Study of methods of chemisorption purification of hydrogen sulfide in natural gases with natural sorbent

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Abstract. We know from the literature that the cost-effectiveness of using zeolites to purify natural gas is much higher than other natural resources. In the laboratory, $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ were prepared by treating bentonite obtained from local raw materials with calcium, zinc, and magnesium salts. Local raw materials are activated by mechanical-thermal and chemical processing and are delivered in the form of dark-colored granules (tablets) up to 5 mm in diameter.
The sorption potential of high-silica zeolite obtained from local raw materials by metal salts and heat treatment was studied, and a technological scheme was developed. A catalyst containing $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ was developed for drying the obtained high-silica zeolite oil satellite and natural gas from water vapor and purification from sulfur compounds, and its texture and sorption properties were studied. The total amount of SiO_2, Ca^{2+}, $Zn^{2+,}$ and Mg^{2+} ion phases was studied in the radiological analysis of the surface of the catalyst $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ. According to IR spectroscopy data, surface adsorption of hydrogen sulfide at 25°C occurs in the presence of hydroxyl groups. UZBEKGAZ JSC - Mubarek Gas Processing Plant conducted experimental tests to study the sorption properties of this catalyst, as well as a comparative study of the possibility of sorption of sulfides with the participation of catalysts $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ and CaA (5A). The tests showed that another experimental test of the selected CaA (5A) compound catalyst was also performed. The absorption of this adsorbent hydrogen sulfide showed that the catalyst $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ has a total capacity of 8.3% by mass and 14.3% by mass.

1 Introduction

To ensure gas quality, it is necessary to remove sulfur and mercaptan compounds from the gas. Several sources, such as natural gas, satellite gas, coke, and fuel gases, including sulfur compounds in the gas released from biogas wastes, are important tasks in gas purification. In gases, sulfur has toxic and corrosive properties, so these wastes must be cleaned before use [1, 2]. The chemical processes that can purify the gas from sulfur are important, but

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such processes require a high cost. The severe operating conditions of the catalytic reactor are calculated to achieve the desired results. Without exception, all the processes mentioned earlier of processing and using gas raw materials require pre-treatment of sulfur compounds and, first of all, hydrogen sulfide and mercaptans [3,4]. Methods based on separating sulfide compounds from gas streams in oil fields using absorbents are the most promising work [5]. Currently, the extraction and processing of bentonite minerals found in the Navbahor area are of practical economic interest in petrochemistry [6]. The practical significance of the research is that the basics of the adsorption purification process for drying oil and natural gas from water vapor and purification from sulfur compounds have been developed. The basics and techniques of drying oil and natural gas from water vapor and simultaneous purification from sulfur compounds with high-silicon zeolites have been developed, as well as recommendations for use in various industries of the chemical industry [7]. To achieve the set goals, it is necessary to solve the following tasks: Determination of the relative (comparative) activity of new generation silica gels in a method close to industrial conditions of natural sulfur gas purification. Study the laws of the simultaneous purification of natural sulfur gas from liquid hydrocarbon vapors and moisture with new generation catalysts and propose a semi-industrial device [8].

2 Materials and methods

Experimental tests were conducted at the Mubarek Gas Processing Plant in a semi-industrial facility with a mass fraction of hydrogen sulfide of 2.9% and a mass fraction of sulfur in thiols of 0.5%. The absorption process was carried out in glass columns with an adsorbent height of 120 cm and a diameter of 3.2 cm. A Drexel bottle filled with 10% sodium hydroxide solution was installed to absorb unsaturated hydrogen sulfide and thiols at the exit of the glass column reactor. The amount of gas transferred was determined using a gas clock [9].

The process was carried out in the following mode:

- process temperature -55 ° C;
- Argon consumption -0.1-0.30 l / min;
- consumption of hydrogen sulfide or methyl mercaptan - 5.0-30 ml/min;
- the initial sulfur content of hydrogen sulfide or methyl mercaptan - 1000 ppm;
- the volume of catalyst loaded in the reactor - 26 ml.

A schematic diagram of hydrogen sulfide and methylmercaptan gas purifier is shown in Figure 1.

1. The main part of the equipment is a glass cylinder reactor1, which is operated by a heating system 2, and temperature control is carried out 3,4,5, and 6. The carrier gas to the reactor is passed through the 8th cylinder, which is controlled by 9 rotometers. Hydrogen sulfide or methyl mercaptans transfer is controlled by a rotameter from cylinder 8a to cylinder 9a. The gas is transferred to the reactor through a glass disperser 10. The purified gas is sent to the Libix cooler over reactor 7; then, the absorber 11.12 Drexel is released into the atmosphere through an alkaline solution through a spare bottle for 13 and 14 gas hours.

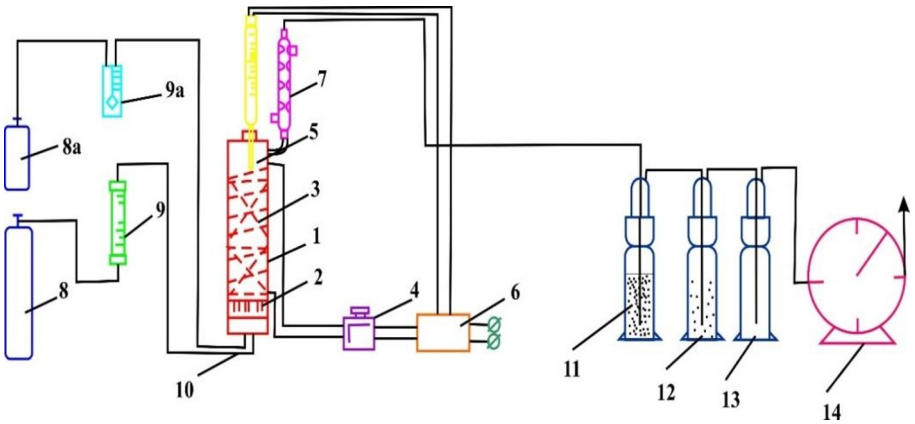


Fig. 1. Gas purification semi-industrial experimental device: 1 is glass cylinder reactor, 2 is heating system, 3,4,5,6 are temperature control, 7 is to the Libix refrigerator, 8 is carrier gas to the reactor, 9 is rotometer, 10 is bottle dispersant, 11,12 are winning Drexel bottle, 13 is spare bottle, 14 is gas hours.

3 Results and Discussion

In the laboratory, HQZ were prepared by treating high-silicon zeolite obtained from local raw materials (bentonite) with calcium, zinc, and magnesium salts. To purify petroleum products from various gases, a 20% solution of $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ was ingested for 2 hours under strong shaking on high silicon zeolite obtained by the above method. As a result, a sample containing HQZ was obtained [10-14]. Local raw materials are activated by mechanical-thermal and chemical processing and are delivered in the form of dark colored granules (tablets) up to 5 mm in diameter. The technological process of natural gas purification using these high-silicon zeolites was studied.

X-ray phase analysis of the catalyst surface analyzed the total amount of SiO_2, Ca^{2+}, $Zn^{2+,}$ and Mg^{2+} ion phases. The diffraction appearance of the catalyst HQZ differs from the onset of linear modification of the sulfur obtained from the original substances. Hence, the adsorption of hydrogen sulfide on the surface of the catalyst $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ continues with the formation of metal sulfides and sulfur Fig. 2. As it is then saturated with hydrogen sulfide, the adsorbent darkens, which may also indicate the formation of metal sulfides and wetting of the adsorbent.

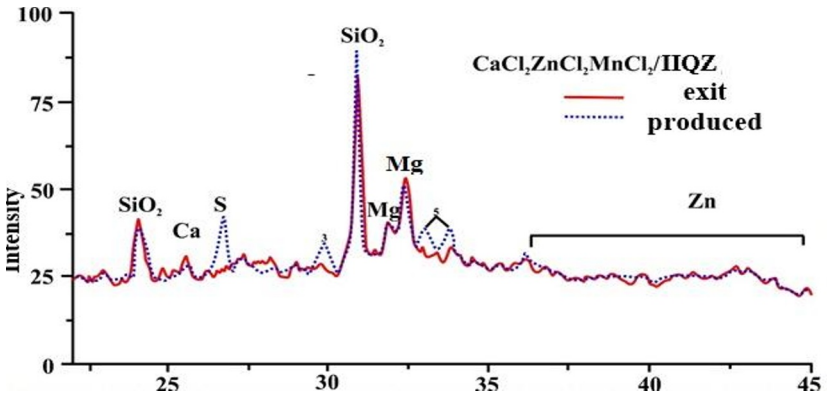
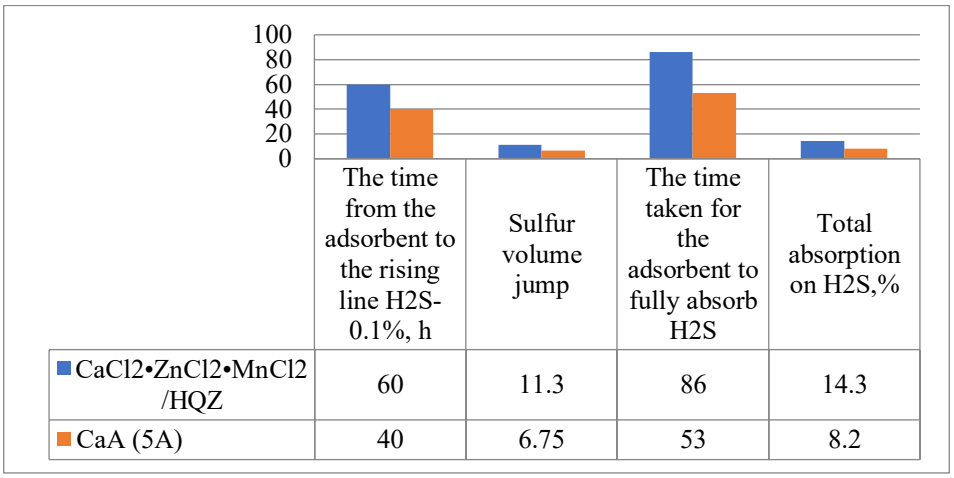


Fig. 2. Diffraction scheme of $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ samples.

According to the IR-spectroscopy data of the test, surface adsorption of hydrogen sulfide at 25°C occurs in the presence of hydroxyl groups, indicating the presence of SH- and H + ions. From the data of this radiographic analysis, it can be concluded that hydrogen sulfide is initially sorbed and absorbed without chemical action. The next part of the work will be the comparative use of the catalyst $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ and CaA (5A) in purifying petroleum gases from hydrogen sulfide and mercaptan. (UZBEKGAZ JSC - Mubarek Gas Processing Plant) conducted experimental tests to study the sorption properties of this catalyst. In this case, the catalyst $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ was selected, consisting of high-silicon zeolite activated by calcium zinc manganese ions. An experimental test of another CaA (5A) compound catalyst of our choice was also performed. Studies have shown that the adsorption of this adsorbent is hydrogen sulfide with a mass of 8.2% by mass $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ catalyst with a total capacity of 14.3% by mass. We investigated the possibility of hydrogen sulfide sorption with $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ and CaA (5A) catalysts (Fig. 3).



	The time from the adsorbent to the rising line H2S-0.1%, h	Sulfur volume jump	The time taken for the adsorbent to fully absorb H2S	Total absorption on H2S,%
CaCl2•ZnCl2•MnCl2 /HQZ	60	11.3	86	14.3
CaA (5A)	40	6.75	53	8.2

Fig. 3. Results of experiments of chemisorbents $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ and CaA (5A) in process of purification of satellite gases from hydrogen sulfide and thiols.

In the presence of catalysts $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ and CaA (5A), the amount of hydrogen sulfide dynamic capacity H_2S sorption concentration was determined Figures 4 and 5.

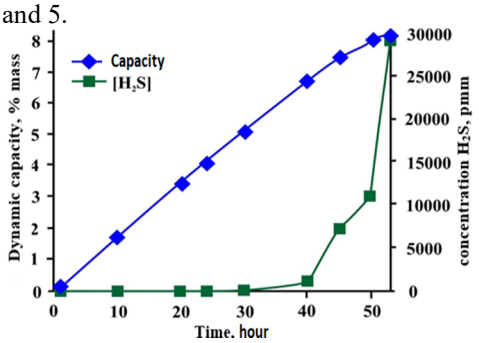


Fig. 4. Capacitance of CaA (5A) dynamic capacitance and adsorber absorbed hydrogen sulfide concentration.

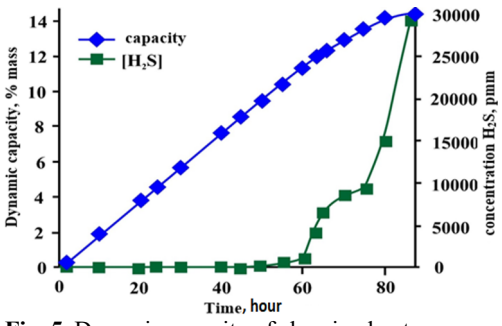


Fig. 5. Dynamic capacity of chemisorbent $CaCl_2{\cdot}ZnCl_2{\cdot}MnCl_2$/HQZ and change in concentration of hydrogen sulfide absorbed in adsorber.

When the adsorbents (CaA (5A), $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HQZ) are fully saturated with hydrogen sulfide, the concentration of mercaptan sulfur leaving the next reactor does not exceed 100 ppm. This suggests that mercaptans compete with hydrogen sulfide during chemisorption. The low amount of mercaptans can also be explained by their oxidation to disulfides. The concentration is selected as 1000 ppm because (boilers, furnaces) equipment begins to actively corrode when hydrogen sulfide gas concentrations exceed 100-1000 ppm. Based on the research, the following basic technological scheme of adsorption purification of hydrogen sulfide from petroleum gas was proposed (Fig. 6).

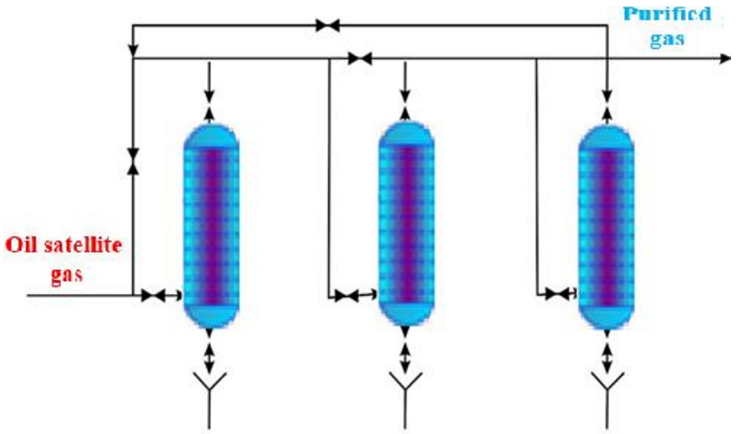


Fig. 6. Basic technological scheme of purification of petroleum gas from hydrogen sulfide.

The device consists of three alternating adsorbers. In the working case, there are two adsorbers. One is in reserve and operates during regeneration. The petroleum gas is purified by passing through a series of adsorber 1 and 2, respectively. In 1, after the adsorber is fully saturated, the gas flow from 2 to 3 is diverted. It is currently undergoing 1st regeneration. Once the 2nd adsorbent is completely saturated, the 3rd passed gas stream to the 1st and the 2nd now to the regeneration state. The total dynamic capacity of H_2S adsorbents is higher than 20-25% relative to the increased concentration, so it is advisable to fully use their adsorption capacity, which was recommended in the scheme of purification of natural gas from hydrogen sulfide.

4 Conclusions

Methods for obtaining high-silicon zeolite from Navbahor bentonite "Sol-gel" and hydrothermal synthesis were developed, and the texture, sorption, physico-mechanical properties, and physicochemical characteristics of the obtained high-silicon zeolites were studied.

A catalyst based on high-silicon zeolite synthesized from Navbahor bentonite is capable of simultaneously drying oil and natural gas from water vapor and removing sulfur compounds.

$CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HQZ and CaA (5A) catalysts can purify petroleum gases from hydrogen sulfide and thiols. In this process, the catalyst acts as a chemisorbent. Experimental tests of a catalyst containing $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HQZ were conducted at the Mubarek Gas Processing Plant. Investigations showed that the adsorption of this adsorbent hydrogen sulfide has a total capacity of 8.2% by weight $CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HQZ catalyst with a total capacity of 14.3% by mass. The possibility of hydrogen sulfide sorption with

$CaCl_2 \cdot ZnCl_2 \cdot MnCl_2$/HQZ and CaA (5A) catalysts was studied and analyzed. As a result of studying the laws of the process of drying oil and natural gas from water vapor and simultaneous purification of sulfur compounds from high-silica zeolites and determining the relative activity of new generation silica gels under industrial conditions, generalized technological processes for bentonite processing and bentonite modification technology.

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