Extraction-membrane technology for processing oil-based mud

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Abstract. The article presents the methods of waste oil-based mud (OBM) treatment by the combined extraction-membrane separation method. The efficiency of various solvents for the hydrocarbon base extraction from drill cuttings is considered and it is found that hexane is the most promising one. The estimation of operating costs for carrying out the OBM treatment using the organic solvent nanofiltration technology are of 0.6-0.84 $/l.

1. Introduction

In the process of well construction and drilling, special technological fluids called drilling fluids are used.
There are several types of drilling fluids, including oil-based mud (OBM). OBM is a multicomponent mixture, which contains mineral oil (hydrocarbon base), various mineral additives and surfactants, which vary physical characteristics of the solution depending on the well characteristics. A typical OBM composition is shown in table 1 [1-2].

| Reagent             | Concentration, kg / m³ |
|---------------------|------------------------|
| Mineral oil         | 500-700                |
| Water               | 100-200                |
| Emulsifiers, surfactants | 15-20        |
| Organophilic clay   | 10-15                  |
| Calcium carbonate   | 80-100                 |
| Additional reagents | If necessary           |

After a well drilling, the drilling fluid composition is enriched with impurities: gas (air), water, oil and solids. The mixture is a stabilized multiphase system with direct and inverse emulsions and suspensions that are difficult to separate.

After separation of the solid phase on vibrating screens, hydrocyclones and centrifuges, the OBM’s liquid phase is sent to the cycle for reuse. The solid phase, which contains 15-20 wt. % [3-4] of the hydrocarbon base, as well as waste mud, goes to special storage facilities (mud pits) and must be subjected to further (or secondary) processing.

The most countries’ environmental standards require the residual hydrocarbon content in the sludge less than 1 wt. % [3]. Otherwise, damage to the environment is caused: withdrawal of forest land for
the placement of mud pits; ground and surface waters depletion and pollution; soils’ waterlogging, dehydration and salinization; pollution by harmful substances and chemical elements of atmospheric air [5].

In addition, the absence of mud treatment causes the loss of valuable component - a hydrocarbon base, the cost of which varies from 0.7 to 4 $/kg [2; 6]. Furthermore, the most of the oil wells are located in hard-to-reach regions, and the introduction of on-site drill cuttings and regeneration treatment, i.e. reuse of the hydrocarbon base of OBM, solves economic, logistic and economic problems.

Therefore, waste muds and drill cuttings are to be recycled.

To our opinion, extraction is the most promising technology of hydrocarbon base recovery from drill cuttings. It allows almost completely to extract oil from cuttings at the required level of purification.

Also, we consider, that the use of membrane purification methods - ultrafiltration and / or nanofiltration is necessary to increase the efficiency of the extraction process and the possibility of reusing both the hydrocarbon base and the solvent (extractant).

2. Materials and methods

A real drilling mud from a mud pit was used to study the extraction and select the optimal solvent.

The following solvents were used to study the extraction process:

- Acetone – 99 wt. %;
- Toluene, high purity – 99,5 wt. %;
- Hexane – 98,48 wt.%;
- Isopropanol, chemically pure – 99,8 wt. %.

The effectiveness the extractant use was evaluated by the mass of the hydrocarbon base released during the distillation process.

Atmospheric pressure and temperature were measured in the laboratory before each experiment. All experiments were carried out in a ventilating hood due to the toxicity and high volatility of solvents and hydrocarbons that make up the drilling fluid.

A fixed volume of thoroughly mixed waste drilling fluid was poured into the graduated cylinder. A fixed volume of organic solvent was poured into the second graduated cylinder; after which it was added to the first cylinder to the waste drilling fluid. The mass of the resulting mixture was determined; the data were recorded in the experiment log. The neck of the graduated cylinder was closed to avoid solvent loss during the experiment due to its high volatility. Separation of solid and liquid phases was carried out by settling. After separating the mixture into liquid and solid phases, their masses were measured. The liquid fraction was distilled to obtain the mineral oil.

The selected drilling fluid was placed in a 200 ml round-bottom flask and connected to a distillation unit. The temperature of the coolant in the container should not exceed the boiling point of the organic solvent by more than 20-30 °C. The distillation process was completed at the moment the vapor temperature rose higher than the boiling point of the organic solvent. After carrying out the distillation, the mass of the organic solvent and extracted mineral oil were measured. The data obtained were recorded in the experiment log.

The solid phase, which contains a hydrocarbon base and a solvent, was thermally treated. Organic solvent was obtained in the distillate, - a precipitate and non-extracted oil - in the still residue. The mass of the organic solvent was determined, and the still residue was put to evaporation. The flask with the solid phase was placed in a silicone oil bath and the residual liquid was removed at a temperature of about 170 °C. After evaporation the flask with dry sediment was weighed.
3. Results
The results of the experiments are presented in Table 2 (the volume ratio of the waste drilling fluid to solvent is 1 to 10).

Table 2. Result of extraction of mineral oil from waste drilling muds.

| Solvent    | OBR weight, g | Solvent weight, g | Mineral base weight, g | Solvent after distillation weight, g | Sediment weight, g |
|------------|---------------|-------------------|------------------------|-------------------------------------|--------------------|
| Acetone    | 9.97          | 78.78             | 4.90                   | 74.60                               | 2.20               |
| Toluene    | 10.00         | 86.45             | 6.32                   | 78.18                               | 1.79               |
| Hexane     | 10.01         | 65.82             | 6.56                   | 62.11                               | 1.79               |
| Isopropanol| 10.01         | 78.30             | 4.50                   | 75.92                               | 1.59               |

In figure 1 shows a comparison of the OBM extraction process by hexane and acetone. The separation of the solid and liquid phases by acetone occurred almost instantly, but the efficiency of the hydrocarbon base extraction was relatively low.

![Figure 1. Extraction of mineral oil from drilling mud by acetone (left) and hexane (right).](image)

Taking into account the economic component, the studies carried out show that hexane is the most promising extractant,

4. Discussion
It is known that membrane separation processes have advantages over traditional separation processes (evaporation, rectification) - there is no phase transition and additional heating in the separation process, which leads to significant savings in specific energy consumption (an order of magnitude lower than distillation [3]), the ability to separate thermolabile (temperature-sensitive) compounds, high selectivity of separation, relative ease of use and modularity of the system.

As applied to OBM purification, it is proposed to use ultrafiltration and nanofiltration of organic media (OSN - Organic Solvent Nanofiltration).
Ultrafiltration (UF) - used to separate high molecular weight (molecular weight 30 - 150,000 Da) and low molecular weight compounds.

The UF process is used after extraction to isolate a finely dispersed solid phase and liquid phase purification, as a preparatory stage before nanofiltration.

The nanofiltration process using special membranes resistant to organic solvents (polymeric and inorganic), providing high values of the specific solvent flux through the membrane and, at the same time, a high retarding characteristic of a solute (hydrocarbon base) with a molecular weight of 100 to 1000 g/mol seems very promising.

To characterize the separating properties of the membrane, such a concept as the cut-off factor for molecular weight (MW) is used. Thus, the higher the value of the cutoff coefficient for MW, the larger, bulky molecules can penetrate through the membrane.

For binary systems (in our case, “mineral oil-extractant (hexane)”), a substance with a lower molecular weight (hexane) predominantly penetrates through the membrane, and the hydrocarbon base of the drilling mud, which has a higher molecular weight, is retained.

Currently, several patented technologies have been developed using nanofiltration to separate aqueous-organic and organic mixtures, and a number of commercial membranes for OSN are being produced. The most promising commercial membranes for OSN and related technologies are:

- BORSIG Membrane Technology (Germany) - PDMS-based membranes for use in the chemical and petrochemical, food industries for solvent extraction and regeneration of the oil base, fractionation of hydrocarbons, decolorization and dewaxing, separation of thermally unstable organic compounds [7];
- SolSep BV (Holland) – spiral wound membrane modules (membrane based on PDMS) for carrying out the process of nanofiltration of organic media such as: recovery of solvents, dewaxing, fractionation of oligomers and polymers, recovery of dyes and solvents, etc. [8];
- SelRo (Koch, USA) - composite membranes with a non-porous selective PDMS layer [9];
- DuraMem and PuraMem (Evonik) - a series of asymmetric polyimide membranes and modules based on them for OSN, stable in most solvents even at elevated temperatures [10-12].

Naturally, it is impossible to carry out the process of purification and regeneration of the extractant and mineral base in one stage.

The performed analysis and search for possible solutions assumes the following road map.

The extractant and the spent drilling fluid are fed into the reactor with a stirrer, where they are separated into a three-component system: solid phase - extractant + mineral oil - water. The resulting mixture is supplied to an ultrafiltration unit, where the process of separation of solid (dispersed) and organic, liquid (extractant and mineral oil) phases takes place. The liquid phase is fed to the OSN membrane unit, where it is separated into a stream of permeate - extractant and concentrate - enriched to 70-80 wt. % mineral oil. Oil through an intermediate tank is supplied to the evaporator for concentration up to 99,5 wt. %. The extractant after the stages of nanofiltration and evaporation is returned to the reactor, the losses of the extractant do not exceed 5 wt. %.

The main costs in the operation of this technology are: electricity spent on pumping and increasing pressure in ultra- and nanofiltration units; heat costs (steam, hot water and other sources of thermal energy); replenishment of the extractant; reagents for technological processes and chemical cleaning of equipment.

Table 3 presents the main items of operating costs and their estimated costs.

Thus, the cost of mineral oil obtained by our technology is about 0,60-0,83 $/l, the oil return is 90-95%.
Table 3. Cost calculations of refined and recovered mineral oil (hydrocarbon base).

| Types of costs                  | Unit quantity | Cost, $ for 1 l of refined oil |
|---------------------------------|---------------|-------------------------------|
| Electricity                     | 2-3 kW·h/l    | 0.14-0.2                      |
| Heat costs                      | 0.02 Gcal/l   | 0.27                          |
| Replenishment of extractant     | 0.2-0.4 l/l   | 0.16-0.32                     |
| Other reagents                  | -             | 0.04                          |
| Total                           |               | 0.60-0.83                     |

5. Conclusion
Our analysis shows that OSN can be effective for separating waste oil-based drilling fluids, the disposal of which is a serious task from the point of view of solving environmental problems and increasing energy and resource conservation. The estimated calculations also show the economic benefit of the proposed process - the cost of the regenerated oil is 0.60-0.83 $/l, as well as the possibility of reusing the extractant.

The conducted research shows that hexane is the most effective solvent for separating hydrocarbon base from mineral oil.

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