

ENVIRONMENTAL FACTORS

Environmental factors are external factors that affect how corrosion occurs. This includes the selection of the cathode reaction, the rate of the redox reaction and formation of protective coatings. The environmental factors that affect corrosion in pipelines with CO₂ present are reviewed.

pH

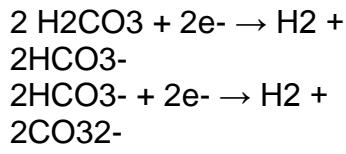
The pH of the solution strongly influences two different factors of the corrosion reaction, the electrochemical reactions that lead to iron dissolution and the precipitation of protective films on the pipe wall.

When there is an increase in the pH, the solubility of the Fe²⁺ and CO₃²⁻ ions is reduced, sometimes drastically depending on the pH. Precipitation of Fe(CO₃)₂ begins around a pH of 6 however it isn't until the pH is around 6.8, that the formation of a dense protective Fe(CO₃)₂ film begins. The precipitate that is formed below the pH of 6.8 is porous and relatively unattached to the pipe and does not offer very much protection. And can encourage pitting and mesa attack corrosion.

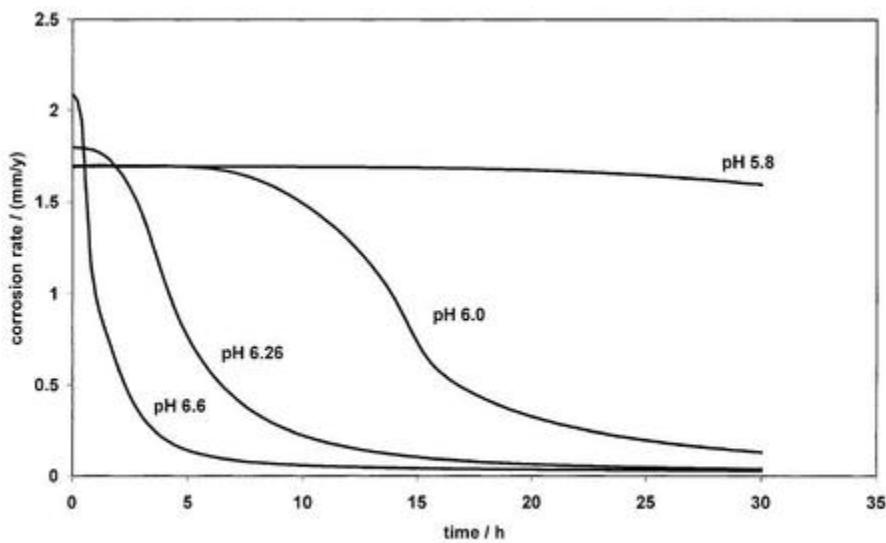
The effect that the pH has on the electrochemical reactions differs between the half reactions.



- The anode reaction (the oxidation of Fe) is not strongly dependent on the pH.



- Of the three reduction reactions available,



The predicted effect of pH on the corrosion rate for T=80°C, $P_{\text{CO}_2}=0.54$ bar, $c_{\text{CO}_2}=250$ ppm, $v=1$ m/s.

- When the pH < 4, the direct reduction of H⁺ is the dominant cathode reaction.
- Between 4 < pH < 6, the reduction of H₂CO₃ is the dominant reaction.
- Above a pH > 6, the cathode reaction takes on many different pathways.

A note on the reduction reactions, the direct reduction of H⁺ is largely flow dependent, which the reduction of H₂CO₃ is not, so the dominant cathode reaction can change at lower pH's depending on the pipe flow. Around a pH of 4, when there is high pipe flow the reduction of H⁺ is the dominant, and at low pipe flow, the reduction of H⁺ and H₂CO₃ are in similar amounts.

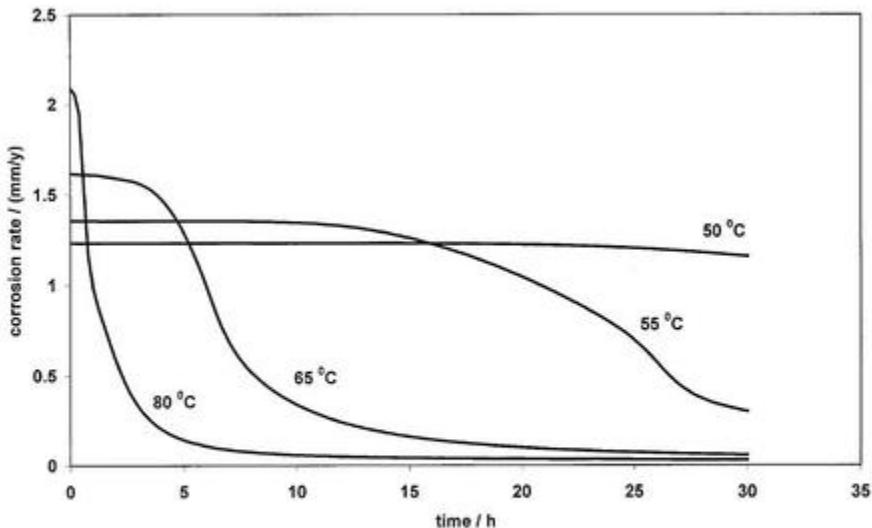
Temperature

Temperature affects the rate of corrosion indirectly, through the formation of a protective film. The solubility of FeCO₃ (which is the main compound that makes a protective film) decreases as the temperature increases, creating a supersaturated environment. As the water becomes more supersaturated with FeCO₃ the rate of precipitation increases to the point which the film formed is dense enough to create a barrier between the metal and oxidizing agents.

- When the temperature, T < 60 °C, the solubility of FeCO₃ is high and no film is formed unless the pH is increased. The rate of corrosion increases

- Between 60 °C < T < 80 °C the solubility of FeCO₃ decreases with temperature and the protective film starts to form, so the rate of corrosion starts to decline.

- When T > 80 °C FeCO₃ precipitate forms a dense film which drastically reduces corrosion rates.



The predicted effect of temperature on the corrosion rate for pH 6.6, $P_{CO_2} = 0.54$ bar, $c_{Fe^{2+}} = 250$ ppm, $v=1$ m/s.

Temperature also directly affects the rate of corrosion due to kinetics, so there is more heat or energy available, more molecules of Fe are oxidized because the activation energy is easier to achieve.

- So as the temperature increases, the rate of corrosion increases until at temperature in between 60 °C and 80 °C, where the formation of a protective film reduces the area of reaction.
- If no film was formed then the rate of corrosion would continue to increase with temperature.

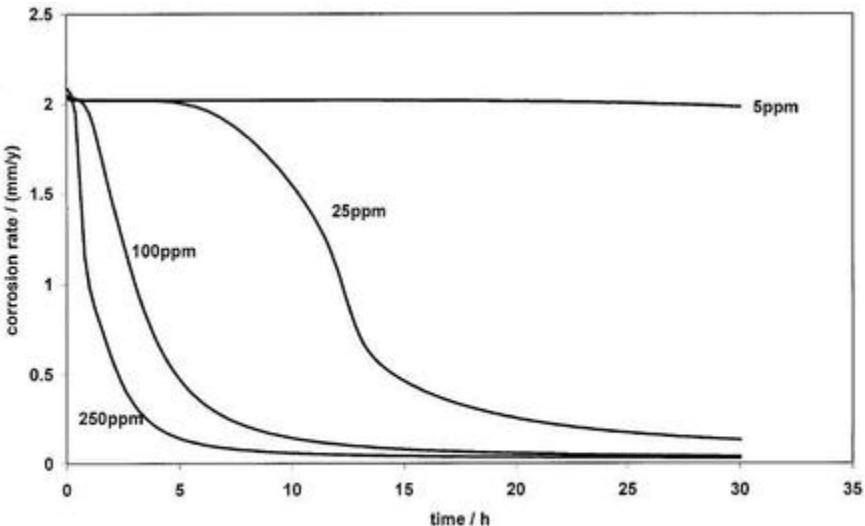
- When the temperature is about 90°C, any break in the protective film leads to heavy local corrosion.

Concentration of Fe²⁺ Ions

The concentration of Fe²⁺ ions has a direct effect on the rate of corrosion, as it is part of the anode reaction.



So when Fe²⁺ concentration is reduced, the reaction equilibrium is shifted to the product side and the rate of corrosion increases.

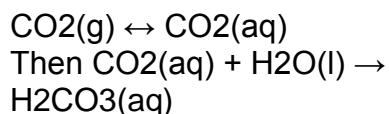


The predicted effect of Fe²⁺ concentration on the corrosion rate for T=80°C, pH 6.6, P_{CO₂} = 0.54 bar, v=1 m/s.

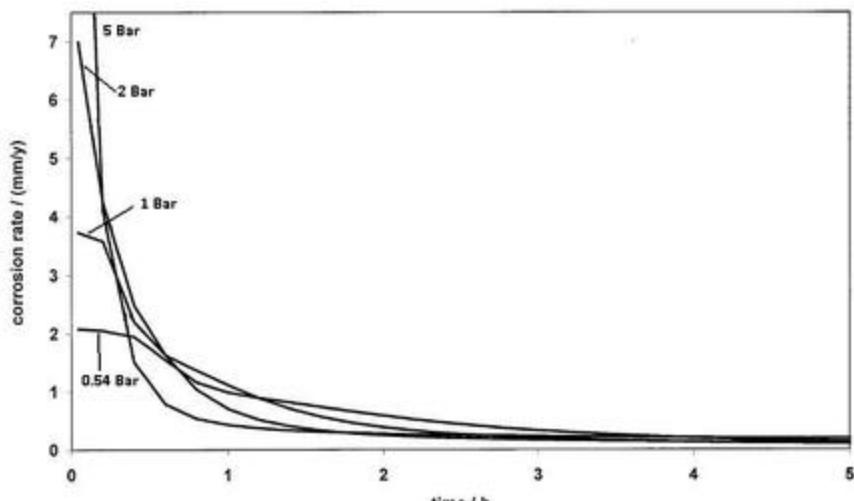
Partial Pressure of CO₂

The effects that the partial pressures of CO₂ have on corrosion are complicated and not yet fully understood, however there are still some general relationships that can be used.

First the partial pressure of CO₂ does not directly affect the corrosion reaction; CO₂ is a reactant in the formation of H₂CO₃.

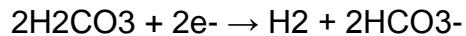


The higher the partial pressure of CO₂ the more dissolved CO₂ there is in the water, which shifts the equilibrium of the H₂O-H₂CO₃ system towards



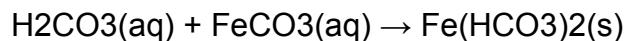
The predicted effect of CO₂ partial pressure on the corrosion rate for T=80°C, pH 6.6, c_{Fe²⁺} = 250 ppm, v=1 m/s.

the production of H_2CO_3 . So the partial pressure of CO_2 only effects one potential half reaction.



This means that the partial pressure of CO_2 only affects the rate of corrosion when the reduction of H_2CO_3 is the dominant or semi-dominant cathode reaction and usually means that the rate of corrosion increases.

The other way that the partial pressure of CO_2 can effect corrosion is by supersaturating the solution and causing $\text{Fe}(\text{CO}_3)_2$ to precipitate, forming a protective film on the metal. Again this is through the formation of H_2CO_3 .



However the formation of the protective film is dependent on the pH as well, so the partial pressure of CO_2 affects the rate of corrosion differently at different pH's.

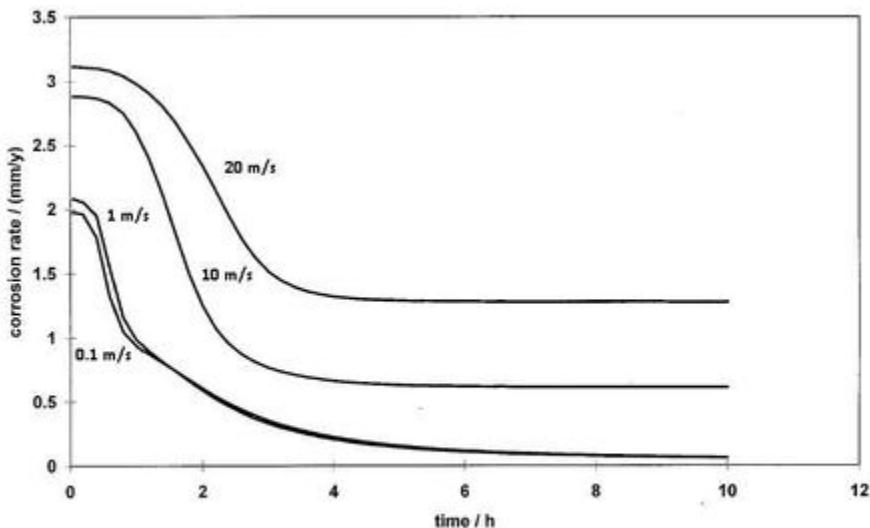
- $6 > \text{pH}$: No film is formed, corrosion rate increases with CO_2 partial pressure
- $6 < \text{pH} < 6.8$: A film is formed, but it is very porous and unattached to the wall, so it offers little corrosion protection, corrosion rate increases with CO_2 partial pressure
- $\text{pH} > 6.8$: A dense protective film forms, corrosion rate decreases with CO_2 partial pressure

So only at pH's above 6 does increasing the partial pressure of CO_2 cause more $\text{Fe}(\text{HCO}_3)_2$ to precipitate into a dense film that stops contact between the metal wall and the oxidizing agents in the water.

Hydrodynamics

The flowing velocity of the fluid effects corrosion two ways, the destruction of protective films and the reduction of ion concentration near the pipe wall.

When the flow rate is increased the rate of corrosion is only slightly increased due to removal of Fe^{2+} ions from near the wall. Because of the shift of the reaction equilibrium to the product side.



The predicted effect of velocity on the corrosion rate for $T=80^\circ\text{C}$, $\text{pH } 6.6$, $P_{\text{CO}_2}=1 \text{ bar}$, $c_{\text{Fe}^{2+}} = 250 \text{ ppm}$.



The flow regime of the fluid is very important as it largely affects the formation of protective films. When the flow is laminar, films can form without being stripped off. However, when the flow regime becomes transient or turbulent the protective film is removed and any further formation of a protective layer is prevented.

Transient and turbulent flow occurs at either high flow rate or when there is a change in geometry, so when the pipe diameter changes, there are irregularities on the pipe wall or where there is a bend in the pipe. However the general trend is the higher the flow rate, the faster the corrosion rate.

It is also noted that at high flow rates, the removal of Fe^{2+} ions from the bottom of pits begins to occur, and because the saturation of ions near the wall is decreased, the film formed in the pits are not as effective at corrosion prevention as the film is more porous and loose.

Wettability of Pipe Wall

The wettability of the pipe wall affects the contact area of corrosion, as hydrocarbons usually don't induce corrosion. It is the contact with H_2O , which carries the oxidizing agents, that allows corrosion to progress. The oil/gas being flowed through the pipeline typically contains water, and often, especially with oil, there is water added to aid flow. Oil is mainly discussed here.

The wettability of the wall is dependent on the fluid that touches the wall more, so when water is the fluid mainly in contact with the wall, it is called water wet. The more water wet the wall, the more the oxidizing agents carried by the water reacts with the pipe wall. At a low water cut (percent of total flowing volume) there is competition between the water and oil for contact to the pipe wall, so there is not continuous water contact with the wall. However for many oils, the water cut is over 30% which leads to having continuous contact with the wall. So the more water wet the pipe wall is, the more corrosion occurs.

Source : <http://co2corrosionchem409.wikispaces.com/Environmental+Factors>