

# Studies on the CO<sub>2</sub> Adsorption Mechanism of Na-X and Na-Ca-X Coal Fly Ash Zeolites

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**Abstract** Coal fly ash zeolites (CFAZ) of Na-X and Na-Ca-X types were synthesized using as raw materials fly ashes generated by the combustion of lignite from various deposits with low and medium limestone content. It has been found that CFAZs with higher calcium content superior those containing less calcium with respect to their ability to capture CO<sub>2</sub>. This provoked our interest to elucidate the role of Ca in the CO<sub>2</sub> adsorption process. CFAZs of Na-X and Na-Ca-X types were investigated in dynamic CO<sub>2</sub> adsorption cycles, as the thermal regeneration of the adsorbents is carried out at low temperatures at which only the physically adsorbed molecules can be released. Desorption was investigated by thermogravimetric TG-DTG analyses over a wide temperature range.

**Keywords:** Carbon capture, Circular economy, Coal fly ash utilization, Coal fly ash zeolites

## 1. Introduction

Post-combustion carbon capture is one of the leading technological solutions for reducing carbon emissions from fossil fuel Thermal Power Plants (TPPs) (Liang et al., 2015). The improvement of this technology for its wider implementation requires development of environmentally friendly, cost-effective and regenerable adsorbents at low energy consumption (Shi et al., 2015). Zeolites are among of the most studied adsorbents for CO<sub>2</sub> retaining due to their developed specific surface, defined pore size, environmental compatibility, and availability as natural minerals, strong chemical and thermal resistance and affordable regeneration process (Kumar et al., 2020). Recently, zeolites derived from coal fly ash have been intensively studied regarding their ability to capture CO<sub>2</sub>. The increased interest in these materials is provoked by the technologically accessible opportunity to exploit the potential of coal ash to obtain products of practical importance. The study of the technological opportunity for coal ash processing to effective adsorbents for post-combustion carbon capture technologies is of significant concern of the strategy for development of circular economy and raw materials saving, which will contribute to huge environmental

benefits. Coal fly ash zeolites (CFAZ) reveal high adsorption capacity toward CO<sub>2</sub> comparable to those of the pure synthetic and natural zeolites stipulated by their compositional and textural peculiarities despite their lower specific surface area (Zgureva and Boycheva, 2020). CFAZs also possess high selectivity in the presence of water vapor and nitrogen, which are typical flue gas components (Boycheva et al., 2021). In our previous studies it was found that the increased lime content in the raw ash results in a higher adsorption capacity of the obtained CFAZ (Boycheva et al., 2021). However, this observation will not be practically useful if the calcium transferred into the zeolite framework is involved in a chemisorption process with the formation of calcium carbonate, which will increase the regeneration temperature.

The present study aims to elucidate the function of calcium incorporated in CFAZ in the capture of CO<sub>2</sub> and the mechanism of the adsorption process.

## 2. Experimental

CFAZ were synthesized by ultrasonic-assisted double stage alkaline conversion of coal fly ash with low (4.45 wt %) and medium (9.36 wt %) CaO content. The synthesis procedures and the characterization of the raw and derived products are described in (Boycheva et al., 2021). CO<sub>2</sub> adsorption was performed on a dynamic reactor with on line GC analysis. The samples were preliminary dried *in situ* at 423 K for 2 h. In each experiment, 0.40 g sample of 20–80 mesh and 3 % CO<sub>2</sub>/N<sub>2</sub> at a flow rate of 30 mL/min were used and the effluent gas was analyzed on-line by GC TCD analysis (25 m PLOT Q capillary column). The amounts of CO<sub>2</sub> cumulated in the materials at room temperature were determined and used to calculate the adsorption capacity. After desorption of CO<sub>2</sub> at 80 °C the adsorption was repeated.

TG-DTG analyses were performed for determination of adsorbed and desorbed CO<sub>2</sub> in STA449F5 Jupiter type instrument, NETZSCH Gerätebau GmbH. In a typical measurement 150 mg of sample was placed in a

microbalance crucible and heated in a flow of N<sub>2</sub> (100 cm<sup>3</sup>/min) up to 500 °C with 5 °C/min and a final hold-up of 1 h. The system was cooled down and CO<sub>2</sub> adsorption was performed at 35 °C for 1 h with CO<sub>2</sub> (30 ml/min)/N<sub>2</sub> (30 ml/min) flow. The system was purged at 35 °C in N<sub>2</sub> (100 cm<sup>3</sup>/min) for 30 min and CO<sub>2</sub> desorption was performed up to 500 °C with temperature rate of 5 °C/min.

### 3. Results and Discussions

Both tested samples with different calcium content are of zeolite type X and are characterized by specific surface area values exceeding 400 m<sup>2</sup>/g. Breakthrough curves of three adsorption cycles are presented in Fig. 1. After three regeneration cycles no changes in the adsorption dynamics were detected in CFAZ Na-X (Fig. 1,a). The adsorption capacity remains constant after all regeneration cycles (Table 1). This is indicative for a physisorption mechanism, as the complete adsorbent recovery is achieved at low temperatures (80 °C). At CFAZ Na-Ca-X a decrease in the breakthrough time was

established after the first regeneration cycle (Fig. 1b). No reduction of the adsorption zone was observed in the following adsorption cycles. The adsorption capacity of CFAZ Na-Ca-X decreases after the first regeneration, and further it maintains a constant value exceeding that of CFAZ Na-X (Tabl. 1). This trend of the breakthrough curve shows a mixed mechanism of adsorption in the presence of calcium. Some part of the calcium is involved in chemisorption, most likely forming calcium carbonate, which does not decompose at the applied regeneration temperature. However, the larger share of calcium electrostatically retains CO<sub>2</sub> molecules by a physisorption mechanism, and it is easily recovered. This contributes to the increased adsorption capacity at the zeolites with higher content of Ca. The stable adsorption behavior of CFAZ Na-Ca-X in subsequent adsorption cycles indicates that only Ca in a determined state is reactive. It could be assumed that lime particles transferred to the zeolite are involved in the chemisorption process due to their high reactivity.

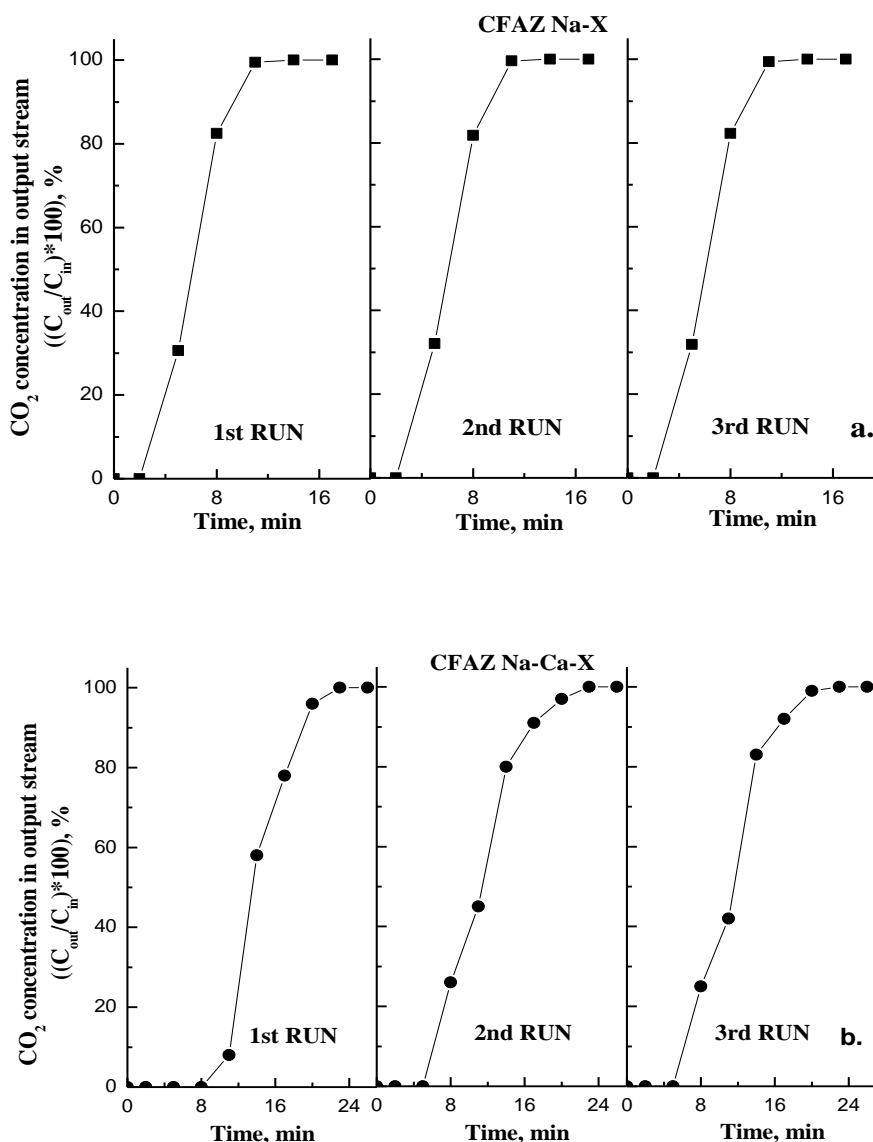
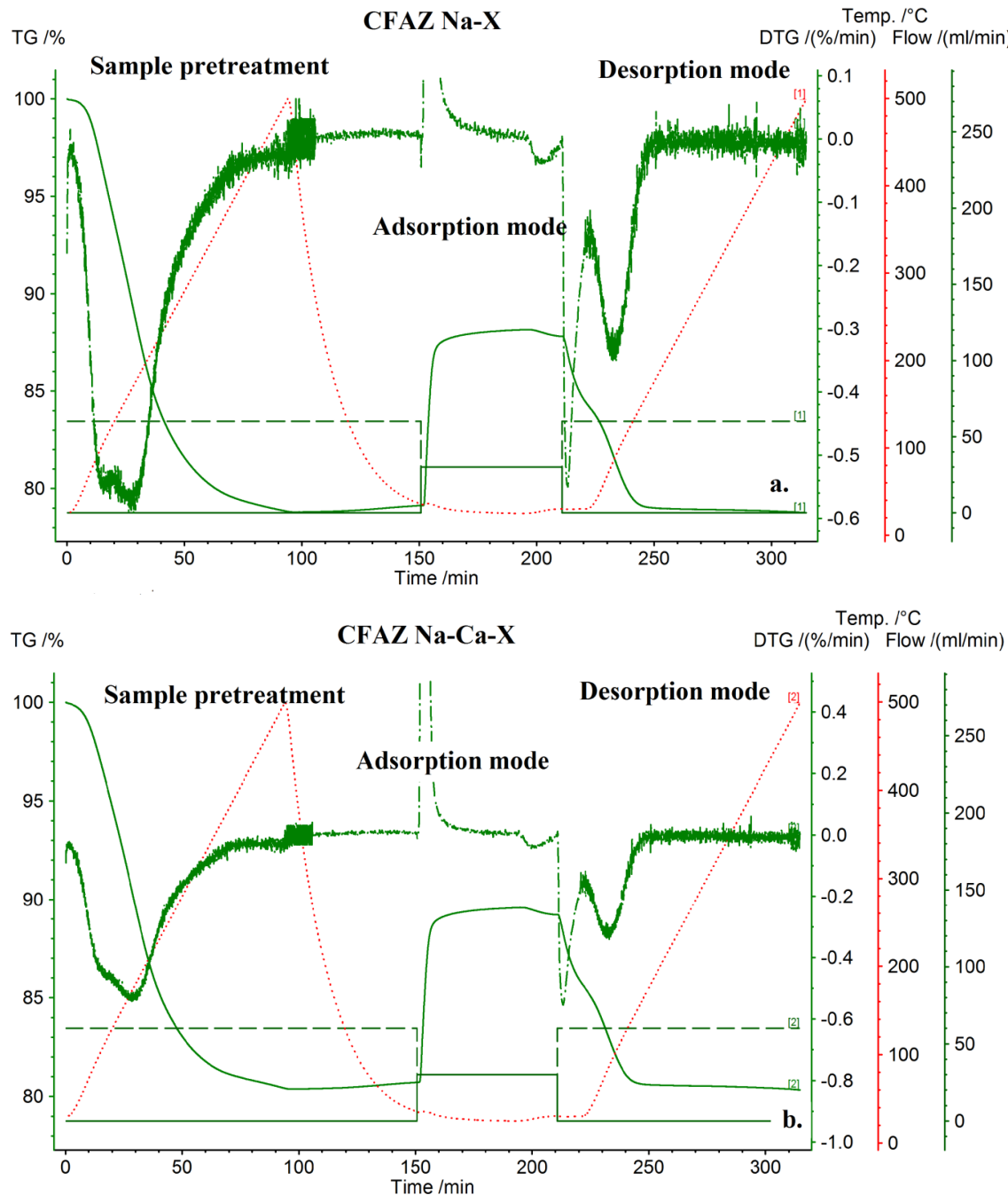


Figure 1. Breakthrough curves of CO<sub>2</sub> cyclic adsorption onto CFAZ.

It could be assumed that a significant part of calcium turns into an ionic state during the synthesis procedure and calcium ions occupy together with sodium ions the position of charge compensators in the structural framework of the zeolite. It is expected that these calcium ions act as electrostatic centers of CO<sub>2</sub> capture and due to their higher degree of oxidation as compared to the sodium ions retain more molecules of the adsorbate. Desorption process was studied by thermal gravimetric analysis. The experimental TG-DTG plots are presented in Fig. 2.

**Table 1. Capacities of CO<sub>2</sub> capture in adsorption cycles.**

Adsorption	Adsorption capacity, mmol/g	
	CFAZ Na-X	CFAZ Na-Ca-X
Run 1	2.9	4.0
Run 2	2.9	3.5
Run 3	2.9	3.5



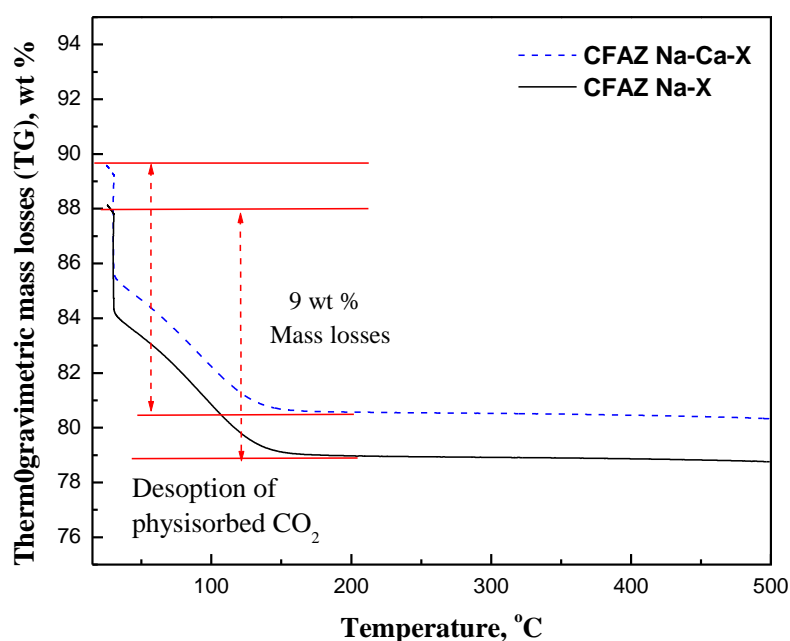
**Fig.2. TG-DTG experimental plots**

CFAZ samples were pretreated by heating to remove the accumulated moisture and loaded with CO<sub>2</sub> by exposing in CO<sub>2</sub>/N<sub>2</sub> gas mixture. In the DTG experimental plots of desorption recorded up to 500 °C, one broad endothermic peak is observed in both studied

samples assigned to the release of physically adsorbed CO<sub>2</sub>. Under the applied heating conditions, maximum recovery of CFAZ is achieved in about 40 min. Thermogravimetric mass loss vs. temperature is plotted in Fig.3. The dependences reveal an instant mass drop

after output of CO<sub>2</sub> exposure, and rapid release of the adsorbate with the temperature increase to 140 °C. In CFAZ Na-Ca-X and CFAZ Na-X comparative mass losses were observed, despite the stronger CO<sub>2</sub> capture in CFAZ Na-Ca-X confirming the observations from the dynamic adsorption that part of the calcium interact chemically with CO<sub>2</sub>. The results of the chemical composition studies show surface content of Ca in CFAZ Na-X about 1.7 at. %, and in CFAZ Na-Ca-X about 2.5 at.% (Boycheva et al., 2021). Studies in adsorption cycles and thermogravimetry of desorption do not indicate chemisorption in CFAZ Na-X. X-ray diffraction of low-calcium coal fly ash does not reveal reflexes of portlantite, while in the medium-calcium ash such are observed (Boycheva et al., 2021). Therefore, it

could be supposed that the calcium contained in the aluminosilicate components is transferred to the zeolite network as a compensating ion, while the part of portlantite is incorporated as particles, which carbonize during the CO<sub>2</sub> adsorption process. However, this remains to be further investigated. The part of calcium in CFAZ Na-Ca-X, which is involved in the chemisorption will not participate in subsequent adsorption/regeneration cycles. However, the remaining part, which retains CO<sub>2</sub> by Van der Waals forces is regenerable and benefits the capturing ability. Moreover, the previous studies have shown that the increased Ca content in CFAZ leads to an enhanced mesopore yield (Boycheva et al. 2021).



**Fig.3. Thermogravimetric analyses of CO<sub>2</sub> loaded CFAZ**

## Conclusions

Studies on the utilization of coal fly ash from by its conversion into zeolites applicable as adsorbents of CO<sub>2</sub> reveal a significant effect of calcium content on the carbon capture ability in dynamic conditions. Calcium contributes to higher CO<sub>2</sub> retaining capacity through chemical and physical adsorption. A significant part of Ca is involved in the regenerative adsorption.

## Acknowledgements

This work was financially supported by the National Science Funds, Ministry of Education and Science of R. Bulgaria under contract DN 17/18 (2017).

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