

STUDY OF RATE OF CORROSION BY HIGH CO₂ ON PRESSURE PIPELINE MADE OF STEEL

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Abstract— The paper deals with the effect of pressure, temperature and time on corrosion rate of pipeline steels in CO₂ saturated water and in humid saturated CO₂ gas in the range from 25 to 60°C and pressure from 20 to 145 bar, up to 400 hours of exposure. The results of weight loss tests show very high rates in the aqueous phase, one or two order of magnitude higher than the values obtained in CO₂ saturated with water. Depending on temperature and pressure, cementite and iron carbonate scales can grow on metallic surface reducing corrosion rate. SEM and metallographic analysis evidenced the evolution of scale from defective cementite-based layer to protective compact carbonate scale. An experimental setup has been designed, taking various measures from different references to get an idea about corrosive effect due to flow of waste gases under higher pressure. Material grade was selected same as used for CO₂ capture, transport and storage.

Index terms- Corrosion, Carbon steel, Scale formation, Supercritical CO₂, CO₂ capture, transport and storage.

I. INTRODUCTION

Steel is the most commonly employed metallic material in open-air structures and is used to make a wide range of equipment and metallic structures due to its low cost and good mechanical strength. Much of the steel that is manufactured is exposed to outdoor conditions, often in highly polluted atmospheres where corrosion is much more severe than in clean rural environments. There have been a lot of studies on the effects of flow on CO₂ corrosion of carbon steel. However, only few studies have attempted to address the flow effect in high partial pressure CO₂, *i.e.*, 10 bar and above. This is especially true for flow effects in supercritical CO₂; despite the wide interest in CO₂ transport in carbon capture and storage (CCS) and enhanced oil recovery (EOR), almost all studies in CO₂ corrosion at supercritical CO₂ were carried out in stagnant conditions. Although one study simulated the effects of velocity on supercritical CO₂ corrosion, the focus of the study was more on the effects of crude oils/water mixture on super-critical CO₂ corrosion at one particular velocity: 1 m/s.

Due to increasingly emission of CO₂ gaseous waste, it is necessary to take preventive action regarding capturing carbon from combustion exhaust gas produced at electric power plants, its compression, transport in pipelines, and storage in geological sites. Steel used to keep this waste gas should be provided prevention against corrosion. Despite the significant

ecological benefits, there are still unsolved issues, mainly related to economics and risks of accidental release into the atmosphere of large amounts of CO₂. Plant reliability requires accurate material selection and a deep knowledge of material corrosion in presence of very high pressure of wet CO₂. Main solutions in order to control transport costs consider carbon steel pipelines and the transport of dense phase, under supercritical conditions, for maximizing the amount of the mass flux.

Although dry carbon dioxide is not aggressive for carbon steel, the presence of water and other chemical aggressive species can accelerate corrosion. The solubility of water in CO₂ is determinant in the separation of the aqueous phase, which is necessary for the corrosion to take place. The CO₂ corrosion, commonly named “sweet corrosion”, occurs by hydration of CO₂ to carbonic acid in the aqueous phase. The phenomena have widely been studied in the Oil & Gas industry by experimental researches and data collected from plants, mainly at CO₂ partial pressures up to 10 bar. Only few works on corrosion in the supercritical conditions of CCTS systems above the critical pressure of 73.9 bar and critical temperature of 31°C are reported in literature. The aim of this experimental work is the evaluation of corrosion rates of a HSLA steel under high CO₂ subcritical and supercritical partial pressures.

II. METHODOLOGY AND EXPERIMENTAL SETUP

To evaluate the effects of flow in high partial pressure CO₂ environment at various pCO₂, pH values and temperatures, many experiments have already been done at low pressures as high as 10 bar as simulated the study of corrosion behaviour on carbon steel. Corrosion rate was evaluated by means of weight loss tests on grade X65 steel by using two different types of specimen: 24x20x16 mm prismatic, and Ø20 mm × 2 mm cylindrical (taken from reference for convenience). The surface was prepared by grinding with silicon carbide emery paper up to 1000 grit and cleaning with acetone in ultrasonic bath. Glass cylinders or PTFE gaskets insulated the specimens for preventing any galvanic coupling. The specimen holder was placed in a 6 liters autoclave filled with 3 liters of distilled water in order to achieve different exposure conditions: the specimens on the upper side were in humid CO₂ phase, whereas the specimens in the lower side were soaked in water saturated by CO₂. Before testing, cycles of pressurization and depressurization with nitrogen removed oxygen in the chamber

before heating. Finally, the autoclave was pressurized with CO₂.

The tests were performed at constant pressure and temperature, in the range from 20 to 145 bars and 25 to 60°C, with exposure time from 48 up to 400 hours. Part of tests were executed by using a mechanical stirrer rotating at 180 rpm in the aqueous phase. The weight loss was measured after pickling in 6N hydrochloric acid inhibited with 3 g/L hexamethylenetetramine. at 60°C, for 1 min, and drying. SEM analysis of metallographic cross-sections was performed to view the scale formed on the steel surface.

III. RESULTS AND DISCUSSION

A. Corrosion rates

The effect of exposure time and temperature on corrosion rate in water saturated with CO₂ and humid saturated CO₂ gas at pressures of 123-145 bars was considered. The corrosion rate is expressed as average value of the specific weight loss over the exposure time of the specimen. It decreases over the time according an exponential law. In the water phase, for short-term exposure, the corrosion rate increases with temperature: the highest rate was during short-term tests at 60°C. The reduction over exposure time is more pronounced at 60°C than at 40°C and 25°C, producing average rates after 300 hour exposure that become very close for all three temperatures. Therefore, at 60°C, instant corrosion rate reduces to values below the rates at 40°C and 25°C.

In humid saturated CO₂ gas, the corrosion rate is much lower than in the water phase. For long testing time, above 300 hours, the corrosion rate decreases and approaches similar level, regardless of the temperature. The testing conditions at 25°C and 135 bar of CO₂ induced abnormal initial high corrosion rates. In these conditions, CO₂ is liquid and we suppose that during early stage of test, during entering of icy liquid, a condensed layer also wet the specimens placed in the upper side of autoclave. The subsequent heating probably removed the layer, which, however, produced more emphasized attacks. The stirring had negligible effect, indicating that liquid CO₂ did not emulsify with the water phase. For comparison, the figure also shows the corrosion rates estimated at temperatures of 25, 40 and 60°C, by De Waard and Milliams model.

$$v_{cor} [mm/year] = 10^{\left(5.8 - \frac{1710}{T(^{\circ}C) + 273}\right)} \cdot (f_{CO_2} [bar])^{0.67} \quad \text{-----(1)}$$

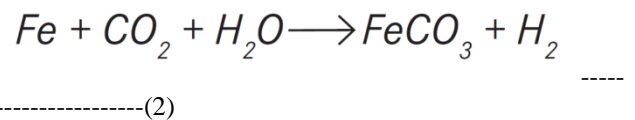
(fCO₂ is the fugacity of CO₂).

The model describes the typical conditions of oil extraction, with CO₂ partial pressures that do not exceed 20 bar, and estimates the maximum corrosion rate of carbon steel in absence of any formation of corrosion product scales. There is a good correlation between the model and the experimental data only at low CO₂ partial pressure (20 and 30 bar) and 40°C. At 50 and 60°C, the increase of corrosion rate with CO₂ partial pressure is below the values extrapolated by De Waard and Milliams and its only evident in the early period. Exceeding 90 hours exposure, the corrosion rate tends to stabilize between 5

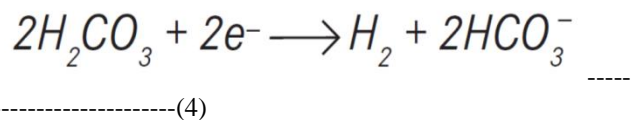
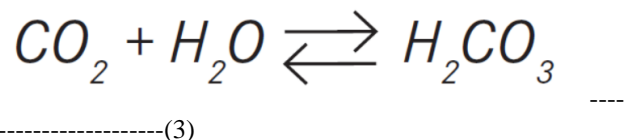
and 20 mm/year, regardless of the pressure, in accordance with literature data. One stated that the corrosion rate in supercritical CO₂ was very high, above 20 mm/year, in absence of adherent iron carbonate scale formation; on the contrary, it can reduce below 1 mm/year. In humid saturated CO₂ for exposure times between 160 and 190 hours at 40 and 50°C, the corrosion rate considerably decreases as CO₂ partial pressure increases and it is not affected by temperature. At 60°C, data are quite scattered and do not show clear effect of CO₂ pressure. The data collected in this experimentation confirm the values were reported and measured corrosion rates from 0.2 to 0.3 mm/year after 24 hours at 50°C and CO₂ partial pressure equal to 40, 60 and 80 bar. However, negligible corrosion rates of carbon steel in humid supercritical CO₂ at 80°C was recorded.

B. Corrosion mechanism

Steel corrosion at very high CO₂ partial pressure shows complex influence of temperature, pressure and time. Different phenomena act in synergistic or counteracting way. The corrosion of carbon steel in the presence of CO₂ and water involves the anodic oxidation of iron to ferrous ions and the cathodic process of hydrogen evolution, according to the general reaction:



Calculations of the composition of water saturated with CO₂ gas, liquid or supercritical were done. At pressures above 20 bar and temperatures between 25 and 85°C, pH values between 3.1 and 3.3 are expected due to the increase of carbonic acid concentration. The acidity promotes the cathodic process by direct reduction of hydrogen ions. Moreover, the corrosivity of CO₂ derives from the chemical reaction of hydration of CO₂ in the electrolyte to carbonic acid and the further electrochemical cathodic process connected with the direct reduction of carbonic acid.



An increase of temperature produces a reduction of CO₂ solubility. Thus, lower amount of carbonic acid is available for supporting the reduction process. On the other hand, it increases the rate of the chemical process of hydration. The temperature generally affects mass transport mechanisms and the processes occurring under limiting current conditions, but it should be outlined that direct reduction of carbonic acid is controlled by the rate of hydration and not by the diffusion rate of carbonic acid into water [1,7]. Moreover, the temperature modifies kinetics of electrochemical anodic and cathodic reactions.

C. Morphology of corrosion product scale

The temperature can also influence corrosion rate because it can affect the solubility of corrosion products, favouring their precipitation and scale growth. The SEM analysis of specimens after testing showed the formation of iron carbonate and iron carbide scales having different morphology depending on temperature and time. The carbides due to the preferential dissolution of ferrite that leaves the cementite lamellae of pearlite. The characteristic morphology of this structural component can be clearly observed on both the corroded surface and metallographic section of the scale. The cementite lamellas have a dual role on corrosion process. Because of their noble nature, they act as low hydrogen overvoltage cathode, promoting anodic attack on ferrite. As far as scale growth process is concerned, the cementite acts as a network in which the iron carbonate precipitations are favoured owing to the increase of iron ions and pH due to the anodic and cathodic reactions, respectively. Thus, in suitable conditions, iron carbonate fully seals the porosity within the network of cementite and a mixed iron carbonate and carbide protective film forms, leading to relevant reduction of the corrosion rate.

Protective behaviour of the scales formed in environment relevant for "sweet corrosion" of Oil & Gas Industry was noticed. Concluded that iron carbonate mixed iron carbonate/iron carbide scales at the metal/scale interface are necessary to reduce the corrosion rate. On the contrary, the only presence of cementite at the interface does not produce a protective scale. For this reason the protective properties of carbonate scale is poor at temperatures below 80°C. However, the experimental results obtained at very high pressures of CO₂ show that precipitation of iron carbonate scale can reduce significantly the corrosion rate at 40°C and 60°C.

After tests at 25°C in CO₂ saturated water with stirring, the film partially covers the specimen surface. It is mainly composed by cementite and the corrosion rate, although lower than that observed at higher temperatures, only evidences a limited variation over the time. At 40°C, essentially a cementite based layer covers the specimens after short-term tests. Cubic carbonate crystals became evident within the cementite only on the specimens exposed for 331 hours but they did not completely seal the cementite. At 60°C, a continuous mixed film of cementite and iron carbonate gradually grows. After short-term exposure, SEM observations did not show uniform scales; they evidenced the simultaneous presence of areas with compact and thick layer and zones with thin and fractured film. Increasing the exposure time, the precipitation of cubic crystals of iron carbonate fully sealed the cracks and porosities of the scale. The metallographic sections confirm chiefly cementite based layer in the scale formed at 25°C and 135 bar CO₂ partial pressure and the presence of a mixed film of cementite and iron carbonate at higher temperatures, still porous at 40°C and becoming continuous at 60°C. Without stirring, the film at 60°C forms a cementite layer at the interface that remains critical for the scale stability. The precipitation of the carbonate takes place above the cementite

network, remaining in this way less adherent to the substrate. On the contrary, the stirring of the solution leads to very high initial corrosion rates and promotes direct formation of the mixed Fe₃C - FeCO₃ scale without any intermediate.

The scale is protective and resists to the mechanical action of flow, confirming the observation of Crolet et al [16]. The CO₂ partial pressure did not primarily affect the scale morphology, but in supercritical CO₂, probably due to the elevated concentration of CO₂, less porous films grew (Figure 6). In humid saturated CO₂ phase, the formation of a layer of condensed water on the metal surface controls the corrosion process. Corrosion takes place in a restricted volume of condensate electrolyte which is rapidly saturated by corrosion product favouring precipitation of iron carbonate crystals. At low temperature and CO₂ pressure, the scale is not adherent and it is easily detached from the metal surface. The carbonate scale becomes more compact and adherent by increasing the CO₂ pressure, significantly reducing the corrosion rate. At 60°C the scale specimens present not corroded areas and areas covered by a compact and adherent scale consisting of iron carbonate and iron carbide. Some localized attacks filled by the corrosion products were observed.

IV. CONCLUSIONS

The corrosion rates of HSLA steel under high CO₂ subcritical and supercritical partial pressures were evaluated in CO₂ saturated water and in water saturated CO₂.

The corrosion rate in water saturated with CO₂ showed values between 1 and 28 mm/year. The highest corrosion rates were reported for short-term exposure; on the contrary, low values were observed in the case of long term exposure due to the precipitation of corrosion

product scales. The scale formation primarily depends upon the temperature and exposure time. At 60°C in stirred solution a compact and protective film of iron carbonate and cementite was observed. The presence of cementite at metal/scale interface promotes the formation of not adherent scale in absence of stirring at the same temperature. At lower temperature, the film is more porous and less able to reduce the dissolution of metal. The corrosion rates in humid saturated CO₂ gas are significantly lower than those obtained in the water phase and they are controlled by the formation of scale. The corrosion rates were lower at 60°C, temperature at which the CO₂ pressure effect was negligible.

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