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### «ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ» РҚБ «ХАЛЫҚ» ЖҚ

### ХАБАРЛАРЫ

### ИЗВЕСТИЯ

РОО «НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН» ЧФ «Халык»

## NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF
KAZAKHSTAN
«Halyk» Private Foundation

# SERIES OF GEOLOGY AND TECHNICAL SCIENCES

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NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАНРК сообщает, что научный журнал «Известия НАНРК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.



#### ЧФ «ХАЛЫК»

В 2016 году для развития и улучшения качества жизни казахстанцев был создан частный Благотворительный фонд «Халык». За годы своей деятельности на реализацию благотворительных проектов в областях образования и науки, социальной защиты, культуры, здравоохранения и спорта, Фонд выделил более 45 миллиардов тенге.

Особое внимание Благотворительный фонд «Халык» уделяет образовательным программам, считая это направление одним из ключевых в своей деятельности. Оказывая поддержку отечественному образованию, Фонд вносит свой посильный вклад в развитие качественного образования в Казахстане. Тем самым способствуя росту числа людей, способных менять жизнь в стране к лучшему – профессионалов в различных сферах, потенциальных лидеров и «великих умов». Одной из значимых инициатив фонда «Халык» в образовательной сфере стал проект Ozgeris powered by Halyk Fund – первый в стране бизнес-инкубатор для учащихся 9-11 классов, который помогает развивать необходимые в современном мире предпринимательские навыки. Так, на содействие малому бизнесу школьников было выделено более 200 грантов. Для поддержки талантливых и мотивированных детей Фонд неоднократно выделял гранты на обучение в Международной школе «Мирас» и в Astana IT University, а также помог казахстанским школьникам принять участие в престижном конкурсе «USTEM Robotics» в США. Авторские работы в рамках проекта «Тәлімгер», которому Фонд оказал поддержку, легли в основу учебной программы, учебников и учебно-методических книг по предмету «Основы предпринимательства и бизнеса», преподаваемого в 10-11 классах казахстанских школ и колледжей.

Помимо помощи школьникам, учащимся колледжей и студентам Фонд считает важным внести свой вклад в повышение квалификации педагогов, совершенствование их знаний и навыков, поскольку именно они являются проводниками знаний будущих поколений казахстанцев. При поддержке Фонда «Халык» в южной столице был организован ежегодный городской конкурс педагогов «Almaty Digital Ustaz.

Важной инициативой стал реализуемый проект по обучению основам финансовой грамотности преподавателей из восьми областей Казахстана, что должно оказать существенное влияние на воспитание финансовой грамотности и предпринимательского мышления у нового поколения граждан страны.

Необходимую помощь Фонд «Халык» оказывает и тем, кто особенно остро в ней нуждается. В рамках социальной защиты населения активно проводится

работа по поддержке детей, оставшихся без родителей, детей и взрослых из социально уязвимых слоев населения, людей с ограниченными возможностями, а также обеспечению нуждающихся социальным жильем, строительству социально важных объектов, таких как детские сады, детские площадки и физкультурно-оздоровительные комплексы.

В копилку добрых дел Фонда «Халык» можно добавить оказание помощи детскому спорту, куда относится поддержка в развитии детского футбола и карате в нашей стране. Жизненно важную помощь Благотворительный фонд «Халык» оказал нашим соотечественникам во время недавней пандемии COVID-19. Тогда, в разгар тяжелой борьбы с коронавирусной инфекцией Фонд выделил свыше 11 миллиардов тенге на приобретение необходимого медицинского оборудования и дорогостоящих медицинских препаратов, автомобилей скорой медицинской помощи и средств защиты, адресную материальную помощь социально уязвимым слоям населения и денежные выплаты медицинским работникам.

В 2023 году наряду с другими проектами, нацеленными на повышение благосостояния казахстанских граждан Фонд решил уделить особое внимание науке, поскольку она является частью общественной культуры, а уровень ее развития определяет уровень развития государства.

Поддержка Фондом выпуска журналов Национальной Академии наук Республики Казахстан, которые входят в международные фонды Scopus и Wos и в которых публикуются статьи отечественных ученых, докторантов и магистрантов, а также научных сотрудников высших учебных заведений и научно-исследовательских институтов нашей страны является не менее значимым вкладом Фонда в развитие казахстанского общества.

С уважением, Благотворительный Фонд «Халык»!

#### Бас редактор

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### «ҚР ҰҒА» РҚБ Хабарлары. Геология және техникалық ғылымдар сериясы».

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### © O.V. Rozhkova<sup>1,3\*</sup>, D.M.-K. Ibraimova<sup>2,4</sup>, K.B. Musabekov<sup>2</sup>, V.I. Rozhkov<sup>3,4</sup>, M.T. Ermekov<sup>1</sup>, 2024

<sup>1</sup>AO «Science and Technology Solutions», Almaty, Kazakhstan;

<sup>2</sup> NJSC Al-Farabi Kazakh National University, Almaty, Kazakhstan;

<sup>3</sup> NJSC Saken Seifullin Kazakh Agrotechnical Research University», Astana, Kazakhstan;

<sup>4</sup> Altai Geological-Ecological Institute LLP, Ust-Kamenogorsk, Kazakhstan.

E-mail: rozhkova.o@stsolutions.kz

# DEVELOPMENT OF ANHYDROUS DRILLING FLUIDS BASED ON TAGAN DEPOSIT'S SUPERHYDROPHOBIC CLAY FOR DRILLING OIL WELLS AT THE KUMKOL FIELD

**Rozhkova O.V.** — Doctor of Chemistry, Professor of NJSC «Saken Seifullin Kazakh Agrotechnical Research University», Astana, Kazakhstan; JSC «Science and Technology Solutions», Astana, Kazakhstan E-mail: rozhkova.o@stsolutions.kz; https://orcid.org/0000-0001-8163-7035;

**Ibraimova D.M.-K.** — candidate of Chemical Sciences, Senior Lecturer of the NJSC «Al-Farabi Kazakh National University, Almaty, Kazakhstan; LLP «Altai Geological and Ecological Institute», Ust-Kamenogorsk, Kazakhstan E-mail: dana kereevna@kaznu.kz; https://orcid.org/0000-0002-1761-9745;

**Musabekov K.B.** — Doctor of Chemical Sciences, Academician of the National Academy of Natural Sciences of the Kazakhstan; professor of the NJSC «Al-Farabi Kazakh National University», Almaty, Kazakhstan E-mail: musabekov40@mail.ru; https://orcid.org/0000-0003-1114-1901;

**Rozhkov V.I.** — Candidate of Technical Sciences, NAO «Saken Seifullin Kazakh Agrotechnical University», Astana, Kazakhstan; LLP «Altai Geological and Ecological Institute», Ust-Kamenogorsk, Kazakhstan E-mail: Vitalrza1983@gmail.com; https://orcid.org/0000-0002-3232-5972;

**Ermekov M.T.** — Head of the Project and Asset Management Department of Science and Technology Solutions JSC, Almaty, Kazakhstan

E-mail: yermekov.m@stsolutions.kz; https://orcid.org/0000-0002-5226-2710.

**Abstract.** This work shows a method for producing superhydrophobic clays from the Tagan deposit bentonite (the East Kazakhstan region) has been developed for use in the production of anhydrous drilling fluids for the oil industry. A wide range of the most diverse cationic surfactants have been used as superhydrophobizing agents. An organophilic (superhydrophobic) clay with a contact angle of 170° was obtained in the presence of tetrakis(decyl) ammonium bromide (TKDAB). It has been proved that the particles of organophilic clays have been obtained by modification TKDAB form a stable suspension in diesel fuel and do not mix at all with the aqueous phase at all. A new technological scheme for the production of organoclay has been developed. The formula for the obtained anhydrous

drilling fluids has been presented and its technical characteristics have been determined. A technological scheme for producing drilling fluids based on organoclay has been developed. This drilling fluid is manufactured in accordance with the characteristics and thixotropic properties of oil at the Kumkol oilfield (Kyzylorda, Kazakhstan). It has been shown that drilling fluid can be used in oil drilling operations at the Kumkol field and other similar fields

**Keywords:** bentonite, montmorillonite, superhydrophobic clay, drilling fluids, Kumkol oil deposit, technological characteristics, surfactants

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## © О.В Рожкова<sup>1,3\*</sup>, Д.М-К. Ибраимова<sup>2,4</sup>, К.Б. Мусабеков<sup>2</sup>, В.И. Рожков<sup>3,4</sup>, М.Т.Ермеков<sup>1</sup>, 2024

<sup>1</sup> «Science and Technology Solutions» АҚ, Алматы, Қазақстан;

2 «Әл-Фараби атындағы Қазақ ұлттық университеті» КЕАҚ, Алматы, Қазақстан;
 3 «С.Сейфуллин атындағы Қазақ агротехникалық зерттеу университеті» КЕАҚ. Астана, Қазақстан;

<sup>4</sup>«Алтайский геолого-экологический институт ЖШС», Өскемен, Қазақстан. E-mail: rozhkova.o@stsolutions.kz

# «ҚҰМКӨЛ» МҰНАЙ ҰҢҒЫМАЛАРЫН БҰРҒЫЛАУҒА АРНАЛҒАН «ТАҒАН» БЕНТОНИТ КЕНОРНЫНЫҢ СУПЕРГИДРОФОБТЫ САЗЫ НЕГІЗІНДЕ СУСЫЗ БҰРҒЫЛАУ ЕРІТІНДІЛЕРІН ӘЗІРЛЕУ

**Рожкова О.В.** — химия ғылымдарының докторы, «Сәкен Сейфуллин атындағы Қазақ ғылыми-зерттеу агротехникалық университеті» КЕАҚ профессоры, Астана, Қазақстан; «Science and Technology Solutions» АҚ, Астана, Қазақстан

E-mail: rozhkova.o@stsolutions.kz; https://orcid.org/0000-0001-8163-7035;

**Ибраимова** Д. М.-Қ. — химия ғылымдарының кандидаты, әл-Фараби атындағы Қазақ ұлттық университетінің аға оқытушысы, Алматы, Қазақстан; «Алтай геологиялық-экологиялық институты» ЖШС, Өскемен, Қазақстан

E-mail: dana kereevna@kaznu.kz; https://orcid.org/0000-0002-1761-9745;

**Мұсабеков Қ.Б.** — химия ғылымдарының докторы, Қазақстан Республикасы Ұлттық жаратылыстану ғылымдары академиясының академигі, әл-Фараби атындағы Қазақ ұлттық университетінің профессоры, Алматы қ., Қазақстан

E-mail: musabekov40@mail.ru; https://orcid.org/0000-0003-1114-1901;

**Рожков В.И.** — техника ғылымдарының кандидаты, «Сәкен Сейфуллин атындағы Қазақ агротехникалық университеті» КЕАҚ, Астана, Қазақстан; «Алтай геологиялық-экологиялық институты» ЖШС, Өскемен, Қазақстан

E-mail: Vitalrza1983@gmail.com; https://orcid.org/0000-0002-3232-5972;

**Ермеков М.Т.** — «Ғылым және технологиялық шешімдер» АҚ Жоба және активтерді басқару департаментінің директоры, Алматы, Қазақстан

E-mail: yermekov.m@stsolutions.kz; https://orcid.org/0000-0002-5226-2710.

Аннотация. Бұл жұмыста мұнай өндіру өнеркәсібінде сусыз бұрғылау ерітінділерін өндірісте қолдануды қамтитын Шығыс Қазақстан облысының «Таған» кенорнының бентонитінен супергидрофобты саздарды алу тәсілі әзірленді. Супергидрофобизаторлар ретінде катионды беттік белсенді заттардың (КБАЗ) кең ассортименті қолданылды. Тетракис (децил) аммоний бромиді (ТКАБ) 170° жұғу бұрышы бар органофильді (супергидрофобты) саз алынды. ТКАБ-дан алынған органофильді саз бөлшектері дизельде тұрақты суспензия түзетіні және су фазасымен мүлдем араласпайтыны дәлелденді. Органосазды алудың жаңа технологиялық сызбанұсқасы жасалды. Алынған сусыз бұрғылау ерітінділерінің формуласы ұсынылған және олардың техникалық сипаттамалары анықталған. Органосаз негізінде бұрғылау ерітіндісін алудың технологиялық сызбанұсқасы жасалды. Бұл бұрғылау ерітіндісі «Құмкөл» (Қызылорда, Қазақстан) мұнай кенорнындағы мұнайдың сипаттамалары мен тиксотроптылығына сәйкес дайындалды. «Құмкөл» кенорнында және осыған ұқсас кенорындарында мұнай бұрғылау кезінде Бұрғылау ерітіндісін пайдалануға болатындығы көрсетілген.

**Түйін сөздер:** бентонит, монтмориллонт, супергидрофобты саз, бұрғылау ерітіндісі, «Құмкөл» кенорны, технологиялық сипаттамалар, беттік активті заттар

# © О.В. Рожкова<sup>1,3\*</sup>, Д.М.-К. Ибраимова<sup>2,4</sup>, К.Б. Мусабеков<sup>2</sup>, В.И. Рожков<sup>3,4</sup>, М.Т. Ермеков<sup>1</sup>, 2024

 $^1$  AO «Science and Technology Solutions», Алматы, Казахстан;  $^2$  HAO «Казахский национальный университет имени аль-Фараби», Алматы, Казахстан;

<sup>3</sup> НАО «Казахский агротехнический исследовательский университет им. С. Сейфуллина», Астана, Казахстан;

<sup>4</sup> TOO «Алтайский геолого-экологический институт», Усть-Каменогорск, Казахстан. E-mail: rozhkova.o@stsolutions.kz

### РАЗРАБОТКА БЕЗВОДНЫХ БУРОВЫХ РАСТВОРОВ НА ОСНОВЕ СУПЕРГИДРОФОБНОЙ ГЛИНЫ МЕСТОРОЖДЕНИЯ «ТАГАНСКОЕ» ДЛЯ БУРЕНИЯ НЕФТЯНЫХ СКВАЖИН НА МЕСТОРОЖДЕНИИ «КУМКОЛЬ»

**Рожкова О.В.** — доктор химических наук, профессор НАО «Казахский научно-исследовательский агротехнический университет имени Сакена Сейфуллина», Астана, Казахстан, Астана, Казахстан; АО «Science and Technology Solutions», Астана, Казахстан

E-mail: rozhkova.o@stsolutions.kz; https://orcid.org/0000-0001-8163-7035;

**Ибраимова** Д. М.-К. — кандидат химических наук, старший преподаватель НАО «Казахский национальный университет имени аль-Фараби», Алматы, Казахстан; ТОО «Алтайский геолого-экологический институт», Усть-Каменогорск, Казахстан

E-mail: dana kereevna@kaznu.kz; https://orcid.org/0000-0002-1761-9745;

**Мусабеков К.Б.** — доктор химических наук, академик Национальной академии естественных наук Республики Казахстан, профессор НАО «Казахский национальный университет имени аль-Фараби», Алматы, Казахстан

E-mail: musabekov40@mail.ru; https://orcid.org/0000-0003-1114-1901;

**Рожков В.И.** — кандидат технических наук, НАО «Казахский агротехнический университет имени Сакена Сейфуллина», Астана, Казахстан; ТОО «Алтайский геолого-экологический институт», Усть-Каменогорск, Казахстан

E-mail: Vitalrza1983@gmail.com; https://orcid.org/0000-0002-3232-5972;

**Ермеков М.Т.** — директор Департамента Управления проектами и активами АО АО «Science and Technology Solutions», Алматы, Казахстан

E-mail: yermekov.m@stsolutions.kz; https://orcid.org/0000-0002-5226-2710.

В работе был разработан Аннотация. данной способ получения супергидрофобных глин из бентонита месторождения «Таганское» Казахстанской области с целью применения в производстве безводных буровых растворов для нефтедобывающей промышленности. В качестве супергидрофобизаторов был использован широкий ряд самых разнообразных катионных поверхностноактивных веществ (ПАВ). В присутствии тетракис(децил) бромид аммония (ТКБА) была получена органофильная (супергидрофобная) глина с углом смачивания 170°. Доказано, что частицы органофильной глины, полученные на основе ТКБА, образуют стабильную суспензию в дизельном топливе и совершенно не смешиваются с водной фазой. Разработана новая технологическая схема получения органоглины. Представлена формула полученных безводных буровых растворов и определены их технические характеристики. Разработана технологическая схема получения бурового раствора на основе органоглины. Данный буровой раствор изготовлен в соответствии с характеристиками и тиксотропностью нефти на нефтяном месторождении «Кумколь» (Кызылорда, Казахстан). Показано, что буровой раствор может быть использован при бурении нефти на месторождении «Кумколь» и аналогичных месторождениях.

**Ключевые слова:** бентонит, монтмориллонт, супергидрофобная глина, буровой раствор, местрождение «Кумколь», технологические характеристики, поверхностно-активные вешества

#### Introduction

The development of the oil and gas industry and the increase in hydrocarbon production at a level that ensures the energy security of Kazakhstan should be accompanied by an increase in drilling volumes.

One of the important directions for improving the quality of well construction is the use of efficient and cost-effective drilling fluids formulations in order to prevent technological issues and reduce costs during the drilling process.

The construction of deep wells in difficult mining and geological conditions, caused by the alternation of unstable clay and salt deposits, the presence of zones of abnormal reservoir pressures, elevated temperatures, and large depths of hydrocarbon deposits, is associated with complications related to problems managing the properties of drilling fluids.

It is known that most complications and accidents are associated with the instability of water-based drilling fluids when drilling at elevated temperatures, increasing the cost of well construction.

Thus, effective drilling fluids can help avoid many problems during drilling, development, and testing of wells. They clean the borehole, create a filter crust on its walls to prevent water from seeping into the ground. They also maintain the stability of the borehole walls, help prevent tool failure and jamming, and protect equipment from aggressive fluids and dirt. Effective drilling fluids increase drilling speed by reducing surface friction

The construction of wells at the oil from Kumkol field, located 150 kilometers northeast of Kyzylorda and covering an area of 23,143 hectares, is being carried out under difficult geological conditions.

The field is multi-layered and contains six productive oil and gas deposits. Two of these are confined to the Lower Neolump Cretaceous deposits (horizons M-I and M-II) at depths of 1,063 m and 1,270 m respectively, while the remaining four are located in the «Yu» deposits (horizons Yu-I, Yu-II, Yu-III and Yu-IV). The deposits in the Cretaceous strata are predominantly composed of petroleum, with the Yu formation consisting of gas and oil. These deposits are stratified and arch-shaped, with elements of tectonic and lithologic shielding. Due to the fact that the productive section consists of terrigenous rock types (sandstones and siltstones), challenges in the form of faulting, scree, and collapse of well walls at the Kumkol field are observed during well drilling operations, making the effectiveness of drilling fluids used critically important.

Improving the quality of well construction and preventing technological complications during drilling at elevated temperatures (up to 150 °C) and in unstable deposits are possible through the use of new drilling fluid compositions and ways to control their properties.

Therefore, the development of new formulations of drilling fluids that can ensure high-quality well construction under these conditions seems like a very urgent task.

It is known that clay is one of the most active components in drilling fluids. This applies to clay powders as well as clay rocks, especially weakly polymerized ones. Clays are fine-grained mixtures of minerals with a predominantly crystalline structure that were formed as a result of physicochemical weathering of rocks (Ianchis et al., 2014). The main part consists of clay minerals. In addition, quartz, feldspar, calcite, pyrite, and so on, are present. Of course, the most important role is played by clay minerals, which are highly dispersed (the maximum size of clay particles according to geologists does not exceed 2 microns), and are relatively stable mineral compounds belonging to the group of aqueous aluminosilicate layered or layered ribbon structures. High dispersion, the shapes of minerals, as well as the properties of basal surfaces of micro-crystals, cause their high physical and chemical reactivity.

In (Hodhaifa et al., 2021) the use of bentonite clays for drilling wells was studied because they have good hydrophilic and dispersing properties. Montmorillonite, which is the basis for bentonite powder, is one of the most active ingredients. It consists of two tetrahedron grids with an octahedron sublayer between them. All the vertices of tetrahedrons face the center of a structural layer, forming a common layer with oxygen atoms at the vertices shared by the sublayers and hydroxides at the vertices not shared by tetrahedrals.

A characteristic feature of the montmorillonite structure is that the oxygen surface of one layer contacts the similar oxygen surface of the neighboring layer. This is a prerequisite for swelling processes, as molecules of water and other polar liquids can penetrate between the structural layers of montmorillonites and further reduce interaction between them. The c-distance varies depending on the amount of water in the interlayer space from  $9.6 \cdot 10-8$  to  $140 \cdot 10-8$  cm (and possibly up to complete delamination). Substitutions of Al<sup>3+</sup> to Mg<sup>2+</sup> and Fe<sup>2+</sup> in octahedral sublayers prevail in montmorillonites, but Al<sup>3+</sup> can partially replace Si<sup>4+</sup> in tetrahedral positions (Ianchis R. et al., 2014).

The charge deficit varies widely and depends on the degree of substitution. The maximum value of the density of negative charges in the lattice is approximately 0.66 elementary charges per structural cell. This negative charge is compensated for by exchangeable hydrated cations, usually sodium, calcium, or magnesium ions, which are located between the structural layers and together with water molecules form a montmorillonite interlayer complex. These exchangeable cations are called interlayer exchangeable ions.

Due to their structural features, chemical composition and dispersion, clay

minerals have significant activity and are able to interact with components of drilling fluids such as high molecular weight water-soluble compounds and inorganic electrolytes.

In this regard, we are interested in conducting research on bentonite clay from the Tagan deposit in order to obtain organoclays for drilling fluids, as they are characterized by a high montmorillonite content of about 95%.

Due to the peculiarities of genesis, three types of bentonite clay were identified at the Tagan deposit (Tarbagatai district, East Kazakhstan region, Republic of Kazakhstan): alkaline, alkaline-earth, and pharmaceutical. These types have different properties and montmorillonite content, which allows them to be used in various industrial applications, including the production of drilling fluids.

Bentonite clay from the 12th horizon of the Tagan deposit is far and away the most famous, as it exceeds reference Wyoming bentonite (USA) in terms of quality characteristics. Its adsorption properties are so good that the clay is exported to France as an enterosorbent.

The uniqueness of our research lies in the fact that methods for superhydrophobizing montmorillonite from Tagan deposits have not previously been used. Results from our previous studies were presented in an article published in 2021 (Hodhaifa et al., 2021), where octadecylamine was used as the superhydrophobic agent, with a contact angle of 157 degrees.

Also, in some studies (Ianchis et al., 2014), production of organoclays from clays was investigated using various modifiers. The wetting angle in these studies reached 150°.

In this work, we faced the task of obtaining orgonoclay that will be injected into a liquid with very low polarity. To obtain thixotropic drilling fluids with stable properties, we propose creating an optimal orgonoclays. For this, the unique Tagan bentonite clay, due to its high content of montmorillonite, offers more opportunities for superhydrophobicity and supramolecular intercalation with modifier molecules.

Thus, the purpose of this work is to study a method for obtaining organophilic clay from montmorillonite from the Tagan deposit, with an edge angle closer to 180°, which, at the same time, has high stability in an organic medium. A method to create drilling fluids based on this material that exhibits thixotropic properties in an anhydrous medium will be proposed.

The novelty of this work lies in the fact that, for the first time, we obtained superhydrophobic organoclays based on bentonite from the Tagan deposit. The wetting angle of these organoclay was 170°. We determined the suitability of these organoclays for the preparation of drilling fluid, and we proposed technological schemes for producing organoclay and creating drilling fluid based on them..

#### Research materials and methods

In this work, Na-montmorillonite was used. It was obtained from bentonite clays of the Tagan deposit (quarry 12). The basis is the conditional chemical formula of bentonite  $(OH)_4Si_8Al_4O_{20}\cdot n(inter-layer)\cdot H_2O$ . Tagan bentonite has a light pink color with dark pink spots. Due to the fact that in most cases there are different types of it, this type is sometimes referred to as Tagan pharmaceutical bentonite.

Montmorillonites, as an ordinary material, do not exhibit pronounced catalytic or adsorption activity, so they must be pre-activated or transformed. To purify the clay from impurities, it is washed by decantation and then the thermal acid activation method is used. The montmorillonite first dried at 90 °C for 2 hours. Clay was mixed 1:3 with 15 % sulfuric acid and continuously mixed at 90 °C for 4 hours. Heated in an acidic solution in a hot water bath, bentonite filtered, placed on porcelain plate, washed with an ammonia solution and distilled water to pH neutrality. Bentonite filtrates are dried in laboratory oven at 80 ° C.

Dried montmorillonite clay is obtained, sieved and placed in glass conical flask with polished stopper.

The X-ray diffraction (XRD) technique was employed in this study using an automatic diffractometer DRON 3.0 equipped with  $CuK_{\alpha}$ -irradiation and a  $\beta$ -filter. The diffractogram acquisition conditions were as follows: U=35kB; I=20mA;  $\theta$ -2 $\theta$  scanning; detector speed of 2 degrees per minute. Semi-quantitative X-ray phase analysis was performed on powder samples using diffractograms obtained by the method of equi-suspensions and artificial mixtures, with the aim of determining the quantitative ratio of crystalline phases. The interpretation of diffractograms was based on data from the International Center for Diffraction Data (ICDD) file, specifically the PDF2 powder diffraction database and diffractograms of pure minerals. Calculations for the content were performed for the main phases.

Several surfactants were used as hydrophobic agents for the treatment of Namontmorillonite (Mehri et al., 2019; Elias et al., 2016; Zare et al., 2017; Guanzheng et al., 2019):

- 1) Tetrakis (decile)ammonium bromide (TKDAB) C<sub>40</sub>H<sub>84</sub>BrN
- 2) Didecyldimethylammonium bromide (DDMAB)  $\tilde{C}_{22}H_{48}$ BrN
- Trimethyloctadecylammonium bromide (TMODAB) C<sub>21</sub>H<sub>46</sub>BrN
- 4) Cetylpyridinium bromide (CPB) C<sub>21</sub>H<sub>28</sub>BrN
- 5) Octadecylamine (ODA) C<sub>18</sub>H<sub>39</sub>N

6)

Reagents needed to produce the drilling fluid:

- A) Superhydrophobic clay was used as organo-modified clay (orgonoclay), obtained by modifying Tagan Na-montmorillonite with TKDAB. Orgonoclays are typically used as a structural component, a rheological property, modifier in drilling fluids, and as a crust-forming agent to reduce water absorption in boreholes.
- B) Limestone (Ca(OH)<sub>2</sub>) was used to prevent the accumulation of carbonates in water-based drilling fluids. It increases the pH and amount of calcium cations in the drilling fluid and improves the resistance of the drilling fluid to the aggressive effects of hydrogen sulfide.
- C) Polyacrylamide (PAA) film was used to cover and protect the wall of the well to prevents the penetration of filtrate into the rock structure. This promoted the formation of a strong filtration crust and improved the lubricating properties of the solution.
- D) Halite NaCl was used to aid in making the walls of the well stronger
- E) Diesel fuel with a low dielectric permeability was used as the liquid medium.

Many various methods were used in the research process and it listed below:

- 1) Preparation of solutions of hydrophobizers and clay treatment In the process of hydrophobization, 100 ml of surfactant solutions were prepared in concentrations of 1 M and 0.1 M. Na-montmorillonite clay was placed in the prepared solutions in the range of 1–5 G and mixed for 5–6 hours in a heated laboratory magnetic stirrer at a temperature of 70 ° C. The powder was placed in a Petri dish and dried in a laboratory dryer until the weight was stabilized, then crushed and sieved to a size of 0.315 microns. After that, the hydrophobicity of the organoclay types was determined.
- 2) The method of transmission electron microscopy was used to characterize the morphological features of clay.

- 3) The Goniometer LK-1 was used to measure the contact angle of a drop lying on the surface of a hydrophobic clay powder using the method of a stationary lying stationary drop. The Goniometer LK-1 is based on a horizontal microscope and a digital HD video camera and has the ability to calculate the contact angle of a stationary droplet with a display. Before determining the contact angles of water droplets on the surface of a hydrophobic organoclay powder, the powder was pressed through two glass plates and smoothed.
- 4) Determination of the stability of superhydrophobic clay species in organic compounds. Diesel fuel (diesel) was used as a liquid with a low dielectric constant to test the ability of superhydrophobic clays to disperse in organic media. The approximate chemical formula of diesel is C8H18–C17H36. Diesel fuel is a complex mixture of paraffin limiting 10–40 % (general formula  $C_nH_{2n+2}$ ), naphthenic polymethylene 20–60 % (general formula  $C_nH_{2n}$ ) and arene-aromatic 14–30 % (general formula  $C_nH_{2n-6}$ ) hydrocarbons. The average molecular weight is around of 110–230 gramm/mole, and boils between 170–380° C. The dielectric constant of diesel fuel is approximately  $\epsilon$ =2.05.
- 5) The stability of the dispersed medium was determined by measuring precipitation in an organic medium using a photoelectric colorimeter.
- 6) Thermogravimetry and differential scanning calorimetry (TGA and DSC) were used to monitor the effect of chemical changes on the composition of organoclay under the influence of temperature. Drilling fluids can be subjected to extremely high temperatures within the bowels of the Earth, so these methods were employed to study the physical, chemical, and chemical processes that occur in a substance as its temperature changes.
- 7) The rheological properties of the drilling fluids and oils at the Kumkol field were determined using simple indirect methods, using samples taken from the field. Measurements such as determining the density of the liquid using a hydrometer, the pH of the solution using a pH meter and the viscosity using a rheometer, were carried out to determine these properties. The relationship between shear rate and shear stress for Kumkol oil and drilling fluids obtained by TKDAB was determined using a MCR 702 MultiDrive (Anton Paar).

#### Results

hich are the main types that replace each other naturally over billions of years (Mehri et al., 2019). The aluminosilicate structure in clay consists mainly of two-dimensional parallel layers formed by alternating silicate tetrahedra and aluminum octahedra (Elias et al., 2016; Zare et al., 2017). The location, degree, and nature of the exchange in these layers determine the chemical and physical properties of the materials, including adsorption characteristics.

Natural aluminosilicates can be divided into two groups depending on their crystal lattice - crystalline and amorphous (Guanzheng et al., 2019). Amorphous aluminosilicates are characterized by the ability to swell during ion exchange, similar to ion exchange resins.

There are three types of bentonite clay found in the Tagan deposit – alkaline (pink), alkaline-earth and pharmaceutical. Due to the unique geological characteristics of the Tagan deposit, these different types of montmorillonite and bentonite have specific properties that make them suitable for use in various industrial processes.

Alkaline bentonites, in particular, are used in the production of drilling fluids. In order to fully understand the chemical composition of these clays, an X-ray fluorescence analysis has been conducted (Table 1).

Table 1. Oxide chemical composition of bentonite clay from the Tagan deposit

The amount of oxides in the mineral	CaO	MgO	Fe <sub>2</sub> O <sub>3</sub>	$Al_2O_3$	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Residues after burning
The quantitative ratio of oxides in the crude mineral montmorillonite, %	15	4	6	10	30	1,5	4	69,5
The quantitative ratio of oxides in the mineral Namontmorillonite, %	4	0,9	4	9,8	31	0,6	0,91	84,8

It has been found that bentonite clay contains a variety of elements and oxides in addition to Fe, Al, Si, Zn, Ti, and Ca. When analyzing the elemental composition, it was determined that montmorillonite originating from the Tagan deposit has a calcium-sodium composition, which is due to the high level of calcium. During the stages of decanting washing, thermal activation, and acid activation of the montmorillonite from Tagan, calcium and magnesium ions are eliminated. As a result, swelling, ion-exchange capacity, and interlayer spacing of the clay are increased. Montmorillonite is known to naturally disperse in an aqueous environment and break down into individual plates up to one nanometer thick and 200–250 nanometers in diameter (Rogers et al., 2005; Pegoretti et al., 2008).

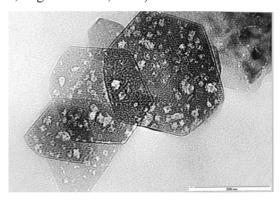


Fig. 1. The results of the analysis conducted using transmission electron microscopy on montmorillonite samples from the Tagan deposit.

In order to determine the mineral composition of bentonite and organoclay from the Tagan deposit, an X-ray phase analysis has been conducted. The results of this analysis are presented in Table 2 below:

Table 2. Mineral Composition of Tagan Bentonite

The mineral	Formula	Quantity, %
Montmorillonite	(Na,H) <sub>0.3</sub> (Al,Mg,	96,4
	Ca),Si <sub>4</sub> O <sub>10</sub> (OH),·xH,O	

Quartz	$\mathrm{SiO}_2$	3,6

Table 3. Mineral Composition of Organoclays Obtained Using a TKDAB

The mineral	Formula	Quantity, %
Montmorillonite	$(Na,H)_{0.3}(Al,Mg, Ca)_2Si_4O_{10}(OH)_2\cdot xH_2O$	94–97
Quartz	$\mathrm{SiO}_2$	2–4
Amorphous phase	-	1–2

As a result of determining the mineral composition of bentonite from the Tagan deposit and orgonoclays using X-ray diffraction analysis, other minerals were found in the clay in addition to montmorillonite, including quartz and amorphous phases. Currently, several methods for hydrophobizing montmorillonite are employed. The most commonly used methods for hydrophobizing montmorillonites include surface modification techniques, intercalation of modifying agents, and biohydrophobization methods (Atyaksheva et al., 2022; Musabekov et al., 2023). Each of these methods has its own advantages and disadvantages. The selection of a particular method depends, for example, on the purpose of the research and the requirements for the final product. (Musabekov et al., 2023) Organomodification, or the intercalation method, may be more suitable for this area of work because it is necessary to take into account the crystal structure of montmorillonite. In structural schemes, some Si<sup>4+</sup> ions are replaced with Al<sup>3+</sup> ions, creating an excessive negative charge in the crystal. This charge is compensated by mobile cations of alkaline and alkaline earth metals, which are not fixed in specific places in the lattice. These cations can be exchanged for other ions. (Rogers et al., 2005; Pegoretti et al., 2008; Yermekov et al., 2022; Musabekov et al., 2023).

Accordingly, clay particles may have an uncompensated negative charge on their surface. When clay particles rise, they can interact with amino groups through hydrogen bonding. The adsorption of cationic surfactants onto the surface of clay particles occurs through electrostatic interactions. This interaction can be illustrated using a diagram, for example, by considering the interaction between clay particles and any alkylated Ammonium Bromide (AlkAB) compounds (Fig. 2).:

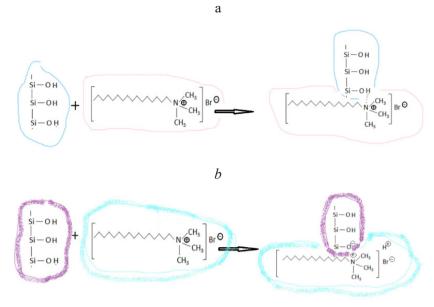


Fig. 2. Schemes of AlkAB interaction by hydrogen bonding (a) and electrostatic attraction (b) with the surface of montmorillonite particles

Since the scientific results use clay minerals and the intercalation method is effective as a hydrophobization method. The main focus is on choosing the optimal hydrophobe for this type of mineral. A drop of water was placed on an organoclay powder that had been treated with different hydrophobes, and their contact angles were then measured using a goniometer. Table 4 shows the contact angle values obtained for each organoclay (Amankeldi et al., 2022; Yerlan et al., 2022).

Table 4. Contact angles of water droplets applied on the surface of various types of organomodified clay powders

Spatial formula of modifiers	Concentrations of modifiers' solutions	Contact angle for montmo- rillonite with organo- philic coating	Images of organoclay, in the presence of various hydrophobizers
	Montmorillonite	31º	

Br CH <sub>3</sub> N+-CH <sub>3</sub>	TMOD- AB	0.1 M	39°	no image
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CH <sub>2</sub> CH <sub>3</sub> CH <sub>3</sub>		1 M	9º	
N Br	СРВ	0,1M	139º	
		1 M	128º	no image
		0,1M	135º	no image
H <sub>3</sub> C CH <sub>3</sub>	DDMAB	1 M	161º	
H <sub>3</sub> C N <sup>+</sup>	TKDAB	0,1M	141º	no image
H <sub>3</sub> C H <sub>3</sub> C H <sub>3</sub> C H <sub>3</sub> C		1 M	170°	
		0,1M	131º	no image
Light CH <sub>3</sub>	ODA	1 M	157°	9]

Among orgonoclays, as indicated in Table 4, the maximum contact angle was 170 °C TKDAB. This can be explained by the structure of the TKDAB molecule, i.e., the TKDAB has 4 long, nonpolar hydrocarbon chains that give it four times the hydrophobic properties of other molecules. The end sides of the TKDAB hydrocarbons do not have much space when packed together tightly, compared to CPB. The CPB molecule has a benzene ring at the end side. Therefore, even at high concentrations, the maximum angle of absorption did not exceed 128 °. Regarding the rest of the data, an interesting situation arises here (see table 4). At a low concentration of hydrophobizers (0.1M), the values for contact angles of water droplets were higher than at high concentrations (1M). In particular, for PBC, the angle decreased from 39 ° to 9 °, while for TMODAB, it decreased from 135 ° to 129 °. In other cases, with an increase in the concentration of the hydrophobizer, the contact angle of orgonoclay also increases. This decrease depends on the characteristics of these molecules, specifically on the position and

length of their chain on the surface of a solid particle. At an excessively high concentration, surfactant molecules form a layer, causing reverse hydrophilization of the surface (Fig. 3).

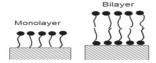


Fig. 3. A schematic representation of the independent interaction of surfactant molecules, forming a double layer, and reverse hydrophilization on the surface of clay particles.

With an increase in the concentration of surfactant molecules, the contact angles of water droplets increased in another group of hydrophobizers.

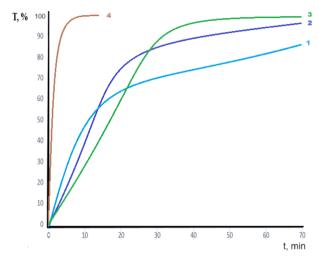


Fig. 4. Kinetics of sedimentation of organoclay particles based on montmorillonite in diesel fuel studied by optical methods.

1-TKDAB; 2-DDMAB; 3-CPB; 4-TODMAB.

Figure 4 shows the change in the optically observed values of the light conductivity of an organoclay suspension obtained using various hydrophobizers in diesel fuel over a certain period of time. The results showed that organoclays obtained in the presence of TKDAB have the lowest light transmission and an equivalent of 82 %. For further studies, organoclays with the highest contact angles were used. It was decided to continue with organoclay produced only in the presence of TKDAB, as this surfactant appeared to be the most optimal superhydrophobic agent.

Figure 5 shows the results of IR spectroscopy to ensure the adsorption of TKDAB onto the clay surface.

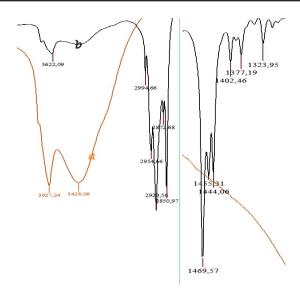


Figure-5: IR spectra of (a) Na-montmorillonite and (b) modified organoclay TKDAB

Accordingly, bands and peaks in the infrared Fourier transform indicate the intercalation of surfactant molecules into the interlayer spaces of montmorillonite clay. Currently, infrared spectroscopy is one of the most versatile techniques for studying solids, especially for determining the surface groups of clay minerals and vibrations of their structural elements. It also allows us to observe changes in chemical bonds during adsorption of reagents.

Figure 5 shows the fluctuations in Si-O-Si bonds, which are observed in a broad band corresponding to 1036 cm<sup>-1</sup>. Frequencies of 470.65 and 527 cm<sup>-1</sup> reflect vibrations of Me-O bonds, while peaks at 914 and 3100–3500 (almost 3627) cm<sup>-1</sup> correspond to bound water molecules and deformations reflecting hydrogen bonds. In the frequency range of 1444 to 1469 cm<sup>-1</sup>, there are peaks that indicate carbon-hydrogen (C-H) bonds. The peaks at 2,850.97, 2,954, 2.87268, and 2, 994.66 cm<sup>-1</sup> centimeters per minute show fluctuations in the -CH<sub>2</sub> bond. Therefore, we have confirmed that the adsorption of TKDABs on the surface of montmorillonite has occurred.

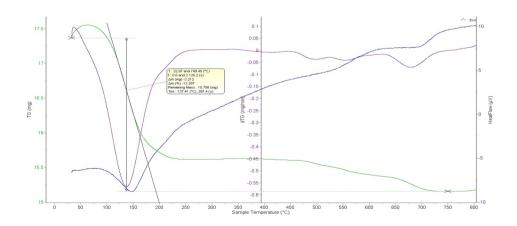


Fig. 6. Results of TGA and DSC for Na - montmorillonite

This analysis demonstrates that, as temperature increases from 140 °C to 200 °C, the weight of the sample under study decreases. This indicates that various phase transitions are occurring (green line).

During the experiment, it was observed that as temperature increased, the weight decreased, indicating that the composition is beginning to separate from its water content and crystallize (Hadj-Hamou et al., 2017; Kurmangazhi et al., 2021; Wang et al., 2023). The rate of weight change slowed by 15.788 mg, and the melting point appeared to be shifting (purple line).

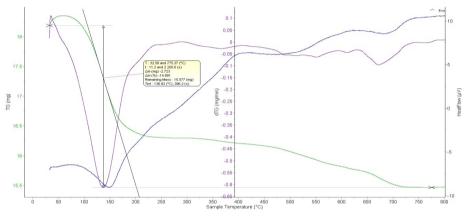


Fig. 7. Analysis of DSC and TGA of organoclay obtained in the presence of TKDAB

The same phenomenon is observed, but the loss of mass from the organical produced by TKDAB occurs more rapidly, indicating that the hydrocarbon chain present in TKDAB is being oxidized in the presence of oxygen and breaking into smaller molecules that escape as CO2 gas.

During the experiment, a decrease in the mass of the organoclay produced by TKDAB was observed to slow down to 15.577 milligrams. Given the increasing interest in producing drilling fluid with an organic medium rather than an aqueous one, despite the lack of such work in Kazakhstan, a diesel-based drilling fluid has been produced and its technical characteristics have been determined.



Fig. 8: Images of the drilling fluid obtained in the time interval



t = 48 hours

The composition of the drilling fluid is as follows: diesel fuel - 100 G; lime (Ca(OH)<sub>2</sub>) - 4 G; organoclay - 4 G; polyacrylamide - 3 G; and halite - 4 G. This composition was selected based on a gradual addition of components and monitoring of the fluid's technological properties.

Table 5. Description of the Drilling Fluid Sample

Properties	$\rho$ , kg/m <sup>3</sup>	η, Pa.sec	рН
Drilling Fluid	1720	16,5	7

Table 6. Description of the Kumkol Oil Sample

Properties	ρ, kg/ m <sup>3</sup>	η, Pa.sec	рН	Mechanical additives, %
Kumkol oil	850	9,6	7	7

The drilling fluid was prepared in accordance with the specifications for all drilling fluids. Its characteristics were then determined, including density, viscosity, and pH. The relevant data are presented in Tables 5 and 6.

By comparing the characteristics of the drilling fluid with of Kumkol oil field, we can conclude that it is suitable for use in oil drilling operations. Thixotropic properties, which are typical of high-viscosity and bituminous oils, can be attributed to the presence of complex high-molecular compounds that are prone to structuring, such as paraffins, resins, and asphaltenes. Figure 9 illustrates the study of fluid viscosity as a function of time under shear stress.

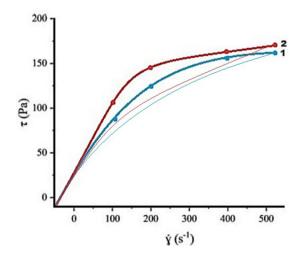


Fig. 9. The relationship between shear rate and shear stress for oil from the Kumkol field and drilling fluid based on organoclay TKDAB.

1- Drilling fluid; 2 - Oil from the Kumcol field

According to the results obtained, studies on the thixotropic properties of drilling fluid consisting of organoclay were carried out over a period of 24 hours, and it was found that rheological changes take place within 24 hours. The technical specifications of the drilling

fluid and oil from the Kumkol field are relatively similar, and the polymer solution present in them can create a slip layer in the wellbore, providing an optimal effect on smooth wellbore movement. Therefore, this drilling fluid can be used for oil drilling in the Kumkol and similar fields.

#### Conclusion

- 1. Four types of organical were developed from bentonite of Tagan origin in the East Kazakhstan region at different concentrations of cationic surfactants: 1 TKDAB; 2 DDMAB; 3 CPB; and 4 TMODAB.
- 2. The contact angle was measured using a drop of water on the surface of the organophilic clay powder, and it was found that, at high concentrations of TKDAB, the contact angle of a water drop was  $170^{\circ}$  and, in the presence of other TKDAB concentrations, the contact angles were only  $140^{\circ}$ .
- 3. Stability of organophilic clays in organic media was studied using optical methods, and the superhydrophobic clays obtained by TKDAB showed the highest stability, with turbidity equal to 82%.
- 4. A method for producing modified organoclays by TKDAB has been established during research, as well as a method for producing organoclays: diesel fuel 100 G; limestone Ca(OH)<sub>2</sub> 4G; organoclay 4G; polyacrylamide 3G, halite 4G.
- 5. As a result of the experimental research work conducted, a drilling fluid with an organic medium based on diesel fuel has been developed, with the optimization of its composition parameters and the determination of technical characteristics. Based on the gradual addition of components and monitoring of technological fluid properties, the composition of the drilling fluid was optimized and it was shown that the fluid can be used in oil drilling at the Kumkol field and other similar fields.

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