Study on Acid Corrosion Characteristics in Low-Pressure Stage Initial Condensation Zone of Supercritical H$_2$O/CO$_2$ Turbine

Zi-yue Ma, Xiao-fang Wang*, Tao Jiang, Wei Wang, Yang Xu
School of Energy and Power Engineering, Dalian University of Technology, Dalian 116024, China

Email: dlwxf@dlut.edu.cn

Abstract. Compared with the traditional steam turbine, the supercritical H$_2$O/CO$_2$ turbine has a relatively high CO$_2$ content in the working fluid. In the initial condensation zone, CO$_2$ dissolves in the condensed water to form carbonic acid, which intensifies the corrosion of blade. In order to study the acid corrosion characteristics in the initial condensation zone of supercritical H$_2$O/CO$_2$ turbine, the acid corrosion rate of the blades in the initial condensation zone of supercritical H$_2$O/CO$_2$ turbine was calculated and analyzed based on the numerical model of non-equilibrium condensation flow and a numerical model of CO$_2$ corrosion reaction. The results show that the temperature, pressure, proportion of CO$_2$ in the gas phase and thickness of the solution on blade surface are the main factors affecting the acid corrosion rate in the initial condensation zone of the turbine. The influence of temperature and pressure is more significant. Overall, the acid corrosion rate decreases stage by stage.

1. Introduction

Coal plays an important role in China’s energy structure. However, the process of using coal causes nonnegligible waste and inevitable pollution. Therefore, in order to build a resource-conserving and environment-friendly society, China has adopted Clean Coal Technology as a main focus of the energy development strategy in the 21st century. The National Key Research and Development Project, Integrated Investigation on Supercritical Water Gasification of Coal for Hydrogen Production and Thermal Power Generation with H$_2$O/CO$_2$ Mixtures, proposed a new technology for clean coal utilization. Supercritical H$_2$O/CO$_2$ steam turbine is the key equipment of this technology to achieve thermal power conversion. The supercritical H$_2$O/CO$_2$ steam turbine has a relatively high CO$_2$ content in its working fluid (CO$_2$ accounts for about 10-12% in the main steam), much higher than the content of CO$_2$ in the working fluid of traditional steam turbines. In the initial condensation zone, CO$_2$ will dissolve in condensed water to form carbonic acid, which shows strong corrosiveness. This scenario is harmful to turbine blade and will reduce aerodynamic performance, safety, and reliability. In order to provide a design basis for supercritical H$_2$O/CO$_2$ steam turbines, it is necessary to investigate the corrosion characteristic of CO$_2$ in the initial condensation zone of supercritical H$_2$O/CO$_2$ steam turbines.

Many researchers have investigated the mechanism and influencing factors of CO$_2$ corrosion. For example, Tanupabrungsun[1] proposed a mechanism for the CO$_2$ corrosion of which the temperatures ranging from 25°C to 250°C. Nordsyen et al.[2] studied the chemical reactions and mass transfer in
CO₂ corrosion process. Main influencing factors of CO₂ corrosion are pH, temperature, partial pressure of CO₂ and flow rate. Nordsveen et al.[2] found the corrosion rate decreases with the increase of pH. Many research[3-8] suggested that the CO₂ corrosion rate shows different characteristics in different range of temperature. Choi et al.[9] calculated the interaction of the pressure on the solubility of CO₂. Wei Liang[8] investigated the effect of flow on the corrosion rate.

Although the current research on CO₂ corrosion is relatively complete, working condition in the supercritical H₂O/CO₂ steam turbine is complex. The corrosion environment is different with most condition(due to the relative motion between blade and working fluid, changing high temperature and high pressure and stress on the blade). Therefore, it is significant to investigate the characteristics of CO₂ corrosion in the turbine internal environment.

2. Corrosion process in supercritical H₂O/CO₂ steam turbines initial condensation zone

2.1. An application of the CO₂ corrosion mechanism in the low-pressure stage initial condensation zone of steam turbines

The corrosion phenomenon of CO₂ to metal materials occurs in the initial condensation zone. The reason is that the steam starts to condense into droplets due to temperature and pressure factors as the working fluid flows, and the CO₂ dissolving in condensed water to form carbonic acid. Specifically, CO₂ dissolves in condensed water on turbine blades, then forms carbonic acid that corrodes the blades. From the electrochemical perspective, the corrosion reaction on the blade includes two half-reactions, including the oxidation reaction of iron at the anode and the reduction reaction of H⁺, H₂CO₃, HCO₃⁻ and H₂O. This reactions are summarized in Table 1.

**Table 1.** Electrochemical reactions of carbon dioxide corrosion.

| Reaction Name                | Reaction Formula                      |
|------------------------------|---------------------------------------|
| H⁺ reduction reaction        | 2H⁺(aq) + 2e⁻ → H₂(g)                  |
| Cathodic Reaction H₂CO₃ reduction reaction | 2H₂CO₃(aq) + 2e⁻ → 2HCO₃⁻(aq) + H₂(g) |
| HCO₃⁻ reduction reaction    | 2HCO₃⁻(aq) + 2e⁻ → CO₂(g) + H₂(g)     |
| H₂O reduction reaction      | 2H₂O(l) + 2e⁻ → 2OH⁻(aq) + H₂(g)      |

2.2. Main factors of CO₂ corrosion in supercritical H₂O/CO₂ steam turbines

The internal environment of turbines is extremely complex. In order to build a simple and effective corrosion model, it is necessary to determine the main factors of CO₂ corrosion in turbines.

2.2.1. pH. The pH of condensed water in turbines depends on the dissolved CO₂ amount and temperature. Therefore, the effect of pH is essentially the effect of the partial pressure of CO₂ and temperature of condensed water.

2.2.2. Temperature. The temperature on CO₂ corrosion rate is another central factor as shown in previous works [1,3-6,11-12]. It is effected by two fundamental factors. On one hand, the corrosion rate increases with temperature due to the kinetic rate of electrochemical reactions being accelerated by temperature. On the other hand, the protective FeCO₃ forms on the steel surface with increasing temperature and the FeCO₃ will slow down both anodic and cathodic reactions. As a result, under the interaction of these two phenomena, the CO₂ corrosion rate reaches peak value when the temperature is ranging from 60 °C to 90 °C. However, its effect can be negligible as the temperature decreases further. Therefore, when temperature is relatively low, the corrosion rate is mainly effected by the reactant activity, will gradually decrease.

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2.2.3. Partial pressure of CO$_2$. The effect of CO$_2$ partial pressure on the rate of carbon dioxide acid corrosion is mainly reflected in the solubility of CO$_2$ and the concentration of reactant in solution. In a steam turbine, the partial pressure of CO$_2$ decreases as the working fluid flows. However, the condensation of steam will increase the proportion of CO$_2$ in working fluid.

2.2.4. Flow rate. The flow rate mainly affects the corrosion rate by affecting the formation of the corrosion product film on the metal surface. Notably, the flow rate of working fluid in the steam turbine is much higher than most existing corrosion studies[9] and the working blade surface of steam turbines will be subject to great stress, so it is difficult to form a protective corrosion film on the blade surface. In this paper, the effect of corrosion products on corrosion rate is ignored. The effect of flow rate is reflected in the effect of mass transfer.

3. Numerical analysis of two-phase non-equilibrium condensation of wet steam in supercritical H$_2$O/CO$_2$ steam turbines initial condensation zone

In this study, the steady and viscous three-dimensional numerical simulation for a 5MW supercritical H$_2$O/CO$_2$ steam turbine initial condensation zone is carried out using the commercial software CFX. The Turbogrid is utilized to generate the mesh of stators and rotors. The geometry of blades is built based on one-dimensional design results. The SST turbulence model is used and a no-slip wall boundary condition is applied for the solid wall. The stage interface is set between stators and rotors. In order to simplify calculations, the steam based on IAPWS-IF97 is used as the working fluid. The total pressure of 200kPa and total temperature of 418 K are specified at the inlet of the domain and the static pressure of 5kPa is defined as outlet boundary condition with a rotating speed of 5000rpm. The distribution of thermal parameters is shown in Figure.1-3.

The pressure, velocity, and temperature at the surface of blades are obtained according to the calculation results, and these parameters will be used to calculate the CO$_2$ corrosion rate. The condensed water appears at the trailing edge of the second stage stator (as shown in Figure.4). Therefore, the parameters are collected after the second stage stator. The pressure, fluid velocity and condensed water temperature are collected at 10%, 50% and 90% heights of blades after the second stage stator for corrosion rate calculations.

![Figure 1](image1.png)

(a) 0.1 blade height  (b) 0.5 blade height  (c) 0.9 blade height

**Figure 1.** Speed distribution in blade-to-blade view

![Figure 2](image2.png)

**Figure 2.** Liquid temperature distribution on blade surface

![Figure 3](image3.png)

**Figure 3.** Pressure distribution on blade surface

blade surface
4. Numerical analysis of CO₂ Corrosion in supercritical H₂O/CO₂ steam turbines initial condensation zone

4.1. CO₂ Corrosion model in Supercritical H₂O/CO₂ steam turbines initial condensation zone

In this study, the CO₂ corrosion rate is calculated using the Corrosion Module from the commercial software Comsol Multiphysics. An one-dimensional acid corrosion model is used as shown in Fig.4. The thickness of the boundary layer depends on the Reynolds number. The diffusion and turbulent sublayers vary and are accounted for with the mass transfer parameters. All species are assumed to be diluted in water and the mass transfer is modeled by diffusion. CO₂ hydration, water dissociation, thress reduction reactions, and iron dissolution are accounted fro, resulting in seven species in the model. The species and diffusion coefficients are tabulated in Table.2.

![Figure 4. Droplet number distribution on blade surface](image)

**Figure 4.** Droplet number distribution on blade surface

![Figure 5. Description of the boundary layer adjacent to the steel surface](image)

**Figure 5.** Description of the boundary layer adjacent to the steel surface

The turbulent sublayer is modeled by adding a turbulent diffusivity term to the diffusion coefficient. The term depends on the flow rate, viscosity, density of the liquid, and distance from the steel surface[2].

The electrode surface boundary feature is used to calculate the corrosion potential at the blade surface using the mixed potential theory. The total current of all electrochemical reactions is set to 0, which leads to the following equation:

\[
\sum_{j} i_j = 0, \tag{1}
\]

where \(i_j\) (SI unit: A/m²) is the current density of \(j\) number of electrochemical reactions. The initial value is set to -0.5V around the free corrosion potential[10]. The outer point of the boundary layer is set to the bulk concentrations of the species. Fluxes of species converted in the electrochemical reactions are applied on the blade surface as \(i_j/F\) (Faraday’s constant = 96485 C/mol).

**Table 2.** Modeled species with their respective diffusion coefficients

| Species               | Diffusion Coefficient |
|-----------------------|-----------------------|
| CO₂                   |                       |
| H₂O                   |                       |
| H₂                    |                       |
| O₂                    |                       |
| H₃O⁺                  |                       |
| CO₃²⁻                 |                       |
| H⁺                    |                       |
| OH⁻                   |                       |

...
| Species     | Diffusion Coefficient D(m²/s) × 10⁹ |
|------------|-----------------------------------|
| CO₂        | 1.96                              |
| H₂CO₃      | 2.00                              |
| HCO₃⁻      | 1.11                              |
| CO₂⁺       | 0.92                              |
| H⁺         | 9.31                              |
| OH⁻        | 5.26                              |
| Fe⁺        | 0.72                              |

Except for the physical quantities calculated by CFD, some parameters involved in the reactions also need to be obtained from theoretical or empirical formulas.

The concentration of CO₂ in condensed water is calculated by Henry’s Law. The Henry constant of CO₂ at different temperatures is estimated by the following formula:

\[
K_{CO₂} = 0.0454 \times [1.6616 - 5.736 \times 10^{-5} \times (T - 273) + 1.031 \times 10^{-3} \times (T - 273)^{2} - 9.68 \times 10^{-6} \times (T - 273)^{3} + 4.471 \times 10^{-8} \times (T - 273)^{4} - 7.912 \times 10^{-11} \times (T - 273)^{5}] \tag{2}
\]

The ionization equilibrium constant of water is:

\[
K_{H₂O}^{+} = 10^{-7.93 \times 10^{-4}} \times (2.9368 - 0.0737549 \times T + 7.47881 \times 10^{-3} \times T^2) \tag{3}
\]

The first ionization constant of H₂CO₃ is:

\[
K_{H₂CO₃}^{+} = 387.6 \times 10^{-2} \times (6.41 \times 10^{-2}T + 8.52 \times 10^{-6}T^2 - 3.07 \times 10^{-8}T - 0.4727 + 0.118T) \tag{4}
\]

The ionization equilibrium constant of HCO₃⁻ is:

\[
K_{HCO₃⁻} = 10^{-10.61 - 4.97 \times 10^{-3}T + 1.331 \times 10^{-5}T^2 - 2.624 \times 10^{-7}T + 1.166 \times 10^{-10} - 0.3466 \times I}, \tag{5}
\]

where \(T_F\) (°F) is Fahrenheit temperature, and \(I\) (mol/L) is ionic strength. \(I\) is set to 0.185mol/L in this study.

According to Henry's Law, the concentration of dissolved CO₂ in the solution is:

\[
c_{CO₂} = K_{CO₂} \times \rho_{CO₂}, \tag{6}
\]

and the concentration of H₂CO₃ can be calculated by:

\[
c_{H₂CO₃} = K_{CO₂} \times c_{CO₂}, \tag{7}
\]

where \(K_{CO₂}\) is the equilibrium constant of CO₂ hydration.

Steam is condensed into droplets as the working fluid flows, which makes the volume fraction and the partial pressure of CO₂ increase. In this study, the volume changing laws of CO₂ and steam under the effect of temperature and pressure are assumed to be the same. According to the dryness of each stage obtained from the one-dimensional design results, the proportion of steam reduction in gas phase is calculated to obtain the new volume fraction and partial pressure of CO₂. The dryness after each stage is listed in Table 3. The concentration of other substances can be calculated based on the concentration of H₂CO₃ and the equilibrium constant of each reaction.

The expression of electrode kinetics to control the progress of the reaction is:
\[ i_{\text{loc}} = i_0 \times 10^{\eta/A}, \]  
(8)

where \( i_{\text{loc}} \) (SI unit: A/m\(^2\)) is the local current density, \( i_0 \) (SI unit: A/m\(^2\)) is the initial current density. \( \eta \) (SI unit: V) is overpotential, which characterizes the difference between the disequilibrium potential and the equilibrium potential of this electrode reaction. \( A_\text{a} \) (SI unit: V) is the Tafel slope of the electrode reaction that characterizes the effect of current density on overpotential.

After consulting the literature, the Tafel slope of each substances involved in electron transfer are taken as follows:

\[ A_\text{Fe} = 0.04 \text{ V}, \text{A}_\text{H}_2\text{O} = 0.118 \text{ V}, \text{A}_\text{H}_2\text{CO}_3 = 0.12 \text{ V}, \text{A}_\text{H}_2 = 0.118 \text{ V}.\]

The equilibrium potential is necessary for overpotential calculation. The potential of each reduction reaction can be calculated by the Nernst equation:

\[ E_{\text{rev}} = 2.303 \frac{RT}{nF} \cdot \lg c_i, \]
(9)

where \( R \) is the standard gas constant, \( n \) is number of reaction transfer electrons, and \( F \) is Faraday’s constant. For the reduction reactions involved in this study, \( H^+ \) gets electron to generate \( H_2 \), so the \( c_i \) is just the concentration of \( H^+ \). Therefore, the Nernst equation can be written as:

\[ E_{\text{rev}} = -2.303 \frac{RT}{F} \cdot \text{pH} \]
(10)

Furthermore, the initial current density needs to be converted from the reference current density in standard state. The initial current density of each substance involved in the electron transfer is calculated by:

\[ i_{\text{0}\text{H}_2\text{O}} = i_{\text{refH}_2\text{O}} \cdot \frac{[300-1.107(\text{mol})]}{R \cdot \{1 - \frac{1}{T_{\text{refH}_2\text{O}}}\}} \]
(11)

\[ i_{\text{0}\text{H}_2\text{CO}_3} = i_{\text{refH}_2\text{CO}_3} \cdot \frac{c_\text{H}}{c_{\text{HHeFFH}_2\text{CO}_3}} \left( \frac{c_{\text{H}_2\text{CO}_3}}{c_{\text{H}_2\text{CO}_3,\text{refH}_2\text{CO}_3}} \right)^{a_{\text{H}_2\text{CO}_3}} \cdot \frac{[300-1.107(\text{mol})]}{R \cdot \{1 - \frac{1}{T_{\text{refH}_2\text{CO}_3}}\}} \]
(12)

\[ i_{\text{0}\text{H}_2} = i_{\text{refH}_2} \cdot \frac{c_\text{H}}{c_{\text{HHeFFH}_2}} \left( \frac{c_{\text{H}_2}}{c_{\text{H}_2,\text{refH}_2}} \right)^{a_{\text{H}_2}} \cdot \frac{[300-1.107(\text{mol})]}{R \cdot \{1 - \frac{1}{T_{\text{refH}_2}}\}} \]
(13)

\[ i_{\text{0}\text{Fe}} = i_{\text{refFe}} \cdot \left( \frac{c_\text{H}}{c_{\text{HHeFFe}}} \right)^{a_{\text{Fe}}} \cdot \left( \frac{c_{\text{CO}_2}}{c_{\text{CO}_2,\text{refFe}}} \right)^{a_{\text{Fe}}} \cdot \frac{[300-1.107(\text{mol})]}{R \cdot \{1 - \frac{1}{T_{\text{refFe}}}\}} \]
(14)

where the values of constants are as follows:

\[ i_{\text{refH}_2\text{O}} = 3 \times 10^{-5} \text{ A/m}^2, i_{\text{refH}_2\text{CO}_3} = 0.06 \text{ A/m}^2, i_{\text{refH}_2} = 0.05 \text{ A/m}^2, i_{\text{refFe}} = 1 \text{ A/m}^2, T_{\text{refH}_2\text{O}} = T_{\text{refH}_2\text{CO}_3} = 25^\circ \text{C}, T_{\text{refH}_2} = 20^\circ \text{C}, c_{\text{HHeFFH}_2\text{CO}_3} = 0.1 \text{ mol/m}^3, c_{\text{HHeFFH}_2} = 0.1 \text{ mol/m}^3, c_{\text{H}_2\text{CO}_3,\text{refH}_2\text{CO}_3} = 0.1 \text{ mol/m}^3, c_{\text{H}_2\text{CO}_3,\text{refH}_2} = 0.1 \text{ mol/m}^3, c_{\text{HHeFFe}} = 0.1 \text{ mol/m}^3, c_{\text{H}_2\text{CO}_3,\text{refFe}} = 0.1 \text{ mol/m}^3, c_{\text{H}_2\text{CO}_3} = 0.0366 \times 10^{-3}, a_{\text{H}_2\text{CO}_3} = -0.5, a_{\text{H}_2}\text{CO}_3 = 1, a_{\text{H}_2} = 0.5, a_{\text{Fe}} = 1 \times p_{\text{CO}_2}.\]

After calculating the corrosion current density of the Fe electrode, commercial software can be adopted in realizing this model to calculate the \( \text{CO}_2 \) corrosion rate.

### 4.2. Prediction and analysis of corrosion rate in the supercritical \( \text{H}_2\text{O}/\text{CO}_2 \) steam turbine initial condensation zone

The numerical calculation results of the internal flow field of turbine initial condensation zone are imported into the \( \text{CO}_2 \) corrosion model presented in part 4.1. The results of corrosion rate calculation
are shown in the following figures (Figure.6 to 11) where the abscissa represents the non-dimensional distance along streamwise and the ordinate represents the corrosion rate. First of all, as the steam flows, the temperature and pressure of the steam gradually decrease and part of steam condenses into water. However, the corrosion rate does not increase with the increase of humidity. In contrary, it gradually decreases. In this process, temperature and pressure are the dominant factors that affect the corrosion rate. The decrease of temperature will reduce the ionization of water and CO$_2$. And the ionization equilibrium reaction will be reversed, which will reduce the concentration of H$^+$, increase the pH, and reduce the reaction rate. When the pressure decreases greatly, the partial pressure of CO$_2$ will decrease and make CO$_2$ more difficult to be dissolved into water. As a result, the concentration of H$_2$CO$_3$ decreases, and pH eventually increase. Due to the comprehensive effect of temperature and pressure, the corrosion rate in the initial condensation zone of steam turbine gradually decreases stage by stage.

In the same way, as the steam flows, the temperature and pressure of steam gradually decreases, and the corrosion rate of stators is larger than that of rotors in the same stage. On the surface of a single blade, the corrosion rate of leading edge is larger than other position of the blade. This is because the fluid is at the stagnation state at leading edge, and the temperature and pressure of fluid decrease as the fluid flows in the cascade flow-path. At different height of a blade, the load of blade is different and the degrees of temperature and pressure reduction are diverse. The corrosion rate increases with the increase of blade height. However, in some positions of flow-path, the partial pressure of CO$_2$ increases due to the condensation of steam. It makes the corrosion rate larger than the other positions.

Another important influential factor of the corrosion rate is the thickness of liquid. At leading edge of the blade, the thickness of the boundary layer is minimal. The boundary layer thickens with the flow of fluid. The smaller the thickness of the liquid, the smaller the resistance of the mass transfer between main fluid area and the metal surface. It makes the progress of the corrosion reaction more conducive. Therefore, the corrosion rate at leading edge correspondingly increases. At the other position of the blade where the thickness of liquid is relatively large, the resistance of mass transfer between main fluid area and the metal surface is larger than the leading edge. For example, as shown in Figure.10 and 11, the thickness of the solution layer is small at leading edge point, and the difference in concentration of each substance on the metal surface and the outer surface of the solution is smaller than that at the throat of blade. A large concentration of the reaction product will hinder the reaction and decrease the corrosion rate.

![Figure 6. Corrosion rate of the third stator](image1)

![Figure 7. Corrosion rate of the third rotor](image2)
Figure 8. Corrosion rate of the forth stator

Figure 9. Corrosion rate of the forth rotor

Figure 10. Deviation in concentration of the species compared to the bulk along the liquid boundary layer at the leading point, 50% blade height in the third rotor

Figure 11. Deviation in concentration of the species compared to the bulk along the liquid boundary layer at the throat, 50% blade height in the third rotor

5. Conclusions
Supercritical H₂O/CO₂ steam turbine is the key equipment for realizing thermal conversion in supercritical water gasification of coal for hydrogen production and thermal power generation with H₂O/CO₂ mixtures technology. However, ensuring its safety and reliability might be of great significance. In this study, a novel CO₂ corrosion model is constructed for the environment of the initial condensation zone of a supercritical H₂O/CO₂ steam turbine, and the internal fluid field calculations of a 5MW supercritical H₂O/CO₂ steam turbine are used to analyze the corrosion characteristics. The main conclusions are:

1) In supercritical H₂O/CO₂ steam turbine, the main factor that affects the CO₂ corrosion rate is temperature and pressure of working fluid. Temperature affects the corrosion rate by changing equilibrium constants of reactions. Pressure is mainly related to the partial pressure of CO₂ in the working fluid, and then affects the dissolution of CO₂ in condensed water as well as the concentration of corrosive substances in solution. The corrosion rate decreases with temperature and pressure stage by stage.

2) For a single blade, the corrosion rate gradually decreases within the cascade flow-path while in some position the condensation of steam may make the corrosion rate larger than the other positions. Also, the corrosion rate will be larger at a larger blade height.
3) The thickness of the solution on blade surface also affects the CO$_2$ corrosion rate. Large distance between the blade surface and the main flow area (the greater the thickness of the solution) will lead to large resistance of mass transfer between the blade surface and the main fluid area, large concentration difference between product and reactant, and unfavorable the progress of the reaction. Eventually, the corrosion rate is reduced.

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