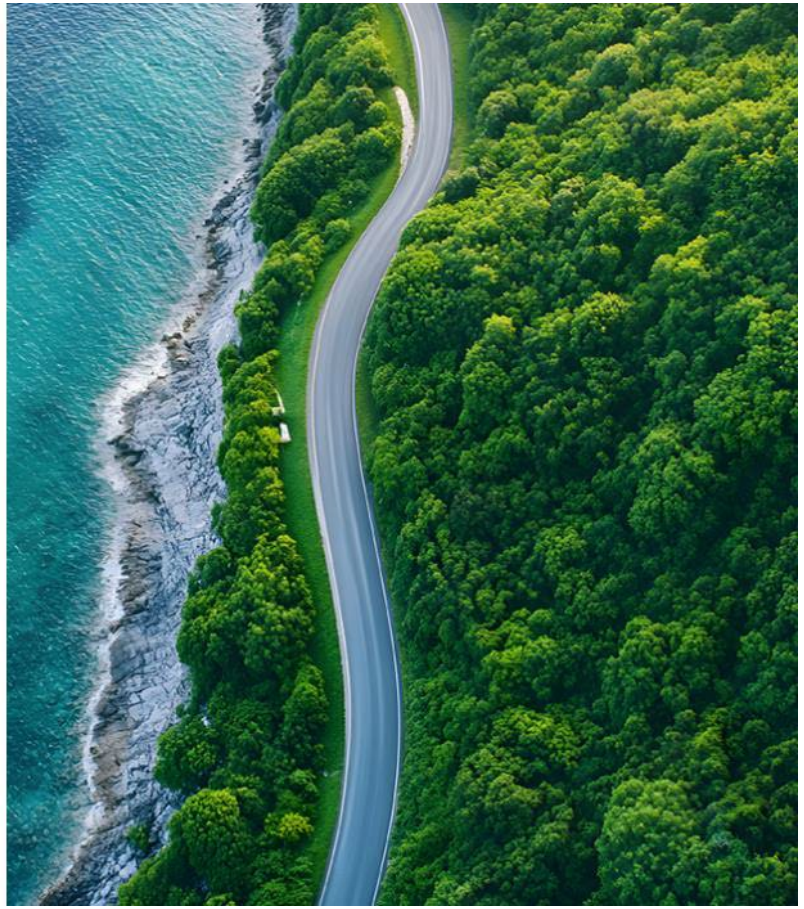
Screening of leaching conditions: a high-throughput approach



Anne-Sophie Gay, Elodie Devers, Jérôme Danguin, Mathieu Vidalie, Sylvie Lopez

PROMETIA, 12th Scientific Seminar – Naples – November 2025

IFPEN PRESENTATION

IFPEN AT A GLANCE

Public sector **R&I** institution

Training center

Industrial **Group**

INTERNATIONAL SCOPE in the field of
ENERGY, MOBILITY and **THE ENVIRONMENT**

1,543 employees

incl. **1,087** R&I engineers & technicians

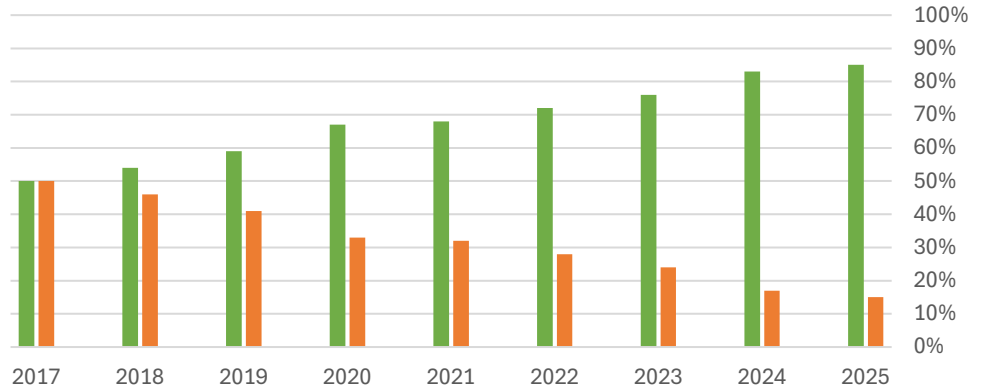
€122 M Budget allocation in 2024

€154 M Own resources in 2024

Research & Innovation activities

Green technologies

Responsible & profitable Oil & Gas



OUR GREEN INNOVATIONS

- Carry out **scientific and technical research** and promote the value of its outcomes
- From fundamental research to the support of industrial-scale deployment

ENERGY

- Wind
- Energy storage
- Energy management systems
- Geothermal energy
- Natural hydrogen, H2 transport and storage
- Subsurface modeling for the energy transition
- Renewable gas processing

MOBILITY

- Biofuels and e-fuels
- Electric mobility:
  - Electric machines and power electronics
  - Batteries
- Hydrogen mobility: IC engines & fuel cells
- Environmental analysis of transport & digitalization of mobility

ENVIRONMENT

- Biobased products
- Advanced plastics recycling
- Recycling of metals from catalysts and batteries
- Industrial decarbonization: CCS/CCU
- Air/Soil/Water:
  - Environmental monitoring
  - Sustainable soil management
  - Water management & treatment

- Technical, economic and environmental analyses (multi-criteria life cycle analyses)

THE LEGACY OF OIL AND GAS

- Innovate to improve solutions and carry out expert studies, to meet energy and chemical product demands in a more environmentally sustainable way

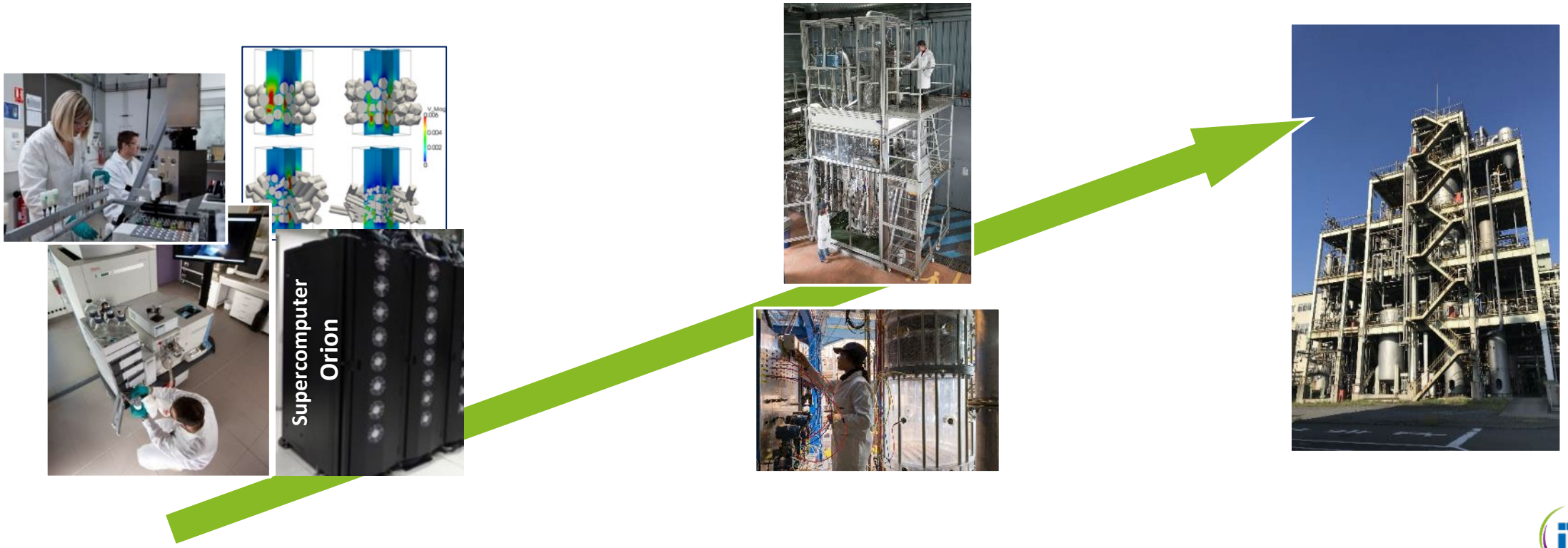
OIL AND GAS

- Fuels
- Petrochemicals
- Natural gas processing
- Risers and production lines

Contributing to the funding of research on green technologies

FROM FUNDAMENTAL RESEARCH TO INDUSTRIAL DEVELOPMENT

- R&I work on a variety of scales
  - Experimental setups from lab scale to pre-industrial pilot
  - Advanced digital tools: modeling and high-performance computing (HPC)
- In collaboration with academic and industrial partners



IFPEN SUBSIDIARIES AND SHAREHOLDINGS *

4,000 COLLABORATORS (IFPEN + SUBSIDIARIES)

Eco-energies & mobility

- 75% GreenWITS
- 24% DRIVE QUANT
- 18% la Cie des Mobilités
- 11% K-Ryole carry on
- 11% so sponge
- 6% Tec E Mouv

Processes & products, oil and gas, biomass, water, CO_2, materials recycling

- 99% Axens — Powering integrated solutions — An IFP Group company
  - 50 % EURECAT
- 16% nacre
- 10% BioTJet

Geosciences consulting & software

- 100% BeicipFranlab
  - 50 % CFG GEOTHERMAL
- 100% TECH advantage

Training

- 62% IFP Training

CONSOLIDATED TURNOVER OF €1,100 MILLION

* February 2025

EDUCATION AND TRAINING @ IFPEN

Training the next generation to become active players in the energy transition

Training through research

~150
PhD students per year

Specialized engineering graduate programs

~500
graduates per year

Continuing professional training

~15, 000
professionals per year

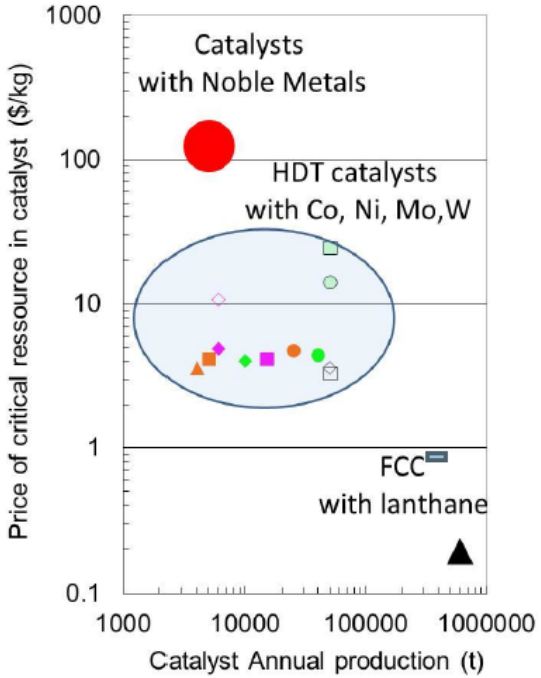
CATALYST MANAGEMENT
ROLE OF RECYCLING

REFINING AND CATALYSTS

Inside reactor

- Refining
  - More than 600 refineries in the world
  - Crude oil world capacity 90 MBD
  - Complex scheme, combining different processes
    - Separation / conversion / transformation / purification
    - Most of these processes are (thermo)catalytic

- Catalysts in refinery
  - Amount: 800-900 kt/y (loaded per year) / Market : 60 000-70 000 M$/y
  - Different types of heterogeneous catalysts
    - FCC Catalyst : Biggest catalyst volumes but low prices (~1$/kg) ; Catalyst based on zeolite (ZSM-5) and alumina Doped with rare earth (La, few wt%)
    - Noble metal based catalysts (Pt, Pd,...) : precious metal belongs to the refiners. After catalyst end-of-life, precious metals are separated from support (pyro- or hydrometallurgy process), purified and used as recycled raw chemical materials
    - Sulfide catalysts (mainly group VI & VIII: Ni, Co, Mo, W) : Process of regeneration / rejuvenation to make several catalyst cycles with same catalyst batches. Market = 170 kt/y.



HOW TO PREPARE A HYDROTREATING CATALYST?

MoO_3
$Co(OH)_2$ ou $Ni(OH)_2$
H_3PO_4

+ Organic additives in solution
= performance booster

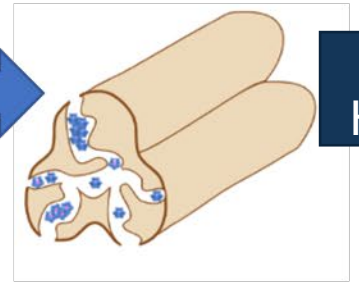
Aqueous metallic precursors solution

Alumina support

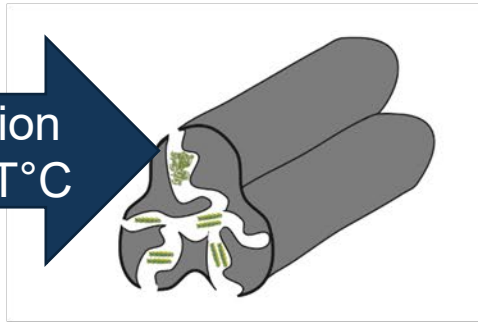
Impregnation

Ageing

Drying (calcination)



Sulfidation
H_2/H_2S T°C

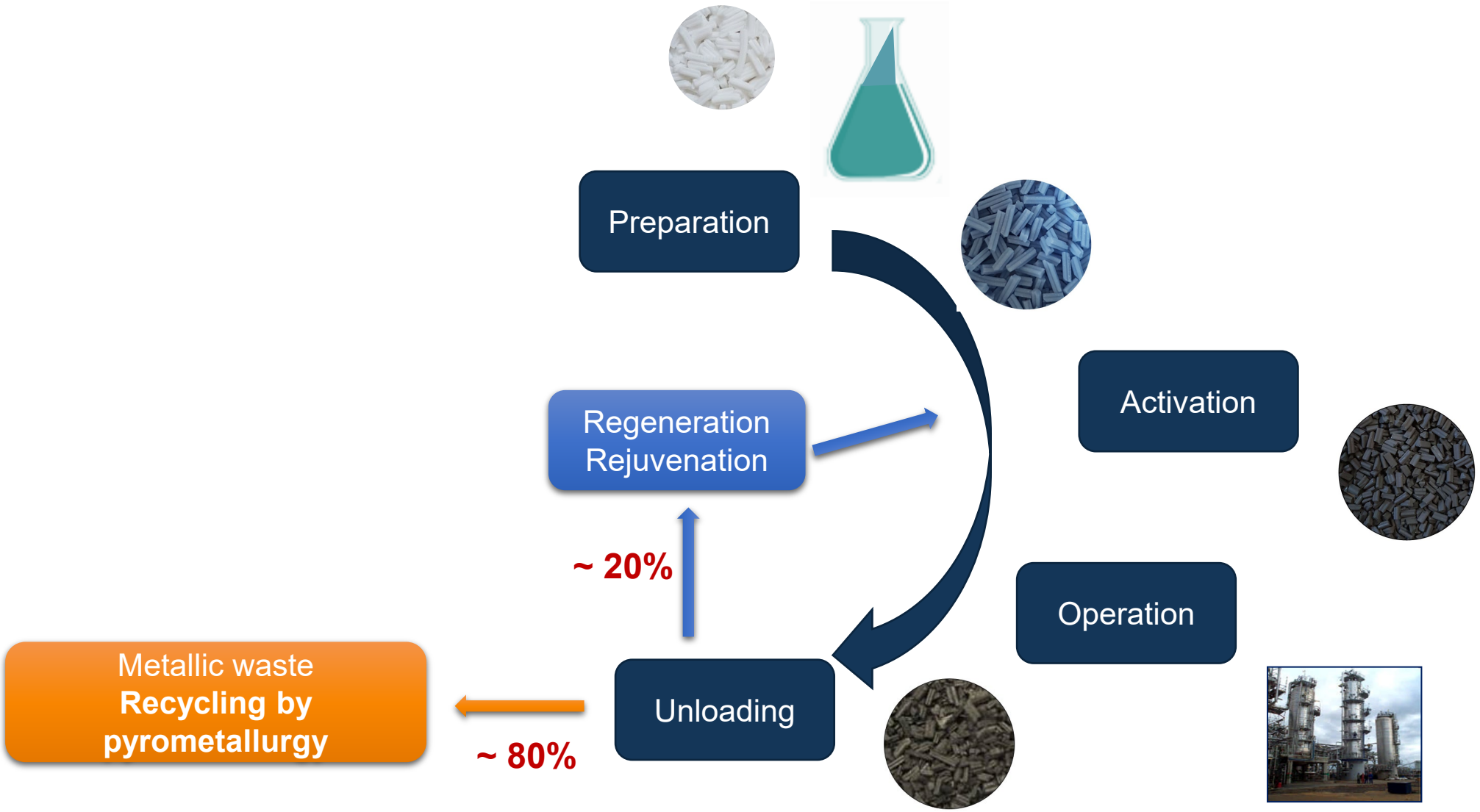


- => most HDT catalyst constituents are now part of EU critical materials list

Aluminium/Bauxite	**Coking Coal**	**Lithium**	**Phosphorus**
Antimony	**Feldspar**	Light rare earth elements	Scandium
Arsenic	Fluorspar	Magnesium	Silicon metal
Baryte	Gallium	**Manganese**	Strontium
Beryllium	Germanium	Natural Graphite	Tantalum
Bismuth	Hafnium	Niobium	Titanium metal
Boron/Borate	**Helium**	Platinum group metals	Tungsten
Cobalt	Heavy rare earth elements	Phosphate Rock	Vanadium
		Copper	**Nickel**

https://single-market-economy.ec.europa.eu/sectors/raw-materials/areas-specific-interest/critical-raw-materials_en (2023)

HDS CATALYST LIFE CYCLE: CURRENT CONTEXT



HDS CATALYST LIFE CYCLE: CURRENT CONTEXT

Objective: Improve the circular economy of HDT catalysts

Preparation

Activation

Operation

Unloading

~ 80%

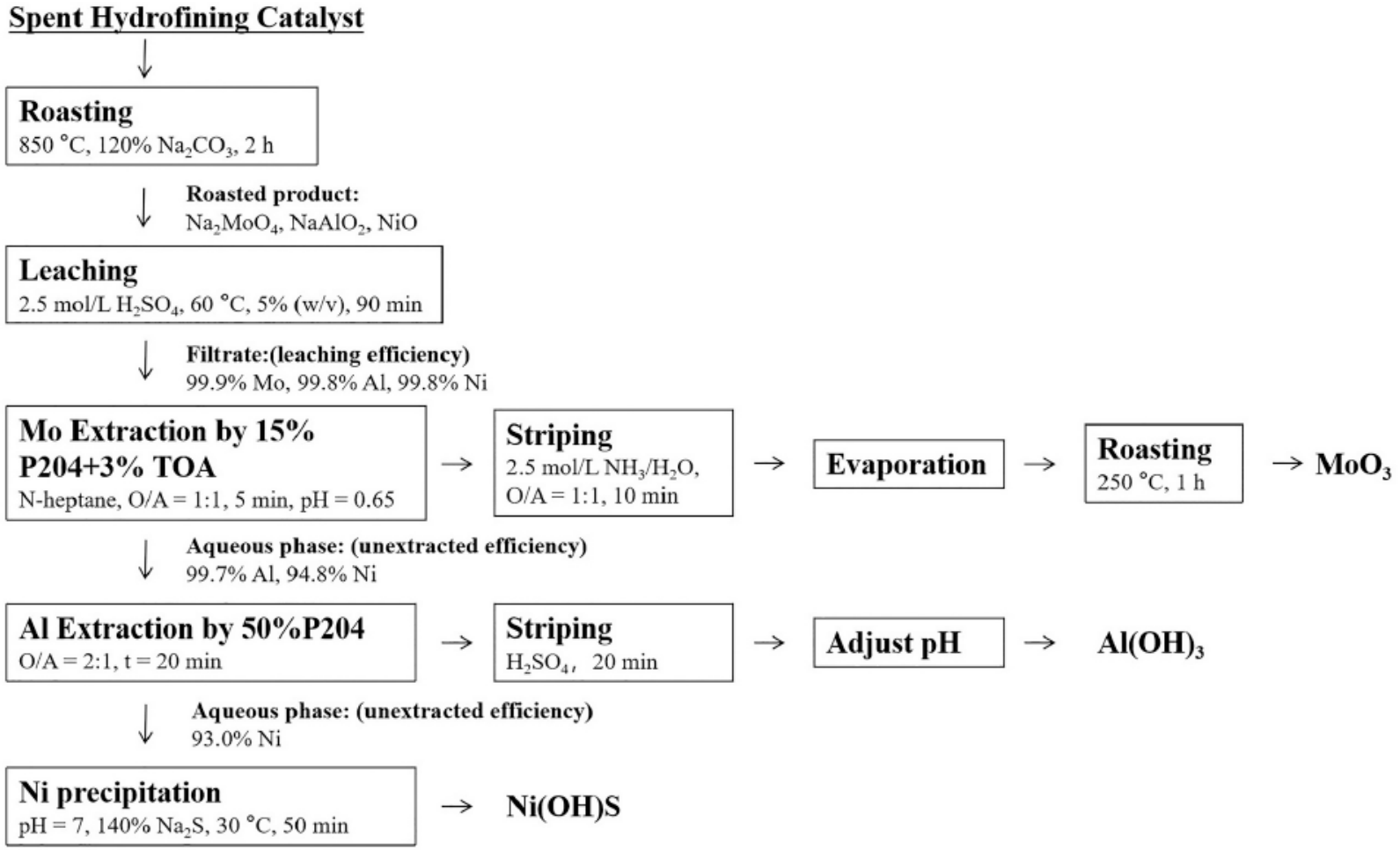
Metallic waste
Recycling by pyrometallurgy

~ 20%

Regeneration
Rejuvenation

Recycling

EXAMPLE OF FLOWSHEET FOR THE TOTAL RECYCLING OF ALL CONSTITUENT METALS FROM A SPENT NIMO HDT CATALYST



- Complete and complex hydrometallurgy scheme leading to extraction, separation and refining of all components of the catalyst
  - Molybdenum
  - Nickel
  - Alumina

Y. Cai et al. Hydrometallurgy 208 (2022) 105800 Comprehensive recovery of metals in spent Ni–Mo/γ–Al2O3 hydrofining catalyst

IFPEN IMPLEMENTATION

- An innovative opportunity to break with existing processes: recycle of polymetallic solutions
  - It is not necessary to separate metals from each other or from phosphorus.
  - Leaching with organic acids📖 = additives for catalyst preparation

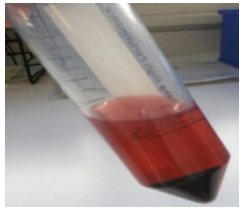
Regenerated catalyst

Organic Acid

Leaching

Filtration

Residual catalyst



Leachate

Evaporation

Polymetallic (Co,Ni)MoP impregnation solution

Impregnation

Catalyst with recycled metals

⇒ **Catalysts prepared with recycled metals deliver the same performance as catalysts with 100% fresh metals**

⇒ **Paving the way for a circular economy for these materials**

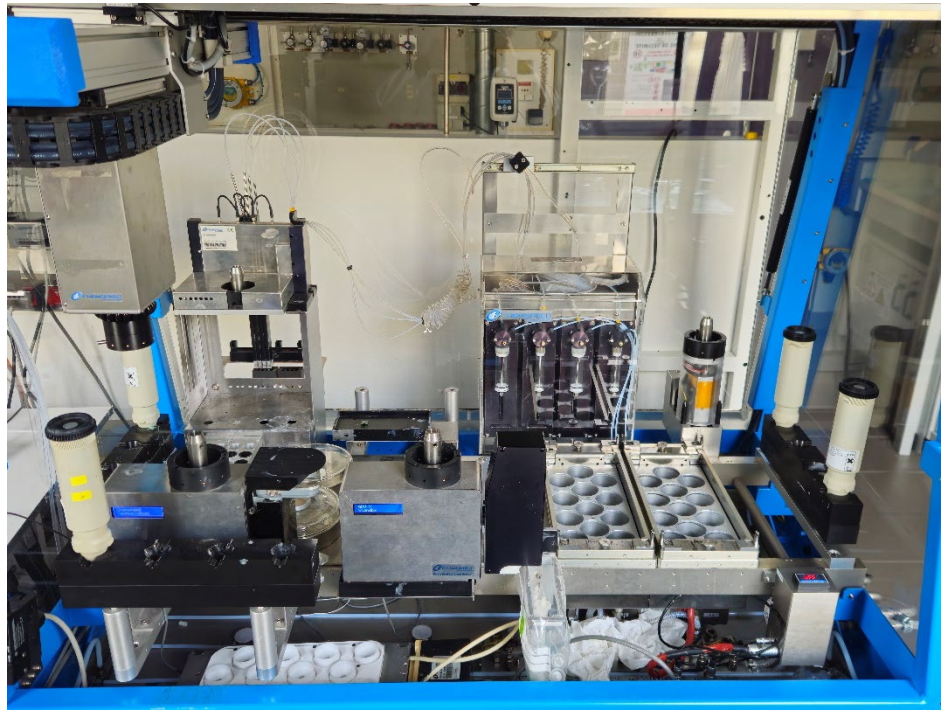
📖 Pathak A., Mani Vinoba M., Kothari R.(2020): Emerging role of organic acids in leaching of valuable metals from refinery-spent hydroprocessing catalysts, and potential techno-economic challenges: A review, Critical Reviews in Environmental Science and Technology

HIGH-THROUGHPUT LEACHING

LEACHING IN HIGH-THROUGHPUT EXPERIMENT

- « Chemspeed » automated tool used for catalyst preparation
  - Preparation of aqueous solution containing metal precursors by dilution (impregnation solution)
  - Dispense of the impregnation solution on an alumina support
  - Stirring for ageing ; drying

- Adapted for acid leaching of spent catalysts
  - Preparation of acid leaching solution by dilution
  - Dispense of acid leaching solution on spent catalysts
  - Stirring (+ heating)
  - Sampling of leachates
  - Drying of leaching residues



↳ **Validation of the protocol by comparison with lab experiments**

LEACHING IN HIGH-THROUGHPUT EXPERIMENT

- Step 1 : coding the automated protocol for leaching

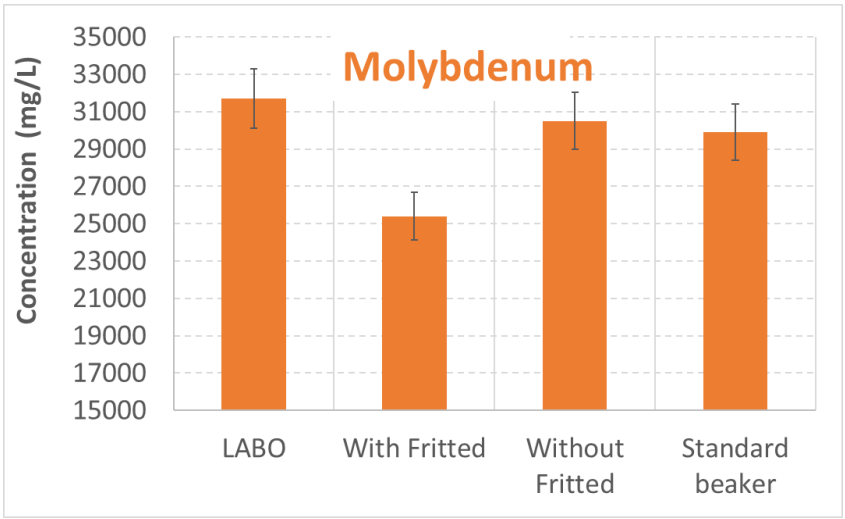
Task	Name	Parameter	Description	Estimated Time	Task Number
1	Initialisation	Execute Once		00 sec	1
2	Prép sol	Execute Once		07 min 56 sec	2
1	Dispense eau dilution	Execute Once		02 min 54 sec	2.1
2	Dispense sol mère	Execute Once		00 sec	2.2
3	Stir	Agitation ON on zone variable 'RackPrepSoll		02 sec	2.3
4	Wait	Waiting for 5:00 minutes		05 min 00 sec	2.4
5	Stir	Agitation OFF on zone variable 'RackPrepSol		00 sec	2.5
<insert sub tasks here>					
3	Lixiviation	Execute Once		02 hours 30 min 0	3
4	Prélèvement solutions MTX	Execute Once	OK² : maturation et sechage	16 min 00 sec	4
1	Transfer Volumetrically	Transfer liquid from Rack_Lixi to Rack_Stock_	Préciser les réglages lors du test avec	16 min 00 sec	4.1
<insert sub tasks here>					

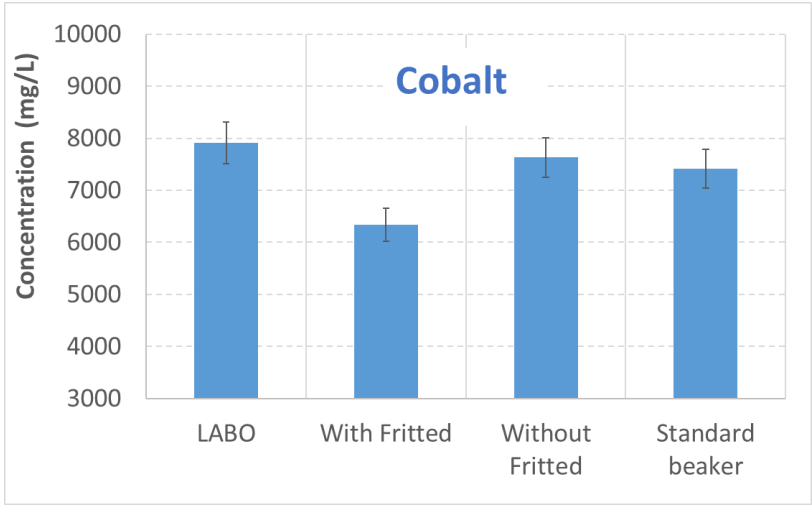
- Step 2 : validation of the protocol
  - Sampling of the leachate solution
    - Lab : filtration of the solution vs Chemspeed : sampling with a syringe
  - Geometry of the beakers
  - Stirring speed

LEACHING IN HIGH-THROUGHPUT EXPERIMENT
GEOMETRY OF THE BEAKER

- Standard beaker
- Beaker with a fritted glass filter
  - Facilitates the liquid sampling without the presence of fine particles

- Roasted spent CoMo catalyst
- Citric acid 180 g/L
- L/S= 3.2 ml/g
- 2.5h, room temperature
- Stirring speed 220 rpm



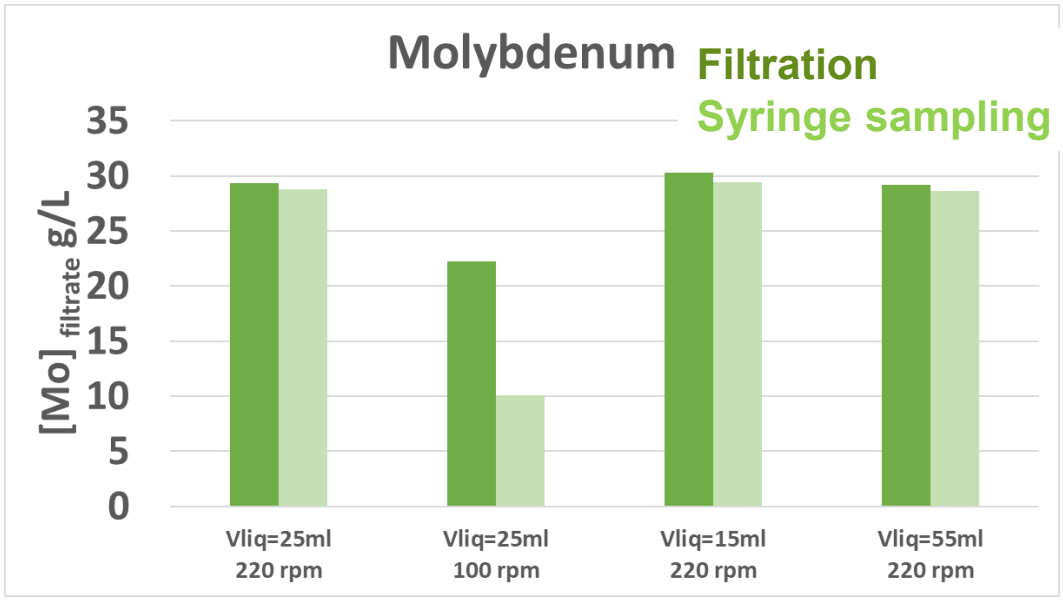


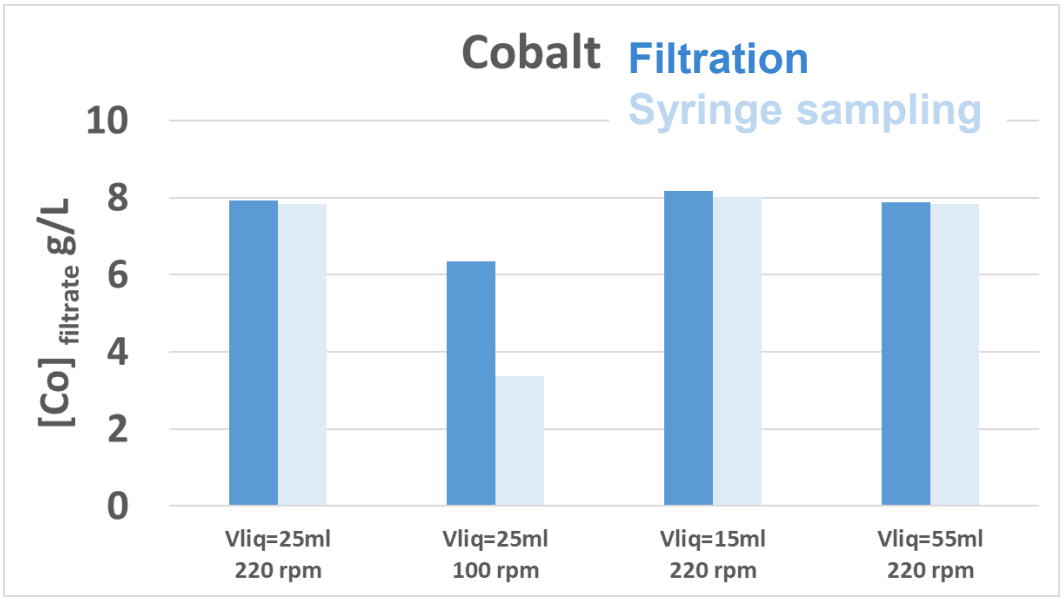
- Presence of the fritted limits the extraction. Bad diffusion of metals from solid to liquid
  - Problem of poor stirring

LEACHING IN HIGH-THROUGHPUT EXPERIMENT
EFFECT OF STRIRRING SPEED AND SAMPLING METHOD

- Stirring speed : 100 or 220 rpm
- Leachate solution recovery
  - Filtration on buchner
  - Sampling with syringe

- Roasted spent CoMo catalyst
- Citric acid 180 g/L
- L/S= 3.2 ml/g
- 2.5h, room temperature
- Standard beaker



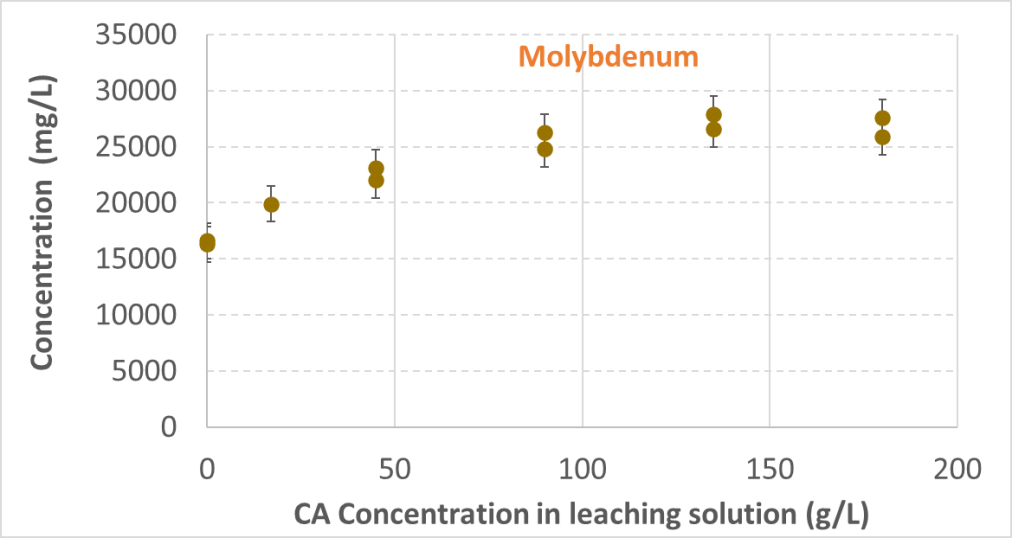


- Low stirring speed leads to low extraction rates, and heterogeneity of the solution concentration
- If high enough, no difference between filtration and syringe sampling : good homogeneity of the solution concentration
  - Whatever the liquid volume

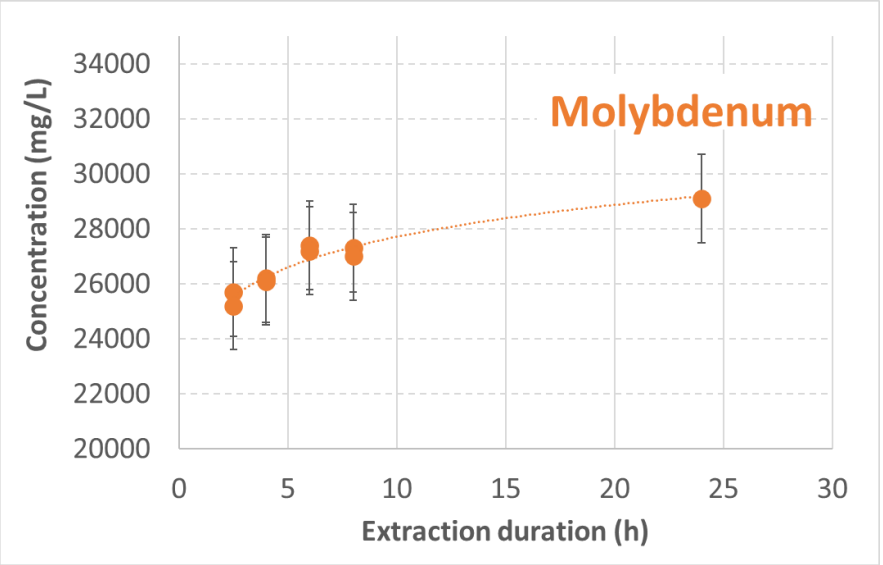
LEACHING IN HIGH-THROUGHPUT EXPERIMENT
FIRST SCREENING EXPERIMENTS

- Roasted spent CoMo catalyst
- L/S= 3.2 ml/g
- room temperature
- Standard beaker, 220 rpm

- Citric acid concentration (2.5h)



- Extraction duration (at [CA]=180g/L)



- 12 experiments performed in 3 hours !

CONCLUSION

- Development of an innovative route for circular economy of catalyst
  - Direct re-use of polymetallic leachate solutions to prepare catalysts

- Settlement of different tools to screen operating conditions for leaching
  - Automated tool for leaching
  - ICP analysis screening protocols
  - Can be used to screen operating conditions, catalysts pre-treatment protocols….

Innovating for a low-carbon and sustainable world

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