

**Corrosion in Confined Environments -  
The Importance of High Supersaturation of Dissolved Corrosion Products**

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**ABSTRACT**

Flexible pipes used in oil and gas production are composed of densely packed steel wires enclosed in an annulus confined by inner and outer thermoplastic sheaths. Hydrocarbons, water, CO<sub>2</sub>, and H<sub>2</sub>S from the bore permeate through the thermoplastic sheaths and form a corrosive environment in the confined space between the sheaths. Generally, low corrosion rates (<0.01 mm/y) are experienced. This is attributed to the low water volume to steel surface ratio (V/S ratio) causing rapid accumulation of dissolved corrosion products and precipitation of protective corrosion product films.

The relationship between the supersaturation of dissolved FeCO<sub>3</sub> (SR<sub>FeCO3</sub>), the precipitation rate of FeCO<sub>3</sub>, and the protective properties of the precipitated corrosion product film was studied in a series of experiments performed at different V/S ratios and different temperatures (10 °C, 25 °C and 60 °C). The experiments showed a large effect of temperature and duration of exposure.

The paper discusses how SR<sub>FeCO3</sub> affects the stability of the corrosion product films and how SR<sub>FeCO3</sub> can be used to estimate the equilibrium pressure of H<sub>2</sub>S in the annulus.

Key words: Flexible pipe, corrosion, FeCO<sub>3</sub> saturation ratio, H<sub>2</sub>S consumption

**INTRODUCTION**

Unbonded flexible pipes used in oil and gas production have a layered structure with densely packed carbon steel pressure and tensile armor wires in an annulus enclosed by the inner liner and outer sheath,

as illustrated in Figure 1. A detailed description of the design and operation of flexible pipes is presented elsewhere.<sup>1</sup>

Water, CO<sub>2</sub>, H<sub>2</sub>S, and light hydrocarbons from the bore fluids permeate through the inner liner, resulting in a corrosive environment in the confined space between the polymer sheaths. Low corrosion rate (<0.01 mm/y) is experienced under normal operation.<sup>2-8</sup> This is attributed to the confined annulus volume (V) and large steel surface area (S), where the aqueous phase quickly becomes supersaturated with dissolved corrosion products, enabling formation of protective FeCO<sub>3</sub> on the wires surface. The V/S ratio is typically below 0.1 ml/cm<sup>2</sup>.

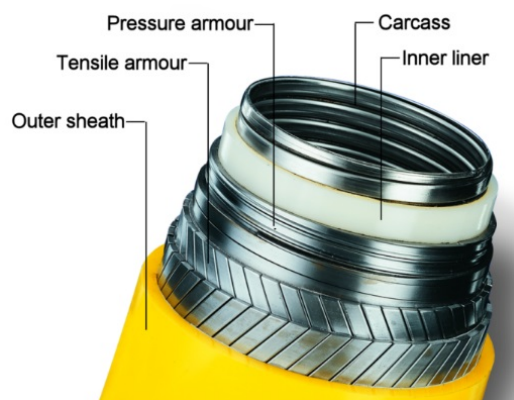
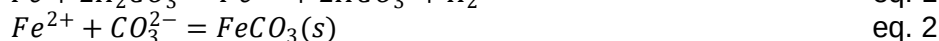
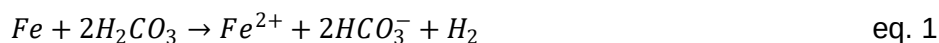


**Figure 1: Typical cross section of a flexible pipe<sup>2</sup>**

Figure 2a shows the buildup rate of corrosion products for various corrosion rates and V/S ratios. The horizontal lines included in the figure indicate the saturation concentration of dissolved FeCO<sub>3</sub> for the test conditions studied in the present paper. As shown in the figure, it takes less than 3 days to exceed the saturation concentrations for all the conditions. It has been assumed that the entire steel surface in the annulus is attacked and corrodes uniformly. This is usually the case in laboratory experiments where pieces of steel wires are exposed. In a real flexible pipe, the steel wires will be covered with various types of oil and grease, and part of the wires might also be covered with tape or liner material. The actual corroding steel area can therefore be much smaller than the total steel area, and the effective V/S ratio will then be much larger. A larger V/S will require more time to build up the concentration of dissolved corrosion products required for formation of protective corrosion product films.

When the steel corrodes, Fe<sup>2+</sup> and an equivalent amount of alkalinity are released as shown in equation 1. The pH and SR<sub>FeCO<sub>3</sub></sub> in the solution increase as shown in Figure 2b until precipitation of FeCO<sub>3</sub> (eq. 2) commences. When solid FeCO<sub>3</sub> is formed at the same rate as the steel corrodes, the pH becomes constant. As shown, the pH and the saturation ratio for a certain level of dissolved corrosion products is very different for the two cases simulated in the figure.



Precipitation of protective FeCO<sub>3</sub> can start when the solubility limit is exceeded, but experiments show that a large SR<sub>FeCO<sub>3</sub></sub> is required for significant FeCO<sub>3</sub> precipitation to occur, particularly at low temperature (< 30 °C).<sup>9</sup> Experiments also show that the protective properties of the precipitated films are closely related to the SR<sub>FeCO<sub>3</sub></sub> level and “the history” of when a certain SR<sub>FeCO<sub>3</sub></sub> level is achieved.<sup>10</sup> There is therefore a need to understand the mechanisms controlling the SR<sub>FeCO<sub>3</sub></sub> in the annulus and develop a procedure for simulating the appropriate SR<sub>FeCO<sub>3</sub></sub> in corrosion, fatigue, and cracking experiments.

The present paper discusses the results of a study where 3 or 6 different armor wire steels were exposed at different V/S ratios (0.7 and 2.4 ml/cm<sup>2</sup>), different surface conditions (degreased and abraded),

different temperatures (10, 25 and 60 °C), different CO<sub>2</sub> partial pressures (0.01 and 0.1 MPa), and different water compositions (modified ASTM seawater and condensed water).

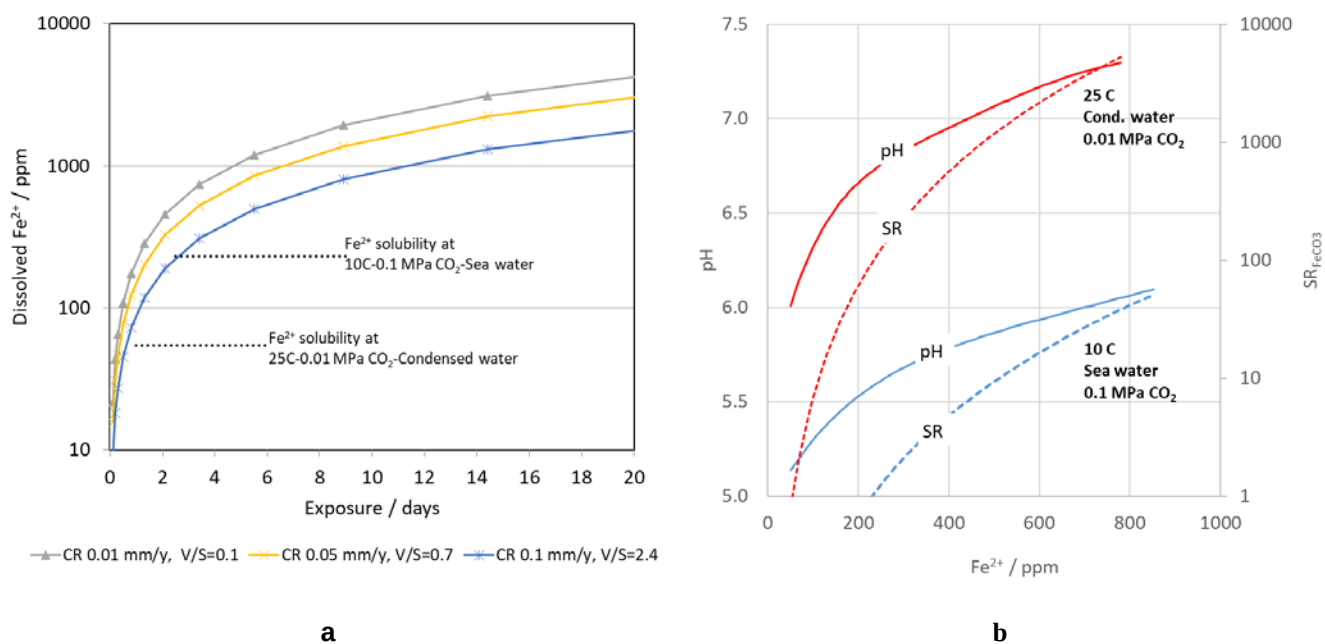


**Figure 2: Left (a): Accumulation of dissolved FeCO<sub>3</sub> as a function of exposure time for various corrosion rates and V/S ratios. Right (b): Calculated<sup>11</sup> pH and SR<sub>FeCO<sub>3</sub></sub> as a function of the concentration of FeCO<sub>3</sub>.**

## EXPERIMENTAL PROCEDURE

Armor wire specimens were exposed in small plastic containers (boxes/cylinders) mounted in a large test cell with temperature and gas composition control. An illustration of the test set up is shown in Figure 3. The experiments were performed at ambient pressure and the test cells were continuously bubbled with test gas to prevent ingress of air/O<sub>2</sub>.

The test specimens were either exposed in seawater without Ca (S.W.) or in distilled water with 1.65 g/l NaCl (C.W.).

Nine different wire steels were exposed in the experiments. The carbon content varied from 0.28 to 0.83 wt% and the yield strength from 616 to 1252 MPa. The wire specimens were exposed either “as received”, i.e. only degreased in acetone and isopropanol, or slightly abraded to remove previous corrosion film and/or features. The abrasion removed on average 2-3 μm steel.

The size of the specimens and the test containers were adjusted to give a V/S ratio of 0.7 and 2.4 ml/cm<sup>2</sup>. This corresponds to an annulus with a V/S ratio of 0.1 ml/cm<sup>2</sup> where the effective V/S ratio becomes 0.7 and 2.4 ml/cm<sup>2</sup>, respectively, when 14% and 4 % of the steel surface is actively corroding.

The concentration of dissolved FeCO<sub>3</sub> was measured in water sampled (0.05 ml) from the containers at various time intervals. A slight loss of water due to sampling and evaporation required occasional water replenishment to maintain the water level in the containers.

The average corrosion rates of the exposed specimens were estimated from mass loss after stripping of the corrosion film in inhibited hydrochloric acid. The corrosion rate is highest in the beginning of the exposure when pH and  $[\text{Fe}^{2+}]$  are low. Since the concentration of dissolved  $\text{Fe}^{2+}$  was measured frequently it is possible to estimate the corrosion rate in the first part of the exposure (i.e. before the onset of precipitation) based on the dissolved  $\text{Fe}^{2+}$  accumulation rate. The average corrosion rate in the second part of the exposure is then the mass loss corrected for the corrosion rate in the first part.

When  $[\text{Fe}^{2+}]$  is used to indicate the concentration of dissolved corrosion products in text and figures it is always assumed that the alkalinity in the liquid has increased with the same amount (equation 1).

A commercial software package was used to estimate pH,  $\text{pH}_2\text{S}$  and  $\text{SR}_{\text{FeCO}_3}$ .<sup>11</sup>



**Figure 3: Test setup for  $\text{SR}_{\text{FeCO}_3}$  experiments. Wires are exposed in small containers mounted in large test cells. The test cells are continuously gas flushed. Water samples are taken with a syringe through holes in the lids.**

## RESULTS

Test conditions and results are summarized in Table 1. The third column in the table shows the number of exposed specimens, the number of tested steel types, and the type of surface conditions, respectively. Column 7 shows the average  $[\text{Fe}^{2+}]$  for all the specimens (different steels and different surface conditions) at the end of the exposure. The corresponding standard deviation is given in column 8. Column 9 shows the estimated  $\text{SR}_{\text{FeCO}_3}$  for the average  $[\text{Fe}^{2+}]$  given in column 7. Corrosion rates estimated from mass loss and iron counts are given in column 10. Columns 11 and 12 show the estimated  $[\text{Fe}^{2+}]$  and  $\text{SR}_{\text{FeCO}_3}$  when the system is at steady state, i.e. a situation where the precipitation rate of  $\text{FeCO}_3$  equals the rate of releasing new dissolved corrosion products in the corrosion process.

Six different types of steel and two different surface conditions, altogether twelve different specimens, were exposed in experiment 1 (10 °C), 2 (25 °C) and 3 (60 °C). Figure 4a, c, and e show the measured  $[\text{Fe}^{2+}]$  as a function of time for all specimens. The  $[\text{Fe}^{2+}]$  vs. time curves followed the same trend, but the absolute values varied somewhat. The standard deviation of the measurements performed at the end of the exposure is given in column 8 in Table 1. A comparison of the average  $[\text{Fe}^{2+}]$  measured for all the abraded and all the degreased specimens are shown in Figure 4b, d, and f. Almost no difference in the average  $[\text{Fe}^{2+}]$  was observed for the two surface conditions. The spread in the  $[\text{Fe}^{2+}]$  vs. time curves seems therefore to be related to the steel composition/microstructure.