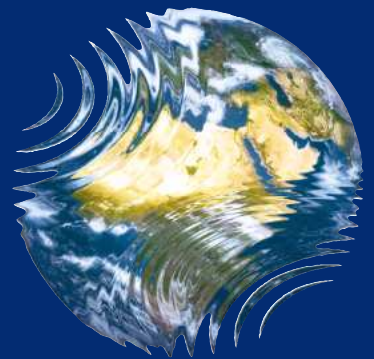




*Enhancing  
Polymer  
Flooding  
Performance*

*30 Years of  
Experience  
in EOR*



**SNF FLOERGER**



# Index

1. OVERALL PRESENTATION OF SNF	2
A. Generalities	3
B. Oil Field Division	3
2. POLYMER FLOODING	4
A. Facts and figures about EOR	5
B. What is polymer flooding?	6
C. Surfactant - Polymer flooding	6
D. Alkaline - Surfactant - Polymer flooding	6
3. SNF POLYMERS AND THEIR CHEMISTRY	8
A. Raw materials	9
B. Processes of polymerization	9
C. Range of products and their stability	10
D. Conclusion and transition	15
4. FROM DESIGN TO INJECTION	16
A. Laboratory testing: selection of the best polymer	17
B. Polymer flooding facilities – from Design to Operation	19
5. WATER TREATMENT	22
A. Mechanical treatment of viscosity	23
B. Physical-Chemical treatment of viscosity	24
Conclusion	25



## Overall Presentation of SNF

Since its early beginning, SNF has experienced a continuous growth to become the world leader in polymer technology for water treatment and Enhanced Oil Recovery. It has been achieved by applying high technical and ethical standards throughout the development of the company. Our development strategy has always taken into account the environmental and social concerns; it allowed SNF to set an example on the environmental front to maintain a sustainable and environment-minded growth. SNF has remained an independent company which reinvested all the cash flows to obtain the highest rate of growth. We also focus on continuously improving the chemistry and the quality of our products to meet the performance goals of our customers. Our leadership also encompasses strategic alliances with service providers and a wide geographical coverage to efficiently serve all our clients. Every day, highly skilled people in SNF strive to tackle every new challenge provided by the energy industry. From chemistry to conceptual studies, from laboratory to the field, from design to injection.



## Corporate Overview

SNF is a privately held chemical company created in 1978. SNF manufactures polyacrylamide-based polymers for various applications such as water treatment, enhanced oil recovery, hydraulic fracturing, mining, cosmetics, paper making, agriculture and textile. Throughout 30 years of organic growth, SNF has become the world leader in polymer technology for water treatment and enhanced oil recovery. Today, with more than 3,300 employees and worldwide manufacturing facilities, we are able to meet all the demands of our customers.

SNF has heavily invested in manufacturing capacities across the globe.



Andrézieux



Riceboro



Plaquemine



## SNF Oil Field Division

In the Oil and Gas industry, SNF products are used within a wide range of applications:

- **FLODRILL**: products for water based drilling fluids. It comprises fluid loss agent for mud and cement, viscosifiers, thinners, shale inhibitor, bentonite extender.
- **FLOJET DR**: products for drag reduction and hydraulic fracturing.
- **FLOPERM**: products for reservoir stimulation (gels, microgels), sand control, and well conformance.
- **FLOPAM, FLOQUAT, FLOSPERSE**: products for scale inhibition, coagulation & flocculation, OIW and TSS reduction, oil sands MFT dewatering.
- **FLOPAAM**: products for Enhanced Oil Recovery (EOR).

Chemical EOR, and especially polymer flooding has experienced a major increase in the past few years because of the energy demand and therefore the necessity to recover more oil. In order to meet this growth, SNF has built a plant in Plaquemine (LA, USA) to deliver products specially dedicated to this market.

SNF manufactures products either in liquid (water in water or water in oil emulsion) or solid form (powder) to meet implementation requirement and facilities. A brief comparison is given in the table on the side. The main difference is the percentage of active matter which is >95% with the powder but 30% with the emulsion. Handling an emulsion is for instance easier in Offshore applications ( + in the table, advantageous), but this type of product is more expensive compared to powder ( - in the table, disadvantageous).

Product	Emulsion	Powder
Form	Liquid	Solid
Handling	+	-
Active content	-	+
Price	-	+
Equipment footprint	+	-
CAPEX	+	-
OPEX	-	+



## Polymer flooding

Nearly  $2.0 \times 10^{12}$  barrels ( $0.3 \times 10^{12} \text{ m}^3$ ) of conventional oil and  $5.0 \times 10^{12}$  barrels ( $0.8 \times 10^{12} \text{ m}^3$ ) of heavy oil will remain in reservoirs worldwide after conventional recovery methods have been exhausted.<sup>1</sup> It is important for the O&G industry to recover more hydrocarbons to supply the increasing world energy demand. To maximize the recovery of hydrocarbons from a reservoir, several methods can be implemented after the natural depletion stage is over. The secondary methods which comprise water or gas injection help in maintaining the reservoir pressure to ensure hydrocarbon flow to the production wells. The recovery factor at the end of this stage often remains below 40% of the OOIP. Tertiary methods are then developed to overcome this issue and reach recovery factors above 60%. Polymer flooding belongs to chemical enhanced recovery; it is a well-known method (over 40 years of commercial application) with low risk and application over a wide range of reservoir conditions. It consists of dissolving polymer in the injected water to increase its viscosity and to improve the sweep efficiency in the hydrocarbon reservoir.

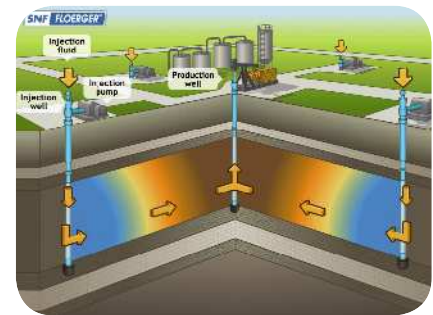


## Facts and figures about EOR

Polymer flooding has a long commercial history. In the 80's, because of the US tax incentives linked to the 70's & 80's technologies, companies were eager to implement polymer flooding in their fields. But a lack of comprehensive reservoir studies led to poor results and a progressive abandonment of this recovery method. A renewed interest was expressed in the 90's in China with the Daqing oil field polymer flooding.

In 1992, SNF constructed the world's largest polyacrylamide manufacturing plant in Daqing for the National Oil Company of China. Polymer flooding at industrial scale started in 1996. With more than 3000 wells on polymer flood, the Daqing field is the largest current polymer flood with about 220,000 bbl/day incremental oil production and 12% OOIP incremental recovery.

Today, with more than 150 references throughout the world and 30 years of experience in polymer flood, SNF is a partner of choice in designing any polymer flooding project.



## What is polymer flooding?

Polymer flooding can yield a significant increase in oil recovery compared to conventional waterflooding techniques. A typical polymer flood project involves mixing and injecting polymer over an extended period of time until  $\frac{1}{3}$  –  $\frac{1}{2}$  of the reservoir pore volume has been injected.

When water is injected into a reservoir, it follows the path of least resistance to flow (usually the layers with higher permeability) directly to the lower pressure region of the offset producing wells.

If the oil in place has a higher viscosity than the injected water, the water will finger through this oil and bypass it. The result will be a lower sweep efficiency and a loss in recovery. The goal of polymer injection is to improve the sweep efficiency in the reservoir and to decrease the mobility contrast between water and oil, with an ultimate goal of a mobility ratio of one.

### Polymer flooding screening criteria

Reservoir Property	Preferred conditions
Permeability	From 50 mD to 10 D
Temperature	Up to 120°C
Lithology	Sandstone
Oil viscosity	From 10 cP to 10,000 cP
Oil Gravity	> 15° API
Salinity	< 250,000 TDS
Oil Saturation	> 20%
Water Injectivity	Good

## SP (Surfactant Polymer)

Surfactant-Polymer flooding consists in injecting a surfactant – often a mixture containing co-surfactants, co-solvents, stabilizers...- to lower the interfacial tension to values as low as 10 mN/m. An initial fresh water preflush is sometimes required to decrease salinity and especially divalent ion concentration in the reservoir. This preflush is then followed by surfactant and polymer injection; these can be injected via different slugs or simultaneously.

## ASP (Alkali Surfactant Polymer)

### Components of ASP flooding

ASP involves the injection of a solution containing polymer, alkali and surfactant. Polymer flooding is designed to increase the volumetric sweep efficiency as well as the displacement efficiency. Alkali and surfactants processes are designed to recover residual oil. An overview of the mechanisms is given below.

### Polymer

As described above, Polymer flooding involves the property of water soluble polymers to uncoil and swell in brine resulting in a thickening of the solution. The injection of thickened water into the reservoir will improve the areal and vertical sweep efficiency of the injection. The increased sweep efficiency results in higher oil production rates for an equivalent volume injected. Conventional wisdom states that polymer does not reduce the residual oil saturation. However, recent work suggest that polymer viscoelasticity can play a role in enhancing microscopic sweep efficiency.

### Surfactant

A surfactant (Surface Active Agent) is an amphiphilic molecule composed of a hydrophobic tail and a hydrophilic head. This molecule will adsorb at the oil/water interface and thus lower the oil-water interfacial tension (tension existing between two immiscible fluids), leading to the mobilization of the trapped residual oil droplets. The main criteria to select the appropriate surfactant are its temperature stability, its resistance to salinity and hardness and its adsorption on rocks which must be as low as possible.

$$M = \frac{(k_{rw} / \mu_w)}{(k_{ro} / \mu_o)}$$

where  $k_r =$  relative permeability (water or oil)

$$\mu =$$
 apparent viscosity (water or oil)

Carbonate and Polymer Skid Mounted Silos





## Alkali

Carboxylate soaps are created when a crude oil with acidic components reacts with hydroxide ions in alkaline solution. These petroleum soaps are capable of adsorbing at the oil-water interface and lowering the interfacial tension.

The combination of Alkali, Surfactants and Polymers leads to synergistic effects between the chemicals. The key roles of each component are summarized below.

## Polymer

- Increase viscosity of water

## Surfactant

- Lower IFT between oil and water
- Change the wettability of the rock
- Generate emulsions

## Alkalies

- Reacts with crude oil to generate soaps
- Increase pH and adjust salinity
- Alter rock wettability
- Alter rock chemistry reducing adsorption

Most floods will fail without mobility control, and polymer addition is a pre-requisite. Moreover, the dosage of each chemical is very different and large amount of surfactants are often required to accommodate the high level of adsorption within the reservoir. The dosage of alkali could also be an issue, because it requires a costly water softening system.

## Water treatment in ASP

One of the major issues to address when designing an ASP flood is the prevention of scale formation.

The increase in pH due to the injection of alkali will lead to the precipitation of divalent ions such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which will form carbonate and/or hydroxide.

To prevent or at least significantly reduce these reactions, it is necessary to soften the injection water to reduce the concentration of divalent ions.

Alkaline solution improves oil recovery by several mechanisms:

- Emulsification and entrainment
- Decreasing IFT
- Wettability reversal

The **capillary number ( $N_c$ )** is a dimensionless ratio between viscous and capillary forces, which provides a measure of how strongly trapped residual oil is within a porous medium.

$$N_c = V \mu / \sigma$$

where,

- $V$  = Darcy velocity
- $\mu$  = Viscosity of the displacing phase
- $\sigma$  = IFT between displaced and displacing phases

## SNF Polymers and their chemistry

SNF is the world leader in the polyacrylamide chemistry and manufacturing. With more than 40% of market share, we continue to develop and improve our products and facilities to meet the continuous growth in demand. Our R&D team still optimizes the chemistry and the properties of the existing products as well as the development of new ones. With a dedicated engineering team, SNF is also able to build its own facilities to manufacture the polyacrylamide products.

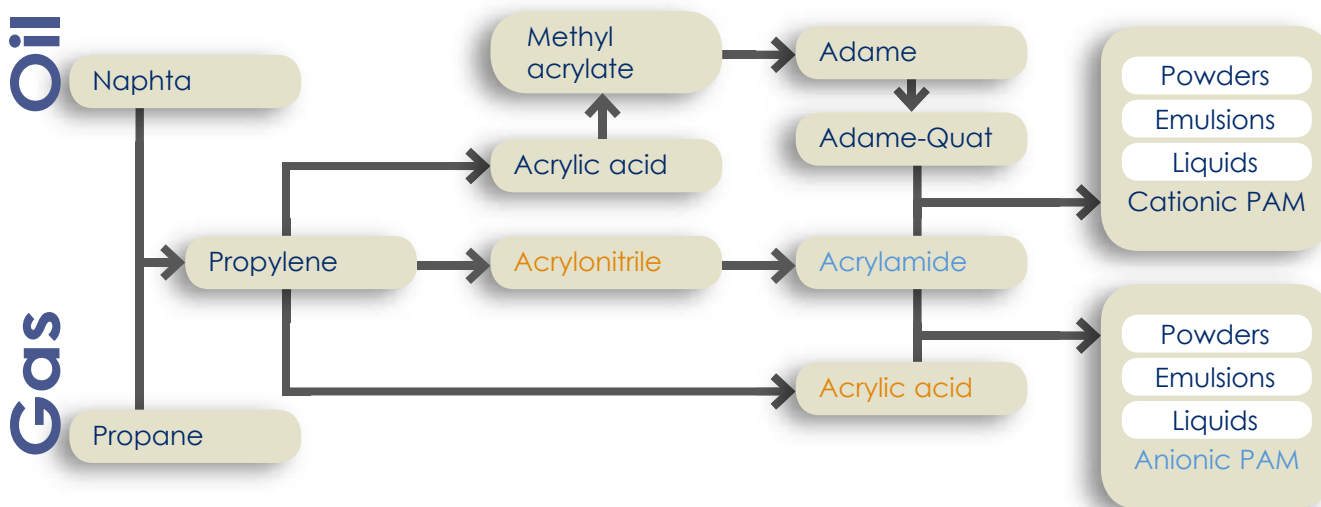
Considering the demands of the Oil and Gas industry and because each hydrocarbon reservoir is unique, we continuously fine-tune our polymers to fit any reservoir condition, even at high temperatures and high salinities.



## Raw materials

The raw material for the synthesis of polyacrylamide polymers is propylene which is a derivative of crude oil. Acrylamide is the basic monomer for the polymerization process. It is obtained from Acrylonitrile which is a derivative of propylene. Propylene can also lead to acrylic acid after an oxidation reaction. The figure below shows the different stages needed to obtain acrylamide and acrylic acid from oil.

What should be remembered is that our cost base fluctuates with propylene prices and therefore with the prices of crude.



## Processes of polymerization

There are several different technologies to produce polyacrylamides and each one yields polymers with diverse characteristics, including the amount of hard and soft gels. Below are listed the most widely used processes:

### Co-polymerization

Acrylamide and acrylic acid are polymerized together. It produces polymer with a narrow distribution of anionicity, a maximum molecular weight (MW) of about 20 million Dalton and also an excellent solubility.

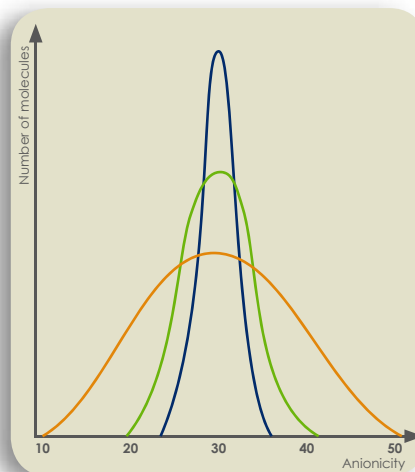
### Co-hydrolysis

Acrylamide is homo-polymerized in the presence of a base in order to be hydrolyzed during the reaction. Polymer produced by this technique has a wide range of anionicity, an upper limit of 18 million MW, a good solubility and a very sharp distribution of anionicity.

### Post-hydrolysis

Homo-polymer of acrylamide is post-hydrolyzed with a base while it is a gel, and then dried. Polymer with a MW of around 22 million can be produced but it has a very wide range of anionicity and problems with solubility in presence of divalent cations.

Polydispersity vs. polymerisation process



■ Co-polymerization  
 ■ Co-hydrolysis  
 ■ Post-hydrolysis



During the manufacturing process of polyacrylamide, there is a possibility that 2 types of insoluble gel particles can form. These can be categorized as soft or hard gels, depending on the flexibility of the particle. Soft gel particles are able to deform and propagate due to the shear forces during injection whereas hard gels particles do not deform and can cause plugging of the pores at the sand-face and in the reservoir.

Generally speaking, the higher the molecular weight, the more the solubility and the filterability are affected. Especially, polymers produced by the co-polymerization technology contain very low levels of soft gels and almost no hard gels, whereas those produced by post-hydrolysis contain the highest amount of hard gel particles. The amount of hard gel formed increases with the molecular weight. To compare the efficiency, it is necessary to test industrially produced polymers in the laboratory under field conditions with procedures that take into account several parameters like mechanical, chemical or thermal degradations. These will be discussed later on.

The amount of insoluble formed during the polymer manufacturing process depends on the type of catalysts, chain transfer agents, stabilizers as well as the:

- Quality of monomers and chemicals used in production
- Manufacturing equipment, especially dryers and the precision of temperature control
- Production process and procedures
- Molecular weight of the final product

## Range of products and their stability

The quality of the polymers for EOR and the range of applications have been greatly improved for the past 10 years. Today, polymer flooding is a viable technology which can be implemented even with hard reservoirs conditions; products are available for temperature up to 120°C, with salty brines and low permeability (10 mD).

SNF has developed a full range of polymers for polymer flooding applications. With our expertise, we are able to determine the best polymer to fit any reservoir conditions. We also developed the know-how to implement such a technology successfully in the field, avoiding degradation of the polymer.

### Chemical degradation

In a typical polymer flood, the polymer is first dissolved before dilution with "dissolution water" and then diluted with "dilution water". The diluted solution is then injected into the reservoir.

These waters contain two types of chemical products which are reactive: oxidizers and reducers.

- Oxidizers are mainly: dissolved oxygen, peroxides found in the oxidized hydrocarbon compounds...
- Reducers are  $H_2S$ , oxygen scavenger (ammonium bisulfite),  $Fe^{2+}$ , which can be an oxidizer or a reducer depending on the other chemical products present in the water, sulfato-reducing bacteria or ammonia...

### Overview of polymer degradation

The very high molecular weight products are sensitive to different degradation mechanisms, which are cumulative in the overall injection lifecycle within an oilfield:

- Chemical degradation which is promoted by free radicals,
- Thermal degradation enhanced by brine composition,
- Mechanical degradation due to shear,
- Absorption and precipitation,
- Biodegradation, which is low with regard to polyacrylamides.

Each of the above degradation mechanisms is addressed below.

In the brine, the reaction between an oxidizer and a reducer will form a free radical and this free radical will react on the polyacrylamide molecules by cutting them. This reaction is a chain reaction and one free radical can cut many molecules.

In addition to optimizing the MW of the polymer to reduce its sensitivity to chemical degradations, different techniques can be used to reduce the presence of free radicals.

## Free radical scavengers

The use of oxygen scavengers (ammonium bisulfite for instance) decreases free oxygen in water to 0-20 ppb prior to injection. However, the reaction between oxygen and scavenger will itself lead to the formation of free radicals harmful to the polymer. This problem can be partially solved by the use of free radical scavenger.

**All SNF polymers dedicated to EOR have a minimum protection package. When required, SNF has developed full protected polymers (F3P) that contain an improved protective package added at the manufacturing stage. The result is a powder which can be handled more safely.**

## Removal of oxygen

To efficiently address the above situation and to minimize the reactions leading to the creation of free radicals, it is very important to obtain a brine for injection with a very low level of oxygen and a limited amount of necessary oxygen scavenger.

To achieve this objective, it is necessary to have a de-oxygenated brine and to protect it from oxygen dissolution by blanketing with nitrogen all the equipment used to produce the injection polymer solution. The use of produced-gas for blanketing is not recommended for complicated feed systems.

H<sub>2</sub>S without the presence of an oxidizer will not promote the degradation of the polymer.

## Thermal degradation

### Polymer selection

Above a certain temperature, precipitation occurs between the hydrolyzed polyacrylamide and divalent ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>) resulting in a significant loss of viscosity. Copolymers of acrylamide/acrylic acid are unstable above 80°C. Above this temperature, it is necessary to use copolymers acrylamide/ATBS, which are stable, up to 90-100°C, depending upon the brine composition and the amount of ATBS.

### Polymer hydrolysis

Even at low temperatures (50°C) and depending on the pH of the brine, hydrolysis of the polymer occurs resulting in an increase of the anionicity of the polymer. Above a certain hydrolysis degree (35 to 45%) precipitation of Calcium-Magnesium salts of the polymer occurs along with an increase in absorption especially in carbonate reservoirs.

Nitrogen Blanking Test



Glove Boxes



When the temperature increases, it is important to select a low anionicity product (15-25%) with a lower apparent viscosity. Through the above mentioned mechanism, the further hydrolysis of the polymer will increase the viscosity and if the polymer selection is correct, no subsequent precipitation of the polymer will occur.

### Mechanical degradation

Polyacrylamides are sensitive to shear which degrades the polymer into smaller pieces and forms free radicals which again cut the polymer molecule in a chain reaction.

The higher the MW the higher the degradation for a given shear. The velocity of the fluid in equipment or pipes must not exceed  $5 \text{ ms}^{-1}$ . If the dissolution and injection plants are well designed, the main shear occurs in the injection lines due to restriction or chokes. Shear will also result from a combination of different factors including:

- Surface equipment (chokes, pipes, valves, pumps, dissolution equipment)
- Well completion design (Horizontal/Vertical drilling, perforations, well height, shots per feet, nozzles...)the permeability of the reservoir...
- Polymer type (average molecular weight and poly-dispersity)

### Absorption - Precipitation

#### Divalent metal precipitation

Divalent metal will precipitate with an increase in pH as a carbonate or a hydroxide. In ASP applications, the pH is increased by the addition of sodium hydroxide or sodium carbonate. In this case, to avoid the precipitation of divalent metal, it is necessary to soften the injection water by precipitation, ion exchange or membrane treatment.

Precipitation will then occur in the reservoir at the injection point, and also at the production wells leading to potential mechanical problems for the equipment and a flow reduction.

#### Other precipitants

Many substances are found in the injection lines. Some of them will propagate into the first phase of the reservoir: rust, sand, clay, ferrous sulfate, sulphur, calcium carbonate, magnesium hydroxide, barium and strontium sulfates, molds,...

In ASP projects, sodium hydroxide will dissolve silica which will precipitate at the production side, impairing the functioning of equipment such as pumps.

#### Compatibility with other chemicals

It is important to test the compatibility of the different additives with the polymer. This is especially true with biocides or anti corrosion products, which are often cationic can precipitate with the anionic polymer. This problem of compatibility occurs also on the production side of the operation as cationic emulsion breakers, coagulants for oil separation and flocculants for flotation are precipitated and neutralize each other.





## Biodegradation

Polyacrylamides are very insensitive to bacteria. However, in some cases, for example Sulfate Reducing Bacteria (SBR), a complex mechanism forms  $H_2S$  with low pH, corrosion and redox reactions resulting in the degradation of the polymer.

Fortunately, these reactions take place in a very limited space and have therefore little influence on the average viscosity of the polymer.

**This paragraph provides basic technical information on SNF polymers range for chemical EOR. Keeping under control both the chemistry and the molecular weight, SNF polymers go from the simplest copolymers to thermally stable ATBS based series, salt resistant SUPERPUSHER series, or very high molecular weight polymer Flopaam 60 series. New types of products are continuously developed for more difficult applications. Below are listed all SNF products available for EOR, depending on field characteristics like temperature, salinity...**

## Standard polymers

Co-polymers of acrylamide and acrylate are suitable for reservoirs with temperature up to 70°C (158°F) and 35 000 ppm TDS, with maximum 1000 ppm of divalent ions



		Anionicity	MW
Flopaam	1430 S	Low	Low
Flopaam	1530 S	Low	Medium
Flopaam	1630 S	Low	High
Flopaam	2430 S	Low	Low
Flopaam	2530 S	Low	Medium
Flopaam	2630 S	Low	Medium-High
Flopaam	3130 S	Medium to High	Ultra Low
Flopaam	3230 S	Medium to High	Very Low
Flopaam	3330 S	Medium to High	Low
Flopaam	3430 S	Medium to High	Medium
Flopaam	3530 S	Medium to High	Medium-High
Flopaam	3635 S	Medium to High	High
Flopaam	3630 S	Medium to High	High
Flopaam	6030 S	High	Very High
Flopaam	6040 D	High	Very High

## Co-polymers of ATBS and acrylamide

ATBS-based polymers are less sensitive to temperature and salinity. They are recommended for reservoir temperatures up to 95°C (203°F).

	Anionicity	MW
Flopaam AN 105	Very Low	Low
Flopaam AN 105 SH	Very Low	High
Flopaam AN 105 VHM	Very Low	Very High
Flopaam AN 110	Low	Low
Flopaam AN 110 SH	Low	High
Flopaam AN 110 VHM	Low	Very High
Flopaam AN 113	Low	Low
Flopaam AN 113 SH	Low	High
Flopaam AN 113 VHM	Low	Very High
Flopaam AN 118	Medium	Low
Flopaam AN 118 SH	Medium	High
Flopaam AN 118 VHM	Medium	Very High
Flopaam AN 125 VLM	Medium	Very low
Flopaam AN 125	Medium	Low
Flopaam AN 125 SH	Medium	High
Flopaam AN 125 VHM	Medium	Very High
Flopaam AN 132	High	Low
Flopaam AN 132 SH	High	High
Flopaam AN 132 VHM	High	Very High

Initial mechanical degradation takes place within a matter of seconds or minutes. The degree of degradation depends on:

- Flow of the polymer solution,
- Available area of injection which changes with time due to plugging by precipitates,
- Permeability of the reservoir.

## Acrylamide/ATBS/Acrylic acid polymers

	Anionicity	MW
Flopaam 5205	Medium	Medium
Flopaam 5205 SH	Medium	High
Flopaam 5115 VLM	Medium	Very Low
Flopaam 5115 BPM	Medium	Low
Flopaam 5115 MPM	Medium	Medium
Flopaam 5115	Medium	Medium
Flopaam 5115 SH	Medium	High
Flopaam 5115 VHM	Medium	Very High
Flopaam 5220	High	Medium
Flopaam 5220 SH	High	High
Flopaam 5220 VHM	High	Very High

## Terpolymers of Acrylamide, ATBS and NVP

These polymers are composed of acrylamide, ATBS and NVP. They are suitable for reservoirs with temperature as high as 120°C, with high salinity.

	Anionicity	MW
Superpusher SAV 225	Medium	Low
Superpusher SAV 226	Medium	Low
Superpusher SAV 333	Medium	Low
Superpusher SAV 441	High	Low
Superpusher SAV 442	High	Low
Superpusher SAV 522	Medium	Low

## Associative polymers

Associative Polymers contain both hydrophobic and hydrophilic moieties. They can resist high salinities and moderate temperature and provide very high resistance factors in reservoirs.

	Anionicity	MW
Superpusher B192	Low	Low
Superpusher S255	Medium	Low
Superpusher S265	Medium	Low
Superpusher C319	High	High
Superpusher P329	High	High
Superpusher D118	High	High
Superpusher C1205	Medium	High

As highlighted in the previous paragraphs, the selection of a polymer is related to the field conditions (temperature, salinity, target viscosity) but also to the type of injection, the additives used during injection and the surface facilities. SNF has developed the full range of expertise to implement successfully a polymer flood: from the laboratory studies to select the appropriate polymer to the design and building of facilities required for the injection.

## Calcium Tolerant Polymers

SNF has developed a full range of calcium tolerant polymers for very hard and salty brines. The FloComb series is detailed below.

	Anionicity	MW
FloComb C3025	Medium	High
FloComb C3125	Medium	High
FloComb C3225	Medium	High
FloComb C3525	Medium	High
FloComb C6025	Medium	Very High
FloComb C6125	Medium	Very High
FloComb C6225	Medium	Very High
FloComb C6525	Medium	Very High





## From Design To Injection

Polymer flooding projects are more and more challenging and require a full set of integrated expertise, from chemistry to system engineering. In order to design such a project, a wide variety of variables must be considered such as monomer selection, polymer structure, polymer dissolution, injection system, water pre-treatment and supply chain. SNF provides the full range of expertise required to support the need of EOR as evidenced by a recent large-scale multi-year contract for the engineering and construction of a polymer flooding project in the Marmul field in the south of Oman. Our dedicated teams are ready to find out the best solution and equipment to fit the requirements of each company and each reservoir. Delivering large quantities of products throughout the world also requires strong logistic capabilities. SNF is able to assess and meet all the demands to deliver the products to the customers in a right time, at right price.

SNF provides the full range of expertise required to support the need of EOR as evidenced by a recent large-scale multi-year contract for the engineering and construction of a polymer flooding project in the Marmul field in the south of Oman. SNF can provide:

- Reservoir engineering
- Monomer integration
- Polymer selection design
- Polymer manufacturing
- Polymer storage and dissolution equipment
- Injection equipment
- Treatment of injection and produced water
- Engineering and system design
- Training, start-up and commissioning

Polymer flooding projects are more and more challenging and require a full set of integrated expertise, from chemistry to system engineering. In order to design such a project, a wide variety of variables must be considered:

- Selection of monomer
- Polymer structure
- Polymer dissolution
- Injection system
- Water pre-treatment
- Supply chain

## Laboratory testing: selection of the best polymer

Several tests are performed in SNF laboratory to select the best polymer for each polymer flooding project. Our full set of expertise will allow our customers to considerably reduce the risks and uncertainties linked to the implementation of polymer flood in their field. All our products are extensively tested and improved to continuously provide the industry with the cutting-edge products, for the most challenging conditions. The tests performed are listed and described briefly below.

### I. Solution preparation

To carry out these experiments, we need to synthesize the brine used in the field for the injection.

With dry powder polymers, the brine is stirred using a magnetic stirrer at a speed high enough to make a strong vortex. The powder is introduced slowly into the side of the vortex to avoid formation of fisheyes which can be formed if the powder is not wetted evenly. The solution is then stirred slowly for 90 minutes to ensure complete dissolution. The solution is then diluted to the final concentration used for the testing.

Polyacrylamide emulsions are not simple concentrated solutions of polymers so a simple dilution in water is not possible. When making a solution from an emulsion, two physical phenomena take place: phase inversion and dissolution. When the emulsion comes into contact with water, the inverting surfactant dissolves and emulsifies the oil in the water (inversion). The actual polymer particles then come into contact with water and dissolve (dissolution). Emulsion polymers are mixed by adding the emulsion via a syringe to the rapidly moving brine. A high shear, mechanical stirrer is recommended for the initial dilution rather than a magnetic stirrer.



## II. Viscosity

After the polymer solution has been prepared, viscosity measurements are performed using a low shear viscometer such as Brookfield LVT with UL adaptor. The standard SNF procedure measures the viscosity of a 1000 ppm (1g/l) solution at 25°C. Other types of viscosity measurements can be made to evaluate polymers for use in a specific project. These include viscosity as a function of polymer concentration, shear rate at a given polymer concentrations and as a function of temperature.

## III. Filter ratio

The filter ratio test is important to ensure that a polymer solution is free of aggregates which could lead to formation plugging.

A 1.0 g/l solution is pumped through a 5 micron filter membrane with a differential pressure of 2 bars. The flow rate is measured and should remain nearly constant during the test for a product that is free of aggregates. Filter Ratio (FR) is defined as the time for 300<sup>th</sup> ml minus the time for 200<sup>th</sup> ml all divided by the time for the 200<sup>th</sup> ml minus the time for the 100<sup>th</sup> ml, calculated by:

$$FR = (t_{300} - t_{200}) / (t_{200} - t_{100})$$

## IV. Thermal stability

Long-term thermal stability of polymer solutions at field temperatures is determined under anaerobic conditions in sealed glass ampoules. A special procedure allows vacuum degassing down to 10-20 ppb (parts per billion) of oxygen. Temperatures up to 120°C can be studied. Thermal stability is expressed as percent of the viscosity retained after a chosen period of high temperature exposure. Viscosity may be measured initially and finally at room temperature or at the designed temperature. Tests can be performed during several months to one year.

## V. Core flooding

Sand-packs and core floods on actual reservoir core material can be used to measure:

- RF (Resistance Factor)
- RRF (Residual Resistance Factor)
- Oil recovery
- Injectivity
- Adsorption

The whole study can be performed within a period of 6 months to one year, depending on the company requirements and the number of polymers tested.



## Polymer flooding facilities – from Design to Operation

### Introduction

To ensure proper injection in the reservoir, it is important for the polymer to be dissolved properly, for the equipment to be compatible with the polymer and for the solution to be handled properly and injected on continuous basis.

In order to optimize the different phases of a project, SNF offers a wide range of engineering services and polymer flooding equipment to customers all around the world, thanks to dedicated EOR Engineering teams.

### Conceptual studies

During preliminary phases of polymer flooding project, SNF can develop conceptual studies of facilities to evaluate the technical feasibility, CAPEX budget and assess flooding project risks (facilities/logistics aspects). Different technical options for polymer storage, dissolution and injection are studied and compared: main process principles are described, logistics issues are highlighted and basic cost and high level planning are proposed.

### Injectivity test

Also during the preliminary phase of a project, SNF is able to provide a very specific service to oil companies: polymer injectivity test. The main interest of this injectivity test will be to establish and validate the flow rate and pressure at which the polymer solution can be pumped into the reservoir without fracturing the formation.

SNF's scope of work for this type of tests includes the supply of a stand-alone polymer injectivity test skid, the mobilization of a dedicated operating crew (which will operate the unit and run basic viscosities measurements) and obviously the supply of polymer chemical to be tested.

### Pilot and full field equipment

As soon as the polymer selection and the injection parameters have been validated, the next step of the polymer flooding projects could go through a continuous pilot injection or directly to a full field development. This is really the core business of SNF EOR engineering department, which can propose either skid mounted units (for pilot or small size full field projects) built in SNF partners' workshops or field erected plants (for large pilot or full field projects), where typically equipment is sent and assembled at site.

Typically, the following deliverables are provided by SNF at the end of the study:

- Process description
- Supply chain description
- Process flow diagram (PFD), for polymer storage, preparation and injection
- Preliminary mass balance
- Preliminary equipment list
- Estimated electrical power consumption
- Preliminary general layout and land requirement
- Basic operating & control philosophy
- HAZOP
- Preliminary material selection report
- Level 2 schedule for polymer facilities
- Identification of the long lead items
- Proposed SNF vendor list
- Cost estimation of facilities ( $\pm 30\%$ )
- Comparison of different options and SNF recommended solution



## Basic & Detailed Design

In order to manufacture in the most efficient way the skids or field erected plants, design work is carried out. For each project SNF is able to mobilize a dedicated team. For specific disciplines such as civil and pipelines, SNF will work with consultants who have knowledge of the local rules and regulations.

All along this project development phase, specific attention is focused on HSE issues through risk analysis session, ergonomic reviews,... in accordance with the client policy.

## Equipment selection

Based on its long experience in polymer flooding, SNF defines, selects and implements equipment based on efficiency and robustness proven on past experiences and site field conditions.

Due to the polymer shearing sensitivity, specific attention is paid to the equipment which handles the polymer solution, such as low pressure transfer pumps, tanks agitators, high pressure injection pumps, static mixers... Design and selection of equipment will also be engineered to minimize oxygen ingress in the system, which leads in presence of contaminants (Iron,  $H_2S$ ) to polymer degradation.

In the past, when hydrating powder with conventional systems such as educators, many challenges and short-comings were encountered. In response, SNF has designed and patented specific dissolution equipment, called Floquip PSU™. This equipment has quickly become a standard in EOR applications in the USA and Canada. It has also been used in other projects all around the world (Oman, Indonesia, Angola...).

Polymer Slicing Units: FLOQUIP PSU™



### Manufacturing - Construction

To limit costly activities in field, SNF develops units with equipment mounted on stand-alone structures (either closed or opened). These structures are then shipped and installed at site.

Manufacturing and especially welding can be carried out following different construction standards: ASME, API, DIN...

If construction and installation activities, carried out on the field, are part of the scope, SNF uses local construction companies which have knowledge of the country applicable rules and oil consortium or company specific requirements and all accreditations required to conduct jobs in the field.

### Training, commissioning, operation

After completion of the construction site, SNF mobilizes its dedicated commissioning team. This team composed of engineers and technicians with different skills is able to perform all commissioning steps and start-up of the facilities in accordance with company specific specifications. In addition to the installation start-up; the team collects polymer solution samples and main parameters are analyzed (yield viscosity, filter ratio...) in order to optimize the process parameters of the system. In parallel of these start-up operations, training sessions are conducted by SNF for the different company personnel teams: operations, maintenance and laboratory.



Full scale ASP facility running test before shipment



## Water Treatment

When dealing with water treatment, two points have to be tackled. The first one concerns the quality of the dissolution or injection water. The presence of contaminants such as oxygen,  $H_2S$  and iron has to be limited in order to avoid the degradation of the polymer solution. Sometimes the water has to be treated to remove the excess of iron or oxygen.

The second point concerns the treatment of the produced water. SNF is constantly acquiring knowledge and new skills to tackle the degradation of the back-produced polymer. Because not all the polymers are degraded, it is necessary to implement specific treatments (preferentially after the Oil/Water separation so as not to affect the quality of the crude) to cut the remaining polymer backbones and therefore decrease the water viscosity. Among the possible treatments, chemical and mechanical are the most used.





At the pilot stage, there is no need to assess in detail the effect of the back-produced polymer since the dilution effect in the reservoir will lead to negligible concentration of polymer within the water treatment facilities. When dealing with a full field project, two different aspects have to be considered in the treatment processes. The first one is related to the separation of the crude and the produced water. The next one deals with the treatment of the produced water once it has been separated from the crude, in order to be re-used or disposed of.

Each case is specific and needs demonstrative studies to pre-engineer the equipment.

There is a compulsory necessity if the produced water is to be re-injected and that is to keep the water at a minimum concentration of oxygen, in the range of 10 to 50 ppb. Therefore, all equipment have to be blanketed under a minimum pressure of gas or nitrogen to avoid oxygen pollution. The main methods of treatment are as follows.

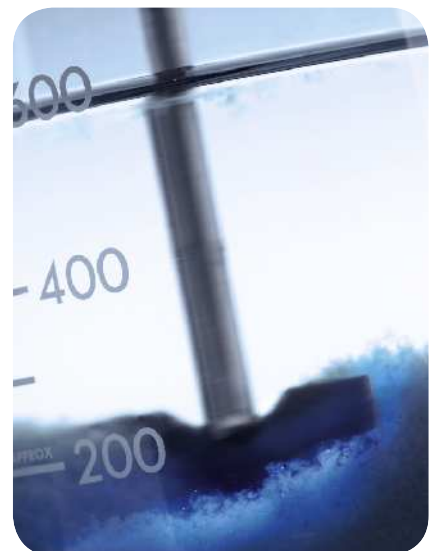
## Mechanical Treatment of Viscosity

### Increase the size of equipment

It is possible, if the viscosity is not too high to increase the size of the equipment to take into account the change of separation velocity. The majority of equipment is designed for a maximum viscosity of 2 to 4 cps. And in water flooding applications the viscosity ranges generally between 1.57 (@ 4 °C) and 0.367 (@ 80 °C). It is therefore possible to treat viscous water with standard equipment by calculating  $V_o$  under the different operating conditions.

Obviously gas flotation systems have efficiency limits in viscous systems because the coalescence of the gas bubbles is increased with a decrease of efficiency of micro bubble systems. In general, hydrocyclones are very sensitive to viscosity and their test results are not positive. On the other hand, filters and especially nutshell filters keep their efficiency in viscous systems but they are often overloaded by the lack of efficiency of the other equipment.

The shear between equipment (pumps, valves, pipes, restrictions) normally gives an average particle size under 50 microns. Coalescence occurs in the different equipment that remove the largest particles first, then smaller and smaller ones. The use of gravity transfer or low shear pumps will improve the size of the droplets and the quality of the treatment.





## Add stabilization tanks before each treatment unit

This improves the coalescence if the transfer between the storage tank and treatment equipment is made by gravity at very low shear.

## Coalescers

Coalescers are used for particles ranging 5 - 15 microns, but in viscous systems they show an improvement with higher particle sizes in low shear.

# Physical-Chemical Treatment of Viscosity

This treatment is difficult as the anionic polymer will generally react with cationic products.

## Surfactant emulsion breaker

With the new composition of the produced water it is necessary to confirm the emulsion breaker used in quality and quantity. This is particularly important in ASP or SP systems where the oil emulsion is stabilized by the surfactant.

## Acidification

In ASP systems the acidification destabilizes the alkaline salts and decreases the HLB of the system. But the surfactant effect with sulfonic surfactants is maintained and is difficult to overcome.

## Coagulation - Flocculation

Coagulants and flocculants are added in the process at gas flotation and filtration steps. These cationic compounds precipitate with the anionic polymer used for flooding. They will have no effect at the concentrations normally used. Nevertheless water treatment can still be achieved by total or partial precipitation of the anionic polymer by cationic flocculants beforehand.

## Oxidizers

The addition of oxidizer or redox systems break down very quickly the viscosity of the produced water allowing for instance sea disposal.

The most efficient oxidizers are sodium hypochlorite, sodium persulfate, hydrogen peroxide, and the activity increases with temperature.



## Mechanical degradation

As polyacrylamides are sensitive to mechanical degradation it is possible to shear the solution to decrease the viscosity. This can be done just before any treatment or just after the skimmer tank. To achieve a good degradation, it is necessary to apply high shear, in the range of 50 to 100 000 s<sup>-1</sup> with high pressure pumps, 30 to 80 bars, with the flow passing through perforated plates with holes having a diameter of 1 to 2 mm.

## Thermal degradation

It is possible to decrease the MW of the polymer down to 1 - 2 million, by heating for one minute at 180 °C - 200 °C. This can be achieved at low cost by a double loop heat exchanger and a boiler using produced gas. The main problem is corrosion with brines and specific alloys or titanium are necessary to build this equipment.

## Biotreatment

Biotreatment is inefficient for MW over 2000.



## Conclusion

At the pilot stage, the impact of polymer on produced water is minimal since dilution likely occurred in the reservoir or at the water treatment facilities. For larger EOR projects, several degradation methods exist and are under implementation to maximize the efficiency of the water treatment process by degrading the residual polymer.



## Notes

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## Notes

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## Enhancing Polymer Flooding Performance

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