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Field Technology for Desulfurization of Associated Petroleum Gas

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Abstract—Applicability of gas desulfurization technologies for sulfur-containing gases under conditions of the limited choice is analyzed. Data on efficiency of a new process for catalytic desulfurization of sulfur-containing gases through H_2S and RSH conversion in sulfur and disulfides, respectively, is demonstrated. The technology is approved in pilot projects of gas desulfurization at a flare line, on a gas-processing plant. The equipment is developed and certificated. Installations for catalytic desulfurization are intended to be equipped with a complete set of blocks for gas preparation and power-generating equipment directly at deposits. This solution substantially decreases both capital and operational expenditures compared to the traditional multi-stage absorption/desorption technologies such as expensive Claus process.

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It is well-known that resources of sulfur-containing gases in the CIS-countries are estimated at more than 25 trln. m^3. The problem of sour gases utilization cannot be solved without development of economically feasible desulfurization processes, at least, at one-third of the Russian deposits. On the other side, the practice of flaring crude associated petroleum gas or discharging it into the atmosphere, which still exists, damages the environmental situation in the oil regions and contradicts the fundamental principles of rational nature management. Utilization of associated gases that are extracted from sour crude oil fields and contain hydrogen sulfide and mercaptans requires new solutions. The existing desulfurization processes cannot ensure the achievement of normative values for utilization of associated petroleum gas (APG) due to a high level of capital and/or operational costs.

In this connection, economic challenges and problems related to the quality of gas processing come to the fore. Russia developed adsorption technologies for preparation of natural gas for transportation; however, these methods are of little applicability for APG processing. This fact is largely connected to the presence of sulfur compounds such as H_2S (and in some cases, mercaptans and COS), which are toxic for adsorbents, in APG. On the other side, low pressures and high concentrations of water vapors also require new processing methods. The currently applied desulfurization technologies often cause additional environmental problems.

As is well-known, the reduction of hydrogen sulfide to sulfur is a key stage in cleaning of raw gases [1–3] ensuring compliance of the marketable products and atmospheric emissions with the normative requirements to sulfur content. A high toxicity and aggressiveness of sulfur impurities define the upper limit of their content in gases for household and industrial purposes at a level of 10–20 ppm. For application of such raw materials in gas chemical production it is necessary to achieve much lower concentrations of hydrogen sulfide and mercaptans in order to avoid poisoning of the catalysts.

At present, the major method of hydrogen sulfide utilization and sulfur production is based on application of the Claus reaction. In Russia the annual output of sulfur manufactured on the basis of the Claus process exceeds 6 mln. t $year^{-1}$.

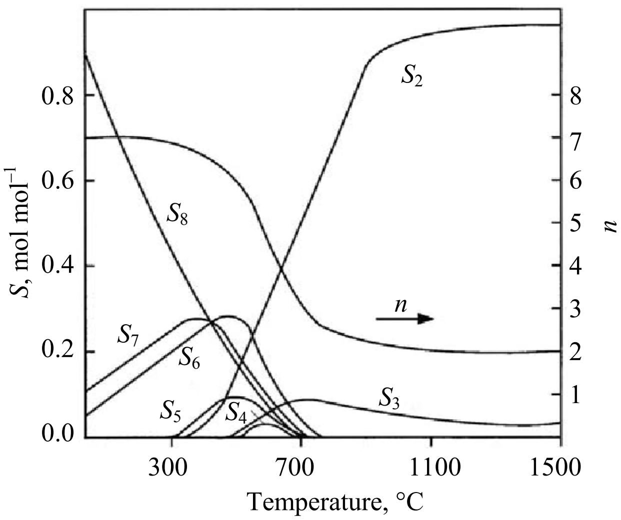

Fig. 1. Equilibrium content of sulfur at various temperatures.

Before considering the major aspects of this most wide-spread technology it should be noted that there is a wide variety of methods for cleaning of gases from sulfur impurities. They include application of special sorbents, catalytic techniques for oxidation of hydrogen sulfide to sulfur by liquid-phase processes (methods like LOCAT), and alkali treatment. However, due to high costs these techniques are only applicable within a limited range of processing capacity with regard to gas and sulfur.

Below we consider alkali treatment of gas as an example. This technique is presently applied for desulfurization of APG at minor deposits. The method is based on acid-base interaction of hydrogen sulfide with an alkali described with the following reactions:

$$H_2S + 2NaOH \rightarrow Na_2S + 2H_2O, \qquad (1)$$

$$H_2S + NaOH \rightarrow NaHS + H_2O. \qquad (2)$$

Stoichiometry of hydrogen sulfide interaction with the alkali determines the consumption of the reagent exceeding 1 t per each ton of hydrogen sulfide extracted from hydrocarbon raw materials. Costs of the alkali range from 400 to 1200 rubles for desulfurization of 1000 m^3 of gas containing 1–2% of hydrogen sulfide.

Therefore, the costs of reagents required for alkali treatment of APG are quite high and set bounds on applicability of the technique limiting it with low-capacity processes with regard to hydrogen sulfide. Moreover, application of alkalis causes additional environmental problems related to utilization of alkaline wastes. However, alkali treatment basically remains the most realistic way of treatment in field conditions.

As is known, the main method of gas purification from hydrogen sulfide at gas-processing plants with an APG gathering system is amine treatment in combination with the Claus process for sulfur recovery [1–4]. The process of desulfurization includes a number of stages. During the amine treatment the flows of gas and hydrogen sulfide are separated. During the amine regeneration stage hydrogen sulfide is separated and sent to the Claus process reactors.

The first thermal stage of the Claus process is oxidation of hydrogen sulfide with excess oxygen resulting in sulfur dioxide formation:

$$H_2S + 3/2O_2 = H_2O + SO_2. \qquad (3)$$

The formed sulfur dioxide reacts with hydrogen sulfide in a cascade of catalytic reactors:

$$2H_2S + SO_2 \leftrightarrow 2H_2O + 3S. \qquad (4)$$

As is well-known, in order to ensure quantitative conversion of hydrogen sulfide the process is usually performed in a cascade of reactors due to the reversibility of the Claus reaction. The yield of sulfur is related to the equilibrium concentration (Fig. 1) [2].

After implementation of the Claus reaction in a cascade of reactors the gas contains up to 1–2% of hydrogen sulfide and other sulfur compounds [3]. Therefore, the waste gases of the Claus process go through advanced treatment. There is a wide range of methods for advanced treatment of the Clause process waste gases based on oxidation of all sulfur compounds to sulfur dioxide or their recovery to hydrogen sulfide [1–4]. In the advanced treatment processes hydrogen sulfide is also oxidized to sulfur in accordance with the following reaction:

$$H_2S + 1/2O_2 = S + H_2O. \qquad (5)$$

Unlike the Claus process, this reaction (5) is irreversible, which ensures high selectivity of hydrogen sulfide oxidation to sulfur. Despite a great number of scientific and patent publications on catalysts applied for direct oxidation of hydrogen sulfide into sulfur, the choice of catalytic systems for industrial use is limited. The most widely applied catalysts are based on metal oxides in solid or deposited form [6–9].

The Superclaus process developed by Comprimo B.V., VEG-GasInstitut N.V. (Netherlands) ensures the

Fig. 2. Pilot unit for APG desulfurization on flare line.

sulfur recovery rate exceeding 99.5% [5–10]. When the reaction involves application of the catalyst [12], the residual concentration of hydrogen sulfide can be reduced to 1–10 ppb, i.e. to 10^{-3} ppm. The optimal range of hydrogen sulfide content in the source gas, coming for oxidation in accordance with the reaction (5), is 2–3%.

It should be noted that it is quite a common range of hydrogen sulfide content in APG. Desulfurization of gas through direct oxidation of hydrogen sulfide can significantly simplify the purification due to transition from amine treatment multistage processes (including the Claus process for sulfur utilization) to the described reaction (5).

There is a number of technological, environmental, and economic prerequisites for development of a commercial-scale technology for desulfurization of APG on the basis of the specified reaction. In fact, this reaction (5) is widely applied for purification of the Claus process waste gases from hydrogen sulfide. In countries of the European Union there are dozens of processes for advanced treatment of this type. However, there is no practice of applying this reaction (5) for desulfurization of APG directly in the flow of source hydrocarbon materials.

It is evident that appearance of domestic catalysts for the reaction (5) can change the situation significantly and simplify the process of gas desulfurization. Such simplified approaches are in the highest demand especially in the case of APG treatment, when it is necessary to ensure APG purification directly at mining and production sites in order to use the gas for the extracting companies' own needs or for power generation purposes.

Fig. 3. Catalyst unit and pelletized catalyst.

Specialists of the Start-Katalizator Research and Innovation Company in cooperation with researchers of the Chemical Faculty of Lomonosov Moscow State University and Topchiev Institute of Petrochemical Synthesis developed a process for desulfurization of APG directly in the sour gas flow based on adaptation of the technology and application of the equipment for purification of the Claus process waste gases in compliance with the reaction (5).

The process ensures selective oxidation of hydrogen sulfide and mercaptans with the catalysts [12–14] according to the reactions (5) and (6).

$$2RSH + 1/2O_2 \rightarrow RSSR + H_2O, \qquad (6)$$

where R = mostly C_1–C_3-alkyl.

Conditions of APG Desulfurization Process

Gas from a standby flare line was sent to desulfurization. The composition of the gas was as follows (wt %): methane 49.9, ethane 3.7, propane 14.0, *n*-butane 7.2, *iso*-butane 2.8, and C_5^+ 4.39. The gas density amounted to 1.25 kg m^{-3}, the moisture content reached 39%, and the calorific value amounted to 55.08 (gross) and 50.37 (net) MJ mol^{-1}. The hydrogen

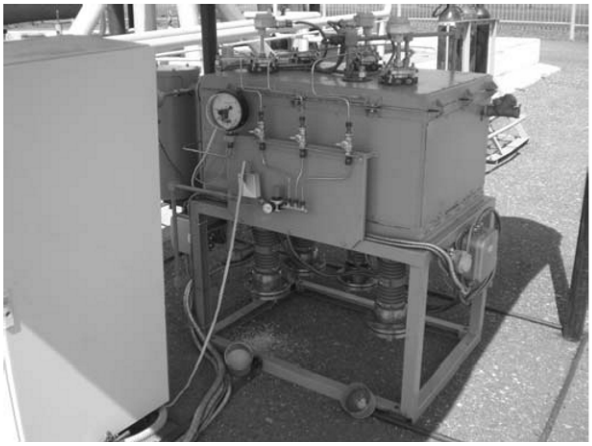

Fig. 4. Sulfur in sulfur-collecting units.

sulfide content in the crude gas amounted to 35.06 g m^{-3} at average and the content of mercaptans (in terms of sulfur) reached 14.85 g m^{-3}. The volume rate of the gas flow at the inlet of the unit was varied within a range of 300–600 l h^{-1}; the air was supplied at a rate reaching 80 l h^{-1}. The gas initial temperature was changed from 6 to 27°C.

The design of the equipment envisaged two processing zones for desulfurization:

– zone of catalysis, T > 200°C, where hydrogen sulfide and mercaptans are converted to sulfur and disulfides, respectively;

– zone of sulfur condensation, T = 140°C.

The flow of associated petroleum gas mixed with air is supplied to the catalyst unit with pelletized catalyst. Together with the hot gas flow the oxidation products formed in compliance with the reactions (5), (6) go through the zone of sulfur and disulfide condensation, and the clean gas leaves the unit.

After as little time as 10 minutes from the moment when the gas mixture started passing through the desulfurization unit, concentrations of hydrogen sulfide and mercaptans at the outlet of the unit decreased. The time to stationary temperature amounted to 105 min. The difference of the gas temperatures at the inlet and outlet of the reactor ranged within 20–70°C. No cases of sharp heating were observed. Oxidation products in the amount of 300–500 g were accumulated in the sulfur-collecting units during 10–12 h of operation.

It was found that residual concentrations of hydrogen sulfide and mercaptans amounted to 20–6 ppm. The desulfurization rate reached 99.6–99.9%.

Calculation of the material balance with regard to hydrogen sulfide and mercaptans is given in Table 1.

As follows from the data of Table 1, the material balance is more than 95%. Losses of sulfur are related to the specific design features of sulfur-collecting units and partial dissemination of sulfur on the ground during the removal of sulfur-collecting units (see Fig. 4). It should be noted that under laboratory conditions the material balance was minimum 98%.

Table 1. Material balance of the pilot desulfurization unit with regard to hydrogen sulfide and mercaptans. Gas volume rate of 600 l h^{-1}

Sulfur content	At the inlet		At the outlet	
	testing time of 3 h	testing time of 11 h	testing time of 3 h	testing time of 11 h
H_2S, g m^{-3}	33.24	33.26	0.12	0.12
RSH, g m^{-3}	15.81	15.81	0.14	0.14
Total weight of sulfur in H_2S and RSH, g	88.29	323.8	0.47	1.73
Sulfur accumulated in sulfur-collecting units, g:				
de facto			85.8	308.18
estimated amount S, g			87.82	322.14
Difference between theoretical and actual yield of sulfur:				
g			2.02	13.96
%			2.3	4.33

Table 2. Compliance of calorific values of C_1–C_6 and C_1–C_4 hydrocarbon fractions in purified gas with GOST requirements

Gas composition after desulfurization, vol %		Calorific value (net), kcal m^{-3}
N_2	31.76	
Methane	33.03	2635.5
Ethane	15.01	2146.7
Propane	10.2	2108
Butanes	3.1	845.6
Pentanes	0.88	302.9
Hexanes	0.29	111.9
Heating value, kcal m^{-3}		
Mixture of C_1–C_6 hydrocarbons		8150.6
Mixture of C_1–C_4 hydrocarbons		7735.8
All-Union State Standard GOST 5542-87		7600

Table 3. Temperatures and concentration limits for auto-ignition of hydrocarbon-air mixtures at atmospheric pressure

Hydrocarbon	Calorific value, kcal kg^{-1}	Standard auto-ignition temperature, °C	Lower limit, C_l, vol %	Upper limit, C_u, vol %
Methane	11 910	537	5.0	15.0
Ethane	11 300	515	3.0	12.5
Propane	11 100	466	2.1	9.5
Butane	10 900	405	1.8	8.5
Pentane	11 600	260	1.4	7.7

No formation of sulfur dioxide was observed either under laboratory conditions or during pilot tests.

Therefore, purification of APG from hydrogen sulfide and mercaptans can be performed using the catalysts [12–14] with high efficiency. The tests of the desulfurization/demercaptanization technology under conditions of the existing gas-processing plant confirmed this conclusion and demonstrated that after the treatment residual concentrations of hydrogen sulfide and mercaptans could be significantly lower than the requirements of the GOST (All-Union State Standards).

Below we analyze possible limitations for application of the catalytic desulfurization technology.

The content range of sulfur compounds amounted to 2–3% for one stage. However, as was demonstrated by the results of the pilot tests, in case of dosed air supply at several points along the gas passage can proportionally increase the range of the initial content of sulfur compounds in APG and raise the upper limit at least by a factor of 2–3.

The reaction (5) was carried out using atmospheric oxygen. The behavior of the reaction (5) with participation of atmospheric oxygen is connected to certain dilution of the gas with nitrogen. Let us assess the calorific value of the gas with the initial content of hydrogen sulfide of 3.0% and nitrogen of 31.76% after desulfurization in terms of compliance with the normative requirements [15, 16]. The data on the gas composition and calorific value of the mixture after desulfurization according to the reaction (5) are given in Table 2. In compliance with the reaction equation, oxidation of hydrogen sulfide with atmospheric oxygen can increase the nitrogen content by 6–7%, i.e. to 37–38%.

During oxidation of hydrogen sulfide with atmospheric oxygen the contribution of nitrogen amounts to approximately 22% of its initial content in case the gas of the specified composition is used. In this case the heating value of the clean gas is in compliance with the normative value [15, 16].

It should be noted that at present the prevailing practice involves the use of APG for power generation

Table 4. APG extraction volumes and concentrations of pollutants on sites

Deposit	Extraction volume, m^3 $year^{-1}$	$[H_2S]$, g m^{-3}	[RSH], g m^{-3}	H_2S emissions, t $year^{-1}$	RSH emissions, t $year^{-1}$
no. 1	3000000	40	20	120	60.0
no. 2	1200000	36	18	43.2	21.6

Table 5. Standard penalty rates for emitting pollutants into the atmosphere

Pollutant	Standard rates for 1 t of polluting emissions		
	Within the range of permissible standards, RUR t^{-1}	Within the range of fixed limits, RUR t^{-1}	Exceeding fixed emission limits, RUR t^{-1}
H_2S	257	1285	6425
RSH	20498	102490	512450

Table 6. Penalties for emitting hydrogen sulfide and mercaptans (RUR $year^{-1}$) taking into account coefficients [20] for different degrees of APG utilization

Deposit	APG processing of 90%		APG processing of 80%	
	H_2S	RSH	H_2S	RSH
no. 1	346950	11530125	1040850	34590375
no. 2	124902	4981014	374706	14943042

at oil-production sites. Associated petroleum gas is a high-energy fuel. Taking into account high energy consumption of crude oil production, it should be noted that the practice of using APG for power generation to satisfy the field needs is quite feasible and spread all over the world. At the same time, the gas that is supplied to power units has to comply with a number of requirements. In a wide range of cases, introduction of a certain additional quantity of nitrogen can play a positive role optimizing the value of the raw material heating capacity in compliance with the requirements of the power-generating equipment. Moreover, reduced temperature in the wet gas combustion zone contributes to a significant increase in the equipment operating life and a reduction in atmospheric emissions of nitrogen oxides. Addition of nitrogen into the gas in order to reduce the combustion temperature and ensure the optimal heating capacity is a widely applied technique [17]. In case of catalytic oxidation (5), it is done automatically. Due to the indicated reasons development of a compact desulfurization unit to be supplied to oil fields in a complete set with power-generating equipment is seen as the optimal technological solution for utilization of APG which is currently flared.

The main advantages of the desulfurization technology based on oxidation of hydrogen sulfide and the use of gas for power generation are as follows:

– possibility to ensure that residual concentrations of hydrogen sulfide and mercaptans are in compliance with the requirements set by manufacturers of the power-generating equipment;

– increased operating life of the power-generating equipment;

– compactness of the technology and reduced capital investment costs;

– versatility in terms of the gas content and operating conditions.

Compliance of the engineering solutions with the safety requirements is ensured by the use of gas-air mixtures containing significantly less oxygen compared to the lower flammable limit (see Table 3) [18] and by the dosed air supply along the gas passage in each oxidation reaction zone in amounts meeting the GOST (All-Union State Standard) requirements with regard to the oxygen content in household gas.

Therefore, as demonstrated by the data from Table 2 and 3, addition of atmospheric oxygen to crude hydrocarbons in accordance with the reaction equation (5) has no significant impact on the quality of marketable products and safety of the manufacturing process.

The desulfurization/demercaptanization technology is characterized by versatility and can be applied even at small- and medium-scale oil fields, gas-compressor stations, and gas-processing plants. By this, such solution compares favorably with the currently applied technology combining amine treatment and the Claus process for processing of hydrogen sulfide into sulfur. Moreover, due to the special design features, the latter technology can be only applied at large-scale plants. The proposed desulfurization technology is also versatile with regard to climatic factors. Its efficiency does not depend on weather conditions, unlike the efficiency of amine treatment, which is often reduced during hot seasons due to a shift of the adsorption-desorption equilibrium of hydrogen sulfide.

In conclusion, we will analyze the relevance of the task to provide minor deposits with APG desulfurization equipment in the context of imposed penalties. We will use two small-scale oil fields with the production capacity ranging from 1 to 3 mln m^3 of gas per year as an example. Table 4 provides data on annual volumes of sulphur-containing emissions at these two objects.

Table 5 illustrates sizes of penalties to be paid for emitting polluting components of sulfur-containing gases into the atmosphere [19]. The penalty rates are increased due to k_1 additional coefficient for emissions exceeding the fixed APG flaring limit of 5% and k_2 regional coefficient [20]. Table 6 provides the assessment of penalties at $k_1 = 4.5$ and $k_2 = 2$.

Introduction of such prohibitive penalties makes it commercially viable to build purification units even at minor deposits. It should be noted that the volume of the main reactor for APG desulfurization at deposits 1 and 2 amounts to 100–300 l, respectively (material – carbon steel). The catalyst life reaches 2 years without regeneration. The catalyst contains no rare or expensive components; the production time for manufacturing of the catalyst at the plant is 9 days for a lot of 30 t. It is obvious that the complete set of equipment includes more than the catalytic reactor of the specified volume. However, the value of the reactor volume can illustrate the compactness of the equipment within the framework of the process under description.

Therefore, oxidation of hydrogen sulfide and mercaptans directly in the flow of APG significantly facilitates the process of crude hydrocarbons desulfurization. As a result, the number of the processing stages and the dimensions of the basic equipment are reduced, which makes it possible to perform APG desulfurization directly at small sour crude oil fields.

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