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PHYSICAL AND CHEMICAL PROPERTIES OF PURIFYING SULFUR-CONTAINING GAS EMISSIONS FROM PRODUCTION

Abstract. *To further purify sulfur-containing flue gas emissions, we have proposed a method for utilizing these gases using an aqueous solution of ammonium* *carbonate in the presence of a 2% limestone solution $Ca(OH)_2$. The developed procedure for this method describes the sequence of activities that must be performed to successfully test a sulfur production plant to ensure the required standards for the degree of utilization of harmful sulfur emissions into the atmosphere. The renewability of adsorbents gives them a technological advantage, with repeated cycles of use for the purification of similar colloidal disperse systems.*

Key words: *adsorption, absorption, regeneration, recycling, composite absorbents, scrubber, sulfur, waste sulfur-containing process gases.*

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ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ОЧИЩЕННЫХ ПРОМЫШЛЕННЫХ СЕРО-СОДЕРЖАЩИХ ВЫБРОСОВ

Аннотация. *Для доочистки серосодержащих дымовых газовых выбросов, нами предложен метод утилизации этих газов с применением водного раствора аммония карбоната в присутствии 2% ного раствора известняка $Ca(OH)_2$. В разработанной процедуре этого метода описывается последовательность мероприятий, которые необходимо выполнять для успешного проведения апробации установки получения серы с целью обеспечения требуемых норм степени утилизации вредных сернистых выбросов в атмосферу. Возобновляемость адсорбентов даёт им преимущество в технологии, при многократном цикле использования для очистки подобных коллоидных дисперсных систем.*

Ключевые слова: *адсорбция, абсорбция, регенерация, утилизация, композиционные абсорбенты, скруббер, сера, отходящие серосодержащие технологические газы.*

An analysis of foreign and domestic production practices accumulated in the field of natural gas purification shows that for the purification of sulfurous natural secondary gases, alkanol amines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), methyldiethanolamine (MDEA) are most often used), diisopropanolamine (DIPA), diglycolamine (DGA), composite absorbent – MDEA+DEA and others [1-4]. When replacing DEA with MDEA, it becomes possible to selectively extract H_2S and its mixtures with CO_2 in cases where complete gas purification from CO_2 is not required or the H_2S concentration in the extracted acid gases (H_2S+CO_2) must be no higher than 40%, which allows process them in Claus plants.

In recent years, large natural gas fields have been discovered in Uzbekistan (Ustyurt, Kandym, etc.), containing significant amounts of H_2S

and CO_2. In the gas processing industry of our republic, an alkaline cleaning process is used to utilize flue gases. We have proposed a new option for conducting the technological process and recycling flue gases using an aqueous solution of NaOH alkali in the presence of a 2% solution of limestone $Ca(OH)_2$. The use of limestone (2-5% aqueous solution) in the presence of ammonium carbonate and the resulting interaction of these reagents, such as ammonium hydroxide NH_4OH, makes it possible to replace the currently used NaOH to purify gases from SO_2 using calcium and ammonium containing reagents on an industrial scale, for example in ShGChC.

When wet scrubbing sulfur dioxide waste gases using limestone in the presence of ammonium carbonate, the resulting ammonium sulfide $(NH_4)_2SO_3$ can be remixed with $Ca(OH)_2$ according to the equation

$$(\mathrm{NH_4})_2\mathrm{SO_3} + \mathrm{Ca(OH)_2} = \frac{\mathrm{CaSO_3}}{\text{осадок}} + 2\mathrm{NH_4OH} \quad (4)$$

and calcium sulfide can be treated with oxygen to produce gypsum $CaSO_4 \cdot 2H_2O$. The NH_4OH obtained according to this scheme can be additionally sent to a scrubber for wet cleaning of sulfurous waste gases. However, for this, the concentration of the aqueous solution of NH_4OH will need to be brought to the required value, i.e. up to a concentration of 5-10%. To save financial costs on the purchase of new process equipment, it is recommended to use a 5-10% aqueous solution of NH_4OH for post-purification of waste tail sulfur dioxide gases for a sulfur production plant, instead of the 10% aqueous solution of NaOH alkali proposed in the project for a sulfur production plant.

Based on the research carried out on the proposed scheme for post-purification of waste gases from sulfur production, the main changes were made: replacement of process water with mineralized water; preparing a 5-10% aqueous solution of NH_4OH and feeding it into a wet scrubber; regulation of the temperature of the exhaust gases after the scrubber after complete evaporation by supplying demineralized water through the control valve to the upper part of the scrubber; supply of NH_4OH solution to the pump discharge line, i.e. directly, for irrigation, and not into the bottom part of the scrubber, as is currently carried out under the project; into a container intended to supply demineralized water for the preparation of a 5-10% NH_4OH solution, as well as circulating the ammonium hydroxide solution with a pump and pumping the prepared NH_4OH solution into the supply container; replacement of pumping equipment with more efficient ones; recommend installing additional equipment with a larger capacity for preparing NH_4OH solution; selection and installation of a flow meter on the supply line of a 5-10% NH_4OH solution in a wet scrubber.

A method for purifying sulfur-containing exhaust gases using an ammonium hydroxide solution is carried out by the interaction of NH_4OH reagents and sulfur dioxide, i.e. by the following chemical reaction.

$$\mathbf{2SO_2+O_2=2SO_3} \ (5)$$

$$\mathbf{SO_2+H_2O=H_2SO_3} \ (6)$$

$$\mathbf{2NH_4OH+H_2SO_3=(NH_4)_2SO_3+2H_2O} \ (7)$$

$$\mathbf{or\ \ 2NH_4OH+SO_3=(NH_4)_2SO_3+4H_2O} \ (8)$$

Based on this interaction process, we can say that with increasing concentration of sulfur dioxide, the degree of its purification should increase to a certain value. Experiments were carried out to study the effect of SO_2 content in the gas phase on the degree of purification using a 5-10% NH_4OH solution. At the same time, the SO_2 content in the model solution varied from 0.85% to 0.26% volume. The research results are shown in Fig. 3. With a SO_2 concentration in the gas mixture of 0.85%, the degree of purification (depth) is 85-78% volume. A decrease in the SO_2 content in the exhaust tail gas leads to an increase in the degree of purification, for example, at C_{SO2} = 0.33% and C_{SO2} = 0.26%, the degree of purification is, respectively, 95-96% and 97-99% of the volume. The reaction temperature of sulfur dioxide flue tail gases using NH_4OH solutions has a significant impact on the chemical capture process. Thus, the efficiency of binding sulfur dioxide with NH_4OH increases in the temperature range of 200-300 °C.

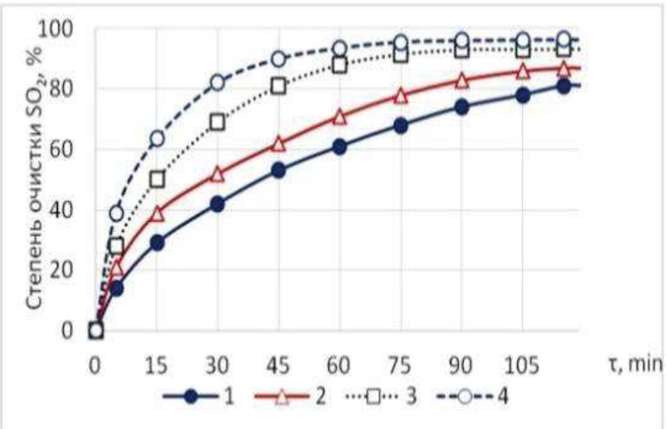

Fig.1 - The influence of the content in the gas mixture on the degree of purification using ammonium hydroxide: $C_{NH_4OH} = 5 \div 10\%$, $C_{SO_2} = 26 \div 85$. 1 – C_{SO_2} – 0,85%; 2 – C_{SO_2} – 0,65%;3 – C_{SO_2} – 0,33%;4 – C_{SO_2} – 0,26%.

In the low-temperature zone (200-400 °C) the main product is $(NH_4)_2SO_3$. In this regard, the use of the NH_4OH reagent makes it possible to purify gases from sulfur dioxide SO_2 calcium, and ammonium-containing reagents on an industrial scale.

Calcium carbonate $CaCO_3$ obtained by the interaction of $Ca(OH)_2$ and $(NH_4)_2CO_3$ can be recommended as a secondary raw material for the production of technical soda (Na_2CO_3). Solid waste ammonium sulfide can be partially oxidized with atmospheric oxygen to produce ammonium sulfate

$(NH_4)_2SO_4$, which can be recommended as an ingredient in ammonium-containing mineral fertilizer. The reaction of tail flue gas sulfur dioxide with $Ca(OH)_2$ has a significant impact on the chemical capture process.

Based on the multi-component nature of exhaust gas emissions from gas processing plants, to increase the selectivity and efficiency of post-treatment and utilization of sulfur-containing substances, we have proposed a dry SO_3 separation method in combination with wet purification of such tail gases using $Ca(OH)_2$, $(NH_4)_2CO_3$ and NH_4OH at the sulfur recovery plant. For this purpose, a new adsorbent has been proposed, synthesized based on waste from the chemical industry of the republic. Adsorbents conventionally designated AK-1 and AK-2 are in solid form with a grain size of 0.3 mm. Testing of new adsorbents was carried out at the Central Factory Laboratory of ShGChC. The initial H_2S content in the natural gases tested was 0.0654 mol%. The weight of the AK-1 adsorbent was 106.41, and the AK-2 was 105.05 g. The SO_3 adsorption isotherm using AK-1 and AK-2 is shown in Fig. 2.

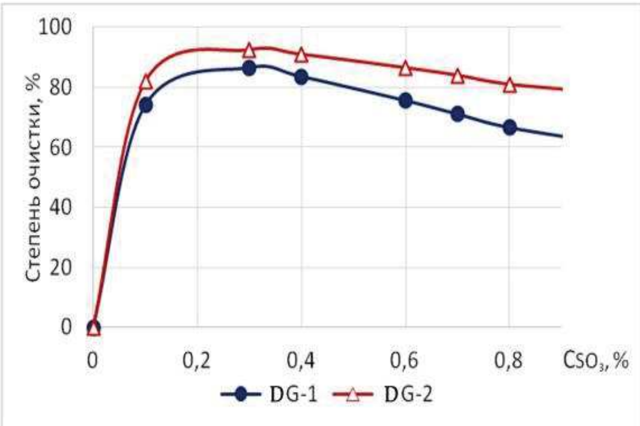

Fig.2 - Dependence of the degree of purification SO_3 (adsorption isotherm) on its concentration: 1-AK-1; 2-AK-2 (at 25°C)

When using adsorbent AK-1, the degree of purification of natural gas H_2S was 93.0% and with AK-2 - 91.0%, and in addition, the adsorption of SO_3 from AK-1 goes up to 98.9% (0.3% C_{SO_3}) and with AK-2 to 88-89% (0.25-3.0% C_{SO_3}). The dependence between the concentrations of the adsorbed substance (mol/mol of adsorbent) on temperature is shown in Fig. 3.

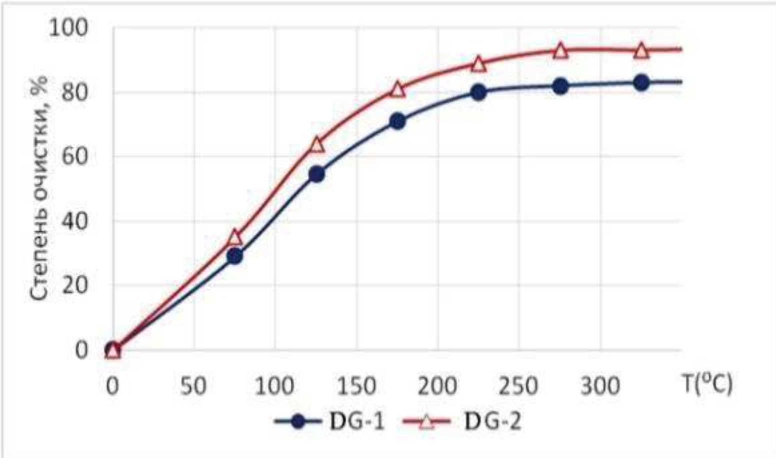

Fig.3 - The influence of temperature on the degree of purificationSO_3: C_{SO_3}= 0,025 mol; 1-AK-1; 2-AK-2.

With increasing adsorption temperature, the equilibrium concentration of the adsorbed substance decreases; it has also been revealed that the activity of adsorbents AK-1 and AK-2 depends on the temperature of the gas mixture being purified and the concentration of the component absorbed in it.

To effectively purify a composite absorbent solution by filtration through a sorbent, some characteristics of activated carbon, γ-alumina, silica gel, and zeolite are considered (table 1 and table 2).

Table 1 - Physical and colloidal characteristics of sorbents

Name of sorbents	P, kg/m³	S,cm²	V, cm³
Activated carbon	765	560	760
Alumina, Al_2O_3	1205	480	680
Silica gel Al_2O_3+SiO_2	1800	540	700
Zeolite NaO+Al_2O_3+SiO_3+CaO	1456	600	750

The given adsorbents in all respects are acceptable for clarification and filtration of a composite absorbent solution from mechanical impurities.

As can be seen from the data presented, the sorbents used (activated carbon, aluminum oxide, and silica gel) showed various positive results in their absorption properties, but in terms of service life, solid sorbents will exceed the properties of activated carbon. The renewable nature of adsorbents (regeneration with hot water steam) gives them a technology advantage, with repeated cycles of use for the purification of similar colloidal disperse systems.

Table 2 -Comparative characteristics of cleaning the working solution using various adsorbents

Indicators of working solution	Saturated solution for regeneration	Regenerated 20% solution of MDEA+DEA+ additive after purification on sorbents		
		Activated carbon	**Sorbent (Al_2O_3)**	**Silica gel**

Solution color	Gray green	Light yellow	Light yellow	Light yellow
Density (ρ), gr/m^3	1,092	1,045	0,040	0,034
Composition: H_2S, mg/l	863	38,5	21,8	16,8
CO_2, % mol	2,19	0,24	0,02	0,02
Hydrocarbons (C_nH_{2n+2}),%	26,8	30,0	30,8	30,7
pH	8,1	10,8	10,9	11,0
Solution viscosity, mm^2/sec.	5,1	4,4	4,1	4,0

Based on the testing of adsorbents synthesized using waste from the chemical industry of the republic, new adsorbents AK-1 and AK-2, it was established that the adsorbent, conventionally designated AK-1, can be recommended for the dry method of purification of sulfur-containing gas tail emissions.

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