

Analysis on Influence of High Temperature on Morphology Features of CO₂ Corrosion Product Film

Zhengmao Chen

Management School, China West Normal University, Nanchong, 637000, China

Abstract: At current stage, the CO₂ corrosion is very common in oil and gas pipeline, which brings great economic loss and disastrous consequence on oil industry. Through testing on materials from oil and gas field Chuandong gas field and Tarim gas field, this paper makes an observation on morphology features of CO₂ corrosion product film, and makes a conclusion for the influence of high temperature on the morphology features of CO₂ corrosion product film.

Key words: high temperature; CO₂ corrosion product film; morphology; feature; influence

In the oil and gas production system of oil and gas field, CO₂ mainly has two sources: on one hand, it exists in oil and gas as one of compositions of natural gas or crude oil; on the other hand, because CO₂ is used to enhance mining technology in crude oil production-increasing technique, CO₂ is brought into drilling, extracting, gathering and transportation system. Under the temperature of oil and gas production system, in normal dry environment, CO₂ will not corrode steel; however, in humid environment, it is very easy to have a partial and even comprehensive corrosion on steel. This paper gives a discussion based on Chuandong gas field and Tarim gas field.

I. Test materials and test method

The metal materials used in the test are oil, casing steel P110, J55, and N80 which are commonly used in Chuandong gas field and Tarim gas film, and the compositions are shown as below respectively:

Serial No.	C	Mn	Si	P	Cr	S	Mo	Ti	Ni	Cu
P110	24	119	22	1.3	3.6	0.4	2.1	1.1	2.8	<1.9
J55	19	139	31	1.4	1.9	0.4	9.2	4	1.7	<1
N80	26	140	20	0.9	1.5	0.3	1	3	1.2	<1

The steel shall be processed into sheet and then polished via abrasive paper for metallograph. After

being polished, the steel shall be washed and then have deoiling via acetone, and then it can be used after it is dry.

The test equipment is American static-state high-temperature autoclave; the test specimen is hung on specimen frame which is placed into autoclave; and then the corrosion medium is placed into autoclave and the equipment is sealed; the nitrogen is added to remove oxygen for 6 hours, and then CO_2 is added for 8 hours. As the temperature continuously rise, it is required to regulate CO_2 gas and keep the pressure within 1.4-2.1MPa after the scheduled temperature is reached, and the corrosion time is set as 4 days. After completion of test, the distilled water is used to wash away the corrosion medium on surface of material, and the anhydrous alcohol is used to remove the water; after the corrosion medium is dry, it is placed in the dryer for standby application.

The SEM observation is applied to observe the morphology of corrosion product, and the scanning condition is longitudinal scanning; later, the ruler attached on electron microscope is used to measure the scanned picture and obtain the size of surface grain and film thickness.

II. Observation on morphology and structure of corrosion product film after test

(I) Morphology features on surface of corrosion product film

It can be seen that the corrosion product films obtained from 3 kinds of materials are dark brown, and their main component is FeCO_3 , as well as few Fe_2O_3 , Fe_3O_4 and CaCO_3 or Fe. The crystal structure of FeCO_3 is very similar to the morphology of CaCO_3 we commonly see, and it can form compound salt structure or isomorphous mixed crystal.

The crystallization on the surface of corrosion product films obtained from these 3 kinds of materials is most regular at 100 °C, and then

as the temperature rises; this is because FeCO_3 has decomposition function, and the solubility of FeCO_3 has negative temperature effect. When there is no change in the pressure of CO_2 , the solubility and corrosion rate of FeCO_3 determine the concentration of Fe^{2+} in the solution.

While the temperature is higher than 150 °C, the corrosion rate will decrease with temperature rise, which is caused by the corrosion inhibition of film; with the temperature rise, the solubility of FeCO_3 will gradually decrease, but its decrease degree is still larger than the decrease degree of corrosion rate; in this way, the deposition rate is larger than dissolution rate, and the deposition process of FeCO_3 crystal is not under a dynamic balance between deposition and dissolution. With the temperature rise, the gap between them is gradually expanded, the grain becomes smaller and

smaller, and the crystalline form becomes more and more irregular.

With continuous temperature rise, the decomposition degree of FeCO_3 continuously expands, and the crystalline form also changes with the addition of content of Fe_2O_3 and Fe_3O_4 in the crystal. There are also some other factors: for example, there are mutual winding and crossing between crystals, the surface space is not fixed or suffers certain limitations, all of which will cause incomplete shape of crystal. Therefore, the complete crystal particles are few.

(II) Longitudinal morphology features of corrosion product film

As for J55 steel, while the CO_2 pressure is 4MPa and the temperature is 90°C , the longitudinal morphology in SEM reflects there are 2 layers of CO_2 corrosion product films on the surface of metallic matrix; the crystal particles on one layer are relatively regular, and there is also a kind of solid film outside, just like mud, and it exists between external layer and metallic matrix and it is called secondary film. Although these 2 layers are different, there is no great difference between them; the secondly film mainly includes FeCO_3 , as well as Fe_3C left after the metallic matrix is corroded, and few Fe_2O_3 and Fe_3O_4 .

As for P110 steel, under the condition that CO_2 pressure is 0.8MPa and the temperature is 100°C , it is shown via SEM that the corrosion resistance phenomenon appears in partial steel; this is because the large hole and gap appear in the structure of corrosion product film formed on metallic surface; when there are large hole and gap in the film, the corrosion medium can contact partial metallic surface, and then the partial corrosion happens.

(III) Superficial morphology features of secondary film after damage on corrosion product film

As for J55 steel, under the condition of 1MPa CO_2 pressure and a temperature of 80°C , some crystal particles on the margin extrude each other in the formation process, which causes the phase separation with internal layer; this result is caused by surface blistering of corrosion film. In the test, a kind of aciform crystal is observed; it is not the shape after the internal-layer solid film falls off, but the crystal formed on the surface of internal layer after the surface-layer film falls off under the condition that the FeCO_3 in corrosion medium exceeds saturated degree. Due to corrosion inhibition of CO_2 corrosion product film, the crystallization and dissolution happen at the same time; in this way, the aciform crystal is formed on the internal-layer surface.

The new superficial film is formed from the surface of original secondary film, thus we can imagine that the secondary film is formed between corrosion medium and superficial film after the

corrosion medium reaches the matrix surface. However, the previous superficial film is formed at an early time, and there is large binding force between new superficial film and original secondary film.

III. Influence of temperature on morphology feature of corrosion product film

(I) Influence of temperature on thickness of corrosion product film

Under the condition of 1.4-2.1MPa CO₂ pressure, the thickness of corrosion product film changes with the temperature; it shall be noted that the thickness of corrosion product film measured via SEM is an average value under general condition, and such value can't stand for all conditions. As for the above 3 kinds of materials, they have a roughly consistent curve of change of thickness of corrosion product film as the temperature and all curves are S shape, with a maximum value and a minimum value.

While the temperature is lower than 120°C, the thickness of corrosion film is in direct proportion to the temperature, and N80 and J55 steel have a more obvious change than P110 steel; under this temperature, the corrosion film obtained via N80 and J55 steel is also thicker than that obtained via P110 steel. While the temperature is within 120°C~200°C, the thickness of corrosion film varies as the temperature corresponding to the change low-ebb of temperature; for example, when N80 and J55 steel are at 160°C, P110 steel is at 180°C; although the thickness of corrosion film is minimum while N80 steel is at 160°C, such thickness is almost equal to the thickness while N80 steel is at 180°C.

While the general iron-base alloy has a temperature below 60°C, the main component of its corrosion product film is FeCO₃, and the corrosion belongs to uniform corrosion; the metallic surface is smooth and soft without adhesive force, thus the starting point of test temperature shall be selected at 80°C. Therefore, the Fe²⁺ concentration increases as the increase of solubility and corrosion rate of FeCO₃ solution. However, the corrosion rate still depends on the influence of film formation corrosion inhibition and temperature on corrosion rate; if these two opposite factors have larger opposite degree, the corrosion rate will be larger, which shows that the temperature is higher, the compactness of film formation is thicker and thicker, and the corrosion rate is smaller accordingly.

In general, the film grain of P110 steel has a small size and large density in same temperature interval, thus the grain is compactly arranged; in some places, there is only small accumulation

space, thus the partial corrosion is serious. By comparison, the corrosion product film of P110 steel is thin, but the corrosion product film in partial area may be thick.

(II) Influence of temperature on grain size of corrosion product film

In the test of simulating CO₂ corrosion product film, the grain size measured is just an average value which can't stand for all conditions. These 3 kinds of materials have a similar aspect, that is, the quantity of grains decreases while the temperature rises, but this situation is temporary, and then the quantity of grains will increase, with a minimum value and a maximum value; these two values are corresponding to the peak and low ebb of film thickness in temperature change. As for these 3 kinds of materials, their maximum grain value appears at 80°C, but the minimum value appears at different temperature; as for N80 and J55 steel, the minimum value appears at 160°C, but the minimum value for P110 steel appears at 180°C. The place with the minimum film formation grain is the place with the thinnest film, and the corresponding temperature is the temperature at which the iron-base metallic materials have the strongest compactness, thus the film thickness and grain of these 3 kinds of materials change with the temperature. In other words, at the temperature of the strongest compactness, the corrosion product film formed can effectively prevent the medium from diffusing on surface of metallic matrix; besides, the strong adhesive force and compactness can mitigate metallic matrix to suffer further corrosion.

It can be found via the test that the grain size on the surface of corrosion product film of these 3 kinds of materials shows a shape of inverted S with the temperature change. Upon testing, while the temperature is within 80°C ~ 180°C, the grain of corrosion film of P110 and N80 steel is very small; with the temperature change, the grain also slowly changes accordingly, which shows that the grain size of these 2 kinds of materials is not sensitive to the temperature change. However, the average grain size of corrosion film of J55 steel changes greatly with temperature change; based on the average situation, the grain is thick, which shows that this material is sensitive to the temperature change.

Besides, upon high temperature (such as 180°C), there is a similar change in grain size of corrosion film formed by these 3 kinds of materials with the temperature change, that is to say, there is a small increase; therefore, the grain size of CO₂ corrosion product film formed by these 3 kinds of materials has not strong sensibility to the temperature change.

IV. Conclusion

In recent years, there are some progresses in research on CO₂ corrosion, but the research is still not deep; in the process of developing the oil gas construction with acid gas corrosion medium in oil and gas field, there are many factors influencing the corrosion; as for equipments, the damage caused by CO₂ corrosion is often partial corrosion, and the corrosion rate and corrosion form are determined by corrosion product film, thus this research is very necessary. In the oil and gas development of Chuandong gas field and Tarim gas field, the attention shall be also paid to some problems such as humid acid gas environment.

Acknowledgments

This paper is the basic application project of Sichuan Provincial Department of Science and Technology (project title: Safety Assessment on Sulfur Gas Well under Annular Pressure; project No.: 2013JY0093).

References

- [1] Lin Guanfa, Xu Xunyu, Bai Zhenquan, Feng Yaorong: Analysis on Energy Spectrum of CO₂ Corrosion Product Film of 13Cr Oil Casing Steel [A], Collected Papers (I) of The 7th National Surface Engineering Academic Conference & The 2nd Surface Engineering Youth Academic Forum [C], 2008.
- [2] Sun Jianbo, Liu Wei, Chang Wei, Zhang Zhonghua, Xu Lining, Zhang Lei, Lu Minxu: Features and Formation Mechanism of CO₂ Corrosion Product Film of Low-chromium X65 Pipeline Steel [A], Special Issue of The 6th Corrosion and Protection Technology Academic Exchange of Shandong Petroleum Society, [C], 2008.
- [3] Deng Hongda, Li Chunfu, Cao Xianlong: Influence of CO₂ on Hydrogen Embrittlement Behavior of P110 Casing Steel under High H₂S Content [A], Collected Papers of 2010 China – Chongqing 7th Surface Engineering Technology Academic Forum & Exhibition [C], 2010.
- [4] Zhao Yan, Lin Changjian, Hu Ronggang, Du Ronggui, Wang Jingrun: Research on Corrosion Electrochemistry Behavior of Copper Clad Laminate in NaCl₂ Solution [A], Collected Papers of 2006 National Corrosion Electrochemistry and Test Method Academic Conference [C], 2006.
- [5] Ibrahim, Yu Guoxian, Wang Ping, Zhou Xiaolong: Influence of Oleophylic Chain Structure of Imidazoline Derivative on Its Corrosion Inhibition in Saturated CO₂ Solution [A], Collected Papers of 2008 Academic Annual Conference of Shanghai Chemistry and Chemical Engineering Society [C], 2008.
- [6] Chen Changfeng, Zhang Zhonghua, Guo Jinbao, Lu Minxu: Development Status of Economic

Low-Cr CO₂ Corrosion-resisting Alloy Petroleum Tubular Steel [A], Collected Papers of The 3rd Corrosion and Protection Technology Academic Exchange of Shandong Petroleum Society [C], 2005.

[7] Jin Lei, Wang Xinqiang, Zhao Xingqiang, Zhang Wenting, Guo Pei, Fang Liang: Research on Formation Process of Carbon Steel Phosphate Film [A], Collected Papers of 2007 High-tech Materials Industrial Development Seminar & Annual Meeting of Materials Review Editorial Board [C], 2007.

[8] Wu Hongyan, Zhou Qiongyu, Zhong Qingdong, Sheng Minqi, Wang Yi, Lin Hai: Array Electrode Research – Influence of F on Corrosion Electrochemistry Behavior of Copper in Na₂SO₄ Solution [J], The Chinese Journal of Nonferrous Metals, 2011 (07).

[9] Chen Wu, Meiping, Ai Junzhe, Gao Qiuying: Research Progress in CO₂/H₂S Coexistence Corrosion and Corrosion Inhibition Technology [A], Collected Papers of 2006 Annual Meeting of Hubei Chemistry and Chemical Engineering Society & Circular Economy Expert Forum [C], 2006.

[10] Hao Shengzhi, Zhang Xiangdong, Wu Pingsheng, Wu Aimin, Gao Bo, Zou Jianxin, Qin Ying, Dong Chuan: Influence of High Current Pulsed Electron Beam Irradiation Treatment on Superficial Tissue and Performance of Steel and Magnesium Alloy [A], Collected Papers of 2006 National Charged Particle Source and Particle Beam Academic Conference [C], 2006.