# Pilot-scale testing of Metal Organic Frameworks (MOFs) for post-combustion $CO_2$ capture at Technology Centre Mongstad (TCM)

G. De Weireld(1), A. Henrotin(1), N. Heymans(1), A. Wakaa(2), T. Oliveira(2),

D. **Siozos** (2), R. Blom(3), S. Krishnamurthy(3), J. Casaban(4)

*(1) Thermodynamics and Mathematical Physics Unit, University of Mons (UMONS), Place du parc 20, 7000 Mons, Belgium.*
*(2) Technology Centre Mongstad, 5954 Mongstad, Norway*
*(3) SINTEF Industry, Norway*
*(4) MOFTECH, Belfast, UK*
*Email: guy.deweireld@umons.ac.be*

The accelerating frequency and severity of extreme weather events, driven by rising anthropogenic greenhouse gas emissions, highlight the urgent need for effective decarbonization strategies to achieve climate neutrality. Carbon Capture and Storage (CCS) or Use (CCU) has emerged as a leading approach for $CO_2$ mitigation, particularly in carbon-intensive, post-combustion industrial processes. Among various CCUS technology, adsorption is a promising technology that can address, at least partially, a number of absorption problems such as high thermal energy consumption, solvent loss or toxicity. The use of metal-organic frameworks (MOFs) has an important potential due to the high $CO_2$ adsorption capacity, selectivity, and efficient regeneration capabilities of these materials. Although extensive lab-scale studies highlight the potential of MOFs for $CO_2$ capture, industrial-scale application remains limited, and the effects of real operational conditions on factors like productivity, purity, and energy consumption are not yet fully understood.

Addressing the issue, a consortium of 14 partners from 8 different countries has collaborated to establish the MOF4AIR project. The initiative aims to develop and demonstrate the performance of promising MOF materials in post-combustion $CO_2$ capture contexts. Technology Centre Mongstad (TCM) is one of the three selected demonstration sites to test the MOF-based $CO_2$ capture technology at industrial scale as part of the MOF4AIR project.

In the project's initial phase, a screening process was conducted on 24 pre-identified MOF materials, selected from various structural families for their high $CO_2$ selectivity, working capacity, and low regeneration costs. This selection was subsequently refined based on comparative results for the following criteria: (i) $CO_2$ adsorption capacity at 0.15 bar and temperatures of 298 K and above, (ii) $CO_2/N_2$ selectivity at 0.15 bar by IAST, (iii) working capacity between 0.15 bar (feed) and 0.015 (purge) which corresponds to a VPSA operating between 1 bar and 0.1 bar for a 15/85 $CO_2/N_2$ mixture, (iv) resistance to water, (v) stability in the presence of contaminants (SOx, NOx…), , (vi) impact of water on $CO_2$ adsorption capacity, and (vii) enthalpy of adsorption. Experimental $CO_2/N_2$ selectivity by breakthrough curve measurements was also determined for the most promising samples to confirm the IAST predictions. On this basis, a list of 6 promising candidates has been established to be synthesized and shaped at 100-200 g scale also considering their potential easy scalability and the ligand availability. Each material was reassessed across the same $CO_2$ adsorption parameters for a thorough comparative analysis. Finally, the effects of different binders on $CO_2$ adsorption capacity, including the influence of binder type, amount, and shaping techniques, were evaluated across all materials.

Following evaluations across various scales—including stability tests with impurities, binder selection for shaping, and lab-scale pilot testing, MIL-160(Al) (formula: $Al(OH)(O_2CC_4H_2OCO_2)$) [1-2] emerged as a promising MOF candidate for scaling up to pilot demonstration (60 kg) using a vacuum pressure swing adsorption (VPSA) process for carbon capture. MIL-160(Al) features an inorganic aluminum chain linked by five-membered 2,5-furan dicarboxylate rings, forming helical chains with interactive sites that selectively adsorb $CO_2$ (or $H_2O$) over $N_2$. With an adsorption enthalpy of -33 kJ/mol for $CO_2$, this MOF allows efficient regeneration. MIL-160(Al) was synthesized through a mechanochemical process and shaped by extrusion at MOFTECH facilities, where process optimizations were made to meet the required crushing strength (minimum 10 N) while minimizing porosity losses. The demonstration pilot setup at TCM (see Figure 1) is designed to treat 50 to 100 $Nm^3/h$ of flue gas coming from a residual fluid catalytic cracking unit (RFCC) or from a steam boiler (Mongstad heat plant (MHP)). The pilot includes (i) a scrubber, (ii) a water removal unit, (iii) a contaminants removal unit, and (iv) the MOF section, which comprises three 41 L columns filled with pelletized MOF material. The pilot operates a 6-step cycle composed of an adsorption step, heavy reflux, co-current evacuation, counter-current evacuation, light reflux and light product pressurization [3].

This demonstration unit was firstly optimized with a simulation model developed with the results obtained with the laboratory scale VPSA pilot using an aliquot of the 60kg of MIL-160(Al) [4]. Breakthrough curves measured on the TCM pilot were used to adjust the heat transfer coefficients of the adsorption bed, and validate the simulation model at this scale. A design of experiments (DOE) was constructed to create a surrogate model including (i) adsorption time, (ii) light reflux time, (iii) co-current evacuation time, (iv) feed flow rate, (v) light reflux flow rate, and (vi) feed $CO_2$ concentration. Results obtained from the DOE were used to fit an artificial neural network giving a value of $R^2$ >99.9% for recovery, purity and energy consumption. Optimization of the unit using a genetic algorithm (NSGA-II) was performed with the surrogate model to maximize purity and recovery while minimizing energy consumption. From simulation, the demonstration unit is able to reach purity and recovery higher than 90% for $CO_2$ concentration ranging from 5 to 15% at 50 $Nm^3/h$ of flue gas. The optimization procedure made through the simulation enabled optimum conditions to be found for each concentration of gas to be treated, defining test conditions for the demonstration unit.

Performance tests were carried out based on an experimental plan derived from VPSA simulations. Various VPSA adaptation were tested to improve $CO_2$ recovery and purity. During the test campaign, parameters such as co-current evacuation time, co-current flow rate, and counter-current flow rate were found to significantly influence the adsorption process. However, achieving the target levels for $CO_2$ capture and purity has been challenging, with fine-tuning hindered by the process's inherent complexity.
The VPSA unit was extensively modified to enhance performance. Final optimization efforts were focused on reducing flow and pressure in the co-current evacuation step, as well as reducing light reflux flow rate. After more than one year of tests and improvements, current results indicate solid overall performance of both the VPSA system and the plant's operational flow.
The results from the TCM site demonstration reach to project objectives with a recovery higher than 90% and a purity higher than 95% and demonstrates the feasibility of using MOFs in a post-combustion $CO_2$ capture process.

**Figure 1: Pictures of the TCM MOF4AIR pilot**

**References**

[1] A. Cadiau et al., "Design of Hydrophilic Metal Organic Framework Water Adsorbents for Heat Reallocation," Adv. Mater. 2015, 27(32), 4775–4780.
[2] D. Damasceno Borges et al., "Gas Adsorption and Separation by the Al-Based Metal–Organic Framework MIL-160," J. Phys. Chem. C. 2017, 121 (48), 26822–26832.
[3] M. Khurana and S. Farooq, "Simulation and optimization of a 6-step dual-reflux VSA cycle for post-combustion $CO_2$ capture," Chem. Eng. Sci., vol. 152, pp. 507–515, 2016.
[4] A. Henrotin et al., "Lab-scale pilot for $CO_2$ capture vacuum pressure swing adsorption: MIL-160(Al) vs zeolite 13X," Carbon Capture Sci. Technol., vol. 12, p. 100224, 2024.

*Acknowledgement:*
*This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 831975 (MOF4AIR project).*