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<p>(21) International Application Number: PCT/US90/02438 (22) International Filing Date: 2 May 1990 (02.05.90) (30) Priority data: 352,733 16 May 1989 (16.05.89) US (71) Applicant: THE UNIVERSITY OF KANSAS [US/US]; Office of the General Counsel, 227 Strong Hall, Lawrence, KS 66045 (US). (72) Inventors: BULLER, Clarence, S. ; 2920 Lawrence Avenue, Lawrence, KS 66046 (US). VOSSOUGH, Shapour ; 1035 Lakecrest Road, Lawrence, KS 66044 (US). (74) Agents: COLLINS, John, M. et al.; Hovey, Williams, Timmons & Collins, 1101 Walnut Street, Suite 1400, Kansas City, MO 64106 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report.</i> <i>With amended claims.</i></p>
<p>(54) Title: SUBTERRANEAN PERMEABILITY MODIFICATION BY USING MICROBIAL POLYSACCHARIDE POLYMERS</p>		
<p>(57) Abstract</p> <p>A secondary (or tertiary) oil recovery process is disclosed involving the injection of a polysaccharide polymer naturally produced by certain bacteria in a solubilized form into the oil sand or horizon. When such polymer is injected, it is solubilized in alkali solution such as sodium hydroxide. Solubilized (unprecipitated) polymer may be used as a secondary recovery sweep fluid, <i>per se</i>. Within the formation, the polysaccharide polymer may be precipitated by the later injection of an acid solution or carbon dioxide. The order of injection of the acidic materials and the solubilized polymer is not critical, except with respect to carbon dioxide injection, which must follow the solubilized polymer injection. By such precipitation, high permeability zones are selectively blocked off, giving sweep access primarily to the lower permeability zones containing mostly oil.</p>		

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SUBTERRANEAN PERMEABILITY MODIFICATION
BY USING MICROBIAL POLYSACCHARIDE POLYMERS

5 BACKGROUND OF THE INVENTION

As herein disclosed, a strain of aerobic bacteria has been isolated which encapsulate themselves, from which a bio-polymer can be extracted. Neutralization of the alkaline extract with mineral acids, organic acids or CO₂ results in gel formation. Polymer in hydrated gel is resistant (and tolerant) to repeated cycles of redissolving in
10 alkali followed by precipitation by acid or CO₂. The subject invention sets forth methods of using this microbial polymer for permeability modification and reversible blocking of undesirable flow channels in petroleum sands, horizons and reservoirs.

Most of the Kansas oil reservoirs have been water flooded in secondary recovery. The water/oil ratio in most of them has reached or passed the economic level. Therefore,
15 devising and providing a technique which will selectively and reversibly plug the water channels has great economic prospects. Our invention establishes that the bio-polymer has potential for application in microbially enhanced oil recovery (EOR). The potential and capacity for generating the reversibly gelable polymer from inexpensive, renewable cellulosic, hemicellulosic or cornstarch stocks greatly enhances the usefulness of the
20 subject process.

Permeability modification has been a subject of interest since the introduction of water-flooding as a secondary oil recovery technique. Because of variations in the reservoir's permeability, bypassing of the displaced fluid is unavoidable even in the most homogenous reservoir. Early breakthrough of the displacing fluid causes the secondary
25 recovery project to become uneconomical and leaves a large portion of the initially present oil in place and unrecovered.

Several processes such as injection of polymer solution or cross linking of polymers in situ in the reservoir (in situ gelation) have been developed and are presently under investigation. Near well-bore treatment is easier to achieve than treatments requiring deep penetration of the reservoir.
30

Clearly, it is desirable to devise a method which is time independent and reversible. In such case, materials could be injected as far in the reservoir as desired, then be activated to gel. Process reversibility would allow breaking the first in situ gel, moving it further down in the reservoir and then repeating the gelation process. One
35 objective of the subject method is to disclose and provide a technique using a reversible gel generated by a bio-organism.

The in situ growth of bacteria and the accumulation of the products of their growth have been considered for use in enhance oil recovery (EOR) processes. Products of anaerobic bacterial growth which may enhance flow characteristics of in situ oil include gases such as carbon dioxide and methane, solvents such as ethanol or butanol, and acetic, propionic, or butyric acid. Potentially useful products of aerobic bacteria growth include surfactants produced by hydrocarbon oxidizing bacteria and polysaccharide gums which increase the viscosity of water.

In addition to problems attendant to the creation of environments suitable for the in situ growth of bacteria, the biomass may eventually accumulate in amounts sufficient to cause clogging. Problems involved in the in situ use of bacteria may be contrasted with the relative ease with which desirable microbial products can be produced in large scale cultures. Such products can then be injected into the wells. One such product is xanthan, a polysaccharide polymer which is injected into wells in order to increase the viscosity of water.

The present invention is concerned in part with the use of microbial polymers capable of gel formation for reversible blocking of undesirable channels. Such polymers can readily be obtained from a newly isolated strain of cellulolytic bacteria as well as such bacteria previously known.

DESCRIPTION OF THE PRIOR ART

Recoverable oil-in-place is directly proportional to the volume of the reservoir which is swept by the injected fluids. The volumetric sweep efficiency can be effected by any one, several or all of the properties of the injected or displaced fluids, their interaction with the porous rock, and the heterogeneity of the porous rock. Therefore, increase in volumetric sweep efficiency can be expected if alteration in any of the above properties is achieved in the desired direction.

The topic of oil sand permeability modification is an active research area. There have been many attempts to control fluid movement in the reservoirs in order to improve sweep efficiencies or to reduce water production rates in water-flooding. Polymers have been added to the displacing fluid to reduce its mobility. Early treatments involve polymer flooding or polymer augmented water flooding. Although the technique works to some extent, there are many reservoirs that do not benefit from polymer flood. Factors responsible for such failures are polymer degradation due to mechanical shear, high salinity of injected or resident water and the existence of fractures or large

permeability variations. In addition, polymer retained by absorption or mechanical entrapment has a tendency to be washed from the porous rock over a long period of time. Thus, retention of polymer cannot produce sufficient permeability reduction over desirable periods of time for many reservoirs.

5 Recent processes have aimed to produce large permeability reductions in porous media, involving cross linking or in-situ gelation of polymers. A typical gelled polymer process involves the reaction of a polymer with a metal ion to yield a three-dimensional cross-linked system. Mixtures with different gelation times can be provided, based on the concentration of the mixture, temperature, pH and other properties. Such techniques fail
10 in most of the field applications. Near well-bore treatment is easier to achieve than the treatment requiring deep penetration in the reservoir. Failure is mostly due to the large number of variable involved. Controlling these variables, such as concentration of the metal ions, polymer, reducing agent, etc., at the necessary field scale is extremely difficult.

15 It is, therefore, desirable to devise a process which is time independent and reversible. Gelable materials in solution could be injected as far into the reservoir as desired, then activated to gel. Process reversibility would allow breaking the gel thereafter and moving the initial charge of materials further down in the reservoir, where the gelation process may again be repeated.

20 SUMMARY OF THE INVENTION

 The preferred polymer that should be used in this new process and method is a water insoluble alkaline beta 1, 3 polyglucan. It is produced by a new strain of Cellulomonas flavigena. The strain was selected from chemostat cultures in which ammonium chloride was the growth limiting substrate. When the polymer is produced,
25 it is stored as a capsule which surrounds the bacteria. The polymer itself has been determined to be a polysaccharide. Under optimal growth conditions, as much as 90% of the dry weight of encapsulated bacteria can be accounted for as polysaccharide.

 The polymer is completely soluble in 1 N NaOH. When its solutions are neutralized with any of mineral or organic acids or CO₂, a water insoluble gel is formed.
30 Polymer in hydrated gel is resistant to repeated cycles of redissolving in alkali followed by precipitation by acid or CO₂. If the gel is macerated and diluted in water, then subjected to centrifugal forces of 16,000 g for 15 minutes, 97% of the weight of the precipitated gel is accounted for as water.

Polymer solution, even in dilute form, exhibits much higher viscosity than plain water or dilute sodium hydroxide.

Two of the physical properties associated with the above polymer can be taken advantage of in enhancing oil production from subterranean oil sands or reservoirs. These two properties are increased solution viscosity in dilute state and reversible gel formation of the alkaline solution by acid titration. The subject invention is directed to all aspects of oil reservoir treatment wherein the above and below mentioned polymer any be used.

The polymer being soluble in alkaline solution makes it an attractive additive to alkaline flooding. Since the viscosity of the alkaline solution is significantly increased, it provides much more favorable mobility ratios which enhance sweep efficiency. The technique can be used as a straight polymer flood, if such is cost effective, or as slug with or without buffer zones. Such may be referred to as "polymer augmented caustic flood".

Perhaps the most important factor which effects volumetric sweep efficiency in secondary oil recovery is the variation of rock permeability with respect to spatial position in the reservoir. Reservoir rock is frequently heterogeneous and sometimes anisotropic. Permeability typically varies both horizontally and vertically across the sand. The largest changes commonly occur in the vertical cross section. When there are large differences in permeability in the vertical cross section, injected fluids tend to flow into and in those regions with highest permeability, bypassing portions of the reservoir which have lower permeability. A significant quantity of oil remains in these bypassed or unswept regions at the time operation of the secondary recovery displacement process becomes uneconomical.

The present invention provides simple and effective techniques to modify the permeability heterogeneity of oil horizons and sands and to block the already swept zones. In a first form of this approach, the pH of the displacing fluids, i.e. water in most cases, is reduced below the pH required for the polymer solution to gel. Injection of the altered pH water may be continued until it is detected in the production well. Injection is then switched to fresh water to insure that the flow lines and the near well-bore zone are free from acidic solution. Injection of polymer in alkaline solution is then undertaken. Polymer solution will gel upon contact with the acid solution blocking the already swept zone.

In some instances it may be desirable to alternate the treatment to make it cost effective. Injection of the acid, fresh water and alkaline-polymer solution are repeatedly

made in the noted sequence to minimize the required quantities of injections of the acid and alkaline-polymer solutions. In this approach, there will be no need for monitoring the produced water from the production well and the effect of higher oil production should be felt sooner.

5 In an alternative approach, alkaline-polymer solution can be injected first, followed by fresh water or brine, if necessary to clear the flow lines and near wellbore zone, then acidic water or CO₂ may be injected. The already positioned polymer solution, presumably at least partly located in the water flooded high permeability zone will gel upon contacting the acidic water or CO₂ being injected which will force any thereafter
10 used displacing fluid such as water flood, polymer flood into the residual oil containing formation zone.

The procedures described above are well suited for even the most homogenous reservoirs. Intrusion of displacing fluid into displaced fluid zones is not because of the heterogeneity of the rock alone, but also because of the relative viscosities of the fluids
15 involved. Viscous fingering, gravity segregation or tonguing are such examples.

Very large permeability contrast in oil sands and formations which have been water flooded in secondary oil recovery result in channels of displacing fluid from injection to production wells. These can be fractures, thief zones or high-permeability zones. Channel detection can be easily achieved by a simple tracer test. The time of
20 tracer detection in the production well is typically very short. Channel blocking can be simply achieved by applying the same techniques as those described above.

One of the major difficulties in open-hole completion of unconsolidated or poorly consolidated sandstone reservoirs, is sand production. Artificial cementation can be achieved in near well-bore treatment by first injecting acid solution, then alkaline-
25 polymer solution (or vice versa also including CO₂). In situ gelation of the polymer solution provides artificial cementation which will inhibit objectionable sand production. Sufficient flow channels into the reservoir from the wellbore can be created by subsequent injection of alkaline solution.

The distinctive features of the present invention in comparison with prior art in
30 situ gelation processes can be elaborated. This is not a cross linking process, but a change in physical morphology due to the reduction of pH. pH is the only variable involved in precipitating polymer from alkaline solution, does not require to be monitored but just requires that the alkaline polymer solutions be lowered to neutrality. The process is time independent and requires no skilled operator to be successful in use.

More importantly, it is reversible. An already gelled zone can be washed by alkaline solution, thus resolubilizing the gelled polymer, and such fluid be moved to lower or deeper regions in the reservoir by fluid drive, then the solution gelled again by injecting acidic solution or CO₂ where the latter is called for. The repeated solubilize/gel cycles do not effect the strength or the effectiveness of the gelation process.

Carbon dioxide is soluble in oil, and the solubility increases as pressure is increased. The dissolved carbon dioxide swells the oil and increases its volume. Solution of carbon dioxide also causes a large reduction in oil viscosity. These two characteristics result in an improvement of immiscible displacement of oil by carbon dioxide.

If the pressure is increased to the minimum miscibility pressure (mmp), the oil and liquid CO₂ become miscible in all proportions. Miscible displacement between oil and carbon dioxide results from hydrocarbon vaporization from the oil into the carbon dioxide. This occurs at the mmp, a relatively high pressure.

Although the pore to pore (microscopic) displacement efficiency of oil by CO₂ is very high in the area reached by CO₂, the overall displacement efficiency over a large block of porous material is often hindered by mobility problems resulting in poor CO₂ sweep efficiency through the reservoir. These mobility problems are largely a result of the lower viscosity and density of the CO₂ phase as compared to the reservoir oil and brine or water phases.

If the displacing fluid is less viscous, and thereby can move more readily than oil, the displacement front will spread into the oil and early breakthrough occurs. Intrusion of the displacing fluid into the oil bank can also occur because of the density contrast. Both conditions, i.e. unfavorable viscosity and density ratios, exist in the case of CO₂ displacement.

Previous studies that were aimed at improving the macroscopic displacement efficiency, or sweep efficiency of the CO₂ recovery process can be categorized in the following areas.

The injection of alternating slugs of CO₂ and water is referred to as the "WAG" (water alternating gas) process. The purpose of the water injection is to decrease the CO₂ permeability relative to the oil permeability, thus retarding adverse movement of CO₂.

The injection of an aqueous surfactant solution in conjunction with the CO₂ phase, which causes a foam to occur. The composite mixture has been found to have lower mobility than CO₂ by itself.

With respect to the direct thickening of CO₂, attempts were made to find a polymer that was soluble in liquid or supercritical CO₂. It was thought that, if such a polymer could be found, the viscosity of the mixture would be higher than CO₂ by itself, thereby improving the sweep efficiency of the CO₂ phase. It has been attempted to achieve the same goal by searching for monomers that are soluble in CO₂ under conditions similar to reservoir conditions. An initiator would then be added to the mixture in an attempt to generate a polymerization reaction.

Despite this multiplicity of approaches, no workable scheme has yet been devised to substantially reduce the mobility of carbon dioxide, thereby to eliminate its early breakthrough. With the subject process, a breakthrough in CO₂ mobility control has emerged.

The herein disclosed invention has resulted, when utilizing CO₂ as a neutralizing agent, in providing a simple and workable technique to reduce carbon dioxide mobility. Early breakthrough of CO₂ occurs because of its channeling through the oil zone. Plugging of these created channels should effectively substantially eliminate CO₂ production at production wells. Such plugging can be achieved by in situ polymer gelation initiated in such channels by the injection of CO₂. The subject bio-polymer is ideal for this purpose. Such polymer dissolves in alkaline solution, yet gels upon reduction of the pH of the solution below 7 or substantial neutralization thereof. The reduction of pH can be achieved by flow of CO₂ through the solubilized, in situ, injected polymer solution.

The polymer is produced by an aerobic type microorganism belonging to the Cellulomonas group of bacteria or others noted herein. The polymer itself has been determined to be a glucan-type polysaccharide. The polymer is completely soluble in 1N NaOH. When its solutions are neutralized or acidified to pH below 7.0 with mineral or organic acids or CO₂, a water insoluble gel is formed.

The two processes below described illustrate of the gelling of alkaline solubilized polymer in situ in oil sands by CO₂:

1. A cylindrical plexiglas tube of approximately one inch diameter and two foot length was filled with the aqueous polymer solution. Carbon dioxide gas was introduced from the bottom of the tube in the form of rising bubbles. The upper outlet of this tube was open to the atmosphere. The rise of the bubbles slowed down upon gelation of the solution. The viscosity of the gelled solution in the tube was measured

using a Brookfield viscosimeter before and after the CO₂ flow, thus confirming the gelation process.

2. An apparatus as shown in Fig. 4 was used in this part of the investigation. The main components are a pump, pressure transducers, a fraction collector and a Berea sandstone core or sandpack.

The core was initially saturated with brine. The permeability of the core was determined knowing the pressure drop and brine flow rate. The brine was then displaced by oil to its connate water saturation, i.e. the saturation that cannot be reduced further by passage of more oil through the core. CO₂ injection was then initiated and the oil recovery thereby was measured. Injection of CO₂ continued until breakthrough of CO₂ occurred. Polymer solution injection was then initiated after the latter stage and any additional oil recovery was measured. Polymer solution injection was then stopped at polymer breakthrough and CO₂ injection was resumed.

In situ gelation of the polymer was induced by the latter CO₂ injection. A change in the pressure gradient along the core was observed. Using a series of pressure transducers equally spaced along the core, as seen in Fig. 4, the pressure gradient along the front segments of the core was plotted versus time. Higher pressure gradients indicated successful gelation. Spread of the length of the gelation zone was evident from the spread of the zone of high pressure gradient combined with increased oil production from the core.

DESCRIPTION OF THE DRAWING FIGURES

Fig. 1 is a schematic procedural delineation of the successive steps in the extraction and purification of exopolysaccharides.

Fig. 2 is a graph showing the effect of nitrogen concentration on biomass and hydrogel production. Bacteria were grown in flask cultures in CM9 medium containing the indicated amounts of ammonium chloride and 4% glucose. Cultures were incubated with shaking (250 rpm) at 30°C for 72 hours. The triangular symbols show biomass, the circular symbols hydrogel.

Fig. 3 shows the time course of growth and polysaccharide production. Bacteria were grown at 30°C, with rapid aeration, in a Biostat table top fermentor (with pH maintained at 6.7). CM9 Culture Medium contains 0.02M NH₄Cl and 2% glucose. Symbols: circular dots, acid; triangles, biomass; squares, polymers; A aggregation first observed by phase contrast microscopy; B macroscopic aggregation.

Fig. 4 is a schematic drawing of a test process to evaluate the injection into an oil sand core of one of the alkaline polymer solutions of this invention with alternate injections of CO₂ gas.

Fig. 5 is a schematic diagram of a process useable to measure oil production from an oil sand core after water drive therethrough.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Cellulomonas flavigena (819) strain KU produces an exocellular polysaccharide which apparently enables the bacteria to adhere to each other, resulting in their aggregation. The polysaccharide is not lost upon extensive subculture, differing at the least in that respect from a glycocalyx. Although the polysaccharide accumulates extracellularly it nevertheless is used as an energy reserve. Energy reserves most commonly accumulate as intracellular deposits or granules.

The specific bacterium noted was originally isolated from leaf litter and has been characterized as Cellulomonas flavigena strain KU (ATCC 53703). Several other species of Cellulomonas which are able to produce a polymer identical to that produced by Cellulomonas flavigena strain KU can also be used. These include Cellulomonas flavigena (ATCC 482), considered to be the type species, Cellulomonas uda (ATCC 491) and Cellulomonas spp. (ATCC 21399).

Cellulomonas flavigena strain KU differs from American Type Culture Collection (ATCC) #482, the strain which is considered to be the type species of Cellulomonas flavigena, in its morphology and the amount of extracellular polysaccharide produced.

Cellulomonas flavigena can be grown in simple salts media that contain carbohydrates as the carbon and energy source and ammonium salts as the nitrogen source. After growth in such media, the bacteria are densely aggregated and when the cultures are allowed to stand the bacteria rapidly settle out of suspension. Electron microscopic examination of cross sections of such cells reveals that they are surrounded by a large capsule. The bacteria contained large amounts of the polymer only when aggregated and encapsulated. Growth of C. flavigena in complex media, such as tryptone broth or nutrient broth, does not result in aggregation of the cells and they are not encapsulated.

When aggregated cells are incubated in a starvation medium, i.e., a medium without a carbon source, they will utilize the capsule as an energy reserve.

The high glucose content of hydrolysates of aggregated cells suggest that capsular energy reserve is, at least in part, a polysaccharide. Figure 1 outlines the steps in a procedure that was used to extract polysaccharide from aggregated C. flavigena strain KU. This procedure takes advantage of the fact that C. flavigena cells that have formed capsules and have become aggregated will rapidly settle out from the growth media when agitation of the culture is terminated. After standing briefly, the cell free upper phase, usually consisting of about 75% of the culture volume, can be removed by aspiration. The remaining cells are then collected by centrifugation and, after being washed with water, are resuspended in 1.0 N NaOH, at a concentration of 1 gm of cells (wet weight)/4 ml of 1.0 N NaOH. Two extractions are sufficient for the removal of at least 95% of the polysaccharide. When the supernatants of the first and second extractions are neutralized with either 50% (w/v) acetic acid or 6 N HCl, the polysaccharide separates out of solution and, in the process, the entire volume of the supernatants congeals. Purification of such hydrogels is readily accomplished by resuspending them in 10 to 20 volumes of water and, after stirring, allowing the water insoluble polysaccharide to settle out. The clear upper phase may then be removed by aspiration. This process may be repeated until the preparation is free of inorganic phosphate and protein.

The chemical composition and solubility characteristics of the polysaccharide extracted from aggregated C. flavigena cells and some properties of the hydrogel formed by it are:

A. Chemical composition

1. Glucose homopolymer in which glucose subunits are joined via B-1,3-glucosidic bonds.
2. Infrared (IR) - nuclear magnetic resonance (NMR) spectra similar but not identical to B-1,3-glucans known as curdlans.

B. Solubility characteristics

1. Soluble in 0.1 N (or greater) sodium- and/or potassium-hydroxide.
2. Soluble in 85% (or more concentrated) formic acid.
3. Soluble in dimethyl sulfoxide (DMSO).
4. Poorly soluble in ammonium hydroxide.
5. Insoluble in water, methanol, ethanol, isopropanol, and acetone.

C. Properties of the hydrogel

1. Resuspension of the polymer at a concentration of 2 mg/ml of water leads to formation of a hydrogel. After centrifugation at 15,000 x g for 15 min 97% of the weight of the hydrogel is accounted for by the entrained water.
2. Heating the hydrogel does not result in solubilization of the polymer.

Exopolysaccharide synthesis often is enhanced by the growth of bacteria in media containing limiting amounts of nitrogen and an excess of the carbon and energy source. The relationship of the nitrogen concentration of the growth medium to the growth of C. flavigena strain KU and the amount of polysaccharide synthesized is shown in Fig. 2. Cellulomonas flavigena strain KU was grown for 72 hours in flasks containing media with the indicated NH₄Cl concentrations. Samples were removed for the estimation of bacterial growth and of the amount of extractable polysaccharide. Growth was estimated on the basis of the wet weight of biomass/ml of culture and estimates of polysaccharide production were based upon the amount of hydrogel which could be obtained from alkaline extracts of the bacteria. To standardize the determination of the wet weights the samples were always centrifuged for 15 min at 15,000 x g. Figure 2 shows that an increase in the concentration of NH₄Cl from 0.005 M to 0.015 M was accompanied by an increase in biomass. Polysaccharide synthesis also increased, but the maximum yield was observed in the medium with 0.01 M NH₄Cl. The decrease in biomass and hydrogel at higher concentrations of NH₄Cl was accompanied by a decrease in pH of the media. Cellulomonas species are facultatively anaerobic and may produce considerable amounts of acid from glucose.

The decrease in the polysaccharide/biomass ratio which was observed in cells grown in media with increasing NH₄Cl concentration presumably was a consequence of the low final pH of the culture media. Accordingly, growth of the bacteria in a 1 liter table top fermentor which provided automatic pH control was examined. Figure 3 shows the results from a culture in which the starting NH₄Cl concentration was 0.02 M and the pH was maintained at 6.7. At the indicated times samples were withdrawn for the determination of biomass and the amounts of reducing sugar in alkaline extracts of them. Examination of the samples by phase contrast microscopy indicated that the cells had begun to aggregate at 22 h and by 24 h the extent of aggregation was such that the cells rapidly settled out of suspension. The final yield of biomass was 71.1 mg/ml (wet weight), in contrast to the yield of 34 mg/ml obtained in shake cultures which also were 0.02 M

with respect to NH_4Cl but which lacked pH control (Fig. 2). The dry weight yield of biomass, determined only on the final sample from the pH controlled culture, was 14.9 mg/ml.

Thus, as has been reported for other bacteria, the synthesis of polysaccharide by C. flavigena is enhanced by low concentrations of inorganic nitrogen. With C. flavigena, however, the inhibitory effect of increasing the nitrogen is a consequence of a drastic decrease in pH, occurring presumably as a consequence of increased cell metabolism. This may also explain why the production of an extracellular polysaccharide by C. flavigena has not been previously reported. It may have been unnoticed because the bacteria do not produce it when they are grown in standard minimal salts media, such as M9, containing the usual 0.018-0.02 M NH_4Cl unless the glucose concentration is at least 1% (w/v). At higher concentrations of glucose the culture becomes so acidic that growth and polymer production are decreased.

The modification of the permeability of subterranean formations can be accomplished either by the use of alkaline suspensions of encapsulated bacteria or by the use of crude extracts of the polymer. Alkaline suspensions can be prepared by simply resuspending the bacteria in 1N NaOH. This step takes advantage of the fact that C. flavigena cells that have formed capsules and have become aggregated will rapidly settle out from the growth media when agitation of the culture is terminated. The resuspension of the cells in alkali results in the extraction and solubilization of the polymer while leaving the bacterial residue in suspension. If partially purified polymer is desired, then the bacteria can be mechanically removed (e.g., by centrifugation) from such suspensions. Neutralization of the alkaline extract which contains cells and/or the cell-free extracts results in gelation of the polymer.

The principal reason for removing the bacterial debris from alkaline suspensions would be to obviate the possibility of an unwanted "plugging" of subterranean strata and/or oil sands. However, starvation of bacteria result in decreasing the size of bacterial cells. Such cells flow into and through high permeability zones in earth formations and oil sands, without any unwanted permeability reduction.

Plugging occurred only when nutrients were introduced, resulting as a consequence of the growth associated increase in size of the bacterial cells. Electron microscopy has been used to demonstrate that, although alkali extracted cells remain structurally intact, they are very prominently reduced in size. Because of their small size, the suspended bacteria also will be able to flow into zones of high permeability, but

because they have been killed by the alkali, they will not be able to grow and cause undesired plugging. Plugging would occur only upon gelation of the polymer dissolved in the sodium hydroxide solution NaOH which also happens to contain the resuspended cells.

5 Certain other polysaccharide, belonging to a family of polymers known as the curdlans, also can be used for permeability modifications in processes identical to those described for the exopolysaccharide product of Cellulomonas. The chemical compositions of the polyglucan produced by the various Cellulomonas species and that of the curdlans are similar, if not identical. All are polyglucan homopolymers in which the glucose
10 subunits are joined via B-1, 3-gluoside bonds. They may differ in degree of polymerization and possibly in the occurrence of a small amount of branching. Because of their solubility in NaOH and their ability to form gels upon neutralization of the alkali, they all are suitable for the in situ permeability modifications of subterranean strata described hereinbefore and hereinafter. The noted curdlans are produced by Alkaligenes faecalis
15 subsp. myxogenes (ATCC 21680, Alkaligenes faecalia (ATCC 31749) and Agrobacterium radiobacter (ATCC 21679).

Looking at Fig. 1, it should be noted that level 2 (allow aggregated cells to sediment) after the supernatant is poured off produces a condition of the bacteria and capsules which may be fed into an earth strata, oil sand or oil formation, per se. At level
20 4, "cell pellet-1", this status of the process may be employed as an input to oil sands or oil formations after the supernatant 1 is discarded therefrom.

With respect to the description of the applications of the new process and methods disclosed herewith, it is assumed for the discussion of the following that there is an oil sand or formation of a given thickness into which at least one injection well has
25 been bored or prepared from an old production well. Primary production has ended in the oil sand and formation with respect to one or more production wells spaced away from and around the injection well, as well as at the injection well itself. The injection well may have been, initially, a production well through which primary production was completed. Thereafter, for at least the said injection well, the wellbore is prepared for
30 input of fluid injection media by any of the well known, standard, conventional and adequate means.

As a typical example, a casing may be run from the surface into and typically through the oil sand in the originally drilled wellbore. This casing may then be perforated by conventional means through the casing and surrounding cement across any

selected vertical portion of the wellbore and cemented casing in the oil sand or the entire face thereof. Then, typically, but not limiting, an injection pipe is run in the wellbore into or through the oil sand, then an injection zone is packed off, above and below the zone which is to be fluid or water injected or yet the entire sand so that the injection pipe perforated zone is exposed only to the casing perforated zone which is desired to be injected or pressurized. The face of the wellbore in or at one or more levels of the height of the sand, in addition to having been perforated, may also have been fractured by conventional means and methods.

Thereafter, in any conventional manner, such as, packing off the perforated sand face or any portion thereof, water flood or water drive or other conventional secondary production method may be undertaken from at least the said injection well to the production well or wells positioned away from but around the injection well. Eventually all of the production wells will be reached by injected fluids, unless thief zones, high permeability zones, etc., delay or screen one or more of the production wells from water drive or other system oil production in secondary recovery.

In the process of fluid drive in secondary oil production, only a certain amount of the oil is driven through the formation to one or more of the production wells. The water or other fluid injected into the injection well usually essentially spread out circumferentially therefrom optimally in a concentric circle manner, but actually in differing profiles as the water flood or other injection encounters low permeability zones, thief zones and the like. Eventually one or more of the production wells produces so much water with any oil produced from the well that it is not economical to continue the water drive. As each production well reaches a selected water/oil-production ratio such well may be closed down from production. This outward fluid migration leaves the circumferential zone around the injection well, to the distance to which the water or other drive has penetrated in any direction through the formation and with respect to the vertical cross section of the formation, with a lot of fluid in thief zones, high permeability zones and zones from which oil has been driven and, typically, with an even greater amount of oil being retained in the sand bypassed by the flow of the fluid fronts circumferentially outwardly through the sand compared to oil produced.

Depending on what is to be accomplished in the previously fluid flooded oil formation, with respect to any given injection well, its wellbore and surrounding sand zones, the following steps take place, in the subject process and variations thereof.

First, a quantity of either acidic water or reversibly gelable, alkaline polymer solution which solution gels upon neutralization and acidification thereof is injected from the injection well into the formation. There is a difference in treatment of the sand available between either first injecting the acidic water or first injecting the polymer solution. That is, the acidic water injection has substantially the same effect as injecting water or brine. Thus, it drives itself into the permeable zones and thief zones following the initial water drive pattern set up therein, probably producing no better results with respect to oil/water ratios in production from the reopened production well or wells. Accordingly, a predetermined quantity of acidic water is injected into the oil sand at the injection well in the quantity needed. Thus, if it is desired to treat a portion of the oil sand relatively close to the injection well, a limited quantity is injected. This quantity can be increased to the extent desired by operator attempting to penetrate with acidic water the original water zones between the injection well and one or more of the production wells. Alternatively, this injection can be continued until acidic water is produced in one or more of the production wells. CO₂ is not used in the subject process as a first injected precipitating fluid or substance.

If the reversibly gelable alkaline polymer solution is first injected into the oil formation or oil sand, considerably different results may be achieved. That is, because of the greater viscosity of this polymer solution, it may cause the production of oil and water in one or more of the reopened production wells at a higher oil/water ration than was produced by fluid drive from the beginning. Accordingly, the injection into the injection well of the quantity of reversibly gelable, alkaline polymer solution (which solution will gel upon one of neutralization and acidification thereof) may be continued for only a short time, effecting only a relatively near portion of the sand surrounding the injection well, any greater quantity and time interval, or until the polymer solution is produced from one or more of the production wells. Thus it is a first advantage of the subject, reversibly gelable alkaline polymer solution here disclosed that it will make more effective and efficient the original fluid drive as the polymer solution is injected further and further into the formation.

The next stage is to preferably clear the inside wellbore injecting zone of either the acidic water or the polymer solution, at least into the face of the formation. Alternatively, this clearing of the acidic water or polymer solution can be effected for a lesser or greater circumferential distance out into the sand from the injection well. This is to insure that the gelling of the polymer upon interaction of the acidic water (or CO₂

when polymer is first injected) and polymer solution will not block or prevent large area injection of the acidic water (or CO₂ when polymer is first injected) or polymer solution.

If, inadvertently, the injection equipment and piping, the annular wellbore in the injection zone and/or the face of the injection zone casing and/or formations are plugged by gelled polymer, injection of NaOH solution will clear such impedances.

The herein described processes may be employed before secondary oil production is used in formation. However, most typically, the depleted oil formation (of gas pressure, formation liquids and the like) has been subjected to any one or more of a conventional secondary recovery process, most particularly considering a water of other fluid drive(s) any one of before, with or after utilizing the secondary recovery process.

A first improved process of the subject methods here disclosed comprises first injecting a selected quantity of acidic (mineral or organic acid) water into the said formation through a well thereinto selected as an injection well. Presumably there are one or a number of surrounding wells to the injection well which will serve as production wells. After the quantity of acidic water has been injected into said formation, most preferably, there is next injected a sufficient quantity of one of water or brine into said formation (after the acidic water injection) whereby to clear the injection equipment, the fluids in the injection portion of the wellbore, and the wellbore face to any predetermined depth of the acidic water injection. The point of this is to avoid immediately clotting and clogging in or at the injection equipment, the wellbore annulus around and/or in the injection well, and the face of the well formation immediately around the injection zone, with the polymer gel to be produced as to be described.

It should be noted that there may be numerous sets of wellbore conditions where the sequential differing injections comprising the subject improvement are involved. For example, a wellbore casing may be cemented from the top of the formation to a considerably level thereabove, whereby materials introduced under pressure have only the oil formation face in the wellbore to impact against. There may have been fracture performed in the wellbore to aid production of oil in the initial stages of production through initial pressure, loss of initial pressure, pumping, etc. The oil horizon may be cased off entirely and shot perforated and/or fractured at one or more levels.

Another variation of preparing the wellbore for the injections is to set a single packer at the bottom of the oil sand, if the wellbore vertically extends past the oil sand face. Still further, one or more additional packers may be employed (together with the positioning of perforations on the vertical injection pipe while closing the bottom end

thereof) to force pressure only against a limited portion of the oil formation or two or more such.

These techniques of isolating the formation and portions thereof do not constitute a part of the subject invention. The invention here is the materials used and the manner and order in which they are used, not in any particular mechanical arrangements of oil formation isolating, oil formation sealing, limitation of portions of the oil formation with respect to injection of fluids and recovery of fluids.

Returning to the first example, there is first injection of a quantity of acidic water into the said formation through the injection well to the extent desired. This may be a very considerable quantity of such, yet, since most injections into oil formations are into the circumferential wellbore around the level of injection, a very considerable quantity of acidic water may be absorbed by the circumferential formation both horizontally and vertically thereinto without moving the water (acid) any great distance radially from the injection well. One extremity of injection of the quantity of acid water into the formation through the injection well would be where the acidic water is injected into the formation in the injection well until is detectable at a production well or several or all thereof. During this injection, any oil or fluids that become available at one or more production wells may be produced, including by pumping from the wellbore.

Secondly, after the injection of a quantity of acidic water into the formation through the injection well, to whatever actual extent and degree such is done, and, as well, after clearing the injection wellbore and sand face of acid, thereafter there is injected a quantity of reversibly gelable, alkaline polymer solution, which solution gels upon one of neutralization and acidification thereof, into said injection well.

When the injection of a quantity of reversibly gelable, alkaline polymer solution begins and continues, penetrating the formation circumferentially and peripherally to the injection well, it is assumed that such gelable alkaline polymer solution will tend to seek zones, areas, paths, etc. of relatively high permeability. However, to the extent that the acidic water is in place therein, there will be, upon neutralization and/or acidification of the gelable alkaline polymer solution, gelling of said latter solution along the line or faces of the bodies of acidic water in the sand, also thrusting somewhat thereinto until the gel builds up into a condition where it repels further penetration of the reversibly gelable alkaline polymer solution into a given acidic water body or quantity located in a given place or zone in the formation.

Two things must be noted with respect to this second injection. In the first place, if pure water drive has been used as a secondary recovery method, the reversibly gelable alkaline polymer solution may not penetrate or will pass along the surface of not only acidic water containing high permeability zones, but also the water or brine containing such. This means that this more dense solution well may produce additional oil at one or more production wells surrounding the injection well both by sealing off acid water containing zones by gelling and penetrating, and driving oil from less permeable zones in the wellbore clear out to the recovery well or production well, not displacing water and brine deposits to any great degree.

There are a number of options which follow after a substantial injection of acidic water into a given injection well and, thereafter, a substantial injection of gelable alkaline polymer solution.

Assuming substantially stoichiometrically equal quantities of acid water and polymer solution have been injected into the well, thereafter water drive may be reinstated until, once again, the oil/water ratio at the production well becomes unacceptable.

If the polymer solution injection is continued until it is detected at the production well, or near such, again, when the oil/water ratio in the production well drops, this injection may cease. In this particular case a further injection of acidic water may follow until such is detected at the production well or, again, oil production at the recovery well drops below commercial.

Once quantities of acidic water and polymer solubilized alkaline mixture injections have been made substantially stoichiometrically equal, a further injection of acidic water may be made at the injection well. This may acidify some or all of the waterlogged high permeability zones deeper in the formation away from the injection well, thus to prepare for another injection of reversibly gelable alkaline polymer solution. The latter gelling will, to a greater or lesser extent or entirely, bar a further penetration of later used drive liquid in the presumably water filled and/or acidic water filled high permeability zones deeper in the formation. Or the gel block of the nearby high permeability zones may be lessened or removed in the event NaOH is injected.

There is the option of thereafter injecting a further quantity of acidic water into the injection well, but this will make some higher permeability zones deeper in the formation acidic. The second option is injecting quantities of reversibly gelable alkaline polymer solution to block off and isolate more permeable formations from less such

before or after the former. Since this solution is always more dense than plain water, at each point it may be used partially, fully or deeper than the penetration of the first and/or second acidic water injection. Still further, after the second gel block off of the depths of the formation beyond the first gel block off, drive water may be injected into the well to further scavenge the lower permeability zones until the water/oil ration at the production well is again uneconomic.

The option of injecting acidic water into the formation through said injection well or wells can extend until the acidic water is detected at one or more of the production wells. This would signal that some of the high permeability zones of water left over from the earlier water flood have been acidified sufficiently to cause gel of the alkaline polymer solution in question. The gelable alkaline polymer solution may further be injected into the injection well until such is detected at one ore more production wells or the oil/water recovery ratio becomes uneconomic.

With respect to the injection of alternative quantities of acidic water and polymer solution in either order, the operator will preferably inject a quantity of one of water or brine into the formation after the first type of injection (acidic water or polymer solution) before the second active ingredient injection (polymer solution or acidic water injection) into the sand whereby to clean out the injection equipment, and clean out the wellbore surface and some depth thereof, before permitting gelation of the polymer.

It should also be understood that fracturing of the formation between two set packers on an injection pipe may be employed before, during or after a first phase of acidic water/alkaline polymer solution injection. Yet further, a casing may be run initially into the well before any of the subject treatment or at any stage thereof, cemented and perforated in the zone of the oil formation in which it is desired to inject the materials.

It is understood that all of these processes may also be carried out in an oil formation wherein there are a plurality of injection wells spaced among a plurality or pluralities of production wells. Optimally for production from one injection well is the case where at least two or more production wells surround or are relatively evenly radially displaced around the injection well.

Where there is an oil formation with a group of wellbores penetrating same in a fairly dense, closely related manner, it should be understood that one or more central wells may serve for a considerable time as an improved injection well with the closest surrounding wells thereto serving as production wells. After the subject process is exhausted from one or one set of injection wells, any one of the production wells or other wells in

the formation related or spaced near the original injection well itself, may be pressed into service as an injection well. The original injection well itself may be changed to a production well or at least sensor containing well.

5 One group of polymer solutions which are reversibly gelable is an alkaline solution of polysaccharide polymer produced by cultivating bacteria of the genus Cellulomonas including at least one of ATCC 21399 (Cellulomonas sp.), ATCC 482 (Cellulomonas flavigena), ATCC 53703 (Cellulomonas flavigena strain KU or 819), and ATCC 491 (Cellulomonas uda.) in a suitable solubilizing medium.

10 With respect to the subject method for the enhanced recovery of oil by injection of flooding reversibly gelable fluid into a subterranean oil bearing formation through an injection well extending from the surface of the earth into the formation, the purpose and effect of such injection being to displace oil within the formation from the injection well towards at least one production well spaced at a distance away from the injection well, the following are the second basic procedures involving initial polymer solution injection.

15 There first is injected into the formation through the injection well a quantity of alkaline, reversibly gelable, polymer solution, which solution gels upon one of neutralization and acidification thereof. This is the reverse of the previously described process and procedure where the acid water initially was injected into the injection well and the formation around the injection well. To ungel a formed gel, NaOH or its alkaline equivalent (KOH or alkaline polymer solution) is injected.

20 As with respect to the initial acid injection method, any part or parts of the formation wellbore face may be isolated for the subject injection. There may or may not be one or more fractures already produced in the wellbore face in the oil formation. One or more fractures may be produced prior to the injection of the first constituent of this process, here the alkaline, reversibly gelable, polymer solution. After this injection water/brine or air injection is carried out to a sufficient extent to clear the injection equipment, the wellbore and some depth into the formation.

25 After any one of the polymer solution quantity injections noted above, a quantity of acidic water of CO₂ may be injected into the same formation or parts thereof through the same injection well, whereby, when the acidic water of CO₂ contacts the polymer solution in situ, such, whether it is in largely high permeability zones or portions thereof or yet in lesser permeability zones, at least some of the polymer solution in the formation, when neutralized or acidized, will gel within the formation, thus tending to block off or restrict entry into the relatively higher permeability zones into which the

polymer solution has penetrated and the zones scavenged by the polymer solution in the initial injection.

While this is done, any oil driven by the acid/CO₂ injection may be produced at the production borehole. To the extent the acidic water or CO₂ penetrates the oil formation and contacts any of the quantity of polymer solution therein contact of the acid water and polymer solution will, to the degree the acid water retains its acidity and, further, to the degree the polymer remains in the polymer solution to be contacted by the acid water, cause gelling and sand pore blocking to take place. Relatively less dense, relatively denser and relatively densest gelation of the polymer by the acid may take place, thereby giving gel layering which layers of gel in the formation may resist penetration thereinto of other fluids yet to be injected.

A first option is to inject enough acidic water to have such be traceable at one or more of the production wells. While this may not produce any additional oil at the production well, this acid injection will prepare those parts or some parts of the formation not yet having any gel treatment thereof to be gelled. Thus, a logical decision for the sequentially third injection (after polymer solution, then acid water) is more polymer solution.

To the extent acid water has preceded it, this injection of polymer solution will gel and block off more high permeability zones as well as swept zones and drive oil before it to the production well where such may be produced. When the gelation of polymer in the oil formation with respect to a given injection well or set thereof has been essentially completed out to said production well or close to it, then further injection of water, or polymer solution will drive oil out of the lower permeability areas of the formation, thus to produce considerably more oil at the production well.

This situation is analogous to the sequence of acid water injection, then polymer solution injection discussed above. In either case, where a gelation has been produced, following a first injection of acid water or a first injection of polymer solution, if there is a gel of greater or lesser dimension produced, in the first case, by polymer solution injection and, in the second case, by acid water injection, any NaOH or alkaline equivalent injection thereafter may tend to dissolve the gel formed. To the extent a dissolved gel, acidizing or neutralizing fluid, or alkaline/water polymer solution exist in the oil sand, further injection of polymer solution thereinto will tend to cause more gelling to the extent such polymer solution is neutralized or acidified. Acid fluid or CO₂ injection will tend to regel and/or gel.

When a third agent such as water or brine is employed in the sequence of the injections, in order to effect gelations within the formation, the alkaline polymer solution must reach a neutral or an acidified state or where polymer solution is present, an acidified solution of CO₂ must reach same, whereby to form gels by neutralization.

5 Where limited quantities of materials are desired to be utilized for limited additional production time at the production well the following may occur:

 A quantity of acidic water is first injected into the formation through the injection well; thereafter, a quantity of reversible gelable alkaline polymer solution is injected, which solution gels upon one of neutralization and acidification thereof into the formation around said injection well.

10 Oil may be producible from the production well during the injection of acidic water, and, thereafter, during injection of said polymer solution. After at least some formation gelling, a drive liquid or fluid may be injected into the injection well while producing at least some oil from said production well. Another quantity of acidic water may thereafter again be injected into the formation through the injection well and, following this:

 Another quantity of reversibly gelable alkaline polymer solution of the same previously described sort may be injected into the injection well to extend the gelling. Oil may be produced from the production well during, first, the second injection of acid water and, thereafter, during the second injection of said polymer solution. Thereafter, a drive liquid may be injected into the injection well whereby to produce at least some oil from said production well.

20 NaOH injections may be employed to dissolve earlier gellings, such solutions moveable further into the formation by water, brine or polymer solutions of this and other type, later to be elsewhere gelled by subsequent acid or CO₂ injections.

25 As previously noted, the options of water or brine may be used for the drive liquid or more alkaline polymer solution, and/or more acidic solution, or another liquid with or without other substances.

30 The acidic water may initially be injected in the formation until it is detectable at the production well. Next, the polymer solution may be injected into the formation in one or more injections until it is detectable at the production well, including possibly producing oil in commercial quantities available in the formation at the production well in said latter process.

In any case, in order to avoid plugging, clogging and coating the injection equipment, gelling materials in the wellbore and gelling across the annulus and into the wellbore face, some neutral (non-gel causing liquid or gas) preferably is used to clean out the injection equipment, the wellbore annulus and the injection face of the formation before further injecting reacting or gelling substances thereinto. (Or NaOH, which is not preferred, except in an actual foulup gelling.)

The opposite method involves first injecting a substantial quantity of reversibly gelable alkaline polymer solution, which solution gels upon one of neutralization and acidification thereof, into the formation through and surrounding the injection well.

Thereafter, a substantial (such as stoichiometrically equal) quantity of acid or CO₂ (which solution gels upon one of neutralization and acidification thereof), is injected into the injection well.

With respect to each above sequential injection, if oil appears at any of the production wells in commercial quantities, such may be produced.

Thereafter, a further quantity of reversibly gelable alkaline polymer solution is injected into the injection well.

Next, a substantial quantity of acidic fluid or CO₂ is injected into the said formation through the injection well whereby to gel, upon one of neutralization and acidification thereof, at least some of the second injected quantity of reversible gelable alkaline polymer solution in the formation; and, producing at the production wells any additional oil appearing during said second set of injection.

Thereafter, a drive fluid (water, brine, acidic water, CO₂, air or additional reversibly gelable alkaline polymer solution) may be injected into said injection well whereby to produce at least some additional oil from said production well.

It should be understood that one of the drive fluids (not acidic water, CO₂, or soluble polymer solution) disclosed in the prior art, including other polymer containing liquids, such also including water, may be employed at any time in these processes as a drive liquid to substitute for water, brine or other components of the specific process here disclosed.

Where sequential alkaline polymer solution and acid water solution or CO₂ injections, in whatever order, are employed preferably some nonreactable or nongelling liquid or fluid, such as air, water or brine, should be employed to clear the injection equipment, the wellbore, and the immediate wellbore formation face before the opposite member of the pair of the gel producing materials follows. Alkaline solution injection

will clear any actual equipment, wellbore and formation face and deeper gel effects not desired.

To carry the maximum amount of polymer into the depths of the sand/formation, gelled earlier stages may be dissolved in alkali and driven further into the sand by injection of more alkaline polymer solution and then this deeper penetrating body of alkaline polymer solution gelled by acid or CO₂ injection.

It is best to clean out the injecting equipment, the wellbore annulus and the face of the formation or perforated casing between successive reactant or reagent injections. This may be accomplished, first, by injecting air, water or brine following each injection to have a circumferential plug of such fluid through which, in the next stage, the first one of the gelling agents may dissolve backwards thereinto to ultimately make gelling contact. On the other hand, where there is a wellbore annulus surrounding the injection pipe or tubing, a liquid may be used to backflash the annulus and the injection equipment forced into the annulus and back up the injection pipe or tubing such as water, brine or drilling mud. Gases such as air and nitrogen may also be used in this procedure.

If there is a any gel plugging that interferes with the process in or on the injection equipment, wellbore annulus or wellbore face, alkaline solution or polymer alkaline solution (KOH or NaOH polymer solution, etc.) should be injected to dissolve the gel.

In addition to the preferred acids comprising hydrochloric acid (HCl) and acetic acid, sulfuric and nitric acids will also work as a reactant or reagent, but are considerably more corrosive. With respect to hydrochloric acid, for example, the polymer solution in 0.1 N sodium hydroxide requires an equivalent amount of 0.1N HCl to get all the polymer precipitated. Likewise, the polymer solution in 1.0 N alkaline polymer solution requires an equivalent amount of 1.0 N hydrochloric acid to get the solution.

Where there are a plurality of production wells and any particular stage in the subject process is being used and one or more of the production wells begin producing a lower than satisfactory oil-water ratio, while the other wells are producing satisfactory oil-water ratios, the operator may close off the less productive wells. Alternatively, with respect to a less productive well, this well can be used as an alkaline polymer solution injection well until the production oil-water ratio at that well is corrected.

Alkaline (NaOH, KOH, polymer solution, etc.) injection serves these useful purposes: To clear the clogged injection wellbore, injection equipment and wellbore faces; dissolve the gel body or bodies of polymer in the formation and move same deeper

into the formation; and clear any production well gel cloggings if such occur. Injecting the alkaline polymer solution, particularly with a stronger alkalinity, will achieve the same purposes as alkali itself.

5 The portion of the oil formation and the wellbore that is to receive the injection of the fluids of the subject invention may be isolated in any suitable conventional manner. Thus, if the wellbore casing is merely cemented to the top of the oil sand or well formation, then an input pipe or tubing (with a plugged lowest end and perforations opposite the wellbore zone to be treated) inside the casing may be rigidly set in the wellbore with packers filling the annulus between the injection pipe and the wellbore face, provided that the wellbore face will hold the seal at the packers under the necessary 10 pressurization. In this process, the packers are set above and below the vertical area of the wellbore face to be worked. Such portion of the wellbore face portion intended to increase permeability and recovery and/or injection efficiency in the zone fracture. Further, after the packers are set or the critical portion of the wellbore face is otherwise 15 isolated, then fracturing may or may not be employed either before the beginning of the subject process or thereafter at any stage during same.

In another alternative, the wellbore casing is extended through and cemented through a portion or the entire vertical cross sectional face of the sand. In this case, in 20 certain heights and portions of the face of the casing and the cement surrounding, same may be perforated or shot in conventional manner to give access therethrough to the formation. In this case, an injection tubing with the lower end closed and perforations in the wall of the tubing to be set opposite the perforated zone and the oil sand may be run into the wellbore and set in position with packers to the casing above and below the wellbore face zone to be worked.

25 Where the particular oil horizon, sand or formation includes a highly porous, readily collapsing wellbore face or there is a particular quantity of loose formation or sand in the wellbore itself, the following process is useful. It is first desired to consolidate any loose formation or particles or sand into the mass at the bottom of the wellbore. Either polymer solution or acid is run into the wellbore in the critical zone 30 followed either by equipment clearing brine, water, nitrogen or air or, alternatively, the excess first fluid may be backflushed as set forth above. Then other reagent is injected to gel the loose mass of sand. If it is desired to plug the horizon in the wellbore or wellbore annulus, one need run in only as much air, water or brine required to clear the injection pipe or tubing.

If a lot of loose sand has been gelled in the lower portion of the wellbore, in the formation, or below the formation, after the initial gelling to consolidate the loose sand, packers may isolate the portions of the wellbore face or perforated wellbore casing for treatment by one or more of the subject processes.

5 Referring to Fig. 1, therein is shown a schematic procedural delineation of the successive steps in the extraction and purification of the exopolysaccharides useable in this invention. At 10 is the culture of the bacteria in its suitable medium. At 11, with respect to the Cellulomonas bacteria, the aggregated cells may be permitted to sediment. At this point, after pouring off the supernatant above the aggregated cells, the aggregated
10 cells may be dissolved in alkali (NaOH or KOH) thus giving solubilized polymer and the bacterial cells. This stage, at 11, after pouring off the supernatant, may be employed in the subject process once the polymer is dissolved in alkali with the cells remaining in suspension at 11a.

At 12 there is a centrifugation step as indicated resulting with supernatant 1 to
15 the right at 13. This supernatant is discarded. The discard of supernatant 1 at 13 leaves at 14, to the left, the first cell pelletization which includes both the cell bodies and the precipitated polymer. At 15 alkali (here typically 1N sodium hydroxide) is added to the first cell pelletization step and, upon stirring, the polymer is dissolved. After another centrifugation step at 16, the second supernatant at 17 is poured off, neutralized with acid
20 at 18 which precipitates the insoluble polysaccharide polymer at 19. Most of the polymer is recovered at this stage.

The residue from centrifugation step 16 is a second cell pelletization stage at 20 and has a small amount of polymer. As in the case of the first pelletization stage, one normal sodium hydroxide may be added with stirring at 21. There is then a third
25 centrifugation step at 22 which leaves, after pouring off the supernatant, the third stage of cell pelletization at 23. Supernatant 3 at 24 is then neutralized with acid at 25, whereby to precipitate the remainder of the insoluble polysaccharide at 26. The material at stages 19 and 26 may be used in the process by dissolving the polysaccharide in alkali to achieve an alkaline polymer solution without the cell bodies therein. If there is no
30 objection to the cell bodies being included in the alkaline polymer solution used in the processes, which is usually the case, such is useable at stages 11a and 15.

Fig. 4, is a schematic flow diagram of producing carbon dioxide induced gelation in an oil sand core. The main components of Fig. 4 are a container or flask of alkaline solution at 27, line 28 to pump 29 and line 30 from pump 29 to three-way valve 31.

From one of the two outputs from the valve, line 32, having pressure gauge 33 thereon, receives carbon dioxide from carbon dioxide cylinder 34. Line 35 goes from the second output of valve 31 to the input side of core 36. Thus it can be seen that, alternatively, alkaline polymer solution and carbon dioxide may be fed to the core 36 through line 35. One or more inlets to the valve may be added as discussed herebelow. Pressure transducers 37 and 37a-37d, inclusive are linked to successive portions of the core sample. From the output side of core 36, line 38 goes to fraction collector 39.

Core 36 is initially saturated with brine. The permeability of the core is determined, knowing the pressure drop and the brine flow rate. The brine is then displaced by oil to its connate water saturation, i.e., the saturation that cannot be reduced further by passage of more oil through the core. A carbon dioxide injection is initiated and the oil recovery is measured. Injection of carbon dioxide continues until the breakthrough of CO₂ occurs. Alkali solubilized polymer injection will then be initiated at this stage and the additional oil recovery will be measured. Polymer injection will be stopped at polymer breakthrough and CO₂ injection will be resumed.

When in-situ gelation of polymer induced by CO₂ occurs, then a change in the pressure gradient along the core will be observed. Using a series of pressure transducers, equally spaced along the core, the pressure gradient along different segments of the core will be plotted versus time. Higher pressure gradient is an indication of successful gelation. A spread in the length of the gelation zone will be evident from the spread of the zone of high pressure gradient. Such an observation, combined with the increased oil production is an indication of successful process.

Fig. 5 shows a simple core testing process wherein container or flask 40 may contain either alkaline polymer solution or acidic water or two flasks may be provided with one having the alkaline polymer solution and the other having the acid therein. Through line 41 one of acid or alkaline polymer solution is first passed to pump 42 whose discharge line 43 has pressure gauge 44 thereon. Line 43 leads into the selected input side of oil sand core 45. The outlet line 46 from the other (selected output) end of the core preferably has gauge 47 thereon. A battery of transducers like that seen in Fig. 4 is connected to successive longitudinal zones of the core 45.

With respect to Fig. 5, the core or sand pack 45 is initially saturated with brine. The permeability of the sand core, sand pack or sand bed is determined, knowing the pressure drop and the brine flow rate. Porosity of core 45 is determined by knowledge

of the volume of the core, the weight of the core and its density. Brine is then displaced in core 45 by oil to its connate water saturation.

Oil injection is then switched to a solution of the polymer in container 27 (polymer dissolved in alkali). This solution is injected through lines 41 and 43 into the sand pack until at least the first segment of the core or sand pack is flooded. This is determined by the pressure drop reading of the first segment compared to the rest of the sand pack. The difference in the pressure drop reading is due to the difference in the viscosity of the bio-gel solution with respect to that of the brine.

The injection of the polymer solution may be stopped at this stage and switched to an acidic solution such as hydrochloric acid, acetic acid, or gas such as CO₂. Such acid or gas would come from another line (not shown) joining line 43 with a pump thereon. Gelation starts in the first segment of the core of the sand pack because of the direct or delayed mixing of the acidic solution, or CO₂, with the alkaline polymer solution already residing in that segment. This is detected by increased pressure readings because of the partial plugging caused by the precipitated gel.

Input of the acid solution or CO₂ is then switched to input of alkali, or the alkaline polymer solution. The first gel breaks in the presence of the alkali or the solubilized polymer solution, at least in part, thus to produce a more dilute alkaline polymer solution. Injection of the alkali or alkali solution polymer is continued until the resolubilized alkaline polymer solution reaches the second or third segment of the sand pack. Input is then switched back to input of the acid solution or CO₂ such through line 32, to create the reoccurrence of the gelation in the second or third segment of the sand pack.

Alternatively, the acid solution, preferably hydrochloric or acetic acid, is first injected into the core through lines 41 and 43 followed by the injection of the polymer solution from container 40 and lines 41 and 43 before or after nonacidic water injection. This latter order of events will not work with carbon dioxide.

The sequential injection of the acid and alkaline polymer solution, or vice versa, including optional use of CO₂, is continued until the alkaline polymer solution is produced from the exit end of sand pack 45. The use of this method and process produces significantly higher oil recovery. Such recovery depends on how well the water bypassing channels are plugged during the periods of gelation and gel recurrence.

As many possible embodiments may be made of the invention without departing from the scope thereof, it is to be understood that all matter herein set forth or shown

in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

CLAIMS

1. In a method for enhanced recovery of hydrocarbon fluids by the injection of a flooding fluid into a subterranean hydrocarbon fluid bearing formation through an injection well extending from the surface of the earth into the formation, to
5 displace in situ hydrocarbon fluids from the formation towards at least one production well spaced at a distance away from the injection well, the improvement which comprises:

(1) injecting a quantity of acidic water into the said formation through said injection well,

(2) injecting a quantity of reversibly gelable, water insoluble, alkaline beta 1,3 polyglucan polymer solution, which solution gels immediately upon one of neutralization and acidification thereof, into said injection well and
10

(3) injecting a drive fluid into said injection well and producing at least some hydrocarbon fluids from the said production well.

2. A process as in Claim 1 wherein the polymer solution is produced by cultivating bacteria of the genus Cellulomonas, including at least one of ATCC 21399 (Cellulomonas sp.), ATCC 482 (Cellulomonas flavigena), (Cellulomonas uda) ATCC 491 and ATCC 53703 (Cellulomonas flavigena 819).
15

3. A process as in Claim 1 wherein the polymer solution which is reversibly gelable is a solution of polysaccharide polymer produced by cultivating bacteria including at least one of Alkaligenes faecalis sub sp. myxogenes (ATCC 21680), Alkaligenes faecalis (ATCC 31749) and Agrobacterium radiobacter (ATCC 21679).
20

4. A process as in Claim 1 wherein the polymer solution which is reversibly gelable is an alkaline solution of polysaccharide polymer produced by cultivating bacteria including at least one of Alkaligenes faecalis subsp. myxogenes (ATCC 21680), Alkaligenes faecalis (ATCC 31749), Agrobacterium radiobacter (ATCC 21679), Cellulomonas sp. (ATCC 21399), Cellulomonas flavigena, (ATCC 482), Cellulomonas uda (ATCC 491) and Cellulomonas flavigena 819 (ATCC 53703).
25
30

5 5. In a method for the enhanced recovery of hydrocarbon fluids by injection of a flooding fluid into a subterranean hydrocarbon fluid bearing formation through an injection well extending from the surface of the earth into said formation, whereby to displace hydrocarbon fluids within the formation towards at least on production well spaced at a distance away from the said injection well, the improvement which comprises:

 (1) first injecting into the formation through the injection well a quantity of alkaline, reversibly gelable, polymer solution, which solution gels upon one of neutralization and acidification thereof,

10 (2) thereafter, second, injecting a quantity of one of acidic water and CO₂ into the said formation through the said injection well, whereby to neutralize at least some of said polymer solution in the formation and thus gel same in said formation, and

15 (3) thereafter, third, injecting a drive fluid into said injection well and producing hydrocarbon fluids driven thereby from the production well.

6. A process as in Claim 5 wherein the said reversibly gelable, basic polymer solution, which solution gels upon one of neutralization and acidification thereof, is produced by cultivating at least one of the bacteria of the genus Cellulomonas, such as ATCC 21399 (Cellulomonas sp.), ATCC 482 (Cellulomonas flavigena), ATCC 53703 (Cellulomonas flavigena 819), and ATCC 491 Cellulomonas uda.

7. A process as in Claim 5 wherein the polymer solution which is reversibly gelable is a solution of polysaccharide polymer produced by cultivating bacteria including at least one of Alkaligenes faecalis subsp. myxogenes ATCC 21680, Alkaligenes faecalis (ATCC 31749) and Agrobacterium radiobacter (ATCC 21679).

8. A process as in Claim 5 wherein the polymer solution which is reversibly gelable is a solution of polysaccharide polymer produced by cultivating bacteria including at least one of Alkaligenes faecalis subsp. myxogenes (ATCC 21680), Alkaligenes faecalis (ATCC 31749), Agrobacterium radiobacter (ATCC 21679), Cellulomonas sp. (ATCC 21399), Cellulomonas flavigena (ATCC 482), Cellulomonas flavigena 819 (ATCC 53703) and Cellulomonas uda (ATCC 491).

9. A process as in Claim 4 wherein the said drive fluid is selected from the group consisting of water, brine, acidic water, a polymer solution and CO₂.

5 10. In a method of enhanced recovery of hydrocarbon fluids by injection of a flooding fluid into a subterranean hydrocarbon fluid bearing formation through an injection well extending from the surface of the earth into the formation, whereby to displace in situ hydrocarbon fluids within the formation toward at least one production well at a distance from the injection well, the improvement which comprises the following steps:

10 Step 1: injecting a quantity of acidic water into the said formation through said injection well, and producing hydrocarbon fluids from said production well;

15 Step 2: injecting a quantity of reversibly gelable alkaline polymer solution, which solution gels upon one of neutralization and acidification thereof into said injection well, and producing hydrocarbon fluids from said production well;

Step 3: injecting a drive fluid into said injection well and producing hydrocarbon fluids from said production well;

20 Step 4: injecting a quantity of acidic water into the said formation through said injection well, and producing hydrocarbon fluids from said production well;

25 Step 5: injecting a quantity for reversibly gelable, alkaline polymer solution, which solution gels upon one of neutralization and acidification thereof, into said injection well, and producing hydrocarbon fluids from said production well;

Step 6: injecting a drive fluid into said injection well and producing hydrocarbon fluid from said production well.

11. In a method of producing enhanced recovery of hydrocarbon fluids by the injection of a flooding fluid into a subterranean hydrocarbon fluid bearing formation through an injection well extending from the surface of the earth into the formation, to displace in situ hydrocarbon fluids from the formation towards at least one production well at a distance from the injection well, the improvement which comprises:

5 (1) first injecting a substantial quantity of acidic water into the surrounding formation through said injection well, said quantity insufficient to be detected at the production well;

10 (2) thereafter, second, injecting another substantial quantity of reversibly gelable, alkaline polymer solution, which solution gels upon one of neutralization and acidification thereof, into said injection well,

(3) with respect to each said first and second sequential injections into the formation, producing any additionally available hydrocarbon fluids at the production well;

15 (4) thereafter injecting (third) a further quantity of reversibly gelable alkaline polymer solution, which solution gels upon one of neutralization and acidification thereof, into said injection well in substantial quantity and

20 (5) next injecting (fourth) a comparable quantity of acidic water into the said formation through the said injection well whereby to gel, upon one of neutralization and acidification thereof, at least some of any yet ungelled, gelable, alkaline polymer solution, and

producing hydrocarbon fluids at the production well.

12. In a method for the enhanced recovery of hydrocarbon fluids by injection of a flooding fluid into a subterranean, hydrocarbon fluids bearing formation through at least one injection well extending from the surface of the earth into the formation, to displace hydrocarbon fluids within the formation towards at least one production well spaced away a substantial distance from said injection well, the improvement which comprises:

(1) first injecting into the formation through the injection well a quantity of reversibly gelable alkaline polymer solution, which solution gels upon one of neutralization and acidification thereof,

(2) thereafter, second injecting one of a quantity of acidic water and CO₂ into the said formation through the said injection well whereby to at least neutralize some of said polymer solution in the formation thereby to gel same in said formation,

(3) further injecting, third, a second quantity of alkaline, reversibly gelable, polymer solution, which solution gels upon one of neutralization and acidification thereof, and

(4) thereafter injecting, fourth, a quantity of one of acidic water and CO₂ into the formation through the said injection well whereby to neutralize at least some of said polymer solution in the formation and gel same while in the formation, and

(5) producing hydrocarbon fluids at said production well.

13. In a method for enhanced recovery of hydrocarbon fluids by the injection of at least one flooding fluid into a subterranean hydrocarbon fluid bearing formation through an injection well extending from the surface of the earth into the formation, whereby to displace in situ hydrocarbon fluids from the formation toward at least one production well spaced at a distance away from the said injection well, the improvement which comprises:

(1) first injecting a substantial quantity of acidic water into said formation through said injection well,

(2) thereafter injecting into said formation a quantity of reversibly gelable, water insoluble alkaline beta 1, 3 polyglucan homopolymer solution, which solution gels immediately upon one of neutralization and acidification thereof into said injection well, and

(3) producing at least some hydrocarbon fluids from the said production well.

14. In a method for the enhanced recovery of hydrocarbon fluids by injection of a flooding fluid into a subterranean hydrocarbon fluid bearing formation through an injection well extending from the surface of the earth into said formation, whereby to displace hydrocarbon fluids within the formation toward at least one production well spaced at a distance away from said injection well, the improvement which comprises:

(1) first injecting into the formation through the injection well a quantity of reversibly gelable water insoluble, alkaline beta 1,3 polyglucan homopolymer solution, which solution immediately gels upon one of neutralization and acidification thereof,

(2) thereafter, second, injecting a quantity of one of acidic water and CO₂ into the said formation through the said injection well, whereby to neutralize at least some of said polymer solution in the formation and thus gel same in said formation, and

(3) producing hydrocarbon fluids from the production well.

15. A method of selectively sealing relatively more permeable, undesirable, fluid passing porous sand strata in an earth formation exposed to an input well of an artificial, fluid drive, secondary recovery hydrocarbon fluid producing system without sealing off less permeable, desirable, fluid less passing strata exposed to the input well, comprising the steps of:

(1) stopping the fluid drive into said input well;

(2) injecting into said input well an alkaline solution of reversibly gelling polysaccharide polymer, whereby the said polymer containing solution preferentially flows into the pores of the more permeable, undesirable fluid passing, porous and strata and not preferentially into the pores of the less permeable, desirable, initially fluid nonpassing and sand strata;

(3) subsequently injecting one of a mineral acid, an organic acid and CO₂ to neutralize the initially injected alkaline polymer solution, such neutralizing resulting in precipitating of at least some of the said polymer in said pores of the more permeable, less desirable, fluid passing strata, thus to at least partially seal off said last strata and at least partially confine further fluid injection into the less permeable, more desirable, initially fluid nonpassing, porous sand strata; and

(4) reinstating the fluid drive into the said input well utilizing one of air, water, brine, acidic water, alkaline polymer solution and CO₂.

16. The method of selectively sealing relatively more permeable, undesirable, fluid passing, porous sand strata in an earth formation exposed to an input well of an artificial, fluid drive, secondary recovery, hydrocarbon fluid producing system without sealing off less permeable, more desirable, fluid-nonpassing sand strata exposed to the input well, comprising the steps of:

5

(1) stopping the fluid drive into the said input well;

(2) injecting one of a mineral acid and an organic acid into said input well, whereby said acid injection is preferentially received in the said relatively more permeable, undesirable, fluid-passing porous sand strata;

10

(3) subsequently injecting into said input well an alkaline solution of a reversibly gelling polysaccharide polymer, whereby at least some of the polymer is precipitated at least in the outer pores of the said more permeable, undesirable, fluid passing, porous sand strata, thus to at least partially seal off said last strata and at least partially confine further fluid injection into the less permeable, more desirable, initially fluid nonpassing, porous sand strata,

15

(4) and reinstating the fluid drive into the said input well, utilizing at least one of water, brine, acid water, solubilized alkaline polymer solution and CO₂.

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17. A method for carrying out a secondary recovery crude oil recovery operation from a crude oil and water containing earth formation, wherein fluid is injected through a fluid input well and then into the oil and water bearing formation in a fluid drive, such producing an oil and water flow into an oil output well, said oil and water being produced from said output well, comprising:

(1) stopping any fluid drive into said input well;

(2) injecting a reversibly gelable, solubilized polysaccharide polymer in an alkaline medium into said input well and thence into at least some of the water wet portions of said formation, whereby the said solubilized polymer solution primarily contacts pore surfaces of the water-wet portions of the formation,

(3) while said latter portion of said formation is wet with said polymer solution, injecting one of acidic water and carbon dioxide into said formation through said input well to at least partially precipitate some of said polymer in said water wet formation portion, and

(4) reinstating said fluid drive at said input well and producing oil and water from said output well in said crude oil recovery operation, said oil and water being produced in a higher oil to water ratio than prior to injection of the said alkaline medium polymer solution into said formation.

18. A method for carrying out a crude oil secondary recovery operation from a crude oil and water containing earth formation, wherein fluid is injected through a fluid input well and then into the oil and water bearing formation, such producing an oil and water flow into an oil output well, said oil and water being produced from said output well, comprising:

(1) stopping any fluid drive into said input well,

(2) injecting acidic water into said input well and thence into at least some of the water-wet portions of said formation, whereby the said acidic water primarily contacts pore surfaces of the water-wet portions of the formation,

(3) while said latter portion of said formation is wet with said acidic water solution, injecting a reversibly gelable, solubilized polysaccharide polymer in an alkaline medium into said input well to at least partially precipitate some of said polymer in said water wet formation portions; and

(4) reinstating said fluid drive at said input well and producing oil and water from said output well in said crude oil recovery operation, said oil and water being produced in a higher oil to water ratio than prior to injection of said acidic water into said formation.

19. A process of carrying out a fluid drive system in a permeable, porous earth formation body having hydrocarbon fluids therein comprising injecting into said body an alkaline medium containing solubilized, reversibly gelable, water insoluble beta 1,3 polyglucan homopolysaccharide polymer which solution gels immediately upon one of neutralization and acidification thereof, and recovering hydrocarbon fluids from said body.

20. In the recovery of oil from a reservoir having at least one high permeability zone therein by injecting a drive fluid to displace oil toward a second well, the method comprising the steps of:

5 (1) injecting as said driving fluid in said first well an alkaline solution of regelable polysaccharide polymer until the drive fluid containing said polymer breaks through into the second well,

(2) producing oil from the second well until said solution breaks into the second well,

10 (3) terminating the injection of fluid into said first well,

(4) introducing into the reservoir from the second well one of a mineral acid, an organic acid and CO₂ which will neutralize at least part of the said driving fluid and precipitate at least some of said polymer within said reservoir, and

15 (5) thereafter injecting a driving fluid into one of said wells comprising one of water, brine, acidic water, solubilized polymer solution and CO₂ and producing oil from the other well.

21. In the recovery of oil from a reservoir having at least one high permeability zone therein by injecting a driving fluid into a first well to displace oil toward a second well, the method comprising the steps of:

20 (1) injecting a first driving fluid of acidic water into said first well;

(2) producing oil from the second well until the acidic driving fluid breaks through into the second well,

25 (3) terminating the injection of fluid into the first well;

(4) introducing into the reservoir from said second well an alkaline medium in which there is solubilized, regelable polysaccharide polymer, whereby to precipitate at least some of said polymer from said alkaline medium upon neutralization thereof by contact with said previously injected acidic driving fluid, and

30 (5) thereafter injecting a driving fluid comprising one of water, brine, acidic water, solubilized polymer and CO₂ into one of said wells, and

(6) producing oil from the other of said wells.

22. A method of selectively plugging earth formations with a gel-like precipitate of a regelable polysaccharide polymer comprising the steps of:

(1) injecting into the formation an alkaline medium containing regelable, solubilized polysaccharide polymer; and

(2) thereafter injecting into said formation one of a mineral acid, an organic acid and CO₂ whereby to precipitate at least a portion of said polysaccharide polymer in said earth formation.

23. A method of selectively plugging earth formations with a gel-like precipitate of regelable polysaccharide polymer comprising the steps of:

(1) injecting into the formation a quantity of one of a mineral acid and an organic acid; and

(2) thereafter injecting into said formation an alkaline medium containing regelable, solubilized polymer, whereby to precipitate at least a portion of said polysaccharide polymer in the said earth formation.

24. A process for recovering crude oil from a subterranean oil formation, which comprises injecting into said formation through an input well communicating with said formation on alkaline flooding medium having dissolved therein a reversibly gelable water insoluble beta 1,3 polyglucan homo polysaccharide polymer, which solution gels immediately upon one of neutralization and acidification thereof whereby oil is displaced in the formation toward at least one output well communicating with the same formation.

25. A method for recovering oil from heterogeneous oil bearing formations penetrated by an injection well and a spaced production well, which comprises:

selectively readjusting the permeability of the said formations by introducing thereinto through said injection well, in sequence:

a solution of a first reactant material;

a solution of a second reactant material that reacts with said first reactant material, on contact therebetween in the formation, to produce a plugging precipitate at least at the interface between said injected solutions; and

the plugging precipitate being resolubilizable upon introducing into said formation a solution of at least one component of one of said reactant materials.

26. A method of consolidating an unconsolidated underground zone penetrated by a well which comprises:

(1) injecting an alkali medium solution of a reversibly gelable polysaccharide polymer through said well into said zone; and

(2) thereafter injecting one of a mineral acid, an organic acid and CO₂ able to neutralize said alkaline polymer containing medium and precipitate at least some of said polymer in said zone.

27. A method of consolidating an unconsolidated underground zone penetrated by a well which comprises:

(1) injecting one of a mineral acid and an organic acid through said well into said zone; and

(2) injecting thereafter an alkaline medium solution of reversibly gelable polysaccharide polymer through said well into said zone, whereby said acid is able to neutralize at least some of said alkaline polymer containing medium and precipitate at least some of said polymer in said zone.

AMENDED CLAIMS

received by the International Bureau on 3 October 1990 (3.10.90);
original claim 1 amended; other claims unchanged (1page)]

1. In a method for enhanced recovery of hydrocarbon fluids by the injection of a flooding fluid into a subterranean hydrocarbon fluid bearing formation through an injection well extending from the surface of the earth into the formation, to
5 displace in situ hydrocarbon fluids from the formation towards at least one production well spaced at a distance away from the injection well, the improvement which comprises:

(1) injecting a quantity of acidic water into the said formation through said injection well,

10 (2) injecting a quantity of reversibly gelable, water insoluble, alkaline beta 1,3 polyglucan homopolymer solution, which solution gels immediately upon one of neutralization and acidification thereof, into said injection well and

(3) injecting a drive fluid into said injection well and producing at least some hydrocarbon fluids from the said production well.

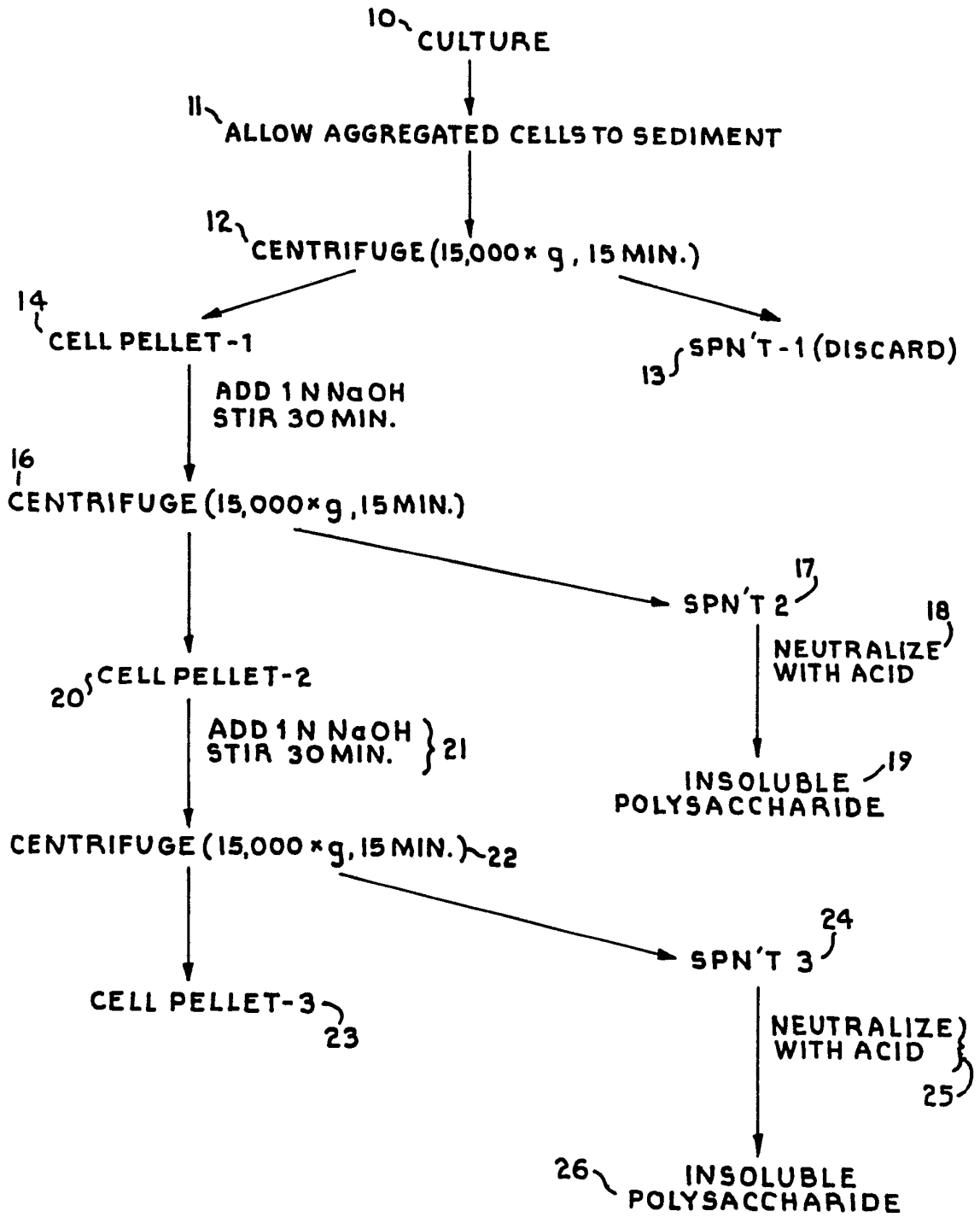
15 2. A process as in Claim 1 wherein the polymer solution is produced by cultivating bacteria of the genus Cellulomonas, including at least one of ATCC 21399 (Cellulomonas sp.), ATCC 482 (Cellulomonas flavigena), (Cellulomonas uda) ATCC 491 and ATCC 53703 (Cellulomonas flavigena 819).

20 3. A process as in Claim 1 wherein the polymer solution which is reversibly gelable is a solution of polysaccharide polymer produced by cultivating bacteria including at least one of Alkaligenes faecalis sub sp. myxogenes (ATCC 21680), Alkaligenes faecalis (ATCC 31749) and Agrobacterium radiobacter (ATCC 21679).

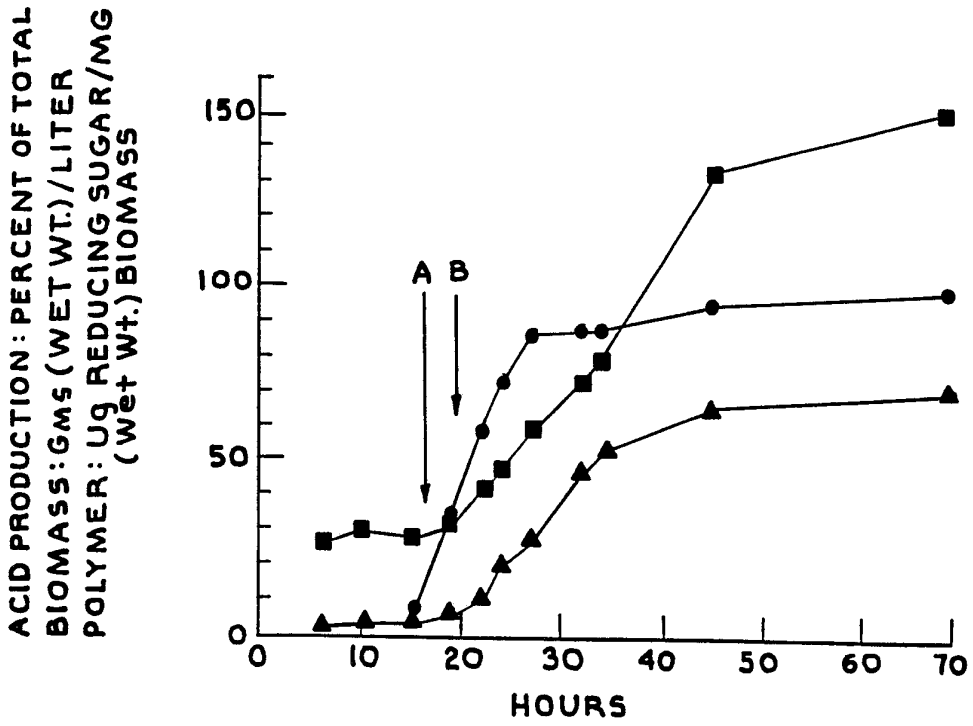
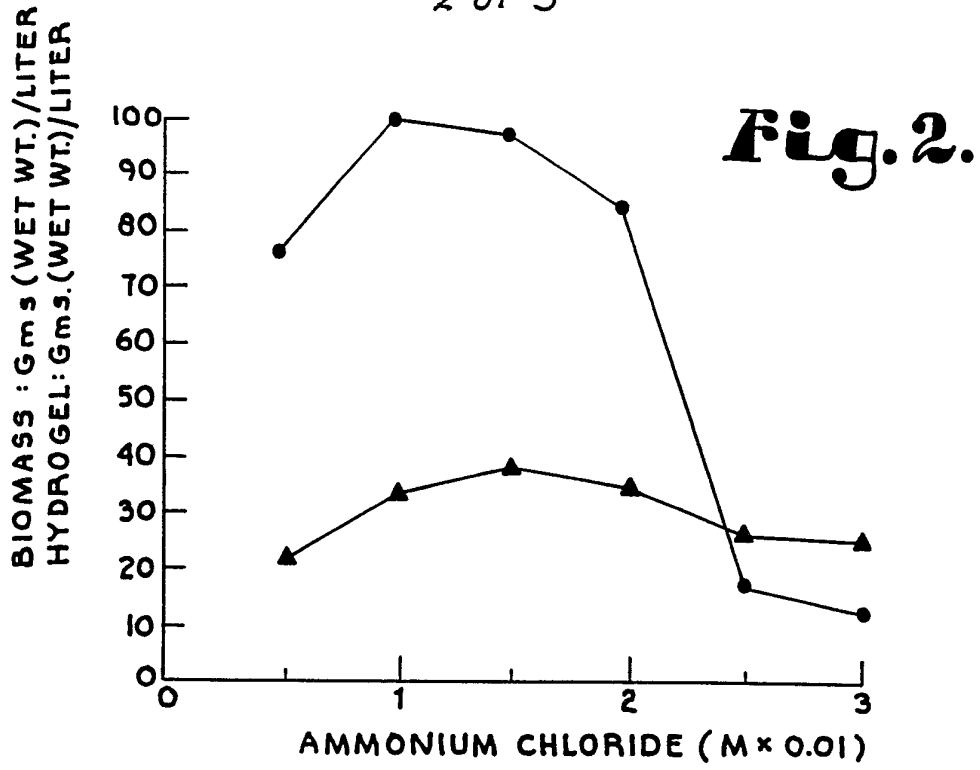
25 4. A process as in Claim 1 wherein the polymer solution which is reversibly gelable is an alkaline solution of polysaccharide polymer produced by cultivating bacteria including at least one of Alkaligenes faecalis subsp. myxogenes (ATCC 21680), Alkaligenes faecalis (ATCC 31749), Agrobacterium radiobacter (ATCC 21679),
30 Cellulomonas sp. (ATCC 21399), Cellulomonas flavigena, (ATCC 482), Cellulomonas uda (ATCC 491) and Cellulomonas flavigena 819 (ATCC 53703).

1 of 3

Fig. 1.



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Fig. 4.

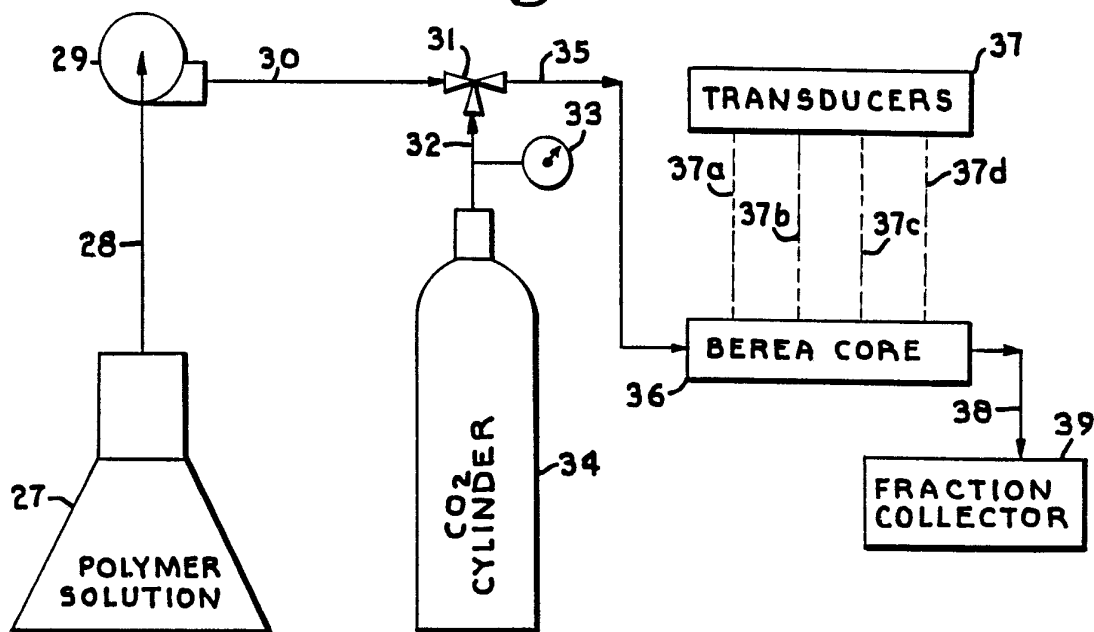
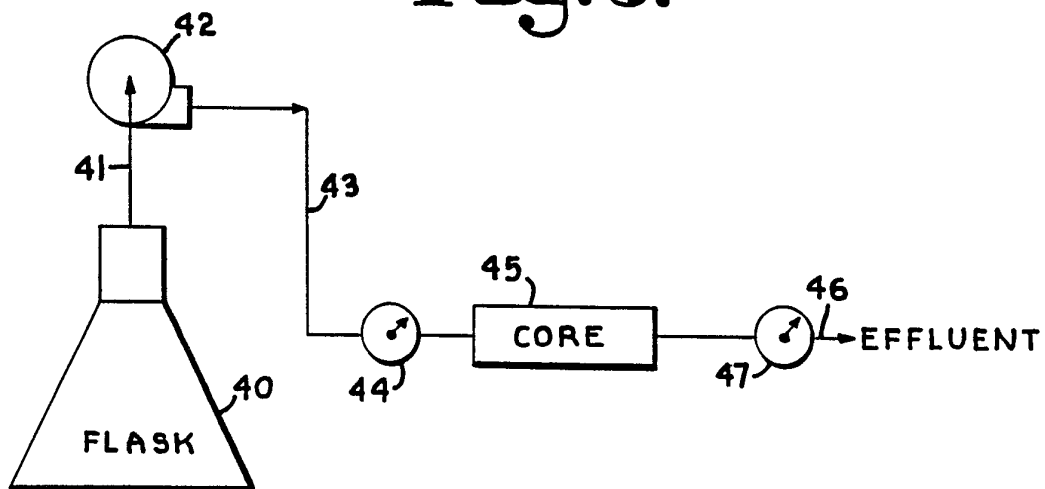
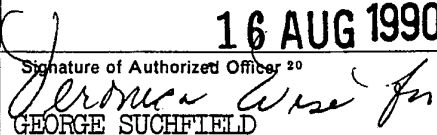


Fig. 5.



INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/02438

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC(5): E21B 33/138; E21B 43/22; E21B 43/27; E21B 47/00 U.S. CL.: 166/252,246,270,271,273,294,300		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	166-246,252,270,271,273,274,275,281,292,294,295,300 252-8.554 530-130,132 536-114	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 2,747,670 (KING ET. AL.) 29 May 1956.	
A	US, A, 2,903,065 (HOLBROOK ET. AL.) 08 September 1965.	
A	US, A, 3,208,518 (PATTON) 28 September 1965.	
A	US, A, 3,372,748 (COOK) 12 March 1968.	
A	US, A, 3,404,734 (RAIFSNIDER) 08 October 1968.	
A	US, A, 4,384,044 (KIM ET. AL.) 17 May 1983.	
A	US, A, 4,413,680 (SANDIFORD ET. AL.) 08 November 1983.	
A	US, A, 4,548,268 (STIPANOVIC) 22 October 1985.	
A	US, A, 4,569,393 (BRUNING ET. AL.) 11 February 1986.	
A	US, A, 4,658,898 (PAUL ET. AL.) 21 April 1987.	
A	US, A, 4,670,550 (BLEEKER ET. AL.) 02 June 1987.	
<p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ²	
19 JULY 1990	16 AUG 1990	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 GEORGE SUCHFIELD	