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DECARBONISATION OF INDUSTRIAL GAS EMISSIONS BY ADSORPTION METHODS

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Abstract. The article is dedicated to the problem of decarbonising industrial gas emissions using adsorption methods. The article examines promising approaches to reducing carbon dioxide (CO_2) emissions using adsorption materials with high selectivity and efficiency in capture processes. The purpose of the study is to determine the adsorption capacity of various types of adsorbents, including synthetic and natural materials, in particular, fly ash synthesised by the hydrothermal method, zeolite obtained by the sintering method, natural zeolite, and fly ash from thermal power plants. The research showed that the most effective adsorbent for absorbing CO_2 is zeolite synthesised by hydrothermal, demonstrating a high adsorption capacity among the studied materials. Natural zeolite and thermal power plant fly ash have a much lower adsorption capacity, but they can be used as cost-effective alternatives for processes with moderate performance requirements. The study also highlights the importance of selecting adsorbents depending on operating conditions, such as temperature and pressure, which affect adsorption. According to the research results, synthetic zeolites have a significant advantage in adsorption efficiency due to their high specific surface area and porous structure, which allow effective absorption of CO_2 even at relatively low gas concentrations. The generalised conclusions of the article indicate that the use of adsorption methods for decarbonising industrial emissions can significantly reduce the level of greenhouse gases in the atmosphere. This research has the potential to significantly impact the field of environmental science and engineering, providing valuable insights for future studies and practical applications.

Keywords: decarbonisation, adsorption, greenhouse gases, zeolite, fly ash.

1. Introduction

Production energy (electricity, heat) in the world annually increases, which leads to the burning of large volumes of fossil fuel. Coal part fuel, in the burning process, turns into dioxide of carbon (CO_2) by reaction (Sabadash et al., 2023):

$$C + O_2 \xrightarrow{t} CO_2$$

This carbon dioxide, together with flue gases, is released into the atmosphere, which increases its concentration in it (Cinke et al., 2003). Dioxide carbon absorbs infrared radiation on Earth because its spectrum absorption hits the lengths of waves in this region. This absorption of infrared radiation by CO_2 leads to the so-called' greenhouse effect', a phenomenon that contributes to global warming and is part of the global pollution atmosphere. The “greenhouse effect” is a natural process that warms the Earth’s surface. When the sun’s energy reaches the Earth, some is absorbed, and the rest is radiated back into space. Greenhouse gases like CO_2 trap some of this energy, preventing it from escaping into space and warming the Earth.

The world’s ocean and vegetation world part compensate for the growth concentration of CO_2 by adsorbing it through absorption and photosynthesis. However, the amount of absorption in oceans is limited, and the forest covering the Earth continues to shrink due to logging, urbanisation, and changes in land use, which worsen the situation. As a result, the concentration of CO_2 in the atmosphere grows, strengthening the negative impact on the climate system.

In connection with this, the international community has already spent decades trying to regulate emissions of greenhouse gases. In 1997, the Kyoto Protocol was approved, and in 2015, the Paris Protocol

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climate agreement set quotas for CO_2 emissions and provided a gradual transition to low-carbon and renewable sources of energy (Peng et al., 2021). These initiatives stimulate the search for new technologies and approaches, in particular, the implementation of non-carbonated species energy, as well as technologies, capture, utilisation and storage of CO_2 (CCUS), which aimed at lowering carbon emissions into the atmosphere. Significant growth emissions of carbon dioxide (CO_2) and other greenhouse gases from industrial sources, particularly metallurgical and chemical enterprises, promote accelerating global climatic changes and deterioration of ecological situations (Abd et al., 2020). Existing methods of capture and declining concentration of CO_2 in industrial gas flows do not always provide high efficiency at relatively low energy expenses, making it necessary to search for new approaches to reduce carbon industry (Cinke et al., 2003). One of the promising directions is applicable adsorption methods, mainly by using zeolite molecular sieves, which can selectively grab molecules of CO_2 due to their unique physical and chemical properties (Park al., 2020). Zeolites demonstrate high selectivity and adsorption capacity for carbon dioxide even when present with other impurities in the gas plant mixture, making them promising materials for decarbonising gas emissions on an industrial scale. However, despite the potential zeolites, the effectiveness of such adsorbents may depend on the gas flow, temperature, humidity, and other conditions (Wijaya, Lee, 2020). Thus, research and improvement are relevant adsorption methods using zeolite molecular sieves to decarbonise industrial gases. The impact of different efficiency factors CO_2 adsorption and development will create optimal process conditions and an effective cleaning system capable of significantly decreasing carbon emissions and reducing the negative impact on the environment.

Zeolite molecular sieves are crystalline, microporous materials with a three-dimensional honeycomb-like structure. They have size incoming windows close to the diameters of polar molecules such as SO_2, CO_2, NH_3, water vapour and others. This unique structure gives them high selectivity and adsorption capacity concerning these adsorptives (Arista, 2023). Particular interest represents using synthetic zeolites in processes of decarbonisation gases (Liet et al., 2023). It includes creating controlled atmospheres, preparing biogas for its further use as fuel, the concentration of CO_2 in soda production, purification of air for separation at low temperatures and cleaning of ethylene before it is processed into polyethene.

Dioxide carbon has a diameter of about 0.31 nm, allowing its molecules to penetrate the internal structure of most molecular sieves. Although these molecules do not have a dipole moment, their high quadrupole moment ($3.2 \cdot 10^{-26}$ X·m^2) provides particular interaction with cations alkaline metals that are a part of crystalline grids zeolites (Wang et al., 2021). This makes zeolites effective in processes of selective adsorption that is important for environmentally friendly extraction and concentration gases.

The work aims to research the efficiency of different adsorption materials, such as synthetic and natural zeolites and ash takeaway, to catch carbon dioxide gas from industrial emissions and reduce greenhouse gases in the atmosphere.

Analysis of previous research and publications. In our previous studies, the adsorption of carbon dioxide by carbon nanotubes was investigated (Sabadash et al., 2023). Studies show that the efficiency of CO_2 adsorption on carbon nanotubes depends on such parameters as the type and size of the sorbent, temperature and pressure in the system. Manometric and volumetric methods make it possible to accurately measure the amount of gas absorbed on the surface of the sorbent and to study the features of the interaction of CO_2 with various structures of carbon nanotubes (Gautam, Mondal, 2023). In particular, it was established that multilayered carbon nanotubes modified with metal oxides, particularly iron oxide, are effective sorbents. Their high surface area and ability to specifically interact with gas molecules make them promising for capturing CO_2. Research in the field of carbon dioxide adsorption has shown a significant potential for the use of natural and synthetic sorbents, in particular carbon nanotubes, metal-organic framework structures (MOFs), porous silica materials and activated carbon (Wang et al., 2023). Carbon nanotubes, due to their high specific surface and the possibility of modification, particularly with the use of metals and oxides, demonstrate increased efficiency in the absorption of CO_2, making them promising for cleaning industrial emissions. In particular, using multilayered carbon nanotubes doped with metal oxides proves their ability to remove carbon dioxide from gas mixtures effectively (Hayawin et al., 2023). An important research direction is the development of metal-organic framework structures, which show high stability and variability in porosity adjustment, which allows high selectivity of CO_2 adsorption in complex industrial flows.

Further experiments show that particle size, pressure and process temperature are the key parameters that affect adsorption efficiency, while manometric and volumetric analysis methods allow detailed estimation of the amount of carbon dioxide absorbed by different types of sorbents (Yuan et al., 2023). Several works also pay attention to hybrid membrane materials, particularly organosilicate, which, thanks to special coatings, can improve the selectivity of CO_2 capture. The development of fluorinated porous materials for capturing and separating carbon dioxide opens up opportunities for creating sorbents with a high capacity for selective adsorption of gases. In addition, modern research is actively studying biomass as a source for the production of carbon materials, which is an economically beneficial and, at the same time, ecologically safe way to reduce the concentration of greenhouse gases in the atmosphere.

2. Experimental part

Methodology research adsorption carbon dioxide

The study studied the process of carbon dioxide (CO_2) adsorption from air streams with a CO_2 content of 1 to 10 vol. % at a temperature of 20 °C. The study of CO_2 adsorption by zeolites was carried out in a flow dynamic installation, the main element of which was an adsorption column filled with sorbents, in particular, natural zeolite from the Sokyrnytsky deposit and various types of synthetic zeolites produced by the hydrothermal method and the sintering method. The micropore volume of the studied adsorbents ranged from 0.3 to 0.36 cm³/g (Sabadash et al., 2023). Before each experiment, the zeolites were subjected to thermal regeneration for 1 hour at a temperature of 350 °C in an environment of dried air to remove residual moisture and prepare them for adsorption. The gravimetric method carried out the study of the adsorption capacity of zeolites concerning CO_2.

The technique of gravimetric analysis of CO_2 adsorption by zeolites included the following stages:

Preparation of zeolite:

The selected sorbent (zeolite) was thoroughly cleaned and subjected to thermal regeneration to remove residual moisture and other adsorbed substances. Regeneration was carried out in a drying cabinet at about 350 °C for 1 hour in dried air. After regeneration, the zeolite was cooled to room temperature in a dry atmosphere to prevent the re-adsorption of moisture from the air.

Weighing the sample: The prepared zeolite sample was weighed on an analytical balance with an accuracy of 0.0001g before and after the experiment to determine its initial mass.

CO_2 adsorption:

The experiments were conducted on a specially designed installation. The central element was a quartz tube with a perforated grid at the bottom, and it was equipped with a heating and thermostatic system to maintain a stable temperature. This design allows the creation of a fluidised layer of the adsorbent, which improves the contact of the gas mixture with the zeolite. To obtain a gas mixture with the required concentration of CO_2, cylinders with air and CO_2 were used, which were fed into the mixer. The gas flow was adjusted and recorded using rotameters, and the CO_2 concentration was monitored both at the inlet and outlet of the installation using a Mahiak Finor 710 analyser connected to a computer. This analysis made it possible to obtain both numerical results of the analysis and a graphical representation in the form of an output curve. The device worked in the range of CO_2 concentrations from 1 to 10 % or with an accuracy of ±1 %, which ensured high measurement accuracy. The parameter for evaluating the adsorption activity of zeolite was the value “a” – the mass of adsorbed CO_2 per 100 g of zeolite. The composition of the supplied gas mixture corresponded to the flue gases of power plants, with a CO_2 concentration of 1 % to 10 % by volume.

A 10 g weight of zeolite was loaded into the adsorber, after which the system was transferred to the specified temperature and hydrodynamic mode. After stabilisation, the gas mixture supply was turned on, and the start of the experiment was recorded with a stopwatch. The experiment’s duration was chosen to achieve complete saturation of the zeolite with carbon dioxide. After reaching saturation, the integration of the original curve made it possible to determine the static adsorption activity of the zeolite for the corresponding experimental conditions.

Measurement of the mass of absorbed CO_2 during adsorption: During the passage of gas through the adsorbent, CO_2 is adsorbed, which leads to an increase in the mass of the zeolite. The increase in mass was recorded at certain time intervals, which allows us to estimate the kinetic parameters of the adsorption process.

Calculating the adsorption capacity: The amount of adsorbed CO_2 expressed in milligrams of CO_2 per gram of sorbent was calculated based on the mass change results. The initial mass of zeolite, temperature, concentration of CO_2 in the gas mixture, and experimental conditions were considered for accurate calculations. The equilibrium capacity of the adsorbent was calculated using data on the maximum saturation of zeolite CO_2.

Analysis and processing of results: The obtained data were processed in MS Excel. Based on the obtained results, adsorption isotherms were constructed.

3. Results and Discussion

This section presented the results of experimental research on the adsorption ability of different types of carbon dioxide sorbents, in particular zeolites, synthesised by hydrothermal, sintering, and natural zeolite and ash removed from the thermal power plant. Analysis of received data allows us to evaluate the efficiency of each of the materials for use in decarbonising industrial gas emissions. Figure 1 shows the experimental data of static CO_2 adsorption on the studied adsorbents at a temperature of 20 °C. Isotherms were also shown to compare carbon dioxide adsorption on the synthetic zeolite samples obtained using hydrothermal and sintering methods. It allows us to evaluate differences in the ability of different adsorbents to capture CO_2 under the same conditions and determine the influence of the synthesis method on their adsorption properties. The analysis received isotherm allows us to compare the natural capacity and synthetic zeolites at different CO_2 concentrations. In addition, research shows how structural features, microporosity and manufacturing method synthetic zeolites can affect the efficiency of adsorption of dioxide carbon, which is essential for optimisation processes to capture and decline CO_2 emissions.

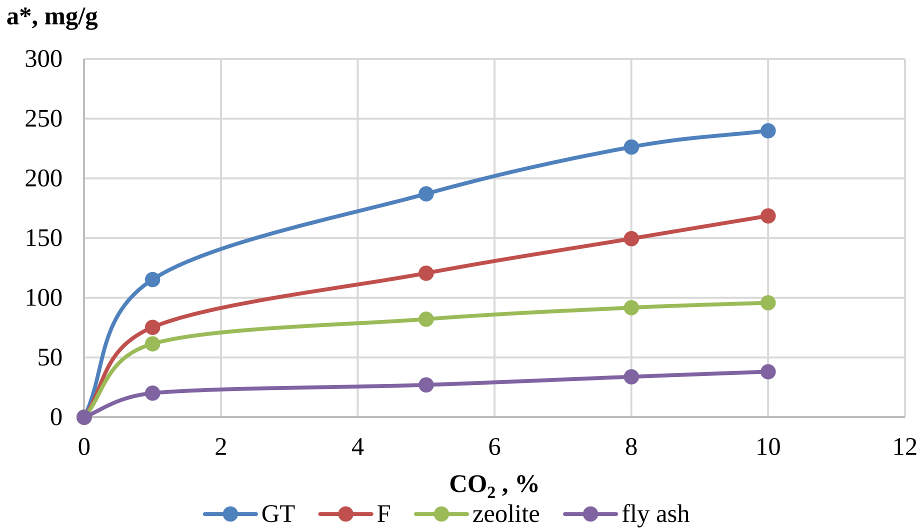

Fig. 1. Isotherms adsorption of CO_2 in column-type apparatus depending on the concentration of CO_2 in the gas stream: GT - zeolite synthesised by the hydrothermal method; F - zeolite synthesised by the sintering method; zeolite - natural zeolite; - fly ash - ash removal from CHP

It is evident that all obtained isotherms belong to the first type according to Brunauer's classification: the adsorption capacity increases with increasing CO_2 concentration in the gas stream. The highest carbon dioxide adsorption capacity in the range of concentrations was demonstrated by zeolite synthesised by the hydrothermal method. The sintering method's adsorbent made from fly ash shows slightly lower but still high activity. For example, at the initial concentration of CO_2 in the air mixture at the level of 10 % of volume particles, the static adsorption capacity of these adsorbents is 243 mg/g for hydrothermal synthesis and 176 mg/g for ash adsorbent, respectively.

Comparative analysis shows synthetic zeolites have a significantly higher adsorption capacity than natural materials. In particular, synthetic zeolites exceed the capacity of natural zeolite and fly ash by 2.5–4 times. Thus, the capacity of natural zeolite under similar conditions is only 40 % of the capacity of zeolite synthesised by the hydrothermal method, and for fly ash – about 20 %. This significant performance gap indicates the potential of synthetic zeolites for CO_2 capture in industrial settings, especially when high adsorbent capacity was required at variable gas mixture concentrations. The experimental data were linearised to obtain the Langmuir adsorption equations, and the results were presented in Fig. 2.

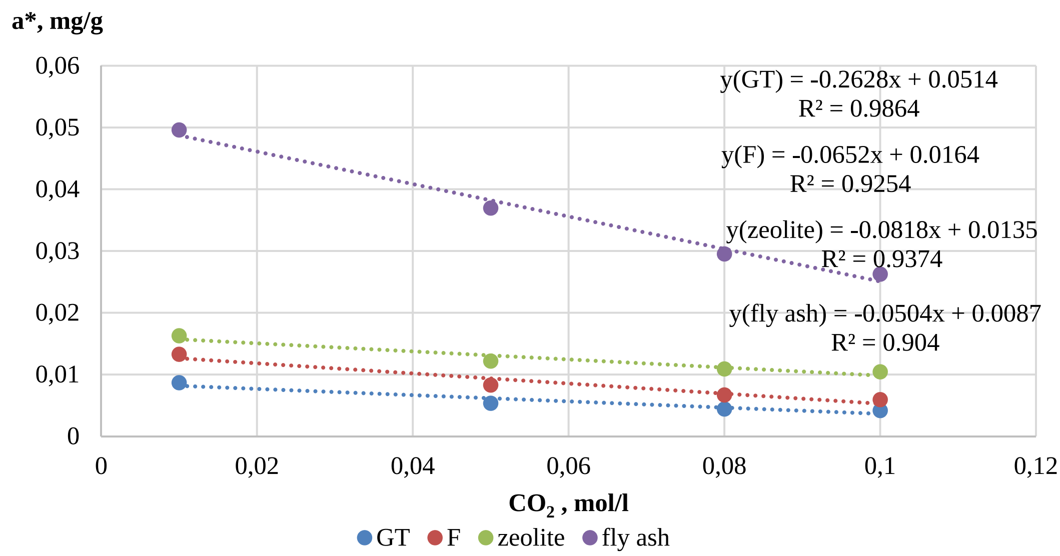

Fig. 2. Linearised isotherms adsorption of CO_2 in column-type apparatus depending on the concentration of CO_2

The Langmuir equation in nonlinear form can be written as:

$$a = a_{\max} \cdot \frac{KC}{1 + KC}, \qquad (1)$$

where a is the equilibrium amount of adsorbed substance, $a_{\max}$ is the maximum adsorption capacity, K is the adsorption equilibrium constant, C is the adsorbate concentration in the gas phase.

The parameters $a_{\max}$ and K were determined for each of the given isotherms, so we could write down the equation for each adsorbent.

1. For zeolite synthesised by the hydrothermal method:

$$a^*_{GT} = 0{,}1955 \cdot \frac{0.2628 \cdot C}{1 - 0.2628 \cdot C}. \qquad (2)$$

2. For zeolite synthesised by the sintering method:

$$a^*_{F} = 0{,}165 \cdot \frac{0.0652 \cdot C}{1 - 0.0652 \cdot C}. \qquad (3)$$

3. For natural zeolite:

$$a^*_{Zeolite} = 0{,}165 \cdot \frac{0.0818 \cdot C}{1 - 0.0818 \cdot C}. \qquad (4)$$

4. For the ash removed from the CHP:

$$a^*_{Fly\ ash} = 0{,}1726 \cdot \frac{0.0504 \cdot C}{1 - 0.0504 \cdot C}. \qquad (5)$$

The use of adsorption methods to reduce the concentration of CO_2 has several advantages, including high efficiency, the possibility of application at different conditions of temperature and pressure, and the ease of scaling technologies for different types of industrial emissions. Studies have shown that adsorption efficiency depends on the physicochemical properties of adsorbents, such as specific surface area, pore volume, and their distribution. Zeolites show a high adsorption capacity due to their porous structure, but their efficiency depends significantly on the process temperature (Sabadash et al., 2023). It is also worth noting the challenges associated with the regeneration of adsorbents, which may require additional energy costs, reducing the overall economic benefit of the decarbonisation process. Developing combined technologies involving adsorption and other methods, such as membrane systems or chemical capture, is a promising direction for further research. Such combinations can improve the performance of decarbonisation processes due to increased selectivity and reduced energy consumption. Research shows that adsorption methods are most effective under high-pressure and low-temperature conditions. In general, adsorption methods of decarbonising industrial emissions have a significant potential for reducing greenhouse gas emissions but require further research to improve their economic feasibility, the stability of adsorbents to various operating conditions, and the optimisation of regeneration processes.

4. Conclusions

The conducted studies confirmed the effectiveness of the adsorption method for decarbonising industrial gas emissions, particularly for capturing carbon dioxide from air streams containing from 1 to

10 % vol. CO_2. Among the studied adsorbents, synthetic zeolites obtained by the hydrothermal method showed the highest adsorption capacity for carbon dioxide due to their high specific surface area and structural features that contribute to the effective adsorption of CO_2. Zeolites synthesised by the method of sintering from fly ash had a slightly lower adsorption capacity but showed acceptable results, which makes them potential materials for use in decarbonisation in industrial conditions. Natural zeolite and fly ash from thermal power plants had lower adsorption characteristics than synthetic sorbents. However, their availability and low cost make these materials promising for large-scale projects for cleaning gas emissions. It was established that process parameters, in particular temperature, pressure, and CO_2 concentration, are essential for achieving the maximum adsorption capacity, which requires additional research to optimise adsorption conditions in industrial conditions. The obtained results can be used to develop practical recommendations for implementing adsorption systems in industrial processes to reduce greenhouse gas emissions into the atmosphere effectively.

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