Industrial Applications of Fine Desulfurizers in Natural Gas Processing

in China

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ABSTRACT

The H2S content of most natural gas in China, supplied to users by pipeline, is typically 10-30ppm, but can be 500-1000ppm in associated gas.

This paper describes the sulfur-removal principles and main industrial applications for T703 Ferric Oxide Fine Desulfurizer, DS-1 Combined Oxides Fine Desulfurizer, and the JTL-7 Process which have been developed by Hubei Research Institute of Chemistry (HRIC) since 1996. Test data show that the sulfur capacities of T703 for fine removal [outlet H2S less than 0.03ppm] and bulk removal [outlet H2S 1-10ppm] are 4 times and 3.5 times higher than those of common ferric oxide desulfurizers. The products also have the advantages of good strength and do not powder in the presence of water. However, T703, like common ferric oxide desulfurizer, works well only with O2/H2S = 5-10. DS-1 solves this problem and can be applied in feeds with oxygen absent. The JTL-7 Process can remove H2S, COS, CS2, RSH, RSR, RSSR at 350-400°C [633-752°F] to solve the problem of fine desulfurization of natural gas to replace the traditional high temperature process.

Some of the main industrial applications to date have been:
[1] T703 is applied by Tianjin Dagang Oilfield to remove H2S from natural gas to protect equipment from corrosion. The outlet H2S content has been below 0.03 ppm for one year, thereby completely solving the problem of corrosion.
[2] T703 is used by the Luzhou Natural Gas Chemical Plant to protect steam reforming and other catalysts in an 850 tonnes/day ammonia plant. Trace oxygen is added to the feed because the O2/H2S ratio is less than 3.0 in the natural gas. The fine desulfurizer has been used beneficially for more than two years.
[3] DS-1 is used to remove H2S from oxygen-free associated gas to prevent equipment corrosion in the Hubei Jianghan Oilfield. The outlet H2S content is below 0.03 ppm, copper strip corrosion of LPG is less than 1b and separate LPG desulfurization is not required.
The JTL-7 Process is used by Chengdu Yulong Natural Gas Chemical Plant to protect steam reforming and other catalysts. There have been clear economic benefits.

INTRODUCTION

General Situation of Natural Gas in China [1]

Natural gas (NG) is abundant in China, the total quantity is about $38 \times 10^{12} \text{ m}^3$, of which about 41% is in the Tarim and Sichuan basins. Recently a large gas field (more than $1 \times 10^{11} \text{ m}^3$) was discovered in the Daqing oilfield.

China has published a new national natural gas standard (GB 17820-1999), see Table 1

<table>
<thead>
<tr>
<th>Items</th>
<th>First grade</th>
<th>Second grade</th>
<th>Third grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calorific value (MJ/m³)</td>
<td>31.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S/(mg/m³)</td>
<td>≤6</td>
<td>≤20</td>
<td>≤460</td>
</tr>
<tr>
<td>Total sulfur (mgS/m³)</td>
<td>≤100</td>
<td>≤200</td>
<td>≤460</td>
</tr>
<tr>
<td>CO₂ /%, v/v</td>
<td>≤3.0</td>
<td>≤3.0</td>
<td>---</td>
</tr>
<tr>
<td>Dew point</td>
<td>5°C[9°F] lower than lowest environmental temperature under the pressure and temperature of the connection point</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: * Standard reference conditions: 101.325 kPa, 20°C [68°F].

In NG pipes built before this standard was published, there should be no free water in the NG at the pressure and temperature of the connection point, ie no free water should separate through the separation plant.

To satisfy these requirements, NG needs purification as follows:

1. Desulfurization: The main wet desulfurization processes are MDEA, improved MDEA and Sulfinol solutions.

2. Water-removal: Most NG in China contains saturated water vapor which must be removed to satisfy the requirement for pipeline transportation.

At present, pipeline construction is still developing in China; the pipeline network does not yet cover the whole country. Existing pipelines are mainly in the Sichuan, Shanganning, Chaidamu and Talimu gas fields. In recent years, many pipeline construction projects have been opened. The four main pipelines in China are:

1. Shanxi-Beijing pipeline: the pipeline traverses Shaanxi province, Shanxi province, Hebei province and Beijing municipality. The total length is 918.42 km, diameter is 660mm, design pressure is 6.4MPa [960psi], maximum carrying capacity is $33 \times 10^8 \text{ m}^3$ per year.

2. Sichuan-Chongqing pipeline: the pipeline connects five gas mines and scores of gas fields. The total length is 1800 km, diameter is 720mm, design pressure is 6MPa [900psi], throughput capacity is $30 \times 10^8 \text{ m}^3$ per year.
3. West-East pipeline: this pipeline is one of the key projects of the China West Region Development; it is from Sinkiang to Shanghai municipality, traversing nine provinces or municipalities. The total length is 4176 km, diameter is 1016mm, design pressure is 10 MPa [1500psi], the capacity is $200 \times 10^6 \text{m}^3$ per year.

4. Chongqing-Wuhan pipeline: total length is 718 km, diameter is 711mm, design pressure is 4MPa [600psi], the capacity will reach $25 \times 10^6 \text{m}^3$ per year in 2020.

NG is also an important chemical raw material for production of synthetic ammonia, methanol, ethane and chloromethane; the main products are synthetic ammonia and methanol.

**Introduction to Fine Desulfurization**

There are many sulfides in NG, mainly H$_2$S with some CS$_2$, COS, thiols, disulfides, thioethers, etc. NG needs crude desulfurization before transportation by pipeline. When NG is used as chemical raw material, it needs fine desulfurization because sulfides will poison catalysts, reduce product quality and pollute the environment. In many cases, total sulfur must be less than 0.1ppm.

There are three processes: moderate temperature ZnO desulfurization, Co-Mo hydrogenation catalyst plus ZnO fine sulfur removal process, and the ambient temperature fine sulfur removal (ATFSR) process. The first two ways have some disadvantages as follows:

1. The energy consumption and operating expenses are higher than for the ATFSR process.
2. The outlet sulfur content is not sufficiently low. ZnO desulfurizer can only remove H$_2$S and, partially, organic sulfides. The Co-Mo plus ZnO sulfur removal process can remove organic sulfides, but the outlet H$_2$S content after ZnO desulfurizer may not be less than 0.4mg/m$^3$.
3. The price of desulfurizer is higher than for the ATFSR process.

**PRODUCTS AND PROCESSES**

Addressing the disadvantages above, HRIC has developed many ambient temperature desulfurizers which have been successfully applied in many plants, has improved the Co-Mo hydrogenation catalyst plus ZnO high temperature fine sulfur removal process and has developed the JTL-7 Process which has advantages compared to the Co-Mo + ZnO high temperature fine sulfur removal process.

**Improved High Temperature Fine Sulfur Removal Process [2]**

T703 Fine Desulfurizer is placed before Co-Mo hydrogenation catalyst plus ZnO high temperature fine sulfur removal process, the flow sheet is shown in Figure 1

**Figure 1 - Flow Sheet of Improved High Temperature Fine Sulfur Removal Process**
The advantages of this process are:

[1] Reducing the load on the ZnO desulfurizer, so decreasing the cost of fine desulfurization;


These benefits will be more obvious in cases of high H₂S content.

**JTL-7 New Process**

This process consists of EZ-2 Wide Temperature Zinc Oxide Fine Desulfurizer and MZX Conversion-Absorption Fine Desulfurizer and can remove H₂S, COS, CS₂, RSH, RSR, RSSR at 350-400°C [633-752°F], outlet total sulfur is less than 0.1ppm. The flow sheet of the JTL-7 Process is shown in Figure 2

![Flow Sheet of JTL-7 Process](image)

Compared to the conventional process, the JTL-7 Process has the advantages shown in Table 2

<table>
<thead>
<tr>
<th>Item</th>
<th>JTL-7</th>
<th>Co-Mo catalyst + ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlet total sulfur</td>
<td>&lt;0.1ppm steady</td>
<td>&lt;0.1ppm but fluctuates</td>
</tr>
<tr>
<td>Start-up and operation</td>
<td>Needs no sulfiding, simple</td>
<td>Needs sulfiding, complicated</td>
</tr>
<tr>
<td>Production</td>
<td>No H₂ addition</td>
<td>Needs H₂ addition</td>
</tr>
</tbody>
</table>

The expenses of catalyst and operation of the JTL-7 Process are only respectively half those of the Co-Mo + ZnO sulfur removal process.

**The Specification of Fine Desulfurizers**

1. **T703 Ferric Oxide Fine Desulfurizer**

Low outlet sulfur content: outlet sulfur content is less than 0.03 ppm compared with, typically, 1 ppm from common ferric oxide desulfurizers.

   High reaction rate: space velocity for T703 is 1000-2000 h⁻¹, which is about 3 times higher than that of common ferric oxide desulfurizer (typically 300-500 h⁻¹).

   High working sulfur capacity: with space velocity 2000 h⁻¹, normal pressure, water-saturated, inlet H₂S content 10,000 ppm, outlet H₂S below 0.03 ppm, original size absorbent, the working sulfur capacity of T703 is 20%, which is about 3-10 times that of common ferric oxide desulfurizers [3][4].

   High strength and water-resistance: when boiled for two hours or dipped in water for 30 days, T703 does not powder and still has good strength, while most common ferric oxide
desulfurizers powder.

Wide temperature range: test data show that the working sulfur capacity of T703 does not vary significantly over the range 5-100°C [41-212°F].

**Sulfur-removal principle:**

\[
\text{Fe}_2\text{O}_3 + \text{H}_2\text{S} + \text{O}_2 \rightleftharpoons \text{FeS} + \text{FeS}_x + \text{S} + \text{H}_2\text{O}
\]

Depending upon the oxygen content of the feed gas, the reaction between \(\text{Fe}_2\text{O}_3\) and \(\text{H}_2\text{S}\) produces \(\text{FeS}, \text{FeS}_x\) and \(\text{S}\) [4].

**Properties**

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Yellow Extrudate, diameter 3-4 mm × length 3-15 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density, kg/l</td>
<td>0.5-0.8</td>
</tr>
<tr>
<td>Crushing Strength, N/cm</td>
<td>(\geq 50)</td>
</tr>
<tr>
<td>(\text{H}_2\text{S}) Sulfur Capacity, %(wt)</td>
<td>(\geq 20)</td>
</tr>
<tr>
<td>Outlet (\text{H}_2\text{S}) content, ppm</td>
<td>(\leq 0.03)</td>
</tr>
</tbody>
</table>

2. **DS-1 Combined Oxides Fine Desulfurizer**

DS-1 can be used in gas or liquid feeds with oxygen absent; its working sulfur capacity is three times higher than that of other similar desulfurizers in China.

Low outlet sulfur content: when inlet \(\text{H}_2\text{S}\) is 15,000 mg/m\(^3\), outlet \(\text{H}_2\text{S}\) content is \(< 0.03\) ppm.

High reaction rate: gas space velocity is 500-1500 h\(^{-1}\), liquid space velocity is 1-3 h\(^{-1}\).

Water-resistance: DS-1 does not powder when boiled for two hours or dipped in water for 30 days.

Wide temperature range: DS-1 can be used over the range 5-100°C [41-212°F].

**Sulfur-removal principles:**

\[
\text{MO} + \text{H}_2\text{S} \rightleftharpoons \text{MS} + \text{H}_2\text{O} \quad \text{MO} + \text{COS} \rightleftharpoons \text{MS} + \text{CO}_2 \quad \text{[M = metal]}
\]

DS-1 can also partially remove COS at high temperatures.

**Properties**

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Yellow Extrudate, diameter 3-4 mm × length 3-15 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density, kg/l</td>
<td>0.8-0.9</td>
</tr>
<tr>
<td>Crushing Strength, N/cm</td>
<td>(\geq 25)</td>
</tr>
<tr>
<td>(\text{H}_2\text{S}) Sulfur Capacity, %(wt)</td>
<td>(\geq 13) (Oxygen absent, single tower)</td>
</tr>
<tr>
<td>Outlet (\text{H}_2\text{S}) content, ppm</td>
<td>(\leq 0.03)</td>
</tr>
</tbody>
</table>

3. **EZ-2 Wide Temperature Zinc Oxide Fine Desulfurizer**

Low outlet sulfur content: when inlet \(\text{H}_2\text{S}\) is 15,000mg/m\(^3\), outlet \(\text{H}_2\text{S}\) content is \(< 0.03\) ppm.

EZ-2 can also partially remove COS at high temperatures.
High reaction rate: space velocity of EZ-2 is 1000-3000 h\(^{-1}\).

High working sulfur capacity: as determined by the National Quality Supervision and Test Center for Chemical Catalysts, the working sulfur capacity of EZ-2 is 20-30% higher than the requirement of the Chinese national standard (Table 3).

Table 3 - Working Sulfur Capacity [%w/w] of EZ-2 at Different Temperatures

<table>
<thead>
<tr>
<th>Item</th>
<th>National chemical standard</th>
<th>Test data</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C [212°F]</td>
<td>-</td>
<td>12.1</td>
</tr>
<tr>
<td>220°C [428°F]</td>
<td>≥20.0</td>
<td>24.4</td>
</tr>
<tr>
<td>350°C [662°F]</td>
<td>≥22.0</td>
<td>29.2</td>
</tr>
</tbody>
</table>

High strength and water-resistance: when boiled for two hours or dipped in water for 30 days, EZ-2 does not powder and still has good strength.

Wide temperature range: EZ-2 can be used over the range 30-400°C [86-752°F].

Sulfur-removal principles:

\[
\begin{align*}
\text{ZnO} + \text{H}_2\text{S} & \rightleftharpoons \text{ZnS} + \text{H}_2\text{O} & \text{ZnO} + \text{COS} & \rightleftharpoons \text{ZnS} + \text{CO}_2 \\
\text{ZnO} + \text{C}_2\text{H}_5\text{SH} & \rightleftharpoons \text{ZnS} + \text{C}_2\text{H}_6 + \text{H}_2\text{O} & 2 \text{ZnO} + \text{CS}_2 & \rightleftharpoons 2 \text{ZnS} + \text{CO}_2
\end{align*}
\]

Properties

- **Appearance**: White Extrudate, diameter 4 mm \(\times\) length 4-10 mm
- **Bulk Density, kg/l**: 1.00-1.10
- **Crushing Strength, N/cm**: ≥40
- **H\(_2\)S Sulfur Capacity, % (wt)**: 
  - ≥12 at 100°C [212°F]
  - ≥24 at 220°C [428°F]
  - ≥29 at 350°C [662°F]
- **Outlet H\(_2\)S content, ppm**: ≤0.10

4. **MZX Conversion-Absorption Fine Desulfurizer**

Simple operation: does not need presulfiding nor H\(_2\) addition.
Low outlet sulfur content: outlet total sulfur content is less than 0.1 ppm.
High working sulfur capacity: the sulfur capacity of MZX is over 18% when two towers are operated in series.
High reaction rate: space velocity for MZX is 1000-2000 h\(^{-1}\).

Sulfur-removal principles:

\[
\begin{align*}
\text{RSH} + \text{H}_2 & \rightleftharpoons \text{H}_2\text{S} + \text{RH} & \text{RSR’} + 2\text{H}_2 & \rightleftharpoons \text{H}_2\text{S} + \text{RH} + \text{R’H} \\
\text{RSSR’} + 3\text{H}_2 & \rightleftharpoons 2\text{H}_2\text{S} + \text{RH} + \text{R’H} & \text{RSR} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{S} + \text{ROH} \\
\text{RSR} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{S} + 2\text{ROH} & 2\text{CH}_3\text{SH} & \rightleftharpoons 2\text{H}_2\text{S} + \text{C}_2\text{H}_4
\end{align*}
\]
\[
\begin{align*}
\text{CH}_3\text{SCH}_3 & = \text{H}_2\text{S} + \text{C}_2\text{H}_4 & \text{H}_2\text{S} + \text{MO} & = \text{MS} + \text{H}_2\text{O} \\
\text{RSH} + \text{MO} & = \text{MS} + \text{ROH}
\end{align*}
\]

**Properties**

- **Appearance**: Black-brown extrudate, diameter 3-4mm × length 3-15 mm
- **Bulk Density, kg/l**: 1.10 - 1.30
- **Crushing Strength, N/cm**: ≥40
- **Organic Sulfides Capacity, % (wt)**: ≥14 (single tower)
- **Outlet total sulfur content, ppm**: ≤0.1

**INDUSTRIAL APPLICATIONS**

Some HRIC catalysts have been applied in many natural gas based plants achieving good economical and social benefits. Now some applications are introduced as follows:

**Application of T703 Fine Desulfurizer in Tianjin Dagang Oilfield [5]**

NG from Tianjin Dagang Oilfield was transported to Hebei Cangzhou Fertilizer Plant as raw material and to Tianjin for civil fuel through pipeline.

Most of the sulfides in natural gas of the oilfield is H₂S; there are 23 ppm, 11.6 ppm and 3.4 ppm H₂S respectively in three source gases. Formerly, NG was pumped directly into a compressor (supplied by Pro-Quip Company, USA in 1994) without desulfurization, the compressor was corroded seriously and had to be repaired every week to remove blockages; about 100 tons LNG were lost per stoppage. 10 million RMB were lost annually. The oilfield decided to instal sulfur-removal equipment and, after comparing with other desulfurizers, chose T703 Fine Desulfurizer.

1. **Flow sheet and operating conditions:**

The flow sheet is shown in Figure 3

![Flow Sheet of Desulfurization in the Tianjin Dagang Oilfield](image)

The inner diameter of the two sulfur-removal towers is 2600 mm, the height is 7000 mm, the volume of T703 Fine Desulfurizer is 2 x 35 m³. The components of the NG are shown in Table 4

**Table 4- Components of NG in the Tianjin Dagang Oilfield**

<table>
<thead>
<tr>
<th>Component</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Components | CH$_4$ | C$_2$H$_6$ | C$_3$H$_8$ | C$_4$H$_{10}$ | CO$_2$ | $\Sigma$
|---|---|---|---|---|---|---|
volume % | 81 | 12 | 3 | 1 | 3 | 100

Operating conditions: gas flow 48000 m$^3$/h [43 MMscfd]; pressure 3.0 MPa [450 psi]; temperature 30-40°C [86-104°F]; inlet H$_2$S about 20 ppm; required outlet H$_2$S < 1ppm.

2. Operating experience:

The sulfur-removal equipment has run very well for more than one year since 1997, the operating data are shown in Table 5.

Table 5 - Operating Data in Tianjin Dagang Oilfield

<table>
<thead>
<tr>
<th>Date</th>
<th>Inlet H$_2$S content /ppm</th>
<th>Outlet H$_2$S content /ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1997-10-26</td>
<td>18.15</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1997-11-06</td>
<td>18.65</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1997-12-08</td>
<td>16.69</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1997-12-10</td>
<td>17.00</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1998-02-10</td>
<td>16.65</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1998-03-10</td>
<td>16.63</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1998-04-10</td>
<td>16.73</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1998-05-10</td>
<td>16.40</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1998-06-10</td>
<td>16.67</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1998-07-10</td>
<td>16.66</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1998-08-10</td>
<td>17.16</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>1998-09-10</td>
<td>17.02</td>
<td>&lt;0.03</td>
</tr>
</tbody>
</table>

Note: the above data were analyzed by an HC-2 Trace Sulfides Analyzer of HRIC. Outlet H$_2$S content was less than 0.03 ppm, corrosion and blockage were resolved completely, thus 10 million RMB of economic loss were avoided. Moreover 3.35 million RMB of new benefits were achieved.

T703 Fine Desulfurizer shows the following advantages:
[1] It runs smoothly at ambient temperature.
[4] Expense is less than 1000 RMB per one million Nm$^3$ NG.

Application of T703 Fine Desulfurizer in Luzhou Natural Gas Chemical Plant [6]

Luzhou Natural Gas Chemical Plant is a large-scale synthetic ammonia plant using natural gas as raw material. There is some H$_2$S in feed gas, formerly the plant adopted wet process to remove H$_2$S before high-temperature fine sulfur removal process (Co-Mo hydrogenation catalyst plus ZnO), which is complicated and high operating expenses, to solve the problem, the plant adopted our improved high-temperature process (mentioned above), it means T703 Fine
Desulfurizer is used to remove $H_2S$ before high-temperature Co-Mo hydrogenation catalyst plus ZnO process, trace oxygen is added to the feed because the $O_2/H_2S$ ratio is less than 3.0 in the NG.

1. **Flow sheet and operating conditions:**

   The flow sheet is shown in Figure 4

   ![Flow Sheet](image)

   Figure 4 - Flow Sheet of Desulfurization in the Luzhou Natural Gas Chemical Plant

   The inner diameter of two sulfur-removal towers is 4200 mm, the height 7000 mm, the volume of T703 Fine Desulfurizer is 91 m$^3$.

   The components of NG is shown in Table 6

<table>
<thead>
<tr>
<th>Components</th>
<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_8$</th>
<th>N$_2$</th>
<th>CO$_2$</th>
<th>Ar</th>
<th>∑</th>
</tr>
</thead>
<tbody>
<tr>
<td>volume %</td>
<td>96.88</td>
<td>0.65</td>
<td>0.10</td>
<td>1.20</td>
<td>1.15</td>
<td>0.02</td>
<td>100</td>
</tr>
</tbody>
</table>

   Operating conditions: gas flow 60,000 Nm$^3$/h [54 MMscfd]; pressure 1.0 MPa [150 psi]; temperature 35°C [95°F]; inlet H$_2S$ about 20 ppm; required outlet total sulfur < 5ppm.

2. **Operating experience:**

   The sulfur-removal equipment has run very well for about two years since December 2003, the operating data are shown in Table 7.

   ![Operating Data](image)

   Table 7- Operating Data in Luzhou Natural Gas Chemical Plant

<table>
<thead>
<tr>
<th>Date</th>
<th>Inlet H$_2S$ content (ppm)</th>
<th>Outlet H$_2S$ content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003-12-28</td>
<td>4.5</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>2003-12-29</td>
<td>5.1</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>2004-04-05</td>
<td>16.2</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>2004-04-06</td>
<td>15.0</td>
<td>&lt;0.03</td>
</tr>
</tbody>
</table>

   Note: the above data were analyzed by an HC-2 Trace Sulfides Analyzer of HRIC

   The data of Table 7 show that outlet H$_2S$ content is always less than 0.03 ppm, so the load on the ZnO fine desulfurizer is decreased, corrosion of the pipeline and compressor is eliminated and the expense of desulfurization is decreased.

   **Application of DS-1 Fine Desulfurizer in the Hubei Jianghan Oilfield [6]**

   The Zhong City Processing Station of the Jianghan Oilfield processes oxygen-free
associated gas. Two feeds contain 800ppm and 200ppm H₂S respectively. First the two associated
gases are mixed then the mixed gas enters the sulfur removal equipment to remove H₂S in order to
decrease corrosion of equipment and copper strip of LPG in the next section.

1. Flow sheet and operating conditions:

The flow sheet is shown in Figure 5

![Flow Sheet](image)

Figure 5 - Flow Sheet of Desulfurization in the Hubei Jianghan Oilfield

The inner diameter of two sulfur-removal towers is 1800 mm, the height is 5500 mm, the
volume of DS-1 Fine Desulfurizer is 12m³.

The compositions of the associated gases are shown in Table 8

Table 8 - Components of Associated Gases in the Zhong City Processing Station of Jianghan Oilfield

<table>
<thead>
<tr>
<th>Components</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>C₄H₁₀</th>
<th>C₅H₁₂</th>
<th>C₆H₁₄</th>
<th>CO₂</th>
<th>N₂</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 associated gas /V%</td>
<td>56.2</td>
<td>12.5</td>
<td>16.7</td>
<td>7.10</td>
<td>1.75</td>
<td>0.63</td>
<td>1.92</td>
<td>3.2</td>
<td>100</td>
</tr>
<tr>
<td>#2 associated gas /V%</td>
<td>5.9</td>
<td>12.4</td>
<td>46.5</td>
<td>28.7</td>
<td>4.88</td>
<td>0.37</td>
<td>0.94</td>
<td>0.34</td>
<td>100</td>
</tr>
</tbody>
</table>

Operating conditions: gas flow 700 Nm³/h [0.63 MMscfd]; pressure 0.4 MPa [6 psi];
temperature 70-80°C [160-175°F]; inlet H₂S about 230ppm.

2. Operating experience:

The sulfur-removal equipment has run very well for more than three years since June 2002,
outlet H₂S content of DS-1 Fine Desulfurizer is always less than 0.03 ppm and corrosion of
equipment is avoided completely. Moreover copper strip corrosion of LPG is less than 1b, LPG
desulfurization is avoided and the economic benefits are obvious.

Application of the JTL-7 Process in Chengdu Yulong Natural Gas Chemical Plant [7]

Chengdu Yulong Natural Gas Chemical Plant is a synthetic ammonia plant using NG as raw
material. There are two systems of synthetic ammonia; the plant first adopted a manganese mineral
to desulfurize in the two systems but the outlet total sulfur content did not satisfy the requirement.
In 2003 the JTL-7 Process was adopted in the two systems to solve the problem.

1. Flow sheet and operating conditions:

The flow sheet is shown in Figure 6
The components of the NG are shown in Table 9.

Table 9 - Components of NG in Chengdu Yulong Natural Gas Chemical Plant

<table>
<thead>
<tr>
<th>Component</th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>C₄H₁₀</th>
<th>C₅H₁₂</th>
<th>C₆⁺</th>
<th>N₂</th>
<th>CO₂</th>
<th>Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol %</td>
<td>91.48</td>
<td>5.17</td>
<td>0.94</td>
<td>0.36</td>
<td>0.15</td>
<td>0.04</td>
<td>1.63</td>
<td>0.15</td>
<td>100</td>
</tr>
</tbody>
</table>

Operating conditions:
Gas flow: #1 system: 4000 m³/h [3.6 MMscfd]; #2 system: 5000 m³/h [4.5 MMscfd];
Pressure 1.2-1.3 MPa [18-19.5 psi]; EZ-2 operating temperature 350-360°C [662-680°F];
MZX operating temperature 340-350°C [644-662°F]; inlet total sulfur content about 20 ppm.

2. Operating experience:

The #1 sulfur removal equipment has run very well for about 2.5 years since 2003; the #2 sulfur removal equipment has run very well for more than one year since 2004. The operating data are shown in Table 10. These data show that the outlet total sulfur content is always less than 0.1 ppm which totally satisfies the requirement of next section, so the JTL-7 Process has completely solved the problem.

Table 10 - Operating Data in the Chengdu Yulong Natural Gas Chemical Plant

<table>
<thead>
<tr>
<th></th>
<th>#1 system</th>
<th>mgS/Nm³</th>
<th>#2 system</th>
<th>mgS/Nm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sulfides of</td>
<td></td>
<td>Sulfides of</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Raw material</td>
<td>Outlet sulfides</td>
<td>Raw material</td>
</tr>
<tr>
<td>2005-10-25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>4.1</td>
<td>&lt;0.02</td>
<td>1.7</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>COS</td>
<td>1.2</td>
<td>&lt;0.02</td>
<td>1.1</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>CH₃SH</td>
<td>14</td>
<td>&lt;0.02</td>
<td>11</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C₂H₅SH</td>
<td>3.0</td>
<td>&lt;0.02</td>
<td>2.7</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>CH₃SCH₃</td>
<td></td>
<td>&lt;0.02</td>
<td></td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C₃H₇SH</td>
<td>0.2</td>
<td>&lt;0.02</td>
<td>0.2</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>CH₃SSCH₃</td>
<td>0.16</td>
<td>&lt;0.02</td>
<td>0.1</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>2005-10-26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2005-10-27</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>--------</td>
<td>------------</td>
<td>----------</td>
<td>--------</td>
<td>----------</td>
</tr>
<tr>
<td>H₂S</td>
<td>3.6</td>
<td>&lt;0.02</td>
<td>1.8</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>COS</td>
<td>1.1</td>
<td>&lt;0.02</td>
<td>1.1</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>CH₂SH</td>
<td>13</td>
<td>&lt;0.02</td>
<td>11</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C₂H₅SH</td>
<td>3.3</td>
<td>&lt;0.02</td>
<td>3.0</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>CH₃SCH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₇SH</td>
<td>0.23</td>
<td>&lt;0.02</td>
<td>0.22</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>CH₃SSCH₃</td>
<td></td>
<td></td>
<td>0.19</td>
<td>&lt;0.02</td>
</tr>
</tbody>
</table>

Notes: [1] the above data were analyzed by an HC-2 Trace Sulfides Analyzer of HRIC.
[2] It is difficult to separate C₂H₅SH and CH₃SCH₃ in raw material feed by the HC-2 Trace Sulfides Analyzer, so the sum is shown in the above tables.

REFERENCES