Research Progress on Corrosion of Oil and Gas Field Gathering Pipeline in H₂S-CO₂-Cl⁻ System

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Abstract. With the development of the oil and gas field industry, the corrosion of metal materials in the H₂S/CO₂ environment has greatly restricted the development of the oil and gas industry. The corrosion of metal materials has gradually been paid attention to. The corrosion of steel under the H₂S-CO₂-Cl⁻ system has been studied. In this paper, the corrosion and types of H₂S and CO₂ in steel for gathering pipelines, focusing on the reaction mechanism of corrosion, so as to achieve a more accurate grasp of corrosion laws and provide a theoretical basis for the development of new protection technologies.

Keywords. H₂S/CO₂ environment; gathering pipeline steel; corrosion.

1. Introduction
With the rapid development of economy and society, China’s demand for natural gas, petroleum and other resources is increasing, and the exploration level of oil and gas fields is gradually increasing, which has greatly promoted the development of petroleum pipeline engineering [1]. However, during the use of the pipeline, it is often corroded by strong corrosive media, and the buried pipeline will undergo corrosion and perforation in the early stage of service [2].

The common local corrosion types of oil and gas pipelines are somewhat etched, crevice corrosion, and scale corrosion [3]. During the development of highly acidic and high-sulfur gas fields, pressure and temperature are continuously decreasing along the wellbore, and sulfur is continuously precipitated due to its reduced solubility in hydrogen sulfide. The precipitated sulfur will not only hydrolyze with water, but also Combined with H₂S, HS⁻, Cl⁻, the formation of elemental sulfur deposits corrosion, causing corrosion perforation, oil and gas leakage and other phenomena [4, 5]. Therefore, the corrosion problem has become a difficult problem in this type of oil and gas field gathering pipeline system.

In this paper, the corrosion type and mechanism of oil and gas field gathering pipelines in this kind of environment are reviewed in the complex oil and gas field corrosion environment in H₂S-CO₂-Cl⁻ system. The research content will help to improve the corrosion characteristics of H₂S and CO₂ corrosive environments. The understanding and research progress have provided some theoretical support for the development of anti-corrosion work.
2. Corrosion under Different Media

2.1. \( H_2S \) Corrosion

In oil and gas field mining, due to the thermal effects of organic sulfides in oil and gas, bacteria or hydrocarbons in drilling fluids, different degrees of \( H_2S \) are generally dissociated [3]. Under normal temperature conditions, \( H_2S \) is a highly toxic gas with special odor, colorless, flammable and chemically unstable. In the oil and gas field environment, \( H_2S \) is extremely harmful to the corrosion of pipes. The corrosion status of \( H_2S \) is shown in Table 1.

| Corrosion type               | Corrosion characteristics                                                                 | Research status                                                                 |
|------------------------------|-------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| General corrosion            | The local wall thickness is thinned, plaque or perforation, and the corrosion product film formed on the surface of the material is relatively uniform and complete [6]. | Liu [7] used electrochemical technology and static hanging piece experiments to investigate the corrosion behavior of carbon steel in low concentration \( H_2S \) solution. The results show that the corrosion rate and concentration of carbon steel are nonlinear. |
| Pitting                      | Pitting is caused by cracking of the passivation film formed on the metal surface, and the exposed portion is small and concentrated, which can be used as an anode region. During the electrochemical corrosion process, the anode region is corroded and pitting pits appear on the metal surface [6]. | Zhang [8] studied the corrosion behavior of heat exchanger tube bundle steel in \( H_2S \) containing medium, and found that the steel studied had obvious pitting tendency in the presence of both oxidant and aggressive ions. |
| Hydrogen bubbling (HB)       | In the process of \( H_2S \) corrosion, \( H_2S \) provides hydrogen atoms to prevent the formation of hydrogen molecules. Hydrogen atoms will diffuse into the defective metal to form hydrogen molecules. Hydrogen molecules will gradually increase, internal stress will be generated inside the metal, and then drums will be formed on the metal surface [3, 6]. | Hou et al. [9] studied the hydrogen bubbling behavior of pipelines in high hydrogen sulfide-containing environments. It was found that this was mainly due to the accumulation of sulfur and the accumulation of hydrogen, which caused cracks to crack along the grain boundaries. |
| Hydrogen induced cracking (HIC) | Inside the metal that generates hydrogen bubbling, hydrogen bubbling increases, internal pressure increases, and small bubbling tends to connect with each other to form stepped cracks in parallel tube walls [6]. | He [10] found that the larger the grain size, the greater the sensitivity of stainless steel to hydrogen cracking. |
| Sulfide Stress Corrosion Cracking (SSCC) | The SSCC is due to the diffusion of hydrogen atoms generated by \( H_2S \) into the interior of the metal, which causes cracking under the action of external stress. | Huang [11] found that the corrosion behavior of L360QCS steel did not show SSCC cracks in all tests under simulated conditions. It shows that L360QCS steel has good anti-SSCC performance. |

2.2. Mechanism of \( H_2S \) Corrosion

Steel does not corrode in a dry \( H_2S \) environment, and only if it is dissolved in a solution or a thin film
of liquid, it is corrosive to steel [1]. The corrosion process is as follows:

\[
H_2S \rightarrow H^++HS^- \quad (1)
\]
\[
HS^- \rightarrow H^++S^{2-} \quad (2)
\]
\[
H_2S+Fe+H_2O \rightarrow FeHS_{\text{Adsorption}}+H_3O^+ \quad (3)
\]
\[
FeHS_{\text{Adsorption}} \rightarrow FeHS_{\text{Adsorption}}^++e^- \quad (4)
\]
\[
FeHS_{\text{Adsorption}} \rightarrow FeHS_{\text{Adsorption}}^++e^- \quad (5)
\]
\[
FeHS_{\text{Adsorption}}^++H_2O \rightarrow Fe^{2+}+H_2S+H_2O \quad (6)
\]

Finally, a corrosion product is generated:

\[
Fe^{2+}+HS^- \rightarrow FeS+H^+ \quad (7)
\]

2.3. \(CO_2\) Corrosion

\(CO_2\) is an associated gas in natural gas and petroleum, mainly in oil and gas layers and formation water. The dry \(CO_2\) is not corrosive. If it is formed in a wet \(CO_2\) environment with water, it will cause corrosion on the metal surface. The corrosion caused by the wet \(CO_2\) environment is called “sweet corrosion” [3]. The corrosion status of \(CO_2\) is shown in table 2.

| Corrosion type    | Corrosion characteristics                                                                 | Research status |
|-------------------|------------------------------------------------------------------------------------------|-----------------|
| General corrosion | \(CO_2\) dissolves in water to form carbonic acid, which reacts with \(Fe\) to cause uniform corrosion. During the corrosion process, the corrosion cathode reaction area where the material reduction reaction and the metal anode dissolution reaction are performed is small, and the position is not reaction of hydrogen ion fixed, so that the corrosion distribution is very and surface adsorbed \(CO_2\). uniform. | Zhang [3] believes that the corrosion cathode reaction is divided into two types, the metal anode dissolution reaction are which are the reduction performed is small, and the position is not reaction of hydrogen ion fixed, so that the corrosion distribution is very and surface adsorbed \(CO_2\). uniform. |
| Pitting           | The corrosion pattern of pitting is generally concave and smooth. The temperature at which pitting occurs is generally between 80-90 °C. This type of corrosion is generally concave, the bottom is relatively flat, and the periphery is vertically concave. However, such membranes are defective, not dense enough to stabilize or fall off to cause such damage [6]. | Ikeda [12] found that pitting is due to defects in the corrosion product film on the surface of the metal substrate. |
| Mesa corrosion    | Flow induced local corrosion, which is in the form of a groove. This corrosion produces a layer of precipitate on the surface of the metal substrate, but does not protect the substrate [6]. | |
| Localized corrosion |                                                                                                                                               |                 |

2.4. Mechanism of \(CO_2\) Corrosion

\(CO_2\) itself is not corrosive, mainly caused by the dissolution of water to form carbonic acid, causing corrosion of oil and gas pipelines. For the corrosion mechanism of \(CO_2\), the reaction system can be described as follows:

\[
H_2O+CO_2 \rightarrow H_2CO_3 \quad (8)
\]
\[
H_2CO_3 \rightarrow HCO_3^-+H^+ \quad (9)
\]
\begin{align*}
    \text{HCO}_3^- & \rightarrow \text{CO}_3^{2-} + \text{H}^+ \quad (10) \\
    \text{Fe} + 2\text{H}^+ & \rightarrow \text{H}_2 + \text{Fe}^{2+} \quad (11)
\end{align*}

Generate corrosion products:
\[ \text{CO}_3^{2-} + \text{Fe}^{2+} \rightarrow \text{FeCO}_3 \quad (12) \]

The total response is:
\[ \text{H}_2\text{O} + \text{CO}_2 + \text{Fe} \rightarrow \text{FeCO}_3 + \text{H}_2 \quad (13) \]

3. Conclusion
(1) For highly acidic and high-sulfur gas fields, the pressure and temperature decrease continuously along the wellbore, and the sulfur is continuously precipitated due to its reduced solubility in hydrogen sulfide. The precipitated sulfur and water are hydrolyzed, and simultaneously with \( \text{H}_2\text{S} \) and \( \text{HS}^- \), \( \text{Cl}^- \) and so on, the formation of elemental sulfur deposit corrosion, causing corrosion perforation, oil and gas leakage and other phenomena.

(2) In order to solve the corrosion problem of buried metal pipelines, it is necessary to establish a more complete anti-corrosion monitoring system to improve the service life of pipelines and prevent corrosion and perforation.

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