IMT Atlantique
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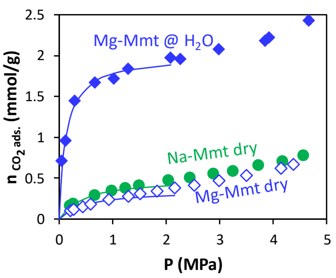
# PhD offer: Design of clay-based adsorbent materials for $CO_2$ capturing from biogas.

*Context:* The production of "green" methane from biogas is one of the most dynamically developing markets of renewable energy sources in Europe, especially in the context of its injection in the natural gas (NG) pipeline grid or utilisation as a fuel for transportation. Prior to storage or injection in NG grid biogas has to be upgraded, *i.e.* enriched in methane (from 55-80% up-to > 96%) by $CO_2$ removal and purified from minor impurities such as $H_2S$, $H_2O$, $H_2$, $N_2$, $O_2$ and VOC.

Numerous processes exist for $CO_2$ separation. Adsorption-based technologies, such as Pressure and Vacuum Swing Adsorption – "PSA VSA" process, which consist of $CO_2$ selective capture from $CH_4/CO_2$ stream by a porous solid inside a column, are employed on about 20 % of average- and small- size bio-methane production plants. In these process the separation is driven by the difference in $CO_2$ and $CH_4$ adsorption capacity or the rates of their diffusion into micropores with opening comparable to the molecular cross-section. The basic PSA cycle involves two parallel columns, which operate in antiphase the phases of: (1) pressurization, (2) feeding with biogas and production of a stream enriched in $CH_4$, (3) blowdown (depressurization) to desorb $CO_2$ and (4) purge with a part of downstream $CH_4$ to completely remove $CO_2$ from the column and regenerate the adsorbent. PSA/VSA process have several advantages over other separation technologies, such as good ratio between $CH_4$ purity and energy consumption and handling of inert solids instead of volatile/corrosive/toxic liquids. Also these process have a great potential for future development owing to cycle design flexibility and existence of numerous classes of adsorbent materials with tuneable adsorption capacity and selectivity.[1] The choice of adsorbent materials is one the key steps of PSA process design. Regardless recent progress in the domain of the discovery and development of adsorbent materials, traditional zeolites and microporous activated carbon are still commonly employed for $CO_2$ separation, owing to their robustness and efficiency. Zeolites exhibit high $CO_2$ selectivity over methane and their micropore filling with $CO_2$ usually occurs below 5 bar. On the other hand, they are highly sensitive to moisture, the adsorption of which dramatically decreases zeolite performances and ability to efficiently capture $CO_2$. Carbonaceous materials feature much lower selectivity to $CO_2$ *vs* $CH_4$ and their working capacity can be spread over a large range of pressures, but in contrast to zeolites they are more inert vis-à-vis gas stream humidity.[2] The combination of the advantages of traditional adsorbents such as high $CO_2$ selectivity and resistivity to moisture sounds attractive from application point of view.

Over the past decade gas adsorption properties of swelling clay minerals (smectites) have extensively been studied and it was shown that under partially hydrated state, their interlayer spaces can be accessible for the incorporation of $CO_2$ and $CH_4$, and not only for water, as considered earlier. In fact, the hydration of the interlayer cations results in the increase of their effective size, which leads to the increase of the interlayer distances to values superior than kinetic diameters of gas molecules, allowing the later to enter. As illustrated in the figure, partially-hydrated Mg-exchanged montmorillonite adsorbs much higher amounts of $CO_2$ than its completely dehydrated counterpart or other clays exhibiting collapsed state of the interlayers.[3]




*Objectives and work program:* The proposed PhD project is a part of ANR CLAYGAS (AAPG 2021) project and its main goal is to evaluate the ability of different clay minerals to efficiently separate $CO_2$ from biogas (model $CH_4/CO_2$ mixture).

The envisaged work program includes four main tasks:

1) To prepare a series of cation-exchanged smectites from different sources.

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2) To characterize their structural (composition and charge of phyllosilicate sheets) and textural (micropore volume and surface area) properties.
3) To characterize equilibrium and dynamic $CO_2$ and $CH_4$ adsorption properties in a large range of P, T conditions and establish how these characteristics correlate with structure/texture of the minerals.
4) To perform column assays through breakthrough curves on selected materials to evaluate their dynamic separation performances.

The following experimental methods will be employed: Powder XRD (+profile refinement), elemental analysis using AAS, cation exchange capacity (CEC) measurement, TGA, TEM/SEM, low-pressure/high pressure $N_2$, $CO_2$, $CH_4$ adsorption assays and measurement of breakthrough curves.

*Host institution and environment:* The PhD project is proposed at the Department of Energy Systems and Environment – DSEE at IMT Atlantique (https://www.imt-atlantique.fr/fr), Nantes – France, in VERTE research group (https://www.imt-atlantique.fr/fr/departement-systemes-energetiques-et-environnement). The Department is a part of UMR CNRS 6144 Gepea laboratory and its research is focused on the development of the process of bio-resource and waste conversion as well as eco-technologies. The position is offered for 3 years (from November 2021) with net month salary ~1450 €. Several stays at ISTERRE Grenoble (https://www.isterre.fr) are envisaged to perform structural characterization of clay materials. Thus, future PhD student will benefit from interdisciplinary environment of the project.

*Candidate profile*: We are looking for candidates passionate about materials/minerals characterization and interface phenomena, like adsorption or mass transfer process. Applicants should hold Master degree, M2 or equivalent, in one of the following fields: physical chemistry, materials science, mineralogy or chemical engineering (with solid knowledge of materials science). Previous experience in characterization of clays will be an asset.

PhD student will be supervised by Denys Grekov (denys.grekov@imt-atlantique.fr), Pascaline Pré (pascaline.pre@imt-atlantique.fr) and Laurent Truche (laurent.truche@univ-grenoble-alpes.fr).

Interested candidates should send their CV and cover letters to Denys Grekov (denys.grekov@imt-atlantique.fr). Two reference letters from internship supervisor and coordinator of Master program are requested.

(1) Wilken, D.; Strippel, F.; Hofmann, F.; Maciejczyk, M.; Klinkmüller, L.; Wagner, L.; Bontempo, G.; Münch, J.; Scheidl, S.; Conton, M.; et al. Technical Rapport: Biogas to Biomethane. *Unido* **2017**, 9.
(2) Grande, C. A. Biogas Upgrading by Pressure Swing Adsorption. *Intech* **2013**, *32* (July), 137–144.
(3) Grekov, D. I.; Suzuki-Muresan, T.; Kalinichev, A. G.; Pré, P.; Grambow, B. Thermodynamic Data of Adsorption Reveal the Entry of CH4 and CO2 in a Smectite Clay Interlayer. *Phys. Chem. Chem. Phys.* **2020**, *22* (29), 16727–16733. https://doi.org/10.1039/d0cp02135k.