INTRODUCTION

Controlling water production is an increasing concern to oil companies as currently developed hydrocarbon fields mature. Reduced well productivity, increased costs associated to produced water treatment and premature well abandonment (in gas fields) are typical drawbacks caused by excessive water production.

Many technologies, like cement squeeze and injection of polymer gels, require identification and isolation of the water producing levels in order to eliminate the risk of damaging the hydrocarbon-bearing zones. They are therefore very difficult to apply in micro-layered formations and/or in presence of gravel-pack completions, where zone isolation is often unfeasible.

A theoretically viable option, that has often been field-applied since the late 70’s, is the injection of a selective-permeability-modifying-agent (usually a polymer solution) in the entire pay zone in order to reduce the water permeability with a small effect on the permeability to hydrocarbons. Because these treatments are relatively simple and inexpensive, and the risk of impairing the permeability of the hydrocarbon producing layers is small, many field tests have often been carried out in the absence of definite rules for candidate and chemical selection. This approach has prevented the development of a mature technology, up to the point that the low success ratio and the difficulties in interpreting field-test results have induced some companies to withdraw completely from these treatments.

Besides the trial-and-error approach adopted in many field applications, various studies have also been developed in the last 10 years facing the problem from a more fundamental point of view. From these studies it is possible to identify some general issues that are critical at the different scales in the reservoir, i.e.:

- A successful treatment requires a significant polymer adsorption onto the rock surface, though this might not be a sufficient condition.
- The reduction of the dimensions of pore throats and bodies caused by the adsorbed polymer layer seems to play an important role in reducing the permeability of the porous medium.
- Achieving selective permeability reduction is not sufficient to ensure a successful job, as the post-treatment well performance strongly depends on the mechanism by which water was produced.

Many specific problems (such as the mechanism of selective permeability reduction, the relationship between polymer adsorption and permeability reduction, etc.), however, are still open and need to be solved in order to make significant improvements in the technology.

In this work we present some preliminary results of adsorption studies and coreflood experiments that have helped to improve the understanding of polymer adsorption and its effect on fluid flow in porous media. In a first series of experiments we studied the effect of the polymer charge on its adsorption on Clashach sandstone. Static adsorption measurements showed a clear trend in the amount of adsorbed polymer according to the polymer charge. The effect of the adsorbed polymer on fluid flow was then investigated by coreflood experiments, in which the absolute permeability was modified by adsorbing the polymer within the porous medium.
In a second series of experiments we considered a more complex sand obtained from a gas reservoir in southern Italy and a number of polymers that were different in charge, structure and molecular weight. Results from static adsorption measurements and brine/gas corefloods showed trends that were similar to those observed with Clashach sandstone, confirming the ionic character of the polymer to be a critical parameter. Furthermore, the trends observed in brine/gas corefloods provided an insight in the mechanism of selective permeability reduction and some clues for future work in this area.

**EXPERIMENTAL**

** Fluids/chemicals properties

A 2% KCl solution in deionised water was used in all our experiments as the brine phase.

The polymers used, schematically grouped in Table 1, were all commercially available systems.

<table>
<thead>
<tr>
<th>Name</th>
<th>Type / Structure</th>
<th>Ionic character</th>
<th>MW</th>
<th>pH in brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAM</td>
<td>Polyacrylamide</td>
<td>Non ionic</td>
<td>5x10^5</td>
<td>7.23</td>
</tr>
<tr>
<td>HPAM_23</td>
<td>23% Hydrolysed PAM</td>
<td>Anionic</td>
<td>5x10^5</td>
<td>7.42</td>
</tr>
<tr>
<td>CAT1</td>
<td>Base PAM / Unknown</td>
<td>Cationic</td>
<td>4x10^6</td>
<td>4.25</td>
</tr>
<tr>
<td>CAT2</td>
<td>Similar to CAT1</td>
<td>Cationic</td>
<td>8x10^5</td>
<td>4.25</td>
</tr>
<tr>
<td>CP1</td>
<td>Copolymer / PAM+AMPS</td>
<td>Non ionic</td>
<td>5x10^5</td>
<td>6.38</td>
</tr>
<tr>
<td>CP2</td>
<td>Copolymer / VSA</td>
<td>Amphoteric</td>
<td>1x10^6</td>
<td>6.83</td>
</tr>
<tr>
<td>TP</td>
<td>Terpolymer / PAM+AMPS+VP</td>
<td>Non ionic</td>
<td>N.A.</td>
<td>6.66</td>
</tr>
</tbody>
</table>

Tab 1 Polymers used in the present study. AMPS = “Acrylamido-3-Propansolphonic-acid”, VP = Vinylpyrrolidone, VSA = “Vinyl-Sulphonate-Acrylamide”, N.A. = Not Available.

Polymer solutions were prepared in brine and filtered through a 2.7 µm glass-fibre filter; at concentrations up to 2000 ppm the viscosity was always less that 4 cP and the rheological behaviour ranged from newtonian to weakly shear-thinning, for shear rates up to 1000 s^-1. All the fluids were degassed prior to corefloods experiments. In the coreflood experiments with Clashach cores the polymer solution was shear-degraded by flow (at a rate of 500 cm/h) through a 4 cm-long sacrificial Clashach core and then refiltered prior to the actual coreflood.

**Porous media**

Two types of porous media were used: (i) Clashach sandstone cores (8 x 2.54 cm, ~16% porosity) and (ii) sandpacks (7 x 2.54 cm, ~40% porosity) containing a reservoir sand (hereafter referred to as: sand PC16). Clashach sandstone is composed mainly by quartz and silicates, with very small amounts of clays (< 2%); sand PC16 contains silicates, aluminosilicates and a relatively high amount of calcite (about 20%).

Clashach sandstone was crushed in order to obtain a sand that was suitable for static adsorption measurements.

**Static adsorption test procedure**

Static polymer adsorption experiments were performed to evaluate the adsorption properties (adsorption kinetics and adsorption isotherm) of the different polymers on the two sands. These tests were conducted at room temperature by adding 3 grams of sand to a given amount of polymer solution (10 cm^3). At the end of the test the supernatant was filtered and the amount of polymer remaining in solution was determined by

* NMR and IR spectra of CAT1 and CAT2 were essentially identical
Total Organic Carbon (TOC) measurement. The amount of polymer retained by the sand was then calculated by difference, after correcting for the organic carbon released by the sand itself.

Corefloods procedures

A schematic of the coreflood apparatus for brine/gas corefloods is shown in Figure 1.

Two different coreflood experiments have been performed to study the effect of the polymer adsorption in the porous medium, i.e.: (i) reduction of absolute permeability (with Clashach cores at room temperature) and (ii) reduction of end-point permeabilities to brine and gas (with PC16 sandpacks at 48 °C).

The initial saturation with brine was established under vacuum. The gas used was nitrogen, that was firstly saturated with water vapour (by flow through a humidifier) to maintain water saturation within the core and then injected at constant pressure (1.2 bar). Saturation of water-based fluids (brine and polymer solution) was determined by tracer test experiments; potassium iodide at 20 ppm was used as a tracer and detected by a UV spectrophotometer at 234 nm wavelength. The saturation of gas at the irreducible water saturation was determined by weighing the water displaced during the gas flow.

Polymer treatment was performed by injecting at least 10 PV of the solution at constant flow rate (25 cm³/h in Clashach sandstone cores and 50 cm³/h in PC16 sandpacks), shutting-in the system for 18 hours and then displacing the solution with brine at the same injection flow rate. During polymer injection and displacement the effluents were collected with a fraction collector and the polymer concentration was measured by TOC. In this manner, we were able to determine the amount of polymer retained in the porous medium.

RESULTS

Clashach sandstone

In this first series of experiments we investigated the adsorption of polymers of different charge and their effect on fluid flow within the porous medium. Therefore we chose three polymers (CAT1, PAM and HPAM_23) with similar structure and molecular weight but different charge (positive, neutral and negative, respectively). Because Clashach sandstone is composed entirely by silicates, at pH values close to neutral the rock/brine interface is negatively charged; thus it was reasonable to expect a strong effect of the polymer charge on the adsorption onto the sand surface. This is clearly shown in Fig. 2, that reports the adsorption, after 24 hours, of the three polymers at 1000 ppm concentration. The adsorption kinetics of CAT1 and PAM at 1000 ppm is shown in the insert.

Although coreflood experiments (see Fig. 3) showed that PAM and CAT1 were much more effective than HPAM_23 in reducing the absolute permeability, we observed a less well-defined trend. In fact (i) PAM and CAT1 determined the same permeability reduction although they showed distinct adsorption behaviour (cf. Fig. 2), and (ii) HPAM_23 appeared to reduce somewhat the permeability although it did not show any adsorption onto Clashach sand.

The latter can be easily explained invoking polymer filtration, while the behaviour of CAT1 and PAM suggests that although CAT1 adsorbs more strongly than PAM, it presumably forms a thinner layer, because of the strong electrostatic interactions that increase the tendency of the polymer to lay flat on the rock surface.

PC16 sand

This second series of experiments were aimed at selecting a polymer to be tested in a gas field located in southern Italy. An initial screening, based on static adsorption measurements, was performed on the polymers listed in Table I (see Fig. 4) and allowed us to select three polymers (CAT1, CAT2 and PAM) to be further tested in porous media. Also in this case the cationic polymers showed the highest adsorption, which confirms the key role of electrostatic interactions in the adsorption process. An intriguing result, that we have not been able to explain yet, was the negligible adsorption of anionic polymers on PC16 sand, which contains a significant amount of calcite, positively charged in brine at pH values less than 10.

From the adsorption isotherms and kinetics of the three selected polymers (see Figs. 5 and 6), we fixed the
optimal polymer concentration and shut-in time at 2000 ppm and 18 hours, a compromise between the objective to maximise polymer adsorption and field constraints such as the formation fracturing pressure and the minimisation of the shut-in time.

The effect of the adsorbed polymer on end-point permeabilities to brine and gas is shown in Figs. 7 and 8, that also report the initial permeabilities and saturations at the end-points. After the treatment we did not observe significant changes in the residual gas and irreducible water saturations, except in two cases (indicated in Fig. 8 with black bars) in which the irreducible water saturation increased from 14% to 26% (polymer CAT2) and from 39% to 46% (polymer CAT1). In these two cases the observed reduction in the gas permeability cannot be ascribed only to the presence of the polymer layer, but also to the increase in water saturation.

All the tested polymers proved effective in selectively reducing the water permeability. This selectivity, however, cannot be explained considering only the reduction of pore-throats cross-sections caused by the polymer layer, as in this case the permeability reduction would be dependent only on the initial permeability and not on the particular fluid phase.

The cationic polymers CAT1 and CAT2 showed similar performance whereas PAM was less effective; this trend was also consistent with the calculated amount of polymer retained in the porous media, that was around 2.4 mg/g for CAT1 and CAT2 and 1.7 mg/g for PAM. Comparison of these values with Figs. 5 and 6 shows that, in these experiments, retention by mechanical entrapment was negligible.

Even though the results showed consistent trends, we are aware of some limitations in the experimental procedures that could have an influence on the experimental output. In particular we had to use short sandpacks (because of limited availability of reservoir sand) and Hassler cells without internal pressure taps. Furthermore, saturation measurements were limited by the pore-volume/dead-volumes ratio that was close to 1, therefore not optimal for precise determinations. Further studies will try to overcome these limitations and give more definitive and general answers to these issues.

CONCLUSIONS

Controlling polymer adsorption is a key issue in treatments with the objective of selectively reducing the permeability to water. To this aim a correct match between the polymer and the surface charges can greatly increase the adsorption.

Although a significant polymer adsorption is necessary, other factors, such as the disposition of the adsorbed polymer on the rock surface, can influence the ultimate effectiveness in terms of permeability reduction.

Mechanical entrapment of polymer molecules within the porous medium can also reduce the permeability to water and/or hydrocarbons. In general this is an unwanted effect than can be estimated by comparing the polymer retention in the porous medium with static adsorption measurements.

Further studies will be addressed at understanding the mechanism of selective permeability reduction and defining the role of the different chemical properties of the adsorbing polymer with the adsorption process and, ultimately, with its effect on multiphase flow.

REFERENCES


Fig. 1 Schematic diagram of the coreflood apparatus

Fig. 2 Adsorption of polymers with different charge onto Clashach sandstone

Fig. 3 Reduction of the absolute permeability after polymer treatment in Clashach sandstone cores. The initial permeability is shown on the graph for each experiment.
Fig. 4 Static adsorption of different polymers on PC16 sand after 24 hours

Fig. 5 Adsorption isotherms on PC16 sand after 24 hours

Fig. 6 Kinetics of adsorption on PC16 sand from 3000 ppm polymer solutions

Fig. 7 Reduction of the brine permeability after polymer injection in PC16 sandpacks. Initial brine permeability at residual gas saturation (in parentheses) is shown on the graph for each experiment

Fig. 8 Reduction of the gas permeability after polymer injection in PC16 sandpacks. Initial gas permeability at irreducible water saturation (in parentheses) is shown on the graph for each experiment. Black bars indicate two experiments in which irreducible water saturation increased after polymer treatment.