METHOD FOR ADSORPTION PURIFICATION OF ASSOCIATED OIL GASES FROM MERCAPTANS

Abstract. The paper examines methods of utilization of zeolite regeneration gases to assess the possibility of using them in an industrial adsorption unit for drying and purifying gases from hydrogen sulfide and mercaptans. The most promising is the method of decomposition of mercaptans to hydrogen sulfide and hydrogen on solid catalysts, which is carried out at a pressure and temperature of 200-350 °C, as well as the method of direct gas-phase catalytic oxidation of mercaptans with atmospheric oxygen. We carried out experiments on the purification of zeolite regeneration gases of the Orenburg GPP by oxidation with atmospheric oxygen using an iron oxide catalyst at a temperature of 180-250 °C. They showed that the gas purified from mercaptans contained elemental sulfur and disulfides as the main oxidation products, and 0.2% vol. of sulfur dioxide was present as a by-product. The method of purification from mercaptans and heavy hydrocarbons gas regeneration of composite absorbent by thermocatalytic oxidation is also proposed. To reduce the yield of undesirable sulfur dioxide in the regeneration gas purified from mercaptans, it is proposed to divide the regeneration gas stream into two streams, while the larger part, comprising about 80-90% vol., is sent to oxidation on a zinc-iron catalyst at 200 °C, the second stream is mixed with oxidation products in a volume ratio in terms of mercaptans and sulfur dioxide equal to 1.5-2.2:1, respectively, then the resulting mixture is passed at 160-200 °C through a titanium oxide catalyst with a gas volumetric velocity of 4000-6000 h⁻¹. The proposed scheme for gas purification from mercaptans and heavy hydrocarbons on a composite absorbent with oxidative regeneration makes it possible to carry out the subsequent process of amine purification of gas from hydrogen sulfide without the complications associated with foaming of the working solution. Furthermore, it becomes possible to transport gas purified from mercaptans and hydrogen sulfide through the pipeline without precipitation of condensate.

Keywords: adsorption; gas purification; associated gas; mercaptans; hydrogen sulfide; regeneration gases; thermocatalytic decomposition; oxidation; sulfur; disulfides; recirculation gases.

The relevance of the topic. Adsorption treatment using aluminosilicates is widely used in the gas and petrochemical industry for drying and purifying natural gases from mercaptans. The process of drying and purification of natural gas from sulfur compounds is carried out in an adsorber system, which is filled with zeolites and work alternately at the stages of adsorption of impurities from raw materials, regeneration, and cooling of zeolites. During the adsorption treatment of gas, impurities such as water, hydrogen sulfide, mercaptans pass into the primary porous structure of the adsorbent. When the adsorbent is saturated with extracted impurities, its high-temperature regeneration is performed by a gas stream, into which previously extracted impurities pass [1]. The degree of gas adsorption treatment and its economic efficiency largely depends on the technology of adsorbent regeneration, the choice of regeneration gases.
(i.e. desorbing gas), and the method of their utilization (i.e. gases of desorption or regeneration) of adsorbents. In addition to mercaptans, hydrogen sulfide and water vapors, carbon dioxide, and sulfur compounds from the source gas are concentrated there.

Thus, current research projects are aimed at developing methods for adsorption purification of associated petroleum gases from mercaptans.

**Discussion of problems.** Regeneration of the adsorbent of the drying process and purification of natural gas from sulfur compounds is carried out by heating the layer by purging the gas heated up to 320-380 °C through it. Moreover, as the regeneration gas, one can use 17-23% of raw gas that is delivered for drying and purification [2]. In industry as regeneration gas and cooler for zeolite, a natural gas adsorption drying unit usually uses 5-15% of gas (in terms of crude gas), which is supplied for drying and purification, and drained and purified from sulfur compounds [3]. It is possible to achieve deep regeneration of zeolite when the adsorbent is purged with a methane fraction extracted from a part of the natural gas, which is drained and purified from sulfur compounds and mixed with the nitrogen-methane fraction. This fraction is a waste of the helium concentrate production that ensures the calorific value of the fraction mixture to be no lower than 7600 kcal/m3 at the corresponding ratio [4]. Also, there is a well-known method of zeolite regeneration, which is applied for the drying and purifying of natural gas, where a methane fraction is used to purge the regenerated CaA zeolite [5].

A common disadvantage of the above-mentioned methods of zeolite regeneration at units of drying and purification of hydrocarbon gases is that adsorbent regeneration gases are obtained when using as a desorbing agent of hydrocarbon gases (methane fraction or part of the purified source hydrocarbon gas). Later, those adsorbent regeneration gases are used as fuel that is contaminated with the same sulfur-containing substances as the initial purified hydrocarbon gas. The purpose of the adsorption process is to concentrate sulfur-containing and other undesirable impurities of the source gas (then used as fuel) in its part, which is then also used as fuel for the needs of the enterprise. It pollutes the industrial zone instead of distribution in the environment by numerous consumers in the absence of purification of the hydrocarbon fuel gas. The process of adsorption treatment without the utilization of regeneration gases does not reduce the amount of sulfur oxide release into the atmosphere. Furthermore, the burning of valuable sulfur-containing substances leads to their irretrievable loss to the economy. The validity of extracting and processing of sulfur-containing substances present in zeolite regeneration gases is of ecological and economic importance.

**Materials and methods of research.** The production conditions where the adsorption installation operates, the composition of the purified gas, nature, and concentration of sulfur compounds, which are present in it, largely influence the choice of a rational method of utilization of zeolite regeneration gases or other adsorbents used in the drying processes and purification of the gas from sulfur compounds. The following three thermocatalytic methods are the most promising for gas processing plants (GPP). The first of them is based on the reaction of decomposition of mercaptans to hydrogen sulfide and hydrogen on solid catalysts, which is carried out at a pressure and temperature (200-350 °C) of the adsorbent regeneration [6-12]. The practical implementation of this method at GPP is facilitated by the availability of energy at the plant for further purification of regeneration gas from hydrogen sulfide formed during the decomposition of mercaptans, and its utilization by the Claus process. In addition to hydrogen sulfide, thermocatalytic decomposition of mercaptans is accompanied by the production of saturated and unsaturated hydrocarbons, and parallel reactions of the destruction of amines, methanol, and other impurities contained in the zeolite desorption gas [13-15].

The third method is more attractive, and that is direct thermocatalytic gas-phase oxidation of mercaptans to sulfur by atmospheric oxygen. We carried out experiments on the purification of zeolite regeneration gases of the Orenburg GPP by oxidation with atmospheric oxygen using an iron oxide catalyst at a temperature of 180-250 °C. They showed that the gas purified from mercaptans contained elemental sulfur and disulfides as the main oxidation products, and 0.2% vol. of sulfur dioxide was present as a by-product [16-17]. In these experiments, it was found that hydrogen sulfide and other sulfur-containing compounds (carbonyl sulfide, carbon disulfide, sulfides), which are contained in small amounts in zeolite regeneration gases, are also subjected to oxidation, and the product of their oxidation is elemental sulfur. Most of the sulfur-containing oxidation products can be separated from the reaction gas by condensation when cooled to ambient temperature, which greatly simplifies the process.
One of the crucial processes for purification of zeolite regeneration gases is alkaline-free direct oxidation of mercaptans based on the conversion of H₂S and mercaptans to non-toxic forms (di- and polysulfides) by atmospheric oxygen directly in hydrocarbon media [18]. Oxidation reactions occurring in hydrocarbon raw materials are significantly accelerated in the presence of metal-complex catalysts based on transition metals [19-22]. This technology eliminates the stage of alkaline extraction and, consequently, the need for disposal of toxic sulfur-alkaline effluents. The effectiveness of such catalytic systems was established in the laboratory conditions on model mixtures of thiols and hydrocarbons, for example, which is shown in [18].

Most of the works of Kazakh scientists are devoted to the purification of oil gases.

The authors of the following work conducted research on the use of liquefied petroleum gas as a raw material for the production of liquid oxygen-containing organic compounds [23].

Research results. This article describes a method for purification of composite adsorbent regeneration gas, which, in contrast to aluminosilicate sorbents, can absorb not only mercaptans but heavy hydrocarbons contained in associated petroleum gas or processing gases of light hydrocarbon raw materials. The composite adsorbent is porous coal or natural sorbent impregnated with a moisture-absorbing substance, which has a high dynamic capacity for water [24]. During the development of the technology of gas regeneration of composite adsorbent by direct oxidation, a few new technical solutions were found that ensured the achievement of the following positive results [25]:

1) simplification of the catalytic stage by conducting the process in a single stage and lack of need for precise control of the ratio of components in the catalytic oxidation of mercaptans;

2) increase of purification degree of hydrocarbon gases by removing, along with mercaptans, both heavy hydrocarbons, and volatile oxidation products and sulfur vapors when gas purification on composite adsorbents is applied;

3) reduction of the energy consumption of the process due to the use of pre-concentration of mercaptans on composite adsorbents;

4) reduced material consumption by decreasing the volume of the catalytic oxidation reactor and loading the catalyst while decreasing the volume flow of the purified gas.

Figure 1 illustrates the scheme of a hydrocarbon gas treatment installation on a composite adsorbent with the utilization of regeneration gases by direct oxidation and recirculation into the stream of purified gas.

![Figure 1 - The scheme of a hydrocarbon gas treatment installation on a composite adsorbent with the utilization of regeneration gases.](image)


*Devices: 1 - gas separator; 2,3 - adsorbers; 4 - composite adsorbent; 5 - oxidation reactor; 6 - liquid-ring pump; 7 - catalyst*
According to this technology, the hydrocarbon gas is pre-mixed with the oxidation products, and the mixture is separated with the release of liquid oxidation products and separation gas. This gas is subjected to adsorption treatment on a composite adsorbent, using as porous coal, for example, the Sibunit brand, while indirectly cooling the adsorbent to the adsorption temperature, which should not be lower than the freezing point of water or hydrate formation. The adsorbent regeneration is carried out by blowing off the purified gas at low pressure and indirect heating the adsorbent with coolant to the regeneration temperature, and the regenerated adsorbent is cooled indirectly with a refrigerant to the adsorption temperature.

After that, the regeneration gas is mixed with air at a mass ratio of mercaptans to atmospheric oxygen equal to 2.2\(\div\)3.1, which is higher than the stoichiometric ratio equal to 2:1, and it is passed through the oxidation catalyst at the volume rate and oxidation temperature. The oxidation products are recirculated into the purified gas stream, compressed to the pressure of the hydrocarbon gas utilizing a liquid-ring pump using the liquid oxidation products as the working fluid. In this case, for example, atmospheric air can be used as a refrigerant, and the coolant can be atmospheric air heated with a catalytic air heater by direct mixing of the oxidation products of hydrocarbon condensate or dry gas with atmospheric air.

Pre-mixing of hydrocarbon gas with oxidation products and separation of the mixture with the release of liquid oxidation products and separation gas allows to remove the liquid products of the oxidative conversion of mercaptans from the process, to obtain a working fluid for a liquid-ring pump that recirculates the regeneration gas, as well as to recirculate the non-reacting mercaptans for re-oxidation. This prevents contamination of the adsorbent and increases its lifetime.

The purification of hydrocarbon gas from mercaptans, heavy hydrocarbons, volatile oxidation products, and sulfur fumes is possible thanks to adsorption treatment of separation gas using carbonaceous adsorbent at simultaneous indirect cooling of the adsorbent to the adsorption temperature, but not below the freezing point of water or hydrate formation. It is achieved through making the most favorable conditions for adsorption with a maximum dynamic capacity of the adsorbent, preventing its heating because of the heat release of adsorption. This reduces the adsorbent load and the metal content of the equipment.

Regeneration of the adsorbent by blowing off the purified gas at low pressure and simultaneous indirect heating the adsorbent with coolant to the regeneration temperature (200 °C) allows for deep regeneration of the adsorbent with minimal purge gas consumption. The optimal regeneration temperature depends on the chemical composition of purified gas and the type of adsorbent, the desired degree of purification of hydrocarbon gas from mercaptans, and heavy hydrocarbons (desired dew point by hydrocarbons), energy costs, etc.

The optimal flow rate of the purified gas for the regeneration of the adsorbent depends on the chemical composition of the gas being treated, the type of adsorbent, as well as the condition of the thermal balance of the mercaptan oxidation stage. When the concentration of mercaptans in the regeneration gas is high, the purified gas consumption for regeneration is increased to keep the temperature during the oxidation stage below the permissible level and to ensure the selectivity of the oxidation of mercaptans to disulfides and sulfur without the formation of sulfur dioxide. As the concentration of mercaptans in the regeneration gas decreases, the consumption of the purified gas for regeneration is reduced, and, if necessary, indirect heating of the catalyst with coolant is additionally performed to maintain the oxidation temperature.

The usage of indirect heating of the adsorbent by coolant to regeneration temperature in the regeneration stage and the indirect cooling of the regenerated adsorbent by the refrigerant to the adsorption temperature allows to control the temperature of the adsorbent and reduce the total duration of the regeneration stage and adsorption cycle, as well as to reduce the load of the adsorbent and metal content of equipment.

Oxidation of mercaptans present in the regeneration gas in a mixture with air has a mass ratio of mercaptans to atmospheric oxygen equal to 2.2\(\div\)3.1, which is higher than the stoichiometric ratio for the oxidation reaction to sulfur and disulfides, and it prevents the formation of sulfur dioxide, which can potentially contaminate the purified gas during a slip in the adsorber. A raise in the mass ratio of mercaptans to atmospheric oxygen higher than 3:1 leads to an increase in the recirculation of non-reacted mercaptans and an overload of the adsorbent. When the mass ratio of mercaptans to atmospheric oxygen becomes lower than 2.2:1, it leads to the formation of sulfur dioxide in the oxidation products, which
pollutes the purified gas. The experiments have shown that the optimal temperature and volume rate of oxidation depend on the type of catalyst.

The loss of hydrocarbon gas with the regeneration gas is prevented by recirculation of the oxidation products into the purified gas stream compressing it to the pressure of hydrocarbon gas. This is achieved by utilizing a liquid-ring pump that uses liquid oxidation products as the working fluid. Besides, it becomes possible to conduct regeneration at a reduced pressure of up to 5-15 kPa, which is determined by the characteristics of the pump and the initial pressure of the gas being treated. During compression, the oxidation products are cooled due to the contact of the gas with the working fluid, the liquid oxidation products are condensed, and most of the mercaptans contained in the hydrocarbon gas are absorbed. These processes take place without the use of additional cooling and separation equipment. As a result, the load of the adsorbent and the material consumption of the process can be reduced, whereas the degree of purification of hydrocarbon gas can be increased.

For example, the use of atmospheric air as a refrigerant and, as a coolant, atmospheric air heated with a catalytic air heater by direct mixing of the oxidation products of a hydrocarbon fuel with atmospheric air, allows providing effective heating and cooling of the adsorbent with the minimal technological difficulties.

The use of a catalytic air heater instead of a conventional fire furnace reduces the cost of equipment, the fire and explosion hazard of the installation and increases the reliability of its operation, as well as reduces the release of nitrogen oxides and carbon monoxide into the atmosphere due to controlled flameless combustion (oxidation) of gaseous or liquid distillate fuel at temperatures below 900 °C.

The efficiency of the described purification method of associated petroleum gas and regeneration gas is shown by the data of the following experiment at the pilot installation. The composition of the gas supplied for treatment, vol.% is oxygen 0.03, nitrogen 10.90, carbon dioxide 0.28, methane 70.10, ethane 5.61, propane 4.02, n-butane 2.65, isobutane 1.14, isopentane 1.35, pentane and higher 2.06, hydrogen sulfide 1.64, mercaptans 0.24. Chromatographic analysis reveals the absence of mercaptans in the purified gas, the content of other components is oxygen 0.13, nitrogen 11.66, carbon dioxide 0.29, methane 71.7, ethane 5.73, propane 4.10, n-butane 2.40, isobutane 1.12, isopentane 1.18, and pentane and higher hydrocarbons are absent.

Conclusions. Thus, the lack of heavy hydrocarbons in gas purified from mercaptans on composite adsorbent enables a subsequent process of its amine purification from hydrogen sulfide without the complications associated with the foaming of the working solution. Furthermore, it becomes possible to transport gas purified from mercaptans and hydrogen sulfide through the pipeline without precipitation of condensate.

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ИЛЕСПЕ МУНАЙ ГАЗЫН МЕРКПАННАН АДСОРБЦИЯЛЫК ТАЗАРТУДЫҢ ТәСІЛІ

Аннотация. Целочитр регенерация газын қаде ҝарату оларды тәтіру және газды құқырт сүтегі мен меркаптанан тазартудың өнерқасіпін адсорбциялық қондырысында пайдалану мүмкіндігін бағалу үшін талдау жұрғізілді.

Жұмыста композитті адсорбент регенерация газын тазарту әдісі сипатталған, оның алуомосииндикті сорбенттерден ғарғыларығы – меркаптандармен жататын кванттик шығаруының қосымша қысқақты жайға әкелу ғана болмаса, дәл өлімді, оңай және құдайығы көздерінің құрақтығына жақында қадедеетін алуым квантты сорбенттердің лейтінұлысына байланысты.

Текелей тәтінің есімдін композитті адсорбентті регенерациялдағы газын алу техникасының әрекетінің негізінде бірнеше оң затық екі жеткізді камтамасыз ететін бірқатар әрекет және техникалық үшін қажетілген.

– процесті жүргізу үшін бір саты әлемінде өткізу үшін және меркаптананың қалалыққа қатысты тәтінің кезінде компоненттердің аракетісін дәл реттеу қажеттілігінің болмауы есебінен қалалыққа қатысты анықталым қарая айналдыру.
– меркаптанылырмен қатар, ауыр қоюрсықтерді де және сонымен қатар тәзгірдің ұша өнімі мен күкірт буын өшіру және композиттіқ адсорбенттердің газ тазартуды қолдану әрқылы газ тазарту денгейін арттырыңыз;
– композиттіқ адсорбенттерге меркаптанылырды алын ала әкімшілік қолдану әсібінен әр тәріздің энергия әр түрлі дайындық азайту;
– тәттігі қаталитикалық реакторының қоғамдары және тазарылыс ғызғының колемдік шығынының азайту кезінде қаталитикалық қолдану әсібінен материалдық әр түрлі дайындық тығықты әдеміді.

Негізгілі, перспектив болып, 200–350 °С температура аралығында жұлдызамен меркаптанылыр күкірттің сұтегі мен сұтегіне дейінгі және қатама қаталитикалық өмірі тәзгірдің өмірін әйдіт қолдаңыз. 180–200С температураларда темпераураға қарсы козгатын ауызы өткізген өмірін өзгертетін қатынас өндірісті құрылыс үшін 0,2% денінен 0,8% түсінілген көрсеткішті. Сонымен қатар, меркаптанылыр ғызғын өздерінің әсібінен композиттіқ адсорбент рөліндерін және олардың қолданылуына дейінгі ауа өткізілген тәзгірдің өміріне қарсы қарқынылып, құрылыс және әкімшілік қолданылуы өзгерісін қорғайды.

Меркаптанылыр қолданылып, газотропа козгатын өмірін өзгертеді. Егерінен репозициялық тәзгірдің өмірін әйдіт қолдаңыз.

Тәттіқ қозгатын ықысы мен ауыр қоюрсықтердің композиттіқ адсорбент рөліндерін және рөліндерін және олардың қолданылуына дейінгі ауа өткізілген тәзгірдің өміріне қарсы қарқынылып, құрылыс және әкімшілік қолданылуы өзгерісін қорғайды.

Түйін сөзлер: адсорбция, газ тазарту, әкімшілік, меркаптанылыр, қуырсық, Қауіпсіздік, рөліндері, қолданылып, бойынша. 84.
- упрощение катализитической стадии за счет проведения процесса в одну стадию и отсутствия необхо-
димости точного регулирования соотношения компонентов при катализическом окислении меркаптанов;
- повышение степени очистки углеводородных газов за счет удаления наряду с меркаптанами, как
tяжелых углеводородов, так и легких продуктов окисления и паров серы, путем применения очистки газов
на композитных адсорбентах;
- уменьшение энергоемкости процесса за счет применения предварительного концентрирования
меркаптанов на композитных адсорбентах;
- снижение материалоемкости за счет уменьшения объема катализитического реактора окисления и
загрузки катализатора при уменьшении объемного расхода очищаемого газа.

Наиболее перспективными являются метод разложения меркаптанов до сероводорода и водорода на
твердых катализаторах, который проводится при давлении и температуре 200–350 °С, а также метод прямого
газофазного катализитического окисления меркаптанов кислородом воздуха. Опыты, проведенные нами по
очистке газов регенерации цеолитов Оренбургского ГПЗ путем окисления кислородом воздуха на
железооксидном катализаторе при температуре 180-250°С показали, что в очищенном от меркаптанов газе в
какие основных продуктов серы находится на уровне 0,2 % об. Предложен также метод очистки от
меркаптанов и тяжелых углеводородов газов регенерации композитного адсорбента методом термоизоли-
тического окисления меркаптанов до серы кислородом воздуха.

Для снижения выхода нежелательной двукиси серы в очищенном от меркаптанов газа регенерации
предложено поток газа регенерации делить на два потока, при этом большая по объему часть, составляющая
примерно 80-90 % об., направляют на окисление на железохромнициновом катализаторе при 200°С, а второй
попутники с продуктами окисления в объемном соотношении в пересчете на меркаптаны и двукись
серы, равном 1,5-2,2–1, соответственно, и полученную смесь пропускают при 160-200°С через титаноксида-
ный катализатор при объемной скорости газа 4000-6000 ч⁻¹.

Предложенная схема очистки газов от меркаптанов и углеводородов композитного адсорбента с окисительной регенерацией дает возможность вести последующий процесс аминовой очистки
газа от сероводорода без охлаждения, связанного с вспениванием рабочего раствора, и осуществлять
транспортировку очищенного от меркаптанов и сероводорода газа регенерации по трубопроводу без
выпадения конденсата.

Использование в качестве хладагента, например, атмосферного воздуха, а в качестве теплоносителя
- атмосферного воздуха, нагретого с помощью катализитического нагревателя воздуха прямым смещением
продуктов окисления углеводородного топлива с атмосферным воздухом, позволяет с наименьшими
технологическими сложностями обеспечить эффективный нагрев и охлаждение адсорбента.

Использование катализитического нагревателя воздуха вместо обычно применяемой печи огневого
нагрева позволяет снизить стоимость оборудования, уменьшить пожаро- и взрывоопасность установки и
повысить надежность его работы, а также сократить выбросы окислов азота и окиси углерода в атмосферу за
 счет контролируемого беспламенного сжигания (окисления) газообразного или жидкого дистиляционного
tоплива при температуре ниже 900°C.

Ключевые слова: адсорбция; очистка газов; попутный газ; меркаптаны; сероводород; газы
регенерации; термокатализитическое разложение; окисление; сера; дисульфида; газы рециркуляции.

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