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WO 2010/080867 A1
US 5462672 A
US 20070199872 A1
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(54) Title of the Invention: **Method of separation**
Abstract Title: **Separating an emulsion of oil, water and solid matter**

(57) A method of separating an emulsion of oil, water and solid matter includes the steps of providing an emulsion of oil, water and solid matter; adding a solid to the emulsion in an amount of at least 50% of the oil by content by volume; adding a flocculent to the emulsion; filtering the mixture where filtering involves applying a first pressure to the mixture to force the water through the filter and applying a second pressure which is higher than the first to force oil through the filter.

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Method of separation

This invention relates to a method of separation and more particularly but not exclusively to a method of separating a mixture of water, solids and oil.

When seeking hydrocarbon natural resources, e.g. oil and gas, it is common for drilling to occur. Drilling often involves the use of a drill rig which drives a cutting head into rock, for example at the sea bed. Cutting heads are generally lubricated by the provision of a drilling liquid. The drilling liquid provides lubrication and acts as a viscous transporter, transporting some or all of the debris cut by the drilling head away from the drill head, and/or drill bit to which the drill bit is attached. The drilling liquid, which is taken away from the drill head and/or drill bit, is then roughly filtered to remove some or all of the debris cut away during drilling. The drilling liquid is re-used following rough filtration until it is deemed exhausted because it contains too much debris and/or water.

Drilling liquid is used in many other industrial scale drilling scenarios, e.g. for lubricating drill heads when drilling quarries or foundations for bridges and other large structures.

Typical drilling liquids are an oil, for example paraffin and/or kerosene, and water emulsion stabilised with solid material, for example dispersed clay or organophilic clay. The emulsion is chosen to be stable so that it does not break down at the drilling head/rock (or other material to be drilled) interface. The stability of the emulsion makes it difficult to break down into the component parts for safe and environmentally sound disposal.

Typically, exhausted drilling liquids are referred to as oil slops. The disposal of oil slops is governed by local legislation. Taking the example of a drilling rig at sea, it is not acceptable to place oil slops in the sea because they pose a hazard to wildlife, can be toxic and are difficult to recover once placed in the sea.

Treatment systems have been developed for dealing with oil slops. However, on oil rigs where space is at a premium, there is little or no room for an onsite treatment plant. Therefore, oil slops are typically sent from oil rigs to shore for cleaning. This results in a large overhead cost for the safe removal and cleaning of oil slops.

Exhausted drilling liquid, i.e. oil slops, taken from drilling sites typically comprise 80-95% water by volume, 1.0-2.5% solids by volume and 10-2.5% oil by volume, or any combination of values within these ranges adding up to 100%. Common oil slops, taken from drilling sites, typically comprise 90% water by volume, 5% solids by volume and 5% oil by volume.

There a number of problems associated with separating oil slops down into their constituent parts, namely, substantially pure water, solids and oil. The addition of well known flocculants often does not produce a separable mixture. Passing exhausted drilling liquid, oil slops, through a filter results in binding of the filtrate material to itself and the filter so that little, or no, material is passed through the filter. Use of a centrifuge can separate solids from the exhausted drilling liquid but the resulting water and/or solids are contaminated with oil. Thermal desorption, i.e. heating exhausted drilling liquid, oil slops, and taking off the water and oil in fractions is time consuming, requires specialist equipment and is expensive. Dilution of the oil content by addition of lime and/or clay to minimise the amount of oil per unit of volume is problematic because the oil remains in the material.

According to a first aspect of the present invention, there is provided a method of separating an emulsion of oil, water and solid matter comprising the steps of:

providing an emulsion of oil, water and solid matter;

adding a solid to the emulsion in an amount of at least 50% of the oil content by volume;

adding a flocculant to the emulsion in an amount to flocculate the solid matter;

filtering the resultant mixture through a filter; where filtering the resultant mixture through the filter includes the steps of:

applying a first pressure to the resultant mixture to force substantially all of the water through the filter;

applying a second pressure, the second pressure being higher than the first pressure, to the resultant mixture to force substantially all of the oil through the filter.

Preferably, wherein the step of adding a solid to the emulsion includes adding the solid in an amount between 60% and 150% of the oil content by volume.

Further preferably, wherein the step of adding a solid to the emulsion includes adding the solid in an amount at least 100% of the oil content by volume.

Advantageously, wherein the step of adding a solid to the emulsion includes adding the solid in an amount at least 60%, or 70%, or 80%, or 90%, or 100%, or 110%, or 120%, or 130%, or 140%, or 150%, or more, of the oil content by volume.

Preferably, wherein the step of adding a solid to the emulsion includes adding a generally inert solid to the emulsion.

Further preferably, wherein the generally inert solid is a filler.

Advantageously, wherein the solid is gypsum, barites, clay, fly ash residue, diatomaceous earth, recovered fines from drilling, coal, crushed calcium carbonate, precipitated calcium carbonate, crushed rock, waste sludge of aluminium salts, ferric sludge from water treatment, ferrous sludge from water treatment, residues form paper making such as de-inking plant sludge or any other generally inert solid, or a combination of one or more of these solids.

Preferably, wherein the step of adding a flocculant to emulsion includes adding flocculant in an amount at least 0.01%, or more, of the oil content by volume, optionally, wherein the step of adding flocculant to emulsion includes adding flocculant in an amount of from 50 to 300ppm, preferably 50 to 500 ppm, based on the volume of the slurry to be flocculated.

Further preferably, wherein the flocculant is an anionic or cationic acrylic flocculant, optionally, polyacrylamide polymers cationic or anionic, polydiallyl dimethyl ammonium chloride (PolyDadmac), polyamine polymers, natural flocculants such as guar gum derivatives, carboxymethylcellulose derivatives, optionally, Treatchem 1040C or combinations of flocculant.

Advantageously, further comprising the step of diluting the emulsion with water prior to filtering the resulting mixture through a filter.

Preferably, wherein the step of diluting the emulsion with water includes diluting the emulsion by from 1% to 200%.

Further preferably, wherein the ratio of dilution of the emulsion to water is from 1:1 to 4:1, optionally, 1:1, 2:1, 3:1 or 4:1.

Advantageously, wherein the first pressure applied is 7 bar, plus or minus 25%.

Preferably, wherein the second pressure applied is 25 bar, plus or minus 25%.

Specific and non-limiting embodiments of the invention, in all its aspects, will now be described, strictly by way of example only.

This invention is concerned with a method of separating a mixture of oil, water and solid matter. In particular, the present invention is concerned with separating oil slops so that the oil, water and solid matter are separated to allow safe disposal and/or re-use of each of the oil, water and solid matter.

Samples of typical exhausted drilling liquid, i.e. oil slops, were obtained from a processing facility servicing North Sea drilling rigs. The approximate content of the exhausted drilling liquid was (by volume) 5% oil, 5% solids and 90% water.

Samples were passed through a membrane filter press after undergoing different pre-conditioning steps. Examples of membrane filter presses are those manufactured and/or supplied by Ashbrook Simon-Hartley™ of Stoke-on-Trent, UK. A membrane filter press is a device which includes a filter cloth and a chamber adjacent the filter cloth which can be pressurised to push filtrate through the filter cloth under pressure. The surface of the plate in the active membrane constitutes an inflatable sac which may be inflated with a fluid (gas or water). The surface of the plate is outside the filter cloth – it allows two surfaces of a chamber to close in on each other by application of pressure. Inflation of the sac is performed by an external but separate pump. The sac is configured to provide a desired pressure. As the sac inflates behind the filter cloth of a given chamber, a compression of matter within the chamber takes place, for example at the filter cloth surface. This means the applied pressure (commonly called the ‘squeeze’) is applied directly to the matter within the chamber without any loss of pressure; loss of pressure could be experienced, for example, by pumping a viscous mixture into the original chamber. The achievable pressure of the ‘squeeze’ is limited by press design and materials of construction. Pressures of greater than 20 bar are used in certain aspect of the present invention.

Samples were processed through a press which was equipped with 2 chambers, on filling by external pumping of the sample mixture into the chambers of the press the maximum obtainable pressure was 7 bar, once filled the surface of the chamber behind the cloth pressure could be increased to 30 bar maximum by separate pumping of water into the squeeze membrane sacs.

Samples were prepared separately in stainless steel mixing vessels, where additions of any flocculants and/or fillers (i.e. generally solid material) could be made to precondition the slurry before admission to the press.

The samples of pre-conditioned material were then admitted to the press by a double diaphragm air operated pump until such time as the pump pressure was overcome by the back pressure of the press inlet. In the examples, the pump would stall at 7 bar. At the stalling point the pump was isolated and the inlet valves to the press closed.

A membrane inflation pump was then activated, when desired, and the pressure within the press raised to a maximum of 25 bar allowing the membranes to close in on the particular sample inside the press.

For the first set of tests (treatments 1, 2 and 3), the sample material contained approximately 12 % oil, 5% solids and 83% water.

Treatment 1: Flocculant was added, in this example Treatchem 1040C HMW (a cationic polyacrylamide polymer, with approximately 40% charge density) as a 0.5% solution at 200ppm, no addition of filler, 11 litres of sample added to press, press filled to 7 bar in 1.5 hours

- Flocculation appeared good with water production from the sample.
- When higher pressure membrane squeeze was applied, up to 25 bar, oil and residual water release through the filter was slow.
- After 4 hours some oil was recovered; approximately 1 litre. Most of the oil is removed, but very slowly and the remaining oil in the solids along with the water produces a material that is sticky, is not a true solid and has an oil content above allowable levels for landfill. The press requires hand scraping to clean and the press cloths must be renewed.
- Resulting solid material was sloppy and layered with a soft centre.
- The filter material was impervious to water suggesting blocking of the filter pores.
- Unable to reuse the filter cloth material.
- Overall, this is not a suitable method.

Treatment 2: Flocculant added, the same type and amount as in treatment 1, Gypsum added, no dilution

- Approx 30 litres of sample, 2 litres of dry gypsum (the source of the gypsum was wall plaster from a commercial DIY store) added (nominally 6.6% by volume of the total sample), followed by mechanical mixing.
- Flocculant added at 300ppm based on volume.
- The press was then filled to 7 bar over 1.5 hours.
- 11 litres of sample was admitted to the press; subsequently a pressure membrane squeeze was applied up to 25 bar resulting in 6 litres of primary filtrate, the filtrate being essentially pure water, and about 1 litre of oil removed after squeeze.
- The resulting solid material was soft and layered and stuck to press.
- The filter cloth material could be re-used.

Treatment 3: Flocculant added, the same type and amount as in treatment 1, Gypsum added, with dilution

- Since 11 litres were forced into the press in treatment 2, treatment 3 investigated the possibility of faster filtration and complete separation of constituents by dilution and adding extra filler (in this example, Gypsum).
- 11 litres of sample taken and diluted with water to make 40 litres of dilute sample.
- 4 litres of gypsum was added to the dilute sample (nominally 36% by volume on starting material).
- The resulting sample was mechanically stirred and flocculant was added, in this example the flocculant was Treatchem 1040C HMW at 80 ppm as 0.5% solution.
- Large floccs were observed which dewatered well.
- The press was filled quickly (within 15 minutes) to 7 bar. Some oil was seen coming through the filter during filling.
- After pressure membrane squeeze applied up to 25 bar; the press was held at this pressure for 1.5 hours.
- The resulting solid material was hard.
- Oil production was 1.3 litres.
- The resulting solid material had a dry matter content of 79% solids, owing to the amount of filler added, with an oil content of 0.9% by weight; this solid was deemed suitable for landfill.

Treatment 3 was repeated with fly ash residue from a municipal incinerator as the filler, i.e. in place of Gypsum. This produced a similar result to treatment 3 with the resulting solid material having a dry matter content of 86% and oil content of 0.75% by weight.

In each of treatments 1, 2 and 3 above, the initial filling the press allows water to selectively flow out of the press. Some of the oil, due to low viscosity, also passes through the solid matter and out of the matrix of solid matter before the matrix closes up tightly at around 7 bar. So a large ratio of water to oil filtrate is achieved in the primary fill; i.e. most of the filtrate up to 7 bar is water (with some oil). When the press is subsequently squeezed to a higher pressure, the water is the first thing to come out but, as the water in the solid material leaves (as filtrate) the oil becomes a greater proportion of the filtrate. It is believed that this is due to surface tension and viscosity differences in the two fluids. As some of the fractions of the filtrate contain both oil and water, but no solid, the water and oil of the filtrate can be separated by, for example, standing, i.e. the filtrate does not form a stable emulsion.

Treatments 1, 2 and 3 suggest that by adding a filler, i.e. a generally inert solid substance, to the mixture of oil, water and solid material prior to flocculating and then applying a first pressure and a second pressure higher than the first pressure, results in the separation of each of oil, water and solid matter so that the solid matter can be safely disposed of, e.g. in landfill.

Some further tests were carried out to study the process in more detail:

A sample was taken of a slurry, the slurry being sourced from a processing unit of shore spent muds received from the North Sea. The slurry which had been treated by centrifuging to remove nearly all coarse material and presented as a stable emulsion. The slurry contained oil 27% by weight, solids 5% by weight and water 68% by weight.

The slurry was diluted 4:1 with fresh water to produce a model slurry which contained oil 5.4% by volume, solids 1% by volume and water 93.6% by volume.

a. Flocculation only:

On adding a flocculant, the flocculant being the same type and amount as used in treatment 1, this material flocculated but upon admission to the press immediately blocked the filtration membrane; this permitted little or no passage of liquid through the filter membrane.

b. Flocculation and gypsum:

Gypsum was added to the sample at 10% by weight of the slurry. Given that the density of the gypsum is approximately 2.3 g/ml this equates to an addition of 4.34 % by volume to the mixture, i.e. close to the oil content by volume of 5.4%. (For oil, the density is slightly less than water, approximately 0.9, this means weight and volume percentages may generally be used interchangeably).

The mixture was then flocculated with a cationic flocculant 85 ppm of Treatchem 1040C, a cationic acrylamide based flocculent. The mixture flocculated readily and separated into flocculated solid matter and water. The mixture was placed in a press and water was forced through the filter material at around 7 bar of pressure. A substantial amount of oil was released during filling of the press. When the press was filled with the water/flocculated matter mixture, the inlet valve was shut off, pressure within the press was increased to 25 bar over 1 hour and the removal of the residual oil and water took place within an hour.

c. Flocculation and gypsum (less gypsum):

An attempt to run at lower added solids (gypsum, in this example) where the volume percentage of the added gypsum was 2% by volume resulted in a blocked press, as in a. above.

Results a., b. and c. indicate that, in order to achieve good flocculation and subsequent separation of the sample in a press, the amount of added solids should approach the volume % of the oil content of the starting oil, water and solids emulsion.

This general rule discounts the presence of solids in the material before treatment since the solids present in oil slops are of very small particle size, often the particles are in the sub micron range, and a large percentage of the solids are present as organophilic clays. Without wishing to be bound by theory, organophilic clay stabilises the emulsion; particles of organophilic clay tend to act as a sealant and offer a surface upon which oil may bind. When there are no particles of filler (i.e. in the absence of addition of solids, e.g. gypsum) to entrap and compress the oily particles during the pressure filtration, the original hydrophobic mixture tends to form films which are stable under high pressure. This is the mechanism by which drill bit lubricants work.

Without wishing to be bound by theory, the addition of solids, e.g. gypsum, permits the pressure of the membrane system to compress the matrix of solid matter and prevent the filtration material becoming clogged. There is no theoretical minimum for the addition of solids except insomuch as there is a requirement to overwhelm the ability of the slurry to block the filtration material.

When used in this specification and claims, the terms "comprises" and "comprising" and variations thereof mean that the specified features, steps or integers are included. The terms are not to be interpreted to exclude the presence of other features, steps or components.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

Claims

1. A method of separating an emulsion of oil, water and solid matter comprising the steps of:

providing an emulsion of oil, water and solid matter;

adding a solid to the emulsion in an amount of at least 50% of the oil content by volume;

adding a flocculant to the emulsion in an amount to flocculate the solid matter;

filtering the resultant mixture through a filter; where filtering the resultant mixture through the filter includes the steps of:

applying a first pressure to the resultant mixture to force substantially all of the water through the filter;

applying a second pressure, the second pressure being higher than the first pressure, to the resultant mixture to force substantially all of the oil through the filter.

2. A method according to claim 1, wherein the step of adding a solid to the emulsion includes adding the solid in an amount between 60% and 150% of the oil content by volume.

3. A method according to claim 1, wherein the step of adding a solid to the emulsion includes adding the solid in an amount at least 100% of the oil content by volume.

4. A method according to claim 1, wherein the step of adding a solid to the emulsion includes adding the solid in an amount at least 60%, or 70%, or 80%, or 90%, or 100%, or 110%, or 120%, or 130%, or 140%, or 150%, or more, of the oil content by volume.

5. A method according to any one of claims 1-4, wherein the step of adding a solid to the emulsion includes adding a generally inert solid to the emulsion.

6. A method according to claim 5, wherein the generally inert solid is a filler.

7. A method according to any one of the previous claims, wherein the solid is gypsum, barites, clay, fly ash residue, diatomaceous earth, recovered fines from drilling, coal, crushed calcium carbonate, precipitated calcium carbonate, crushed rock, waste sludge of aluminium salts, ferric sludge from water treatment, ferrous sludge from water treatment, residues form paper making such as de-inking plant sludge or any other generally inert solid, or a combination of one or more of these solids.

8. A method according to any one of claims 1-7, wherein the step of adding a flocculant to emulsion includes adding flocculant in an amount at least 0.01%, or more, of the oil content by volume, optionally, wherein the step of adding flocculant to emulsion includes adding flocculant in an amount of from 50 to 300ppm, preferably 50 to 500 ppm, based on the volume of the slurry to be flocculated.

9. A method according to claim 8, wherein the flocculant is an anionic or cationic acrylic flocculant, optionally, polyacrylamide polymers cationic or anionic, polydiallyl dimethyl ammonium chloride (PolyDadmac), polyamine polymers, natural flocculants such as guar gum derivatives, carboxymethylcellulose derivatives, optionally, Treatchem 1040C or combinations of flocculant.

10. A method according to any one of the previous claims, further comprising the step of diluting the emulsion with water prior to filtering the resulting mixture through a filter.

11. A method according to claim 10, wherein the step of diluting the emulsion with water includes diluting the emulsion by from 1% to 200%.

12. A method according to claim 11, wherein the ratio of dilution of the emulsion to water is from 1:1 to 4:1, optionally, 1:1, 2:1, 3:1 or 4:1.

13. A method according to any one of the previous claims, wherein the first pressure applied is 7 bar, plus or minus 25%.

14. A method according to any one of the previous claims, wherein the second pressure applied is 25 bar, plus or minus 25%.

15. A method of separating an emulsion of oil, water and solid matter substantially as hereinbefore described.

16. Any novel combination of features disclosed herein.

Application No: GB1211574.7 **Examiner:** Dr Lyndon Ellis
Claims searched: 1-15 **Date of search:** 5 August 2012

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	US2006/0032820 A1 (Reddy)
A	-	US2007/0199872 A1 (Mueller)
A	-	US5462672 A (Masahiro)
A	-	WO2010/080867 A1 (Jackson)

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

E21B

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI

International Classification:

Subclass	Subgroup	Valid From
E21B	0021/06	01/01/2006