



Study and application of corrosion mechanisms and corrosion prevention design for the sour gas wells under adverse corrosion environments

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ABSTRACT

For natural gas well in sour gas reservoirs, very serious corrosion in the well producing system is an important factor of gas production system life. In order to ensure the long-term development of gas wells, this paper mainly introduces material corrosion prevention technology in the well producing system, such as corrosion-resistant alloy steel corrosion control technology, corrosion inhibitor technology and so on. By taking YB-L Gas Field as an example, which is a typical sulfide containing gas field, statistics generated from the natural gas analytical data of gas wells at YB-L Gas Field shows that the content of hydrogen sulfide is 8.3%~10.2%, with the average of 9.4%, and the content of carbon dioxide is generally 4.6%~8.9%, with the average of 6.5%. The average relative density of natural gas is 0.676. It can be observed from the above that YB-L gas reservoirs is a typical sulfide containing gas field under adverse corrosion environments. This paper introduces the material corrosion prevention technology and corrosion inhibitor technology in the well producing system in YB-L Gas Field. For application in the well producing system in YB-L Gas Field, the technology above have good performance of corrosion resistance.

Keywords: Corrosion, sour gas field, electrochemical corrosion, well producing system, corrosion-resistant material, corrosion inhibitor

INTRODUCTION

For sour gas fields, dangerous safety accidents and environmental problems may be generated by corrosion; Fig. 1 is the completed well system material corrosion in a sour gas reservoir. The natural gases of many gas reservoirs contain a certain quantity of hydrogen sulfide and carbon dioxide and there is stress corrosion and electrochemical corrosion generated by sour gas. Therefore, the tubings and casings selected and used in sour gas-containing gas wells should be made of sour media-resistant steel, or corrosion inhibitor is added. This paper mainly introduces corrosion mechanisms and corrosion prevention design for the sour gas wells under adverse corrosion environments and application.

Corrosive Media and Corrosion Environment of Gas Wells

Corrosion of gas wells is related to the corrosive media in produced fluid, the corrosion environment, the material selected and structure, and so on[1], among which there is interaction, thus generating even obvious differences in corrosion severity between wells, in different positions in the same well, and at different producing times for the same well. In gas production systems, there also are many nonmetallic component parts such as plastic and rubber products, for which attention to corrosion should also be paid.

Corrosive Media of Gas Wells

1. Corrosive components in dynamically produced fluid include: a. Carbon dioxide; b. Hydrogen sulfide, elemental sulfur, organic sulfur, and so on; c. Formation water with high-concentration chloride ions, water injected during water flooding, and condensate water in a gas well; d. Oxygen or other acidic materials that enter the well during well construction and down hole operations (such as acidizing); e. Sulfate, sulfate reducing bacteria and carbonate.
2. Corrosive components that are injected include:
 - a. Spent acid during acidizing, polymer injected for enhancing recovery factor, carbon dioxide reinjected during enhanced oil recovery, and so on;
 - b. Carbon dioxide injected into condensate gas reservoir and carbon dioxide reinjected during gas recycling;
 - c. High-temperature steam injected during thermal production.
3. Corrosive components in non-productive formations include: a. Acidic gases. H₂S, CO₂, and H₂; b. Dissolved oxygen gas; c. Salt ions; d. Bacteria. Sulfate-reducing bacteria, oxyphilous bacteria, and so on; e. Interzonal crossflow due to poor cement job quality or improper downhole operation.

Corrosion Environment of Gas Wells

The corrosion environment of oil and gas wells includes the pressures, temperatures, flow regimes, and flow fields in various positions[2,3]. These factors may cause a change of the phase state of the system. The change process is accompanied by the dissolution and escape of gas, the disruption of bubbles, and so on. Shear and cavitation may be generated on the flow passage wall. Corrosion may be aggravated under the action of combined mechanical force and electrochemical corrosion. The changes of flow passage diameter and flow direction may also generate changes of pressure, temperature, flow regime, and flow field; thus, corrosion may be aggravated. During oil and gas well production, the contents of corrosive components are changeable. With the prolongation of the production period, the content of formation water will increase and the content of H₂S may also increase. Contact or connection between different materials may generate an electric potential difference. Some formations or intervals may generate an electric potential difference with casing. Electric potential difference is an important component part of the oil and gas well corrosion environment.

The stress state and stress level of structural members (such as tubing, casing and wellhead assembly) are important in the corrosion environment.

Corrosion Mechanism

The deterioration or failure by chemical or electrochemical action generated between metal and its environmental media is known as metallic corrosion[4,5]. The mechanisms or types of corrosion during oil and gas well production include: 1. Electrochemical corrosion; 2. Chemical corrosion; 3. Environment-assisted fracture and stress corrosion; 4. Flow- and phase change-induced corrosion.

Electrochemical Corrosion

Tubing, casing, and equipment made of steel are good electric conductors. Various salts or CO₂ and H₂S, and so on, are dissolved in the water that oil and gas well fluid produced contains. When steel contacts the aforementioned media, the protective metal-oxide film that has been formed in air may be dissolved in an electrolyte solution. When metal is exposed, the metal as a good electric conductor and the solution as a good ionic conductor form a return circuit. Ferrous ions with positive charges tend to dissolve in electrolyte solution and form ferrous salts. Electrons tend to congregate at the metal end and a certain electric potential difference is formed. Electrons flow toward the solution. This is an oxidation reaction process and is known as anodic reaction. The metal end is known as the anodic area. In addition, the electrons that enter solution are bound with hydrogen ion, and hydrogen molecules are formed. This is a reduction reaction process and is known as cathodic reaction. The solution end is known as the cathodic area. In an aerobic environment, hydroxide radicals are formed[6].

Proper selection of the material of tubing is a key problem in corrosion prevention of oil and gas wells. Improper selection of material may not only cause waste, but it may also generate unsafe conditions.

Effect of coexisting hydrogen sulfide and carbon dioxide on corrosion

Sulfide-containing well production practice indicates that when sulfide-resistant carbon steel or low-alloy steel is selected, electrochemical corrosion (metal thinning and pitting corrosion, and so on) will be predominant in comparison with corrosion due to coexisting H₂S and CO₂. Electrochemical corrosion is not fully dependent on the contents and partial pressures of H₂S and CO₂ due to the interaction of corrosive components and is related to the specific dynamic corrosion environment of each gas reservoir. There may be differences between laboratory evaluation and the on-site situation and greater differences between software prediction and the on-site situation. Software prediction may overestimate corrosion severity.

The effect of hydrogen sulfide on carbon dioxide corrosion includes two aspects. Hydrogen sulfide may speed up carbon dioxide corrosion due to cathodic reaction and mitigate corrosion due to FeS precipitation. The change is directly related to temperature and hydrogen sulfide content. In general, at low temperature (30 °C), a small quantity of hydrogen sulfide (0.2%) may doubly speed up carbon dioxide corrosion, while high hydrogen sulfide content (such as 21.5%) may reduce the corrosion rate. At high temperature, the corrosion rate is lower than that of pure carbon dioxide when hydrogen sulfide content is higher than 2.1%. When temperature is higher than 150 °C, the corrosion rate may not be affected by hydrogen sulfide content. At the same time, low hydrogen sulfide concentration may aggravate corrosion because hydrogen sulfide may directly attend the cathodic reaction, while high hydrogen sulfide concentration may mitigate corrosion because hydrogen sulfide may react with iron to form FeS film. In addition, hydrogen sulfide may greatly reduce the corrosion resistance of the corrosion-resistant steel, which contains Cr, to cause serious local corrosion and even stress corrosion cracking.



Fig.1: Producing system corrosion of natural gas well under adverse corrosion environments

The produced gas with high content of CO₂, H₂S, and elemental sulfur, and so on, in some gas wells make the corrosion in the gas production system and station and field equipment very serious. In general, hydrogen sulfide-containing natural gas also contains a certain quantity of carbon dioxide [4]. Fig.1 is the producing system corrosion of natural gas well under adverse corrosion environments.

CORROSION PREVENTION FOR SOUR GAS RESERVOIRS

Tubing and casing corrosion control for sour gas reservoirs is a type of system engineering. Metal material or corrosion inhibitor alone cannot achieve the desired corrosion control effectiveness, and corrosion-resistant material (metal and nonmetal), chemicals, cathodic protection, and coating should be comprehensively applied. In oil and gas fields, the application of corrosion-resistant metal material has obtained obvious effectiveness in combination with corrosion inhibitor.

Proper selection of the material of tubing, casing, downhole accessories, Christmas tree, and surface equipment is a key problem in corrosion prevention of oil and gas wells. Improper selection of material may not only cause waste, but it may also generate unsafe conditions. Carbon steel and low-alloy steel are commonly used in sour environments of hydrogen sulfide[7]. Environment-assisted fracture should be predominantly considered when the material is selected in corrosion prevention design that is in light of sour environments of hydrogen sulfide. The ISO 15156-2 standard can be used for selecting the cracking-resistant material in a sour environment. After sulfide-resistant carbon steel and low-alloy steel are selected, electrochemical corrosion should be emphatically considered. A corrosion inhibitor may be used for preventing or mitigating electrochemical corrosion. Its feasibility is dependent on technical feasibility, reliability, and risk assessment; medium- and long-term cumulative investments and rate of return; and the cost of replacing tubing during well servicing and the loss assessment.

APPLICATION

In this paper, we take YB-L gas field as an example, which is a typical sulfide containing gas field. Statistics generated from the natural gas analytical data of gas wells at YB-L Gas Field shows that the content of methane, as the principal constituent of natural gas, is generally 8.3%~10.2%, with the average of 9.4%, and the content of carbon dioxide is generally 4.6%~8.9%, with the average of 6.5%. The average relative density of natural gas is 0.676.

It can be observed from the above that YB-L gas reservoirs are principally of methane, being dry gas reservoir with high-hydrogen sulfide-content and moderate carbon dioxide content.

Application status of down hole tubing

For down hole tubing application status of the completed gas well of YB-L Gas Field, please refer to Table 1.

Table 1: Application Status of Down hole tubing of YB-L Gas Field

Well Code	Basic Status	Material Used for Lowered Down Tubing at Present
YB-L No.1	Well completion done	VM80SS
YB-L No.2	Well completion done	G3-110
YB-L No.3	Well completion done	G3-110
YB-L No.4	Well completion done	NKAC80SS

Application plan of corrosion inhibitor

1. Corrosion types and their influences

1) Corrosion type

a. Down-hole corrosion type

Since natural gas in the down-hole tubing contains free water, H₂S and CO₂, electrochemical corrosion and sulfide stress cracking (SSC) on the inner wall surface of the tubing are unavoidable. Normally SSC is dealt with by way of careful selections of material and the fabrication process of the tubing, and the problem of electrochemical corrosion is solved by adding corrosion inhibitor (for normal sulfur resisting carbon steel).

b. Corrosion types of gathering and transmission pipeline

Electrochemical corrosion, sulfide stress cracking (SSC) and hydrogen induced cracking (HIC) might occur in the gathering and transmission pipeline on the ground. Principally, SSC and HIC are resolved by way of careful selections of material and the fabrication process of the pipes. The problem of electrochemical corrosion is generally resolved through adding of corrosion inhibitor.

2) Influences

a. Influence of temperature

After going through water-jacketed heater, the temperature of well-head feed gas is 50°C or so, dropping to about 24°C before arriving at dehydration device. As long as electrochemical corrosion is concerned, temperature from 50 to 80°C is a sensitive temperature range. For SSC and HIC, normal temperature is the sensitive temperature range, however.

b. Influence by flow velocity

Too high flow velocity can result in erosion corrosion on the valves and other equipment on one hand, and on the other hand, the iron sulfide on the inner wall surface of the pipe, which is the corrosion product, will be damaged by washing out reaction or made unable to adhere firmly to the wall. As a result, the inner wall surface is corroded rapidly at the initial corrosion rate. Too low flow velocity can cause collection of liquid in the pipeline and in the equipment, resulting in water-line corrosion and under-deposit corrosion, etc. As a result, localized corrosion damage occurs. Flow velocity is generally controlled at 3~8m/s.

c. Influence by elemental sulfur

Under high-acid environment, elemental sulfur is highly corrosive. It can expedite the corrosion of material at the contact point if contacted with the material of the pipe.

2. Corrosion-proof plan in the completed well

1) Corrosion-proof plan of corrosion-resistant alloy tubing and normal sulfur-resistant tubing

The project chooses corrosion-resistant alloy tubing material to solve corrosion problem (SSC and electrochemical corrosion) of tubing. Normal sulfur-resistant carbon steel (VM80SS and NKAC80SS) will be used for well completion of 3 wells, i.e. YB-L No.11, YB-L No.14H and YB-L No.16H-1 (YB-L No.14H well is provided with capillary tube filling system). SSC-resistant capacity of the tubing is solved through material selection. Electrochemical corrosion problem in the production process can be solved by way of adding corrosion inhibitor.

For YB-L No.14H well provided with capillary tube filling system, method of continuous filling of corrosion inhibitor can be adopted, the quantity of inhibitor shall be determined according to production allocation of the well. For YB-L No.11 and YB-L No.16H-1 wells, filling of corrosion inhibitor in the tubing can be completed at one time only, the quantity of inhibitor shall be determined according to production allocations of the wells.

2) Corrosion-proof plan of filling corrosion inhibitor in casing-tubing annulus

When a corrosion inhibitor is used, a protective film should be rapidly generated on the metal surface as fast as possible; otherwise, a large quantity of corrosive product may be formed to disturb the formation of backwall. If some part of the surface has not been protected, corrosion may be aggravated and pitting corrosion may be generated.

Different media or steels often require different corrosion inhibitors [7]. Even for the same type of medium, the corrosion inhibitor used may also be required to be changed when the operating conditions are changed. During oil and gas production from bottomhole to wellhead and then to treatment plant, temperature, pressure, and flow velocity may be greatly changed. Deep gas wells have high bottomhole temperature and pressure. Different production periods of oil and gas wells have different proportions of oil, gas, and water. In general, with the increase of water production, failure by corrosion may be aggravated. In order to select correctly the corrosion inhibitor that is appropriate for the specific system, not only should the media composition, operational parameters, and possible types of corrosion in the system be considered, but also the necessary evaluation tests of corrosion inhibitor are required in accordance with actual use conditions (Tables 2).

TABLE 2 Static Selection Results of Different Types of Corrosion Inhibitors at 120 °C

Corrosion Inhibitor	Addition (mg/l)	Phase State	Corrosion Rate (mm/a)	Inhibitor Efficiency (%)	Surface State of Coupon
No corrosion inhibitor	0	Gas	0.8382	0	Pitting corrosion
		Liquid	0.4832	0	Pitting corrosion
CT2-1	1000	Gas	0.1610	80.8	Local corrosion
		Liquid	0.3899	11.5	Local corrosion
CT2-4	1000	Gas	0.3670	56.2	Local corrosion
		Liquid	0.2640	45.4	Uniform corrosion
BT-1	1000	Gas	0.1701	79.7	Local corrosion
		Liquid	0.0798	83.5	Pitting corrosion

The application of corrosion inhibitors (CT 2-1 and CT 2-14) in YB-L gas field has obtained good effectiveness. YB-L No.1, 6 and 7 wells have all been filled with independently developed annular protection liquid, which is found to be of good effect as verified from the inspections made on the status of the drawn out oil tubing.

a. Selection of annular protection liquids

Water-base annular protection liquid: Water solution of annular protection liquid with water-soluble corrosion inhibitor CT2-4 as the main constituent is recommended. The application concentration of CT2-4 inhibitor shall be 10%.

Oil-base annular protection liquid: Diesel annular protection liquid with oil-soluble corrosion inhibitor CT2-1 as the main constituent is recommended. The application concentration of CT2-1 corrosion inhibitor shall be 5 to 10%. It is recommended that oil-base annular protection liquid to be used in the newly completed wells in the future.

b. Filling process of annular protection liquid

The annular protection liquid is filled with fracturing truck. The quantity of annular protection liquid required can be calculated according to the volume of the annulus space.

CONCLUSION

For natural gas well in sour gas reservoirs, very serious corrosion in the well producing system is an important factor of gas production system life. In order to ensure the long-term development of gas wells, this paper mainly introduces material corrosion prevention technology in the well producing system, such as corrosion-resistant alloy steel corrosion control technology, corrosion inhibitor technology and so on. By taking YB-L Gas Field as an example, statistics generated from the natural gas analytical data of 9 gas wells at YB-L Gas Field shows that the content of hydrogen sulfide is 8.3% ~ 10.2%, with the average of 9.4%, and the content of carbon dioxide is generally 4.6% ~ 8.9%, with the average of 6.5%. The average relative density of natural gas is 0.676. It can be observed from the above that YB-L gas reservoirs is a typical sulfide containing gas field under adverse corrosion environments. By taking YB-L Gas Field as an example, this paper introduces the material corrosion prevention technology in the completed well system in YB-L Gas Field. For application in the completed well system in YB-L Gas Field, the technology above have good performance of corrosion resistance. The study above has a good applicability by testing, and can provide reference for corrosion preventing of the similar high sour gas fields under adverse corrosion environments.

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