



Sour Natural Gas Corrosion Protection and Purification

China National Petroleum Corporation

China holds a vast amount of sour gas reserves, which accounts for about 25% of the nation's total natural gas reserves, and mainly in the Sichuan Basin and the Ordos Basin.

CNPC started to tap sour gas resources in the Sichuan Basin since the 1960s. Through years of research and practice, we have tackled the difficulties in corrosion control, deep desulfurization of a large volume of poisonous sulfide, and efficient sulfur recovery. A complete set of related technologies have been developed.

Sour natural gas corrosion protection

An overall anti-corrosion technical package for sour gas fields has been developed based on the studies of sour gas properties, evaluation of corrosion-resistant materials, research of corrosion inhibitors, and corrosion monitoring and detection measures.

1. Downhole corrosion protection

Based on the analysis of corrosion behavior inside the borehole and material evaluation, we have developed applicable corrosion-resistant alloy steels and corrosion inhibitors, and invented protective annular fluids which are mainly composed of water-soluble inhibitors.

2. On-line corrosion test and on-site material evaluation

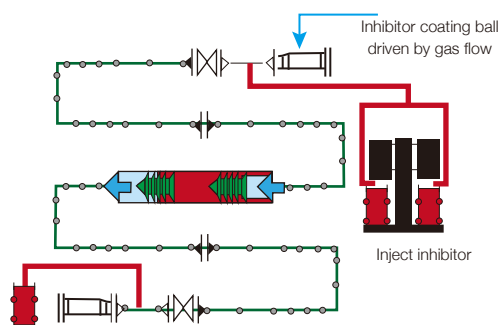
Tests on the anti-corrosion performance of metal materials were made in the site of gas producing wells. Two technologies, for anti-corrosion testing and material evaluation respectively under varied flow rate, gas-liquid phases and high pressure, have been formed to verify the reliability of materials and welding techniques.



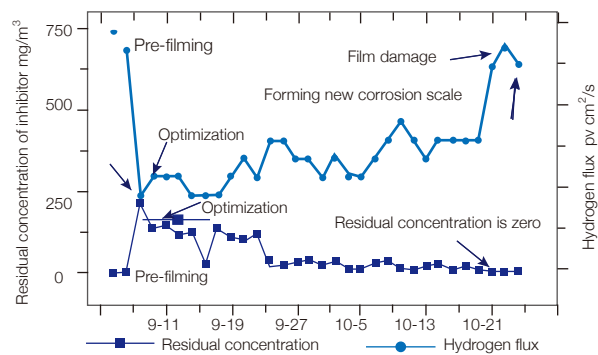
On-line sour gas corrosion test unit
max. pressure 35MPa, max. temperature 80°C

3. Corrosion inhibitors

We have invented the long-acting film-forming corrosion inhibitors. By adding special chemical groups, the absorption between inhibitor and metal surface is enhanced, and the acting period of the hydrophobic film is extended to 45 days from 10 days.



Quantitative inhibitor injection by using a pig



Protection effect of inhibitor

4. Overall corrosion monitoring

Overall sour gas corrosion monitoring is enabled by integrating inhibitor residual concentration analysis, electrochemical on-line corrosion detecting, FSM corrosion monitoring, and hydrogen flux testing.

Sour natural gas purification

Sour natural gas purification aims to greatly remove the poisonous and noxious substances such as H₂S and CO₂ in the produced sour gas in order to meet the requirements for commercial gas, and meanwhile collect the sulfide for recycling use.

1. H₂S and CO₂ removal by amine

The technology for sour gas desulfurization and decarbonization by amine has been developed, as well as the formulated H₂S and CO₂ removal solvents, which are adaptable to various sour gas complexes and different purification requirements. The purification effect is better than mono MDEA solvents.

National Standards for Natural Gas in China GB 17820—2012

Major index	First-class	Second-class
H ₂ S, mg/m ³	≤6	≤20
Total Sulfur, mg/m ³	≤60	≤200
CO ₂ , %	≤2.0	≤3.0

- ▶ Strengthened selective absorption—selectively absorb more H₂S and less CO₂, reducing energy consumption of purification units
- ▶ Deep desulfurization and decarbonization—simultaneously remove H₂S and CO₂, to meet the requirements for downstream natural gas processing
- ▶ Organic sulfur removal—greatly remove carbonyl sulfide, mercaptan, thiophene and other organic sulfides, to meet the requirements for pipeline transportation

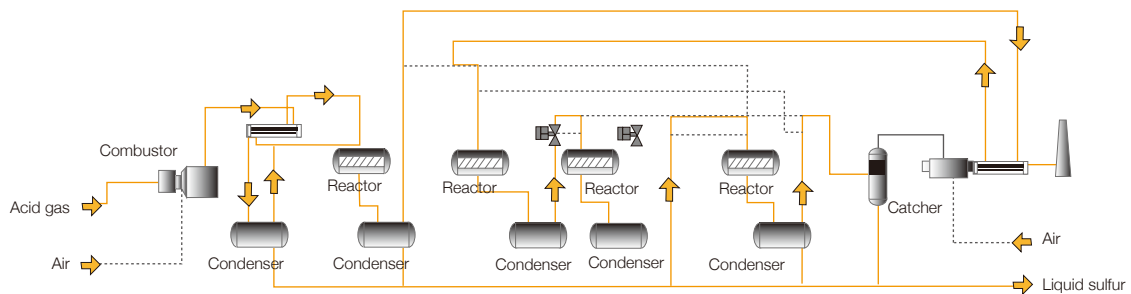
A computational model for H₂S and CO₂ removal process with formulated solvents has been established, which can accurately simulate the solvent purification effect with the error less than 5%.

We have also developed 17 kinds of analysis methods, including the determination of total sulfur content and H₂S content in natural gas, all being adopted as China's national standards. In particular, the Natural gas—Determination of sulfur compounds—determination of total sulfur by oxidative microcoulometry method was officially issued as an international standard ISO 16960:2014 in October 2014.

2. Sulfur recovery and tail gas treatment

An improved low-temperature Claus sulfur recovery process was invented, with the recovery rate of 99.45%.

- ▶ Raise regenerated gas temperature and add pre-cooler to avoid operating fluctuation
- ▶ Set sulfur pre-separation to improve conversion rate during regeneration stage
- ▶ Recycle heat energy of flue gas, reducing energy consumption by 10%



Improved low-temperature Claus sulfur recovery process

Catalyst series for sulfur recovery and tail gas treatment, represented by titania-based sulfur recovery catalysts and Claus tail gas low-temperature hydrogenation hydrolysis catalysts have been developed.

- Organic sulfur hydrolysis rate of process gas increased from 50% to 85%
- Operating temperature of reactor decreased by 60-80°C

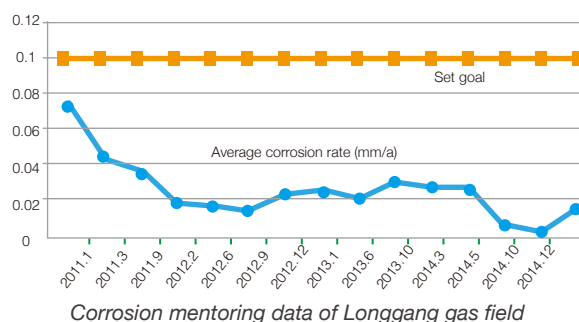
3. Natural gas purification pilot test center

CNPC has built a natural gas purification pilot test center in Sichuan, which consists of five testing units and ancillary facilities. The whole process for sour gas purification, including H₂S and CO₂ removal, sulfur recovery and tail gas treatment, can be tested at the center with the largest flow of 10,000 m³/d and highest pressure of 9.0 MPa.

Application

In the Longgang gas field, where the maximum H₂S content and maximum CO₂ content in the produced gas are 130.3g/m³ and 95.6g/m³ respectively, the application of the above technologies and measures has resulted in an average corrosion rate much less than the set goal of 0.1mm/a. Additionally, the circulation volume of solutions was decreased by 15%, usage of regenerating steam reduced by 17%, operating temperature of the reactor dropped by 60°C, and tail gas emissions meet relevant national standards.

In the Longwangmiao gas field, corrosion rate was less than 0.076mm/a, H₂S content in the processed gas was less than 6 mg/m³, the circulation volume of solutions was decreased by 20% and sulfur recovery rate reached 99.45%.



Corrosion mentoring data of Longgang gas field



Longgang Natural Gas Purification Plant