	PhD GRANT
	ÉCOLE DOCTORALE SCIENCES EXACTES ET LEURS APPLICATIONS - ED 211 / NATURAL SCIENCES DOCTORAL SCHOOL Avenue de l'université BP 1155 64 013 PAU Cedex – France

PhD SUBJECT

TITRE / TITLE: Dynamic selective storage of hydrogen in a pressurized gas mixture in porous media

ABSTRACT:
The aim of this thesis is to contribute to a better understanding of the phenomena of diffusion and transport of pressurised gaseous mixtures containing hydrogen for the purpose of separation or storage of this compound in porous media. For this, a new experimental device will be developed for the dynamic study of permeability and selective separation of gaseous compounds under pressure on porous materials. It will also include a theoretical part dedicated to the modeling and numerical simulation of the flow of pressurized gas mixtures through porous media, taking into account the phenomenon of adsorption and possible swelling of the microporous matrix of the adsorbent.

Mots clés (Keywords): Dynamic adsorption, Diffusive transport, Adsorbent swelling

WORKING CONDITIONS

Laboratoire : : Laboratoire des Fluides Complexes et leurs Réservoirs (LFCR) et Laboratoire de Mathématiques et de leurs applications (LMAP) **Site web :**https://lfc.univ-pau.fr/fr/index.html et https://lma-umr5142.univ-pau.fr/fr/index.html	
PhD Director : MOCHO Pierre (Associate Professor, LFCR, UPPA) **PhD co-Director :** PERRIER Laurent (Associate Professor, LFCR, UPPA) **In Collaboration with** MIQUEU Christelle (Associate Professor, LFCR, UPPA) et AMAZIANE Brahim (Associate Professor, LMAP, UPPA)	
Place : LFCR, Groupe Géomécanique et Milieux Poreux (G2MP), Anglet, FRANCE	
Start : September 2021	**Duration):** 3 years
Employer : Université de Pau et des Pays de l'Adour (UPPA)	
Monthly salary before taxes : 1768 €	

HOST LABORATORY PROFILE

Laboratoire des Fluides Complexes et leurs Réservoirs :
The LFCR is a joint research unit linked to the UPPA, the CNRS and the TOTAL. The LFCR is a research unit whose research ranges from nanometers to hundreds of kilometres, from nanoseconds to a million years, from the physics and chemistry of interfaces, through the thermodynamics of fluids under flow, to the geology of reservoirs, geomechanics and geophysics. The G2MP (Geomechanical/ Porous Media) group focuses on the mechanical behaviour of porous media, fluid-solid couplings and general transport properties in these media. The group develops both experimental characterization and modelling activities using numerical simulation tools at different scales. Its current activities focus on: (1) understanding the behaviour of fluids in microporous networks, (2) poro-mechanical modelling of micro and mesoporous environments and the transition from nano-scale to continuum mechanics, (3) understanding the relationships and couplings between permeability and damage, (4) storage and separation of gases by adsorption.

Laboratoire de Mathématiques et de leurs Applications :
The Laboratoire de Mathématiques et ses Applications de Pau is part of the CNRS and the University of Pau et de l'Adour. It is a member of the Federation IPRA FR 2952. The LMAP comprises four groups covering a broad spectrum in pure and applied mathematics: algebra and geometry, optimization, analysis and numerical simulation, partial differential equations, probabilities and statistics.

Projet NewPores :
NewPores is an international hub dedicated to the mechanics and physics of porous materials, which aims to meet the new challenges of Energy and Environment. This is a joint effort of the group on Geomechanics and Porous Materials (G2MP) of the Laboratory of Complex Fluids and their Tanks at E2S UPPA (France), the Center for Sustainable Engineering of Geological and Infrastructure Materials (SEGIM) at Northwestern University (USA), the University of Vigo (Spain), the Technical University of Madrid (Spain) and the University of Liège (Belgium).

MISSION – PRINCIPAL ACTIVITIES

I. *Scientific Context*
Since August 2015, when the Energy Transition for Growth Act was enacted, there has been an acceleration in the development of renewable energy. Energy recovery in the form of hydrogen requires its storage on different scales, from porous media to geological reservoirs.
The study of the phenomena of gas diffusion and permeability of porous media is part of the adsorption dynamics of gas mixtures. In dynamic adsorption experiments, a fluid phase containing the adsorbate(s) flows through a fixed bed of adsorbent. The temporal monitoring of the concentration of an adsorbate in the fluid at the column outlet enables the breakthrough curve of the adsorbate in question to be obtained. In the literature, most studies mention experiments carried out under atmospheric pressure and few of them concern high pressure conditions. One advantage of high-pressure adsorption is that it allows both separation (by pressure-oscillating adsorption process) and gas storage. High-pressure studies have been commonly applied to the separation of the carbon dioxide-methane mixture by adsorption processes (adsorption with variation of pressure) [1]. However, the implementation of high-pressure adsorption requires consideration of the potential deformation of the adsorbent due to gas adsorption in micropores or contained storage materials. In nanopores (pore size less than 50 nm) [2], the fluid is contained and the fluid/solid and fluid/fluid interactions drastically change its state compared to the «free» fluid. The direct consequence of adsorption is macroscopically a volumetric swelling of the microporous matrix [3]. This swelling causes a change in the transport porosity of the material [4], inducing a disturbance of the flow of the fluid into the porous medium, characterized by its permeability. This phenomenon may be important to consider in the context of the dynamic adsorption of gas mixtures on adsorbent column under high pressure and is not, to our knowledge, studied to date. From a modelling point of view, numerical models have been developed to provide information for determining migration and fluid interactions in underground storage porous media [5-6]. These models are based on porous media characteristics such as porosity and permeability. Rare papers have been devoted to the prediction of breakthrough curves of various mixtures of hydrogen, nitrogen, methane and high-pressure carbon dioxide [7, 8]. But to our knowledge, no study specifically addresses the effect of swelling on the shape of the breakthrough curve.

II. *Objectives*
The major interest of this work lies in the development of a new device for high-pressure measurement of permeability and breakthrough curves of hydrogen-containing gas mixtures. It will provide access to a better knowledge of the processes of transport and dynamic storage of gaseous components under pressure (dihydrogen H2, methane CH4, carbon dioxide CO2, ...) in porous media. The originality of our approach lies in measuring the permeability of dihydrogen from a cover rock

and a hybrid material as well as the diffusion of pure or mixed H_2 in the porous matrix under high pressure conditions. These two physical properties are key elements in the security of storage of renewable energies in the form of H_2 at high pressure. Another objective is to obtain theoretical breakthrough curves of gaseous mixtures (for example H_2/CH_4 or H_2/N_2) by filtering porous media on a fixed bed with possible consideration of the phenomenon of swelling. This part should lead to diffusion and adsorption data of gaseous compounds, useful for purifying biogas for energy recovery or storage purposes.

III. *Work plan*

The scientific programme consists of five parts: 1- Development of an experimental high-pressure device (up to 60 bar) for the continuous measurement of:
- Permeability of porous materials;
- Breakthrough curves of gas mixtures on adsorbents;

2- Validation of the experimental device:
- permeability using a granodiorite rock from a benchmark (KG2B)
- $C0_2/CH_4$ gas mixture breakthrough curve on a zeolite

3-Experimental studies of permeability (H_2) and breakthrough curves of gaseous mixtures (H_2/CH_4, H_2/N_2, $CH_4/C0_2$) on the following porous media:
- Geological storage material such as argillite, limestone;
- Hybrid H_2 storage material following the results of the ongoing HYGIE II project study;

4- Modelling and numerical simulation of breakthrough curves incorporating a porometric model to introduce the deformation of the porous structure of the adsorbent, in parallel with Parts 2 and 3.

5- Exploitation of results:
- Comparison experiments/model (analysis of diffusion coefficients of constituents in porous media);
- Correlation research between permeability, loss of media load, adsorption; microporous, swelling and porosity.

IV. *Literature References*

[1] Poursaeidesfahani A, Andres-Garcia E, de Lange M, Torres-Knoop A, Rigutto M, Nair N, Kapteijn F, Gascon J, Dubbeldam D, Vlugt TJH. (2019). Prediction of adsorption isotherms from breakthrough curves. Microporous Mesoporous Mater, 277: 237 – 44.

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[5] Kilinçer, N. and F. Gümrah, 2000, A Numerical Simulation Study on Mixing of Inert Cushion Gas with Working Gas in an Underground Gas Storage Reservoir, in Energy Sources, vol 22, pp. 869-879

[6] Sáinz-García, Á. (2017). Dynamique de stockage souterrain de gaz. Aperçu à partir de modèles numériques de dioxyde de carbone et d'hydrogène (Doctoral dissertation, Université de Toulouse, Université Toulouse III-Paul Sabatier).

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[8] Ma S, Tong L, Ye F, Xiao J, Bénard P, Chahine R. (2019). Hydrogen purification layered bed optimization based on artificial neural network prediction of breakthrough curves. Int J Hydrogen Energy, 44(11): 5324–33.

REQUIRED COMPETENCES

The candidate must have either a Master’s degree or equivalent in Physics, Chemical Engineering or Materials Engineering. Good numerical modeling/simulation skills are expected to study fluid dynamics in porous media.

REQUIRED DOSSIER,

Send an e-mail with your candidature containing :

- CV
- Cover letter detailing candidate's motivations
- Copy of the diploma
- Candidate's MSc or equivalent : marks and ranking
- Any letters of recommendation)
- Contact details for 2 referees)

LIMITING DATE : 30 May 2021

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