Increasing efficiency of use of dryers at the gas-processing enterprises

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Abstract. Gas is the most environmentally friendly type of fuel and its role only increases over time. According to experts' forecasts by 2050 its role in the world's energy balance will be 28-30%. The main technological process used in gas production and transportation is the drying process. Annually, about 20-25 billion cubic meters of associated petroleum gases are processed at gas processing plants. In Russia, the production of liquefied natural gas is becoming more popular. The quality of associated petroleum gas intended for processing is subject to high demands, such as purification of methanol, mercury and gas dehydration. Mostly dehydration is carried out using zeolites. The paper presents the result. On the territory of Russia, a significant proportion of gas fields contain hydrogen sulfide and organosulfuric compounds, without purification from which gas can not be sold to the main gas pipeline system and consumers. The organization of gas production at the Orenburg and then Astrakhan fields required the use of technologies for gas purification from hydrogen sulfide, production of gas sulfur and post-treatment of tail gases of sulfur production, as well as gas purification from organosulfur compounds.

1. Introduction
Currently, gas processing plants (GPPs) use the mandatory stage of natural gas preparation to prevent a number of serious problems in the transportation of associated petroleum gas (APG). During gas processing and transportation due to lowering the temperature in the system, condensation of water vapor occurs, which leads to the formation of condensate formed with the components of natural gas hydrates, which, deposited in gas pipelines, reduce their cross-section. In addition, the presence of water in the system enhances equipment corrosion. Therefore, one of the most important stages of processing is gas dehydration [1,2].

Adsorption drying, used for deep drying of gases. The main advantage of adsorption plants is the possibility of simultaneous removal of water and a number of impurities, such as hydrocarbons, acid gases, etc. The adsorbent in the plants is zeolite. Depending on the requirements we need at the output, several layers of adsorbent are filled up, each of which carries the function of removing unwanted components [3,4].

At gas-gasoline plants, the use of moderate and deep cold in technological processes allows increasing the degree of recovery of light fractions of hydrocarbons, solving the problem of natural gas liquefaction, and separating the non-condensed helium residue. Gas liquefaction plants cool down to -160 °C, and helium plants cool down to -170 °C. This technology has become available thanks to the
use of zeolites, which ensure long-term continuous operation of separation equipment in these conditions. Deep and reliable drying of the transported gas in a cold climate by land transport is possible with the use of zeolites [5].

Taking into account import substitution, the issue of replacing imported zeolites with domestic synthetic zeolites becomes relevant, for their use in gas processing plants.

2. Materials and methods

The purpose of this work is a study of the properties of synthetic zeolites in laboratory facilities. Zeolites are aluminosilicates containing oxides of alkaline and alkaline earth metals. Zeolites are characterized by a strictly regular pore structure, which under normal temperature conditions are filled with water molecules [6].

The General chemical formula of zeolites is Me_{2/n}O•Al_{2}O_{3}•xSiO_{2}•yH_{2}O. (where Me is the alkali metal cations and n is its valence). In nature, as cations, usually the composition of zeolites includes sodium, potassium, calcium, rarely barium, strontium and magnesium. The crystal structure of zeolites is formed by SiO_4 and AlO_4 tetrahedra (al and Si atoms are usually classified as T atoms), connected to each other by a common oxygen ion.

In nature, zeolites are widely distributed and often occur. They were formed as a result of changes in volcanic tuffs in marine and continental basins and thus represent the tuff-sedimentary type of deposits. Cations that are part of zeolites can be replaced by ions of other metals under the action of the medium. Varying conditions of hydrothermal synthesis and the course of cation exchange reactions in natural conditions predetermined a wide variety of types of natural zeolites [7, 8].

Synthetic zeolites are obtained by heating aqueous alkaline aluminosilicate mixtures, i.e. mixtures containing water, alkali, SiO_4 and AlO_4 as mandatory components. In this way, synthetic zeolites were obtained in the last century, but until the end of the 40s of this century, work in the field of zeolite synthesis was episodic, and the resulting crystal phases were often not clean and reliably identified.

Research part. The study of the physicomechanical adsorption characteristics of zeolites was carried out in a pilot installation simulating the conditions of the gas dehydration process in industry, which makes it possible to evaluate the effect of impurities on the properties of adsorbents and the uniform distribution of the gas flow [9-11].

The pilot plant is made in accordance with similarity criteria for industrial devices. A typical design of a pilot plant is shown in Figure 1.

![Figure 1. Typical design of a pilot plant for APG adsorption dehydration.](image)
Ka zeolite Sorbs He, H₂, H₂O, NaA zeolite Sorbs inert gases CH₄, hydrocarbons C₂, C₃H₆, O₂, CO₂, H₂O, CH₃ON, CH₃CN, CH₃NH₂, CH₃Cl, CH₃Br. CaA zeolite Sorbs n-alkanes C₅H₁₂ON, C₃H₇Cl, C₃H₇Br, CH₂Br₂, (C₃H₇)₂NH, CaX zeolite Sorbs branched alkanes and alcohols, benzene, cyclohexane and it’s lower homologues; NaX Zeolite 1,3,5 Sorbs-triethylbenzene, 1,3-dichlorobenzene [(h-C₆F₉)₃N].

3. Results
At the research stage, experiments were conducted to identify the physicochemical and adsorption characteristics of potassium zeolites. The results are shown in the table 1. According to the results of comparative tests, zeolites of SkatZ LLC KA-BS Russia possess the best physicomechanical and adsorption characteristics (producer of ISKhZK LLC) and 3A-DJ 1/8 UOP (producer of Honeywell Company Italy).

Table 1. Physico-mechanical and adsorption characteristics of potassium zeolites.

| Sorbent                          | Dynamic capacity, mg / cm³ | Bulk density, g / cm³ | Mechanical strength | Water resistance, % wt. | TTR during tests, °C |
|----------------------------------|-----------------------------|-----------------------|---------------------|--------------------------|-----------------------|
| according to the regulations     |                             |                       |                     |                          |                       |
| 1...2 (1 - data at the beginning of the test…2 - data at the end of the test) |
| LLC ISKhZK KA-U, Russia          | 150...141                   | 0.82                  | 3.1...1.67          | 96.5...64.0              | 99.0 -70...-75        |
| SkatZ LLC, KA-BS, Russia         | 145...142                   | 0.80                  | 2.16...1.87         | 99.2...97.9              | 99.3 -70...-73        |
| UOP A Honeywell Company, 3A-DG 1/8, Italy | 112 | 0.73 | 1.75...1.64 | 98.5...94.8 | 99.9 -68...-69 |
| Axens IFT Group Technolo-gies, AxSorb 531, France | 122...120 | 0.80 | 1.97...1.41 | 99.0...98.7 | 99.9 -76...-79 |
| ZAO BASF, 3A, Germany            | 111...108                   | 0.80                  | 0.67...0.63         | 99.9...83.9              | 99.8 -70...-71        |
| ISKhZK LLC KA-U, Russia, 2008 ГГИК | 130.24...125.27             | 0.83                  | 4.27               | n/a                      | 99.87 -74.6...-75.7  |
| ISKhZK LLC KA-U, Russia, 2010, GPK | 140.82...128.24             | 0.79                  | 3.48               | n/a                      | 99.64 -86.3...-84.0  |
| ISKhZK LLC KA-U, Russia, 2010 M GPK LLC "RealSorb", KA-PNG, Russia, 2008 | 143.35...139.81             | 0.76                  | 2.9                | n/a                      | 99.75 -89.5...-84.9  |
| LLC "RealSorb", KA-PNG, Russia, 2008 | 53.16...29.30               | 0.88                  | 0.91               | n/a                      | 95.56 -70.5...-67.9  |
| LLC "RealSorb", KA-PNG, Russia, 2011 | 145.05...133.71             | 0.81                  | 2.25               | n/a                      | 99.33 -89.8...-89.5  |
| LLC "RealSorb", NaA-PNG, Russia, 2011 | 159.03...136.84             | 0.85                  | 2.33               | n/a                      | 99.75 -89.8...-89.5  |
| Nizhny Novgorod Sorbents CJSC, NaA, Russia, 2010 | 140.33...97.84             | 0.82                  | 2.66               | n/a                      | 99.25 -77.1...-75.5  |
These studies have allowed us to identify several important criteria that determine the optimal conditions for the selection and operation of zeolites and, as a result, their service life. One of these criteria is the quality of zeolites, which includes a number of interrelated components [12]:

- constant monitoring of the quality of zeolites from manufacturers and interaction with them, the purpose of monitoring is to constantly monitor, identify and select the best quality zeolites, both domestic and foreign;
- incoming inspection prior to loading on the conformity of the actual quality indicators passport or certificate;
- control of operating conditions (regulatory or recommended), which allows to determine the absence or presence of violations of the technological mode of operation the constancy or change of gas composition and evaluate the quality of the adsorbent after discharge with regard to the conditions;
- complex tests of spent zeolites after discharge from the adsorbers, carried out to identify the main reasons for reducing the adsorption activity and mechanical strength of the sorbent during operation at a specific plant.

Progressive reduction of the adsorption capacity with each cycle of "adsorption-regeneration" requires constant adjustment of the operating mode of industrial plants [13, 14]. Tested measures in production conditions aimed at increasing the service life of zeolite, reducing the degree of its coking do not bring the desired effect, which makes it necessary to further search for solutions to improve the efficiency of adsorption drying of natural gas.

4. Discussion
Industrial surveys of the gas drying process on zeolites and experimental studies in laboratory conditions were carried out, based on the results of which the estimation of the residual resource of zeolite was calculated for the first time [15, 16]. It was found that uneven gas distribution leads to irrational use of zeolite - the third part of the zeolite has a high residual resource (production of less than 50%). About a third of the zeolite load could also serve as more (production of 50-60%).
Special laboratory and pilot installations have been created that simulate desulfurized gas drying conditions in industrial conditions, and original methods have been developed to assess the uniformity of gas flow distribution in the adsorber [17,18].

It is shown that to ensure the efficiency of adsorption drying of gas and maintain high dynamic activity of zeolite, it is necessary to maintain the gas temperature at the inlet to the adsorber no higher than 25°C, to conduct regeneration in three stages: at temperatures of 90°C, 210°C and 350°C, respectively, for the purpose of sequentially removing hydrogen sulfide, carbon disulfide, mercaptans and moisture [19,20].

The efficacy of the developed improved junction ring device is provided with permanent magnets, enabling to eliminate "dead" zones in the layer of the zeolite and thereby increase the service life of the zeolite with 2"x 3-4"x, to extend the time between repairs and replacement of equipment ipso period in the drying unit.

5. Conclusions

Zeolites are the most optimal adsorbents. The main difference from other adsorbents, for example, from silica gel is the ability to adsorb at a temperature of 100 °C. The adsorption capacity at normal temperatures and pressures of about 200 PA is unique. High rates of moisture adsorption make it possible to use their short adsorbent layer in dynamic processes. The scope of application of zeolites is very extensive from air drying to catalyst in chemical reactions, as well as drying in the gas and oil refining industries.

Based on comparative tests, the following zeolites were noted as the best indicators:

- Sample ISKhZK LLC, KA-U, part. 221: has a high dynamic capacity. After pilot tests for the sample, there is a decrease in crushing strength by 47% and abrasion by 35%. The coking ability of zeolite is high (1, 34% coke);
- A sample of LLC "SkattZ", KA-BS: has a high dynamic capacity after pilot tests is reduced by 2.1%. After testing, there is a smaller decrease in crushing strength and abrasion than for the sample KA-U, ISKhZK LLC (by 13-20% and 2.1%, respectively). After testing, the proportion of broken granules is - 0.1%. The coking ability of zeolite is lower than for KA-U, LLC ISKhZK;
- Sample UOP A Honeywell Company, 3A-DG 1/8: has a capacity below the regulated value, after testing the dynamic capacity does not drop (112 mg / cm³). The crush strength after pilot testing in the sample is reduced by 6%, the abrasion resistance drops by 5%. After testing, the sample contains broken granules - 0.1%. Low coking ability (0.63%).

Drying of gas and liquid media is of great importance in modern conditions of operation of high-intensity technologies associated with the use of high pressures and temperatures, environmentally unfavorable components, significant electrical voltage, as well as high requirements for accuracy and rhythmicity of equipment operation. The use of inorganic sorbing materials makes it possible to dry liquid and gas media to low humidity values, up to -70 °C at the dew point. At the same time, high requirements for the strength of the adsorbents used cause their use in the form of block sorbing products characterized by the absence of dusting. Manufacturing of such products is possible using technologies that provide for fixing adsorbents in products on polymer matrices of various nature. Regeneration of sorbing materials using electrothermal and electromagnetic effects on the adsorbent allows to significantly increase the resource of the sorbing material.

From the above conclusions, it follows that the isolated samples of zeolites will have a potentially longer service life.

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