State-of-the-art overview of pipeline steel corrosion in impure dense CO₂ for CCS transportation: mechanisms and models

Yong Xiang, Minghe Xu & Yoon-Seok Choi

To cite this article: Yong Xiang, Minghe Xu & Yoon-Seok Choi (2017) State-of-the-art overview of pipeline steel corrosion in impure dense CO₂ for CCS transportation: mechanisms and models, Corrosion Engineering, Science and Technology, 52:7, 485-509, DOI: 10.1080/1478422X.2017.1304690

To link to this article: http://dx.doi.org/10.1080/1478422X.2017.1304690

Published online: 28 Mar 2017.
State-of-the-art overview of pipeline steel corrosion in impure dense CO$_2$ for CCS transportation: mechanisms and models

Yong Xiang$^{a,b}$, Minghe Xu$^c$ and Yoon-Seok Choi$^d$

$^a$College of Mechanical and Transportation Engineering, China University of Petroleum, Beijing, PR China; $^b$Beijing Key Laboratory of Process Fluid Filtration and Separation, China University of Petroleum, Beijing, PR China; $^c$Department of Thermal Engineering, State Key Laboratory of Power Systems, Tsinghua University, Beijing, PR China; $^d$Department of Chemical and Biomolecular Engineering, Institute for Corrosion and Multiphase Technology, Ohio University, Athens, OH, USA

**ABSTRACT**

This review works the existing open literature concerned with pipeline steel corrosion in CO$_2$-rich phase with impurities for carbon capture and storage purpose. The intent of this review was to provide information on the corrosion mechanisms, which is crucial for establishing the mechanistic prediction models. The primary focus was placed on key affecting parameters and their corresponding mechanisms, while the corrosion control strategies and research prospects are also discussed. This review covers the effects of: impurities, pressure, temperature, flow, exposure time, product layers, and steel chemistry. The influences of flow dynamics, amines, sulphur, and solids that had received little systematic attention need to be further addressed. Contradictory conclusions regarding the influence of H$_2$O and O$_2$ on the corrosion rates should be re-evaluated. The localised corrosion and cathodic reaction mechanisms also require further investigation, especially under synergistic conditions with multiple impurities.

**Nomenclature**

- $A_0$: Debye–Hückel equation constant
- $b_i$: modified TCPC model parameter
- $c_i$: mole concentration for species $j$, mol L$^{-1}$
- $CR$: corrosion rate, mm a$^{-1}$
- $d_i$: product film thickness, m
- $D_j$: diffusion coefficient for species $j$, m$^2$ s$^{-1}$
- $EW$: equivalent mass, kg
- $i_{H^+}$: hydrogen electrode current density, A m$^{-2}$
- $i_{O_2}$: oxygen electrode current density, A m$^{-2}$
- $i_{Fe}$: anode current density, A m$^{-2}$
- $I$: ionic strength, mol kg$^{-1}$
- $k_{GC}$: effective crystal growth rate constant
- $K_{cor}$: corrosion rate equation coefficient
- $K_{fract}$: fracture toughness of product scale, MPa m$^{1/2}$
- $n_i$: modified TCPC model parameter
- $R_{ch}$: chemical reaction rate for species $j$, mol m$^{-3}$ s$^{-1}$
- $R_{prec}$: precipitation rate, kg m$^{-2}$ s$^{-1}$
- $S_i$: modified TCPC model parameter
- $t$: time, s
- $T$: temperature, K
- $\varepsilon$: volumetric porosity of product scale
- $\nu_c$: chemical equivalent coefficient of cation
- $\nu_a$: chemical equivalent coefficient of anion
- $x$: x coordinate
- $z$: component charge number
- $\rho$: density, kg m$^{-3}$
- $\Delta c$: mass concentration difference, kg kg$^{-1}$
- $\gamma$: activity coefficient

**Introduction**

Pipeline transportation is one of the main ways to transport CO$_2$ to sequestration sites, either in the oil and gas industry for the purpose of enhanced oil recovery (EOR) or in carbon capture and storage (CCS) systems for the purpose of greenhouse gas control. CO$_2$ transportation by pipeline has been in progress for more than 40 years, and over 6000 km of CO$_2$ pipelines currently exist for EOR, mainly situated in the U.S.A and Canada. The existing CO$_2$ transportation systems, which are summarised in Table 1, always require high-purity CO$_2$ streams, especially for EOR, which transports CO$_2$ from natural sources [1]. However, for future anthropogenic CO$_2$ transportation in the CCS industry, the CO$_2$ stream will further contain a certain amount of flue gas impurities (SO$_x$, NO$_x$, HCl, CO, O$_2$, Ar, and H$_2$), in addition to H$_2$S, CH$_4$, N$_2$, and H$_2$O, depending on fuel sources, combustion methods and CO$_2$ capture technologies. Unfortunately, purifying the CO$_2$ stream to relatively high purity will be costly, which will not be an option in future large-scale CCS system. Although the co-sequestration of CO$_2$ and impurities may greatly reduce the cost of the purification process, further evidence is needed to show whether it is safe for long-distance transportation and permanent geological sequestration. The CO$_2$ commercial projects under construction or planning are summarised in Table 2, and all the CO$_2$ involved is from anthropogenic sources.

Usually, the pipeline steel type for CO$_2$ transportation is carbon steel, such as X52, X65, and X70. These CO$_2$ pipeline steels may suffer severe corrosion degradation problems due to the attack by impurities, thus deteriorating the operational integrity of CO$_2$ pipeline transportation systems. According to a report by Det Norske Veritas (DNV) based on the data provided by the Pipeline and Hazardous Materials Safety Administration (PHMSA) of the US Department of Transportation, 29 incidents with regard to CO$_2$ transmission were reported from 1986 to 2008, and 45% of these incidents were caused by corrosion, ranking first among all causes [2]. Corrosion is also a common concern in all CCS processes, including capture, transportation, and injection [3–9]. Unlike
the corrosion of steels under low CO₂ partial pressure conditions, which has been widely addressed in the oil and gas industry, the steel corrosion issue under high partial CO₂ pressure during the CCS transportation process, either in the supercritical phase or the liquid CO₂ phase (both can be called dense CO₂ or a CO₂-rich phase), still lacks adequate related research.

Research on the corrosion of carbon steel in dense CO₂ was initiated in 1975, aiming at the material selection of CO₂ pipeline transportation for EOR. This study showed no localised corrosion on X60 steel and fairly low general corrosion rates [10]. The US Department of Energy also performed some research related to supercritical CO₂ corrosion in 1979 [11] and 1996 [12], which also indicated a low corrosion rate of steel when the water concentration was low. Currently, studies on steel corrosion in dense CO₂ with impurities for CCS have mainly focused on influential parameters, corrosion product layers (structure, morphology, composition) [13–15], corrosion mechanisms [16–18], and mathematical prediction models [19–21]. The studies on influential parameters are crucial, since they provide basic information to uncover the correlations between corrosion phenomena and mechanisms, based on which the corrosion prediction models, corrosion control strategies and pipeline integrity management can be further manipulated.

The internal corrosion of pipeline steel in dense CO₂ with impurities is influenced by a variety of parameters, including environmental, metallurgical, and physical variables. A number of these influential parameters have been preliminarily investigated, such as the impurities (moisture, acidic gases, O₂, and the other impurities), partial pressure, temperature, flow, exposure time, product scales, and materials [13,15,16,19,21–52]. These parameters not only affect the extent of corrosion independently but also accelerate or mitigate macroscopic corrosion through cross-reactions and interactions between them, thus generating synergistic or competitive effects. Systematically checking whether all the important influential parameters have been addressed in the open literature and the research progress in relation to dense CO₂ corrosion is essential for further understanding of the corrosion mechanisms of steel in a dense CO₂ environment, as well as for establishing mechanistic prediction models.

Therefore, this work reviews the existing research development in the open literature and focuses on the influential mechanisms of various parameters on pipeline steel corrosion in dense CO₂ with impurities. The influential parameters neglected by the current research are also mentioned and analysed. The existing mathematical prediction models for dense CO₂ corrosion prediction are highlighted. Moreover, the knowledge gaps and areas requiring further research are proposed in this work.

Table 1. Summary of the existing long-distance CO₂ pipelines [59,60].

<table>
<thead>
<tr>
<th>Project name</th>
<th>Operator</th>
<th>Country</th>
<th>Capacity (Mt a⁻¹)</th>
<th>Length (km)</th>
<th>Diameter (mm)</th>
<th>Pressure (MPa)</th>
<th>Completion time</th>
<th>CO₂ source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cortz</td>
<td>Kinder Morgan</td>
<td>U.S.A</td>
<td>19.3</td>
<td>808</td>
<td>762</td>
<td>18.6</td>
<td>1984</td>
<td>McElmo Dome</td>
</tr>
<tr>
<td>Bravo</td>
<td>BP</td>
<td>U.S.A</td>
<td>7.3</td>
<td>350</td>
<td>508</td>
<td>16.5</td>
<td>1984</td>
<td>Bravo Dome</td>
</tr>
<tr>
<td>Transpetco Bravo</td>
<td>Transpetco</td>
<td>–</td>
<td>3.3</td>
<td>193</td>
<td>324</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Central Basin</td>
<td>Kinder Morgan</td>
<td>U.S.A</td>
<td>11.5</td>
<td>278</td>
<td>508/660/610/508/406</td>
<td>15.1/15/15.8/16.5/17.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Este</td>
<td>Exxon Mobil</td>
<td>U.S.A</td>
<td>4.8</td>
<td>191</td>
<td>305/356</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>West Texas</td>
<td>Trinity</td>
<td>U.S.A</td>
<td>1.9</td>
<td>204</td>
<td>203-305</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SACROC</td>
<td>–</td>
<td>U.S.A</td>
<td>4.2</td>
<td>354</td>
<td>406</td>
<td>17.5</td>
<td>1972</td>
<td>Gasification</td>
</tr>
<tr>
<td>Val Verde</td>
<td>–</td>
<td>U.S.A</td>
<td>2.5</td>
<td>130</td>
<td>–</td>
<td>–</td>
<td>1998</td>
<td>Val Verde Gas Plants</td>
</tr>
<tr>
<td>Canyon Reef Carriers</td>
<td>Kinder Morgan</td>
<td>U.S.A</td>
<td>4.6</td>
<td>225</td>
<td>406</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bati Raman</td>
<td>Turkish Petroleum</td>
<td>Turkey</td>
<td>1.1</td>
<td>90</td>
<td>–</td>
<td>17.0</td>
<td>1983</td>
<td>Dodan field</td>
</tr>
<tr>
<td>Snehvit</td>
<td>StatoilHydro</td>
<td>Norway</td>
<td>0.7</td>
<td>153</td>
<td>203</td>
<td>15</td>
<td>2007</td>
<td>LNG plant</td>
</tr>
</tbody>
</table>

Table 2. Summary of CO₂ commercial projects under construction or planning [61].

<table>
<thead>
<tr>
<th>Country</th>
<th>Project</th>
<th>Operator</th>
<th>Fuel</th>
<th>Scale/MW</th>
<th>Capture technology</th>
<th>CO₂ purpose</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.A</td>
<td>Kemper County</td>
<td>Southern</td>
<td>Coal</td>
<td>582</td>
<td>Pre</td>
<td>EOR</td>
<td>Under construction</td>
</tr>
<tr>
<td>Petra Nova WA Parish</td>
<td>NRG Energy JX Nippon</td>
<td>Coal</td>
<td>240</td>
<td>Post</td>
<td>EOR</td>
<td>Under construction</td>
<td></td>
</tr>
<tr>
<td>HECA</td>
<td>TCEP Summit Power</td>
<td>Petcoke</td>
<td>405</td>
<td>Pre</td>
<td>EOR</td>
<td>Planning</td>
<td></td>
</tr>
<tr>
<td>Canada</td>
<td>Bow City</td>
<td>BPCL</td>
<td>Coal</td>
<td>1000</td>
<td>Post</td>
<td>EOR</td>
<td>Planning</td>
</tr>
<tr>
<td>Norway</td>
<td>Longyearbyen</td>
<td>Unis CO₂</td>
<td>Coal</td>
<td>N/A</td>
<td>Post</td>
<td>Saline</td>
<td>Planning</td>
</tr>
<tr>
<td>Korea</td>
<td>Korea CCS</td>
<td>KCR</td>
<td>Coal</td>
<td>500</td>
<td>Oxy</td>
<td>Saline</td>
<td>Planning</td>
</tr>
<tr>
<td>European Union</td>
<td>ROAD</td>
<td>EON</td>
<td>Coal</td>
<td>250</td>
<td>Post</td>
<td>Depleted oil or gas</td>
<td>Planning</td>
</tr>
<tr>
<td>Serum</td>
<td>Muñoz</td>
<td>Various</td>
<td>Coal</td>
<td>1200</td>
<td>Pre</td>
<td>Depleted oil or gas</td>
<td>Planning</td>
</tr>
<tr>
<td>Peterhead</td>
<td>Shell and SSE</td>
<td>Gas</td>
<td>385</td>
<td>Post</td>
<td>Depleted gas</td>
<td>Planning</td>
<td></td>
</tr>
<tr>
<td>Captain</td>
<td>Summit Power</td>
<td>Coal</td>
<td>570</td>
<td>Post</td>
<td>Saline</td>
<td>Planning</td>
<td></td>
</tr>
<tr>
<td>White Rose</td>
<td>Capture Power</td>
<td>Coal</td>
<td>426</td>
<td>Oxy</td>
<td>Saline</td>
<td>Planning</td>
<td></td>
</tr>
<tr>
<td>Killingholme</td>
<td>CGEN</td>
<td>Coal</td>
<td>470</td>
<td>Pre</td>
<td>Saline</td>
<td>Planning</td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>Damning</td>
<td>Alistom &amp; Datang</td>
<td>Coal</td>
<td>350</td>
<td>Pre</td>
<td>EOR</td>
<td>Planning</td>
</tr>
<tr>
<td>Dongguan</td>
<td>Dongguan Taiyangzhuo Power Corporation</td>
<td>Coal</td>
<td>800</td>
<td>Pre</td>
<td>EOR</td>
<td>Planning</td>
<td></td>
</tr>
<tr>
<td>Shengli Oil Field</td>
<td>Sinopec</td>
<td>Coal</td>
<td>250</td>
<td>Post</td>
<td>EOR</td>
<td>Planning</td>
<td></td>
</tr>
<tr>
<td>GreenGen</td>
<td>GreenGen</td>
<td>Coal</td>
<td>400</td>
<td>Pre</td>
<td>EOR</td>
<td>Planning</td>
<td></td>
</tr>
<tr>
<td>Lianyungang</td>
<td>Lianyungang Clean Energy</td>
<td>Coal</td>
<td>1200</td>
<td>Pre</td>
<td>Saline or EOR</td>
<td>Planning</td>
<td></td>
</tr>
</tbody>
</table>
Generally, two types of dense CO₂ corrosion problems can occur: corrosion in a water-saturated dense CO₂ phase and corrosion in a dense CO₂-saturated water phase. The former scenario is usually encountered in the dense CO₂ transportation system of CCS, while the latter may occur when an aqueous phase forms at the bottom of a dense CO₂ transportation pipeline (especially for upset conditions) or in down-hole material corrosion problems in the oil and gas industry. The corrosion of steel in a dense CO₂-saturated water phase with impurities will not be the main focus of this present work. The review of steel corrosion in supercritical CO₂ in nuclear systems and of CO₂ corrosion in oil and gas pipelines, for which the related articles can be easily found in the open literature [53–58], are also outside the scope of this work. CO₂ is not corrosive, and its carbonic acid that speciates in situ is the issue. CO₂ corrosion refers to the carbonic acid corrosion in this work.

**Influential parameters and mechanisms**

**Impurities**

Impurities are crucial parameters in causing and determining the extent of degradation of steels in dense CO₂. The quality recommendations for the CO₂ transportation provided by the DYNAMIS and EOR projects are shown in Table 3. If impurities can be completely removed from CO₂, corrosion will never be a concern in safe dense CO₂ pipeline transportation. However, no international consensus on the quality standards for the specification of CO₂ mixtures has yet been achieved for pipeline transmission systems [59], for either EOR or CCS purposes. Based on the degree of corrosion attack by combinations of contaminants, four regimes with different risks of pipeline integrity degradation were outlined for CCS dense CO₂ transportation by Cole et al. [7]:

(i) Very low contaminant levels and extremely low water content.
(ii) Low contaminant levels and water content below the solubility limit.
(iii) Low contaminant levels and water content above the solubility limit.
(iv) Moderate contaminant levels and water content above the solubility limit.

It has not yet been determined which regime will be followed in future CCS systems. Before establishing the criteria, corrosion issues must be addressed. A series of studies have followed the four regimes to study the corrosion risk of pipeline steels in dense CO₂ environments, and a number of them have shown that impurities such as SO₂, NOₓ, H₂S, HCl, and O₂ exhibit remarkable effects on the corrosion rate of steel in the CO₂-rich phase [16,17,23,24,30–32,36–38,40–42,45,62–65]. The test conditions for steel corrosion in dense CO₂ with impurities to date are summarised in Appendix A, for convenient searching and citations. The separately summarised test conditions related to supercritical CO₂ corrosion can also be found in the works by Wei et al. [66], Barker et al. [67], and Hua et al. [13,28,29,32].

**H₂O**

The water content plays a critical and principal role on the corrosion behaviours of pipeline steels in dense CO₂.
environments because the existence of water provides the basic conditions for electrolyte formation on the steel surface and further determines the extent of general and localised corrosion. Very strict limitations on the water content have been implemented for EOR CO₂ transportation, but the open literature still lacks the specifics of the dehydration process for the EOR CO₂ stream [6]. It has been found that the water content within each CO₂ stream for EOR projects varies from 20 to 630 ppm, with the exception of the Sleipner project, which transports CO₂ with saturated water using corrosion resistant alloy (CRA) pipelines [67].

A number of studies [1,10,27,28,35,39,68] have shown that when CO₂ is water-free or has relatively low moisture content, the corrosion rates of pipeline steel are zero or negligibly low. Field experience also indicates very few problems in relation to dry CO₂ transportation in carbon steel pipelines [69]. However, once CCS is applied on a large scale, it will be impossible to dry the dense CO₂ stream to a dew point well below the ambient temperature in all cases [70]. It has been estimated that with a less restricted water removal limit (increasing to 400 ppmv), the total cost for impurities been estimated that with a less restricted water removal limit and is another representation of the moisture degree in on the ratio of the actual water content and the water solubility limit and is another representation of the moisture degree in addition to the actual water content (usually in units of ppmv). The sharp increase in corrosion rate occurring at the critical RH is believed to be closely related to the change in corrosion mechanism, that is, the corrosion type argued to change from chemical corrosion to electrochemical corrosion, since a thin water layer forms as RH increases [46].

Thus, the solubility of water in high-pressure CO₂ is a critical issue for dense CO₂ corrosion, and it has been studied by a few researchers, including both experiment [72,73] and model studies [74,75]. However, the solubility of water in high-pressure CO₂ is believed to be considerably influenced by other impurities [39,46]. Above which the corrosion rate increases dramatically with increasing RH. RH (usually in units of %) is defined as the ratio of the actual water content and the water solubility limit and is another representation of the moisture degree in addition to the actual water content (usually in units of ppmv). The sharp increase in corrosion rate occurring at the critical RH is believed to be closely related to the change in corrosion mechanism, that is, the corrosion type is argued to change from chemical corrosion to electrochemical corrosion, since a thin water layer forms as RH increases [46].

For the case with very low RH, no continuous water layer forms, and the anodic process of corrosion will be suppressed along the hydration of the metal ion. The passivation of the anodic process is the main reason for the low corrosion rate under low RH conditions [82]. That is, in the case of RH below the critical RH, the corrosion process is mainly controlled by the anodic process, while for a higher RH, the corrosion process is subject to cathodic process control [82]. Although the study of corrosion in supercritical CO₂ with thin electrolyte layers can refer to a few new methods employed in atmospheric corrosion studies [83,84], the high-pressure environment restricts the employment of certain in situ technologies. Despite some research on electrochemical test technologies in the CO₂-rich phase [85,86], the use of electrochemical methods in supercritical CO₂ systems remains questionable and is not widely applied.
Overall, there is no consensus on the tolerable water content required for dense CO₂ transportation, either for a CO₂ stream with only SO₂ and H₂O or for a CO₂ stream with multiple impurities (SO₃, NO₃, H₂O, O₂, H₂S).

SOₓ
SO₃ stands for SO₂ and SO₃, and SO₂ can be oxidised to SO₃ by O₂. Dissolved SO₂ can ionise in two steps as follows [87]:

\[
\begin{align*}
H₂O + SO₂ & \rightarrow H^+ + HSO₃^- \\
HSO₃^- & \rightarrow H^+ + SO₃²⁻
\end{align*}
\]

SO₂ was found to accelerate the corrosion rates when the SO₂ concentration increased [23,27,45,88]. The presence of SO₂ results in the formation of sulphuric acid by reacting with H₂O and further reacting with O₂ to form sulphuric acid in the aqueous phase, thus lowering the pH and providing more H⁺ ions to participate in and enhance the cathodic reactions. Although it remains unclear whether SO₂ first reacts with water in the bulk dense CO₂ phase to form acid, which then condenses onto the steel surface, or if a thin water layer first forms on the steel surface and then reacts with SO₂ and O₂, or if both of these processes co-exist in dense CO₂ systems. The general corrosion mechanism in dense CO₂ with SO₂ and H₂O has been suggested in detail by several authors [23,28,46].

When a relatively high concentration of SO₂ (for example, 2% mol) is present, the corrosion behaviour of steel in dense CO₂ is not dominated by CO₂ but by SO₂. Choi et al. [23] and Xiang et al. [45] found that when SO₂ was added to the supercritical CO₂ system, iron sulphite was the main corrosion product instead of FeCO₃. It is easy to understand that when SO₂ concentration is high, a high concentration of sulphuric acid will form in the condensates on the steel surface, and once FeCO₃ is formed, it will be dissolved by sulphurous acid. However, if the SO₂ concentration is extremely low, the amount of sulphuric acid cannot dissolve all the FeCO₃, resulting in a mixed and complex composition of corrosion products, thus enhancing the difficulty of product detection.

In terms of the interaction between SO₂ and H₂O, it was found that SO₂ concentration tends to lower the tolerable water content for avoiding pipeline corrosion in supercritical CO₂ transportation [30]. Hua et al. [30] found that the introduction of 50 ppm SO₂ and 20 ppm O₂ resulted in a significant reduction in the tolerable water content required to stay below a general corrosion rate of 0.1 mm/y, reducing it to ~2120 ppm, and further increasing the SO₂ content to 100 ppm reduced the critical water content to ~1850 ppm. They also noted that corrosion can occur with water content of 300 ppm, well below the solubility limit of water in supercritical CO₂, in the presence of 0, 50, and 100 ppm SO₂ [30].

Similar results were also reported by Dugstad et al. [89]. Therefore, the introduction of SO₂ will inevitably increase the risk of pipeline integrity degradation by enhancing the extent of corrosion.

NOₓ
NO₃ stands for NO and NO₂, and NO can be oxidised to NO₂ by O₂. Both NO and NO₂ were found to cause very severe corrosion issues in pipeline steels [90,91]. The presence of NO₂ leads to the formation of HNO₃ in the condensates, which is an extremely strong acid with high causticity [92]:

\[
3NO₂ + H₂O → 2HNO₃ + NO (3)
\]

HNO₃ has a similar accelerant effect on the corrosion behaviour of steel to HCl [22]. However, the diffusion ability of HNO₃ is higher than for HCl and H₂SO₄, which means it may more easily induce severe corrosion problems on the internal surface of supercritical CO₂ pipelines [37]. The neural network modelling results by Sim et al. [21] also showed that HNO₃ had the most notable impact on the corrosion rate of all the potential acids.

Another reason for the high corrosion rates in HNO₃ is derived from the rapid autocatalytic reduction of HNO₃, known as a strong oxidising agent [93]. The mechanism is explained as the primary displacement of hydrogen ions from the aqueous, which is followed by reduction of HNO₃ rather than hydrogen evolution since the acid reduction leads to a marked decrease in free energy [94]:

\[
Fe + 4HNO₃ → Fe(NO₃)₂ + 2H₂O + 2NO₂ (4)
\]

HNO₃ has a strong oxidation effect on Fe²⁺, leading to the formation of a rust-like dusty product, which was always fluffy and exhibited poor protection on the substrate, without the ability to efficiently reduce the corrosion rate [92]. A blackish/orange coloured dusty film was found forming on the X65 steel surface in wet supercritical CO₂ with NO₂ [63]. The composition of the products formed in a continuous flow of CO₂ containing NO₂, SO₂ and CO was found to be very complex [36].

H₂S
When H₂S exists in dense CO₂, it can dissolve in the water layers and promote corrosion by affecting both the anodic and cathodic processes. Aqueous H₂S is a mild acid that can partially dissociate in two steps [97]:

\[
\begin{align*}
H₂S & → H^+ + HS^- \\
HS^- & → H^+ + S²⁻
\end{align*}
\]

Based on records of CO₂/H₂S corrosion in oil and gas industry, ignoring the cracking aspects of corrosion problems, H₂S can either enhance CO₂ corrosion by acting as a promoter of anodic dissolution through sulphide adsorption...
and lowering the pH or reduce CO2 corrosion by forming a protective sulphide scale [55]. The formation reaction of the corrosion products is the following solid-state reaction [98]:

\[
\text{Fe} + \text{H}_2\text{S(aq)} \rightarrow \text{FeS}_{1-x} + x\text{HS}^- + (2-x)\text{H}^+ + 2\text{e}^-(7)
\]

Usually, the H2S-induced corrosion is always highly localised (pitting or mesa-type attack). The formation of iron sulphide layers (such as mackinawite, pyrrhotite, and greigite) is related to the localised corrosion, and their physical properties and protectiveness vary with the conditions [99,100]. The electrode potential gradients created by the local galvanic cells between the iron sulphide and the uncovered area are believed to drive the localised corrosion [101].

Localised corrosion was found to be dominant for low alloy steels (P110 and 3Cr steel), while 316L stainless steel was highly resistant to corrosion in the supercritical CO2 phase with H2S impurity [102]. Choi et al. [24] showed that the addition of 200 ppm H2S in the supercritical CO2 phase dramatically increased the corrosion rate of all tested materials (carbon steel, 1Cr and 3Cr steels) in CO2 with saturated water. However, lowering the water content to 100 ppm in supercritical and liquid CO2 with 200 ppm H2S reduced the corrosion rate to less than 0.01 mm/y [24]. A small amount of H2S was reported to change the adsorbability of H2O onto the steel surface [42], causing the adsorption of H2O on the whole steel surface, thus accelerating the general and localised corrosion of carbon steel in the supercritical CO2 phase. Like nitrates, hydrogen sulphide can also cause internal SCC in CO2 pipelines, which requires more consideration when the transported CO2 contains H2S.

**O2**

Oxygen will inevitably be encountered in the CO2 stream in CCS systems that capture CO2 from coal-fired plants, especially for the oxy-fuel capture technology. Dugstad et al. [27] and Choi et al. [23] preliminarily studied the effect of O2 content on the corrosion rate of pipeline steel in supercritical CO2. It was previously believed that the presence of O2 generally increased the corrosion rate. However, the experimental results by Hua et al. [31] revealed that increasing the O2 concentration from 0 to 1000 ppm caused a progressive decrease in the general corrosion rates of X65 and 5Cr steel in water-saturated supercritical CO2 but tended to increase the extent of localised corrosion observed on both materials. Additionally, Zeng et al. [103] concluded that the influence of oxygen on corrosion is related to the existence of water and the CO2 stream pressure, and there is a threshold pressure (~10 MPa) of a supercritical CO2 stream containing water and oxygen, above which the corrosion rates of pipeline steels become noticeable. Ayello et al. [104] found that a small amount (100 ppm) of O2 had essentially no impact on the corrosion rate of steel in supercritical CO2. Xu et al. [105] found that high O2 concentrations exerted no influence on uniform corrosion rates of X70 steel in supercritical CO2 at a relative water content of 45%, enhanced the general corrosion at a relative water content of 50–60% and localised corrosion at a relative water content of 50–88%, but decreased the general corrosion at a relative water content of 75–100% and localised corrosion at a relative water content of 100%. They also found that the addition of O2 decreased the tolerable water content of the transport system. These controversial results imply that more corrosion experiments related to different amounts of O2 in dense CO2 are needed to reveal the complex effects of O2 on corrosion behaviours, especially under conditions of multiple impurities.

When O2 is the only gas impurity in a normal-pressure CO2 system, it will induce the formation of porous iron oxides with low protectiveness and inhibit the formation of a protective FeCO3 film, resulting in poor protectiveness of the product scales [106], which will eventually induce localised corrosion. It was proven that increasing the O2 content in water-saturated CO2 in the presence of X65 and 5Cr.
suppressed the growth of iron carbonate (FeCO₃) on the steel surface and resulted in the formation of a corrosion product consisting mainly of iron oxide (Fe₂O₃) [31]. When SO₂ and O₂ co-exist in the CO₂ system as gas impurities, O₂ can react with water and SO₂ to form sulphuric acid, which is more corrosive than sulphurous acid. O₂ can also provide more depolarising agents to the cathodic reactions [107,108] and oxidise SO₃⁻ in the following reaction [109]:

$$2\text{SO}_3^- + \text{O}_2 \rightarrow 2\text{SO}_4^-$$  \hspace{1cm} (8)

**Other impurities**

HCl can exist in the CO₂ stream, especially for CO₂ captured from the flue gas of biomass boilers. According to Cole et al. [78], the addition of HCl decreases the solubility of water in CO₂ so that the mass of the aqueous phase progressively increases with increasing HCl. They presumably concluded that the increasing ionic nature of the water content is the cause of the decrease in solubility in the carbon dioxide phase. Another study by Ruhl and Kranzmann [37] found that both apparently amorphous and angular corrosion products were found on samples immersed in supercritical CO₂ with HCl and H₂O impurities, and the crystalline structures appeared hollow at higher magnifications, indicating that the scales could not provide much protection to the substrate.

The existence of HCl will also introduce another problem: the introduction of Cl⁻. At room temperature, Cl⁻ ions may have an inhibitory effect on CO₂ corrosion [110]; however, at high temperature, Cl⁻ ions may cause localised corrosion of the alloy steel. In contrast, Gao et al. [111] argued that localised corrosion of X65 steel in a CO₂ aqueous environment under ambient pressure could be initiated by changing the solubility of iron carbonate and the subsequent changes in the ionic strength of the solution, which was not directly caused by high Cl⁻ concentration.

For pre-combustion technology, CO will inevitably exist in the captured CO₂. CO has a similar effect as NO₃, which can induce an SCC problem that has been observed for approximately 40 years in CO₂–CO–H₂O environments, with the partial pressure of CO₂ below 2.0 MPa [96]. For high-pressure conditions in dense CO₂, the task of elucidating this issue remains. No evidence currently exists to show that CO can promote or depress general corrosion or induce localised corrosion in dense CO₂ environments.

Since most of the CO₂ is captured by organic amines, it is possible that organic amines will be present in the CO₂ stream. The results of Thodla et al. [80] indicated that the presence of monoethanolamine (MEA) decreased the corrosion rate, while Collier et al. [26] found that the presence of diethanolamine (DEA) increased the corrosion rate. MEA might serve as an inhibitor, adsorbing on the steel surface [4], while DEA might provide cathodic depolarising agents.

The presence of acidic gases markedly affects the pH value of the liquid film on the steel surface under supercritical CO₂ environments, by forming strong acids. They thereby result in more H⁺ ions for the hydrogen evolution cathodic reaction, thereby increasing the corrosion rates. Cole et al. [78] found that at the minimum level of HCl contamination (2 ppm), the pH of condensates falls below 1.5 under both liquid and supercritical CO₂ conditions. The research results of CO₂ corrosion in the oil and gas industry showed that pH had a significant impact on the corrosion behaviour of mild steel. It can influence both the electrochemical reactions that lead to iron dissolution and the precipitation of protective scales which governs the various transport phenomena associated with the former [55]. The corrosion mechanisms could be related to the changes of localised pH; however, this issue has not been addressed yet in the supercritical CO₂ environment by the experimental study. A mechanistic prediction model for supercritical CO₂–SO₂–O₂–H₂O corrosion by Xiang et al. [19] showed that the localised pH on the steel surface increased due to the depletion of H⁺ ions and the accumulation of HSO₃⁻ and SO₃⁻.

The hydrogen-induced cracking (HIC) have to be considered when an aqueous phase and impurities such as H₂S and NO₂ exist. The threat and mitigation of HIC and SCC must be addressed in future standards related to the design and construction of pipelines for anthropogenic CO₂ transportation.

**Pressure**

Pressure herein includes the total pressure, the partial pressure of CO₂, the partial pressure of O₂ and other gas impurities. Experimental results on CO₂ corrosion in the oil and gas industry showed that there was almost a linear growth relationship between the CO₂ partial pressure and the corrosion rate of pipeline steel at low CO₂ partial pressure [112]. For dense CO₂ environments with impurities, CO₂ becomes the solvent and the impurities become the solutes, making the CO₂ partial pressure substantially equal to the total pressure of the mixtures. Changing the total pressure can change the bulk phase state (gas, liquid, or supercritical), the total amount of corrosive medium, the solubility of impurities in the bulk phase, the morphology, and the properties of the product layers, thus influencing the corrosion behaviour of the pipeline steel. Changing the partial pressure of the impurity is equivalent to changing the concentration of impurity.

Choi and Nesic [25] preliminarily studied the effect of total pressure on the corrosion rate of X65 steel in a high-pressure CO₂ environment with saturated water, and the experimental results revealed that the corrosion rate increased when the total pressure increased from 6.0 to 8.0 MPa, with the CO₂ phase changing from gas to a supercritical state. Moreover, the increase in O₂ partial pressure can also generally increase the corrosion rate in a supercritical CO₂ system; however, the corrosion rate reaches a maximum value at 3.3 bar O₂ [23]. Meanwhile, increasing the partial pressure of SO₂, which means increasing the SO₂ concentration, can also dramatically increase the corrosion rate of X70 steel and iron in a supercritical CO₂ system [45]. Recently, the results by Xu et al. [113] showed that the corrosion rates of pipeline steels at 8 MPa are higher than at 10 MPa when the water concentration is below 3000 ppmv, while the situation is the opposite when the water content was 3000 ppmv. They also found that the pitting rates were high, especially for the cases with 3000 ppmv water concentration.

The experimental data at higher total pressures are sparse, especially for the pressure more than 20 MPa. It has to be mentioned that for the high pressure environment, the non-ideality of gases will play an important role [55]. Instead of the CO₂ partial pressure, the CO₂ fugacity should be used...
Since Henry’s law can only be used in diluted solutions, non-ideal equilibrium models must be applied to precisely predict the solubility of the impurities in the condensed phase under high-pressure condition.

**Temperature**

The temperature in a dense CO₂ transportation system can vary from -56.7 to above 31°C, with the CO₂ phase changing from liquid to supercritical, based on the CO₂ phase diagram. Temperature is an operating parameter as critical as pressure, since it can affect the corrosion behaviour in many ways. It can affect the solubility product of FeCO₃ according to the following equation [115]:

\[
\log K_{sp} = -59.3498 - 0.041377T_k - \frac{2.1963}{T_k} \\
+ 24.5724 \log (T_k) + 2.5181^{0.5} - 0.657I
\]

where \( K_{sp} \) is the solubility product of FeCO₃, \( T_k \) is the temperature in Kelvin and \( I \) is the ionic strength of the solution.

In addition to the effect on the bulk phase, temperature directly influences the exchange current density, chemical reaction equilibrium constants, chemical reaction rate constants, fluid viscosity, and fluid density. Moreover, temperature can affect the morphology and properties of product layers and the component diffusion coefficients, thus indirectly influencing the corrosion behaviours.

Notwithstanding, the corrosion rates of X70 steel in supercritical CO₂ mixtures first increased with temperature, reaching a peak value near 75°C, and then decreased with temperature [43,48], which showed a similar influence trend of temperature on the corrosion rate of pipeline steel in a low partial pressure CO₂ environment [116]. The effect of temperature on increasing the corrosion rates of pipeline steel in supercritical CO₂ compared with liquid CO₂ was suggested by several researchers [27,43]. In contrast, Ruhl and Kranzmann [36] found that the corrosion rates became more pronounced with decreasing temperature and increasing humidity, though the tests were under ambient pressure instead of high pressure. Meanwhile, Hua et al. [28] revealed that the corrosion rate of X65 steel increased as the temperature decreased from 50 to 35°C when the water content was lower than 1600 ppm (mol). These paradoxical experimental results require deep investigations to explain.

It is noteworthy that temperature has a great impact on the surface morphology of corroded samples, as shown in Figure 3, further affects the protectiveness of product layers, thus eventually determining the general and localised corrosion. Under supercritical CO₂ conditions, the porosity test results of the product scales indicated that the loose product layer with poor protectiveness was related to low temperature, while a more compact product layer with better protectiveness was related to high temperature [43].

**Flow**

CO₂ corrosion studies for low partial pressure conditions have shown that the increase in flow velocity would usually increase the corrosion rate, which derives from accelerating the speed with which the depolarising agent reaches the sample surface to participate in the electrode reaction, i.e. enhancing the cathodic depolarisation process and accelerating the transfer rate for the reaction products to move away from the steel surface, thus eventually enhancing the corrosion process [112]. However, after the formation of the corrosion product layers, the impact of flow velocity on the corrosion rate was found to be weakened [117].

![Figure 3. Surface morphology of X70 steel in supercritical CO₂ mixtures (10 MPa, 120 h, 5 g H₂O, 0.02 mol O₂ and 2% mol SO₂) changes with temperature [43]. (a) 298 K; (b) 323 K; (c) 348 K; (d) 366 K.](image-url)
which may be related to the greatly diminished flow velocity by porous corrosion product layers. It is noted that the flow shear stress near the pipeline wall might also affect the formation and stability of the product layer and inhibitor film [55], though the recent results by Li et al. [118] revealed that the mechanical removal of an FeCO₃ layer solely by wall shear stress, typically observed in multiphase flow lines, is highly unlikely under ambient pressure. Moreover, the flow regime may have great impact on the pipeline internal corrosion in dense CO₂, which implies that the desired properties of CO₂ should be adequately monitored to avoid the phase changes and ensure the maintenance of a single-phase flow throughout the pipelines [119]. Furthermore, flow-induced localised corrosion and erosion problems in the presence of particulates may also occur in dense CO₂ environments.

To date, sparse studies with relevance to the flow effect under a dense phase CO₂ environment have been conducted in closed autoclave systems. The work by Dugstad et al. [27] revealed that in supercritical CO₂ at 50°C, the corrosion rate of X65 steel at a flow velocity of 3 m s⁻¹ condition was approximately 10 times the value with no flow, as shown in Figure 4. The similar effect of the flow on the corrosion rate was also found in liquid CO₂ [27]. In contrast, the work by Farelas et al. [120] revealed that a 1000 rev min⁻¹ rotating speed in the autoclave can depress the corrosion rate of X65 in the supercritical CO₂ system distinctly. Hua et al. [32] stated that the flow can reduce the amount of water condensing onto the sample surface, thereby depressing the corrosion.

Meanwhile, only a few of the existing supercritical CO₂ corrosion tests were completed in the flow loop [79,121], and the test results in the flow loop were believed to show better reliability than the test results obtained in the sealed autoclaves. There is no doubt that more studies under different flow conditions in the flow loop are needed, especially for multiphase flow conditions in the CO₂ pipeline with different flow regimes, which may represent a gas–liquid flow in the worst-case scenario. The gas–liquid flow could be encountered when the pressure was reduced due to CO₂ pipeline rupture or other disrupted conditions.

**Exposure time**

A number of tests by different researchers have shown that, as the corrosion reactions proceeded, the corrosion products gradually accumulated on the sample surface, thickening the corrosion product layers with exposure time [15], both in a supercritical CO₂-saturated water phase and a water-saturated supercritical CO₂ phase, as shown in Figure 5 [29]. As the exposure time extended, the mass of corrosion product layers increased and the corrosion rate decreased, which suggested that the presence of the corrosion product layers effectively protected the substrate metal and reduced the corrosion rate. In a 454 h test conducted by Xiang et al. [44], the pitting corrosion beneath the product layers was highlighted as a serious problem.

Notably, the autoclave test method was employed in most studies. Since the autoclave is a closed system, the corrosive species will be gradually consumed, decreasing the corrosive species concentrations, which might contribute to the decrease in corrosion rates with exposure time. This issue was first mentioned by Xiang et al. [15] in the supercritical CO₂ environment, then elaborated in detail by Hua et al. [30] and Barker et al. [67]. If the impurity concentrations are high enough to make up for the consumption of corrosion reaction, the impact of decreasing the impurity concentration is limited. When the impurity concentration is low, the impact of the consumption of impurities on the corrosion rate might not be discounted. Brown et al. [62] claimed that a large portion of the corrosive phase can be trapped in dead legs or wet the autoclave walls preferentially. They also noted that the interaction of impurities in the bulk phase was another reason for the decrease of the active corrosion phase concentrations [62].

A system with impurity replenishment was another method to diminish the effect of decreasing the impurity concentration, which was employed by Yevtushenko and Bäßler to test the corrosion behaviour of steel in supercritical CO₂ [79]. A rocking autoclave with an impurity replenishing system and venting lines for CO₂ composition online analyses was also employed for dense CO₂ corrosion...
studies to overcome the shortcomings of the impurity consumption [89].

Product layers

In CO2 corrosion, if a protective layer forms on the steel surface, a diffusion process controlled by the product layer may become the rate-determining step (RDS) in the corrosion process [122]. Four characteristics are generally used to judge the protectiveness of the product layer: layer density, adhesion, stability, and surface coverage [55].

To date, there have been limited studies on the formation mechanisms of the product layer in supercritical CO2 environments with impurities and their properties, while studies related to the FeCO3 layer formation in supercritical CO2-saturated water environments have been performed in detail [14,29]. If the supersaturation exceeds the solubility of FeCO3 in the solution, FeCO3 will precipitate on the steel surface.

In a supercritical CO2-saturated water environment, the mechanical properties of the FeCO3 layer and the relationship between the corrosion rate and the fracture toughness, as shown in Equation (10), were proposed by Zhang et al. [14] as follows:

\[ CR = \frac{3.25}{K^{3/6}} - 0.908 \]  

(10)

Another study conducted by Hua et al. [29] indicated that the FeCO3 layer formed in a supercritical CO2-saturated water environment consisted of two layers: the loose amorphous FeCO3 inner layer and the compact FeCO3 crystal outer layer. However, the localised corrosion rates were still high, even though the layers seemed to be compact, in water-saturated supercritical CO2.

The composition of the product layer and the effect on corrosion behaviour become more complicated when the acidic gases are contained in a dense CO2 stream. Taking SO2 as an example, FeSO3·3H2O and FeSO4·H2O crystals are usually detected in the product layers [46], while FeCO3 cannot be found in the product unless the SO2 concentration in the corrosion environment is fairly low [32]. A mixed product layer containing FeSO3·3H2O and FeCO3 was found under conditions of 50 and 100 ppm SO2 and 20 ppm O2, and the ratio of FeSO3·3H2O to FeCO3 increased with increasing SO2 concentration [32]. Moreover, Ruhl and Kranzmann [38] suggested that the inner part of the FeSO3·3H2O and FeSO4·H2O layers changed to iron sulphide (FeS) under ambient pressure. The changing process was characterised by the following equation [123]:

\[ \begin{align*}
SO_2 & \rightarrow SO_4^{2-} \rightarrow S_2O_8^{2-} \rightarrow S_2O_7^{2-} \rightarrow S \rightarrow S^2 \rightarrow S_4 \rightarrow S_3 \rightarrow S_2 \rightarrow S^- \\
\end{align*} \]  

(11)

When NO2 and SO2 were present, ammoniojarosite \((\text{NH}_4)_2\text{Fe}_2(SO_4)_3(OH)_6\) was found to be the main corrosion product under ambient conditions [36], while Fe(NO3)3·9H2O, O and FeO2·H2O were detected as the main corrosion products for X65 steel in water-saturated supercritical CO2 with 1000 ppm NO2 [91]. NO3 present in the solution might be reduced to ammonium (NH4+) within the aqueous film and in the presence of hydronium ions (H3O+) [37], according to the following equation [124]:

\[ 4\text{Fe} + \text{NO}_3^- + 10\text{H}^+ \rightarrow 4\text{Fe}^{2+} + \text{NH}_4^+ + 3\text{H}_2\text{O} \]  

(12)

Ammoniojarosite \((\text{NH}_4)_2\text{Fe}_2(SO_4)_3(OH)_6\) formed according to [125]:

\[ 3\text{Fe}^{3+} + \text{NH}_4^+ + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow \text{NH}_4\text{Fe}_2(\text{SO}_4)_3(\text{OH})_6 + 6\text{H}^+ \]  

(13)

For the case with SO2, H2S, and O2 impurities, the complex product has been identified by Sun et al. [16], while for the case with NO3, SO2, H2S, O2, and HCl coexisting, there is still no experimental result that can be cited here to clearly show the exact composition of the product layers.

The following equations describe the other potential corrosion products of mild steel in the supercritical CO2 environments:

\[ \begin{align*}
\text{Fe} + \text{SO}_2 + \text{H}_2\text{O} & \rightarrow \text{FeSO}_3 + \text{H}_2 \\
2\text{Fe} + 2\text{SO}_2 + 2\text{H}_2\text{O} + \text{O}_2 & \rightarrow 2\text{FeSO}_4 + 2\text{H}_2 \\
x\text{Fe} + y\text{H}_2\text{S} & \rightarrow \text{Fe}_x\text{S}_y + y\text{H}_2 \\
\text{Fe} + 2\text{HCl} & \rightarrow \text{FeCl}_2 + \text{H}_2 \\
\end{align*} \]  

(14) \hspace{1cm} (15) \hspace{1cm} (16) \hspace{1cm} (17)

A protective corrosion product layer on the one hand, tends to reduce the flux of corrosive media reaching the metal surface, and on the other hand, may directly isolate part of the substrate metal from the corrosive media completely, thus substantially lowering the corrosion rate. Vitse and Nesic proposed the concept of surface coverage to describe the ability of the product layer to isolate the steel from the corrosive media [126].

The mechanisms of product layer formation under different conditions also need to be specified. Sun et al. [41] speculated the mechanisms of water layer and product layer formation for a water-saturated supercritical CO2 system with O2 and H2S impurities, as shown in Figure 6. The exact product compositions and structures might be affected by impurity types and concentrations and the surface roughness of the inner wall of the CO2 pipeline. Xu et al. [47] found that the initial surface roughness has no influence on the corrosion rate at a RH of <55% (45, 50, and 55%) and >88% (88, 100%). However, a rougher surface leads to higher corrosion rate at a RH between 60 and 75%.

Steel chemistry

The metallurgical variables (composition, heat treatment, and microstructure) play important roles in the corrosion of steels in dense CO2 environments. Russick et al. [127] showed that carbon steel suffered corrosion problems in water-saturated supercritical CO2, while 316 SS and 304L SS are corrosion resistant in the same environment. Hua et al. [31] found that when O2 is present in water-saturated supercritical CO2, 5Cr offers more resistance to pitting corrosion than X65 steel. They also found that with a concentration of O2 above 500 ppm, the general corrosion rate of 5Cr steel was less than 0.04 mm/y, half the value measured for X65 steel [31]. However, the experimental results by Choi et al. [23] showed that the corrosion rates of X65 steel and 13Cr steel showed no outstanding differences in water-saturated supercritical CO2 with SO2 and O2 impurities, revealing that 13Cr steel does not show higher corrosion resistance in the water-saturated dense CO2 environment with SO2 and O2. Yevtushenko and Bäßler [79] also found that X20Cr13 steel showed severe pitting problems in supercritical CO2 with H2O, SO2,
NO, CO, and O₂ impurities. Dugstad et al. [64] even found that high concentrations (>1000 mg L⁻¹) of Ni, Mo, and Cr were dissolved in the greenish liquid after corrosion testing, which indicated that the Hastelloy C autoclave was attacked in liquid CO₂ with H₂O, SO₂, NO₂, H₂S, and O₂ impurities. It was indicated that the ions generated from the pipeline steel alloy elements, such as Mn²⁺, would be a catalyst to accelerate the oxidation reaction of SO₂⁻³ to SO₂⁻⁴. The differences between the physical properties of the FeSO₃ hydrate and the FeSO₄ hydrate products, such as the different solubility in water, may indirectly affect the corrosion process. However, the roles of other alloying elements in the corrosion of steels remain unknown in dense CO₂ with acidic gas impurities.

The effect of heat treatment on the corrosion behaviour of stainless steels during CO₂-sequestration into a saline aquifer was investigated by Pfennig et al. [8]. Low corrosion rates were obtained for steels with martensitic microstructures exposed to supercritical CO₂ at 100 bar, whereas normalised steels showed better corrosion resistance at ambient pressure [8].

### Discussion of corrosion mechanisms

#### Synergistic effect

NO₂ and SO₂ were reported to have a synergistic effect that can intensify atmospheric corrosion, and moreover NO₂ had a catalytic effect on corrosion reactions [128]. Recently, Sun et al. [16] found that the synergistic effect of O₂, H₂S, and SO₂ impurities on the corrosion behaviour of X65 steel in water-saturated supercritical CO₂ systems was remarkable. Weight-loss tests revealed that the synergistic effect of multiple impurities significantly increased the corrosion rate of X65 steel. The complicated synergistic effects among CO₂, O₂, H₂S, and SO₂ resulted in the highest corrosion rate, as shown in Figure 7 [16]. The corrosion scales consisted of FeOOH, FeSO₄·2H₂O, FeSO₄·4H₂O, FeS, FeCO₃, and S [16], which implied a complex corrosion mechanism. The weak protective ability of the product scale might be one of the reasons for the synergistic increase in the effect of impurities on the corrosion rates.

The interactions among the impurities in the bulk phase have also attracted attention. Dugstad et al. [89] found that there was some elemental sulphur in the autoclave after the test for steel corrosion in supercritical CO₂ containing NO₂, SO₂, H₂O, H₂S, and O₂. The initiation of pitting corrosion by the presence of sulphur in a CO₂ environment has been reported by Fang et al. [129], which indicates that sulphur-initiated pitting may also occur in a supercritical CO₂ environment. Although the mechanism of sulphur formation is elusive, Dugstad et al. [89] speculated that the following reactions might occur:

1. \[2H₂S + 3O₂ \rightarrow 2SO₂ + 2H₂O\] (18)
2. \[2H₂S + SO₂ \rightarrow 3S + 2H₂O\] (19)
3. \[2H₂S + O₂ \rightarrow 2S + 2H₂O\] (20)

Brown et al. [62] also suggested a similar reaction mechanism to Equation (20) between H₂S and O₂ at very low H₂S and O₂ concentrations. The formation of sulphur will lead to a...
sulphur sedimentation problem that may block the pipelines and affect the accuracy of the electrical resistance electrode. Then elemental sulphur can react with H₂O to produce H₂S and sulphuric acid [130]:

\[
8S + 8H₂O \rightarrow 6H₂S + 2H₂SO₄
\]  

Dugstad et al. [89] also discussed the interaction between NO₂ and SO₂, that is, when NO₂, SO₂, O₂, and H₂O are present, SO₂ will be catalytically oxidised to H₂SO₄ by NO₂ (Lead Chamber Process) [131]:

\[
\begin{align*}
\text{NO}_2 + \text{SO}_2 + \text{H}_2\text{O} & \rightarrow \text{NO} + \text{H}_2\text{SO}_4 \quad \text{fast} \\
2\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \\
2\text{NO}_2 + \text{H}_2\text{O} & \rightarrow \text{HNO}_2 + \text{HNO}_3 \quad \text{slow} \\
3\text{HNO}_2 & \rightarrow \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}
\end{align*}
\]

More possible cross chemical reactions between impurities and their corresponding acids were proposed by Dugstad et al. [64]:

\[
\begin{align*}
\text{H}_2\text{S} + 2\text{NO}_2 & \rightarrow 1/2\text{SO}_2 + 2\text{NO} + \text{H}_2\text{O} + 1/2\text{S} \\
\text{H}_2\text{S} + \text{H}_2\text{SO}_4 & \rightarrow \text{S} + \text{SO}_2 + 2\text{H}_2\text{O} \\
3\text{H}_2\text{S} + 2\text{HNO}_3 & \rightarrow 3\text{S} + 2\text{NO} + 4\text{H}_2\text{O} \\
4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{HNO}_3
\end{align*}
\]

For the case with SO₂, O₂, and H₂O impurities, the ferrous sulphate product formed at anodic sites oxidises to ferric sulphate which in turn hydrolyses to produce iron oxyhydroxide, with the generation of sulphuric acid; the overall reaction is [132]:

\[
4\text{FeSO}_4 + 6\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{FeOOH} + 4\text{H}_2\text{SO}_4
\]

To date, there is no open published model that can predict which of the above reactions are thermodynamically and kinetically possible and favourable under supercritical CO₂ test conditions, though an online measurement system was applied to determine the consumption rate of impurities in dense CO₂ [64]. However, the existing work offers some important information about the impurity interactions in the dense CO₂ phase.

**Anodic and cathodic reactions**

In addition to the bulk phase reactions among the impurities, the electrochemical reactions on the steel surface are the crucial steps in corrosion processes. The widely accepted anodic dissolution of iron in strong acid is the Bockris mechanism (BDD) [133]:

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} & \rightarrow [\text{FeOH}]_{\text{ad}} + \text{H}^+ + e^- \\
[\text{FeOH}]_{\text{ad}} & \rightarrow [\text{FeOH}^+]_{\text{ad}} + e^- \\
[\text{FeOH}^+]_{\text{ad}} + \text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}
\end{align*}
\]

The total anodic reaction is as follows:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- 
\]

The above total anodic reaction is pH dependent in acidic solutions, with a typical measured Tafel slope of 40 mV [56]. This description can be applied where H₂S is not present in the system. In the presence of H₂S, the iron dissolution mechanism can be expressed as follows [134]:

\[
\begin{align*}
\text{Fe} + \text{HS}^- & \rightarrow [\text{FeSH}]_{\text{ad}} \\
[\text{FeSH}]_{\text{ad}} & \rightarrow [\text{FeSH}]_{\text{ad}} + e^- \\
[\text{FeSH}]_{\text{ad}} + e^- & \rightarrow [\text{FeSH}]_{\text{ad}}^{2+} + e^-
\end{align*}
\]

The question remains whether the anodic dissolution mechanisms of iron in dense CO₂ are consistent with the iron dissolution mechanism under low partial pressure conditions. In particular, when acidic gas impurities exist, the synergistic effect of impurities on the anodic dissolution mechanism is elusive.

For the cathodic reactions, the most important confirmed reaction is the hydrogen evolution process:

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2
\]

The following cathodic reactions are also possible for the ingress of impurities [97,107,135]:

\[
\begin{align*}
\text{O}_2 + \text{SO}_2 + 2e^- & \rightarrow \text{SO}_4^{2-} \\
\text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow 2\text{H}_2\text{O} \\
2\text{H}_2\text{S} + 2e^- & \rightarrow \text{H}_2(g) + 2\text{HS}^-
\end{align*}
\]

Due to the low pH conditions in dense CO₂ with acidic gas impurities, it seems that the following cathodic reactions that occur in low partial pressure CO₂ corrosion may not occur here:

\[
\begin{align*}
2\text{H}_2\text{CO}_3 + 2e^- & \rightarrow \text{H}_2 + 2\text{HCO}_3^- \\
2\text{HCO}_3^- + 2e^- & \rightarrow \text{H}_2 + 2\text{CO}_3^{2-} \\
2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2 + 2\text{OH}^-
\end{align*}
\]

Currently, no research has clearly illustrated the exact reactions of the cathodic processes. Other possible reactions might occur under the synergistic effect of impurities. The lack of research on the anodic and cathodic corrosion mechanisms is partly because of the limited methods of investigating corrosion mechanisms that can be applied to the dense CO₂ environment. Conducting electrochemical experiments in the aqueous phase saturated with supercritical CO₂ is expected to be helpful for investigating the corrosion mechanisms. Meanwhile, electrochemical investigation under ambient pressure might also be useful and valuable to provide some insight into the corrosion mechanism under high pressure. Tang et al. [86] recently developed a setup for in situ electrochemical measurements in H₂O-saturated supercritical CO₂ phase by using Ag/AgCl reference electrode, as illustrated in Figure 8. Their work is creative and the setup could be further used to investigate the cathodic and anodic corrosion mechanisms of steel in dense CO₂ phase.

**Localised corrosion**

For traditional CO₂ corrosion, localised corrosion is a common concern, in addition to general corrosion. A similar localised corrosion problem also occurs in dense CO₂ corrosion, even without acidic gas impurities and with high enough water content [30,62]. Most of the current published works focus on the general corrosion behaviour and mechanism of carbon steel, while few of them focus on localised corrosion issues. Moreover, most of the literature reports that mention the localised corrosion issue only note that the samples...
encountered localised attack or that visible pitting regions were found on the sample surface, and the penetration rates were seldom determined.

Actually, localised corrosion is one of the serious threats to pipeline integrity in dense CO₂ transportation, as well as SCC and HIC. Localised corrosion also has a great impact on determining the upper limit of water content to avoid corrosion. The work of Xiang et al. [46] established a systematic method to determine the upper limit of water content for dense CO₂ pipeline transportation, by considering both the control of the general corrosion rate and the temperature variation of the fluids inside the pipes. However, Hua et al. [30] noted that the impact of localised corrosion should also be considered, and the authors concluded that the critical water content required to minimise the significant level of localised attack was substantially lower than the value required to prevent general corrosion (0.1 mm/y) and was determined to be approximately 500 ppm, regardless of SO₂ content (0, 50, or 100 ppm). When other impurities exist, such as NOₓ, HCl, and H₂S, this estimated tolerable water content needs to be re-evaluated.

Barker et al. [67] discussed a series of fundamental questions relating to the localised corrosion of steel in dense CO₂. They suggested the investigation of the initiation, propagation, and stability of pits in a dense CO₂ environment to verify whether they would be the real threat to long-term operation in the field [67]. Currently, there is no literature identifying whether the pits are stable and continue to propagate, and the propagation kinetics also needs further investigation.

Sun et al. [91] recently found that the pits lie right under the spherical corrosion products in water-saturated supercritical CO₂ with NO₂ impurity, and other investigators have also shown localised corrosion under iron sulphate deposits in water-saturated dense CO₂ with SO₂ and O₂ impurities [44]. The localised penetration rates under the corrosion product were much higher than the general corrosion rates. It is essential to investigate the evolution rules of the corrosion products on the sample surface and their relation to the initiation and propagation of pits in dense CO₂ environments.

**Mechanism differences for different CO₂ phase conditions**

The corrosion mechanism differences between low partial pressure and supercritical condition (aqueous phase) have been studied by Zhang et al. [18]. They found that under both low CO₂ partial pressure and supercritical CO₂ condition, the corrosion behaviours of X65 steel, including characteristics of CO₂ corrosion product scale and the variation rule of corrosion rate with temperature, were similar. They concluded that the change in CO₂ partial pressure does not change the corrosion mechanism. They also explained that the corrosion rate was enhanced under supercritical CO₂ condition due to the higher carbonic acid concentration. Zhang et al. [136] stated that there was no essential difference in the electrochemical corrosion mechanism under supercritical CO₂ and non-supercritical CO₂ environments for the N80 steel in the aqueous phase.

Actually, corrosion in CO₂ environments can be divided into six circumstances: corrosion in aqueous phase with low CO₂ partial pressure (gas CO₂), wet gas phase with low CO₂ partial pressure (gas CO₂), aqueous phase with high CO₂ partial pressure (liquid CO₂), liquid CO₂ phase, aqueous phase with high CO₂ partial pressure (supercritical CO₂), and supercritical CO₂ phase. When the phase state of CO₂ is changed, the corresponding parameters (solubility, diffusion coefficient, viscosity, ionic strength, etc.) will change. With the presence of acidic gas impurities (SO₂, NO₂, H₂S, etc.), the corrosion mechanism will be thoroughly altered. The carbonic acid corrosion will change to sulphurous acid corrosion, nitric acid corrosion, and H₂S corrosion, or a mixed type of them. The corrosion products will also vary for different acidic gas impurities, which will affect the corrosion process in turn. For the corrosion in the dense CO₂ phase, the corrosion happened in the confined aqueous phase (water film), which is apparently different from the corrosion in the bulk aqueous phase. This characteristic has notable impact on the mass transport of species, and also affects the solubility of corrosion products, which will eventually affect the protectiveness of product layers to the substrate. The investigations on the effects of multiple acidic gas impurities on the corrosion

![Figure 8. Schematic diagram of the setup for in situ electrochemical measurements in H₂O-saturated supercritical CO₂ environment [86].](image-url)
behaviours and their effects on the corrosion mechanisms are necessary and urgent, which is required by establishing the mechanistic prediction models.

**Mathematical prediction models**

**CO₂ and H₂S corrosion prediction models**

The development of a mathematical corrosion prediction model based on physico-chemical processes is among the research hotspots in the fields of corrosion science and technology because it can assist engineers in foreseeing the corrosion issue and thus making decisions related to corrosion prevention and control issues [56]. There are three main types of mathematical prediction models [56,137]:

- **Mechanistic models**: These models describe the mechanisms of the underlying reactions and have a strong theoretical background. Most of the constants appearing in this type of model have a clear physical meaning.

- **Semi-empirical models**: These models are only partly based on firm theoretical hypotheses. Some of the constants appearing in these models have a clear physical meaning, while others are arbitrary best-fit parameters.

- **Empirical models**: These models have very little or no theoretical background. Most constants used in them have no physical meaning.

Corrosion prediction is particularly important in the oil and gas industry, since the corrosion issue is highly connected with the safe operation of wells, pipelines and other facilities. CO₂ corrosion is the most common corrosion type in the oil and gas industry, and the earliest CO₂ corrosion model was published in 1975 by de Waard and Milliams [138], including only the CO₂ partial pressure and the temperature as the model input. It was then improved to kinds of CO₂ corrosion prediction models with more key parameters as the input variables, such as water chemistry, pH, scaling tendency, total pressure, fluid flow velocity, and hydraulic diameter. The famous CO₂ prediction models include the NORSOK model [139], the LIPUCOR model [140], the KSC model [141], the TULSA model [142], as listed in Table 4. The FREECORP [143,144] and MULTICORP [145] models are the most recently developed models, and the latter considers the complex effects of multiphase flow and product layers.

H₂S corrosion is another common corrosion problem in the oil and gas industry. A mechanistic prediction model was established for H₂S corrosion by Zheng et al. [97], based on the hypothesis that there is a direct reduction of H₂S on the steel surface, as shown in Equation (41). Another mechanistic prediction model for CO₂/H₂S corrosion was also established by Zheng et al. [146–148] and is a useful reference when establishing supercritical CO₂ corrosion with H₂S and other impurities. It is also important in predicting liquid CO₂ corrosion, though there still remains a series of challenges to overcome.

Although there are many CO₂ corrosion prediction models, they can only be employed within the CO₂ partial pressure range of 0–2 MPa. When these models were applied to higher CO₂ partial pressure conditions, the predicted values were almost an order of magnitude higher than the experimental values [20,70]. The reason for this discrepancy should be attributed to the different corrosion characteristics under high-pressure conditions.

**Mechanistic prediction model for corrosion in impure dense CO₂**

Corrosion in dense CO₂ always occurs with a thin water layer with high ionic strength, and the dissolution behaviours of the impurity gases are non-ideal; thus, a new model should be generated for dense CO₂ conditions.

Currently, there is only one mechanistic model that specifically addresses the prediction of carbon steel corrosion in dense CO₂ phase with SO₂–O₂–H₂O impurities. A six-layer mechanistic model was established by Xiang et al. [19] by integrating the traditional CO₂ corrosion models [141,143,150–154] and the atmospheric corrosion model by Graedel [155]. The corrosion region was divided into six regions, namely, supercritical CO₂, interface, water film, deposition, electroic, and solid (SIWDES), as shown in Figure 9. The effects of SO₂ and O₂ on the corrosion rate were considered, while the contribution of CO₂ to the corrosion rate was ignored. Only Equations (38) and (39) were considered as the cathodic reactions, and the mass transfer process was assumed to be diffusion controlled.

This model applied the following equation to calculate the diffusion rate of all components in the water and porous product scales for various components [19]:

\[
\frac{\partial (\varepsilon c_j)}{\partial t} = - \frac{\partial}{\partial x} \left( \varepsilon^{1.5}D_j \frac{\partial c_j}{\partial x} \right) + \varepsilon R_j - \left( CR - \frac{\partial d_j}{\partial t} \right) \frac{\partial c_j}{\partial x} \tag{45}
\]

The modified Three-Characteristic-Parameter Correlation (TCPC) model was introduced to modify the impact of the ionic strength on the activities of the species in the water film, allowing simple and accurate calculation of the ion

<table>
<thead>
<tr>
<th>Model</th>
<th>Developer(s)</th>
<th>Temperature (°C) Min</th>
<th>Pressure (bar) Max</th>
<th>CO₂ partial pressure (bar) Min</th>
<th>pH Min</th>
<th>pH Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>de Waard-Milliams</td>
<td>de Waard and Milliams</td>
<td>0</td>
<td>140</td>
<td>–</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>HYDROCOR</td>
<td>Shell</td>
<td>0</td>
<td>150</td>
<td>200</td>
<td>–</td>
<td>20</td>
</tr>
<tr>
<td>Cassandra 98</td>
<td>BP</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>NORSOK</td>
<td>Statoil, Saga, IFE</td>
<td>20</td>
<td>150</td>
<td>1000</td>
<td>–</td>
<td>10</td>
</tr>
<tr>
<td>CORMED</td>
<td>Elf</td>
<td>–</td>
<td>120</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>LIPUCOR</td>
<td>Total</td>
<td>20</td>
<td>150</td>
<td>250</td>
<td>–</td>
<td>50</td>
</tr>
<tr>
<td>KSC</td>
<td>Shell</td>
<td>5</td>
<td>150</td>
<td>250</td>
<td>–</td>
<td>50</td>
</tr>
<tr>
<td>TULSA</td>
<td>University of Tulsa</td>
<td>38</td>
<td>116</td>
<td>–</td>
<td>17</td>
<td>–</td>
</tr>
<tr>
<td>PREDICT</td>
<td>InterCorr International</td>
<td>20</td>
<td>200</td>
<td>–</td>
<td>–</td>
<td>100</td>
</tr>
<tr>
<td>SweetCor</td>
<td>Shell</td>
<td>5</td>
<td>121</td>
<td>0.2</td>
<td>–</td>
<td>170</td>
</tr>
<tr>
<td>Ohio</td>
<td>Ohio University</td>
<td>10</td>
<td>110</td>
<td>20</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
The product film formation rate was calculated as follows [157]:

\[ R_G = k_G \Delta c^{d_h} \]  

(47)

For the hydrogen electrode current density \( i_{H^+} \), the method proposed by Nordsveen et al. [150] was used. After the limit diffusion current density of oxygen was calculated, and according to current conservation, the anodic current density can be expressed as follows:

\[ i_{Fe} = i_{H^+} + i_{O2} \]  

(48)

The relationship between the corrosion rate and the anode current density is as follows [158]:

\[ CR = K_c \frac{i_{Fe}EW}{\rho} \]  

(49)

A comparison of the corrosion rates predicted by this model and measured results is illustrated in Figure 10. The accuracy of this model seems to be high, especially for cases with high SO2 concentration and RH. However, for cases with extremely low SO2 concentration, the accuracy of this model seems to be low. These results suggested that the effect of dissolved CO2 should be considered for conditions with low SO2 concentrations. For low-RH conditions, the results of this model were also not satisfactory.

Notwithstanding, this model only included the influence of SO2, O2, and H2O, while the impact of the other possible impurities (such as NOx and H2S) was not addressed. This model was also based on several assumptions, including the RDS and the cathodic processes of the corrosion. The corrosion product layer growth model was based on the FeCO3 layer growth model, which might be questionable. There seems to be a need to develop a more reliable mechanistic prediction model for steel corrosion in dense CO2 with multiple impurities. This task will not be easy, as researchers must find accurate mathematical descriptions for the physical and chemical processes in several different layers, which will strongly rely on experimental mechanistic studies of the dense CO2 corrosion.

Knowledge gaps for mechanistic model of corrosion in impure dense CO2

The following challenges still remain for establishing the mechanistic prediction model for general corrosion in impure dense CO2 environments:

(i) The bulk phase reaction mechanisms and kinetics with multiple impurities;
(ii) The phase equilibrium model considering all the possible impurities, to determine the amount of dissolved impurities in the condensed phase;
(iii) The water condensation mechanisms and kinetics, to determine the water layer thickness and water chemistry;
(iv) The ionisation equilibrium model of the dissolved species;
(v) The constitution of the anodic and cathodic reactions and their corresponding kinetics;
(vi) The formation mechanisms and kinetics of the product layers and their corresponding properties.
(vii) The mass transfer models in the dynamic bulk CO₂, aqueous phase and product layers.

Notably, all of the above discussion addresses general corrosion prediction, while the prediction of localised corrosion in both dense CO₂ and low partial pressure CO₂ is a huge challenge. Apart from the mechanistic models, semi-empirical and empirical models may be better choices until almost all the above fundamental questions are correctly solved. The neural network model created by Sim et al. [21] through applying the potentiodynamic polarisation data from the corrosion tests also seems to be a good approach.

Corrosion control strategies

Generally, if water is not thoroughly removed from the impure CO₂ streams, using CRAs, coatings, and inhibitors are the usual corrosion control measures for CCS CO₂ pipelines. Usually, the compact layer of FeCO₃ can have a favourable protection to the substrate metal, and Sim et al. [6] noted it as a potential source of corrosion protection for CO₂ transportation; however, the presence of acidic gases will definitely weaken the protectiveness of FeCO₃ layer, since it can be dissolved by the stronger acids. Stainless steels usually show excellent corrosion resistance, but due to their high costs, they are unlikely to be the best option for CO₂ pipeline transportation in a large scale. Barker et al. [67] pointed out that it is unlikely that CRAs will offer any significant benefit in terms of mitigating corrosion as the protective passive film will not be stable under the conditions in the aqueous phase due to the low pH.

The detailed material selection issue for supercritical CO₂ transport can be referred to the work by Paul et al. [159–161]. Appropriate steels suitable for CO₂ transportation for the CCS purposes need to be developed and selected based on laboratory testing and the evaluation of the application limits [33]. The other two corrosion control methods are discussed as follows:

Coatings

Coatings are thought to be among the most important corrosion control strategies. Morks et al. [50] indicated that the inhibition efficiency of Mn–Mg–Zn phosphate coatings was low when the pH was low. One of the coatings was selected by Zhang et al. [52] as a good candidate for internal coatings of the CO₂ pipeline when testing the performance of three polymer coatings in CO₂ containing impurities and possible solutions.

Recently, Paul [51] reported the use of a thermal spray CRA coating to mitigate the corrosion of carbon steel in an environment containing supercritical CO₂, H₂S, and an aqueous phase. Thermally sprayed CRA coatings were proposed as a cost-effective corrosion mitigation method for infrastructure that is likely to be in contact with wet supercritical CO₂ containing H₂S. However, they also stated that care must be taken to ensure that the thermally sprayed layer does not have any through porosity. Otherwise, such coatings with through porosity may accelerate corrosion of the underlying steel due to galvanic interactions.

However, Sim et al. [6] argued that internal pipeline coatings such as polymeric coatings are not feasible as anti-corrosion technology for long-distance dense CO₂ transportation, due to the high operating pressure and potentially accelerating corrosion in the presence of likely defects. It seems that such coating is not appropriate for CO₂ pipeline corrosion control.

Inhibitors

If dehydration is not applied to the CO₂ purification process, inhibitors can be selected to control the internal corrosion of the CO₂ pipeline, which is similar to the internal corrosion control strategy in oil and gas pipelines. Taking natural gas transportation as an example, wet gas transportation is usually adopted rather than dry gas transportation, even for some gas fields with high H₂S concentrations (e.g. Puguang Gas field in China and East Crossfield in Canada), due to the lower operational cost for wet gas transportation.

The performance of various inhibitors in CO₂-saturated aqueous phase has been studied for the oil and gas transportation purpose [3,162–171], and most of the tests were under low CO₂ partial pressure conditions. Imidazoline-based inhibitors are extensively used in oil and gas industry to mitigate CO₂ corrosion. When they are used in supercritical CO₂ phase, the performance of these inhibitors remains questionable and must be further verified. Therefore, corrosion inhibition practices employed in oil and gas fields must be carefully applied to CCS [6].

The performance of several inhibitors in a supercritical CO₂-saturated water environment was tested by Zhang et al. [49]; however, the performance of inhibitors in a water-saturated supercritical CO₂ environment has seldom been addressed. Morks et al. [50] tried a vanadate inhibitor for CCS CO₂ transportation, but the inhibition efficiency was almost nil when the pH was between 1 and 3, even in combination with Mn–Mg-zinc phosphate coating.

The challenge of using inhibitors in dense CO₂ is that it is hard to find an inhibitor to reduce the corrosion rate of steel in the presence of a number of acidic gas impurities, which can always induce extremely low pH in the condensates. The diffusion ability of an inhibitor in dense CO₂ is another issue to be considered. For CCS purpose, CO₂-soluble inhibitors or high diffusion rate of corrosion inhibitors in CO₂ is required [6]. They also have to be the water-soluble inhibitors, for they will eventually dissolve in the water film on the steel surface to inhibit corrosion in dense CO₂ phase.

Neutralising amines (pH stabilisation) is a potential option to mitigate corrosion caused by strong acids in systems where water condenses onto a steel surface, and choosing a proper amine always requires considering a number of properties, including boiling point, the effect of excess amine, the vapour–liquid equilibrium, the base strength and potential salt formation [67]. This technique can be rarely used with formation water systems for it has the drawback of leading to excessive scaling. The side effects of the chemicals used to inhibit corrosion on the environment must be also considered when selecting the chemicals.

It is still difficult to choose the best way to control the corrosion problems of impure CO₂ pipelines, though most of the existing CO₂ projects choose controlling the water content as solving method, while they always transport CO₂ from the natural sources with less acidic gas impurities rather than the anthropogenic CO₂.
**Research prospects**

The summarised influential parameters of supercritical CO₂ corrosion are illustrated in Figure 11. Overall, studies related to the corrosion of pipeline steel in dense CO₂ transportation systems remain relatively limited, and more investigations are required to improve the understanding of corrosion mechanisms. A number of influential parameters with great impact on the corrosion process require further and deeper studies. The urgent topics to be investigated include the following:

(i) The impact of flow dynamics, amines, sulphur, and solids. The flow dynamics have a significant influence on the mass transfer process and product scales. Solids may not exist in the CO₂ pipeline, but the corrosion product scales falling off from the inner wall of the pipeline by the mechanical force might act as solids, and their corrosion–erosion effect should be considered. The influence of possible hydrates on the corrosion also requires further evaluation. The impact of the amines and their degradation products, such as formate and acetate, needs to be reconsidered in supercritical CO₂ systems. The influence of sulphur on corrosion in the supercritical CO₂ environment also needs to be evaluated. The impact of H₂O and O₂ on the corrosion rate should be re-evaluated, since there are opposite conclusions in the open literature.

(ii) More online research methods are also desirable to investigate the intermediate steps of the corrosion process. Using electrochemical techniques in the dense CO₂ phase, aqueous phase, and under ambient pressure conditions might be valuable and useful for the investigation of mechanisms, especially for the cathodic processes. The composition of product scales under multiple acidic gas impurity conditions and the mechanical property studies of corrosion product scales. *In situ* observation tools can be applied to observe the evolution process of product scales, to obtain the real surface morphology excluding the influence of environmental change (when bringing the specimens from a high-pressure to a normal-pressure environment).

(iii) The synergistic corrosion mechanism of steel under supercritical CO₂ with multiple acidic gas impurities (SO₂, NOₓ, H₂S, and HCl). The synergistic corrosion mechanism is complicated by these acidic gases and needs systematic investigation. The cathodic process of the corrosion is not clear, especially for conditions with various impurities. The cross chemical reaction mechanisms of impurities also need to be examined. These are all crucial for establishing a mechanistic prediction model with high accuracy. Localised corrosion, HIC and SCC mechanisms of CO₂ pipeline steel and the prevention methods and corresponding standards under supercritical CO₂ environments also need to be addressed and formulated.

(iv) The establishment of mechanistic prediction model for steel corrosion in dense CO₂ phase with various acidic gas impurities. There are many CO₂ corrosion prediction models, but they are not accurate for predicting corrosion in dense CO₂ phase with thin water films. The defects of the SIWDES model should be overcome, including the consideration of more impurities, dissolution, and ionisation equilibrium models, anodic and cathodic reaction mechanisms and kinetics, a mass transfer model and the kinetics of the product layer formation, etc. The setting up of mathematical mechanistic model for uniform corrosion prediction that can reflect the effects of the primary variables with high accuracy is challenging in dense CO₂ environment with various impurities.

(v) Research on anti-corrosion measures for CO₂ pipeline transportation with multiple acidic gas impurities: inhibitors and new CRAs are needed for the transportation of CO₂ with multiple acidic gas impurities. The inhibitors with high corrosion inhibition efficiency in the dense CO₂ phase are needed, including the selection of the existing inhibitors or the synthesis of new inhibitors. The diffusion behaviours of potential inhibitor candidates in the dense CO₂ phase need to be addressed.
Using the existing CRAs seems to be not economically feasible, and there is an urgent need for developing the new CRAs with low cost and excellent corrosion resistance under low pH condition for CCS. The role of alloying elements needs to be determined to find the optimised steel compositions to satisfy the corrosion resistance, strength, properties, and weldability targets required for the transportation of dense CO$_2$ with various acidic gas impurities.

**Conclusions**

Steel corrosion in dense CO$_2$ phase is affected by various factors, including physical, environmental, and metallurgical variables. Based on the experimental results in the open literature, this paper systematically analyses the influential parameters and their impact mechanisms on pipeline steel corrosion in dense CO$_2$ phase with impurities. The mathematical models are also reviewed and highlighted. Several conclusions can be drawn:

(i) The effects of impurities, pressure, temperature, flow, exposure time, product layers, and steel chemistry are reviewed. Neglected influential parameters by the current researchers have been highlighted, including the impact of flow dynamics as well as various amines, sulphur, and solids. Further research prospects for pipeline steel corrosion in dense CO$_2$ phase with multiple acidic gas impurities are also suggested to further understand the corrosion mechanisms and establish mechanistic corrosion prediction models, such as synergistic corrosion mechanisms, compositions and properties of product layers, and corrosion control strategies.

(ii) The knowledge gaps regarding a dense CO$_2$ corrosion prediction model include bulk phase reaction mechanisms, a phase equilibrium model for impurities, water condensation mechanisms and kinetics, anodic and cathodic reaction mechanisms and kinetics, kinetics of product layer formation, and mass transfer models.

(iii) New CRAs with high corrosion resistance and inhibitors with high inhibition efficiency are needed for the transportation of CO$_2$ with multiple acidic gas impurities, though it seems to be difficult to find an effective inhibitor that works well under dense CO$_2$ and low pH conditions. pH stabilisation is a potential option to mitigate corrosion caused by strong acidic gases in dense CO$_2$.

(iv) It is still difficult to select the best ways to control corrosion in dense CO$_2$ transportation for large scale CCS among options such as controlling the water content, eliminating acidic gas impurities, employing inhibitors and coatings, and using CRAs. The understanding, prediction, and control strategies for supercritical CO$_2$ corrosion still remain key challenges in meeting the safety requirements of CO$_2$ transportation for CCS purpose at a large scale.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work was financially supported by National Natural Science Foundation of China (Grant No. 51604289), Beijing Natural Science Foundation (Grant No. 2172048), Science Foundation of China University of Petroleum, Beijing (Grant Nos. 2462014JRC043 and 2462015YQ0402), and Open Foundation of China State Key Lab of Power Systems (Grant No. SKL16KZ10).

**References**


[61] Zhao X. Overview of CCUS corrosion control technologies and discussion on the problems. 2nd Corrosion and Protection Technologies of Petroleum and Petrochemistry Conference of China, Pengshan, China; 2016.


[99] Pessu F, Barker R, Neville A. Early stages of pitting corrosion of UNS K03014 carbon steel in sour corrosion environments: the influence of CO₂, H₂S and temperature. CORROSION/2015, Dallas, TX, USA, 2015, NACE International.


[110] Chen C. Research on electrochemical behavior and corrosion scale characteristics of CO₂ corrosion for tubing and casing steel [PhD thesis]. Xi’an: Northwestern Polytechnical University; 2002.


[124] Alowitz MJ, Scherer MM. Kinetics of nitrate, nitrite, and Cr(VI) hydrolysis of elemental sulfur in natural gas pipelines. First International Conference on the


[140] Alowitz MJ, Scherer MM. Kinetics of nitrate, nitrite, and Cr(VI) hydrolysis of elemental sulfur in natural gas pipelines. First International Conference on the


### Table A1. Summary of the test conditions for steel corrosion in dense CO2 with impurities

<table>
<thead>
<tr>
<th>Year</th>
<th>Researchers</th>
<th>Materials</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>Time (h)</th>
<th>Impurities</th>
<th>Flow (rev min⁻¹)</th>
<th>General corrosion rate (mm/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1975</td>
<td>Schremp and Roberson [10]</td>
<td>X60, A51 4140</td>
<td>276, 295</td>
<td>13.8</td>
<td>1008</td>
<td>H2O: 800–1000 ppm</td>
<td>Loop</td>
<td>Less than 5.08 × 10⁻⁴</td>
</tr>
<tr>
<td>1975</td>
<td>Russick et al. [127]</td>
<td>304 LSS, 306 SS, C1018</td>
<td>323</td>
<td>24.138</td>
<td>24</td>
<td>H2O: 800–1000 ppm</td>
<td>Static</td>
<td>Weight change: −1.06 to +0.77 μg cm⁻²</td>
</tr>
<tr>
<td>1975</td>
<td>Propp et al. [12]</td>
<td>Iron</td>
<td>304 SS, 316 SS</td>
<td>473</td>
<td>3.3–16.5</td>
<td>Methanol: 10 wt-%</td>
<td>Loop</td>
<td>2.54 × 10⁻⁵</td>
</tr>
<tr>
<td>2009</td>
<td>Thodla et al. [80]</td>
<td>CS</td>
<td>304 SS</td>
<td>297</td>
<td>8.2</td>
<td>H2O: 1 wt-%</td>
<td>Static</td>
<td>About 0.01–2</td>
</tr>
<tr>
<td>2009</td>
<td>Choi and Nesić [25, 172]</td>
<td>X65</td>
<td>323</td>
<td>8.0</td>
<td>24–120</td>
<td>H2O: saturated SO₂: 1 vol.-%</td>
<td>Static</td>
<td>Up to 7</td>
</tr>
<tr>
<td>2011</td>
<td>Dugstad et al. [27]</td>
<td>X65</td>
<td>323</td>
<td>8.0</td>
<td>24, 120</td>
<td>H2O: 650–3000 ppmv</td>
<td>Rotating autoclave: 3 rev min⁻¹</td>
<td>Up to 1.6</td>
</tr>
<tr>
<td>2011</td>
<td>Choi [174]</td>
<td>X65</td>
<td>298</td>
<td>10</td>
<td>3–20 days</td>
<td>H2O: saturated</td>
<td>Static</td>
<td>0.19–0.88, 0.34–1.35</td>
</tr>
<tr>
<td>2011</td>
<td>Zhang et al. [48]</td>
<td>X70</td>
<td>323</td>
<td>10</td>
<td>288</td>
<td>H2O: saturated</td>
<td>Static</td>
<td>0.005–1.46</td>
</tr>
<tr>
<td>2012</td>
<td>Paschke and Kather [90]</td>
<td>X12Cr13 X5CrNiCuNb16-4 L360NB L485MB</td>
<td>333, 423</td>
<td>11</td>
<td>168</td>
<td>H2O: 0–1000 ppmv</td>
<td>Static</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>2012</td>
<td>Ruhl and Kranzmann [37]</td>
<td>X42</td>
<td>333</td>
<td>10</td>
<td>120</td>
<td>H2O: 0.5–1 mL</td>
<td>Static</td>
<td>Weight loss &lt; 500 mg</td>
</tr>
<tr>
<td>2012</td>
<td>Xiang et al. [46]</td>
<td>X70</td>
<td>323</td>
<td>10</td>
<td>120</td>
<td>H2O: 0.5–1 mL</td>
<td>Static</td>
<td>0.005–1.46</td>
</tr>
</tbody>
</table>

(Continued)
<table>
<thead>
<tr>
<th>Year</th>
<th>Researchers</th>
<th>Materials</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
<th>Time (h)</th>
<th>Impurities</th>
<th>Flow (rev min(^{-1}))</th>
<th>General corrosion rate (mm/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>Collier et al. [26]</td>
<td>304L, 316L, X42, X60</td>
<td>307–322</td>
<td>9.48–10.3</td>
<td>110–120</td>
<td>H(_2)O: 0.17–3.0 g</td>
<td>100</td>
<td>&lt;4 mpy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO(_2): 2 vol.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O(_2): 1000 ppmv</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_2)O: 10–100 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O(_2): 3 vol.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_2)O: 650 ppmv</td>
<td>1000</td>
<td>Up to 3.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO(_2): 0.08, 0.04 bar</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Farelas et al. [88,120]</td>
<td>X65</td>
<td>298, 323</td>
<td>8</td>
<td>24</td>
<td>Nitric acid (65 wt-%): 22.7 µL</td>
<td>Static</td>
<td>Weight increase &lt; 5 mg</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_2)O: 10 g L(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NaCl: 1 g L(^{-1})</td>
<td></td>
<td>Mass loss: 1.63–2.40 mg</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Na(_2)SO(_4): 1–3 g L(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>NaNO(_3): 1–3 g L(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>HNO(_3): 1 g L(^{-1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pH 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ruhl and Kranzmann [175]</td>
<td>X42</td>
<td>333</td>
<td>10</td>
<td>Up to 240</td>
<td>H(_2)O: 10 g L(^{-1})</td>
<td>Static</td>
<td>Mass loss: 1.63–2.40 mg</td>
</tr>
<tr>
<td></td>
<td>Sim et al. [40]</td>
<td>CS</td>
<td>323</td>
<td>7.6</td>
<td>168</td>
<td>H(_2)O: 10 g L(^{-1})</td>
<td>Static</td>
<td>Mass loss: 1.63–2.40 mg</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO(_2): 0.17–3.0 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O(_2): 1000 ppmv</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_2)O: 10–100 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O(_2): 3 vol.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_2)O: 650 ppmv</td>
<td>1000</td>
<td>Up to 3.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO(_2): 0.08, 0.04 bar</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xiang et al. [43]</td>
<td>X70</td>
<td>298–366</td>
<td>10</td>
<td>120</td>
<td>H(_2)O: 5.0 g</td>
<td>120</td>
<td>1.10–3.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO(_2): 2 vol.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O(_2): 0.02 mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xiang et al. [15]</td>
<td>X70</td>
<td>323</td>
<td>10</td>
<td>24–192</td>
<td>H(_2)O: 15 g</td>
<td>120</td>
<td>0.73–1.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO(_2): 2.5 vol.%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(_2)O: 70 g</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Xiang et al. [44]</td>
<td>X70, Iron</td>
<td>323</td>
<td>12</td>
<td>454</td>
<td>Loop</td>
<td>Up to 0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Yevtushenko et al. [121]</td>
<td>Alloy 31, L360 NB, Iron</td>
<td>333</td>
<td>10</td>
<td>168</td>
<td>Loop</td>
<td>Up to 0.03</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>Hua et al. [28]</td>
<td>X65</td>
<td>308, 323</td>
<td>8</td>
<td>14–48</td>
<td>H(_2)O: 300–34 000 ppm</td>
<td>Static</td>
<td>Mass loss: 2.07–5.47 mg</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO(_2): 70 ppmv</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>Sim et al. [39]</td>
<td>CS</td>
<td>313</td>
<td>8</td>
<td>168</td>
<td>H(_2)O: 50–100 000 ppm</td>
<td>Static</td>
<td>Mass loss: 2.07–5.47 mg</td>
</tr>
<tr>
<td>2014</td>
<td>V. Yevtushenko and Baßler [79]</td>
<td>X52</td>
<td>333</td>
<td>10</td>
<td>7, 30, and 186 days</td>
<td>Loop</td>
<td>Mass loss: 2.07–5.47 mg</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>Brown et al. [62]</td>
<td>X65</td>
<td>277, 323</td>
<td>10</td>
<td>168</td>
<td>H(_2)O: 300 ppmv</td>
<td>Rotating autoclave: 3 rpm</td>
<td>Up to 0.275</td>
</tr>
<tr>
<td>2014</td>
<td>Patchigolla et al. [119]</td>
<td>X60</td>
<td>308</td>
<td>9.5</td>
<td>50–1100</td>
<td>H(_2)O: 300 ppmv</td>
<td>Rotating autoclave: 3 rev min(^{-1})</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>2015</td>
<td>Zeng et al. [103]</td>
<td>X42, X60, X80, and X100</td>
<td>308, 318</td>
<td>5.86–10.34</td>
<td>120</td>
<td>H(_2)O: saturated</td>
<td>0–500</td>
<td>0–0.163</td>
</tr>
<tr>
<td>2015</td>
<td>Jiang et al. [34]</td>
<td>X65</td>
<td>298, 308</td>
<td>8</td>
<td>3, 14 days</td>
<td>H(_2)O: 100 ppmv</td>
<td>Static</td>
<td>Mass loss: 2.07–5.47 mg</td>
</tr>
<tr>
<td>2015</td>
<td>Choi et al. [24]</td>
<td>CS, 1Cr, 3Cr</td>
<td>298, 353</td>
<td>8–12</td>
<td>48</td>
<td>H(_2)O: saturated, 100 ppmv</td>
<td>Static</td>
<td>Mass loss: 2.07–5.47 mg</td>
</tr>
<tr>
<td>2015</td>
<td>Hua et al. [29]</td>
<td>X65</td>
<td>323</td>
<td>8</td>
<td>14–48</td>
<td>H(_2)O: 50, 500 ppmv</td>
<td>Rotating autoclave: 3 rpm</td>
<td>Up to 0.275</td>
</tr>
<tr>
<td>2015</td>
<td>Hua et al. [13]</td>
<td>X65</td>
<td>308</td>
<td>8</td>
<td>14–168</td>
<td>H(_2)O: 300 ppmv</td>
<td>Rotating autoclave: 3 rev min(^{-1})</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>2015</td>
<td>Hua et al. [32, 176]</td>
<td>X65</td>
<td>308</td>
<td>8</td>
<td>48</td>
<td>H(_2)O: 300 ppmv</td>
<td>Rotating autoclave: 3 rev min(^{-1})</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Year</td>
<td>Authors</td>
<td>Material</td>
<td>Temperature</td>
<td>Humidity</td>
<td>Water (g)</td>
<td>Acid (ppmv)</td>
<td>Oxygen (ppmv)</td>
<td>Other (ppmv)</td>
</tr>
<tr>
<td>-------</td>
<td>------------------</td>
<td>----------</td>
<td>-------------</td>
<td>----------</td>
<td>-----------</td>
<td>-------------</td>
<td>---------------</td>
<td>--------------</td>
</tr>
<tr>
<td>2015</td>
<td>Hua et al. [30]</td>
<td>X65</td>
<td>308</td>
<td>8</td>
<td>48</td>
<td>H₂O: saturated</td>
<td>SO₂: 0–100 ppm mol</td>
<td>O₂: 0, 20 ppm mol</td>
</tr>
<tr>
<td>2015</td>
<td>Hua et al. [31]</td>
<td>X65</td>
<td>308</td>
<td>8</td>
<td>48</td>
<td>H₂O: 0–34 000 ppm</td>
<td>SO₂: 0–100 ppm mol</td>
<td>O₂: 0, 20 ppm mol</td>
</tr>
<tr>
<td>2016</td>
<td>Sun et al. [41]</td>
<td>X65</td>
<td>323</td>
<td>10</td>
<td>240</td>
<td>H₂O: 10 g</td>
<td>SO₂: 1000 ppmv</td>
<td>O₂: 1000 ppmv</td>
</tr>
<tr>
<td>2016</td>
<td>Sun et al. [16]</td>
<td>X65</td>
<td>323</td>
<td>10</td>
<td>120</td>
<td>H₂O: saturated</td>
<td>SO₂: 1000 ppmv</td>
<td>O₂: 1000 ppmv</td>
</tr>
<tr>
<td>2016</td>
<td>Sun et al. [91]</td>
<td>X65</td>
<td>323</td>
<td>10</td>
<td>24, 120</td>
<td>O₆, SO₆, H₂S, and NO₂: 1000 ppmv</td>
<td>H₂O: saturated</td>
<td>Static</td>
</tr>
<tr>
<td>2016</td>
<td>Wei et al. [102]</td>
<td>P110, 3Cr, 316L</td>
<td>353</td>
<td>10</td>
<td>240</td>
<td>H₂O: saturated</td>
<td>SO₂: 2.0 vol-%</td>
<td>O₂: 1.0 vol-%</td>
</tr>
<tr>
<td>2016</td>
<td>Wei et al. [42]</td>
<td>X65</td>
<td>353</td>
<td>10</td>
<td>240</td>
<td>H₂O: saturated</td>
<td>H₂S: 30 ppm</td>
<td>1 m s⁻¹</td>
</tr>
<tr>
<td>2016</td>
<td>Xu et al. [47]</td>
<td>X70</td>
<td>323</td>
<td>10</td>
<td>72</td>
<td>H₂O: RH 45–100%</td>
<td>SO₂: 2.0 vol-%</td>
<td>O₂: 1.0 vol-%</td>
</tr>
<tr>
<td>2016</td>
<td>Xu et al. [113]</td>
<td>X60, X65, X70, X80</td>
<td>323</td>
<td>8–12</td>
<td>72</td>
<td>H₂O: 1600–3000 ppmv</td>
<td>SO₂: 3000 ppmv</td>
<td>O₂: 1000 ppmv</td>
</tr>
<tr>
<td>2017</td>
<td>Xu et al. [105]</td>
<td>X70</td>
<td>323</td>
<td>10</td>
<td>72</td>
<td>H₂O: RH 45–100%</td>
<td>SO₂: 2.0 vol-%</td>
<td>O₂: 1.0 vol-%</td>
</tr>
<tr>
<td>2017</td>
<td>Tang et al. [86]</td>
<td>X65</td>
<td>323</td>
<td>8</td>
<td>96</td>
<td>H₂O: 100 mL</td>
<td>O₂: 0–475 mg L⁻¹</td>
<td>Static</td>
</tr>
</tbody>
</table>