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Development of effective chemicals for drilling fluid based on local and raw materials

Opracowanie skutecznych odczynników chemicznych do płuczek wiertniczych na bazie surowców lokalnych

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ABSTRACT: The paper presents the current state of chemical reagents used in the development and production of drilling fluids for oil and gas well drilling, based on local and raw materials from Uzbekistan. A novel and effective chemical reagent, MBR (drilling fluid lubricant), has been obtained from gossypol resin, a by-product of cotton oil production. Types of weighted water-based drilling fluids using bentonite, carboxymethylcellulose (CMC), MBR (Moylovchi burg'ilash reagent), barite, and hematite and their physical and chemical properties were investigated. Methods for testing drilling fluid properties were studied, and the compositions and contents of chemical reagents and weighting agents for the preparation of weighted drilling fluids have been provided. The water-soluble modified powdery resin contains hydrophobic additives based on sodium salt of fatty acids and ionic surfactants. The use of these reagents in drilling fluids for oil and gas wells ensures the preservation of regulated rheological and filtration properties of polymer systems at 80–190°C for 30–40 hours. A method for obtaining new effective chemical reagents based on the physical and chemical modification of initial materials under various ratios, environments, and regimes has been developed. The requirements for chemical reagents and weighting agents according to geological conditions of oil and gas boreholes have been studied. A new formulation of weighted drilling fluids based on MBR, barite, and hematite using salt water with densities of 2.15 and 2.41 g/cm^3 has been developed and recommended for use in oil and gas well drilling. The application of these research results is expected to increase the lubricity of drilling fluid due to the use of the MBR lubricant, enhance the mechanical speed of drilling, and can help address certain ecological problems in the country through the utilization of cotton oil and fat production waste.

Key words: chemicals, drilling fluid, drilling, oil, gas, well, gossypol, CMC, barite, properties.

STRESZCZENIE: W artykule przedstawiono aktualny stan odczynników chemicznych wykorzystywanych do opracowywania i produkcji płuczek wiertniczych do wiercenia odwiertów naftowych i gazowych na bazie surowców lokalnych pochodzących z Uzbekistanu. Otrzymano nowy, skuteczny odczynnik chemiczny – MBR (dodatek smarujący do płuczki wiertniczej) – będący produktem ubocznym w procesie wytwarzania oleju z nasion bawełny. Zbadano rodzaje obciążonych płuczek wiertniczych na bazie wody zawierających bentonit, karboksymetyloceluloz (CMC), MBR, baryt i hematyt oraz ich właściwości fizykochemiczne. Przeanalizowano metody badania właściwości płuczki wiertniczej, a także przedstawiono skład i zawartość odczynników chemicznych i materiałów ciężkich używanych do sporządzania obciążonych płuczek. Rozpuszczalna w wodzie modyfikowana żywica w proszku zawiera dodatki hydrofobowe na bazie soli sodowej kwasów tłuszczowych i anionowych środków powierzchniowo czynnych. Zastosowanie tych środków w płuczkach przeznaczonych do wiercenia odwiertów ropnych i gazowych pozwala na zachowanie regulowanych właściwości reologicznych i filtracyjnych układów polimerowych w temperaturze 80–190°C przez 30–40 godzin. Opracowano metodę uzyskiwania nowych, skutecznych środków chemicznych poprzez fizykochemiczną modyfikację materiałów wyjściowych w różnych proporcjach, środowiskach i warunkach. Przeanalizowano wymagania dotyczące odczynników chemicznych i materiałów ciężkich w zależności od warunków geologicznych panujących w otworach naftowych i gazowych. Opracowano nową recepturę obciążonych płuczek wiertniczych na bazie MBR, barytu i hematytu, z użyciem wody solankowej o gęstości 2,15 i 2,41 g/cm^3,

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którą zarekomendowano do stosowania w wierceniach otworów ropnych i gazowych. Wdrożenie wyników tych badań pozwala zwiększyć właściwości smarne płuczki wiertniczej dzięki zastosowaniu środka smarującego MBR, poprawić mechaniczną prędkość wiercenia, a także przyczynić się do rozwiązania niektórych problemów ekologicznych w kraju poprzez zagospodarowanie odpadów z produkcji olejów i tłuszczów z nasion bawełny.

Słowa kluczowe: chemikalia, płuczka, wiercenie, ropa, gaz, odwiert, gossypol, CMC, baryt, właściwości.

Introduction

At present, more than 3000 types of chemicals are used globally for the preparation and stabilization of drilling fluids used for oil and gas well drilling. These include carboxymethylcellulose (CMC), polyacrylamide, hydrolyzed polyacrylonitrile, ferrochrome-lignosulphonate, graphite, chromium picolinate (chrompic), NaOH, Na_2CO_3 and others. In the Republic of Uzbekistan, approximately 2,500–3,000 thousand tons of chemical reagents are used annually for drilling oil and gas wells (Kobilov et al., 2023).

During the drilling process, it is essential to configure an appropriate mud system to ensure the proper operation of the drilling rig. This requires suitable values for viscosity, specific gravity, water loss, and some other parameters. These indicators must be adjusted to suit different regions, drilling depths, and mud types. The addition of CMC helps adjust these parameters, reduce water loss, and improve operational efficiency (Fagundes et al., 2018).

With an annual cotton production of approximately 1 million tons of fiber (4–5% of global production), and exports of 700,000–800,000 tons (10% of global exports), Uzbekistan ranks as the eighth-largest producer and the eleventh-largest exporter of cotton in the world. Cotton is often referred to as "white gold" (Uzbek: *oq oltin*) in the country. Carboxymethylcellulose, derived from cotton cellulose, is one of the most important cellulose derivatives due to its versatility as a thickener, binding agent, emulsifier, and stabilizer. The presence of $–CH_2– COONa^+$ substituent groups on the cellulose backbone is responsible for its high solubility in aqueous media. Polymer concentration, salt content, pH, the presence of surfactant, molecular structure, molecular weight, and degree of substitution significantly influence the properties of CMC solutions. This polysaccharide has found applications across numerous industries, including food, pharmaceuticals, biomaterials, cosmetics, and electronics, as well as in oilfield operations such as drilling fluids (Caenn et al., 2017).

CMC added to drilling mud can reduce water loss by forming a thin but dense, low-permeability filter cake on the borehole wall. It also enables the rig to achieve a low initial shear force, which facilitates the release of trapped gas and the effective removal of debris. CMC-containing mud is stable and can effectively reduce water loss even at temperatures exceeding 150°C. Additionally, CMC, as an effective stabilizer, extends the service life of drilling mud and helps protect both the mud and the drill bit from damages caused by soluble salts.

Sodium CMC is produced by "Carbonam" JSC. As sodium salt, CMC is used in drilling fluids, completion fluids, and fracturing fluids. In drilling fluids, it functions as a viscosifier, filtration reducer, and rheology controller; in completion fluids, it helps control fluid viscosity, suspend heavy solids, and prevent fluid loss; in fracturing fluids, it is used to carry proppants and minimize fluid loss. The requirements for CMC viscosity and degree of substitution vary depending on the region, mud type, and drilling depth.

In all cotton-producing countries and factories, gossypol resin is formed as a by-product during cottonseed processing. This substance has a viscous, fluid-like consistency and is now being explored for more effective utilization. Transforming viscous gossypol resin into a powdered form by modifying it with various organic and inorganic ingredients offers commercial potential and could expand its large-scale applications (Negmatova et al., 2012).

In line with a governmental resolution, the State Committee on Geology and Mineral Resources of Uzbekistan conducted in the years 2010–2024 a geologic survey at perspectives fields – Oraylyk, Agata, Kichi-Arsagan, Karakiya, Guldurama. It is anticipated that barite ores from these fields will be processed in Almalyk, Tashkent region, where processing facilities with a capacity of up to 15,000 tons a year will be established. In the future, barite concentrate production will also be organized in Almalyk. The plant will produce 15,000 tons of barite concentrate annually from ores extracted at the Sarybulak and Kushrabad fields. "Uzbekneftegaz" JSC will finance the mining of barite ore at the Sarybulak field and the experimental-industrial production at the prospective fields – Oraylyk, Agata, Kichi-Arsagan, Karakiya, Gulduram with the production of barite concentrate.

Materials and methods

For stabilization and preparation of weighted drilling fluids, the following materials were used: water-soluble modified powdered gossypol resins, carboxymethylcellulose sodium (produced by "Carbonam" JSC, with a polymerization degree of 500), soda ash (Na_2CO_3), and caustic soda (NaOH). The weighting agents used included red clay, marble flour, dolomite, scale, hematite, and barite.

In the development of new chemical reagents for the stabilization of drilling fluids used in oil and gas well drilling, the primary raw materials included waste from cotton oil and fat production (gossypol resin) and low-mass carboxymethylcellulose. Gossypol resin consists of 52–64 free fatty acids (FFA) and their derivatives, with the remainder comprising products of gossypol condensation and polymerization, as well as transformation products formed during the distillation of fatty acids from soapstock in the cottonseed oil extraction process. Gossypol resin also contains 12% nitrogen-containing compounds and 36% gossypol transformation products including fatty acids and their oxidized derviatives. It is a homogenous fluid mass ranging in color from dark brown to black. A new chemical reagent was obtained based on gossypol resin and conditionally (preliminary) named MBR (drilling fluid lubricant) (Kobilov et al. 2023).

In the Republic of Uzbekistan, approximately 3,000–4,000 tons of gossypol resin and over 2,000 tons of oil sludge are generated annually. These waste materials pose serious environmental threats and are very harmful to human health. Oil sludge, a by-product of crude oil processing and transportation, presents significant ecological risks, including soil and water contamination, air pollution, and potential harmful effects on living organisms. These issues arise from the presence of various hazardous compounds within the sludge, such as polycyclic aromatic hydrocarbons (PAHs), heavy metals, and volatile organic compounds.

The process of obtaining the MBR lubricant is based on the modification of gossypol resin and oil sludge using solutions of caustic alkali (8–10%) and calcined soda (3–5%) at a temperature of 70–80°C. All reagents are then mixed for 30–40 minutes until a homogeneous mass is obtained. This technology enables complete recycling of the aforementioned industrial wastes.

The American Petroleum Institute (API) publishes standards relating to oilfield operations, including drilling fluids testing procedures (Parate, 2021). Investigations of drilling fluids properties are carried out according to the API (ANSI/API RP 13b-1, 2017) standards. As with all laboratory procedures involving potentially hazardous chemicals and equipment, users are expected to have appropriate training and knowledge regarding the use and disposal of such materials. Users are also responsible for compliance with all applicable local, regional, and national health, safety, and environmental regulations (Kobilov et al., 2023).

Polymers are widely used in the oil industry to control the properties of drilling fluids and for enhanced oil recovery applications, particularly for extracting heavy oil. Polymer flooding is a crucial method for extracting heavy oil from thin and heterogeneous reservoirs (Mohamed et al., 2017). Screening criteria and algorithms should be developed to optimize oil recovery techniques (Omland et al., 2007). Artificial intelligence and data mining can assist in managing reservoirs for polymer flooding, especially in thin and heterogeneous heavy oil reservoirs.

Determination of physical and chemical properties of drilling fluids

- **Determination of mud density**
  The density of the mud samples was determined using a Baroid mud balance. After calibration, the cup was completely filled with the mud sample. Excess mud was expelled and cleaned, and the balance arm was placed back on the base, with the knife edge resting on the fulcrum.
- **Determination of mud viscosity**
  The viscosity of the mud samples was measured using a Fann V-G meter. The meter was filled with the sample to the 350 cm^3 mark and placed on the movable work table. The table was adjusted until the mud surface aligned with the scribed line on the rotor sleeve. The motor was started in the high-speed position (600 rpm), and the reading was taken from the steady indicator dial. A second reading was obtained at the low speed of 300 rpm.
- **Determination of pH**
  The pH of the analyzed muds was determined using a pH meter consisting of a glass electrode system, an electronic amplifier, and a meter calibrated in pH units. The electrical connection with the mud was established through a saturated KCl solution contained in a tube surrounding the calomel cell. The electrical potential generated in the glass electrode system by the hydrogen ions in the drilling mud was amplified, and pH was displayed on the calibrated meter.
- **Determination of stability index**
  Stability refers to the ability of a drilling fluid to maintain its density over time. The stability index (C) is determined by the difference in densities between the lower and upper parts of a settled drilling mud sample over a specified period. Procedure of determination using a TS-2 stability cylinder:
  – pour a thoroughly mixed sample of the solution into a 720 cm^3 cylinder until full;
  – place the filled cylinder in a quiet place and leave it undisturbed for 24 hours;
  – after 24 hours, open the tap and drain the upper part of the sample along with the separated water;
  – mix the drained portion thoroughly and measure its density, ρ_1;

– close the tap with a stopper, mix the remaining lower portion thoroughly, and measure its density, ρ_2;
– the stability index is calculated by the difference in densities:

$$C = \rho_1 - \rho_2 \text{ [g/cm}^3\text{]}$$

- **Determination of water filtration (water loss)**
  To measure the water filtration of drilling fluids, the API filter press test is commonly used. Briefly, a sample of drilling fluid is placed in the cell of press, and a filter paper is positioned on the mesh in the base. A specific pressure (usually 100 psi) is applied, and the filtrate volume passing through the filter paper is measured over a set time, typically 30 minutes [cm^3/30 min]. The resulting filter cake is also examined for its quality and thickness.
- **Determination of shear stress**
  To measure the shear stress of drilling fluids, a viscometer is used to assess the fluid's behavior under different shear rates. The shear stress is measured at various shear rates after 10 seconds and 10 minutes of resting period. This process helps determine the fluid's gel strength and other rheological properties, which are crucial for understanding how the fluid will behave in the wellbore.

Results and discussion

A technology has been developed for the production of effective MBR-type reagents using low molecular weight sodium carboxymethylcellulose, alkali, and organic-mineral additives in various ratios to enhance the physical and chemical properties of drilling fluids. The water-soluble modified powdery resin contains hydrophobic additives based on sodium salt of fatty acids and ionic surfactants. The use of these reagents in drilling fluids for oil and gas wells ensures the preservation of regulated rheological and filtration properties of polymer systems at temperatures of 80–190°C for 30–40 hours. The method involves the physical and chemical modification of the initial materials under varying ratios, environments, and regimes.

CMCs are not as shear-thinning as fermentation biopolymers and exhibit little to no suspending ability. However, they are excellent fluid loss control agents. Hydroxyethyl celluloses (HECs) are primarily used as a bulk viscosifiers in saturated brines, such as chlorides and bromates, for completion fluids. They also lack suspending ability and have low particle-carrying capacity under annular flow conditions. Table 1 lists the various oilfield cellulosic products.

Barite weighting additive is a barium sulfate-based material used to increase the density of drilling mud and cement slurries. Typically, 85 to 90% of barite additive passes through a 325-mesh sieve. It is effective at bottom-hole temperatures (BHTs) between 80°F and 500°F (27°C and 260°C). A barite additive concentration of 135 lb/sk of cement yields a maximum slurry weight of 19 lb/gal.

Barite and other weighting materials are compounds that are dissolved or suspended in drilling fluid to increase its density. They are used to control formation pressures and to resist the effects of sloughing or heaving shales that may be encountered in stressed areas. Barite is often added as a weighting agent to counteract pressure in the geologic formations being drilled, thereby preventing blowouts. Some commercial drilling mud barites contain elevated (compared to marine sediments) concentrations of several metals. If bioavailable, these metals may harm the local marine ecosystem. The bioavailable fraction of metals is defined as the portion that dissolves from nearly insoluble, solid barite into seawater or sediment porewater. Barite-seawater and barite-porewater distribution coefficients (Kd) were calculated to determine the predicted environmental concentration (PEC), i.e. the bioavailable fraction of metals from drilling mud in the water column and sediments. The analysis of current state of API specification (ANSI/API 13A, 2019) is presented in Table 2.

Barite, derived from the Greek word for "heavy", has a specific gravity of approximately 4.2 to 4.6 g/cm^3. Its hardness ranges from 2.5 to 3.5. This mineral is used in different densities and hardness levels to meet the requirements of various drilling formations. The amount of alkaline earth metals soluble in water should be less than 250 mg/kg. In addition, barite used

Table 1. Modified cellulosic products: differences and applications
Tabela 1. Modyfikowane produkty celulozowe: różnice i zastosowania

Oilfield cellulosic		
Carboxymethylcellulose (CMC)	Polyanionic cellulose (PAC)	Hydroxyethyl cellulose (HEC)
Low Degree of substitution	High Degree of substitution	High Degree of substitution
Anionic	Anionic	Nonionic
Subject to precipitation with calcium	Can tolerate calcium	Viscosifiers high density, saturated brines
Routine fluid loss control	Fluid loss control in fresh and brine water-based fluids	Bulk viscosifiers for saturated high-density brines

Table 2. Physical and chemical properties and API specifications for barite-based drilling mud (ANSI/API, 13A, 2019)

Tabela 2. Właściwości fizyczne i chemiczne oraz specyfikacje API dla płuczki obciążonej barytem (ANSI/API, 13A, 2019)

Parameters	Barite-based drilling mud	API specification
Specific Gravity	3.85–4.01 g/cm^3	4.10 or 4.20 g/cm^3 min
$BaSO_4$	80–85%	85% or 90% min
Extractable Carbonates	2580 mg/l	3000 mg/l max
Hg	0.95 ppm	1.00 ppm max
Cd	2.80 ppm	3.00 ppm max
Water Alkaline Earth Metals (as Calcium)	2600 ppm	250 ppm max
Moisture	1.05%	1.00% max
Residue >75 micrometers	5.00%	3.00% max
Particles <6 micrometers in equivalent spherical diameter	20.00%	30.00% max

in offshore drilling rigs must meet environmental regulations regarding mercury and cadmium content.

The developed drilling fluid fromulations based on CMC-HV, MBR, barite, and hematite, and their physical and chemical properties are provided in Tables 3–4.

According to the results of the experiment provided in Table 3, when weighting the drilling fluid with barite content of up to 80%, in a drilling fluid formulation containing 5% bentonite, 0.5% CMC-HV, 0.4% Na_2CO_3, and 2% MBR drilling solution, the fluid density increases to 2.15 g/cm^3. The water loss remains nearly constant at 4 cm^3/30 min, and the pH is stable at 9 – the addition of barite does not cause any changes to these parameters, so they are considered constant. The apparent viscosity of the drilling fluid ranges from 56 to 78 s and the shear stress of the fluid ranges from 36 to 42 mgf/cm^2 after 10 minutes.

Table 3. Physical and chemical properties of drilling fluid based on MBR and barite

Tabela 3. Właściwości fizyczne i chemiczne płuczki wiertniczej na bazie MBR i barytu

Drilling fluid composition	Physical and chemical properties					
	ρ [g/cm^3]	*V* [s]	*W* [cm^3/30 min]	*SS* (1/10 min) [mgf/cm^2]	*C* [g/cm^3]	pH
N1: 1000 ml saline water + 5% bentonite + 0.5% CMC-HV + + 0.4% Na_2CO_3 + 2% MBR	1.05	25	4	18/25	0.02	9
N1 + 20% Barite	1.28	30	4	20/26	0.03	9
N1 + 40% Barite	1.52	34	4	22/27	0.04	9
N1 + 60% Barite	1.75	56	4	28/36	0.05	9
N1 + 80% Barite	2.15	78	4	34/42	0.06	9
ρ – density, *V* – apparent viscosity, *W* – water loss, *SS* – static shear stress, *C* – stability index.						

Table 4. Physical and chemical properties of drilling fluid based on MBR and hematite

Tabela 4. Właściwości fizyczne i chemiczne płuczki wiertniczej na bazie MBR i hematytu

Drilling fluid composition	Physical and chemical properties					
	ρ [g/cm^3]	*V* [s]	*W* [cm^3/30 min]	*SS* (1/10 min) [mgf/cm^2]	*C* [g/cm^3]	pH
N1: 1000 ml saline water + 5% bentonite + 0.5% CMC-HV + + 0.4% Na_2CO_3 + 2% MBR	1.05	25	4	16/23	0.02	9
N1 + 20% Hematite	1.37	28	4	18/25	0.03	9
N1 + 40% Hematite	1.63	32	4	21/26	0.04	9
N1 + 60% Hematite	1.92	53	4	27/34	0.05	9
N1 + 80% Hematite	2.41	66	4	32/42	0.06	9
ρ – density, *V* – apparent viscosity, *W* – water loss, *SS* – static shear stress, *C* – stability index.						

To ensure optimal drilling conditions, implement effective circulation technologies and prevent potential complications, it is necessary to consider several factors. The developed MBR lubricant was applied during gas well drilling in the Chilkuvar field of Uzbekistan. Salt-bearing anhydrite strata are present at depths of 2800–3200 m. According to geological and technological assessments, the required weighted drilling fluid parameters include a density of 1.8–2.2 g/cm^3, apparent viscosity of 60–80 s, filtration index of 4–5 cm^3/30 min, shear stress of 35–45 mgf/cm^2 (after 10 minutes), and pH of 9–10.

The stabilization of drilling fluids refers to the ability of a solution to keep solid particles suspended. For fluids not weighted with barite, this value is 0.02 g/cm^3. With the addition of weighting materials, the stabilization index increases by 0.02 up to 0.06 g/cm^3. However, according to the results of the experiment provided in Table 4, when the hematite content in the drilling fluid is increased up to 80%, the fluid density reaches 2.41 g/cm^3. The water loss remains virtually constant at 4 cm^3/30 min, and the pH remains stable at 9. The apparent viscosity ranges from 25 to 66 s, while the shear stress is in the range of 34–42 mgf/cm^2 after 10 minutes. The water loss remains virtually constant at 4 cm^3/30 min, and the pH is stable at 9 – the addition of hematite does not cause any changes of these parameters, so they are considered constant. All tested parameters of the drilling fluids meet the geological and technical requirements for oil and gas wells. The use of the developed MBR-type lubricants reduces the coefficient of friction and increases drilling speed by 10–15%. In addition, the fatty acids present in the lubricant composition inhibit corrosion of metal components and extend the operational lifespan of drilling rigs and bits.

Conclusion

A new formulation of weighted drilling fluids based on MBR, barite, and hematite, using salt water with densities of 2.15 and 2.41 g/cm^3, has been developed and is recommended for use in the drilling of oil and gas wells with abnormally high reservoir pressure (AHRP). Furthermore, the application of the research findings will enhance the lubricity properties of drilling fluids due to the use of the MBR lubricant, increase the mechanical rate of penetration, and contribute to solving certain environmental issues through the utilization of cotton oil and fat production waste. The findings also demonstrate that barite additives offer the following benefits: by increasing slurry density, they help control high formation pressures and improve mud displacement efficiency. These formulations are suitable for use in deep, high-temperature wells.

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List of abbreviations

AHRP	Abnormally high reservoir pressure
API	American Petroleum Institute
BHTs	Bottom-hole temperatures
CMC	Carboxymethylcellulose
DS	Degree of substitution
FFA	Free fatty acids
HECs	Hydroxyethyl celluloses
HV	High viscosity
JSC	Joint stock company
LV	Low viscosity
MBR	Moylovchi burg'ilash reagent – drilling fluid lubricant
PAC	Polyanionic cellulose
PAH	Polycyclic aromatic hydrocarbons
PEC	Predicted environmental concentration
TS-2	Stability cylinder

Nomenclature

ρ	Density
V	Apparent viscosity
W	Water loss-filtration
SS	Shear stress
pH	Acidity
Kd	Distribution coefficients
NaOH	Caustic soda
Na_2CO_3	Soda ash
C	Stability index

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