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SPECIAL ISSUE
Behavior of confined
fluids and media



Porous media have in common to develop a large interface that divides the space with a varying degree of complexity, potentially with hierarchical structuring. Such environments are central to IFPEN's research on geological formations and certain industrial materials.

The thermodynamic, dynamic and rheological properties of the fluids present in the porous network are strongly influenced by the nature of interfacial interactions (wettability and adsorption) and by the degree of confinement of the pore space. This dual dependency makes it possible to cover a rich phenomenology of behaviors associated with molecular adsorption, thermodynamic phase diagrams, micro or even nanorheology of confined fluids, more or less complex (foams, emulsions, etc.), and with their transport and reactivity. For the latter field, searching optimized reaction conditions remains a real challenge.

This issue presents recent research in this rich and dynamic field, in which the dual top-down and bottom-up approach is very promising for crossing time and space scales, from macroscopic through to nanoconfinement, a research area still full of surprises.

I hope you enjoy reading this issue,

Pierre Levitz,
CNRS - Sorbonne University
Expert for IFPEN's Scientific Board

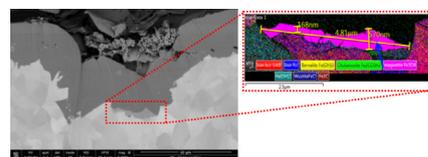
Carbon steel in self-defense mode against corrosion

Carbon or low-alloy steel corrosion, by aqueous media containing CO₂, hampers the development of numerous technologies^a for the energy transition. Among the electrochemical processes involved, the reaction between metal cations and anions present in the electrolyte produces the precipitation of compounds that are deposited on the surface of the steel and modify corrosion kinetics through processes that are not yet fully understood.

A collaborative project conducted with ANDRA (French National Agency for Radioactive Waste Management) demonstrated experimentally, at a temperature of 80°C and under 0.54 bars of CO₂, that increasing pH beyond 6.6 led to a reduction in corrosion kinetics, due to the formation of a film qualified as "pseudo-passive" (final corrosion rate below 0.05 mm/year)^[1].

A study combining different techniques^b demonstrated that the effect of this protective porous film on corrosion rate was primarily due to its surface-coating action on the metal, thereby reducing active dissolution zones. SEM-EBSD^c analysis (figure) revealed that this film is made up of layers of a variety of compositions. Below the outer part made up of siderite (FeCO₃), a magnetite (Fe₃O₄) layer developed in some zones, contributing to the capacity to protect against corrosion^[2].

This improved understanding of the pseudo-passivation mechanisms, at the



Cross section of the steel-corrosion deposit interface formed at 80°C, under 0.54 bars of CO₂ at pH=6.6 after 12 days. The different phases were detected using SEM-EBSD analysis.

confined interface between the surface of a carbon steel and a corrosion deposit, is being used as the basis for a study currently under way on the influence of some contaminant compounds dissolved in the aqueous phase, such as oxygen. ■

- a - For example: CO₂ capture, transport and conversion, underground gas storage, conversion of biomass into fuels and chemicals.
- b - Electrochemical impedance measurement, surface chemical analysis and local pH measurements.
- c - Scanning electron microscopy analysis via electron backscatter diffraction.

[1] R. De Motte, R. Mingant, J. Kittel, F. Ropital, P. Combrade, S. Necib, V. Deydier, D. Crusset, Near, *Electrochimica Acta*, 290 (2018) 605-615. doi.org/10.1016/j.electacta.2018.09.117

[2] R. De Motte, R. Mingant, J. Kittel, F. Ropital, P. Combrade, S. Necib, V. Deydier, D. Crusset, *The Use of Electrochemical Impedance Spectroscopy and Surface Analysis to Study the Formation of a Protective Film*, submitted to *Corrosion Science*.

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IFP Energies nouvelles (IFPEN) is a major research and training player in the fields of energy, transport and the environment. From research to industry, technological innovation is central to all its activities.



Foam rheology in porous media

For processes involving gas injection, such as enhanced oil recovery (EOR^a) and CO₂ storage operations, the use of foam makes it easier to control gas mobility. Improving these processes requires thorough knowledge of the foam's flow properties in porous media.

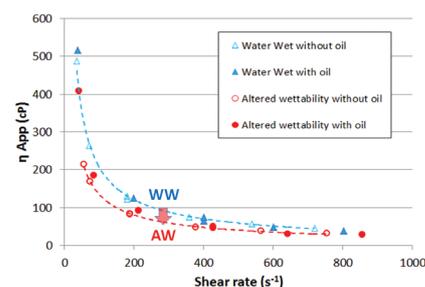
However, the structure of the confining medium, the pore surface state (wettability), the presence of oil and the composition of the injected gas are all parameters that can influence the stability of the foam and its flow properties. Experimental research is thus required to study these phenomena under various temperature and pressure conditions.

The tests conducted to date have involved the co-injection of brines (containing surfactants) and gases of variable compositions (CO₂ and CO₂ + CH₄, N₂). They were carried out in the presence and absence of oil, and in water-wetting or partially oil-wetting porous media. The determination of the role of these parameters and their combined

influences was facilitated by the use of an experimental set-up reducing the experimentation time by 30%.

The results obtained^[1, 2] demonstrate, in particular, a significant reduction in foam viscosity in porous media with altered wettability (AW curve on the figure).

Future experiments with transparent porous micromodels, coupled with an in situ foam observation technique, will provide invaluable information for understanding the complex interactions between porous media, injected fluid properties and the flow of the foams formed. ■



Foam rheology in sandstone, for different experimental conditions.

a - Enhanced Oil Recovery.

[1] N. Gland, E. Chevallier, A. Cuenca, G. Batôt, SPE Adipéc 2018
DOI: 10.2118/193201-MS

[2] V. Beunat, N. Pannacci, G. Batôt, N. Gland, E. Chevallier, A. Cuenca, SPE MEOS 2019
DOI: 10.2118/194963-MS

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Phase equilibria in confined media

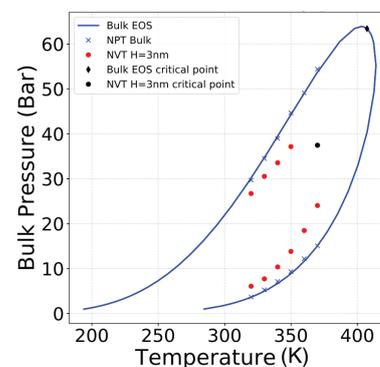
In many geological reservoirs, pore size distribution is highly heterogeneous (from 2 to 50 nm). While the molecular size of the confined fluids is between 0.5 and 10 nm, their interaction forces with the micropore wall (~2 nm) are of the same order of magnitude as their intermolecular interactions, which can radically alter their thermodynamic behavior. Understanding this phenomenon is of significant interest to various industries: oil, chemicals, food, pharmaceutical, etc.

However, obtaining the required thermodynamic properties experimentally^a remains technically challenging. Molecular simulation was recently employed at IFPEN to model phase equilibria in confined fluids. This alternative makes it possible to produce reference data for equations of state used in reservoir simulation.

A new Monte Carlo calculation method^b, with a modified version of the Gibbs ensemble, was used to obtain the thermodynamic properties at equilibrium of the confined mixtures and their liquid and vapour pressures^[1].

The method was tested for pure hydrocarbons (C₂, C₅ and C₁₀) and mixtures (C₂/C₂, C₂/C₅). Pores were modeled using slits with various sizes of graphite walls. Hydrocarbons were modeled with an anisotropic united atom potential, for different C₂/C₅ mixture proportions (figure). It is observed that the phase envelope of the confined fluid shifts and its size reduces. Simulations confirm that the critical temperature and pressure are shifted downwards and the bubble point pressure decreases while the dew point pressure increases.

This information will be used to optimize the description of confined fluids via the calibration of equations of state. ■



P-T diagram of a C₂/C₅ mixture (59.7%/40.3%) in a 3-nm nanopore^c.

a - Critical temperature, critical pressure and phase density.
b - Adaptation of the method fixing the bubble point pressure in order to initialize a constant temperature calculation.
c - The symbols represent simulation results while the continuous lines represent the results obtained from a cubic equation of state for unconfined fluids.

[1] N. Sobecki, C. Nieto-Drachi, A. Di Lella, D. Yu Ding, Phase behavior of hydrocarbons in nano-pores, Fluid Phase Equilibria [2019].
<https://doi.org/10.1016/j.fluid.2019.05.025>

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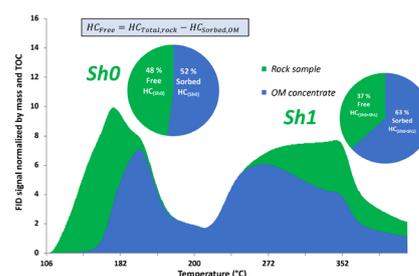
What percentage of free compounds in porous media?

The energy mix required to satisfy global needs will include fossil hydrocarbons for some time to come. Therefore, estimating existing reserves, i.e., the quantity of liquid organic compounds present in natural porous media, remains crucially important. These free compounds represent the fraction of oil potentially recoverable and the easiest to extract. The adsorption phenomena within sedimentary organic matter (OM) significantly affect both this proportion and the composition and retention mechanism of oils in source rocks.

In order to optimize the characterization of this phenomenon, an analytical methodology was developed to estimate the total amount of free vs adsorbed compounds. It is based on a specific method of the Rock-Eval^{®a} technology, widely used to estimate the type and thermal maturity of OM⁽¹⁾ using pyrolysis. The idea is to record the global surface area under each thermal peak (parameters Sh0 and Sh1) measured during vaporization by an FID^b between 100 and 350°C. These

values are first obtained from a whole rock sample, to estimate the total free and adsorbed liquids, and then from the corresponding OM isolated from the mineral matrix^c, which corresponds only to the adsorbed oils. The free liquid hydrocarbon fraction is finally calculated as the difference between these last two values (figure).

In oil exploration, this methodology could be used to identify potential producible free liquid zones most suitable for successful development. Making modifications to Rock-Eval^{®d} operating conditions and detectors, the proposed methodology could be applied to new research topics such as the characterization of OM from soil, organic-rich rocks and recent sediments, as well as oils and lubricants. ■



Principle of the new methodology.

- a - Physico-chemical apparatus used to quantify the organic carbon content of rocks.
- b - Flame Ionization Detector.
- c - Using non-oxidizing acid treatments.
- d - Analysis temperature and conditions during pyrolysis and oxidation phases.

[1] M.-F. Romero-Sarmiento, 2019, AAPG Bulletin DOI: 10.1306/02151918152

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Adsorption, a key factor for geological storage

Low permeability geological layers, already known within the context of oil exploration, are once again becoming a focus of interest for energy (compressed air), gas (CO₂, H₂, CH₄) and waste storage. Their integrity is fundamental to their roles as both cap rock and host rock. All the retention, trapping and transport mechanisms within these rocks are reflected in two petrophysical properties that it is important to determine: permeability and porosity⁽¹⁾.

Several methods exist to determine the permeability – by definition very low – of these media and IFPEN is equipped with high-performance experimental set-ups to do so. However, the impact of adsorption on transport mechanisms within them is still poorly understood and difficult to measure, despite its significance. This is because if a chemical species is adsorbed in a rock's porous network, this limits the network available for flow. This is known as effective flow porosity and/or kinematic porosity.

A new G-KwAD experimental methodology, coupling permeability measurements

with a tracing experiment, was recently developed⁽²⁾ making it possible, by means of a kinematic porosity measurement experiment with gas, to determine, for a single, ultra-low-permeability sample:

- not only its permeability k and its kinematic porosity ω_c^a ,
- but also its adsorption capacity (in g/kg of rock), which depends on pressure conditions and the concentration of the species injected.

For several of the applications mentioned above, the G-KwAD method represents significant progress: it makes it possible to easily access the values of key properties for numerical modeling of geological storage site longevity and safety. ■



Experimental apparatus for the G-KwAD method.

[1] P.-F. Boulin, P. Bretonnier, N. Gland, J.-M. Lombard. Oil & Gas Science and Technology – IFP Energies nouvelles journal, 3, issue 67 (2012), 387-401

[2] G. Berthe, F. Martin, F. Al Sahyouni. Patent FR1857508, 2018

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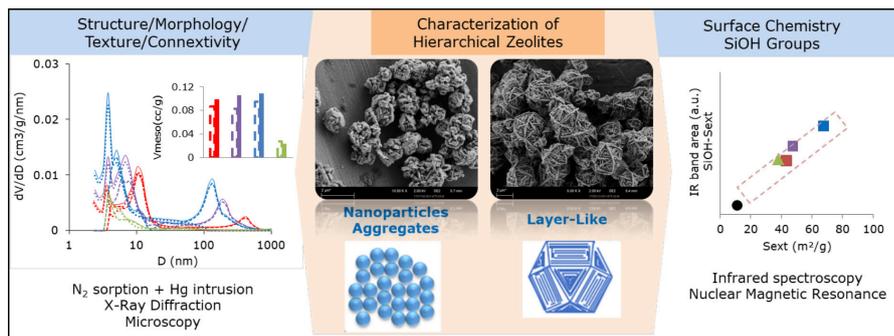
a - Which takes adsorption into account.

For xylene separation, hierarchy is not all bad

The three xylene^a isomers are each employed in numerous growth market applications (polymers, plastifiers and resins). It is thus vital to improve the efficiency of the separation processes for these isomers, the most widely used process being liquid phase adsorption on zeolite materials. For the competitiveness of the process, these materials must be optimized while maintaining a subtle balance between their adsorption capacity, their selectivity with respect to the different isomers and the accessibility of the latter to selective regions. These properties are directly linked to the texture and topology of the zeolite support, made up of agglomerated crystallites.

Recourse to zeolites with a network of auxiliary pores makes it possible to improve liquid phase accessibility to the selective regions located in the microporosity. However, during the synthesis of these supports, the introduction of the secondary porous network must be carried out while minimizing its impact on the selective regions due to a modification to the microporosity access surface.

To achieve this, a range of characterization methods^b was used to relate the adsorptive behavior of the different isomers to the textural and surface properties



Morphological, textural and surface characterization of different zeolites with hierarchized porosity used for xylene separation.

(figure) of the zeolites⁽¹⁾. This exhaustive characterization makes it possible to rationalize the impact of the secondary pore network and paves the way for optimization of the “hierarchical” zeolite synthesis process for xylene separation.

Combining these experimental results with atomistic models will lead to a better understanding of the impact of surface chemistry on adsorbent selectivity with respect to the different isomers. ■

- a - Ortho, meta and paraxylene.
b - Comprising XRD, microscopy, nitrogen physisorption, mercury intrusion, IR, NMR, xylene adsorption by gas phase thermogravimetry and liquid phase batch experiment.

[1] I. Medeiros-Costa, C. Laroche, J. Pérez-Pellitero, B. Coasne. *Microporous & Mesoporous Materials* (2019), Special Issue “Patarin (1985-2019)”

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News

- **François de Rugy**, Minister of State, Minister for Ecological and Inclusive Transition was hosted at our Lyon site. He was given a tour of the site to learn about IFPEN's research in the fields of electric and hybrid powertrains, connected mobility, electricity storage and energy management, the Organic Rankine Cycle (ORC), biomass chemistry and biofuels, biogas purification and plastics recycling.
- **iMust**, the “Institute for Multi-scale Sciences and Technologies” to which IFPEN belongs as a member, has just been given a five-year extension following the outstanding nature of its scientific and technological results.
- With 182 patent applications published in 2018, **IFPEN Group climbed one place in the INPI (French National Industrial Property) rankings**, and is now in 12th position.

Upcoming scientific events

- **Workshop e³CAV – Connected and Automated Vehicles for Energy Efficiency and Environmental Impact** – 30 September and 1st October – IFPEN, Rueil-Malmaison - www.WS-e3CAV.com
- **Rencontres Scientifiques d'IFP Energies nouvelles – Microfluidics 2019: from laboratory tools to process development** – 13-15 November 2019 – IFPEN, Rueil-Malmaison - www.rs-microfluidics.com
- **Rencontres Scientifiques d'IFP Energies nouvelles – SimRace 2019: Numerical methods and HPC for industrial applications** – 4-6 December 2019 – IFPEN, Rueil-Malmaison - www.rs-simrace.com

Awards

- **Céline Pagis**, IFPEN catalysis researcher, has won the 2019 Denise Barthelemy prize, awarded by the French Zeolites Group. It should be remembered that Céline Pagis was also the recipient of the 2018 L'Oréal-Unesco “For Women in Science” award, in October 2018.

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