



In collaboration with  **AFESA**

Extensive research on the factors affecting the behaviour of heavy metals originating from pyrite ash in an estuarine area:

From lab and pilot test to remedial design

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Summary

- 1 *Injectis and the SPIN® Injection Technology*
- 2 *Context*
- 3 *Lab tests*
- 4 *Pilot test*
- 5 *Conclusions*



INJECTIS and the SPIN[®] injection technology

- Founded 2014
- Patented SPIN[®] injection technology
- Specialized in direct injections in heterogeneous and low permeability soils or complex geology



Dr. Eng. Jeroen Vandenbruwane
Managing Director



Patented SPIN[®] injection bit



Real time
control system



INJECTIS and the SPIN® injection technology

Manu-SPIN®



Macro-SPIN®



Delta-SPIN®



Maxi-SPIN® (2)



Micro-SPIN®



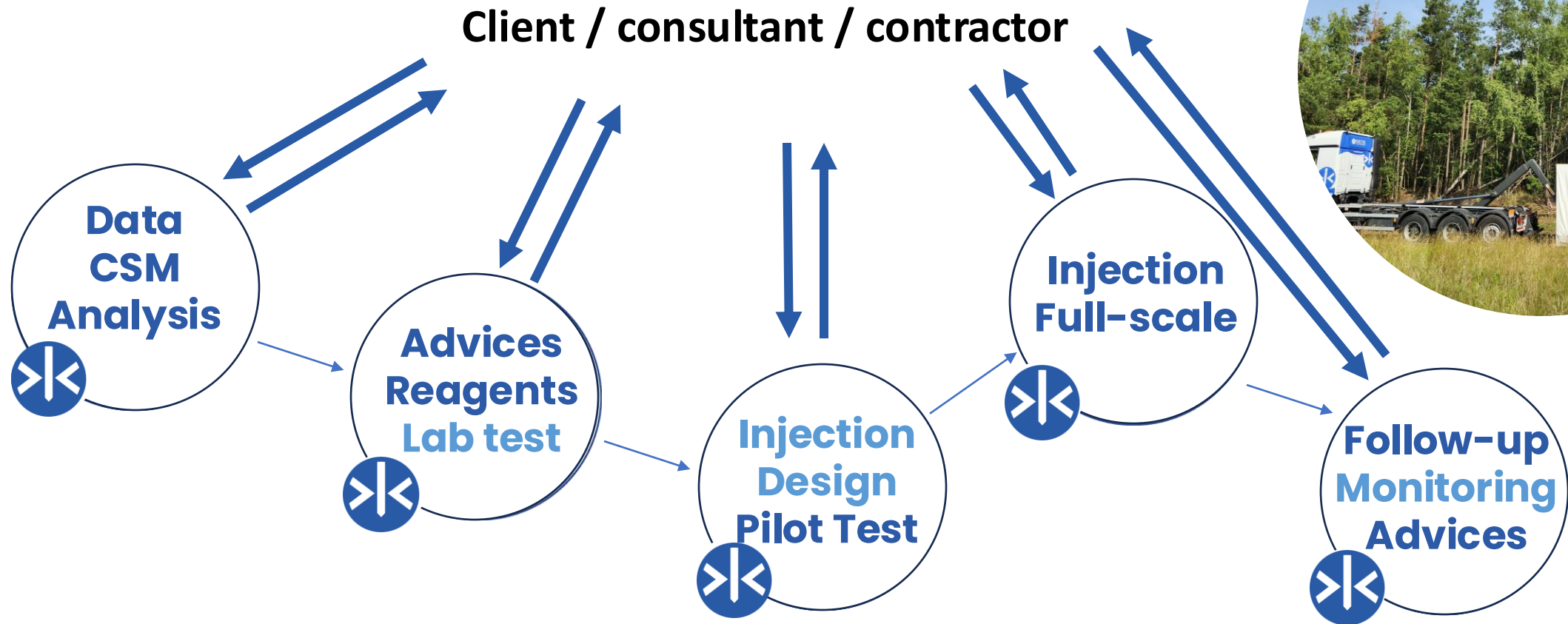
Multi-SPIN®



HD-SPIN®



INJECTIS and the SPIN[®] injection technology



INJECTIS and the SPIN® injection technology

- 170 projects carried out in Europe
- For consultants, remediation contractors, problem owners



Innovative solution for in situ soil remediation

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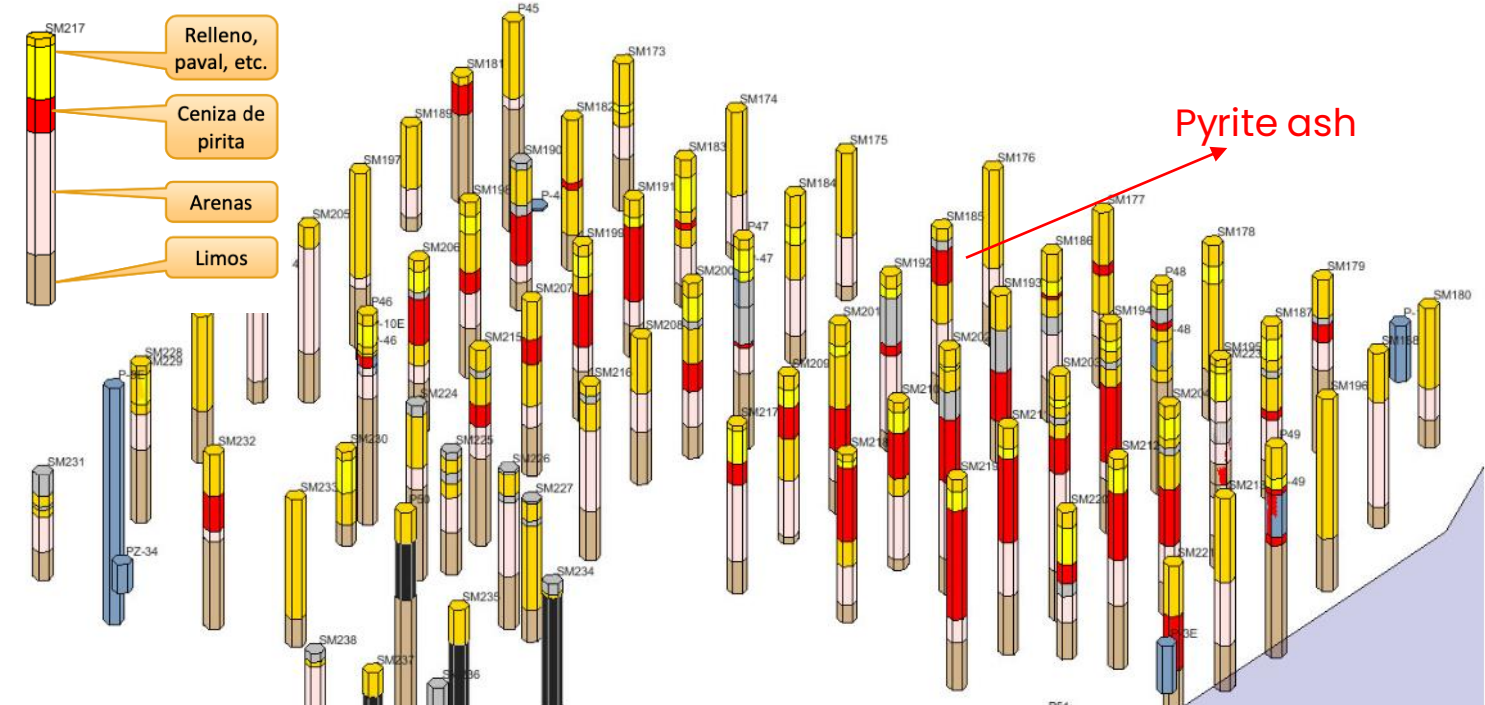
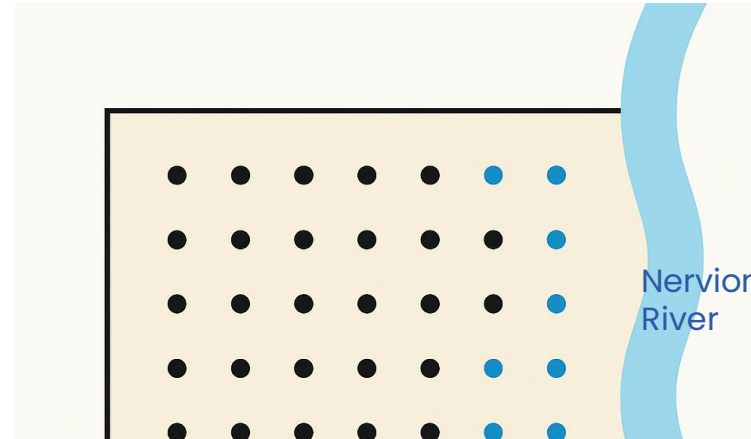


Context

SITE

- Bilbao (Spain)
 - Industrial production zone $\approx 5.000 \text{ m}^2$
 - Site **next to the Nervion river**
 - Potential influence of marine tides
-
- Former sulfuric acid production site
 - Heterogeneous **backfill** of **pyrite ash**
 - Contamination > **heavy metals GW/soil**
 - **Risks:** solubilization and mobility of HMs

Consultant :



Context

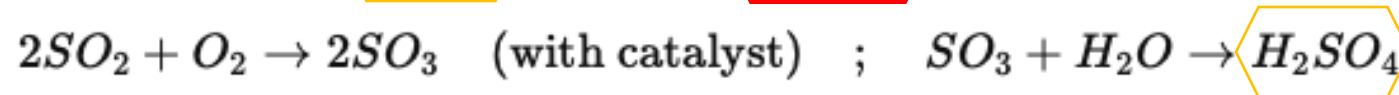
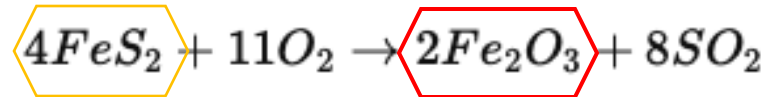


Pyrite mineral
 FeS_2

Pyrite ash
 $\rightarrow \text{Fe}_2\text{O}_3$ (hematite)

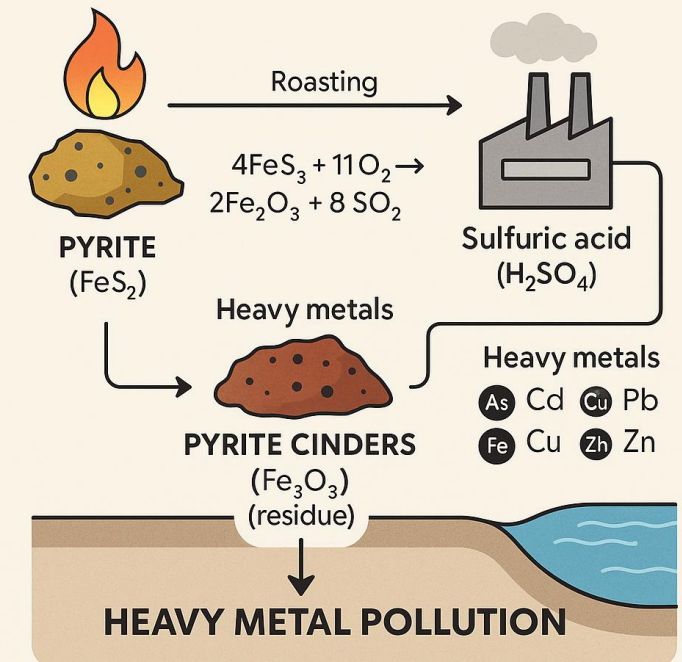
CONTAMINATION

- Origin : **sulfuric acid** (H_2SO_4) production by **oxidizing pyrite** (FeS_2):



- solid residue** produced = **pyrite ash**
 - rich in ferric oxide (hematite Fe_2O_3 + magnetite Fe_3O_4)
 - And Pb, Zn, Cu, As, Cd, etc. (natural HM present)

- ⚠ **Potentially highly acidic** (pH often < 3).
- ⚠ Contain **partially leachable metals** under natural conditions.
- ⚠ **Mobile metals**, leading to soil and GW contamination and dispersion risk.



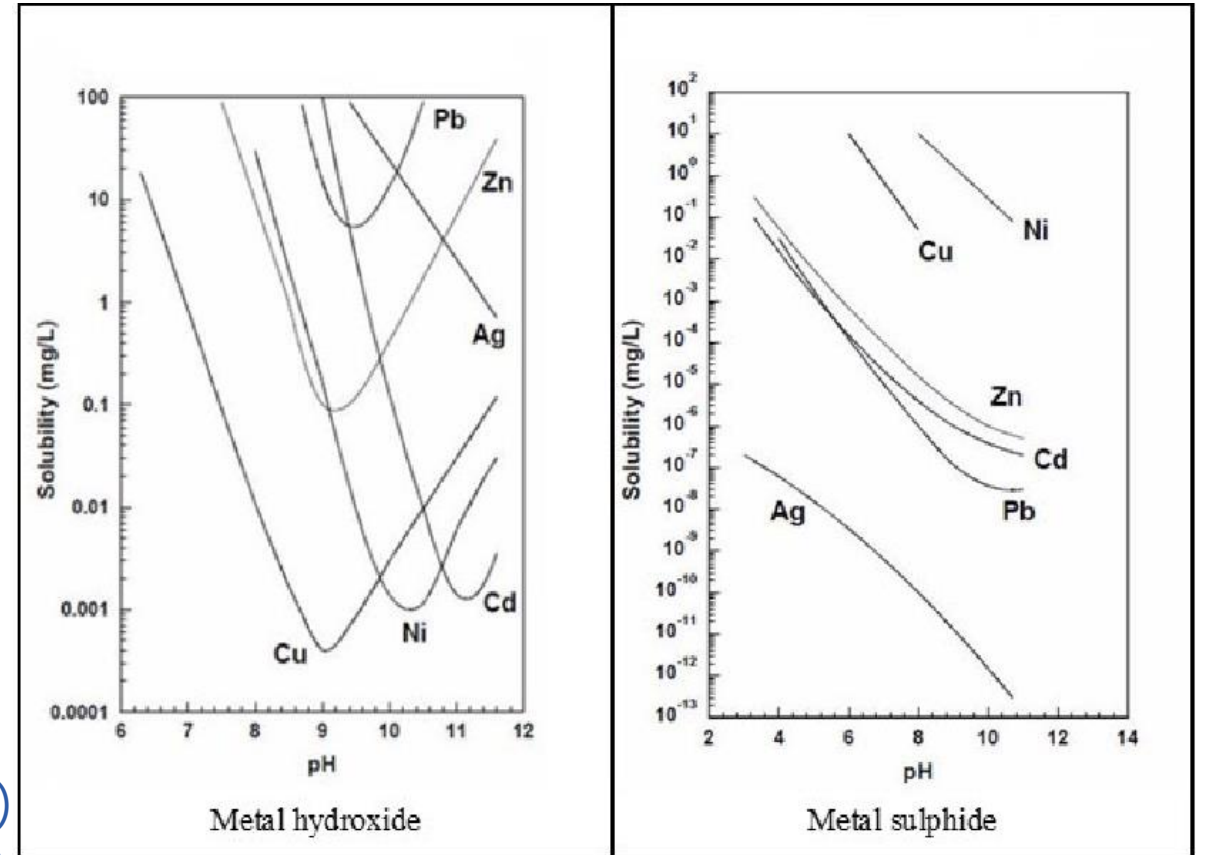
Context

CONTAMINATION

- **Mobile heavy metals**, leading to soil and GW contamination

As, Cd, Cu, Ni, Pb, Zn

- The contamination is mainly determined by their **solubility and mobility** which depends on the :
 - **pH**
 - existing **redox** potential (dissolved oxygen)
 - ionic strength and composition (chlorides, sulfates)
 - **presence** and content of « **(ad)sorbent** » materials (including cation and anion exchange capacity; CEC and AEC)



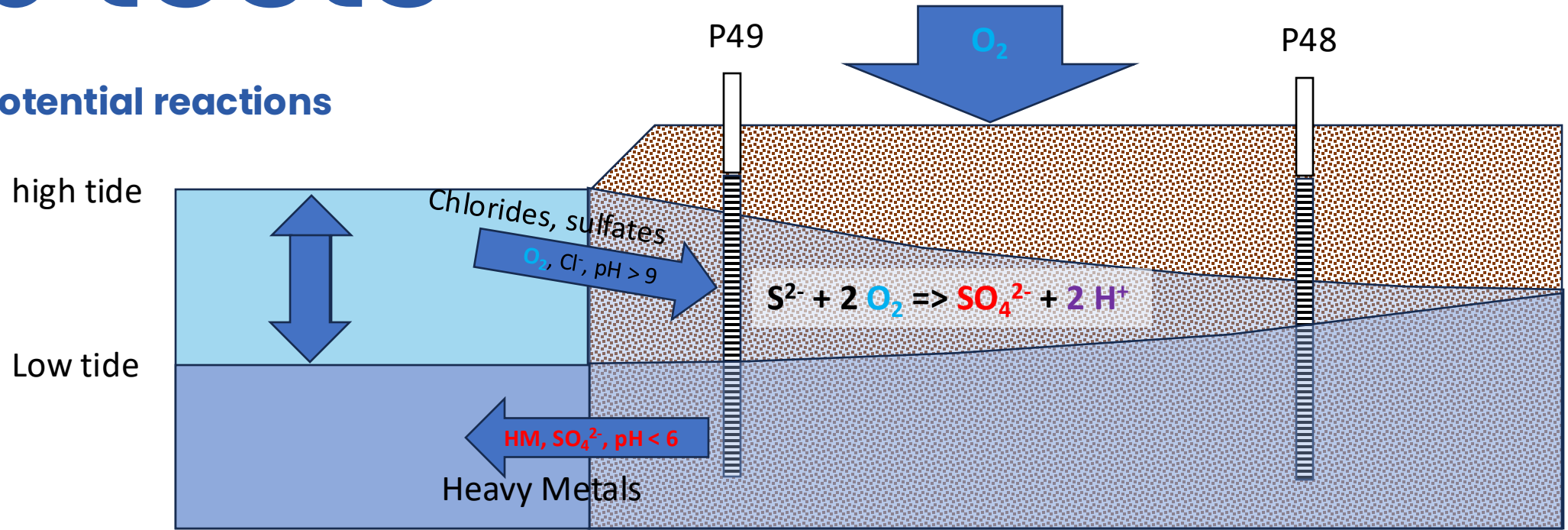
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Lab tests

Occuring potential reactions



Working hypotheses of HM solubilization :

- ❖ Oxygenation / redox ?
- ❖ pH : Acidification ?
- ❖ Chlorides (saline sea water entrance) ?
- ❖ Anion Exchange Capacity ?



NJECTIS

Innovative solution for in situ soil remediation

Lab tests

 **Preliminary lab tests** – before stabilization test

Based on **HYPOTHESES** on HM solubilization :

1. Oxygenation :

- **Oxygenation does not have a significant effect** on heavy metal mobilization
- **Acid pH** seems to be significant for HM solubilization
- **Chlorides** concentrations = influence HM Solubilization

2. Chlorides (addition KCl) :

- **Chlorides** ≈ Sea water entrance
- **Significantly increases** the HM Solubilization
- Acid pH confirmed to influence HM Solubilization
- USZ is a source of HM through the lixiviation process



	Units	Blank 1	Blank 2	Treat 1	Blank 3	Blank 4	Blank 5
Groundwater	400 mL	P49	P49	P49	P48	P48	P48
Soil	100 cm ³	-	SS SM194	SS SM194	USS SM194	SS SM194	-
Aeration	8 days	no	no	yes	no	no	no
pH	-	5,49	6,10	≈ 6,39	6,44	7,05	6,58
ORP	mV	186,00	89,20	≈ 87,20	114,60	90,60	81,46
EC	μS/cm	9 400	9 380	9 260	830	1 551	5 498
Arsenic (As)	μg/L	<5,0	560	≈ 190	<5,0	34	<5,0
Cadmium (Cd)	μg/L	42	26	≈ 39	24	7,6	1,3
Chromium (Cr)	μg/L	<1,0	<1,0	<1,0	<1,0	<1,0	<1,0
Copper (Cu)	μg/L	940	25	≈ 7,6	2800	<5,0	5,3
Mercury (Hg)	μg/L	<0,050	<0,050	<0,050	<0,050	<0,050	<0,050
Nickel (Ni)	μg/L	39	120	≈ 240	330	70	<5,0
Lead (Pb)	μg/L	270	710	≈ 130	940	100	<5,0
Zinc (Zn)	μg/L	5 100	18 000	≈ 18 000	4 400	7 500	220
Sulfate	mg SO ₄ /L	2 500	2 400	≈ 2 400	1 000	1 900	1 800
Chloride	mg/L	5 730	5 140	≈ 5 120	12	280	320

SS: Saturated Soil = Zona Saturada; USS: Unsaturated Zone = Zona no Saturada

Lab tests

 **REAGENTS RESEARCH** for the stabilization lab test

Key Properties of Selected Reagent(s):

- ☐ can reduce O₂ intrusion (?) (by solidification or impermeabilization)
- ☐ can reduce Cl⁻ intrusion (by solidification or impermeabilization)
- ☐ **raise the pH (precipitation)**
- ☐ raise the CEC (Cation Exchange Capacity) (by adsorption)

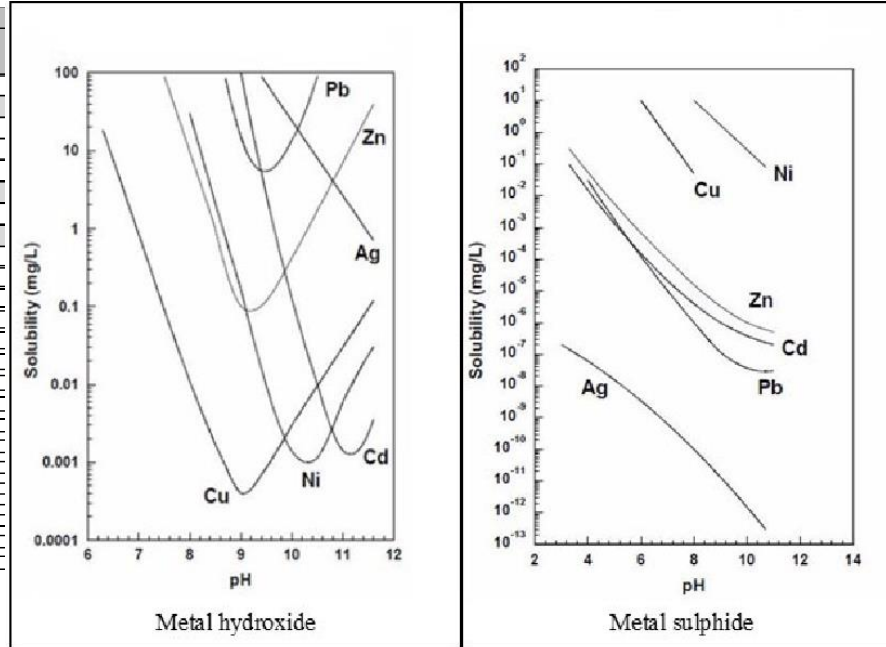
We decide to test 3 different reagents for the **stabilization test**

1. **Silicate** (**Na₂SiO₃**)
2. **Aluminate** (**NaAlO₂**)
3. **Cement** (**Portland**)

Lab tests

Stabilization effect on Unsaturated Zone (USZ) and Saturated Zone (SZ)

Saturated zone		
blank	no acid	no aluminate
sodium silicate	no acid	aluminate to pH 8,5
sodium silicate	no acid	aluminate to pH 8,5
sodium silicate	5 mL H2SO4	aluminate to pH 8,5
sodium silicate	10 mL H2SO4	aluminate to pH 8,5
sodium silicate	15 mL H2SO4	aluminate to pH 8,5
sodium silicate	20 mL H2SO4	aluminate to pH 8,5
sodium silicate	2 mL H2SO4	aluminate to pH 8,5
sodium silicate	4 mL H2SO4	aluminate to pH 8,5
sodium silicate	6 mL H2SO4	aluminate to pH 8,5
sodium silicate	8 mL H2SO4	aluminate to pH 8,5
sodium silicate	2,5 g NaHCO3	aluminate to pH 8,5
sodium silicate	5 g NaHCO3	aluminate to pH 8,5
sodium silicate	10 g NaHCO3	aluminate to pH 8,5
sodium silicate	20 g NaHCO3	aluminate to pH 8,5
blank	7,5 g NaHCO3	aluminate to pH 8,5
portland cement (60 g/m)	7,5 g NaHCO3	aluminate to pH 8,5
portland cement (100 g/m)	7,5 g NaHCO3	aluminate to pH 8,5
portland cement (160 g/m)	7,5 g NaHCO3	aluminate to pH 8,5
portland cement (200 g/m)	7,5 g NaHCO3	aluminate to pH 8,5
portland cement (260 g/m)	7,5 g NaHCO3	aluminate to pH 8,5



	pH_initial	pH_after acid	pH_after acid equilibrium	pH_end	pH_end (shaken)
7500	6,77	0,05	11,49	-	solid
<10	7,2	-	9,4	0,9	get after sulfuric acid
41	6,83	1,18	solid	-	solid
<10	6,85	1,19	12,82	0,3	12,82
<10	6,75	1,19	12,79	0,19	7,65
<10	6,57	1,19	12,57	0	12,57
26	6,55	1,19	12,52	0	8,96
160	6,49	1,19	12,93	0,94	12,93
190	6,57	1,19	12,93	0,59	7,21
<10	6,52	1,19	4,12	1,4	4,12
69	6,59	1,19	3,97	0,21	3,97
<10	6,56	1,19	12,53	0,27	12,53
19	6,44	1,19	12,72	0,02	9,82
11	6,43	1,19	10,78	0,83	10,78
<10	6,54	1,19	11,02	0,75	4,12
53	6,5	1,19	6,62	5,44	6,7
75	6,36	1,19	6,34	12,4	12,4
180	6,54	1,19	6,33	12,64	12,64
250	6,36	1,19	6,44	12,77	12,77

Results :

→ Significant reductions in **Ni, Pb, and Zn** were observed **with many treatments**, often significantly below blank values.

→ **pH is a key factor** in stabilization (best result at moderate alkaline **pH: 9,2**)

→ **Final pH after stabilization** is the most relevant indicator

→ **Best results of stabilization for**

→ **USZ : Sodium Aluminate + sulfuric acid**

→ **SZ : Sodium Aluminate + sulfuric acid OR without acid**

→ Results confirmed by lixiviation column test

→ **BEST : Sodium Aluminate alone (USZ + SZ)**

⇒ Co-precipitation/co-agulation, surface complexation, inclusion in crystal structure, adsorption (Fe-Al oxy-hydroxides)

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Pilot test

Sodium aluminate injection test

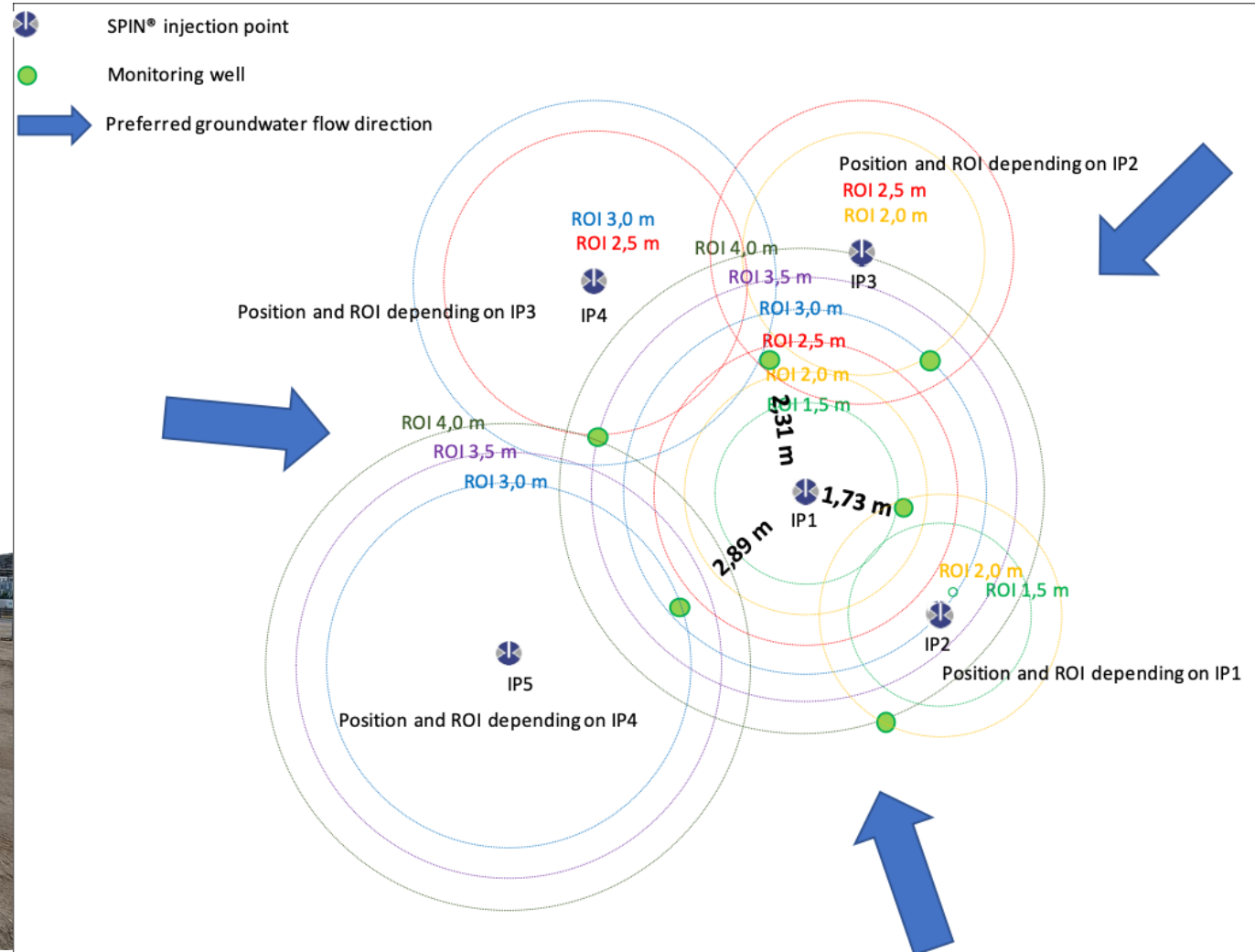
→ Preliminary “on site” lab tests:

- ❖ **pH titration :**
 - on slurry samples (Soil + GW)
 - 2 different depths : USZ and SZ
 - evolution 30 min/1H/2H/24H/15 days
- ❖ **NaAlO₂ dosage determination > objective : pH 9,2**
- ❖ **Applied dosage**
 - USZ dosis ≈ SZ dosis
 - = 10% Sodium Aluminate



Pilot test

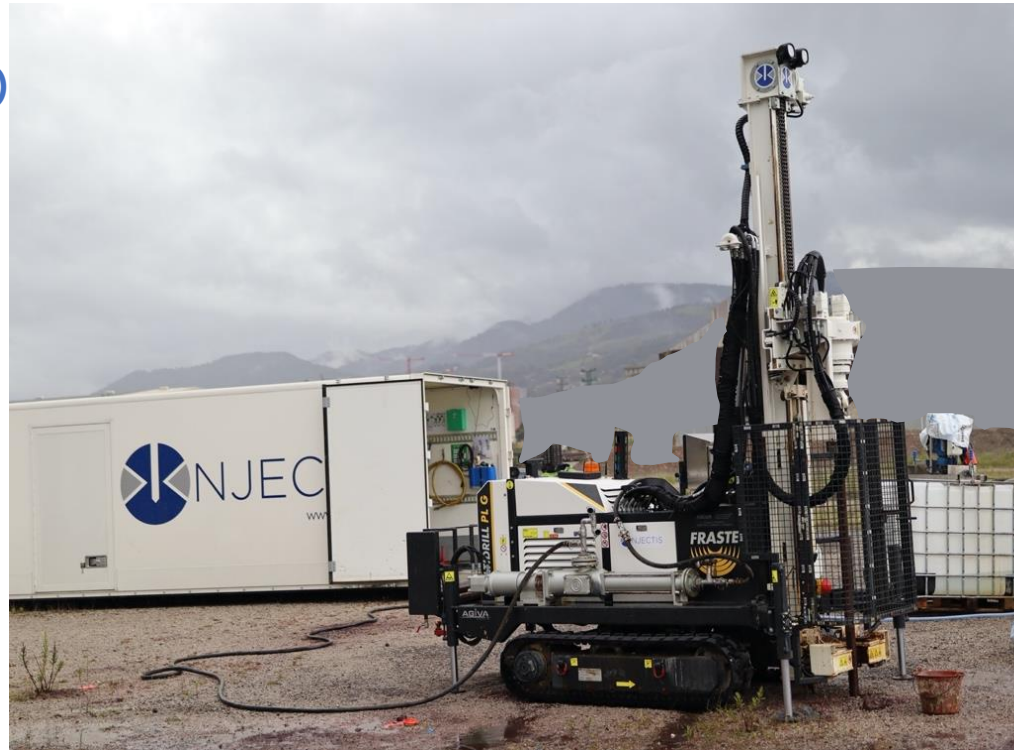
Injection design



Pilot test

Results : Injections

- ❖ Injection bottom-up :
 - ❖ 4,5 – 1,5 m-bgl
 - ❖ 1000 L/meter (3.000 L/point)
 - ❖ IP5 → up till 2.000 L/m (6.000 L/point)
 - ❖ 10% of Sodium Aluminate
- ❖ ≈ 15.000 liters in total
- ❖ ROI reached : up to 3 m



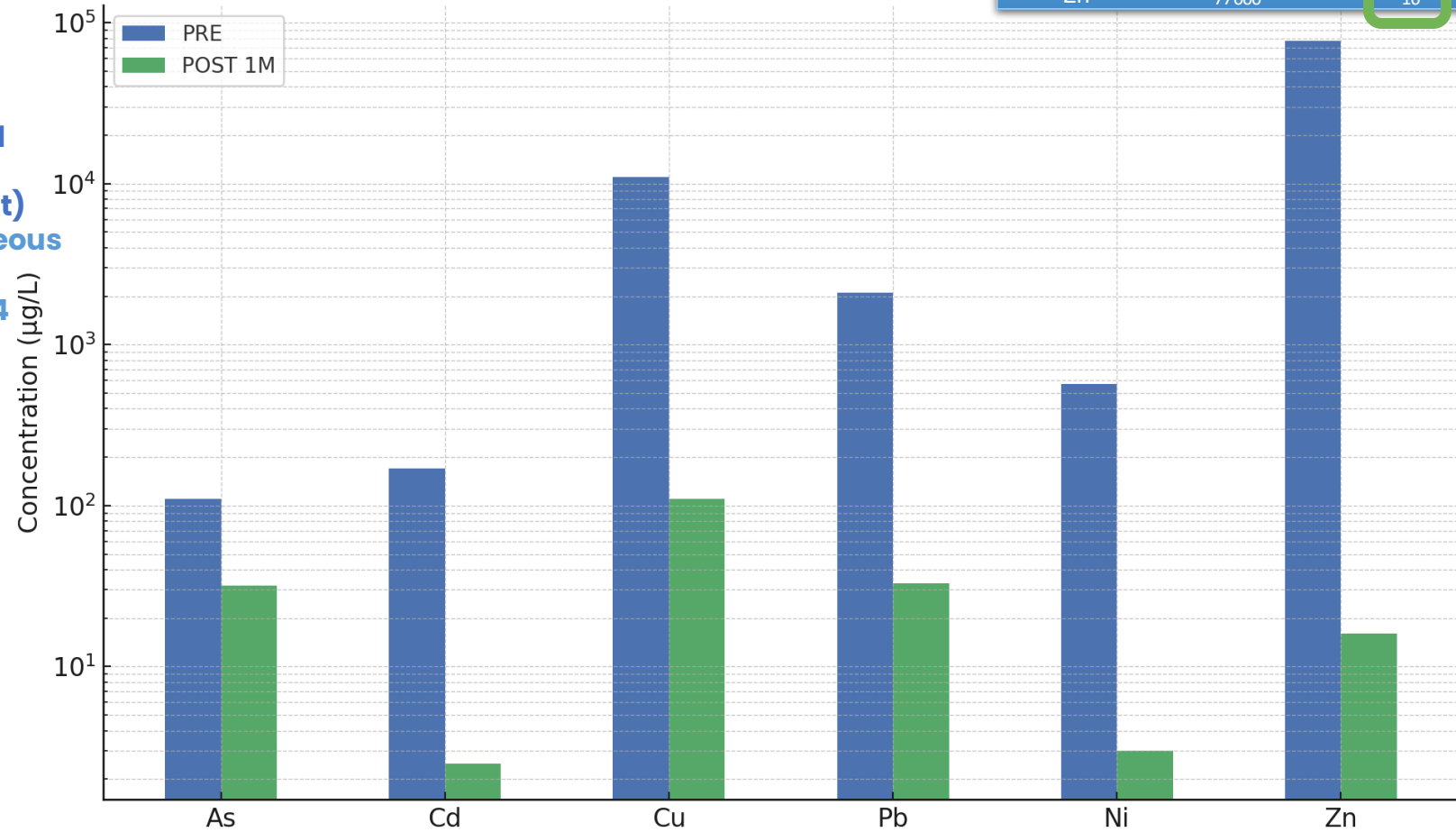
Pilot test

1 month after injection

	PRE	POST 1M
As	110	32
Cd	170	2.5
Cu	11000	110
Pb	2100	33
Ni	570	<3
Zn	77000	16

Results : concentrations

- ❖ Significant decrease observed
- ❖ Better effect in PC5
 - ❖ Where pH : 8,5 (9,2 target)
 - ❖ Distribution + homogeneous
- ❖ Same Results for PC3
- ❖ Lower decrease in PC1,PC2,PC4



Pilot test

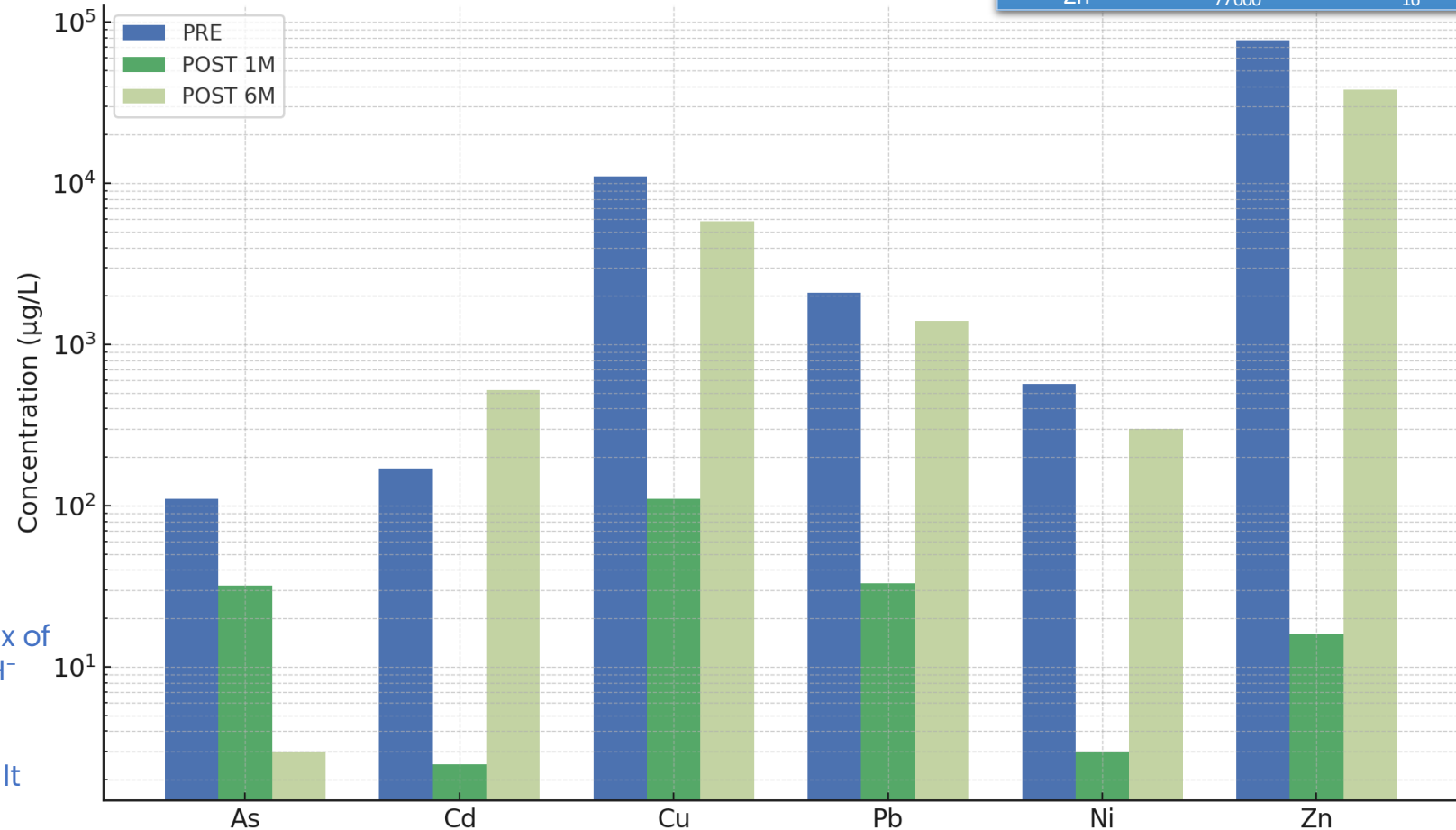
6 months after injection

	PRE	POST 1M	POST 6M
As	110	32	3.0
Cd	170	2.5	520
Cu	11000	110	5800
Pb	2100	33	1400
Ni	570	<3	300
Zn	77000	16	38000

Results : concentrations

Why this rebound?

- An important **under-dosage** of aluminate to stabilize pH around 9 (after 6M : pH: 5-6)
- **Larger volume per point required :**
 - larger ROI (during pilot: 1 inj.)
 - Improve distribution
- **Small pilot test area** compared to external influences :
 - **River influence** (2x/day) : influx of Cl^- , sulfates, O_2 , leaching of OH^-
 - **O_2 intrance** that influence HM precipitates behavior after injection (acidification as result of FeS_2 -oxydation)



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Conclusions

- **Lab tests :**
 - has been an important preliminary step to understand HM solubilization in complex situation
 - **NEVER REPLACES IN SITU (PILOT) TEST (with dynamic conditions)**
- **Pilot test injection :**
 - SPIN® Injection technology allowed to **inject reagents in LARGE VOLUMES**
 - Confirm a very **good correlation** between injection volume and ROI to predict and design a full-scale project
- **Mid- and long-term pilot test results :**
 - The injection of Aluminate has a **positive effect on the pH of the GW**
 - **The increase in pH** of the GW and co-precipitation has a **significant effect on the concentration of HMs** in solution
 - In the longer-term, this increase in pH (and therefore the effect on HMs) was not confirmed because:
 - **Underdosing** of reagents that was only visible after the injections were completed (field lab test 15 days).
 - **Limited area impacted** by the injections
 - In combination with the significant **water flows** (general + weekly)

Perspectives

- the **"on-site" laboratory test** must be conducted at least 2 months before the pilot test
- **Adjust injection volume** : the strong heterogeneity of the terrain is very important to be taken into account.
- Add an additional reagent able to **adjust and maintain the pH at 9** (more accurately) and that is not mobile (e.g. $\text{Mg}(\text{OH})_2$?



Thank you

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Thank you for their trust
and good collaboration



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