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INSTITUTE OF CHEMICAL ENGINEERING SCIENCES


# Nanoparticle-based suspensions and emulsions for enhanced oil recovery

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# Introduction

**Problem**

- Energy consumption worldwide is expected to increase by 50% relative to current levels by the end of 2030.
- This growth is unlikely to be met by renewable resources, and thus there is a strong and growing demand for oil as a predominant energy resource.

**Objectives**

- Globally the overall oil recovery factors for primary and secondary recovery range from 35% to 45%.
- A tertiary recovery method can enhance the recovery factor by 10-30%, which could contribute to energy supply
- The use of nanoparticles in enhanced oil recovery (EOR) processes comprises an emerging and well-promising approach.

# Overview

Synthesis of Fe NPs

- polyphenols from parsley leaves
- $FeCl_3$

Characterization of Fe NPs properties

- Density , Contact angle
- Surface – Interfacial tension
- Size , z-potential
- Rheology of emulsion

Experiments into porous media

- transparent glass-etched pore networks

# Synthesis of Fe NPs

Polyphenols
(parsley leaves)

+

$FeCl_3$ 0.1M

| Measurements of Fe NPs suspension | | |
|---|---|---|
| pH | 6,02 | |
| Eh (mV) | 499,1 | |
| Surface Tension(mN/m) | Wilhelmy plate<br>53.84 | DuNouy Ring<br>55.12 |
| Interfacial Tension (mN/m) | 19.41 (with n-C12) | |
| Size (nm) | 132,43 | |
| Z-potential (mV) | -25,5 | |


Image : Solution of FeNPs

# Properties of FeNPs

## *Density:*

| fluids | Density d (g/mL) |
|---|---|
| Paraffin oil | 0.829 |
| NaCl 0.25M | 1.002 |
| Fe NPs 0.25(g/L) | 0.9931 |
| Fe NPs 0.25 (g/L) – NaCl 0.25M | 0.9814 |
| Fe NPs 0.25 (g/L) – NaCl 0.25M (Emulsion) | 0.833 |

## *Measurement ST and IT of suspensions:*

The ***static*** surface/interfacial tension of aqueous phase/air and aqueous phase/oil was measured by using a tensiometer with DuNouy Ring.

| suspension | Surface tension (mN/m) | Interfacial tension (mN/m) |
|---|---|---|
| NaCl 0.25M | 66.42 | 30.59 |
| Fe NPs 0.25(g/L) | 52.87 | 27.93 |
| Fe NPs 0.25 (g/L) – NaCl 0.25M | 50.03 | 20.72 |

# <u>*Contact angles:*</u>

| Solutions | CA (°)/air | image | CA (°) / paraffin | Image |
| --- | --- | --- | --- | --- |
| NaCl 0.25M | 53.85 |  | 54.45 |  |
| Fe NPs 0.25 g/L | 53.05 |  | 39.2 |  |
| Fe NPs 0.25 g/L – NaCl 0.25M | 55.0 |  | 43.95 |  |

# ***Size and z-potential:***

The suspended nanoparticle size distribution was determined with dynamic light scattering (DLS), while the stability of the nano-colloids was confirmed by measuring the ζ-potential.

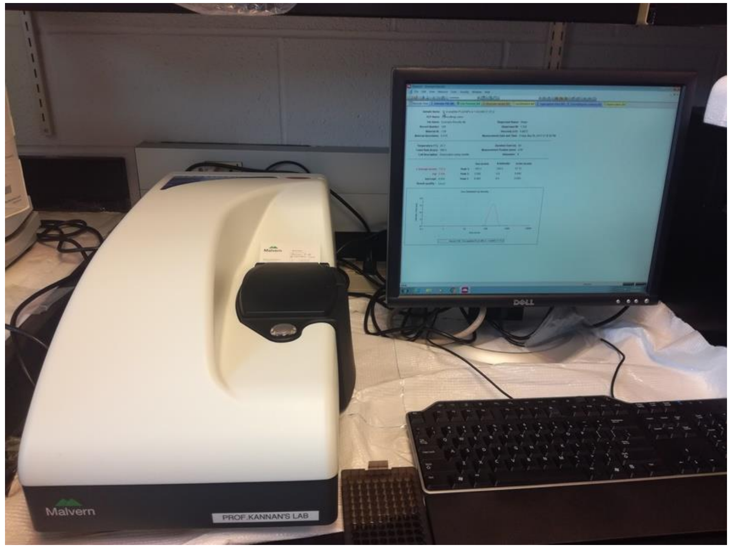
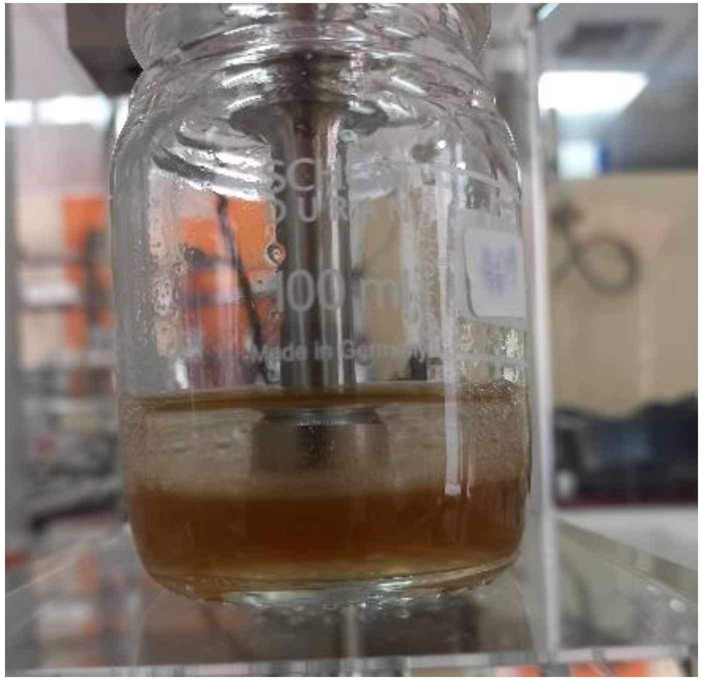



Image : Dynamic light scattering

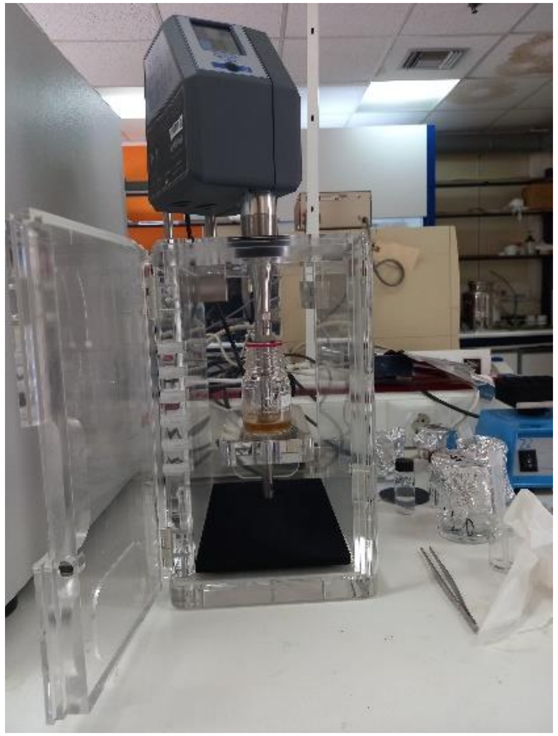
| solutions | Size (nm) |
|---|---|
| Fe NPs 0.25 (g/L) | 36.39 |
| Fe NPs 0.25(g/L) – NaCl 0.25M | 35.26 |
| Fe NPs 0.25(g/L) – NaCl 0.25M (Emulsion) | 220.2 |

Zeta potential of FeNPs 0.25 (g/L) is -22.1 mV.

# Pickering Emulsion



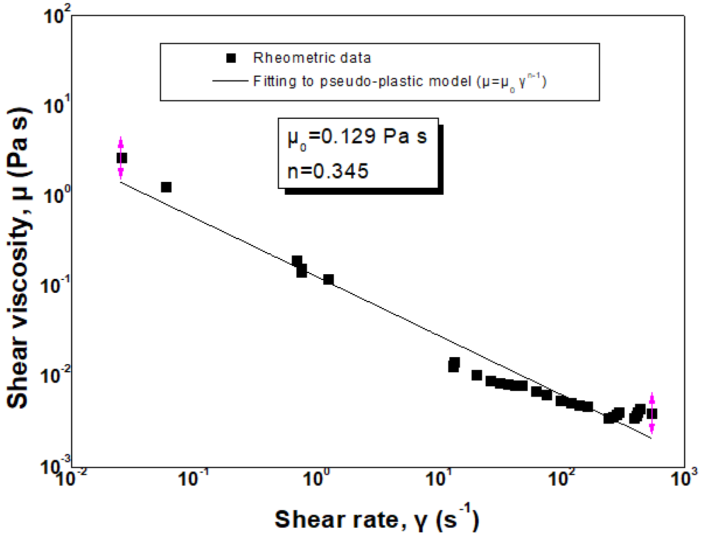
Suspension of FeNPs - oil (n-decane)
Volume ratio 1:1



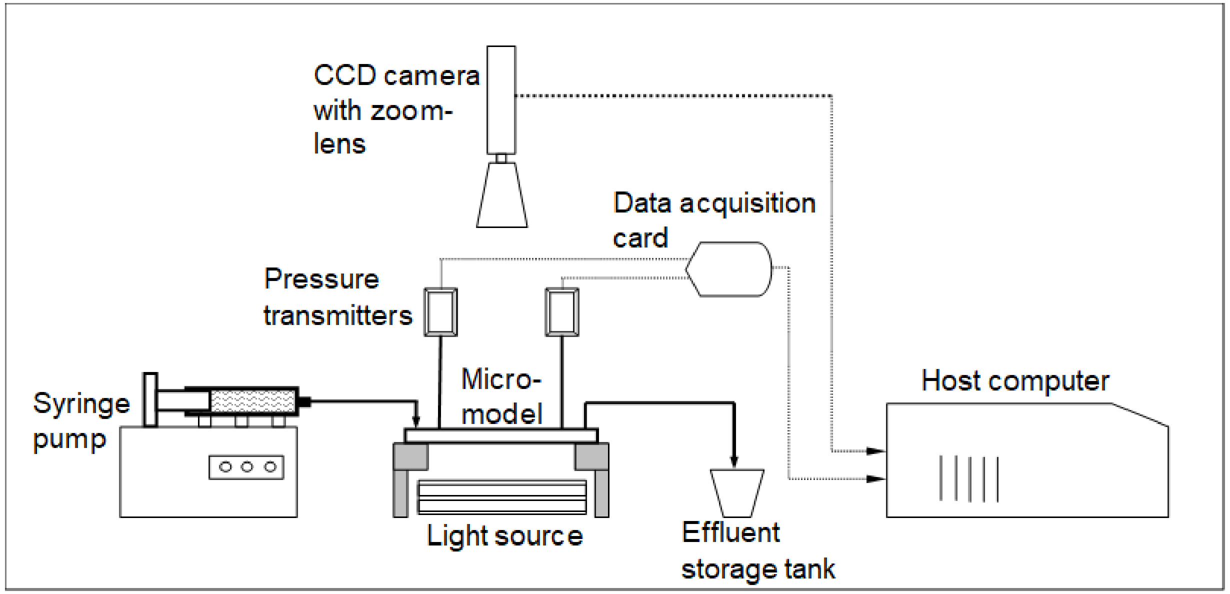
Ultrasound probe

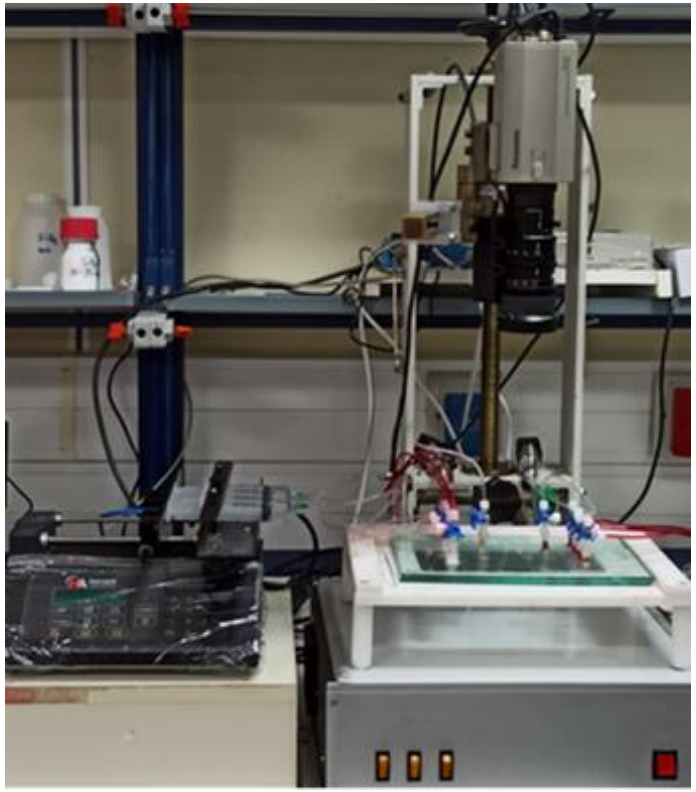
Pickering emulsion

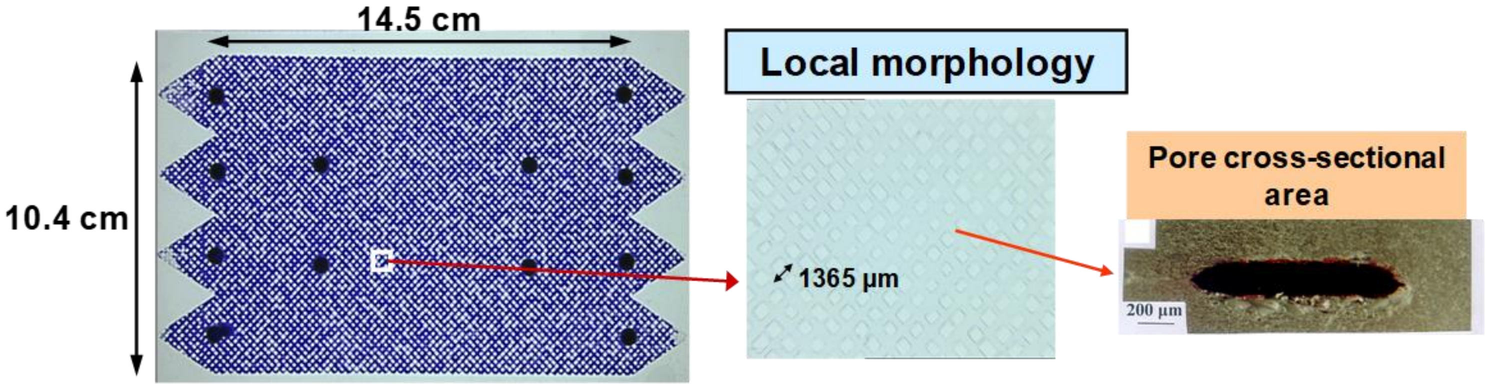
With the aid of an ultrasound probe, the nano-colloids were mixed with oil (n-decane) to prepare Pickering emulsion of FeNPs 0.25g/L -NaCl 0.25M .



# Experimental setup of visualization tests on transparent pore networks





# Values of Ca and κ

Capillary number $Ca = \frac{\mu_{displacing}\, U}{IT}$

Viscosity ratio $\kappa = \frac{\mu_{displacing}}{\mu_{displaced}}$

$\mu_{emulsion}$ = 0.01246 Pa s

$\mu_{paraffin}$ = 0.026 Pa s

$\mu_{water}$ = 0.001 Pa s

Ca pore scale -> **$Ca_{L1}$=Ca*factor**

Ca network scale -> **$Ca_{LN}=Ca_{L1}*L_N/L_p$**

Drainage: $Ca_{L1}$=0.0324, $Ca_{LN}$=3.2

Imbibition: $Ca_{L1}$=0.0038, $Ca_{LN}$=0.38

*Tsakiroglou et al., AIChE J. 49(10), 2472 (2003)*

| fluid | Flow rate($10^{-6}$/60) m3/s | U ( $10^{-5}$ m/s) | μ (Pa s) | IT (mN/m) | Ca ($10^{-6}$) | κ |
|---|---|---|---|---|---|---|
| paraffin | 0.08 | 0.94 | 0.026 | 30.5 | 8.0 | 26.0 |
| NaCl 0.25M | 0.2 | 2.35 | 0.001 | 25.0 | 0.94 | 0.038 |
| FeNPs 0.25 g/L | 0.2 | 2.35 | 0.001 | 25.0 | 0.94 | 0.038 |
| FeNps 0.25 g/L – NaCl 0.25M | 0.2 | 2.35 | 0.001 | 25.0 | 0.94 | 0.038 |
| FeNps 0.25 g/L – NaCl 0.25M (emulsion) | 0.2 | 2.35 | 0.01246 | 25.0 | 1.17 | 0.48 |

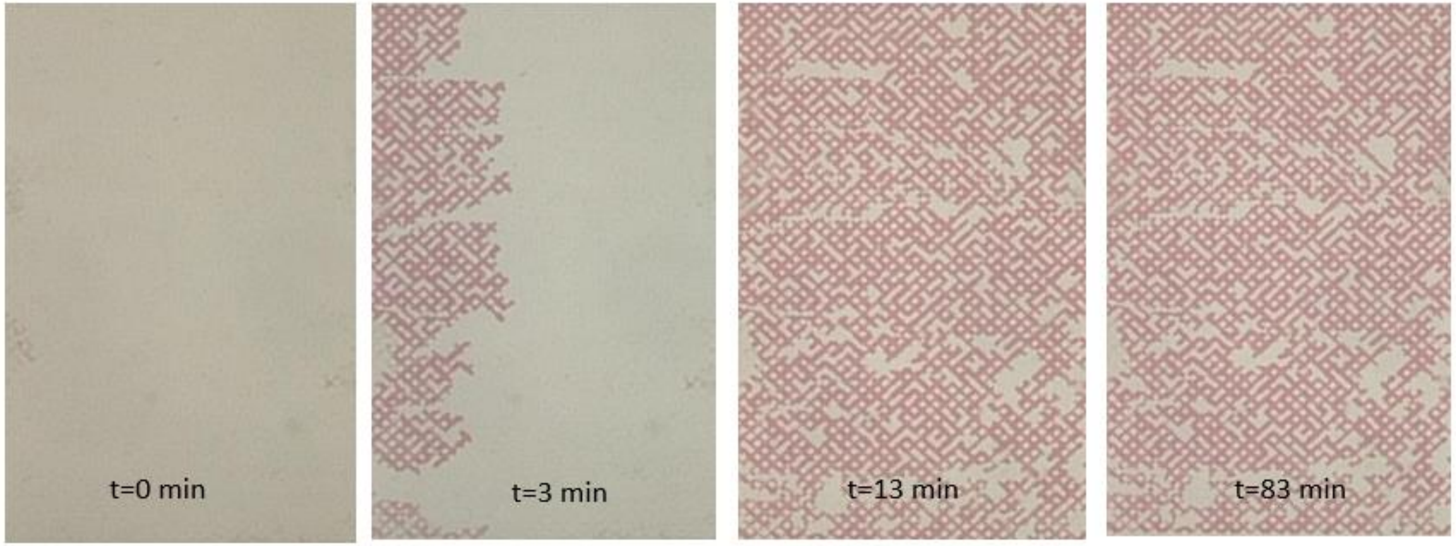
# Transient two-phase flow patterns

Primary Drainage

Displacement NaCl 0.25M by **paraffin oil** (red- colored)

κ= 26.0

Ca = $8x10^{-6}$

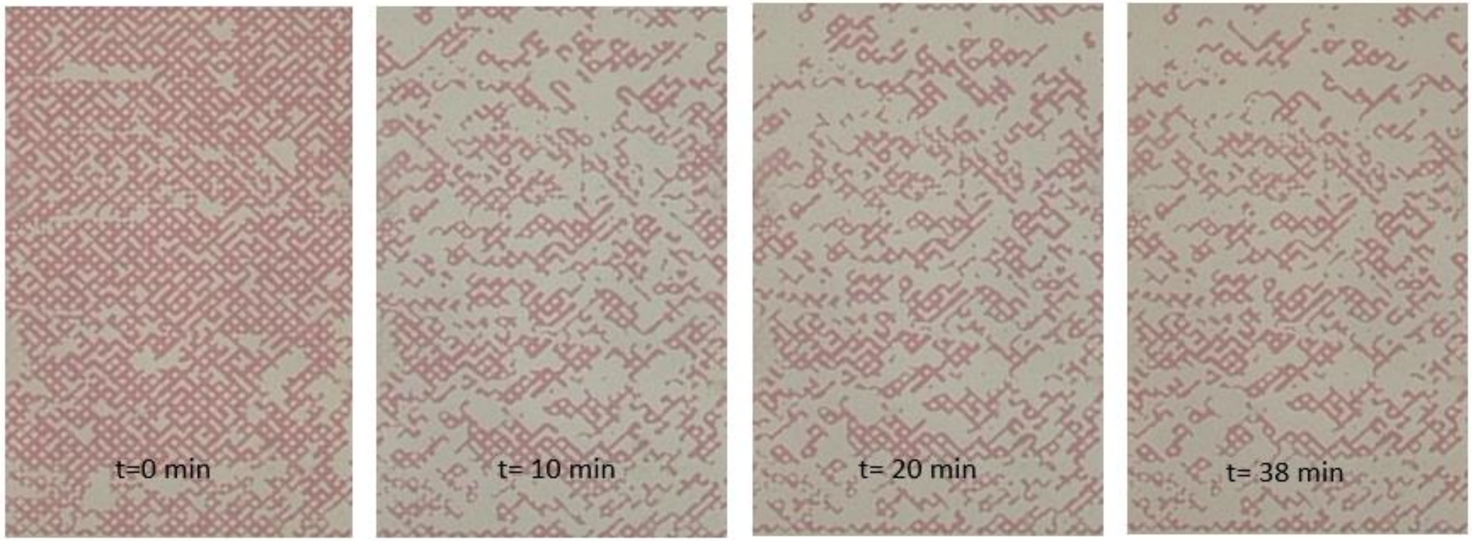



Primary Imbibition

**NaCl 0.25M**

κ = 0.038

Ca = $0.94x10^{-6}$



# Transient two-phase flow patterns

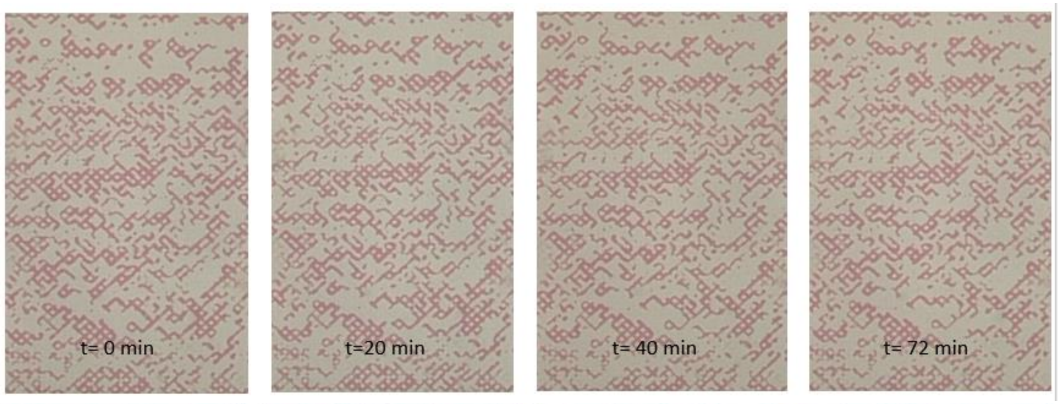
*Secondary Imbibition*

$$\kappa = \frac{\mu_{displacing}}{\mu_{displaced}}$$

**FeNPs 0.25 g/L**

κ≈ 0.038

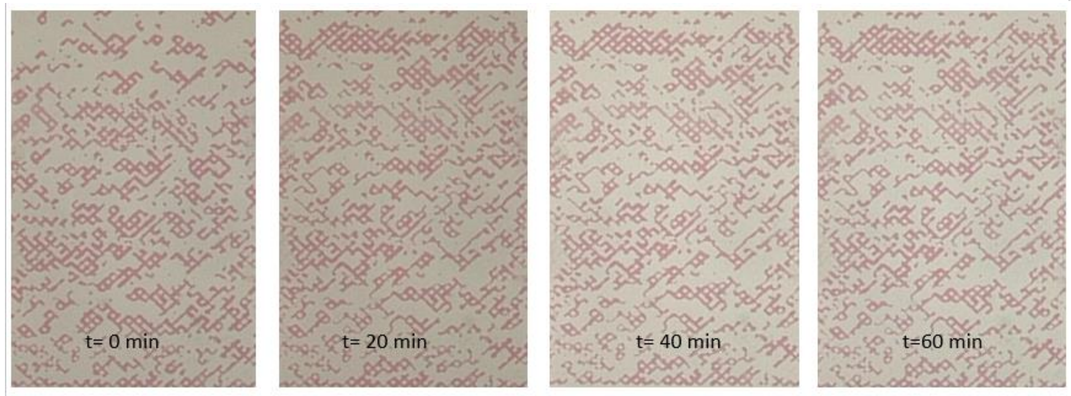
Ca = $0.94 \times 10^{-6}$




**FeNPs 0.25 g/L – NaCl 0.25M**

κ≈ 0.038

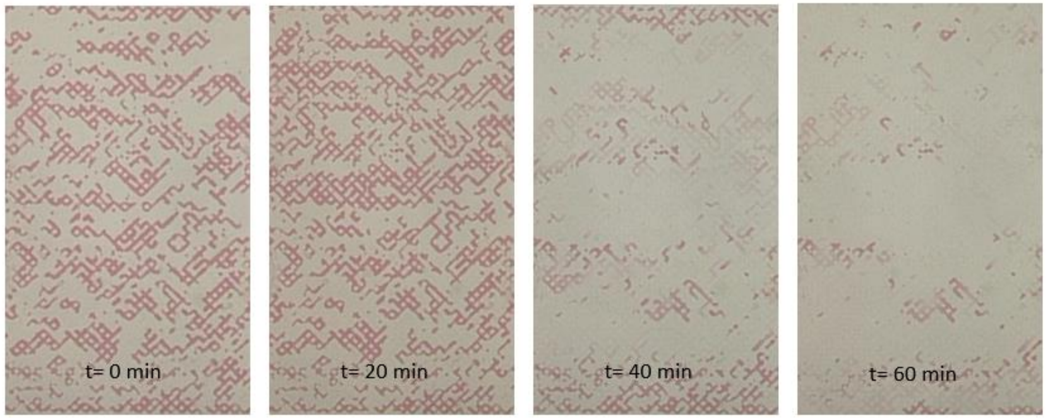
Ca = $0.94 \times 10^{-6}$




**FeNPs 0.25 g/L – NaCl 0.25M**
**Emulsion**

κ=0.48

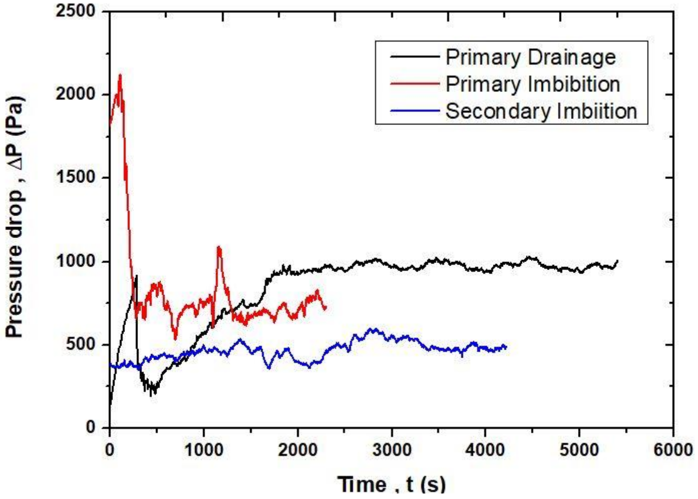
Ca = $1.17 \times 10^{-6}$

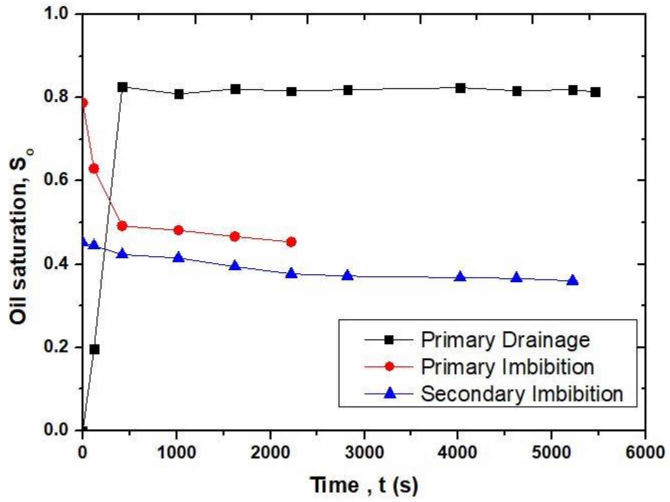



*Tsakiroglou et al., J. Coll. & Interface Sci. 267, 217-232 (2003)*
*Tsakiroglou, J. Non-Newt. Fluid Mech. 117, 1–23 (2004)*

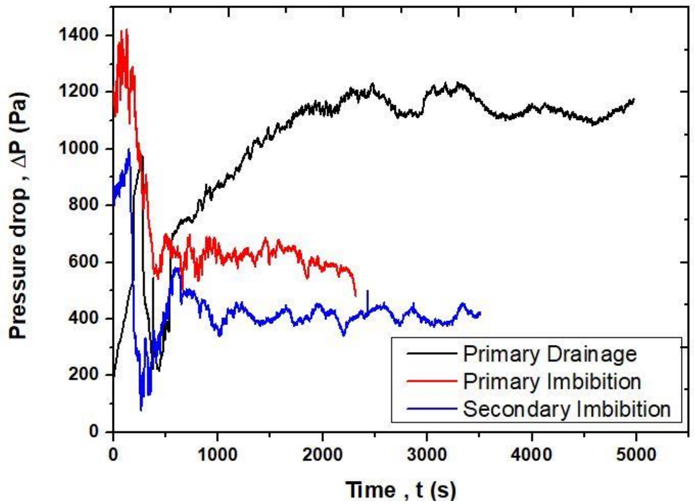
# Plots of tests for EOR

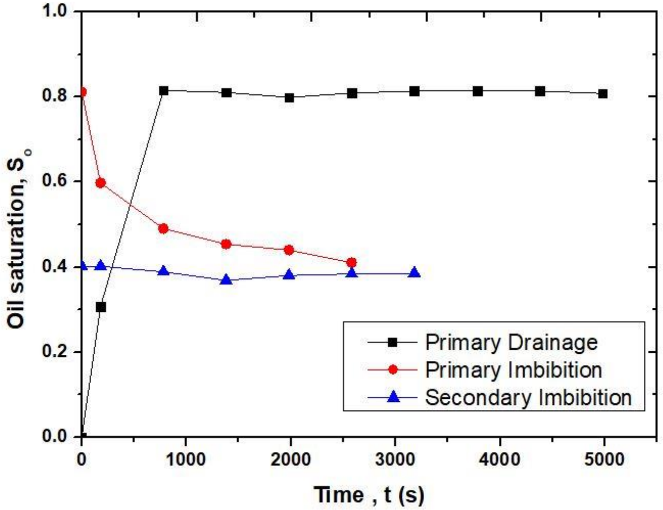
## Fe NPs 0.25 (g/L)



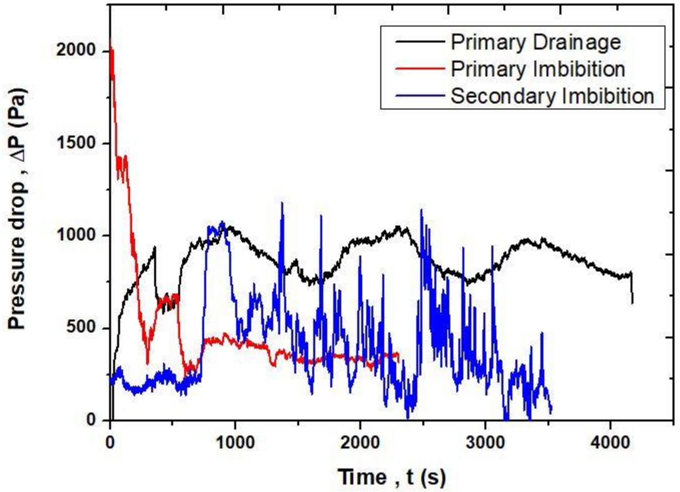



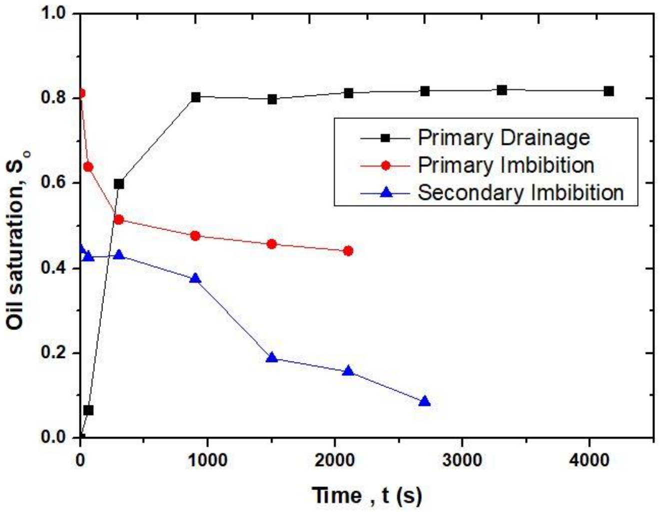

## Fe NPs 0.25 (g/L) – NaCl 0.25M




## Fe NPs 0.25 (g/L) – NaCl 0.25M Emulsion



# Results

| Type of displacement | Displaced fluid | Displacing fluid | Flow rate (mL/min) | Injected volume (mL) | Oil saturation | Oil removal efficiency (%) |
|---|---|---|---|---|---|---|
| **Drainage** | NaCl 0.25M | Paraffin oil | 0.08 | 8.0 | 0.82 | - |
| **Prim. Imbib.** | Resid. paraffin oil | NaCl 0.25M | 0.2 | 8.0 | 0.45 | 46.25 |
| **Sec. Imbib.** | Resid. paraffin oil | FeNPs 0.25 (g/L)-water suspension | 0.2 | 14.4 | 0.36 | 20.0 |
| **Drainage** | NaCl 0.25M | Paraffin oil | 0.08 | 8.0 | 0.82 | - |
| **Prim. Imbib.** | Resid. paraffin oil | NaCl 0.25M | 0.2 | 8.0 | 0.41 | 50.0 |
| **Sec. Imbib.** | Resid. paraffin oil | FeNPs 0.25 (g/L)-NaCl 0.25M suspension | 0.2 | 14.0 | 0.39 | 4.88 |
| **Drainage** | NaCl 0.25M | Paraffin oil | 0.08 | 8.0 | 0.82 | - |
| **Prim. Imbib.** | Resid. paraffin oil | NaCl 0.25M | 0.2 | 8.0 | 0.44 | 46.34 |
| **Sec. Imbib.** | Resid. paraffin oil | Emulsion | 0.2 | 12.0 | 0.09 | 79.55 |

# Conclusions

- The potential to increase the residual oil recovery efficiency by injecting suspensions of iron oxide nanoparticles synthesized and stabilized by the polyphenols of parsley extracts is investigated with visualization tests on a glass-etched pore network.
- The nanoparticles mobilize trapped oil by transferring it from upstream to downstream through a mechanism of successive steps of drainage (local increase of oil saturation) / imbibition (local decrease of oil saturation).
- It seems that the oil recovery efficiency of secondary imbibition tests is favored when using low iron concentration Fe NPs suspension without the presence of NaCl . On the other hand, the oil recovery efficiency increases respectably when using Pickering emulsions stabilized by FeNP with NaCl.

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