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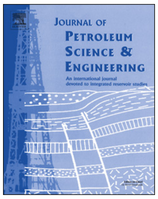

Corrosion of C110 carbon steel in high-pressure aqueous environment with mixed hydrocarbon and CO_2 gas

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ABSTRACT

Corrosion is a major issue in the oil industry, especially in presence of aqueous carbon dioxide under high-pressure high-temperature (HPHT) conditions. Exposing tubular materials to aqueous CO_2 (carbonic acid) environment causes severe corrosion. This paper presents results of an experimental study conducted to investigate effects of CO_2 partial pressure ratio (i.e. ratio of CO_2 partial pressure to the total pressure) and total pressure on corrosion behavior of C110 carbon steel. In addition, effect of CO_2 corrosion on mechanical strength was investigated to identify presence of microscopically undetectable localized corrosion such as intergranular attack that can cause substantial mechanical degradation.

To perform corrosion experiments, test specimens were cut from C110 casing and machined. In order to improve accuracy and reduce machining-induced defects, water-jet cutting and milling machines were utilized. Corrosion tests were conducted by exposing the specimens (three specimens in one batch) to 2% NaCl solution saturated with mixed gas containing CH_4 and CO_2. CO_2 partial pressure ratio (CPPR) and total system pressure were varied. Tests were performed at a constant temperature (38 ± 1 °C) for one week duration. Corrosion rate was measured using weight loss technique. In addition, corroded specimens were examined using a digital microscope to inspect corrosion product and detect presence of localized corrosion. Localized corrosion is known for degrading mechanical properties of carbon steel. To identify existence of undetectable localized corrosion, the specimen load-carrying-capacity (LCC) was measured using tensile strength measuring apparatus.

When CPPR was varied from 0 to 100%, similar corrosion rate trends were observed at 41.37 and 62.05 MPa. Corrosion rate increased to a maximum value and subsequently decreased as the CPPR was increased to 100%. A dense and compact corrosion product was formed at 41.37 MPa and 100% CPPR. To detect presence of localized corrosion, total reduction in Load Carrying Capacity (LCC) and reduction in LCC due to uniform corrosion were determined and compared. Results show no mechanical property degradation after exposure indicating absence of localized corrosion. The total reduction was slightly higher than the reduction due to uniform corrosion. One possible explanation for this observation could be minor variation of corroded specimen thickness, which resulted in underestimation of LCC reduction due to uniform corrosion.

1. Introduction

Oil-field tubulars are often exposed to carbonic acid due to CO_2 injection for the purpose of enhanced oil recovery or geological storage (sequestration). In addition, production of aqueous formation fluid that contains carbonic acid can cause severe tubular corrosion in oil and gas wells. CO_2 corrosion is commonly known as sweet corrosion. Usually, two types of reactions are involved in CO_2 corrosion process: i) homogeneous chemical reactions in surrounding bulk solution, and ii) electrochemical reactions, which take place at steel surface. In CO_2-brine system, certain amount of CO_2 dissolves in brine:

$$CO_{2(g)} \rightarrow CO_{2(aq)} \quad (1)$$

Subsequently, dissolved CO_2 hydrates and generates carbonic acid:

$$CO_{2(aq)} + H_2O \rightarrow H_2CO_3 \quad \text{(Hydration of aqueous } CO_2\text{)} \quad (2)$$

After hydration, carbonic acid dissociates forming hydrogen, bicarbonate and carbonate ions:

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Nomenclature

Symbols

A	exposed area
CR	corrosion rate
t	exposure time
w	specimen width
W_1	initial weight of specimen
W	final weight of specimen
ρ_{st}	density of steel
ΔT	average specimen thickness reduction due to corrosion

Acronyms

HPHT	high-pressure high temperature
CPPR	CO_2 partial pressure ratio
LCC	load carrying capacity
LCC_{uncorr}	load carrying capacity of un-corroded specimen
LCC_{corr}	load carrying capacity of corroded specimen
UTS	ultimate tensile strength
ΔLCC_T	total reduction in carrying capacity
ΔLCC_{uc}	reduction in load carrying capacity due to uniform corrosion

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \quad \text{(Dissociation of carbonic acid)} \tag{3}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \quad \text{(Dissociation of bicarbonate)} \tag{4}$$

Due to concentration gradient, carbonic species and hydrogen ions move toward steel surface at which electrochemical reactions take place as anodic and cathodic reactions. Anodic reaction results in iron dissolution (Nordsveen et al., 2003; Nesic et al., 1996; Forero et al., 2014):

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{5}$$

Reduction of hydrogen ions, carbonic acid and bicarbonate ions occur due to cathodic reaction:

$$2H^+ + 2e^- \rightarrow H_2 \tag{6}$$

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^- \tag{7}$$

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-} \tag{8}$$

Solution pH determines the most dominant cathodic reaction (Nesic et al., 1996). For instance, at low pH (less than 4), the reduction of hydrogen ions is a dominant cathodic reaction. At intermediate pH (between 4 and 6), reduction of carbonic acid becomes a leading reaction. However, at high solution pH (greater than 6), direct reduction of bicarbonate ions (HCO_3^-) becomes an important cathodic reaction in addition to the reduction of H^+ and H_2CO_3.

During CO_2 corrosion, there is a possibility of iron carbonate scale formation on steel surface. This occurs when concentrations of $Fe^{2+}$and CO_3^{2-} ions exceed their solubility limits. Hence, the overall reaction that takes place in aqueous CO_2 environment is expressed as:

$$Fe_{(s)} + CO_{2(aq)} + H_2O \rightarrow FeCO_{3(s)} + H_2 \tag{9}$$

Mass loss during CO_2 corrosion is generally related to environmental conditions such as temperature, pressure, salt concentration, solution pH and CO_2 partial pressure in the gas phase. The impacts of CO_2 partial pressure and protective scale on corrosion rate are considerable. In addition, CO_2 partial pressure is indirectly related to other environmental parameters such as solution pH and ionic concentration, which have a great influence on precipitation and formation processes of protective scale. Typical trend of CO_2 corrosion rate in scale-free condition is increasing with partial pressure of CO_2 (Wang et al., 2002; Choi et al., 2013; Nesic et al., 2003).

With increase in CO_2 partial pressure, H_2CO_3 concentration increases in surrounding aqueous solution and reduces solution pH, resulting in accelerated cathodic reaction and corrosion rate. However, high CO_2 partial pressure increases concentrations of bicarbonate and carbonate ions in the solution and that results in super saturation of $FeCO_3$. This accelerates the scale formation and consequently reduces corrosion rate (Nesic et al., 2002). Consequently, increasing CO_2 partial pressure does not often accelerate the corrosion process (Sun and Nesic, 2004; Seiersten, 2001). Presence of aqueous CO_2 in contact with carbon steel promotes corrosion by accelerating the cathodic reaction (Sun et al., 2004; Choi et al., 2014; George et al., 2004; Elgaddafi et al., 2015). Tran et al. (2015) conducted a study using electrochemical techniques to investigate mechanisms of cathodic reaction in presence of H_2CO_3. Two possible cathodic reaction mechanisms (direct reaction and buffering effect) were identified. The direct reaction occurs when H_2CO_3 molecules are consumed at steel surface due to: i) reduction of proton produced in the first and the second dissociation processes of carbonic acid (Eqs. (3), (4) and (6)); and ii) direct reaction of carbonic acid with steel surface. Reduction of hydrogen ions dominates the cathodic reaction. The reduction mechanism is considered as buffering effect or phenomenon, in which hydration of aqueous CO_2 creates carbonic acid, which subsequently dissociates and provides additional hydrogen ions in addition to dissociation of water. Then, proton ions move toward the steel surface due to diffusion process. This means that carbonic acid works as a source for hydrogen ions. As presented in Fig. 1, cathodic reaction mechanisms affect the trend of corrosion rate with CO_2 partial pressure (Tran et al., 2015).

A number of studies (Suhor et al., 2012; Tanupabrungsun et al., 2013; Ueda and Takabe, 2001; Dugstad, 1998) demonstrated that protective film/scale that forms on corroded steel surface has a strong impact on corrosion process in CO_2 environment. The film can delay the corrosion process by building up a diffusion barrier for ionic species involved in electrochemical process. Moreover, by covering steel surface, the film impedes dissolution of iron as its density and thickness increase. The most common type of scale

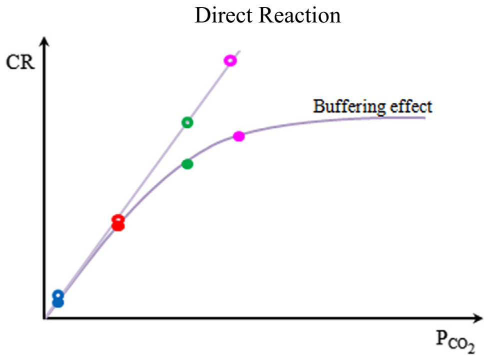

Fig. 1. Corrosion rate change as function of CO_2 partial pressure.

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