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ADSORPTION DRYING OF NATURAL GAS BY CARBONATE SLUDGE

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Experimental results for absorption drying of natural gas by a developed granulated material based on chemical water-treatment sludge of Kazan TAC-1 are presented. A batch adsorber with a fixed bed of this material is calculated. A technological scheme for a recuperative adsorption plant for drying natural gas is proposed.

Keywords: adsorption drying, natural gas, granular sorbent, batch adsorption, fixed bed, technological scheme of drying

Natural gas recovered from deposits contains many impurities [1]. Moisture is found in many hydrocarbon gases and has adverse effects on their refining. The technical and economic parameters of an installation are degraded if moist gases are processed. Water condenses in pipelines and readily corrodes them if moist gas is transported. Also, crystal hydrates are formed, can narrow openings, and increase hydraulic resistance to gas streams passing through pipelines. Therefore, natural gas must be dried [2].

Hydrocarbon gases are dried by absorption, adsorption, and combinations of these methods [3]. The degree of gas drying is evaluated from the frost point, which characterizes the degree of saturation of the gas with water vapor.

Let us examine adsorption drying of hydrocarbon gas to produce low frost points with low gas humidity.

The advantages of adsorption drying of natural gas (before absorption) are the ability to produce frost points to – 70°C and lower, insignificant temperature and pressure effects on adsorption, relatively simple apparatus, and low operating costs.

Disadvantages of adsorption drying are high pressure drops, relatively high heating costs, and abrasion of sorbents.

Adsorption methods for separating gas mixtures are based on selective absorption of hydrocarbons and moisture by solid sorbents that adsorb well higher hydrocarbons and do not absorb methane. The requirements applicable to adsorbents are high adsorption capacity, mechanical strength, and selectivity; ability to be regenerated; stability during prolonged operation; low toxicity; corrosion resistance; and low cost.

The present work proposes using granulated sorbent based on carbonate sludge from Kazan TAC-1 as an adsorbent for drying natural gas. Carbonate sludge (homogeneous powder colored light-yellow to brown) is waste from thermal power plants (TPPs) that is formed by water treatment during preliminary purification. X-ray diffraction phase analysis on a D8 Avance diffractometer (Bruker) gave the chemical composition as calcite ($CaCO_3$) 73%, brucite [$Mg(OH)_2$] 9%, portlandite [$Ca(OH)_2$] < 1%, (SiO_2) and other matter 17.5%. The processing characteristics of the sludge as a sorbent were bulk density 560 kg/m^3, water capacity 57%, adsorption capacity (for water vapor) 1.1 g/g, total pore volume 0.41 cm^3/g, and specific surface area 23.2 m^2/g [4].

As a rule, granular adsorbers are used to dry natural gas (in order to decrease hydraulic resistance in the bed). Sludge of particle size 0.01–0.09 mm is mixed with liquid sodium glass (LSG) in a 2:1 ratio (selected

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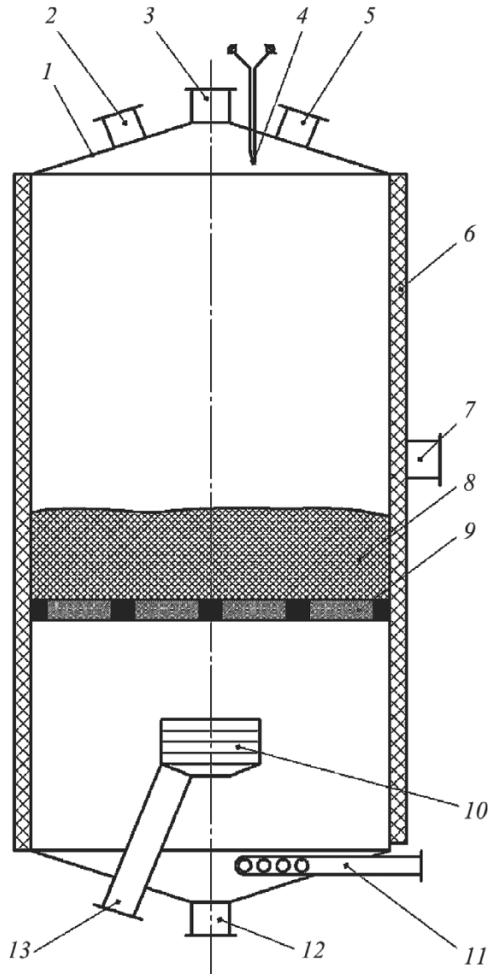

Fig. 1. Reactor column with GS fixed bed: Body (1); adsorbate outlet (2); dried gas outlet (3); thermocouple (4); hatch for loading adsorbent (5); electrical heater (6); hatch for unloading adsorbent (7); GS layer (8); steel grid with openings of diameter < 1 mm (9); diffusion cap (10); compressed air inlet (11); condensate outlet pipe (12); gas mixture inlet (13).

experimentally) to produce finely disperse granules. The sludge was not fully soaked with LSG at lower ratios (the granules disintegrated upon annealing) and consumed too much binder at higher ratios. Then, the mixture was homogenized by stirring. Granules were produced by rolling manually, storing in an oven at t = 400°C for 3 h, and cooling to room temperature in a desiccator. The obtained granules had diameters of 0.5–2.5 mm.

The processing characteristics of the obtained granules were adsorption capacity for water vapor 2.4 g/g, moisture capacity 49 wt.%, bulk density 536 kg/m^3, total pore volume 0.592 cm^3/g, and specific surface area 46.2 m^2/g.

Natural gas can be dried with minimal cost and the greatest efficiency because of the low cost of the water-treatment sludge adsorbent and its availability and ability to be regenerated.

A model plant with a fixed bed of sludge that was built in the Department of Water and Fuel Technology, Kazan State Energy University, was used to study the sorption properties of the granulated sorbent (GS) in a gaseous medium simulating the composition of natural gas.

The plant included a stainless-steel reactor column as a laboratory adsorber (Fig. 1). Gas mixture was fed in and taken out through fittings 3 and 13. Diffusion cap 10 was screwed onto the inlet fitting to distribute the gas

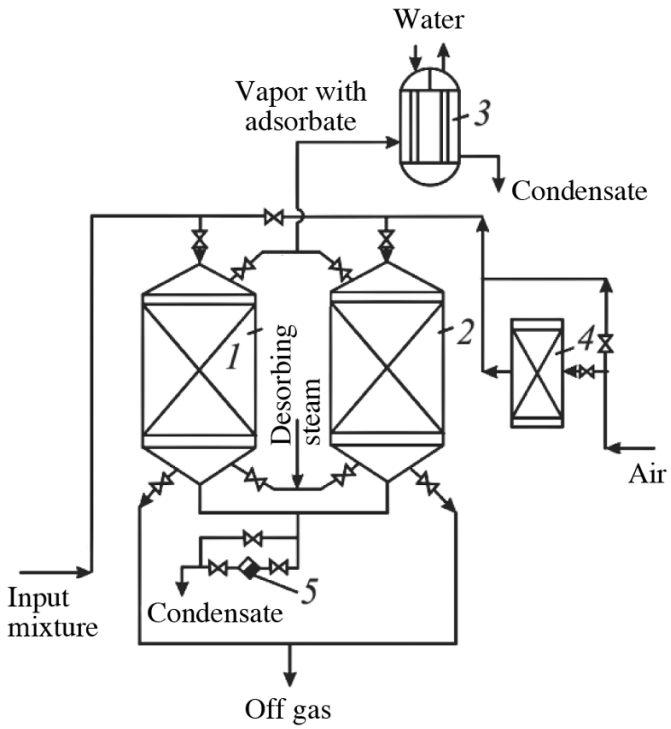

Fig. 2. Diagram of recuperative adsorption plant: Adsorbers (1, 2); condenser for steam and desorbed vapors (3); hot-air blower (4); condensate outlet (5).

evenly over GS bed 8 (situated on grid 9) without entraining particles. The column was heated using a thermostat and electric heater 6. The gas temperature was 40°C.

The gas composition (%) was O_2, 4.0–5.7; CH_4, 75–79; H_2O, 3; and CO_2, remainder. The moisture concentration varied in the range 0–10 mg/m^3 as it was adsorbed. The gas flow rate adjusted to normal conditions was $4 \cdot 10^{-4}$ m^3/sec. Methane was produced in the laboratory using the reaction

$$Al_4C_3 + 10H_2O \rightarrow 4Al(OH)_3 + 3CH_4. \quad (1)$$

Water absorption by the adsorbent was determined gravimetrically.

This adsorber was proposed for inclusion in a recuperative plant for drying natural gas (Fig. 2). The adsorption plants operated continuously, despite the batch operation of the fixed-bed apparatuses, because they included several adsorbers (their number was determined according to the duration of the adsorption—desorption cycle).

The starting gas mixture was fed into adsorber 1 that was filled with the developed GS. The bed in adsorber 1 was saturated and then switched to the desorption stage with the starting mixture fed into adsorber 2. The adsorbent was regenerated by dynamic penetrating steam (fed into the adsorber lower part) that carried adsorbate vapor into condenser 3. The adsorbate condensate with water was sent for further separation. Adsorbent was dried by hot air sent into the adsorber through hot-air blower 4 and cooled by room air entering through a by-pass line.

The following input data were used for technological calculations of a batch adsorber: gas–air mixture with CH_4 concentration $C_0 = 0.0045$ kg/m^3 of volume $L = 2{,}000$ m^3 passes through the adsorber in one batch;

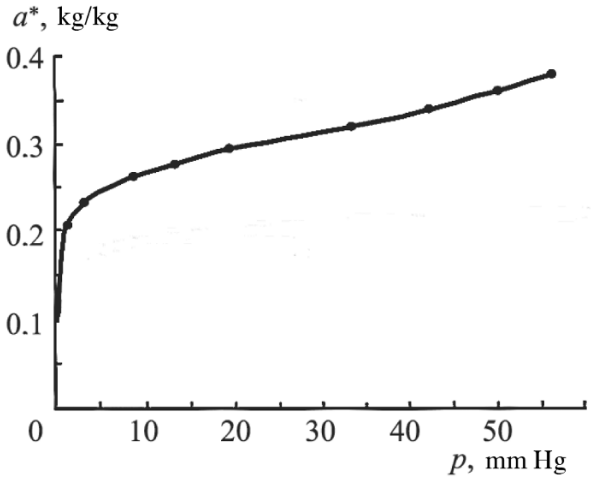

Fig. 3. Adsorption isotherm of methane vapor on sorbent under absorption conditions [5].

process temperature, 20°C; atmospheric pressure; gas–air mixture flow rate $w_i = 0.22$ m/sec; post-adsorber mixture concentration $C = 3 \cdot 10^{-5}$ kg/m^3; GS (grain diameter $d_g = 1.0$–2.5 mm; bulk density $\rho_b = 536$ kg/m^3); bed height $H = 0.5$ m; specific surface area $a_v = 720$ m^2/m^3, and specific free pore volume $\varepsilon_{fr} = 0.375$.

The adsorption isotherm of methane at 20°C on the developed GS was plotted for an analytical calculation of the adsorber (Fig. 3).

The static activity a^* of the GS for moisture at gas-air mixture concentration $C_0 = 0.0045$ kg/m^3 (considering the gas—air mixture partial pressure p_0) was determined from the isotherm:

$$p_0 = C_0 RT = 5.13 \text{ mm Hg}, \tag{2}$$

$$a^* = 0.155 \text{ kg/kg}.$$

The amount of GS for a single adsorber load was:

$$G_1 = \frac{LC_0}{a^*} = 58 \text{ kg}. \tag{3}$$

The sludge volume was

$$V_a = \frac{G_1}{\rho_i} = 0.108 \text{ m}^3. \tag{4}$$

The adsorber diameter was calculated from

$$V_a = \frac{\pi D_a^2}{4} H = 0.108 \text{ m}^3, \tag{5}$$

hence

$$D_a = 0.52 \text{ m}. \tag{6}$$

The duration of the process was calculated using the following formula because the point corresponding to the starting gas-air mixture concentration C_0 fell on the linear part of the isotherm:

$$\sqrt{\tau} = \sqrt{\frac{\Gamma}{w_\text{i}}}\sqrt{H} - b\sqrt{\frac{\Gamma}{\beta_y}}, \tag{7}$$

where τ is the adsorption time (sec); Γ, dimensionless Henry coefficient; w_i, gas-air mixture flow rate (m/sec); H, sludge bed height (m); b, coefficient considering initial and final adsorbate concentrations (table value); and β_y, volume mass-transfer coefficient (sec^{-1}).

$$\Gamma = \frac{a^* \rho_\text{i}}{C_0} = 18\,462,$$

$$\beta_y = \beta a_v,$$

where β is the mass-transfer coefficient (sec^{-1}) and a_v, specific surface area (m^2/m^3).

The mass-transfer coefficient in the absorber fixed bed could be calculated from theoretical equations [5] for laminar flow (Re < 40).

Let us determine the flow regime in the bed. The Reynolds number is

$$\text{Re} = \frac{d_\text{e} w_\text{i} \rho}{\mu} = 29.3, \tag{8}$$

where $d_\text{e} = 4\varepsilon_\text{fr}/a_v = 0.002$ m is the equivalent diameter; ρ, gas–air mixture density (kg/m^3); and μ, kinematic viscosity coefficient of gas—air mixture at 20°C (Pa·sec).

Thus, the bed had laminar flow.

The Prandtl diffusion criterion is

$$\text{Pr}' = \frac{\nu}{D} = 1.74, \tag{9}$$

where

$\nu = \mu/\rho = 0.15 \cdot 10^{-4}\,\text{m}^2/\text{sec}$ is the gas-air mixture dynamic viscosity coefficient;

$D = 0.0864 \cdot 10^{-4}\,\text{m}^2/\text{sec}$, the methane–air molecular diffusion coefficient at 20°C and 1 atm.

The pressure drop in the bed is determined using

$$\Delta p = \lambda \frac{H}{d_\text{e}} \frac{\rho \omega_\text{i}^2}{2}, \tag{10}$$

where λ is a friction coefficient depending on the friction mode: For Re < 50, $\lambda = 220/\text{Re}$; Re = 50–7200, $\lambda = 11.6/\text{Re}^{0.25}$; Re > 7200, $\lambda = 1.26$.

In this instance, $\lambda = 7.5$ whereas $\Delta p = 54.45$ Pa.

Table 1

Parameter	Value
Diameter, m	0.52
Specific surface area, m^2/m^2	720
Specific free pore volume	0.375
Amount of sorbent in single load, kg	130.44
Time of adsorption:	
minutes	306
hours	5.1
Height of granulated sorbent layer, m	0.5
Moisture content of granulated sorbent, %	3.0

The mass-transfer coefficient:

$$\beta = 0.62\left(\frac{\Delta p \varepsilon_{fr} v}{a_v H L \rho}\right)^{1/3} (\mathrm{Pr}')^{-2/3} = 0.029 \text{ m/sec}, \tag{11}$$

$$\beta_y = \beta a_v = 20.88 \sec^{-1}, \tag{12}$$

$$\sqrt{\tau} = 135.6,$$

$$\tau = 5.1 \text{ h}.$$

Let us determine the amount of gas–air mixture passing through the adsorber during this time:

$$V = \frac{\pi D_a^2}{4} w\tau = 859 \text{ m}^3. \tag{13}$$

According to the conditions, 2,000 m^3 of gas—air mixture should pass through the adsorber in one operating batch. Therefore, the adsorber diameter must be increased:

$$D_a = \sqrt{\frac{2000 \cdot 4}{\pi w \tau}} = 0.8 \text{ m}.$$

The amount of sludge per adsorber load must also be increased:

$$G_1 = \frac{\pi D_a^2}{4} H \rho_b = 130.44 \text{ kg}.$$

Table 1 presents the processing parameters of the batch adsorber.

CONCLUSION

The processing characteristics of a batch adsorber based on GS of chemical water-treatment sludge from Kazan TPP-1 were obtained. The maximum adsorption capacity of the GS for moisture on a laboratory apparatus was 2.4 g/g. A processing scheme for a recuperative adsorption plant for drying natural gas was proposed.

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