Mechanism analysis of bubbling corrosion caused by boiler flue gas on metal material

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Abstract. Hydrogen bubbling is a typical corrosion morphology caused by hydrogen sulfide corrosion. In order to explore hydrogen sulfide corrosion of iron, the composition of flue gas under actual conditions was simulated in this research. Hydrogen sulfide corrosion in flue gas of four kinds of materials selection of ground process pipeline and underground pipe string was researched experimentally. The pressure and temperature of hydrogen bubbling corrosion morphology under actual flue gas conditions were obtained. The electrochemical corrosion mechanism between iron and hydrogen sulfide was investigated.

1. Introduction
Steam injection boiler is a special gas injection equipment for heavy oil recovery in oilfields. In the process of heavy oil recovery assisted by steam injection boiler flue gas, CO\textsubscript{2}, SO\textsubscript{2}, NO\textsubscript{2} and a small amount of H\textsubscript{2}S in boiler flue gas are corrosive to pipeline materials, which threaten the safe operation of heavy oil recovery equipment and its auxiliary equipment. Therefore, it is necessary to study the corrosion behaviour of candidate materials in the flue gas environment at different temperatures and pressures, which is able to provide reference for materials selection of ground process pipeline and underground pipe string.

An immersion test was performed by X S Huang et al. \cite{1} in order to analyse the influence of partial pressure of H\textsubscript{2}S/CO\textsubscript{2} and sulfur deposition for the corrosion behaviour of L360QCS pipeline steel in H\textsubscript{2}S/CO\textsubscript{2} environment. The results indicated that the corrosion rate of steel firstly decreased and then increased with the increasing of H\textsubscript{2}S/CO\textsubscript{2} partial pressure. Jean Kittel et al. \cite{2} studied the hydrogen induced cracking (HIC) of pipeline steel via immersion test and hydrogen permeation test. The extent of HIC depended on exposure time until it reached a stable level when the H\textsubscript{2}S partial pressure was constant. According to Li et al. \cite{3}, the corrosion rate (CR) of 110S tube steel decreased first and then increased with increasing temperature. The minimum CR appeared at 110°C. Yin et al. \cite{4} studied the corrosion behaviour of SM 80SS tube steel in stimulant solution containing H\textsubscript{2}S and CO\textsubscript{2}. Corrosion attacks increase in the initial stage and then decrease with the increase in \(p_{CO_2}/p_{H_2S}\) range from 31 to 520.

In this study, four typical materials for ground equipment and underground pipe string are tested. According to the actual working conditions, corrosion tests were performed and the mechanism of bubbling corrosion was studied.

2. Experimental

2.1. Materials
Four different materials are steel 20#, 35CrMo steel, steel 45# and N80 steel. The standard compositions of samples are shown in table 1 [5]. Dimensions of all samples were 3*3*5mm. According to the actual flue gas detection report, the flue gas is used as corrosion medium. The compositions of the corrosion medium are shown in table 2.

### Table 1. Standard compositions of materials used in the experiment

| Material       | C   | Si  | Mn  | Cr  | Mo | Al | P  | S  | Ni |
|----------------|-----|-----|-----|-----|----|----|----|----|----|
| Steel 20#      | 0.20| 0.25| 0.45| 0.20| -  | -  | 0.03| 0.04| 0.02|
| 35CrMo steel   | 0.35| 0.21| 0.55| 0.90| 0.20| -  | -  | -  | -  |
| Steel 45#      | 0.46| 0.27| 0.65| 0.22| -  | -  | 0.04| 0.04| 0.21|
| N80 steel      | 0.22| 1.00| 1.00| 13.00| -  | -  | 0.02| 0.01| 0.50|

### Table 2. Compositions of corrosion medium

| composition | CO₂ | NO₂ | H₂  | H₂S | O₂  | N₂  | H₂O          |
|-------------|-----|-----|-----|-----|-----|-----|--------------|
| Volume fraction (%) | 11  | 0.005| 0.001| 0.001| 7   | surplus saturation |

2.2. Procedure and apparatus
The matrix was polished in the sample polishing machine, and then was cleaned in the ultrasonic material emulsifier and disperser. The matrix was cooled naturally and weighed. The experiments were performed using high pressure tubular furnace. The pressure in the adjusting furnace is 3.0 MPa, 5.0 MPa, 7.0 MPa and 9.0 MPa, respectively. The temperature is 120°C, 150°C, 200°C and 250°C, respectively, and the corrosion time is 48 hours. Samples were stored in a vacuum drying oven.

2.3. Sample analysis
The identification of the corroded sample was performed by scanning electron microscope (Model JEOL 7800F). Energy-dispersive X-ray spectroscopy (Model X-Max Extreme Oxford) was used in X-ray energy spectrum analysis of sample.

3. Results and discussion

3.1. Occurrence conditions of hydrogen bubbling corrosion
Bubbling corrosion morphology was found via scanning electron microscope (SEM) images. Figure 1 shown the typical morphology of bubbling corrosion. It can be seen that a small amount of bubbling corrosion products was produced on the surface of the matrix and most of bubbles are cracked, which can only be observed through SEM. In addition, it can be seen that the solid corrosion product layer was raised from the matrix, and there was a certain distance between the layer and matrix through the observation of the fracture of corrosion product.

It is noteworthy that this bubbling corrosion product usually occurs in the “wet hydrogen sulfide” environment that the content of H₂S ≥ 0.0075% in acid gas. In this study, the content of H₂S = 0.0075% in flue gas, which didn’t form the so-call “wet hydrogen sulfide” environment.

In this research, experiments have been done at different temperatures and pressures. Table 3 shown that the conditions of appearing bubbling corrosion product, it indicated that bubbling corrosion morphology mainly appeared in a certain range of experimental condition that 9MPa, 200°C and 7MPa, 120°C. It can be considered that bubbling corrosion happened mainly in high pressure region.
(7MPa, 9MPa), and it happened in higher temperature region (7MPa, 120℃; 9MPa, 200℃) with the increased of pressure. In the flue gas environment containing water, the state of water in the high pressure and low temperature environment is super-cooled water, and the solubility of H₂S is high. However, the diffusion coefficient of H₂S is relatively high in the region of higher temperature, so that there is an equilibrium point between pressure and temperature. Therefore, 9MPa, 200℃ and 7MPa, 120℃ may be such an equilibrium points.

![Figure 1. SEM images of two typical bubbling corrosion morphology. (a)(b). 20 steel in 9MPa and 200℃. (c)(d). 45 steel in 9MPa and 200℃.](image)

### Table 3. The conditions of appearing bubbling corrosion product in experiments

| Material    | Pressure | Temperature |
|-------------|----------|-------------|
| 35CrMo      | 9        | 150         |
| All Materials | 9        | 200         |
| 35CrMo      | 9        | 250         |
| All Materials | 7        | 120         |

3.2. Formatting the title

3.2.1. Anodic reaction mechanism. On the metal surface, zero-valent Fe lost electrons to generated divalent Fe, and then combined with HS⁻ (from H₂S) to formed FeHS⁺. On the other hand, H⁺ (from H₂S) combined with H₂O to formed hydronium ion (H₃O⁺). FeHS⁺ couldn’t exist stably, and it will eventually be transformed into a more stable FeS [6]. The chemical reaction equations are as follows:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{(1)}
\]

\[
\text{Fe}^{2+} + \text{HS}^- \rightarrow \text{FeHS}^+ \quad \text{(2)}
\]

\[
\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ \quad \text{(3)}
\]

\[
\text{FeHS}^+ + \text{H}_2\text{O} \rightarrow \text{FeS} + \text{H}_3\text{O}^+ \quad \text{(4)}
\]
In the case of the concentration of H₂S is higher than 0.02% and the temperature is higher than 40℃, iron-rich sulfide FeS_{(1-x)} will be formed; On the contrary, sulfur-rich sulfide FeS_{(1+x)} will be formed when both the concentration and temperature are low [7]. In this study, the concentration of H₂S was 0.001%, and the temperature of environment was 120-250℃. It was considered that the corrosion product film should contained FeS, it can protected metal materials from further corrosion in a way due to their compactness [6]. The energy spectrum analysis of corrosion product films and cracks is shown in figure 2. It can be seen that the content of sulfur in corrosion products was very low, but oxygen was relatively high. It indicated that the main component of corrosion product film was still iron oxide. The content of H₂S was relatively low, therefore, corrosion product film was not as compact as FeS, so it was prone to rupture.

![Figure 2. Spectral analysis of bubbling region. (a)(b). Position of analysis. (c)(d). Spectrum analysis spectrogram at specified locations.](image)

3.2.2. Anodic reaction mechanism. The hydrolysis process of H₂S was carried out in two steps, in water, with the production of H₃O⁺, HS⁻ and S²⁻. The chemical reaction equations are as follows:

\[
\begin{align*}
H_2S + H_2O & \rightarrow H_3O^+ + HS^- \\
HS^- + H_2O & \rightarrow H_3O^+ + S^{2-}
\end{align*}
\]

Hydronium ions that produced on metal surfaces were gave to electrons and generated hydrogen atoms adsorbed on metal surfaces. The chemical reaction equations are as follows:

\[
\begin{align*}
H_3O^+ + e^- & \rightarrow H + H_2O \\
Fe + H & \rightarrow Fe \cdot H_{(adsorption)}
\end{align*}
\]

There were two trends for hydrogen atoms adsorbed on metal surfaces. Some of the hydrogen atoms were further transformed into dissolved hydrogen atoms and diffused into metal materials, it were captured by steel defects such as plane defects, crystal lattice dislocation and stress concentration in the process of diffusion, and then became interstitial atoms in metal. In this case, the pressure in the position of defects increasing, which led to embrittlement of steel, flaws are initiated and propagated to form cracks. The chemical reaction equations are as follows:

\[
Fe \cdot H_{(adsorption)} \rightarrow Fe \cdot H_{(dissolution)}
\]

The other part of hydrogen atoms compounded formed gaseous hydrogen molecules and escaped from the metal surface. The chemical reaction equations are as follows:

\[
\begin{align*}
2Fe \cdot H_{(adsorption)} & \rightarrow Fe \cdot H_2 + Fe \\
Fe \cdot H_2 & \rightarrow Fe + H_2 \uparrow
\end{align*}
\]

Hydrogen gas accumulated continuously between the matrix and the compact solid corrosion products, so that the surface of the material gradually bubbled up with a growing pressure difference between two sides. When the pressure difference reached a critical value, the corrosion product film fractured and the surface of matrix contacted newly with corrosion medium. In such a case, matrix began to corrode again.
The general chemical reaction equation could be expressed as follows:

\[ \text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2 \uparrow \]  

(12)

In this study, the concentration of \( \text{H}_2\text{S} \) was lower than the standard of “wet hydrogen sulfide” environment, but there was still bubbling corrosion morphology. The possible reason is that there were a lot of \( \text{CO}_2 \) and \( \text{NO}_2 \) in flue gas, which lead to the increase of pH value of corrosion medium. To some extent, hydrogen bubbling corrosion was promoted.

4. Conclusions
In this research, the hydrogen bubbling corrosion of four metal materials caused by hydrogen sulfide was studied experimentally in the flue gas of boilers under the conditions of 3MPa - 9MPa and 120\(^\circ\)C - 250\(^\circ\)C. The temperature and pressure conditions of hydrogen bubbling corrosion morphology were analyzed. The results indicated that hydrogen bubbling analysis mainly occurs under corrosion conditions of high pressure region (7MPa, 120\(^\circ\)C; 9MPa, 200\(^\circ\)C), but the higher pressure has not been studied. According to the corrosion medium of metal, the mechanism of hydrogen bubbling corrosion caused by hydrogen sulfide was proposed. In the process of corrosion, corrosion cell were formed with steel as anode and hydrogen sulfide as cathode. The results of this research provided a basis for the further study of corrosion mechanism of iron in boiler flue gas.

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