ gas flow rate, V/S ratio and test duration as those for Set 1- 40 barg CO₂¹².

EXPERIMENTAL PROCEDURE

Conditions investigated

The experimental conditions of the tests presented in the current paper are summarized in Table 1. For these test conditions, tests were carried out also at 1barg CO₂, 5 barg CO₂ and 10barg CO₂ at 30 and 60°C. Same test conditions were used for tests at 40barg CO₂ (Set 1) presented in previously published work¹².

Table 1: Test conditions

Parameter	Conditions		
Temperature, (°C)	30	40	60
NaCl Solution (wt.%)	3.5		
Normalised CO ₂ volumetric flow rate (per steel surface area, ml/min/cm ²)	0.001		
Level of Dissolved Oxygen (ppb)	<10		
Test Duration (months)	2		

Materials preparation

High strength steel extracted from flexible pipes were used for the tests. These wires have a very fine pearlitic microstructure and a composition shown in Table 2.

Table 2: Chemical composition of high strength steel subjected to testing

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Cu	Al	As
Content (%m/m)	0.67	0.20	0.64	0.005	0.009	0.044	0.009	0.048	0.050	0.026	0.007

The general appearance of the wire specimens used in the experiments is shown in Figure 1. All specimens were cleaned using Clarke's reagent solution, as per BS ISO 8407:2014 standard¹³ to remove grease and pre-existing corrosion products before the initial mass of the specimens was determined. Note that some evidence of minor corrosion from previous service of the wires was apparent on the surface of the specimens. All specimens were stored in a desiccator prior to use.



Figure 1: Images of the test material after cleaning as per BS ISO 8407:2014 standard, prior testing for tests in current study

Test equipment and test execution

Three 10L autoclaves, were loaded with wires and de-aerated solution to achieve the V/S required and heated to the required temperatures (Figures 2a and 2b). A detailed schematic diagram is given in previously published work¹². Each autoclave is supplied with CO₂ at the specified rate and pressure via electronic mass flow and back pressure controllers. A 1l probe vessel connected to the autoclaves is used to regularly measure the pH from each autoclave. To obtain the in-situ measurement of pH, the solution from the autoclave of interest is circulated through the probe vessel, which is itself maintained at the same pressure and temperature as the main vessel. Following measurement of the pH, the probe vessel is isolated and an aliquot of solution is collected from the for analysis of the dissolved iron. After measurement, the solution is returned back to the main test vessel under a slight positive gas pressure. Between the measurements, the probe vessel was isolated from the rest of the system and thoroughly cleaned with DI water and air dried prior to each measurement.

Pressure gauges allowed visual checks, while calibrated pressure transducers in each vessel allow accurate logging of the pressure during testing. The solution temperature was continuously monitored via thermocouples linked to the computer system. A 1mm PTFE liner was fitted to each of the main test vessels to avoid contact of the flat wire specimens with the vessel walls. CO₂ gas with 99.999% purity was used throughout the experiments. A higher flux was used at the start of the experiment to achieve quick saturation and pressurization of the solution.

A number of commissioning tests were carried out to ensure that the required conditions could be maintained over the long test period. Further details regarding the commissioning tests and test execution are provided in previously published work¹².

Prior to the corrosion tests, in situ pH measurements were carried out without the presence of steel in order to obtain the pH values of the test environments without the presence of steel.

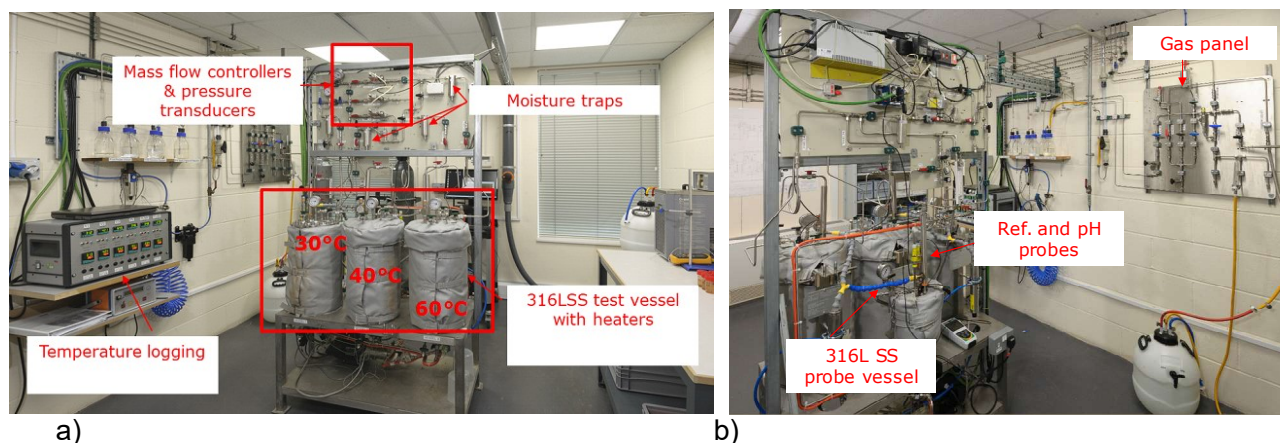


Figure 3 a) the 316L SS main test vessels with heaters on and relevant tubing/equipment/accessories connected b) 316L SS probe vessel with heater on and relevant tubing/equipment/accessories connected.

Post-test examination

Immediately after the end of the tests, the specimens were removed from the vessels, lightly rinsed with deionized water and acetone, dried and stored in a desiccator for further examination. Metallographic sections were extracted and prepared for each test condition. The sections were examined using light microscopy. The morphology of the inner and out surfaces of the specimens was assessed and pit depth and scale thickness measurements were carried out at various locations on each metallographic section. The pit depth measurements were carried out relevant to the apparent surface. The cross sections were also examined using scanning electron microscopy (SEM) and backscatter electron imaging provided information on scale density in the form of brightness/contrast differences, which was beneficial for differentiating the layers of corrosion product. Energy dispersive x-ray spectroscopy (EDX) and X-ray diffraction (XRD) were used to elucidate the local chemical composition of the corrosion products. The corrosion products were removed according to the instructions in ISO 8407:2014, to allow determination of final mass and corrosion rate¹³. Following removal of the corrosion products the specimens were examined by profilometry in order to assess the extent of localized damage.

RESULTS AND DISCUSSION

pH and dissolved $[\text{Fe}^{2+}]$ results

Figures 4a presents the evolution of the in situ measured pH and dissolved iron concentration at 20 bar CO_2 over 58 days of testing. The pH values remained higher than those without Fe (pH3.1-3.4), throughout the experiment. Maxima values were observed within the first 10 days, beyond which the values appeared to stabilise be close to one another at a value of approximately 4.6. The pH evolution was slightly different to that at 40barg CO_2 , where the pH exhibited a decreasing trend immediately after establishment of 40barg CO_2 in the test solution and stabilised after a much longer period, i.e. 30 days (see Figure 4b). The pH obtained at 20barg CO_2 was consistently higher than at 40barg CO_2 .

Similar to the pH evolution, the maximum dissolved iron concentration was measured 48 hours after establishment of 20barg CO_2 in the vessels: 4773mg/L, 2634mg/L and 1111mg/L at 30°C, 40°C and 60°C. A pronounced decrease in Fe^{2+} took place within the initial period of the tests (9 days at 60°C, 15 days at 40°C and 30 days at 30°C), with the rate of decrease reducing towards the end of the tests. The initial trend was slightly different to that at 40barg CO_2 , where a rapid decrease in dissolved iron concentration started after only 24h and never quite stabilised. The minima measured at the end of the test durations were: 1006mg/L, 587mg/L and 357mg/L at 30°C, 40°C and 60°C respectively. These are lower than final measured values at 40barg CO_2 and above the equilibrium saturation concentrations (calculated using water chemistry models), which range between 167mg/L - 93mg/L respectively.

The dissolved iron is associated with the CO₂ corrosion of steel as illustrated in the literature^{16,17}. Dissolution of CO₂ acidifies the solution and accelerates the anodic dissolution of steel. The solubility of CO₂ increases with partial pressure explaining the more rapid acidification of solution and dissolution of Fe at 40 barg CO₂. For both cases, at 20 barg CO₂ and 40 barg CO₂, super saturated conditions existed over the entirety of the test, but approached equilibrium saturation values towards the end of the experiments at 60°C (for both 20 barg CO₂ and 40 barg CO₂¹²). For a given temperature and CO₂ pressure, the pH increased with the dissolved iron concentration. However, the pH values appeared to substantially converge towards the end of the tests whereas differences in dissolved iron concentration vs. temperature persisted. Water chemistry models agreed well with the pH measurements, when the [Fe²⁺], CO₂ pressure and temperature were inputted.

The evolution of the pH is related to that of the dissolved iron concentration, precipitation kinetics and scale formation on the surface of the specimens. Upper bound values are linked with initial high concentrations of [Fe²⁺] in the solution (as outcome of the corrosion process of the steel upon contact with CO₂-reactant species during the initial stage of exposure) when specimens were relatively free of iron carbonate scale. Lower bound values are representative of longer durations at the same conditions after extensive precipitation had occurred. The stabilisation in pH values for all test temperatures at 40 barg CO₂ and 20 barg CO₂ over the long term, can be attributed to the stability, structure and thickness of formed scales on the tested specimens.

Figure 5 presents the steady state pH values vs. the different partial pressures of CO₂ and test temperatures for current and previous data. The average of the last three measured pH values at each test pressure and test temperature were used as steady state values. Despite fluctuations the overall trend appears to be that the pH decreases as temperature and CO₂ pressure increase. The results of the 10 barg 60°C test do not conform well with the trend. Looking back over the original data it was clear that pH had not stabilised during the test period for these particular conditions and may have been to sensor issues. The change in measured values during a prolonged period of stable controlled variables highlights the challenge of obtaining accurate and useful data for determination of the annulus environment.

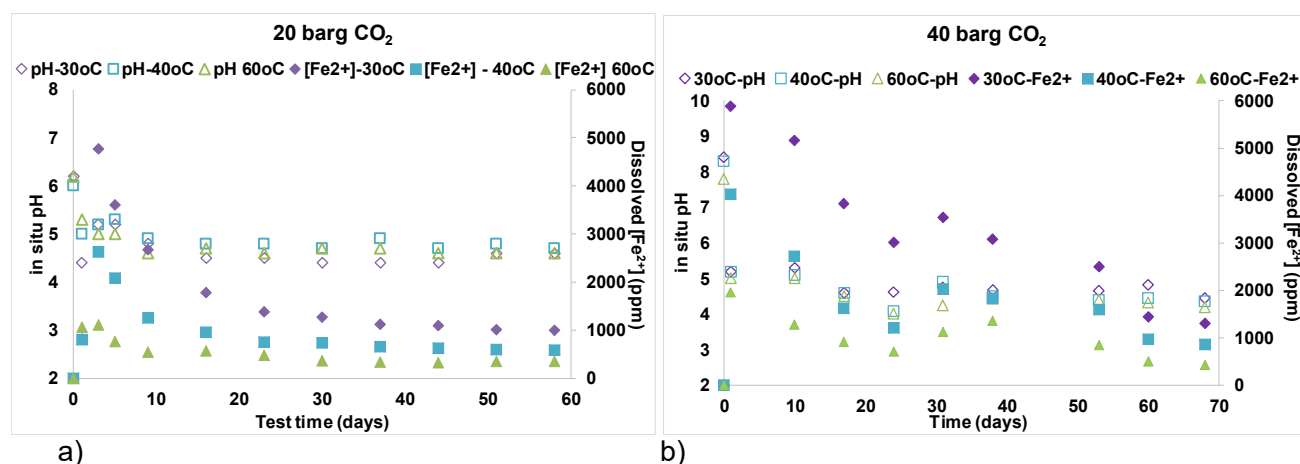


Figure 4: Evolution of measured in-situ pH and dissolved iron concentration vs. time at 30°C, 40°C and 60°C, at a) 20 barg CO₂ and b) 40 barg CO₂¹²