Application of a Newly Discovered Biopolymer in Enhanced Oil Recovery

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The polymer under investigation is a β-1,3-polyglucan, which is produced by certain bacteria known as Alcaligenes faecalis. The polymer dissolves in alkaline solution and gels upon neutralization. The gelation process is reversible. A new delayed gel system from the alkaline biopolymer solution and an organic cross-linker was discovered in test tube experiments and successfully tested in a sand pack. Attempts to devise a gelation system by hydrolysis failed for the precipitation of polymer in presence of alcohol that is produced due to the hydrolysis of esters. A hydrolysis/hydration scheme was formulated and tested in tubes with some level of success. An alternative technique for reducing the pH of the gelling solution was found to be precipitation of OH^- ions by Ca^{++} and Mg^{++} ions. This can be especially attractive for reservoirs that have already undergone water flooding by sea water.

A self-adjusting polymer slug was successfully tested in a sand pack which produced a high oil recovery of 90%. Finally, a gel plug that can be placed anywhere along the core was successfully tested in a four-segment sand pack.

In conclusion, results presented in this paper will indicate a wide range of possible applications of the new biopolymer for the petroleum reservoirs.

INTRODUCTION

Production of oil from petroleum reservoirs can be divided into three stages. Primary recovery refers to the first stage of production in which the oil is driven to the production well by the reservoir natural energy. This could be one or a combination of drive mechanisms such as gas in solution, gas cap expansion, water influx from an active aquifer, expansion of connate water and/or compaction of the pore space due to the overburden pressure.

Recovery from the primary stage varies from zero to a maximum of around 30% depending on the drive mechanism and how effectively it is utilized. Primary recovery is ceased upon depletion of the natural energy. At this stage, some kind of secondary recovery scheme is needed to produce some additional oil. In some cases, the economic incentive might dictate entering the secondary stage for the purpose of increasing production rate even before the reservoir natural energy is depleted.

In the secondary recovery process, some kind of fluid is injected into the reservoir to displace oil to the production well. The fluid most commonly injected during the secondary recovery stage is water in waterflooding and gas in gas injection schemes. In any case,

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the displacing fluid tends to by-pass the oil and eventually channels toward the production well. Production of displacing fluid increases with time and reaches a level where further injection becomes uneconomical. In most cases, more than 70% of the oil initially in place will be still trapped in the pore geometry even after the secondary recovery stage has been successfully accomplished. This is because of the heterogeneous nature of the reservoir rocks and existence of high permeable streaks in even the most uniform sandstone reservoir. In addition, most of the oil reservoirs are composed of several productive layers with different permeabilities. The injected fluid, therefore, tends to enter the more permeable layer and live behind the oil in the less permeable layer. This indicates that a large portion of the oil initially in place is targeted for the tertiary stage of oil recovery phases. The tertiary stage requires some kind of modification of the reservoir and/or injected fluid characteristics to overcome, or at least to suppress, the heterogeneity of the reservoir to some extent.

In situ gelation aims to achieve the above goal. The conventional in-situ gelation schemes are characterized as cross linking the polymer molecules with heavy metal ions such as chromium. The appropriate recipe designed in the lab is injected into the reservoir in anticipation of plugging the already-flooded zone. Hence, the subsequent injection of the displacing fluid will hopefully enter that portion of the reservoir that has not yet been swept. This scheme has been applied to a few reservoirs with some level of success.

A new in-situ gelation process, based on a newly discovered biopolymer, was presented earlier [1,2]. The polymer is a β-1,3-polyglucan which is produced by certain bacteria known as Alcaligenes faecalis. Production of the polymer is patented under U.S. patent No.4,908,310 [3] and its application in subterranean permeability modification is patented under U.S. patent No. 4,941,533 [4]. The polymer dissolves in alkaline solution and gels upon neutralization by acid. The gelation process is reversible. The in situ gelation process based on this new scheme was successfully tested in sand packs as well as in Berea sandstone cores, the results of which have been published elsewhere [1,2]. This paper focuses on the additional experimental investigation undertaken at the research laboratory of Elf Aquitaine to further enhance the application of the biopolymer in the petroleum reservoirs.

DELAYED GEL SYSTEM

It was discovered that the biopolymer in sodium hydroxide solution produced a delayed gel system with orthoboric acid. The gelation time varied depending on the concentration of the orthoboric acid and the temperature of the process. The gelation seems to be a cross-linking type reaction, hence, kinetically controlled. Mixtures of 3% polymer solution in 1 N NaOH with various concentrations of orthoboric acid were prepared to determine the respective gelation times. The study was limited to room temperature and 60° C. Table 1 presents the results of the observed gelation time. All the tests were performed in test tubes with screw-type caps. The range of the gelation time observed was from a few hours to a few days. For the mixtures of 3 g polymer solution and less than 1.5 g of 1/2 M orthoboric acid, evaporation of the solution in an oven of 60° C for a period of two weeks did not allow accurate determination of the gelation time. Therefore, the long gelation time tests should be performed in better sealed tubes to eliminate the evaporation effect.

Delayed gelation system was also tested in a sand pack. A sand pack 20 cm long was prepared in the same fashion as reported earlier [2]. The permeability of the sand pack was measured to be 4.51 D. The injected solution consisted of 100 cm^3 of 2% polymer solution in 0.5 N NaOH and 50 cm^3 of 1/2 M orthoboric acid in sea water. The sea water used had the same composition as ASTM synthetic sea water except for the magnesium and calcium ions. To

Table 1. Gelation time of orthoboric acid delayed gel system.

Pol./O.B.A. wt/wt	Gelled?		Gelation Time	
	R.T.	60° C	R.T.	60° C
3/0.1	No	No	—	—
3/0.3	No	No	—	—
3/0.5	No	Yes	—	19 days
3/0.7	No	Evaporated	—	—
3/0.9	No	Soft gel	—	6 days
3/1	No	Soft gel	—	6 days
3/1.5	No	Soft gel	—	7 hours<G.T. <24 hours
3/2	Yes	Yes	8 days <G.T. <11 days	7 hours<G.T. <24 hours
3/2.5	Yes	Yes	4 1/2 days	7 hours<G.T. <24 hours
3/3	Yes	Yes	4 1/2 days	7 hours<G.T. <24 hours
3/3.5	Yes	Yes	4 1/2 days	4 1/2 hours
3/4	Yes	Yes	4 1/2 days	4 1/2 hours
3/4.5	Yes	Yes	4 days	4 1/2 hours
3/5	Yes	Yes	11 hours	1 hour

O.B.A. : Orthoboric Acid
Pol. : Polymer
wt/wt : weight/weight
R.T. : Room Temperature
G.T. : Gelation Time

avoid precipitation of magnesium and calcium ions in a sodium hydroxide environment, these salts were eliminated from the synthetic sea water preparation.

After saturating the sand pack, it was left overnight for the solution to gel. Permeability measurement after gelation revealed 0.14 md, which corresponds to a permeability reduction of greater than 32,000. The sand pack was then subjected to a constant head of water column while monitoring the fluid production to study the long term stability of the gelation system. Permeability measurement after 5 months revealed a permeability of 0.16 md, which corresponds to a permeability reduction of more than 28,000.

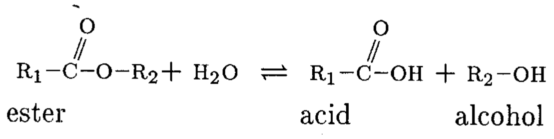
GELATION BY HYDROLYSIS

The gelation system reported earlier [1,2] was based on in situ acidification of the polymer solution in alkaline by injecting acid into the porous media intermittently. The process, although effective, does not seem to produce uniform gel. Gelation is achieved only where mixing within the pore space occurs. This was probably one reason that complete plugging was hard to achieve. Therefore, it is desirable to have a system which changes its pH internally by hydrolysis and/or by disintegration of some kind of chemical compound which produces an acid to reduce the pH of the solution to below 10, which is required for gelation to occur.

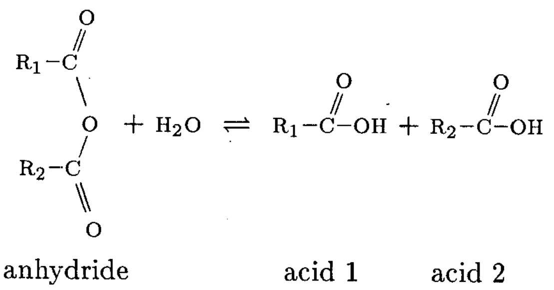
Table 2. Test tube results of gelation by hydrolysis.

Chemical Compound	Gelation Time
C_2-formiate	1 hour 5 min.
C_3-formiate	1 hour 51 min.
nC_4-formiate	polymer precipitated
iC_5-formiate	> 2 days
C_1-acetate	12 min.
C_2-acetate	1 hour
iC_4-acetate	> 7 1/2 hours
nC_4-acetate	polymer precipitated
iC_5-acetate	polymer precipitated
nC_5-acetate	polymer precipitated
$2-C_2-C_6$-acetate	phases remained separated
acetic anhydride	$\approx$ 1 min.
maleic anhydride	instantaneous
maleic anhydride in formaldehyde	8 min.

An extensive test tube investigation with a variety of chemical compounds was undertaken. Results are presented in Table 2. Two groups of compounds of prospective utility seem to be alkyl esters and organic anhydrides, as shown below.



$$R_1-\overset{O}{\overset{/\!/}{C}}-O-R_2 + H_2O \rightleftharpoons R_1-\overset{O}{\overset{/\!/}{C}}-OH + R_2-OH$$



Investigation was limited to the chemicals available in the lab. The gelation time produced was in the range of a few minutes to a couple of days. The following general observations were made:

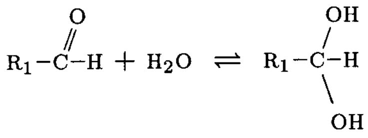
a. Alkyl esters of longer carbon chains produced longer gelation time. However, as expected, solubility in the aqueous phase was reduced drastically by increasing the carbon chain length.

b. Polymer was precipitated in the presence of C_4-alcohol and higher. Since hydrolysis of alkyl esters produces alcohol, polymer precipitation became a major difficulty.

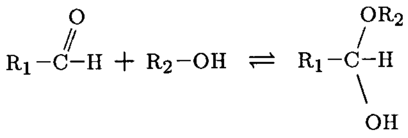
c. Organic anhydrides did not produce alcohol; therefore, polymer precipitation was not a problem. However, the limited number of available organic anhydrides that were studied in the lab did not produce a reasonable gelation time. The mixtures gelled either instantaneously or in a few minutes.

GELATION BY HYDROLYSIS/HYDRATION

The major difficulty of gelation by ester hydrolysis, as mentioned above, was precipitation of the polymer in the presence of long chain alcohol. Therefore, the possibility of removing the alcohol from the mixture upon production by some other type of reaction was investigated. Hydration of the aldehydes in the presence of water and alcohol seemed to be a promising approach.



$$R_1-\overset{\overset{O}{\|}}{C}-H + H_2O \rightleftharpoons R_1-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}}-H$$



$$R_1-\overset{\overset{O}{\|}}{C}-H + R_2-OH \rightleftharpoons R_1-\underset{\underset{OH}{|}}{\overset{\overset{OR_2}{|}}{C}}-H$$

The equilibrium constant for addition of H_2O to formaldehyde is 41 M^{-1} and for addition of ethanol and methanol to formaldehyde is 860 M^{-1} and 1300 M^{-1} respectively [5]. Therefore, formaldehyde should be able to remove the excess alcohol effectively. Test tube observation supported the theory and much clearer gel was produced in the presence of formaldehyde. However, since the equilibrium constant reduces with increasing carbon chain, its effectiveness vanishes for higher chain alcohols.

GELATION BY IN SITU PRECIPITATION

An alternative approach for reducing the pH of the gelling solution within the porous rock is to precipitate OH^- ions. This can be effectively achieved in presence of Ca^{++} and/or Mg^{++} ions. Gels of reasonable strength were produced by addition of synthetic sea water to the polymer solution. The process deserves further investigation, especially for reservoirs that have already been flooded by sea water.

SELF-ADJUSTING POLYMER SLUG

Polymer flood is most cost effective if a slug of polymer is injected. However, this creates the problem of viscous fingering of the tail water, which eventually breaks through the slug. Different schemes with some reasonable success have been suggested, such as gradual decrease of polymer concentration instead of a sharp concentration gradient between the polymer slug and the chase water. Because of the inherent nature of the present system, a self-adjusting slug seems to be achievable. A sand pack test was undertaken to elucidate the effectiveness of this new scheme.

A sandpack similar to the one reported earlier [2] was used. It was composed of three modular cells, each made of 20 cm long lucite tubes with both ends grooved to fit rubber O-rings for sealing purposes. Each cell is separated from the next one by a one inch lucite male connector grooved to fit the O-ring. The main cells and the middle pieces were each equipped with two pressure taps. It was initially saturated with sea water without Ca^{++} and Mg^{++} ions. The total pore volume of the sandpack was 143 cm^3. Water was then displaced by a 5 cp crude oil at a rate of 40 cm^3/hr to a connate water saturation of 39.5%.

Waterflood was initiated by injecting sea water and continued until no more oil production was observed. Total oil production at this stage was 55% of the oil in place. Water was switched to 1 N HCL and its injection at a rate of 60 cm^3/hr continued until acid breakthrough occurred. A polymer solution of 3% polymer in 1 N NaOH was then injected at the same flow rate. After injecting a slug of 25 cm^3 of polymer solution, it was switched back to acid injection at the same rate of 60 cm^3/hr. Pressure drops along different segments of the sandpack and fluid production were continuously monitored. Injection of acid continued until fluid production became clear and free from oil production.

The total oil production achieved was around 90%. That is, an additional 35% of oil in place was produced by injecting the self-adjusting polymer slug. Creation of the oil bank ahead of the polymer slug became obvious upon observation of fluid production consisting of 100% oil which persisted for a reasonable length of time.

The mechanism behind such an effective displacement process is rather obvious. A polymer slug sandwiched between two acid zones practically eliminates fingering possibilities and the front and tail end of the polymer slug become very similar to those of a piston-like displacement. Any fingering of acid into the polymer slug or polymer solution into the acid zone is diminished by the tendency of the polymer solution to gel instantaneously in the presence of acid.

GEL PLUG

Creation of a gel layer at the interface between the acid and the polymer solution phases at the front and tail end of a polymer slug, as shown above, protects the integrity of the slug while it is moving from the injection to the production port. Therefore, combining this with the delayed gel characteristics of the orthoboric acid/polymer system makes it possible to locate the slug anywhere along the core and create a gel plug at that location. This was tested in a sandpack composed of four 10 cm long segments similar to the one described earlier. Permeabilities of the segments from the bottom to top were 3.65 D, 3.41 D, 3.95 D and 3.20 D respectively; and the corresponding pore volumes were 26.56 cm^3, 27.45 cm^3, 27.43 cm^3 and 25.84 cm^3 respectively.

The sandpack was initially saturated with the synthetic sea water without Ca^{++} and Mg^{++} ions. Then it was preflushed with 1 N HCL solution. At the time of acid breakthrough, a slug of polymer solution was injected. The polymer solution consisted of 3% by weight polymer in 1 N NaOH with 0.5 M orthoboric acid solution in synthetic sea water (no Ca^{++} and Mg^{++} ions) at a weight ratio of 3/2 polymer/orthoboric acid. Total volume of slug injected was 20 cm^3. The polymer slug was followed by 1 N HCL solution. The pressure drop along each segment of the sandpack was monitored continuously. Acid injection was stopped when the pressure drop readings indicated the slug had reached the third segment from the bottom of the sandpack. The inlet and the outlet taps were closed and the sandpack was left for gelation of the slug to occur at room temperature.

Gelation of the same polymer solution that was injected in the sandpack occurred in a test tube after nine days at room temperature which was much longer than expected. The cause of the delay in gelation time is not known. It could be due to the aging effect of the polymer solution, orthoboric acid solution, room temperature, or a combination of all of them. Permeability measurements performed 20 days after gelation revealed permeabilities of 1.46 D, 0.56 D, 0.23 D and 3.43 D from the bottom to the top segments respectively. It was noticed that the top segment was more or less at its initial permeability and, as expected, the permeability reduction was highest for the second segment from the top, where the slug was located.

Permeability reduction for this segment was expected to be much higher. The lower than expected value is probably because of a combination of two effects; loss of some polymer due to the adsorption to the sand surface area and the long period of time elapsed after gelation before permeability measurements were performed. Examination of the gel in the test tube at the time of permeability measurement revealed some syneresis. Therefore, the gel within the sandpack had also undergone some level of syneresis. The lower values of permeabilities for the first two segments were not expected to that extent. The permeability reductions of the lower two segments are probably due to the adsorption of the polymer solution mixture onto the sand surface while the slug was passing through and its subsequent gelation.

CONCLUDING REMARKS

Results presented in this paper are an indication of the wide range of possible applications of the new biopolymer system for the petroleum reservoirs. The uniform permeability reduction and its reversibility, which was established earlier and reported elsewhere [1,2], makes it unique among other competitive systems. Creation of a layer of gel at the interface, which is re-dissolved and re-gelled and possibly moves in the direction of the flow path, can be taken advantage of in creating a self-adjusting polymer slug. The oil recovery mechanism under this scheme of slug injection would be enhanced to an extent that is impossible to achieve under any other immiscible processes known to the authors.

The delayed gel system presented here is a still further extension of its applicability in different circumstances, e.g., plugging off fractures and/or thief zones. Its combination with in situ acidification, as shown in this paper, provides conditions to create gel plugs positioned deep in the reservoir.

Further study is required in gelation by hydrolysis and/or disintegration of chemical compounds to produce in situ acid. Organic anhydride compounds seem particularly promising in producing acid. Precipitation of the polymer from its solution in the presence of alcohols which are produced by the esters hydrolysis needs to be overcome to make it possible to design a gelation system by hydrolysis with reasonably long gelation time.

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