Halloysite as Mineral Adsorbent of Co₂ – Kinetics and Adsorption Capacity

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Summary

Physical adsorption of carbon dioxide on various mineral adsorbents is becoming extremely interesting in the field of energy and environment where CCS technology is an option for CO_2 emission reduction. In the article the halloysite from Dunino deposit was assessed in terms of its potential use as a CO_2 adsorbent. Results of tests indicate that modified halloysite (i.e. calcinated or modified by acid treatment) has a relatively low adsorption capacity which should be easily increased by other surface modification methods. Sorption kinetic is rather fast and over 85-89% of CO_2 adsorption is accounted by a rapid sorption step i.e. 7 to 16 seconds.

Keywords: physical adsorption, carbon dioxide, halloysite, adsorption kinetics

Introduction

Physical adsorption of carbon dioxide on various mineral (eg. zeolites, silica gels) and organic adsorbents (eg. activated carbons) is becoming extremely interesting in the field of energy and environment where CO_2 emission reduction targets are a challenge for countries where fossil fuels are a dominant source of energy. These adsorbents have application in CO_2 capture technologies where Pressure Swing Adsorption (PSA) or Temperature Swing Adsorption (TSA) methods are used. Despite the widespread use of amine-based technologies for CO_2 capture (absorption) these technologies are too energy intensive to be commercially applied. A viable solution is to develop an inexpensive method of CO_2 removal using adsorption technology (eg. PSA, TSA or hybrid methods) and convenient adsorbent. An ideal adsorbent should have the following properties [1]:

- high CO2 sorption capacity,
- selectivity towards CO2 adsorption,
- regeneration efficiency,
- availability,
- low cost.

After analyzing the CO_2 adsorption characteristics of many minerals i.a.: kaolin, montmorillonite, bentonite, zeolite [2]–[5] it was considered to examine the halloysite from Dunino Deposit which is a mineral belonging to the kaolinite group. Halloysite may be used for many purposes in the environment protection engineering e.g. for the manufacturing of coagulants for municipal and industrial wastewater treatment, rehabilitation of industrial degraded areas, as a component of geosynthetic clay liners, catalysts and filler for nanocomposites. The halloysite derivatives feature high sorption capacity for hydrogen sulfide, ammonia and other substances like pesticides, formaldehyde, heavy metals [6]–[8].

Analysis of findings of other researchers [2]–[5] prompted the authors to consider the possibility of improving the characteristics of sorption and desorption properties of halloysite. Therefore it was decided to conduct a series of studies with the aim of answering the question whether modified Dunino halloysite is suitable for use as CO_2 adsorbent. The authors of this paper decided to examine CO_2 adsorption properties of two modified types of halloysite marked for this article as HBS and KRP.

Materials and methods
Materials

Halloysite is a two-layer mineral belonging to the kaolinite subgroup which is represented by the same chemical formula $Al_2Si_2O_5(OH)4•nH_2O$, where n is the number of water molecules that occupy the interlayer spaces of the clay aggregates. The value of n is zero for kaolinite and up to 4 for halloysite. It was shown [4] that in montmorillonite CO_2 adsorption depends on the degree of hydration and similar phenomenon can occur in halloysite. The halloysite mineral contains a layer of water in its interlayer space which results in an increase in layer thickness up to 10.1 Å. The interlayer water molecules of halloysite can easily and irreversibly be removed by a slight increase in the temperature which in turn results in formation of the 7 Å halloysite characterized by the interlayer distance ranging from 7,15 Å up to 7,5Å [9], [10]. However, after a dehydration process, the halloysite platelets stay separated. The structural unit of halloy-

site consists of two sheets: Si-tetrahedra and Al-octahedra. The octahedral external surface is built up from the hydroxyl groups with outstanding hydrogen and has a positive surface charge when the oxygen surface of the tetrahedral sheet is, usually and like with montmorillonite, negatively charged.

The halloysite for tests was acquired from Dunino Mine in Poland. Dunino deposit is located in the Lower Silesia and contains over 10 million tons of a homogeneous raw material mined using open pit method. Halloysite extracted from this deposit is a product of basalt weatherEng. Raw halloysite from Dunino is characterized by a specific easy to modify and large surface area and high porosity. For the purpose of the study it was decided to use modified halloysite i.e.: calcinated at the temperature of 600ºC referred in article as HBS and the second one treated with sulfuric acid and dried, named in article as KRP. The structure of this two types of material was shown on SEM images (Fig. 1 a-d). Both samples have granule structure with irregular plates which structure was not consistent and ranged between 0-4 µm, averaging 0-1 µm. Occasionally halloysite nanotubes (HNT) were found. The KRP halloysite derivate morphology is illustrated in Fig. 1b and 1d and seems to have more porous structure then than HBS samples.

In order to measure sorption capacity and kinetics of adsorption the samples were dried in an oven
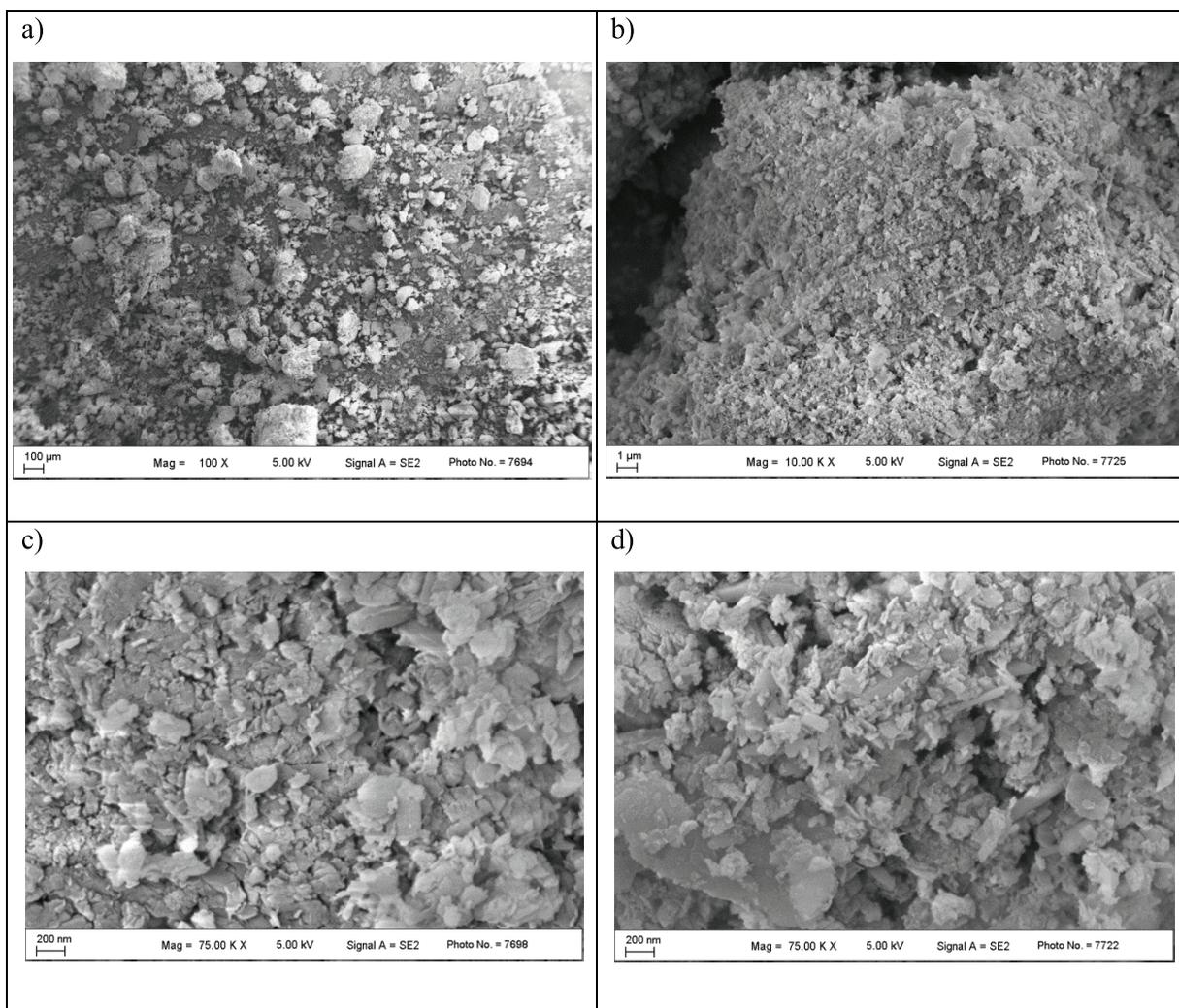

Fig. 1. SEM scans of the structure of modified halloysite from Dunino deposit:

a,c) HBS, b,d) KRP

Rys. 1. Zdjęcia elektronowego mikroskopu skaningowego (SEM) struktury modyfikowanego

haloizytu ze złoża Dunino, próbki:

a,c) HBS, b,d) KRP

for 24h at 373.15K. Then, the samples were quickly transferred to the sample cell in order to avoid contact with air and degassed under vacuum for 24 h at the temperature of 318 K. The amount of HBS and KRP used for the measurements was 122.5 g and 66.1 g respectively.

Methods

Sorption experiments were performed using the manometric technique with custom made sample cells and setup. The process of adsorption removes sorbate gas molecules from the free gas phase and thus results in a decrease of the gas pressure within the experimental system. The most fundamental operational procedure to quantify gas adsorption is the Gibbs approach where the amount of adsorbed gas ($n_{adsorbed}$) is defined as the difference between the total amount of gas (n_{total}) presents in the system and the amount occupying the void volume (V_{void}), i.e. the volume not occupied by the solid sample. This latter quantity is calculated from the molar concentration (c_{gas}) in the gas phase which is obtained from an equation of state of the gas for the corresponding pressure and temperature conditions with the formula:

$$n_{sorbed} = n_{total} - c_{gas} \cdot V_{void} = n_{total} - c_{gas} (V_{(sample\ cell)} - V_{sample}) \quad (1)$$

Prior to the start of the actual experiment void volume of the sample cell (V_{void}) must be measured. For this purpose a non-adsorptive gas (Helium) was used. The density of gas was calculated with McCarthy equation of state [11]. Multiplication of the void volume by the density of the gas ($V_{void} \cdot \rho^{CO2}(T,P)$) gives the "non-sorption" reference mass, i.e. the amount of gas that would be accommodated in the measuring cell if no sorption occurred. Whereas, the excess sorption mass is the difference between the mass of gas that has been actually transferred into the measuring cell up to a given pressure step and the "non-sorption" reference mass:

$$m_{excess}^{CO2} = m_{transferred}^{CO2} - V_{void} \cdot \rho^{CO2} (T,P) \quad (2)$$

Sorption measurement is done in consecutive steps and the mass of gas transferred from the reference cell into the sample cell at each step (N) can be calculated with the use of the following formula:

$$m_{excess}^{CO2} = m_{transferred}^{CO2} - V_{void} \cdot \rho^{CO2} (T,P) \quad (3)$$

Superscripts in the equation i.e. f, CO_2 and e, CO_2 refer to the density of the gas in the filling phase (when the reference cell is not connected with the sample cell) and equilibrium phase (when the sample cell is connected with the sample cell and the pressure is equilibrated), respectively. Densities of CO_2 were calculated with the use of highly accurate Span&Wagner equation of state [12]. Due to the long equilibration time for CO_2 each sorption step took approximately 24 hours.

In order to measure the kinetics of sorption the pressure data are recorded with the use of data acquisition system every 5 seconds right after the valve between the Reference Cell and Sample cell is open.

Setup description

The manometric setup used for the experiments consists of a sample cell, reference cell, valves, tubing, pressure transducers and temperature sensors (Fig. 2). There are two identical setups allowing two parallel measurements to be performed at the same time. The gas is injected into the setup by the MAXI-MATOR DLE 5-30-GG high pressure pump and prior to the start of the experiment the system is evacuated with the use of the vacuum pump. Pressure is monitored with the use of WIKA P-30 pressure transducers of 0.05% F.S. accuracy. Pressure transducers are connected to the data acquisition system recording pressure readings at desired intervals with WIKA Easy-Com 2011 software.

The temperature is monitored with Pt100 sensors of 1/3B class resistance tolerance. Temperature sensors are connected to the multi-channel temperature data-logger APAR AR205 which communicates with the data acquisition system. Sample cells designed and constructed at the Silesian University of Technology are made from 314L stainless steel. The volume of the cells is 183.7 cm³ and 184.5 cm³. Sample cells are joined to the rest of the circuit with a ¼" NPT ISO thread. Reference cells have a volume of 151.3 cm³ and 152.5 cm3³. Fittings and valves used in the setup are high pressure SWAGELOK fittings made of stainless steel with ¼" tubEng. Setup is immersed in demineralized water in custom made thermo bath with electronic temperature stabilization of 0.1ºC manufactured by LABO-PLAY.

Results

The sorption of CO_2 was measured up to the pressure of approximately 1100 kPa. The excess adsorption isotherms of each sample are shown as a function of gas pressure in Fig. 3. The isotherms were type I isotherm according to IUPAC classification (with unfavorable slope i.e. low uptake at low pressures). The Langmuir model provided excellent fit to the experimental data and is shown as dashed line in Fig. 3. The calculated constants for the model with coefficient of determination are shown in Table 1.
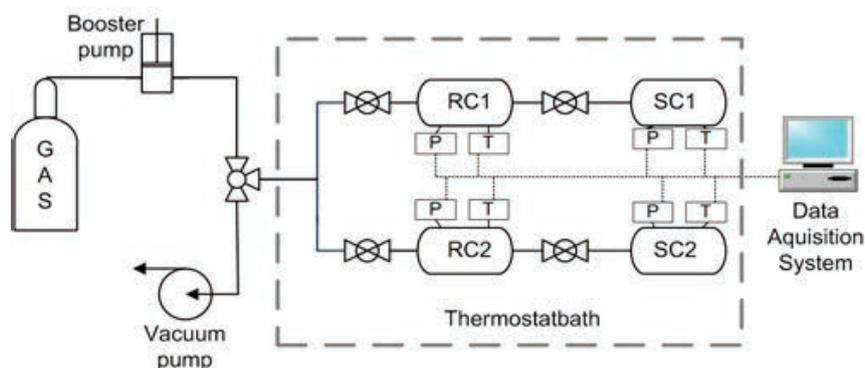
Fig. 2 Scheme of the high-pressure manometric setup

Rys. 2 Schemat budowy wysokociśnieniowego aparatu sorpcyjnego.

Tab. 1 Parameters of Langmuir model for CO_2 adsorption on halloysite.

Tab. 1 Parametry modelu Langmuira dla adsorpcji CO_2 na próbkach haloizytu.

Sample	Q_{max} (mmol/g)	P_L (kPa)	R^2
HBS	0.416	1325.15	0.9997
KRP	0.746	992.73	0.9980

Tab. 2 Kinetic parameters of two first-order rate model.

Tab. 2 Parametry kinetyki procesu dla modelu pierwszego rzędu.

Sample	Q_0' (%)	$t_{1/2}'$ (s)	Q_0'' (%)	$t_{1/2}''$ (s)	R^2
HBS	89.5	7	10.5	1635	0.9933
KRP	85.3	16	14.7	4718	0.9945

Obtained data show that modified by acid treatment halloysite sample (KRP) adsorbs almost double of the HBS sample. The maximum monolayer capacity calculated from Langmuir model is 0.746 mmol/g and 0.416 mmol/g for KRP and HBS respectively. Lower value of Langmuir pressure (PL) shows that the maximum sorption capacity can be reached at lower pressure which is desirable in case of CO_2 capture technologies. Considerable difference in adsorption of the same mineral shows that the halloysite is prone to surface modifications which enhance the sorption capacity. Nevertheless, the adsorption of the samples is significantly lower than other mineral or organic adsorbents where adsorption is of a few orders of magnitude higher.

In order to describe the kinetics processes, a combination of two first-order rate functions with two different rate constants were used similar to the approach in [13]:

$$Q_{residual} = Q_0' \bullet e^{(-k' \bullet t)} + Q'' \bullet e^{(-k'' \bullet t)}$$

Here $Q_{residual}$ is the residual sorption capacity expressed as a function of time, Q_0' and Q_0'' are the normalized sorption capacities with $Q_0' = 1 - Q_0''$, t is the time and k' and k'' are the independent two first-order rate constants.

$Q_{residual}$ was obtained for each step as a pressure ratio dependent on time:

$$Q_{residual} = \frac{P(t) - P\infty}{P_0 - P\infty}$$

Where P_0 and P_∞ denote the initial and the final pressure of the system of a given pressure step, and
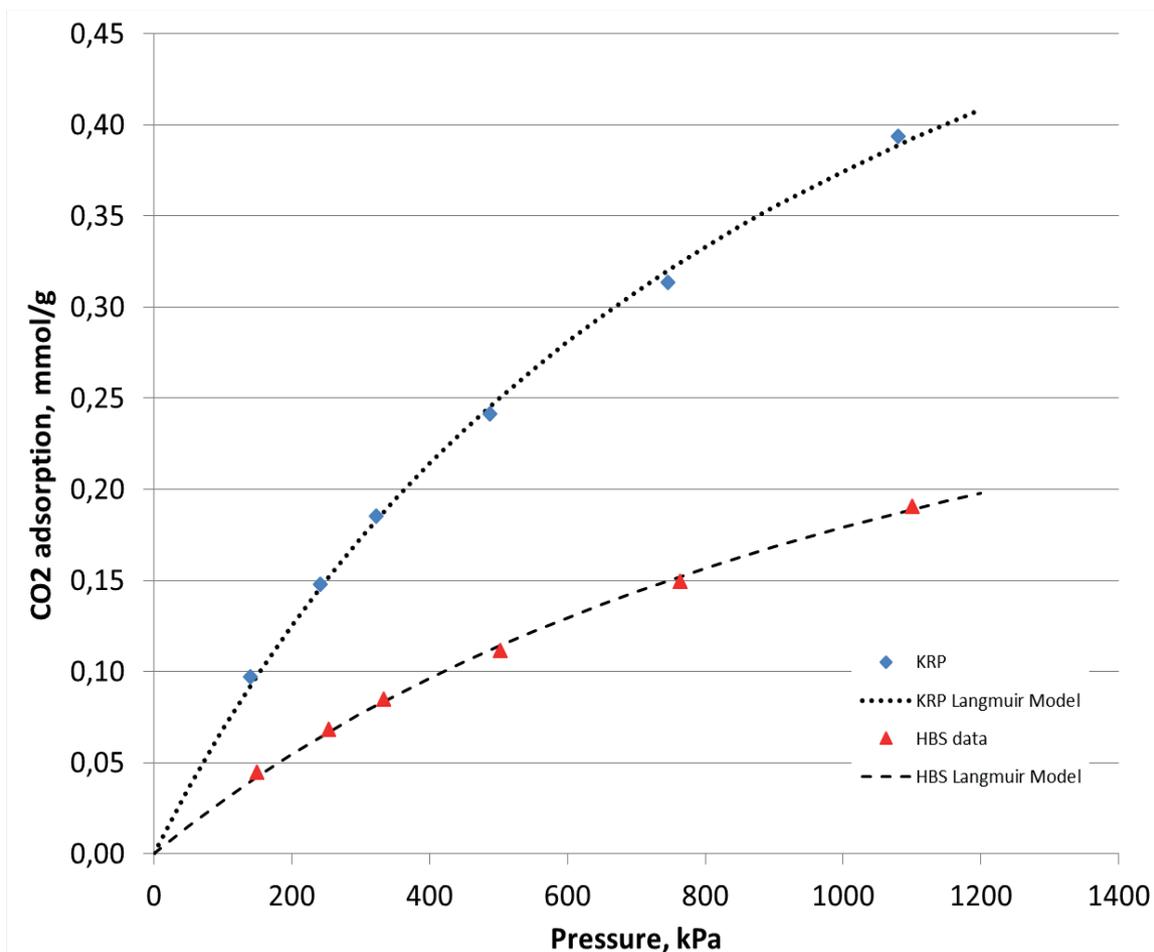
Fig. 3 Carbon dioxide adsorption isotherms on halloysite (at 45ºC) with Langmuir model fitted

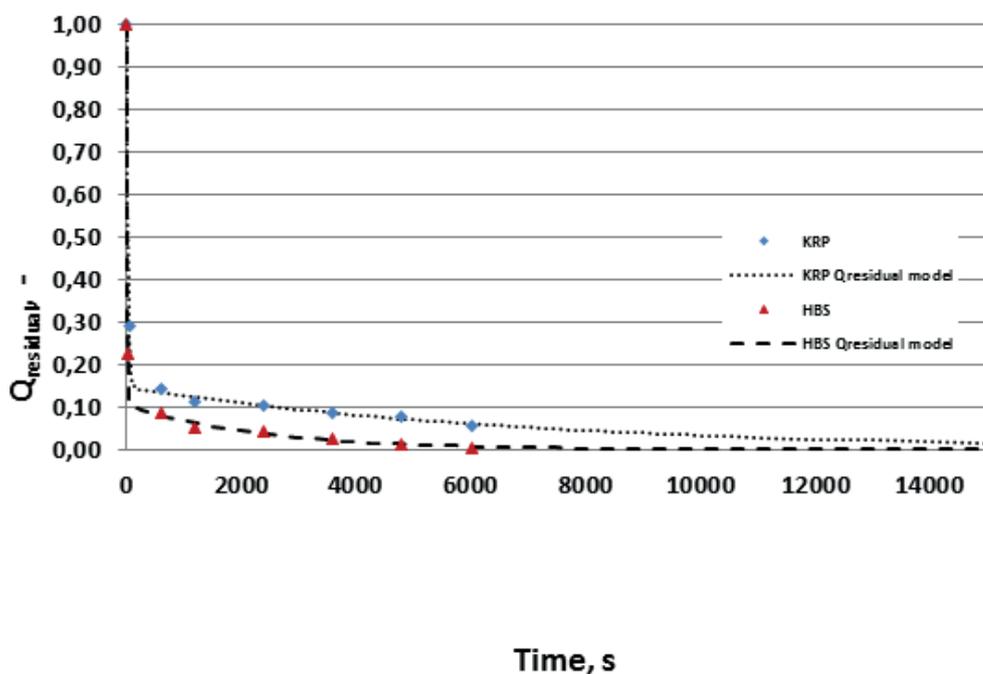Rys. 3 Adsorpcja dwutlenku węgla na haloizycie (w temp. 45 ºC) wraz z dopasowanym modelem Langmuira.

Fig. 4 Adsorption kinetics of CO_2 on halloysite.

Rys. 4 Kinetyka adsorpcji CO_2 na halozycie.

$P(t)$ is the system pressure at time t.

Half–life times are used as indicators of the speed of each one of the adsorption processes in the system, being $t_{1/2'}$ and $t_{1/2''}$ values for the fast and the slow sorption processes respectively. Values of $t_{1/2}$ are calculated using the equation for the first-order rate law where $t_{1/2} = ln(2)/k$. In Table 2, kinetics parameters from the two first-order rate function are shown and in Fig. 4 both models with the experimental data are plotted.

In case of the adsorption kinetics the HBS sample reached equilibrium almost twice faster than the KRP sample. Although for both samples the total equilibrium time was rather long the half times of the fast adsorption process were fast i.e. 7 and 16 seconds for HBS and KRP sample respectively. Over 85-89% of CO_2 adsorption is accounted by a rapid sorption step. This is a considerably faster time in comparison to organic adsorbents such as e.g. activated carbon where the kinetics is in the order of minutes [14]. A slightly faster adsorption of HBS sample can be attributed to the fact that the KRP sample is treated with sulfuric acid forming acidic groups on the surface. This can cause repulsion to the CO_2 gas particles and slow the overall adsorption process.

Conclusions

The study was focused on the assessment of sorption properties of halloysite as a possible adsorbent of CO_2. It was revealed that the adsorption of CO_2 depends mainly on the halloysite treatment method. In case of temperature treated halloysite (HBS) the adsorption was almost half of the adsorption of the chemically i.e. with sulfuric acid treated sample (KRP). In both cases the adsorption capacities were rather low in comparison to other commercially available adsorbents such as activated carbons or silica gels. Nevertheless, given the fast adsorption rate of the CO_2 adsorption on halloysite and surface of this mineral which is prone to modification this adsorbent might be an interesting solution for CO_2 capture methods. However, future work is required to understand the possible mechanisms linking chemical and physical CO2 adsorption properties of halloysite.

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Streszczenie

Procesy adsorpcji fizycznej CO_2 na różnego rodzaju adsorbentach mineralnych są istotne z punktu widzenia technologii wychwytywania i separacji tego gazu z dużych źródeł stacjonarnych (CCS). W artykule przedstawiono wyniki adsorpcji CO_2 na haloizycie ze złoża Dunino, który może mieć potencjalne zastosowanie w technologiach adsorpcyjnych. Rezultaty badań wskazują, że adsorpcja CO_2 na modyfikowanym haloizycie tj. kalcynowanym oraz kwasowanym jest relatywnie niska w porównaniu z innymi adsorbentami mineralnymi, jednakże odpowiednia metoda jego modyfikacji może zwiększyć znacznie jego chłonność sorpcyjną. Przeanalizowano również kinetykę sorpcji, gdzie oszacowano iż 85-89% CO_2 adsorbuje się w czasie 7-16 sekund.

Słowa kluczowe: adsorpcja fizyczna, dwutlenek węgla, haloizyt, kinetyka adsorpcji