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Material selection research into casings in natural gas wells in a high-corrosion environment

Yifei Yan[2,6], Bing Shao[2], Shengli Song[3], Jianjun Wang[4], Xiangzhen Yan[5]

Abstract. The different guidelines of five companies in three countries and the material selection method for oil country tubular goods (OCTG) are analyzed in a high-corrosion environment in which CO_2 and H_2S coexist. The main factors that influence such material selection are also generalized. The OCTG material selection software is developed on the basis of relevant guidelines. The research on material selection and operation steps is conducted. The main factors that influence the material selection for OCTG are H_2S pressure, CO_2pressure, temperature, and Cl^- content. The safety and corrosion-resistant properties of different materials recommended by six guidelines in specific sour conditions are compared to develop synthetic guidelines and optimum suggestions. Three high-gas wells in the Xinjiang oil field are used as examples. Results of the five guidelines and those of the synthetic guidelines are obtained, and the formula to calculate the anti-corrosion characteristic of the materials is shown. The material selection method is determined with the different characteristics of the materials.

Key words. CO_2 and H_2S, sour environment, oil country tubular goods, material selection, corrosion gas.

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[2]Workshop 1 - College of Mechanical and Electronic Engineering, China University of Petroleum, Qingdao,Shandong, 266580, China

[3]Workshop 2 - Petroleum Engineering Technology Research Institute of Zhongyuan Oilfield. Sinopec,Puyang,Henan, 457001, China

[4]Workshop 3 - CNPC Tubular Goods Research Institue, Xi'an Shanxi 710077, China

[5]Workshop 4 - Oil and Gas CAE Technology Research Center, China University of Petroleum, Qingdao,Shandong, 266580, China

[6]Corresponding author: Yifei Yan; e-mail: `yanyf163@163.com`

1. Introduction

For a long time, corrosive gases such as CO_2 and H_2S in oil and gas fields have caused substantial damage to tubing and casing strings and have considerably reduced the security and reliability of these components. Traditional carbon steel materials such as API, N80, and P110 have been mostly used in acidic gas fields. However, strings made from these materials are ineffective in a production environment with high temperature and high CO_2/H_2S concentrations. This characteristic leads to unnecessary production losses.

Corrosion resistant alloys (CRAs) are increasingly being used to reduce the losses caused by the corrosion of CO_2 and H_2S. Currently, numerous studies pay attention to the condition in which either CO_2 or H_2S is present, but the condition in which these gases coexist is rarely explored. The guidelines for the selection of CRAs are mainly regulations or references used by oil companies and enterprises. These guidelines are scattered and not systematic [1–2]. Therefore, additional studies must be conducted on the selection of appropriate CRAs under a corrosive environment. In addition, the cost of CRAs with different levels varies. Hence, the scientific and suitable selection of the materials of tubing and casing strings can effectively prevent and reduce string damage caused by acidic conditions, minimize risks of safety accidents during the exploitation of oil and gas fields, and save production cost.

A few computing models for steel corrosion rate consider the coexistence of CO_2 and H_2S. On the basis of the models of De Waard and Mishra for the sole existence of CO_2 or H_2S and the data obtained from autoclave simulative experiments [4–5], a computing model for corrosion rate that considers the coexistence of CO_2 and H_2S can be established as follows:

$$\ln r_{corr} = A - \frac{Q}{KT} + \frac{B}{T} - C \cdot \mathrm{pH} + D \cdot \left[1 - \exp\left(-\frac{Q'}{P_{H_2S}}\right)\right] \ln P_{CO_2} \qquad (1)$$

where $A, B\ C\ D\ E\ F\ G$ are the constants and coefficients based on the experimental data that consider the influence of solution flow rates and ions, such as Cl^-, Mg^{2+}, and Ca^{2+}; Q' is the activation energy for the formation of the FeS film, and K is the universal gas constant.

The corrosion rate of steels in conditions in which CO_2 and H_2S coexist is related to factors such as the partial pressures of CO_2 and H_2S, temperature, pH, concentration of Cl^-, and so on. The guidelines for the selection of materials widely used today are also based on these conditional parameters.

2. Materials and Methods

2.1. Sumitomo selection criterion

The Sumitomo selection criterion is widely used worldwide. The steel used in the acidic environment of Chinese oil and gas fields is mainly from the Sumitomo

Corporation. The Sumitomo Metal Company has developed a series of products to meet the stringent requirements of material properties in an acidic environment. Fig. 1 shows the Sumitomo selection criterion for an acidic environment.

With the Sumitomo criterion, materials are selected according to the partial pressures of CO_2 and H_2S. Temperature and Cl^- concentration are used as constraint conditions. For example, the service temperature of SM 13CRS-80 should not be higher than 175 C, and SM 9CR should be used in case the concentration of Cl^- is less than 50,000 ppm. Additionally, the valid parameter range of the Sumitomo Module is extensive. The valid range of the partial pressures of CO_2 and H_2S reaches 100 MPa, and the limitative temperature reaches 300 C. The Sumitomo Company has also developed new SM-Series steels with excellent performance in high temperature, high CO_2/H_2S pressure, and high Cl^- concentration environment to prevent the corrosion of CO_2 and H_2S. Such development is one of the reasons for the extensive application of the Sumitomo guidelines.

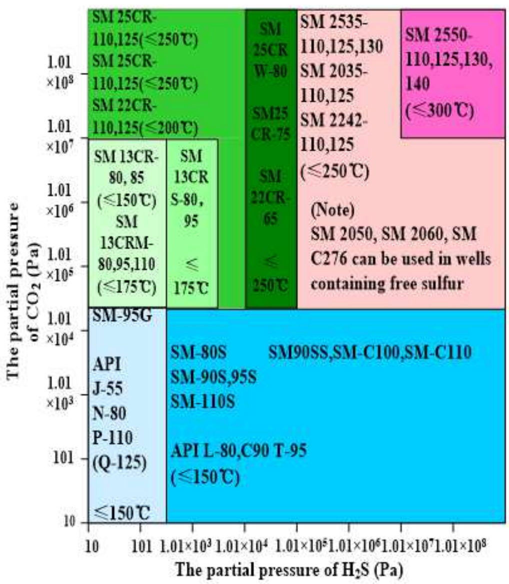

Fig. 1. Material selection program of the Sumitomo Metal Company (Japan)

2.2. *Kawasaki selection criterion*

With the Kawasaki selection criterion, materials are selected according to the partial pressures of CO_2 and H_2S, temperature, and pH; the effect of Cl^- concentration is excluded. Temperature and pH are secondary parameters that serve as necessary inputs in a specific CO_2/H_2S pressure range. These inputs can be used according to software guidelines. The selection scheme is shown in Fig. 2. The Kawasaki Module is partly similar to the NKK Module, that is, a certain temperature limit exists when the partial pressure of CO_2 is greater than 345 Pa.

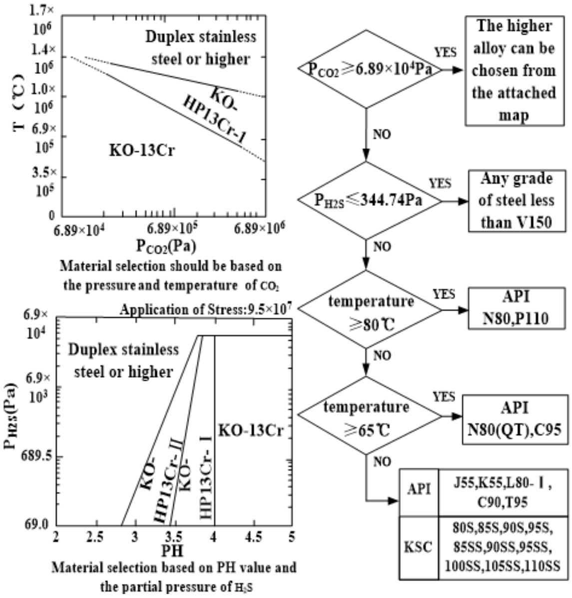

Fig. 2. Material selection program of the Kawasaki Company (Japan)

3. Results

The Xinjiang oil field is one of the main working districts of the China National Petroleum Corporation. The working environment in this oil field is severe, and the casing completion of complex deep wells is in a high-temperature, high-pressure, and high-acid environment. The environmental parameters based on known environmental conditions are shown in Table 5. The recommended materials for well completion are as follows: SM 2535/SM 2242 for T: 132 C–149 C and $P_{H2S}<$ 1.4 MPa or T < 132 ?C when no free sulfur exists; SM 2535/SM 2242 for T < 132 C, SM 2550 for T: 132 C–149 C when free sulfur exists.

Table 1. Environmental parameters

Partial pressure of CO_2	Partial pressure of H_2S	Temperature	Cl^- concentration
15 MPa	1.4MPa	150 C	15,000 ppm

The environmental condition is specified in No. 33 of Table 3, and the different selection criteria are shown in Table 6.

Table 2. Recommended materials of different material selection criteria

Selection criterion	Selection results
Sumitomo selection criterion	SM 2535-110, 125, 130; SM 2035-110, 125; SM 2242-110, 125 (250 C) Note: SM 2050, SM 2060, and SM C276 can be used in wells that contain free sulfur.
NKK selection criterion	The NK NIC series of high-nickel alloys, SANICRO 28 (27% Cr–31% Ni–3.5% Mo), INCONEL 825 (22 Cr–42 Ni–3 Mo)
Kawasaki selection criterion	Beyond the scope of the evaluation
DMV selection criterion	Austenitic steel DMV 928 (27 Cr–32 Ni–3.5 Mo); DMV C-276 (C-276; AlloyC -276) also applies to a free sulfur-containing environment.
Cabval selection criterion	ALLOY 825 (nickel–iron–chromium alloy 42 Ni–22 Cr–3 Mo)

The materials in Table 6 are all high-alloy steels, and they can be discussed in terms of the existence of free sulfur.

4. Discussion

On the basis of the analysis and comparison, we obtain the following suggested materials: SM 2535, SM 2035, SM 2242 (ALLOY 825), or DMV 928 without free sulfur; SM 2050, SM 2060, or SM C276 with free sulfur, which correspond to the materials selected with the synthetic module.

Currently, the pitting resistance equivalent number (PREN) [6] is widely used to compare the corrosion resistances of different alloys.

A large PREN generally equates to good corrosion resistance. The standard formula (Equation. (2)) is used to calculate the PREN of stainless steel.

$$\mathrm{PREN} = \omega_{\mathrm{Cr}} + 3.3\left(\omega_{\mathrm{Mo}} + 0.5\omega_{\mathrm{W}}\right) + 16\omega_{\mathrm{N}} \tag{2}$$

where ω_{Cr}, ω_{Mo}, ω_{W}, and ω_{N} refer to the respective percentages of alloy.

The abovementioned formula does not apply to nickel-based alloys, whereas Eqation. (3) provides the formula to calculate the value of PREN for Ni–Cr–Mo alloy in a variety of media [7].

$$\mathrm{PREN} = \omega_{\mathrm{Cr}} - 0.8\omega_{\mathrm{Cu}} + 1.5\left(\omega_{\mathrm{Mo}} + \omega_{\mathrm{W}}\right) \tag{3}$$

The PREN of materials selected with different selection criteria can be calculated by the abovementioned formula. With the use of the standard NACE MR0175/ISO 15156, the restrictions for the maximum temperature, maximum H_2S partial pressure, maximum chloride content, and pH can be provided.

Without consideration of material strength, the most conservative selection program can be determined from the analysis and calculation, that is, DMV 928/SANICRO 28 without free sulfur and DMV C-276/SM C276 with free sulfur. The comprehensive selection program provides not only the recommended materials with different selection criteria but also the most conservative materials.

In general, a high alloying element content equates to the good performance of CRAs. However, the cost can be considerably high. Therefore, economic factors should be considered in making the final selection. Given that the material selection methods proposed in this study are established on the basis of safety and corrosion resistance, the most conservative scheme is also the most costly scheme. In this case, the most inexpensive materials are SM 2242 without free sulfur and SM 2050 with free sulfur. Hence, we can conclude that SM 2535 or SM 2242 is suitable when no free sulfur exists and that SM 2050 is suitable when free sulfur exists.

5. Conclusion

The differences between six different selection specifications are compared, and the safety and steel corrosion resistance of proper materials are analyzed according to the norms and standards under acidic conditions. We find that the partial pressure of CO_2 and H_2S, temperature, and chloride concentration are the main factors that influence the selection of OCTG. The application scope of the Sumitomo selection criterion and the DMV Module is broader than that of the other selection criteria.

The corresponding selection software is developed to achieve the selection of different pipes during the process of well completion under different environmental conditions. Thus, users are provided with multiple choices while meeting the requirements of safety and corrosion resistance. The Xinjiang oil field is used as an example to describe and generalize the typical methods of the comprehensive selection program. The PREN formula is presented to measure the corrosion resistances of materials. Specifically, it provides the corresponding SM criterion when free sulfur exists, as well as then DMV criterion when no free sulfur exists.

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