

Fundamental Aspects of CO₂ Metal Loss Corrosion

Part I: Mechanism

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ABSTRACT

Carbon steel is thermodynamically unstable in water with dissolved CO₂ and the only reason that carbon steel is so attractive and can be so widely used in oil and gas production is that the steel surface becomes covered by a protective layer of corrosion products, oil, mineral scale or inhibitors. It is relatively easy to predict and explain the high corrosion rates on bare steel. The real challenge is to reduce the corrosion and that requires knowledge about the performance of the protective layers, means to predict the breakdown of the layers and methods and techniques to ensure that robust layers form on the surface.

The paper discusses how CO₂ affects the water chemistry, the electrochemical reactions on the bare steel surface, and the initiation and growth of protective corrosion product films. As many sweet systems contain organic acids that affect the solution chemistry and the formation and stability of the FeCO₃ corrosion product films, organic acids need also to be considered when the effect of CO₂ is discussed.

Keywords: CO₂ corrosion, carbon steel, internal corrosion, mechanisms, corrosion films

INTRODUCTION

The mechanism of carbon steel corrosion in a CO₂ containing environment has been studied and debated for decades. Hundreds of papers related to CO₂ corrosion have been published and a large variety of corrosion rates and mechanisms have been reported. Oil companies and research institutions

have analyzed the data and developed a number of prediction models¹ to take account of the various parameters that determine the corrosion rate. The models give up to two decades difference in the predicted CO₂ corrosion rate and it all depends on how the various parameters are treated and how much conservatism that is built into the model.

In order to explain the confusion and the apparently contradictory observations and results that have been seen and reported, it is important to realize that the term “CO₂ corrosion” and the effect of CO₂ is not related to one mechanism only. A large number of CO₂ dependent chemical, electrochemical and mass transport processes occur simultaneously on and close to the corroding steel surface. The various reactions respond differently to changes in CO₂ partial pressure, temperature, water chemistry, flow and other operational parameters. All the reactions should be taken into account when corrosion in a CO₂ containing environment is to be quantified and explained.

Many researchers have studied and discussed the electrochemical reactions taking place on the bare steel surface. The mechanisms that control the rate of the electrochemical reactions are of great academic interest, but are less important when it comes to the practical application of carbon steel. When carbon steel is directly exposed to water and CO₂ the bare steel corrosion rate will under almost all circumstances become prohibitively high for practical use in oil and gas production. This is illustrated in Figure 1 where the corrosion rate has been predicted² for various CO₂ partial pressures and pH values as a function of temperature. The corrosion rate predicted up to 40 °C apply for bare steel, while partly protective films are formed at higher temperature. It is seen that the corrosion rates are in the order of several mm/year, even at CO₂ partial pressures below 0.5 bar, i.e. pressures where the old “rule of thumb” says that carbon steel can be applied without any treatment³.

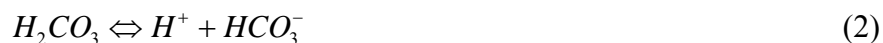
In the present paper it is focused on fundamental corrosion mechanisms in sweet systems. Three major effects of CO₂ will be addressed: The effect on the water chemistry, the effect on the electrochemical reactions, and the impact on the initiation and growth of corrosion product films. As many sweet systems contain organic acids that affect the solution chemistry and the formation and stability of the FeCO₃ corrosion product films, organic acids also have to be included in the discussion. The effect of other parameters is discussed in the paper “Fundamental Aspects of CO₂ Metal Loss Corrosion, Part II: Influence of different Parameters on the CO₂ Corrosion Mechanism”⁴

CO₂ AND THE EFFECT ON WATER CHEMISTRY AND pH

When CO₂ is dissolved in water it is partly hydrated and forms carbonic acid:

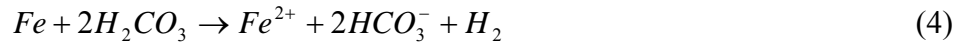


Carbonic acid is diprotic and dissociates in two steps:



The resulting pH is a function of the CO₂ partial pressure. This is illustrated in Figure 2 where the pH has been calculated [#] as a function of CO₂ partial pressure in unbuffered water and in water with 1, 10 and 100 mM alkalinity respectively. The pH decreases with increasing CO₂ partial pressure. When the water is buffered, the pH increases but the dependency of the CO₂ partial pressure follows the same trend as for pure water.

When the steel corrodes, Fe²⁺ and an equivalent amount of alkalinity are released in the corrosion process.



The pH in the solution increases and when the concentrations of Fe²⁺ and CO₃²⁻ ions exceed the solubility limit, precipitation of FeCO₃ can occur:



When solid FeCO₃ is formed at the same rate as the steel corrodes, the pH becomes constant in the corroding system.

The solubility of FeCO₃ is strongly dependent on the pH and the CO₂ partial pressure. This is illustrated in Figure 3 where the amount of Fe²⁺ needed to be produced by corrosion to reach FeCO₃ saturation is plotted as function of pH at the start of the corrosion process (1 wt% NaCl). It is seen that [Fe²⁺]_{sat} is much higher in condensed water than in typical formation water with a pH above 5. When the system is pH stabilised at pH 6.5-7.5, [Fe²⁺]_{sat} is only a fraction of a ppm and is reduced 100 times per unit pH increase. It is important to note that the solubility curves in Figure 3 are not parallel and they cross in the range pH 4.5 to 5. The consequences are illustrated in Figure 4 where the pH is kept constant while the Fe²⁺ solubility is plotted as a function of CO₂ partial pressure. It is seen that the solubility of Fe²⁺ goes through a maximum for pH 5 and 5.5. At lower pH the solubility increases with increasing CO₂ partial pressure while the trend is opposite at pH 6. As the pH is often used as an indicator for the corrosivity of produced water it should be noted that corrosion films form more easily at pH 5 with very high CO₂ partial pressures (>> 1 bar) than with 1 bar CO₂⁵. When comparing the corrosivity of various waters, a higher pH will always give less contribution from the H⁺ reduction reaction, but the pH cannot be used directly to predict the likelihood for formation of protective corrosion product films.

The presence of HAc and other organic acids makes the water chemistry much more complex. The interaction of HAc has been discussed in detail in two recent review papers by Crolet and Bonis⁶ and by Gulbrandsen⁷. HAc is a weak acid that is readily soluble in water. The equilibrium HAc partial pressure over a 1 mM HAc solution is less than 1 Pa at temperatures up to 100 °C. As pointed out by several authors^{7,8}, HAc is often referred to as a stronger acid than carbonic acid in the literature. The source of this confusion is that dissolved CO₂, and not only H₂CO₃, is often erroneously included in the term “carbonic acid”. The dissociation constant K_a of H₂CO₃ according to eq. (2), expressed as

[#] Sol1.81: IFE in-house pH and solubility program developed for water and mixed water and glycol systems

pK_a , is about 3.5 at 25 °C, i.e. lower than for HAc, which has a pK_a of about 4.8. Accordingly, H_2CO_3 , which is the main cathodic reactant in CO_2 corrosion,⁹⁻¹¹ is a stronger acid than HAc. A consequence of this is that H_2CO_3 has a higher reaction rate constant than HAc⁸.

The concentrations of HAc in the water can typically be a few mM. Crolet and Bonis¹² have proposed a classification where less than 0.1 mM HAc is regarded to give only slightly increased risk of corrosion, while concentrations of more than 1 mM significantly increases the corrosivity. Undissociated HAc concentrations of more than 10 mM have been reported in some fields.

Acetic acid dissociates according to equation 6:



The three equilibria in eqs. 2,3 and 6 are linked through the same H^+ concentration and form a two-buffer system. The shift in pH due to the presence of acetic acid and the effect on $FeCO_3$ solubility can be calculated by solving these equations together with eq. 5 for $FeCO_3$ solubility. The shift in $[Fe^{2+}]_{sat}$ at 0.1, 1 and 10 mM HAc respectively is given in Figure 5. The relative increase in solubility is highest at low pH. The increase was about 0.2, 3 and 8 times when the undissociated HAc concentration was 0.1, 1 and 10 mM respectively in condensed water.

As discussed by Gulbrandsen⁷, Fe^{2+} and Ca^{2+} can form acetate complexes^{13,15} according to eqs. 7-9:



In formation waters with high content of calcium, a significant fraction of Ac^- can therefore be present as $CaAc^+$. Since the concentration of bicarbonate and $HAc+Ac^-$ is used to estimate the in situ pH in formation water, it might be important to take complex formation into account, particularly for high Ca^{2+} brines and high temperatures.

ELECTROCHEMICAL REACTIONS AT THE BARE STEEL SURFACE

Cathodic reactions

A large number of papers have proposed and discussed various cathodic and anodic reactions on the steel surface in the presence of CO_2 . Most of these reactions have recently been reviewed, discussed and summarized by Nestic et al^{11,14,16} and Garsany et al⁸. The three main cathodic reactions appear to be:



Equations 10-12 are the overall reaction routes and do not indicate the detailed mechanisms of the proton reduction. The relative contribution from each of these reactions depends on the concentrations, temperature, pH, convection etc. The presence of CO₂ affects all the reactions directly or indirectly by affecting the H⁺ concentration and the amount of undissociated HAc and H₂CO₃.

In strong acids, which are fully dissociated, the rate of hydrogen evolution occurs according to eq 10 and cannot exceed the rate at which H⁺ ions are transported to the surface from the bulk solution (mass transfer limit). Its contribution to the corrosion rate is small above pH 5, a typical pH in formation water. H₂CO₃ serves as an additional source of H⁺ ions¹⁷ that enables the hydrogen evolution reaction to proceed at a much higher rate than in a solution of a strong acid at the same pH.

Although it is still debated, it seems to be widely accepted that cathodic reduction of protons from molecular H₂CO₃, also referred to as “direct H₂CO₃ reduction”, may take place^{8,11,18-22} (eq 11) and thus contribute to an increase in the corrosion rate beyond the limits of the H⁺ reduction rate. One suggested mechanism is that H₂CO₃ adsorbs and reacts on the electrode^{18,19,20}. Another proposed mechanism is formation of H₂ from direct reduction of H₂CO₃. The rate determining step is assumed to be slow hydration of CO₂^{8,11,21-24}, at least at temperatures below 50-60°C. It was found to be activation controlled above this temperature¹¹. It should be noticed that the term “direct reduction” has not been well defined and the actual mechanism is unclear.

It has been well documented that the presence of HAc has a detrimental effect on the corrosion rate and the morphology of the attack in sweet systems when the concentration of undissociated HAc exceeds 0.1-1 mM. The effect of organic acids was debated in the early 40'sies, and then almost forgotten before the topic was revitalized by Crolet and Bonis in the 80'sies. Recently Crolet and Bonis presented a review paper that sums up much of their work⁶. In this paper it is focused on the effect of the water chemistry, the pH and how the stability of the iron carbonate films is reduced in the presence of HAc. Crolet and co-workers found that HAc increased the cathodic limiting current²⁵ and that the anodic reaction was inhibited by HAc²⁶. Although HAc affects both the cathodic and anodic reaction mechanisms, the effects have been regarded as secondary, with minor consequences for the corrosion attack seen in the field⁶.

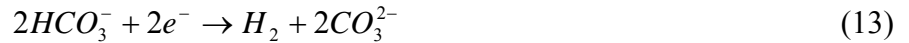
Over the last 10 years there has been a growing awareness amongst operators and researchers for the accelerated corrosion caused by organic acids. A large number of papers have addressed the HAc issue and tried to shed more light on the mechanisms. Most of these papers have been discussed and summarized in Gulbrandsen's review⁷.

Little work addresses directly the basic effects of HAc on the anodic and cathodic reactions. The increased cathodic limiting current and the inhibition of the anodic reaction reported by Crolet et al have been seen also by other workers^{7,8,9,10}. Gulbrandsen⁷ reported that localised attacks were formed

at low temperature. This was attributed to the inhibition of the anodic reaction, not the formation of a corrosion product film.

As for the case of H_2CO_3 , it has not been fully agreed whether HAC is directly reduced at the surface or only acts as an extra source of H^+ . Sun et al reported that the H_2 evolution from HAC was activation controlled at room temperature and that HAC acts solely as an additional source of hydrogen ions. Garsany et al did voltammetry studies that showed two waves related to H^+ and HAC reduction respectively^{8,9}. Since the dissociation of HAC is very fast, it was not possible to distinguish between the reduction of HAC and the reduction of H^+ after dissociation.

It has been suggested that direct reduction of the bicarbonate ion^{27,28} and water^{11,29} can become important at low pCO_2 partial pressure and high pH:



The concentration of HCO_3^- increases with pH and becomes more than 300 times the H_2CO_3 concentration at 1 bar CO_2 and pH 6. Although the concentrations can be high, the low dissociation constant makes bicarbonate (pK ca. 10) and water poor proton donors and it is believed that the contribution from these reactions will be negligible under normal sweet conditions. However it is difficult to experimentally distinguish the effect of this particular reaction mechanism for hydrogen evolution from eqs 10 and 11.

A high bicarbonate concentration might also affect the corrosion rate by enabling the regeneration of the reactant (H_2CO_3)³⁰. It is therefore not necessary to consider bicarbonate reduction to explain the observed increase in current at $pH > 6$.

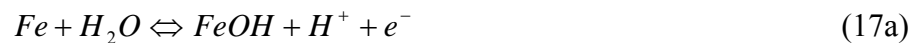


Anodic reactions

The overall anodic dissolution of iron is given in equation 16:



This reaction, which has a pH dependent rate in accordance with Bockris experimental results³³, has been extensively studied and the various reaction steps have been discussed in detail by Drazic³¹ and Lorenz and Heusler³². The mechanism suggested by Bockris et al.³³ for strong acids



has frequently been assumed to apply in CO₂ solutions^{18,20,21,28}. As pointed out by Nescic¹⁴, it has been overlooked that the experimental data indicated that the pH dependency decreased rapidly with increasing pH. The reaction order with respect to OH⁻ was 2 at low pH but decreased towards 1 and 0 at pH>4. In a study by Nescic et al.³⁴ it has been confirmed that the anodic dissolution of iron does not depend significantly on OH⁻ concentration above pH 4, but is affected by the presence of CO₂, as previously indicated by Davies and Burstein³⁵ and Videm³⁶.

The following iron dissolution rate equation was derived from experimental results and proposed by Nescic et al³⁴:

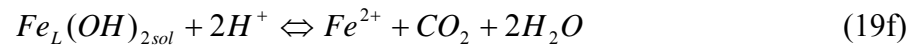
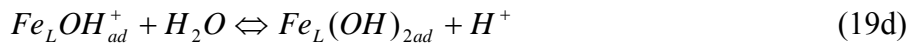
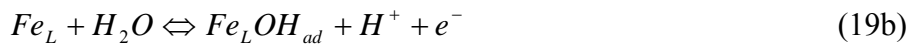
$$i_a = k[OH^-]^{a_1} (p_{CO_2})^{a_2} 10^{\frac{E}{b_a}} \quad (18)$$

where for:

pH<4	→	a ₁ = 2	b _a =0.03 V per decade
4<pH<5	→	a ₁ = 2-0	b _a =0.03-0.12 V per decade
pH>5	→	a ₁ = 0	b _a =0.12 V per decade

pCO ₂ < 10 ⁻² bar	→	a ₂ = 0
10 ⁻² <pCO ₂ < 1 bar	→	a ₂ = 1
pCO ₂ > 1 bar	→	a ₂ = 0

They also proposed a mechanism to explain the experimental results at pH>5:



where Fe_L denotes the complex Fe-CO₂. They assumed that the complex is formed as an adsorbed species at the electrode surface that catalyses the dissolution of iron. For pH<4, it is postulated that the rate of charge transfer step 19c will increase, and the desorption step 19e will then be rate-

determining. The problem in such model consideration is to document the existence of the intermediates.

CO₂ AND HOW IT AFFECTS THE PROTECTIVE FILM FORMATION

Film formation is a complex process and the precipitation rate of iron carbonate is the main controlling factor in sweet systems. The morphology and the composition of the film determine whether an attack develops as worst case corrosion, low corrosion with protective films or mesa corrosion. The layer also influences the corrosion inhibitor access and availability at the surface and therefore plays an important role for inhibitor performance^{37,38}

A number of papers address the film properties and how the films are formed. Much of this work has recently been discussed and referenced by Kermani³⁹. In the present paper it will only be focused on some fundamental principles and trends.

The driving force for precipitation is the supersaturation of FeCO₃. The precipitation rate is generally slow, and a high degree of supersaturation of iron carbonate in the water is necessary in order to get sufficient amounts of iron carbonate deposits on the steel surface. Whether it deposits or not depends amongst other factors on the kinetics of precipitation and on how it is anchored to the surface.

In principle there are two steps involved in the precipitation processes; nucleation and particle growth. It is assumed that the rates of these processes are related to the relative supersaturation (RS) where S is the supersaturation, Q is the concentration of the solute at any instant, Q_{eq} the equilibrium solubility and K_{sp} the solubility product for FeCO₃

$$S = \frac{C_{Fe^{2+}} \cdot C_{CO_3^{2-}}}{K_{sp}} \quad (20)$$

$$RS = \frac{Q - Q_{eq}}{Q_{eq}} = (S - 1) \quad (21)$$

The rate of nucleation is believed to increase exponentially with relative supersaturation, whereas the rate of particle growth bears an approximately linear relationship to this parameter. Growth should therefore predominate at low relative supersaturation. When the supersaturation is high, the exponential dependency of nucleation rate may cause this process to occur to the near exclusion of particle growth and a colloidal solution might form close to the steel surface or inside the film. Coagulation might therefore be important for protective film formation under these conditions. Coagulation is accelerated by heating, and increasing ionic strength.

Calculated supersaturation for a sweet system with various CO₂ partial pressures is given as a function of the pH in the brine in Figure 7. It is assumed that a steady state corrosion process is established that gives 30 ppm dissolved Fe²⁺ in the water, and that the pH referred to is the pH in the brine before corrosion products are dissolved. It is seen that the supersaturation in a brine with a certain pH increases substantially when the CO₂ partial pressure is increased. The higher supersaturation gives a higher precipitation rate and increased likelihood for film initiation and formation. The results fit with the observation that a higher pH is required for protective film initiation/formation when the CO₂ partial pressure is low.

Fe²⁺ will be produced in the solution at the metal surface while the H⁺ concentration is reduced on the steel surface or on the film surface if the film is of the conducting type (iron carbide). The resulting concentration gradients might give a higher supersaturation in the film and on the metal surface and that will increase the precipitation rate locally. These effects have been modeled in detail by Nesic et al^{14,16} and have been included as an integral part of the corrosion models developed at IFE¹⁶ and Ohio University⁴⁰.

It has been reported several studies on the growth rate of FeCO₃^{41,42,43}. Calculated growth rates based on Johnson and Tomson's work⁴¹ is shown as an example in Figure 6. It is seen that the predicted growth rate is very low at 20 °C, but increases fast when temperature and supersaturation increase.

The general description of the growth and nucleation mechanisms given above fit with many of the observations in the authors laboratory⁴⁴. Figure 8 shows some corrosion films formed in various experiments. At high temperature (> 60 °C) the precipitation rate is fast and the supersaturation low. Under these conditions dense crystalline films are formed which often give good protection. At lower temperature (< 40 °C) a much lower precipitation rate is experienced, and the relative supersaturation can therefore become very high when dissolved iron carbonate is accumulated. Under these conditions where the relative supersaturation is high a corrosion film with low crystallinity is expected. The expectation is consistent with the appearance of the films actually formed, which are porous, loosely adherent, more or less non crystalline and much less protective than those formed at higher temperatures.

The critical part of the film forming process is the initiation. If the temperature and the supersaturation in the bulk phase are high, a massive precipitation takes place and a dense iron carbonate film can form on most steel surfaces. At lower temperatures and precipitation rates, however, protective film may never form if the steel surface is cleaned (sand blasted, descaled) and continuously exposed. A stagnant period or a semi dry period where high local supersaturation can be achieved⁴⁴ may therefore be necessary in order to start the deposition of iron carbonate on the steel surface. Experiments have indicated that quenched and tempered low carbon steel are more dependent on such a trigger mechanism than ferritic pearlitic steels, where the pearlite colonies can form a porous network on the surface suitable for anchoring iron carbonate precipitate when the steel is corroded. Once a protective film has formed, however, there is apparently no systematic difference in the ranking of the two steel types when it comes to the development of localized attack. Since small differences in the steel composition and the microstructure can affect the anchoring properties and the development of localized attack, it is not surprising that large differences in the performance of similar carbon steels have been seen in both field applications and laboratory work.

Protective film formation is accelerated by all measures which restricts the transport of reaction products from the surface and which can anchor the corrosion product. Freshly ground specimens studied in the laboratory are therefore much more susceptible to high corrosion rates compared to real pipelines, where an oxide layer is grown during rolling and storage. It can be discussed whether it is the oxide films, which keep the corrosion rate low in the long run, or if the oxide films play an intermittent role only as an initiator for protective iron carbonate films.

Experiments have shown that an apparently dense corrosion film is attached directly to the metal surface when good protection is obtained, while a porous film, sometimes filled with iron carbonate in the outer part only, is formed when poor protection is obtained. A mechanism for how iron carbonate film can form close to the metal surface has been suggested⁴². It is assumed that the growth rate of iron carbonate has to be equal or higher than the corrosion rate. If the growth rate is less than the corrosion rate, the gap between the iron carbonate filled part of the film and the steel surface will never be filled with dense iron carbonate, and the corrosion film thus formed will be porous or non adherent, see Figure 8b. In order to get an iron carbonate growth rate matching a corrosion rate of 1 mm/y at 40 °C, about 50 times supersaturation is necessary according to Figure 6. Such high supersaturation can apparently be established close to the steel surface when the dissolved iron content is high and a surface layer like rust, mill scale etc restrict the transport of reactants and corrosion product. The maximum supersaturation will then be a balance between the corrosion rate, nucleation rate and the rate of transport.

Once a reasonably dense corrosion product film has formed it can be speculated on whether it is the reduced transport through the iron carbonate film or the formation of a passive film which reduces the corrosion rate⁴⁵. Experiments showed that the steel shows passive-like behavior at high pH. High pH can be obtained close to the steel when the transport of reactants and corrosion products are restricted by the deposited corrosion products.

CONCLUSIONS

Carbon steel is unstable in water with dissolved CO₂ and the only reason that carbon steel can be so widely used is that the surface becomes covered by a protective layer of oil, corrosion products, mineral scale or inhibitors.

CO₂ is assumed to contribute to the cathodic reaction rate in two different ways. H₂CO₃ can be directly reduced and dissociation of H₂CO₃ can serve as a source of H⁺ ions. The rate determining step is the CO₂ hydration reaction below 50-60 °C. Activation control has been reported at higher temperatures.

The presence of CO₂ does not seem to affect the anodic reaction significantly in the pH range 4-6 when the acetate concentration is low.

Acetic acid serves as an additional source of H⁺. It is uncertain whether it also can be directly reduced.

The presence of CO₂ affects all the proposed cathodic reactions directly or indirectly by affecting the H⁺ concentration and the amount of undissociated HAc and H₂CO₃. When a sweet system contains

HAc, the relative contribution from the various reactions depends on the concentrations, temperature, pH, convection etc.

The solubility and precipitation of FeCO_3 is a function of a large number of parameters where $p\text{CO}_2$, $\text{HAc}+\text{Ac}^-$ concentration, temperature and the amount of dissolved corrosion products are the most important parameters. A computer program is necessary in order to account for all the parameters. Some general trends and special effects are:

- The amount of FeCO_3 that can be dissolved in a brine goes through a maximum at around 1-2 bar CO_2 for a given pH in the range 4.5-5.5.
- The supersaturation of FeCO_3 at a given pH and Fe^{2+} concentration increases with increasing CO_2 partial pressure.
- Formation of the CaAc^+ complex can give a too low estimation of pH in high Ca-brine if it is not compensated for the Ac-bounded to the complex.

Increased understanding of the CO_2 material loss mechanisms can increase the application range of carbon steel and reduce the risk for loss of the pipeline due to misjudgment and wrong treatment. Research areas that should be addressed in the future includes:

- Fundamental studies of film growth in complex water chemistry
- Interaction between corrosion films and oil. How are the growth and the morphology of the corrosion film affected? How is oil wetting affected by the various solid products that can accumulate on the steel surface?
- Inhibitor performance on steel covered or partly covered with corrosion products, scale and other deposits.

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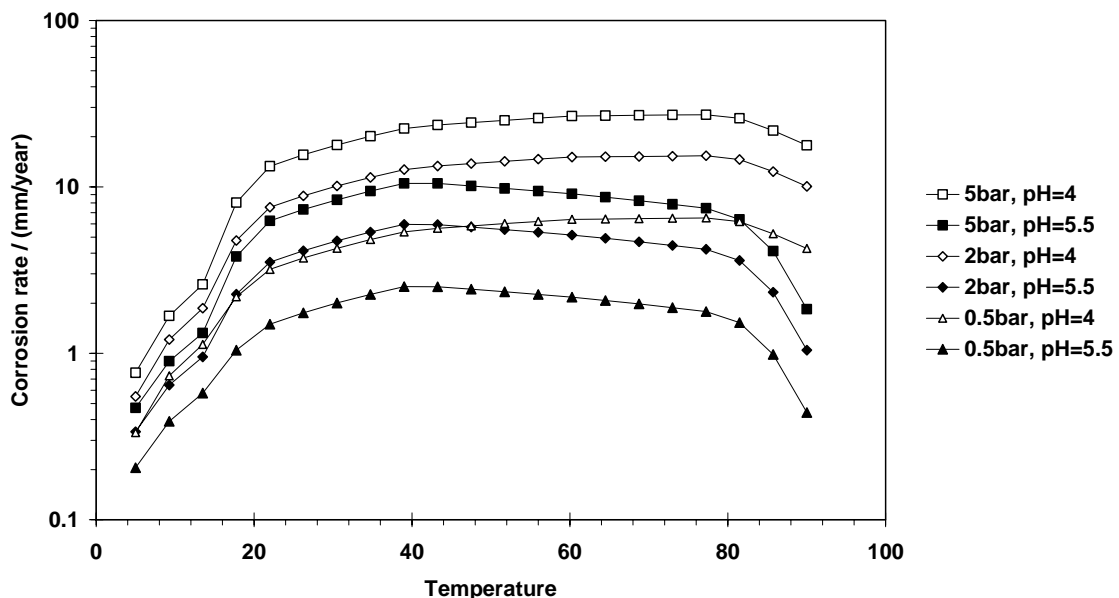


FIGURE 1. Calculated² corrosion rates as a function of temperature at 0.5, 2 and 5 bar CO₂ partial pressure and pH 4 and 5.5 respectively. Wall shear stress 20 Pa.

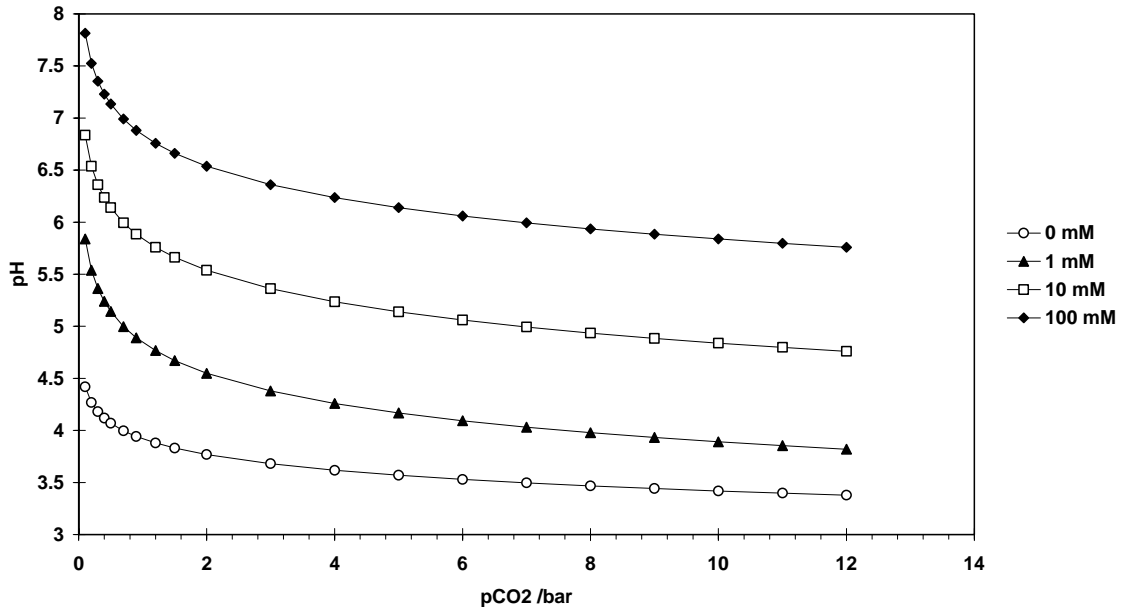


FIGURE 2. pH as a function of CO₂ partial pressure in water with various concentration of NaHCO₃. Temperature 60 °C, NaCl=1 wt%

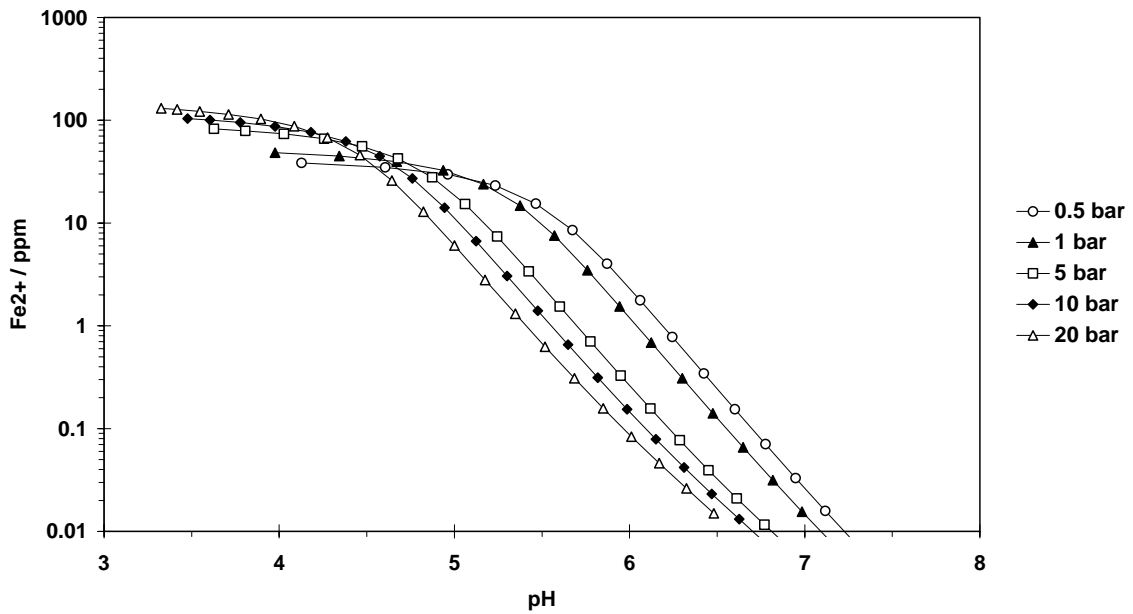


FIGURE 3. Amount of Fe²⁺ needed to be produced by corrosion to reach FeCO₃ saturation, plotted as function of pH in the brine. The brine pH is the pH before corrosion has started. (1 wt% NaCl).

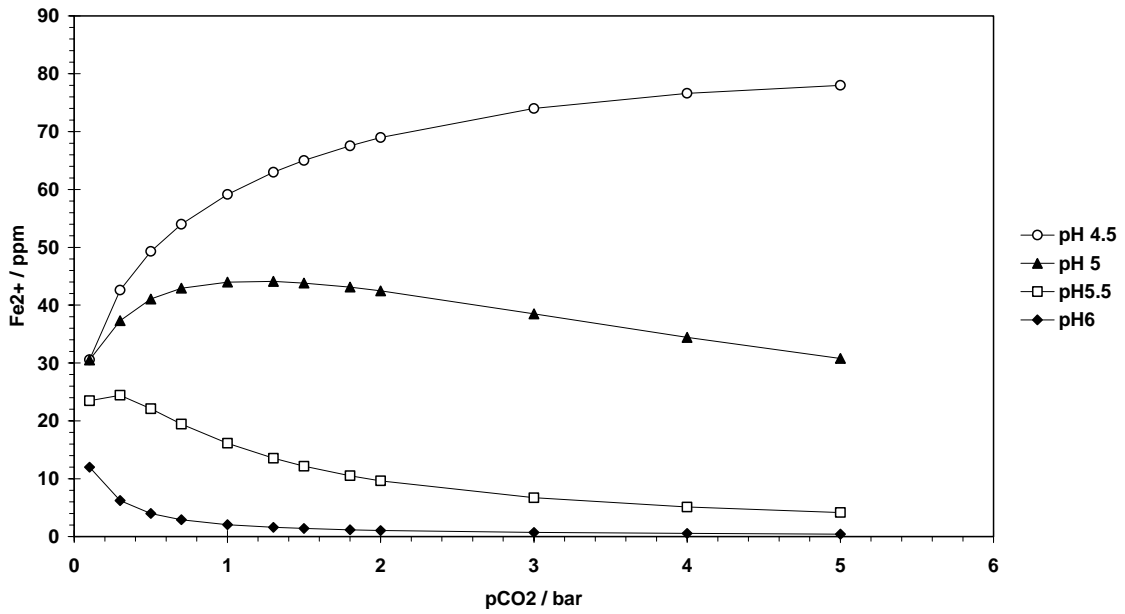


FIGURE 4. Amount of Fe^{2+} needed to be produced by corrosion to reach FeCO_3 saturation, plotted as function of pCO_2 for various pH's in the brine. The brine pH is the pH before corrosion has started. (3.5 wt % NaCl, 60 °C).

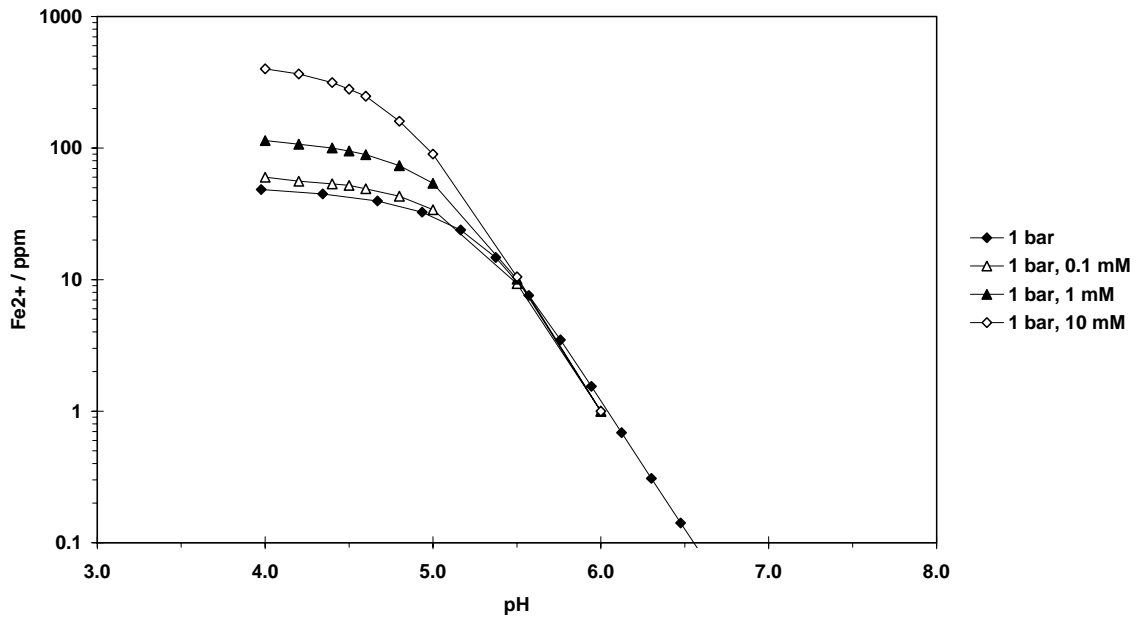


FIGURE 5. Amount of Fe^{2+} needed to be produced by corrosion to reach FeCO_3 saturation, plotted as function of pH in the brine. The given brine pH is the pH before corrosion has started. 1 bar CO_2 and 0, 0.1 1 and 10 mM HAc respectively. 1 wt% NaCl,

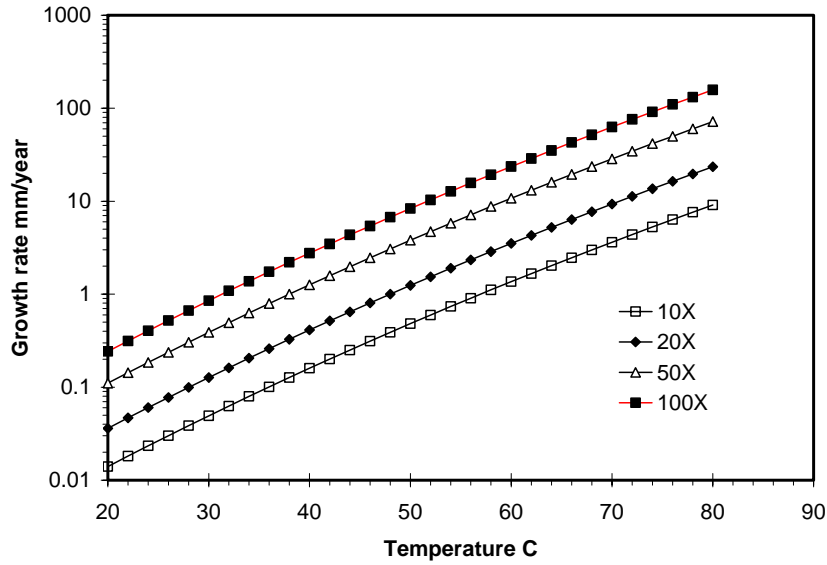


FIGURE 6. Calculated⁴¹ growth rate of iron carbonate as a function of temperature and different supersaturation. NaCl = 1 wt%.

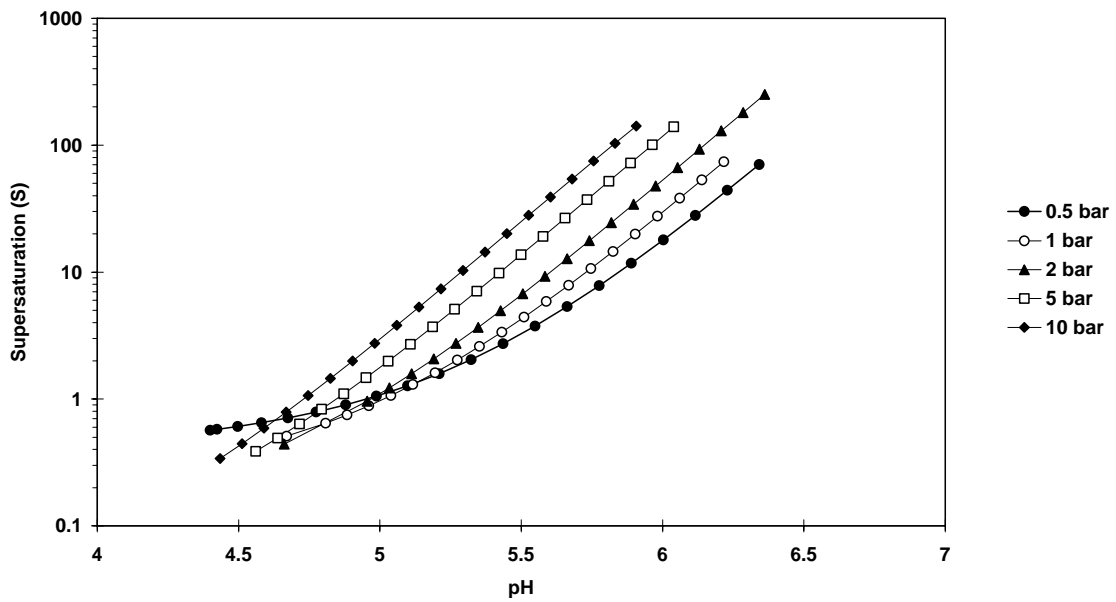


FIGURE 7. Supersaturation obtained in the brine when it is assumed that the corrosion process releases 30 ppm dissolved Fe^{2+} in the water. The pH is the pH in the brine before corrosion starts. NaCl=1 wt%.

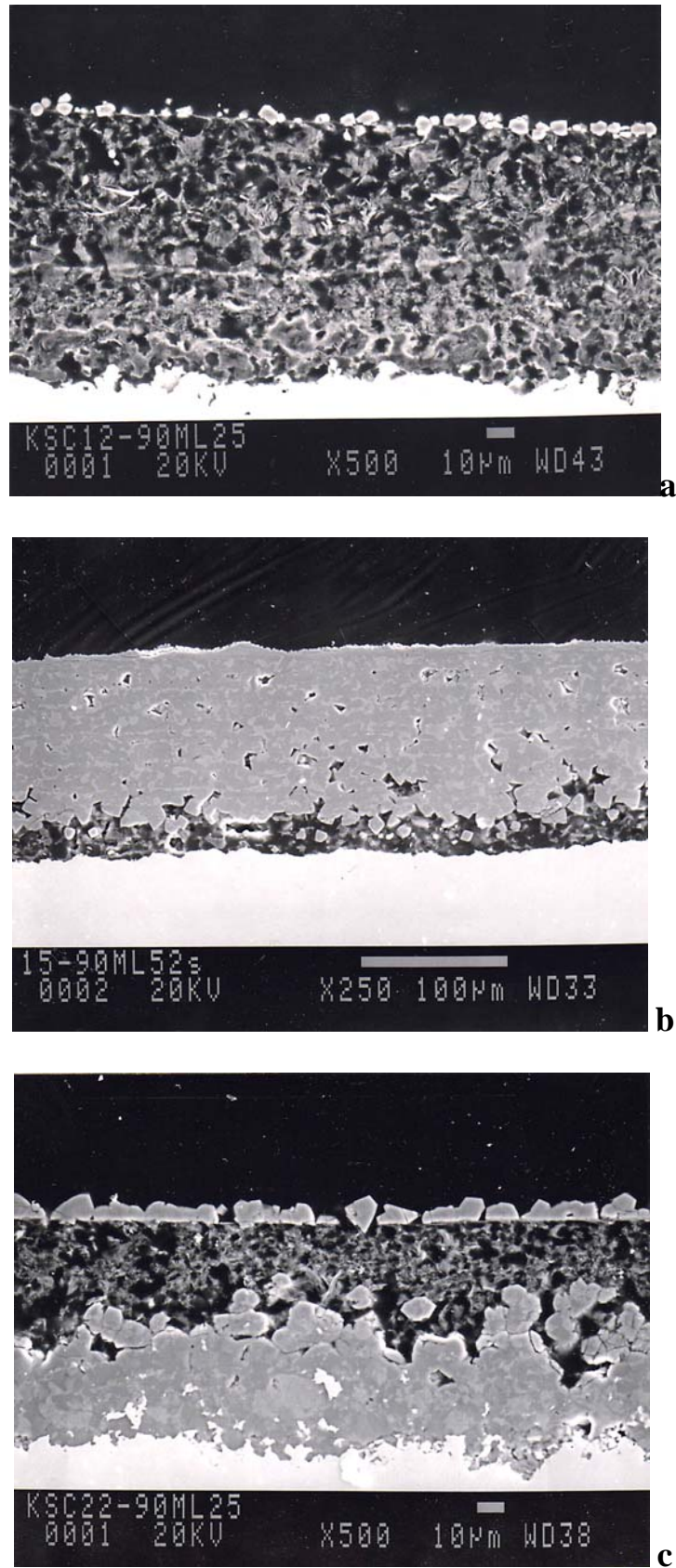


FIGURE 8. Corrosion films formed under various conditions. a) 40 °C and SR < 40 in bulk solution, b) 40 °C and SR > 40 in bulk solution, c) 80 °C and SR < 10 in bulk solution.