# Heat of Adsorption in the Fly Ash Zeolite – $CO_2$ System at Dynamic Conditions

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**Abstract**

Recently, the global warming is one of the major world problems considering that coal-fired power generation accounts for 40 % of the total $CO_2$ emissions. The post-combustion capture of $CO_2$ based on physical adsorption has the greatest potential to meet the industrial needs. The nature of the adsorption processes is complex and is described by many empirical constants that are determined experimentally for individual contact systems.

In this study, the heat of adsorption in the fly ash zeolite (FAZ) – $CO_2$ system was investigated experimentally. The technique used includes online measurements of temperature rise during the exothermic adsorption process carried out by passing $CO_2$ through a laboratory-assembled column filled with FAZ. Based on the experimental results, the calculated specific heat of adsorption amounts to $H_{ads}$=-36.83 kJ/kg.

**Keywords:** post-combustion carbon capture, fly ash zeolite, adsorption, heat of adsorption

## 1. Introduction

The global environmental problems related to the occurrence of natural disasters caused by the emission of carbon dioxide ($CO_2$) in the atmosphere from fossil fueled power plants requires development and implementation of effective and economically feasible technological solutions to reduce these emissions (Yang et al.). Investing in low-carbon technologies to achieve a threefold reduction in greenhouse gas emissions compared to 1990 levels is a part of the long-term European strategy for the 2020-2050 timeframe. Post-combustion capture based on physical adsorption of $CO_2$ has the greatest potential to meet the industrial needs and requirements (Modal et al.). The adsorption processes are characterized by a complex nature, described by many empirical constants, which are determined experimentally for individual contact systems. Typical for the adsorption of gases onto solid surface is the strong exothermic effect due to the conversion of surface energy into heat. The strength of the interaction between the gas molecules and solid surface can be estimated by the change of the enthalpy or so called heat of adsorption (Builes et al.). The value of the heat of adsorption in each individual system can be determined by direct calorimetric analyses or by equilibrium adsorption studies at different temperatures. The aim of this study is to investigate experimentally the heat of adsorption in the fly ash zeolite (FAZ) – carbon dioxide system. This research is a part of a broad scientific program of our team to develop novel sorbents of $CO_2$ produced by utilization of solid wastes from combustion of coal in thermal power plants (TPP).

## 2. Experimental

Fly ash (FA) obtained from the burning of lignite coal in Bulgarian TPP "AES Galabovo" was used as a raw material for synthesis of zeolites. A mixture of 5g FA and 10g NaOH was fused at 550 $^oC$ for 1 hour, magnetically stirred in 100 ml distilled water and hydrothermally activated at 90 $^oC$ for 4 hours. The obtained FAZ was characterized by XRD and SEM analyses. The surface properties of the sample were determined by $N_2$ equilibrium adsorption/desorption analyses at 77 K in a Micromeritics TriStar 3020 analyzer. The specific heat capacity ($C_{p,\ solids}$) of FAZ was measured in the range of 40-120 $^oC$ in $N_2$ inert atmosphere after pretreatment at 370 $^oC$ by Perkin Elmer Thermal Analyzer DDSC 7. The heat of adsorption ($H_{ads}$) in the FAZ-$CO_2$ system was determined via a laboratory approach for direct measurement of the temperature increase ($\Delta T$) in the exothermic process - Figure 1. Studied FAZ was preliminary treated at 260 ° C in a stream of He for 2 hours to release the adsorbed moisture. Glass laboratory adsorption column was filled with 1.4 g FAZ and Ni-CrNi thermocouple with C = 41 μV/°C was inserted. $CO_2$ gas with a constant flow rate of 30 ml/min was fed into the column with all gas lines thermostated at T=25 °C. The experiment was performed for 15 minutes, recording in real time in 1 second the signal from the warm thermoelectrode to the voltmeter MS 82-12. The cold end of the thermocouple was kept at room temperature as the accurate temperature was measured by RTD Pt100.

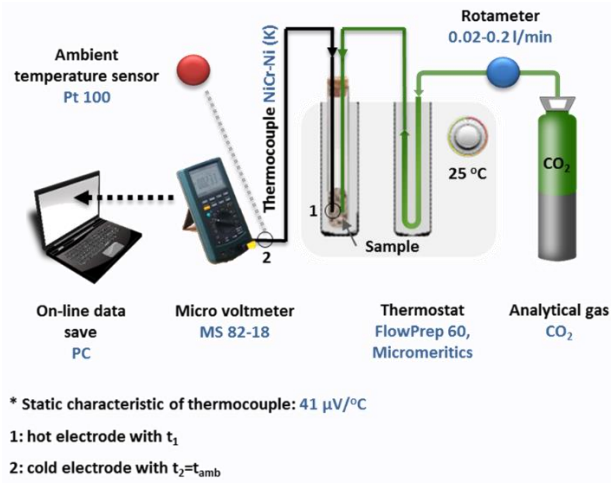


**Figure 1.** Experimental set-up for heat of adsorption.

## 3. Results and discussions

SEM and XRD analyses reveal that FAZ is a phase of faujasite type. The sample has a specific surface area of 388 $m^2/g$ and total pore volume of 0.271 $cm^3/g$. The resulting differential voltage data are converted to a differential temperature based on the static characteristic of the NiCr-Ni thermocouple, and the results are shown in Figure 2.

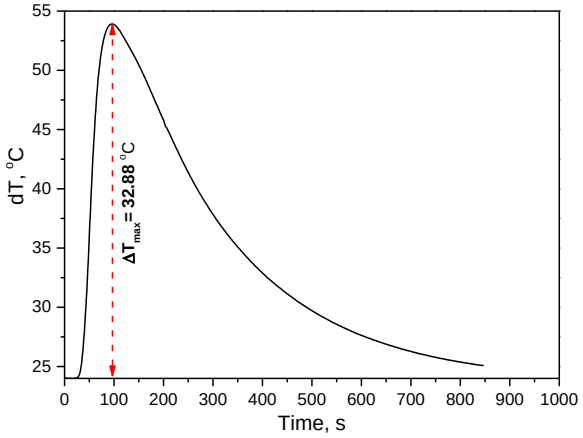


**Figure 2.** Time dependence of the differential temperature.

The heat of adsorption in the closed gas-solid system is determined by the temperature increase by the following dependence:

$$H_{ads} = C_{p,solid} m_{solid} \Delta T + C_{p,gas} m_{gas} \Delta T ,$$

Where: $C_{p,solid}$ and $C_{p,gas}$ are the specific heat capacities of FAZ and $CO_2$, J/gK; $m_{solid}$ and $m_{gas}$ are their weights, g; $\Delta T$ is the temperature increase, K.
From the DTA-DSC analyses of the FAZ, $C_{p,solid}$ was measured of 1.12 ± 0.06 J/gK at 40 °C, Figure 3.

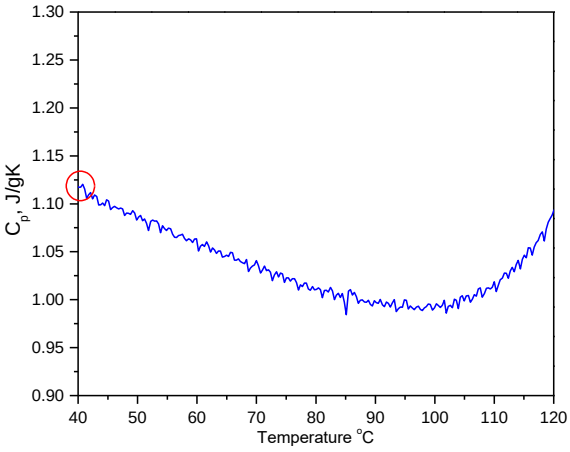


**Figure 3.** Temperature dependence of $C_{p,solid}$.

The calculated enthalpy released during the experiment was $H_{ads}$ = -51.56 J or the specific heat of adsorption in the FAZ-$CO_2$ system is $H_{ads*}$ = -36.83 ± 1.84 kJ/kg.

## 4. Conclusion

The performed experiments to assess the heat of adsorption in the fly ash zeolite-carbon dioxide system revealed an intensive exothermic effect of the process. The experimental results obtained from the investigations on the temperature dependence of the specific heat capacity of FAZ in the range 40-120 °C will be used for further computation of post-combustion carbon capture processes from laboratory to to the pilot plant scales, and for evaluation of economical and technological aspects. It is expected that the development of novel sorbents, especially when solid wastes are utilized, will improve the parameters of post-combustion $CO_2$ capturing process in terms of economical feasibility and environmental protection.

**Acknowledgements**
This work was financially supported by the National Science Fund, Ministry of Education and Science of Bulgaria under contract DM 17/6.

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