



HAL
open science

Mobilization of LNAPL by using polymer-based alcohol emulsion in contaminated aquifers

Bexultan Sabyrbay, Dorian Davarzani, Christophe Dicharry, Sagyn Omirbekov, Amir Alamooti, Mélanie Lorthioy, Mohamed Krimissa, Stéfan Colombano

► **To cite this version:**

Bexultan Sabyrbay, Dorian Davarzani, Christophe Dicharry, Sagyn Omirbekov, Amir Alamooti, et al.. Mobilization of LNAPL by using polymer-based alcohol emulsion in contaminated aquifers. Aqua-ConSoil 2023, Sep 2023, Prague, Czech Republic. hal-04374819

HAL Id: hal-04374819

<https://hal.science/hal-04374819>

Submitted on 5 Jan 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Mobilization of LNAPL by using polymer-based alcohol emulsions in contaminated aquifers.

Bexultan Sabyrbay^{a, b, c}, Hossein Davarzani^a, Sagyn Omirbekov^{a, d}, Amir Alamooti^a, Mohamed Krimissa^b, Christophe Dicharry^c, Stéfan Colombano^a

^a*Bureau de Recherches Géologiques et Minières (BRGM), 3 Avenue Claude Guillemin, Orléans, 45100, France*

^b*Electricité de France (EDF), Recherches & Développements, Laboratoire National d'Hydraulique et d'Environnement (LNHE), 6 Quai Watier, Chatou, 78400, France*

^c*Université de Pau et des Pays de l'Adour (UPPA), Laboratoire des Fluides Complexes et leurs Réservoirs (LFC-R), Avenue de l'Université, Pau Cedex, 64013, France*

^d*Nazarbayev University, 53 avenue Qabanbay Batyr, Astana, 010000, Kazakhstan*

Keywords: soil remediation, porous media, biopolymer, alcohol, LNAPL

Abstract

Environmental pollution, notably soil pollution, is one of the urgent problems at present. Light refined petroleum products (gasoline, diesel, engine oil, etc.) which represent light non-aqueous phase liquids (LNAPL) are among the most dangerous environmental pollutants. Penetration of LNAPL into the soil or groundwater makes it unsuitable for plant, animal, and microorganism life. Therefore, the search for effective ways to dispose of hydrocarbon pollution is of great importance. One of the most widely known LNAPL remediation methods is Pump-and-treat (PT), which is considered inefficient due to long operation, and low recovery efficiency (around 60%). Injecting non-Newtonian fluids such as polymers presents a significant industrial application interest for in situ remediation of contaminated soil, especially for aquifers with significantly high permeability and strong heterogeneity. Nevertheless, there is some limitation to using high-viscosity fluids. For instance, the injection of a high-viscosity polymer solution during soil remediation can harm the environment by increasing the injection pressure, leading to aquifer erosion or soil uplift. Hence, developing eco-friendly, sufficiently viscous, and biodegradable fluid is highly in demand.

The main goal of this study is to improve the removal of LNAPL (here diesel fuel) with a new polymer-based formulation that promotes its dissolution or mobilization. The use of viscous polymer solutions can contribute to stable oil displacement in heterogeneous porous media and simultaneously carry active matters (surfactants, co-solvents) to hard-to-reach low-permeability media.

To embody the goal, the remediation of diesel was tested in one-dimensional 30 cm long silica-based sand-pack columns. Biopolymer “xanthan gum” was used due to its rheological and biodegradability properties. Primary flushing by xanthan gum with a concentration of 0.1% w/w, promoted stable displacement in saturated porous media and allowed the recovery of up to 80% of diesel fuel. Further, the polymer solution was formulated with the addition of alcohol solvents to improve sweeping performance. Therefore, fifteen types of biodegradable homologous alcohols (from ethanol to n-octanol) were applied for batch experiments to formulate polymer-based alcohol mixtures. These homologous alcohols are known to exhibit different partitioning behavior upon contact with diesel fuel. Environmentally friendly surfactant sodium dodecyl sulfate (SDS) was used to stabilize a mixture of alcohol and polymer solution. To obtain a stable formulation, batch experiments were carried out at various surfactant concentrations and various volume fractions of polymer solution, alcohol, and diesel fuel.

Batch experiments were carried out in small polypropylene vials to test the mechanisms of alcohol partitioning in the presence of diesel fuel. According to the results of batch experiments, ethanol, 1-propanol, and 2-propanol exhibit a mechanism of diesel dissolution into an aqueous phase, which leads

to a decrease in the volume of diesel fuel. Homologous alcohols from n-butanol to n-octanol promoted partitioning into the organic phase. As a result, swelling of the volume of diesel fuel was observed, which is typical for the mobilization mechanism. However, only 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 2-octanol among mobilization alcohols showed stable emulsions when mixed with a xanthan-SDS solution.

Further, the rheological behaviors of xanthan-SDS-alcohol mixtures were characterized through a rheometer. The preliminary results showed that they exhibit non-Newtonian shear-thinning behavior. Rheological experiments are still ongoing to select the best formulation regarding viscosity properties. Thus, the final polymer-based alcohol emulsion will be used for the secondary flushing (after polymer flushing) in a 1D column to remove residual diesel.

Mobilization of LNAPL by using polymer-based alcohol emulsions in contaminated aquifers

ID: 138

Bexultan Sabyrbay^{a, b, c}, Dorian Davarzani^a, Christophe Dicharry^c, Sagyn Omirbekov^{a, d}, Amir Alamooti^a, Mélanie Lorthioy^b, Mohamed Krimissa^b, Stéfan Colombano^a

b.sabyrbay@brgm.fr

^aBureau de Recherches Géologiques et Minières (BRGM), 3 Avenue Claude Guillemin, Orléans, 45100, France

^bElectricité de France (EDF), Recherches & Développement, Laboratoire National d'Hydraulique et d'Environnement (LNHE), 6 Quai Watier, Chatou, 78400, France

^cCNRS/TOTAL ENERGIES/UNIV PAU & PAYS ADOUR, Laboratoire des Fluides Complexes et leurs Réservoirs - IPRA, UMR5150, 64000, Pau, France

^dNazarbayev University, 53 avenue Qabanbay Batyr, Astana, 010000, Kazakhstan

1 Introduction and objectives

- ❖ **Light Non-Aqueous Phase Liquids (LNAPL)** spills are a significant environmental concern, particularly for groundwater resources. Classical pump-and-treat method's efficiency rarely exceeds 60% due to the subsurface heterogeneity [1].
- ❖ The use of polymers in soil remediation has already proven to be a promising method for in-situ remediation of NAPLs by improving homogeneity displacement even in heterogeneous mediums [2].
- ❖ However, applying a high-viscous polymer solution may negatively impact the environment by raising the injection pressure which tends to erode the aquifer or uplift the soil [3].
- ❖ This study exhibits how an injection of a **biopolymer-surfactant-alcohol** mixture will improve the recovery of the residual LNAPL in a porous media.

Main objectives of the study:

- ❑ Development of a new biopolymer-based formulation using alcohols and surfactants to improve the recovery of residual LNAPL.
- ❑ Determination the alcohol partitioning mechanism in porous media in the presence of diesel and aqueous phases.
- ❑ Performance of the newly developed formulation in multiple scales (batch experiments, rheological measurements, 1D column experiments).

2 Materials & Methods

Batch experiments:

- **Biopolymer** – Xanthan Gum (XG)
- **Surfactant** – Sodium Dodecyl Sulfate (SDS)
- **15 biodegradable homologous alcohols** –

N°	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Alcohol	Ethanol	1-propanol	2-propanol	1-butanol	2-butanol	Isobutanol	Tert-butanol	2-methyl-1-butanol	1-pentanol	2-pentanol	3-pentanol	1-hexanol	1-heptanol	1-octanol	2-octanol

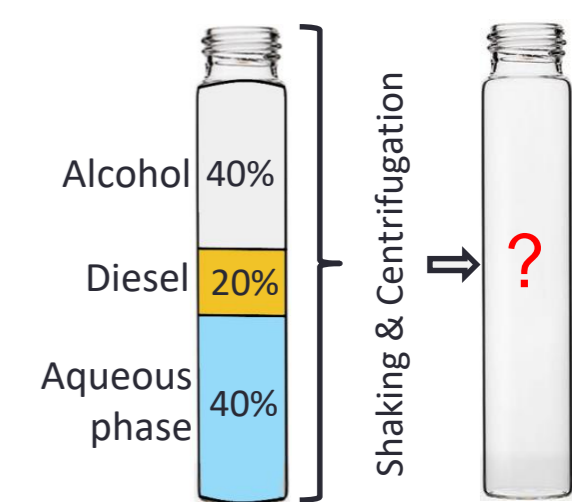


Fig. 1: Methodology of batch experiments

- **LNAPL** – Diesel Fuel

Rheological experiments:

- Rheology of fluids → Rheometer Haake Mars 60 (Thermofisher)

1D column experiments:

Porous media	Grain size diameter, d (mm)	Porosity, ϕ (%)	Permeability, K (m ²)
Extra siliceous sand	0.4-1.3	36 ± 1	290 (±10) × 10 ⁻¹²

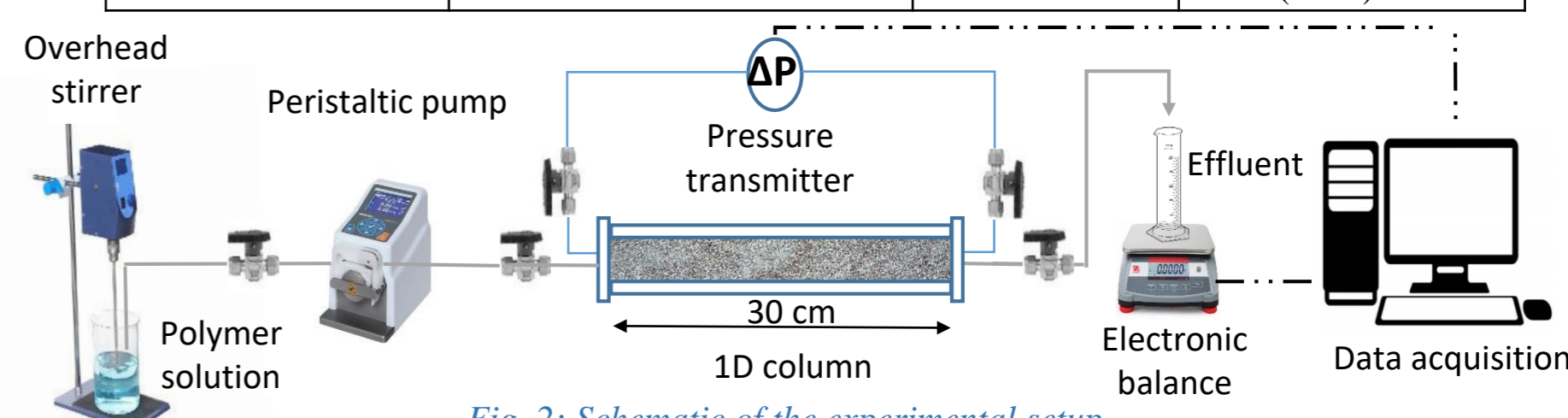


Fig. 2: Schematic of the experimental setup

3 Results & discussions

Batch experiments: development of new formula

Alcohol partitioning type

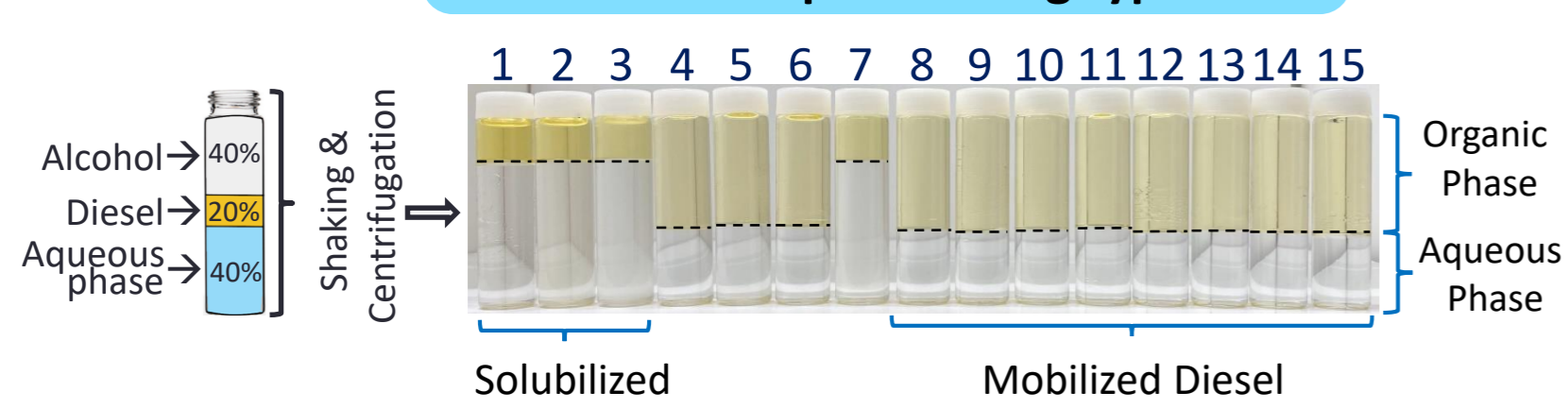


Fig. 3: Alcohol partitioning mechanism in the presence of water and diesel

- ✓ Diesel **"solubilization"** alcohols: 1, 2, 3, 7 → **water-soluble**
- ✓ Diesel **"mobilization"** alcohols: 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 15 → **water-insoluble**

Generation of single-phase XG-SDS-ALCOHOL mixture:

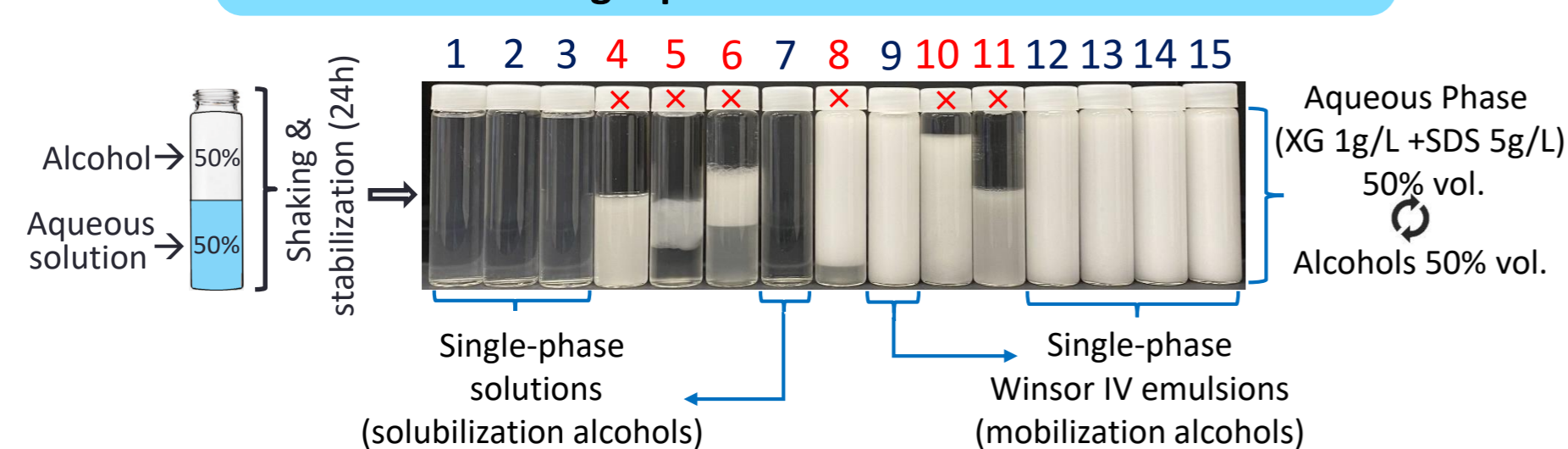


Fig. 4: Development and selection of a new single-phase formulation

- ✓ Single-phase **"solubilization"** XG-SDS-ALC solutions → 1, 2, 3, 7
- ✓ Single-phase **"mobilization"** XG-SDS-ALC emulsions → 9, 12, 13, 14, 15

Rheological experiments:

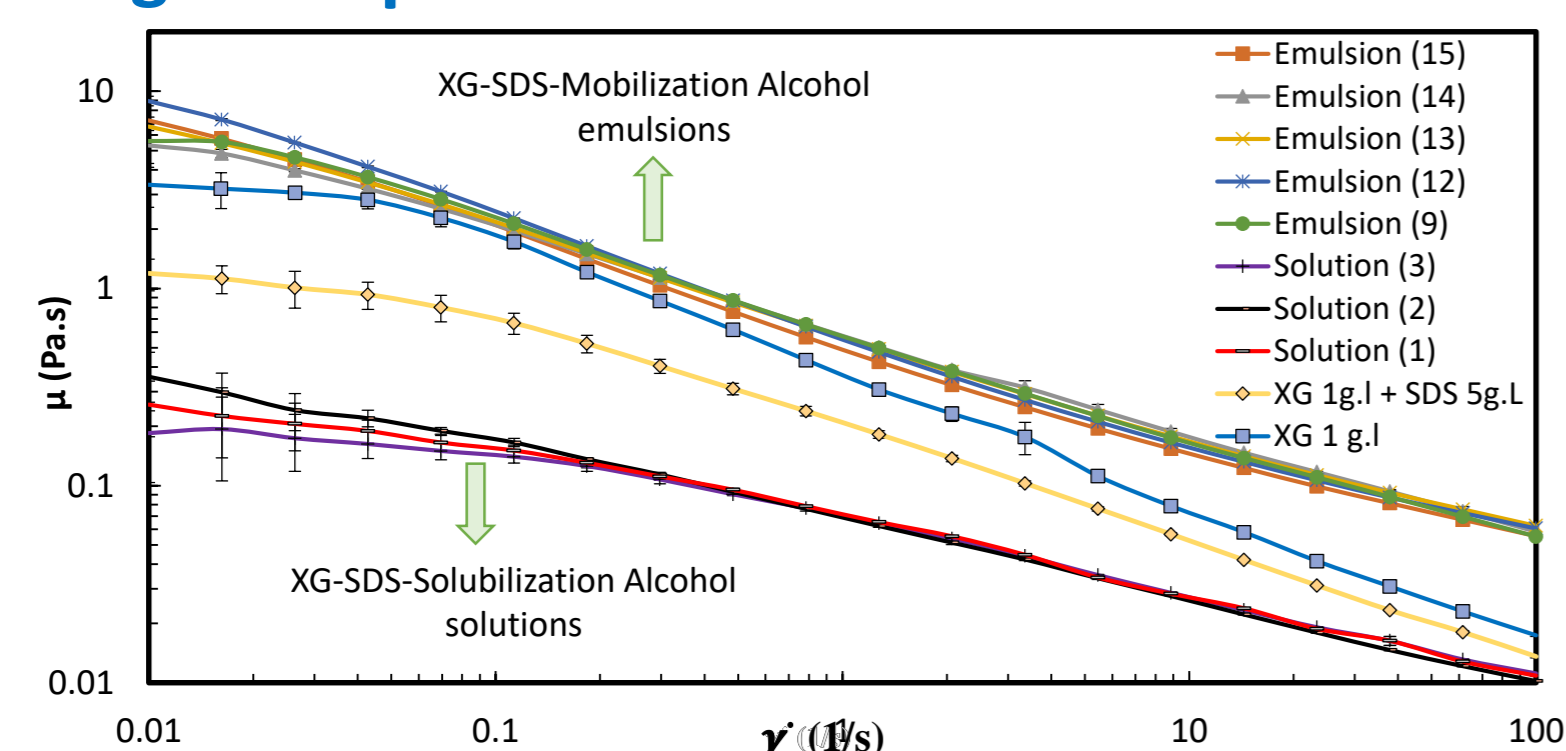


Fig. 5: Rheological behavior of the displacing fluids

- ✓ All mixtures → non-Newtonian shear-thinning behavior.
- ✓ SDS decreases the viscosity of XG solution due to repulsive electrostatic forces.
- ✓ Water-insoluble **"mobilization"** alcohols (50% vol.) increase the viscosity
- ✓ Water-soluble **"solubilization"** alcohols (50% vol.) decrease the viscosity

when mixing with XG-SDS solution

1-D column experiments:

- ✓ **"COCKTAIL 50%"** → XG-SDS-1-Pentanol emulsion at 50% alcohol content.
- ✓ **1-pentanol** → lower toxicity and higher biodegradability.

Post-treatment: LNAPL saturated Porous Media

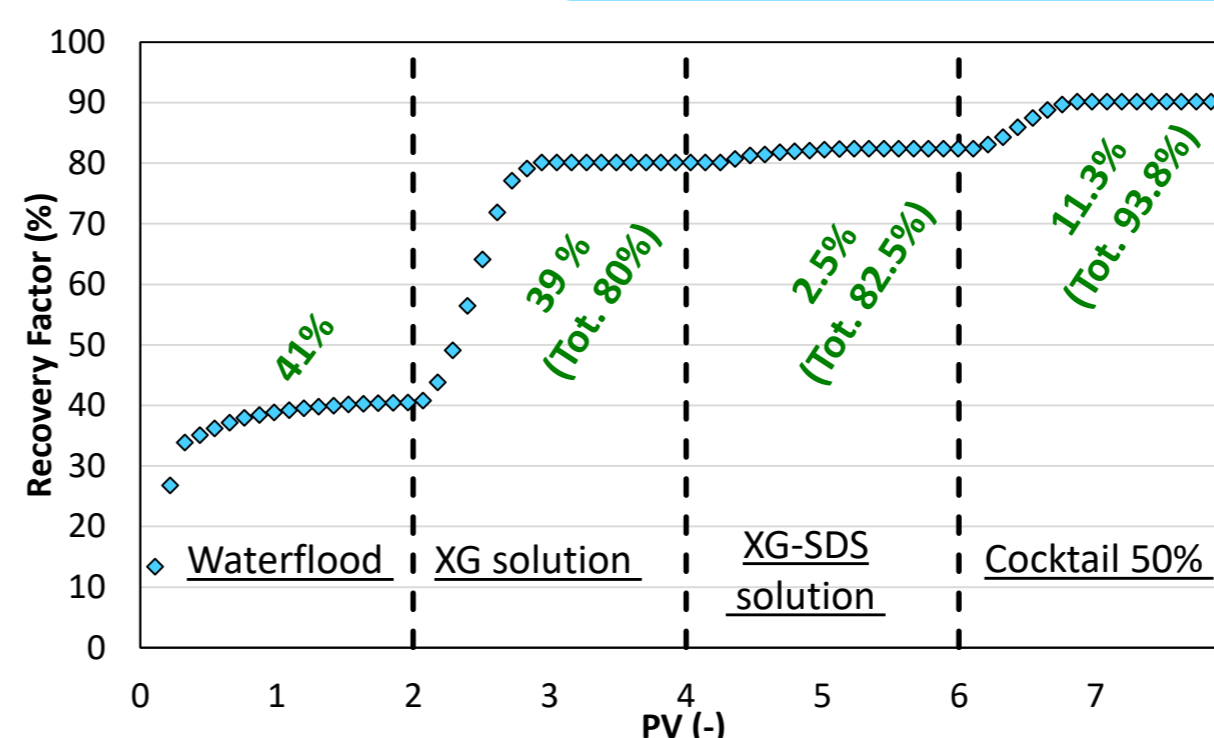


Fig. 6: LNAPL displacement in 1D column by post-treatment

Main findings:

- ✓ Post-injection of **"Cocktail 50%"** after **Waterflood** → **XG** → **XG-SDS** showed an improvement in recovery to 11.3% (tot. 93.8%)
 - ✓ **"Cocktail 50%"** exhibits an effective recovery of the residual LNAPL in porous media.
- Remark: industrial "classical" field application is waterflooding (i.e. pump-and-treat)

Direct treatment: LNAPL saturated Porous Media

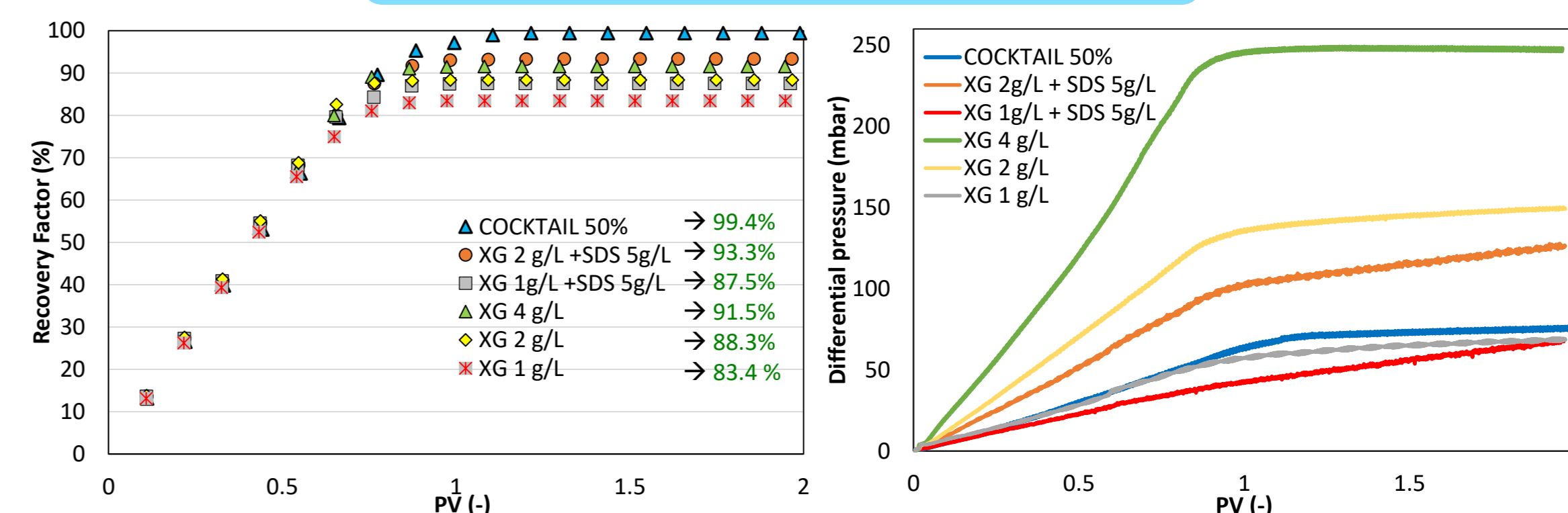


Fig. 7: LNAPL displacement in 1D column by direct-treatment

Fig. 8: Pressure drop as a function of injected PV for different formulations

- ✓ **"Cocktail 50%"** → improved recovery of 99.4%
- ✓ **"Cocktail 50%"** → low column pressure drop and higher diesel recovery (easier injection)

4 Main Conclusions

- ❑ The new-developed XG-SDS-1-pentanol emulsion called **"COCKTAIL 50%"** exhibited an improved recovery of 99.4% upon direct treatment in 1D columns.
- ❑ Post-injection of **"COCKTAIL 50%"** after XG-SDS flushing improved diesel removal to 11.3% (total 93.8%).
- ❑ **COCKTAIL 50%** emulsion preserves non-Newtonian shear-thinning behavior despite the addition of alcohol.
- ❑ The main mechanism of 1-pentanol in **"Cocktail 50%"** is the swelling of the diesel phase in a porous media and thereby its further mobilization.