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TECHNOLOGICAL SOLUTION FOR COMBATING HYDROGEN SULFIDE AT THE FIELD

Abstract: One of the urgent problems in the production of hydrogen sulfide-containing oils is the problem of increasing the efficiency of hydrogen sulfide removal. Optimization of costs associated with the production, transportation and preparation of oil is very important at the present time.

In order to reduce the costs of oil preparation, the use of a differentiated approach to solving the problem of its purification from hydrogen sulfide at the Kashagan field depends on the volumes of oil preparation, the mass fraction of hydrogen sulfide in the oil, the presence of gas near the high-sulfur oil preparation unit (UPVSN) that does not contain hydrogen sulfide, the presence of a gas collection system and the possibility of transporting increased volumes of hydrogen sulfide-containing gas to the sulfur purification unit.

Taking these factors into account, it is necessary to identify the maximum values of the volume fractions of methane, ethane, nitrogen and carbon dioxide in the composition of the stripping gas, at which the mass of oil will be preserved, as well as the conditions under which it will be purified from hydrogen sulfide in the conditions of the Kashagan field.

Studies have shown that with an increase in the oil heating temperature and a decrease in the pressure in the desorption column, the maximum total volume fraction of methane and nitrogen in the mixture in the composition of the stripping gas decreases. A decrease in the mass fraction of hydrogen sulfide in oil below 100 ppm and maintaining the mass yield of oil depending on the proportion of these components in the composition of the stripping gas is possible if the oil temperature and pressure in the column are optimized. An increase in the total volume fraction of methane and nitrogen in the composition of the stripping gas leads to a decrease in its required consumption to achieve a certain efficiency of oil purification from hydrogen sulfide at specified operating parameters of the column.

Key words: hydrogen sulfide, stripping, mass oil yield, stripping gas, multicomponent mixture, cleaning efficiency.

Introduction. The gradual depletion of oil and gas reserves on land and the aggravation of the global energy crisis have necessitated an ever-wider development of oil and gas resources on the continental shelf, in the depths of which almost three times more oil and gas is concentrated than on land. In this regard, hydrocarbon production on the continental shelves of the seas around the world is rapidly developing.

Removing hydrogen sulfide from oil is becoming an increasingly urgent task every year. The need to purify oil from hydrogen sulfide is caused by several reasons: the presence of these volatile toxic components creates serious environmental problems, causes accelerated corrosion of pipelines and oil storage facilities, and leads to accelerated wear of equipment. At the moment, there are many ways to purify oil from impurities, such as catalytic, reagent, sorption, adsorption, chemisorption. Commercial oil contains many impurities, one of which is sulfur-containing compounds, which are unacceptable in a commercial product, and these impurities also affect the fuel's environmental class. At the moment, for existing neutralizers of sulfur compounds, and in particular mercaptans and hydrogen sulfide, specific reagents are used that must be synthesized, purchased and certain technical conditions must be met, under which these reagents will work effectively.

Currently known methods for combating hydrogen sulfide and related complications in the processes of oil production, collection and preparation are recommended to be divided into four groups according to their functional focus [1, 2]:

– removal of hydrogen sulfide from well products;
– prevention of biogenic hydrogen sulfide formation;
– prevention of hydrogen sulfide corrosion of oilfield equipment;
– prevention of iron sulfide deposits in the productive formation and well equipment.

Hydrogen sulfide is removed from oil during its collection and preparation at separation units, where hydrogen sulfide is separated from oil together with other petroleum gases. However, the efficiency of the process, even with hot oil separation, does not exceed 10-30% [3].

Among the physical methods, three main ones should be distinguished: separation, rectification (stripping), and stripping.

There are various fundamental technological schemes for cleaning oil from hydrogen sulfide. The simplest of the listed methods is separation. In this regard, when developing oil fields containing hydrogen sulfide, it is advisable to focus the oil separation process on its maximum possible removal. Theoretically, the following ways to increase the intensity of hydrogen sulfide extraction from oil during separation are possible [3]:

- reducing the number of separation stages;
- reducing the separation pressure below atmospheric (vacuuming);
- increasing the process temperature;
- feeding an additional volume of sulfur-free gas into the oil (separation with stripping).

The effectiveness of the listed methods is ambiguous. Thus, it was found that reducing the number of separation stages slightly intensifies the extraction of hydrogen sulfide from oil. In addition, in practice, the use of this method can lead to a significant increase in the cost of commercial oil, since the optimal number of separation stages is taken at the minimum specific costs.

During vacuumization, the efficiency of hydrogen sulfide desorption increases almost linearly with increasing vacuum depth and reaches 60-65% at a pressure of 0.06 MPa at the separation stages. Higher efficiency of oil purification from hydrogen sulfide (70-75%) is achieved at the atmospheric separation stage with an increase in oil temperature to 80 °C [4]. The same results are observed when mixing oil at the separation stage with sulfur-free hydrocarbon gas in a volume of 3-5 m3/m3 (Fig. 1)

At the Kashagan field with an abnormally high content of hydrogen sulfide, it is necessary to use rectification (stripping) and stripping using mass-exchange column equipment, which ensure an oil purification efficiency of more than 95% [5].

During rectification, deep selection of gaseous components from oil, including hydrogen sulfide, is achieved. The latter is extracted in the stripping part of the rectification column when the oil is heated from 120 to 280 °C, depending on the process pressure. The pressure can vary from 0.2 to 0.8 MPa.

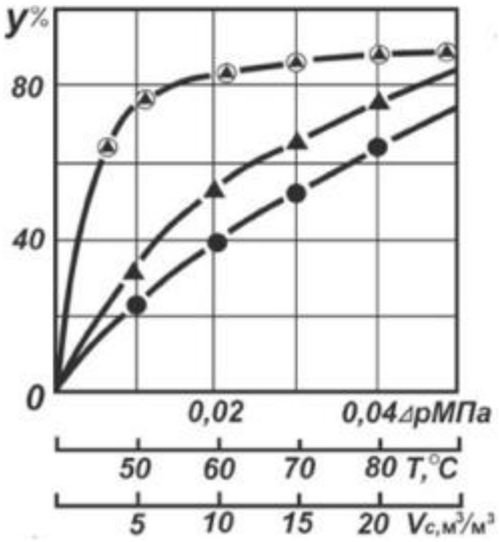

Figure 1 – Classification of methods for removing hydrogen sulfide and low molecular weight mercaptans

The upper strengthening part of the column allows for a clear separation of hydrocarbon components and has little effect on the efficiency of hydrogen sulfide extraction. In this regard, the method of purification in a stripping column that does not have a strengthening part should be considered close to rectification in terms of efficiency. The disadvantages of this method include the high temperature regime of the process, the presence of bulky and metal-intensive heat exchange equipment and the complexity of the operation of the rectification column due to the large number of adjustable parameters.

The simplest method of action in terms of technology, which does not require large material costs, is the stripping of hydrogen sulfide in the feed oil pipeline of separation units or a special desorption column.

The essence of the most effective technology for stripping hydrogen sulfide from oil in a desorption column is the counter-current passage of gas that does not contain hydrogen sulfide

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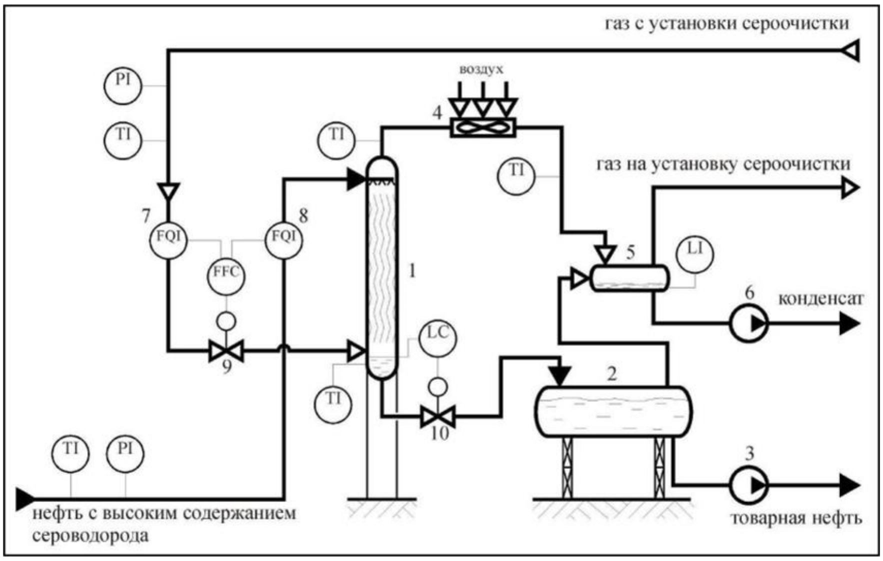
or with a low content of it through the volume of oil (Fig. 2). This allows, by bubbling the oil with gas and by contacting the phases on special packing, to significantly increase the gas-liquid phase interface surface and, consequently, to increase the interphase mass transfer. In this case, the chemical composition and properties of the oil do not change after processing.

Hydrogen sulfide is stripped from the oil in a column apparatus after the final separation stage with a counter-current of gas coming from below and oil fed from above [6].

Oil with a temperature of 50-60°C after the electric dehydrators is fed under its own pressure to the upper part of the stripping column 1, distributed over a special packing and flows to the lower part of the column, from where it flows by gravity into buffer tanks 9. Commercial oil is pumped out by pump 8. Hydrogen sulfide is stripped in the column by gas coming from the gas desulfurization unit, moving in the column in a counter-current with the oil. The gas after the stripping column, contaminated with hydrogen sulfide, is cooled to a temperature not exceeding 25°C in refrigerator 5.



1 - stripping column; 2, 4 - flow meters; 3, 10 - control valves; 5 - air cooling device; 6 - condensate collector; 7 - condensate pump; 8 - pump; 9 - buffer tank

Figure 2 - Flow chart of oil purification from H_2S by stripping it in a column

One of the current areas in the development and operation of oil fields is the optimization of costs associated with the extraction, transportation and preparation of oil. To reduce the costs of oil preparation, it is necessary to use a differentiated approach to solving the problem of its purification from hydrogen sulfide at the Kashagan field, depending on the following conditions:

- volumes of oil preparation;
- mass fraction of hydrogen sulfide in oil;
- the presence of gas near the UPVSN that does not contain hydrogen sulfide;
- the presence of a gas collection system and the possibility of transporting increased volumes of hydrogen sulfide-containing gas to the sulfur purification unit.

Taking into account the above, the goal of our scientific research is to identify the maximum values of the volume fractions of methane, ethane, nitrogen and carbon dioxide in the composition of the stripping gas, at which the mass of oil will be preserved, as well as the conditions under which it will be purified from hydrogen sulfide in the conditions of the Kashagan field.

Materials and methods of the study. The studies were conducted on a desorption column model, which was a glass tube with a diameter of 34 mm, in the lower part of which there was a Schott filter designed for uniform distribution of gas over the cross-section of the model. Before filling with oil, the desorption column model was purged with hydrocarbon gas for 15 minutes. Gas purging was carried out to remove air from the model. After that, 150 ml of oil was fed into it. Gas from the preliminary water discharge unit (PDU) with a volume fraction of hydrogen sulfide equal to 0.5% was used for purging. Hydrocarbon gas for oil purging was fed with a syringe through the Schott filter.

Results and discussion. The physicochemical properties of oil and gas at the Kashagan field were determined based on the results of studies of reservoir and degassed samples. Despite the large number of studied reservoir and surface oil samples collected in different zones of the field both at depth and along the strike, no pattern in the change in the properties and composition of reservoir oil was found. In calculating reserves, the composition of reservoir oil was assumed to be average for the entire deposit. With increasing depth, pressure and temperature increase. At the same time, an increase in pressure increases the density and viscosity of oil, and an increase in temperature decreases them. As a result, the density and viscosity of reservoir oil remain almost constant along the height of the deposit. Calculations show that at the -4300 m mark, the density of reservoir oil is 620.6 kg/m3, and the viscosity is 0.32 mPa s, at the -5300 m mark, respectively 617.6 kg/m3 and 0.2296 mPa s. The difference is comparable with the measurement errors [5, 6].

Therefore, the data on the properties of oil and gas, including differential degassing at reservoir temperature, are assumed to be the same throughout the deposit.

According to the results of studies and calculations, the average density of reservoir oil is 620.6 kg/m3, the saturation pressure of oil with gas at reservoir temperature is 25.26 mPa, the gas content during a single degassing of reservoir oil is 585.9 m3/t, the dynamic viscosity of reservoir oil is 0.232 mPa s. [7, 8]

After differential degassing under operating conditions, the oil density is 785.0 kg/m3, the gas content is 514.5 m3/t, the volumetric coefficient is 1.936, the dynamic viscosity of degassed oil is 2.10 mPa s. [9]

The molar content of the components in the mixture of gases released from the oil during differential degassing under operating conditions: hydrogen sulfide 16.12%, nitrogen 1.34%, methane 57.66%, ethane 11.49%, propane 5.99%, higher hydrocarbons (propanes + higher) 9.46%, helium 0.02%. The relative density of air is 0.869 [10].

Due to the hydrogen sulfide saturation of gas from the Kashagan wells in the range of 18-20%, the field will supply "sour gas" with one of the highest levels of H2S content encountered in offshore oil and gas production. When oil production reaches 14 million tons per year, according to AGIP, the largest volume of hydrogen sulfide will need to be re-injected into coastal high-pressure reservoirs, avoiding the production of large quantities of gas sulfur and flaring of gas. The efficiency of oil purification from hydrogen sulfide and the mass yield of oil are significantly affected by the concentration of methane, ethane, nitrogen and carbon dioxide in the stripping gas. In this case, the total share of these components in oil is insignificant and has a similar value at different sites due to the fact that degassed oil is fed for stripping. An increase in the share of these components in the gas fed to the column, under certain process conditions, leads to a decrease in its required consumption, as well as the mass of commercial oil. Figures 3 and 4 show the values for the required specific consumption of methane, ethane, nitrogen and carbon dioxide used separately as gases for stripping hydrogen sulfide, and the loss in oil mass provided that its residual mass fraction of 95 ppm is achieved, depending on its temperature at an absolute pressure in the column of 0.14 MPa.

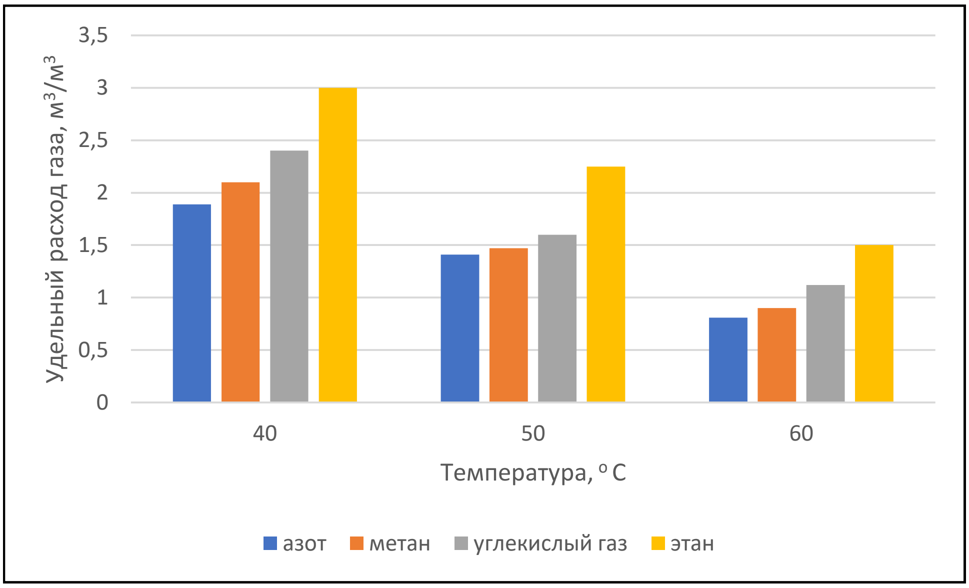


Figure 3 – Dependence of the required specific gas consumption values on temperature

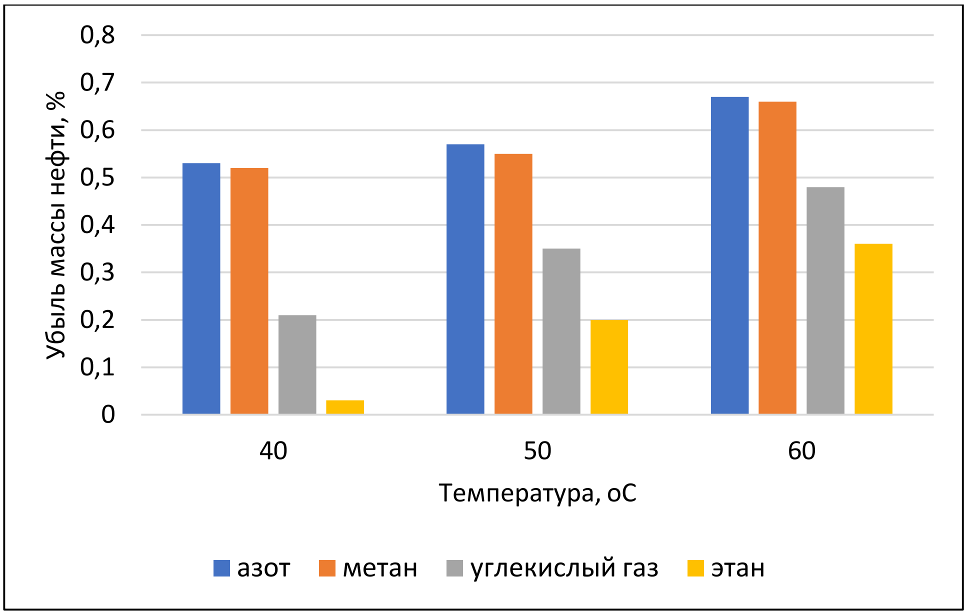


Figure 4 – Dependence of oil mass loss under blowing conditions with different gases on temperature

It is evident that when methane and nitrogen are supplied to the column, the required gas consumption is minimal, and the amount of oil mass loss is maximal, and the specified indicators for both gases are close. When carbon dioxide is supplied to the column, its required consumption and oil mass loss are intermediate values between methane and ethane. With increasing temperature, the effect of gas composition on these factors is less pronounced.

Using propane as a stripping gas, even at a maximum temperature of 60°C and a minimum absolute pressure in the column of 0.12 MPa, does not lead to a decrease in the concentration of hydrogen sulfide in oil below 100 ppm.

The main share of propane passes into oil, which leads to an increase in its mass. Consequently, under certain operating parameters of the desorption column, a decrease in the proportion of C3+b components in the gas composition and, as a consequence, an increase in the total proportion of methane, ethane, nitrogen and carbon dioxide leads, on the one hand, to an increase in the efficiency of oil purification from hydrogen sulfide, and on the other hand, to a decrease in its mass. Figure 5 shows the maximum values of the volume fraction of light components in the stripping gas, which is their mixture with C3+b, at which the mass of oil is preserved.

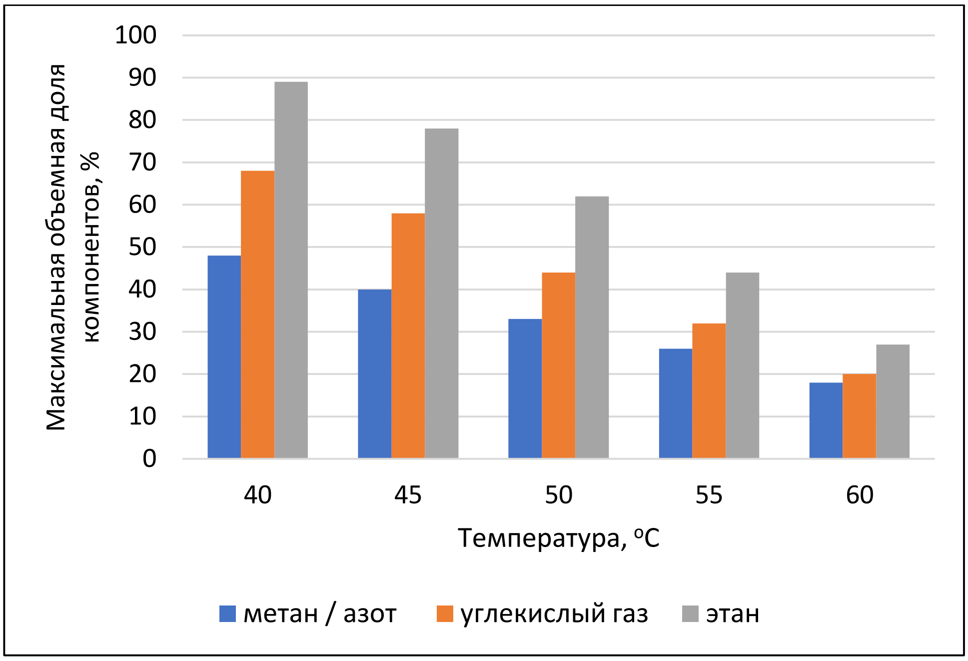


Figure 5 – Dynamics of the values of volume fractions of methane, ethane, nitrogen and carbon dioxide in a mixture of C3+b under the condition of maintaining the mass of oil (at a pressure of P=14 MPa)

When using nitrogen and methane, the values of oil mass loss have similar values (Figure 5). Therefore, when determining the maximum volume fraction of components in a mixture with C3 + in the composition of the stripping gas, the concentrations of nitrogen and methane are summed up. For example, at a temperature of 40 °C, oil mass conservation is possible with a total value of the volume fractions of methane and nitrogen not exceeding 47% and C3 + > 53%. Associated petroleum gas used for oil stripping is a multicomponent mixture that differs in composition. Each individual component has a certain effect on oil mass loss (Figure 5). Provided that the oil mass is preserved, an increase in the concentration of nitrogen and methane leads to a significant decrease in the permissible volume fraction of ethane and carbon dioxide. From the data presented in Figure 5, it is clear that oil mass conservation is possible at a temperature of 40 °C and an ethane volume fraction of 89%. With a volume fraction of nitrogen and methane of 20%, the maximum permissible concentration of ethane decreases from 89 to 49%. An increase in the proportion of ethane has a lesser effect on reducing the maximum permissible concentration of nitrogen and methane.

With an increase in the oil heating temperature and a decrease in the pressure in the column, the maximum total volume fraction of methane and nitrogen in the mixture in the stripping gas decreases. To reduce the mass fraction of hydrogen sulfide in oil below 100 ppm and maintain the mass yield of oil depending on the proportion of these components in the stripping gas, the oil temperature and pressure in the column are optimized.

An increase in the total volume fraction of methane and nitrogen in the stripping gas leads to a decrease in its required consumption to achieve a certain efficiency of oil purification from hydrogen sulfide at given column operating parameters.

Conclusions. Thus, the maximum values of the volume fractions of methane, ethane, nitrogen and carbon dioxide in the stripping gas have been identified, at which the mass of oil is preserved.

It has been established that in order to preserve the mass of oil, the process of its purification from hydrogen sulfide in the desorption column at oil preparation facilities at the Kashagan field should be carried out at the lowest possible temperature and elevated pressure, ensuring a reduction in the mass fraction of hydrogen sulfide below 100 ppm, as well as the transport and utilization of stripping gas.

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КЕН ОРНЫНДА КҮКІРТСУТЕКПЕН КҮРЕСУДІҢ ТЕХНОЛОГИЯЛЫҚ ШЕШІМІ

Аңдатпа: Құрамында күкіртті сутегі бар майларды өндірудегі өзекті мәселелердің бірі күкіртсутекті жоюдың тиімділігін арттыру мәселесі болып табылады. Мұнай өндіруге, тасымалдауға және өңдеуге байланысты шығындарды оңтайландыру қазіргі уақытта өте өзекті болып табылады.

Мұнай дайындаудың өзіндік құнын төмендету үшін Қашаған кен орнында оны күкіртсутектен тазарту мәселесін шешуде сараланған тәсілді қолдану мұнай дайындау көлеміне, мұнайдағы күкіртсутектің массалық үлесіне, газдың болуына байланысты. құрамында күкіртті сутегі жоқ (жоғары күкіртті мұнай өңдеу қондырғысы) UPVSN, газ жинау жүйесінің болуы және күкірт сутегі бар газдың ұлғайтылған көлемін күкіртті тазарту қондырғысына тасымалдау мүмкіндігі.

Осы факторларды ескере отырып, мұнай массасы сақталатын аршу газындағы метанның, этанның, азоттың және көмірқышқыл газының көлемдік үлестерінің максималды мәндерін, сондай-ақ пайдалану шарттарын анықтау қажет. ол Қашаған кен орны жағдайында күкіртсутектен тазартылады.

Зерттеулер көрсеткендей, мұнайды қыздыру температурасының жоғарылауы және десорбциялық колоннадағы қысымның төмендеуі кезінде аршу газындағы қоспадағы метан мен азоттың максималды жалпы көлемдік үлесі азаяды. Мұнайдағы күкіртсутектің массалық үлесін 100 промилледен төмен төмендету және аршу газындағы осы компоненттердің үлесіне байланысты мұнайдың массалық шығымын сақтау, егер мұнай температурасы мен колоннадағы қысым оңтайландырылған жағдайда мүмкін болады. Аршу газындағы метан мен азоттың жалпы көлемдік үлесін арттыру колоннаның берілген жұмыс параметрлерінде мұнайды күкіртсутектен тазартуда белгілі бір тиімділікке жету үшін оның қажетті шығынының төмендеуіне әкеледі.

Кілт сөздер: күкіртсутек, аршу, мұнай массасы шығымы, аршу газы, көп компонентті қоспа, тазалау тиімділігі.

ТЕХНОЛОГИЧЕСКОЕ РЕШЕНИЕ БОРЬБЫ С СЕРОВОДОРОДОМ НА МЕСТОРОЖДЕНИИ

Аннотация. Одной из актуальных проблем при добыче сероводородсодержащих нефтей является проблема повышения эффективности удаления сероводорода**.** Оптимизация затрат, связанных с добычей, транспортом и подготовкой нефти весьма актуальны в настоящее время.

Для снижения затрат на подготовку нефти использование дифференцированного подхода к решению проблемы её очистки от сероводорода на месторождении Кашаган зависит от объёмов подготовки нефти, массовой доли сероводорода в нефти, наличия вблизи (установки подготовки высокосернистой нефти) УПВСН газа, не содержащего сероводород, наличия системы газосбора и возможности транспорта повышенных объёмов сероводородсодержащего газа до установки-сероочистки.

Учитывая эти факторы, необходимо выявить максимальные значения объёмных долей метана, этана, азота и двуокиси углерода в составе отдувочного газа, при которых будет сохраняться масса нефти, а также условия при которых будет происходить ее очистка от сероводорода в условиях месторождения Кашаган.

Исследования показали, что с увеличением температуры нагрева нефти и снижением давления в десорбционной колонне максимальная суммарная объёмная доля метана и азота в смеси в составе отдувочного газа снижается. Снижение массовой доли сероводорода в нефти ниже 100 млн$^{-1}$ и сохранение массового выхода нефти в зависимости от доли указанных компонентов в составе отдувочного газа возможно, если оптимизировать температуру нефти и давление в колонне. Увеличение суммарной объёмной доли метана и азота в составе отдувочного газа приводит к снижению требуемого его расхода для достижения определённой эффективности очистки нефти от сероводорода при заданных параметрах работы колонны.

Ключевые слова: сероводород, отдувка, массовый выход нефти, отдувочный газ, многокомпонентная смесь, эффективности очистки.