Failure Analysis on Leakage and Perforation of Natural Gas Pipeline

JU Jianbo, DU Liang, MENG Tao*
China Special Equipment Inspection and Research Institute, Beijing, China
*email: mengtao@CSEI.org.cn

[Abstract] CO2 corrosion is one of the most common corrosion forms in the process of oil and gas field development and oil and gas gathering and transportation. In the process of natural gas gathering and transportation, the problem of pipeline corrosion caused by CO2 is widespread, which often leads to serious local thinning, even perforation and fracture of the pipe body. Once it occurs, it will cause great economic losses and disastrous consequences to the actual production. Therefore, it is of great practical significance to study the mechanism of CO2 corrosion and analyze the influencing factors of CO2 corrosion in order to prevent the safety accidents and improve the efficiency of natural gas transportation. In this paper, a natural gas pipeline wall perforation failure analysis as an example, the sample from the natural gas pipeline corrosion product morphology and composition of micro analysis, and the CO2 corrosion mechanism, influencing factors and other aspects are described in detail.

1. introduction
In the process of oil and gas exploration and development, CO2 is produced as associated gas. Due to the existence of CO2, the whole process of oil and gas exploitation and transportation is facing a serious threat of CO2 Corrosion [1].

CO2 is easy to dissolve in water, forming H2CO3, which reduces the pH of the environment, causing serious corrosion to the pipelines in the oil and gas exploitation and transportation system, and H2CO3 can be directly reduced on the steel surface. Therefore, under the same pH condition, the corrosivity of CO2 aqueous solution is stronger than that of HCl solution [2]. CO2 corrosion perforation is easy to cause leakage accidents, which not only directly wastes resources, but also pollutes water and air resources and damages the environment. In the environment of increasing energy demand, CO2 corrosion has become a very prominent and urgent problem that plagues the development of oil and gas industry.

2. Failure cases of pipe wall perforation
A natural gas pipeline was completed in March 2019, and then went through the process of hydrostatic test, pressure relief, water sweeping, deep water sweeping, ball passing and air tightness test. In December 2019, during the long-term air pressure holding test, the pipeline leaked. The standard of the pipeline is GB/T9711.2-1999, technical delivery conditions for steel pipes for petroleum and natural gas industries - Part 2: Grade B steel pipes. The pipeline material is 1415MB, the specification is Φ508×7.1mm, and the design pressure is 6.3MPa.
3. Corrosion morphology of pipe fitting

The length of the leaking pipeline is about 1.2m. Through the inspection of the external surface of the pipeline, it is found that there are four damage points of the anti-corrosion coating on the external surface of the pipeline, as shown in Figure 1.

![Rupture point of anticorrosive coating](image1)

Figure 1 Leaking steel pipe

Leakage holes are found at each damage point. The leakage holes are needle shaped and the perforation direction is perpendicular to the pipe wall thickness. See Fig.2 (a) - (d). It can be seen that the four leakage holes are symmetrically distributed on both sides of the steel pipe, and each group is in two straight lines roughly parallel to the generatrix of the pipe body.

![Leakage hole on the outer wall of pipeline](image2)

Figure 2 Leakage hole on the outer wall of pipeline

The observation of the inner surface of the leakage pipeline shows that the inner surface of the pipeline is covered by a layer of corrosion products, which indicates that the inner wall of the pipeline has been completely corroded to a certain extent, as shown in Fig. 3 (a) - (c).
As shown in Fig. 3, the corrosion products present two distinct states: one is orange powder, as shown in Fig. 3 (a) and (c); the other is reddish brown flake structure, as shown in Fig. 3 (b) and Fig. 3 (c). Further observation shows that there is a certain relationship between the distribution of corrosion products in two different states and the installation position of the pipeline: the orange corrosion products are located at the bottom of the pipeline, Fig. 3 (b); the reason may be due to the introduction of liquid water during the installation and use of the pipeline and the accumulation of water at the bottom of the pipeline.

After dissecting the pipeline and observing the shape of the internal leakage hole, we can see that the shape of the leakage hole on the inner wall is basically the same as that on the outer wall, and it is also needle shaped, and the direction of perforation is perpendicular to the thickness of the pipe wall.

4. Cause analysis of corrosion

4.1. Chemical composition analysis

Take samples to analyze the chemical composition of the leaking pipeline. The results are shown in Table 1 below. The analysis results show that the chemical composition of the pipeline meets the requirements of GB/T 9711.2-1999 [3].

| element                     | C    | Si   | Mn   | P    | S    | V    | Nb  |
|-----------------------------|------|------|------|------|------|------|-----|
| GB/T 9711.2-1999            | ≤0.16| ≤0.45| ≤1.6 | ≤0.025| ≤0.02| ≤0.08| ≤0.05|
| Leaking steel pipe          | 0.09 | 0.20 | 1.41 | 0.08 | <0.005| 0.018| 0.032|
| element                     | Ti   | Cu   | Ni   | Cr   | Mo   | V+Nb+Ti CEV |
| GB/T 9711.2-1999            | ≤0.06| ≤0.25| ≤0.3 | <0.3 | <0.10| ≤0.15 | ≤0.42|
| Leaking steel pipe          | 0.016| <0.005| <0.005| 0.016| 0.007| 0.066| 0.334|

4.2. Metallographic analysis

Samples were taken from the tube body and leakage hole for metallographic examination. Both of them are ferrite + pearlite with normal structure, as shown in Fig. 4 (a), (b) and Fig. 5 (a), (b).
4.3. Scanning electron microscopy analysis

Scanning electron microscope (SEM) was used to detect the leakage hole in the pipeline. It was found that the inner wall of the leakage hole was covered by corrosion products. Cracks were found on the corrosion products, and no bare metal surface was found.

4.4. Energy spectrum analysis of corrosion products

The corrosion products attached to the leakage hole on the inner wall of the pipeline are analyzed. It is found that the corrosion products at the leakage hole on the inner wall of the pipeline contain C, O, Fe, Cl, Si and other elements. The content of each element is shown in Table 2 below. The maximum content of chlorine is 6.61%, and chlorine is the sensitive substance causing pitting corrosion damage of pipeline steel.

| element    | C   | O    | Si  | Cl  | Fe   |
|------------|-----|------|-----|-----|------|
| Corrosion product content | 4.65 | 34.55 | 0.29 | 6.61 | 53.91 |

4.5. XRD phase analysis

In order to determine the structure of the corrosion products, XRD phase analysis was carried out on the corrosion products at the leakage hole on the inner wall of the pipeline. The results show that the main phases of corrosion products are Fe₃O₄, α-Fe₂O₃ and FeO.

4.6. Water quality analysis

Seven groups of water samples along the leakage pipeline were taken for determination of chloride ion content. The results showed that the highest chloride ion content was 6522mg/L, and the lowest was 250mg/L. It shows that the content of chloride ion has reached a very high level.

5. Analysis of corrosion mechanism

According to the above analysis, the pipeline is in a very bad environment before leakage. Firstly, liquid water with High Cl⁻ content may remain at the bottom of the pipeline; secondly, the pipeline will be exposed to air rich in CO₂ and O₂ for a long time after installation. Under the influence of the above factors, a complex electrochemical corrosion process occurred on the inner wall of the pipeline, which eventually led to pitting corrosion and overall corrosion of the inner wall of the pipeline.

Relevant studies show that in humid environment, the presence of CO₂ can cause both overall corrosion and local corrosion. Cl⁻ and temperature are the two most important factors that affect the corrosion morphology of CO₂. Excluding the influence of other factors, the CO₂ corrosion can be divided into three types according to the temperature: low temperature zone (<60°C), the material has overall corrosion; medium temperature zone (60-150°C), the material has local corrosion (pitting); high temperature zone (>150°C), the formation of passive film to inhibit the occurrence of corrosion.
In this case, it is obvious that the inside of the pipeline is in the low temperature zone, so if there is only CO\textsubscript{2} corrosion, the pipeline will be completely corroded, which will not lead to perforation and leakage in a short time.

Cl\textsuperscript{-} is a very special and important example in the corrosion process of metal materials. It is an important factor to induce and promote pitting corrosion. Firstly, when the protection of corrosion product film is poor, Cl\textsuperscript{-} in the solution will reduce the possibility of the formation of passive film on the surface of materials or accelerate the destruction of passive film, thus causing local corrosion damage; secondly, Cl\textsuperscript{-} can preferentially adsorb on various defects in the corrosion product film induced by the internal stress of metal defects, or squeeze out other adsorbed anions, or directly penetrate through the pores of the film. In addition, the self catalytic effect of Cl\textsuperscript{-} will accelerate the dissolution of the metal, resulting in the metal has been in the active state; finally, in order to maintain the electrical neutrality in the pit, Cl\textsuperscript{-} will also be enriched in the pit, resulting in the decline of local pH value, and Cl\textsuperscript{-} is in the active state inside and outside the pit. The concentration will also lead to local galvanic corrosion, blocking cell effect will be very strong, forming large cathode outside the pit, small anode inside the pit, promoting the dissolution of iron in the pit, eventually leading to high local corrosion rate, forming pitting corrosion pit.

However, in the CO\textsubscript{2} corrosion system, the existence of Cl\textsuperscript{-} does not lead to pitting corrosion, and the pitting corrosion only occurs when the concentration of Cl\textsuperscript{-} is above 30mg/L. In the above cases, the water sample with the lowest concentration of Cl\textsuperscript{-} is also far more than 30mg/L; in addition, the CO\textsubscript{2} corrosion is in the low temperature zone, the FeCO\textsubscript{3} film generated inside the pipeline is loose and has no adhesion, and even can not form a film, which can not effectively prevent Cl\textsuperscript{-} from penetrating into the corrosion layer, and eventually leads to pitting corrosion. The specific electrochemical corrosion mechanism\cite{4} is as follows:

**Anodic reaction:**
\[
\begin{align*}
\text{Fe} + \text{Cl}^- + \text{H}_2\text{O} & = [\text{FeCl(OH)}\text{]_{ad}} + \text{H}^+ + \text{e} \\
[\text{FeCl(OH)}\text{]_{ad}} & \rightarrow \text{FeClOH} + \text{e} \\
\text{FeClOH} + \text{H}^+ & = \text{Fe}^{2+} + \text{Cl}^- + \text{H}_2\text{O}
\end{align*}
\]

**Cathodic reaction:**
\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & = \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 + \text{e} & \rightarrow \text{H}^- + \text{HCO}_3^- \\
\text{HCO}_3^- + \text{H}^+ & = \text{H}_2\text{CO}_3 \\
\text{H}^- + \text{H}^- & = \text{H}_2
\end{align*}
\]

From the above analysis, it can be seen that the pipeline is an oxygen rich environment, and the existence of O\textsubscript{2} will also promote the corrosion of CO\textsubscript{2}. Firstly, O\textsubscript{2} as depolarizer reacts directly with Fe\textsuperscript{2+} to form Fe\textsuperscript{3+} in the presence of oxygen, and Fe\textsuperscript{3+} reacts with OH\textsuperscript{-} formed by O\textsubscript{2} depolarization to form Fe(OH)\textsubscript{3} precipitation. If the oxidation rate of Fe\textsuperscript{2+} to Fe\textsuperscript{3+} exceeds the consumption rate of Fe\textsuperscript{3+}, the corrosion process will be accelerated. At the gas-liquid junction in the pipeline, sufficient O\textsubscript{2} will constantly oxidize Fe\textsuperscript{2+} to Fe\textsuperscript{3+}, which will accelerate the corrosion process and accelerate the growth of pitting pits at the gas-liquid junction. Moreover, with the corrosion reaction in the pit, O\textsubscript{2} in the pit is gradually consumed, while the concentration of O\textsubscript{2} in the outer pit is always high. O\textsubscript{2} concentration difference battery is formed inside and outside the pit. The area with high oxygen concentration has low potential, which is the cathode; the area with low oxygen concentration has high potential, which is the anode. Once again, it leads to the formation of large cathode outside the pit and small anode inside the pit, which promotes the development of the pit. The mechanism of electrochemical reaction is as follows:
\[
\begin{align*}
\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} & = \text{Fe}^{3+} + 2\text{OH}^- \\
\text{Fe}^{3+} + 3\text{OH}^- & = \text{Fe(OH)}_3
\end{align*}
\]

In addition, Ca\textsuperscript{2+} and Mg\textsuperscript{2+} plasma in residual water can also promote the formation of pitting corrosion on the inner wall of pipeline, and the effect of internal load can also promote the development of pitting corrosion.
6. Conclusions
The results show that the leakage of the pipeline is caused by the pitting of the metal inner wall under the joint action of CO₂, Cl⁻, O₂. Especially the existence of high concentration Cl⁻ plays a key role in promoting the rapid development of pitting.

The internal corrosion of natural gas pipeline caused by CO₂ is an inevitable problem. Its corrosion mechanism is complex, and there are many influencing factors, usually many factors work together, and the corrosion modes and forms are diverse. In order to effectively prevent and slow down the corrosion of pipeline metal matrix, it is necessary to deeply understand its corrosion mechanism, analyze the main influencing factors, and take effective protective measures against the synergistic effect caused by various factors.

Acknowledgments
This study was financially supported by the research project of Research and development of key technology and equipment for safety assurance of typical petrochemical process (2018YFC0808600).

References
[1] Jia Zhijun, Corrosion electrochemical behavior and mechanism of Tubing Steel in CO₂ solution [D], Beijing University of science and technology, Doctoral Dissertation,2011:1-1.
[2] Nešič S Nordsveen M,Nyborg R, Stangeland A. A mechanistic model for CO2 Corrosion with protective iron carbonate films[A], Corrosion/01[C], paper NO.40 (Houston,TX:NACE,2001).
[3] State Bureau of quality and technical supervision. GB/T 9711.2-1999. technical delivery conditions for steel pipes for petroleum and natural gas industries - Part 2: Grade B steel pipes[S].Beijing,1999.
[4] De Waard C,Milliams D E. Carbonic acid corrosion of steel[J]. Corrosion,1975,31:131.
[5] Wen-Zheng Xu,Chun Bao Li,Joonmo Choung,Jae-Myung Lee. Corroded pipeline failure analysis using artificial neural network scheme[J]. Advances in Engineering Software,2017,112.
[6] Hossam A. Kishawy,Hossam A. Gabbar. Review of pipeline integrity management practices[J]. International Journal of Pressure Vessels and Piping,2010,87(7).