

Some Key Features to Consider When Studying Acrylamide-Based Polymers for Chemical Enhanced Oil Recovery

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Résumé — Quelques caractéristiques clés à considérer lors de l'étude des polymères à base d'acrylamide en vue de leur utilisation pour la récupération assistée chimique du pétrole — Parmi les méthodes chimiques de récupération assistée du pétrole, l'injection de polymère est une technique simple, connue de longue date et qui a démontré son efficacité. Le principe repose sur l'injection d'eau additionnée de polymère dans un réservoir pétrolier afin d'en améliorer le balayage et de diminuer le contraste de mobilité entre eau et hydrocarbures grâce à l'augmentation de viscosité. Cependant, la mise en œuvre d'une telle technique requiert un savoir-faire spécifique afin d'éviter toute dégradation potentielle du polymère, avec pour conséquence une chute de la viscosité de la solution injectée.

Le succès d'un projet d'injection de polymères commence avec la sélection du produit adapté aux caractéristiques du réservoir telles que la qualité d'eau, la température, la perméabilité ainsi que la présence éventuelle de contaminants comme le fer, l'hydrogène sulfuré et l'oxygène. Des études de stabilité menées à long terme en laboratoire permettent de s'assurer de la bonne tenue du produit tout au long de l'injection, tandis que des expériences d'injection sur carottes sont utiles pour vérifier l'injectivité et la propagation de la solution de polymère à travers le milieu poreux.

L'étape suivante concerne le design et la sélection des équipements qui vont servir à la dissolution et à l'injection de la solution dans le réservoir. Les installations de surface jouent un rôle primordial à ce stade, le but étant d'optimiser les étapes d'hydratation, de maturation et d'injection de la solution de polymère en évitant toute dégradation, soit chimique (introduction d'oxygène), soit mécanique (duses, pompes centrifuges).

La dégradation du polymère présent dans l'eau de production est un autre aspect important du projet d'injection. Plusieurs études ont montré qu'il n'y avait pas d'influence du polymère sur la séparation entre le brut et l'eau de production, le polymère étant uniquement soluble dans l'eau. Une dégradation du polymère résiduel préliminaire au passage des équipements de traitement d'eau peut être mise en œuvre afin d'abaisser la viscosité à 4 mPa.s et éviter toute difficulté dans le déroulement du processus.

Abstract — Some Key Features to Consider When Studying Acrylamide-Based Polymers for Chemical Enhanced Oil Recovery — Among Chemical Enhanced Oil Recovery (CEOR) methods, polymer flooding is a straightforward technique with a long commercial history and proven results. It consists in injecting polymer-augmented water into a subterranean formation in order to improve, thanks to the viscosity increase, the sweep efficiency in the reservoir and provides a mobility control between water and the hydrocarbons. However, implementing successfully a polymer flood in the field requires specific know-how to avoid polymer degradation and associated viscosity loss.

The first stage begins with the selection of the right polymer for the reservoir, depending on the water quality, temperature, permeability and presence of contaminants such as iron, hydrogen sulfide and oxygen. Several laboratory tests have to be performed to ensure the long term stability of the product as well as core flooding experiments to check parameters such as injectivity and propagation through the porous medium.

The next step is the design and selection of equipment for the dissolution and the injection of the polymer solution into the reservoir. Surface facilities are paramount for the quality of the injected solution: the goal is to allow a good hydration, maturation and transport of the solution while avoiding any type of degradation that can occur either chemically (oxygen ingress) or mechanically (choke, centrifugal pumps).

Another aspect that can be assessed is the degradation of the back-produced polymer. Several studies have shown that there is no influence of the polymer on the separation of crude and water; the polymer being water-soluble. However, when the viscosity of the produced water is above 4 mPa.s, a treatment may be operated before the water treatment process to avoid any difficulty in the surface facilities and an optimum efficiency.

INTRODUCTION

An increasing number of oil fields has become mature and has accordingly seen a decline of their production or is on the point of doing so. The recovery rate of these fields is currently about 15% to 35% on average of the oil in place. Hence, they still offer considerable production potential. The crude oil contained in the reservoirs is generally recovered in several steps.

Production first results from the natural energy of the fluids and the rock decompression. Following this depletion phase, the quantity of oil recovered at the surface represents on average some 5 to 15% of the initial reserve. It is therefore necessary, in a second step, to employ techniques designed to boost the recovery yield while maintaining the pressure of the field.

The most frequently used method consists in injecting water into the reservoir through dedicated injection wells. This is commonly referred to as secondary recovery. This second phase stops when the water content in the produced fluid is too high. In terms of additional recovery rate, the gain here is about 10-20%.

The next usable techniques are combined under the name of Enhanced Oil Recovery (EOR). Their aim is to recover between 10 and 35% of additional oil. The term EOR includes thermal techniques, non-thermal techniques such as electrical, miscible, steam or chemical techniques for enhanced recovery of the oil remaining in place (Willhite and Green, 1998).

Among the possibilities, Chemical Enhanced Oil Recovery (CEOR), involving at least the injection of water-soluble polymers in the form of a dilute solution is a straightforward technique with a long commercial history and proven results. It consists in injecting polymer dissolved in water into a subterranean formation in order to improve, thanks to the viscosity increase, the sweep efficiency in the reservoir and provide a mobility control between water and

the hydrocarbons. The injection of a viscous polymer solution can be carried out alone or in combination with other chemical compounds useful for recovering additional oil. Among these other chemical compounds, mention can be made of the use of a weak, strong or extra-strong, inorganic or organic base capable of saponifying the crude oils and forming surfactant species *in situ* for solubilizing the oil. By way of example, these include sodium carbonate, caustic soda, borate and metaborate compounds, silicates, metasilicates, amines, basic polymeric species. Another family of compounds commonly injected with polymers is based on surfactant compounds. The surfactants are mostly anionic and sometimes also zwitterionic, cationic and non-ionic. These compounds can be injected pure or along with a co-surfactant and/or a co-solvent to improve their compatibility and effectiveness in the reservoir.

In all these variations, the propagation of the chemicals is improved by the addition of water-soluble polymers over water injection alone, especially when it is implemented early in the life of a field (Morel *et al.*, 2010).

Synthetic water-soluble polymers and in particular acrylamide based polymers are the most common and advantageous for increasing the viscosity of aqueous solutions and are therefore widely used in EOR. Biopolymers can also be used for EOR but this paper will focus on synthetic polymers due to their industrial significance.

The main polyacrylamides used are anionic in nature. They have already been widely studied and used for EOR, in techniques called “Polymer”, “Surfactant-Polymer”, “Alkali Surfactant Polymer” (P, SP, ASP) techniques.

Many key aspects need to be considered for the design of a polymer flood such as reservoir characteristics (lithology, stratigraphy, fractures), distribution of remaining oil, well pattern and spacing, polymer degradation, rheology of polymer solution, compatibility with other chemicals, cost-effectiveness, etc. This paper does not intend to give a comprehensive overview of polymer flooding design but focuses on several

important aspects that need to be taken into account for a successful field implementation.

1 THE SELECTION OF THE POLYMER

1.1 Polymer Flooding: A Reminder

The value of adding polymer to a conventional waterflood can be explained by considering the mobility ratio which is defined by the following formula:

$$M = \frac{\lambda_o}{\lambda_w} = \frac{\mu_o / k_o}{\mu_w / k_w}$$

where λ , μ and k are the mobility, viscosity and effective permeability respectively and where the subscripts w and o refer to water and oil. Oil is left behind in a waterflood either because it is trapped by the capillary forces (residual oil) or because it is bypassed (Sorbie, 1991). The mobility ratio improvement associated with the use of polymers minimizes the bypassing effect. Another parameter is the viscoelasticity associated with the use of high Molecular weight (Mw) or associative polymers. Some studies (Wang *et al.*, 2000) tend to claim that the viscoelasticity may also contribute to recover additional entrapped oil compared to a conventional Newtonian fluid injection, but there is some controversy whether it applies to real reservoir conditions or not.

Polymer-augmented waterflooding can be divided in two classifications, as described by Willhite and Green (1998). Firstly, when the mobility ratio during a waterflood is unfavorable, continuous injection can increase the microscopic sweep efficiency in the reservoir. Secondly, even with a favorable mobility ratio, if the reservoir is heterogeneous, a polymer-augmented waterflooding can be implemented to reduce the water mobility in the high-permeability layers in order to recover the oil from the low-permeability layers.

A typical polymer flood project involves mixing and injecting polymer over several months for surfactant slugs and several years for polymer alone at concentrations ranging from 300 to 3 000 ppm, until 30% or more reservoir pore volumes have been affected.

Reservoirs that are good candidates can be recognized by poor volumetric efficiency (Willhite and Green, 1998) and selected if the conditions respect the polymer tolerance limits (temperature, salinity). Thanks to the new developments in chemistry, polymer flooding can be implemented in higher salinity, higher temperature and lower permeability reservoirs. At the laboratory scale, the boundaries that can be achieved with new polymers (Vermolen *et al.*, 2011; Kulawardana *et al.*, 2012) are given in Table 1. The success depends also on the viscosity of the oil in place, as described by the permeability factor in the mobility ratio equation.

TABLE 1
Current limits of some relevant parameters for polymer flooding implementation

Reservoir temperature	< 130°C
Reservoir permeability	> 40 mD
Salinity	< 250 000 TDS (hardness dependent)
Oil viscosity	2 mPa.s < μ < 10 000 mPa.s

1.2 Surfactant-Polymer (SP) and Alkali-Surfactant Polymer Flooding (ASP)

It is recognized that capillary forces cause large quantities of oil to be left behind in well-swept zones of waterflooded oil reservoirs (Lake, 1989). Injecting surfactants (surface active agents) can reduce the interfacial tension between oil and water and therefore release trapped oil. Mobility control is assured by the injection of a polymer slug. However, it is often necessary to inject costly dosages of surfactants to balance the adsorption on rocks (0.5 to 1%). This effect can be offset by adding alkalis to the solution. Alkalies, such as sodium carbonate, will adsorb on rocks (reducing surfactant adsorption), increase the pH and generates *in situ* surfactants. However, such process will require expensive water treatment facilities, and combined with the surfactant, can generate difficulties to break the produced emulsion. SP and ASP must therefore be carefully designed and monitored.

New chemicals are currently being developed and studied to decrease the apparent viscosity of oil either by encapsulation or by thinning the micro-emulsion containing the oil. These new strategies have not been implemented in the field yet but may broaden the field of application of CEOR technologies in the forthcoming decades.

1.3 Choosing the Right Polymer

1.3.1 Properties of Polyacrylamide Polymers

The majority of the polymers used in polymer flooding applications is anionic acrylamide-based polymers and derived from:

- copolymerization of acrylamide and sodium acrylate (or/ and sodium Acrylamido-Tertio-Butyl Sulfonate (ATBS));
- cohydrolysis or post-hydrolysis of a polyacrylamide;
- copolymerization or ter-polymerization of acrylamide with other ionic or non-ionic functional monomers. Functional monomers improve polymer thermal or salt tolerances (for example, incorporation of N-Vinyl Pyrrolidone (NVP) for improved thermal resistance).

Depending on the manufacturing process, the repartition of the anionic charges along the backbone chain of the polymer is changed and induces different physical properties when

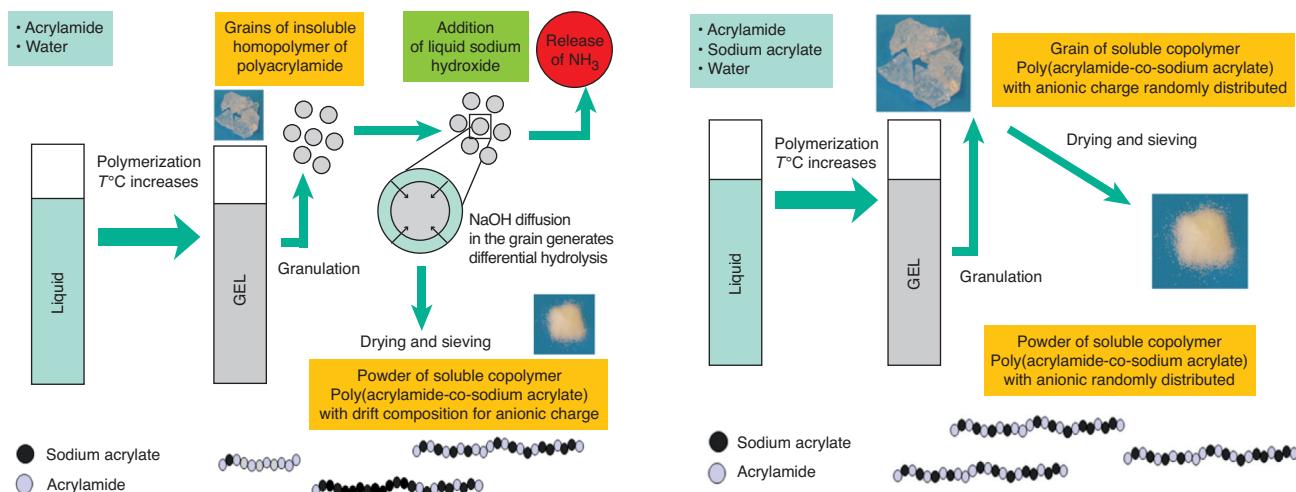


Figure 1

Scheme of the post-hydrolysis manufacturing process.

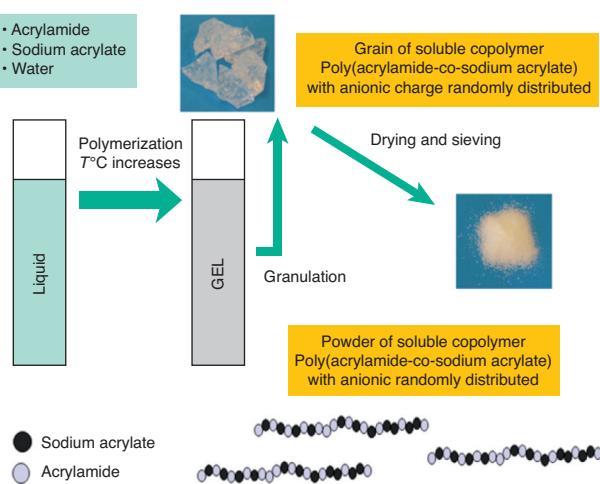


Figure 2

Scheme of the copolymerization process.

TABLE 2
Range of products for several field conditions

Form of product	Type of polymer	Monomer	Example of product	Remarks
Powder	Copolymer	Acrylamide – Sodium acrylate	Flopaam 3630S	$T < 80^\circ\text{C}$ medium hardness
	Homopolymer post hydrolysed	Acrylamide	Flopaam 6030S	$T < 75^\circ\text{C}$ low hardness
	Copolymer	Acrylamide – ATBS	Flopaam AN125SH	$T < 95^\circ\text{C}$ all salinities
	Terpolymers	Acrylamide – Sodium Acrylate – ATBS	Flopaam 5205SH Flopaam 5115SH	$T < 90^\circ\text{C}$ all salinities
	Associative polymers	Acrylamide – Sodium	Superpusher C319	High resistance factor in reservoir
		Acrylate – Hydrophobic monomer		Medium hardness
	Terpolymers	Acrylamide – ATBS-NVP	Flopaam SAV225	$T < 120^\circ\text{C}$ all salinities
Liquid O/W Emulsion	Copolymers	Acrylamide – Sodium acrylate	Flopaam EM533	$T < 80^\circ\text{C}$ medium hardness

dissolved in water. Posthydrolysed polyacrylamides are composed of a wide range of anionic chains (Fig. 1). Some are highly charged, others are less charged. The copolymerization of acrylamide and sodium acrylate leads to polymer with a more uniform repartition of the anionic charges (Fig. 2). These properties are very important for the behaviour of the polymers in aqueous solution especially in the presence of calcium and magnesium.

Anionic polyacrylamides are also characterized by their Mw as well as the molecular weight distribution (polydispersity index: PDI). The range of Mw is between 4 and 30 million g/mol and is determined using intrinsic viscosity measurement. PDI cannot be determined since neither standards with low PDI nor GPC (Gel Permeation Chromatography) techniques exist today for such high Mw. However, like for the anionicity, a wide range of molecular weights is present in one product. Moreover, copolymers are more under control than post hydrolysed structures. Table 2

gives some examples of manufacturing products that can be used in oilfields. Figures 3, 4 and 5 show some common polymer molecules.

1.3.2 Properties of Polyacrylamide Polymers in Water Phase

The thickening capability of anionic polyacrylamides is linked to the level of entanglement of the high molecular weight macromolecules and also to the electrostatic repulsion between polymer coils and between segments in the same coil (Lake, 1989). When polyelectrolytes are dissolved in water containing electrolytes (salts), a reduction in viscosity is observed (Borthakur *et al.*, 1995). This effect is attributed to the shielding effect of the charges leading to a reduction in electrostatic repulsion and thus to a less significant expansion of the polymer coils in the solution. The consequence is a relatively lower hydrodynamic volume and therefore a lower viscosity (Ellwanger *et al.*, 1980). Besides the salt dependency,

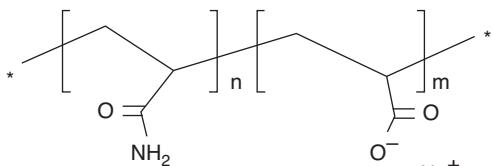


Figure 3

Copolymer of acrylamide and sodium acrylate (Flopaam 30630S type).

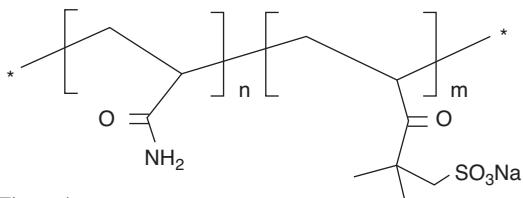


Figure 4

Copolymer of acrylamide and ATBS (Flopaam AN125 type).

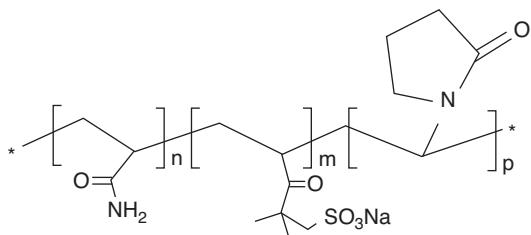


Figure 5

Terpolymer of acrylamide, ATBS and NVP (Flopaam SAV225 type).

other factors influencing the viscosity of Partially Hydrolyzed Polyacrylamide (PHP) solutions are the degree of hydrolysis, solution temperature, molecular weight, tri-dimensional structure and solvent quality (Sukpisan *et al.*, 1998).

At iso-molecular weight and iso-concentration, a polyelectrolyte is susceptible to have different conformations depending on its chemistry. If compatible with the brine, the molecule will uncoil, allowing inter-chain interactions. If not compatible with the brine, coiling will occur, resulting in intra-molecular associations. Other strategies have been developed to enable intermolecular associations independently from the molecular weight of the polymer. The most advanced technology consists in incorporating hydrophobic moieties within a hydrophilic molecule. A concise overview of the technology and the chemistry for these so-called associative polymers is given by Wever *et al.* (2011).

Polyacrylamide fluids behave as non-Newtonian fluids; it means that the viscosity depends on the shear rate applied (Fig. 6). They show a pseudo plastic (or shear thinning) behavior: viscosity decreases when shear stress increases. The viscosity is dependent upon the concentration and the

molecular weight of the polymer (Fig. 7). Moreover, rheology in porous media for synthetic polymers is quite different than in a viscometer but this topic is beyond the scope of this paper.

In the field, polyacrylamides have to be solubilized in injection brine that contains dissolved salts. Total dissolution is achieved when no insoluble or swollen particles remain in filtration test. When high molecular weight ($M_w > 1$ million) or even very high molecular weight (M_w around 18 million) polymers are used, injectivity issues can be observed. Polymers are chemicals that may contain partially soluble species (branched or cross-linked chains) in very few

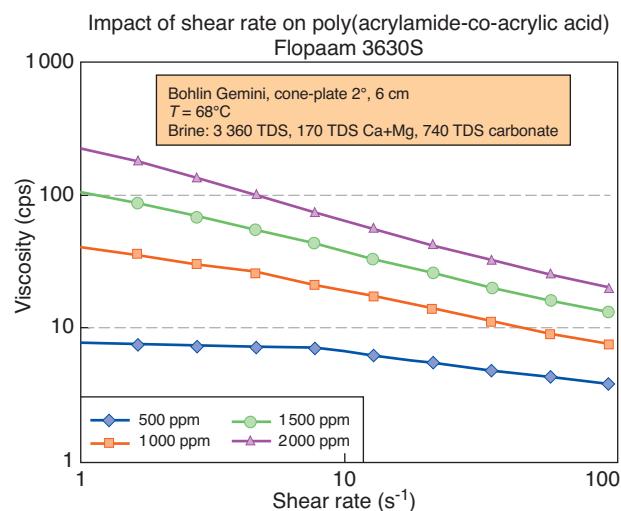


Figure 6

Viscosity as a function of shear rate of FP3630S at different concentrations at 68°C .

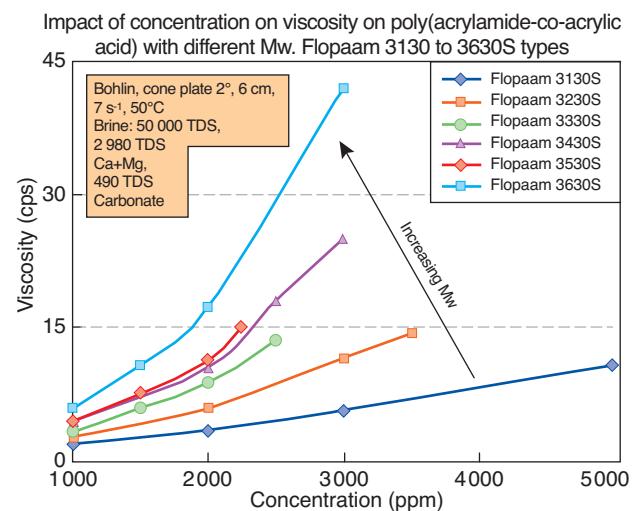


Figure 7

Viscosity as a function of concentration of different Mw polymers.

amounts due to the manufacturing process. When solubilized in water, these species give micro gels that are injected with the polymer in the formation. These micro gels can either propagate or damage the formation since they can plug pores of the rock. Micro gels are detrimental to injectivity (increase in injection pressure) and can block targeted areas. The areas that still contain oil are no more accessible for further EOR techniques. For a polymer flood, it is therefore of importance to avoid accumulation of micro gels in the formation or make sure the gels are small and soft enough to propagate deep in the formation.

Dissolution and viscosity depend on the chemistry of the polymer (manufacturing process, anionic content, type of anionic monomer). In Figures 8 and 9, it can be seen that post-hydrolyzed products FP 6030S is much less tolerant to calcium than polymer obtained by copolymerization process, FP 3630S. Moreover, regular HPAM (Partially Hydrolyzed Polyacrylamide) polymers are known to suffer from modification with time if exposed to high temperature, which can lead to incompatibility of the polymers with the brine if divalent ions are present (Zaitoun and Potie, 1983). It is necessary to change the chemistry to improve their stability. The polymers containing a sulfonated monomer ATBS are the best candidates for calcium tolerance, with an increased resistance for polymers with high ATBS content.

Polyacrylamides are chemicals that can experience degradation. During the dissolution and injection processes three main types of degradations can occur: chemical, thermal and mechanical degradations, briefly described below.

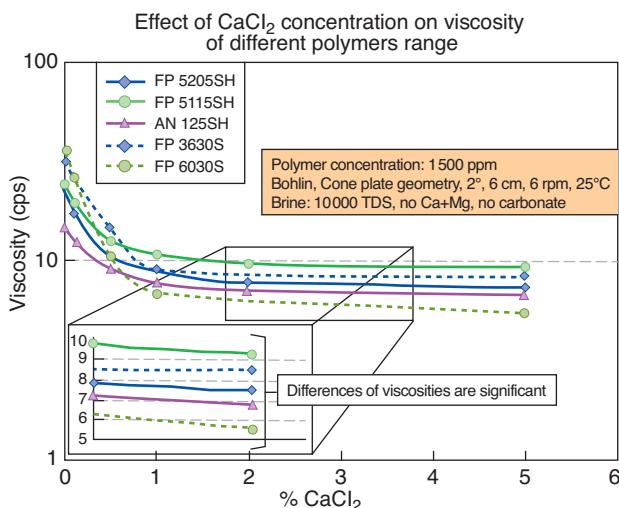


Figure 8

Calcium tolerance of different products, comprising a standard copolymer (FP 3630S), a sulfonated copolymer (AN 125SH), terpolymers (FP 5205SH, FP 5115SH) and a post-hydrolyzed polymer (FP 6030S).

Residual viscosity at the plateau as compared to initial viscosity

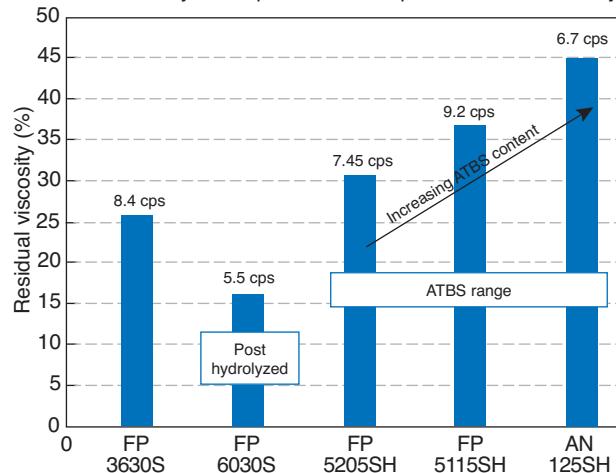


Figure 9

Comparison of the viscosity at the plateau (Fig. 5) for different polymers in the calcium tolerance test.

1.4 The Main Types of Degradation

Few data exist on the quality of the produced fluid when using CEOR techniques. However, from internal reports and papers published by the Daqing and Shengli fields (China), a low viscosity of produced water is frequently reported (Xie and Liu, 2007). Typically, polymer concentration has been reduced by more than a half, anionicity has increased, and molecular weight is five to ten times lower compared to what is injected. The arising question is whether this degradation occurs between surface and down hole or within the reservoir. In any case, preventing any of these degradations, would significantly improve the control over the mobility ratio and consequently the amount of incremental oil recovered using polyelectrolytes.

1.4.1 Chemical Degradation

Chemical degradation is related to the formation of free radicals that can react with the polymer backbone resulting in a drop of molecular weight (Grollman and Schnabel, 1982; Wellington, 1983) and a viscosity drop due to a reduction of hydrodynamic volume. Red/Ox systems are often involved in the generation of free radicals (Fenton, 1894). The presence of chemicals or impurities in the water, as well as oxygen, participates in the formation of such radicals. For instance, Iron II and/or H₂S in contact with oxygen contribute to the degradation of the polymers. Some commercial grade polymers include systematically a minimal amount of stabilizers against the unavoidable occurrence of chemical degradation. Fine-tuning of the type of stabilizers and an increase of their respective dosages is also possible when chemical degradation is expected to be more significant.

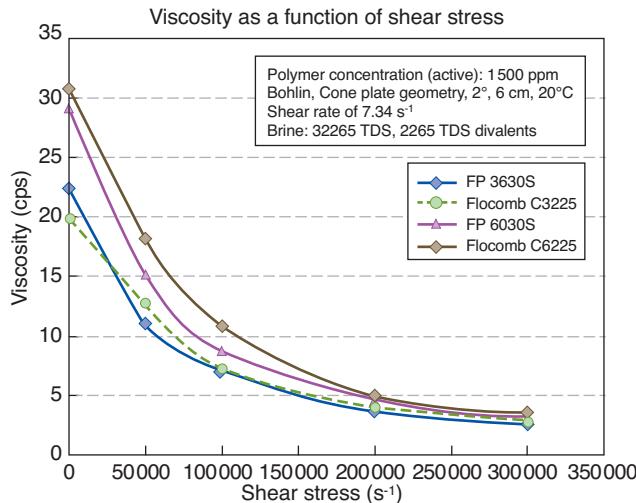


Figure 10

Impact of mechanical degradation on a copolymer (FP 3630S), a post-hydrolyzed polymer (FP 6030S) and recently developed salt tolerant polymers (Flocomb C3525 and Flocomb C6225).

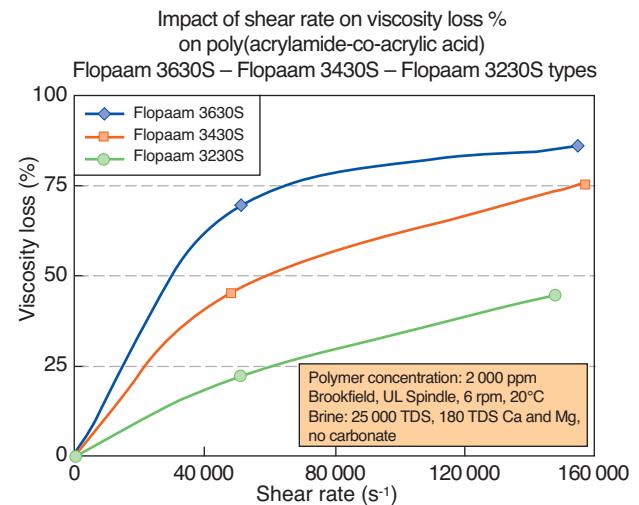


Figure 11

Impact of shear rate on three copolymers with decreasing molecular weights: FP 3630S (high molecular weight), FP 3430S (medium molecular weight) and FP 3230S (low molecular weight).

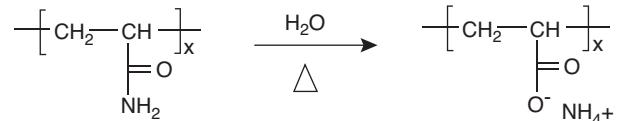


Figure 12

Hydrolysis of acrylamide moieties along the backbone chain.

due to ionic bridges that can ultimately result in precipitation (Moradi-Araghi and Doe, 1987). Figure 13 shows that post-hydrolyzed polymer (FP 6030S) precipitates faster than copolymer (FP 3630S) in presence of calcium at 90°C because of their heterogeneous charge distribution as explained earlier. The incorporation of sulphonated monomer (ATBS) improves the tolerance to calcium (AN 125SH) at high temperature but in general at the expense of the molecular weight and with an increased polymer cost. An optimal composition exists for each salinity and hardness and its determination requires laboratory studies.

Taking into account the aforementioned parameters, it must be understood that it is essential to fine-tune the structure, the composition and the molecular weight to optimize the resistance in a given brine for a given reservoir. Therefore, to select the right polymer, it is necessary to know the reservoir temperature and to analyze the water composition (salinity, divalent cations, dissolved oxygen, iron and hydrogen sulfide). Stability tests are carried out over months to study the stability of the chosen product *versus* time with the appropriate dosage of contaminants defined after brine analysis.

1.4.2 Mechanical Degradation

Mechanical degradation occurs in pipes, through chokes, valves or pumps above a certain velocity or pressure drop as well as down hole through perforations.

The choice of the polymer is very important: the higher the molecular weight, the higher the sensitivity to mechanical degradation. Shearing a high molecular weight polymer can improve the injectivity of the solution into the reservoir with a minor viscosity loss. A drawback to this method can be the loss of the viscoelastic effect which is mainly given by the highest molecular weight fraction of the polymer (Wang *et al.*, 2001). Figures 10 and 11 show the impact of shear degradation on polymers with different molecular weights (Fig. 11) or according to two manufacturing processes (copolymerization for FP 3630S, post-hydrolysis for FP 6030S) (Fig. 10). The experiment was carried out with a pipe of 0.875 mm in diameter and a length of 200 mm. As mentioned before, the higher the molecular weight, the higher the irreversible viscosity loss.

1.4.3 Thermal Degradation

Thermal degradation depends on the type of polymer and the reservoir temperature. For regular HPAM polymers, an increase in temperature will lead to an increase of the hydrolysis of acrylamide moieties (Fig. 12) generating a higher charge density of anionic functionalities along the polymer backbone.

If the brine contains significant amounts of divalent cations such as calcium and magnesium, a viscosity drop is observed

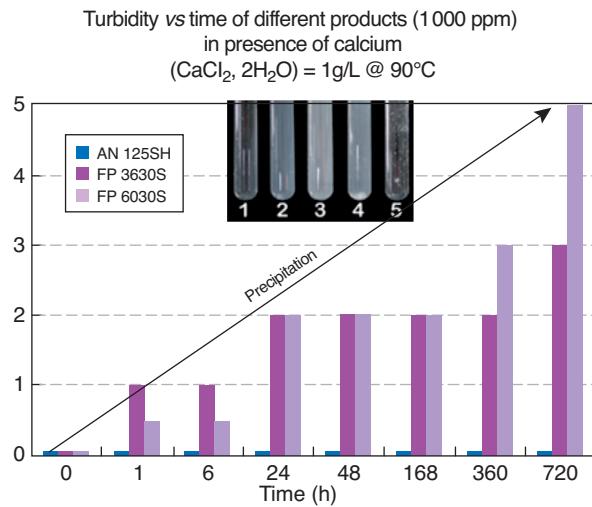


Figure 13

Behavior in salted brines of three polymers: FP 3630S (standard copolymer), AN 125SH (copolymer with ATBS), FP 6030S (post-hydrolyzed product). The numbers from 1 to 5 on the ordinates correspond to the precipitation criterion.

When such contaminants are present, and even in low amounts, it is compulsory to carry these experiments and the associated viscosity measurements in controlled anaerobic conditions to estimate the level of chemical degradation. The use of a glove box with nitrogen blanketing is thus highly recommended.

1.5 Selecting the Right Chemistry

1.5.1 Selecting the Optimized Monomeric Composition

Standard copolymers of acrylamide and sodium acrylate are stable up to 75°C. Above this temperature, sulphonated monomers can be incorporated to resist higher temperatures up to 95°C. Incorporating sodium ATBS to the chain can also provide tolerance to brines containing divalent ions and prevent the polymer from hydrolysis at higher temperatures (Hsieh *et al.*, 1992). Even though, ATBS has its own limitations in temperature and can experience hydrolysis (Parker and Lezzi, 1993) (Fig. 14).

Up to 120°C, it is necessary to change the chemistry by adding NVP monomers. NVP brings better neighboring protection against hydrolysis of acrylamide (Fernandez, 2005; Doe *et al.*, 1987), but because of its low reactivity in polymerization, high molecular weight polymers are harder to obtain and a further over dosage is often necessary to reach the targeted viscosity (Gaillard *et al.*, 2010), with an increase in final EOR cost. Figure 15 shows stability of NVP based polymer (Superpusher SAV series) over 240 days at 105 and 120°C. It can be seen that sulphonated polymer AN125

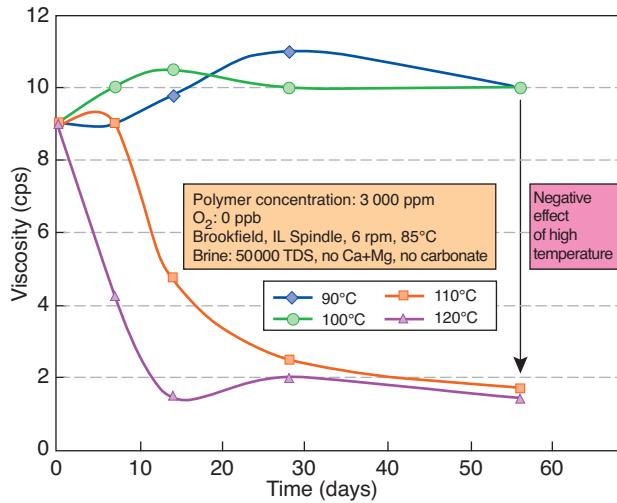


Figure 14

Stability of ATBS-based products as a function of temperature. Hydrolysis occurs at 100°C.

Thermal degradation at 105°C & 120°C of poly(acrylamide-co-ATBS-co-NVP) vs poly(acrylamide-co-ATBS) in middle east brine Superpusher SAV 301, 505, 522 & AN 125 types

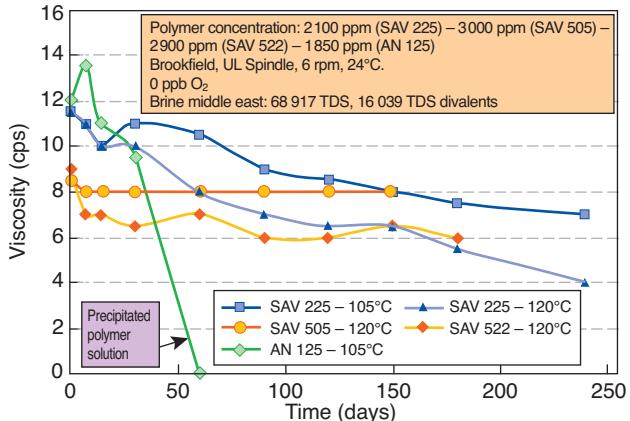


Figure 15

Stability of NVP based polymers at 105 and 120°C in high salinity brine.

precipitates out after 30 days in such conditions and that NVP based polymer, depending on the range, still keep viscosity at high level after more than 180 days at 120°C even in hard brines with 200 000 TDS (Total Dissolved Solids) (Vermolen *et al.*, 2011). The quest for synthetic polymers with both a high viscosity and an improved stability over 110°C is continuing. New monomers are developed and incorporated in polyelectrolytes to push further the application limits of CEOR (patent pending).

Eventually, the ranges of stability detailed above depend on the hardness of the brine and the presence of contaminants;

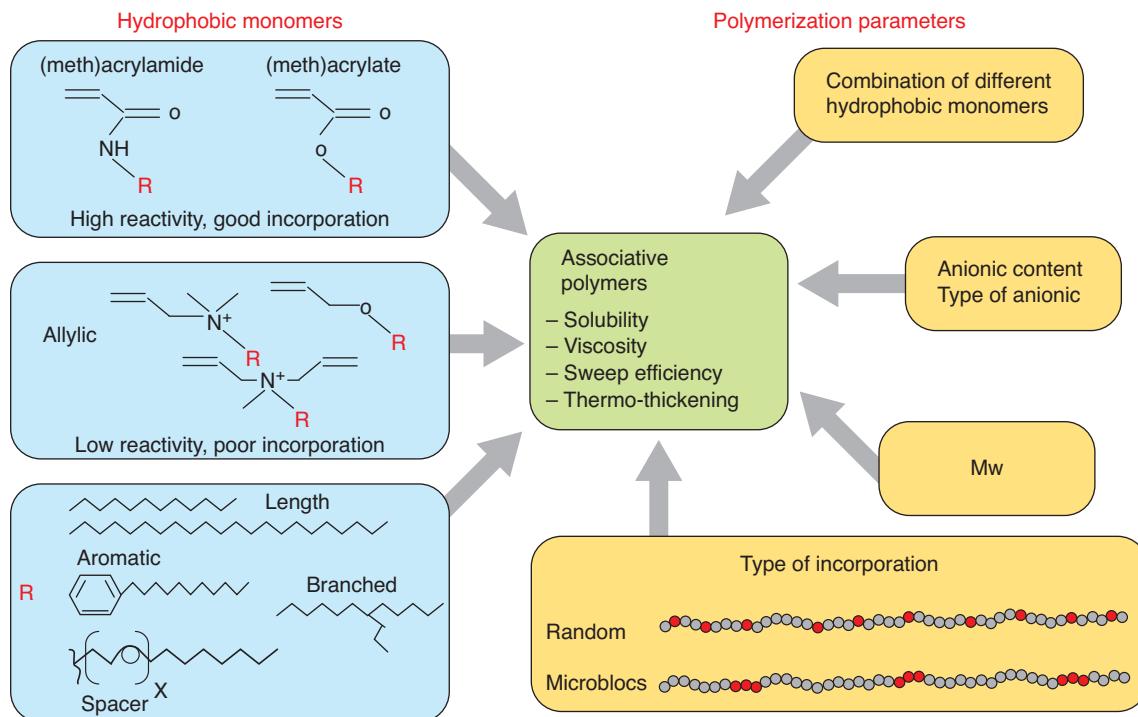


Figure 16

Parameters influencing the final properties of an associative polymer.

both can impair the final viscosity of the solution but can be counter-balanced using protective additives and/or by changing the structure.

1.5.2 Selection of the Right Polymer Structure

Recently, another range of commercial polymers has been developed to obtain very high resistance factors in the reservoir: these are called associative polymers (*Fig. 16*). These polymers contain both hydrophobic and hydrophilic moieties. The hydrophobic parts can associate in water and provide very high viscosities and resistance factors but with a good propagation in cores as shown by Seright *et al.* (2011). Associative polymers can sometimes also be used in conformance jobs (Wassmuth *et al.*, 2012), depending on the amount of hydrophobic moieties in the product. The main advantage is the reversibility of the process. Association can be disrupted either by increasing the shear rate or by the addition of sufficient amount of surfactant. A small amount of surfactant will stabilize the associations whereas a greater amount will encapsulate each hydrophobic moiety and disrupt the associations. Playing on the respective concentration of each chemical can help to select the desired effect. Another area of development is the synthesis of macromolecules with a star or comb structure to limit coiling of the chains.

2 IMPROVING THE STABILITY OF THE POLYMER SOLUTION

To reduce or avoid any Red/Ox degradation, it is possible to either reduce the concentration of contaminants by treating the water or use specific chemicals that are injected with the polymer in solution.

Oxygen

A concentration of oxygen below 5 ppb allows a good stability of the polyacrylamide solution up to 120°C for more than 200 days (Seright and Campbell, 2009). If the oxygen content cannot be maintained at a low level, adding oxygen scavenger such as dithionite and sulfite (Levitt and Pope, 2008; Miron, 1981) to the brine can help in decreasing free oxygen in water. However, re-exposure to any trace of oxygen in presence of residual oxygen scavenger will degrade the polymers. Indeed, the reaction between the oxygen and its scavenger will lead itself to the formation of free radicals harmful to the product as depicted in Figure 17. It is therefore compulsory to keep under control the amount of oxygen and oxygen scavenger present in the brine.

Iron

To limit the effect of degradation of the polymer due to iron, several complexing agents have been studied such as EDTA

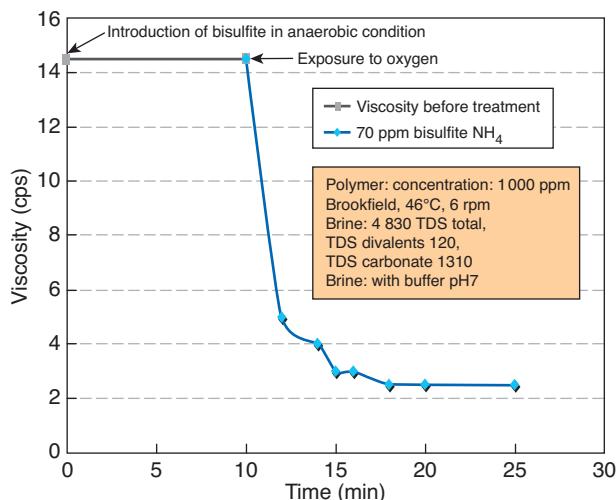


Figure 17

Influence of oxygen scavenger on the viscosity of polymer FP 3630S solution when air is introduced in the system. At time 0 the system is stirred under nitrogen blanketing. At time = 10 minutes the solution is exposed to air atmosphere.

(ethylene diamine tetra-acetic acid). However, using a chelating agent to complex iron can lead to an increase of the degradation of the polymer (Kheramand *et al.*, 1990; Xie and Liu, 2007). Another solution is to partially precipitate the iron by increasing the pH of the solution with sodium carbonate (Levitt and Pope, 2008). Figure 18 depicts the percentage of viscosity loss with different amounts of iron and oxygen added to the solution. The percentage of loss can reach 50% with only 1 ppm of Iron and 300 ppb of oxygen.

Protective additives such as radical scavenger, chelating agents, oxygen scavengers and sacrificial agents can be used to limit chemical degradation of the polymers. Such packages have been implemented in the field to provide significant protection to the polymer. Unfortunately, they can be sometimes hazardous; when using ITW for example (isopropanol thiourea water) (Wellington, 1983). Recent alternatives such as the Flopaam Polymer Protective Package (F3P) contain both polymer and protective additives incorporated at the manufacturing stage. They are fine-tuned according to the amount of contaminants present in the dissolution brine. (Gaillard *et al.*, 2010). The result is a single product that can be implemented as easily as standard polymers in powder or emulsion forms with no changes in surface facilities and a relatively small increase in cost (up to 15% depending on the amount of protective additives added).

From Figure 19, one can notice that the residual viscosity is improved if the powder includes protective agents (F3P), with concentration ranging from 7 to 12%. These results have been obtained with an iron concentration of 5 ppm and 500 ppb of oxygen.

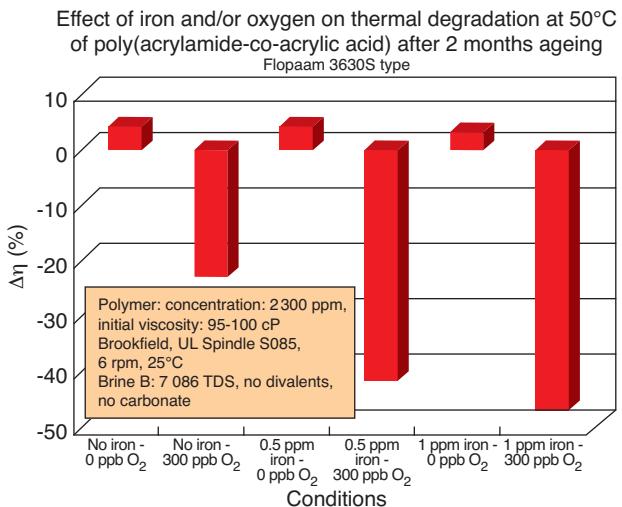


Figure 18

Percentage of viscosity loss of polymer solution with different dosages of iron and oxygen.

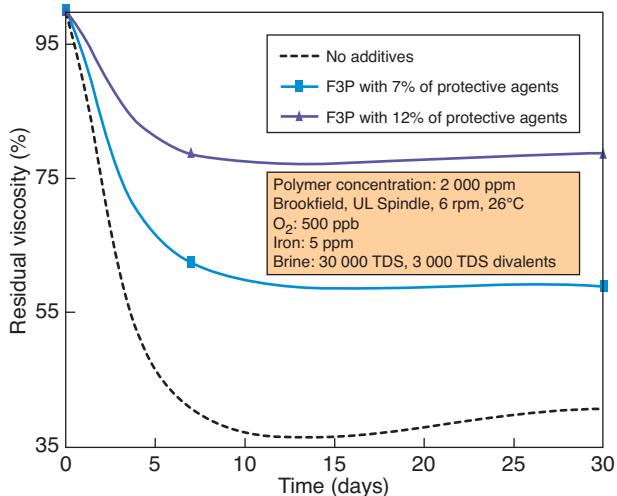


Figure 19

Effect of protective additives on polymer solution stability at 85°C in presence of ferrous iron.

As a conclusion to this part, the success of a polymer flood depends on the selection of the polymer chemistry, molecular weight and structure, the water quality and the protection strategy to ensure an optimized stability during the propagation in the reservoir. In addition, the surface facilities are of paramount importance in order to limit mechanical degradations and ensure the targeted water quality. The quality of the alloys used in surface equipment in contact with the injected fluids will influence the level of soluble iron (corrosion) that can impair the final viscosity of the polymer

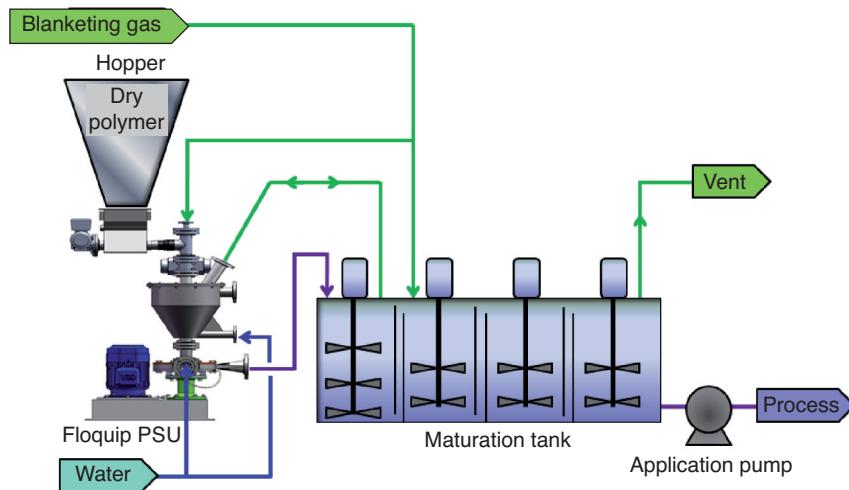


Figure 20

Description of powder polymer dissolution facilities.

solution. The choice of pumps and chokes as well as the dissolution facilities should follow specific guidelines to fulfill polymer flood requirements. For instance, nitrogen blanketed dissolution equipment can prevent oxygen ingress and therefore minimize polymer degradation. The next section presents optimizations of surface facilities to ensure an optimized polymer preparation and injection.

3 OPTIMIZATION OF SURFACE FACILITIES

3.1 Facilities for Dissolution and Injection

Onshore, the polymer dissolution units as well as the maturation tanks and the pumps can be placed into skids. The whole equipment is adapted to the location of the field including its accessibility and local weather conditions. As explained before, it is best recommended to blanket the main equipment with nitrogen to avoid any oxygen ingress and further degradation of the solution viscosity.

Figure 20 shows an example of dissolution facilities. The polymer in powder form is stored in a hopper and distributed *via* a dosing screw into the nitrogen blanketed Floquip PSU where the hydration takes place. Then, the solution goes into maturation tanks where it will achieve its full dissolution. The mother solution is finally pumped and diluted to the target concentration.

Such recently developed and patented equipment is more and more used to dissolve properly the powder in a short time with good efficiency. The Floquip PSU (Polymer Slicing Unit) allows a quick and good hydration of the

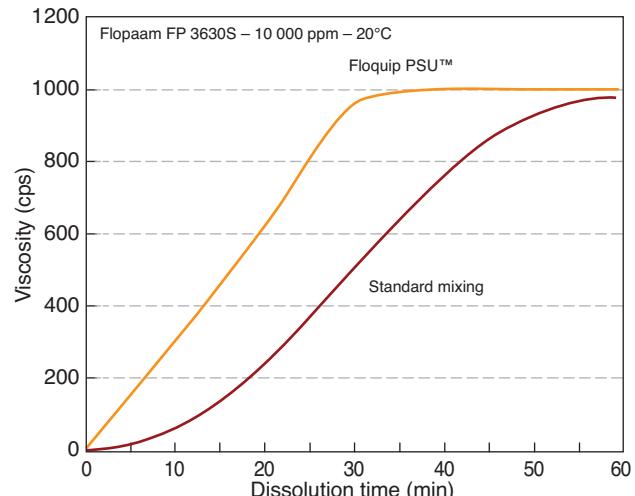


Figure 21

Dissolution time of powder with SNF PSU and a conventional equipment.

polymer (Fig. 21), avoiding fish-eyes, gels and the necessity of filtration. The maturation process occurs in agitated nitrogen blanketed ageing tanks which deliver a concentrated polymer solution which is then diluted to the targeted value before its injection in the reservoir.

When using polymer in emulsion form, in-line static mixers are required to invert the oil-in-water emulsion into a water-in-oil emulsion which is injected in the reservoir. The footprint is much less than in the case of polymer in powder form.

3.2 Minimizing Polymer Degradation

Among the three main types of degradation, chemical and mechanical degradations of the polymer are susceptible to occur at surface facilities.

Chemical degradation can be limited using nitrogen blanketed equipment to avoid any oxygen ingress and monitored by controlling the amount of chemical used in the water for different purposes such as oxygen scavenging. It is also possible to treat the injection water to remove as much contaminants as possible or to add protective additives to the polymer.

Mechanical degradation is an additional issue at this step of the process. Shearing can occur at dissolution and surface equipment such as pumps or in the injection lines if restrictions or chokes are present. For low pressure processes, it is recommended to use progressive cavity or rotary lobes pumps. When dealing with high pressure, plunger or diaphragm pumps (triplex or quintuplex) are preferred. The maximum velocity of the fluid is also paramount and must remain below a critical value, wherever the fluid is moved such as in the agitation process with the impellers or in pipes (short distance). For example, in a two-inch pipe, it must be kept below 7 m.s⁻¹.

Shearing may then occur in the injection line and down hole. Chokes must be removed, by-passed or fully opened to avoid any uncontrolled shearing that would be detrimental to the final viscosity or replaced by non-shearing systems. The type of well completion is also paramount and influences the amount of degradation; for example, the density and number of perforations must be taken into account and correlated to the flow rate of the fluid to assess the potential shearing occurring at this step.

3.3 Key Points for Onshore and Offshore Implementations

Designing an onshore polymer flooding project is often easier than offshore; in the latter case, it is compulsory to optimize the equipment footprint to fit the space available and load limits of the FPSO (Floating Production Storage Offloading) or a platform. Furthermore, logistics are important when transporting large volumes of products either in powder or liquid form. Polymer in emulsion form is easier to handle offshore when the local weather conditions are particularly unfavorable (North Sea for instance). Since it does not require specific dissolution and maturation units, the inversion is made on the fly and the solution can be readily injected into the reservoir. When the conditions are more favorable, polymer in powder form is cheaper to implement. Indeed, the active matter content of the emulsion is 50% to 70% lower than the powder form and suffers from an incremental cost per unit, which means that larger quantities of commercial products are handled to reach the same target viscosity with a higher cost associated.

3.4 Monitoring the Polymer Injection Process

The efficiency of the dissolution and injection processes can be checked with in-line viscometer and periodic sampling at

the well head to ensure that the viscosity of the injected solution is the targeted one. This sampling process has to be carried out carefully to make sure that the measured viscosity corresponds to the reality. Indeed, an inaccurate sampling method can induce shearing or oxygen ingress and trigger chemical reactions between this oxidizer and potential reducers such as iron II and H₂S. It will lead to the formation of free radicals and degrade the polymers, with an immediate viscosity drop. This issue is also valid in the laboratory, where viscosity measurements in presence of contaminants

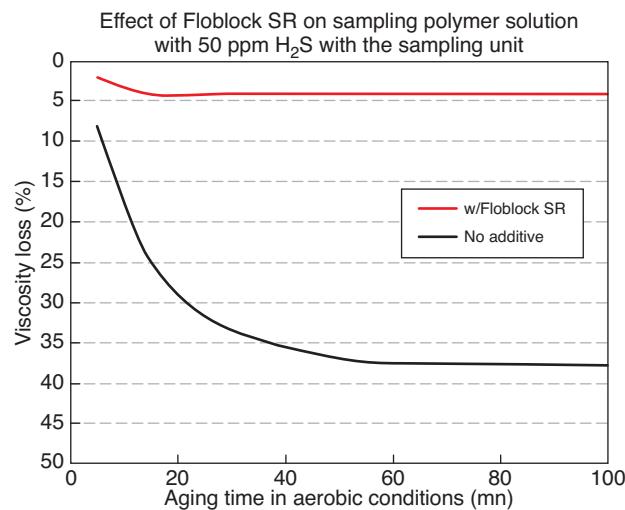


Figure 22

Effect of Floblock SR on the final measured viscosity of a polymer solution.

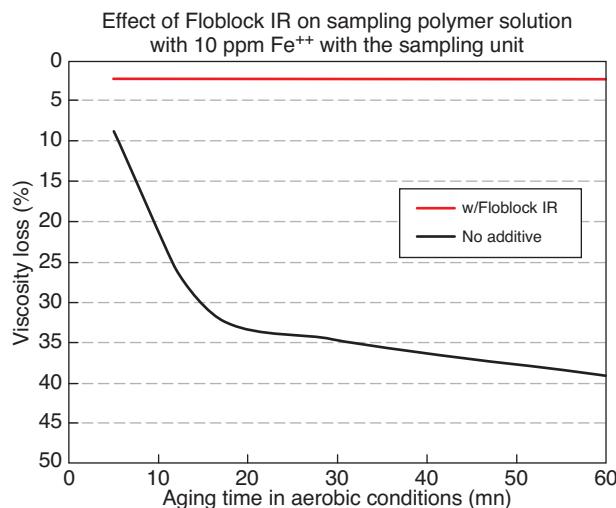


Figure 23

Effect of Floblock IR on the final measured viscosity of a polymer solution.

must be performed under inert atmosphere, in nitrogen blanketed glove boxes for instance.

For field application, a patented sampling tool is available, (Floblock) which contains protective additives that will prevent and quench free radicals that may form from the presence of contaminants, therefore avoiding any viscosity drop at measurement. Figures 22 and 23 show the results of measurements carried out with and without a Floblock treatment, respectively Sulfur and Iron Resistant (SR, IR) formulations. The additives prevent polymer from degradation and viscosity drop, as depicted by the red curves.

4 THE INFLUENCE OF BACK-PRODUCED POLYMER ON THE SURFACE EQUIPMENT

At the pilot stage (with only a small percentage of injecting wells under polymer flooding), there is generally 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. Both aspects are discussed in the following paragraphs.

4.1 Impact on the Separation of Oil and Water

Influence on the separation process

At the production side, depending on the design of the production facilities and the type of injected fluid (presence of surfactant or alkali or both) an emulsion is produced. De-emulsifiers or “breakers” are needed to break this emulsion. The presence of polymer can interact with the breaker and it may result in altered separation. Skilled service companies generally do the selection of the most appropriate and compatible breaker through bottle tests.

Since polyacrylamide polymers are water soluble, they are considered absent from the oil phase.

Presence of suspended solids

Anionic polyacrylamides are efficient flocculating agents of mineral suspended solids. Thus, if the TSS (Total Suspended Solids) is high in the produced fluid, some agglomerates should appear in the water phase in presence of polymer. These precipitates can deposit on the surface of specific equipment such as heater treater used for the separation of oil and water, which contributes to the creation of hot points, which in turn can lead to accelerated corrosion issues. These deposits have to be removed on a regular basis.

4.2 Treatment of Produced Water

Once the main part of the oil has been recovered from the produced fluid, a low amount of oil and TSS still remain in the produced water. Devices for produced water treatment are usually sized to operate with water viscosities below 4 mPa.s. Polymer breakthrough at the production side will contribute to an increase of viscosity and will reduce the efficiency of the treating devices to separate the oil and suspended materials wetted by it. With produced water viscosities of 10 mPa.s for example, the residence time required is five times longer and devices required are five times larger.

Different methods can be applied to decrease the viscosity of the fluid containing polymer in order to improve water treatment efficiency. The principle is to decrease drastically its Mw and thus, the associated viscosity of the fluid by means of mechanical and/or chemical degradations.

4.3 Methods to Degrade the Back-Produced Polymer

4.3.1 Mechanical Degradation of the Polymer

Mechanical degradation can be performed to decrease the Mw of the polymer and thus decrease the viscosity of the solution. A shearing pump or a choke valve can be used to achieve the degradation and decrease the viscosity of the polymer solution (Fig. 24, 25).

4.3.2 Chemical Degradation of the Polymer

Polyacrylamides are chemicals that can experience chemical degradation in presence of oxidizers. Oxidizers generate

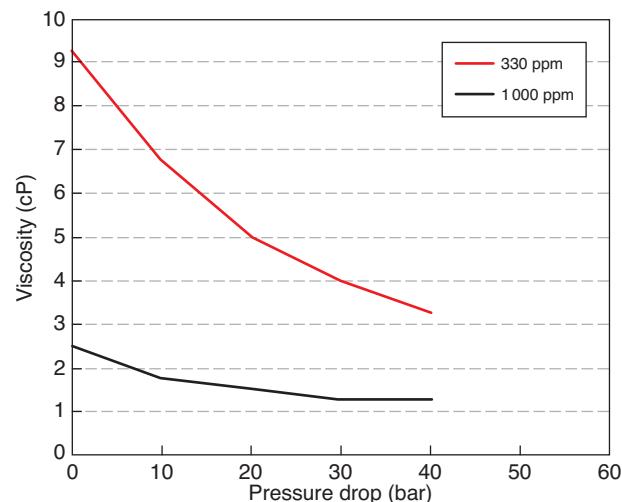


Figure 24

Shear degradation of $M_w = 10$ million g/mol through 1.75 mm perforation.

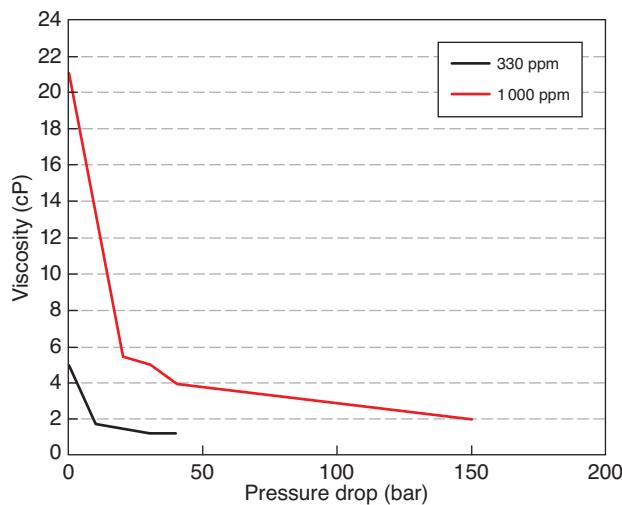


Figure 25

Shear degradation of $M_w = 20$ million g/mol through 0.875 mm perforation.

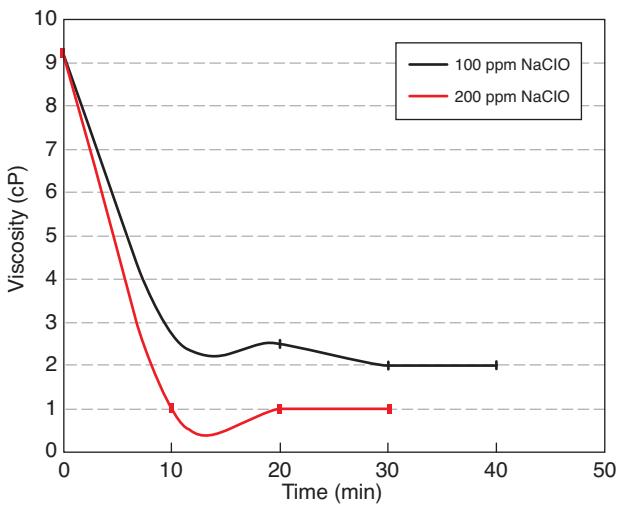


Figure 26

Chemical degradation of 1000 ppm polymer with $M_w = 10$ million g/mol at 46°C using NaClO.

radicals that react with the backbone chain of the polymers, resulting in a decrease of the M_w and a viscosity drop. Preferred oxidizer is sodium hypochlorite (NaClO) (Fig. 26).

Figure 26 shows that 200 ppm of NaClO are enough to reach a viscosity of 1 mPa.s in less than 10 minutes. However, if the treated water needs to be re-used to dissolve polymer for a further injection, any remaining excess of oxidizer has to be neutralized with a reducing agent since any excess of oxidizer would degrade the new dissolved polymer (patented).

For the mechanical and the chemical degradation treatments, polymer is degraded but is still present in the treated water. However, it is in low amount and its M_w has been drastically decreased. The treated water can be used for further polymer dissolution with no impact. This little amount of low M_w polymer will not significantly contribute to the increase of the viscosity or to the extra oil recovery.

4.3.3 Precipitation of the Polymer

Precipitation of the polymer can be performed by using trivalent metal salts (aluminum sulfate, polyaluminum chloride, ferric chloride, etc.). This method entails several disadvantages: the reagents acidify the water, and this must be corrected to prevent the equipment from corrosion. Then, the formed colloidal precipitate is very difficult to treat. A large settler-flocculator and a centrifugation/filtration sludge treatment system have to be installed as well. Then the sludge has to be disposed of in a landfill, when permitted by local regulation or incinerated. Last, it is very difficult to recover the oil absorbed on the precipitate.

Another way to perform the precipitation is to use a cationic polymer. Compared to the previous case, no acidification is required but the precipitate is gummy and sticky and is therefore very difficult to handle and dispose of. As in the previous case, the oil remains co-precipitated and cannot be recovered.

CONCLUSION

When dealing with CEOR methods, polyelectrolytes, surfactant systems and their formulations, as well as the related surface equipment, are developed to fit more and more challenging conditions: higher temperature, higher salinities, lower permeabilities, higher level of contaminants, higher oil viscosities.

The first step, once the candidate reservoir has been selected, is to select the right polymer and to assess its performance as a function of the reservoir characteristics and the water quality. Temperature and salinity are of paramount importance at this stage. The addition of sulphonated monomers or NVP monomers is required when the temperature goes beyond 75°C. A change in polymer morphology improves the rheological properties either in solution or in porous medium. Long-term stability studies are performed to assess the *in situ* behavior of the selected polymer, which requires the development of a protection strategy against contaminants, such as iron, H₂S or oxygen. An alternate approach to the contaminant issue is to pre-condition the water using specific surface equipment and chemicals.

The selection of the dissolution and injection facilities has to be made to avoid any mechanical degradation of the

polymer solution. Nitrogen blanketing is highly recommended since any oxygen ingress would impair the final viscosity of the polymer solution. Moreover, when monitoring the viscosity at the well head or before the injection, adapted sampling tools have to be used to enable a correct measurement with no contaminant ingress that could be misleading the actual performance of the polymer injection. By implementing properly all the aforementioned recommendations, the mobility control will be maintained up to the production side and significantly enhance the results one can expect from polymer injection, compared to existing data. Even though, the higher viscosity at the production will have to be taken into account by designing dedicated water treatment systems.

Polymer flooding is a proven and relatively inexpensive EOR method that gained a lot from chemistry improvements and laboratory experiments. Field testing is the next step to truly validate the behavior of newly developed high temperature and salinity tolerant polymers.

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REFERENCES

- Borthakur A., Rahman M., Sarmah A., Subrahmanyam B. (1995) Partially hydrolyzed polyacrylamide for enhanced oil recovery, *Res. Ind.* **40**, 90-94.
- Doe P.H., Moraghi-Araghi A., Shaw J.E., Stahl G.A. (1987) Development and Evaluation of EOR Polymers Suitable for Hostile Environments. Part 1: Copolymers of Vinylpyrrolidone and Acrylamide, *SPE Reserv. Eng.* **2**, 4, 461-467.
- Ellwanger R.E., Jaeger D.A., Barden R.E. (1980) Use of the empirical hill equation for characterization of the effect of added cations on the viscosity of aqueous solutions of partially hydrolyzed polyacrylamide, *Polym. Bull.* **3**, 369-374.
- Fenton H.J.H. (1894) Oxidation of Tartaric Acid in Presence of Iron, *J. Chem. Soc., Trans.* **65**, 899-910.
- Fernandez I.J. (2005) Evaluation of Cationic Water-Soluble Polymers with Improved Thermal Stability, *SPE International Symposium on Oilfield Chemistry*, The Woodlands, Texas, 2-4 Feb., *SPE Paper* 93003.
- Gaillard N., Giovannetti B., Favero C. (2010) Improved Oil Recovery using Thermally and Chemically Stable Compositions Based on Co and Ter-polymers Containing Acrylamide, *SPE Improved Oil Recovery Symposium*, Tulsa, Oklahoma, 24-28 April, *SPE Paper* 129756.
- Grollman U., Schnabel W. (1982) Free Radical-Induced Oxidative Degradation of Polyacrylamide in Aqueous Solution, *Polym. Degrad. Stab.* **4**, 203-212.
- Hsieh H.L., Moraghi-Araghi A., Stahl G.A., Westerman I.J. (1992) *Makromol. Chem. Macromol. Symp.* **64**, 121-135.
- Kheradmand H., Francois J., Plazanet V. (1990) Effect of Additives on the Degradation of Acrylamide-Acrylic Acid Co-polymers in Aqueous Solution, *J. Appl. Polymer Sci.* **39**, 1847-1857.
- Kulawardana E., Koh H., Kim D., Liyanage P., Upamali K., Huh C., Weerasooriya U., Pope G. (2012) Rheology and Transport of Improved EOR Polymers under Harsh Reservoir Conditions, *Eighteenth SPE Improved Oil Recovery Symposium*, Tulsa, Oklahoma, USA, 14-18 April, *SPE Paper* 154294.
- Lake L.W. (1989) *Enhanced Oil Recovery*, Prentice Hall, New Jersey.
- Levitt D.B., Pope G.A. (2008) Selection and Screening of Polymers for Enhanced-Oil Recovery, *SPE/DOE Symposium on Improved Oil Recovery*, Tulsa, Oklahoma, 20-23 April, *SPE Paper* 113845.
- Moradi-Araghi A., Doe P.H. (1987) Hydrolysis and Precipitation of Polyacrylamides in Hard Brines at Elevated Temperatures, *SPE Reserv. Eng.* **2**, 2, 189-198, *SPE Paper* 13033.
- Morel D., Vert M., Jouenne S., Gauchet R., Bouger Y. (2010) First Polymer Injection in Deep Offshore Field Angola: Recent Advances on Dalia/Camelia Field Case, *SPE Annual Technical Conference and Exhibition*, Florence, Italy, 19-22 Sept., *SPE Paper* 135735.
- Miron R.L. (1981) Removal of Aqueous Oxygen by Chemical Means in Oil Production Operations, *Materials Performance* **20**, 6, 45-50.
- Parker Jr W.O., Lezzi A. (1993) Hydrolysis of sodium-2-acrylamido-2-methylpropanesulfonate copolymers at elevated temperature in aqueous solution via ^{13}C n.m.r. spectroscopy, *Polymer* **34**, 23.
- Seright R.S., Campbell A.R. (2009) Stability of Partially Hydrolyzed Polyacrylamides at Elevated Temperatures in the Absence of Divalent Cations, *SPE International Symposium on Oilfield Chemistry*, The Woodlands, 20-22 April, *SPE Paper* 121460.
- Seright R.S., Fan T., Wavrik K., Wan H., Gaillard N., Favero C. (2011) Rheology of a New Sulfonic Associative Polymer in Porous Media, *SPE Res. Eval. Eng.* **14**, 6, 726-734, *SPE Paper* 141355.
- Sorbie K.S. (1991) *Polymer-Improved Oil Recovery*, CRC Press Inc., Boca Raton, FL.
- Sukpisan J., Kanatharana J., Sirivat A., Wang Y. (1998) The specific viscosity of partially hydrolyzed polyacrylamide solutions: Effects of degree of hydrolysis, molecular weight, solvent quality and temperature, *J. Appl. Polymer Sci. B Polymer Phys.* **36**, 743-753.
- Vermolen E.C.M., Van Haastrecht M.J.T., Masalmeh S.K., Faber M.J., Boersma D.M., Gruenenfelder M. (2011) Pushing the Envelope for Polymer Flooding Towards High-temperature and High-salinity Reservoirs with Polyacrylamide Based Ter-polymers, *SPE Middle East Oil and Gas Show and Conference*, Manama, Bahrain, 25-28 Sept., *SPE Paper* 141497.
- Wang D.M., Jiecheng C., Qingyan Y., Wenchoao G., Qun L. (2000) Viscous-Elastic Polymer Can Increase Microscale Displacement Efficiency in Cores, *Annual Technical Conference and Exhibition*, Dallas, Texas, 1-4 Oct., *SPE Paper* 63227.
- Wang D.M., Huifen X., Zhongchun L., Qingyan A. (2001) Study of the Mechanism of Polymer Solution with Visco-Elastic Behavior. Increasing Microscopic Oil Displacement Efficiency and the Forming of Steady "Oil Thread" Flow Channels, *Asia Pacific Oil and Gas Conference and Exhibition*, Jakarta, Indonesia, 17-19 April, *SPE Paper* 68723.
- Wassmuth F., Green K., Bai J. (2012) Associative Polymers Outperform Regular Polymers Displacing Heavy Oil in Heterogeneous Systems, *SPE Heavy Oil Conference Canada*, Calgary, Alberta, Canada, 12-14 June, *SPE Paper* 157916.
- Wellington S.L. (1983) Biopolymer Solution Viscosity Stabilization - Polymer Degradation and Antioxidant Use, *SPE J.* **23**, 6, 901-912, *SPE Paper* 9296.

Wever D.A.Z., Picchioni F., Broekhuis A.A. (2011) Polymers for Enhanced Oil Recovery: A Paradigm for Structure-Property Relationship in Aqueous Solution, *Prog. Polymer Sci.* **36**, 11, 1558-1628.

Willhite G.P., Green D.W. (1998) Enhanced Oil Recovery, *SPE Textbook Series*, **6**. Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers, Richardson, TX.

Xie J., Liu F.P. (2007) Degradation and Protection of Polymer Used for Enhanced Oil Recovery, *J. Shandong University Sci. Technol.* **26**, 16-20.

Zaitoun A., Potie B. (1983) Limiting Conditions for the Use of Hydrolyzed Polyacrylamides in Brines Containing Divalent Ions, *International Symposium on Oilfield Chemistry*, Denver, Colorado, 1-3 June, *SPE Paper* 11785.

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