

Research Progress of CO₂ Corrosion and Protection in Oil and Gas Pipelines

Na Yang^{1,*}, Kexi Liao¹ and Linshuang Wu¹

¹Southwest Petroleum University, Chengdu 510000, China.

*Corresponding Author

Abstract

Oil transmission pipeline is the most economic, convenient and safe mode of transport, in recent years, along with the crude oil has inferior to, and the increase of the pipeline to use fixed number of year, crude oil pipeline internal corrosion problem increasingly serious, corrosion causes wall thinning, even punch spill, eventually make the pipeline failure, there have been some crude oil pipeline caused by corrosion in the pipeline leakage accidents, Causing serious economic losses. There are many corrosion factors, among which the corrosion caused by CO₂ is more complex and more serious. Based on this, the corrosion mechanism of carbon dioxide and the factors affecting CO₂ corrosion rate of the research is particularly important factors affecting CO₂ corrosion rate is numerous, including crude oil moisture content, the velocity, temperature, ion, O₂, CO₂ partial pressure, etc., and under the action of erosion corrosion rate distribution, at line mutations (tee and elbow) the change of CO₂ corrosion rate, The conclusions obtained from the comparative analysis have important reference significance for predicting the corrosion rate in pipelines, predicting pipeline life and ensuring the safe and stable operation of oil and gas pipelines.

Keywords

CO₂ Corrosion; Corrosion Mechanism; Corrosion Influencing Factors; Corrosion Protection.

1. Introduction

CO₂ usually exists as an associated gas component of natural gas or oil in oil and gas field environment. In addition, CO₂ flooding (CO₂-EOR) and reservoir acidification processes are often used to enhance oil recovery, resulting in high CO₂ content in oil and gas. Dry CO₂ is not corrosive. When it dissolves in water, it generates carbonic acid. Under the same pH value, the total acidity of carbonic acid is higher than that of hydrochloric acid, which is more corrosive to oil well pipes and surface gathering and transportation system than that of hydrochloric acid. CO₂ corrosion seriously affects the development of petroleum industry. In the actual production and transportation, CO₂ corrosion protection is often carried out by correct material selection, coating, process improvement and adding corrosion inhibitor, among which the effect of adding corrosion inhibitor is particularly prominent. Therefore, the development of excellent corrosion inhibitors to extend the service life of oil and gas field equipment is of great significance to the development of petrochemical industry [1]

2. Research Status of CO₂ Corrosion in Oil and Gas Pipeline

CO₂ corrosion causes oil and gas pipeline leakage, burst and other problems often occur, which seriously threatens people's life safety and also causes great harm to the environment, so the CO₂ corrosion problem has been concerned by people. CO₂ aqueous solution itself has a strong corrosive, coupled with the influence of temperature, CO₂ partial pressure, water medium, pH value and other factors, make the corrosion of the pipeline further aggravated. Oil and gas contain S²⁻, Cl⁻, Ca²⁺, Mg²⁺ and many other ionic components, these ions encounter water or pipe matrix will occur different degrees of chemical/electrochemical reaction, and finally pipe due to uneven corrosion and thinning failure.

Due to the serious damage of CO₂ corrosion to gathering and transportation pipelines, many scholars have conducted detailed studies on the mechanism, process, corrosion products and protection of CO₂ corrosion. Liu Xiaowei et al. used high temperature autoclave, weight loss method, scanning electron microscope (SEM), X-ray diffraction (XRD) and other methods to study the corrosion performance of X80 pipeline steel under different CO₂ partial pressures in simulated CO₂ flooding environment of oil field. The test results show that with the increase of CO₂ partial pressure, the corrosion rate of X80 pipeline steel firstly increases and then decreases, and the corrosion rate reaches the maximum value when the CO₂ partial pressure is 1.5 MPa. Li Ming et al. used static weight loss method, SCANNING electron microscope, electron energy spectrum and other methods to simulate the corrosion behavior of pipeline steel with three different chromium contents (316L, 13Cr and 3Cr) in CO₂ corrosion environment in gathering and transportation system. The results show that in the simulated gas-liquid corrosion environment, the corrosion resistance of the three materials is 316L > 13Cr > 3Cr in order, in which 3Cr pipeline steel has extremely serious corrosion, 316L has relatively slight corrosion, and 13Cr pipeline steel has moderate corrosion [2].

3. Influence Factors of CO₂ Corrosions

CO₂ corrosion is complicated, and the corrosion forms are divided into uniform corrosion and local corrosion. The corrosion process is affected by many factors, including temperature, CO₂ partial pressure, pH value, medium composition and flow rate.

3.1 The partial pressure of CO₂

CO₂ partial pressure directly affects the corrosion rate, and has a certain decisive role. At present, it is also the main basis for determining the corrosion strength of CO₂. The research results of Long et al. show that corrosion can occur when the CO₂ partial pressure reaches 0.021mpa, and pitting corrosion occurs when the CO₂ partial pressure increases to 0.05mpa. Aria et al. showed that when the CO₂ partial pressure increased from 0 to 0.1mpa, the corrosion current density only increased slightly. When the CO₂ partial pressure continued to increase to 0.5mpa, the concentration of H₂CO₃ in the solution increased, and the effect of CO₂ hydration reaction became more obvious, leading to a significant increase in the corrosion current density. The increase of CO₂ partial pressure does promote the corrosion process, but it does not have a monotony effect in all pressure ranges. Cui Huaiyun et al. [16] found that there was an inflection point for the effect of CO₂ partial pressure on the corrosion rate of N80 tubing steel. When the temperature is 25°C, the inflection point is about 1MPa; when the CO₂ partial pressure is less than 1MPa, the corrosion rate is fast and the corrosion degree is serious. When CO₂ partial pressure > 1MPa, the corrosion rate decreases.

3.2 Temperature

Temperature generally affects the corrosion rate indirectly by affecting the solubility of CO₂ and the rate of mass transfer between reactants and products. Although the increase of temperature can promote the reaction, the formation rate of product film FeCO₃ will be accelerated with the progress of the reaction, so as to prevent the corrosion reaction. Zhang thought by influencing the CO₂ solubility in the solution temperature, impact on the corrosion process in two aspects: on the one hand, the formation of corrosion product film inhibits by temperature promotes corrosion process, reduces the uniform corrosion rate, on the other hand, in the process of formation of corrosion product film crack in bar or honeycomb, promoted the local corrosion process. The influence of temperature on the corrosion process also has an inflection point. Before the formation of dense corrosion product film, the ability of temperature rise to promote the reaction is greater than the ability of product film to inhibit the reaction.

3.3 The pH of solution

The pH value does not directly affect the corrosion rate, but influences the corrosion rate by influencing the hydrogen evolution reaction of the cathode and the diffusion and dissolution process of the surface product film. In general, when pH value increases, the concentration of hydrogen ions decreases, which inhibits the reduction reaction of hydrogen and thus reduces the rate of corrosion

reaction. With the increase of pH value, the solubility of FeCO_3 decreased, and the Fe^{2+} near the substrate surface was deposited as FeCO_3 film. Zhu et al. studied the CO_2 cathodic corrosion mechanism of low-chromium steel. The results show that when the pH value of the medium is less than 3.5, the cathode reaction is mainly the REDUCTION reaction of H^+ , and the corrosion process is under diffusion control. When the pH value increases to 3.5~5, the cathodic reaction is the reduction of H^+ and H_2CO_3 , and the corrosion is under mixed control (activation-diffusion control). When the pH value is greater than 5, the cathode process has nothing to do with H^+ , H_2CO_3 reduction mainly occurs at the cathode, and corrosion is mainly controlled by activation [3].

3.4 Solution composition

Under actual working conditions, the composition of the corrosive medium is usually complex, including not only Ca^{2+} , Mg^{2+} , HCO_3^- , Cl^- plasma, but also O_2 , H_2S and other dissolved gases, which sometimes cause the change of pH value of the medium. Gu Tan et al. studied the effect of typical ions on carbon steel CO_2 corrosion, and found that HCO_3^- could reduce the corrosion rate by increasing the pH value. Ca^{2+} is involved in the formation of corrosion product membrane, which reduces the porosity of the product membrane, makes the product membrane more dense and enhances its protection. However, the study of Videmk et al. showed that when HCO_3^- coexisted with Ca^{2+} , a protective film could indeed be formed, but if only Ca^{2+} existed, the corrosion would be accelerated. Moreover Cl^- is there is a certain effect on CO_2 corrosion process, when halogen ion concentration is higher, to give priority to the specific adsorption on substrate surface, and catalytic role in the reaction process, with the increase of its concentration, also will improve the catalytic effect, reaction rate soon, but at the same time make the solution quickly saturated solubility product, resulting in precipitation membrane, protect the substrate.

3.5 Velocity and flow pattern of the medium

In addition to the above environmental factors, the velocity and flow state of the medium also have a certain influence on the CO_2 corrosion process. Generally, a more uniform protective film is formed at a low flow rate. With the increase of the flow rate, the uneven cover of the protective film causes local corrosion, namely pitting pits. Compared with static conditions, the flowing medium under dynamic conditions can make the ions produced by corrosion leave the vicinity of the matrix quickly, and the shear force generated by the flowing medium may destroy the corrosion product film already produced and promote the reaction [4].

4. Protection Technology for CO_2 Corrosion

4.1 CO_2 corrosion resistant material technology

The CO_2 corrosion resistant material technology is mainly by adding some alloying elements which can resist or slow down the CO_2 corrosion in steel to achieve the purpose of corrosion resistance. The influence of alloying elements on CO_2 corrosion resistance of steel mainly refers to the influence of Cr on CO_2 corrosion resistance [5].

4.2 Material surface treatment technology

The material surface treatment technology is mainly to treat the steel surface by coating or coating, so that the surface is attached with a protective layer (film) that can prevent CO_2 corrosion, so as to avoid the steel from CO_2 corrosion.

4.3 Cathodic protection technology

Cathodic protection technology is to protect steel from CO_2 corrosion by means of passing current or sacrificial anode. Because CO_2 corrosion is a kind of electrochemical corrosion, according to the principle of electrochemical reaction, enough cathode current can reduce the anode dissolution rate of steel, so as to slow down the corrosion of CO_2 . However, this technology needs electrochemical test and other means to design a reasonable cathodic protection, and the steel structure has a great impact, power consumption is large, so its application is not ideal. The method of protecting steel

from CO₂ corrosion at the expense of anode has been developed greatly in recent years. Currently, sacrificial anodes used in the field are al-based alloys.

4.4 Corrosion inhibitor injection technology

At present, major oil and gas fields at home and abroad mainly use corrosion inhibitor injection technology to solve the PROBLEM of CO₂ corrosion in the process of oil and gas exploitation. The injection of corrosion inhibitor can greatly improve the CO₂ corrosion resistance of casing, pipeline and equipment. And because of its low consumption, low cost, easy to operate, can adapt to many harsh environment and other advantages, it has been widely used in major oil and gas fields.

5. Conclusions and Suggestions

CO₂ corrosion has always been an important problem in oil and gas field development. Major oil and gas fields and scientific research institutions have carried out a lot of research in this regard, and achieved great results [6], but there are still some deficiencies, mainly shown in:

- (1) The research on CO₂ corrosion mechanism is not mature, which leads to the lack of clear CO₂ corrosion law;
- (2) There are some contradictions in the discussion of the factors affecting CO₂ corrosion, which cannot provide guidance for the research on the protection technology of CO₂ corrosion;
- (3) The indoor simulation of corrosion prevention is backward, and the results of many short-term indoor corrosion prevention experiments are inconsistent with the CO₂ corrosion situation in actual oil and gas fields.

These problems restrict the development of CO₂ corrosion protection technology in oil and gas fields. In the future, for the research of CO₂ protection technology, it is necessary to strengthen the research on the mechanism of CO₂ corrosion, deeply discuss the factors affecting CO₂ corrosion and their influence law, and improve the indoor simulation device. Especially in the research of corrosion inhibitors, attention should be paid to the effects of various functional groups on CO₂ corrosion, and the functional groups that can play a role in CO₂ corrosion inhibition should be grafted onto a molecule, and the CO₂ corrosion inhibitors that can adapt to a variety of harsh environment can be developed by means of compounding.

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