Modeling and measuring the transport of foam in porous media in the presence of nanoparticles

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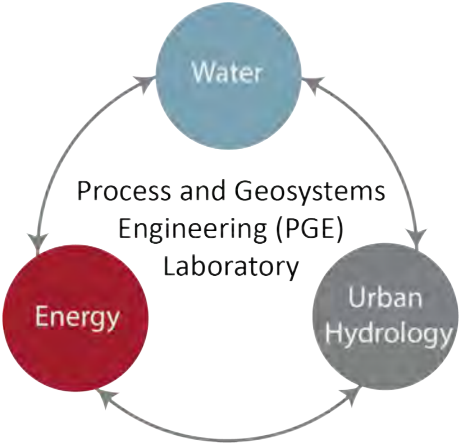
PNNL - Center for the Remediation of Complex Sites (RemPlex) - February 23rd, 2021

Center for Environmental Systems (CES)

- **Mission:** basic and applied research for advanced technology and innovation in environmental engineering.
- **Research:** water, energy, and sustainability with applications to: wastewater and drinking water treatment, renewable energy, and CO_2 utilization and storage.
- **People:** 10 faculty from the Schaefer School of Engineering; 10 PhD students, 5 postdocs; and 2 project managers.
- Research funding on average is: \$ 3M per year.

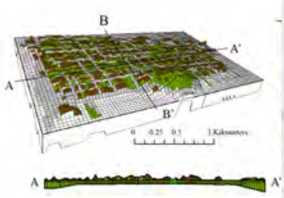
Prigiobbe research group



Urban hydrology

Nuisance flooding due to groundwater

Groundwater modeling



Sewer modeling

Sewer flooding

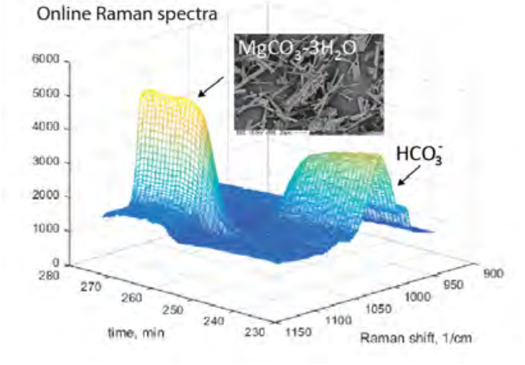
Street flooding

Liu, Su, and Prigiobbe (2018) Water 10(12), 1774.
Su, Liu, Beheshti, and Prigiobbe (2020) Environ Sci Pollut Res 27, 14288—14298
Su, Belvedere, Tosco, and Prigiobbe (202X) Studying nuisance flooding due to groundwater in a coastal urban area. In review.
Liu, Ramirez-Marquez, and Prigiobbe (202X) Combining a statistical model with machine learning to predict groundwater flooding (or infiltration) into sewer networks. In review.

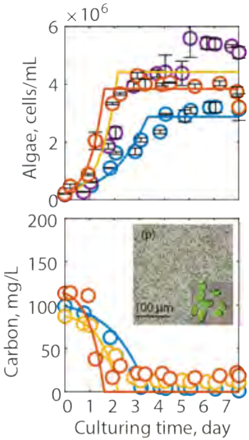
Energy and water

CO_2 mineralization for carbon utilization and storage

Precipitation of nesquehonite



Algae growth using nesquehonite

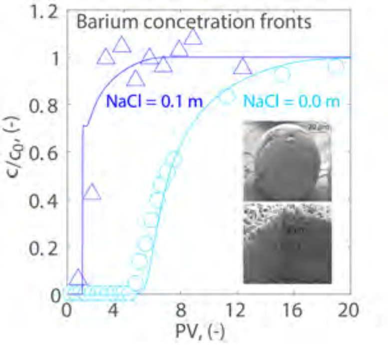


Prigiobbe (2018) *J. Env Chem Eng* **6** 930–936.
Ye, Abraham, Christodoulato, and Prigiobbe (2019) *Energy Fuels* 33 8843–8851.

Energy and water

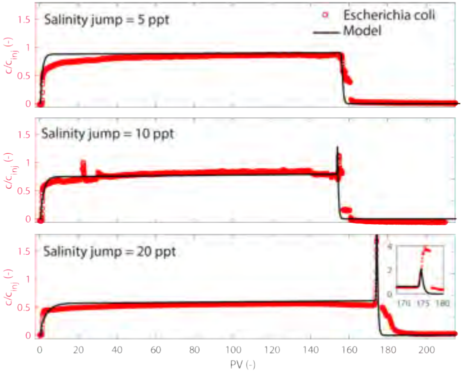
Reactive transport in porous media

Produced water



Ye and Prigiobbe (2018) *J Contam Hydrol* 209 24–32.
Ye and Prigiobbe (2020) *Wat Res* 185 116258.

Virus and bacteria

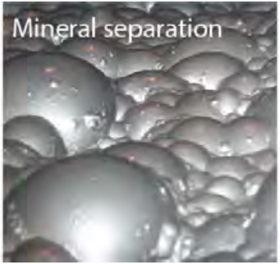


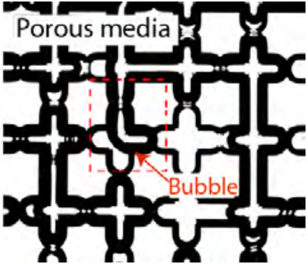
Zhang, Zabarankin, and Prigiobbe, (2019) 127, 252–263.
Zhang and Prigiobbe (202X). Influence of salinity on *E. coli* transport behaviour. In review.

Outline

1. Motivation and introduction
2. Mechanistic model of foam transport in porous media in the presence of nanoparticles
3. Experiments of foam generation in the presence of nanoparticles using a microfluidic system
4. Experiments of foam transport using a column-flood system for model verification
5. Summary and conclusions

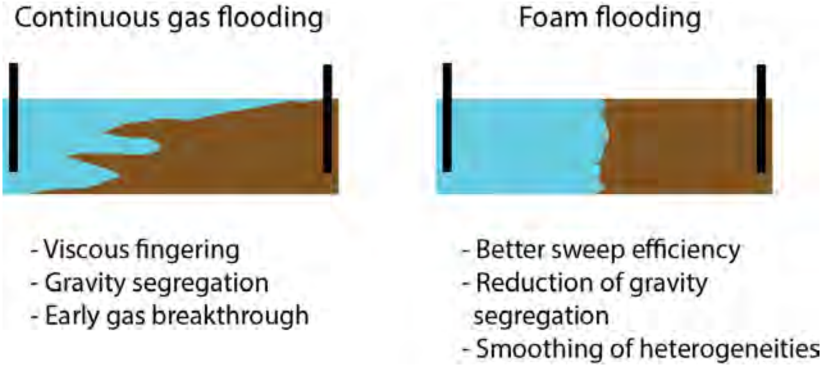
What is a foam?





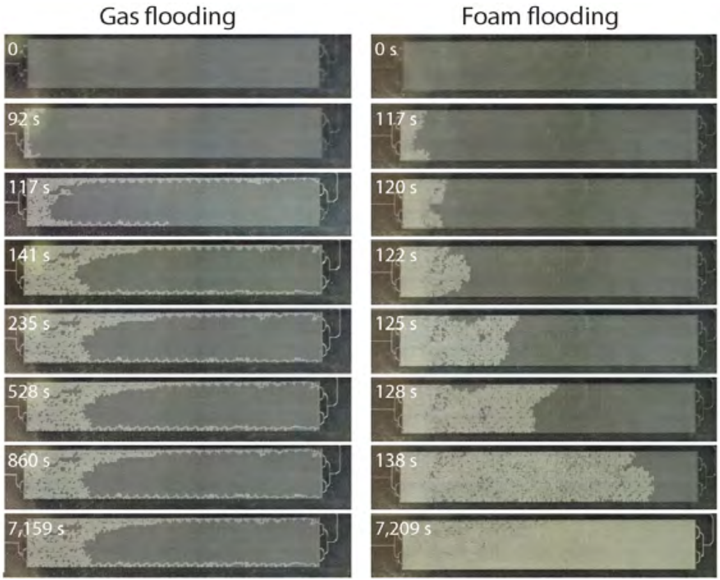
When is foam flooding employed?

Enhanced-oil recovery

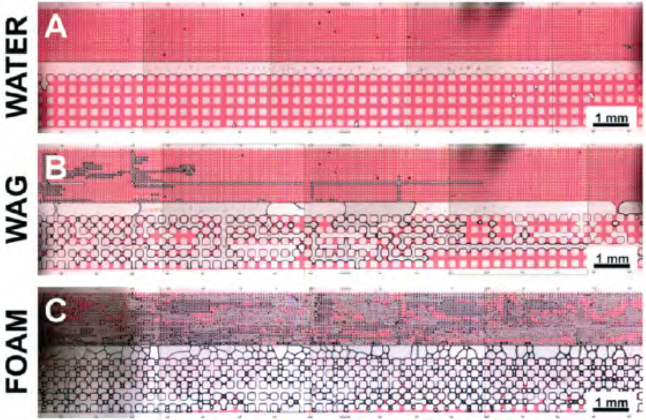


Rossen. Foams in enhanced oil recovery, Marcel Dekker, New York (1996).

Better sweep efficiency and reduced fingering



Smoothing of heterogeneities

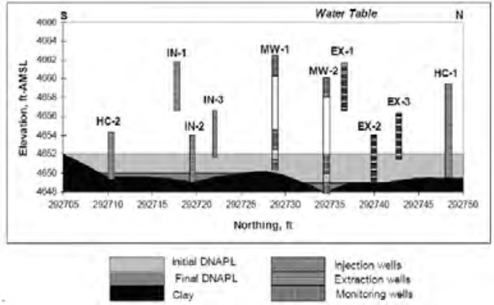


Conn, Ma, Hirasaki, and Biswal (2014) *Lab on a Chip* **14** 3968.

When is foam flooding employed?

Foam flooding for DNAPL removal

- Formation of foam in high-permeability zones to divert surfactant solution to zones of lower permeability.
- Reduction of DNAPL saturation from 22 % to 0.03 %.
- The low water content ($\sim 5\%$) reduces contaminant mobilization.

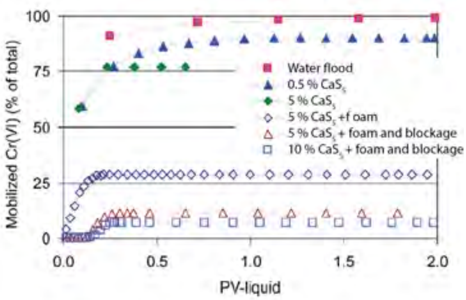


Hirasaki *et al.* (1997) Field Demonstration of the Surfactant/Foam Process for Aquifer Remediation, *SPE 39292*.

When is foam flooding employed?

Foam flooding for the delivery of calcium polysulfide (CaS_5)

- Delivery of amendment with water for the immobilization of metals and radionuclides in the vadose zone is inefficient and can mobilized the contaminants.
- The delivery of CaS_5 with foam to immobilize Cr(VI) was reduced from 70-98% when conventional method were used to 27% when foam combined with foam-blocking was applied.

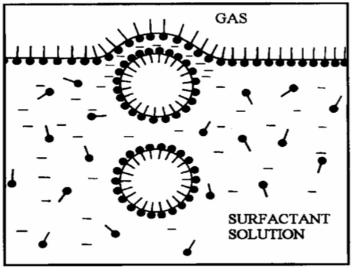


- Reaction: $2CrO_4^{2-} + 3CaS_5 + 10H^+ \rightarrow 2Cr(OH)_3 + 15S_{(s)} + 3Ca^{2+} + 2H_2O$

Zhong, Qafoku, Szecsody, Dresel, and Zhang (2009) *Vadose Zone J.* **8** 976–985.
Zhong, Qafoku, Szecsody, Dresel, and Zhang (2009) WM2009 Conference, March 1-5, 2009, Phoenix, AZ

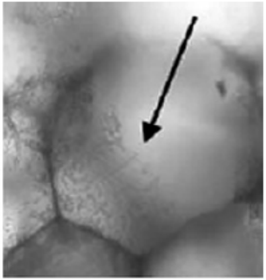
How a foam is stabilized

Surfactant



- Reduction of surface tension/energy.
- Elasticity of the gas-liquid interface.

Particles

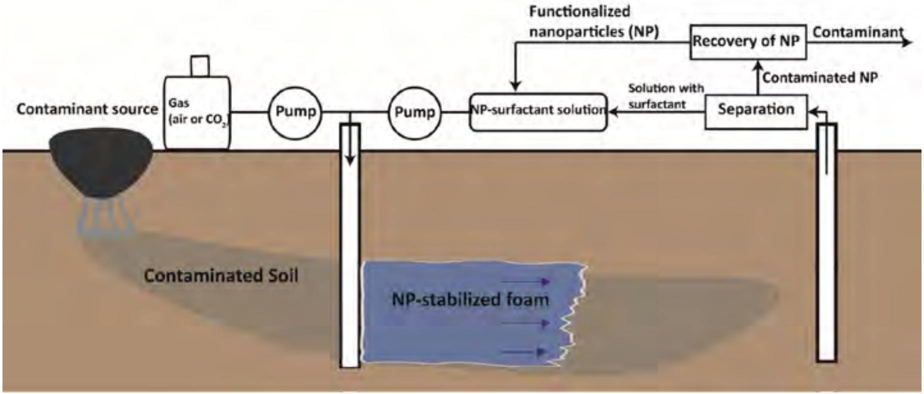


- Reduction of gas diffusion.
- Reduction of drainage.
- Increase of the critical capillary pressure (P_c^*).

Image from: Martinez *et al.* (2008) *Soft Matter* **4**.

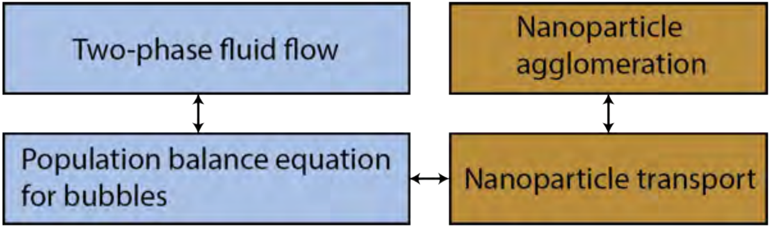
Nano-remediation with foam

Nano-remediation is based on the use of engineered nanoparticles for in situ degradation, transformation, or immobilization of pollutants.
Using foam, nanoparticle mobility control is improved and water is reduced.



Mechanistic model of foam transport in porous media in the presence of nanoparticles

Scheme of the model



Li and Prigiobbe (2019) *Transp Porous Media* **131** 269—288.

Modeling foam transport in porous media

Governing equations*

Fractional flow equation

$$\phi \frac{\partial S_w}{\partial t} + u_t \frac{\partial f_w}{\partial x} = 0,$$

Population balance equation (PBE) for bubbles

$$\phi \frac{\partial (S_g n_f)}{\partial t} + u_t \frac{\partial (f_g n_f)}{\partial x} = \phi S_g (r_g - r_c),$$

- S_w and S_g are the water and the gas saturations, (-);
- ϕ is the porosity, (-);
- u_t is the total flux, where $u_t = u_w + u_g$, m/s;
- n_f is the bubble concentration, $\#/\mathrm{m}^3$;
- r_g and r_c are the rates of generation and coalescence, $\#/(\mathrm{m}^3\mathrm{s})$;
- f_w is the water fraction, (-).

*Kovscek *et al.*, Chem. Eng. Sci. 50(23), 1995; Kam and Rossen, SPEJ 8, 2003.

Modeling foam transport in porous media

Constitutive equations†

Rate of generation

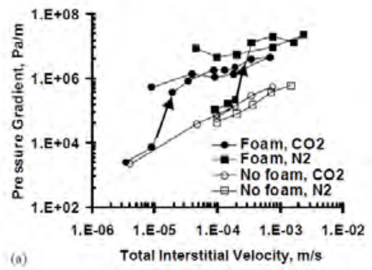
$$r_g = C_g(\nabla p)^m,$$

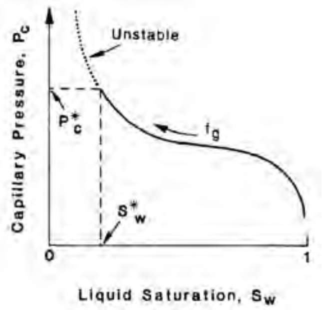
C_g and m are model parameters.

Rate of coalescence

$$r_c = C_c n_f \left(\frac{S_w}{S_w - S_w^*}\right)^n,$$

C_c and n are model parameters and S_w^* is the minimum water saturation.





†Gauglitz *et al.*, Chem. Eng. Sci. 57, 2002. Khatib *et al.*, SPE Reservoir Eng., 1988.

Modeling nanoparticle transport in porous media

Governing equations of nanoparticles transport

$$\frac{\partial(\phi S_w c_w + \rho_b R)}{\partial t} + u_w \frac{\partial c_w}{\partial x} - D\phi \frac{\partial^2 (S_w c_w)}{\partial x^2} = k_b S_w c_w,$$
$$\frac{\partial(\phi S_g c_g)}{\partial t} + u_g \frac{\partial c_g}{\partial x} = -k_b S_w c_w,$$

- c is the nanoparticle concentration, g/m^3; R is the nanoparticle retention, g/kg; ρ_b porous medium density, kg/m^3; D hydrodynamic dispersion, m^2/s; k_b adsorption/desorption rate, g/m^{3}s.

Governing equations of nanoparticles aggregation [‡]

$$\frac{\partial n_p(t,x)}{\partial t} = \frac{1}{2}\int_0^\infty \beta(t, x-y, y) n_p(t, x-y) n_p(t,y) dy - n_p(t,x)\int_0^\infty \beta(t,x,y) n_p(t,y) dy,$$

- n_p is the number of nanoparticle, #/m^3; β is the aggregation kernel; x and y are characteristic length of the particles, m.

[‡] Kumar and Ramkrishna, Chem. Eng. Sci.(1996) 51 1333–1342.

Modeling nanoparticle transport in porous media

Constitutive equations

Attachment/detachment

$$\rho_b \frac{\partial R}{\partial t} = k_{att}\phi c - \rho_b k_{det} R_{max},$$

- k_{att} and k_{det} attachment and detachment coefficients, (-);
- R_{max}, maximum attachment capacity, g/kg.

Aggregation kernel§

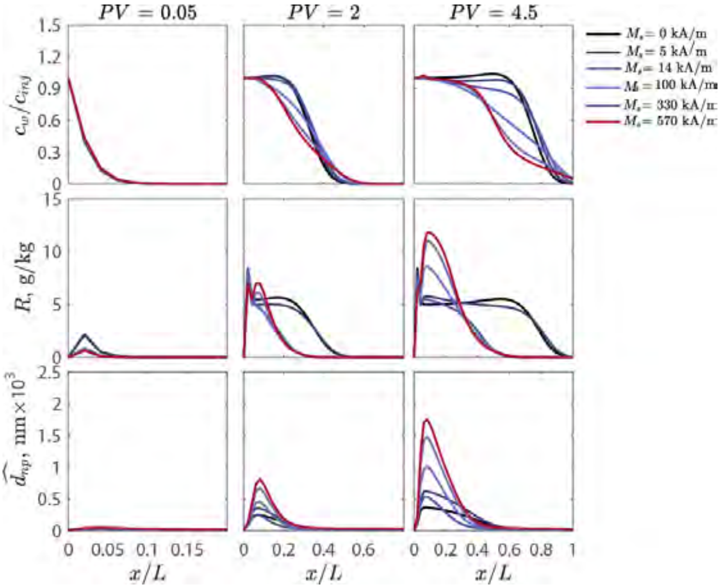
$$\beta_{j,k} = \frac{2k_B T}{3\mu W_{j,k}}(r_j + r_k)\left(\frac{1}{r_j} + \frac{1}{r_k}\right),$$

$$W_{i,k} = (r_j + r_k)\int_r^{\infty} \frac{e^{(V_T/K_B T)}}{r^2}\, dr,$$

- V_T, total interaction energy, i.e, electrostatic, van der Waals, and magnetic energy.

§Hunter and White, Foundations of Colloid Science, Clarendon Press, 1987

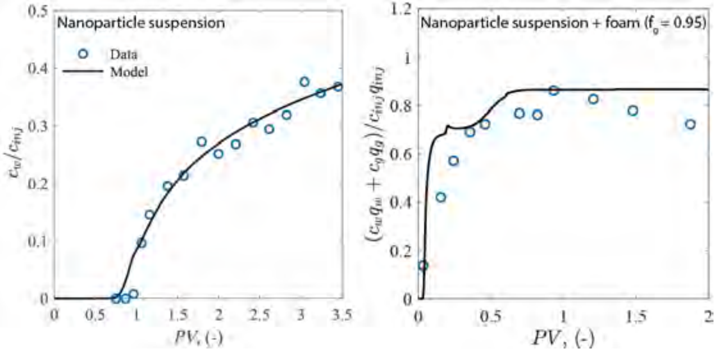
Effect of magnetic properties of the nanoparticles



Li and Prigiobbe (2019) *Transp Porous Media* **131** 269—288.

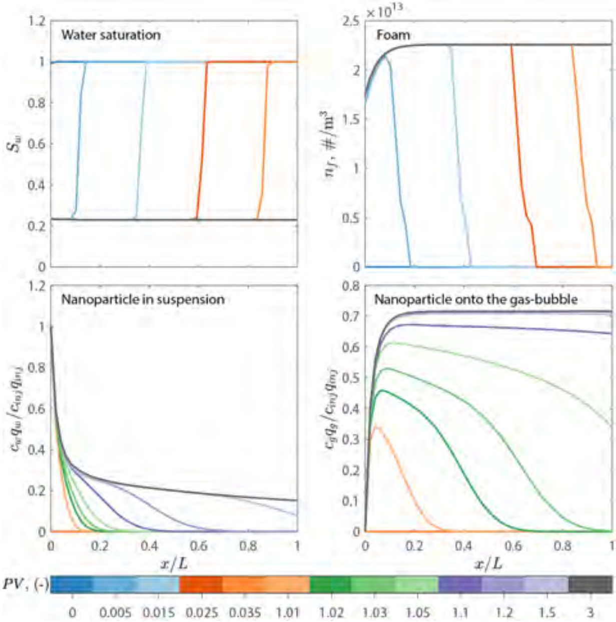
Comparison of the model with literature data

- $Q = 1.3$ mL/min,
- $r_{NP} = 54.5$ nm,
- $k = 1.2 \times 10^{-12}$ m^2,
- $c_0 = 3$ g/L,



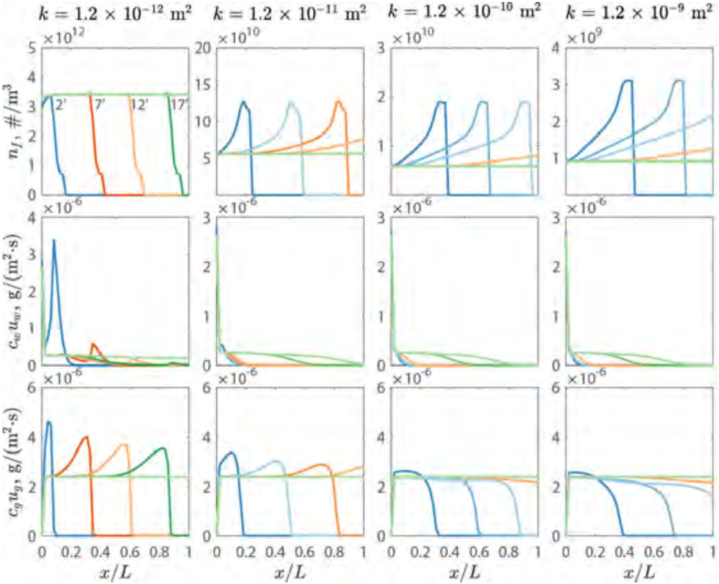
Phenrat *et al.* (2007) *Environ. Sci. Technol.* **41** 284.;
Ding *et al.* (2013) *J. Env. Eng.* **139**(9) 1206.

Simulations of nanoparticle carried with foam



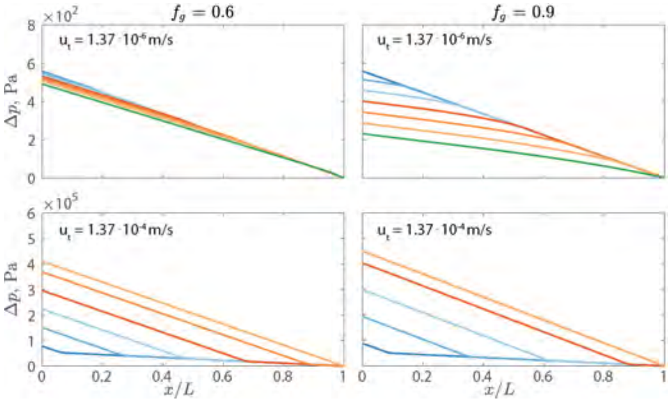
Simulations of nanoparticle carried with foam

Effect of permeability



Simulations of nanoparticle carried with foam

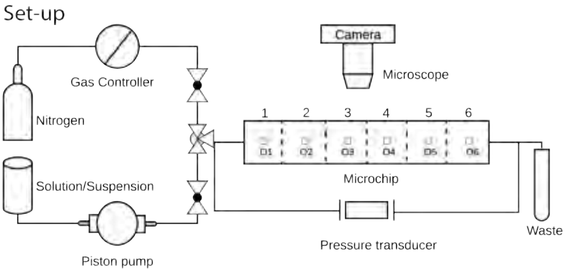
Pressure profiles

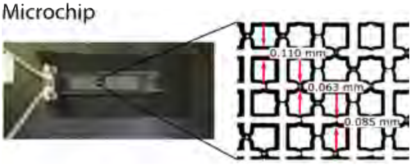


- The pressure within the domain increases with the total flux up to 500 kN/m^2 acceptable for applications of foam flooding in the shallow subsurface.
- For optimal design, aquifer properties should be considered to maximize delivery, minimize the duration of the operation, and contain the pressure.

Experiments of foam generation in the presence of nanoparticles using a microfluidic system

Experiments





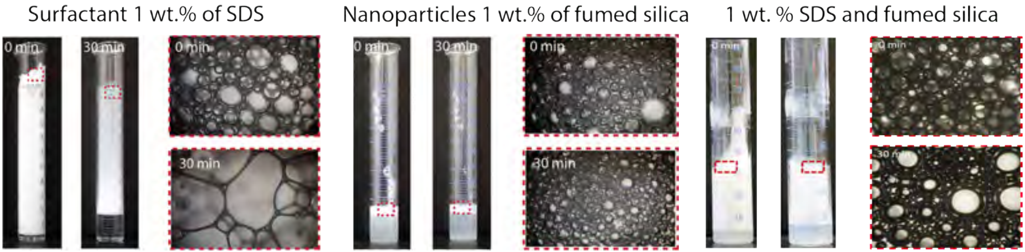
Operating conditions:

- Saturation with a brine of either surfactant (SDS, sodium dodecyl sulfate), nanoparticles (fumed silica, Nycol), or a combination.
- Nanoparticle of $\sim$ 50 nm average diameter.
- Injection of N_2 at the flow-rate of 0.1-0.5 mL/min.
- Experiments were recorded with a high-speed camera in six locations (O1 through O6) and a pressure transducer.

Li and Prigiobbe (2020) *Chem Eng Sci* **215**, 115427.

Experiments

Foamability and stability tests



Experiments

Images of bubble transport across the microchip

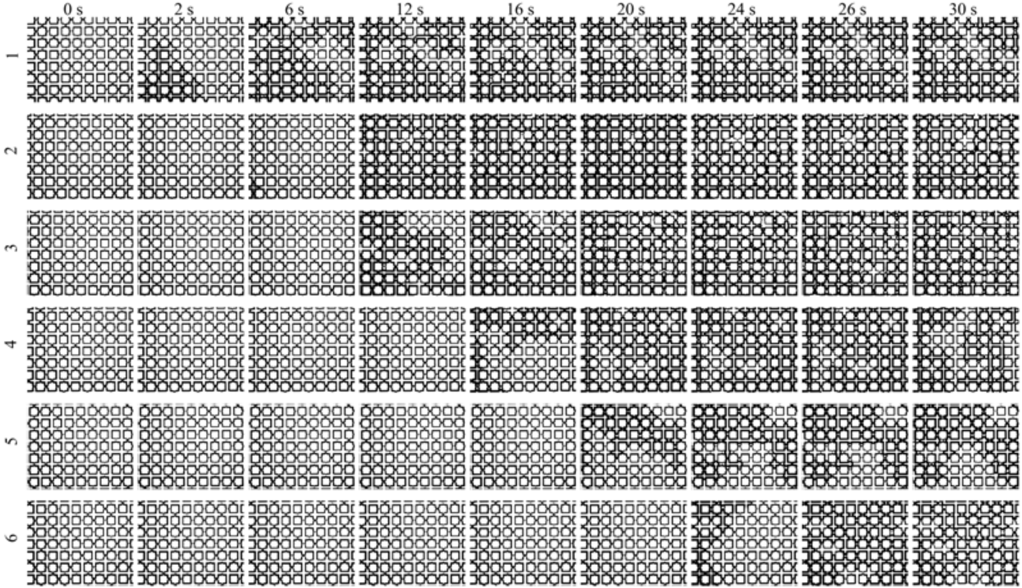
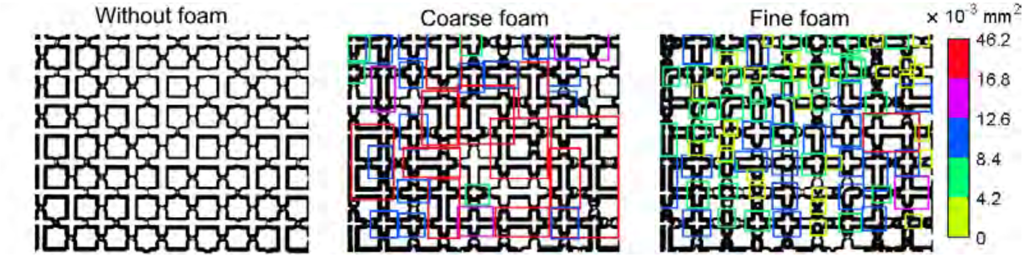


Image processing

- An algorithm based on convolutional neural network (CNN) was implemented for bubble recognition within the recorded images.
- Approximately 6,000 bubbles were labeled as a training data set corresponding to 60 images.
- Hundreds of bubbles in an image could be recognized within one second by using GPU acceleration (Quadro K620 GPU).



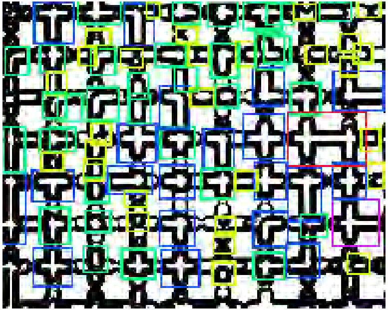
Modeling

Generation rate

$$r_g = \frac{dN(t)}{dt}\frac{1}{V},$$

Bubble number evolution

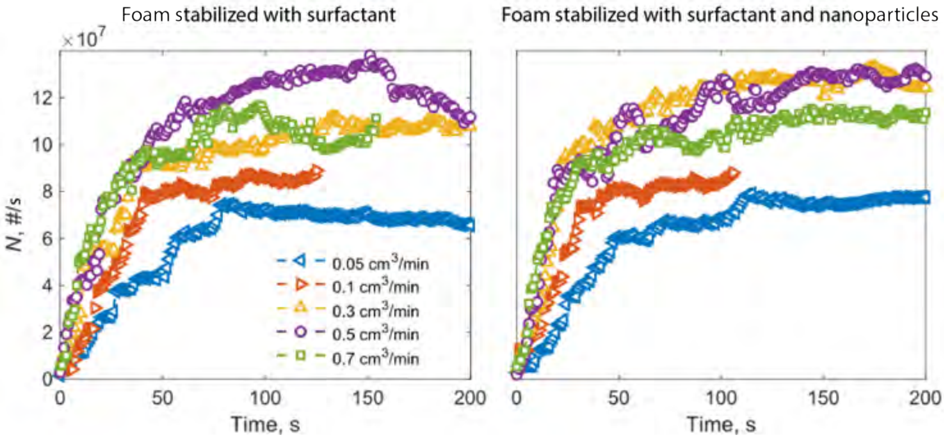
$$N(t) = \sum_{i=1}^{6} \frac{n_i(t)}{a_i} A_i,$$



where:
t is time, s.
$N(t)$ is the total number of bubbles, #/s.
$n_i(t)$ is the bubble number in the ith-view area, #/s.
a_i is the ithview area and A_i is the ith-section area, m^2.
V is the porous medium volume, m^3.

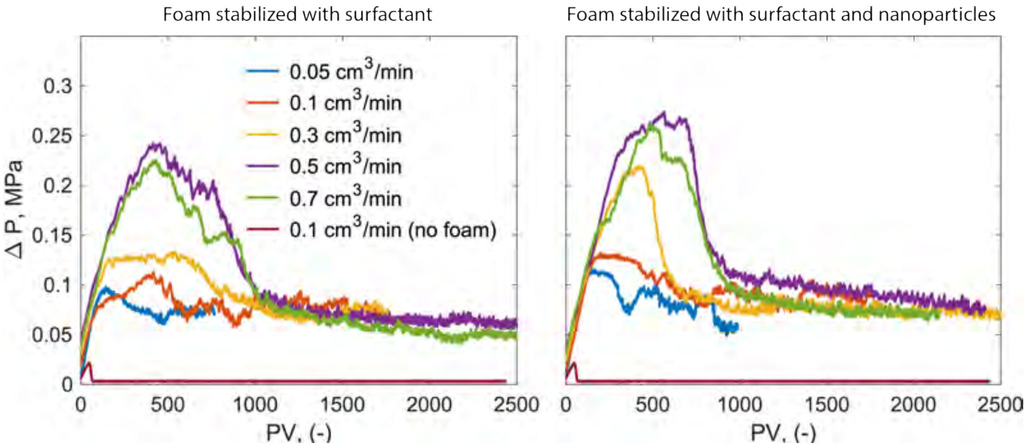
Results

Total number of bubbles (N, #/s)

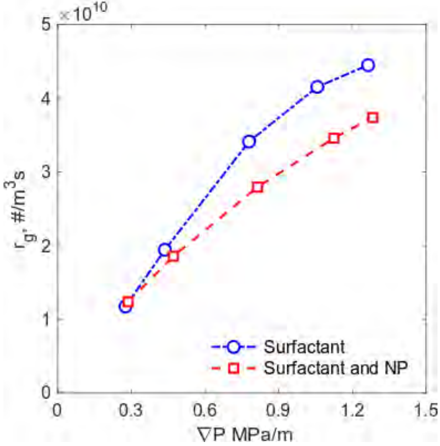


Results

Transport tests



Foam generation rate



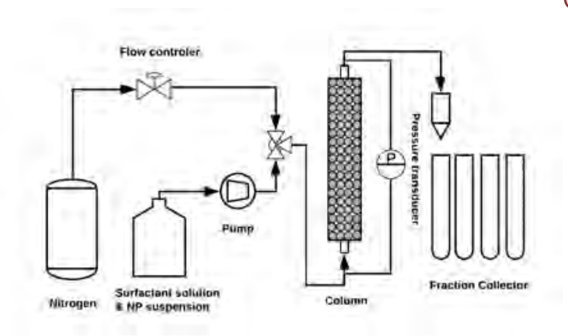
Generation rate, r_g (#/m^{3}s)

$$r_g \propto (\nabla P)^{\alpha},$$

where:
∇P is the pressure gradient, MPa.
α is a model parameter.

Experiments of foam transport using a column-flood system for model verification

Experiments



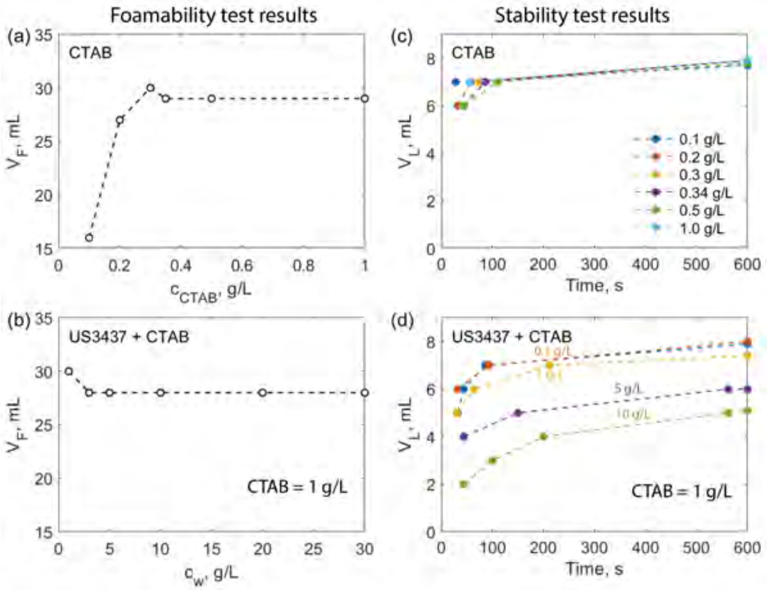
Li and Prigiobbe (202X) Modeling and measuring foam transport in the presence of nanoparticles. *In preparation*.

Operating conditions:

- Saturation with a brine containing either surfactant (CTAB, Cetyl Trimethyl Ammonium Bromide), silica nanoparticles (US3437, US Research Nanomaterials), or a combination.
- Nanoparticle of $\sim$ 50 nm average diameter.
- Injection of N_2 at the flow-rate of 0.1–1.0 mL/min.
- Experiments were monitored with a pressure transducer and sampled collected for nanoparticle concentration determination.

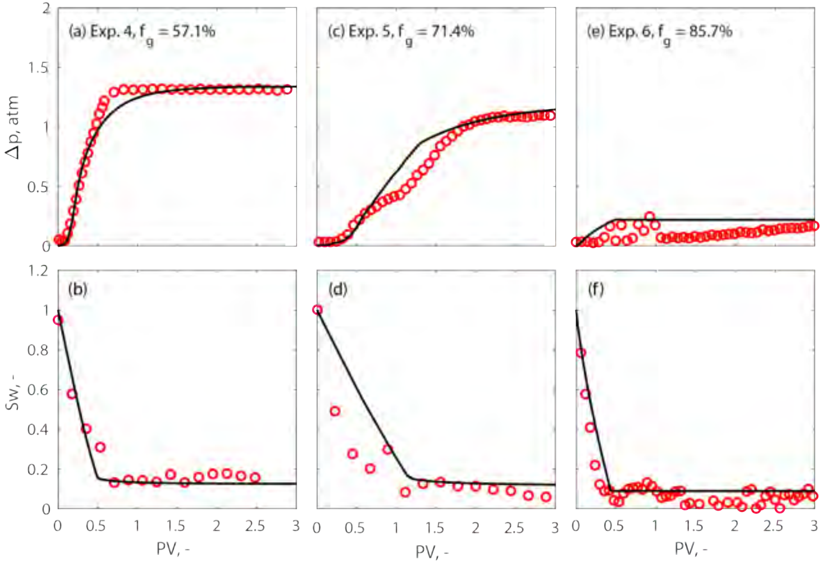
Results

Foamability and stability tests



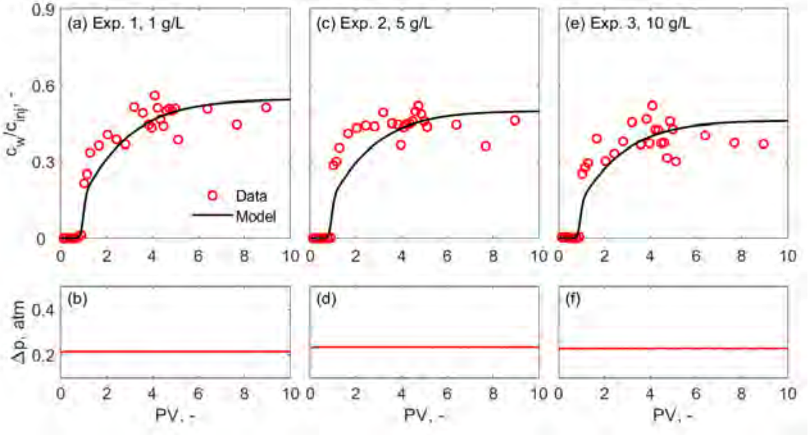
Results

Transport of foam stabilized with only surfactant



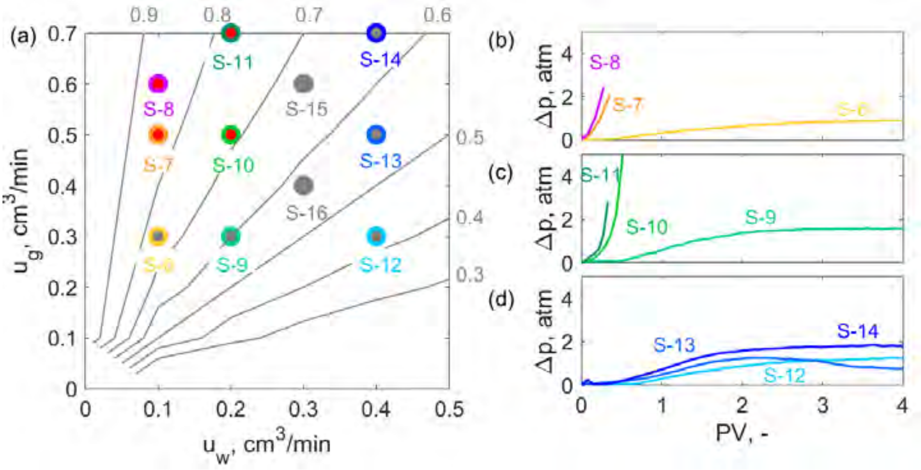
Results

Transport of nanoparticles



Results

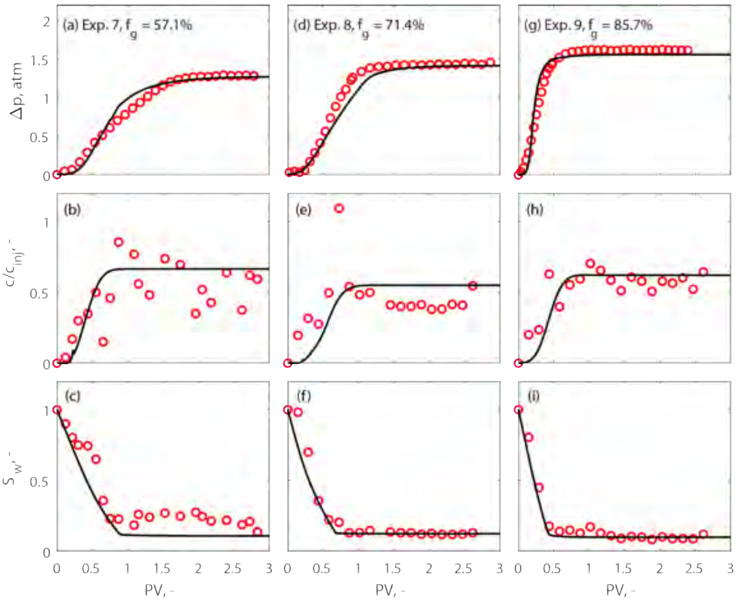
Transport of foam stabilized with surfactant and nanoparticles, $c_w = 5$ g/L



u_g and u_w are the rates of the gas and the water.

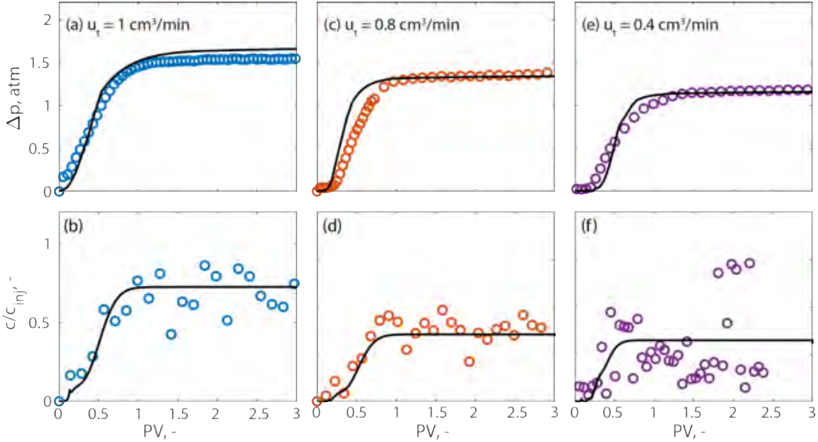
Results

Transport of foam stabilized with surfactant and nanoparticles, $c_w = 1$ g/L



Results

Effect of total flow rate (u_t, cm^3/min) at $f_g = 85.7$ %



Total flow rate: $u_t = u_g + u_w$.

Summary and conclusions

- The use of **foam** has the potential to improve the efficiency of conventional remediation methods for contaminated sites including amendment delivery and nano-remediation where reactive nanoparticles (NPs) are used.
- Challenges are the design and the description of the process. A **mechanistic model** coupling foam and nanoparticle transport was developed and verified with experiments.
- **Simulations** show a very stable high-quality foam can be formed using NPs even in a low permeability medium within the shallow subsurface.
- **Experiments** agree very well with the model and show NPs can be delivered with high-quality foam and much faster when carried by bubbles than by water alone.
- **Future work** will focus on the extension of the model to account for chemical reactions and heterogeneity.

Acknowledgments

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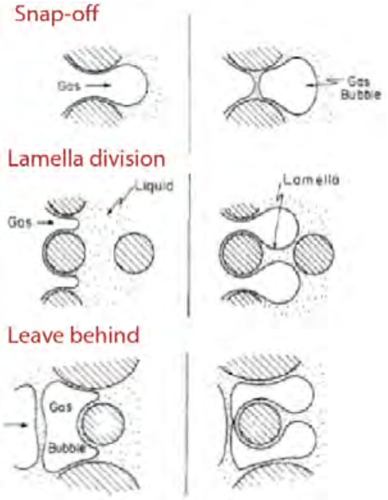
Contact information: Valentina Prigiobbe
Email: valentina.prigiobbe@stevens.edu

How foam is generated

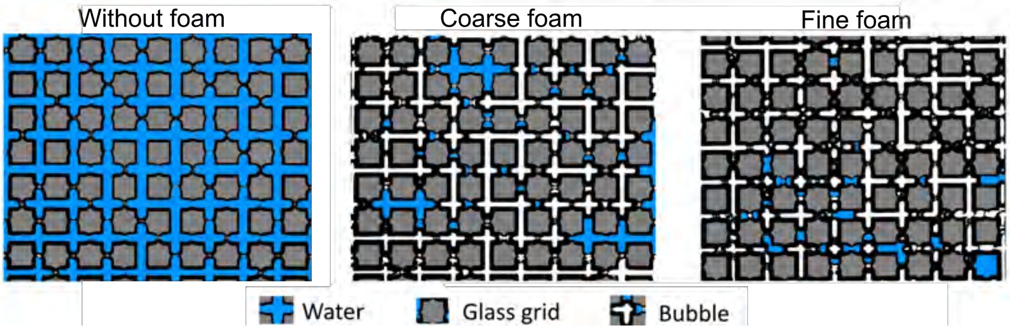
- Snap-off. As the bubble expands, P_c decreases favoring the water flow into the throat. Under a critical P_c value a new gas bubble forms.
- Lamella division. As a bubble flows through separate channels one lamella divides into two lamellae.
- Leave behind. The liquid is constrained into a lamella which might rapture or stay stable. It occurs below critical flow velocities and forms course foam.



Ransohoff and Radke (1988) *J Reservoir Eng of SPE* 3, 573–585.

Results

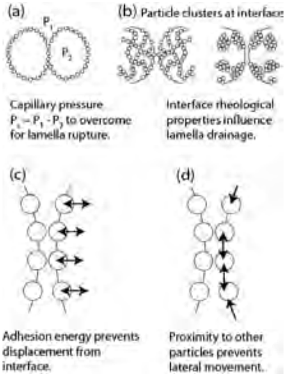
Transport tests



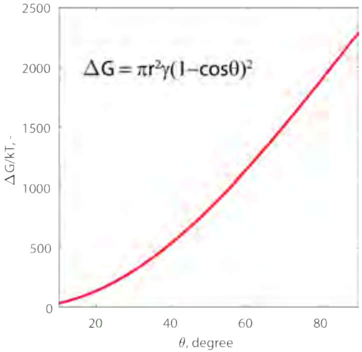
Nanoparticle at the bubble interface

- Particle size, shape, hydrophobicity/wettability, concentration, capillary attraction, and solution composition are the main factors for foam stabilization.
- Flocculation between the armored bubbles and the unadsorbed particles and particle packing reduces drainage and increases foam strength.

Configurations



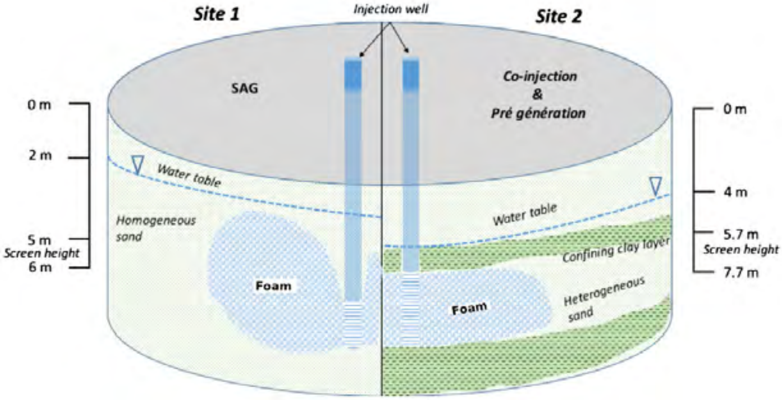
Gibbs free energy of particle desorption



Pugh (2016) *Bubble and Foam Chemistry.* Cambridge.

Application of foam for environmental remediation at the field scale

Foam as a blocking agent



Portois *et al.* (2018) *Transp Porous Med* **124** 787–801.