

# DETERMINATION OF LEAKAGE AND UNACCOUNTED FOR GAS – TRANSMISSION LINES

Class #1070

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With the rewrite of 49 CFR 192 and 49 CFR 195, a different philosophy toward maintaining pipeline integrity has been introduced. Prior to the 1999, regulations were geared toward a more prescriptive approach, than risk based. Over all the safety record for product and gas transmission pipelines were excellent. Events in 1999 at Bellingham and at Carlsbad created a paradigm shift in how pipeline integrity was achieved and maintained.

The focus of this course will be an introduction into the realm of internal corrosion. The basic causes and mechanisms of internal corrosion will be addressed. The influences of flow, materials, and other factors will be covered for introductory purposes.

## PIPELINE CORROSION – THE BASICS

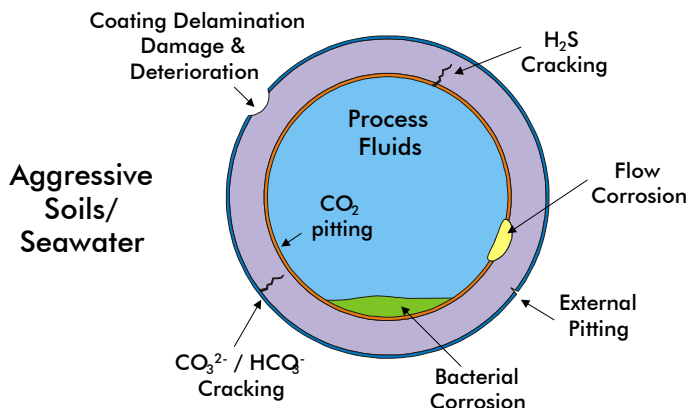
One of the areas of concern dealt with internal corrosion of pipelines. The natural state of iron is in

the form of iron ore. Iron pipe does not want to be iron pipe; it wants to be iron ore. The pipe will utilize whatever mechanisms available to return to the ore state.

Corrosion is the process by which iron pipe attempts to return to the ore state. Corrosion control is the interruption of that process.

Water is the cause of the internal corrosion in every case. Without water, internal corrosion would be all but nil. Water acts as an electrolyte, a carrier of electric charge, which allows corrosion to proceed in the form of a corrosion cell.

A corrosion cell is a reactive site at which the iron is leaving the pipe due to electrochemical reactions. In order for a corrosion cell to exist, four components must be in place in the system: On a pipeline, there are many sites in which corrosion can occur.



Many corrosion cells may be present under a single drop of water. Corrosion cells are extremely complex systems with many different chemical reactions depending upon the corrodents present. Some pipe may be predisposed to an extremely high number of

anodic sites on the interior of the pipe. Pure deoxygenated water is relatively non-corrosive in and by itself. What make water corrosive are the impurities that are added from outside sources or dissolved gases.

## Dissolved Gases

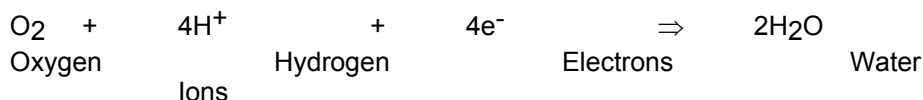
**Oxygen** corrosion is characterized by pitting attack. Dissolved oxygen corrodes steel more rapidly than does an equivalent amount of carbon dioxide or hydrogen sulfide. Also, a small amount of dissolved oxygen can drastically increase the corrosivity of water that contains carbon dioxide but particularly hydrogen sulfide. The oxygen reacts with the hydrogen sulfide to produce active sulfur compounds that are particularly corrosive. Oxygen is usually not present in subsurface waters. Pumps, especially centrifugal pumps, can suck in atmospheric oxygen through mechanical seals. Atmospheric oxygen can also be sucked into a line under pressure through small leaks if the fluid velocity is high or through loose mechanical/threaded couplings.

When oxygen is present, as in seawater, in the electrolyte, two cathodic reactions are possible. The cathodic reaction that occurs depends on the pH of the solution.

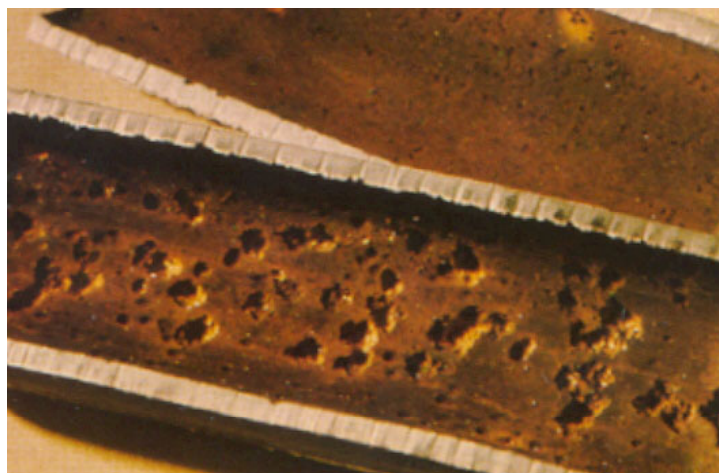
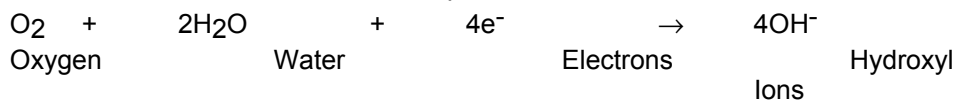
The rate reaction is determined by the availability of oxygen at the cathode area which is limited by the diffusion rate of oxygen from the bulk solution to the metal/solution interface (Concentration Polarization). Dissolved oxygen therefore acts as a cathodic depolarizer even at a concentration as low as 50 ppb in boiler systems and oxygen ingress usually results in pitting corrosion.

### Oxygen reduction reactions

In solutions with an acidic pH, the cathodic reaction is:



In solutions with a neutral or alkaline pH, the cathodic reaction is:



**Figure 1**      **Oxygen Pitting in a Steam Line**

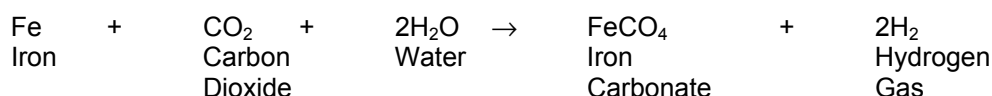
**Carbon Dioxide** (CO<sub>2</sub> corrosion is sometimes called “sweet” corrosion)

Carbon dioxide is a corrosive gas that is very soluble in water. It is usually present in petroleum or natural gas production and can cause significant damage when present at high concentrations.

The precipitation of iron carbonate (siderite) crystals produces a physical barrier on the metal surface but there are pores in the barrier that allow corrosive

species to continue to react with the steel substrate. In some oil fields organic compounds such as acetates will cause increased corrosion while high fluid velocities can result in mechanical (fatigue) damage leading to erosion corrosion. Carbon dioxide corrosion therefore often takes the form of a pitting attack, particularly under high flow conditions; the erosion type corrosion pits are usually deep with steep sides and sharp edges (mesa corrosion).

The overall CO<sub>2</sub> corrosion reaction is:



The solubility of carbon dioxide in water is affected by the pressure, temperature and composition of the water. The solubility of carbon dioxide increases as pressure increases. The partial pressure of carbon dioxide can be calculated to estimate the corrosivity of a fluid as:

$$P_{\text{CO}_2} = (X_{\text{CO}_2}) (p)$$

Where:

$P_{\text{CO}_2}$	=	the partial pressure of carbon dioxide
$X_{\text{CO}_2}$	=	the mole fraction of carbon dioxide in the gas stream
$p$	=	the total system pressure

The mole fraction of a gas, X, is equal to its mole percent divided by 100. In gas analysis, gas composition is usually reported in volume percent. Volume percent is equivalent to mole percent; therefore, the mole fraction of CO<sub>2</sub> is equal to the volume percent divided by 100. For example, the partial pressure of CO<sub>2</sub> in a gas system that operates at 1000 psig and contains 10 percent CO<sub>2</sub> can be calculated as follows:

$$\begin{array}{lclcl} X_{\text{CO}_2} & = & 10\%/100 & = & 0.1 \\ P_{\text{CO}_2} & = & (0.1)(1000) & = & 100 \text{ psi} \end{array}$$

If it is necessary to consider temperature, use the following equation developed by de Waard and Milliams of Shell International. The maximum corrosion rate for a “sweet” system can be calculated at any temperature and partial pressure of carbon dioxide. The equation describes corrosion conditions in systems without protective corrosion deposits. The equation is as follows:

$$\text{Log } r = 8.73 - \frac{2,320}{(T + 273)} - 5.55 \times 10^{-3} T + 0.67 \text{ Log } P_{\text{CO}_2}$$

Where:

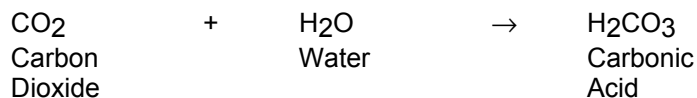
$r$	=	corrosion rate in mils per year
$T$	=	temperature in degrees Celsius
$P_{\text{CO}_2}$	=	partial pressure of CO <sub>2</sub> in pounds per square inch

The nomogram in Figure 2 is used to calculate carbon dioxide corrosion rates using the de Waard and Milliams equation.

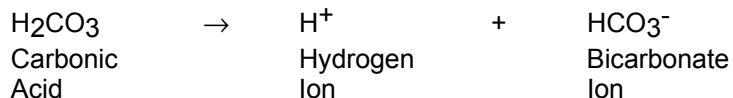
For example, At 120°C and 0.2 bar CO<sub>2</sub> partial pressure, the corrosion rate is 7 mpy.

The scale factor decreases the corrosion rate at high temperatures. Notice that even low partial pressures of carbon dioxide can produce high corrosion rates as the temperature increases.

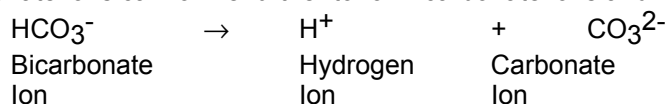
Carbon dioxide may be found in water as free carbon dioxide, disassociated carbonic acid, bicarbonate ions and/or carbonate ions. The following chemical reactions show how carbon dioxide increases the corrosivity of water. Carbon dioxide first dissolves in water to form carbonic acid:



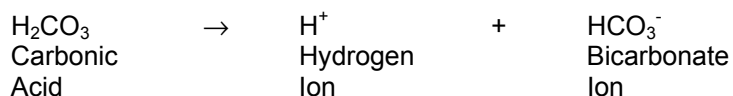
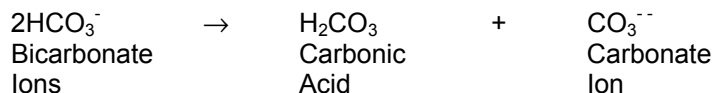
Carbonic acid then ionizes to form hydrogen and bicarbonate ions.



Bicarbonate ions can ionize further to form carbonate ions and more hydrogen ions.

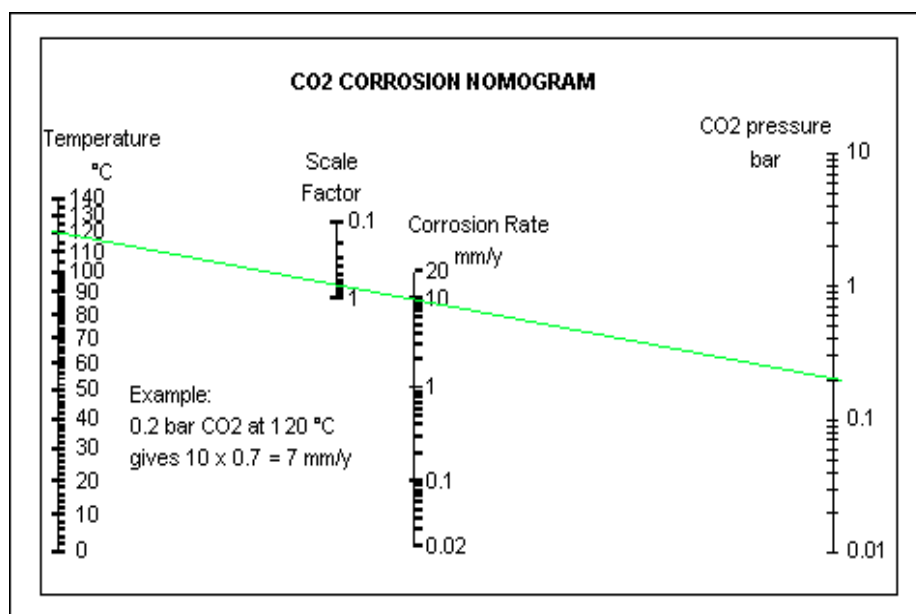


In higher acidic solutions (>pH 5) bicarbonate ions can produce more carbonic acid next to the iron substrate:



Increased cathodic current from the hydrogen ions provided by bicarbonate ions produces more corrosion than indicated by the pH values of produced fluids.

**CONTINUE TO NEXT PAGE...**



**Figure 2 de Waard and Milliams Nomogram for CO<sub>2</sub> Corrosion**

The effect of the concentration of CO<sub>2</sub>, system pressure, temperature and fluid flow can be seen in the simulations Figures 3 to 5 obtained using the NORSOK Standard M-506<sup>1</sup>.

It can be seen that at higher temperatures, above 70°C, the formation of the iron carbonate scale provides some protection.

Increasing the pH also significantly decreases the corrosion rate and in some sub-sea lines pH control is employed in conjunction with glycol injection used to prevent hydrate formation (mixed ice crystals of water and low molecular weight hydrocarbons).

The effect of flow (expressed as a fluid to wall shear stress), Figure 6C, shows an initial increase as the flow changes from laminar to turbulent flow but then only increases gradually. In very high flow conditions the corrosion rate accelerates due to erosion-corrosion (mesa-corrosion).

At low temperature in a sweet environment the surface composition is predominantly iron carbides and only thin iron carbonate films. At temperatures of 70°C and above, depending upon the pH, thicker semi-protective iron carbonate scales tend to form

which give greater protection. Iron carbonate crystals provides a physical barrier at the metal surface.

Sweet corrosion is usually controlled by the injection of corrosion inhibitors or in highly corrosive systems by the use of corrosion resistant alloys. However, in some systems it has been prevented with cement-lined pipe or with pipe that is internally coated with fusion bonded epoxy (FBE).

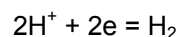
#### Summary of CO<sub>2</sub> Corrosion

The precipitation of iron carbonate scales at temperatures above 80°C results in a decrease in corrosion rates. At lower temperatures the films are relatively thin and corrosion inhibitors are often required to provide the protection necessary for long service life. The surface largely comprises cementite (iron carbide) with a thin layer of iron carbonate attached to the ferrite (iron rich) phase.

Corrosion at low temperatures & low pH (60°C & <pH 4) is determined by the rate of the iron dissolution reaction

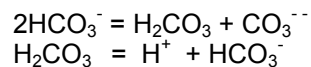


Corrosion at high temperatures (>80°C) is determined by the rate of reduction of hydrogen ions

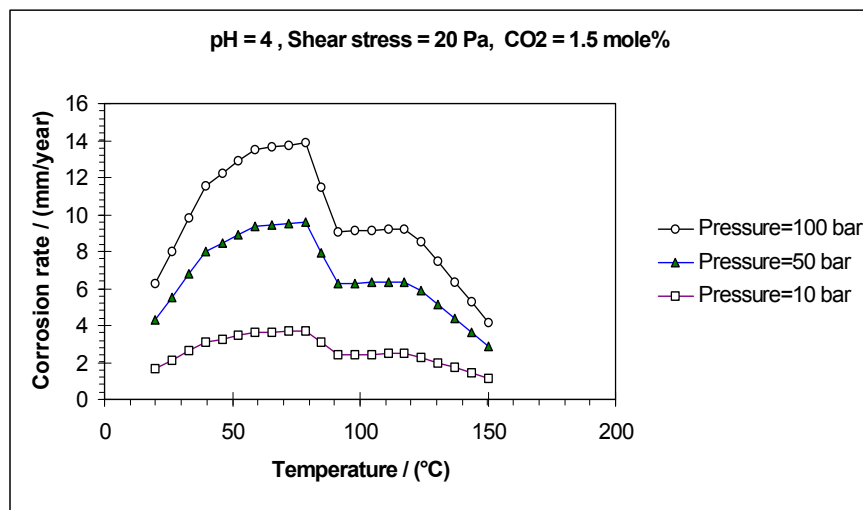


<sup>1</sup> "CO<sub>2</sub> Corrosion Rate Calculation Model" M-506, Norwegian Technology Standards Institution, <http://www.nts.no/norsok>

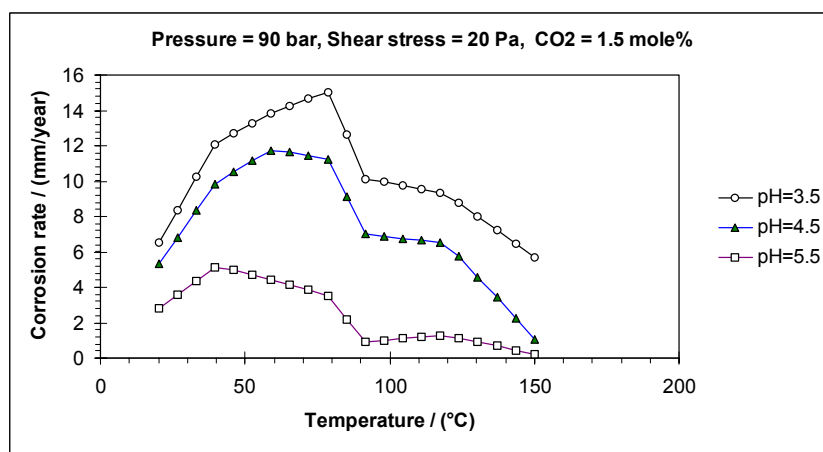
Bicarbonate ions produce carbonic acid next to the electrode to increase the  $H^+$  reduction reaction rate particularly at  $>pH\ 5$



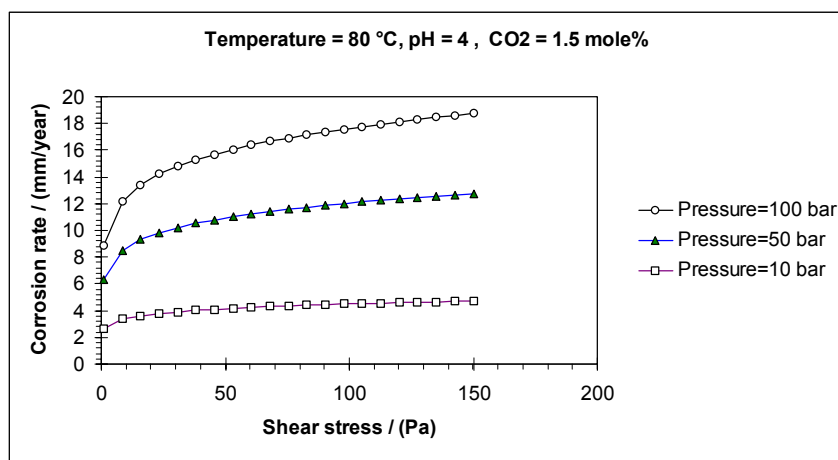
Increased cathodic current from bicarbonate ions produces more corrosion than indicated by the pH values.



**Figure 3 Effect of Pressure on CO<sub>2</sub> Corrosion**



**Figure 4 Effect of pH on CO<sub>2</sub> Corrosion**



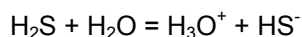
**Figure 5 Effect of Fluid Velocity (Shear Stress) on CO<sub>2</sub> Corrosion**

## Hydrogen Sulfide

Hydrogen sulfide (H<sub>2</sub>S) is a corrosive gas that is often present in produced fluids.

Hydrogen sulfide dissolves in water to form a weaker acid than carbonic acid (lower dissociation constant), but hydrogen sulfide has slightly higher solubility than carbon dioxide which can still give rise to high corrosion rates.

The weak acid dissociates to form hydrogen ions and bisulfide ions.



The hydrogen ions are responsible for the corrosive nature of H<sub>2</sub>S but the adsorption of bisulfide ions on the steel surface to form iron sulfide films also results in the diffusion of atomic hydrogen into the steel that can result in hydrogen damage (cracking processes).

Films are precipitated when the solubility product ( $K_{sp}$ ) of FeS is exceeded. Iron sulfide film formation is easier at high pH. The composition of iron sulfide corrosion deposits varies although the composition is often shown as FeS. Different crystalline structures of iron sulfide have been identified in oil field systems as illustrated in Figure 6.

There is continuing research and discussion regarding the formation and protective nature of sulfide films, however Figure 6 illustrates the major points of interest.

Iron sulfide deposits protect steel surfaces from general corrosion under many conditions but the degree of protection depends on the relative concentrations of H<sub>2</sub>S and CO<sub>2</sub>, the total pressure, temperature and the age of the film.

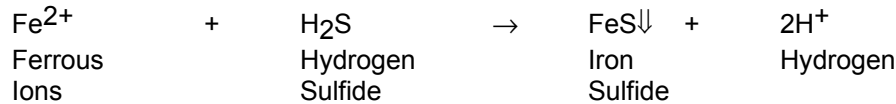
In mixed H<sub>2</sub>S and CO<sub>2</sub> environments with relatively high levels of H<sub>2</sub>S (for example, > 200 ppm in the aqueous phase) and particularly at temperatures above about 40°C black protective films (pyrrhotite) are formed below a gray loose film of carbonate and sulfide. The mechanism probably involves initial iron dissolution and precipitation of a mixture of iron carbonate and iron sulfide (amorphous/mackinawite). This provides a physical but porous barrier and then a compact protective film (passive iron sulfide) grows on the metal surface.

At lower H<sub>2</sub>S concentrations the protection is from mixtures of iron carbonate and iron sulfide films that are less compact, porous and less protective. The surface below the film is often metallic in appearance, indicating a thin carbonate film and cementite as in a CO<sub>2</sub> system.

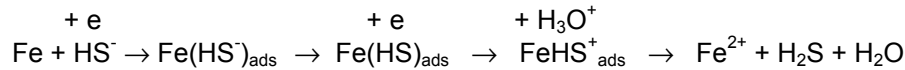
A small amount of H<sub>2</sub>S in a CO<sub>2</sub> system can increase the corrosion rate in a sweet system because ferrous ions are removed by reaction with sulfide ions. This increases the rate of iron carbonate dissolution, Figure 7.

At higher H<sub>2</sub>S concentrations the sulfide ions act in a similar manner as a corrosion inhibitor by forming iron sulfide films that decrease the general corrosion rate.

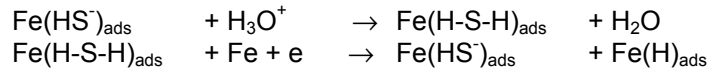
The general corrosion reaction is:



Hydrogen sulfide increases the kinetics of the iron dissolution reaction, the mechanism being catalyzed by adsorbed bisulfide ( $\text{HS}^-$ ) ions:

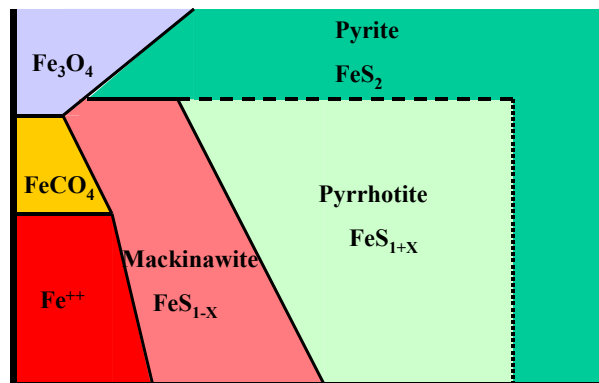


The cathodic reactions are also catalyzed by formation of adsorbed bisulfide ions that aid the reduction of protons to hydrogen atoms with regeneration of adsorbed bisulfide ions:



Adsorbed hydrogen atoms are both combined and evolved as molecular hydrogen gas ( $2\text{Fe}(\text{H})_{\text{ads}} \rightarrow \text{H}_2$ ) or absorbed into the steel substrate. Absorption and diffusion through the steel is the result of 'poisoning' of the combination reaction.

Temperature



Log (Partial Pressure  $\text{H}_2\text{S}$ )

**Figure 6 Surface Films on Steel in  $\text{H}_2\text{S}/\text{CO}_2$  Systems**

Some iron sulfide deposits are rich in iron ( $\text{FeS}_{1-X}$ ), called mackinawite (sometimes referred to as Kansite). Mackinawite is the iron rich sulfide that initially produced in most oil industry sour systems, although this probably crystallizes from an amorphous form of iron sulfide. Other iron sulfide deposits are rich in sulfur. Pyrrhotite ( $\text{FeS}_{1+X}$ ) is produced at higher sulfide concentrations and appears to be more protective against general corrosion than mackinawite. In oxygen free environments the iron rich mackinawite also appears

to convert to the sulfur rich pyrrhotite with time. At high temperatures,  $>200^\circ\text{C}$ , pyrite ( $\text{FeS}_2$ ) is formed. The ratio of iron to sulfur in the deposits depends upon both the environmental conditions of the system, the composition of the electrolyte

Hydrogen sulfide often causes pitting. The susceptibility to pitting depends on the films formed as determined by the temperature and concentrations of the  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , Figure 8.



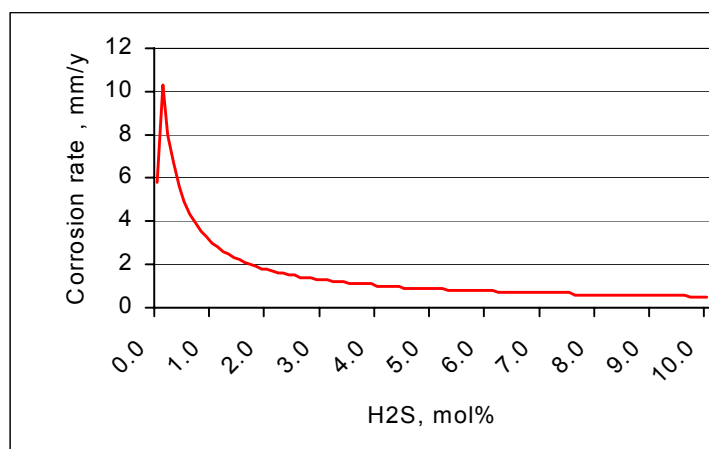
At high ratios of  $\text{CO}_2$  the attack tends to general corrosion but as the ratio of  $\text{H}_2\text{S}$  increases there is increasing localization of attack (but not true pitting). Mixed carbonate and sulfide films are semi-protective, poorly adherent and easily removed. At low  $\text{CO}_2$  ratios the sulfide films are adherent and protective but subject to breakdown and pitting corrosion.

Pitting may be quite severe in some areas, Figure 9, because iron sulfide is cathodic to steel. Any exposed steel becomes the anode of a *galvanic corrosion cell*.

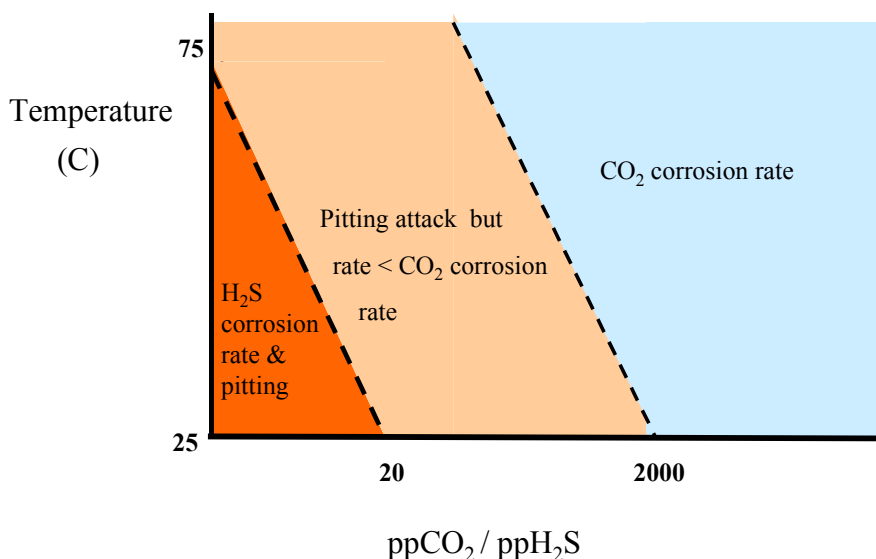
Pitting occurs at areas where protective iron sulfide (pyrrhotite) does not fully cover steel surfaces.  $\text{H}_2\text{S}$  acts like a 'dangerous' anodic inhibitor, a large

amount inhibits corrosion but a small amount may fail to cover up all the possible anodic sites and penetration at these local sites is accelerated. The most important factor is depletion of  $\text{H}_2\text{S}$  (the "inhibitor") within the pit. Depletion occurs because ferrous ions emerging from the pit precipitate  $\text{H}_2\text{S}$  as  $\text{FeS}$  before it can reach the pit surface. This  $\text{FeS}$  that is precipitated away from the pit surface has no protective effect.

Temperature and pressure affect the solubility of oxygen, carbon dioxide, and hydrogen sulfide in the same way. An increase in temperature reduces the solubility of dissolved  $\text{H}_2\text{S}$  in an open system. A very small amount of oxygen can increase the corrosion rate due to the production of active sulfur.



**Figure 7** Effect of  $\text{H}_2\text{S}$  on Corrosion Rates in a 20 mol %  $\text{CO}_2$  System



**Figure 8** Effect of  $\text{H}_2\text{S}$ :  $\text{CO}_2$  Ratios on Corrosion



**Figure 9 Pitting in a Sour System**

Hydrogen sulfide causes various forms of hydrogen damage:

- hydrogen embrittlement
- hydrogen-induced cracking
- blistering of steel
- sulfide stress cracking
- stress orientated hydrogen induced cracking

In most acids hydrogen is generated as gas bubbles in the process fluid. In sour systems the atomic hydrogen produced electrochemically diffuses into, and then through, the steel substrate. Atomic hydrogen can cause embrittlement when the interstitial concentration is high at regions of high stress.

Temperature also affects sulfide stress cracking, hydrogen embrittlement, and hydrogen-induced cracking of steels in  $H_2S$  service. Sulfide stress cracking and hydrogen embrittlement are most likely to occur at temperatures up to  $65^\circ C$  ( $150^\circ F$ ).

<b>Hydrogen Induced Cracking</b>	<p>HIC</p> <p>Stepwise Cracking</p> <p>Hydrogen Blistering</p>	
<b>Sulfide Stress Cracking</b>	<p>SSC</p> <p>A form of stress corrosion cracking often associated with high hardness and high stress, for example welds</p>	
<b>Stress Orientated Hydrogen Induced Cracking</b>	<p>SOHIC</p> <p>Combination of HIC and SSC</p>	

**Figure 10 Typical Hydrogen Damage**