

## Post-combustion CO<sub>2</sub> Capture using Ion-exchanged binder-free NaY beads

E. Aly<sup>(1),(2),(3)</sup>, L. F. A. S. Zafanelli<sup>(1),(2)</sup>, A. Henrique<sup>(1),(2)</sup>, K. Gleichmann<sup>(4)</sup>, A. E. Rodrigues<sup>(5)</sup>, F. A. D. S. Freitas<sup>(3)</sup>, J. A. C. Silva<sup>(1),(2)</sup>

<sup>(1)</sup> Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal.

ezzeldin@ipb.pt

<sup>(2)</sup> Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

<sup>(3)</sup> Aveiro Institute of Materials, CICECO, Department of Chemical Engineering, University of Aveiro, Campus Universitario de Santiago, 3810-193, Aveiro, Portugal

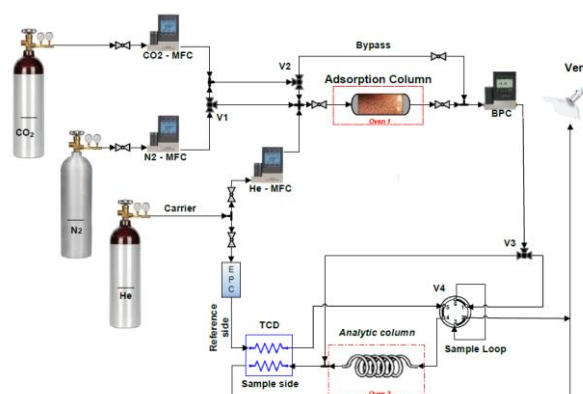
<sup>(4)</sup> Chemiewerk Bad Köstritz GmbH, Heinrichshall 2, 07586 Bad Köstritz, Deutschland / Germany

<sup>(5)</sup> Laboratory of Separation and Reaction Engineering (LSRE), Associate Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering, University of Porto, 4099-002, Porto, Portugal

zafanelli@ipb.pt; adriano\_henrique@ipb.pt; k.gleichmann@cwk-bk.de; arodrig@fe.up.pt; fsilva@ua.pt; jsilva@ipb.pt

**1. Introduction** - Ion-exchange processes on zeolites hold promise for improving adsorption mechanisms critical for post-combustion CO<sub>2</sub> capture (PCC). Zeolites offer advantages such as favourable CO<sub>2</sub> adsorption isotherms, rapid kinetics, non-toxicity, and cost-effectiveness, making them attractive candidates for carbon capture applications. In this study, we focus on exploring the impact of ion-exchange (K<sup>+</sup> and Ca<sup>2+</sup>) on bare NaY zeolite for PCC. Fixed-bed breakthrough experiments were conducted on various ion-exchanged zeolites, including K(23)Y, K(58)Y, K(95)Y, Ca(56)Y, and Ca(71)Y, within a temperature range of 306 K to 344 K and pressures reaching up to 350 kPa. The objective of these experiments is to investigate the equilibrium, kinetics, and dynamic characteristics of the sorption process, covering both single and binary mixtures of CO<sub>2</sub> and N<sub>2</sub>. Performance parameters such as selectivity and working capacity were evaluated based on the experimental outcomes. Following data collection, a mathematical model was calibrated utilizing Aspen Adsorption v10 software to simulate fixed-bed performance under standard PCC conditions.

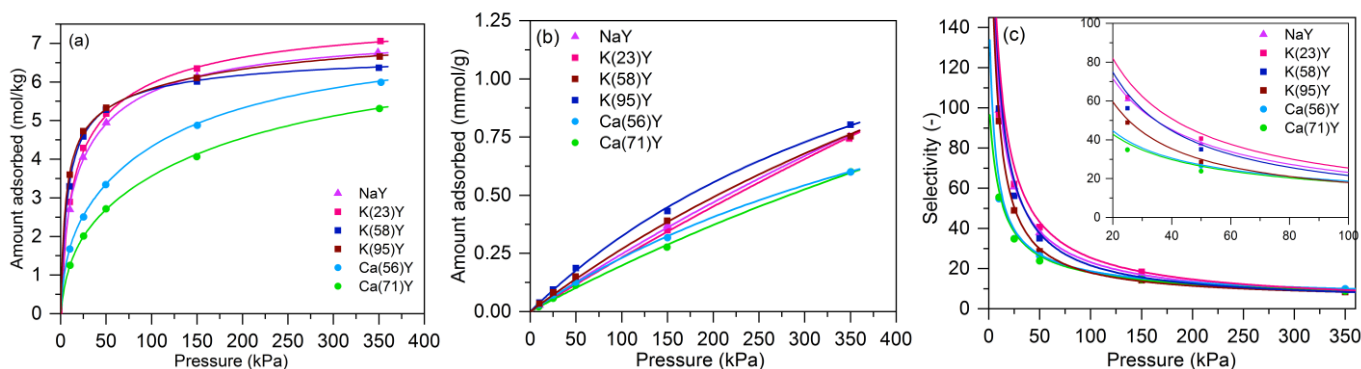
**2. Experimental** - The FAU type-Y zeolites investigated in this study were synthesized in a binder-free form, denoted as Köstrolith NaYBFK, with a Si/Al ratio of 2.5. The synthesis was conducted at the laboratory facilities of Chemiewerk Bad Köstritz GmbH (Germany). A single and multicomponent breakthrough apparatus was employed to investigate the dynamics of fixed-bed adsorption involving CO<sub>2</sub> and N<sub>2</sub>, alongside obtaining adsorption equilibrium data. The apparatus configuration is depicted in Image 1. The isotherms for both single and multicomponent adsorption were modelled using the Dual-site Langmuir (DSL) isotherm. Aspen Adsorption v10 package was used for the numerical simulation of fixed bed adsorption in both single and binary-component breakthrough experiments.



**Image 1.** Schematic drawing of the experimental set-up used to perform single- and multi-component breakthrough experiments

**3. Results and Discussion** - In Image 2, the CO<sub>2</sub> and N<sub>2</sub> adsorption behaviors, along with the CO<sub>2</sub>/N<sub>2</sub> selectivity at 306 K, are shown. These include isotherms for bare binder-free NaY and ion-exchanged zeolites: K(23)Y, K(58)Y, K(95)Y, Ca(56)Y, and Ca(71)Y. Notably, the sorption hierarchy at low pressures (up to 50 kPa) follows the order: Ca(71)Y < Ca(56)Y < NaY < K(23)Y < K(58)Y < K(95)Y.

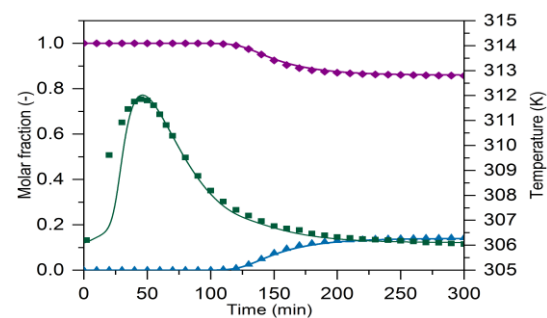
For instance, at 25 kPa and 306 K, CO<sub>2</sub> loading for bare NaY is 4.05 mol·kg<sup>-1</sup>, rising to 4.29 for K(23)Y, 4.59 for K(58)Y, and peaking at 4.72 for K(95)Y, indicating a 16% improvement over NaY. Conversely, Ca(56)Y exhibits a loading of 2.63 mol·kg<sup>-1</sup>, and Ca(71)Y records a lower loading of 2.01 mol·kg<sup>-1</sup>, indicating less than half the adsorption compared to commercial NaY. At pressures exceeding 200 kPa, K(23)Y and NaY exhibit the highest CO<sub>2</sub> loadings, followed by K(58)Y and K(95)Y. The N<sub>2</sub> isotherms show a more linear trend compared to CO<sub>2</sub>, with a similar sorption hierarchy, but with considerably lower loadings. The observed N<sub>2</sub> loadings suggest zeolites containing smaller monovalent cations, like binder-free K(23)Y and NaY, exhibit slightly lower N<sub>2</sub> uptake compared to other K<sup>+</sup> exchanged adsorbents, potentially contributing to higher CO<sub>2</sub>/N<sub>2</sub> selectivities and enhancing CO<sub>2</sub> separation efficiency in industrial applications. Analysis of the CO<sub>2</sub>/N<sub>2</sub> selectivity profile in Image 2c reveals consistent superior performance by binder-free zeolite K(23)Y across various conditions. For instance, at 306 K and 50 kPa, the CO<sub>2</sub>/N<sub>2</sub> selectivity for K(23)Y is 41, surpassing those of NaY (38), K(58)Y (35), K(95)Y (28), Ca(56)Y (26), and Ca(71)Y (24). This sustained elevation highlights K(23)Y's notable proficiency in preferentially adsorbing CO<sub>2</sub> over N<sub>2</sub>, suggesting potential applicability in PCC processes. Under standard PCC conditions, binary breakthrough experiments were performed on all binder-free FAU zeolites using a gas mixture containing 15% CO<sub>2</sub> and 85% N<sub>2</sub> (mol. %) at 101.3 kPa and 306 K. To evaluate CO<sub>2</sub> separation efficiency, various adsorbent metrics, including CO<sub>2</sub> loadings, selectivities, and working capacities, were analyzed. The findings suggest that binder-free K(23)Y exhibits considerable promise for PCC applications, demonstrating the highest binary selectivity at 101, a binary loading of 3.53 mol·kg<sup>-1</sup>, and the highest working capacities of 2.37 mol·kg<sup>-1</sup>, 0.71 mol·kg<sup>-1</sup>, 0.15 mol·kg<sup>-1</sup> across a range of Vacuum Swing Adsorption (VSA) PCC processes, considering regeneration pressures of 3, 10, and 15 kPa, respectively, relative to a feed pressure of 101.3 kPa. Image 3 shows the simulated and experimental breakthrough curves, along with temperature fronts for binary CO<sub>2</sub>/N<sub>2</sub> adsorption in binder-free K(23)Y at 306 K. The simulated data generated with Aspen Adsorption accurately mirrors the dynamic data, capturing both concentration and temperature profiles. This alignment positions Aspen Adsorption as a valuable tool for designing cyclic adsorption processes employing FAU-Y zeolites in PCC applications.



**Image 2.** Comparison of (a) CO<sub>2</sub> and (b) N<sub>2</sub> adsorption isotherms and (c) CO<sub>2</sub>/N<sub>2</sub> at 306 K among binder-free NaY, K(23)Y, K(58)Y, K(95)Y, Ca(56)Y, and Ca(71)Y zeolite. Experimental = symbols; DSL isotherm = lines.

**4. Conclusions** - The results of this study highlight the considerable potential of binder-free K(23)Y as a promising adsorbent for the separation of CO<sub>2</sub> from post-combustion streams. The data derived from this research are actively informing the development of a cyclic process, intended to optimize the practical application and effectiveness of this adsorption system for CO<sub>2</sub> recovery utilizing FAU Y-type zeolites.

**5. Acknowledgments** - This work was supported by national funds through FCT/MCTES (PIDDAC): (1) project PTDC/EQU-EPQ/0467/2020 (DOI:10.54499/PTDC/EQU-EPQ/0467/2020); (2) CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020); (3) CICECO –Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020 & LA/P/0006/2020.



**Image 3.** Breakthrough curves for binder-free K(23)Y zeolite in binary CO<sub>2</sub> (15%) (▲) and N<sub>2</sub> (85%) (◆) fixed bed experiments and temperature fronts (■) at 306 K. Experimental = symbols; Aspen numerical predictions = lines.