



# Corrosion Control in CO<sub>2</sub> Enhanced Oil Recovery From a Perspective of Multiphase Fluids

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Carbon capture and storage (CCS) combined with CO<sub>2</sub>-enhanced oil recovery (EOR), has been recently viewed as an economical and effective method for the reduction of carbon emissions. However, corrosion is a challenging issue in the whole chain process of CO<sub>2</sub>-EOR production if water presents and mild steel pipeline is used. In this paper, the corrosion risk of pipeline at different stages of CO<sub>2</sub>-EOR production is systematically assessed based on a detailed analysis of the fluid characteristics. According to the fluid state of CO<sub>2</sub>, water and crude oil, current understandings on the corrosion behavior of steel materials in multiphase flow conditions are reviewed. Furthermore, the intermittent water wetting phenomena and the fluid behavior of water droplets or clusters in an electrolyte/non-electrolyte emulsion are correlated with the steel corrosion performance, providing new insights into the corrosion phenomena. Besides application of corrosion resistant materials and corrosion inhibitors, tailoring of processing parameters, such as enhancing the water entrainment, shortening the water contact time, and reducing the solution corrosivity, is highly recommended as an effective method for corrosion control in aggressive CO<sub>2</sub>-EOR production conditions. Based on these, some important future research topics on the corrosion in multiphase fluids are suggested.

**Keywords:** CCS, CO<sub>2</sub>-EOR, multiphase flow corrosion, corrosion mechanism, pipeline

## BACKGROUND

Our daily life is closely relied on the technological advancement of a carbon-based civilization. Over eighty percent of the global energy consumption in 2015 is fossil fuels, i.e., coal (29.2%), crude oil (32.9%), and natural gas (23.8%), from which a direct emission of about 36 billion tons of carbon dioxide has become a great challenge in combating its possible environmental impacts. Carbon Capture and Sequestration (CCS) is one of the most promising ways for reducing the buildup of greenhouse gas emissions in the atmosphere.

Combined with CCS techniques, CO<sub>2</sub> enhanced oil recovery (EOR) has proved to be currently applicable in China for reducing CO<sub>2</sub> emissions (Zhang et al., 2013; Lv et al., 2015). The CO<sub>2</sub>-EOR technique may produce a net zero emission of CO<sub>2</sub>, as it can store carbon underground during oil production. Therefore, the crude oil comes from CO<sub>2</sub>-EOR is generally termed as “carbon negative oil” (Hornafius and Hornafius, 2015). A significant improvement of oil production can be observed with CO<sub>2</sub> injection into reservoirs compared to the conventional water injection production. In a pilot scale CCS-EOR project in Shengli oilfield, the improved efficiency of crude oil is around 8%

and the dynamic ratio of carbon storage in reservoir conditions is around 50% (Lv et al., 2015). It provides a green and economical way to improve oil production in an old oilfield.

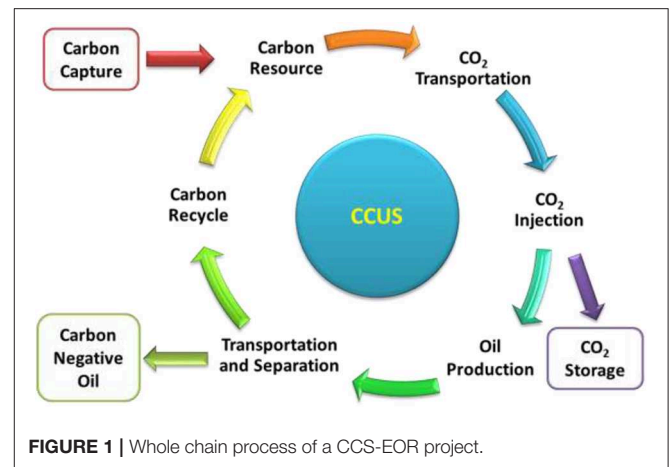
However, corrosion is a big concern in operating a CO<sub>2</sub>-EOR project, as CO<sub>2</sub> becomes corrosive to steel-based facilities when it meets water. For example, in the CO<sub>2</sub>-EOR production section of Shengli oilfield, the presence of a large amount of CO<sub>2</sub> in the production fluids has resulted in an abrupt increase of pipeline leakages within the initial 3 years after the injection of CO<sub>2</sub> into reservoirs (Wang et al., 2015), revealing an averaged corrosion rate of pipeline materials higher than 1.0 mm/y (Zhang J. et al., 2012; Wang Z. M. et al., 2014). According to the field experience from Chevron, the coated tubes can only service for 50 months in CO<sub>2</sub>-injection well conditions (IEAGHG, 2010). Similar damage induced by the presence of high partial pressure of CO<sub>2</sub> has also been reported in other CO<sub>2</sub>-EOR projects (Tzimas et al., 2005; Singh et al., 2010). The corrosion performance of different materials in CO<sub>2</sub>-containing aqueous solutions has been systematically investigated, and some strategies on corrosion control in CCS and CO<sub>2</sub>-EOR production have been suggested based on field experiences (Sim et al., 2014b; Wang et al., 2015). The use of corrosion-resistant alloys (CRA) and corrosion inhibitors is regarded as two of the important ways to mitigate corrosion in aggressive CO<sub>2</sub> conditions (IEAGHG, 2010). However, in operating a large-scale CO<sub>2</sub>-EOR project, corrosion management should be systematically considered at the design and operation stages, which could significantly minimize the cost. Therefore, the corrosion risk of pipeline materials should be carefully evaluated. In this paper, we summarize the current views on corrosion evaluation and control of the CO<sub>2</sub>-containing multiphase flow pipelines in CCS-EOR production, based on which some ideas on corrosion management in the whole chain process of a CCS-EOR project are discussed.

## FIELD ANALYSIS

### Whole Chain Process

There has been a long history of the trial application of CO<sub>2</sub>-EOR technique in oil and gas industry. However, the combination of this technique with CCS was recently adopted. As illustrated in **Figure 1**, the whole chain can be divided into carbon capture, CO<sub>2</sub> transportation, CO<sub>2</sub> injection, and oil production, during which a great portion of CO<sub>2</sub> are permanently stored underground and the other is reutilized in the recycling process. In this whole chain process, CO<sub>2</sub> can be viewed as a feedstock and crude oil is the product. When the net emission of CO<sub>2</sub> is less than zero, i.e., the amount of CO<sub>2</sub> stored underground is larger than that produced after burning the CO<sub>2</sub>-EOR crude oil, the crude oil will become “carbon negative.”

Currently, corrosion is one of the big concerns for wide application of the CCS-EOR technique, as water may be acidified in a CO<sub>2</sub>-containing environment. The presence of crude oil could vastly change the corrosion performance of steel materials, implying that the fluid structure may significantly affect corrosion. Therefore, the state of water and the fluid properties will be highlighted in this paper.



## Fluid Properties

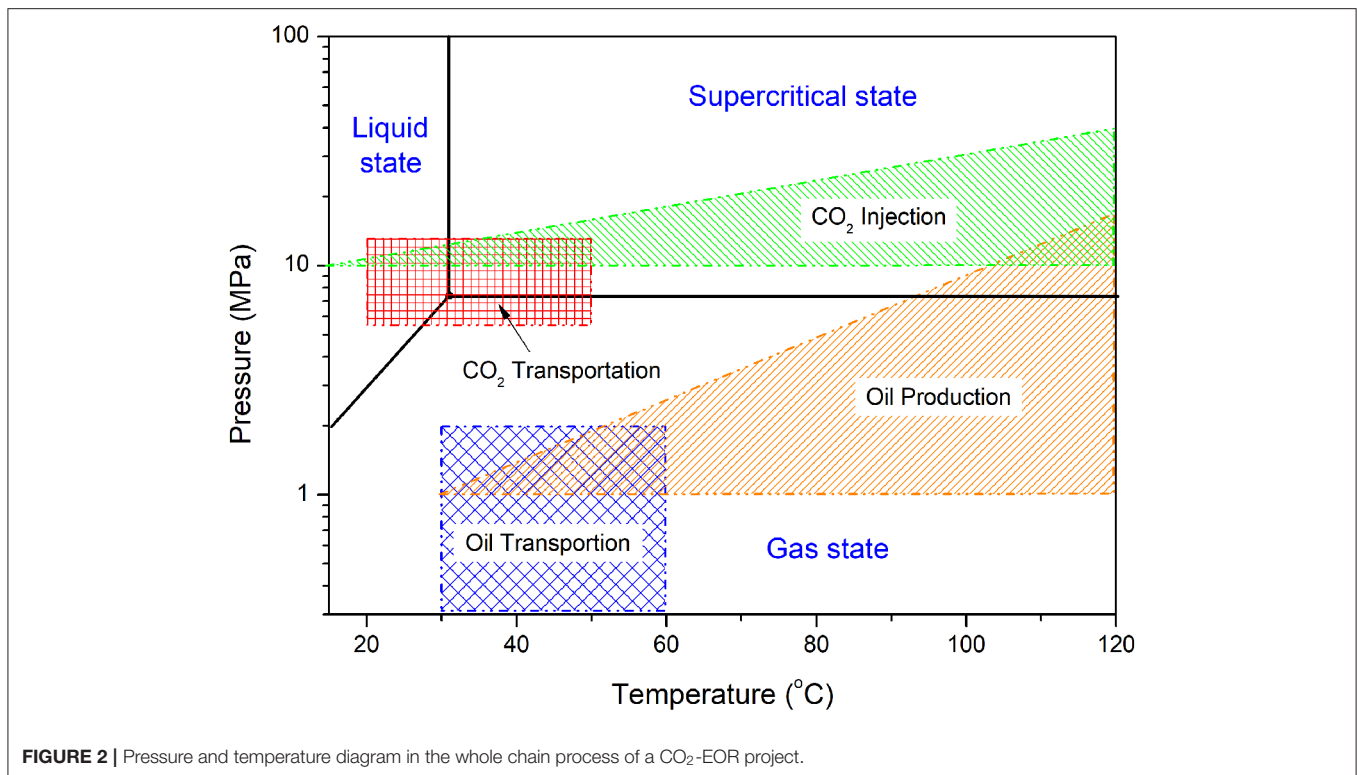
### Pressure and Temperature

Pressure and temperature are two important parameters that determine the properties of the CO<sub>2</sub>-containing fluids, including the state of CO<sub>2</sub> phase, solubility, and pH-values, as well as the properties of crude oils. The diagram of pressure and temperature of CO<sub>2</sub> phase is illustrated in **Figure 2**, where pressure refers to the partial pressure of CO<sub>2</sub>. A transitional point at 7.31 MPa and 31.06°C is indicated and the liquid phase, supercritical phase and gas phase of CO<sub>2</sub> are separated by black lines, as labeled in **Figure 2**.

CO<sub>2</sub> can be transported in different states, but a single-phase state is preferred in pipeline for a security reason. Generally, a supercritical phase or a gas phase is selected, since it needs less energy for long-distance transportation. In some cases, CO<sub>2</sub> is liquefied to a small volume and transported by tanks. Liquid CO<sub>2</sub> may also be encountered when CO<sub>2</sub> is transported in a supercritical state, as the failure of the heat-resistant coatings on the outside surface of a pipeline may result in a decrease of temperature below the critical point. Generally, the pressure of CO<sub>2</sub> transportation pipeline is in a range from 5 to 20 MPa. A high pressure can increase the efficiency of transportation. The temperature may vary in a wide range from below 20°C up to 50°C, depending on the heating or cooling conditions.

CO<sub>2</sub> injection may need a pressure higher than 10 MPa at wellhead and the pressure will be further increased with depth from wellhead. As reported in a previous paper (Wang and Song, 2018), at a depth of 3,000 m, the pressure can be higher than 35 MPa, which is certainly determined by the injection rate and the pressure at wellhead. Temperature is closely related to the depth profile of the ground temperature. According to the field experience in Shengli oilfield, a supercritical state could be kept during continuous injection deeper than 700 m if CO<sub>2</sub> was initially injected in a liquid state. A higher injection rate will push the transitional point to a deeper site in well conditions. The ranges of temperature and pressure of CO<sub>2</sub> fluid in a typical well are schematically shown in **Figure 2**.

In an oil production well, the distributions of pressure and temperature are dependent on well depth. At the wellbore,



temperature and pressure reach their highest values, where CO<sub>2</sub> may be in a supercritical or gas state. As flowing from the well bottom to wellhead, both of the pressure and temperature of the fluids gradually decrease. In some cases, temperature may decrease below 30°C at wellhead and pressure below 1.0 MPa. The fluid must be heated and pressurized in the following transportation process. Different from a CO<sub>2</sub> injection well, the fluid in an oil production well is generally a complex mixture of oil, water and gas. In CO<sub>2</sub>-EOR production, the content of CO<sub>2</sub> in gas phase can be as high as 70% in volume (Wang et al., 2015).

The oil gathering and transportation system is generally operated at a pressure from 0.3 to 2.0 MPa, relatively low compared to the pressure in well conditions. Its temperature is generally lower than 60°C, but for some highly viscous crude oil it may reach 80°C for obtaining a good fluidity. Therefore, the CO<sub>2</sub>-containing aqueous phase in oil transportation pipeline is usually less corrosive than that in oil production well. It is obvious that the flow pattern in a horizontal pipe or a slightly inclined pipe for crude oil transportation is generally different from that in a vertical well tube.

### CO<sub>2</sub> Phase

In CO<sub>2</sub> transportation and injection, the state of CO<sub>2</sub> phase is determined by its pressure and temperature. As shown in **Figure 2**, the supercritical state of CO<sub>2</sub> may be widely encountered in the CO<sub>2</sub> transportation, injection, and oil production processes. Depending on the technology of carbon capture and the resource of CO<sub>2</sub>, trace amounts of impurity gases may remain in the CO<sub>2</sub> after purification. These impurities

generally include water, O<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>, and H<sub>2</sub>S. Water is the most common impurity compound in CO<sub>2</sub> during transportation and injection, whose concentration limit is recommended to be <500 ppm. Although these impurities are generally controlled at a very low level, they may affect steel corrosion in water-containing supercritical (SC) CO<sub>2</sub> conditions.

In the oil production and transportation stages, CO<sub>2</sub> gas is mixed with natural gas at a fraction around 30~70 vol.%, according to the CO<sub>2</sub>-EOR production in Sinopec Shengli oilfield (Wang et al., 2015). At the initial stage of injection, the fraction of CO<sub>2</sub> is similar to that of the conventional oil production, as CO<sub>2</sub> has not migrated to the production well. After continuous injection for months, a sharp increase of the fraction of CO<sub>2</sub> can be observed, finally reaching a value around 50~70% in volume fraction. In this case, besides acidifying the aqueous phase, the large volume of CO<sub>2</sub> gas may also affect the flow patterns.

### Water Phase

During CCS and EOR production, water is saturated with CO<sub>2</sub> forming carbonic acid. The pH-value of the aqueous solution is depending on the partial pressure of CO<sub>2</sub> and the temperature, as well as the salinity of solution (Nesic, 2007); a linear relationship can be observed between pH-value and CO<sub>2</sub> pressure. It should be noticed that the diffusion coefficient of CO<sub>2</sub> in water is around 10<sup>-8</sup> m<sup>2</sup>/s in stagnant conditions, according to which it needs several to tens of minutes to diffuse through the bulk solution layer (Grogan et al., 1988; Farajzadeh et al., 2009). However, in a multiphase flow condition the saturation of CO<sub>2</sub> in water can be greatly accelerated owing to the well-known

migration mechanism. It should be noticed that CO<sub>2</sub> corrosion is generally controlled by cathodic reactions, where different kinds of ionic species (such as H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, and even H<sub>2</sub>CO<sub>3</sub>) would be participated in the reduction process depending on pH-values (Nesic, 2007). The formation of corrosion product layer mainly relies on the local solution chemistry at the vicinity near the steel surface where the concentrations of ferrous ion and CO<sub>3</sub><sup>2-</sup> are above the solubility limit of FeCO<sub>3</sub> for precipitation (Nesic et al., 2004; Ingham et al., 2012; Bian et al., 2015). In turn, the formation of FeCO<sub>3</sub> layer will retard the anodic reaction depending on its morphology and protectiveness (Barker et al., 2018). The presence of a trace amount of S<sup>2-</sup> (Yang et al., 2017) and Ac<sup>-</sup> (Amri et al., 2010) ions in aqueous phase can change the formation and the stability of FeCO<sub>3</sub> layers.

### Crude Oil

Crude oil is a complex mixture of hydrocarbons and it is generally categorized into three types according to its density. A heavy crude oil has an American Petroleum Institute (API) gravity lower than 20, a medium crude oil has an intermediate API gravity of 20–34, while a light crude oil has an API gravity higher than 34. The API gravity is a factor inversely proportional to the density of crude oil. It is generally accepted that heavier oils are more protective than lighter ones with regard to corrosion (De Waard et al., 2003). Another way to classify crude oils is based on the proportions of the organic compounds (Sokolova et al., 1992), such as paraffin, aromatic compounds, and naphthenic compounds. These compounds may have a profound effect on the wettability of crude oil and the chemistry of brine solutions (Efrid et al., 2004), thus affecting pipeline corrosion.

The presence of CO<sub>2</sub> may change the properties of crude oil. The solubility of CO<sub>2</sub> in a crude oil is generally many times higher than that in water (Rostami et al., 2017). The incorporation of CO<sub>2</sub> may induce a volume expansion of crude oil (Yang et al., 2013). The viscosity of crude oil vastly decreases with increasing pressure, as more CO<sub>2</sub> and natural gas can be dissolved into crude oil (Freitag, 2018). A beneficial effect of low viscosity has been reported in multiphase flow loop tests (Kanwar, 1994; Jepson and Menezes, 1995) and recently observed in an oil/water alternate wetted condition (Wang et al., 2019a). These observations are particularly interesting for corrosion evaluation under well conditions where the oil viscosity may be vastly changed with temperature and pressure. One should also notice that a lower viscosity may lead to an easier separation of oil and water and it is harmful for the corrosion mitigation in water-in-oil (w/o) emulsions or dispersions.

### Solid Particle and Scale Deposition

Besides the oil, water and gas phases, solid particles may also be presented in CO<sub>2</sub>-EOR production fluids. The solid phase may come from the reservoir and the precipitation of scales due to variation of brine chemistry. Generally, extremely large (>1 mm) solid particles are rarely observed in the oil and water transportation systems, as a number of filters are equipped on pipeline ahead of a pump. However, in the well conditions or the deep-sea pipeline, where the removal of sand becomes economically unacceptable, erosion corrosion may be

encountered (Pouraria et al., 2016). The precipitation of scales on a pipeline surface can be encountered in CO<sub>2</sub>-containing fluids, especially in a water treatment system, where the CO<sub>2</sub> partial pressure and pH-value have greatly changed, breaking the balance of brine chemistry. This would produce an under-deposit corrosion problem.

## Corrosion Risk Analysis CO<sub>2</sub> Transportation and Injection

Corrosion can only occur when CO<sub>2</sub> meets water. Therefore, the concentration of water in CO<sub>2</sub> during transportation and injection is generally controlled below a critical value. There are several recommendations according to successful project experiences, as summarized in **Table 1**. For example, a recommended value of H<sub>2</sub>O in dense phase CO<sub>2</sub> was 500 ppm in the DYNAMIS project (de Visser et al., 2008). Below this concentration, it was believed that corrosion would not be a problem during CO<sub>2</sub> transportation and injection conditions (Cole et al., 2011; Sandana et al., 2012; Jacobson, 2014). However, in case of CO<sub>2</sub> and water being alternately injected into reservoirs to reduce CO<sub>2</sub> migration, the well tubes may suffer from serious corrosion damage (IEAGHG, 2010). Occasional ingress of water into the transportation pipeline may also induce corrosion.

Another possibility of water ingress is originated from the diffusion of water after injection stops. Theoretically, this takes a few months to form a water saturated CO<sub>2</sub> phase in the well tube usually within a length of several and tens of meters from wellbore, since the diffusion of water in stagnant CO<sub>2</sub> is relatively slow. However, in a long-term sealed well, corrosion induced by water diffusion from the reservoirs must be considered. Even though cement sealing outside the casing pipe is generally believed to be a robust protective layer, it should be borne in mind that CO<sub>2</sub> is actually very corrosive to cement, which has not been widely realized in engineering. After long-term carbonation, the originally protective cement layer might have failed much earlier than expected (Kutchko et al., 2007; Carpenter et al., 2011).

**TABLE 1** | Practical recommendation of water concentrations in CO<sub>2</sub> transportation.

Project name	Operation conditions	Recommended water level
Weyburn (Race et al., 2012; Barker et al., 2017)	18.6 and 20.4 MPa	20 ppm
DYNAMIS (de Visser et al., 2008)	Worst case 4°C, 4.0 MPa	500 ppm
Central Basin (Oosterkamp and Ramsen, 2008; Race et al., 2012)	15.1–17.2 MPa	257 ppmw
Sheep Mountain (Oosterkamp and Ramsen, 2008)	Critical 1.7°C, 8.27 MPa	129 ppmw
Snøhvit (Oosterkamp and Ramsen, 2008; Race et al., 2012)	15 MPa, 25°C	50 ppm
Shengli EOR	15°C, 10 MPa	~200 ppm

There are many reported damage cases of CO<sub>2</sub> transportation pipelines and injection well tubes induced by corrosion. According to the CO<sub>2</sub>-EOR projects in the United States since 1970s, aggressive corrosion damage has been observed in CO<sub>2</sub> injection wells in a water-alternate-gas (WAG) injection condition, although corrosion resistant alloys and liners were adopted for corrosion protection (IEAGHG, 2010). For CO<sub>2</sub> transportation pipelines, corrosion induced damage at the pipeline bottom has also been encountered in the practical operation in east China, owing to the accumulation of the remaining water in CO<sub>2</sub> phase.

### Oil Production Well

The produced fluid is complex and its corrosiveness is determined by many factors, such as the fraction of CO<sub>2</sub>, pH-value, states of oil, water content and water chemistry. Different from conventional oil production, the well fluid contains a large fraction of CO<sub>2</sub> in CO<sub>2</sub>-EOR production. As estimated from a previous reference (Choi and Nešić, 2011), the pH-value at wellbore condition can be as low as 3.0. A greater depth of the well tube can result in a higher partial pressure of CO<sub>2</sub>, which indicates a higher corrosion risk at deeper sites. It should also be noticed that the gas-to-liquid ratio becomes extremely high once a large amount of CO<sub>2</sub> gas is presented in the well tube. It has been reported that the gas-to-liquid ratio could be as high as several hundreds (Wang et al., 2015). Therefore, a highly stirred oil-water-gas three phase flow is a predominant feature of the CO<sub>2</sub>-EOR production fluid. A complete mixture of oil and water may reduce the corrosion risk of well tubes (Cai et al., 2012; Wang et al., 2015), owing to the inhibition effect of crude oil on corrosion. As stated above, the viscosity reduction in oil well conditions may also reduce the corrosion risk of well tubes. Moreover, the accumulation of corrosion released ferrous ion in well tube may in return affect corrosion of steel materials (Bian et al., 2015), through formation of a protective iron carbonate layer. All these make the corrosion process extremely complicated.

### Oil Gathering and Transportation

The produced fluid is subsequently transported by pipelines to a treatment station for separation. Different from the well condition, the transportation pipeline is generally in a horizontal or inclined direction. Its corrosion risk is highly dependent on the mixing state of oil and water, which is determined by the flow parameters (Sarica and Zhang, 2008; Kee et al., 2014), such as the flow rate, fraction and fluidity of different phases and the pressure and temperature of the system. The settlement of free water at the bottom of pipeline can initiate corrosion (Jiang and Cheng, 2013; Wang Z. L. et al., 2014). A large gas-to-liquid ratio will further complicate the mixing state of oil, water, and gas (Wang et al., 2015), which can also result in a significantly increased actual flow velocity of the liquid phase. On one hand, this may lead to flow-accelerated corrosion if water cannot be completely entrained into the oil phase or erosion-corrosion damage when solid particles are involved in the transportation. On the other hand, a mixture of oil and water may reduce the corrosion at the

pipeline bottom, as the water phase may be highly dispersed and thus continuous water wetting of the steel surface is avoided.

### Water Treatment

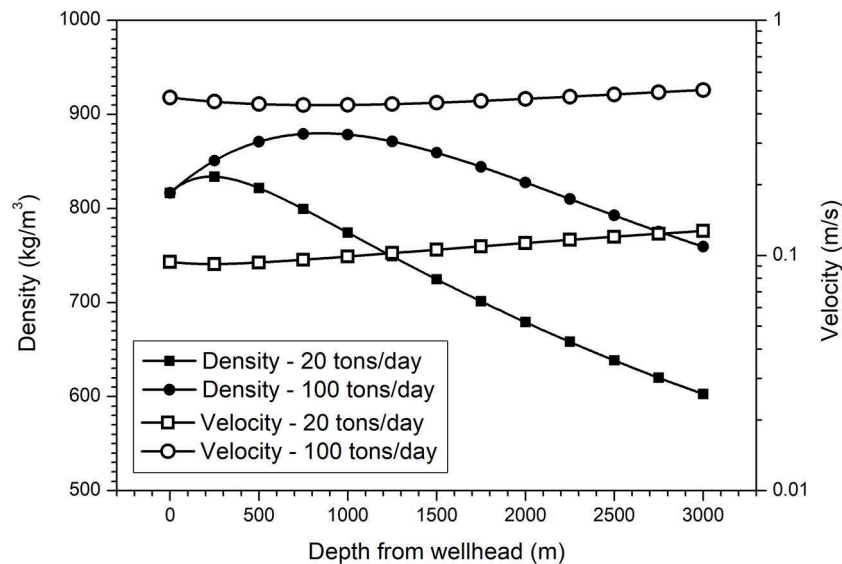
CO<sub>2</sub> cannot be completely removed from water phase after separation of the produced fluid at the treatment station. The partial pressure of CO<sub>2</sub> may be reduced significantly from ~1.0 MPa or higher to <0.2 MPa, and the dissolved CO<sub>2</sub> gas may evolve from the aqueous phase. However, the left fluid remains corrosive to mild steel. Without the presence of crude oil, the CO<sub>2</sub> containing aqueous fluid can become even more aggressive to steel. It can also be less corrosive as the transportation temperature and pressure are lower than the oil production and transportation systems.

In some cases, alkaline solution may be introduced to neutralize the CO<sub>2</sub> containing solution, further reducing its corrosiveness. However, neutralization of the CO<sub>2</sub> containing fluid may induce a scaling problem, owing to the presence of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions. Generally, these scale forming cations are dissolved from the reservoir rocks in CO<sub>2</sub>-EOR conditions. Once the salt scale is formed and attached on the inner surface of pipeline, under-deposit corrosion and crevice corrosion will occur, leading to localized corrosion damage of the pipeline in CO<sub>2</sub>-containing environments (Zhang et al., 2016). A complicated corrosion product layer may be formed owing to the incorporation of Ca<sup>2+</sup> and Mg<sup>2+</sup> cations, which may have improved protectiveness or increased pitting susceptibility (Esmaeely et al., 2013; Tavares et al., 2015). Recently, Shamsa et al. (2019) identified the corrosion products on X65 carbon steel as Fe<sub>x</sub>Ca<sub>y</sub>CO<sub>3</sub> in the presence of Ca<sup>2+</sup> cations. The stoichiometry of Fe<sub>x</sub>Ca<sub>y</sub>CO<sub>3</sub> could vary with immersion time. They also pointed out that incorporation of the Ca<sup>2+</sup> cations in the corrosion product layer may lead to severe localized corrosion damage at a low temperature relevant to oil production (generally below 80°C in the gathering and transportation system).

## MULTIPHASE FLOW CORROSION

### Single-Phase CO<sub>2</sub>

In the temperature range of oil production, completely dry CO<sub>2</sub> is not corrosive to steel. Direct carbonation of steel materials by CO<sub>2</sub> can only occur at a high temperature (Cao et al., 2012). As mentioned above, CO<sub>2</sub> is generally transported and injected into wells in a dense phase state, for example, the supercritical state. The presence of a trace amount of water in the dense phase CO<sub>2</sub> is the origin of corrosion; the formation of CO<sub>2</sub> saturated water layer on steel surface triggers corrosion. In this case, corrosion will be very slight, since this water layer can quickly become saturated with ferrous ion and an iron carbonate layer can be easily formed on the steel surface. The variation of local temperature and pressure is believed to be the primary cause of forming droplets or a water layer on steel surfaces (Choi and Nešić, 2011), just like that in a wet natural gas pipeline. However, CO<sub>2</sub> fluids can have a very high density, vastly different from natural gas. As seen from **Figure 3**, the density of CO<sub>2</sub> can be higher than 800 kg/m<sup>3</sup> in a certain depth in the injection well.



**FIGURE 3** | Distribution of density and velocity of CO<sub>2</sub> fluid as a function of well depth at different injection flow rates, which was calculated based on the field condition of an injection well in Shengli oilfield, where the injection temperature and pressure of CO<sub>2</sub> fluid at wellhead were -20°C and 10 MPa, respectively (Wang and Song, 2018).

Therefore, in a flow condition, such a dense-phase CO<sub>2</sub> may behave more like an oil phase rather than a natural gas phase.

Recently, it was found that the corrosion morphology was highly relied on the flow rate and the degree of water saturation (Liu et al., 2018); a higher flow rate and a higher degree of water saturation produced larger corrosion product particles and patches, implying a possible corrosion mechanism related to the direct bombardment of water droplets on steel surfaces and these droplets are likely entrained in the dense CO<sub>2</sub> phase, rather than directly nucleated on steel surfaces. In SC CO<sub>2</sub> fluids, the entrainment of these water-rich clusters (or droplets) is possible and the presence of such water-rich heterogeneities in wet SC CO<sub>2</sub> has been identified by near-infrared spectroscopy (Wang et al., 2013) and radial distribution function method (Glezakou et al., 2010). Above the solubility limit of water in SC CO<sub>2</sub>, the water-CO<sub>2</sub> mixture may form stable water-in-SC CO<sub>2</sub> micro-emulsions (Lee et al., 1999). Below the saturation limit, the formation of a weak Lewis acid-base H<sub>2</sub>O:CO<sub>2</sub> complex (Thanthiriwatte et al., 2012; Wang et al., 2013) has been reported in SC CO<sub>2</sub> media. As illustrated in **Figure 3**, depending on the flow rate in transportation and injection, the velocity of a CO<sub>2</sub> fluid can be in a wide range from <0.1 to 0.5 m/s or higher. Obviously, decreasing the velocity of CO<sub>2</sub> can reduce the impact of water droplets on steel surface, thus reducing the corrosion risk (Bian et al., 2015). Therefore, to get a high transportation efficiency, pressurizing the CO<sub>2</sub> fluid is better than improving its flow velocity from a corrosion view.

Besides the influence of flow rate and water concentration, it has been reported that some impurity gases may also significantly change the corrosion morphology and increase the corrosion rate. To date, the corrosion performance of steel in presence of trace amounts of O<sub>2</sub> (Xiang et al., 2013; Hua et al., 2014b), SO<sub>x</sub>, NO<sub>x</sub> (Ayello et al., 2010; Dugstad et al., 2013a), H<sub>2</sub>S

(Choi et al., 2015; Sun et al., 2016b), and their mixtures (Choi et al., 2010; Dugstad et al., 2013b; Ruhl and Kranzmann, 2013; Xiang et al., 2013) have been extensively investigated. The results show that these impurity gases may greatly change the water limit for triggering corrosion, as they exacerbates corrosion by influencing corrosion products and participating in corrosion processes. However, it should be noticed that the presence of impurities may also change the stability of the water-CO<sub>2</sub> mixture in a supercritical state (Mohitpour et al., 2012). Visualization tests should be conducted to further explore the initial corrosion and water settlement in SC CO<sub>2</sub> environments. This may finally lead to a better management of the corrosion risk in CO<sub>2</sub> transportation and injection pipelines.

## Water-CO<sub>2</sub> Slugs

Although CO<sub>2</sub> is dried prior to transportation, water ingress may happen in some occasional conditions. It has been reported that the corrosion rate of mild steel in a dense-phase CO<sub>2</sub>-water flowing conditions can be as high as several to tens of mm/y depending on their fluid parameters (Dugstad et al., 2011a; Barker et al., 2017), because the aqueous solution was saturated with high pressure CO<sub>2</sub>. There are many experimental results on the corrosion rates and corrosion morphologies of steel materials in high-pressure CO<sub>2</sub> environments (Cui et al., 2006; Cao et al., 2012; Zhang Y. et al., 2012; Hua et al., 2015), from which it can be deduced that the steel materials suffer from severe corrosion attack and the flow can vastly accelerate corrosion (Dugstad et al., 2011a; Wei et al., 2018) in the presence of a bulk volume of water during the transportation of dense-phase CO<sub>2</sub>.

In practice, CO<sub>2</sub> and water may also be alternatively injected into wells (Rogers and Grigg, 2001; Lv et al., 2015; Dang et al., 2016). For example, in Shengli oilfield, the water alternating gas (WAG) injection technique is planned to be adopted after a

further verification in the pilot-scale CO<sub>2</sub>-EOR project (Lv et al., 2015). This WAG injection process can to some extent retard gas-migration under reservoir conditions (Dugstad et al., 2011b). By adjusting the WAG ratio, a maximum ratio of the oil production to CO<sub>2</sub> injection could be reached (Dai et al., 2014). However, the alternating exposure of the pipe inner wall to water and CO<sub>2</sub> fluids can result in severe corrosion damage. According to field experiences, the water phase may linger for a long time in crevices or dead spots after dry conditions were restored (IEAGHG, 2010), leading to a corrosion problem in aggressive well environments. Temperature and pressure are believed to be the critical factors in corrosion (De Waard et al., 1991), since they directly determine the solubility of water in CO<sub>2</sub> and the pH-value of the water layer (Choi and Nešić, 2011). During the WAG injection process, corrosion occurs when the CO<sub>2</sub> slug begins to drive down the previous water slug, leaving a water layer on the pipe inner wall being acidified by flowing CO<sub>2</sub>. Recently, Wang and Song theoretically evaluated the corrosion risk of steel materials in such WAG conditions by assuming that the steel surfaces were periodically exposed to the wet/dry cycles in CO<sub>2</sub> fluids and the corrosion was dependent on the dissolution of CO<sub>2</sub> in the water layer (Wang and Song, 2018). In their simulation work, the time of forming a CO<sub>2</sub> saturated water layer was simply determined by the diffusion rate of CO<sub>2</sub> through the layer, which was assumed to be very fast and generally less than several minutes (Grogan et al., 1988; Farajzadeh et al., 2009), having little influence on the overall corrosion performance. Therefore, the long-term corrosion behavior relied on the time for drying the steel surface by flowing “dry” CO<sub>2</sub>, and the amount of water absorbed by the “dry” CO<sub>2</sub> fluid was critical for determining corrosion risk, where the “dry” CO<sub>2</sub> meant that the water concentration in CO<sub>2</sub> phase was far below its saturation limit, a shorter drying time meant a less exposure of steel surface to the CO<sub>2</sub> saturated corrosive water, and corrosion was supposed to cease when the water layer was completely absorbed into the CO<sub>2</sub> fluid. In this way, they concluded that the alternate period determined the long-term corrosion performance. The injection rate of CO<sub>2</sub> fluid is another critical factor influencing the distributions of temperature and pressure in well (Lindeberg, 2011; Ruan et al., 2013) and it also affects the drying time of the water layer along the pipe internal wall.

## Oil-Water Mixtures

The presence of crude oil may reduce the corrosion risk of CO<sub>2</sub>-EOR pipelines. The corrosion performance of pipeline may be influenced by crude oil's physical properties, such as its density (Lotz et al., 1991; De Waard et al., 2003; Papavinasam et al., 2007), viscosity (Kanwar, 1994; Jepson and Menezes, 1995; Papavinasam et al., 2007), conductivity (Craig, 1998), and wettability (Craig, 1996; Smart, 2001; Efrid et al., 2004). Recently, Wang and Zhang (2016) summarized four different mechanisms for the inhibition effect of crude oil on corrosion: (1) water entrainment, (2) crude oil wetting, (3) soluble chemical partitioning, and (4) corrosion product layer modification. De Waard et al. (2003) found that heavy oil was less corrosive than light one in an oil-water two-phase flow condition, which could be attributed to the formation of w/o dispersions (Xu, 2007). A simple notion for corrosion

risk analysis has been proposed based on the assumption that corrosion would occur only when free water was separated from w/o emulsion during transportation (Wang Z. L. et al., 2014). At some extremely high water cuts, w/o emulsion can also be formed. For example, the experimentally measured emulsion inversion point (EIP) is generally reported to be as high as 70 wt.% (Fingas and Fieldhouse, 2004; Wang Z. L. et al., 2014), which means that a w/o emulsion can be formed at a relatively high water cut under sufficiently stirred conditions. Free water will be separated within a very short period from a w/o dispersed fluid when the flow is slower than a critical velocity (Xu, 2007). In practical oil production, it is hard to completely emulsify the oil-brine mixtures with a very high water concentration. Generally, a w/o emulsion containing <30 wt.% water is relatively stable under flow conditions (Fingas and Fieldhouse, 2004).

The occurrence of corrosion may be related to the droplet behavior in a w/o emulsion or dispersion, and the droplets may grow to larger ones during transportation, leading to the settlement on pipeline bottom. According to Stokes equation, the settlement rate ( $V_t$ ) of water droplets in a w/o emulsion can be expressed as (Frising et al., 2006),

$$V_t = \frac{d_t^2 g (\rho_w - \rho_o)}{18\mu} \quad (1)$$

where  $d_t$  is the mean diameter of droplets at a test condition,  $g$  is the gravitational acceleration,  $\rho_w$  and  $\rho_o$  are the densities of water and oil phases, and  $\mu$  is the viscosity of oil-water mixtures. It is clear that a larger water droplet is easier to settle down in a lighter oil-water mixture. It should also be noticed that the formation of a stable emulsion may significantly increase the fluid viscosity (Xu, 2007; Wang Z. L. et al., 2014), thus retarding the settlement of water droplets. In practical uses, the theoretical analysis must be verified by the stability of emulsion samples in field conditions. Recently, Paolinelli et al. (2018) examined the correlation of water droplet size distribution with different fluid parameters (flow rate, pressure drop, oil types, and fraction of water) after a globe valve on a pipe flow loop and compared with theoretical analysis, and gave some reasonable hints for the control of water droplets in flow conditions. In this way, before the settlement of water droplets or the formation of water layer at pipeline bottom, corrosion could be totally retarded during the long-distance transportation of oil-water emulsion and a fast transportation could shorten the time from wellhead to treatment station (Wang Z. L. et al., 2014), beneficial for reducing the corrosion risk.

At a higher water cut, where total entrainment of water droplets becomes impossible, the steel surface will be intermittently wetted by water. Flow loop tests indicated that the corrosion rate was retarded under intermittent water wetting conditions compared to continuous water wetting (Li et al., 2006). In a flow condition, the intermittent wetting behavior closely depends on the flow pattern characteristics (Nesic and Carroll, 2003). Several studies have demonstrated that with increasing flow rate, the steel surface can be changed from continuous water wetting to intermittent wetting or even continuous oil wetting (Nesic and Carroll, 2003; Cai et al., 2012),

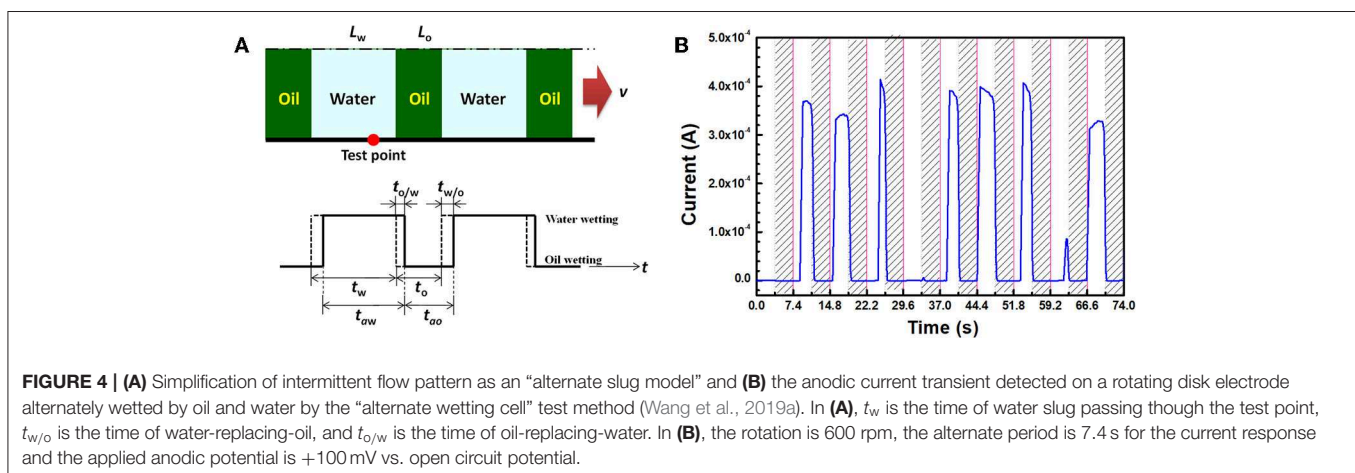
hence reducing the corrosion risk at the pipeline bottom. The intermittent wetting by oil and water at steel surface has been verified by various sensors in flow loop tests (Fordham et al., 1999; Zong et al., 2010; Luo et al., 2017). Efforts have been made to monitor the wetting and corrosion phenomena by electrochemical noise method in oil-water mixtures (Bouazaze et al., 2005). However, the electrochemical noise signals are much complicated. A quantitative and controllable method is urgently needed for analyzing the dynamic wetting and corrosion phenomena in one test. To further reveal the corrosion phenomena in oil-water intermittent conditions, Wang et al. (2019a) recently proposed an “alternate wetting cell” to record the current signals under anodic polarization with a rotating electrode. With a controllable movement of the oil/water interface relative to electrode, it can simplify the intermittent flow pattern as the alternate wetting of the electrode surface by oil and water, as illustrated in **Figure 4**. The actual wetting state could be presented as a series of oil and water slugs (see **Figure 4A**). Interestingly, there is a delay in the actual oil wetting time ( $t_{ao}$ ) and the actual water wetting time ( $t_{aw}$ ), which can be confirmed by the anodic current peaks in **Figure 4B**. The height and width of the current peaks could reflect the corrosion and water wetting on the electrode surface, respectively. Their results indicate that a slow flow and a short alternate period can generate high corrosion mitigation efficiency. The “alternate wetting cell” method provides a possible way to describe the correlation between corrosion and wetting under a controllable manner and a new insight into the corrosion phenomena in a complicated system. It can be used for the evaluation of corrosion inhibitors in an oil-water system (Wang et al., 2019b).

The covering effect of crude oil at the steel surface is widely accepted as the origin for corrosion inhibition. However, a thin layer of crude oil at the steel surface is unstable to prevent corrosion for a long time. For example, Wang Z. L. et al. (2014) observed that a crude oil layer could only persist for about 15 min on a vertically placed steel surface in a stagnant condition. The heterogeneous adsorption of crude oil on steel surface may induce localized corrosion (Sun et al., 2016a). The degree of localized corrosion may be vastly different from the averaged corrosion rate in oil-brine mixed conditions (Choi et al., 1989;

Sun et al., 2016a), but this phenomenon and its mechanisms have not been clearly addressed. Some soluble organic compounds in crude oil can also decisively reduce the corrosion rate in a manner like corrosion inhibitors (Efird and Jasinski, 1989; Castillo et al., 2000; Ayello et al., 2013) and they may produce a possible hybrid effect on corrosion products (Mendez et al., 2001; Yang et al., 2014; Taleb et al., 2017).

## Oil-Water-Gas/Solid Flow

The multiphase fluids are commonly encountered in CO<sub>2</sub>-EOR production, in which a large fraction of CO<sub>2</sub> in the gas phase is involved. Previous efforts were mainly focused on the relationship between corrosion and the flow characteristics of a gas-liquid two-phase flow. Although very limited number of studies have been focused on the corrosion phenomena in CO<sub>2</sub>-EOR multiphase flow conditions, the results regarding corrosion in conventional oil production can be employed for reference. For instance, in a slug flow, the corrosion risk of pipelines can be closely related to the superficial gas velocity (Maley, 1997; Kang et al., 1999), slug frequency (Kang et al., 1996; Maley, 1997; Wang et al., 2015), and Froude number (Kang et al., 1996; Chen and Jepson, 1999). Generally, direct visualization is used to determine the flow patterns. Other methods are also widely accepted, for examples, pressure drop (Sotgia et al., 2008), wetting behavior (Cai et al., 2012), and phase density distribution (Hoffmann and Johnson, 2011). Currently, many research institutes have developed multiphase flow loops for corrosion tests (Kouba and Jepson, 1990; Nyborg, 1998; Li et al., 2006; Zheng et al., 2008; Wang et al., 2015). Based on the flow loop tests, the relationship between corrosion and flow characteristics has been built. It was found that a higher slug frequency may increase the corrosion rate of pipelines, owing to a sharp increase in the local wall shear stress (Yang et al., 2010), which was viewed as an important parameter in corrosion (Wang et al., 2002; Zheng et al., 2008). A higher shear stress may enhance the local corrosion kinetics or damage the corrosion products (Schmitt et al., 2000; Li et al., 2016). It was also observed that a higher gas flow rate could reduce the pressure drop and lower the frequency of liquid slugs at a constant liquid velocity (Kang et al., 1999; Villarreal et al., 2006; Wang et al., 2015), thus reducing the corrosion risk.

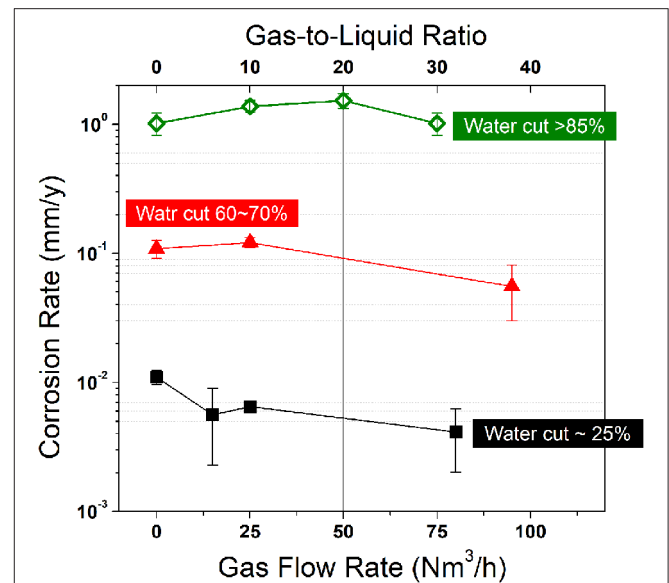




In conducting a flow loop experiment, oil and water may be emulsified during a long-term cyclic test if crude oil was used. The heavier the crude oil is, the easier it can be emulsified. At a fixed pump input fraction of oil and water, the entrainment of water in oil phase may increase the actual water fraction of input fluids. It has been reported that a significantly large amount of water can be entrained into the crude oil phase after 3 days of the cycle test in a closed flow loop (Wang and Zhang, 2016). No free water can be separated from the oil-water mixture within a short period after the cyclic test. Emulsification is the main reason for the use of white oil, instead of crude oil, in most multiphase flow loop tests. To overcome the emulsification problem, a multiphase flow loop was built in a treatment station of Shengli oilfield, where the oil, water and gases were separately introduced into the test loop from the production pipelines and then went back to the production system via the output pipeline after corrosion test. The input of oil, water and gas was also driven by pumps and the process was similar to that of a laboratory-scale setup reported previously (Wang et al., 2015). The only difference is that the mixed fluids after going through the corrosion test section directly flows into the oil production system and never goes back to the pipe section for corrosion tests. Using this “open” flow loop system, field corrosion was monitored at the steel pipe bottom. The corrosion rate can be automatically converted from the galvanic current of a commercial corrosion probe, which has been previously used for corrosion monitoring in an oil-water system (Wang Z. L. et al., 2014). A flat sheet of 20# steel was used as the corrosion probe and the diameter of the pipeline was 80 mm. With changing water cut, a series of field conditions can be simulated.

One may notice that CO<sub>2</sub>-EOR production fluids generally contain an extremely high fraction of gas phase with a gas-to-liquid ratio over 200, in which CO<sub>2</sub> gas can reach a volume fraction of 70% in the gas phase (Wang et al., 2015). Under such a high gas-to-liquid ratio, oil and water may be strongly stirred during transportation, and corrosion can be reduced once the oil phase reaches the bottom of pipeline. In **Figure 5**, the influence of gas-to-liquid ratio on corrosion was further verified at different water cuts in filed conditions. The corrosion rate initially increased and then decreased after the gas-to-liquid ratio increased to a critical value, depending on the water cuts. A higher water cut generally leads to a transition point at a higher gas-to-liquid ratio. However, when the gas-to-liquid ratio is higher than 20, corrosion will be obviously reduced. The result agrees with the theoretical analysis of corrosion mitigation in oil-water-gas three-phase flow conditions (Wang et al., 2015). This is also consistent with the notion that corrosion can be mitigated in an oil-brine mixed flow by increasing turbulence to generate oil wetting (Wicks and Fraser, 1975; Cai et al., 2012). Under a high pressure, the dissolved gas may reduce the viscosity of crude oil, thus changing the flow pattern and the wetting behavior in pipeline (Luo et al., 2017).

Sand or solid particles in CO<sub>2</sub>-EOR fluids may induce erosion or localized corrosion problem. Generally, in the CO<sub>2</sub> injection and water treatment processes, no sand or solid particle is involved. The influence of sand or solid particle on corrosion is usually considered in presence of crude oil. The simulation



**FIGURE 5** | The measured corrosion rate as a function of gas flow rate (or Gas-to-liquid ratio) at different water cuts obtained from the multiphase flow loop test at 0.3 MPa in field condition of Shengli oilfield. The crude oil was heavy oil with a density of 0.92 g/cm<sup>3</sup> at 20°C and a viscosity of 135.3 mPas at the operation temperature of 60°C. The fraction of CO<sub>2</sub> in gas phase was around 50 vol.%. For the present field test, the liquid flow rate was 4.5 m<sup>3</sup>/h. The input fluid was controlled by pumps and the water cut was experimentally estimated by on-site sampling of the oil-water mixtures.

work from Landry et al. (2012) suggested that the settlement of solid particles is much easier onto the pipeline bottom and water may also be accumulated around such solid particles forming a locally water-rich environment. In this condition, corrosion may be preferentially initiated around the solid particle (Han et al., 2013). Tang et al. (2008) observed severe erosion-corrosion damage on steel surface and the contribution of erosion was measured to be around 70% in the oil-sand slurry with different sand concentrations. However, Stack and Abdulrahman (2012) reported the movement behavior of sand particles sealed by an oil layer, which produces a weaker impact on steel surface, and thus reduce the mechanical and electrochemical attacks. A further analysis is essential for understanding the corrosion behavior associated with sand particles and crude oils, which will be helpful to the field corrosion management in CO<sub>2</sub>-EOR well and deep-sea conditions.

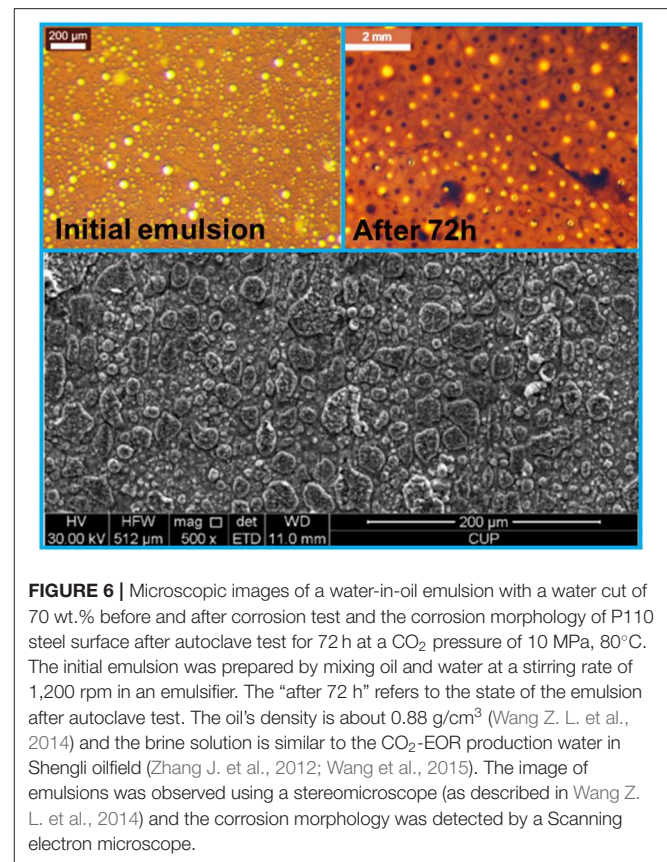
## CORRELATING CORROSION WITH FLUID STRUCTURES

Corrosion control in multiphase flow conditions is technically challenging, owing to the complexity of fluid. In CO<sub>2</sub>-EOR production, the multiphase flow is generally relevant to an oil-water mixture or a dense phase CO<sub>2</sub> containing a trace amount of water, which attributes to oil production and CO<sub>2</sub> injection, respectively. Here, these two cases can both be termed as water/non-electrolyte mixture. In a previous paper, Liu et al.

(2018) believed that the state of water in SC CO<sub>2</sub> phase might behave like the w/o emulsion or dispersion, where a corrosion mechanism was proposed in SC CO<sub>2</sub> environment regarding the impact of water droplets on steel surfaces. It implies that the density and velocity of water clusters in SC CO<sub>2</sub> phase determine the corrosion morphology. Although the corrosion propagation has not been directly monitored, the observation of different types of corrosion product particles on steel surfaces after autoclave test can verify this microscopic mechanism. Actually, similar circular-shaped corrosion product particles can also be observed on steel surface after corrosion in a w/o emulsion for a short period (e.g., 72 h), as typically illustrated in **Figure 6**. For a longer period, the corrosion product particles may be merged to become large patches, finally forming a layer of FeCO<sub>3</sub>. It seems that these corrosion product particles are probably originated from the attachment of corrosive water droplets. Presently, the direct links between the sizes of corrosion product particles and water droplets are still not clear. It is interesting that the corrosion morphologies of steel surface are similar in different types of fluids. It is quite possible that the water droplets or clusters present in the w/o emulsion (Wang Z. L. et al., 2014) and the water containing SC CO<sub>2</sub> (McGrail et al., 2009; Thanthiriwatte et al., 2012; Wang et al., 2013) result in the corrosion product particles on steel surfaces. As proposed by Liu et al. (2018) in CO<sub>2</sub> fluid, the flow and wetting behavior of water clusters are the origin of corrosion damage. This mechanism could be extended to interpret the corrosion performance of steel samples in various electrolyte/non-electrolyte mixtures. This provides a new view on corrosion prediction in complex conditions, where water is highly dispersed in a non-conductive fluid.

The similarity in corrosion mechanism could be firstly testified by the dependence of corrosion rate on water concentration. As an example, **Figure 7** illustrates the corrosion rate of steel samples in different mixtures, such as w/o emulsion and water containing SC CO<sub>2</sub>, where it presents a linear relationship with water concentration. Such a linear dependence of corrosion rate on water concentration could be found in a wide range of water concentrations, regardless of the experimental conditions, which was also observed in correlating the weight-loss data with water concentrations in a SC CO<sub>2</sub> environment when the water concentration is higher than 1,000 ppmw (Sim et al., 2014a). It also reported that the conductivity of a w/o emulsion presented a linear relationship with water concentrations (Craig, 1998). This may be related to the impact of moving water droplets or clusters on steel surfaces. Generally, a higher water concentration may generate a larger volume of water droplets in mixed fluids (Plasencia et al., 2013). Compared with a SC CO<sub>2</sub> fluid, crude oil can entrain a larger volume of water droplets, and thus the corrosion rate was not significantly increased at high water concentrations. This could be explained by the difference in wettability at steel surface. The oil phase is more effective than the dense CO<sub>2</sub> phase against the adsorption of water droplets on steel surfaces.

In multiphase flow corrosion, the state of fluid structure has not been systematically investigated. Water entrainment and water settlement are the control steps in corrosion. The



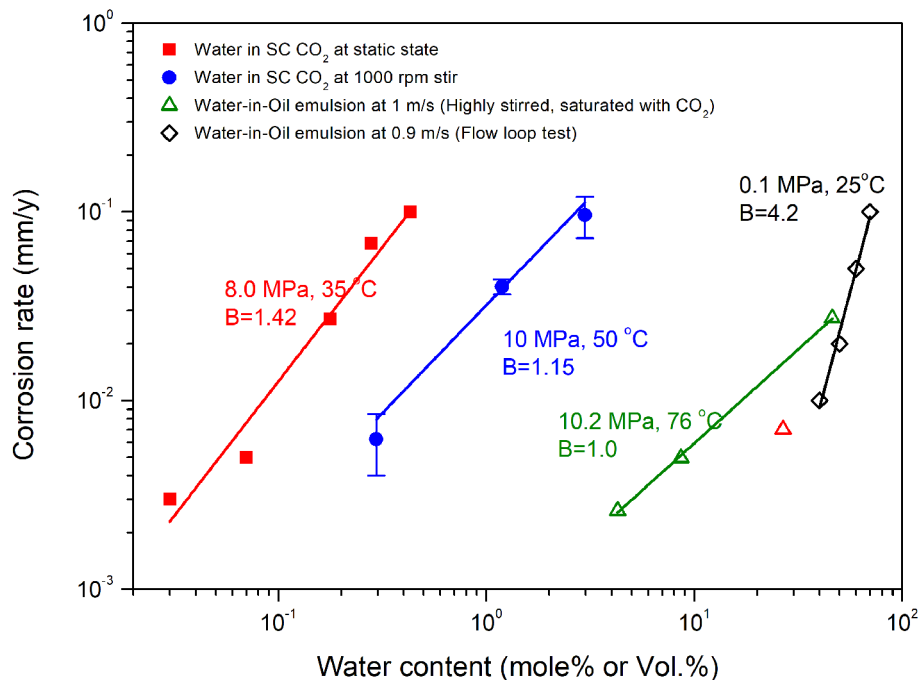
**FIGURE 6** | Microscopic images of a water-in-oil emulsion with a water cut of 70 wt.% before and after corrosion test and the corrosion morphology of P110 steel surface after autoclave test for 72 h at a CO<sub>2</sub> pressure of 10 MPa, 80°C. The initial emulsion was prepared by mixing oil and water at a stirring rate of 1,200 rpm in an emulsifier. The "after 72 h" refers to the state of the emulsion after autoclave test. The oil's density is about 0.88 g/cm<sup>3</sup> (Wang Z. L. et al., 2014) and the brine solution is similar to the CO<sub>2</sub>-EOR production water in Shengli oilfield (Zhang J. et al., 2012; Wang et al., 2015). The image of emulsions was observed using a stereomicroscope (as described in Wang Z. L. et al., 2014) and the corrosion morphology was detected by a Scanning electron microscope.

entrainment of water in crude oil is believed to be beneficial in corrosion mitigation (Wicks and Fraser, 1975; Craig, 1996; De Waard et al., 2003; Cai et al., 2012). Following this idea, methods to stabilize water in SC CO<sub>2</sub> emulsions might also be effective in preventing pipeline corrosion, which has been widely investigated in food and purification industries. However, to date no effort has been made to tailor the SC CO<sub>2</sub> fluid for a corrosion mitigation purpose. If it works, this method can be applied in CO<sub>2</sub> transportation and injection systems.

## CONTROL STRATEGIES

It should be noticed that the operation conditions for CO<sub>2</sub> transportation, injection and oil production are different. As summarized in **Table 2**, their control strategies cannot be the same. Generally speaking, CRAs are most effective, which have been attempted in many projects (IEAGHG, 2010). For example, in a pilot-scale CO<sub>2</sub>-EOR project in Shengli oilfield, stainless steels were employed for the CO<sub>2</sub> injection well tubes. There is no doubt that the use of CRAs is a safe choice when we have little knowledge on the corrosion risk of an operation system, but it is economically unacceptable. Coatings and liners are also adopted in CO<sub>2</sub>-EOR production wells (IEAGHG, 2010), but there are still challenging problems, such as blistering and detachment in deep well conditions.

Recently, several kinds of corrosion inhibitors were tested in simulated CO<sub>2</sub> injection or transportation conditions (Turgoose



**FIGURE 7 |** The dependence of corrosion rate on water concentration in different electrolyte/non-electrolyte binary systems. The red solid square and the blue solid circle refer to the corrosion data in SC CO<sub>2</sub> environment according to Hua et al. (2014a) and Liu et al. (2018). The green open triangle and the black open rhombus refer to the corrosion rates in w/o emulsions or mixtures according to Sun et al. (2016a) and Li (2009). B represents the slope of the fitted line of the experimental data points in a log coordinate system.

et al., 2014; Choi et al., 2017; Xiang et al., 2017; Cen et al., 2019), which may theoretically be a reasonable choice in the aggressive environments. However, the corrosion inhibitors should be effective in high temperature conditions. Corrosion inhibitors have also been widely used in water injection systems where CO<sub>2</sub> was involved. The presence of crude oil in the CO<sub>2</sub>-EOR production system may poison the inhibitors (Gulbrandsen and Kvarekval, 2007; Horsup et al., 2010), reducing their effectiveness. Therefore, the evaluation of corrosion inhibitors in oil-water mixed fluids becomes critical for the practical inhibitor selection (Li et al., 2014, 2016; Wang et al., 2019b). Presently, there is still lack of effective and applicable methods for the evaluation of corrosion inhibitors in oil-water mixed conditions (ASTM G202–12, 2016), which generally relies on a large-scale multiphase flow loop test (Salama and Brown, 2009; Cai et al., 2012; Wang and Zhang, 2016). Most recently, Wang et al. provided a possible method for the fast evaluation of corrosion inhibitors in oil/water alternate conditions by using a specially designed “Alternate Wetting Cell” (Wang et al., 2019a), with which a kind of ODD corrosion inhibitor has been evaluated to be effective (with a high inhibition efficiency of 99.9%) in oil-water media (Wang et al., 2019b). In a multiphase flow environment containing crude oil, the wettability at the oil/water/pipe interface and the emulsion state might be changed by the addition of a trace amount of organic agents, such as corrosion inhibitors (Foss et al., 2009; Li et al., 2014; Wang et al., 2019b) or some surfactant

chemicals (Wang Z. L. et al., 2014; Quej-Ake et al., 2018), finally enhancing or decreasing the corrosion mitigation efficiency of crude oil.

To our knowledge, managing the process parameters is one of the most attractive methods for corrosion control in CO<sub>2</sub>-EOR production (Wicks and Fraser, 1975; Kang et al., 1996; Cai et al., 2012; Wang et al., 2015), as it is generally applicable, effective and inexpensive, but the control strategies must be relied on a deep understanding of the corrosion performance and corrosion mechanism of pipeline materials (Store et al., 2011). For example, to avoid corrosion damage of pipelines, CRAs were usually used and water was strictly limited below a very low concentration in an early pilot CO<sub>2</sub>-EOR project because of little knowledge on steel corrosion in a dense CO<sub>2</sub> phase. Currently, it is generally believed that corrosion will not be a problem if there is no free water or water droplet settlement on the pipeline bottom. However, the critical water concentration threshold to trigger corrosion can be different, depending on pressure, temperature, flow rate, as well as the concentrations of impurities. Nevertheless, limiting water concentration is still the best choice for corrosion mitigation in CO<sub>2</sub> transportation (Sim et al., 2014b; Barker et al., 2017). It can be deduced from the experimental simulation that pressurizing CO<sub>2</sub> could extend the solubility of water (Wang and Song, 2018) and thus reduce the possibility of water wetting on steel surface. Slowing down the flow rate may reduce the probability of the bombardment of water clusters entrained in dense phase CO<sub>2</sub>,

**TABLE 2** | Corrosion control strategies in CCS-EOR systems.

	Materials	Corrosion inhibitors	Process control
CO <sub>2</sub> transportation	Mild steel (e.g., 16 Mn)	Effective in highly acidified, high pressure and high temperature conditions. (e.g., Xiang et al., 2017)	Controlling impurity gases (de Visser et al., 2008; Sim et al., 2014b) Limiting water concentration (Sim et al., 2014b) Slowing down flow and pressurizing (Liu et al., 2018)
CO <sub>2</sub> injection	Mild steel (N80, P110) Stainless steel (304SS, 13Cr) Coatings or liners (IEAGHG, 2010)	Injected with water slugs	Reducing water/gas alternate frequency (Wang and Song, 2018)
Oil production	Mild steel (N80, P110) Stainless steels (304SS, 13Cr)	Effective in the presence of oil, such as tailoring wettability (Li et al., 2014; Wang et al., 2019b) and enhancing emulsification (Wang Z. L. et al., 2014).	Not available.
Oil transportation	Mild steel (20#, X52) Stainless steel for valves Liners for separators		Water separation before transportation (Wang Z. L. et al., 2014) Reducing CO <sub>2</sub> partial pressure (Choi and Nešić, 2011) Flow pattern control: a high flow rate, high gas-to-liquid ratio (Cai et al., 2012; Wang et al., 2015) Enhancing emulsification (Wang Z. L. et al., 2014)
Water treatment	Mild steel (20#, X52) Glass fiber reinforced plastics	Effective in CO <sub>2</sub> aqueous environments Adding pH neutralizer	Reducing dissolved CO <sub>2</sub> by N <sub>2</sub> stripping.

*The recommended materials are based on the pilot-scale CO<sub>2</sub>-EOR project in Shengli oilfield and the reported projects in North American.*

and thus decrease the density of iron carbonate particles on steel surface (Liu et al., 2018). In this way, transporting water containing CO<sub>2</sub> at a high pressure and with a slow rate may be helpful for corrosion mitigation. In a WAG CO<sub>2</sub> injection process, reducing the alternate frequency and increasing the injection rate can extend the service lifetime of well tube (Wang and Song, 2018). Obviously, tailoring the processing parameters in CO<sub>2</sub> transportation and injection should be cautious as the environmental variation may totally change the control strategies.

In oil production, if water could be completely entrained into crude oil, corrosion would cease. Therefore, an effective method is to separate free water from crude oil before transportation. It would be safe if crude oil can be transported to the terminal station before de-emulsification and water settlement. In this way, a fast transportation seems to be beneficial. At the same time, a high flow rate stirs the fluid, hindering the deposition of free water. Similarly, a high gas-to-liquid ratio is also recommended to obtain a turbulent state and reduce the wetting of water at pipeline bottom (Wang et al., 2015). These control strategies are relevant to the management of flow patterns of oil, water and gas in pipeline. In some extreme conditions, emulsification of water into oil may be applicable in reducing the corrosion risk during long-distance transportation. It should be noticed that depressurizing may also reduce the corrosiveness of the CO<sub>2</sub>-containing fluids, which can be employed in the oil transportation and the water treatment stages.

## SUMMARY AND FUTURE IDEAS

In this review, the corrosion of pipeline in CO<sub>2</sub>-EOR production is systematically analyzed from a fluid perspective. Firstly,

the corrosion risk of pipeline at different stages of CO<sub>2</sub>-EOR production was evaluated relevant to the fluid properties. It identified that the presence of water in fluid was the key for triggering corrosion. In CO<sub>2</sub> transportation and injection systems, although water was generally limited well below its saturation limit, the occasional water ingress or the alternate water slug may induce corrosion damage. In oil production and transportation systems, the presence of crude oil may reduce corrosion, while the flow pattern and the mixing state of oil and water were critical for determining the corrosion risk of well tubes and pipelines. In water treatment stage, the scaling problem should be noticed with a reduction in CO<sub>2</sub> partial pressure. After a review of the corrosion behavior of steel materials in multiphase flow conditions according to the fluid states of CO<sub>2</sub>, water and crude oil, corrosion was supposed to be correlated with the fluid structure, in which the dependence of the corrosion rate on water concentrations was attributed to the fluid behavior of water droplet or clusters in an electrolyte/non-electrolyte binary system. An alternate wetting test method was introduced for better understanding the corrosion phenomena in oil/water intermittent flow. Finally, the corrosion control strategies were summarized. Besides the application of corrosion resistant materials and corrosion inhibitors, tailoring the processing parameter was suggested to be an attractive method for preventing corrosion in aggressive CO<sub>2</sub>-EOR production conditions. For the CO<sub>2</sub> transportation and injection systems, limiting water concentrations, slowing down the flow rate and reducing contact time would be beneficial for corrosion mitigation. For the oil production system, enhancing the water entrainment, increasing the turbulence of flow and mitigating the corrosive environment would be helpful.

Future studies on multiphase flow corrosion associated with CO<sub>2</sub>-EOR production should address the flowing issues:

- (1) Broadening ideas on corrosion control for aggressive CO<sub>2</sub>-saturated oil-water mixed fluids, for example, exploring the possibility of using oil/water alternate slugs to reduce corrosion risk of the pipeline bottom.
- (2) Selection of suitable emulsifier agents in water-SC CO<sub>2</sub> environments to extend the water limits for a secure transportation and injection of CO<sub>2</sub>.
- (3) Deciphering the microscopic origin of corrosion initiation and propagation and their relationship with fluid structure in a binary mixed system.
- (4) Developing new electrochemical and analytical methods in badly conductive and harsh environments, such as the water containing SC CO<sub>2</sub> and the oil-water mixtures.

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## AUTHOR CONTRIBUTIONS

ZW and G-LS wrote and finalized the paper. ZW and JZ collected and analyzed the field data.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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