Experimental study of the thermal management process at low-temperature circulating charging of an adsorbed natural gas storage system

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Abstract. Adsorbed natural gas (ANG) technology is a promising alternative to traditional compressed (CNG) and liquefied (LNG) natural gas systems. Nevertheless, energy efficiency and storage capacity of ANG system strongly depends on thermal management of its inner volume because of significant heat effects occurring during adsorption/desorption processes. At the same time low-temperature charging of ANG system provides its higher storage capacity as well as increased fire and explosion safety due to lower operating pressure and “bound-state” of gas molecules with the surface of adsorbent. In present work, a prototype of low-temperature circulating charging system for ANG storage tank filled with shaped microporous carbon adsorbent was studied experimentally in wide ranges of pressures (0.5-3.5 MPa) and gas flow rates (8-18 m³/h).

1. Introduction
ANG storage systems possess a number of significant advantages over CNG and LNG technologies in particular high energy efficiency caused by lack of extremely high pressures and cryogenic temperatures as well as increased fire and explosion safety due “bound-state” of gas molecules with the surface of adsorbent, so-called “nano-dispersed state” [1]. However, it is well known that efficiency of ANG systems strongly depends on significant thermal effects occurring during charge (adsorption) and discharge (desorption) processes, which require development of new approaches to charging processes and thermal management of the ANG tank [2]. Another very important challenge for practical use of ANG is development of new processes for “fast” charging of such systems.

As a rule, to reduce the influence of thermal effects special thermal management systems can be used: heat exchangers installed inside [3, 4] or outside [5, 6] the storage tank including circulation of gas heated or cooled in an external heat exchanger [7, 8].

The main correlations for simulating the characteristics of ANG storage system are presented in [9, 10].

Circulating charging process with thermal management is considered as one of the most promising technique regarding implementation of “fast” charge of the ANG system with advanced efficiency. This article is dedicated to experimental study of full-scale pilot circulating charging system with...
controlled thermal management for charge of ANG tank prototype filled with monolithic microporous carbon adsorbent.

2. Materials and methods

2.1. Monolithic microporous carbon adsorbent
Microporous carbon adsorbents are the most promising materials today for application on ANG due to high activity to methane, mechanical strength and the possibility to increase packing density by shaping under pressure [11, 12], which ensures the maximum indicators of the volumetric storage capacity of the system.

In this work we used AU-1 industrial granulated activated carbon, which possessed remarkable adsorption activity to methane and could be potentially used in ANG systems especially with low-temperature charging process [11-13].

Manufacturing technology of shaped cylindrical monoliths from AU-1 activated carbon is described in [12]. Monolithic adsorbent samples (14 pcs.) were installed in an adsorption tank of 51 liters inner volume. Estimated occupation of inner space of the tank by the monoliths is about 80%. The average diameter and thickness of the monoliths were 196 and 101 mm respectively. To reduce the hydraulic losses of the samples 37 perforating channels with a diameter equal to 4.5 mm were made in the monoliths.

2.2. Adsorptive
Natural gas with the following composition was used in the experiments, vol.: 96.1% methane, 2.2% ethane, 0.8% propane, 0.6% nitrogen and other impurities less than 1%. Theoretical calculations and experimental data analysis were carried out on the basis of 100% (pure) methane.

2.3. Experimental Setup
To study natural gas charge and discharge processes a special multifunctional experimental setup was developed and manufactured, which made it possible to simulate different operation modes: 1 – adiabatic, isothermal and low-temperature charge/discharge processes; 2 – single- and multi-stage charge; 3 – “fast” and “slow” charge. The scheme and description of this experimental setup is presented in [10]. The heat of adsorption released during charge process is removed using circulating natural gas flow, which passes through the channels in adsorbent monoliths located inside the tank with one inlet and two outlets, making it possible to significantly reduce the hydraulic losses. Gas circulation in the circuit is provided by a supercharger. The flow rate of the circulated gas adjusted by changing the supercharger rotation speed.

The charge process is carried out in two stages: 1 – “isothermal” charge with heat removal into environment; 2 – “low-temperature” charge with heat removal employing a cooling unit. A long period of reaching equilibrium was ensured between the stages.

Temperature sensor located on inlet of the adsorber tank, along its axis (4 pcs.) and radially (4 pcs.) were mounted to control temperature distribution inside the tank.

2.4. Methods
Effective charging capacity $\Delta V_a$, i.e. the excess amount of loaded gas in relation to initial state is empirically estimated by the "volumetric method" using the gas mass balance in the experimental setup. The theoretical charging capacity is determined using the current pressure and temperature at a given point in time and data from previous experimental studies of the AU-1 adsorption properties. The temperature of the adsorbent was determined by temperature sensors located inside the adsorber.

The effective circulating charging time $\tau_e$ is counted from the supercharger (circulation) start (differ in experiments) and determined in the experiment by the acceptable final temperature difference $\Delta T_e$ between the incoming gas flow and the average temperature of the adsorbent, which determines the direct loss in the storage capacity of circulating charging. A certain effective charging time
corresponds to a certain (acceptable) loss in storage capacity. For example, the final temperature difference of 5K corresponds to the loss of effective charging capacity in this adsorber from 3.5% at 3.5 MPa to 10% at 0.5 MPa or in absolute value about 0.12-0.20 m$^3$ (STP), where STP is the standard temperature (20 °C) and pressure (101 325 Pa).

The heat exchange efficiency coefficient $K_{he}$ is determined by the ratio between the actual heat flux and the maximum heat flux corresponding to an infinitely high heat transfer coefficient or an infinite large heat exchange surface. The actual heat flux is determined from the theoretical dependences presented in [9, 12] according to the rate of decrease in the measured temperatures of the adsorbent layer. Coefficient $K_{he}$ characterizes the balance between the charging mode and the surface area (structure) of the adsorbent monolithes.

3. Results and discussions

Table 1 provides brief information on the investigated charging modes, as well as a number of results obtained. It should be noted that experiment 5 (pressure 2.0 MPa and gas flow rate 8 m$^3$/h) has the highest heat exchange efficiency coefficient. This is probably due to a combination of both a sufficiently high pressure, which ensures intense heat exchange inside the adsorber, and a low gas flow rate, which allows enough gas heating. Even in experiment 1, the gas flow rate was insufficient for a "fast" (within 5-10 minutes) charging, but $K_{he}$ is enough high, so heat-exchange surface increasing, i.e. monolith structure changing, is weakly efficient at this charging mode. Significant flow rate increasing probably provide target charging time, but in this case it’s necessary to provide a more extended surface area of adsorbent monoliths, because of decreasing $K_{he}$ with flow rate, as can be seen from the example of a pressure of 2.0 MPa. Low values of $\tau_c$ at low pressures are explained smaller amount of released heat of adsorption. Low-temperature charging is more effective in charging capacity at low pressure, but is very ineffective in heat-exchange and charging time.

Table 1. Experimental research modes.

| Parameter                          | Experiment |
|------------------------------------|------------|
| Pressure (MPa)                     | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  |
| Gas flow rate (m$^3$/h)            | 3.5 | 3.5 | 2.0 | 2.0 | 2.0 | 1.0 | 1.0 | 0.5 |
| Initial pressure (MPa)             | 0.13 | 0.13 | 0.12 | 0.13 | 0.14 | 0.14 | 0.13 | 0.14 |
| Initial temperature (°C)           | 16.6 | 18.2 | 19.8 | 18.5 | 21.9 | 20.5 | 21.4 | 23.7 |
| Minimal temperature of adsorbent (°C) | -25.2 | -24.5 | -22.7 | -24.6 | -25.4 | -22.0 | -22.0 | -19.2 |
| $\Delta V_e$ (m$^3$ STP)           | 4.90 | 5.12 | 3.69 | 3.77 | 3.76 | 2.10 | 2.59 | 1.25 |
| isothermal charging                | 6.71 | 7.15 | 5.50 | 5.58 | 5.66 | 3.92 | 4.44 | 2.68 |
| full charging                      | 11.6 | 17.4 | 13.0 | 21.4 | 26.3 | 13.4 | 25.8 | 15.5 |
| $\tau_c$ (min) with $\Delta T_e = 5$ K |
| isothermal charging                | 19.7 | 27.2 | 30.4 | 36.5 | 46.4 | 55.5 | 84.8 | 125.4 |
| low temperature charging           | 0.77 | 0.78 | 0.70 | 0.76 | 0.83 | 0.69 | 0.69 | 0.62 |

Figure 1 shows the dependences of the effective charging capacity for 4 modes of charging at pressures from 0.5 to 3.5 MPa. It should be noted that the experimental and theoretical values of the effective charging capacity are in good accordance. The largest amount of gas charged corresponds, obviously, to the highest charging pressure equal to 3.5 MPa, and is about 6.71-7.15 m$^3$ (STP), in specific values to the volume of the adsorber is 132-140 m$^3$ (gas)/m$^3$ (tank). If the initial gas volume (theoretically about 20 m$^3$/m$^3$) is added to this value, then the total specific amount of storage gas is about 152-160 m$^3$/m$^3$. High capacities can be achieved since the adsorbent occupies only about 80% of the adsorber space. Experimental capacity fluctuations at the beginning of charging are explained by dynamic errors in the used volumetric method.
Figure 1. Time dependence of the effective charging capacity at different modes (the number of the experiment is indicated) at isothermal (stage 1) and low-temperature charging (stage 2). Lines are theoretical values, dots are experimental values, open “stars” – beginning of circulating charging; solid “stars” – achieving effective circulating charging time $\tau_e$ with $\Delta T_e = 5$ K.

4. Conclusions
The results of the study showed the correlation between the charging mode and the charging efficiency indicators. The fastest charging was achieved at a pressure of 3.5 MPa and a gas flow rate of 12 m$^3$/h. The most balanced heat exchange process was observed in the charging mode at a pressure of 2.0 MPa and a gas flow rate of 8 m$^3$/h.

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