ENHANCED REMEDIATION OF LNAPL-CONTAMINATED HETEROGENEOUS AQUIFERS USING POLYMER-ALCOHOL EMULSIONS

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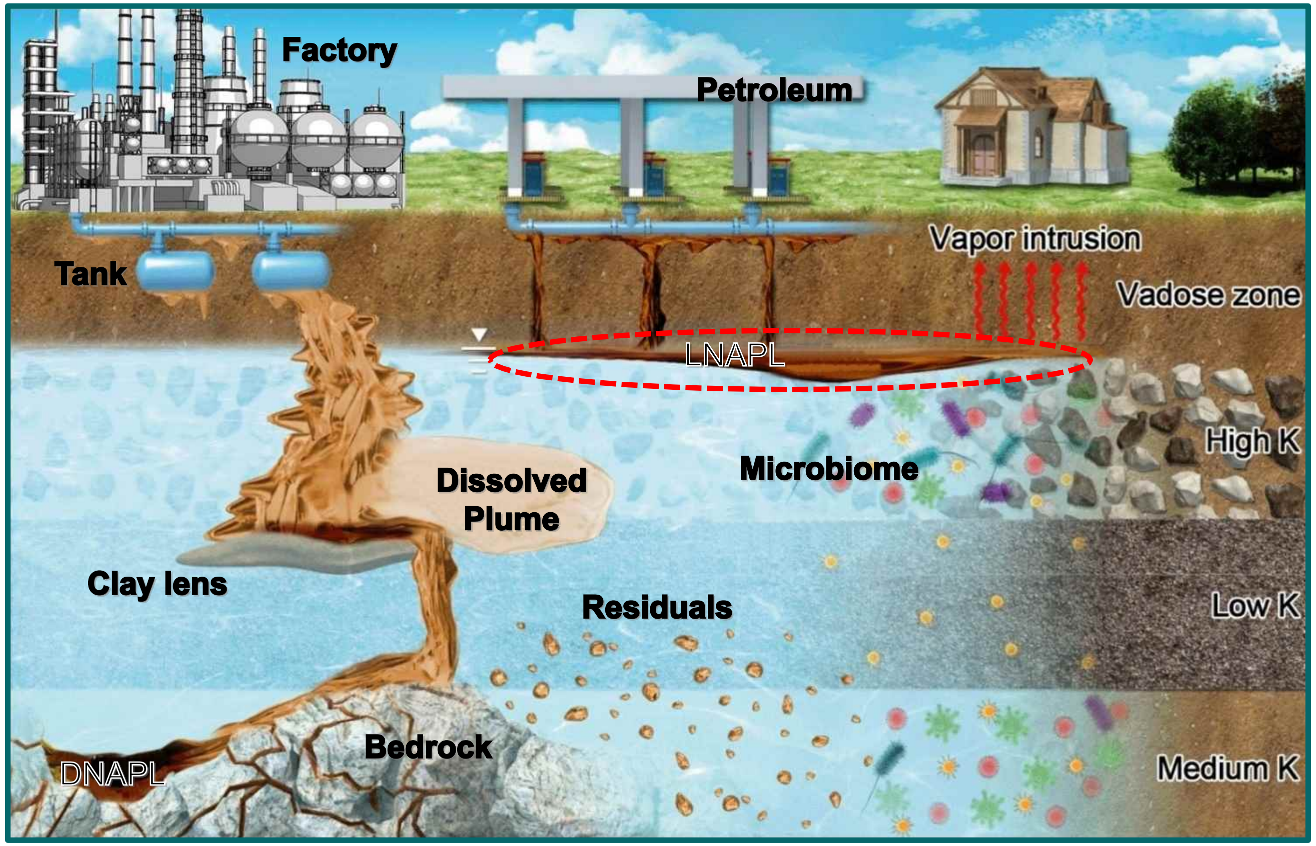
Outline:

- Introduction
  - Context of the problem
- Background
- Objectives of study
- Experimental study
  - Materials and methods
  - Results
- Conclusion

Context

➢ Soil and aquifer contamination



Zhang, et al., 2019

❖ Gasoline ❖ Diesel ❖ Motor oil, etc.

37.22%

MTES (2018)

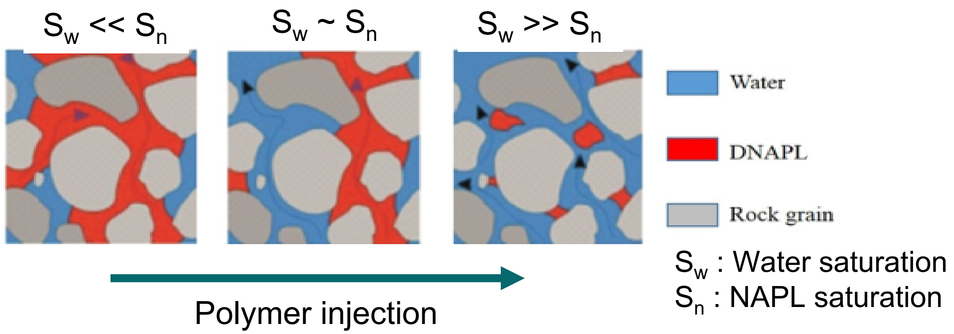
➢ Soil remediation techniques

❑ Conventional

- Pumping and treatment (PT) ➡ Recovery Yields: **60 %** (max.)

❑ Post-conventional

- Thermal remediation
- Co-solvent/surfactant flushing
- **Injection of non-Newtonian fluids (Polymers)**



Residual LNAPL Saturation

➢ How can we improve the recovery of residual NAPL saturation?

Injection of ENHANCED polymer solution

Objectives of study:

❖ **Develop a novel polymer-based formulation to enhance the recovery of residual LNAPL**

- Batch experiments: new formula (polymer/surfactant/alcohol)
- Bulk studies: stability, rheology, interfacial tension

❖ **Evaluate the sweep efficiency of the enhanced polymer-based formulation at multiple scales**

1D column → 2D tank

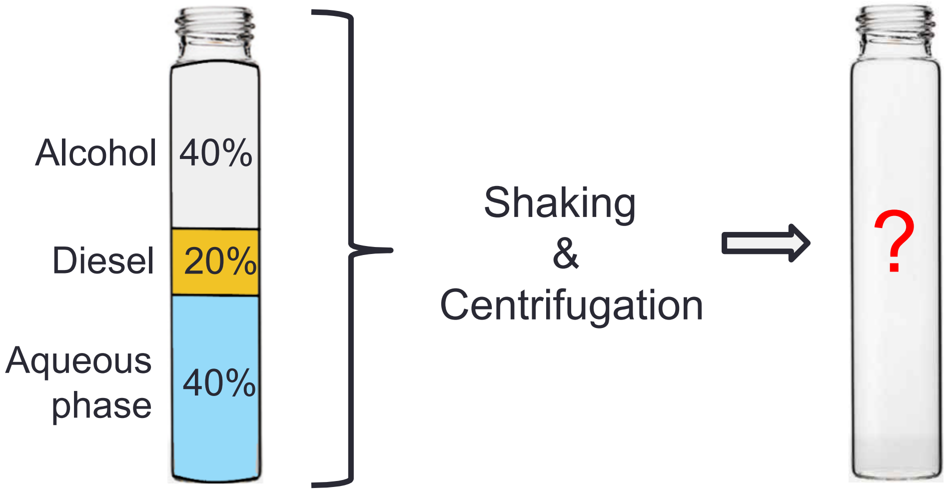
Experimental study

Materials and methods

➢ Batch experiments

- **Biopolymer** – Xanthan Gum (XG)
- **Eco-friendly surfactant –** Sodium Dodecyl Sulfate (SDS)
- **Biodegradable water-immiscible alcohol** – 1-pentanol
- **LNAPL – Diesel fuel**

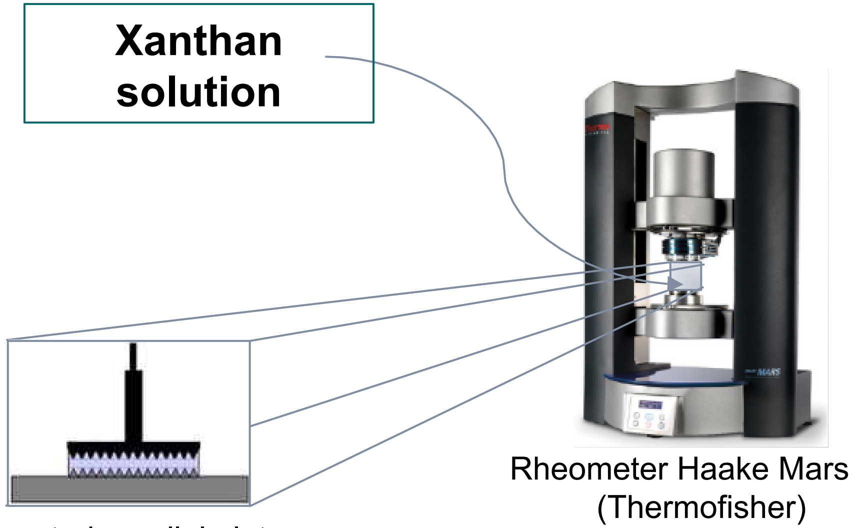
Methodology of batch experiments:



➢ Rheological experiments

- Rheology of all studying here fluids

→ Rheometer Haake Mars 60

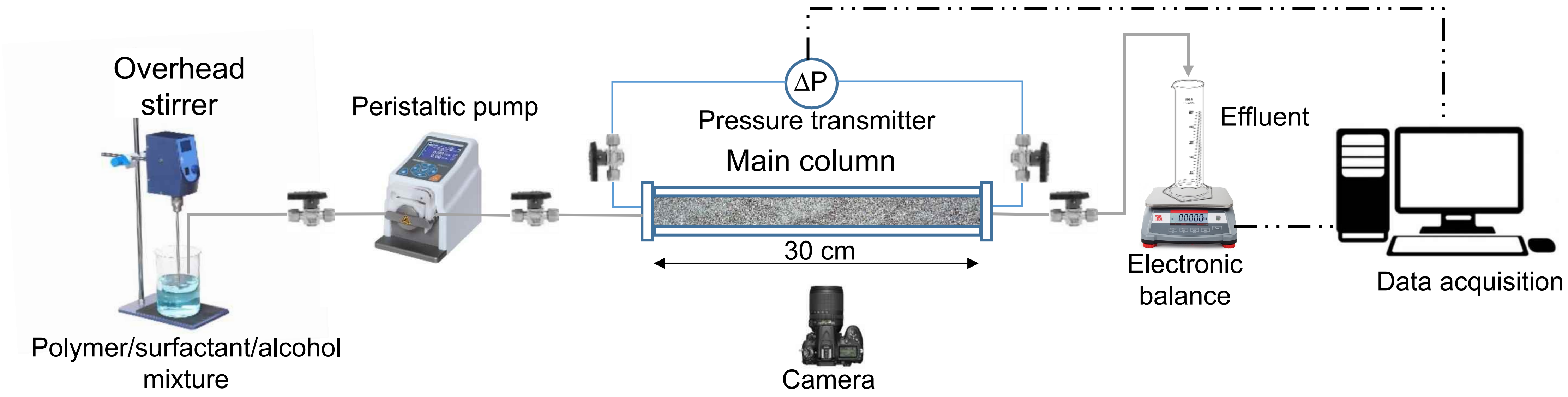


Serrated parallel plate (P60/Ti/SE and TMP60/SE)

Rheometer Haake Mars 60 (Thermofisher)

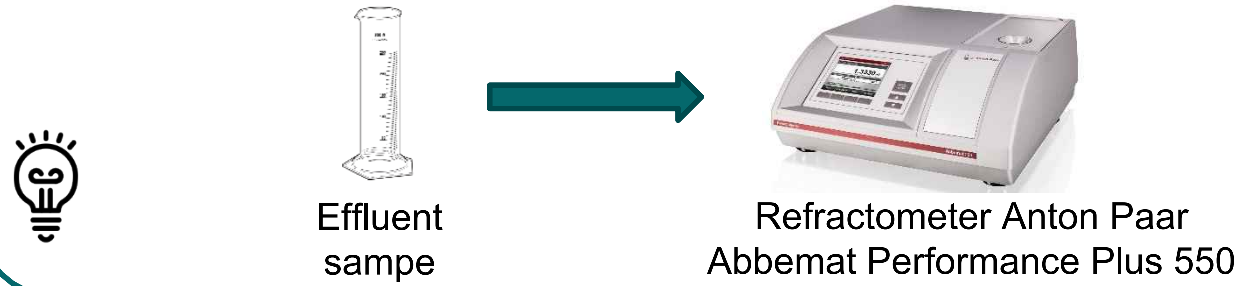
Materials and methods

➢ Schematic of the experimental 1D column setup:



➢ Methodology for effluent sample analysis:

* Determination of Recovery Factor by measuring refractive indices of the samples



Experimental procedure

Protocol:

1. Sand sieving
2. Column packing
3. CO2 flushing
4. Water saturation
5. Porosity and Permeability tests
6. LNAPL saturation

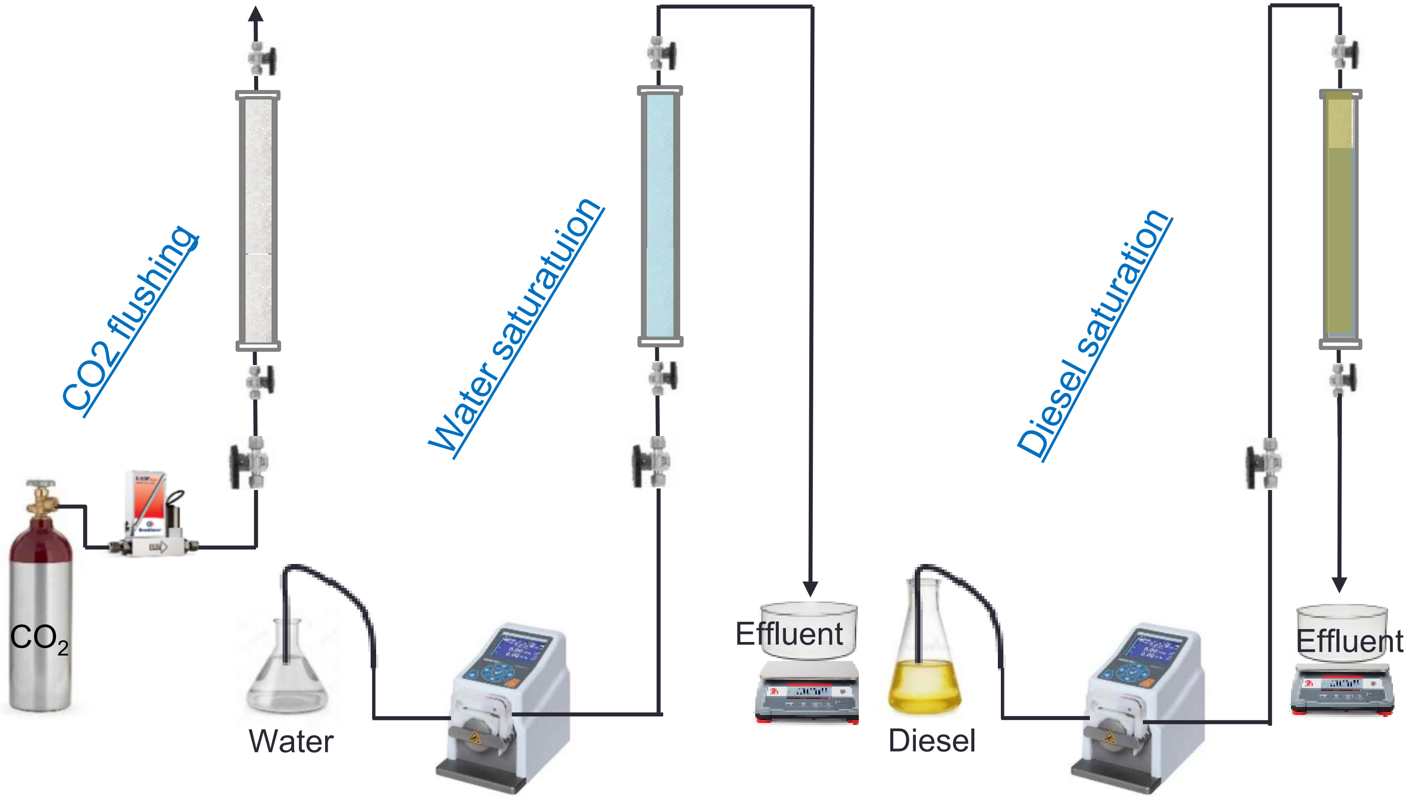


Table 2 Properties of sand-pack

Porous media	Grain size diameter, d (mm)	Pore Volume, PV (mL)	Porosity, ∅ (%)	Permeability, K (m^2)	Mean pore radius, r_{eq} (µm)	Irreducible water saturation, S_{irw} (%)
Extra-siliceous sand	0.4-1.3	136±1	36 ±1	280 (±20) ×10^{-12}	75	17 ±1

Results

➢ Batch experiments:

Alcohol partitioning type

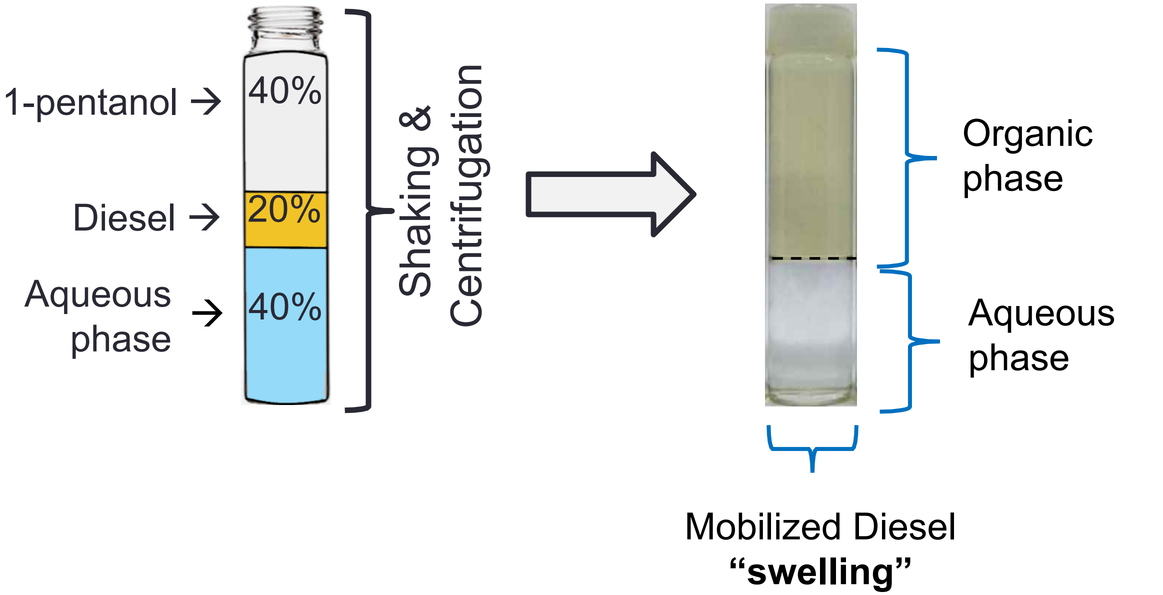


Fig. : Alcohol partitioning mechanism in the presence of water and diesel

Generation of stable POLYMER-SURFACTANT-ALCOHOL mixture:

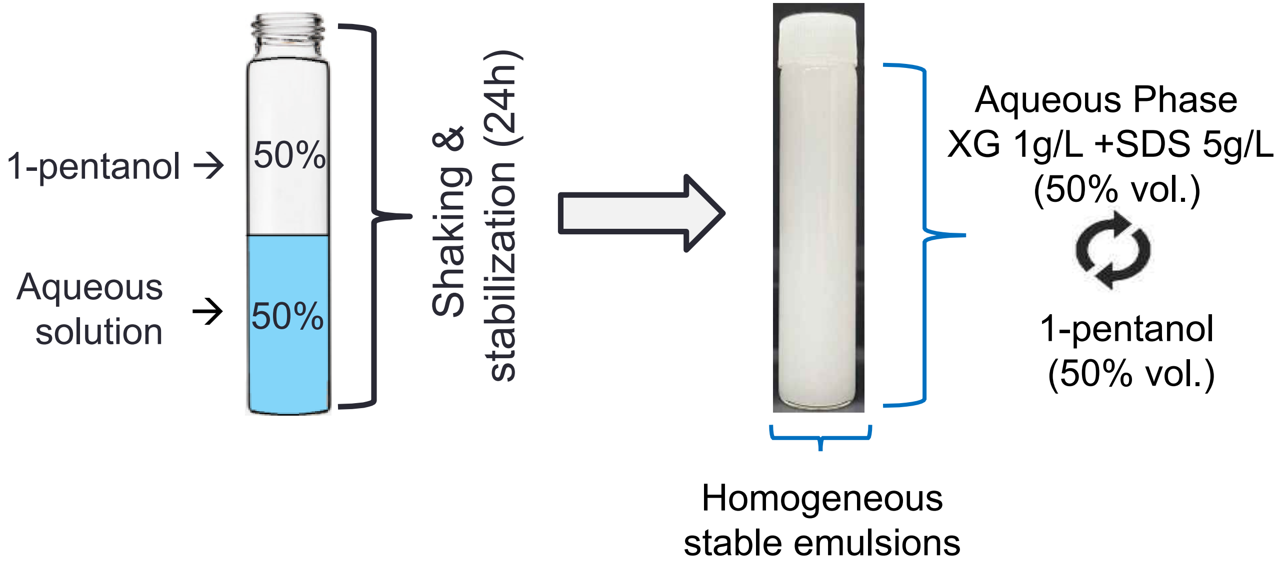


Fig. : Development of a new stable formulation

- ✓ Alcohol partitioning mechanism → **SWELLING** (mobilization)
- ✓ In the presence of diesel and aqueous phases, 1-pentanol preferentially partitions into the diesel oil, promoting an increase in the diesel volume

- ✓ **XG-SDS-1-pentanol** mixture → stable homogeneous cloudy-white emulsion
- ✓ New formulation **"COCKTAIL"** → XG-SDS-1-Pentanol emulsion at 50% alcohol content.

Results

➢ Stability test and emulsion's droplet size:

Stability test over time

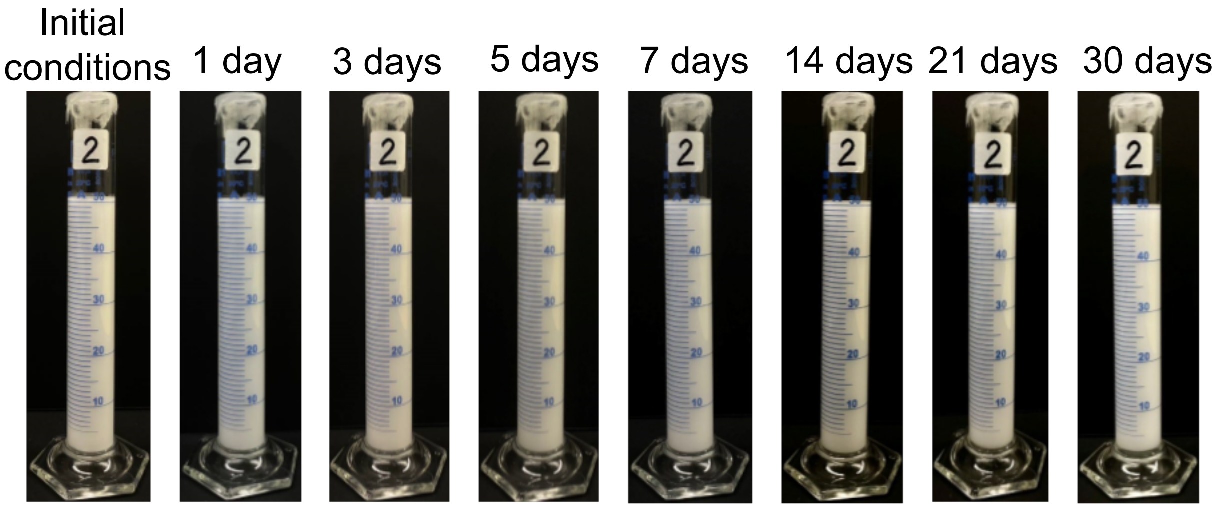


Fig. : Stability of the COCKTAIL emulsion

❖ Stability of emulsion in graduated cylinder with capping →
→ Stable for1 month, no phase separation was observed

Droplet size distribution of emulsion

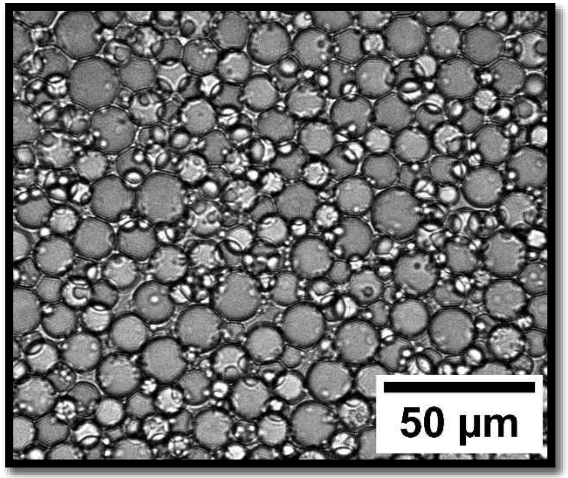


Fig. : Droplet size of emulsion using microscope

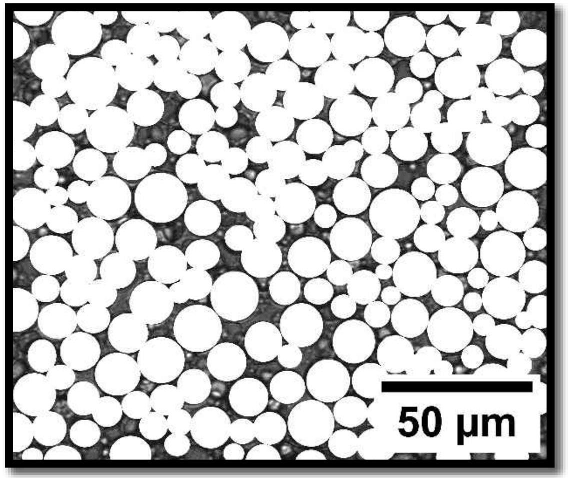


Fig.: Interpretation of droplet size by ImageJ software

❖ The mean droplet size of COCKTAIL emulsion:

D~11 microns

Results

➢ Rheological experiments:

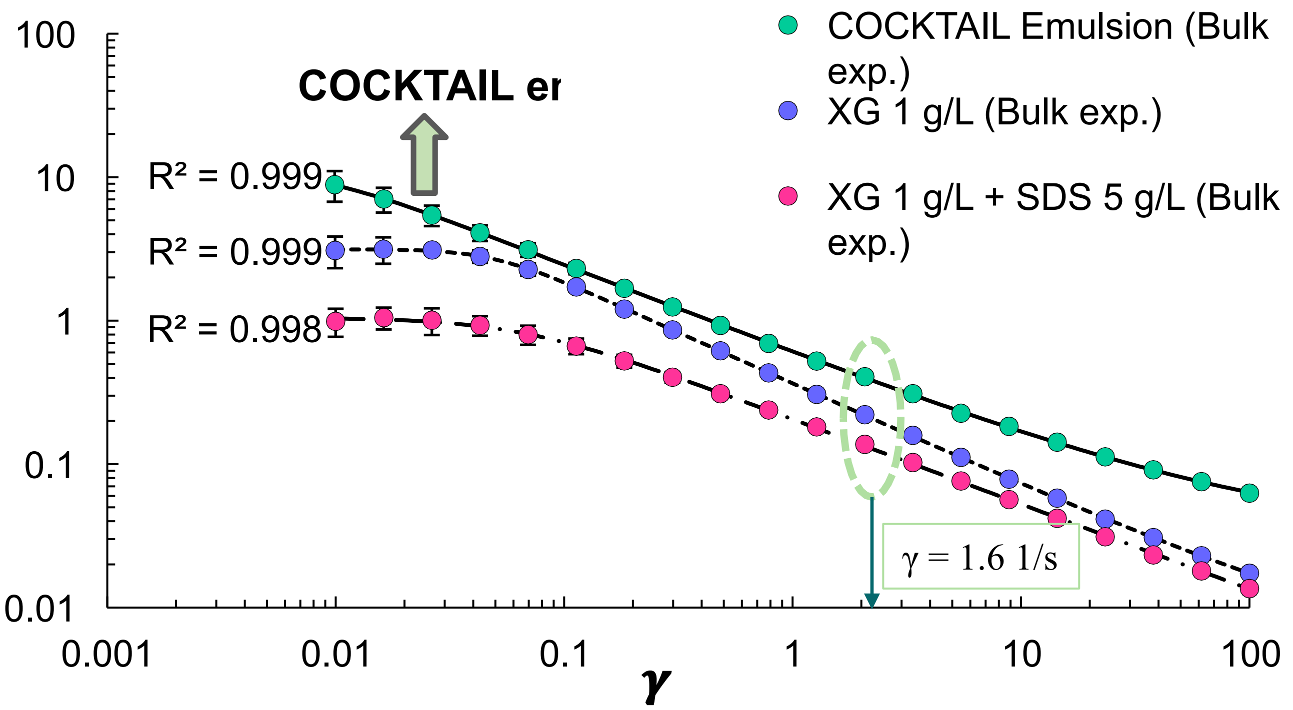


Fig. : Rheological behavior of the displacing fluids

Carreau-Yasuda model:

$$\mu(\dot{\gamma}) = \mu_{inf} + (\mu_0 - \mu_{inf})[1 + (\lambda\dot{\gamma})^a]^{\frac{n-1}{a}}$$

where, μ_0 (Pa.s) and μ_{inf} (Pa.s) are the viscosity at zero and infinite shear rate, λ (s) is the relaxation time, n (−) is the power index, $\dot{\gamma}$ (1/s) is the shear rate, and a (-) is the transition parameter.

At a shear rate of γ = 1.6 1/s (in porous media):

- Viscosity of COCKTAIL emulsion **1.7 times** higher than XG solution
- Viscosity of COCKTAIL emulsion **3 times** higher than XG-SDS solution

✓ All fluids → non-Newtonian shear-thinning behavior.

✓ Experimental results well fitted with Carreau-Yasuda model (R^2 = 0.99)

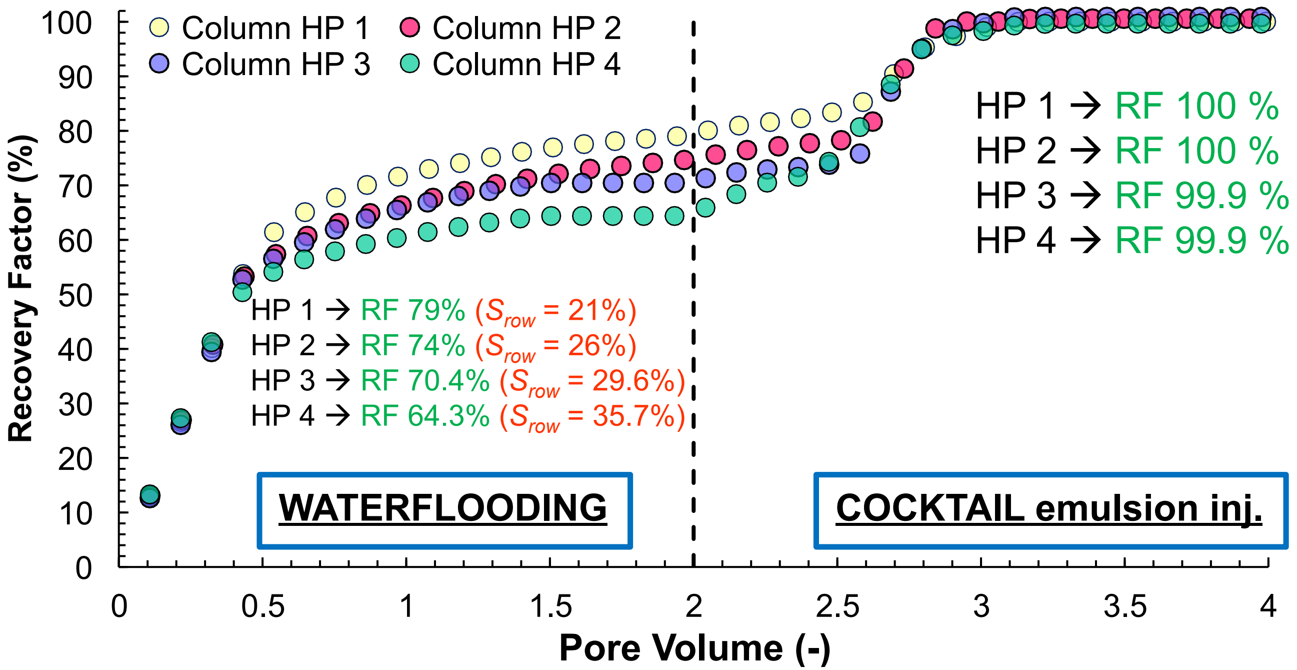
✓ SDS decreases the viscosity of XG solution due to repulsive electrostatic forces.

✓ The viscosity of COCKTAIL emulsion higher than the viscosity of reference fluids XG and XG-SDS solution

Results

➢ 1D column experiments:

Post-treatment by COCKTAILemulsion: LNAPL saturated Porous Media



Main findings:

- ✓ Post-injection of "Cocktail 50%" after Waterflooding showed an improvement in recovery up to 99.95% (± 0.05)
- ✓ No matter how much residual diesel is left after WATERFLOODING, the recovery of residual diesel by COCKTAIL → 100% (just in ≈ 1PV)

Remark: industrial "classical" field application is waterflooding (i.e. pump-and-treat)

WATERFLOOD: 0 PV (i.e. initial conditions)

a) 

WATERFLOOD: after 2 PV injections

b) 

COCKTAIL: after 0.15 PV inj.

c) 

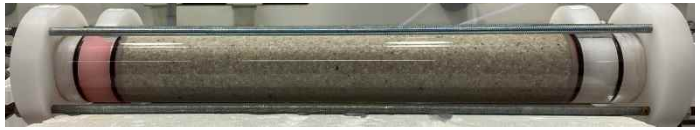
COCKTAIL: after 0.5 PV inj.

d) 

COCKTAIL: after 0.8 PV inj.

e) 

COCKTAIL: after 1.1 PV inj.

f) 

Results

- 1D column experiments:

Direct treatment: LNAPL saturated Porous Media

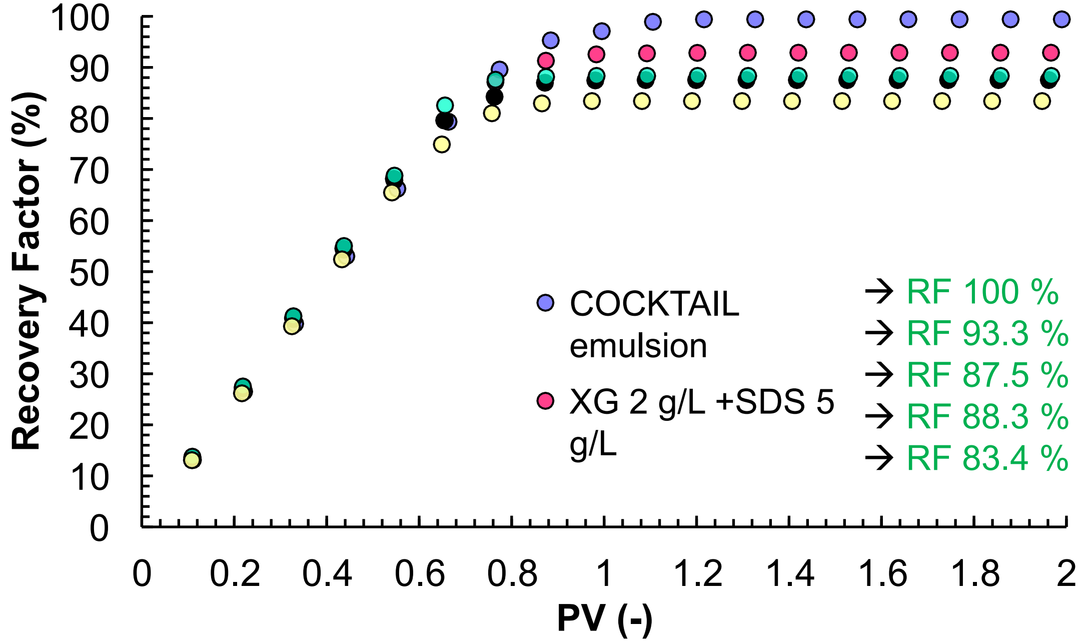


Fig. : LNAPL displacement in 1D column by direct-treatment

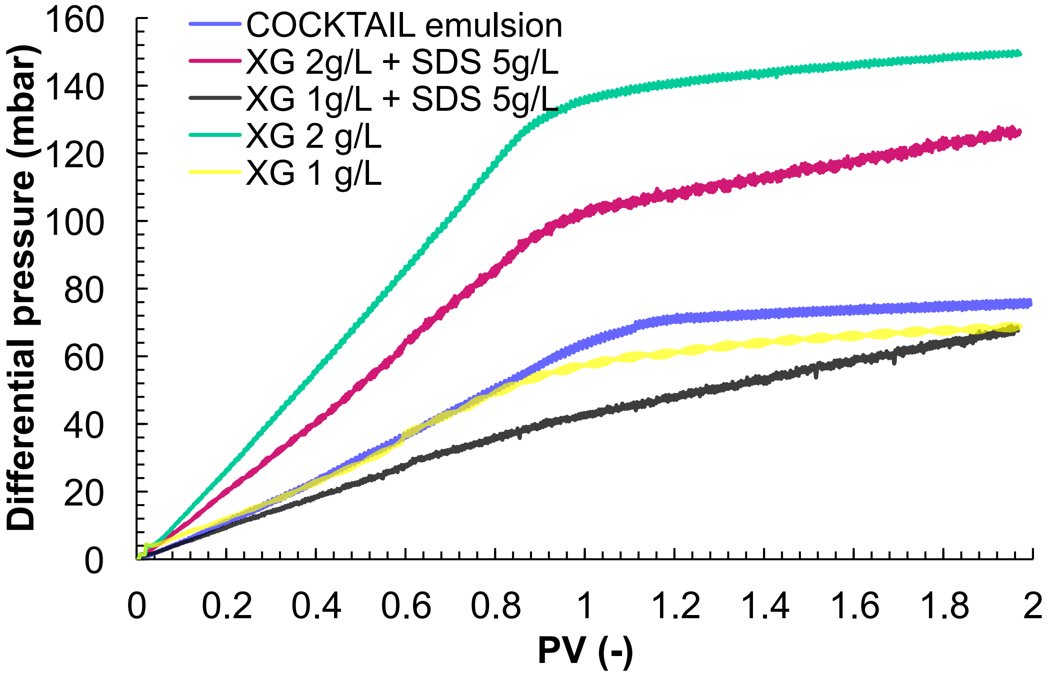
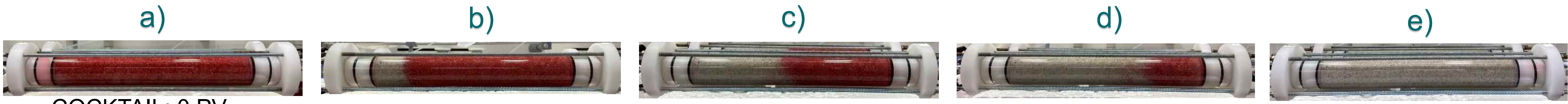


Fig. : Pressure drop as a function of injected PV for different formulations



COCKTAIL: 0 PV (i.e. initial conditions) | 0.15 PV | 0.5 PV | 0.7 PV | 1.1 PV

- ✓ "COCKTAIL emulsion" → improvement of recovery up to 100 %
- ✓ "COCKTAIL emulsion" → low column pressure drop and higher diesel recovery (easier injection)

Schematic illustration of LNAPL swelling by alcohol in porous media

➤ Mechanism of LNAPL displacement in porous media

Mechanism of mobilization "SWELLING"

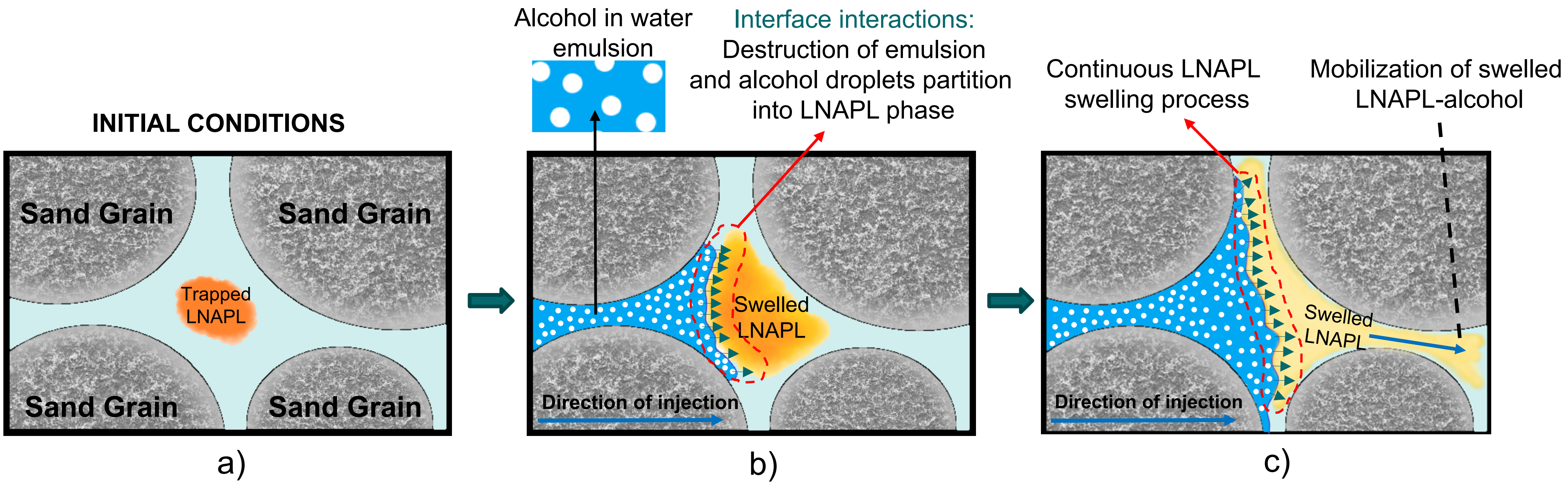
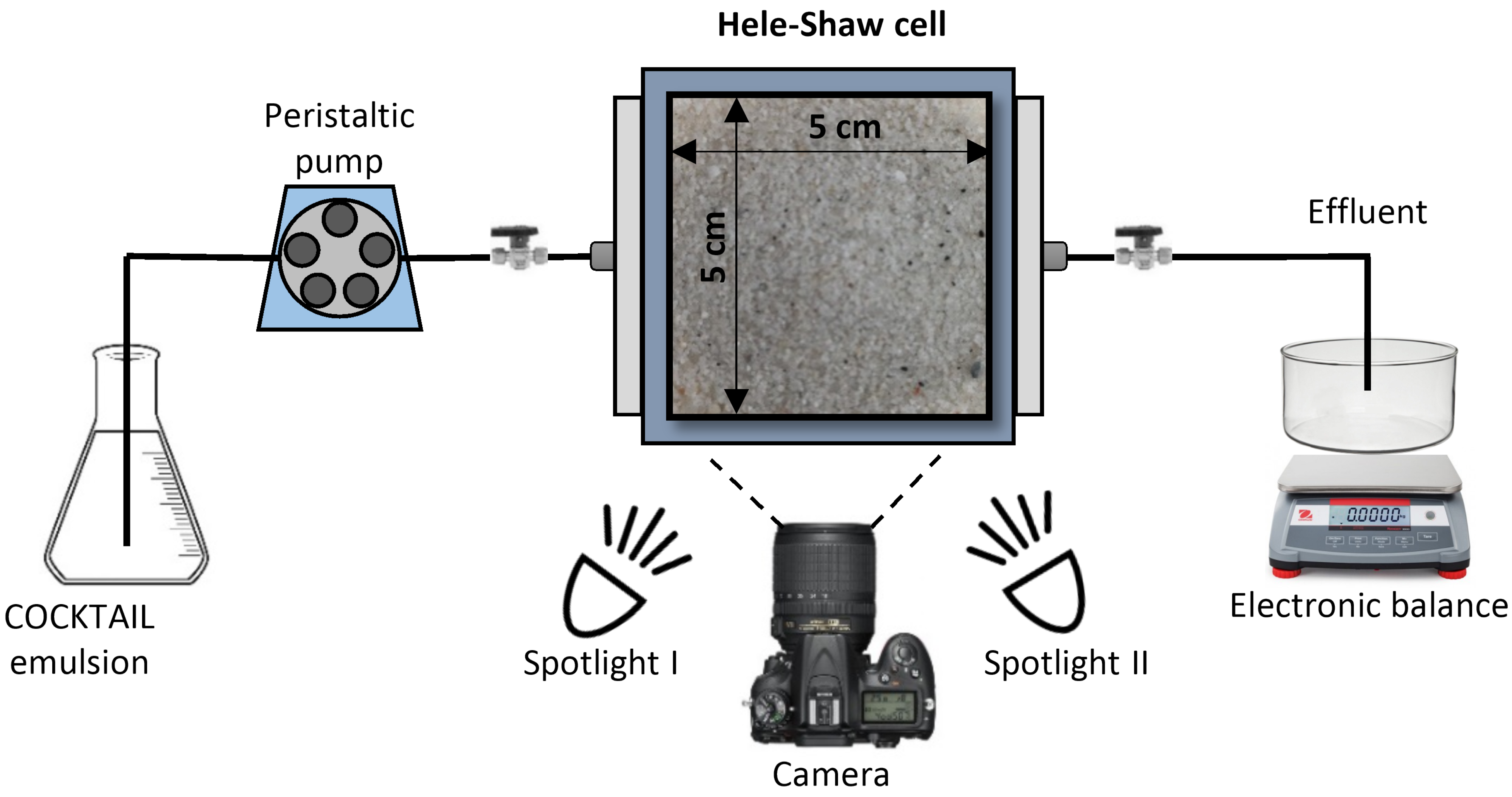


Fig. : Conceptual illustration of LNAPL displacement in porous media by mobilization mechanism

Investigation of LNAPL swelling by alcohol at pore scale

- Schematic of the experimental Hele-Shaw cell setup:



Results

- ➢ LNAPL swelling by alcohol using Hele-Shaw cell: Waterflooding → COCKTAIL emulsion

COCKTAIL emulsion

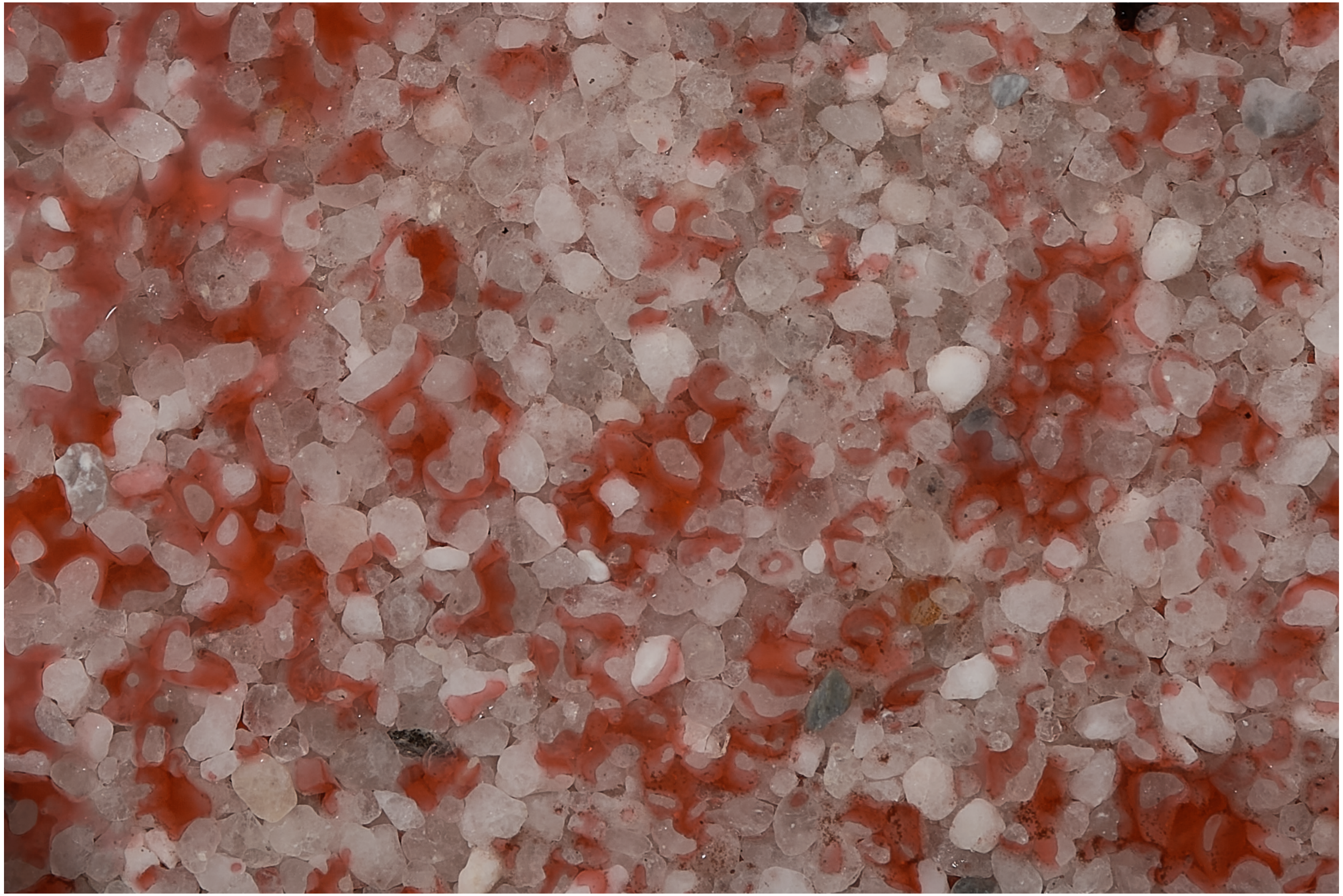


Fig. : LNAPL removal as a function of time in Hele-Shaw cell

Results

- LNAPL swelling by alcohol using Hele-Shaw cell: Waterflooding → COCKTAIL emulsion

COCKTAIL emulsion

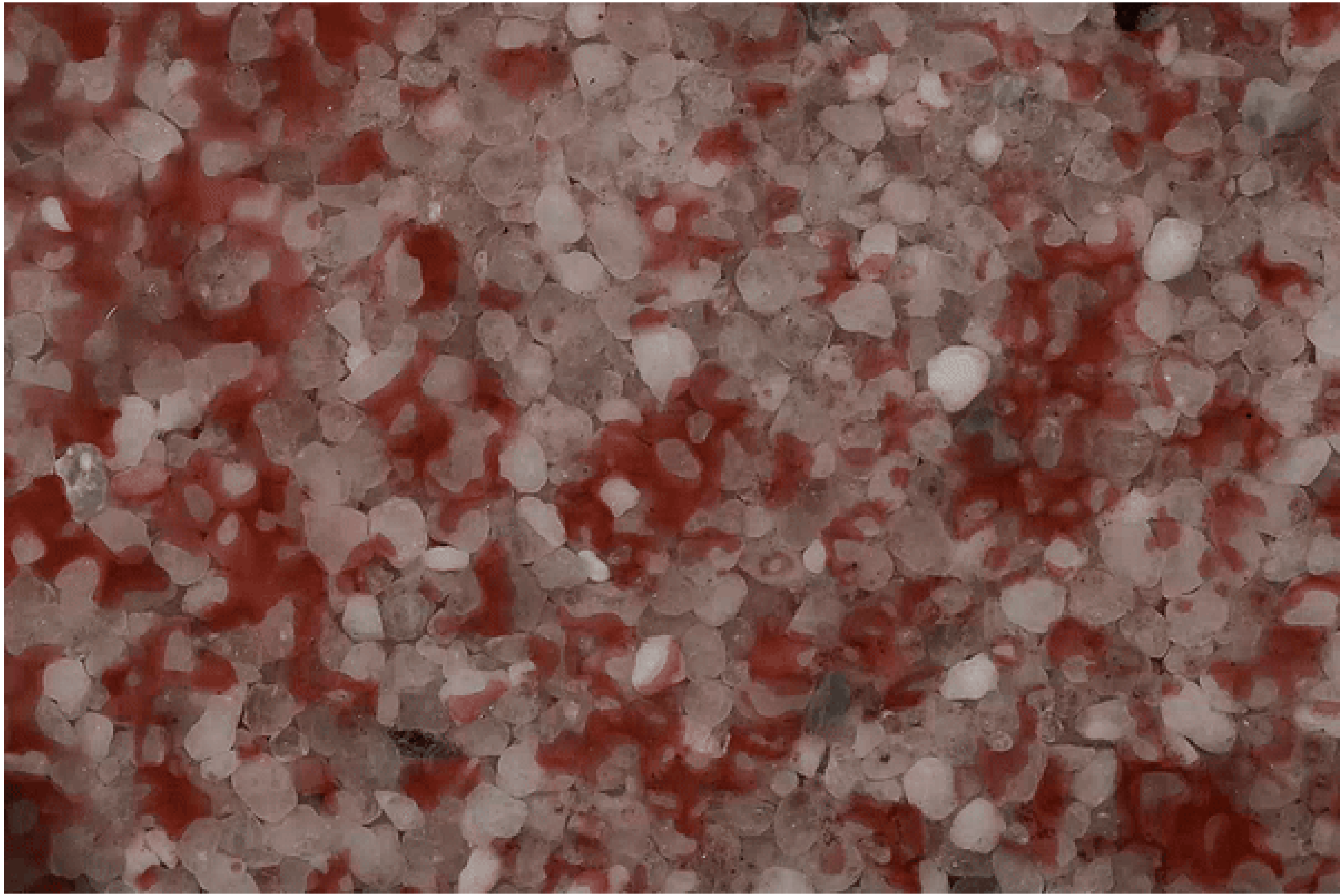


Fig. : LNAPL removal as a function of time in Hele-Shaw cell

Results

➢ LNAPL swelling by alcohol at pore scale during COCKTAIL emulsion injection:

(a)

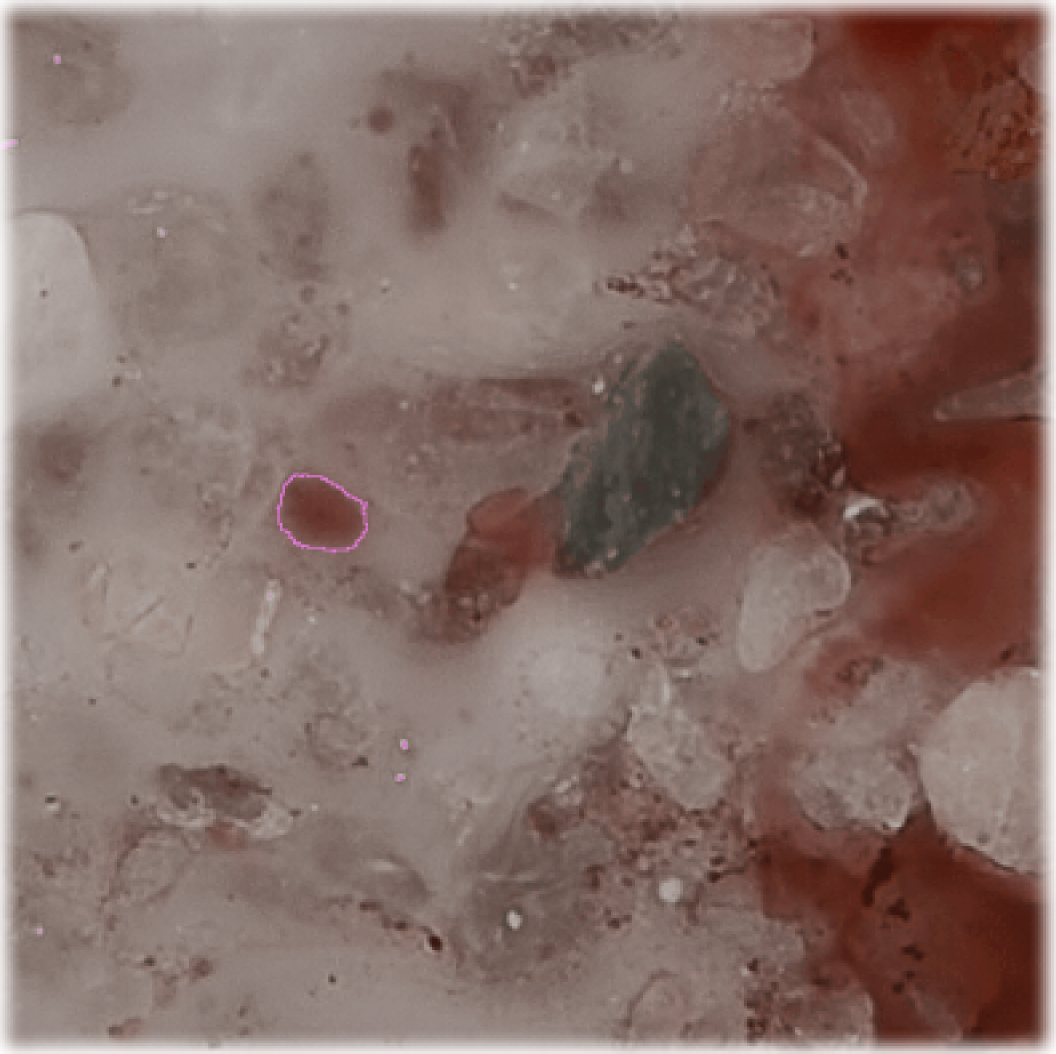


Fig.: Diesel oil swelling as a function of time

(b)

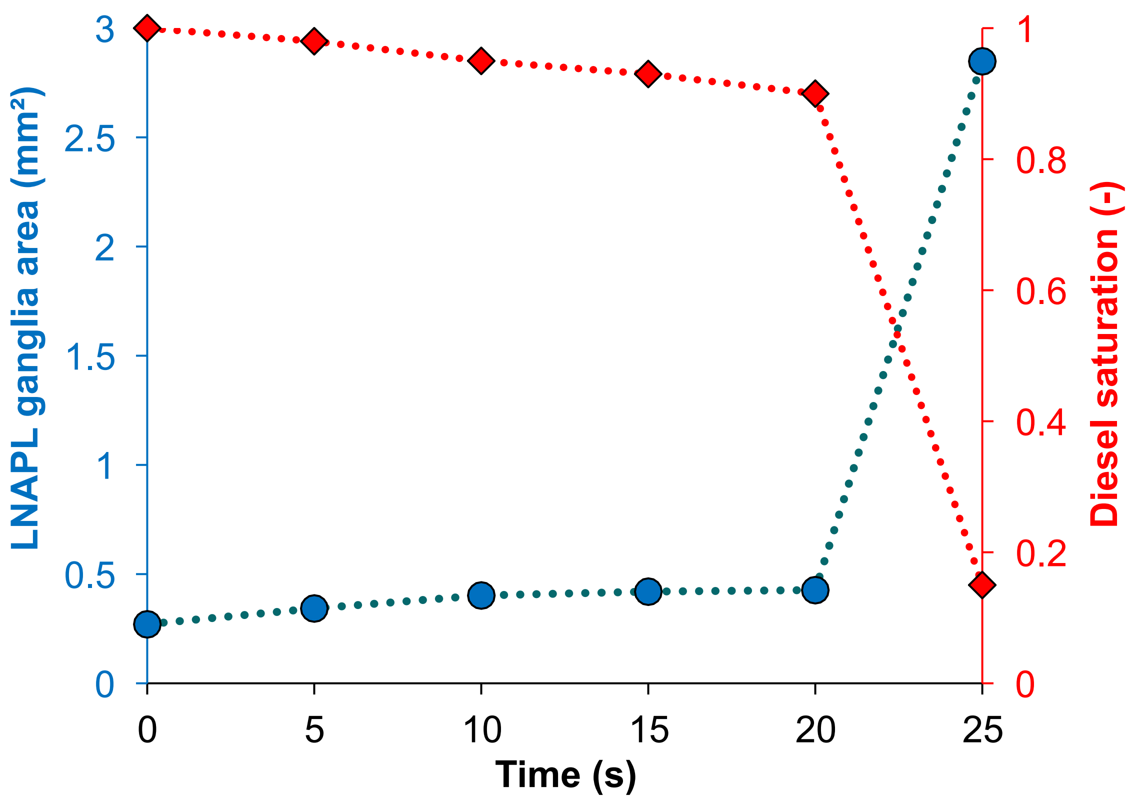


Fig.: LNAPL ganglia area and diesel saturation as a function of time

Main conclusions:

- The new formulation **COCKTAIL emulsion** exhibited an improved recovery of 100% during direct treatment in 1D columns.
- Post-injection of **COCKTAIL emulsion** after **WATERFLOODING** improved diesel removal up to 100%
- The main mechanism of 1-pentanol in **COCKTAIL emulsion** is the swelling of the diesel phase in a porous media and thereby its further mobilization.

REMARK: The main remediation mechanism that enhances diesel recovery is **"swelling".**

To promote the diesel swelling mechanism it is important to deliver alcohol with polymer solution.

Thank you for your attention

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