

Development of Catalytic Technologies for purification of gases from Hydrogen Sulfide based on direct selective Catalytic Oxidation of H₂S to elemental Sulfur

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Abstract

In the Boreskov Institute of Catalysis in cooperation with specialists of All-Russian Institute of Hydrocarbons Raw Materials novel methods of purification of fossil fuels based on oxidation of hydrogen sulfide to elemental sulfur have been developed. In this paper the results of laboratory and pilot plant testing of the technologies are presented.

Introduction

Hydrogen sulfide is known as one of the most toxic atmospheric pollutants. Acid rains, depression of vegetation, dying of aqueous flora and fauna, increase in respiratory and oncological diseases are typical consequences of the adverse effect of hydrogen sulfide and toxic products of its processing, such as sulfur dioxide, carbon oxide-sulfide, carbon disulfide. Sources of hydrogen sulfide emission to atmosphere are mainly man-caused, the most important of them being the extraction and processing of oil and hydrogen sulfide containing natural gas. Natural gases with a high content of H₂S are very common (e.g. Astrakhan gas field in Russia, Karachaganak gas field, Tengiz oil-gas field in Kazakhstan, Jiu-Ji-Lyan` in China, Bearberry in Canada), and they are playing very significant role in the world's energy balance. On the other hand, hydrogen sulfide is an important raw material for elemental sulfur production. Sulfur, in its turn, is a starting material for sulfuric acid synthesis [1]. That is why the problem of the development of environmentally friendly technologies of utilization of hydrogen sulfide containing gases resulting from fossil fuels extraction and processing is a challenge to the world community.

There are many methods of H₂S removal from gaseous mixtures. The ones most developed to date are methods based on the use of different sorbents, such as diethanolamine, monoethanolamine and synthetic zeolites. Despite rich experience accumulated in this field and a rather high efficiency, all these methods only isolate acid components (H₂S and CO₂), and they have to be used in the combination with other processes to produce sulfur, usually with the conventional Claus process based on catalytic oxidation of H₂S by SO₂. At present the Claus process is the most recognized technology for sulfur production from fossil fuels. This process has many stages, and it has evident environmental drawbacks, because initially H₂S is burned in flame resulting in the formation of toxic side products, such as COS, CS₂ and nitrogen oxides. At present the efforts of many companies are directed to the improvement of different stages of the conventional Claus process: the use of oxygen as an oxidizer (COPE[®] process), improved catalysts (CRS-31 by Rhone-Poulenc) and installation of tail-gas purification systems (the cost of which reaches 40% of the total investment), such as SCOTT[®], Superclaus[®], etc.

Another group of methods is based on direct catalytic oxidation of hydrogen sulfide to elemental sulfur, which has been considered in some cases as a more efficient way to solve the problem of purification of fossil fuels from H₂S with simultaneous sulfur production [2]:

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This process has the following advantages:

1. it is continuous;
2. it leads directly to sulfur formation;
3. the operating conditions are very "soft", providing the possibility to oxidize hydrogen sulfide in natural gases without noticeable conversion of hydrocarbon part of these gases.

However, since reaction (1) is highly exothermic ($\Delta H = -221$ kJ/mole) technological problems of efficient heat removal from a fixed catalyst bed limit the application of this technology to gas streams with H_2S concentration below 10 vol.%. There are several commercial processes based on direct oxidation of H_2S to sulfur, like **MODOP**[®], **CATASULF**[®], etc., developed for specific goals, mainly for cleaning tail gas of Claus units.

A few years ago in the Boreskov Institute of Catalysis the technology of hydrogen sulfide direct catalytic oxidation in a fluidized catalyst bed, that has no restrictions on H_2S concentration has been developed. A raw hydrogen sulfide containing gas is supplied to the reactor with a fluidized bed of catalyst, simultaneously oxygen (or air) is fed into the catalyst bed by a separate flow. Prior to reagents supply, the catalyst bed is heated in order to initiate the catalytic reaction. The excessive heat of the exothermic reaction of H_2S oxidation is efficiently removed by a heat-exchanger immersed into the fluidized bed. The bed temperature is controlled by the regulation of the amount of heat removed from the bed with a heat-exchange agent [3-5].

New possibilities extending the range of the application of the technology of direct H_2S oxidation are provided by monolithic honeycomb catalysts recently designed for this process, which possess several technological advantages over granulated catalysts (most important of them low pressure drop), especially for the gases with low excessive pressure and for purposes when the pressure loss is unacceptable. [6]. These catalysts are promising for purification of tail gases and removal of H_2S from geothermal steam.

Results

Catalytic oxidation of hydrogen sulfide in a fluidized catalyst bed

Laboratory study

Experimental study of the reaction of H_2S direct catalytic oxidation was carried out in a flow setup

with a vibro-fluidized catalyst bed. Mixture $\text{H}_2\text{S} + \text{N}_2$ or $\text{H}_2\text{S} + \text{RH}$ was supplied from a gas cylinder to a mixing unit, where it was diluted with air. Reagents ratio $\text{H}_2\text{S}/\text{O}_2$ was varied within 0.3-2.0, depending on experimental goal. Flow rate of H_2S containing mixture was 1L/hour, and that of air was varied according to the reagents ratio. Inlet H_2S concentration ranged from 5 to 20 vol.%. Mixture was analyzed using GC "Tsvet-500" with TCD. Helium was used as a carrier gas, its flow rate being 30 ml/min. Separation of the gas mixture components occurred in two columns - with NaX and Porapak Q. NaX column (1m x 3 mm) worked at $T = 20^\circ\text{C}$ to separate O_2 , N_2 , (CO , CH_4). Porapak Q column worked at $T = 150^\circ\text{C}$ to separate CO_2 , H_2S , SO_2 and H_2O . The reaction was performed at $T = 130-300^\circ\text{C}$ and contact time τ ranging from 0.1 to 3.0 s.

Fig. 1 shows the comparison of H_2S oxidation over alumina and magnesium-chromium oxide catalyst. It can be seen that alumina performance in H_2S oxidation is inferior to that of Mg-Cr catalyst. The sulfur yield determined as the product of H_2S conversion and reaction selectivity to sulfur is less than 60% in all the range of the temperatures studied which may be attributed to the proceeding of the reverse Claus reaction over alumina, i.e. reaction of sulfur with water producing H_2S and SO_2 . Mg-Cr catalyst exhibits a high selectivity up to 300°C , which drops sharply at higher temperatures, possibly due to the initiation of H_2S gas phase oxidation to SO_2 proceeding via radical chain mechanism.

The effect of hydrocarbons in the composition of the initial gas mixture on parameters of the reaction of H_2S direct oxidation is the issue of fundamental importance in the development of processes of purification of fossil fuels from hydrogen sulfide. Initially the separate oxidation of hydrogen sulfide and propane was studied over Mg-Cr catalyst under similar conditions. In the both cases the ratio reagent/oxygen was kept stoichiometric: 2.0 for H_2S partial oxidation and 0.2 for propane deep oxidation. As can be seen from the results obtained (Fig. 2), the temperature regions where these reactions take place are sufficiently separated. Thus, at temperatures $220-260^\circ\text{C}$ when the sulfur yield is close to 100%, the reaction of propane oxidation proceeds at a very

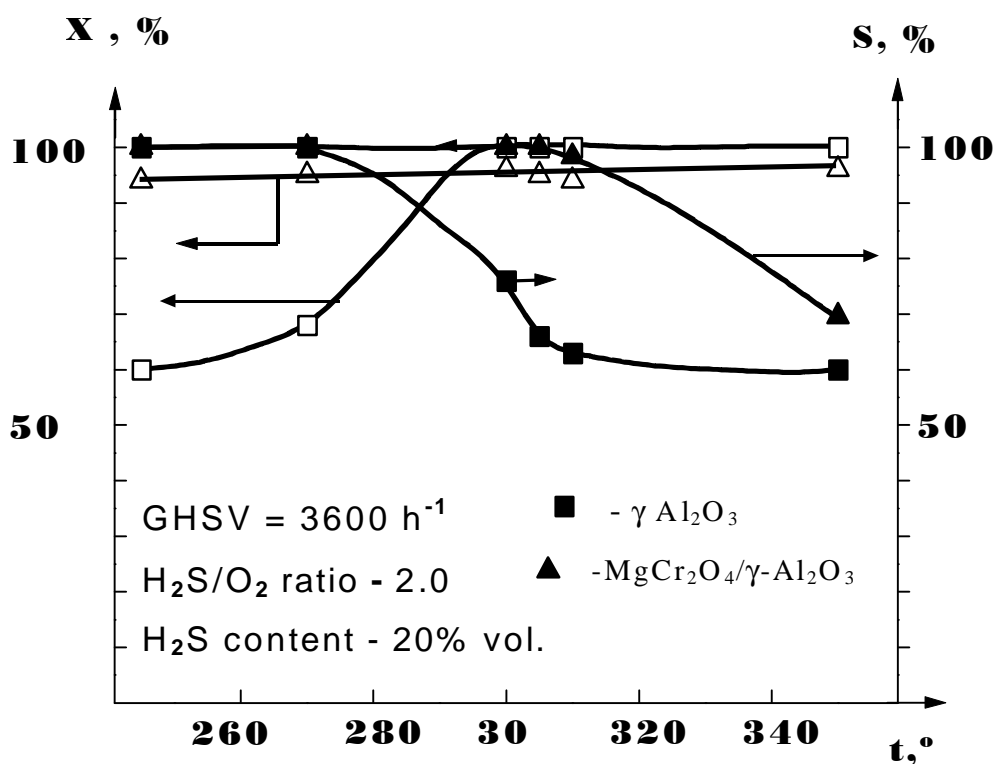


Fig. 1 H₂S conversion and selectivity vs temperature on catalysts γ -Al₂O₃ and MgCr₂O₄/ γ -Al₂O₃

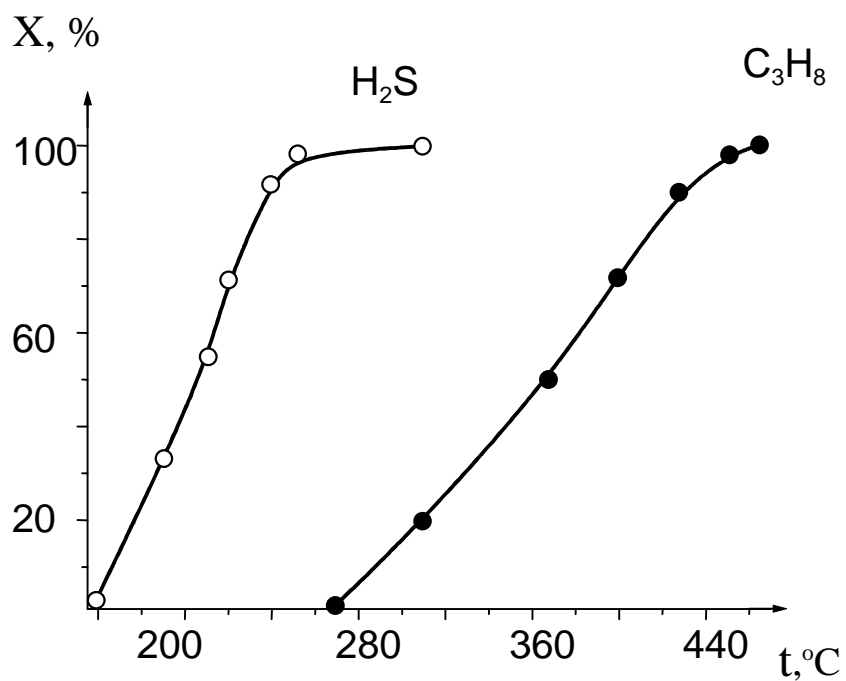


Fig. 2. Temperature dependencies of hydrogen sulfide and propane conversions over MgCr₂O₄/ γ -Al₂O₃

Table 1.Results of study direct catalytic oxidation of H₂S in the composition of hydrocarbon containing

| Gas mixture components | Gas composition, vol. % | |
|---------------------------------|-------------------------|----------------|
| | Reactor inlet | Reactor outlet |
| H ₂ S | 4.6 | 0.03 |
| CO ₂ | 5.1 | 5.2 |
| O ₂ | 2.4 | 0.1 |
| N ₂ | 10.1 | 10.3 |
| CH ₄ | 70.8 | 77.6 |
| C ₂ -C ₅ | 7.1 | 7.6 |
| SO ₂ ³⁰⁰ | - | - |
| SO ₂ ^{330*} | - | 0.02 |

slow rate. It is worth to note also that hydrogen sulfide has deactivating effect of on catalysts for hydrocarbon transformations (deep and partial oxidation, cracking, reforming, etc.) [7-8], thus it should be expected that in the case of the joint presence of H₂S and hydrocarbons in a gas mixture H₂S mainly the reaction of H₂S partial oxidation will take place, because the catalysts will be deactivated with respect to reactions of hydrocarbon transformations retaining sufficient activity for the goal reaction of H₂S oxidation.

The oxidation of H₂S in the composition of complex mixture containing hydrocarbons simulating real natural gas was studied directly over the Mg-Cr catalyst. The results of the experiments performed at 300°C and volume space velocity of 3600 h⁻¹ are given in Table 1. The data obtained demonstrate that the composition of the hydrocarbon portion of the mixture remains unchanged at the maximum temperature 300°C within the optimum range of 250-300°C. It was also shown that the introduction of hydrocarbons to gas mixtures containing H₂S has a positive effect on selectivity to sulfur especially at higher temperatures up to 330°C, which may be attributed to possible reduction of SO₂ to sulfur by hydrocarbons or by CO formed upon hydrocarbon incomplete oxidation.

Pilot tests.

The proposed process of H₂S one-stage catalytic oxidation to sulfur was tested in a pilot installation at the Ufimsky Refinery (Fig. 3) with the mixture simulating the composition of the acid gas formed upon processing of Karachaganak

natural gas. The capacity of the installation with respect to raw gas prepared by mixing H₂S with CO₂ was 10-50 m³/h. The tests were conducted as follows. The raw H₂S containing gas was taken from the monoethanolamine sorption unit at the Ufimsky Refinery and mixed with CO₂ from gas cylinders in a mixing unit. The resulting gas mixture was heated to 200-220°C in the electric heater and fed to the lower part of the catalytic reactor to be oxidized by air stream also preheated to 200-220°C in a fluidized catalyst bed. The reaction of H₂S oxidation proceeds with heat evolution, so in order to maintain optimum temperatures of 250-300°C, the excess heat was removed by a coil heat exchanger immersed into the bed, with 90-100°C water at the inlet and steam at the outlet.

Sulfur vapor produced in the reaction is directed to a sulfur condenser, where it condenses, and the resulting liquid sulfur is collected in a tank. The residual sulfur in the exhaust gas stream is removed by polyethyleneglycol in a sulfur trap at 160°C.

The results of the tests are given in Table 2. The data in the Table show that the H₂S conversion equals 97.8-98.9%, with the selectivity to sulfur being 97-99%. The installation allows to obtain commercial sulfur of the type 99.000 with a quality corresponding to the State Standard.

During testing stable bed temperature and fluidization regimes were maintained, and the catalyst IC-12-72 exhibited stable performance characteristics of activity and selectivity, which is the evidence of efficiency of the process developed and reliability of the design of the installation.

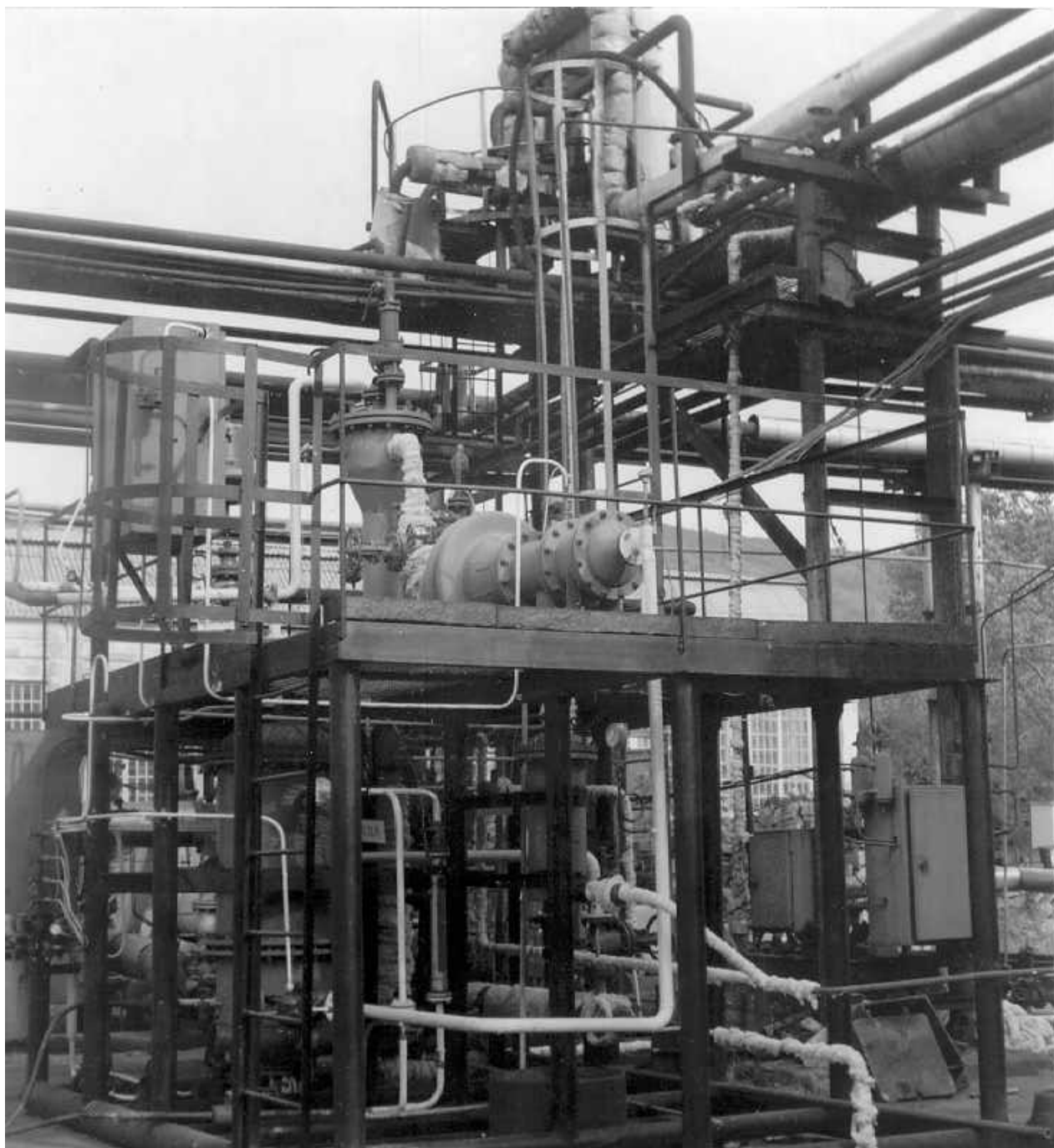


Fig. 3. Pilot installation at the Ufimsky Refinery.

Table 2

Results of the tests of the pilot installation at the Ufimsky Refinery

| T°C | C _{H₂S} , vol.-% | Conversion, % | Selectivity to S, % |
|-----|--------------------------------------|---------------|---------------------|
| 260 | 25 | 97.8 | 99.0 |
| 350 | 30 | 98.9 | 97.3 |
| 300 | 35 | 98.3 | 98.5 |
| 300 | 40 | 98.5 | 99.0 |

Experimental-industrial tests

The technology was tested at experimental-industrial scale at Shkapovo Gas Processing Plant, in Priyutovo, Bashkortan, Russia. This Plant was built for reprocessing of associated gas at Shkapovo oil field. The gas is treated by monoethanolamine absorption unit to remove H₂S and CO₂ and then fractionated to produce commercial products. The acid gas desorbed from monoethanolamine purification unit contains from 20 to 60% H₂S. Up to now, the acid gas was burned in torch and the products of combustion – predominantly SO₂ and unreacted H₂S were emitted to the atmosphere. To prevent the atmosphere pollution and utilize H₂S from the acid gas an experimental-industrial installation for H₂S direct catalytic oxidation was designed and constructed. The schematic diagram of the installation is given in Fig. 4. The raw gas for the installation is the acid gas supplied from the desorber column. The main parameters of the installation are given below:

| | |
|---|---|
| Capacity with respect to acid gas, nm ³ /h | up to 300 |
| Capacity with respect to sulfur produced, t/h | up to 0.2 |
| Catalyst loading, t | 0.1 |
| Catalyst type | IC-12-72(MgCr ₂ O ₄ /γ-Al ₂ O ₃) |

The tests of the installation allowed to optimize operating parameters and ensure the efficiency of H₂S conversion to sulfur at a level of 97%. The capacity of this installation is sufficient for the requirements of the Plant for acid gas reprocessing. Thus, the possibility to replace the Conventional Claus process by a new one-stage process of H₂S catalytic oxidation was demonstrated.

Direct oxidation of hydrogen sulfide to sulfur over monolithic honeycomb catalysts

Purification of tail-gas of the Claus units

The process of Claus unit tail gas purification using honeycomb catalysts was tested at experimental-industrial plant in the Novo-Ufimsky Refinery, Ufa. The conditions of tests are given below:

| | |
|---|------------|
| Gas supply to the plant, Nm ³ /h | up to 7000 |
| H ₂ S concentration, vol.-% | 0.2-3.0 |
| SO ₂ concentration, vol.-% | 0.1-0.3 |
| Catalyst loading, t | 3 |

The efficiency of H₂S removal was up to 95-98%. The experience of one year testing of the plant has shown that the catalyst retains its structural and mechanical properties (mechanical strength changes from 48.0 to 46.2 kg/cm²). The activity measured under standard conditions (250°C, V=7200 h⁻¹) has decreased only by 8-11% for samples taken from various parts of the reactor.

Purification of geothermal steam

Geothermal steam considered as an alternative source of electrical and heat energy usually contains admixture of hydrogen sulfide. It causes equipment corrosion and environment pollution. All modern methods for purification of geothermal steam deal with so called compressor exhaust, i.e. the steam at the turbine outlet. Thus the turbine equipment is not protected from a drastic impact of hydrogen sulfide. Basing on the experience in the development of processes of H₂S direct selective catalytic oxidation, we developed the method of purification of geothermal steam entering the turbine using honeycomb

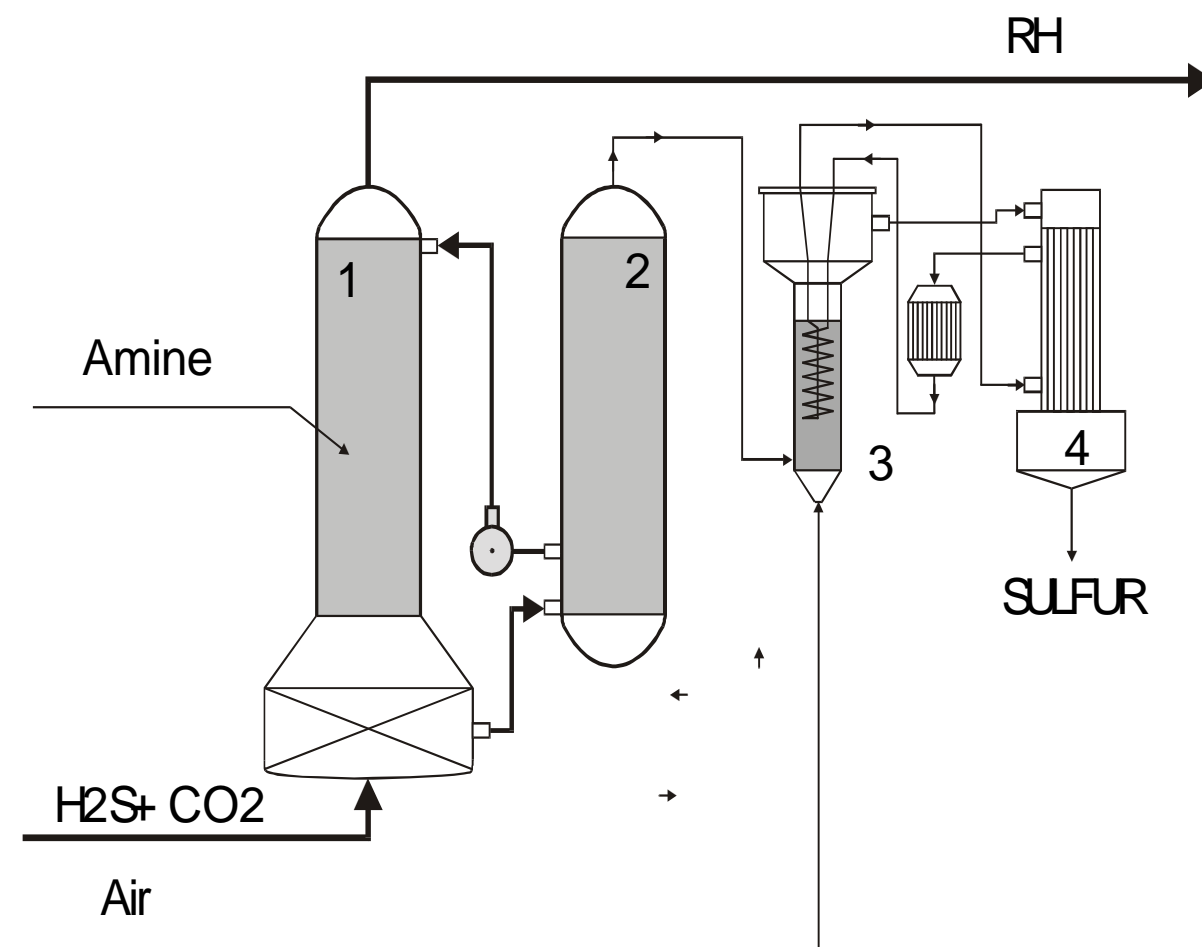


Fig. 4. Schematic diagram of the experimental - industrial plant at Shkapovo Gas Processing Plant:

1. Absorber
2. Desorber
3. Catalytic reactor
4. Sulfur condenser

monolithic catalysts. The unique properties of honeycomb monoliths provide conservation of initial steam parameters, and thus catalytic purification system has no significant effect on the turbine energetic parameters.

The comparative laboratory studies of supported catalytic systems showed that the catalyst based on vanadium pentoxide exhibits the highest activity and selectivity to sulfur in the reaction of hydrogen sulfide oxidation even after long exposure in an autoclave under 2.0 MPa of water vapor.

Based on the results obtained a pilot batch of catalysts was manufactured. The pilot plant with characteristics listed below was designed and built

at Mutnovskoe deposit (Kamchatka peninsula, Russia).

Main characteristics of the pilot plant:

| | |
|----------------------------------|-----------|
| Capacity (geothermal steam), t/h | up to 0.5 |
| Monolithic catalyst loading, kg | 100 |

Operation conditions:

| | |
|--------------------------------|---------|
| T, °C | 150-180 |
| Pressure, MPa | 0.5-0.8 |
| H ₂ S conversion, % | ≥ 99 |

The results of the tests of the pilot plant are given in Table 3. It was shown that at a space velocity of

Table 3

Results of the tests of the pilot plant at the Mutnovsoe deposit of geothermal steam

| N° | Steam pressure, MPa | Steam temperature, °C | Steam feed rate, kg/h | Degree of H ₂ S removal, % |
|----|---------------------|-----------------------|-----------------------|---------------------------------------|
| 1 | 0.62 | 162 | 120 | 80 |
| 2 | 0.73 | 166 | 99 | 93 |
| 3 | 0.81 | 172 | 40 | 95 |
| 4 | 0.72 | 168 | 50 | 97 |
| 5 | 0.66 | 166 | 30 - 35 | 99.9 |
| 6 | 0.65 | 165 | 50 | 99.9 |
| 7 | 0.64 | 164 | 70 | 89 |

3600 h⁻¹ the efficiency of H₂S conversion to elemental sulfur was close to 80%. With space velocity reduced to 1000-1500 h⁻¹ the efficiency of purification increased to 99-99.9%. No sulfur dioxide was detected after the catalytic reactor. The study of the catalyst unloaded from the reactor after 2500 h of continuous operation showed that it retained its mechanical strength and phase composition.

Conclusions

Two modifications of efficient one-stage catalytic technology of direct H₂S oxidation to elemental sulfur were developed and tested - in a fluidized catalyst bed and over monolithic honeycomb catalyst.

We believe the promising fields for the implementation of the developed technologies to be:

1. purification of the natural gas upon the initial blowing of gas wells during well testing procedure,
2. processing of natural gas instead of Claus process
3. H₂S removal from tail gas in gas processing plants and refineries,
4. purification of oil-associated gases,
5. purification of geothermal steam.

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