

Corrosion rate of high CO₂ pressure pipeline steel for carbon capture transport and storage

M. Cabrini, S. Lorenzi, T. Pastore, M. Radaelli

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, but remaining in any case much lower than values extrapolated by De Waard and Milliams model at high partial pressure. 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.

Keywords: Corrosion - Carbon steel - Scale formation - Supercritical CO₂ - CO₂ capture transport and storage (CCTS)

INTRODUCTION

The acronym CCTS (Carbon Capture, Transport and Storage) indicates the technology for capturing waste CO₂ from combustion exhaust gas produced at electric power plants, its compression, transport in pipelines, and storage in geological sites. 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 [1].

Although dry carbon dioxide is not aggressive for carbon steel, the presence of water and other chemical aggressive species can stimulate corrosion [2]. The solubility of water in CO₂ is determinant in the separation of the aqueous phase, which is necessary for the corrosion to take place [3]. The CO₂ corrosion, commonly named "sweet corrosion", occurs by hydration of CO₂ to carbonic acid in the aqueous phase. The phenomena has 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 [4-9] 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.

Experimental

Corrosion rate was evaluated by means of weight loss tests on an API 5L grade X65 steel by using two different types of specimen: 24x20x16 mm prismatic, and Ø20 mm × 2 mm cylindrical. 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 bar and 25 to 60°C (±1°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,

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at 60°C, for 1 min, and drying. SEM analysis of metallographic cross-sections was performed to evidence the scale morphologies.

RESULTS AND DISCUSSION

Corrosion rates

Figure 1 shows 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 bar. 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. The trend confirms the literature data obtained by Cui et al. in turbulent flow at 80°C and 85 bar [10]. In the absence of stirring - under same experimental conditions - the behavior was similar but with lower corrosion rates.

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 (figure 1b). 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 accentuated attacks. The stirring had negligible effect, indicating that liquid CO₂ did not emulsify with the water phase.

Figure 2 shows the effect of CO₂ partial pressure and temperature on the corrosion rate after 160-190 hours exposure. For comparison, the figure also shows the corrosion rates estimated at temperatures of 25, 40 and 60°C, by De Waard and Milliams model (1) (f_{CO_2} is the fugacity of CO₂) [11].

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

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 it is

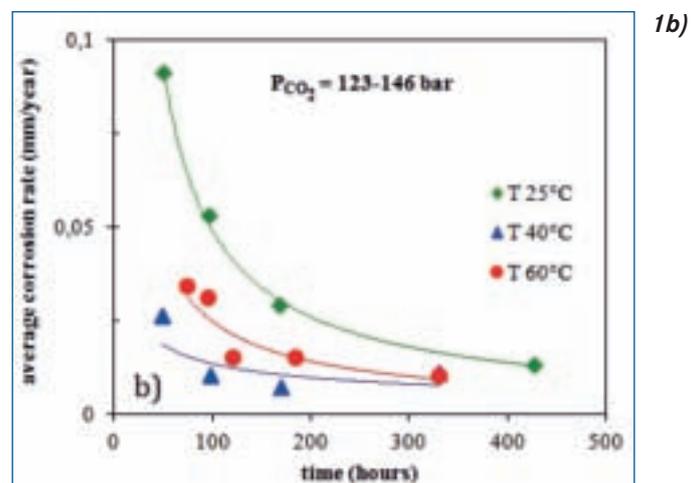
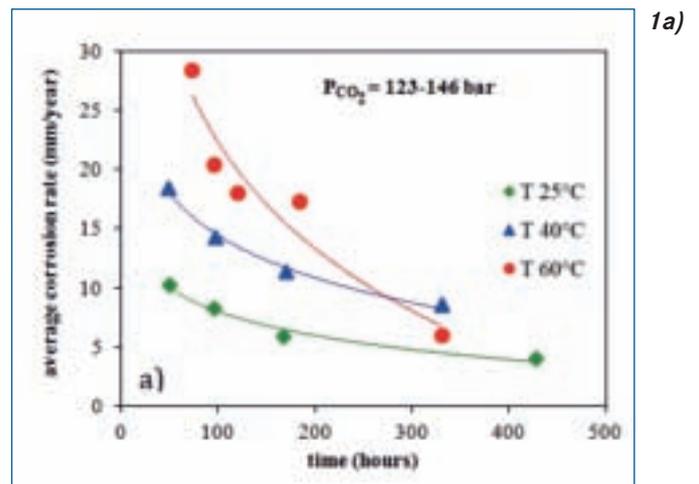


Fig. 1 - Effect of exposure time and temperature on average corrosion rate in water saturated with CO₂ (a) and humid saturated CO₂ gas (b) at 126-146 bar CO₂ partial pressure

Fig. 1 - Effetto del tempo di esposizione e della temperatura sulla velocità di corrosione media dell'acciaio API 5L X65 in acqua saturata di CO₂ (a) e in CO₂ umida saturo (b), a 126-146 bar di pressione parziale di CO₂.

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. Zhang et al remark values significantly lower than the values calculated by using the existing models for sweet corrosion [12]. Choi et al state that the corrosion rate in supercritical CO₂ is very high, above 20 mm/year, in absence of adherent iron carbonate scale formation; on the contrary, it can reduce below 1 mm/year [7,8,13].

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 (Figure 2b). The data collected in this experimentation confirm the

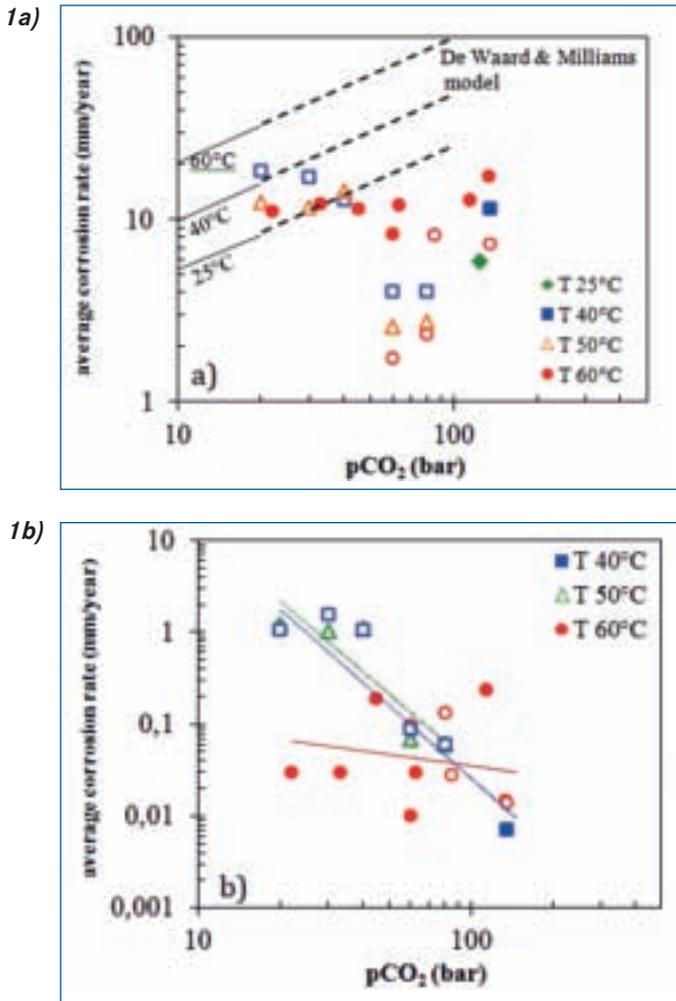


Fig. 2 - Effect of CO₂ partial pressure and temperature on corrosion rate in CO₂ saturated water (a) humid saturated CO₂ (b) for 160-190 hours exposure time. (Empty markers indicated test without stirring, full markers tests with stirring; full and dashed lines indicated extrapolation by DeWaard and Milliams model at 25, 40 and 60°C)

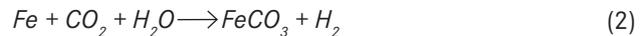
Fig. 2 - Effetto della pressione parziale di CO₂ e della temperatura sulla velocità di corrosione ottenuta in acqua satura di CO₂ (a) e in CO₂ satura (b) per tempi di esposizione di 160-190 ore. (I marcatori vuoti si riferiscono a prove senza agitazione, quelli pieni a prove con agitazione; le linee continue e a tratti indicano i valori estrapolati dal modello di DeWaard e Milliams)

values reported by Choi and Nešić. They 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 [7]. However, Zhang et al point out negligible corrosion rates of carbon steel in humid supercritical CO₂ at 80°C [12].

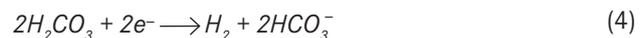
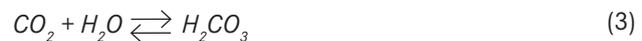
Corrosion mechanism

Steel corrosion at very high CO₂ partial pressure shows a 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 (2):



Choi and Nešić calculated the composition of water saturated with CO₂ gas, liquid or supercritical [8]. 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 (3) and the further electrochemical cathodic process connected with the direct reduction of carbonic acid (4) [11].



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 (4) is controlled by the rate of hydration and not by the diffusion rate of carbonic acid into water [17]. Moreover, the temperature modifies kinetics of electrochemical anodic and cathodic reactions.

Morphology of corrosion product scale

The temperature can also influence corrosion rate because it can affect the solubility of corrosion products, favoring 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 carbide is 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 is favored owing to the increase of iron ions and pH due to the anodic and cathodic reactions, respectively [15-16]. 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.

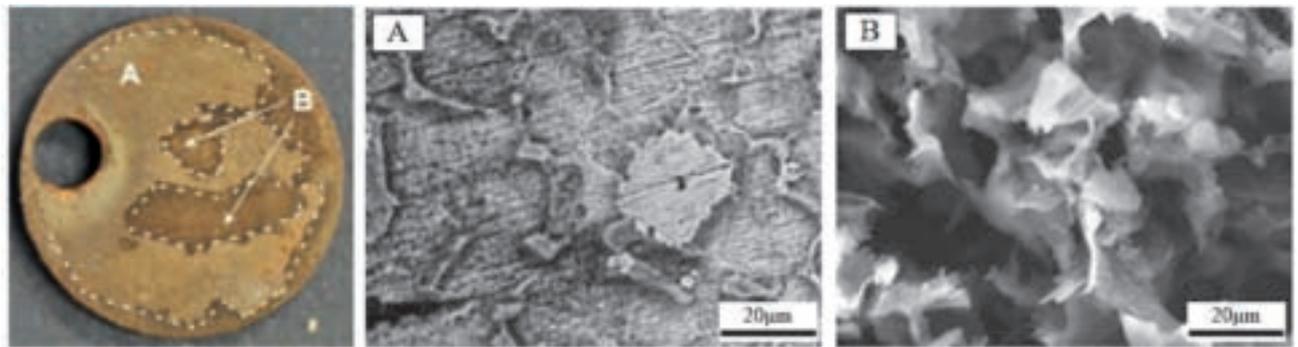


Fig. 3 - Corrosion morphology after 164 hours test in CO_2 saturated water at 135 bar of CO_2 and 25°C with stirring, and details of zones A and B. Non-uniform corrosion and cementite network left by selective corrosion of ferrite

Fig. 3 - Morfologia di corrosione dopo 164 ore di esposizione in acqua saturo a 135 bar di CO_2 e 25°C con agitazione della soluzione (a), particolari della zona A (b) e B (c). Corrosione disuniforme e reticolo di cementite lasciato dalla corrosione selettiva della ferrite.

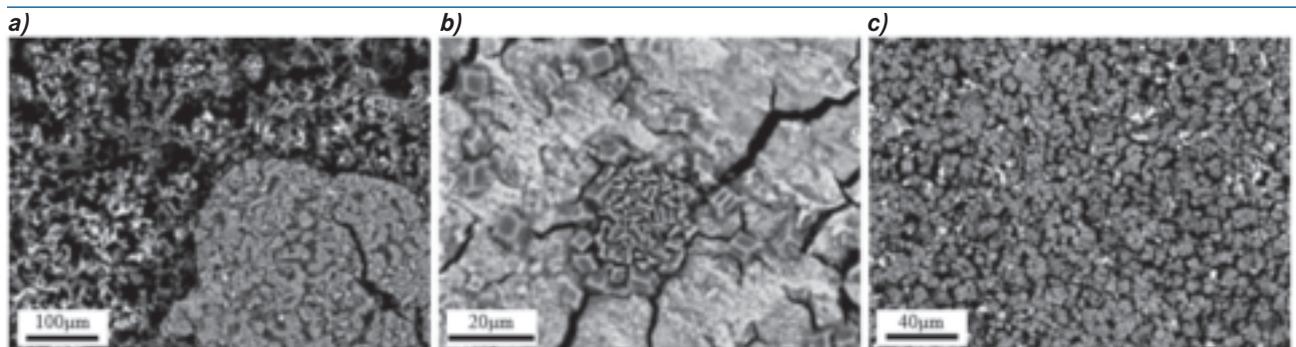


Fig. 4 - Scale morphology of specimens after tests in stirred water saturated by 135 bar CO_2 partial pressure. Morphology of siderite precipitation in the cementite layer. a) 40°C / 170 h, b) 40°C / 331 h, c) 60°C / 331 h.

Fig. 4 - Morfologia della scaglia dopo prova in acqua saturata con 135 bar di pressione parziale di CO_2 , con agitazione della soluzione. Morfologia di precipitazione della siderite nello strato di cementite. a) 40°C / 170 h, b) 40°C / 331 h, c) 60°C / 331 h.

Crolet et al classified the protective behavior of the scales formed in environment relevant for “sweet corrosion” of Oil&Gas Industry [16]. They concluded that iron carbonate or 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 produces a protective scale. Kermani et al [15] emphasized that 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 CO_2 show that precipitation of iron carbonate scale can reduce significantly the corrosion rate at 40 and 60°C, lower than limit usually considered for protective scale formation.

After tests at 25°C in CO_2 saturated water with stirring, the film partially covers the specimen surface (Figure 3). 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 (Figure 4a and b).

At 60°C, a continuous mixed film of cementite and iron carbonate gradually grow. 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 (Figure 4c).

The metallographic sections confirms chiefly cementite based layer in the scale formed at 25°C and 135 bar CO_2 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 (Figures 5 and 6).

Without stirring, the film at 60°C forms a cementite layer at the interface that remains critic for the scale stability (Figure 7a). 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 $Fe_3C - FeCO_3$ scale without any intermedia-

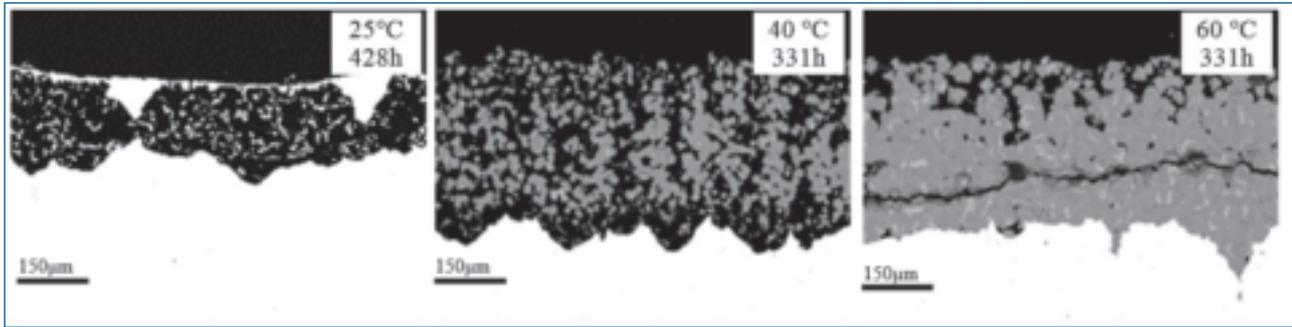


Fig. 5 - Effect of temperature on scale morphology. Metallographic section of specimens exposed in stirred water saturated by 135 bar CO_2 partial pressure. Porosity modification of the scale and cementite network (light zones).

Fig. 5 - Effetto della temperatura sulla morfologia della scaglia. Sezioni metallografiche di provini esposti in acqua saturata a 135 bar di CO_2 in test con agitazione. Modificazione della porosità della scaglia e reticolo di cementite (zone chiare).

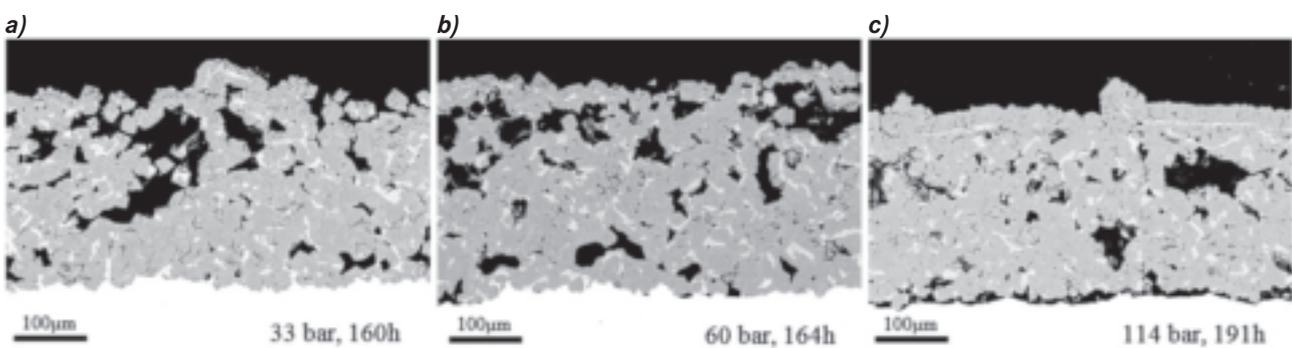


Fig. 6 - Effect of CO_2 partial pressure on scale morphology. Metallographic section of specimens exposed in stirred water at 60°C. Porosity modification of the scale and cementite network (light zones).

Fig. 6 - Effetto della pressione parziale di CO_2 sulla morfologia della scaglia. Sezione metallografica di provini esposti in acqua alla temperatura di 60°C, in test con agitazione. Modificazione della porosità della scaglia e reticolo di cementite (zone più chiare).

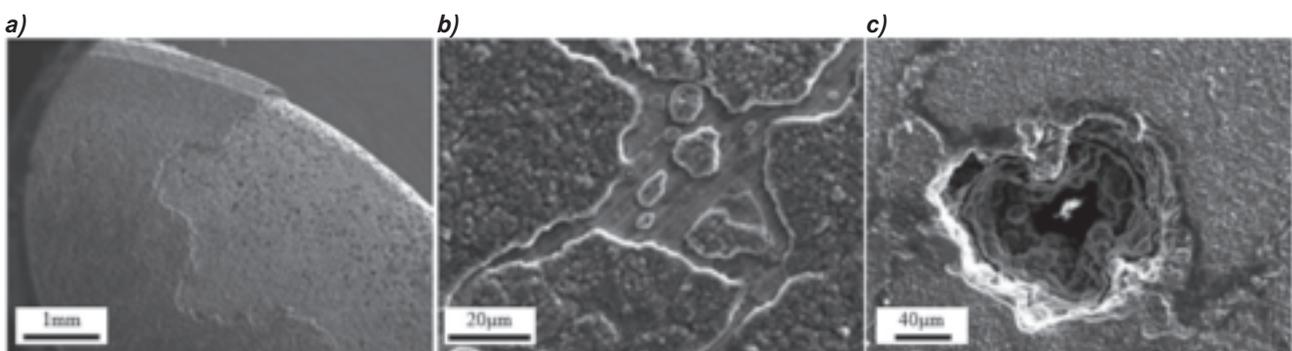


Fig. 7 - Scale morphology after tests at 85 bar CO_2 and 60°C. a) Detached outer siderite layer showing the inner cementite layer, on a specimen immersed in stagnant saturated water. b) Area partially covered by scale on a specimen exposed in the humid gas phase. c) Localized attack partly occluded by corrosion products on a specimen exposed in the gas phase, after prolonged exposure in humid gas phase.

Fig. 7 - Morfologia della scaglia dopo prove a 85 bar e 60°C: a) scaglia di siderite staccata, che evidenzia lo strato di cementite sottostante, del provino immerso in acqua stagnante; b) zona parzialmente ricoperta da scaglia del provino esposto nella fase gas; c) attacco localizzato in parte occluso da prodotti di corrosione sul provino esposto nella fase gas dopo un maggiore tempo di esposizione.

te layer of porous cementite. 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 control the corrosion process. Corrosion takes place in a restrict volume of condensate electrolyte which is rapidly saturated by corrosion product favoring 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 the specimens presents not corroded areas and areas covered by a compact and adherent scale consisting of iron carbonate and iron carbide (figure 7b). Some localized attacks filled by the corrosion products were observed (Figures 7c).

CONCLUSIONS

The corrosion rates of a 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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Valutazione della velocità di corrosione di acciai per tubazioni per il trasporto di CO₂ supercritica (CCTS)

Parole chiave: Caratterizzazione materiali - Acciaio - Corrosione

Il lavoro è volto allo studio della corrosione dell'acciaio al carbonio a contatto con anidride carbonica ad alta pressione, nelle condizioni in cui ne è previsto il trasporto mediante condotte, dall'impianto di abbattimento vero e proprio di un sistema CCTS (Carbon Capture Transport and Sequestration), fino al sito di immagazzinamento geologico [1]. Il trasporto è previsto in condizioni supercritiche, a temperature e pressioni maggiori di 31°C e 73 bar, per rendere massimo il volume di gas trasportato. La CO₂ anidra non è aggressiva nei confronti dell'acciaio, ma lo sono le soluzioni contenenti questo gas disciolto [3].

Lo studio è stato effettuato mediante prove di perdita di peso su un acciaio al carbonio per tubazioni API 5L X65 in acqua distillata satura di CO₂ ad alta pressione o in condizioni supercritiche e in CO₂ satura di vapore, tra 25 e 60°C e pressione tra 20 e 145 bar. I risultati evidenziano che l'effetto maggiore sulla velocità di corrosione è dato dalla formazione della scaglia di prodotti di corrosione e dalle sue caratteristiche di protettività; inoltre, mostrano che la velocità di corrosione nella fase acquosa è sempre molto maggiore di quella nel gas umido. In entrambe le condizioni, la velocità diminuisce con il tempo di esposizione con una legge esponenziale.

Per brevi tempi di esposizione, la velocità di corrosione nell'acqua satura di CO₂ è maggiore a 60° rispetto a 40°C e 25°C, ma diminuisce in modo più accentuato. Dopo circa 300 ore di esposizione, le velocità medie alle diverse temperature si equivalgono (figura 1a). La pressione di CO₂ influenza la velocità di corrosione solo alle più basse pressioni e temperature considerate nelle prove, mentre dopo circa 160 ore di esposizione, questa si assesta in ogni caso tra 2 e 4 mm/anno (figura 2a).

La scaglia è costituita da uno scheletro di carburo di ferro proveniente dalla microstruttura dell'acciaio, lasciato dalla dissoluzione preferenziale della ferrite, e dal carbonato di ferro prodotto dalla corrosione. La precipitazione si ha quando la concentrazione degli ioni Fe²⁺ e carbonato, quest'ultimi provenienti dalla dissociazione dell'acido carbonico, supera il prodotto di solubilità. Lo scheletro di cementite influenza la precipitazione del carbonato di ferro e le caratteristiche della scaglia [15-16]. Elevate pressioni di CO₂, una temperatura di 60°C e l'agitazione della soluzione portano a velocità di corrosione molto elevate nei primi istanti di immersione, ma anche alla rapida formazione di una scaglia protettiva (figura 4c e figura 5c). In assenza di agitazione, la precipitazione del carbonato avviene sopra lo strato di cementite, rimanendo in questo modo meno adesa al substrato e con tendenza a scagliarsi (figura 7a). Alla temperatura di 40°C, invece, la minore velocità di corrosione iniziale riduce la concentrazione degli ioni Fe²⁺; la precipitazione del carbonato avviene in modo incompleto, formando una scaglia porosa e poco protettiva (figure 4a, 4b e 5b). A 25°C, il carbonato di ferro non precipita affatto e i provini sono ricoperti solo dalla cementite (figura 3 e 5a).

Nel gas umido, la velocità di corrosione è molto più bassa, compresa tra 0,01 e 0,3 mm/anno (figura 1b). Nelle condizioni supercritiche, l'aumento della pressione di CO₂ non sembra influenzare le velocità di corrosione (figura 2b); al termine delle prove, la superficie dei provini mostra accanto ad aree praticamente non corrose, aree debolmente corrose, coperte da una scaglia aderente di carbonato di ferro (figura 7b), con punti attacco localizzato (figura 7c). La corrosione in fase gassosa avviene nel sottile strato di acqua che si forma per condensazione. Il ridotto volume di questo, rapidamente saturato dai prodotti di corrosione, favorisce la formazione di una scaglia, soprattutto al crescere della pressione di CO₂ e all'aumentare della temperatura, per la diminuzione del prodotto di solubilità del carbonato di ferro.