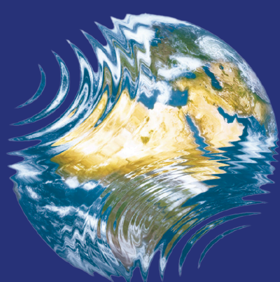
Petroleum Geology
Petroleum Systems

EOR 101



SNF FLOERGER

Summary

Petroleum system

What is a reservoir ?

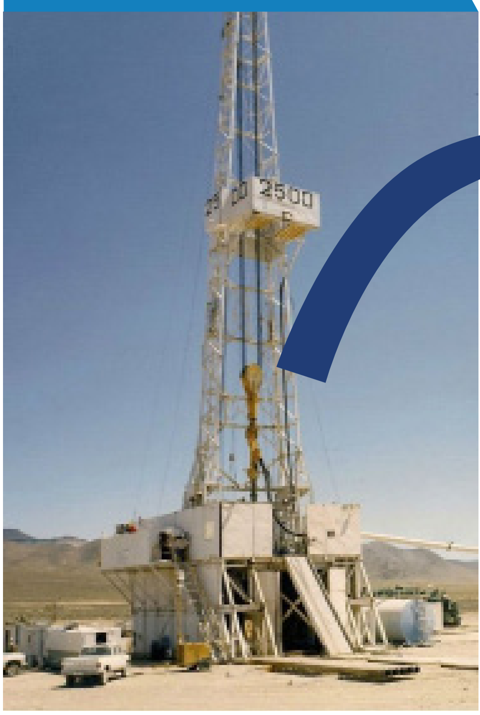
A petroleum reservoir, or oil and gas reservoir, is a subsurface pool of hydrocarbons contained in porous or fractured rock formations. The naturally occurring hydrocarbons, such as crude oil or natural gas, are trapped by overlaying rock formations with lower permeability. The vast majority of hydrocarbons are trapped within sedimentary rocks, formed at the earth surface though several process including weathering, precipitation and biogenic activity. We can distinguish:

Clastic rocks
formed from pre-existing rocks by erosion, transport, transformation and deposition. These include sandstones, conglomerates, silstones and shales.

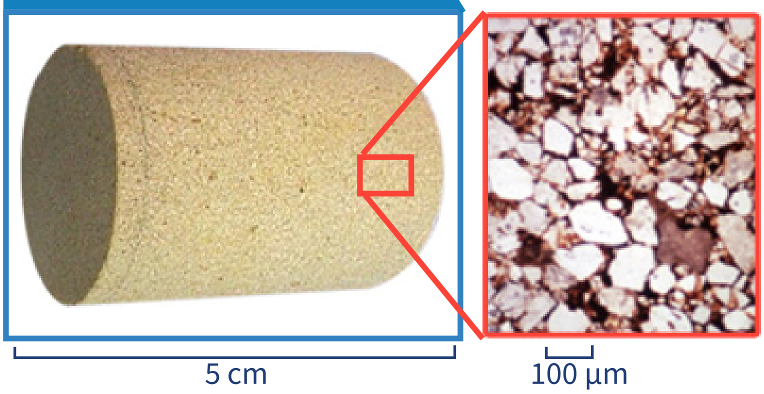
Carbonates
rocks formed from organic constituents and chemical precipitates; including limestones, dolomites and chalks.

Lithology	Oil bearing reservoirs	Abundance of rock type	Production by rock type
Sandstone	60%	21%	37%
Carbonate	30%	37%	61,5%
Other (shale...)	10%	42%	2,5%

Drilling rig

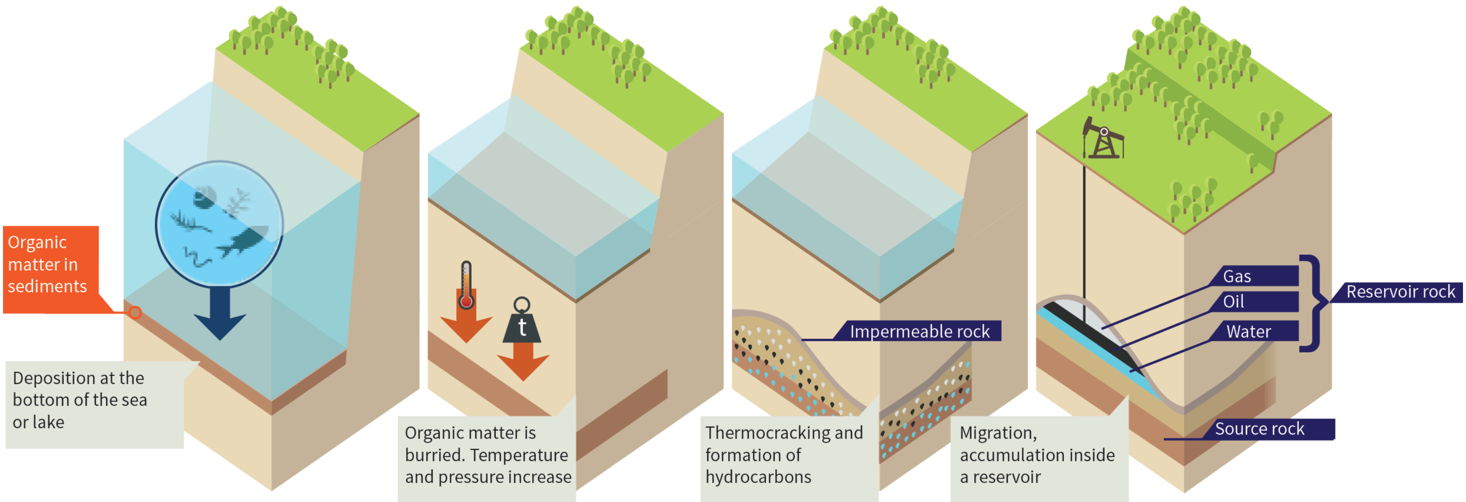


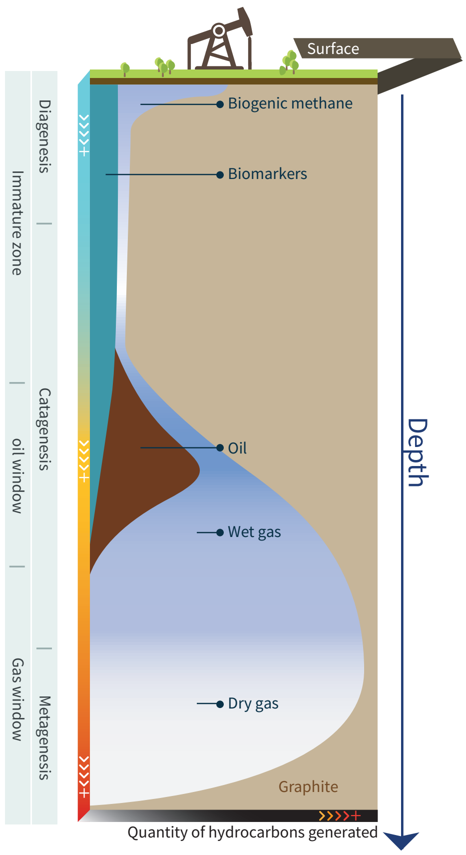
Cores are drilled to study the reservoir



Formation of hydrocarbons

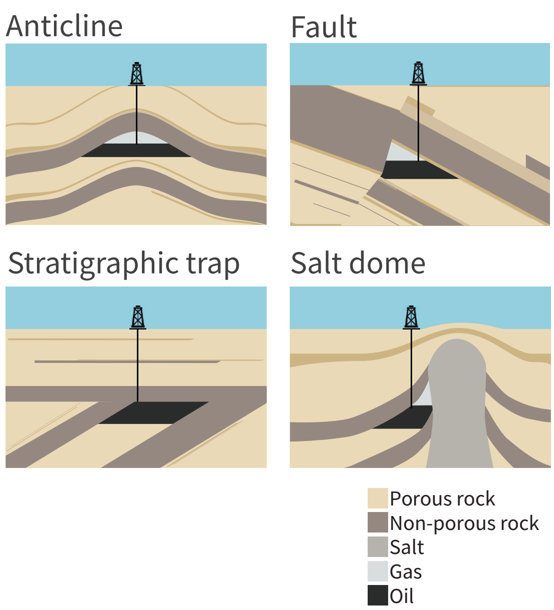
The petroleum system consists of a mature source rock, migration pathway, reservoir rock, trap and seal. Appropriate relative timing of formation of these elements and the processes of generation, migration and accumulation are necessary for hydrocarbons to accumulate and be preserved.
Hydrocarbons are generated from the thermo-cracking of organic matter accumulated in a source rock. It requires temperature (>50°C) and time.





Many types of hydrocarbon traps exist:

Anticline, Fault, Stratigraphic trap, Salt dome, ...



About the reservoirs

Resources

Characteristics of oil and gas generated depend on the type of organic matter and the maturation process. People also make a distinction between conventional and unconventional resources: unconventional plays require specific and often expensive techniques to be produced.

Unconventional resources: example of tight gas reservoirs

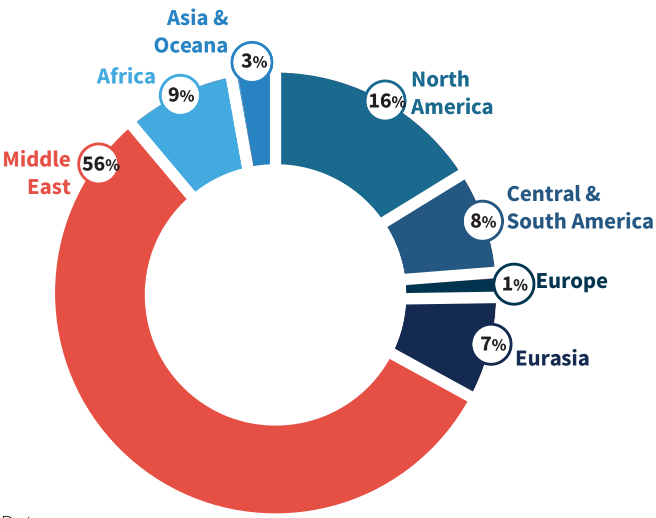
In tight gas reservoirs, the pores are irregularly distributed and poorly connected by very narrow capillaries resulting in very low permeability. Gas flows through these rocks at generally low rates and special methods are necessary to produce this gas such as hydraulic fracturing.

Unconventional play

By opposition with conventional systems, unconventional resources are not easily producible with existing technologies (low permeability reservoirs or viscous oil)

Source-rock hydrocarbons

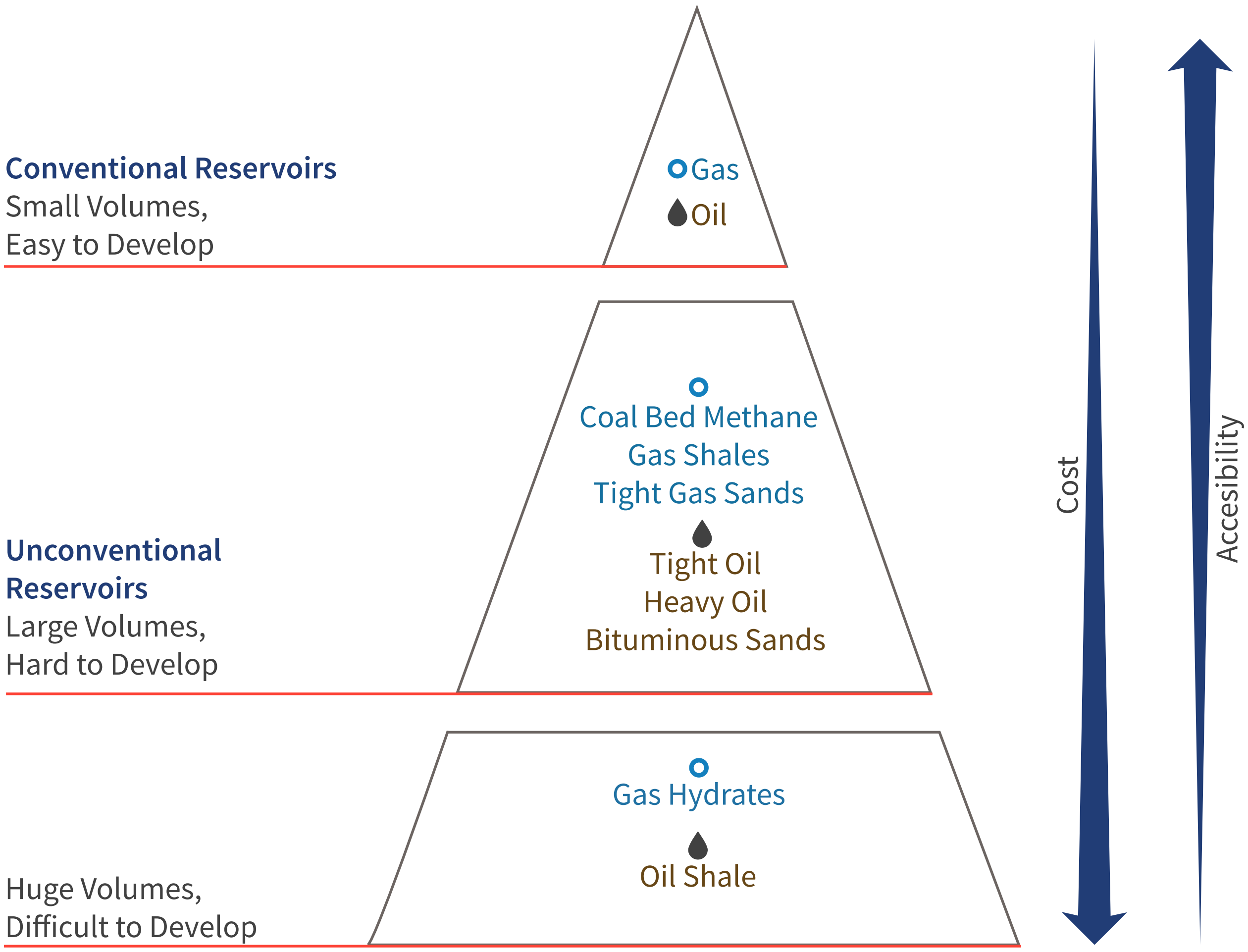
Shale Oil or Shale Gas directly extracted from the source rock by fracturation.



Data source :
US Energy Information Administration from Oil and Gas Journal (2007)
Oil includes crude oil and condensate

Acronyms

OOIP : Original Oil in Place
IOR : Improved Oil Recovery
EOR : Enhanced Oil Recovery
Chem EOR : Chemical EOR
PF : Polymer Flooding
SP : Surfactant and Polymer Flooding
ASP : Alkaline Surfactant Polymer Flooding
PAM : Polyacrylamide
HPAM : Partially Hydrolized Polyacrylamide
MW : Molecular Weight
Da : Dalton (MW unit of measure)
IFT : Interfacial tension
PSU™ : Polymer Slicing Unit
PIU™ : Polymer Injection Unit



Resource pyramid

Tight gas sandstone : (voids in blue).

Enhanced Oil Recovery (EOR)

Why consider EOR ?

The production of hydrocarbons is usually divided into 3 stages :

Primary depletion

Oil is naturally produced thanks to the energy initially stored within the reservoir;

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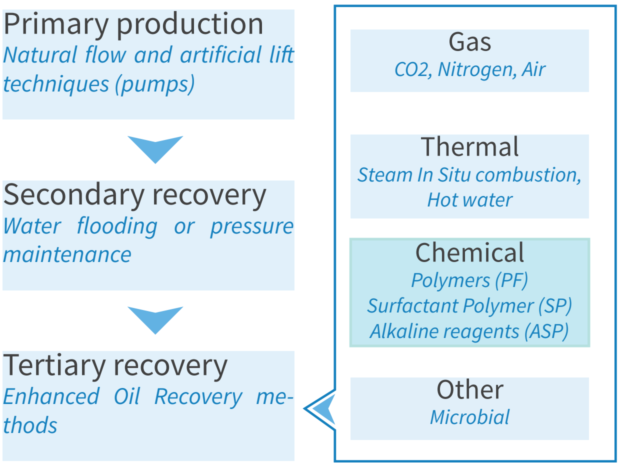
Secondary production

In order to maintain the production and the pressure in the reservoir, water (or sometimes gas) is injected to push the hydrocarbons;

Tertiary production

Injection of specific substances to increase recovery (gas, chemicals, steam...).



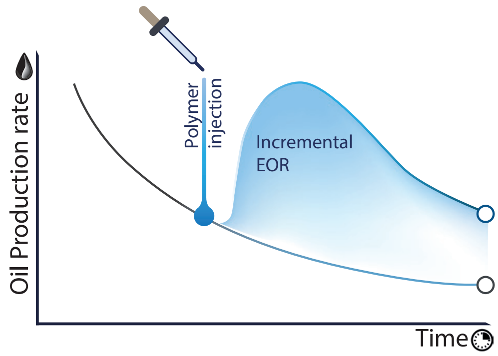
35% of Oil Originally In Place (OOIP) is produced after primary and secondary productions. It means that 65% of oil remains after secondary recovery, trapped into pores by different forces.

There is little doubt that the worldwide demand for oil will increase in the long term. But reserves are not generally replaced and it would require the discovery of new «giant» fields.

Drilling alone is expensive: it requires a large capital investment, and drilling rate is inversely correlated with discovery rate. The costs linked to exploration & extraction increase (ultra-deep offshore, artic circle...). As such, increasing the recovery factor by 1% would translate into 60 billion extra barrels.

EOR applies to known reservoirs, infrastructure is already in place and the market for hydrocarbons is available.

Polymer flooding is a proven, cost-effective EOR

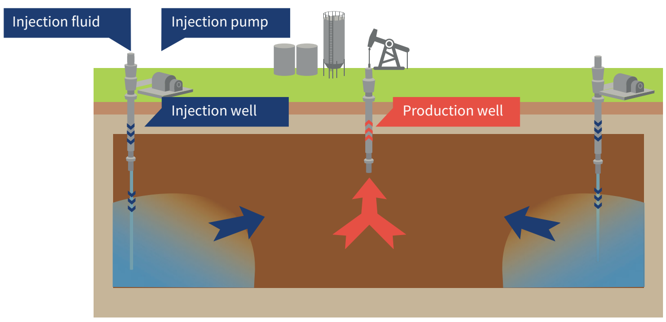


technique with over **40 years** of commercial application that allows recovering from 5 to 15% of additional oil. The best commercial projects have produced about 1 incremental barrel of oil for each \$1 to \$3 of polymer (onshore).

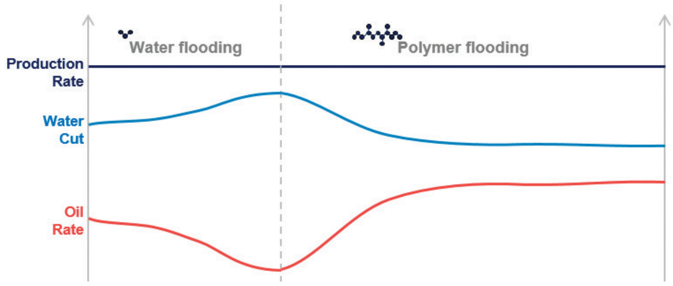
The addition of water-soluble polyacrylamides increases water viscosity and helps push bypassed oil more efficiently. A first step consists in evaluating the potential through a pilot injection.

A pilot is a good way to prove the efficiency:

- Fast deployment (skid-mounted systems)
- Low costs
- Low risks



Modular injection systems can be tied-in to existing injection lines: no need to build new infrastructure, use of available water for polymer injection.
After this stage, full-field deployment can be considered.
Polymer flooding reduces costs related to water handling. The process requires less water to recover the same amount of oil, so the costs linked to water treatment & handling are reduced. Produced water containing polymer can be reused for further injection. In the long-term, polymer flooding can be less expensive than waterflooding. Preferable conditions for polymer injection are light to medium-heavy oil, low salinity, medium to high reservoir permeability, low temperature (below 100°C). Even though, new polymers can resist harsh conditions: 140°C and around 200g/L total salinity.



The earlier, the better: implementing polymer flooding early in the life of a field helps increase the final amount of oil recovered.

History of chemical EOR projects

1976 - 1982

More than 320 chemical injections in the US

East Coalinga
Taber – Manville
West Yellow Creek

North Burbank

1989 - 2000

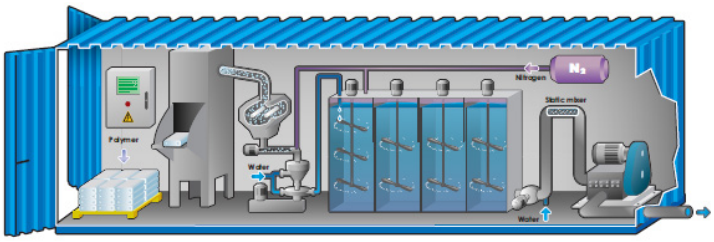
Large success in China

Daqing : world's largest polymer injection, resulting in a 12% increase in recovery of the OOIP.

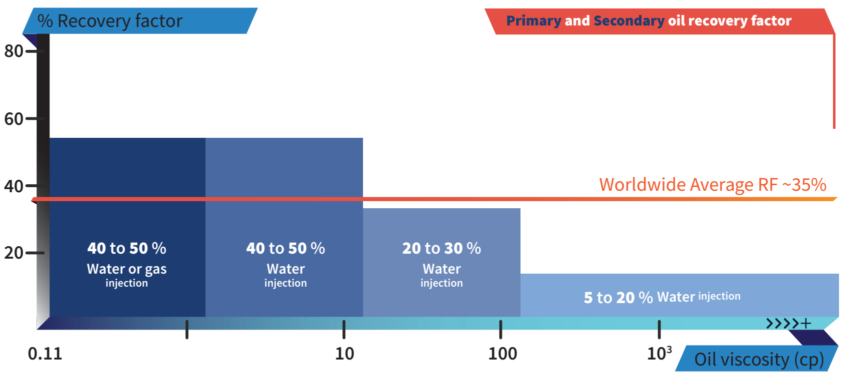
2010 - 2015

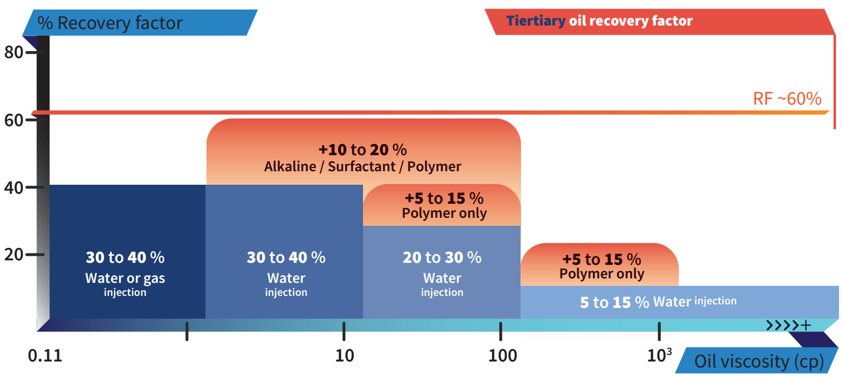
More than 50 polymer injections.
More than 170 projects.

China (Daqing cont'd)
Oman PDO Marmul
Suriname
Indonesia
Canada (more than 30 polymer inj.)
Russia & Kazakhstan
Europe
Latin America
India



Modular systems tied-in to existing injection lines





Principles of Polymer Injection

Polymer injection =
viscous waterflood ▪ limited risk

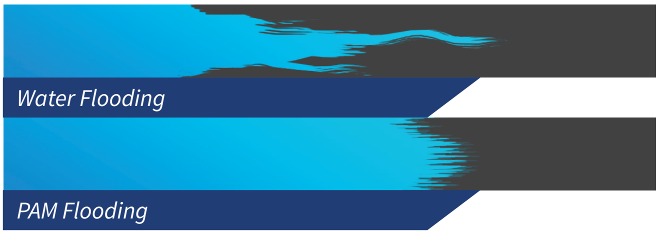
Polymer injection applies when the mobility ratio during a waterflood is unfavorable or when the reservoir is heterogeneous (even with favorable mobility ratio) to recover bypassed oil.

How to design a successful pilot ?

The main criteria to look at when designing a pilot injection are:

- Short spacing /residence time between injection and production well to accelerate the response
- Good connectivity between wells
- Pattern with surrounding offset producers where incremental oil from polymer injection can be isolated for calculation
- Good water injectivity ➤ good polymer injectivity
- Tests to check maximum rates and viscosity accepted by reservoir
- Micro-fractures can be used to improve the overall efficiency
- Relatively high oil saturation (➤ residual oil saturation)

Pilot injection can start very quickly using standard equipment.



Some key figures:

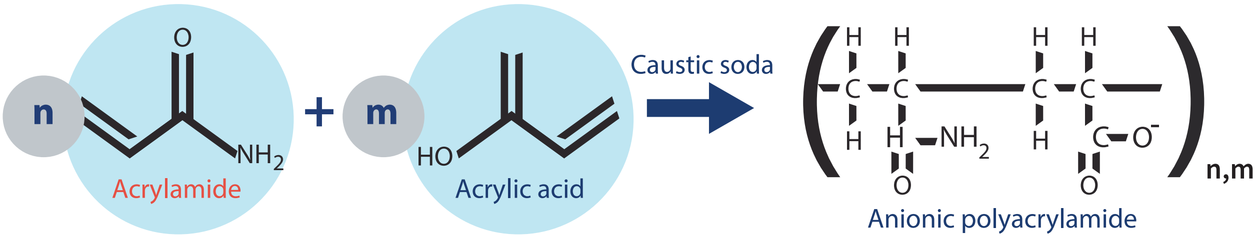
- Polymer is injected over 5 to 25 years.
- Typical injection concentrations range from 1000 to 1500 ppm active.
- Injection of at least 0.3 pore volume: the more the better.
- Injection of high viscosity slug recommended in some cases.
- Incremental oil with polymer ranges from 5% to 15% OOIP.

	Injectivity Test	Pilot	Full Field
	Validation of flow parameters Key learnings	Validation of technology Evaluation of recovery factors	Large scale development
Timeframe	1 to 3 months	6 to 18 months	5 to 25 years
Installations	Portable injection unit	Skids Turn-Key systems	Turn-Key systems On-site injection plants
Critical parameter	Portable selection	Dissolution/ Injection equipement	Logistics Polymer supply Storage Dissolution

Can be run in parallel and shortened (order of weeks) if using standard skids

Polymer selection	Laboratory studies	Equipement Engineering Design	Field installation Commissioning start-up	Operation Maintenance
2 weeks	1-6 months	6-8 months	8 months	5 - 25years

SNF chemistry



Example of an anionic co-polymer of acrylamide and acrylic acid

Two families of polymers:
- Biopolymers
-HPAM: Partially Hydrolyzed Polyacrylamide (synthetic polymers)

Fine-tuning chemistry can help to limit shear and salt sensitivities of synthetic polymers.

SNF develops and manufactures tailor-made polymers based on acrylamide. High molecular weight hydrosoluble polymers are mainly used to increase viscosity.

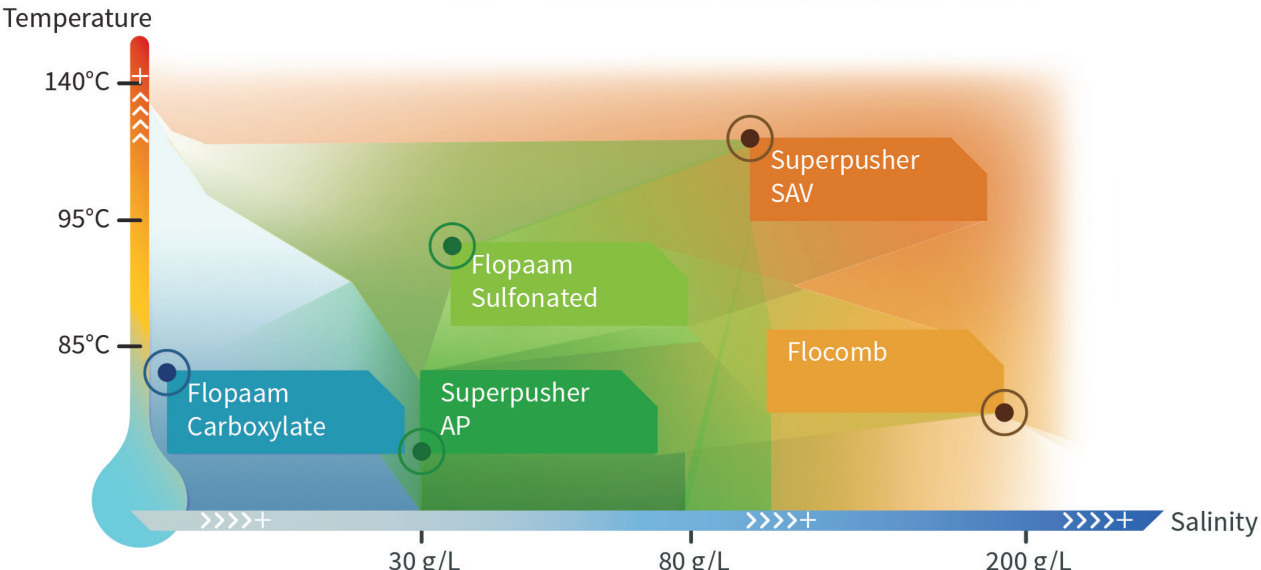
Polymer / Solvent Interaction

Important notions to understand properties of polymers into solution.

A polymer is able to increase the viscosity of the medium only if the chains are uncoiled: this is a medium where the polymer « feels comfortable. » What does it mean ? It means the interactions polymer / solvent should be better on the energetical point of view than the interactions polymer / polymer.

Advantages	Disadvantages
Excellent injectivity and propagation	
High viscosifying power	Shear sensitive
Good and long stability in mild reservoirs conditions	Salt and temperature sensitive
Cost-effective, high production capacity worldwide	Sensitive to chemical degradation
Non toxic	Low biodegradability

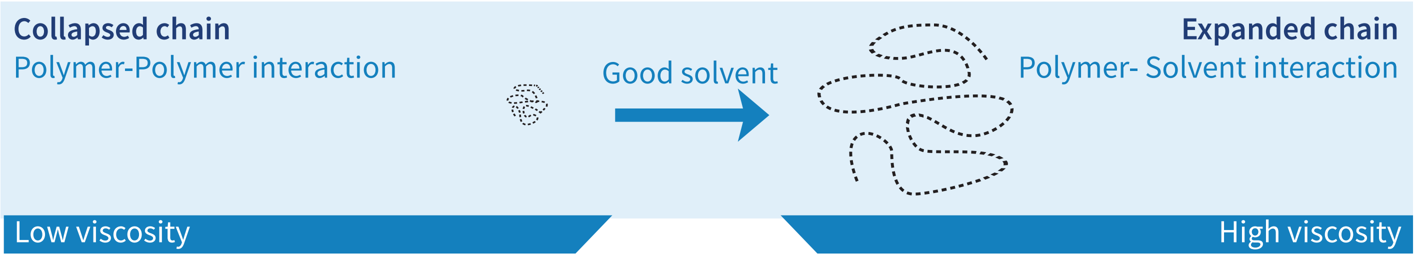
HPAM characteristics

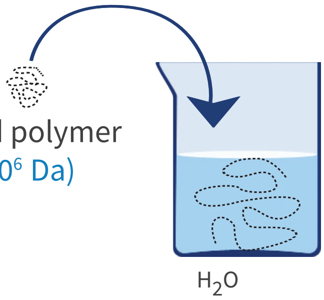


HPAM characteristics

Polymer chemistry needs to be carefully selected
- Importance of brine characteristics.
- Polymer/solvent interactions describe the conformation of the polymer chains (coil) in solution ➤ Efficiency.

If the interactions are good , the macromolecular chain deploys into the medium.
Polymer chain expanded ➤ high viscosity



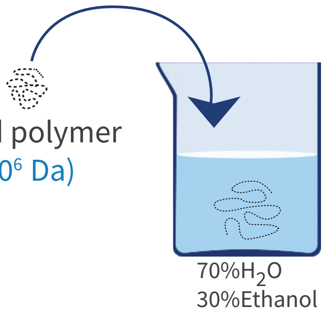


Collapsed polymer
(MW = 8.10^6 Da)

1% Polyacrylamide in H_2O

(viscosity brookfield) **η** = **5.000** to **6.000** mPa.s
(Brookfield UL @6 rpm)

Water is a good solvent.

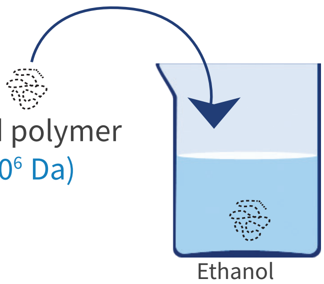


Collapsed polymer
(MW = 8.10^6 Da)

1% Polyacrylamide in H_2O+Ethanol (70/30)

η = **700** to **800** mPa.s
(Brookfield UL @6 rpm)

The medium H_2O/Ethanol is a less good solvent.
The polymer « feels less comfortable . »
The macromolecular chain uncoils partially.



Collapsed polymer
(MW = 8.10^6 Da)

1% Polyacrylamide in Ethanol

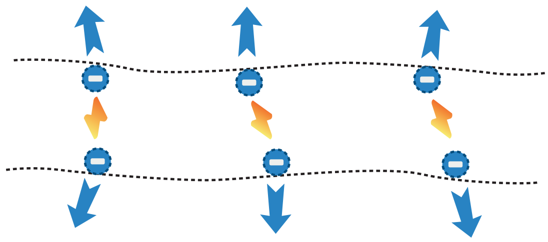
η = **η** of ethanol
(Brookfield UL @6 rpm)

Very bad interactions.
The polymer « feels very uncomfortable ».

Viscosity depends on solvent

Polyelectrolytes

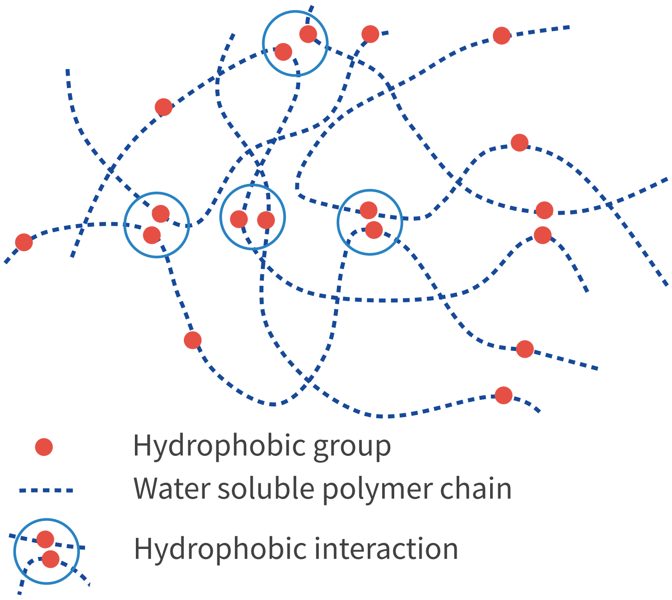
Polyelectrolyte is a polymer containing electrostatic charges into the macromolecular structure.
In a polar medium like H_2O, the polymer is able to expand due to internal electrostatic repulsions (stretching of the chains). It results in a high viscosity.

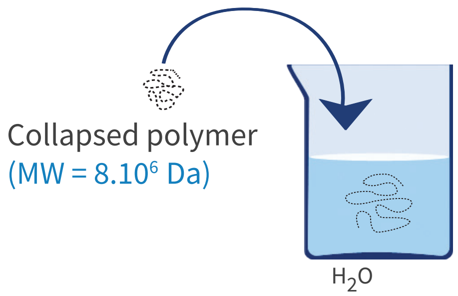


But if salts are present/added, viscosity decreases because of a «screen effect» :
- decrease of repulsions
- the macromolecular chains retract
- viscosity decreases

Associatives Polymers

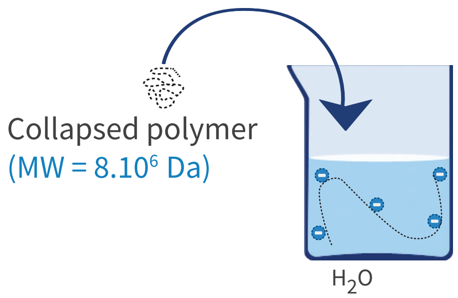
Associative thickener
Associative polymers are hydrophilic polymers containing some hydrophobic groups. A network is created by hydrophobic interactions in water. These interactions create a physical network and very high viscosities can be obtained.





1% Polyacrylamide in H_2O

η = **5.000** to **6.000** mPa.s
(Brookfield UL @6 rpm)



1% Copolymer Acrylamide /AMPS in H_2O

η = **20.000** to **25.000** mPa.s
(Brookfield UL @6 rpm)

Expansion of the macromolecular chain by electrostatic repulsion

The value of adding polymer to a waterflood can be explained by considering the mobility ratio equation with the aim to reach a value close to 1 so that oil and water have the same mobility inside the reservoir. The easiest way is to increase water viscosity as shown by the equation below.
Polyacrylamides are sensitive to mechanical, thermal and chemical degradations. Guidelines exist and have to be implemented to minimize viscosity losses.
There is a need to:

-Select the best chemistry and possible protective packages

-Use specific equipment to avoid shearing and oxygen ingress.

$$M = \frac{k_w \ \mu_o}{k_o \ \mu_w}$$

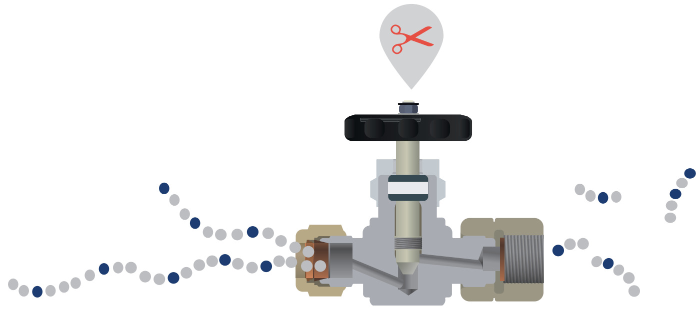
Mobility ratio

End-point relative permeability of water

oil viscosity

water viscosity

End-point relative permeability of oil



Mechanical degradation

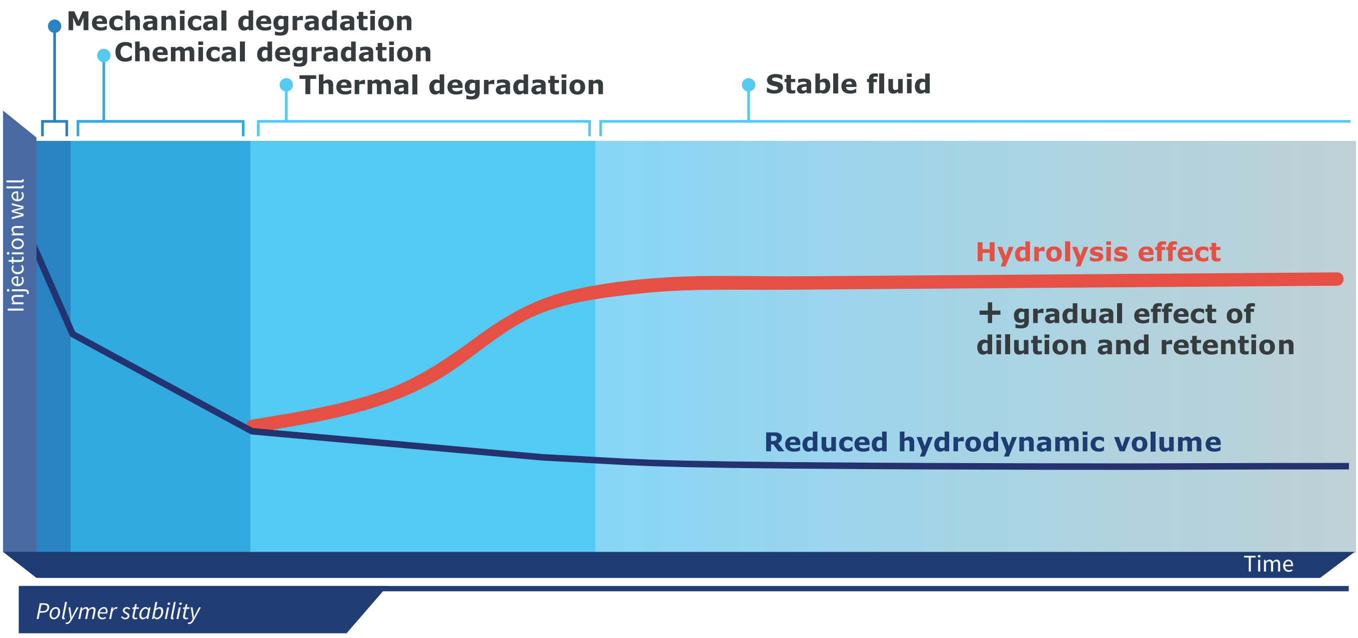
is caused by singular pressure drops.

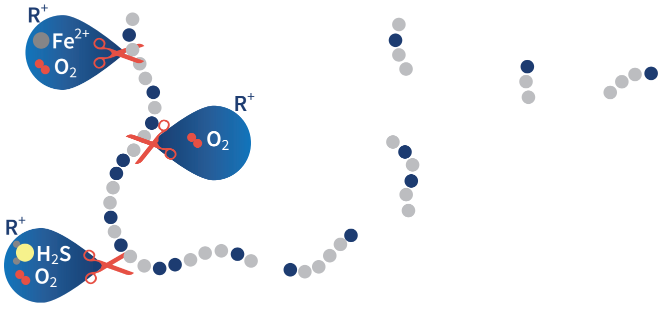
Mechanical degradation through shearing devices can lead to significant reduction in viscosity.

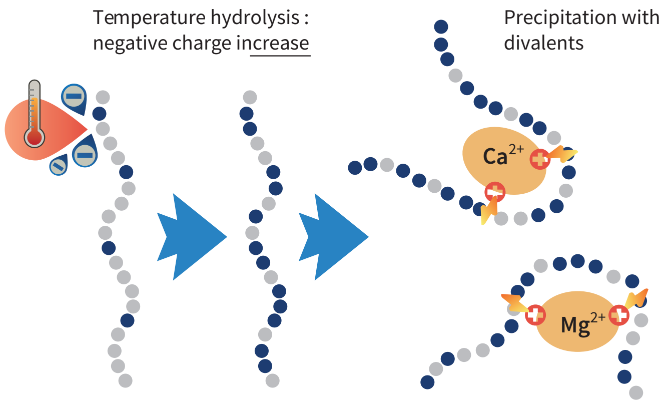
Polyacrylamides are sensitive to shear which degrades the polymer into smaller molecules. Lower molecular weight polymers are much less sensitive to shear.

Special attention should be paid to:
- Dissolution and surface injection equipment,
- Velocity of the fluid,
- Injection lines (restriction, chokes),
- Surface of perforations,
- Permeability of the reservoir,
- Reduction of the injection surface by plugging

SNF has defined a set of engineering guidelines to minimize shear in the surface equipment.







Chemical degradation

is caused by free radicals.

It is essential to minimize chemical degradation by eliminating free radicals, removing oxygen and blanketing dissolution equipment

Free radicals scavenger

SNF sells all its product with a minimal amount of free radical scavenger. For increased protection, specific packages (F3P) are developed by SNF and fine-tuned to every case.

Oxygen removal

Oxygen scavengers (ammonium bisulfite for example) decrease O_2 content below 20 ppb.
The amount of scavenger should be limited to avoid further degradation in case of oxygen ingress.

Nitrogen blanketing

Dissolution equipment can introduce a large amount of oxygen into the injected solution. It is necessary to blanket the installation under Nitrogen in order to prevent oxygen ingress.

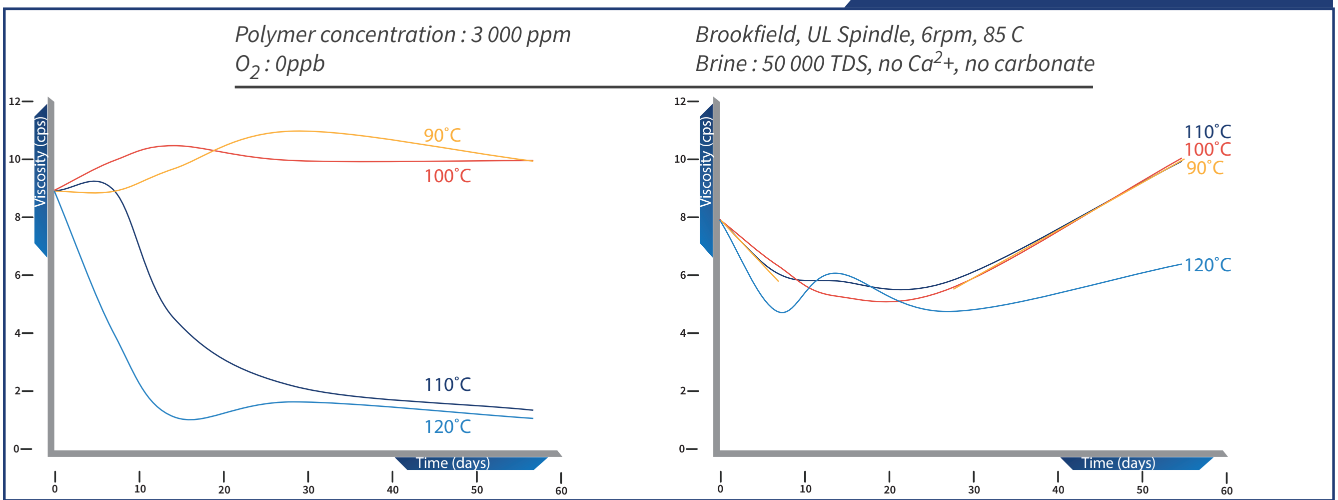
Thermal degradation

is linked to polymer hydrolysis and precipitation with divalent cations.

Polymer microstructure and anionicity should be carefully selected and controlled to minimize thermal degradation

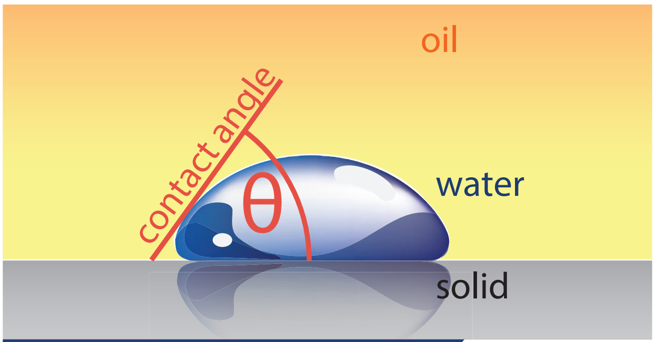
Copolymers acrylamide / acrylic acid are stable up to 75°C. Above 75°C and up to 120°C, polymers containing acrylamide / ATBS or/and other thermal resistant monomers can be used (Flopaam AN 100 & Superpusher SAV series).
Above 50°C, hydrolysis of the polymer will occur resulting in increased anionicity. When anionicity increases above a critical level (35% to 40%) precipitation with divalent ions (Ca^{2+}, Mg^{2+}) will occur resulting in viscosity loss.
With medium to high temperature reservoirs, low anionicity polymers should be privileged. The quality of the manufacturing process of the polymer is essential to avoid high polydispersity.

Negative effect of high temperature

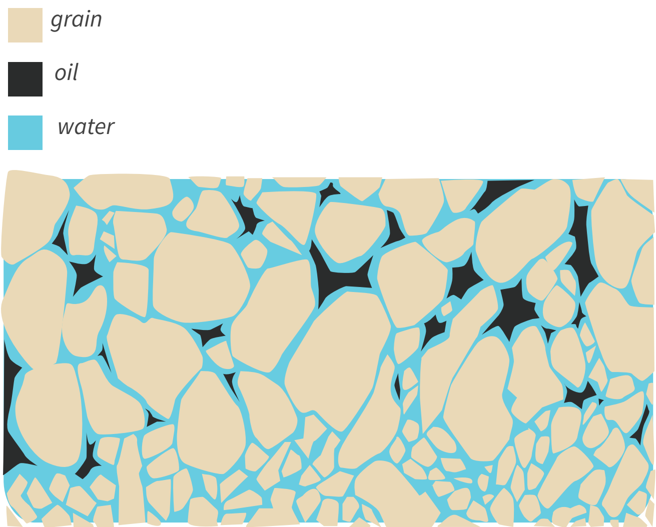


Temperature limits for sulfonated co-polymers AN-125
ATBS based copolymer (Flopaam AN 125) w/o O_2 and divalent cations

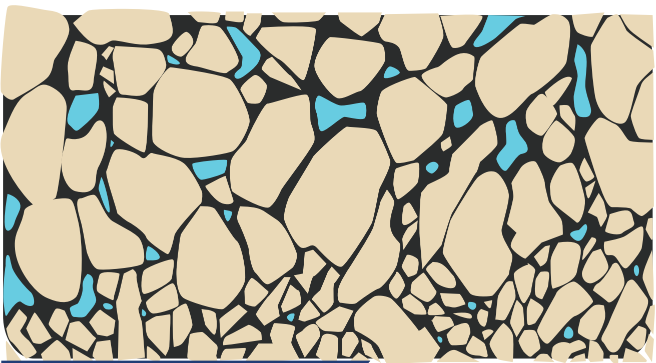
New range of polymer for high temperatures
NVP addition improves stability at high temperature w/o O_2 and divalent cations



Exemple of water-wet medium (□<90°)



water-wet reservoir



oil-wet reservoir

Wettability connotes the preference of a given liquid to spread over a solid surface in the presence of a second liquid. It is quantified by the contact angle which represents a drop of liquid deposited on a flat surface: the smaller the angle, the higher the wettability.
For example, one can distinguish water-wet reservoirs (with water wetting the grains) and oil-wet reservoirs (oil wetting the grains).

Factors affecting reservoir wettability

- Oil composition
- Rock mineralogy
- Connate water composition and pH
- Reservoir pressure and temperature

Interfacial Tension (IFT) It defines the tension (forces) existing between two immiscible fluids (oil and water).

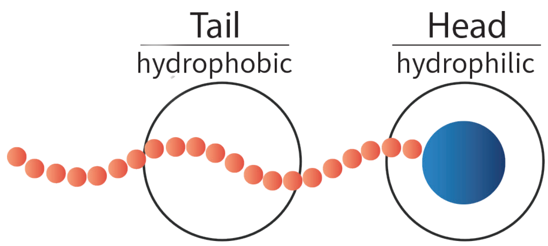
Oil is left behind a waterflood because it can be:
- Trapped by capillary forces
- Bypassed (because of a bad mobility ratio)

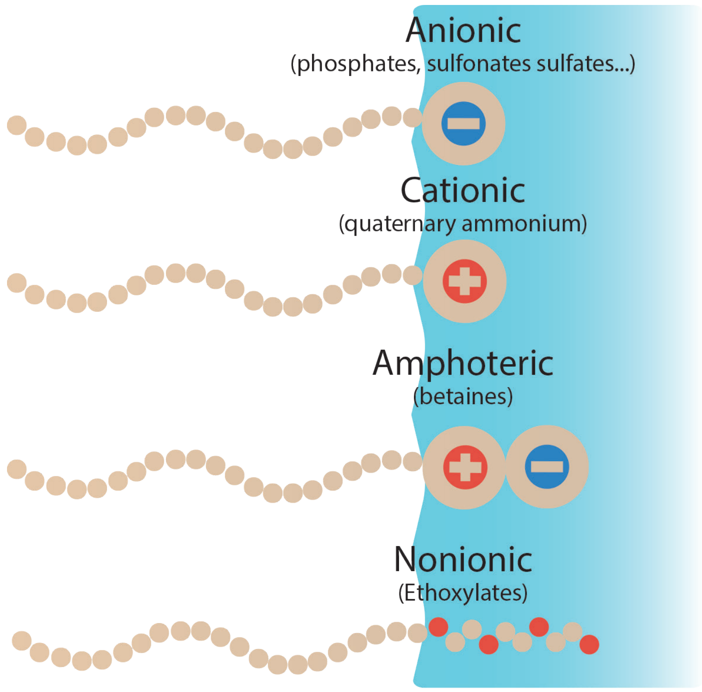
EOR: How to mobilise the oil ?

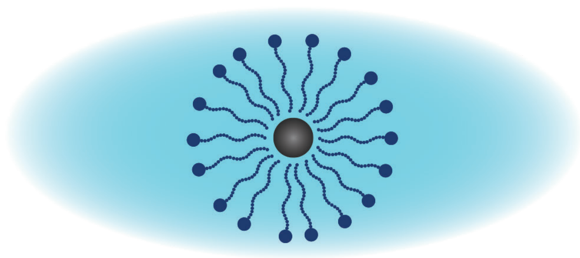
If bypassed: modification of the mobility ratio by increasing the viscosity of water :
- polymer injection

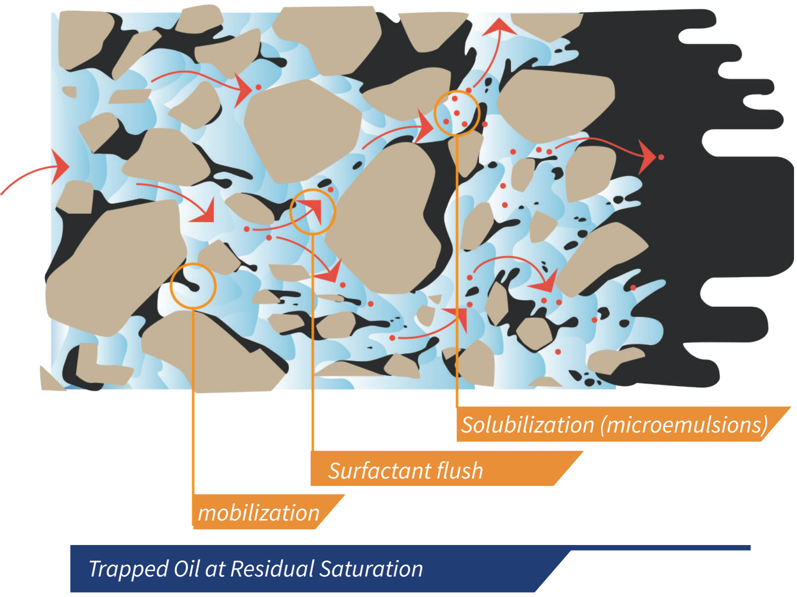
If trapped by capillary force :
- increase capillary number (viscous forces/ capillary forces(IFT))
- lower IFT by surfactant injection for instance

Surfactants are compounds that stabilize mixtures of oil and water by reducing the surface tension at the interface between the oil and water molecules. Surfactants are amphiphilic in nature i.e. they contain 2 distinct structural units:









Tail or hydrophobic group which has little affinity for water – this group is usually a hydrocarbon (alkyl) chain.

Head or hydrophilic group which has strong affinity for water, it can be neutral or charged.

Alkali

Alkaline waterflooding: process where the pH of injection water is increased by addition of alkali (sodium carbonate, sodium silicate, sodium hydroxide, potassium hydroxide). Alkali reacts with acidic compounds of the crude oil leading to lower IFT, emulsification of oil in water and solubilization of rigid interfacial films. Alkali may react with the rock leading to wettability alteration

In a nutshell:

Polymer
Increase water viscosity

Surfactants
Lower IFT
Change wettability of the rock
Generate foams or emulsions

Alkalis
React with crude oil to generate soaps (surfactants)
Increase pH
Alter rock wettability
Alter rock chemistry reducing adsorption of surfactants

EOR: Other processes
Miscible gas injection
In-situ combustion
Steam injection
Microbial degradation

Final goal: recover as much oil as technically and physically possible. Necessity to have a good understanding of the geology, the reservoir, the fluids…

Multi-Purpose Engineering Services

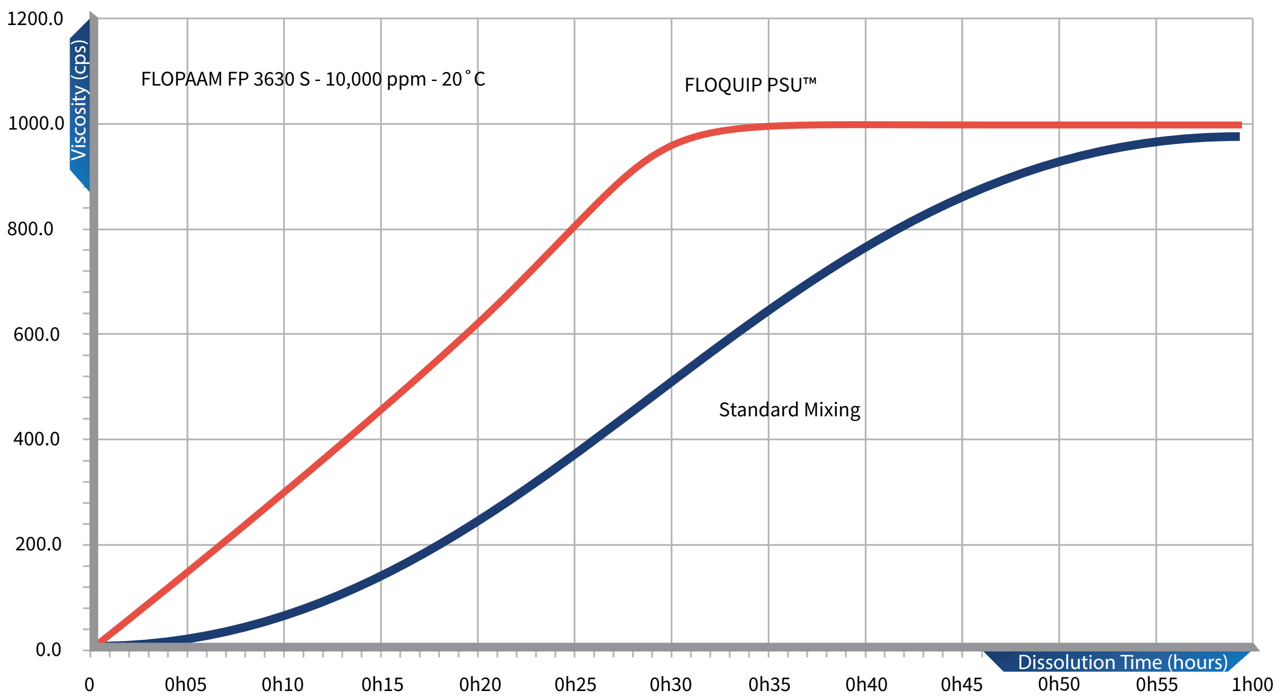
SNF provides dedicated solutions and engineering services to design, build and operate polymer injection systems.

- Frac trailer
- Polymer injectivity trailer
- Standard PIU 100 and PIUC 100 and PIU 300 MS
- Skid based polymer system
- Emulsion inversion, dilution and injection skid
- Skid based ASP system
- On plot polymer / ASP facilities
- Offshore skids
- Offshore modular construction
- …

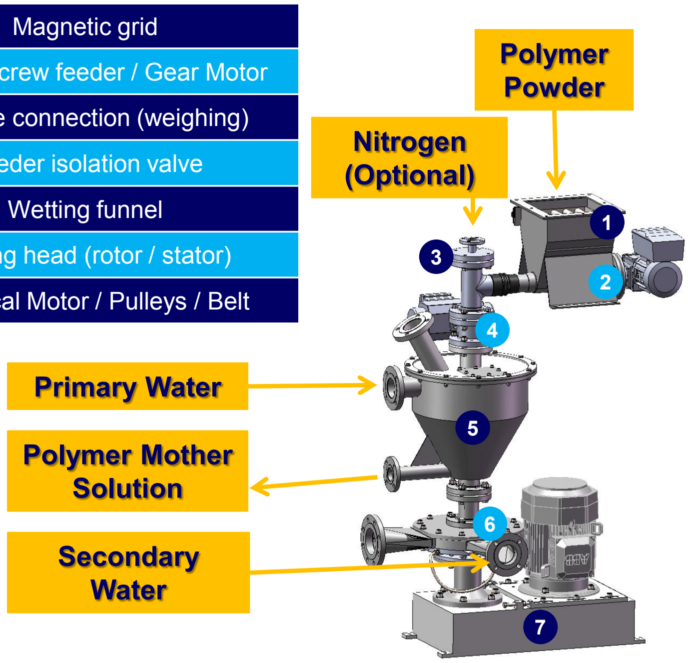
Every system is designed per customer requirements. Standard injection units also exist for fast implementation.

Expertise : Powder Hydration
FLOQUIP PSU™ is a slicing unit that helps decrease the dissolution time of powdered polymer.

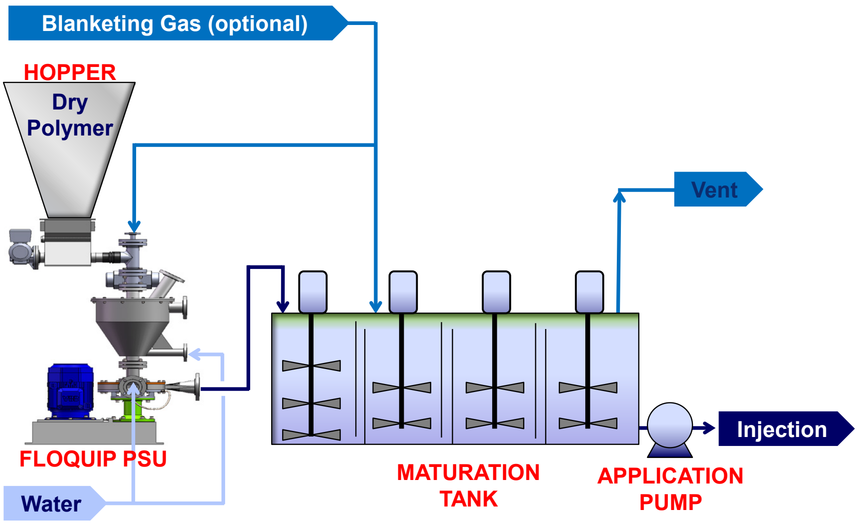
+ Patented technology from SNF
+ Concentration up to 15 000 ppm
+ No fish eyes and no need for filtration
+ Nitrogen blanketing
+ Subsequent equipment reduced by 3x to 4x



1	Magnetic grid
2	Dosing screw feeder / Gear Motor
3	Flexible connection (weighing)
4	Feeder isolation valve
5	Wetting funnel
6	Cutting head (rotor / stator)
7	Electrical Motor / Pulleys / Belt



FLOQUIP™ PSU – Process Connections



FLOQUIP™ PSU – Typical Flowsheet

Unloading system for big bags
Powder storage silo
Mixing unit PSU 100
Agitated Maturation Tank
Mother solution booster pump
High pressure injection pump
Full E& I Package
Electrical control Panel & HMI System
Fire and gas detection system

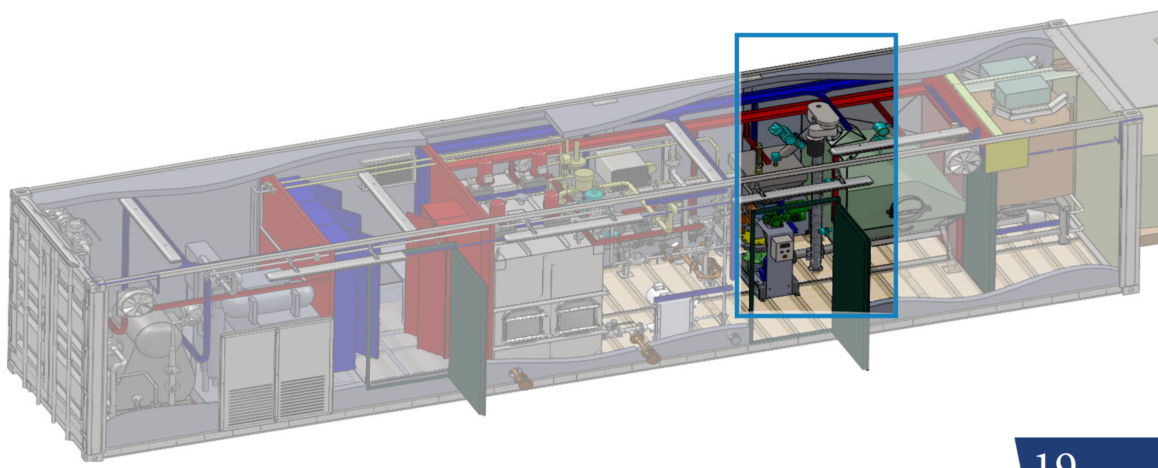
Main Scope

Detailed Design
Procurement & Equipment supply
FAT of the main equipments
Skids Construction
Commissioning, SAT and Start-up
Vendor Data book
E&I package (VSD + MCC)
E& I Cabling
Skid mounted system

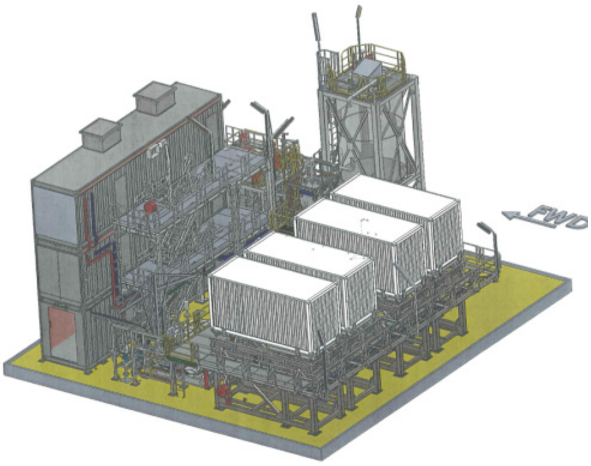
Optional

Water run test
Polymer run test
Training
Operation & Supervision

PIU 100 Standard Polymer Injection Unit



Numerous skid-based project



Offshore projects

Large turn key projects

Turn-key project - Dissolution

PSU 600 - Brazil

PSU 1500 - USA

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Handbook. Edition 2015