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(57) Abstract: The invention relates to the treatment of polymer produced water to enable efficient de-oiling using conventional separation technologies based on turbulent flow, such as hydrocyclones (HCs) and Compact Flotation Units (CFUs). In particular it relates to such treatment involving mechanical degradation of the polymer whereby to reduce its average molecular weight prior to de-oiling. This process is particularly suitable for use in enhancing recovery of crude oil from polymer enhanced oil recovery floods used to maximise the production of crude oil from reservoirs.



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Process

Technical field

The present invention relates generally to the field of enhanced oil production and recovery and, in particular, to the removal of residual oil from water produced from polymer flooded reservoirs (herein referred to as “polymer produced water”).

More specifically, the invention relates to the treatment of polymer produced water to enable efficient de-oiling using separation technologies based on turbulent flow, such as hydrocyclones (HCs) and Compact Flotation Units (CFUs).

Background of the invention

Crude oil is a limited resource and thus it is important to maximise its recovery from existing oil reservoirs. Conventional recovery methods include primary production and secondary water flooding, however these result in a significant quantity of crude oil remaining in the reservoir. Enhanced oil recovery (EOR), also known as tertiary recovery, refers to various techniques for increasing the amount of crude oil that can be extracted from an oil reservoir. Such techniques include thermal recovery, gas injection and chemical injection. Using EOR, 30 to 60% or more of a reservoir's original oil can be extracted compared to 20 to 40% using primary and secondary production methods.

Chemical enhanced oil recovery (cEOR) is expected to play a major role in the future of global crude oil production. cEOR methods include the use of polymer floods, such as surfactant-polymer (SP) floods and alkali-surfactant-polymer (ASP) floods, in which a combination of materials including a water-soluble polymer is injected into the reservoir, typically in a brine solution. The precise nature of the polymer is generally not relevant provided this can increase the viscosity of the injected water.

Polymer flooding is a well-known technique which has been used for many years. It can result in a significant increase in oil recovery compared to conventional water flooding techniques and is now considered to be technically and commercially proven. Compared to other EOR

methods, it is simple, cost effective, low risk and has the advantage that it can be used over a wide range of oil reservoir conditions. The effect of polymer flooding is most pronounced for heavy oils, but also reservoirs with light oils can benefit from polymer flooding, especially when these suffer from severe reservoir heterogeneity.

In polymer flood techniques, a high molecular weight polymer is dissolved in the injected water (typically in an amount ranging from 500 to 2,500 ppm) to increase its viscosity and to increase the sweep efficiency in the reservoir. When water is injected into an oil reservoir it finds the path of least resistance. Where the remaining oil has a higher viscosity than the injected water, the water will finger through this oil and effectively bypass it (this is known as the “fingering effect”). This results in low sweep efficiency and a loss in recovery of oil. By decreasing the mobility ratio between the water and oil, sweep efficiency is enhanced. This results in a higher recovery of oil from the reservoir.

A typical polymer flood process involves mixing and injecting polymer until about half of the reservoir pore volume has been filled. Depending on the oil and reservoir conditions, polymer can either be injected continuously over a period of years to reach the desired pore volume or as a “slug” process. The resulting polymer “slug” is followed by continued long term water flooding to drive the polymer “slug” and the oil bank in front of it towards the production wells. Where polymer is added to the water flood to improve oil recovery from reservoirs, the polymer eventually breaks through from the reservoir and into the production wells. This can typically occur some years after start-up of polymer flooding, and will increase gradually. At polymer breakthrough, the polymer passes into the oil processing train and produced water treatment system topside.

Polymers known for use in polymer flooding are generally categorised into two types: polyacrylamides and polysaccharides (biopolymers). The choice of polymer depends on field characteristics such as reservoir conditions (pH, temperature and pressure) and water chemistry. The most widespread polymer flood technique uses acrylamide-based polymers, for example polyacrylamide (PAM) and hydrolysed polyacrylamide (HPAM); these are much cheaper than polysaccharides and not affected by bacteria. Examples of acrylamide-based polymers which are used in enhanced oil recovery are those sold under the tradename Flopaam® by SNF Floerger.

When used in polymer flooding, polyacrylamides undergo partial hydrolysis which gives rise to anionic carboxyl groups scattered along the backbone of the polymer. Typical degrees of hydrolysis may be in the range of 25-35%; hence the HPAM molecule is negatively charged which accounts for many of its physical properties. The degree of hydrolysis can be selected to optimise certain properties such as water solubility, viscosity and retention - if the degree of hydrolysis is too small, the polymer will not be water-soluble, whereas if it is too large the polymer will be too sensitive to salinity and hardness of the reservoir water. The viscosity-enhancing property of HPAMs lies in their long chain lengths and thus high molecular weights (typically these will have an average molecular weight in the range of 10 to 20 MDa). This property is further enhanced by the anionic repulsion between individual segments in the polymer molecules. This repulsion contributes to chain extension, thereby resulting in high viscosity.

Extensive research and development, as well as field practices have demonstrated improvements in oil recovery using polymer flooding, however, the development of effective methods for processing of the polymer produced water following recovery of the oil is required. The polymer produced water needs to be cleaned, for example to remove any residual oil, but due to its enhanced viscosity and other polymer related properties not all conventional produced water treatment technologies can be used. At present, the treatment of produced water containing polymer (e.g. HPAM) therefore becomes a bottleneck in the oil production process. This is a particular problem offshore where there is less capacity for intensive water treatment methods.

Onshore experience with polymer flooding has shown that effective treatment of polymer produced water is possible, but it involves treatment systems and methods which are large and heavy. These are not suitable for implementation offshore where compact and lightweight technologies are required. Offshore the polymer produced water needs to be cleaned at a surface installation prior to re-injection into the well or discharge into the sea.

Conventional methods for treatment of oil contaminated water (produced water) typically employ turbulent flow to separate and remove residual oil from produced water streams. Hydrocyclones (HCs) and Compact Flotation Units (CFUs) are examples of state-of-the art technologies for the

treatment of produced water offshore to separate residual oil. These utilise accelerated gravity in turbulent flow to increase the de-oiling efficiency. HCs separate oil from produced water by application of a centrifugal force, whereas CFUs use gas flotation and additional centrifugal forces to separate and remove oil from produced water.

Large scale testing has shown that HCs and CFUs do not perform efficiently for de-oiling of produced water when polymer is present. This is a problem for all oils due the rheological properties of the polymer produced water. When polymer is present, the water phase acts like a non-Newtonian system with shear-thinning viscosity. Shear-thickening, viscoelasticity, and drag reduction may also be observed, for example when using HPAM polymers. The high viscosity, drag reduction capability, and non-Newtonian behaviour of the fluid, caused by the presence of the polymer, has a dramatic effect on its separation performance, even at very low polymer concentrations (e.g. as low as 30 ppm). The long chain molecular structure of the polymer also has a negative effect on the centrifugal force in the HC and CFU units – under high velocity (i.e. turbulent flow) the polymer acts as a drag reducer and the chains uncoil and align the flow, reducing the pressure drop and swirl velocity. As a result, oil separation efficiency is dramatically reduced.

A need thus exists for alternative methods for handling of polymer produced water, especially in offshore oil production processes. In particular, a need exists for such methods which are capable of producing an efficient separation and removal of residual crude oil from polymer produced water so that the resulting treated water can either be re-used (i.e. re-injected into the reservoir) or safely discharged into the sea.

The present invention is intended to solve or at least alleviate the problems identified above. An object of the invention is thus to provide a process for enhancing the removal of residual oil from polymer produced water. A further object is to provide a process which improves the separation efficiency of produced water treatment technologies employing turbulent flow, especially those that are typically used offshore such as HCs and/or CFUs.

Specifically, the present inventors now propose a pre-treatment method which involves degradation of the polymer in order to reduce its molecular weight prior to processing of the polymer produced water using separation technologies which rely on turbulent flow. Although

not wishing to be bound by theory, it is believed that degradation of the polymer molecules to reduce their chain length (and thus their molecular weight) is effective to reduce their drag reduction capability and in turn improve the efficiency of a separation process which relies on turbulent flow.

The processes and apparatus herein described represent a significant improvement in the efficiency of separation of residual crude oil from polymer produced water compared to the methods and apparatus known and presently used.

Summary of the invention

In one aspect the invention provides a method of separating residual crude oil from a polymer produced water stream, said method comprising:

- (a) degrading at least a proportion of the polymer contained in said polymer produced water stream; and
- (b) subjecting the resulting degraded polymer produced water stream to turbulent flow whereby to cause separation of at least a proportion of the residual crude oil from said stream.

In a further aspect the invention provides a method of recovering crude oil from a crude oil-containing formation, said method comprising:

- (a) providing a composition comprising water and a water-soluble polymer to a crude oil-containing formation;
- (b) allowing the composition to contact with at least a proportion of the crude oil in said formation;
- (c) recovering from said formation an emulsion which comprises crude oil, water and said polymer;
- (d) subjecting said emulsion to a demulsifying process whereby to produce crude oil and a polymer produced water stream containing residual crude oil;
- (c) degrading at least a proportion of the polymer contained in said polymer produced water stream; and

- (d) subjecting the resulting degraded polymer produced water stream to turbulent flow whereby to cause separation of at least a proportion of the residual crude oil from said stream.

The invention further provides apparatus adapted for use in carrying out the methods herein described. Thus, in a further aspect the invention provides apparatus comprising:

- (a) degradation means configured to degrade at least a proportion of polymer contained in a polymer produced water stream; and
- (b) at least one separator configured to impart turbulent flow to the resulting degraded polymer produced water stream whereby to cause separation of at least a proportion of residual crude oil contained therein.

Detailed description of the invention

The present invention describes a process for treating a crude oil-containing stream which contains a water-soluble polymer added to enhance recovery of crude oil from an oil reservoir (also referred to herein as a “crude oil-containing formation”).

A mixture of crude oil and water (which contains the water-soluble polymer) is collected from the production well and brought to the surface where it is separated into an oil stream and an aqueous stream. In one embodiment, the process of the invention thus involves an initial step of separating water from a stream which contains crude oil, water and the water-soluble polymer, for example using conventional separation techniques such as demulsification. This initial separation of water from oil may be referred to as “bulk separation” and may involve one or more bulk separation steps employing one or more separators, such as demulsifiers or coalescers.

Following bulk separation, the resulting water stream contains residual crude oil, water and the water-soluble polymer (referred to herein as “polymer produced water”). In a process carried out upstream of a further separation step (or steps) to remove residual oil, this water stream is subjected to a polymer degradation process. As will be understood, where more than one bulk separation step is carried out (e.g. in parallel or in series), multiple water streams may be produced. It is envisaged that each of these streams will be treated in accordance with the

methods herein described in order to degrade the polymer material prior to further processing to separate residual oil.

As used herein, the terms “degradation” and “degrading” are to be construed broadly and are intended to encompass any procedure which results in scission of one or more covalent bonds in the backbone of the polymer and thus rupture of the polymer. A “degraded” polymer should be construed accordingly. A “degraded polymer produced water stream” refers to a polymer produced water stream in which at least a proportion of the polymer material has been degraded.

As will be understood, the result of degradation as herein described is a reduction in the molecular weight of the polymer, more particularly a reduction in its average molecular weight (e.g. its weight average molecular weight).

Polymers for use in EOR (e.g. polyacrylamide and HPAMs) will typically have a weight average molecular weight in the region of between 10 and 20 MDa. Degradation of the polymer in accordance with the process of the invention results in a reduction in this weight average molecular weight. The desired extent of degradation will vary depending on the nature of the polymer material, its concentration and its initial molecular weight. Typically, the weight average molecular weight of the polymer might be reduced to below 5 MDa, preferably below 4 MDa, e.g. below 2 MDa. The extent of degradation of the polymer may correspond to a reduction in its weight average molecular weight of the order of about 60 to 90%, preferably about 70 to 80%, e.g. about 75%. The extent of degradation required can be determined by the skilled person taking into account factors such as the nature of the polymer material (e.g. its molecular weight), its concentration, and the method to be used to remove residual oil using turbulent flow.

Degradation of the polymer may also have the effect of reducing the viscosity of the polymer produced water stream. The reduction in viscosity will similarly be dependent on the nature of the polymer material (e.g. its molecular weight) and its concentration, but the desired degree of reduction can be determined by those skilled in the art. In one embodiment, degradation may reduce the viscosity of the polymer produced water stream by about 60 to 90%, preferably about 70 to 80%, e.g. about 75%.

Degradation of the polymer as herein described may be achieved by any suitable means known in the art. This may include chemical or physical means, or a combination of these. Suitable chemical means of degradation include polymer oxidation and hydrolysis. Typically, degradation of the polymer will be achieved by physical means, for example by mechanical means such as mechanical shearing (e.g. mechanical high shearing).

Any mechanical means capable of rupturing one or more bonds in the backbone of the polymer may be employed and suitable processes and apparatus are conventionally known. Mechanical means capable of imparting a rapid change in pressure (e.g. which rapidly accelerate the stream thereby subjecting it to a rapid pressure drop) or which are capable of imparting a shear force (preferably a high shear force) will typically be used.

Equipment capable of imparting a high shear force to the polymer produced water stream includes, for example, pumps such as centrifugal pumps, electric submersible pumps (ESPs), etc. Low shear pumps, for example piston pumps and membrane pumps, may also be used but will be less efficient. Although these are generally less efficient, the required degree of polymer degradation can still be achieved by multiple passes of the stream or, more typically, by using more than one of these pumps connected in series. Any of the pumps herein described may be used singly or degradation may be carried out in stages using more than one pump connected in series.

Examples of equipment capable of imparting a rapid change in pressure include valves, for example choke valves, pressure reducing valves, etc. When using a valve the extent of degradation of the polymer is governed by the pressure drop across the valve and so the choice of particular valve is less important. Depending on the pressure drop which can be achieved across the chosen valve a single valve may be used, however, it is envisaged that multiple valves in series will generally be required to impart the necessary degree and uniformity of polymer degradation.

A further example of equipment which may be used to degrade the polymer is a mechanical coalescer.

Any combination of the various mechanical means herein described may also be used to carry out degradation of the polymer.

The desired degree of polymer degradation will be dependent on various factors, including the nature of the polymer material, its average molecular weight, the initial viscosity of the polymer containing stream, the separation method to be used to remove residual crude oil, etc., but may be selected by the skilled person having in mind these various factors. The extent of degradation should preferably be such that all or substantially all polymer molecules will be reduced in chain length. Uniformity of degradation of the polymer is also considered to be important since even a few remaining long-chained polymer molecules can have a negative impact on the efficiency of the separation method - it is believed that drag reduction is much more sensitive to the concentration of long-chained molecules rather than the absolute viscosity of the fluid. Treatment of the polymer containing stream should thus preferably be carried out in such a way as to reduce (e.g. to minimise) the number of long-chained polymer molecules. Generally, this will necessitate the use of repeated degradation steps. This may be achieved by multiple passes of the stream through a single degradation unit (e.g. a pump or valve) or, more typically, by the use of multiple degradation units. Where more than one piece of equipment is used to achieve degradation, these may be the same or different. Combinations of valves and pumps may, for example, be used.

The extent of polymer degradation may, for example, be calculated according to the measurable change in viscosity of the polymer produced water, e.g. according to the following equation:

$$\text{Mechanical degradation (\%)} = \frac{\eta_0 - \eta}{\eta_0 - \eta_w} \times 100 (\%)$$

where η_0 is the initial viscosity of the solution, η is the final viscosity of the solution following degradation, and η_w is the viscosity of water. A reduction in viscosity in the region of about 60 to 80% may be considered sufficient in some cases, although as discussed above the number of long-chained polymer molecules that may remain in the fluid is also an important factor in influencing separation efficiency. Degradation should preferably result in degradation of substantially all (e.g. all) polymer molecules, e.g. less than 5ppm, preferably less than 2ppm, more preferably less than 1ppm, of the polymer molecules should retain their original chain length.

Water-soluble polymer materials which can increase the viscosity of an aqueous solution and which are thus suitable for use in EOR processes are well known in the art. Those which give rise to problems in separation of residual crude oil from polymer produced water using turbulent flow technologies are those which act as a drag reducer. Examples of such polymers are the acrylamide-based polymers such as polyacrylamide and hydrolysed polyacrylamide (HPAM). Hydrolysed polyacrylamides will usually be partially hydrolysed meaning that the polymer contains repeating units of both acrylamide and acrylic acid (in which the hydrogen of the carboxylic acid may be replaced by an alkali metal cation, e.g. a sodium ion). The degree of hydrolysis may vary and is not critical. Typical degrees of hydrolysis may range from 15 to 35%. These may have a broad molecular weight range, e.g. ranging from $2\text{--}20 \times 10^6$ Daltons up to $50\text{--}60 \times 10^6$ Daltons. State of the art EOR polymers typically have an average molecular weight in the range of about 10 to 20 MDa with a high molecular weight tail at about 50 to 60 MDa.

Several acrylamide-based polymers are commercially available for use in oil recovery methods, for example those sold under the tradename Flopaam® by SNF Floerger. Suitable examples include Flopaam® 3630 (which is a partially hydrolysed polyacrylamide), or Flopaam® 5115 (which is a synthetic sulphonated terpolymer).

Following degradation of the polymer the resulting “degraded polymer produced water” is treated in a downstream process in order to remove the residual crude oil. This step is carried out using a separation method which uses turbulent flow, typically one which is capable of use in a continuous flow system. This step may involve multiple separation steps or a single separation step depending on the efficiency of separation at each stage.

The “degraded polymer produced water” is routed to the separator (or separators). If required, for example where the pressure is low, it may be pumped to the separator. Following separation, the oil-rich flow is routed from a reject outlet of the separator, and the cleaned water (i.e. water-rich flow) is vented from the underflow outlet at the same time.

Suitable devices for separation of oil and water mixtures by subjecting the mixture to turbulent flow are well known to those skilled in the art for use in produced water treatment. Those based on cyclone technology are widely used, e.g. hydrocyclones. Other devices include compact

flotation units (CFUs). More than one separator may be used, e.g. in parallel or series, in order to handle high oil-in-water concentrations. Where more than one separator is used, these need not necessarily be identical. Combinations of HCs and CFUs connected in series may, for example, be employed.

HCs and CFUs are widely used and available from a number of suppliers, including Schlumberger, Cameron, Aker Solutions and FMC Technologies.

For use in offshore treatment, the separators should be lightweight and compact in design. HCs and CFUs are particularly suitable for use in this regard.

Axial flow or tangential hydrocyclones may be used. Axial flow hydrocyclones rely on an axial swirl principle in which fluid enters axially and a swirl element is used in order to develop a spin. In a tangential hydrocyclone fluid enters via multiple tangential inlets.

Hydrocyclones which are conventionally used in oil production may be used. Each liner may be capable of treating several m³ per hour of produced water, and they will be used in a sufficient number to treat the entire water stream. Suitable operating parameters, i.e. inlet pressure, outlet pressure, pressure differential ratios (PDRs) and reject rates may be selected by those skilled in the art - it is envisaged these will be similar or the same as those conventionally used for treatment of ordinary produced water (i.e. where polymer is not present). The pressure drops over water and reject outlets may increase, but not much. The reject rate will also increase if the same PDR is selected.

Compact flotation units use gas flotation and additional centrifugal forces to separate and remove oil from produced water. CFUs conventionally used in oil production methods may be employed in the invention under operating conditions typically used for polymer-free produced water.

The efficiency of separation in the HC or CFU may be determined in accordance with the scaling models which are conventionally used for hydrocyclones and CFUs (without polymer). These take viscosity and droplet size into account, but not drag reduction. When the polymer

produced water has been sufficiently degraded as herein described (i.e. to remove the drag reduction capability, although some viscosity may remain) it follows the established models.

Following separation the treated polymer produced water may be routed to a degasser whereby to release any gases. Further it may then be treated for particle removal, cooled and pumped prior to re-injection.

As a result of the separation process the resulting water phase will have a low oil content and will be "on specification" for re-injection into the formation or discharge into the sea.

When used in EOR processes water-soluble polymer materials will typically be used in combination with at least one surfactant, e.g. a mixture of surfactants. Surface active agents adsorb at the oil-water interface and serve to lower the oil-water interfacial tension. This leads to the mobilisation of trapped residual oil droplets in the reservoir. In addition to water, oil and polymer, the oil / water solutions herein described may thus further comprise at least one surfactant, e.g. an anionic surfactant.

Other components which may be present in the oil / water mixtures herein described include components which may be present in compositions used to aid in the recovery of crude oil from an oil reservoir. This includes, for example, alkaline agents. Carboxylate soaps are formed when crude oil (which contains acidic components) reacts with hydroxide ions in an alkaline solution. These soaps (known as "petroleum soaps") are capable of adsorbing at the oil-water interface and further lowering the oil-water interfacial tension. Alkaline agents which may be present include salts of alkali and alkaline earth metals, e.g. alkali metal carbonate salts, alkali metal bicarbonate salts, and alkali metal hydroxide salts. In these salts the alkali metal ion may be lithium, sodium, potassium or caesium. Typically it will be sodium or potassium. Examples of suitable alkaline agents which may be present therefore include sodium carbonate, sodium bicarbonate, sodium hydroxide, potassium carbonate, potassium bicarbonate and potassium hydroxide.

Further components which may be present in the oil / water mixtures include various production chemicals such as demulsifiers, scale inhibitors, etc.

The invention further relates to apparatus which is specifically adapted for carrying out the methods herein described. Such apparatus comprises degradation means which is capable of degrading at least a proportion of polymer contained in a polymer produced water stream, in addition to a separator configured to impart turbulent flow to the resulting degraded polymer produced water stream. As will be understood, this separator must be positioned downstream of the degradation means. Typically the degradation means and the separator will be directly connected to each other.

The apparatus according to the invention may comprise more than one degradation means and/or more than one separator which employs turbulent flow. Suitable examples of this equipment are provided above in relation to the method of the invention.

Additional components which may be provided as part of the apparatus of the invention include one or more bulk separators positioned upstream of the degradation units. The bulk separators are units capable of separation of oil and water to produce an oil stream and an aqueous stream (which contains the water-soluble polymer). Examples are provided above in respect of the method and include demulsifiers.

The methods and apparatus herein described may be used in de-oiling of any polymer produced water resulting from an EOR treatment. The oil may be any oil, including medium and heavy oils.

The methods and apparatus can be employed both onshore and offshore, but preferably these will be used offshore.

Figure 1 is a schematic representation of one embodiment of a process and apparatus for the treatment of polymer produced water in accordance with the invention. The crude-oil containing emulsion (1) from the formation is subjected to demulsification prior to treatment in a 1st stage separator (2), 2nd stage separator (3) and electrostatic coalescer (4) (these steps are herein referred to as "bulk separation"). Polymer produced water from the 1st stage separator (2) is routed to degradation unit (5) prior to separation in the 1st stage hydrocyclone (6). Polymer produced water from the 2nd stage separator (3) and electrostatic coalescer (4) is routed to degradation unit (7) prior to separation in the 2nd stage hydrocyclone (8). Separated oil exits the

1st stage hydrocyclone (6) through flow line (11) and the 2nd stage hydrocyclone (8) via flow line (12) and is routed back to the bulk separation stage. Water streams containing polymer and any residual oil exit the 1st stage hydrocyclone (6) through flow line (13) and the 2nd stage hydrocyclone (8) through flow line (14), respectively. These water streams are combined and fed into compact flotation unit (9) for further separation of water and any residual oil. The separated oil exits the compact flotation unit (9) via flow line (15) and is routed back into the bulk separation stage. Water containing the degraded polymer exits the CFU via line (16) and is routed into degasser (10). Following the release of any gas, the treated water is either discharged into the sea or, following treatment in a sand cyclone (17), is fed to water-injection pumps ("WI pumps") for re-injection into the formation. Any residual oil released following degassing is pumped via flow line (18) back to the bulk separation stage.

The hydrocyclones utilise the pressure energy of the fluids present in the production separators and convert this into centrifugal swirling flow which generates very high g-forces (800-1000g) over the very short residence time through the equipment. The fluids inside each hydrocyclone produce a double vortex with the heavier water phase migrating to the outside walls and the lighter oil phase displaced towards the inner vortex. The oil is concentrated within the inner vortex and rejected through the overflow for which the flowrate is controlled by the PDR (pressure differential ratio). The separated produced water exits via the underflow and the oil concentration of the water outlet, compared with the inlet, determines the hydrocyclone oil removal efficiency.

The separated produced water from each hydrocyclone is transferred to the compact flotation unit (CFU). While a hydrocyclone uses centrifugal forces to separate oil droplets from the water, a CFU uses gas flotation, i.e. oil droplet-gas bubble coalescence resulting in improved gravimetric separation of lower density oil droplet/gas bubble agglomerates. In the CFU a cyclonic flow pattern may be generated by introducing the fluids via tangential inlets near the top of the vessel. The cyclonic flow pattern makes the flow inside the CFU turbulent and forces the gas bubbles towards the centre, sweeping the entire volume efficiently. The centrifugal force may be of the order of 1G. The separated produced water is then discharged from the bottom of the vessel and the oil/gas reject flow is discharged from the top of the vessel.

Produced water treatment chemicals are typically based on the coagulation and flocculation processes. Coagulation is a process that encourages small droplets of oil to merge or coalesce to form larger droplets. Flocculation is a process that agglomerates small droplets and solids into clusters. Both coagulation and flocculation serve to concentrate the contaminants which helps improve the speed of separation from water. In Figure 1 a flocculant is added upstream of the CFU.

Oil droplet size is an important parameter when it comes to separation of water and oil. Mechanical coalescers provide large surfaces of oleophilic material on which oil droplets can congregate and coalesce into larger droplets. Such mechanical coalescers may be installed upstream of the hydrocyclones and/or the CFU to facilitate oil droplet coalescence and hence improve the performance of the downstream separation process.

The invention is described in more detail by way of the following non-limiting example and the accompanying figures, in which:

Figure 1: Schematic diagram showing a water treatment system in accordance with the invention.

Figure 2: Schematic diagram of the apparatus used in the Porsgrunn water rig.

Figure 3: A typical hydrocyclone liner.

Figure 4: Graph showing the change in differential pressure with changing flow rate in a hydrocyclone.

Figure 5: Graph showing the viscosity change of the produced water during testing.

Figure 6: Graph showing the pressure drop between the inlet and outlet pressure of the hydrocyclone for different concentrations of HPAM.

Figure 7: Graph showing the pressure drop between the inlet and the reject pressure of the hydrocyclone for different concentrations of HPAM.

Figure 8: Graph comparing the pressure drop between the inlet and outlet of the hydrocyclone for two concentrations of HPAM.

Figure 9: Graph comparing the pressure drop between the inlet and reject of the hydrocyclone for two concentrations of HPAM.

Figure 10: Graph showing the reject flow rate for sea water and different concentrations of polymer.

- Figure 11: Graph showing the variation in Johan Sverdrup oil droplet size distribution upstream and downstream of the hydrocyclone when no polymer present.
- Figure 12: Graph showing the variation in Johan Sverdrup oil droplet size distribution upstream and downstream of the hydrocyclone when 500 ppm HPAM is present.
- Figure 13: Graph comparing experimentally obtained and modelled oil removal efficiencies.
- Figure 14: Graph showing the variation in Peregrino oil droplet size distribution upstream and downstream of the hydrocyclone with no polymer present.
- Figure 15: Graph showing the variation in Peregrino oil droplet size distribution upstream and downstream of the hydrocyclone when 500 ppm HPAM is present.
- Figure 16: Graph showing the Peregrino de-oiling efficiency.

Example

Studies were carried out in the Statoil Porsgrunn Water rig to determine the effect of HPAM polymer on de-oiling of synthesised produced water at different concentrations and degrees of mechanical degradation.

1. Materials:

Flopaam® 5115SH is a synthetic sulphonated terpolymer made by SNF Floerger. In addition to acrylamide and acrylate it also contains sulphonated groups that increase the temperature and salt tolerance.

Johan Sverdrup and Peregrino oil were used during the de-oiling tests. Johan Sverdrup oil is medium heavy (API 28) with a relatively high amount of asphaltenes. The Peregrino oil is heavy (API 14) with a high asphaltene content and viscosity.

Polymer solutions were prepared in batches of 900 litres from a concentrated mother solution of Flopaam® 5115SH mixed with sea water. Sea water taken from a 20 meter depth in Frierfjorden was used to simulate formation water (brine) during the testing.

To determine the influence of viscosity, drag reduction and polymer mechanical degradation on the hydrocyclone performance the following focus areas were selected:

- Effects of fresh and mechanically degraded polymer on the hydrocyclone flow rates and pressure drops ($\Delta P_{\text{inlet-outlet}}$ and $\Delta P_{\text{inlet-reject}}$) for two concentrations of HPAM (30 and 500 ppm) (no oil present).
- Johan Sverdrup de-oiling performance for two concentrations of HPAM (30 and 500 ppm) at various degrees of mechanical degradation.
- Peregrino de-oiling performance for one concentration of HPAM (500 ppm) at various degrees of mechanical degradation.

A sketch of the Statoil Porsgrunn Water rig is shown in Figure 2 which shows the hydrocyclone, instrumentation and sampling points ("F" and "P" denote flow and pressure detectors, respectively). This rig was originally built for studying de-oiling of synthetic produced water (sea water) with different oils, but was modified for polymer testing. Pre-mixed polymer solution was stored in a separate tank and connected to the rig upstream of the water pump. The polymer solution could either be circulated in the rig or sent to waste handling (by operating the rig in once-through mode). The shear valve was used to generate oil droplets by setting an appropriate pressure drop across the valve. The amount of oil, seawater and polymer circulating was controlled by valves. All tests were performed at room temperature.

Figure 3 illustrates a typical hydrocyclone liner used in the tests. One single liner typically has a design capacity of 2.5 - 5 m³/h. To be able to handle the process pressure and total flow rate many liners were mounted together inside pressurized vessels.

To evaluate the performance, testing of one single liner is seen as representative due to the straightforward upscaling. An Aker HE2 hydrocyclone liner was used during the testing. This is regarded as representative for conventional last generation hydrocyclone liners with tangential multiple inlets and a characteristic diameter of 20 mm. The HE2 hydrocyclone liner had the following specifications: Liner - HE2 A1 MIKP9; Reject - HE2 C1 MIKP11 with diameter 1.5 mm.

Figure 4 shows the characteristic flow rate vs. differential pressure for the liner at PDR = 1.6. PDR is the Pressure Drop Ratio between the reject outlet side (overflow) and the water outlet side (underflow), and defined according to:

$$\text{PDR} = \frac{dP_{\text{in-reject}}}{dP_{\text{in-outlet}}}$$

2. Methods:

There were 3 sampling points at the hydrocyclone - at the inlet, outlet and reject (see Figure 2). All samples were collected at *in-situ* pressures, and depressurised without shearing of polymer or oil droplets.

The viscosity was measured as a function of shear rate by a Rheolab QC viscometer from Anton Paar using a double gap cylindrical sample holder. All samples were tested shortly after sampling (< 1 hour). The viscosity (at shear rate 100 s^{-1}) was used to calculate the mechanical degradation of the polymer according to:

$$\text{Mechanical degradation (\%)} = \frac{\eta_0 - \eta}{\eta_0 - \eta_w} * 100(\%)$$

where η_0 is the initial viscosity of the solution, η is the measured viscosity, and $\eta_w = 1.1 \text{ cP}$ (the viscosity of sea water).

Oil droplet size was measured by a Malvern Mastersizer immediately after sampling.

Concentrations of oil in water were measured by fluorescence spectroscopy with an ARJAY FluoroCheck 2000 after cyclohexane extraction of the oil.

3. Results:

3.1 *Polymer influence on hydrocyclone pressure drop and flow rates (500 ppm HPAM and 30 ppm HPAM):*

The polymer influence on the hydrocyclone pressure drop and flow rates was the first parameter that was tested; during these tests no oil was present. To study how the presence of polymer influences the hydrocyclone pressure drops (inlet-outlet and inlet-reject) and flow distribution, a batch of 500 ppm HPAM was circulated in the Water rig at various rates and total pressures. Accumulated circulation time of the polymer solution was 6.5 hours spread between 2 days and 5 different test series with different choking of the hydrocyclone outlet. A baseline with pure sea water (no polymer) was also included.

The hydrocyclone was initially run with pure sea water at inlet rate 2000 l/h and PDR = 1.6. When polymer first entered the hydrocyclone the outlet and reject pressures immediately increased and the PDR approached 1. Thus, the pressure drops across the hydrocyclone decreased significantly. Increasing the inlet flow rate to 3000 l/h also increased the pressures, but the outlet and reject pressures did not stabilise, and gradually increasing pressure drops across the cyclone were observed. The flow rate was further increased to 4000 l/h, and then returned to 2000 l/h, where the outlet and reject pressures were much lower than immediately after the polymer was introduced. The PDR was still close to 1.

The immediate decrease in pressure drops after adding the polymer is typical behaviour for a turbulent flowing system where a drag reducer is added. The drag reducer makes the flow less turbulent by damping the local eddies and swirls, and makes the system more laminar-like (although it remains in the turbulent state). The polymer impact on the pressure drops also shows that drag reduction seems to dominate compared to viscosity. If increasing viscosity was the main result of adding polymer the pressure drops would probably increase since even a system with shear-thinning would experience enhanced viscosity compared to the solvent itself.

The decreasing effect of the drag reducer on the pressure drops after increasing the inlet flow rate to 3000 l/h is probably due to mechanical degradation. HPAM molecules are fragile and mechanical shear will quickly inflict molecular scission. The degradation probably starts

immediately after the polymer is introduced, but cannot be observed before recycled polymer returns to the cyclone. Drag reduction is proportional to the molecular weight, typically requiring a minimum chain length, and the polymer has probably lost the majority of its drag reducer capability already during this first test series.

Polymer degradation can also be observed from the viscosity. Figure 5 shows the viscosity of the solution during the testing. The first test series described above constitutes the first 2 hours of the timeline. The initial viscosity was 2.5 cP and after one circulation it was reduced to 2.0 cP. The degradation in the pump had been evaluated earlier and is low (< 5%), and also in other equipment upstream the hydrocyclone the degradation is expected to be low (the shear valve was 100 % open during these tests). The majority of the degradation probably occurred in the hydrocyclone where the main pressure drop took place. After approximately 60 minutes, i.e. during the first test series, the viscosity was reduced to 1.6 cP, corresponding to 60 % degradation. Further circulation in the test rig had no influence on the viscosity which remained more or less constant during the remaining tests. The 60 minutes needed to reach a stable viscosity fits well with the timescale for the observed loss in drag reduction.

During the 4 remaining test series with the polymer batch, the inlet flow rate was varied in the same way as for the first series, but with different choking of the hydrocyclone outlet valve to generate different total pressures in the system. Figure 6 shows the pressure drop over the inlet – outlet for the 5 series (HPAM500 – 1 to 5). It also includes measurement data for pure sea water (no polymer) and vendor's design specification which were in good agreement to each other. The initial drag reducing capability of the polymer and following degradation are very clear (HPAM500 – 1), i.e. initially the pressure drop was significantly reduced compared to the behaviour with pure sea water. After the polymer had been degraded a new pressure drop vs. flow rate curve was established, and maintained for the remaining tests.

A similar behaviour was observed for the pressure drop across the inlet-reject (see Figure 7). The specifications made by the vendor were reproduced when using sea water and PDR 1.6. When polymer was introduced the initial drag reduction decreased the pressure drop significantly, but circulation and accompanying degradation caused the pressure drop to increase again. Without adjustment of the reject rate a new PDR of 1 was established, approximately at the same pressure drop vs. flow rate curve as followed with sea water (at PDR

= 1.6). To reach $PDR = 1.6$ with 500 ppm HPAM it was necessary to open the reject valve further, increasing the reject rate and decreasing the reject pressure, and a new pressure drop vs. flow rate curve was established which was followed as long as the PDR was 1.6.

The same test procedure was followed with batches of 900 litres 30 ppm HPAM. Compared to the baseline test with pure sea water, there were only minor changes to the pressures and flow when the polymer plug of 30 ppm HPAM first entered the hydrocyclone. A small decrease in outlet pressure and flow could be observed, but no drag reduction effect (decreasing pressure drops). Based on the results with 500 ppm this is unexpected, but the concentration may have been too low to detect any effect on the hydrocyclone or the polymer may have degraded upstream. The virgin viscosity was 1.2 cP, and after one circulation in the rig it was not possible to measure any increase to the water viscosity (1.1 cP). However, even at this low polymer concentration a persistent effect of the mechanically degraded polymer on the differential pressure vs. flow rate was observed. It was less prominent than at high concentration, but the pressure drops over the cyclone clearly increased compared to sea water.

Figure 8 shows the comparison of the pressure drops over the cyclone inlet-outlet for the two concentrations of HPAM (after initial degradation), and sea water. The drag reduction effect observed for 500 ppm HPAM is not included in the figure. Presence of polymer clearly increased the pressure drop across the cyclone inlet-outlet.

The inlet-reject pressure drops (for $PDR = 1.6$) are plotted in Figure 9. It showed the same trends as observed for the pressure drop over the hydrocyclone inlet-outlet; i.e. the presence of polymer increased the pressure drop.

Figure 10 shows the reject flow rate for sea water and the polymer batches. During all tests the presence of polymer decreased the PDR below 1.6, and the reject valve had to be opened to reinstall the targeted setting ($PDR = 1.6$). Thus, the reject flow rate increased when polymer was present (at constant PDR).

3.2 Hydrocyclone de-oiling performance with Johan Sverdrup oil:

The polymer batches used for the Johan Sverdrup de-oiling tests were pre-treated in various ways before the tests started, and had variable remaining viscosity due to degradation (see Table 1). The main difference in pre-treatment was the circulation time in the Water rig. Repeated circulations for several hours were assumed to generate polymer with strong degradation and uniform chain length (strong and uniform degradation). With only one circulation the degradation was probably less uniform, i.e. some molecules were strongly degraded while others were less, generating a broader molecular weight distribution.

Table 1: Johan Sverdrup de-oiling: Polymer batches with pre-treatment and corresponding viscosity and degradation

Johan Sverdrup	Pre-treatment	Viscosity (cP)	Pre-degradation (%)
HPAM500 Batch1	Circulation in the Water rig for 6.5 hours at 2000 – 4000 l/h during 2 days	1.5	71*
HPAM500 Batch2	Circulation in the Water rig for 3.5 hours at 3000 l/h	1.6	64*
HPAM500 Batch3	One circulation in the Water rig at 3000 l/h	1.9	43
HPAM500 Batch4	No pre-treatment	2.5	zero
HPAM30 Batch1	Circulation in the Water rig for 6 hours at 2000 – 4000 l/h during 2 days	1.1	*
Baseline tests	No polymer present	1.1	---

* Strong and uniform degradation

During the de-oiling tests the polymer batches were pumped through the rig at 3000 l/h and mixed with 300 ppm Johan Sverdrup oil upstream of the oil shearing valve. The oil contaminated polymer was not circulated, but collected in a separate waste tank for later disposal. During all de-oiling tests with polymer batches the pressure drop across the shear valve was maintained at 7 bar, generating oil droplets at appropriate size. During baseline tests with sea water (no polymer) the pressure drop across the shear valve was varied between 4 and 7 bar to examine corresponding droplet size distributions.

Figure 11 shows the baseline oil droplet size distribution upstream and downstream the hydrocyclone after shearing the Johan Sverdrup oil at 4 bar (no polymer). There was a distinct shift to the left, from high to low droplet size over the cyclone since the larger droplets were removed more easily. The oil removal efficiency in the baseline tests with sea water and 4 bar shear valve pressure drop was 72% at an inlet oil droplet diameter d_{50} of 16.1 μm and 87% at larger inlet droplets of 20.7 μm (see Table 2).

At similar process conditions the presence of polymer increased the oil droplet size. In order to obtain similar inlet oil droplet size as for the baseline with sea water the shear valve pressure drop had to be increased. Figure 12 shows the oil droplet distribution upstream and downstream the hydrocyclone (shear valve pressure drop of 7 bar) for a test with 500 ppm highly degraded HPAM. The upstream distribution was very broad, but the majority of the large droplets were removed in the cyclone, and the downstream distribution was reasonably narrow. Visual inspection of the samples collected from the inlet, outlet and reject clearly demonstrated that the cyclone was separating oil from the water phase. The outlet sample was more transparent than the inlet sample, and there had been an accumulation of oil in the reject. The oil removal efficiency was 76% at an inlet oil droplet diameter of 177 μm (see Table 2).

The results from the de-oiling tests are shown in Table 2. While the oil removal efficiency varied between 20 and 87%, there were also high variations in the droplet size, viscosity and degree of polymer degradation.

Table 2: Results from the Johan Sverdrup de-oiling tests

Johan Sverdrup	Viscosity (cP)	Pre-degradation (%)	Oil _{in} (ppm)	d50 _{in} (μm)	Oil _{out} (ppm)	d50 _{out} (μm)	Oil removal (%)
HPAM500 Batch1	1.5	71*	249	17.7	59	10.3	76
HPAM500 Batch2	1.6	64*	159	20.9	48	14.5	70
HPAM500 Batch3	1.9	43	93	31.3	61	25.8	35
HPAM500 Batch4	2.5	0	260	39.3	209	---	20
HPAM30 Batch1	1.1	*	257	13.3	86	---	66
Baseline, 7 bar	1.1	---	242	11.9	129	10.5	47
Baseline, 5 bar	1.1	---	249	14.9	95	11.2	62
Baseline, 4 bar	1.1	---	141	20.7	19	---	87
Baseline, 4 bar	1.1	---	208	16.1	58	9.2	72

* Strong and uniform degradation

During all de-oiling tests with polymer present the pressure drop across the shear valve was 7 bar. For HPAM the droplet size increased with increasing viscosity or, *vice versa*, the oil droplet size decreased with increasing degree of mechanical degradation.

The hydrocyclone oil removal efficiency (E) for a normally distributed oil droplet distribution can be estimated from the equation:

$$E = \left(1 - \exp \left(-1.8 \left(\frac{d_{50}}{\Delta_{75}} - 0.19 \right) \right)^{1.25} \right) * 100\%$$

where Δ_{75} is the particle size where 75% of the droplets are removed. It can be calculated from the Reynolds number Re and hydrocyclone number Hy_{75} according to the following relationships:

$$Re = \frac{Q\rho_w}{\frac{1}{4}\pi D\mu} \quad Re = \frac{Q\rho_w}{\frac{1}{4}\pi D\mu}$$

$$Hy_{75} = 0.011 Re^{-0.15} Hy_{75} = 0.011 Re^{-0.15}$$

$$Hy_{75} = \frac{(\rho_w - \rho_o) Q \Delta_{75}^2}{\mu D^3} Hy_{75} = \frac{(\rho_w - \rho_o) Q \Delta_{75}^2}{\mu D^3}$$

where Q is the inlet flow, ρ_w and ρ_o are the density of water and oil respectively, D is the characteristic diameter of the hydrocyclone and μ is the viscosity. Combining these equations Δ_{75} is given by:

$$\Delta_{75} = \frac{0.0106 \mu^{1.15} D^{3.15}}{\rho_w^{0.15} (\rho_w - \rho_o) Q^{1.15}} \Delta_{75} = \frac{0.0106 \mu^{1.15} D^{3.15}}{\rho_w^{0.15} (\rho_w - \rho_o) Q^{1.15}}$$

Figure 13 shows the experimental and modelled (based on equation 3 and assuming water viscosity) oil removal efficiencies plotted versus d_{50} / Δ_{75} . Since the viscosity is one of the parameters included in Δ_{75} this allows comparison of test results based on different viscosities. Comparing the model to the experimental data for water, the hydrocyclone is somewhat less efficient than expected, i.e. it underperforms. However, there is good agreement between the water tests and the tests with strongly and uniformly degraded HPAM. For these tests the separation efficiency seems to be governed by the viscosity and droplet size. However, for HPAM with low degree of degradation the model fails (i.e. the two points for HPAM 500 ppm at $d_{50} / \Delta_{75} \sim 1.8$) and can no longer be used to predict the oil removal efficiency. This can probably be understood from the differences in viscoelastic effects (drag reduction) of fresh and degraded HPAM.

3.3 Hydrocyclone de-oiling performance with Peregrino oil:

The polymer batches used for the Peregrino de-oiling tests were also pre-treated in various ways before the tests started, and had variable remaining viscosity due to degradation (Table 3). The tests were performed in the same way as the Johan Sverdrup de-oiling tests with the same flow rate, oil concentration and PDR setting, except for the shear valve pressure drop which had to be increased to 15 bar to generate appropriate oil droplets.

Table 3: Peregrino de-oiling: Polymer batches used during the Peregrino tests with pre-treatment and corresponding viscosity and degradation

Peregrino	Pre-treatment	Viscosity (cP)	Pre-degradation (%)
HPAM500 Batch1	Circulation in the Water rig for 3.5 hours at 3000 l/h and $\Delta P_{\text{shear valve}} = 15$ bar	1.3	82*
HPAM500 Batch2	One circulation in the Water rig at 3000 l/h and $\Delta P_{\text{shear valve}} = 15$ bar	1.6	61
HPAM500 Batch3	One circulation in the Water rig at 3000 l/h and $\Delta P_{\text{shear valve}} = 0$ bar	1.7	52
HPAM500 Batch4	No pre-treatment	2.4	zero
Baseline test	No polymer present	1.1	---

* Strong and uniform degradation

Figure 14 shows the baseline oil droplet size distribution upstream and downstream the hydrocyclone after shearing the Peregrino oil at 15 bar (no polymer). The droplet size was reasonably normal distributed, but were very wide and quite rough with several local minima and maxima. Efficient de-oiling was evident from the distinct shift in droplet size over the cyclone where the larger oil droplets were removed more easily than the smaller, shifting d_{50} from 19.7 μm upstream the cyclone to 11.8 μm downstream. The corresponding de-oiling efficiency was 82% (Table 4). The baseline tests demonstrated the complex nature of the Peregrino oil with rough and asymmetric droplet distribution. The oil was also very sticky and adsorbed to the wall of the sample collector during sampling, increasing the complexity and uncertainty in the droplet size distribution. Several attempts were made to decrease the upstream droplet size distribution by increasing the pressure drop across the shear valve (< 30 bar), but all these failed.

Since the Peregrino oil showed little response upon increasing the shear valve pressure drop above 15 bar it was decided to apply the same condition for the polymer tests. Figure 15 shows the oil droplet distribution upstream and downstream the hydrocyclone for the test with 500 ppm strongly and uniformly degraded HPAM. The upstream distribution was very broad, but the majority of the large droplets were removed in the cyclone, and the downstream distribution was reasonably narrow. At this condition (strongly and uniformly degraded) the polymer had little

influence on the droplet size compared to the baseline tests. The upstream d50 was 19.9 μm and downstream it was 14.6 μm . By decreasing the pre-treatment time of the polymer solutions, and hence decreasing the degree of mechanical degradation, the oil droplets increased and the distribution broadened (see Table 4).

The results from the de-oiling tests are shown in Table 4. Also for Peregrino oil there were large variations in oil droplet size, polymer pre-degradation and de-oiling efficiency (45 – 92 %).

Table 4: Results from the Peregrino de-oiling tests with $\Delta P = 15$ bar

Peregrino	Viscosity (cP)	Pre- degradation (%)	Oil _{in} (ppm)	d50 _{in} (μm)	Oil _{out} (ppm)	d50 _{out} (μm)	Oil removal (%)
HPAM500 Batch1	1.3	82*	236	19.9	19	14.6	91.9
HPAM500 Batch2	1.6	61	238	49.0	61	33.9	74.4
HPAM500 Batch3	1.7	52	293	67.0	110	45.7	62.6
HPAM500 Batch4	2.4	zero	288	89.7	110	50.8	61.8
Baseline test	1.1	---	184	19.7	28	11.8	84.8

* Strong and uniform degradation

The pressure drop across the shear valve was 15 bar for all tests. The Peregrino oil behaved similarly to the Johan Sverdrup oil. Presence of HPAM could increase the droplet size depending on the remaining viscosity (or degree of mechanical pre-degradation). For the strongly and uniformly degraded HPAM solution the oil droplet size was similar to the baseline, i.e. with d50 ~ 20 μm . For HPAM with lower pre-degradation the droplets were very large, and d50 reached 90 μm when the HPAM solution had not been pre-degraded at all.

The Peregrino oil showed similar de-oiling performance as Johan Sverdrup (Figure 16). For highly and uniformly degraded HPAM the efficiency seems to be governed by the remaining viscosity and oil droplet size, and showed reasonable agreement with water data and the removal efficiency calculated from equation 3. For HPAM solutions with low and less uniform degradation (i.e. with short or no pre-treatment) less oil was removed than expected from the model, and it should not be used to predict oil removal efficiency.

4. Discussion:

The tests were performed at room temperature, i.e. below typical working conditions (50-80°C) of the produced water treatment system. One consequence was increased viscosity of the polymer solutions, making de-oiling less efficient. Among the other parameters controlling the de-oiling efficiency (ref. equations 3-7), temperature could also influence possible polymer-oil interaction and thereby oil droplet frictional force, coalescence and break-up.

Flopaam 5115 SH® showed drag reducing capability depending on the degree of mechanical degradation. Drag reduction was detrimental for the hydrocyclone de-oiling performance, reducing the efficiency well below estimates from well-established performance models. It also reduced the pressure drop over the hydrocyclone inlet-outlet and inlet-reject compared to baseline tests with water. Drag reduction could be counteracted by mechanical degradation of the polymer molecules. Upon persistent circulation of the polymer solution in the test rig the polymer molecules were ruptured, and the solution gradually lost the drag reducing capability. HPAM solution with strong and uniform degradation showed no remaining drag reducing capability, and the de-oiling behaved according to the performance model with a penalty compared to baseline tests with water if any rest-viscosity remained.

Claims:

1. A method of separating residual crude oil from a polymer produced water stream, said method comprising:
 - (a) mechanically degrading at least a proportion of the polymer contained in said polymer produced water stream; and
 - (b) subjecting the resulting degraded polymer produced water stream to turbulent flow whereby to cause separation of at least a proportion of the residual crude oil from said stream.
2. A method of recovering crude oil from a crude oil-containing formation, said method comprising:
 - (a) providing a composition comprising water and a water-soluble polymer to a crude oil-containing formation;
 - (b) allowing the composition to contact with at least a proportion of the crude oil in said formation;
 - (c) recovering from said formation an emulsion which comprises crude oil, water and said polymer;
 - (d) subjecting said emulsion to a demulsifying process whereby to produce crude oil and a polymer produced water stream containing residual crude oil;
 - (e) mechanically degrading at least a proportion of the polymer contained in said polymer produced water stream; and
 - (f) subjecting the resulting degraded polymer produced water stream to turbulent flow whereby to cause separation of at least a proportion of the residual crude oil from said stream.
3. A method as claimed in claim 1 or claim 2, wherein the polymer is a polyacrylamide or hydrolysed polyacrylamide.
4. A method as claimed in any one of claims 1 to 3, wherein the step of mechanically degrading the polymer reduces the molecular weight of the polymer.
5. A method as claimed in any one of the preceding claims, wherein the step of mechanically degrading the polymer is carried out by mechanical means capable of

imparting a high shear force or rapid change in pressure to said polymer produced water whereby to rupture the polymer.

6. A method as claimed in claim 5, wherein said mechanical means capable of imparting a high shear force comprises a pump or a plurality of pumps connected in series.
7. A method as claimed in claim 6, wherein said pump or pumps are selected from a centrifugal pump and an electric submersible pump.
8. A method as claimed in claim 5, wherein said mechanical means capable of imparting a rapid change in pressure comprises a valve or a plurality of valves connected in series.
9. A method as claimed in claim 8, wherein said valve or valves are selected from a choke valve and a pressure reducing valve.
10. A method as claimed in any one of the preceding claims, wherein the degraded polymer produced water is subjected to turbulent flow in one or more hydrocyclones and/or compact flotation units.
11. Apparatus adapted for carrying out a method as claimed in claim 1, said apparatus comprising:
 - (a) degradation means configured to mechanically degrade at least a proportion of polymer contained in a polymer produced water stream; and
 - (b) at least one separator configured to impart turbulent flow to the resulting degraded polymer produced water stream whereby to cause separation of at least a proportion of residual crude oil contained therein.
12. Apparatus as claimed in claim 11, wherein said degradation means comprises one or more pumps and/or valves.
13. Apparatus as claimed in claim 11 or claim 12, wherein each separator is a hydrocyclone or a compact flotation unit.

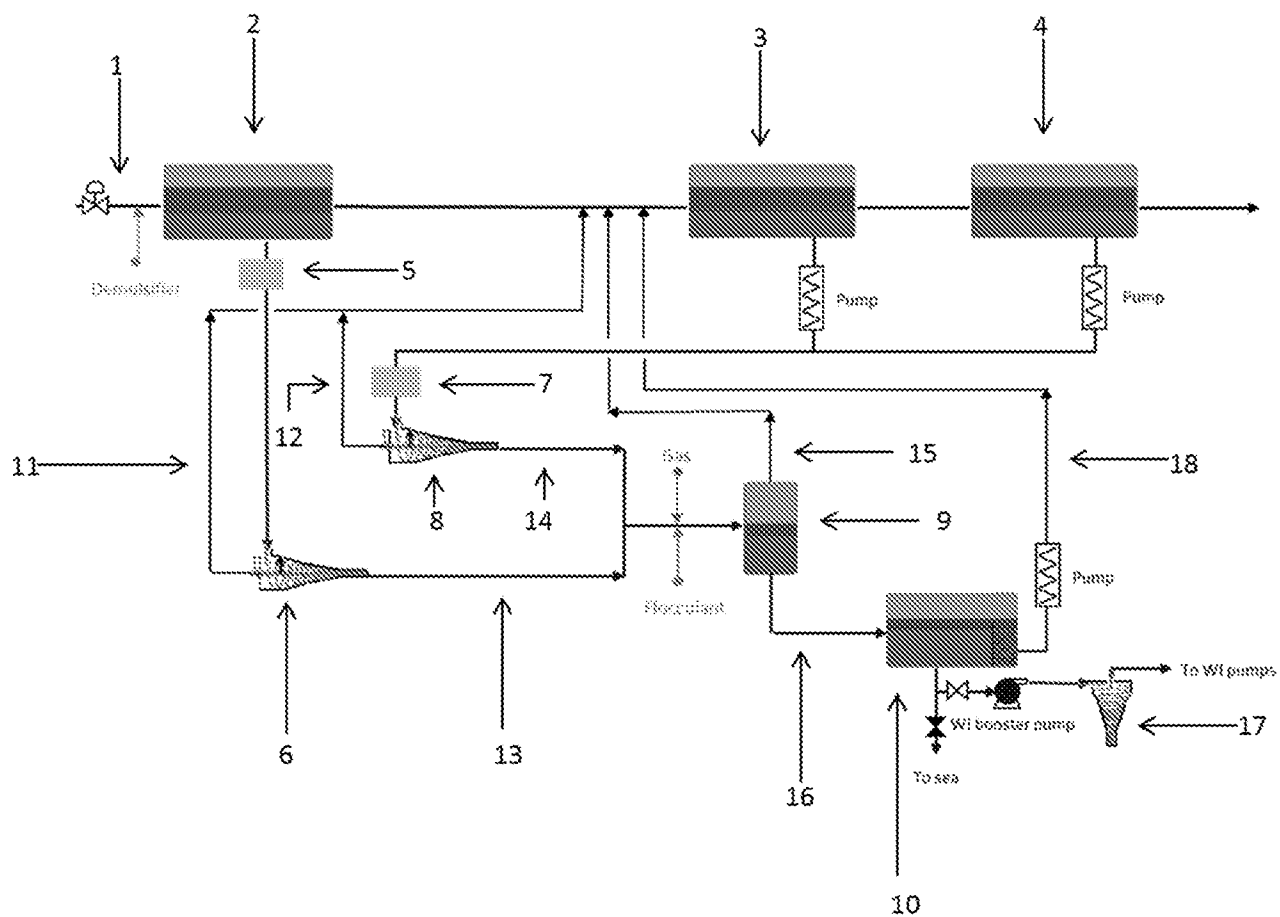


Fig.1

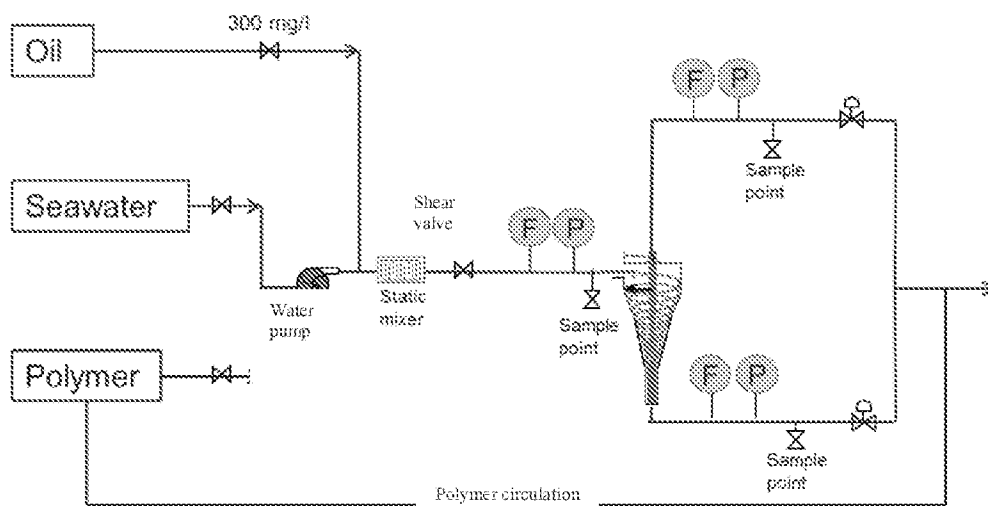


Fig. 2

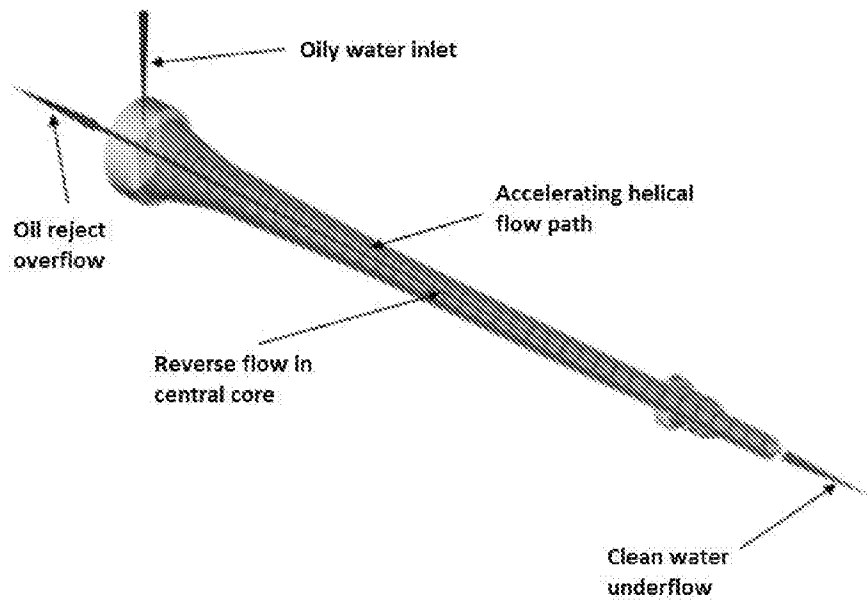


Fig. 3

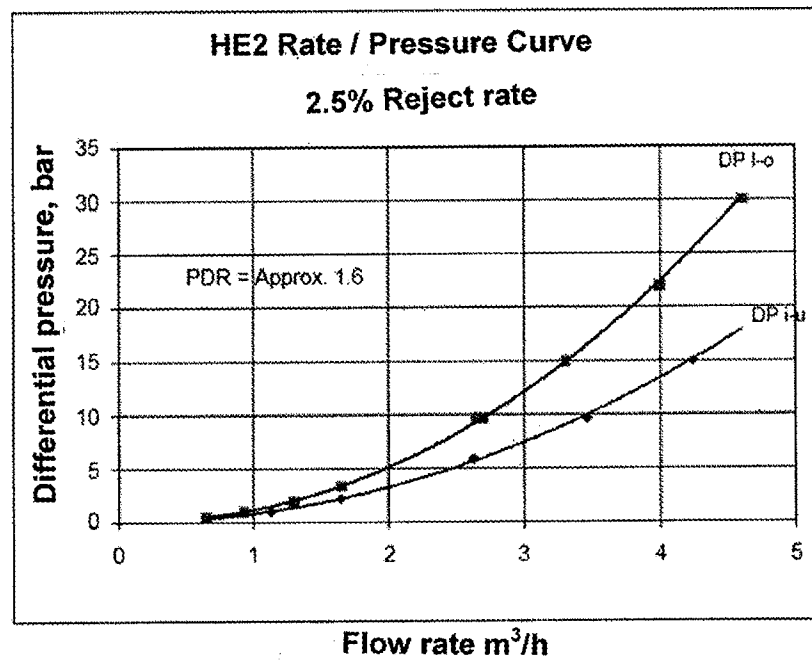


Fig. 4

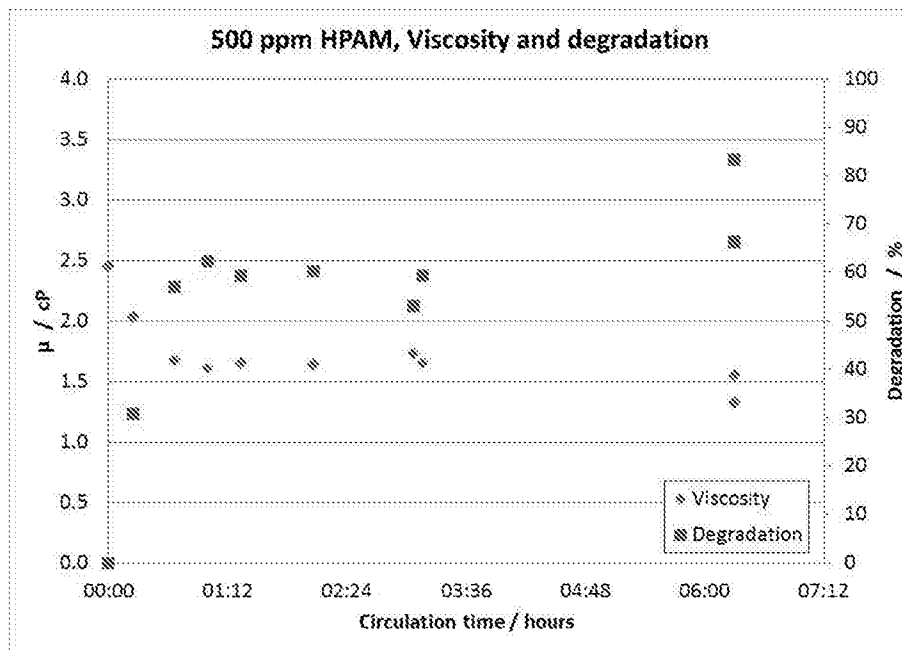


Fig. 5

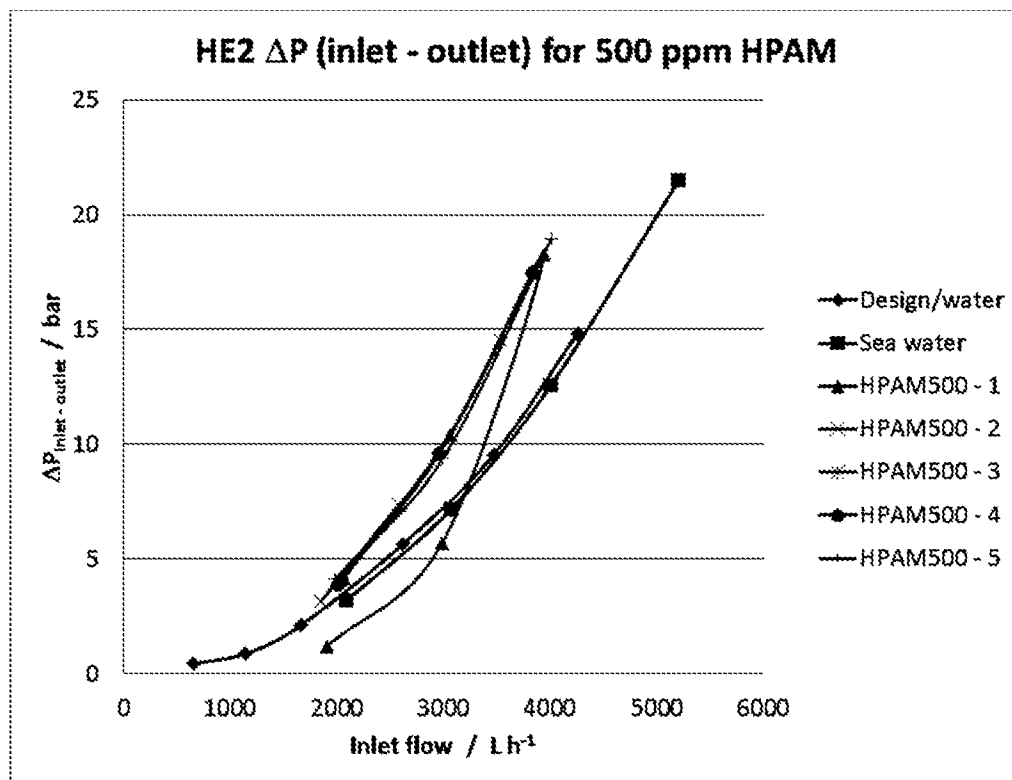


Fig. 6

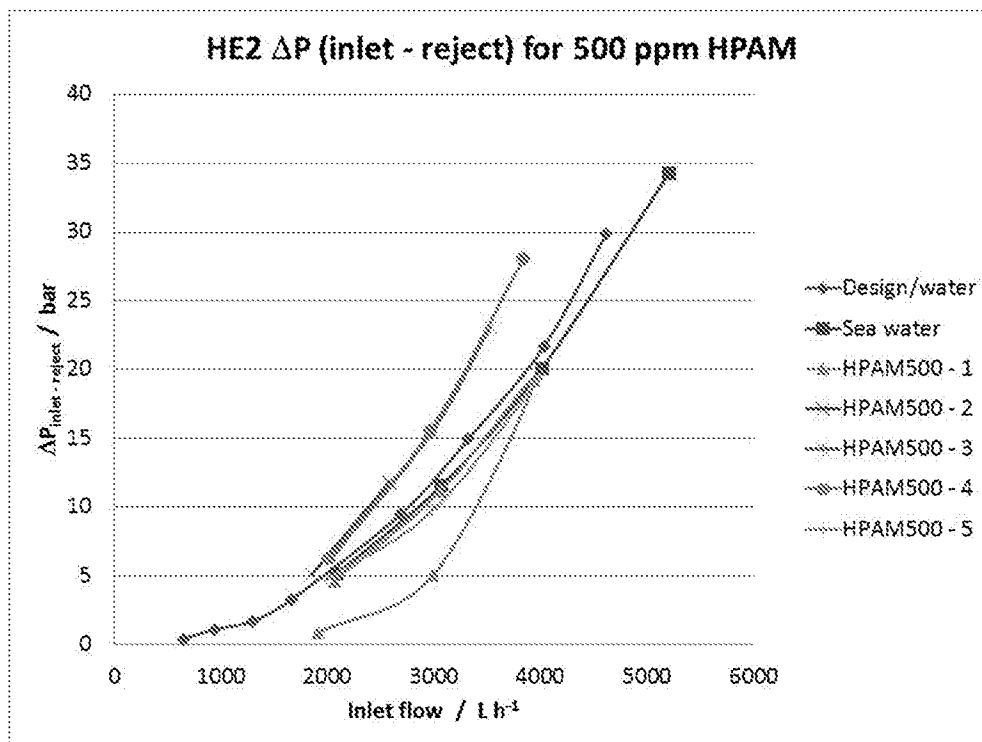


Fig. 7

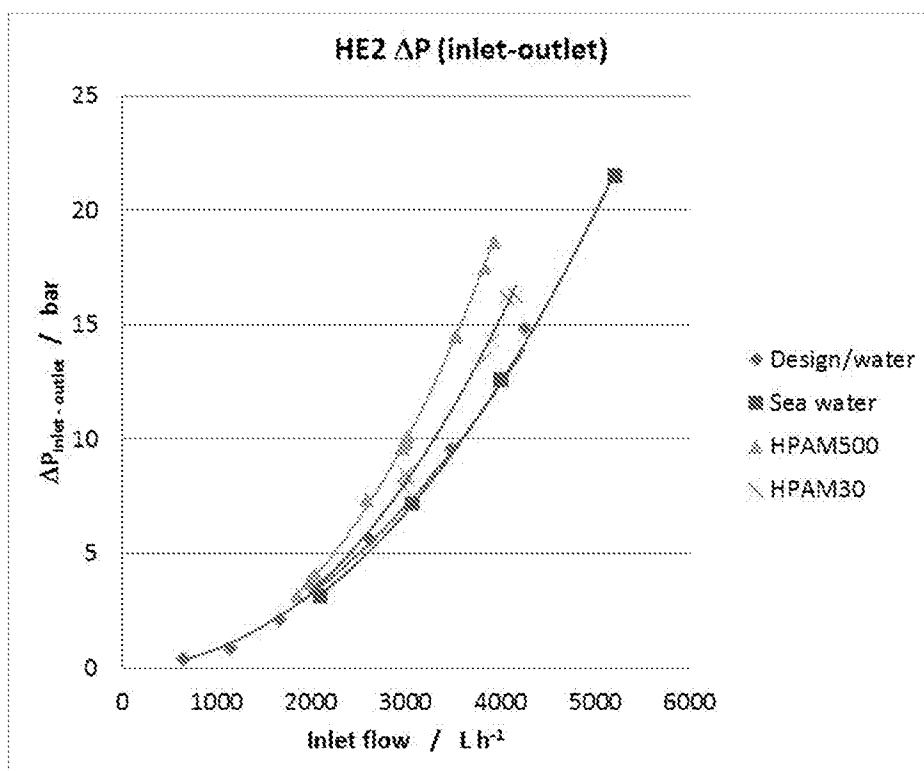


Fig. 8

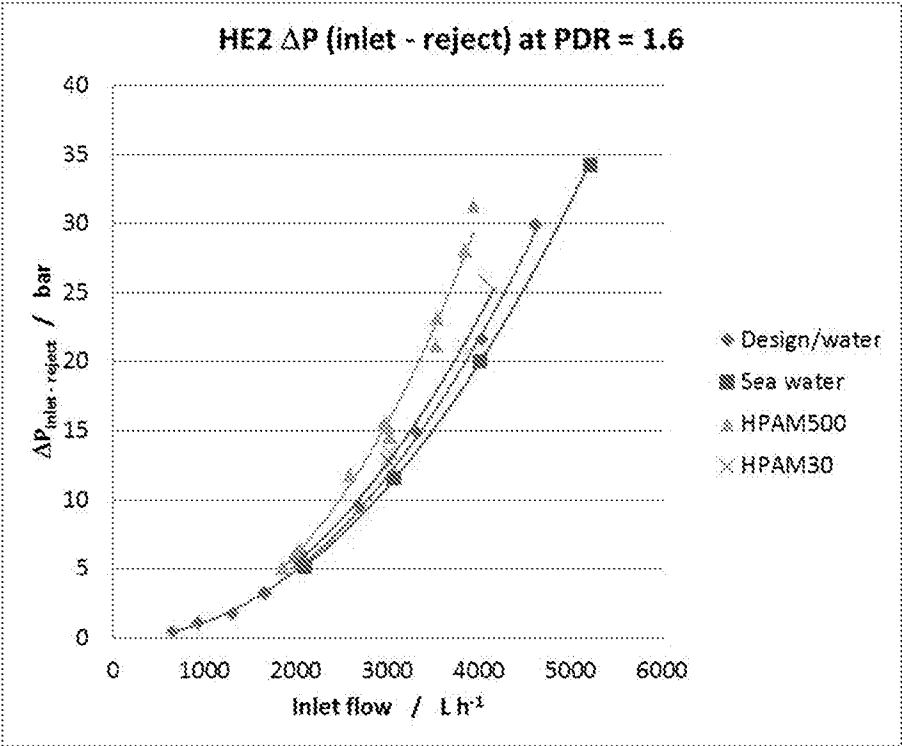


Fig. 9

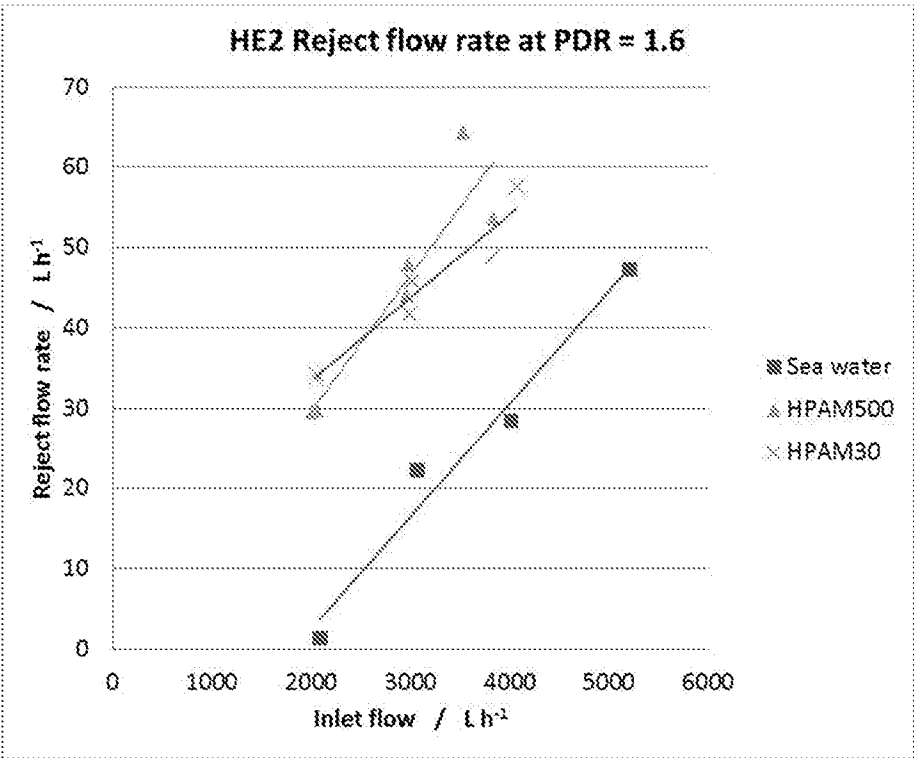


Fig. 10

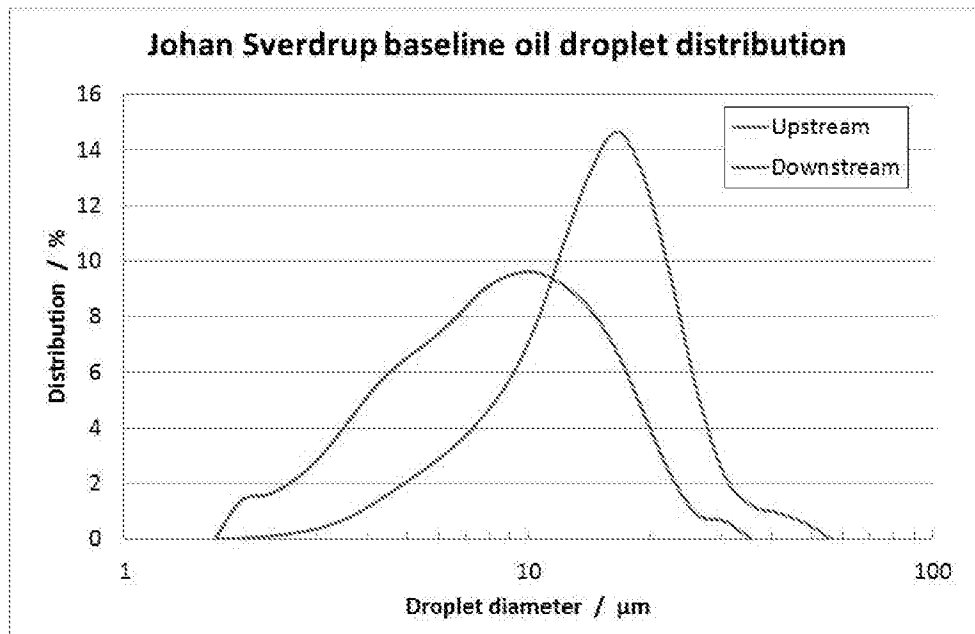


Fig. 11

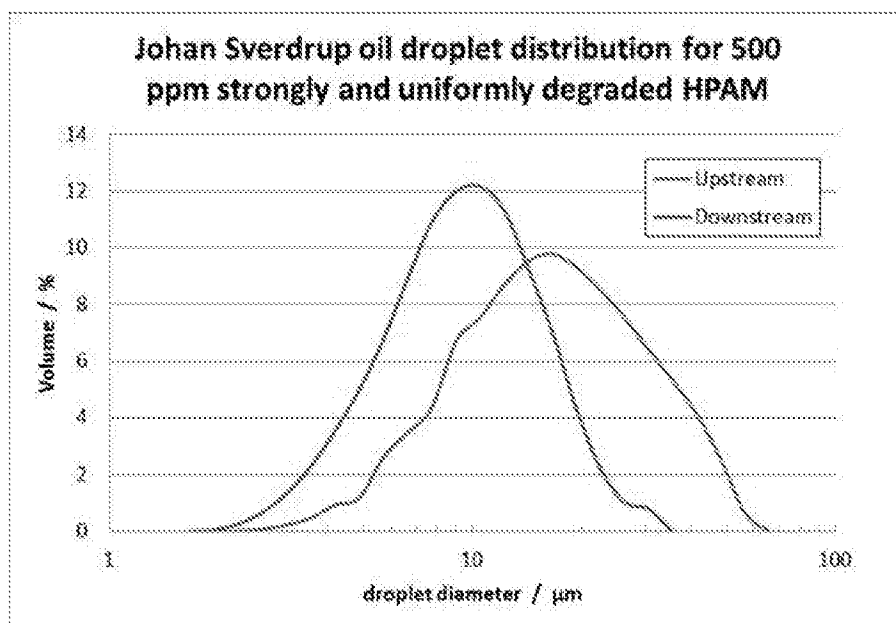


Fig. 12

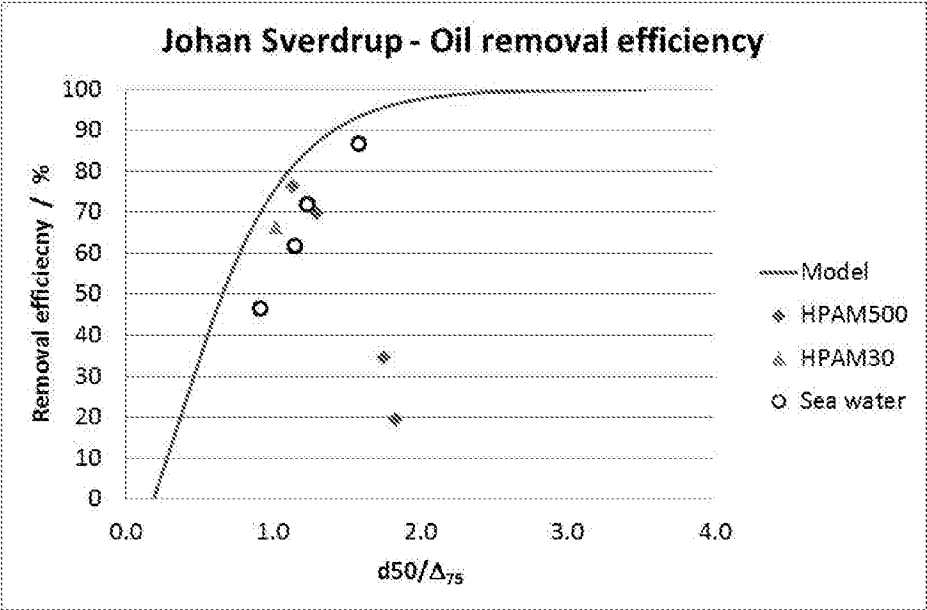


Fig. 13

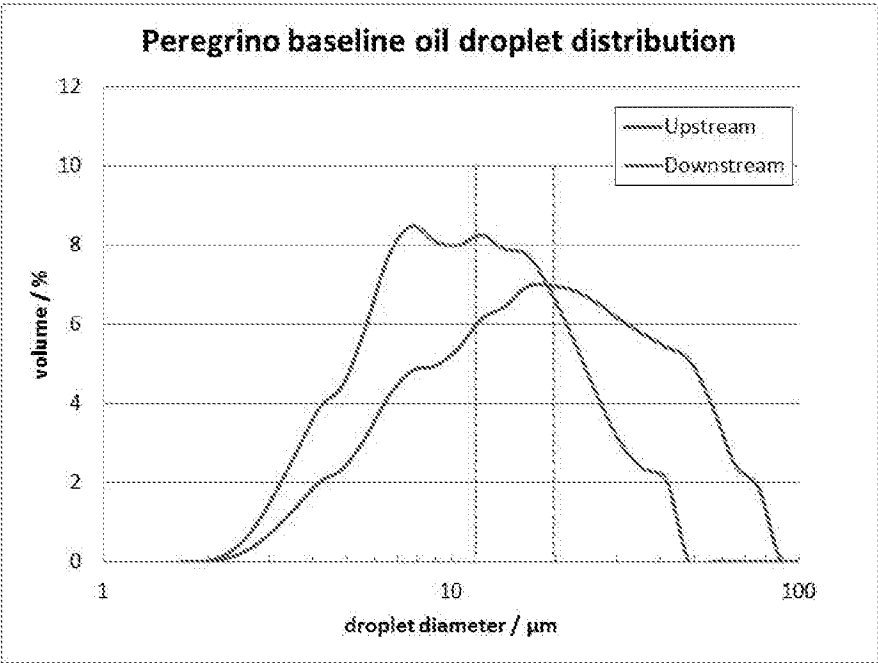


Fig. 14

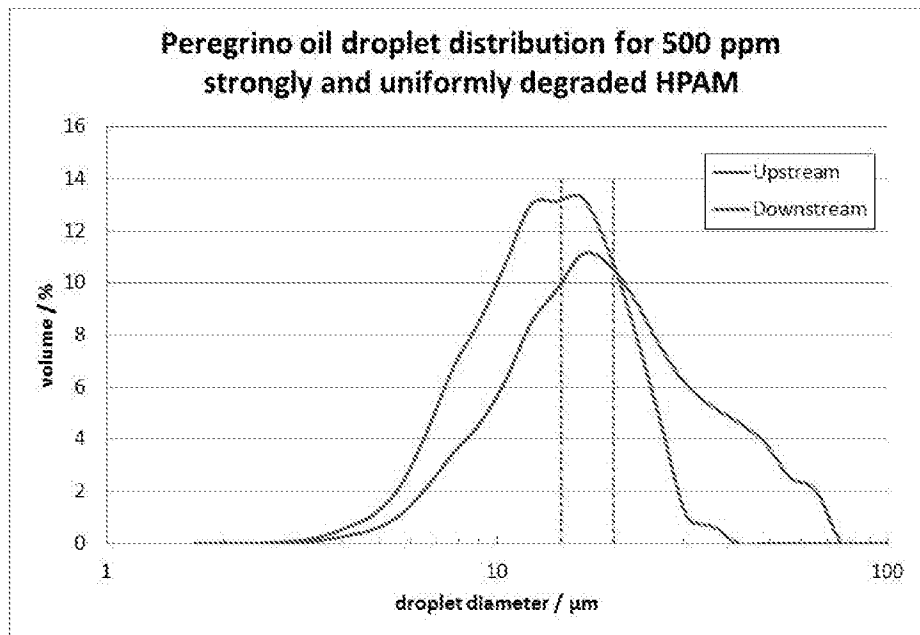


Fig. 15

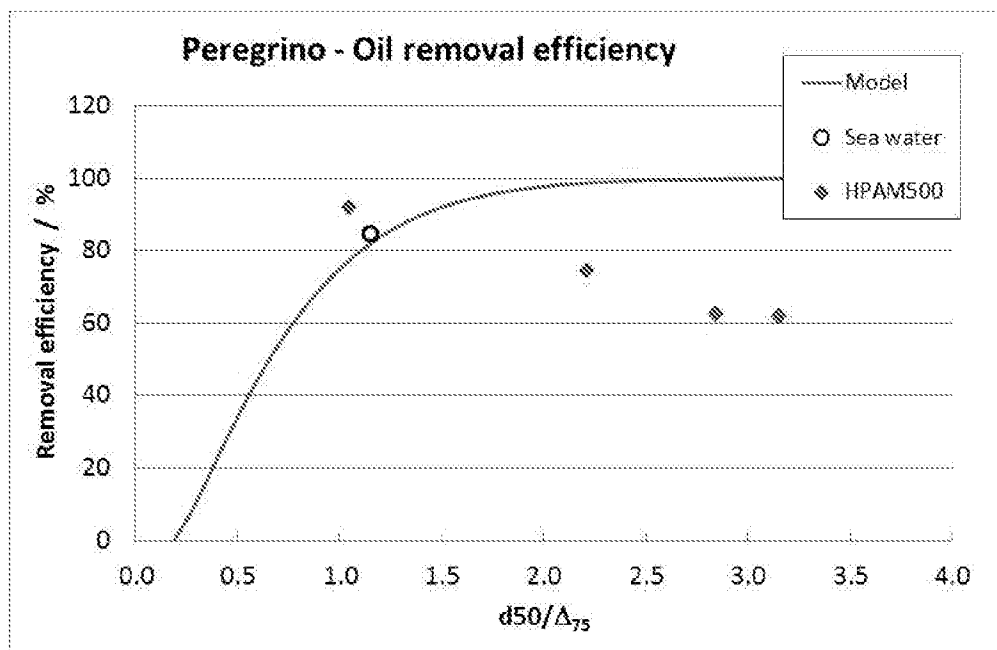


Fig. 16

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO2017/050007

A. CLASSIFICATION OF SUBJECT MATTER B01D 21/00 (2006.01), B01D 21/26 (2006.01), C09K 8/588 (2006.01), E21B 43/16 (2006.01), E21B 43/34 (2006.01) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) E21B, B01D, C09K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched DK, NO, SE, FI: Classes as above.		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPODOC, WPI, FULL TEXT: ENGLISH, GERMAN, FRENCH, COMPDX.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/0107841 A1 (SUIJKERBUIJK et al.), 2015.04.23 [0007], [00339-0040], [0045], [0052], [0055-0056], [0060-0061], [0065-0071] and claim 1.	1-13
Y	Thomas A; Gaillard N; Favero C, "Some Key Features to Consider When Studying Acrylamide-Based Polymers for Chemical Enhanced Oil Recovery", Oil and Gas Science and Technology, Vol. 67, Nr. 6, p 887-902, 2012. Page 887-888, chapter 1.4.2, 3.2, 4.1 and 4.3.1-4.3.2.	1-13
Y	US 5507955 A (Webb), 1996.04.16 Column 1, lines 25-33 and claim 1.	1-13
Y	WO 2010/005312 A (Aker Subsea AS), 2010.01.14 Page 2 lines 21-25, page 3 lines 3-7 and page 6 lines 24-27	1-13
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "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 "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
02/03/2017		03/03/2017
Name and mailing address of the ISA Nordic Patent Institute Helgeshøj Allé 81 DK - 2630 Taastrup, Denmark. Facsimile No. + 45 43 50 80 08		Authorized officer Iren Beisvåg Telephone No. +4790163556

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/NO2017/050007

Patent document cited in search report / Publication date	Patent family member(s) / Publication date
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