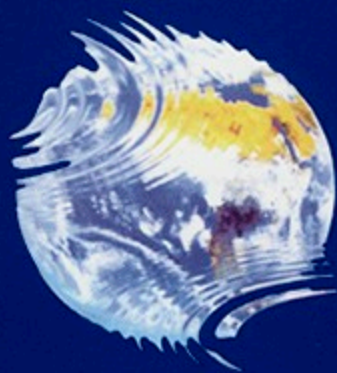


FLOPAAM™

*For Enhanced
Oil Recovery*



SNF FLOPAAM™

FLOPAAM™ *World leader in Polymers*

Viscosifying polymers to control the mobility of injected water have been employed for many years in Enhanced Oil Recovery (EOR) applications. Polymer flooding, to improve volumetric sweep efficiency, reduce channelling and breakthrough, has aided many operators to increase oil recovery and lower the cost per barrel of oil recovered. The same polymers are used with surfactants and alkali agents for increasing the sweep efficiency of these tertiary recovery floods.

SNF has been developing a complete range of polymers for use in EOR for more than 15 years. These products have been developed to accommodate the wide variety of conditions encountered in oil fields throughout the world.

They include the following:

- hydrolysed polyacrylamides of various molecular weights (FLOPAAM™) for temperatures up to 80°C, produced as free flowing powders or as self inverting emulsions.
- sulphonated polyacrylamides for temperatures up to 120°C.
- liquid xanthan gum (FLOCON™ 4800C) for very high salinity brine.

The principle manufacturing sites for EOR polymers are located in St. Etienne, (France), and Riceboro, GA (USA).

■ Polymers used for EOR

SNF manufactures a complete range of anionic polyacrylamides for EOR.

of acrylamide monomers, some of which have been hydrolysed. The molecule is a flexible chain structure known as a random coil and since it is a polyelectrolyte, it will interact with ions in solution.

Polyacrylamide powder

SNF standard polyacrylamides for EOR are the FLOPAAM™ series, S (solid). Molecular weight ranges from less than 2 million up to 22 million Dalton and anionic charge ranges from 0 to 100%. Molecular weight is also dependant on the hydrolysis level (maximum molecular weight is achieved around 40 mole%). These are available in dry powder and emulsion form.

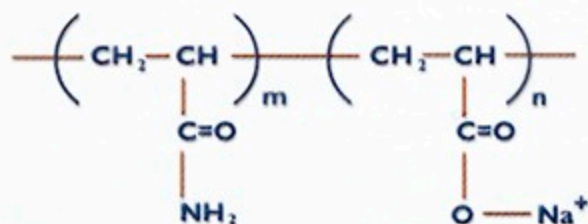
Partially hydrolysed polyacrylamide (HPAM) has been used for mobility control polymer floods since the 1960s. It is a synthetic straight chain polymer

Polyacrylamide emulsion

SNF manufactures polymer in emulsion form having the same chemical characteristics as the powder. These polymers are named under the FLOPAAM™ E series.

Polyacrylamide emulsions are dispersions, also called suspensions, of a hydrogel of water soluble polymer in oil. They are two phases heterogeneous systems and consist of several components. The hydrated polymer is in the shape of microbeads of 1 micron diameter. These microbeads are dispersed in oil and are stabilised by surfactants.

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Chemical Structure of Polyacrylamide

Although the majority of polymer floods have used dry powder polymers, there are field specific conditions that may dictate the use of emulsion polymers. Polymer floods conducted from offshore platforms for example, are a case where emulsion polymers can be more appropriate due to in line, closed loop mixing and easier handling and logistics. SNF EOR emulsion polymers are available in either 30% or 50% active systems. These are easily mixed in the field with the use of static in line mixers.

Inversion of emulsions in the field is straightforward and rapid. Depending on the quality of the makeup

water, an emulsion breaker can be added in the field or incorporated into the oil phase of the emulsion (self inverting). For most EOR applications FLOPAAM emulsions are supplied as self inverting, complete systems, with the inverting surfactant incorporated during manufacture. SNF has an in line static mixing test rig in the laboratory to simulate inversion of emulsion and to analyse the shearing energy required to achieve complete inversion. This is used to be sure that polymer solutions have the required EOR characteristics (filtration, viscosity) for a given field project.

SNF also manufactures the *PUSHER™* brand's products.

It is important to select the proper polymer for a particular field. Reservoir permeability and oil viscosity are used to determine the optimum molecular weight polymer. Rock composition and polymer adsorption level are used to determine the best anionicity (degree of hydrolysis). Preliminary screening for selection of polymer is conducted by reservoir engineers and chemists at SNF.

The table below lists the most common EOR polymers.

| FLOPAAM S and E series | 3630 | 3530 | 3430 | 3330 | 2530 | 2430 | 2330 |
|---|-------|-------|-------|-------|-------|-------|-------|
| Hydrolysis in mole % | 25-30 | 25-30 | 25-30 | 25-30 | 20-25 | 20-25 | 20-25 |
| Approximate Molecular Weight (million Dalton) | 20 | 16 | 12 | 8 | 16 | 12 | 8 |

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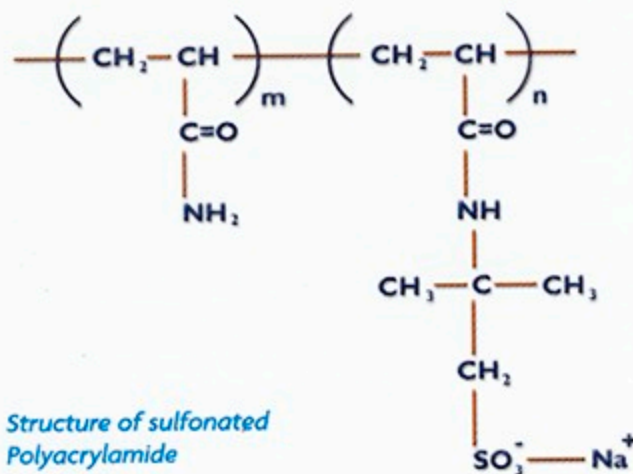
● SNF has developed a complete series of sulfonated, listed in the table below:

| Product Name | AN105 | AN113 | AN125 VLM | AN125 | DP/PT2101B | AN132 |
|---|-------|-------|-----------|-------|------------|-------|
| Sulfonation in mole % | 5 | 13 | 25 | 25 | 25 | 32 |
| Approximate Molecular Weight (million Dalton) | 6 | 8 | 2 | 8 | 12 | 8 |

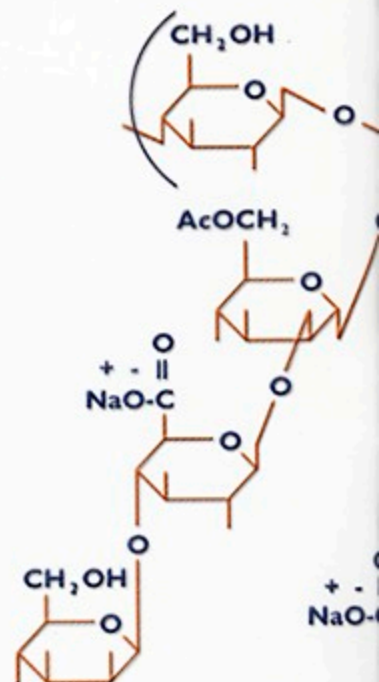
■ Sulfonated polycrylamide powder

SNF "standard" polyacrylamides have better thermal stability than in the past (up to 90°C) due to the addition of anti oxidising agents during the manufacturing process. For higher temperatures up to 120°C sulfonated copolymers are required. These are copolymers of acrylamide and sodium salt of acrylamido propyl sulfonated acid. In addition to thermal stability, they present better stability to

divalent ions, such as Ca^{2+} and Mg^{2+} , present in most hard brines or sea water. Although the molecular weights of these polymers are not as high as the FLOPAAM series, they can reach 14 millions. They also have a lower adsorption levels than standard hydrolysed polyacrylamides.



Structure of sulfonated Polyacrylamide

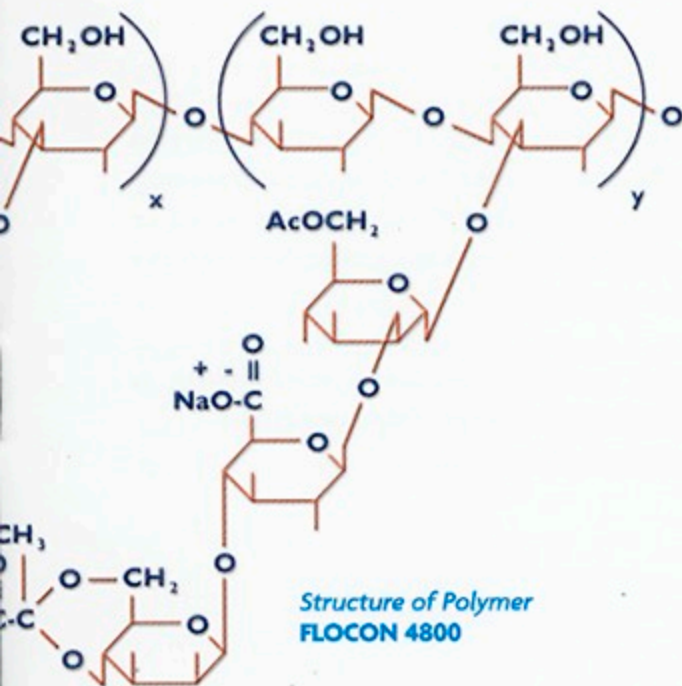


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■ Liquid xanthan gum

Xanthan gum is a polysaccharide, is a bio-polymer. It is produced by the microbial action of *xanthomonas campestris* on a substrate of carbohydrate media, with a protein supplement and an inorganic source of nitrogen. The biopolymer is an extracellular slime which forms on the surface of the cells. The fermented broth is pasteurised to kill the microbes and precipitated from the broth by alcohol, then concentrated.

Xanthan gum is well known to have excellent performance in high salinity brine. SNF obtained all the manufacturing and use patents of Pfizer's FLOCON 4800 xanthan gum, which is recognised by experts around the world as the highest grade xanthan available for EOR projects.



FLOCON 4800

is a liquid broth that can be easily diluted to working concentrations without elaborate shear-mixing equipment. Direct injection of dilute solutions into oil reservoirs is possible without pre-filtration. It is compatible with most surfactants and other injection fluid additives used in tertiary oil recovery formulations. Special manufacturing techniques can impart thermal stability up to 105°C (220°F). FLOCON 4800 is available in broth and concentrate form (FLOCON 4800 C). Both the broth and the concentrate are highly pseudoplastic solutions and are easily pumped.

Typical FLOCON 4800 Physical Properties:

| FLOCON | 4800 | 4800C |
|--------------------|----------------------|----------------------|
| Appearance | Tan gelatinous fluid | Tan gelatinous fluid |
| Active content | 3 - 5% | 7 - 10% |
| Viscosity at 25° | 3,500 - 4,500 cp | 12,000 - 13,500 cp |
| Molecular Weight | 2 - 5 millions | 2 - 5 millions |
| Biocide (ppm HCOH) | 2,000 minimum | 3,000 minimum |

After FLOCON 4800 has been dissolved for use as a mobility control agent, care must be taken to protect it from bacterial attack. Proper use of biocides and oxygen scavengers is essential; the most common biocide used is formaldehyde (HCOH). FLOCON is protected for bulk shipment and storage during manufacture by the addition of 2000–3000 ppm of HCOH.

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■ Manufacturing process

EOR polyacrylamide powder is manufactured using one of 3 different processes:

First is the co-polymerisation process:

co-polymerisation of acrylamide and sodium acrylate at a certain ratio to produce the copolymer. It is the most common.

Second is the co-hydrolysis process:

homo-polymerisation of acrylamide with alkaline hydrolysis in situ during the polymerisation to produce the copolymer.

Third is the post-hydrolysis process:

homo-polymerisation of acrylamide and production of powder. This stage is followed by powder dissolution and post hydrolysis with caustic soda to convert a certain percentage of the acrylamide to sodium acrylate. This can be done in the field or at the manufacturing site.

The first two processes are preferred as they produce a final product that is readily soluble and ready to inject once put into solution. In the case of a post hydrolysis product, the powder, being non-ionic, is more difficult to dissolve and heating is required for the post hydrolysis reaction.

EOR grade emulsion is manufactured by co-polymerisation within a solvent phase to produce an invert emulsion.



SNF - Andrézieux, France

■ Quality control and ISO certification

SNF has achieved the ISO 9001 certification for all products manufactured in SNF plants in France and USA. Very high quality polymers are required for EOR applications and therefore each batch of EOR polymer is carefully tested in our laboratories. This consists of routine tests, such as UL viscosity (test procedure SNF QC400A), active content (SNF QC100A), particle size, free monomer content and can include further EOR related tests such as viscosity measurement at field conditions (injection brine, temperature, concentration), filter ratio and percent hydrolysis (anionicity).

More specific tests are conducted on a reservoir study basis to evaluate the following parameters:

- **Thermal stability under reservoir conditions (anaerobic)**
- **Chemical stability and compatibility with oxygen scavenger, iron chelating agent etc.**
- **Screen factor**
- **Injectivity, adsorption and oil recovery in sandpacks and core floods on actual reservoir core material (core floods are contracted to external laboratories in co-operation with the oil company)**
- **For emulsion products, invertability is optimised for specific field conditions (Brine salinity).**

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■ Principles of polymer flooding

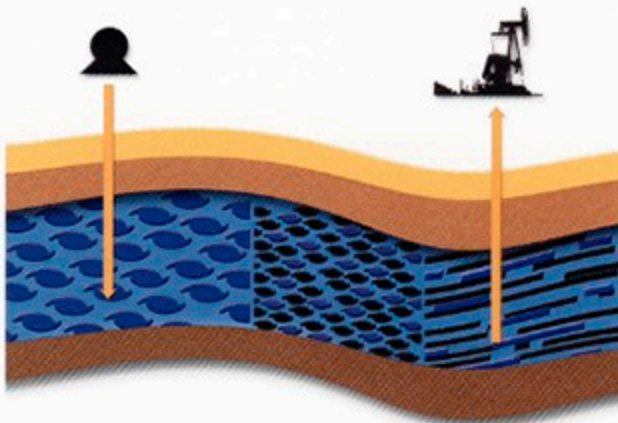
Polymer flooding can yield a significant increase in oil recovery compared to conventional water flooding techniques. A typical polymer flood project involves mixing and injecting polymer over an extended period of time until about 1/3–1/2 of the reservoir pore volume has been injected. This polymer “slug” is then followed by continued long term water flooding to drive the polymer slug and the oil bank in front of it toward the production wells. Polymer is injected continuously over a period of years to reach the desired pore volume.

When water is injected into a reservoir, it seeks the path of least resistance (usually the layers of highest permeability) 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 result in a low sweep efficiency, or bypassed oil.

Polymers improve the mobility ratio and increase the displacement efficiency in the reservoir. One of the routine screening parameters used for a preliminary analysis of a reservoir is the mobility ratio. If the mobility ratio is less than one, the displacement of the oil by the water will be efficient and piston like. If the mobility ratio is greater than one, the more mobile water will finger through the oil and leave behind regions of unswept oil. Polymer concentration ranges from a few hundred ppm to as high as 2000 ppm for typical polymer flood projects. Polymer solutions in this range used for EOR are non-Newtonian (also called pseudoplastic) fluids, because their viscosity is a function of shear rate.

Definitions

The **mobility** of a fluid in a reservoir is defined as the permeability of the reservoir to that fluid divided by the viscosity of that fluid. The **mobility ratio** of water to oil is the mobility of water in the reservoir divided by the mobility of oil in the reservoir.



This is expressed in the following equation:

$$M = (k_w/\mu_w)/(k_o/\mu_o) = (k_w\mu_o)/(k_o\mu_w) = \lambda_w/\lambda_o$$

where :

M = mobility ratio of water to oil

k_w = relative permeability to water

k_o = relative permeability to oil

μ_w = viscosity of water

μ_o = viscosity of oil

λ_w = mobility of water

λ_o = mobility of oil

Common practice is to define mobility using the relative permeability to water at residual oil saturation and the relative permeability to oil at the irreducible or connate water saturation.

Resistance factor is defined as the ratio between the mobility of water to that of polymer solution.

$$RF = (k_w/\mu_w)/(k_p/\mu_p)$$

Residual resistance factor is the ratio of the mobility of water before and after polymer flooding.

$$RRF = \frac{(k_w/\mu_w)_{\text{before polymer injection}}}{(k_w/\mu_w)_{\text{after polymer injection}}}$$

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The resistance factor describes the reduction in water mobility, while the residual resistance factor describes the reduction in water permeability after polymer flooding. The reduction in mobility is partly due to the increase in water viscosity and partly due to permeability reduction.

Permeability reduction is caused by the retention of polymer molecules in the reservoir rock. This is a combination of adsorption, and entrapment and it is not entirely reversible. Thus most of the polymer (and the benefits it provides) remains in the reservoir long after polymer injection is stopped and the field is returned to water injection.

Adsorption is the irreversible retention of polymer molecules on the rock surface. The amount of polymer adsorbed on the rock surface depends on the type and size of the polymer molecules, polymer concentration, and rock surface properties.

Two testing methods are used to measure the amount of adsorption, one is a static condition test and one is a dynamic test, which measures the adsorption in a core flood. Polymer molecules adsorb onto the rock surface as a monolayer with the thickness equal to the diameter of the polymer molecules. Once the monolayer saturation level is reached, no more adsorption will occur.

Anionic polyacrylamide has a greater affinity for the positively charged surfaces such as dolomite than for the negatively charged surfaces such as sandstone. Clay content of sandstone reservoirs also plays a significant role in the total amount of polymer adsorbed, where the higher the clay content the more adsorption there is.

Laboratory Procedures

Solution preparation

Viscosity measurement, filter ratio and screen factor tests are normally conducted in synthetic field water. The polymer is first diluted into a 5000 ppm (by weight) solution and then the working level is made from this mother solution.

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.

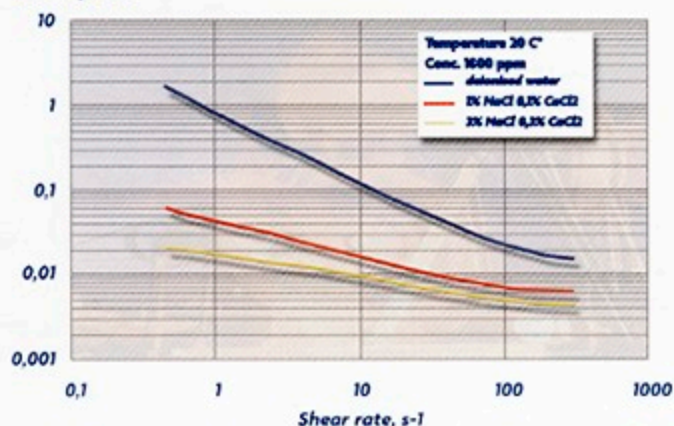
Polyacrylamide emulsions are not simple concentrated solutions of polymer so a simple dilution in water is not possible. When making a solution from an emulsion, two physical phenomenon take place, phase inversion and dissolution. When the emulsion comes into contact with water, the inverting surfactant dissolves and emulsifies the oil in the water (inversion). The actual polymer particles then come into contact with the 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.

As with the dry powder, the recommended initial concentration is 5000 ppm of active polymer, however, the activity of the emulsion must be taken in to account (the emulsions are 30–60% active). Following this initial mixing, the solution only requires 10–15 minutes of additional stirring.

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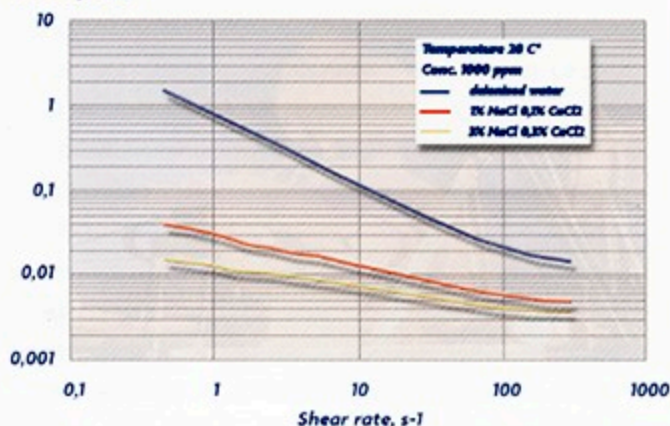
viscosity of FLOPAAM 3630S

Viscosity, Pa.s



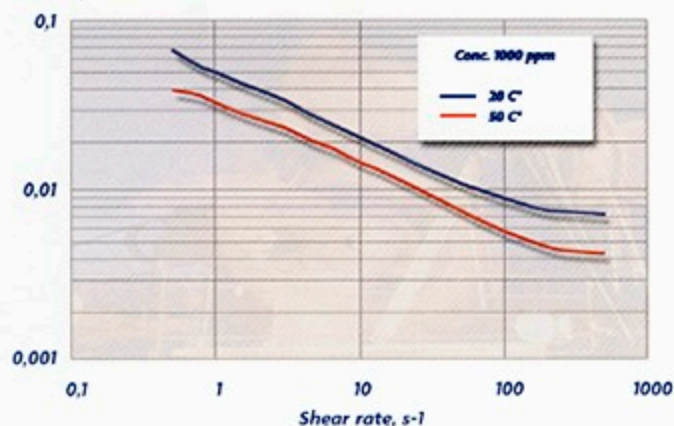
viscosity of FLOPAAM 3530S

Viscosity, Pa.s



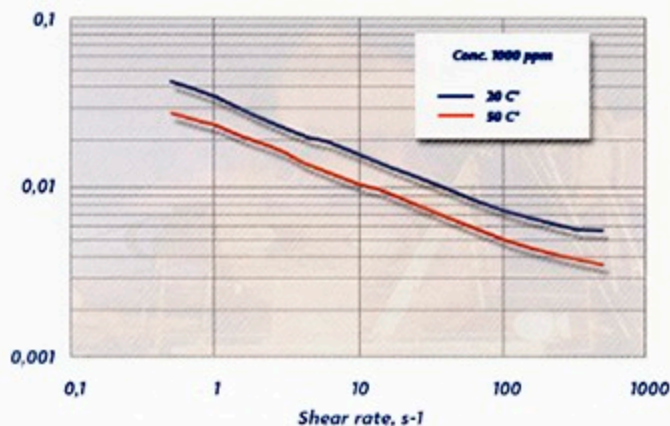
viscosity of FLOPAAM 3630S versus temperature

Viscosity, Pa.s



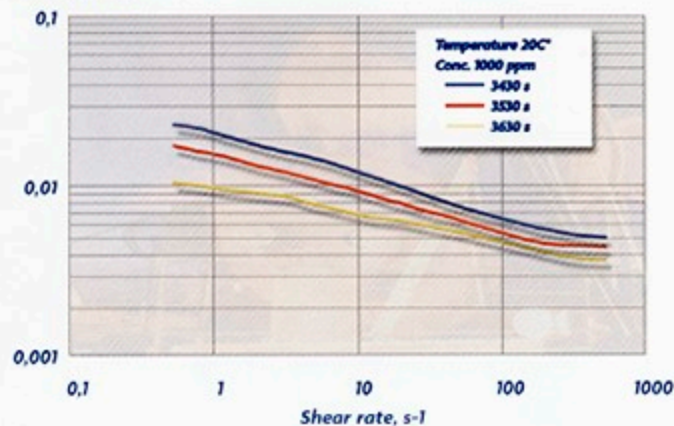
viscosity of FLOPAAM 3530S versus temperature

Viscosity, Pa.s



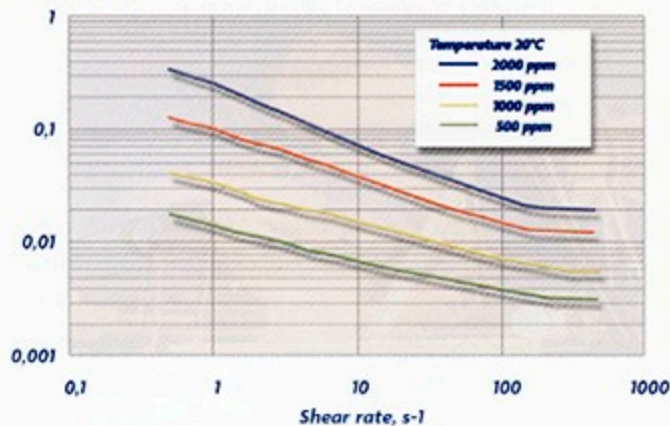
viscosity of FLOPAAM 3530S in synthetic sea water

Viscosity, Pa.s



viscosity of FLOPAAM 3530S in brine (10 g/l NaCl, 1 g/l CaCl₂)

Viscosity, Pa.s



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Viscosity

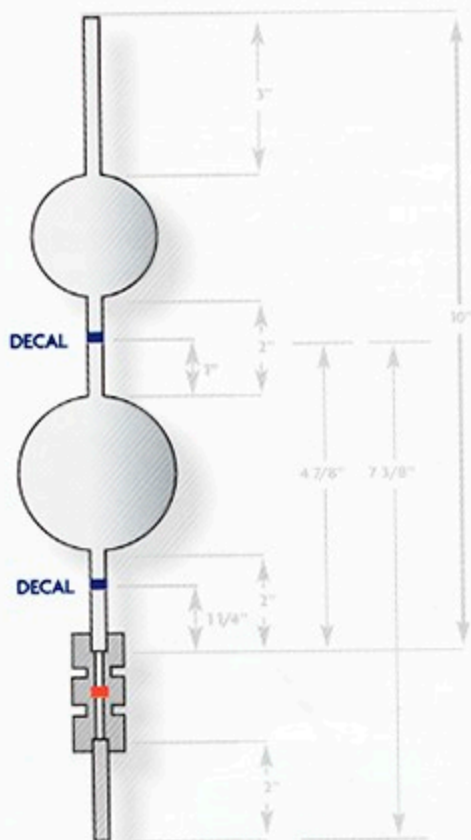
After the polymer solution has been prepared, viscosity measurements can be made using a low shear viscometer such as a Brookfield LVT with UL adaptator. The standard SNF procedure (SNF400A) measures the viscosity of a 1000 ppm (1 g/l) solution at 25°C. Other types of viscosity measurements can be made to evaluate polymers for use in a specific project. These include viscosity as a function of polymer concentration, shear rate at given polymer concentrations and as a function of temperature.

Screen factor

This measurement is related to the viscoelastic nature of solutions of polyacrylamides and is most effected by the larger polymer molecules. Screen factor is easily measured and gives reliable data used for characterising polymer solutions. It is measured with a screen viscometer which consists of a small fluid reservoir above a number of screens of known mesh density, usually three 100-mesh screens. The screen factor, SF, is defined as the following ratio of times:

$$SF = \frac{\text{Flow time of volume of polymer solution through screen viscometer}}{\text{Flow time for same volume of solvent through screen viscometer}}$$

Screen factor is useful as a qualitative characterisation test for comparing different polymer solutions. It is a useful diagnostic test of whether mechanical degradation has occurred by comparing before and after samples of polymer that have been subjected to a given shearing process.

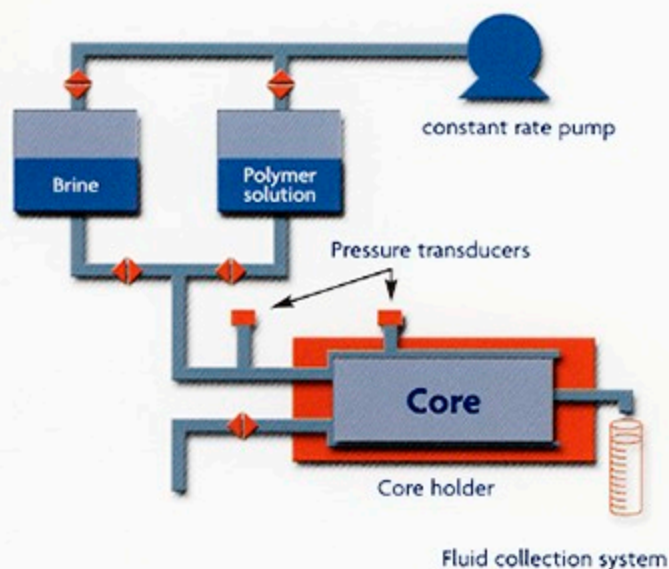


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Filter ratio

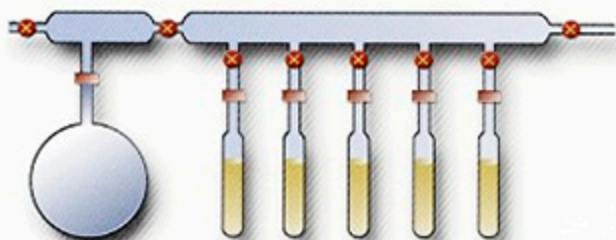
The filter ratio test is important to ensure that a polymer solution is free of aggregates which could lead to formation plugging. A 1.0 g/l solution is pumped through a 5 micron filter membrane with a differential pressure of 2 bar. The flowrate is measured and should remain nearly constant during the test for a product that is free of aggregates. Filter ratio (FR) is defined as the time for 300th ml minus the time for the 200th ml divided by the time for the 200th ml minus the time for the 100th ml and is calculated by:

$$FR = \frac{t_{300ml} - t_{200ml}}{t_{200ml} - t_{100ml}}$$



Thermal stability

Long-term thermal stability of polymer solutions at elevated temperatures is determined under anaerobic conditions in sealed glass ampoules. A special procedure allows vacuum degassing down to 10-20 parts per billion of oxygen. Temperatures up to 105°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.



Core flooding

Sandpacks and core floods on actual reservoir core material can be used to measure the following:

- RF
- RRF
- Oil recovery
- Injectivity
- Adsorption

Core floods are preferably contracted to external laboratories in cooperation with the oil company.



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