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Carbon Dioxide Adsorption Studies on Fly Ash Zeolites

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A B S T R A C T

In this study, the potential of fly ash zeolites (FAZ) Linde (LTA) and faujasite (FAU) to adsorb carbon dioxide (CO₂) was investigated in view of the results of implementation in postcombustion carbon-capture technologies. Adsorption isotherms of selected samples were measured at 273.15 K by a Micromeritics Tristar II 3020 surface analyzer. The highest adsorption capacity was obtained for FAZ with a FAU structure synthesized by a two-stage fusion hydrothermal process from fly ash (FA) that was composed of 65 wt% amorphous components. The adsorption capacity for this sample reached a value of 136.40 mg CO₂/g FAZ at atmospheric pressure, a result comparable to that for commercial FAU. The selectivity coefficients of CO₂ adsorption versus N₂ for FAZ were evaluated from the experimental adsorption isotherms of corresponding gases at 100 kPa. The obtained results are in the range of 23–36, indicating strong affinity of FAZ for CO₂ molecules. The experimental isotherms of CO₂ adsorption fit well with Langmuir and Dubinin-Ashtakov mathematical models. The obtained parameters will be used as input data for calculation and design of a pilot plant carbon-capture installation.

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A R T I C L E I N F O

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1. Introduction

The consumption of electricity and thermal energy is permanently increasing worldwide, with an expected 56% growth between 2010 and 2040 according to the U.S. Energy Information Administration (EIA, 2013). Coal combustion thermal power plants (TPPs) are the major producer of energy. The main disadvantage of coal incineration systems is the numerous by-products, which can cause local and transboundary pollution. These pollutants are solids, for example, coal fly ash (FA), and gases, namely sulfur oxides (SO_x), nitrogen oxides (NO_x), and carbon oxides (CO_x). Carbon dioxide (CO₂) belongs to the group of greenhouse gases, and it is considered that CO₂ causes 55% of global warming (Yang et al., 2008).

Development of effective and economical technologies for carbon-emission control is required to mitigate the global ecological problems and to overcome the natural disasters that carbon emission can cause. The long-term European Union (EU) strategy for the

period 2020–2050 is focused on investments in low-carbon technologies for triple reduction of carbon emissions toward their levels in 1990.

The sequestration of carbon dioxide emitted from TPPs consists of CO₂ separation from other flue gas components and its concentration in a pure flow. Thereafter, CO₂ flow is liquefied by subsequent compression (Boycheva, 2011). The low-carbon technologies have been developed in three directions: (1) fuel incineration in oxygen instead of air (oxy-fuel), thus eliminating nitrogen oxides from the flue gases; (2) integrated with gasification combined gas cycle (IGCC) technologies, realized by gasification of solid fuels for extraction of syngas from flammable components (Figueroa et al., 2008) that is used as fuel in gas turbines; and (3) selective absorption of CO₂ by solutions of amine derivatives. The last technological method belongs to the group of postcombustion capture (PCC) systems, which are the most economically efficient and applicable to existing thermal and industrial plants. The chemisorption of CO₂ by amines is the most studied technology, but it possesses serious disadvantages related to the strong toxicity of the amines and the

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Table 1
Studied fly ash zeolites—raw material properties and synthesis conditions

Sample	Raw material properties		Synthesis conditions				
	SiO ₂ /Al ₂ O ₃ (weight ratio)	Amorphous content (wt%)	Synthesis procedure	Activation temperature, T (°C)	Time of crystallization	NaOH/fly ash (weight ratio)	NaOH (M)
A-1	2.25	43	Self crystallization	22	240 days	0.6	1.5
A-2					300 days		
A-3					360 days		
FH-5	2.00	65	Two-stage hydrothermal with prior fusion at 550°C for 1 h	90	2 h	1.6	2.0
FH-6						2.0	2.5
FH-8					2 h	2.0	2.5
FH-9					4 h		
FH-10					21 h		

high energy consumption for the desorption process (Ben-Mansour et al., 2016). The main challenges of PCC technologies are the development of low-cost porous solids with well-developed surfaces for implementation of physical adsorption (Mondal et al., 2012). As the physical adsorption occurs by the Van der Waals attraction of gas molecules on the solid surface, the energy required for the desorption processes is significantly lower, which is of great benefit for the PCC technologies. Solid sorbents such as carbon, zeolites, mesoporous silicates, alumina, and metal oxides have been intensively studied for gas separation (Songolzadeh et al., 2012). The high adsorption capacity of commercial zeolite 13X is measured at about 325 mg CO₂/g at high pressure (3.4 MPa) and room temperature (25°C) (Cavenati et al., 2004). An adsorption potential of 200 mg CO₂/g has been obtained at conditions similar to those in the real-scale coal-supplied TPP, where after the desulfurization system, the flue gas pressure is slightly lower than 1 atm and the temperature is around 65°C (Kitto and Stultz, 2005).

Coal-combusting TPPs also generate solid wastes, causing environmental pollution after their disposal in open landfills. The coal ash is characterized by low pH value, high salinity, lack of useful soil nutrients, and numerous accumulative toxic components (heavy metals and radionuclides) that are of serious ecological risk (Kim et al., 2003). The main priorities of the EU environmental strategy are the environmentally compatible management of wastes by development of waste-recycling technologies. Because of its predominantly aluminosilicate composition, FA is a suitable raw material for synthesis of zeolites (Lin and His, 1995; Moreno et al., 2001). In practice, synthetic zeolites have numerous applications depending on their specific structure and properties as cation exchangers, adsorbents, catalysts, drug delivery systems, drying agents, and so on. However, because of trace elements, synthetic zeolites obtained

from by-products such as coal FA have some limitation in their application, for example, in desalination of water, in the pharmaceutical and food industries, and in other clean technologies.

Our investigation program is directed to the realization of a closed-cycle environmental protection in TPPs by conversion of coal FA into synthetic zeolites, and their application in flue gas cleaning systems. The main challenge in separation of CO₂ from the flue gas stream is the presence of high concentrations of water vapor and nitrogen in the gas mixture. Synthetic zeolites possess high selectivity of CO₂ to N₂, but their efficiency is reduced in the presence of water because of their strong affinity to its molecules (Li et al., 2011; Ben-Mansour et al., 2016). Researchers have proposed a method for CO₂ separation and a recovery system that combined H₂O and CO₂ adsorption in a dual-bed adsorption column (Takamura et al., 2001). Other approaches for removing H₂O molecules from flue gas could be water vapor condensation from the gas mixture before the CO₂ adsorption process.

In this study, the CO₂ adsorption potential of the synthetic fly ash zeolites (FAZ) Linde (LTA) and faujasite (FAU) will be examined by experimental adsorption isotherms. The selectivity coefficients of CO₂ adsorption for FAZ will be calculated with respect to N₂. The experimental isotherms will be mathematically analyzed for reliable fitting to the existing adsorption models.

2. Materials and Methods

Zeolites were synthesized from lignite coal FA by two different laboratory techniques, self-crystallization and double-stage fusion-hydrothermal activation, as described by Zgureva and Boycheva (2015a). The first procedure consists of long-term incubation (240–360 days) of mixtures of FA and sodium hydroxide solutions

Table 2
Surface properties of fly ash zeolites

Sample	Structure	S _{BET} (m ² /g)	V _{total} (m ³ /g)	V _{micro} (m ³ /g)	d _{micro} (Å)	W _{pore} (Å)
A-1	FAU	226.82	0.174	0.050	10.05	58.42
A-2	FAU	262.40	0.190	0.069	13.42	56.15
A-3	FAU	279.60	0.239	0.113	13.53	58.02
FH-5	LTA	65.24	0.135	N/A	N/A	62.87
FH-6	FAU	176.17	0.124	0.039	13.33	51.50
FH-8	FAU	310.61	0.241	0.083	14.49	45.36
FH-9	FAU	379.20	0.271	0.098	13.62	43.82
FH-10	FAU	176.17	0.261	0.108	14.35	44.89
FA1	Fly ash	10.40	0.012	N/A	N/A	56.28
FA2	Fly ash	9.87	0.010	N/A	N/A	55.87

Note: S_{BET} = specific surface area; V_{total} = total pore volume; V_{micro} = micropore volume; d_{micro} = pore diameter; W_{pore} = average pore width; FAU = faujasite; LTA = Linde.

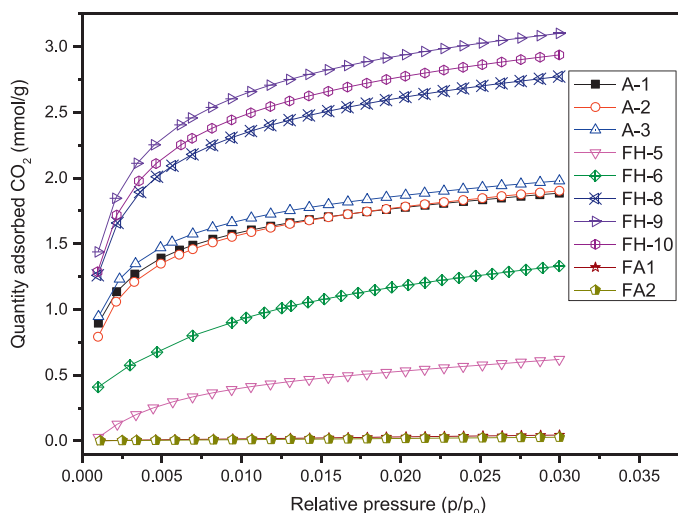


Fig. 1. Experimental adsorption isotherms of CO₂ at 273.15 K for fly ash zeolite. at room conditions; in the second procedure, the solubility of aluminosilicates from FA is accelerated by fusion in NaOH, and thereafter, the crystallization of the reactant solution is enhanced via hydrothermal activation in an autoclave at 90°C. FAZ samples, selected with respect to their crystallinity, and raw FA samples were subjected to studies of CO₂ adsorption via experimental isotherms. The measurements were performed at 273.15 K using a volumetric adsorption analyzer (Tristar II 3020; Micromeritics). Samples were preliminarily degassed at 260°C for 2 hours under helium flow in a FlowPrep 60 (Micromeritics). The adsorption of CO₂ was measured for 25 experimental points in the relative pressure range $P/P_0 = 0.001-0.03$, where P_0 is the CO₂ saturated pressure (3485.6769 kPa at the temperature of analyses). In order to evaluate the selectivity of investigated materials for adsorption of CO₂ versus N₂, similar experiments were performed for nitrogen adsorption.

3. Results and Discussions

3.1. Background studies

Detailed studies on FA characterization, FAZ synthesis, and their structural and morphological investigations have been described previously (Boycheva et al., 2015; Zgureva and Boycheva, 2015b). The FAZ samples from this study are summarized in Table 1. Two types of FA, differing in Si/Al ratios and in the amount of amorphous components, were used as raw materials for zeolite synthesis by two techniques: self-crystallization and two-stage fusion-hydrothermal synthesis. Samples FH-5 and FH-6, obtained from FA with Si/Al ratio of 2.25 by a two-stage fusion-hydrothermal process at increasing NaOH molarities, are characterized by LTA and mixed FAU+LTA zeolite structures, respectively. Samples A-1, A-2, and A-3 were prepared by self-crystallization in an alkaline solution of

Table 3
Dubinin-Ashtakov model parameters of CO₂ adsorption onto fly ash zeolites

	Sample							
	A-1	A-2	A-3	FH-5	FH-6	FH-8	FH-9	FH-10
N	1.36	1.53	1.33	1.23	2.08	1.67	2.71	1.90
E_0 (kJ/mol)	35.34	33.24	36.39	16.44	21.59	35.72	35.36	35.56

Note: N = Ashtakov exponent; E_0 = characteristic energy.

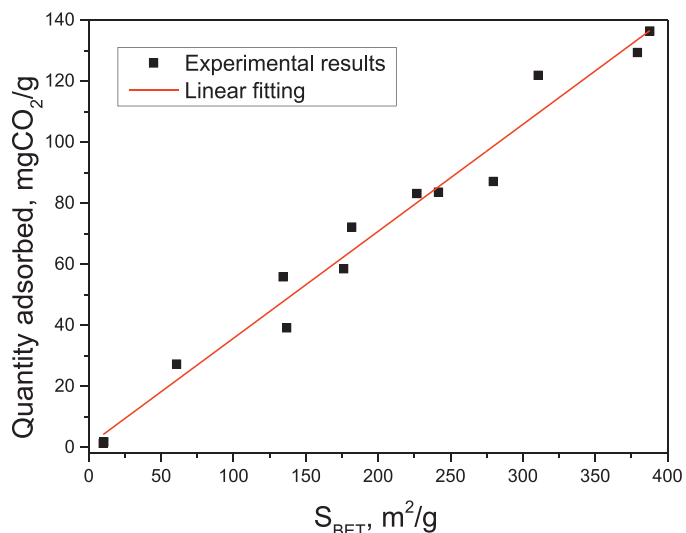


Fig. 2. Correlation between surface area, S_{BET} (m²/g), and the total adsorbed amount of CO₂ (mg CO₂/g): experimental points and linear fit.

the same FA, and they are composed of the FAU phase. Zeolite FAU possesses a well-developed porous texture and free spaces between the separate crystals, favorable for physical adsorption processes (Rouquerol et al., 1999). The FA with the lower Si/Al ratio was subjected to zeolitization by a double-stage fusion-hydrothermal activation. Despite the lower Si/Al value, this results in a FAU structure with a higher surface area and porosity (samples FH-8, FH-9, FH-10) because of the greater amount of amorphous constituents in the raw material. The influence of the amorphous yield on the FA zeolite conversion was discussed in detail in our previous study (Zgureva and Boycheva, 2015b).

The surface properties of FAZ have also been studied (Boycheva and Zgureva, 2016) as main predicting parameters of physical adsorption. The specific surface area (S_{BET}), total pore volume (V_{total}), micropore volume (V_{micro}), pore diameters (d_{micro}), and the average pore width (W_{pore}) were determined from the experimental isotherms of nitrogen adsorption and desorption at cryogenic temperatures applying standardized BET (Brunauer-Emmet-Teller) and BJH (Barrett-Joyner-Hallenda) models (Unger et al., 2000). The obtained results are summarized in Table 2.

3.2. CO₂ adsorption isotherms

The CO₂ adsorption isotherms of the investigated FAZ are plotted in Figure 1 as a function of adsorbed mmol CO₂/g FAZ and the relative pressure P/P_0 . The adsorption of both raw FAs was negligible in the entire studied interval of pressures, a behavior that coincides with the low porosity of the raw material (Table 2). After FA zeolitization, the adsorption ability changed sharply (Figure 1). For sample FH-5, which is an LTA zeolite, a typical isotherm for porous materials is observed, but the adsorption potential for CO₂ is rather low.

Table 4
Langmuir model parameters of CO₂ adsorption onto fly ash zeolites

	Sample							
	A-1	A-2	A-3	FH-5	FH-6	FH-8	FH-9	FH-10
V ₀ (mmol/g)	1.9270	1.9399	2.0065	0.8054	1.6045	2.7839	3.3286	2.9622
b (kPa ⁻¹)	0.1436	0.1326	0.1598	0.0279	0.0389	0.1669	0.1113	0.1609

Note: V₀ = micropore capacity; b = adjustable parameter.

Low CO₂ adsorption activity of the LTA phase, synthesized from both waste materials and pure components, has been reported in other studies (Majchrzak-Kuceba and Nowak, 2005). The isotherm of sample FH-6 reveals improved adsorption of CO₂ owing to the FAU structure. The highest capacity of 1.33 mmol CO₂/g FAZ, obtained at absolute pressure of 104.47 kPa, corresponds very well to the result from previously performed thermogravimetric analysis (Kalvachev et al., 2015). For the experimental isotherms of samples A-1, A-2, and A-3, higher adsorption rates in the low-pressure region are observed, related to the filling of micropores. The CO₂ adsorption in these samples increases with a longer self-crystallization period. Although sample A-3 has the highest adsorption potential in comparison to the others, sample A-1, which was obtained in the shortest time, can also be of interest for industrial purposes from an economical point of view. For samples FH-8, FH-9, and FH-10, kinetic studies on hydrothermal activation have been performed, revealing that after 4 hours, the crystal growth of the FAU phase decreases due to the formation of the more stable sodalite (SOD) crystal structure. The results from the CO₂ adsorption experimental

studies followed the tendency of FAU formation; the highest adsorption capacity of 3.10 mmol CO₂/g FAZ at P = 104.47 kPa was obtained for sample FH-9, while it decreased for FH-10.

3.3. Influence of surface properties on CO₂ adsorption

The correlation between CO₂ adsorption capacity and surface properties of investigated samples was studied by plotting the functions of the adsorbed quantity of mg CO₂/g FAZ at the highest absolute pressure (approx. 104 kPa). Figure 2 represents a linear fit of the experimental results for S_{BET}, and a linear correlation with R² = 0.9729 of the adsorbed CO₂ versus the specific surface area value is evident. For the influence of the other surface characteristics, no trend was observed.

3.4. Model fitting of experimental isotherms

The characteristic energy of CO₂ adsorption for the investigated samples was evaluated by applying the model of Dubinin-Ashtakov to the experimental data:

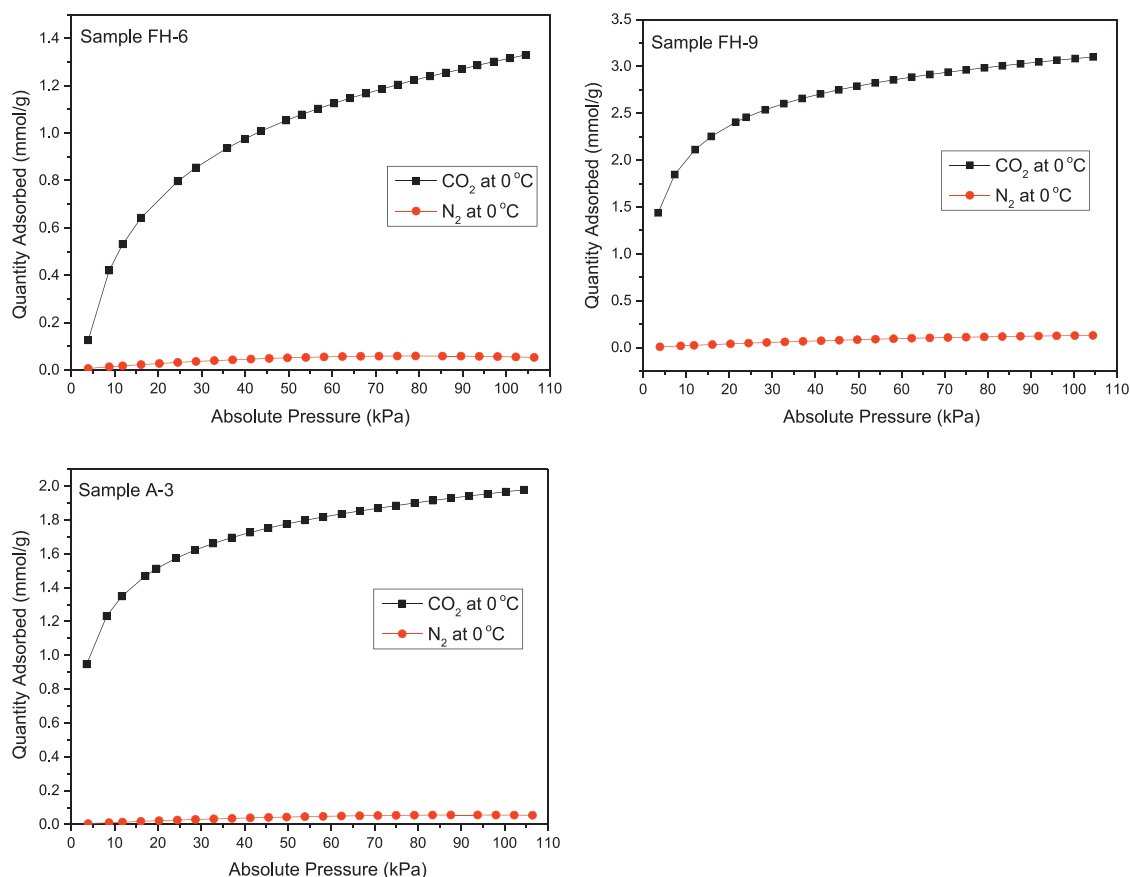


Fig. 3. Experimental CO₂ and N₂ isotherms for fly ash zeolites used for selectivity calculations.

Table 5
Molecular properties of CO₂ and N₂

Molecule	Molecular weight (g)	Kinetic diameter (Å)	Polarizability ($\times 10^{-25}$ cm ³)	Quadrupole moment ($\times 10^{-26}$ esu-cm ²)
N ₂	28	3.64	15.8	1.52
CO ₂	44	3.30	26.5	4.30

$$\log(V) = \log(V_0) - \left[\frac{RT}{\beta E_0} \right]^N \cdot \left[\log \frac{P_0}{P} \right]^N \quad (1)$$

where V is the volume adsorbed at equilibrium pressure (cm³/g); V_0 is the micropore capacity (cm³/g); P_0 is the saturation pressure (3485 kPa at 273.15 K); P is the equilibrium pressure (kPa); R is the gas constant (0.0083144 kJ/mol); E_0 is the characteristic energy (kJ/mol); N is the Ashtakov exponent; and β is the affinity coefficient of CO₂ (0.461).

This model allows optimization of the exponent factor, which is of importance in the case of heterogeneous structures, as in the case of FA zeolites. The optimal value of N is found by recalculation of the linear regression of the function $\log(V)$ vs. $\log(P_0/P)^N$ at the smallest standard error of the y -intercept. The slope of the linear function is applied for the calculation of E_0 using the following equation:

$$E_0 = \frac{2.303 \cdot R \cdot T}{\beta(2.303 \cdot S)^{1/N}} \quad (2)$$

The obtained results are listed in Table 3.

The calculated E_0 values are in agreement with the literature data (Unger et al., 2000) and are used for further computations. The experimental adsorption isotherms of the investigated samples are in agreement with the Langmuir model, described by the following equation:

$$\frac{V}{V_0} = \frac{bP}{bP + 1} \quad (3)$$

where V_0 (mmol/g) and b (kPa⁻¹) are adjustable parameters. These parameters were fitted to the experimental data by mathematical iteration to $R^2 = 0.9998$. The estimated parameters of Langmuir model are listed in Table 4.

3.5. CO₂/N₂ selectivity of FAZ

To evaluate the CO₂/N₂ selectivity of FAZ, N₂ adsorption isotherms were measured at 0°C for samples A-3, FH-6, and FH-9 (Figure 3). The CO₂/N₂ selectivity was estimated as a ratio of the adsorbed CO₂ and N₂ quantities at a pressure of 100 kPa. The obtained selectivity coefficient values for these samples are 35.83, 23.39, and 24.16, respectively, and they reveal strong affinity of the FAZ for CO₂ molecules.

As a rule, the selectivity depends on the difference in either adsorption kinetics or adsorption equilibrium (Ruthven, 1984). In this case, the high CO₂/N₂ selectivity can be explained by the kinetic and polar parameters of the molecules, some of which are listed in Table 5 (Morrison and Hay, 1979). The higher polarizability and quadrupole moments of CO₂ molecules intensify the gas-solid attraction on the charged surface area of zeolites. The CO₂/N₂

selectivity is higher with the increase of the micropore share in the total pore volume of the FA zeolite network.

The experimental data reveal higher CO₂/N₂ selectivity values for FAZ in comparison to the data for commercial FAU zeolites (Takamura et al., 2001; Cavenati et al., 2004). The stronger selectivity of FA zeolites is most probably related to the presence of different metal phases in FAZ, derived from the raw FA (Zhang et al., 2000; Zgureva and Boycheva, 2015a).

4. Conclusions

FA zeolites LTA and FAU synthesized from coal FA by different techniques were studied with respect to their adsorption potential for CO₂. The adsorption capacity of 136.40 mg CO₂/g FAZ measured at atmospheric pressure for the FAU type of FAZ obtained by double-stage fusion-hydrothermal activation is comparable with the capacity of commercial FAU. A strong linear correlation between specific surface area and adsorption capacity of FA zeolites was observed. The CO₂ adsorption isotherms are mathematically compatible with the Dubinin-Ashtakov and Langmuir adsorption models, and the model parameters were calculated, which will be used for further process simulations. FAZ exhibit strong CO₂/N₂ selectivity, found to be in the range of 23–36 for different samples at 273.15 K. The high CO₂ adsorption capacity in combination with the excellent selectivity of the FAU type of FA zeolite are prerequisites for the application of these solids as promising adsorbents for carbon-capture systems.

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References

- Ben-Mansour, R., Habib, M.A., Bamidele, O.E., Basha, M., Quasem, N.A., Peedikakkal, A., Laoui, T., Ali, M., 2016. Carbon capture by physical adsorption: materials, experimental investigations and numerical modeling and simulation—a review. *Applied Energy* 161, 225–255.
- Boycheva, S., 2011. *Systems and Devices for Environmental Protection in Thermal Power Plants*. University Publishing House, Technical University of Sofia, Sofia, Bulgaria.
- Boycheva, S., Zgureva, D., 2016. Surface studies of fly ash zeolites via adsorption/desorption isotherms. *Bulgarian Chemical Communications, Special Issue A*, 101–107.
- Boycheva, S., Zgureva, D., Shoumkova, A., 2015. Recycling of lignite coal fly ash by its conversion into zeolites. *Coal Combustion and Gasification Products* 7, 1–8.
- Cavenati, S., Grande, C., Rodrigues, A., 2004. Adsorption equilibrium of methane, carbon dioxide, and nitrogen on zeolite 13X at high pressure. *Journal of Chemical and Engineering Data* 49, 1095–1101.
- Energy Information Administration (EIA), 2013. *Annual Energy Outlook 2013*. <http://www.eia.gov/todayinenergy/detail.cfm?id=12251>, accessed 15 September 2015.
- Figuerola, J., Fout, T., Plasynski, S., McIlvried, H., Srivastava, R.D., 2008. Advances in CO₂ capture technology—the U.S. Department of energy's carbon sequestration program. *International Journal of Greenhouse Gas Control* 2, 9–20.
- Kalvachev, Y., Zgureva, D., Boycheva, S., Barbov, B., Petrova, N., 2015. Synthesis of carbon dioxide adsorbents by zeolitization of fly ash. *Journal of Thermal Analysis and Calorimetry* 124, 101–106.
- Kim, A.G., Kazonich, G., Dahlberg, M., 2003. Relative solubility of cations in class F fly ash. *Environmental Science and Technology* 37, 4507–4511.
- Kitto, J.B., Stultz, S.C., 2005. *Steam: Its Generation and Use*, 41st ed. The Babcock & Wilcox Company, Barberton, OH.

- Li, G., Xiao P., Xu, D., Webley, P.A., 2011. Dual mode roll-up effect in multicomponent non-isothermal adsorption processes with multilayered bed packing. *Chemical Engineering Science* 66, 1825–1834.
- Lin, C.F., His, H.C., 1995. Resource recovery of waste fly ash: synthesis of zeolite-like materials. *Environmental Science and Technology* 29, 1109–1117.
- Majchrzak-Kuceba, I., Nowak, W., 2005. A thermogravimetric study of the adsorption of CO₂ on zeolites synthesized from fly ash. *Thermochimica Acta* 437, 67–74.
- Mondal, M., Balsora, H., Varshney, P., 2012. Progress and trends in CO₂ capture/separation technologies: a review. *Energy* 46, 431–441.
- Moreno, N., Querol, X., Ayora, C., Pereira, C.F., Janssen-Jurkovicova, M., 2001. Utilization of zeolites synthesized from coal fly ash for the purification of acid mine waters. *Environmental Science and Technology* 35, 3526–3534.
- Morrison, M.A., Hay, P.J., 1979. Molecular properties of N₂ and CO₂ as functions of nuclear geometry: polarizabilities, quadrupole moments and dipole moments. *Journal of Chemical Physics* 70, 4034.
- Rouquerol, F., Rouquerol, J., Sing, K., 1999. *Adsorption by Powders and Porous Solids*. Academic Press, London.
- Ruthven, D., 1984. *Principles of Adsorption and Adsorption Processes*. John Wiley and Sons, New York.
- Songolzadeh, M., Ravanchi, M.T., Soleimani, M., 2012. Carbon dioxide capture and storage: a general review on adsorbents. *World Academy of Science, Engineering, and Technology* 70, 225–232.
- Takamura, Y., Narita, S., Aoki, J., Hironaka, S., Uchida, S., 2001. Evaluation of dual-bed pressure swing adsorption for CO₂ recovery from boiler exhaust gas. *Separation and Purification Technology* 24, 519–528.
- Unger, K.K., Kreysa, G., Baselt, J.P., 2000. *Characterization of Porous Solids V*. Elsevier, Amsterdam, The Netherlands.
- Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R.B., Bland, A.E., Wright, I., 2008. Progress in carbon dioxide separation and capture: a review. *Journal of Environmental Science* 20, 14–27.
- Zgureva, D., Boycheva, S., 2015a. Synthesis of highly porous micro- and nanocrystalline zeolites from aluminosilicate by-products. In: *Nanoscience Advances in CBRN Agents Detection, Information and Energy Security* (Petkov, P., Tsiulyanu, D., Kulisch, W., Popov, C., eds.). Springer, Dordrecht, The Netherlands, pp. 199–204.
- Zgureva, D., Boycheva, S., 2015b. Comparative studies on the zeolitization of fly ash from different Bulgarian power plants TPP “AES Galabovo” and TPP “Maritza East 2”. In: *Proceeding of XXth International Conference of Faculty of Power Machines and Power Engineering 2015, Sozopol, Bulgaria*, pp. 71–78. ISSN 1314-5371.
- Zhang, C., Li, S., Wu, T., Peng, S., 2000. Studies on the decomposing carbon dioxide into carbon with oxygen-deficient magnetite: II. The effects of properties of magnetite on activity of decomposition CO₂ and mechanism of the reaction. *Materials Chemistry and Physics* 62, 52–61.