Written on 01 December 2017 15 minutes of reading
News

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- Hydrogen
- Responsible oil and gas
- Fuels
- Petrochemicals
- Gas treatment
- Risers and flow lines

Special issue: **Publications by Young Doctoral Researchers**

 As a research and training player, IFPEN hosts around **forty new PhD students every year** in an environment that encourages innovation. These students therefore have the opportunity to supplement their scientific training with research work that helps advance the state of the art, in fields falling within the scope of IFPEN's innovation strategy.

This issue is dedicated to the results of recent PhD theses and illustrates the **diversity of disciplines covered by IFPEN's research**, as well as the creativity of our young researchers. In addition to key results, ranging from improvement of our **offshore technologies** to **catalysis for biomass conversion**, via **high throughput experimentation and analysis of terrestrial natural hydrogen flows**, the issue also highlights the work of **Zlatko Solomenko, the 2017 Yves Chauvin prize-winner**. Each year, this prize is given in recognition of a high-quality PhD research project. In this case the field concerned is "**fluid mechanics applied to the treatment of sour gases**" and the research makes it possible to ultimately envisage the **improved capture of CO_2 emitted by large industrial complexes**.

We hope that you enjoy this issue.

Éric Heintzé, Scientific Director

See the PDF of the letter

Les brèves

THESIS BY **ZLATKO SOLOMENKO, 2017 YVES CHAUVIN PRIZE-WINNER**

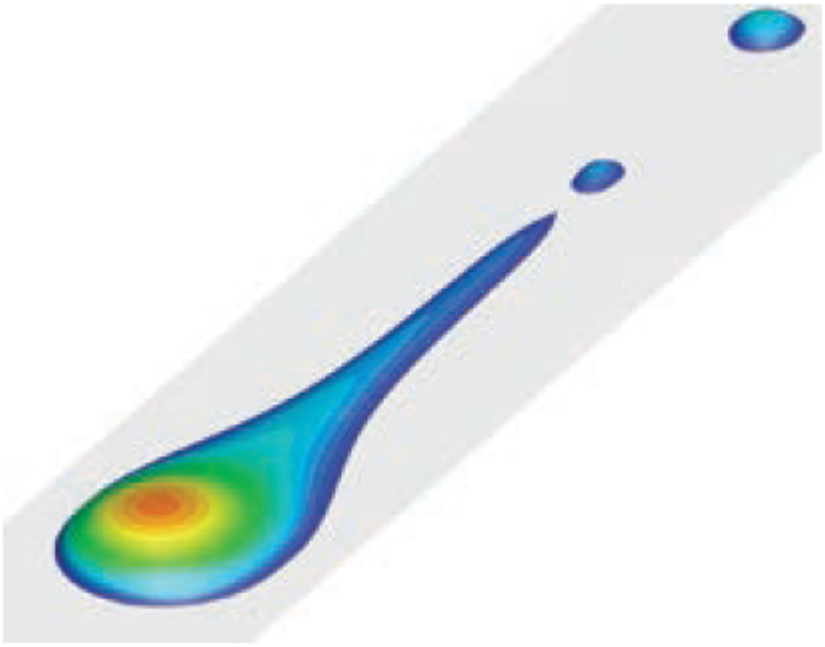
Columns with structured packings are frequently used to treat acid gases (CO_2, H_2S) contained in natural gas. In the future, their use is likely to be extended to the CO_2 recovery from flue gases with the development of carbon capture/use/storage processes.

Packings are also used in **distillation processes**, **gas production or biogas purification**. In these columns, the liquid phase, tasked with capturing the unwanted gases flows over the packing plates, which have a complex geometry designed to maximize the exchange surface.

In order to develop optimized geometries, **numerical hydrodynamics calculations** are used to reproduce **wetting phenomena**. The latter have an impact on liquid film flows on complex surfaces, due to the development of dry zones and hence "***contact lines***" (three-phase), the dynamics of which need to be taken into account.

A CFD (Computational Fluid Dynamics) methodology has been developed to simulate these liquid flows. Since wetting is dependent on **nanometric-scale phenomena** and given that it is impossible to numerically solve equations on this scale, it was examined from **a dynamic contact angle, calculated using a subgrid model**(1).

The results have been validated in the case of a **3D sliding droplet** (figure).



Simulation of a drop sliding down an inclined plane leading to capillary instability(1).

Film thickness and interfacial velocity values, obtained using specially developed methods, will enable **validation of calculations** for structured packing plates. Measurements and calculations will then be reproduced on an arrangement of several plates.

This **new CFD methodology** marks a key step in the development of **predictive models for the flows considered**. Ultimately, it will be useful for the design of **new packing geometries, with a view to improving the performance of gas/liquid contactors**.

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* Thesis entitled ***"Study of dual-phase flows and wetting in structured packings***"

(1) ***Z. Solomenko***, *P. D.M. Spelt,* ***P. Alix****, J. Comput. Phys. 348 (2017) 151-170.*
> DOI: 10.1016/j.jcp.2017.07.011

Scientific contact: Pascal Alix

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How wet is a flow?

THESIS BY **CHARLOTTE GALLOIS***

The **production of alumina catalyst supports** involves a series of individual operations[a] during which the solid fraction of the material varies, from a dispersed state (colloidal fluid) to a porous solid state.

This gradual densification reflects a change in the **structural organization of solid particles on a mesoscopic scale**.

The arrangements adopted depend both **on**:

- **the physicochemical properties of the initial alumina suspensions**,
- and **the densification processes employed**.

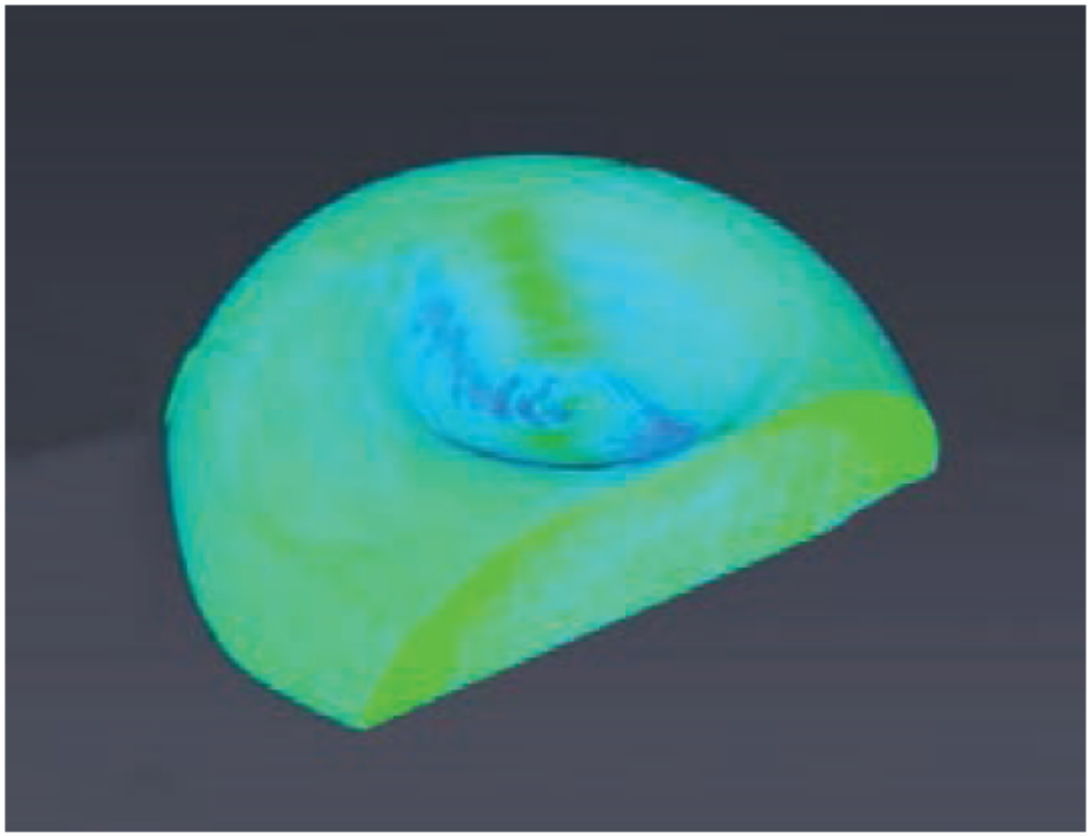
It is crucial to identify and understand the mechanisms at play during densification, since they determine the finished product properties.

A study of colloidal fluid drying was carried out in partnership with the Phenix laboratory at UPMC. A **droplet of alumina suspension, applied to a solid hydrophobic substrate** and placed in controlled drying conditions, was examined **by rapid X-ray microtomography** (on Paul Scherer Institute synchrotron).

These experiments demonstrated that:

- **a droplet of liquid suspension collapses** in the final stages of its drying, due to an accumulation of particles on the outside surface of the drop (particularly at triple line level[b]),
- whereas **a droplet of a suspension in gel state** is deformed in a homothetic manner[(1-2)].

This research will be applied to the study of industrial formulations and be continued in more severe drying conditions.



Collapse of a drop of liquid suspension (Ø = 1.48 mm) during drying: visualization of the solid accumulation (dark green) around the edges.

a- Synthesis of boehmite, filtration and washing, shaping, calcination.

b- Solid-liquid-gas interface.

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* Thesis entitled "***Study of the physicochemical properties of boehmite. Application to catalytic supports***"

(1) ***C. Gallois, E. Rosenberg, L. Barré, A. Bonnin, D. Frot, E. Lécolier, P. Levitz***, *Drying of sessile droplets of anisotropic colloids dispersions. In the process of being drafted.*

(2) ***C. Gallois, D. Frot, E. Lécolier, P. Levitz***, *Colloidal boehmite dispersions under osmotic stress: an in situ DLS investigation of gelation. In the process of being drafted.*

Scientific contact: eric.lecolier@ifpen.fr

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Journey to the center of a droplet

THESIS BY **JULIA GUÉLARD***

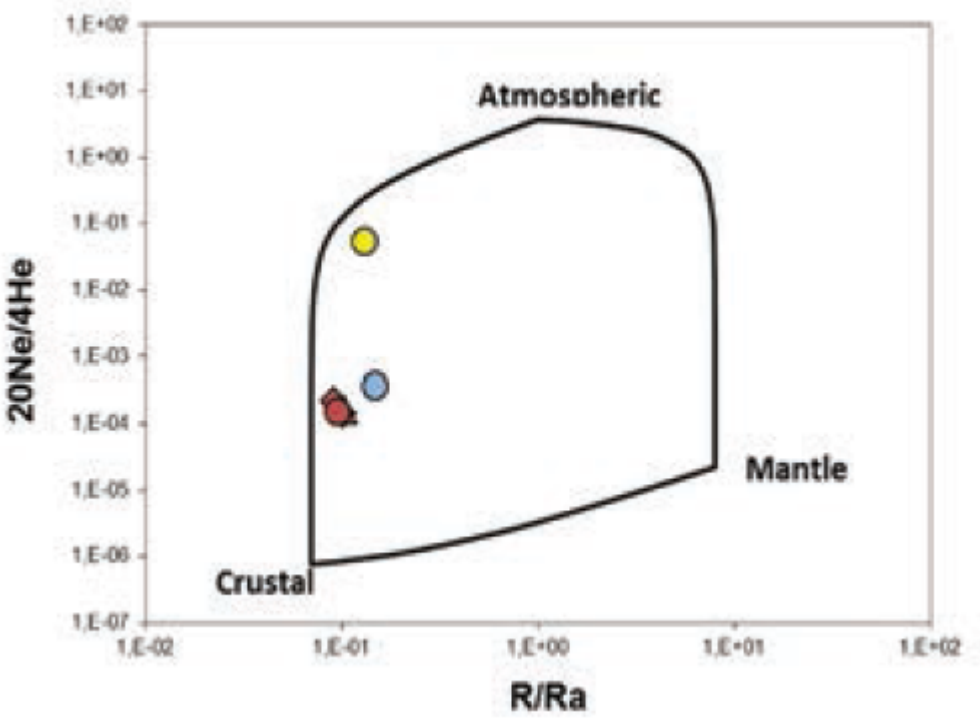
In the 1980s, three wells drilled by an independent prospector, Don Clarke, **revealed the unexpected presence of natural molecular hydrogen (H_2)** in the underground of Kansas, right in the heart of the North American continent.

Since then, **other continental sites have been identified**, in **Mali** and **Russia**, in particular.

However, **the presence of hydrogen in these intracratonic environments**[a] remained unexplained, although fluid/rock interactions in the basement rock were strongly suspected of playing a role.

A new well, drilled in 2008, provided the opportunity to answer the question, by **studying the three elements of the presumed rock/water/gas reactional system**(1). **Variable proportions of H_2/CH_4/N_2**, as well as **helium**, present in substantial quantities, were systematically measured at the site.

Analyses of **noble gases** (figure) indicate a production of H_2 in the basement rocks (so-called "**crustal**"[b]), while **stable C and H isotopes** provide information on the consumption/production reactions between H_2 and CH_4, keys to the dynamic evolution of their concentrations and pressures.



Origin of gases according to the analysis of noble ones.

The oxidation of iron(II), widely present in production waters, was identified as the trigger for the **production of H_2**. Iron(II) is supplied by the minerals of the basement rocks (observed in surrounding wells), coming from the **greenstone belt**.

Therefore **natural hydrogen** may potentially be found on all continents, wherever these rocks are present.

This research has made it possible to identify the ingredients involved in the production of H_2. Now, we need to find out which are the processes responsible for its retention inside sediments.

Future studies will aim to determine the **physicochemical parameters enabling to predict the behavior of this natural hydrogen in the subsurface**.

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* Thesis entitled ***"Characterization of natural dihydrogen emanations in the intracratonic context. Example of a gas/water/rock interaction in Kansas".***

a- A craton is the stable portion of a continental area.
b- Because they are produced by the earth's crust.

(1) *- **J. Guélard**, **V. Beaumont**, **V. Rouchon**, F. Guyot, **D. Pillot**, D. Jézéquel, M. Ader, K. D. Newell, et **E. Deville** (2017), Natural H_2 in Kansas: Deep or shallow origin? - Geochem. Geophys. Geosyst., 18, 1841–1865.*
>> DOI: 10.1002/2016GC006544

Scientific contact: julia.guelard@ifpen.fr

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Natural hydrogen in continental environments: the question of its origin solved

THESIS BY Charles Bonnin*

An essential phase in the **development of catalytic materials** is the assessment of their efficiency, generally performed in the laboratory on specific equipment.

For **catalysts intended for slurry application**[a], **continuous three-phase (gas-liquid-solid)** stirred tank reactors are used. These are complex to operate and require a long testing phase (sometimes lasting several weeks) to access data such as the catalyst selectivity. This experimental difficulty, not to mention the cost, is an obstacle to the development of new materials.

In this context, **high-throughput experimentation (HTE) in micro packed bed reactor is a screening method** offering three advantages:

- direct comparison of the efficiency of several catalysts in identical conditions,
- use of small quantities of substance,
- and short test times.

However, **the conditions specific to HTE make it necessary to reconsider the physical models** used to analyze the results and, in particular, to determine the activity of the catalyst on the basis of measurement of the conversion rate.

Loading of reactors on HTE equipment.

The research therefore focused,

- firstly, **on understanding the physics inside HTE reactors**[1-2], followed by their integration into a numerical model,
- and, secondly, **on a series of experiments with the two types of equipment**.

The model developed, which combines **hydrodynamic and reactional aspects**, **makes it possible to directly access the activity of catalysts and to find the same efficiency classification** in both types of reactor, thereby validating the **new HTE methodology**.

The resulting time savings for the development of catalysts is a major advantage for the exploration of **more disruptive formulations**.

a- Micrometric-sized catalyst suspension in a liquid phase.

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* Thesis entitled ***"Assessment of the high throughput approach in micro packed bed for the Fischer Tropsch catalyst screening"***

(1) **C. Bonnin, L. Brunet-Errard, D. Decottignies**, V. Ordomsky, A. Khodakov, International conferences on Microreaction Technology, Beijing, 2016

(2) **C. Bonnin, L. Brunet-Errard, D. Decottignies, E. Rosenberg,** V. Ordomsky, A. Khodakov, « Microfl uidics: from laboratory tools to process development », Rueil-Malmaison, France, November 2015

Scientific contact: charles.bonnin@ifpen.fr

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HTE in a milli-fixed bed reactor boosts the development of slurry catalysts

THESIS BY Marie Guehl*

The ecological transition requires **the development of new industrial processes making use of renewable resources.**

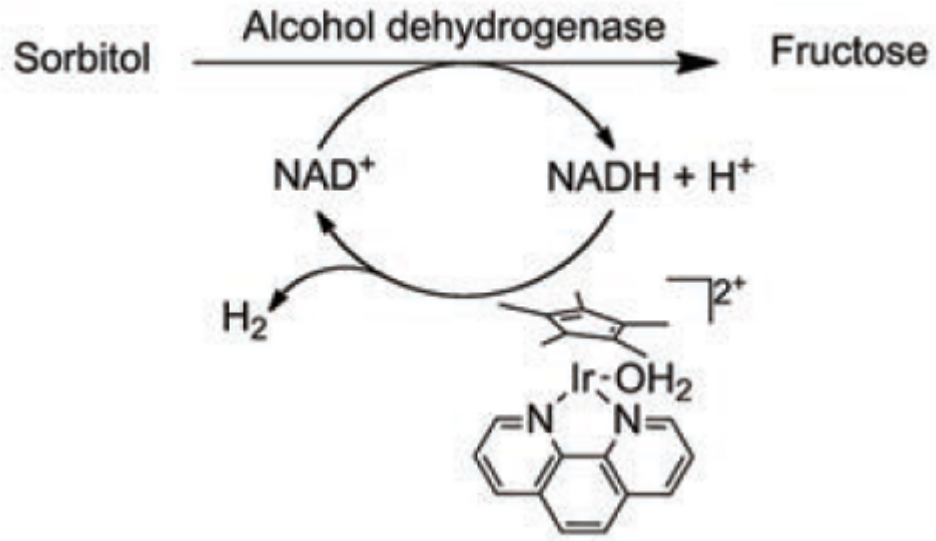
Among them, **sugars from lignocellulosic biomass** can produce derivated products with high added value. Exploiting this rich resource with its multiple chemical functions means coming up with innovative concepts that are radically different from processes aimed at oil and gas.

Biological – especially enzymatic – **catalysis** is particularly suitable for **converting sugars from biomass**, with a very high selectivity, in aqueous medium. However, it presents a number of difficulties, hence the need of a **cofactor[a] to activate the enzyme**, which is expensive to produce and regenerate, by using a second enzymatic step.

An original approach has been adopted to overcome this obstacle: **hybrid catalysis**, combining **the selectivity of enzymes and the robustness of chemical catalysts**. This combination draws on the respective advantages of both types of catalysis to produce "**platform molecules**", which are difficult to obtain using other methods, in a highly selective manner(1).

IFPEN therefore worked with the UCCS[b] at the University of Lille 1 on **converting sorbitol into fructose**, a synthon of choice to obtain products with a high added value.

This research demonstrated the **possibility to combine an enzyme**, called **alcohol deshydrogenase (ADH)**, and an **organometallic chemical catalyst**, capable of regenerating the cofactor in situ (figure).



Hybrid catalysis applied to the enzymatic conversion of sorbitol into fructose with regeneration of the nicotinamide cofactor.

The research focused on:

- the **cohabitation of enzymatic and chemical catalysis**,
- and the **identification of the optimal operating conditions** of the overall system(2).

This initial proof of concept paves the way for new developments for **biomass conversion processes.**

a- A chemical compound that does not contain any proteins but is necessary for the biological activity of a protein.

b- Unité de catalyse et chimie du solide (Solids Catalysis and Chemistry Unit).

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* Thesis entitled***"New hybrid catalysis concept for biomass conversion".***

(1) A. Gimbernat, **M. Guehl**, M. Capron, **N. Lopes Ferreira**, R. Froidevaux, J-S. Girardon, P. Dhulster, **D. Delcroix**, F. Dumeignil, ChemCatChem, 2017, 9, 2080-2084.

(2) Patent FR3031983(A1)

Scientific contacts: damien.delcroix@ifpen.fr - nicolas.lopes-ferreira@ifpen.fr

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Hybrid catalysis can better deal with bio-based substances

THESIS BY Vidit Gaur*

The **i-Clip-Riser®** is a technological product developed by IFPEN, which enables **rapid connection of drilling riser components**[a] **offshore**.

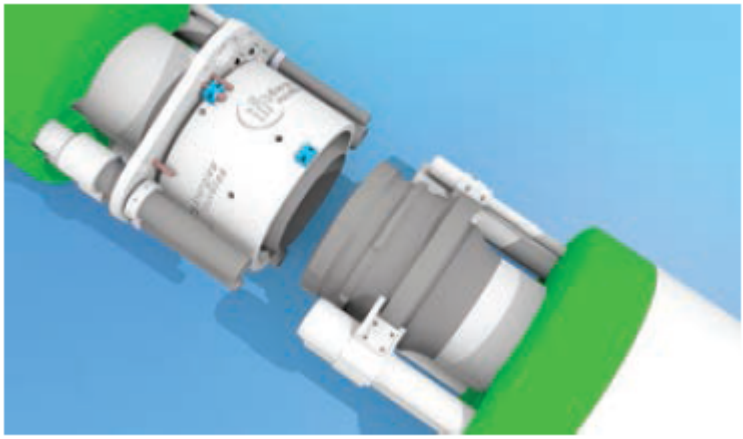
As a result of the weight of the assembly and swell movements, it is constantly subjected to fatigue stresses. A detailed analysis of these, based on **non-linear numerical simulations,** has demonstrated their **multiaxial cyclical nature**, which the conventional fatigue criteria reported in the literature cannot express.

A very comprehensive series of experiments – **dynamic multiaxial mechanical tests**, **SEM and TEM observations**[b], **X-ray diffraction – revealed different crack initiation mechanisms, depending on the stress**

conditions.

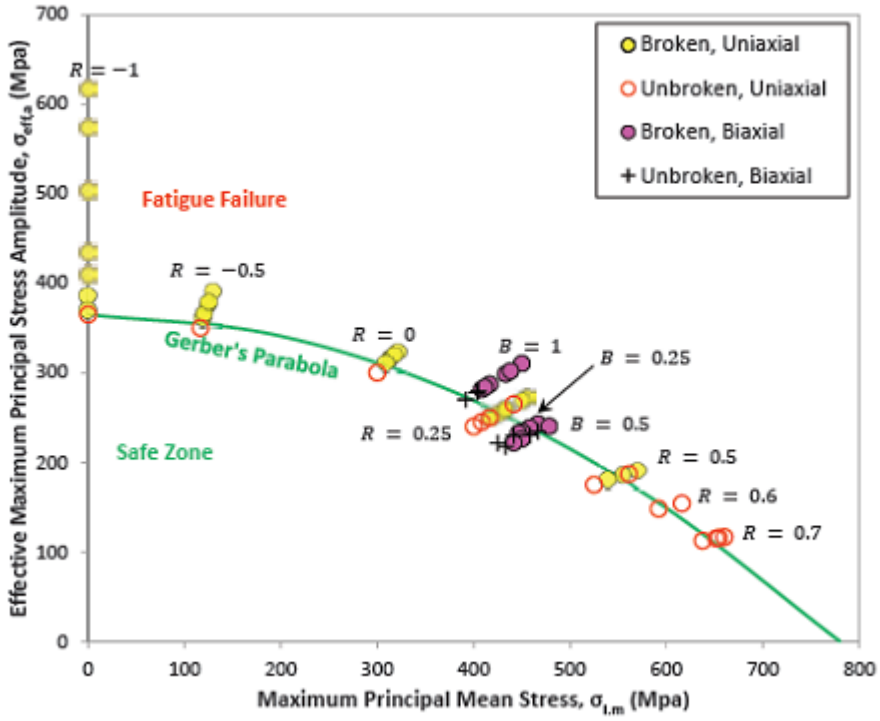
In addition, it made it possible to quantify the impact of several dimensioning parameters, such as:

- **mean stress**,
- the **biaxiality ratio of stresses**,
- or the **presence of the saline environment**[1].



A fatigue endurance limit criterion, including only two material parameters, was defined on the basis of this large-scale testing program and was validated in all the conditions tested[2]. Based on the **Gerber approach**[c], it enables characterization of the resistance of the connector under the multiaxial loads encountered during operation. Easily usable for structure calculations, this enables a more realistic validation of the behavior of the i-Clip-Riser® in response to fatigue.

It is planned to extend this research to predict the life estimation, and also to perform validation tests on a prototype (scale 1:1).



Comparison of the proposed criterion (in green) and the various tests performed (symbol) in the effective stress plane, as a function of the maximum principal stress.

a- A set of tubes, including one main pipeline, connecting the drilling platform to the subsea wellhead.

b- Scanning and transmission electron microscopy.

c- Approach that expresses the effect of mean stress on the endurance limit under uniaxial tension.

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* Thesis entitled: ***Fatigue and corrosion-fatigue in Cr-Mo steel in biaxal tension.***

(1) **V. Gaur**, V. Doquet, **E. Persent**, C. Mareau, **E. Roguet, J. Kittel**, Surface versus internal fatigue crack initiation in steel: Influence of mean stress, International Journal of Fatigue, 2016, 82-3, 437-448.
>> DOI: 10.1016/j.ijfatigue.2015.08.028

(2) **V. Gaur**, V. Doquet, **E. Persent, E. Roguet**, Effect of biaxial cyclic tension on the fatigue life and damage mechanisms of Cr–Mo steel, Int. Journal of Fatigue, 2016, 87, 124-131.
>> DOI: 10.1016/j.ijfatigue.2016.01.021

Scientific contact: eleonore.roguet@ifpen.fr

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The i-Clip-Riser® stands up to fatigue!

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