Effect of Impurities in Supercritical CO2 Environment on Steel Corrosion Behavior – an Overview

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Effect of Impurities in Supercritical CO$_2$ Environment on Steel Corrosion Behavior – an Overview

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Abstract. Carbon capture, utilization, and storage (CCUS) technology is one of the available technologies to reduce presence of greenhouse gasses. Implementation of CCUS technology strongly relates with the CO$_2$ transportation from the capturing facility to the storage in the geological reservoir. The most economical method for large-scale and long-distance CO$_2$ transportation is using pipeline in supercritical phase. Moreover, presence of impurities such as water, O$_2$, SO$_2$, H$_2$S, NO$_2$ may cause detrimental effect towards carbon steel pipeline. This paper intends to provide an initial information for supercritical CO$_2$ pipeline material selection, which review and summarize existing research on corrosion under supercritical CO$_2$ environment. This paper present environment categorization in supercritical CO$_2$ stream, impurities effect toward sample, as well as brief discuss ion about corrosion evaluation method.

Keywords: CCUS; Corrosion evaluation method; Impurities; Supercritical CO$_2$

1. Introduction

Global warming is recently becoming an issue discussed globally that require not only personal contribution, but also collective and even governmental-level contribution (IPCC, 2022). Furthermore, many countries have committed to reach carbon neutrality by a certain target year to limit global temperature increment (Stockwell et al., 2021; Chen et al., 2022). Carbon capture, utilization, and storage (CCUS) technology is one of the available as well as imperative option to reduce emission and presence of greenhouse gasses which in the end contributing to global temperature increment limitation (Lackner, 2003; Pacala and Socolow, 2004; Mac Dowell et al., 2017; Wei et al., 2021).

Depend on the state of CO$_2$ being transported and source of CO$_2$, CCUS cycles generally include 4 stages: CO$_2$ capture from industrial process, CO$_2$ processing (i.e., dehydration, purification, and compression), CO$_2$ transportation, and CO$_2$ utilization and/or storage in a reservoir (Barker et al., 2017; Lu et al., 2020; Millet et al., 2021; Prasad et al., 2023). CO$_2$ can be transported in pipeline, railway, tanker (Gao et al., 2011; Putra et al., 2022; Hadi et al., 2023; Yuliati et al., 2023). Pipeline transportation is considered as the most economical method for large-scale and long-distance CO$_2$ transport (Zhang et al., 2006). As illustrated in Figure 1 (Global CCS Institute, 2018), pipeline is used to transport CO$_2$ to buffer tank from capturing facility, to jetty before shipped using tanker, and to the ocean for storage in the geological reservoir. Furthermore, supercritical phase is considered as the most efficient way of transporting CO$_2$ due
to its unique properties, which at this phase CO$_2$ has a similar density to the liquid phase but has a similar viscosity to the gas phase (Wang et al., 2019). In order to transport CO$_2$ supercritical phase, the CO$_2$ need to be compressed and/or heated above its critical region, pressure above 7.29 MPa and temperature above 31.1°C (Li et al., 2010).

Carbon steel material such as X52, X65, and X70 are the common material used for CO$_2$ transportation (Xiang et al., 2017). It is widely accepted that dry CO$_2$ is considered to be non-corrosive and water content increment in supercritical CO$_2$ has strong relation with the increment of corrosion rate of carbon steel (Hua et al., 2014; Hua et al., 2017; Morland et al., 2017; Jiang et al., 2019). In addition to water presence, presence of impurities (i.e., O$_2$, SO$_2$, H$_2$S, NO$_2$) will lead to corrosive product formation causing carbon steel pipeline material degradation (Xiang et al., 2017; Lu et al., 2020). As an alternative to CO$_2$ dehydration to overcome the corrosion issue, the alternative option is the utilization of corrosion resistant alloy (CRA), which showed promising result in mitigating corrosion threat under influence of various impurities (Wei et al., 2016b; Hua et al., 2017; Xiang et al., 2020).

The purpose of this paper is to provide an initial information for supercritical CO$_2$ pipeline material selection. This work reviews and summarizes the existing research on corrosion under supercritical CO$_2$ environment. This paper reviews environment categorization in supercritical CO$_2$ stream, impurities effect toward sample, as well as brief discussion about corrosion evaluation method.

2. **Environmental Categorizations in Supercritical CO$_2$ Stream**

According to various research previously conducted (Alan et al., 1996; Russick et al., 1996; Hua et al., 2014; Hua et al., 2015a; Wei et al., 2015; Morland et al., 2017; Jiang et al., 2019), supercritical CO$_2$ environment could be generally categorized into 4 types of environments based on water presence and concentration. Those 4 types of environments are: dry supercritical CO$_2$, water-unsaturated supercritical CO$_2$, water-saturated supercritical CO$_2$, supercritical CO$_2$-saturated water.

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2.1. Dry supercritical CO$_2$

Many experiment results have shown that dry SC CO$_2$ is essentially non-corrosive. An experiment utilizing carbon steel (1018), indicated that this material showed no evidence of corrosion when exposed to pure supercritical CO$_2$ at test pressure of 240 bar, test temperature of 50°C, and test duration of 24 hours (Russick et al., 1996). Other experiment also confirms that minimum trace of corrosion observed on iron when exposed to pure supercritical CO$_2$ at test pressure of 87-123 bar, test temperature of 162-183°C, and test duration of 4964 hours (Alan et al., 1996).

2.2. Water-unsaturated supercritical CO$_2$

Water-unsaturated supercritical CO$_2$ means that water content below the solubility limit in the supercritical CO$_2$ and means all water dissolves in the supercritical CO$_2$. Therefore, there is no free liquid water phase in the CO$_2$/H$_2$O system, resulting in the absence of electrochemical reactions, hence the corrosion rate is low (Hua et al., 2015a; Wei et al., 2015; Xiang et al., 2017). Experiment conducted by Hua et al. (Hua et al., 2015a), indicated that carbon steel X65 showed low general corrosion rate when exposed to water-unsaturated supercritical CO$_2$ environment. The test was conducted at test pressure of 80 bar, test temperature of 50°C, and test duration of 48 hours with various water content of 700, 1600, 2650 ppm. While the solubility limit for above experiment is 3400 ppm. The sample showed a general corrosion rate of 0.015 mm/year when immersed in 2650 ppm of water environment. Carbon steel X65 showed no evidence of general corrosion when exposed to water content of 700 and 1600 ppm. In terms of pitting corrosion, carbon steel X65 showed no evidence of pitting corrosion when exposed to water content of 2650 ppm, which over one order of magnitude greater than the general corrosion rate reaching 0.015 mm/year.

2.3. Water-saturated supercritical CO$_2$

Oppositely with water-undersaturated supercritical CO$_2$, water-saturated supercritical CO$_2$ means that water content above the solubility limit in the supercritical CO$_2$, which then clustered together forming a free water (i.e., water droplets), hence providing electrochemical reactions (Hua et al., 2015a; Wei et al., 2015; Xiang et al., 2017). Study conducted by Morland et al. (Morland et al., 2017) and Hua et al. (Hua et al., 2015a) confirmed that presence of free water meaning water content above the solubility limit, leads to higher corrosion rate compared to water-unsaturated supercritical CO$_2$ meaning water content below solubility limit.

2.3. Supercritical CO$_2$-saturated water

Supercritical CO$_2$-saturated water means supercritical CO$_2$ dissolved in water phase present in the system (Hua et al., 2015a; Wei et al., 2015). Choi et al. (Choi et al., 2010) conducted an experiment on carbon steel X65 in supercritical CO$_2$-saturated water environment with test pressure of 80 bar and test temperature of 50°C. the experiment revealed that the general corrosion rate reached 19.2 mm/year at test duration of 24 hours, and the rate decreased to 10.6 mm/year at test duration of 120 hours. Zhang et al. (Zhang et al., 2011) reported similar finding of high corrosion rate occurred on carbon steel X65 tested under supercritical CO$_2$-saturated water environment, 95 bar test pressure and test temperature of 80°C. the test indicated general corrosion rate reached 28.3 mm/year after 2 hours of immersion and gradually decreased to 7.26 mm/year after 168 hours of immersion. Another test conducted by Hua et al. (Hua et al., 2015a)

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using carbon steel X65 material, 80 bar test pressure, test temperature of 50°C in supercritical CO₂-saturated water environment also reported significant corrosion rate. The test reported that the general corrosion rate reached 10.8 mm/year at test duration of 6.5 hours, and the rate decreased to 4.1 mm/year at test duration of 96 hours.

3. **Effect of Impurities in Supercritical CO₂ Stream**

3.1. **Effect of O₂**

Effect of O₂ in supercritical CO₂ have been studied by some scholars (Hua et al., 2015b; Hua et al., 2017; Rosli et al., 2016; Sun, et al., 2016a) in the past. Hua et al. (Hua et al., 2017) conducted a test toward carbon steel X65 and 13Cr steel in water-saturated supercritical CO₂ environment under test pressure of 80 bar, test temperature of 35°C, with influence of 0 and 1000 ppm of O₂ for 48 hours duration. The test reported that both carbon steel X65 and 13Cr steel showed a decrement of general corrosion rate when O₂ introduced in the test environment compared to the environment without O₂. The general corrosion rates of X65 and 13Cr are 0.1 mm/year and 0.003 mm/year respectively for test environment without O₂ and the general corrosion rates of X65 and 13Cr are 0.03 mm/year and 0.001 mm/year under the influence of 1000 ppm of O₂ in the test environment. The test also reported that no localized corrosion is observed on 13Cr under above test environment, whilst X65 shows increment of localized corrosion rate from approx. 0.95 mm/year to approx. 3 mm/year when 1000 ppm of O₂ introduced.

Other research (Hua et al., 2015b; Rosli et al., 2016; Sun, et al., 2016a; Sun et al., 2018a), indicated similar outcome that general corrosion rate of steel is decreasing, and localized corrosion rate is increasing when O₂ is introduced to water-saturated supercritical CO₂. Insignificantly differ from previously mentioned research, Choi et al. (Choi et al., 2010) reported that increment of oxygen content varies from 0% to 6% in water-saturated supercritical CO₂ environment with test pressure of 80 bar, test temperature of 50°C lead to increment of general corrosion rate that peaked at 1 mm/year at O₂ concentration of 4% (3.3 bar). Furthermore, the general corrosion rate decreased to approx. 0.9 mm/year as the O₂ concentration increased to 6% (5.1 bar).

Researcher explains that the phenomenon of reduction of general corrosion rate and increment of localized corrosion rate when O₂ introduced in the test environment were due to the presence of O₂ that inhibit FeCO₃ protective layer formation and forming Fe₂O₃ and Fe(OH)₃ which are considered porous and less protective oxide layer (Choi et al., 2010; Hua et al., 2015b; Rosli et al., 2016; Sun et al., 2016a; Sun et al., 2018a; Cui et al., 2019). Furthermore, other academics (Hua et al. 2015b; Rosli et al., 2016; Sun et al., 2016a) proposed that thickened protective layer causing decrement of O₂ availability to local area, which believed to result in galvanic cell development that leads to localized corrosion.

3.2. **Effect of SO₂**

SO₂ is categorized as highly corrosive gas and various study documented that SO₂ contributed to a substantial detrimental effect on corrosion behavior in supercritical CO₂ environment (Choi et al., 2010; Xiang et al., 2011; Wei et al., 2015; Rosli et al., 2016; Sun et al., 2016a; Xu et al., 2016; Hua et al., 2017; Xiang et al., 2017; Sun et al., 2018a; Yong Hua et al., 2018a; Cui et al., 2019). Presence of SO₂ also inhibit the formation of FeCO₃ and known the be driving the corrosion process over CO₂ (Sun et al., 2018a). Recent study by Hua et al. (Hua et al., 2017) reported a test toward carbon steel X65 and 13Cr steel in water-saturated supercritical CO₂ environment under test pressure of 80 bar, test temperature of 35°C with influence of 0 and 100

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ppm of SO$_2$ for 48 hours duration. The test reported that both X65 and 13Cr steel showed an increment of general corrosion rate when SO$_2$ introduced in the test environment compared to the environment without SO$_2$. The general corrosion rates for X65 and 13Cr are 0.1 mm/year and 0.003 mm/year with no influence of SO$_2$ and significantly increased to 0.65 mm/year and 0.01 mm/year under the influence of 100 ppm of SO$_2$. The test also reported that no localized corrosion is observed on 13Cr under above test environment, whilst X65 shows increment of localized corrosion rate from approx. 0.95 mm/year to approx. 2 mm/year when 100 ppm of SO$_2$ introduced.

Another experiment also captured detrimental effect of SO$_2$ towards carbon steel X70 material under water-saturated supercritical CO$_2$ environment (Sun et al., 2018a). Furthermore, the experiment conducted with test pressure of 100 bar and test temperature of 50°C, the test also captured various SO$_2$ content ranging from 200 to 1000 ppm in the test environment. The general corrosion rates are 0.269 mm/year, 0.345 mm/year, and 0.423 mm/year respectively for 200 ppm, 600 ppm, and 1000 ppm SO$_2$ content.

Presence of O$_2$ and SO$_2$ in the supercritical CO$_2$ could cause more detrimental effect toward steel compared to detrimental effect of O$_2$ and SO$_2$ existed individually in the environment (Choi et al., 2010; Xiang et al., 2011; Sun et al., 2016a; Hua et al., 2017; Hua et al., 2018a; Sun et al., 2018b; Cui et al., 2019). This synergistic phenomenon was caused by oxidation from FeSO$_4$ into FeOOH, and FeSO$_4$ will further oxidize into FeOOH which resulting in H$_2$SO$_4$ formation. H$_2$SO$_4$ formation further reduces pH in the environment, hence exacerbate the corrosion (Choi et al., 2010; Wei et al., 2015; Sun et al., 2018a).

In addition, presence of SO$_2$ in water-saturated supercritical CO$_2$ is not causing increment of stress corrosion cracking (SCC) susceptibility on X65 carbon steel under test condition of 45°C, 100 bar, 3% O$_2$, 100 ppm SO$_2$, 137 hours test duration using four-point bending test method (Zeng and Li, 2020; ASTM International, 2021a). Further long-term duration test was conducted at the same environment test condition as in Zeng and Li previous experiment (Zeng and Li, 2020) with duration up to 480 hours and observes no SCC cracking on X65 carbon steel (Li and Zeng, 2023).

### 3.2. Effect of H$_2$S

H$_2$S presence in supercritical CO$_2$ environment could cause both general and localized corrosion rate of carbon steel and low alloy steel (Choi et al., 2015; Sun et al., 2016a; Wei et al., 2016a; Wei et al., 2016b; Xiang et al., 2017; Sui et al., 2018; Cui et al., 2019). Research conducted by Wei et al. (Wei et al., 2016a), reported that presence of 50 ppm of H$_2$S both in water-saturated supercritical CO$_2$ and supercritical CO$_2$-saturated water could aggravate the general corrosion rate of carbon steel X65. The test was conducted under 80°C, 100 bar, 1 m/s flow and 10 days of exposure duration. It is reported that the general corrosion rate of carbon steel X65 is 0.17 mm/year and 0.24 mm/year for no H$_2$S and with H$_2$S respectively under water-saturated supercritical CO$_2$. Furthermore, the general corrosion rate of the sample reached 8.46 mm/year in environment without H$_2$S and almost doubled to 15.48 mm/year in environment with H$_2$S under supercritical CO$_2$-saturated water. This research explains that the aggravation of general corrosion rate in water-saturated supercritical CO$_2$ occurred due to increment of H$_2$O solubility which increase condensation of H$_2$O in the sample surface, hence aggravating the general corrosion rate. As for the case of supercritical CO$_2$-saturated water, this research explains that HS$^-$ formed in the solution and initiating the formation of porous FeS layer in the steel surface, subsequently the steel can be continuously corroded by the reactive ions in the solutions (i.e., H$^+$, HCO$_3^-$ and CO$_3^{2-}$).

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An interesting finding also captured in the same research (Wei et al., 2016a), specifically in the supercritical CO$_2$-saturated water, where addition of 50 ppm could contribute to the changes of corrosion type from localized corrosion to general corrosion. It is reported that the highest pitting depth is 316 μm in no H$_2$S environment and 81.4 μm for 50ppm H$_2$S environment. The reported pitting rate is 9.19 mm/year and 2.45 mm/year for no H$_2$S and 50ppm H$_2$S environment respectively.

Choi et al. (Choi et al., 2015) reported 0.41 mm/year of general corrosion rate on 200 ppm H$_2$S (80°C, 120 bar, water saturated, 48 hours), Sun et al. (Sun et al., 2016a) reported 0.127 mm/year of general corrosion rate on 1000 ppm H$_2$S (50°C, 100 bar, water saturated, 120 hours), Sui et al. (Sui et al., 2018) reported 0.186 mm/year of general corrosion rate on 1000 ppm H$_2$S (35°C, 100 bar, water saturated, 72 hours).

Wei et al. (Wei et al., 2016b) conducted a test on 316L under same test environment as described in Wei et al. previous work (Wei et al., 2016a). The test reported that both general and localized corrosion rate of 316L in supercritical CO$_2$-saturated water are below 0.04mm/year and no measurable corrosion was observed on the 316L under water-saturated supercritical CO$_2$ environment.

In addition to above, combination of H$_2$S and water could lead to sulfide stress cracking (SSC) if the material is under tensile stress and corrosion, causing hydrogen absorption into the material which ultimately initiating hydrogen embrittlement (Raja and Shoji, 2011; American Petroleum Institute, 2020). SSC phenomenon is further investigated by Li et al. (Li et al., 2021), which reported that no cracks penetrated the carbon steel X65 in water-saturated supercritical CO$_2$ under test condition of 45°C, 100 bar, 3% O$_2$, 100 ppm SO$_2$, 137 hours test duration using four-point bending test method.

3.2. Effect of NO$_2$

Researchers agree that NO$_2$ is corrosive in supercritical CO$_2$ environment (Ayello et al., 2010; Brown et al., 2014; Sun et al., 2016b; Sun et al., 2017; Hua et al., 2018b). Presence of NO$_2$ in water-saturated CO$_2$ environment initiated the formation of HNO$_3$ and led to formation of corrosion product that considered to be loose and insignificantly protective (Dugstad et al., 2013; Sun et al., 2016b). Brown et al. (Brown et al., 2014) conducted test on carbon steel X65 and reported a general corrosion rate of 0.127 mm/year even when small amount of 50 ppm NO$_2$ added in water-unsaturated supercritical CO$_2$ under 100 bar test pressure, 50°C test temperature in 1 day test duration. Significantly higher general corrosion rate up to 11.6 mm/year as calculated by Ayello et al. (Ayello et al., 2010), under supercritical CO$_2$ environment and test condition 75.8 bar, 40°C, 1000 ppm of water, and 100 ppm of NO$_2$.

Other researchers (Sun et al., 2016b; Sun et al., 2017; Hua et al., 2018b) are in agreement that localized corrosion rate are significantly higher compared to general corrosion rate. Sun et al. (Sun et al., 2016b) conducted test on X65 carbon steel in water-saturated supercritical CO$_2$ with 100 bar test pressure, 10 grams of water, 50°C test temperature, 1000 ppmv of NO$_2$, 24- and 120-hours test duration. This experiment reported general corrosion rate of 1.76 mm/year and 0.48 mm/year for test duration of 24 and 120 hours respectively and captured a significantly higher localized corrosion rate of 5.11 mm/year and 1.53 mm/year for test duration of 24 and 120 hours respectively. Furthermore, Sun et al. (Sun et al., 2017) reported a higher localized corrosion rate of approx. 3 mm/year when conducting the same test as conducted by Sun et al. (Sun et al., 2016b), which occurred due to inhomogeneous precipitation of water droplets on the steel surface.

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Hua et al. (Hua et al., 2018b) conducted test on carbon steel X65 in water-saturated supercritical CO$_2$ with 80 bar test pressure, 35$^\circ$C test temperature, 50 and 100 ppm of NO$_2$, 48 hours test duration. This experiment captured the general corrosion rate of general corrosion rate of 0.17 mm/year and 0.23 mm/year for NO$_2$ impurity of 50 and 10 ppm respectively and captured a significantly higher localized corrosion rate of approx. 1.9 mm/year for NO$_2$ impurity of 50 and 10 ppm respectively.

4. Corrosion Behavior Evaluation Method

4.1. Corrosion rate evaluation method

ASTM G193-22 (ASTM International, 2022), provides the definition of corrosion rate which typically declared in thickness loss per unit of time and weight loss per area per unit of time. General corrosion rate calculation, as expressed in Equation 1, is commonly used when corrosion occurs uniformly over the surface area and localized corrosion does not occur or is not considered in separate calculation (ASTM International, 2021b).

\[
GCR = \frac{8.76 \times 10^4 \times \Delta w}{S_a \times \rho \times T_{ex}}
\] (1)

where GCR – general corrosion rate in mm/year, $\Delta w$ – weight loss in gram, $S_a$ – Surface area of the specimen in cm$^2$, $\rho$ – material density in g/cm$^3$, $T_{ex}$ – sample exposure time in hours.

Weight loss measurement should be measured after the test specimens have been properly dried, after previously being cleaned using solutions as prescribed in ASTM G1-03 (ASTM International, 2017). ASTM G 31-21 (ASTM International, 2021b) recommends the test specimens measurement conducted using electronic balance with minimum 1 mg accuracy or better, typically researchers used an electronic balance with an accuracy of 0.1 mg (Zhang et al., 2011; Sun et al., 2016b; Sun et al., 2018a) or even 0.01 mg (Xiang et al., 2011; Hua et al., 2014; Hua et al., 2015a; Hua et al., 2017) to ensure the accuracy of weight data.

Although known as the widely used corrosion evaluation method, general corrosion rate calculation possessed some limitations such as unreliable corrosion rate calculation due to imperfect or excessive process of corrosion product cleaning in the solution, corrosion rate underestimation if the main damage mechanism is pitting or localized corrosion, and absence of information related to the corrosion mechanism (Kutz, 2012; ASTM International, 2017; ASTM International, 2022; Malaret, 2022).

Localized corrosion is a form of damage mechanism which considered to be more destructive than general corrosion due to its difficulty to be detected and its adverse impact toward metal integrity (Akpanyung and Loto, 2019). Accurate determination of localized corrosion rate is important to understand the extent of damage caused by pitting (ASTM International, 2021c). Localized corrosion rate determination is commenced by measurement of pit depth occurred on the specimens. Pit depth measurement can be done by old-fashioned approach using depth gage or by a more sophisticated equipment such as White Light Interferometry (Hua et al., 2015a) or 3D Laser Microscope (Xu et al., 2016) which able to obtain the pit contour without cross sectioning the specimens (ASTM International, 2021c).

Furthermore, extend of damage caused by localized corrosion could be expressed in two approaches, pitting factor captured in Equation 2 and localized corrosion rate captured in Equation 3 (Wei et al., 2016a; Wei et al., 2018; ASTM International, 2021c).

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\[ PF = \frac{DPP \times S_a \times \rho}{1000 \times \Delta w} \]  

\[ LCR = \frac{8.76 \times PP}{T_{ex}} \]

where \( PF \) – Pitting Factor, \( DPP \) – Deepest Pitting Penetration in \( \text{m} \), \( S_a \) – surface area of the specimen in \( \text{cm}^2 \), \( \rho \) – material density in \( \text{g/cm}^3 \), \( \Delta w \) – weight loss in gram, \( LCR \) – localized corrosion rate in \( \text{mm/year} \), \( PP \) – Pitting Penetration in \( \text{m} \), and \( T_{ex} \) – sample exposure time in hours. Pitting factor of 1 can be interpreted as uniform corrosion. Increment of pitting factors number correlate with the increment of pit penetration depth.

4.2. Corrosion product evaluation method

Corrosion product often contains important information which provide insight in determining damage mechanism of a material in a certain environment that can be further utilized to mitigate similar damage mechanism in the future (Eiselstein and Huet, 2011; Pantazopoulos and Vazdirvanidis, 2014). Corrosion products characterization can be done by various method, including Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-ray Diffraction (XRD), Ultraviolet Visible Spectroscopy (UV-vis), Fourier Transform Infrared Spectroscopy (FT-IR), Mössbauer Spectroscopy, Raman Spectroscopy, X-ray Photoelectron Spectroscopy (XPS) (Waseda and Suzuki, 2006).

Corrosion product supercritical \( \text{CO}_2 \) was analyzed by Jiang et al. (Jiang et al., 2019) using electron microscope (i.e., SEM) able to identify different surface morphology of X65 steel coupon as influenced by various water content. The test reported that based on visual observation using SEM polishing marks and thin film of corrosion product were observed under 600 ppm water content whilst porous corrosion product observed under influence of free water. Furthermore, elemental composition investigation was performed using EDS at selected location and reported the same elemental composition with different percentage depend on the water content, which then used as basis to indicate the corrosion product compound formation.

A more complex experiment was conducted by Chong et al. (Chong et al., 2018) involving not only water but also \( \text{CO}_2 \), \( \text{O}_2 \), \( \text{H}_2\text{S} \), and \( \text{SO}_2 \) as the impurities. It was reported that SEM, XRD, XPS and Raman spectroscopy were used to evaluate corrosion product from the tests. The same report also explained that identification of observable corrosion product, exposed to water content below 1500 ppmv, using XRD was not easy due to the limitation of depth of penetration of this equipment. XPS and Raman Spectroscopy were utilized to complement XRD limitation. Both equipment were selected due to their capability of analyzing corrosion product from top zero to ten nanometers and from top zero to several hundred nanometers, respectively for XPS and Raman Spectroscopy (Song et al., 2013; Chong et al., 2018). Furthermore, the experiment (Chong et al., 2018) concluded that the main corrosion product of X65 steel exposed to Water-unsaturated supercritical \( \text{CO}_2 \) with \( \text{CO}_2\text{-O}_2\text{-H}_2\text{S-SO}_2 \) impurity at 10 MPa and 50°C.

5. Conclusions

There are four environments in supercritical \( \text{CO}_2 \) which are dry supercritical \( \text{CO}_2 \), water-unsaturated supercritical \( \text{CO}_2 \), water-saturated supercritical \( \text{CO}_2 \), and supercritical \( \text{CO}_2 \) saturated water. Dry supercritical \( \text{CO}_2 \) is considered non-corrosive, while water-saturated supercritical \( \text{CO}_2 \) and supercritical \( \text{CO}_2 \) saturated water are considered corrosive. Water-unsaturated supercritical
CO₂, depend on the water content, could be classified as corrosive and non-corrosive. O₂, SO₂, H₂S, and NO₂ presence could aggravate corrosion. Coexistence of more than one impurity could accelerate corrosion compared to single-existence impurity. O₃ presence in supercritical CO₂ could decrease general corrosion rate and increase localized corrosion rate. SO₂ presence in supercritical CO₂ could cause the increment of both general and localized corrosion rate. H₂S presence in supercritical CO₂ could lead to both localized and general corrosion, however the existence of this impurity lead to shifting of corrosion mechanism to general corrosion from localized corrosion. NO₂ presence could aggravate significantly the localized corrosion compared to the general corrosion. Research related to corrosion under supercritical CO₂ environment commonly calculate the general corrosion, localized corrosion rate, and pitting factor to quantify the detrimental effect of impurities toward sample. Methods that commonly used for evaluating corrosion product are SEM, EDS, XRD, XPS and Raman Spectroscopy.

References


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Choi, Y S, Neić, S & Young, D J 2010, ‘Effect of impurities on the corrosion behavior of CO2 transmission pipeline steel in supercritical CO2-water environments.’, Environmental science & technology, 44, pp.9233-9238.


doi: https://doi.org/10.7454/jmef.v3i2.1049


Lu, H, Ma, X, Huang, K, Fu, L & Azimi, M 2020, ‘Carbon dioxide transport via pipelines: A systematic review’, *Journal of Cleaner Production*, 266.


Rosili, N R, Choi, Y S, Nesic, S & Young, D 2016, ‘Corrosion of UNS G10180 steel in supercritical and subcritical CO₂ with O₂ as a contaminant’, *Corrosion*.


doi: https://doi.org/10.7454/jmef.v3i2.1049


Sun, J, Sun, C & Wang, Y 2018a, ‘Effects of O\textsubscript{2} and SO\textsubscript{2} on Water Chemistry Characteristics and Corrosion Behavior of X70 Pipeline Steel in Supercritical CO\textsubscript{2} Transport System’, Industrial & Engineering Chemistry Research, 57(6), pp.2365-2375.

Sun, C, Sun, J, Liu, S & Wang, Y 2018b, ‘Effect of water content on the corrosion behavior of X65 pipeline steel in supercritical CO\textsubscript{2}-H\textsubscript{2}O-H\textsubscript{2}S-SO\textsubscript{2} environment as relevant to CCS application’, Corrosion Science, 137, pp.151-162.


doi: https://doi.org/10.7454/jmef.v3i2.1049