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THE HIGH-PRESSURE SORPTOMAT – A NOVEL APPARATUS FOR VOLUMETRIC SORPTION STUDIES UNDER ISOBARIC HIGH GAS PRESSURE CONDITIONS

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Abstract

As part of the work the high-pressure sorptomat – a novel apparatus for sorption tests under conditions of high gas pressure was developed. The sorption measurement is carried out using the volumetric method, and the precise gas flow pressure regulator is used in the device to ensure isobaric conditions and regulate the sorption pressure in the range of 0–10 MPa. The uniqueness and high precision of sorption measurements with the constructed apparatus are ensured by the parallel use of many pressure sensors with a wide measurement range as well as high precision of measurement – due to the use of precise pressure sensors. The obtained results showed, i.a. that the time of reaching the isobaric conditions of the measurement is about 6–7 seconds and it is so short that it can be considered a quasi-step initiation of sorption processes. Moreover, the results of the measurement pressure stabilization tests, during the CO_2 sorption test on activated carbon, have shown that the built-in pressure regulator works correctly and ensures isobaric sorption measurement conditions with the precision of pressure stabilization of ±1% of the measurement pressure. The maximum range of sorption measurement using the high-pressure sorptomat is 0–86 400 cm^3/g, and the maximum measurement uncertainty is ±2% of the measured value. The activated carbon sample used for the tests was characterized by a high sorption capacity, reaching 104.4 cm^3/g at a CO_2 pressure of 1.0 MPa.

Keywords: sorptomat, sorption, high-pressure apparatus, volumetric method.

1. Introduction

Devices for sorption tests in a wide range of gas pressures, especially in near-critical conditions, are extremely expensive, hence their purchase is financially unattainable for many research laboratories. The advantage of sorption devices operating under high pressure conditions is the possibility of conducting sorption measurements in almost full range of the sorbate gas phase, from vacuum to saturated vapor pressure. Determination of the gas sorption isotherm for the relative pressure p/p_0 in the range $0 < p/p_0 < 1$ is the basis for the applicability of theoretical models describing the equilibrium state of the gas sorption process on the solid sorbent surface. The pressure p/p_0 defines the ratio between the measurement pressure (p) and the saturation

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vapour pressure of a specific adsorbate (p_0) at which its gas-to-liquid phase change occurs and vice versa. This value is closely related to the temperature of the measurement, which takes place under isothermal conditions. On the basis of sorption isotherms, using appropriate models, it is possible to determine the basic structural parameters of the sorbent, such as: specific surface area, average pore diameter and pore size distribution [1–5].

The sorption measurement apparatus is used in many fields related to geological [6–9], chemical [10–13], biological [14, 15], environmental [16, 17] sciences as well as many others. From the point of view of methods of measuring the sorption process, there are many techniques, including breakthrough, volumetric, gravimetric, desorption, and many special ones [18]. The breakthrough group is the most popular for measuring the adsorption of gas mixtures, in particular for studies of competitive sorption, selective sorption and gas separation. These devices are not used in sorption measurements under high gas pressure conditions. The most popular group of methods for pure gas sorption measurements under high gas pressure conditions are those with the application of volumetric devices [19]. Typical volumetric sorption devices consist of two containers connected by a valve. The amount of gas sorbed by the sample is determined by measuring the pressure drop in the reference container that accompanies the sorption processes. Volumetric devices have a very simple structure, but their disadvantage is the lack of isobaric measurement conditions. Until the processes of gas transport and sorption in the pore space are completed, the gas pressure in both containers drops, which makes the analysis of the kinetics of the processes taking place problematic. When measuring with the typical volumetric method, the obtained sorption capacity refers to the measurement pressure at which the sorption equilibrium is reached, so the sorption equilibrium pressure is not known before the measurement starts.

An improved version of the sorption volumetric device is the manometric sorptomat – designed and developed at the Strata Mechanics Research Institute of the Polish Academy of Sciences [20]. The manometric sorptomat consists of three connected containers: supply (reference), buffer and sample. The amount of sorbed gas is determined on the basis of the balance of the contents of these three containers. The sorption measurement is performed under isobaric conditions, regulated in the range of 0–1.6 MPa, with a stabilization precision of ±0.003 MPa. The advantage of a manometric sorptomat is the ability to carry out sorption measurements under isobaric conditions, but this device does not allow for measurements at high gas pressures, which makes it impossible to obtain near-critical conditions.

Among the commercially available volumetric devices for sorption studies under high gas pressure conditions the following devices are available: Gas Sorption Analyzer IMI Series (by Hiden Isochema), High Pressure Volumetric Analyzer HPVA (by Micromeritics), High Pressure Gas Sorption Analyzer iSorb HP1/HP2 (by Quantachrome Instruments). These devices operate in the pressure range up to 20 MPa, but most of them do not provide isobaric conditions for sorption measurement.

Gravimetric devices register changes in sample mass related to sorption processes [21]. Measurements are carried out in isobaric conditions, and the amount of sorbed gas in the sample is measured directly on the basis of the registered change in mass of the sample, taking into account the buoyancy force. Gravimetric devices are very precise and sorption measurement is direct, but the design of these devices, compared to volumetric solutions, is extremely complicated. In addition, in the case of measurements at higher pressures, the buoyancy force is so large that it can significantly exceed the changes in the sample mass caused by sorption, which makes it necessary to take it into account [22]. Furthermore, a major problem of gravimetric devices is the lack of pressure step change that initiates the sorption process.

Gravimetric devices for sorption tests under gas high pressure conditions are less popular than volumetric ones, and the commercially available ones include XEMIS-001 (by Hiden Isochema), Gravimetric Sorption Analyzer GSA Series (by Linseis), IsoSORP Sorption Analyzer (by TA Instruments).

Commercially available volumetric and gravimetric devices for sorption tests under high gas pressure are extremely expensive, hence the idea of building such a device was developed in the Strata Mechanics Research Institute of the Polish Academy of Sciences. The requirements of such apparatus include, above all, the possibility of carrying out measurements in isobaric conditions in the pressure range of 0–10 MPa, low complexity of construction of the apparatus, multi-range measurement enabling measurements in both high and low gas pressure, and the scalability of the test sample enabling measurements on various types of materials (granular, raw sample, *etc.*) of small and large masses. Operation of the device in a wide range of pressures will enable the measurement of CH_4 and CO_2 sorption in almost the full range of relative pressure p/p_0.

2. Apparatus

2.1. Construction

The constructed apparatus – the high-pressure sorptomat, enables gas sorption measurements under isobaric conditions in the pressure range of 0–10 MPa. The concept of operation of the device is similar to that of a manometric sorptomat [20], operating in the pressure range of 0–1.6 MPa. The high-pressure sorptomat consists of three containers (Fig. 1):

- Gas supply container – with a volume of 500 cm^3, equipped with a P_S pressure sensor – model S-20 (by WIKA), with a measuring range of 0–16 MPa and a measurement uncertainty of ±0.125%. This container acts as a gas source for refilling the reference container.
- Reference container – with a volume of 40 cm^3, equipped with P_{RH} and P_{RL} pressure sensors model S-20 (by WIKA) – with measuring ranges of 0–16 MPa and 0–1.6 MPa, respectively, and measurement uncertainties of ±0.125%. Depending on the pressure at which the measurement takes place, the pressure is registered on one of these sensors. Based on the pressure drop in the reference container, the amount of gas sorbed in the sample is determined.

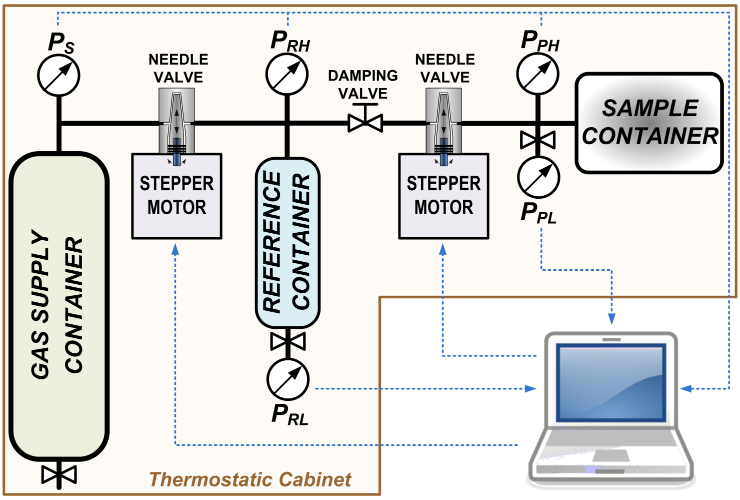

Fig. 1. Scheme of the constructed apparatus – high-pressure sorptomat to study sorption under high gas pressure.

- Sample container – with a volume of 10 cm^3 or 40 cm^3, where the container of the selected volume can be used interchangeably, depending on the size and type of the sample. This container is connected to P_{PH} and P_{PL} pressure sensors model S-20 (by WIKA), with measuring ranges of 0–10 MPa and 0–1.6 MPa, respectively, and measuring uncertainties of ±0.125%. Based on the pressure reading in the sample container, the measurement pressure is stabilized at a set level. Depending on the pressure at which the sorption measurement takes place, the pressure is read from one of these P_{PH} or P_{PL} sensors.

The containers of the high-pressure sorptomat are connected pneumatically by means of pressure regulators, *i.e.*, precise flow needle valves controlled by stepper motors. The operation of the pressure regulator is crucial for the precision of the measurement pressure stabilization.

A photo of the constructed high-pressure sorptomat, with the functional components marked, is shown in Fig. 2.

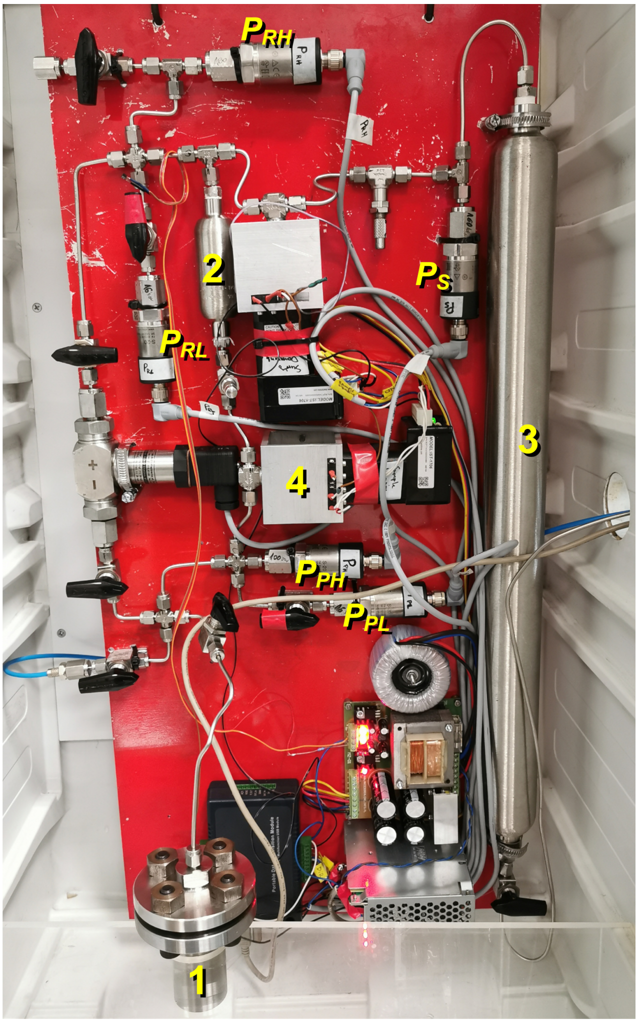

Fig. 2. Photo of the high-pressure sorptomat placed in the thermostatic cabinet: 1 – Sample container; 2 – Reference container; 3 – Gas supply container; 4 – Pressure regulator.

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A major technological challenge in the construction of high-pressure sorption devices is to ensure the tightness of the entire measuring system. The tightness of volumetric devices is particularly important because any leakage affects the uncertainty in the measurement of the amount of sorbed gas. In the constructed high-pressure sorptomat, Swagelok precise gas system components were used to ensure the tightness of the containers and all pneumatic connections. The sealing of the sample container was ensured by the use of a copper gasket. To prevent sample spillage from the container, a sintered filter with a filtration range of less than 40 μm is used. A photo of the sample container is shown in Fig. 3.

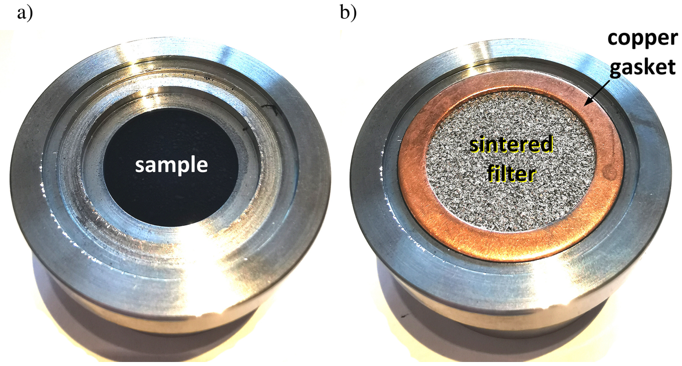

Fig. 3. Photo of a sample container: a) filled with sorbent sample;
b) with sintered filter and copper gasket in place.

Sorption measurements with the high-pressure sorptomat are carried out under isothermal conditions, which is ensured by placing the measuring system in a Q-Cell 240/60 thermostatic cabinet. The thermostatic cabinet provides temperature regulation in the range of 4–60°C and stabilization of ±0.5°C.

2.2. Control system

The operation of the high-pressure sorptomat is controlled by an Advantech USB-4716 universal control and measurement module, which is driven by the DasyLab software. This system also records all measured parameters.

The key element of the operation of the high-pressure sorptomat is the pressure regulator that connects the reference container to the sample container. This regulator (Fig. 4) consists of a flow damping valve (model Swagelok SS-ODKS2), a needle valve (model Swagelok SS-ORS2) driven by a stepper motor (model iST-1706 – 0.6 Nm) and a clutch (model CNC D20xL25) connecting both valves.

The pressure regulator works in feedback with the P_{PH} or P_{PL} pressure sensor (depending on the measurement pressure) to control the flow of gas through the needle valve. Controlling the regulator's operation is extremely important from the point of view of the precision of pressure stabilization. In order to ensure isobaric conditions of sorption, it is necessary to precisely control the operation of the needle valve. A number of factors influence the accuracy of the pressure regulator:

- valve type (needle shape, size of the opening, flow coefficient C_v),
- stepper motor frequency,
- motor step (number of steps per revolution),

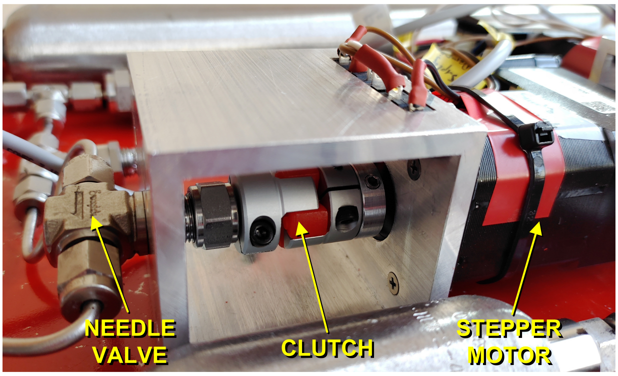

Fig. 4. Photo of the pressure regulator ensuring isobaric conditions for measurement with the high-pressure sorptomat.

- stabilization pressure,
- type of control system (two-position, three-position, PID, *etc.*).

The shape of the needle valve depends on the model of the valve used. In the constructed sorptomat, a Swagelok SS-ORS2 needle valve with a maximum flow coefficient of $C_v = 0.09$ was used.

The stepper motor used (model iST-1706 – 0.6 Nm) is integrated with the controller and enables operation in many modes from 400 to 51200 steps per revolution. It is extremely important from the point of view of the speed of the regulator's response to pressure changes (the fewer steps per revolution, the faster the regulator's response) and the gas flow rate flowing through the regulator (the more steps per revolution, the greater the possibility of obtaining a very low flow). The number of steps per revolution is set in the stepper motor by jumpers, so it cannot be changed during the operation of the device. In the apparatus tests performed, the stepper motor was set to 3200 steps per revolution.

Another parameter that affects the precision of pressure stabilization is the motor frequency, and it can be set using DasyLab in the range of 0-500 Hz. The selection of an appropriate mode and frequency of the stepper motor operation is crucial from the point of view of the precision of pressure stabilization and it is a compromise between the speed of reaction of the needle valve to pressure change and the possibility of obtaining the required gas flow through the regulator. In order to precisely stabilize the measurement pressure, the motor frequency is regulated by the DasyLab software and it is changed automatically during the measurement, using the implemented *proportional–integral–derivative* (PID) controller. The frequency was controlled based on the set measurement pressure, the temporary measured pressure, and the difference of both pressures.

The PID controllerconsists of three parts: the proportional – which is responsible for the current deviation, the integral – associated with the compensation of past deviations and the differential – dealing with the compensation of expected future deviations. The deviation value in the high-pressure sorptomat is understood as the difference between the set value of the measurement pressure and the current value of the pressure in the sample container. The main purpose of the PID controller is to stabilize the measurement pressure at a level as close as possible to the set value in order to ensure isobaric conditions for sorption measurement. The weighted sum of the signals from these three components forms the basis of the pressure signal to the actuator, which in this case is a stepper motor driver connected to a needle valve, to regulate the pressure change and maintain it at the set point.

The use of the PID controller is an effective solution in the absence of specific parameters of the control object. By appropriate selection of the PID controller settings, it is possible to obtain the control adjusted to a given object. The PID controller is one of the most frequently used types of regulators in industrial control systems.

2.3. Sorption balance

The balance of the amount of gas sorbed in the sample is carried out on the basis of recording the pressures in the reference container and the sample container. The gas in the supply container is a reserve to refill the reference container in case the pressure in this container drops below the measurement pressure stabilized in the sample container during the sorption measurement. A schematic diagram of pressure changes in the containers during sorption measurement is shown in Fig. 5.

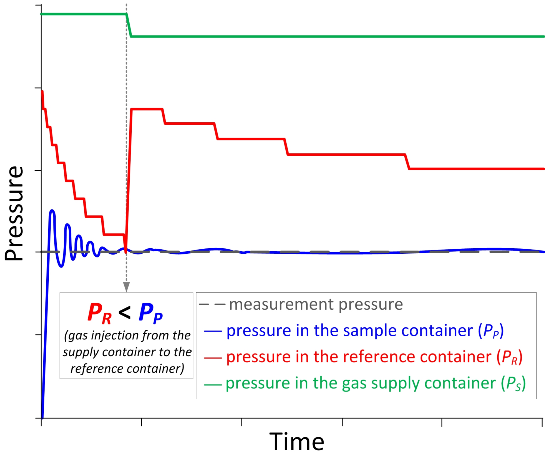

Fig. 5. Schematic diagram of pressure changes in containers during sorption measurement with the high-pressure sorptomat.

Before starting the sorption measurement at a set pressure, there is the starting pressure p_R^0 in the reference container, and the pressure p_P^0 in the sample container respectively. The sorption measurement is started by opening the needle valve of the pressure regulator, which causes the gas to flow from the reference container to the sample container. The needle valve remains open until the pressure p_P in the sample container reaches the set measurement pressure p_{set}. By controlling the position of the needle in the valve, the sample container can be refilled with the correct portion of gas, which is proportional to the amount sorbed in the sample. The amount of sorbed gas is determined from the gas balance in the containers from the formula:

$$a = \frac{V_m}{m \cdot z \cdot R \cdot T} \left(\left(p_R^0 - p_R(t) \right) \cdot V_R - \left(p_B(t) - p_P^0 \right) \cdot V_V \right), \tag{1}$$

where: $a \left[\frac{\text{cm}^3}{\text{g}} \right]$ is the amount of sorbed gas, p_R^0 [Pa], $p_R(t)$ [Pa] is the starting and temporary pressure in the reference container, p_P^0 [Pa], $p_P(t)$ [Pa] is the starting and temporary pressure in the sample container, V_R [m^3], V_P [m^3] is the volume of the reference container and the sample container respectively, V_V [m^3] is the void volume around the sample, m [g] is the sample mass,

z [–] is the compressibility factor of the gas, T [K] is the temperature, R $\left[\frac{\text{J}}{\text{mol}\cdot\text{K}}\right]$ is the universal gas constant, V_m $\left[\frac{\text{cm}^3}{\text{mol}}\right]$ is the molar volume of the gas under normal conditions, t [s] is time.

Sorption measurement by means of a high-pressure sorptomat is carried out using the indirect method, where the amount of gas sorbed in the sample is determined on the basis of pressure, temperature, container volume and sample mass measurements. Hence, the calculation of the measurement uncertainty of the high-pressure sorptomat is related to the complex uncertainty calculus. Based on the measurement uncertainties of the directly measured quantities present in (1), using the uncertainty propagation law, the measurement uncertainty of sorption using a high-pressure sorptomat can be determined as:

$$u(a) = \sqrt{u^2(p_R) + u^2(p_P) + u^2(V_R) + u^2(V_V) + u^2(T) + u^2(m)}\,, \tag{2}$$

where:

$u(p_R)$, $u(p_P)$ is the uncertainty of measurement of the pressure in the reference and sample containers, equal to a measurement uncertainty of $\pm 0.125\%$ of the P_{RH} and P_{RL} sensors used,

$u(V_R)$, $u(V_V)$ is the uncertainty in the determination of the volumes of the reference and sample containers, equal to the estimated 1% uncertainty of the volumes of the containers used,

$u(T)$ is the uncertainty of temperature measurement and stabilization using the Q-Cell 240/60 thermostatic cabinet, amounting to ±0.5°C,

$u(m)$ is the uncertainty of measurement of the sample mass using a Vibra AJH-3200CE laboratory balance with a measurement uncertainty of 0.01 g.

The other constants present in (1) do not have a significant effect on the measurement uncertainty with the high-pressure sorptomat, so they are not included in (2).

3. Apparatus tests

The construction of new laboratory stands is related to a series of tests, preceding the stage of the apparatus implementation into research laboratories. The commissioning and implementation of the high-pressure sorptomat was also started with a series of tests including, among others, tightness tests of the device, tests of its correct functioning, analysis of the precision of pressure stabilization and tests of sorption measurement. The tests related to leak in pneumatic connections and high-pressure sorptomat containers were successfully completed, hence the presentation of their results of has been omitted. Furthermore, each sorption measurement with the apparatus is preceded by a leak test of the sample container and a measurement of the void volume using helium. Other tests of the high-pressure sorptomat operation included:

- tests of the speed of reaching isobaric conditions after a step change of measurement pressure,
- measurement pressure stabilization tests,
- sorption measurement tests.

The order of individual tests is not random, as it results from successive stages of the measurement procedure, where the sorption measurement begins with a step change in gas pressure around the sample, followed by reaching and stabilization of isobaric conditions and, finally, the sorption measurement.

Activated carbon was used as the sorbent to carry out the tests of the apparatus, and CO_2 was used as the gas sorbate. The mass of the sample was 1.45 grams and its density was 2.11 g/cm^3. All tests were conducted under isothermal conditions at 30°C.

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3.1. Tests of the speed of reaching the isobaric conditions of the measurement

The initiation of sorption processes occurring in the pore space of the sorbent takes place by changing the gas pressure around the sample. In the case of volumetric devices operating under conditions of variable gas pressure, sorption initiation is caused by the opening of the valve between the reference container and the sample container. This causes a step change in pressure around the sample, but the sorption processes that occur decrease the measurement pressure, so there are no isobaric measurement conditions. In the case of devices operating under isobaric conditions, the initiation of sorption processes takes place in a similar way, but in this case, it is necessary to limit the gas flow between the containers in order to reach the set measurement pressure, while taking care that this pressure does not exceed the set measurement pressure. In such a case, isobaric conditions are ensured by continuous injection of a gas portion which is proportional to the amount of gas sorbed in the sample, until the sorption equilibrium is reached.

Providing a step change in pressure that initiates sorption is very important when it is necessary to analyse and describe the phenomena of the sorption kinetics and gas diffusion in the sorbent pore space. The determination of the diffusion coefficient of a porous medium is a complicated process and it requires detailed analysis of the saturation kinetics. The diffusion process is described by Fick's second law, the solution of which requires a number of simplifications [23, 24]. One of such assumptions for solving the diffusion equation is that proposed by Crank [25], in which the initiation of the process is triggered by a step change in sorbate concentration/pressure within the sorbent surface. Therefore, it is required that the measuring apparatus used, among other things, to analyze the kinetics of sorption and diffusion processes, provide a step change in the pressure which initiates sorption.

In a high-pressure sorptomat, the sorption measurement is initiated by opening a needle valve, which causes the gas to flow from the reference container to the sample container. This flow is initially damped by the damping valve and then regulated by the needle valve. The operation of the needle valve is controlled by a stepper motor, driven by a PID controller implemented in the DasyLab software. In order to test the speed of reaching the set pressure in the initial phase of sorption measurement, tests of saturation of the activated carbon sample from vacuum to different measuring pressures were carried out: 0.1, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 MPa. The registered pressure changes in the initial measurement phase of the CO_2 sorption process on activated carbon at different saturation pressures are presented in Fig. 6.

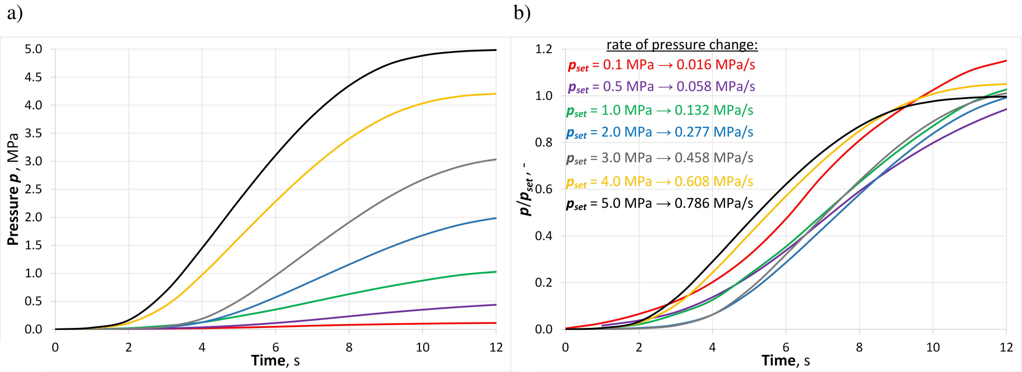

Fig. 6. Pressure changes in the initial measurement phase of the CO_2 sorption process on activated carbon at different saturation pressures: a) absolute pressure changes from vacuum to 0.1–5.0 MPa; b) relative pressure changes.

Figures 6a and 6b show the absolute and relative pressure changes, respectively, in the initial measurement phase with the high-pressure sorptomat, with the measurement pressure equal to 0.1, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 MPa. Presentation of the relative change in measurement pressure, understood as the quotient of the instantaneous pressure to the set pressure (p/p_{set}), enables visualizing what relative value of the set pressure were reached at a given time. As can be seen, at higher measurement pressures p_{set}, the rate of pressure changes in the sample container in the initial phase of the measurement increases. For example, at the measurement pressure $p_{\mathrm{set}} = 0.1$ MPa, the rate of pressure change in the sample container was 0.016 MPa/s, while at $p_{\mathrm{set}} = 2.0$ MPa it was 0.277 MPa/s, and at $p_{\mathrm{set}} = 5.0$ MPa it was 0.786 MPa/s. It follows that the approximate time to reach the measurement pressure is about 6–7 seconds. In comparison, commercially available gravimetric devices, such as the IGA-001, provide a pressure change at a maximum rate of 0.00055 MPa/s, which allows the pressure to change from vacuum to 0.1 MPa approximately 180 seconds after the measurement starts. In volumetric devices, the rate of change of measuring pressure is much faster and the pressure of 0.1 MPa can be reached in just a few seconds, but with these devices pressure overshoot is very common [20].

The speed of reaching the isobaric conditions of the measurement obtained in the tests performed is fast enough to be considered as a quasi-step.

3.2. Measurement pressure stabilization tests

After reaching the set measurement pressure, the sorption measurement is carried out under isobaric conditions provided by the gas pressure regulator. Measurement pressure stabilization tests consisted of saturating the sample from vacuum to CO_2 pressures of 0.1, 0.5, 1.0, and 3.0 MPa, respectively, until the sorption equilibrium was reached, which took approximately 10 minutes. The registered results of pressure changes and accompanying sorption changes are shown in Fig. 7.

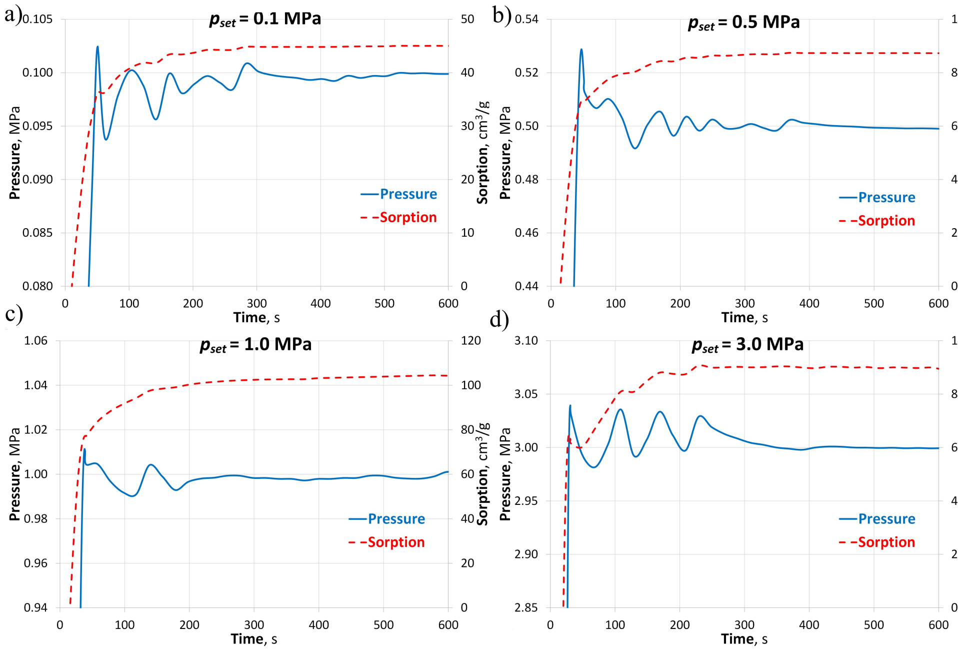

Fig. 7. Pressure changes and accompanying sorption changes measured with a high-pressure sorptomat.

On the basis of the obtained results, it was observed that at the pressure of 0.1 MPa, the precision of pressure stabilization in the initial phase of the measurement was about ±0.005 MPa, which resulted from the overshoot of the stabilization pressure during gas injection from vacuum to the set pressure. At higher measurement pressures, at $p_{\text{set}} = 1.0$ MPa and at $p_{\text{set}} = 3.0$ MPa, in the initial phase of sorption, when the process kinetics is fastest, the precision of stabilization was higher and was about ±1%. As the sorption process progresses, the precision of the measurement pressure stabilization increases significantly due to the operation of the PID controller, and when the sorption equilibrium is reached, after about 5 minutes, the measurement pressure reaches a constant value equal to the set value of p_{set}.

The results of the measurement pressure stabilization tests performed during CO_2 sorption on activated carbon suggest that the pressure controller works correctly to ensure isobaric conditions.

3.3. Sorption measurement tests

The gas sorption in the sorbent is determined from the registered pressure changes in the reference and sample containers during the saturation process. The amount of gas sorbed in the sample is calculated from (1). As part of the sorption measurement tests of the high-pressure sorptomat, CO_2 sorption was carried out at pressures of 0.1, 0.5, 1.0, 2.0 and 3.0 MPa. The sorption measurement at each pressure was preceded by degassing the sample to vacuum for 30 minutes. The kinetics of the saturation process is shown in Fig. 8.

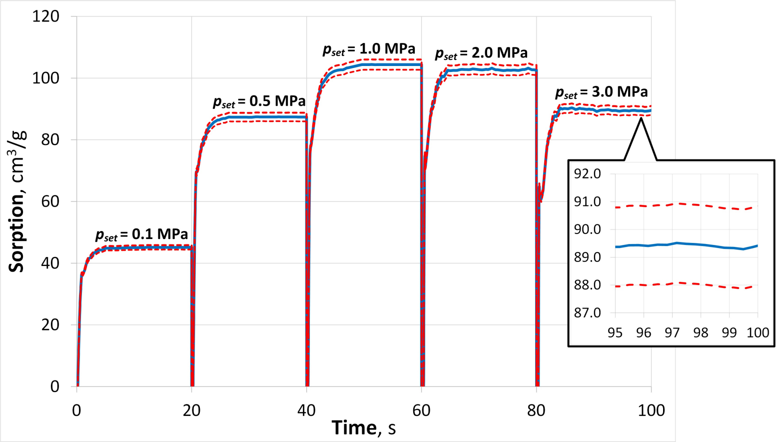

Fig. 8. Kinetics of the sorption process determined from measurements registered with the high-pressure sorptomat.

The time to reach sorption equilibrium was about 10 minutes, and the registration of sorption kinetics was 20 minutes, for each pressure. The red dashed lines indicate the measurement uncertainties determined from (2). The measurement uncertainties were a maximum of approximately ±2% of the sorption value determined from (1), based on the measurement with the high-pressure sorptomat.

Based on the sorption equilibrium points obtained at the measurement pressures, the sorption isotherm can be determined. Figure 9 shows the sorption isotherm of activated carbon relative to CO_2 as a function of measurement pressure and relative pressure. Red lines around the measurement points show error bars on the graph, determined from (2), and they amount to a maximum of

±2%. The measurement uncertainty of the high-pressure sorptomat can be considered low compared to other volumetric sorption devices operating under isobaric high-pressure conditions, where their measurement uncertainty can be as high as 12% [26].

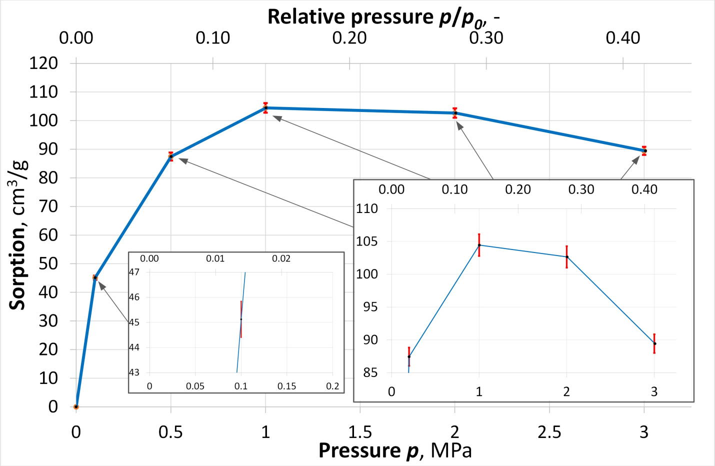

Fig. 9. Sorption isotherm of an activated carbon sample in relation to CO_2 determined from sorption measurements with the high-pressure sorptomat, with the error bars marked.

The sorption isotherm, determined from measurements performed with the high-pressure sorptomat, showed that the maximum sorption capacity of the activated carbon sample to CO_2 was 104.4 cm^3/g, at the pressure of 1.0 MPa. Above this pressure, the sorption capacity began to decrease slightly, which is in line with other studies that confirm that the sorption capacity of coal at a relative pressure above 0.2–0.3 may decrease [27–29]. Due to the decrease of the sorption capacity of the tested sample with the increase of the measurement pressure, further tests at higher CO_2 pressures were abandoned.

The obtained results of sorption studies have shown that it is possible to conduct sorption studies under isobaric conditions with the constructed high-pressure sorptomat, on the basis of which both sorption kinetics and sorption isotherms can be determined.

4. Conclusions

As part of the work, an apparatus for sorption tests under conditions of high gas pressure was developed - the high-pressure sorptomat. Isobaric measuring conditions are ensured by a novel precise pressure regulator working on the basis of a needle valve controlled by a stepper motor. The uniqueness of the developed device, compared to commercial solutions, is due to its high precision with a low degree of complexity of its structure, multi-range measurement enabling measurements at both high and low gas pressures, and the scalability of the test sample enabling measurements on various types of samples. Moreover, the substantial advantage of the constructed device is that it provides isobaric conditions during sorption measurements. Due to isobaric conditions and the step change of the pressure initiating the sorption processes, it is possible to analyse the gas sorption kinetics in the pore space of the sorbent.

Based on the ranges of the components used and the results of the tests performed, it was possible to determine the basic parameters of the apparatus:

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- maximum sorption measurement range: 0–86 400 cm^3/g,
- maximum measurement uncertainty: ±2% of the measured value,
- pressure regulation range: 0–10 MPa,
- precision of pressure stabilization: ±1% of the measurement pressure (after the initial measurement phase),
- temperature control range: 4–60°C,
- temperature stabilization range: ±0.5°C,
- maximum measurement pressure change time: < 10 seconds.

The developed high-pressure sorptomat is another novel laboratory equipment developed at the Strata Mechanics Research Institute of the Polish Academy of Sciences, used to study the rock-gas system.

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