INSTITUT DE CHIMIE
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Ultrasound-assisted soil washing process for the **removal** of **heavy metals** from **clays**

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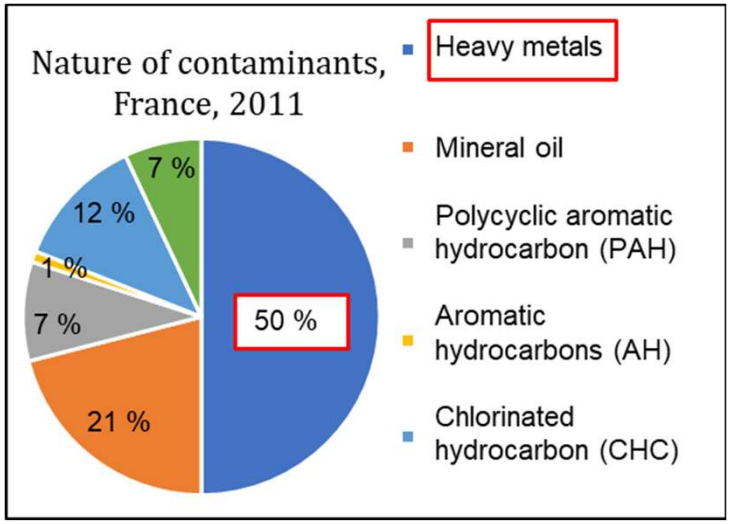
Context and problematic

Past human activities:

- Agriculture (pesticides, fertilizers…)
- Industrial activity (mining, paint production, battery production...)

→ **Source of trace metals harmful to humans and the environment**



Soil/gravel contaminated with heavy metals

Acid leaching
Electroremediation
Phytoremediation

→ Reusable solids + secondary waste

Alternative

Combining leaching + ultrasound (US) treatment

Objective:
A faster, more efficient process in milder conditions.

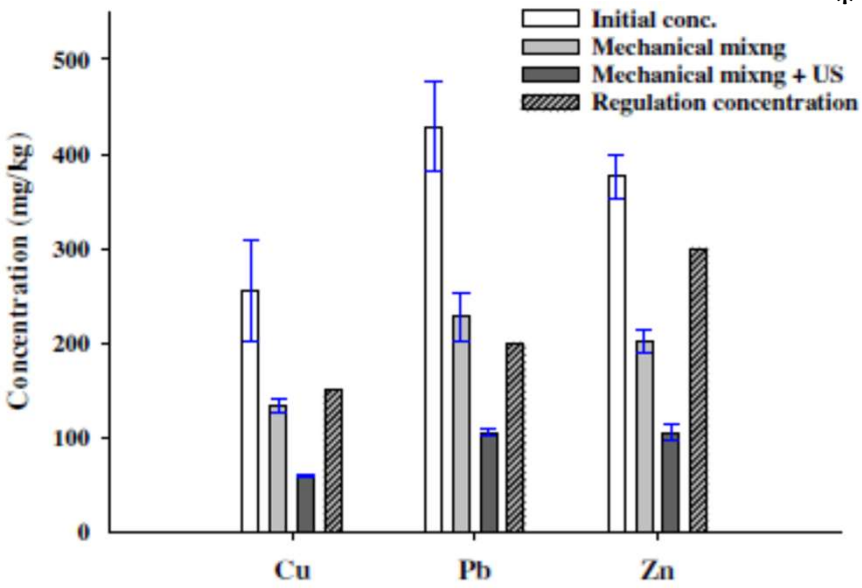
Limited knowledge

In the recent years

Only a few studies focused on combining leaching with ultrasound

Reference	Target metal(s)	Solvent
Choi et al., 2021	Cu, Pb, Zn	EDTA/HCl
Son et al., 2019	Cu, Pb, Zn	HCl
Park et al., 2017*	Cu, Pb, Zn	HCl
Kim et al., 2016	Cu, Zn	HCl
Hwang et al., 2007	Cu, Pb, Cd, Zn	EDTA/citric acid

*



(b) Soil : washing liquid = 1 : 3 (soil 300 g and 1 M HCl 900 mL)

Fig. 2. Heavy metals removal in mechanical and ultrasonic/mechanical soil washing processes using soil:liquid ratio of (a) 1:2 and (b) 1:3 (Washing time: 30 min).

US/Mixing > conventional mixing in terms of:

- ✓ removal efficiency
- ✓ consumption of chemicals

Attributed to :

- Better agitation (macroscale)
- Sonophysical effects (microscale)

However:

- Kinetic aspects neglected
- Poor soil characterisation

Choi, J., Lee, D., & Son, Y. (2021). *Ultrason Sonochem, 74*, 105574.

*Park, B., & Son, Y. (2017). Ultrason Sonochem, 35(Pt B), 640-645.

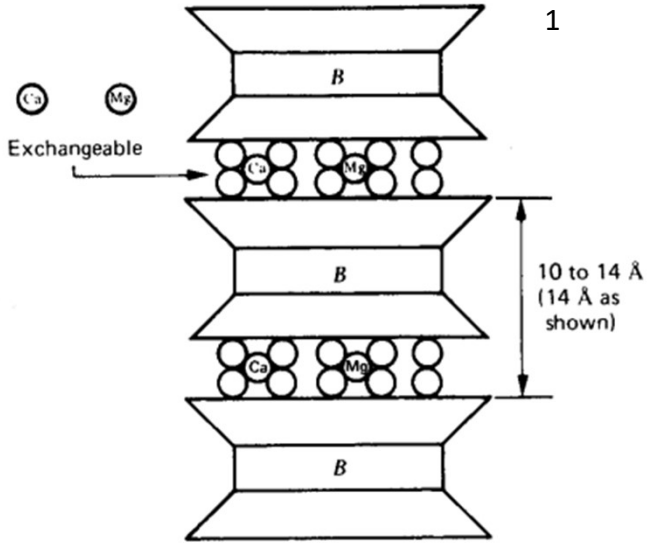
Son, Y., Lee, D., Lee, W., Park, J., Hyoung Lee, W., & Ashokkumar, M. (2019). *Ultrason Sonochem*, 58, 104599.

Kim, S., Lee, W., & Son, Y. (2016). *Jpn. J. Appl. Phys.,* 55(7S1), 07KE04.

Hwang, S.-S., Park, J.-S., & Namkoong, W. (2007). *J Ind Eng Chem*, 13(4), 650-656

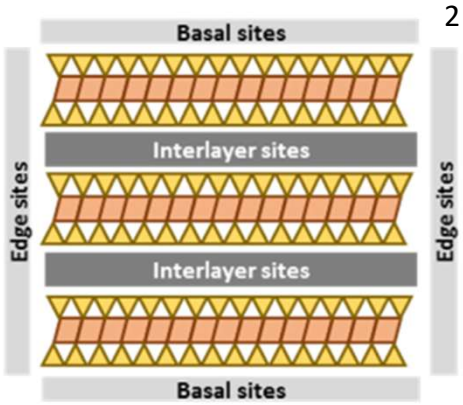
Vermiculite clay : soil model

Structure of a vermiculite (VER) layer *(Cation exchange capacity ≈ 100 – 250 mEq/100g[1])*

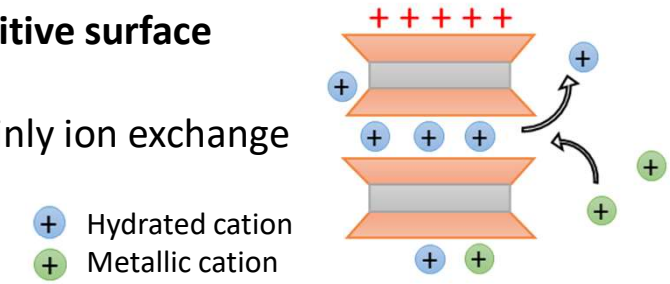


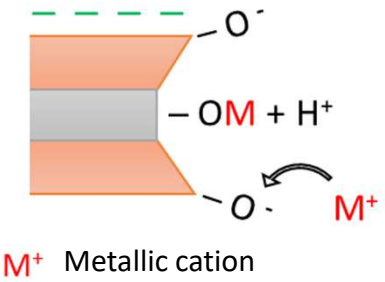
→ **Permanent negative charge** induced by isomorphic substitution

→ Balanced by the **adsorption of cations** within **interfoliar space** and **edges**

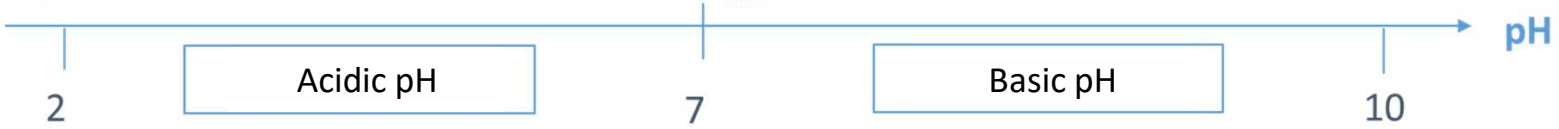


- **Positive surface**
- Mainly ion exchange





- Deprotonation of edge sites → **negative surface**
- **Complexation and precipitation** of metals

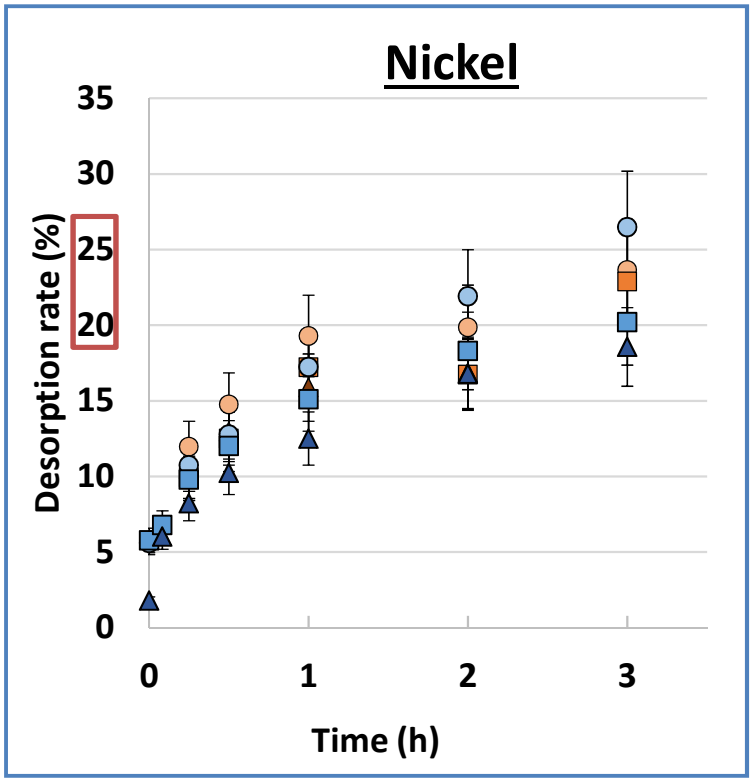


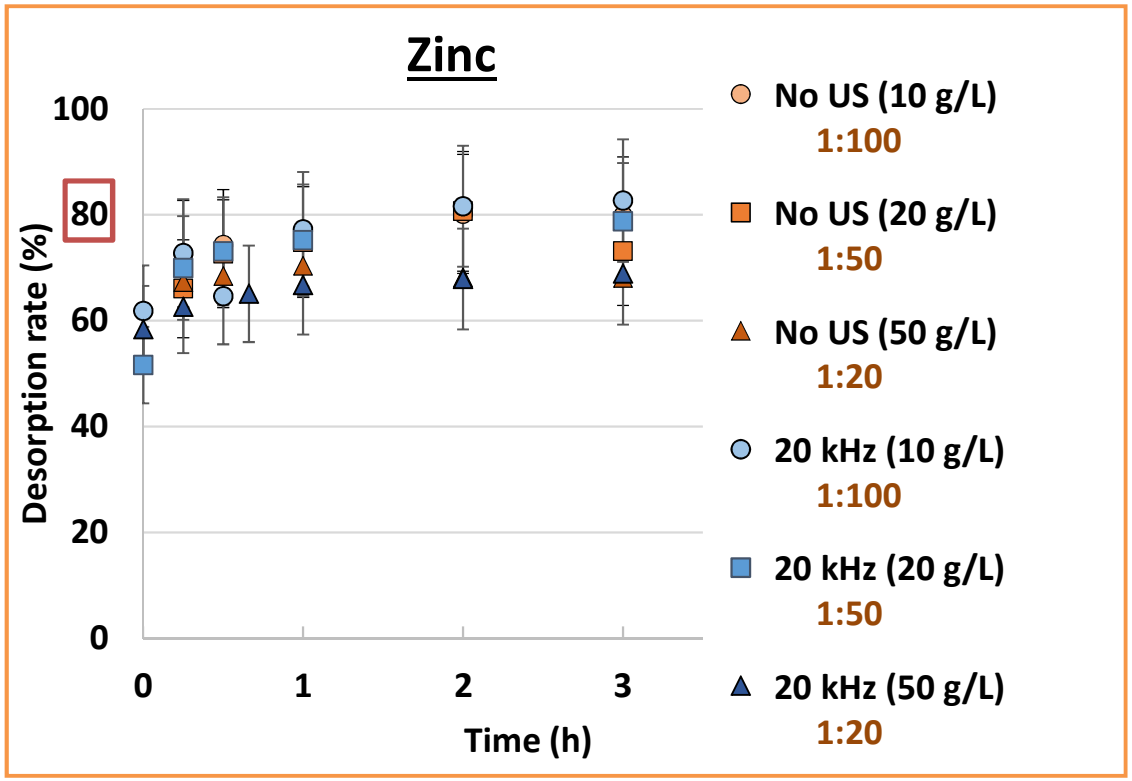
[1] *Mitchell, J. K. (1993). Fundamentals of soil behavior. New York, John Wiley and Sons, Inc.*

[2] *Yin et al., J. Hazard. Mater 326(2017) 47-53*

Desorption with HCl 0.1 M

Acid leaching desorption rates for **different S:L ($m_{vermiculite}$ / $V_{solvent}$) ratios**





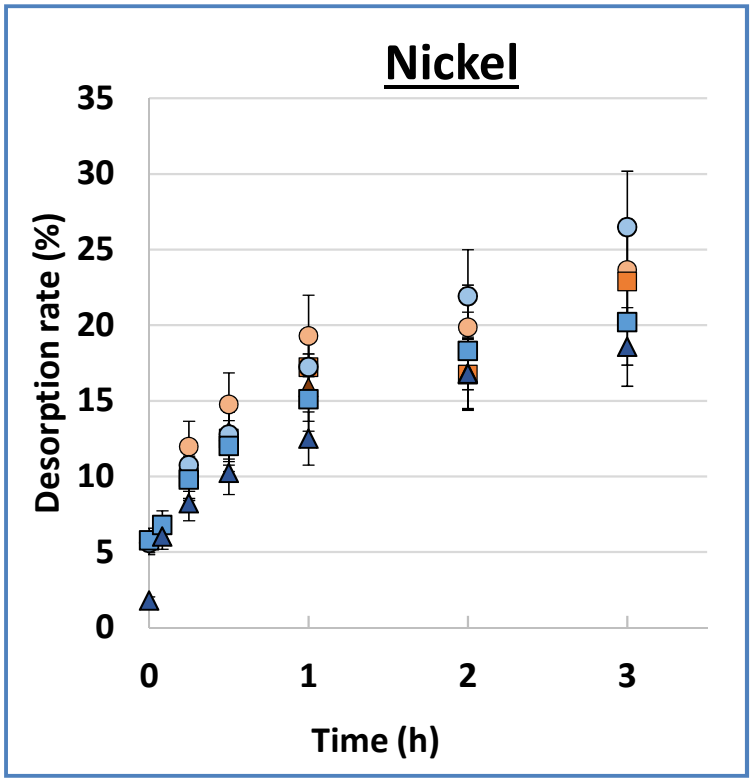
- Zinc is better desorbed than nickel
- The Zn^{2+} desorption kinetic is faster

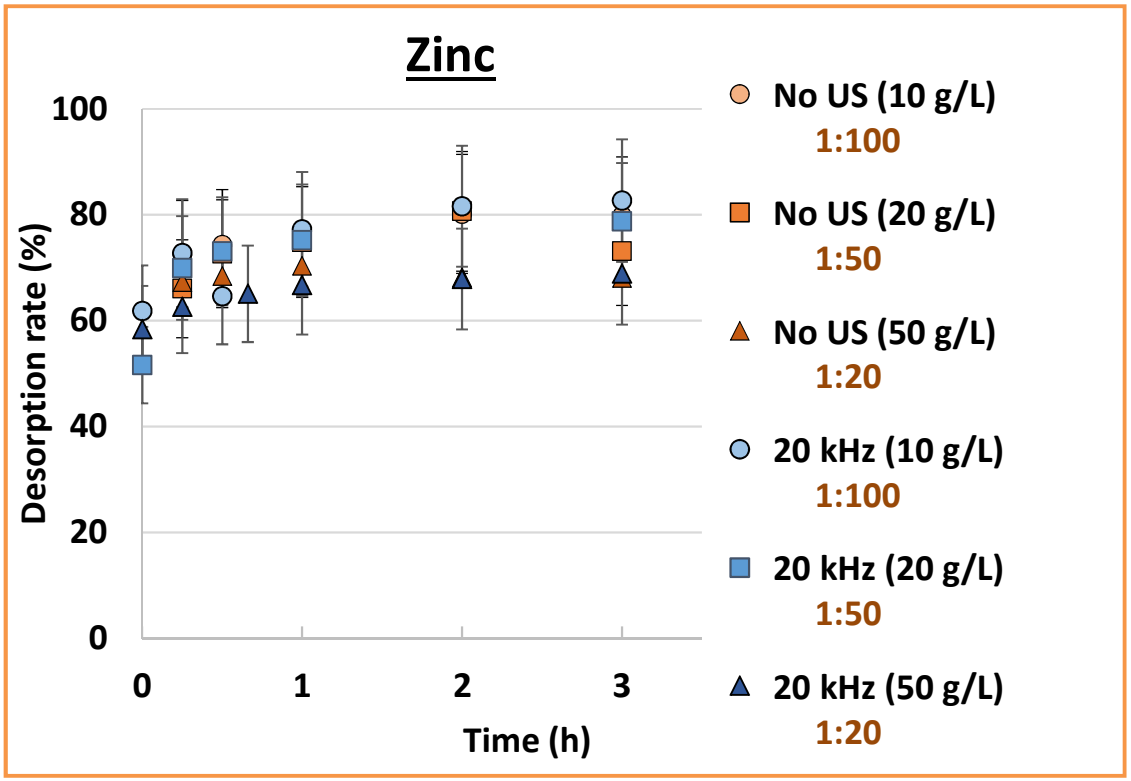
- Solid:liquid ratio :

When S:L ↗ the desorption rates slighly ↘

Desorption with HCl 0.1 M

Acid leaching desorption rates for **different S:L ($m_{vermiculite}$ / $V_{solvent}$) ratios**





- **No significant difference between silent conditions and US**

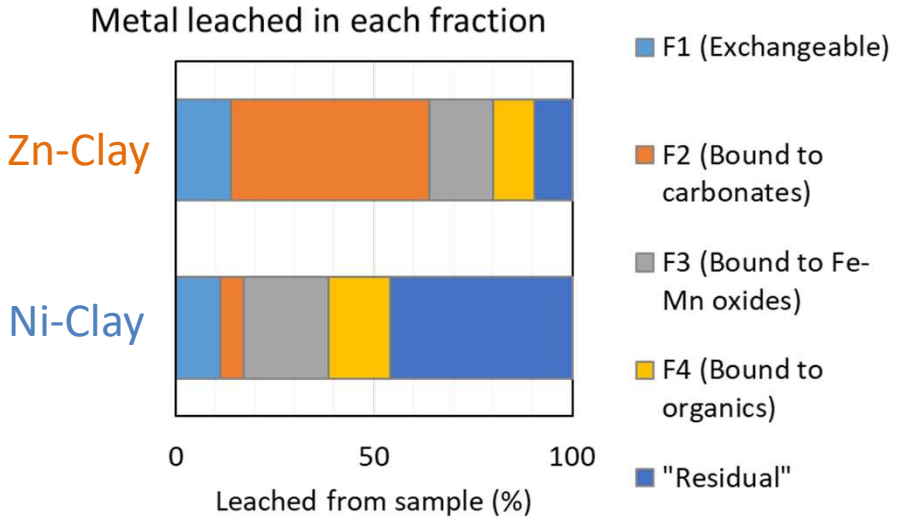
NO improvement !!!

- In maximum desorption rates
- In kinetics

Tessier Sequential extraction

Based on Tessier's protocol (1979)

Fraction	Reagent	Temperature and time
F1	8 mL **$MgCl_2$** (1 M; pH 7)	2 h - 25 °C
F2	8 mL **NaOAc** (1M; pH 5.0 with HOAc)	5 h - 25 °C
F3	20 mL **$NH_2OH{\cdot}HCl$** (0.04 M) in HOAc (25% v/v; pH 2 with HNO_3)	6 h - 96 ±3 °C
F4 - A	5 mL **H_2O_2** (30%; pH 2) 3 mL **HNO_3** (0.02 M)	2 h - 85 ±2 °C
F4 - B	3 mL **H_2O_2** (30%)	3 h - 85 ±2 °C
F4 - C	Cooled down, add 5 mL **NH_4Ac** (3.2 M) in 20%vol **HNO_3** Add 15 mL H_2O	30 min
Residual	Usually from the dissolution with **HF** In our case, we knew the initial metal concentration in the clay and we just subtracted F1+F2+F3+F4 to it.	



The metals don't bind to the same fraction :

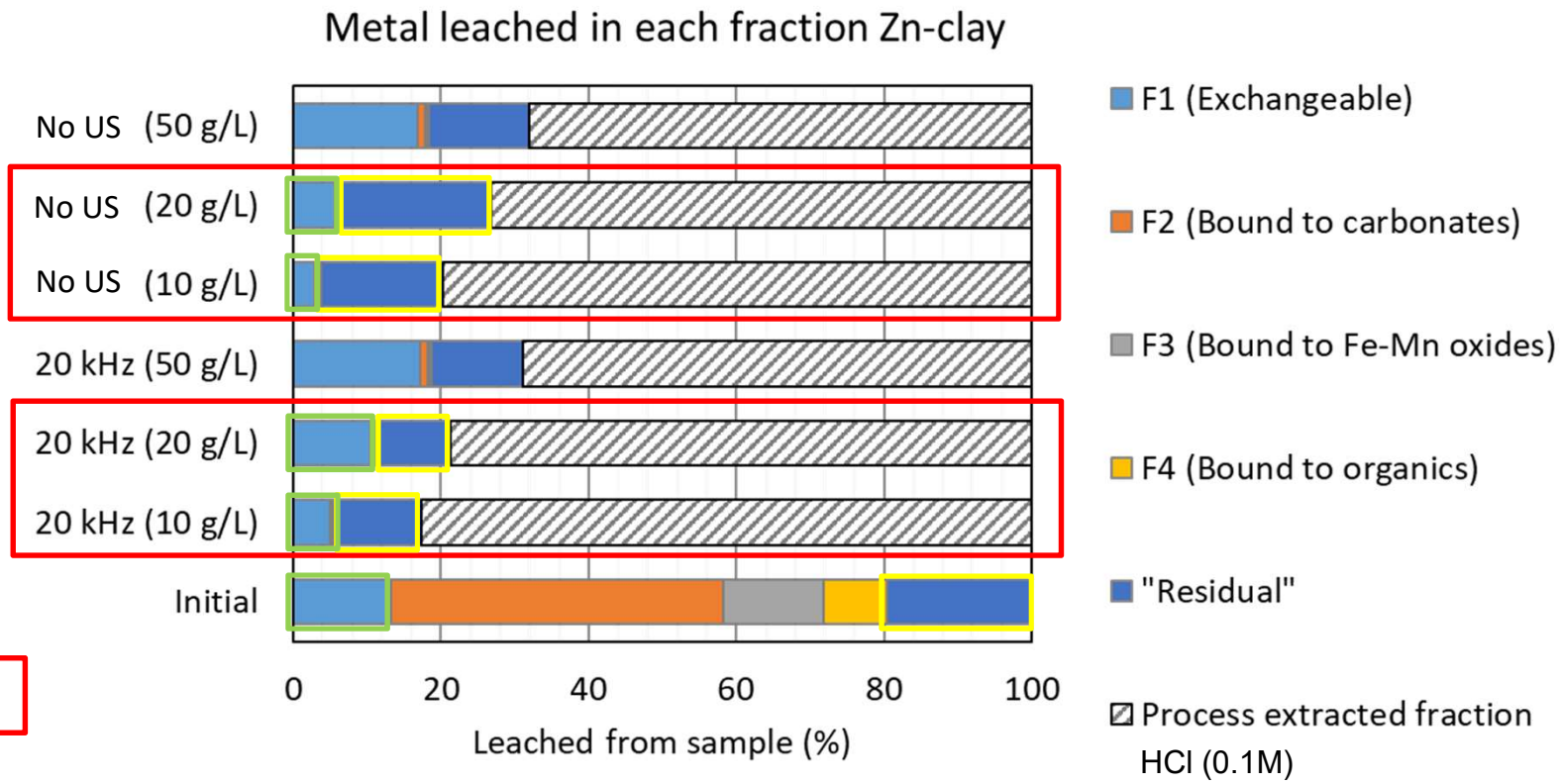
Zn^{2+} mostly binds to the carbonates
Ni^{2+} mostly binds to the residual fraction

→ consistent with the fact that Zn^{2+} desorbs better in HCl which dissolves carbonates

Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Anal. Chem., 51(7), 844-851.

Tessier for Zn-VER post-treatment

Fractions F2+F3+F4 disappear upon acidic treatment



For 10-20 g/L

The residual F5 fraction ↘ more under US (expected impact)

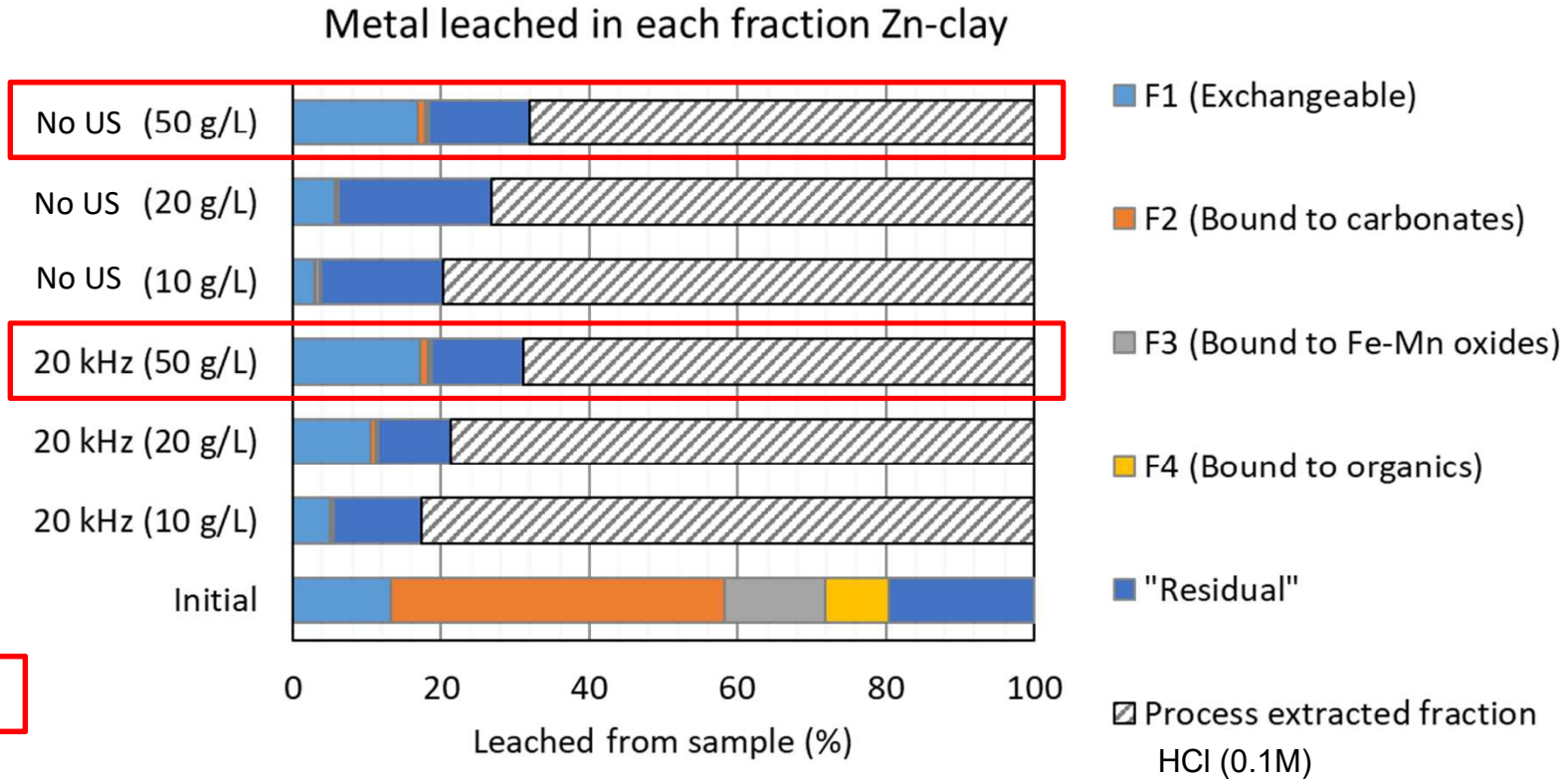
	S:L ratio	No US		US
% F5 removed	10 g/L	16 %	<	40 %
	20 g/L	0	<	51 %
	50 g/L	31 %	=	38 %

F5 Diminution masked by bigger F1 fraction with US

Particle size diminution with US → new adsorption sites
→ more exchangeable metal ions

Tessier for Zn-VER post-treatment

Fractions F2+F3+F4 disappear upon acidic treatment



For 50 g/L

The proportion of fractions <u>seems identical</u> with and without US

<u>F5 = similar</u>

With more particles
→Screening effect
→Efficiency of US ↘

<u>F1 increases</u>

Sonophysical effects + Probability of inter particle collision ↗

→ *Particle size diminution* → *More sites available*

Conclusions

Enhancement of metal desorption from soil is usually witnessed by **adding US** to the leaching process

Our particular case does not allow to draw the same conclusions since we observe the **same desorption rates with and without US**

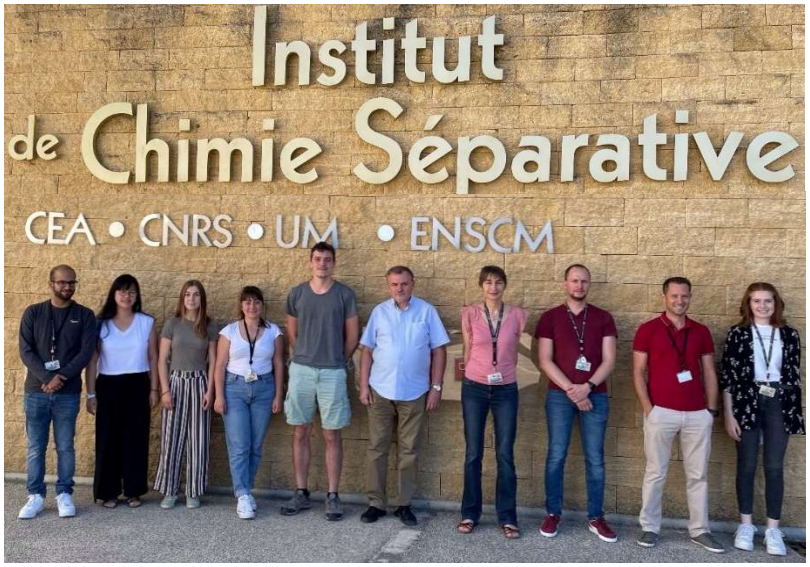
The **Zn-clay residual fraction F5 ↘ under US** but is conterbalanced by the **↗ of F1 exchangeable fraction** due to particle fragmentation → active surface ↗

Prospects

Switch to **HF US (362 kHz)** in order to **minimize mechanical effects** and thus fragmentation while **keeping positive effects from US**

Addition of stirring in order to work with **higher S:L ratios** and expect to see **positive effects of US** on the **removal efficiencies**

Thank you for your attention !



Laboratoire de
Sonochimie dans les
Fluides **C**omplexes

Laboratoire des
Procédés
Supercritiques et de
Décontamination

Thank you to

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