Influence of upgrading natural gas quality standard on purification plant

Chaoyue Yang¹²*, Wenzhao Zhu¹², Linfeng Li¹², Jinjin Li¹² and Xianglin Wang³

¹ Research Institute of Natural Gas Technology, PetroChina Southwest Oil & Gasfield Company, China
² National Energy R&D Center of High Sulfur Gas Exploitation, China
³ Natural Gas Purification Plant General, PetroChina Southwest Oil & Gasfield Company, China

*Corresponding author. Email: yangchaoyue@petrochina.com.cn

Abstract. GB 17820-2018 has been formally implemented, which puts forward higher requirements for the quality index of natural gas entering the long-distance pipeline network. It is required that the H₂S in the first type of natural gas should be less than 6mg/m³ and the total sulfur should be less than 20mg/m³. Because of the high content of organic sulfur in feed gas, MDEA desulfurization can not meet the standard requirements in some purification plants. At present, sulfolamine solvent desulfurization, COS hydrolysis process and molecular sieve desulfurization process are often used to remove organic sulfur. The purification plant can meet the requirements of GB 17820-2018 through solvent upgrading and new process technology. However, each of the three technologies has its own advantages and disadvantages, which should be reasonably selected according to the feed gas situation of the purification plant.

As an important primary energy, natural gas is related to the national economy, people's livelihood and national security, and is an important pillar industry of China's national economic development. In 2020, China's natural gas output will be 130.4 billion cubic meters, of which sulfur-containing natural gas will account for more than 60%. Sour natural gas must be purified before entering the long-distance pipeline network. As the main part of natural gas purification, desulfurization process plays an important role in obtaining high standard commercial natural gas. The requirement of total sulfur and H₂S content in commercial natural gas is more and more strict in China. Since the development of GB 17820-1999, the latest GB 17820-2018 was officially released on November 19, 2018 and implemented on June 1, 2019. In GB 17820-2018, the technical index of natural gas is further improved, especially the index of total sulfur is an order of magnitude higher than that in GB 17820-2012. This latest standard has reached the international advanced level, but it also brings great challenges to China's natural gas purification industry. In this paper, the current situation of gas quality in domestic purification plants is analyzed, and the influence of standard upgrading on purification plants is discussed.

1. Natural gas quality standard

With the increasingly stringent requirements of environmental protection, the upgrading of oil and gas products at home and abroad is also accelerating. At present, the total sulfur content of gasoline and diesel in China has been upgraded from 500 mg/kg in 2003 to 10 mg/kg in 2017. In Europe, America...
and other developed countries, the total sulfur concentration in natural gas is usually 6-30 mg/ m³. However, the total sulfur concentration index of domestic natural gas in China is still 200 mg/m³ as stipulated in 1999. Nowadays, the quality upgrading of natural gas products has attracted wide attention from all walks of life. The proposal No. 4091 of the fifth session of the 12th National People's Congress put forward the "proposal on speeding up the revision of natural gas quality standards". The revision of the standard took four years, and GB 17820-2018 natural gas was officially released on November 19, 2018.

1.1. Foreign natural gas quality standards
The latest EU standard EN 16726-2016 puts forward new requirements for total sulfur content in gas. The natural gas standards of major developed countries abroad are shown in Table 1.

Table 1. Sulfur content in natural gas at abroad.

| National and standard number | mass concentration of total sulfur /(mg·m⁻³) | Mass concentration of hydrogen sulfide /(mg·m⁻³) | mass concentration of mercaptan /(mg·m⁻³) |
|------------------------------|---------------------------------------------|-----------------------------------------------|------------------------------------------|
| European Association for rationalization of gas energy exchange (EASEE gas) | ≤30 | ≤5(H₂S+ COS) | ≤6 |
| European union EN16726-2016 | ≤20(Odorant free) | ≤30(Containing odorant) | ≤5(H₂S+ COS) | ≤6 |
| Germany DVGW G 260:2013 | ≤6(Containing odorant) | ≤5(H₂S+ COS) | ≤6 |
| U.S.A AGA Report No. 4A-2009 | 11.5~460 | ≤5.7~23 | 4.6~46 |
| U.S. Department of oil and gas of Changtan 2005 | ≤17 | ≤5.75 | ≤6.9 |
| Russian industry standards 5542-2014 | - | ≤20 | ≤36 |

1.2. Domestic natural gas quality standards
The latest GB 17820-2018 replaces GB 17820-2012. The main technical changes are as follows.

Table 2. Natural gas indexes of GB 17820-2018.

| Natural gas | High calorific value / (MJ • m⁻³) | Mass concentration of total sulfur/(mg • m⁻³) | Mass concentration of hydrogen sulfide /(mg·m⁻³) | y(CO₂) / % |
|-------------|----------------------------------|---------------------------------------------|-----------------------------------------------|-----------|
| first kind  | ≥34.0 | ≤20 | ≤6 | ≤3.0 |
| second kind | ≥31.4 | ≤100 | ≤20 | - |

2. 2 Natural gas quality and desulfurization process in China

2.1. Natural gas quality and purified gas status in China
Based on the in-depth investigation of the natural gas quality status of the three major domestic oil companies in 2016, according to incomplete statistics, the apparent consumption of natural gas in China reached 1932×10⁸m³. According to PetroChina's statistics, the total volume of class II gas is 185.2×10⁸m³, of which southwest oil and gas field company accounts for about 100×10⁸ m³. Natural gas with total sulfur concentration more than 20 mg/m³ is mainly concentrated in Sichuan and Chongqing.

In 2020, the desulfurization process, total sulfur and H₂S content in purified gas of 11 natural gas purification plants in Sichuan and Chongqing were investigated. The results are shown in Table 3. At present, alcohol amine desulfurization is usually used in domestic natural gas purification plants, and sulfone amine desulfurization is used in a small number of purification plants.
Table 3. Purified gas production and total sulfur content of several natural gas purification plants in Sichuan and Chongqing area.

| Purification plant number | Production of purified gas \((10^8 \text{ m}^3)\) | Desulfurization process | Mass concentration of total sulfur \(/ (\text{mg} \cdot \text{m}^{-3})\) | \(\rho (\text{H}_2\text{S}) / (\text{mg} \cdot \text{m}^{-3})\) |
|---------------------------|----------------------------------|--------------------------|------------------------------------------|-------------------|
| 1                         | 6.88                             | Alcohol amine desulfurization process | 10.4                                      | 2.0               |
| 2                         | 9.331                            | Alcohol amine desulfurization process | 14.0                                      | 2.4               |
| 3                         | 4.881                            | Alcohol amine desulfurization process | 17.4                                      | 2.5               |
| 4                         | 0.255                            | Alcohol amine desulfurization process | 53.1                                      | 6.0               |
| 5                         | 4.661                            | Alcohol amine desulfurization process | 23.0                                      | 2.4               |
| 6                         | 3.201                            | Alcohol amine desulfurization process | 25.0                                      | 2.5               |
| 7                         | 0.393                            | Sulfolamine desulfurization process | 24.0                                      | 3.0               |
| 8                         | 7.947                            | Alcohol amine desulfurization process | 69.0                                      | 3.9               |
| 9                         | 4.625                            | Alcohol amine desulfurization process | 118.3                                     | 10.7              |
| 10                        | 75.693                           | Alcohol amine desulfurization process | 108.0                                     | 7.3               |
| 11                        | 11.27                            | Alcohol amine desulfurization process | 103.0                                     | <1.0              |

According to the requirements of GB 17820-2018, the total sulfur content of domestic purification plants is under great pressure to reach the standard. In order to reduce the total sulfur content in purified gas, on the one hand, it is necessary to remove H\(_2\)S as deeply as possible, and on the other hand, it is necessary to improve the removal capacity of organic sulfur.

2.2. Present situation of desulfurization process

At present, the most commonly used desulfurization process in the field of natural gas purification is still solvent method in the world. According to statistics, 84.4% of natural gas purification plants in the United States use solvent desulfurization. More than 80% of the natural gas produced in Russia every year is treated by solvent desulfurization. In Sichuan and Chongqing area of China, except Puguang purification plant adopts organic sulfur hydrolysis technology due to high carbonyl sulfur content, and some remote scattered wells adopt dry desulfurization due to limited conditions, the rest of feed gas adopts MDEA based solvent desulfurization. It can be seen that solvent desulfurization is still the most mainstream process of natural gas treatment.

Sulfinol process is the most commonly used process for desulfurization of feed gas containing organic sulfur. Commonly used include Sulfinol-M (MDEA based) and Sulfinol-D (Dipa based). The removal rate of organic sulfur of Sulfinol-M is 40% ~ 60%, and the selectivity of CO\(_2\) is equivalent to that of MDEA. The organic sulfur removal rate of Sulfinol-D can reach more than 80%, and even more than 95% after adjusting the process parameters. Due to the removal of all CO\(_2\) by Sulfinol-D, the regeneration energy consumption is greatly increased, which is not conducive to the operation of the downstream sulfur recovery unit.

In China, the natural gas Research Institute of PetroChina Southwest Oil and gas field company independently developed CT8-24 efficient organic sulfur removal solvent in 2011. Under the absorption pressure of 6 MPa in the laboratory, the removal rate of COS can reach 80%-85%, which is better than that of Sulfinol-M solvent. What's more, because of the introduction of key components which can hinder the absorption of CO\(_2\), its selectivity for CO\(_2\) is better than Sulfinol-D, and the CO\(_2\) removal rate is generally 50% ~ 60%. At present, the technology has been applied in industry.
For the gas with a mass concentration of no more than 100 mg/m³ in the raw gas, it is expected to control the total sulfur concentration in the purified gas within 20 mg/m³ after desulfurization by the solvent of organic sulfur removal. However, for the gas with higher organic sulfur content, especially for the gas with organic sulfur concentration more than 200 mg/m³, the CO₂ removal rate will be too high and the product gas output will be reduced by using the solvent method. Therefore, it is necessary to use COS hydrolysis and molecular sieve technology for treatment.

3. Influence of standard upgrade on purification plant

3.1. It is necessary to improve the desulfurization performance of the solvent

Molecular sieve process, COS hydrolysis and other technologies make great changes to the unit, which has high investment and operation cost, and still need to cooperate with amine process to achieve the purpose of removal. At present, MDEA or its formula solvents are mostly used in domestic natural gas purification plants. The solvent upgrading only needs to replace the solvent and adjust some process parameters, which has low cost and short construction period. Therefore, amine desulfurization process is still the best choice for the removal of H₂S and organic sulfur.

Although the amine desulfurization process is mature, there are corresponding technologies for the removal of various sulfur compounds. However, the requirement of total sulfur in GB 17820-2018 is greatly increased, and some purification plants need to upgrade the solvent. The research direction of solvent should focus on improving the purification degree of H₂S and the removal performance of organic sulfur.

In order to improve the purification degree of hydrogen sulfide, it is necessary to use desulfurization solvent which can selectively remove hydrogen sulfide. On the one hand, the co-absorption rate of CO₂ is reduced, on the other hand, the purification degree of H₂S is improved. It can reduce the content of hydrogen sulfide in purified gas and contribute to the reduction of total sulfur content.

In order to improve the removal performance of organic sulfur, the commonly used MDEA chemical desulfurization solvent should be upgraded to the physical chemical solvent with better removal capacity. Such as Sulfinol-D, Sulfinol-M, Sulfinol-X and CT8-24.

3.2. New process technology is added to meet the requirements of the new standard

For natural gas with high mercaptan content, a molecular sieve fine removal unit is added at the back end of amine desulfurization unit. Silica gel adsorbent is used in the upper layer of the refining tower, and NaX molecular sieve is used in the lower layer of the refining tower. The process unit has three absorption towers, which can be switched between each other. The process has the advantages of high removal rate, low energy consumption, simultaneous desulfurization and dehydration, which simplifies the process of purification plant to a certain extent, but needs frequent switching. In addition, the adsorption effect of molecular sieve on carbonyl sulfur is not ideal, and it can also catalyze the reaction of H₂S and CO₂ to produce carbonyl sulfur.

For the feed gas with high cos content, the process of adding organic sulfur hydrolysis unit at the back end of the main absorption tower for fine removal can be adopted. After desulfurization in the main absorption tower, the feed gas is preheated to 140 °C by the preheater and enters the hydrolysis reactor. Under the action of hydrolysis catalyst, the organic sulfur is hydrolyzed to H₂S and CO₂. After heat exchange, it enters the secondary amine absorption tower to further remove a small amount of H₂S and CO₂, and the purified gas reaches the product standard.

Although the above two processes have some research, but the domestic industrial application experience is less, we need to strengthen the engineering research.

3.3. Impact on management

The revision of the existing standards also means higher requirements for the management mode of the existing purification plant. It requires us to manage and maintain it more finely, to consider the
impact of upstream fluctuations and the fluctuations of the device itself, and to consider the impact of
future changes in gas quality and volume; For the purification plants that adopt the new process to
meet the requirements of the revised standard, it is necessary to deeply study the technical points of
the new process, formulate new operating procedures, and strengthen daily management.

4. Conclusions and suggestions
After the upgrading of natural gas quality standards, some domestic purification plants will be affected.
For the purification plants that can not meet the standard of purified gas after MDEA desulfurization,
solvent upgrading is preferred to reduce the total sulfur of purified gas. If the desulfurized solvent can
not meet the standard, the COS hydrolysis process and the molecular sieve refining process should be
introduced according to the form of organic sulfur in the feed gas. In addition, after the upgrading of
the standard, the management requirements of the purification plant are higher, and the management
and maintenance need to be more refined.

References
[1] JENSEN D R. Proceedings of the 62nd Laurance Reid Gas Conditioning Conference. Norman,
Oklahoma: LRGCC, 2012.
[2] LABORIE G, CADOURS R, BARREAU A, et al. Proceedings of the Laurance Reid Gas
Conditioning Conference. Norman, Oklahoma: LRGCC, 2001.F. De Lillo, F. Cecconi, G.
Lacorata, A. Vulpiani, EPL, 84 (2008)
[3] ANDIKA R, NHIEN L C, LEE M. Journal of Industrial and Engineering Chemistry, 2017, 54:
454-463.
[4] LITTLE R J, VERSTEEG G F, VAN SWAAL W P M. Journal of Chemical and Engineering
Data, 1992, 37(1): 49-55.
[5] YANG Chaoyue, Chang Honggang, He Jinglong, et al. Petroleum and natural gas chemical
industry, 2019, 48(1): 1-6.
[6] XIAN Xiangfa, Li Ming. Petroleum and natural gas chemical industry, 2000, 29(1) : 15-20.
[7] CHEN Gengliang. Petroleum and natural gas chemical industry, 2019, 48(1): 1-6.
[8] CHEN Gengliang, Chang Honggang. Beijing: Petroleum Industry Press, 2009: 70.
[9] RIEZQA Andika, Le Cao Nhien, Moonyong Lee. Journal of Industrial and Engineering
Chemistry, 2017, 54 : 454–463.
[10] HU Tianyou, He Jinlong, Peng Xiujun. Petroleum and natural gas chemical industry, 2013, 42
(3): 205-210.
[11] CHEN Gengliang, Chang Honggang. Bei Jing: Petroleum Industry Press, 2008: 80-90.
[12] TIAN yinhua. Petroleum and natural gas chemical industry, 1990, 19(1): 1-10.
[13] HABIB Allah Shirazizadeh, Ali Haqhtalab. J. Chem. Thermodynamics, 2019(133): 111-122.
[14] ZHANG feng, Shen benxian, Sun hui, et al. Chemical industry and engineering progress, 2015,
34(6): 1786-1803.
[15] R. S. Hugo, R. Wagner. Hydrocarbon Engineering, 2005, 5(6): 73-77.
[16] WANG yajun, Li Chunhu, Xue zhen, et al. Natural gas and oil, 2015, 33(3): 28-31.
[17] WANG Kaiyue. Chemical Engineering of Oil & Gas,2007,36(1) : 28-36.
[18] ZHANG Jianhua. Shanghai: East China.