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Synthetic and natural polymers for oil production and development of drilling fluids

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CONTENT

NORMATIVE LINKS

In this dissertation, the references to the following standards are used: This thesis refers to the following standards:

GOST 6.38-90 Unified system of documentation. The system of organizational and administrative documentation. Requirements for registration of documents.

GOST 7.1-2003 System of standards on information, librarianship and publishing. Bibliographic record. The bibliographic description. General requirements and rules.

GOST 7.12-93 System of standards on information, librarianship and publishing. Bibliographic record. Abbreviations of words in Russian. General requirements and rules.

GOST 7.32-2001 System of standards on information, librarianship and publishing. Report on research work. The structure and rules of registration.

GOST 7.9-95 System of standards on information, librarianship and publishing. Summary and abstract. General requirements.

GOST 8.417-2002 State system for ensuring the uniformity of measurements. Units of physical quantities.

LIST OF ABBREVIATIONS

CMC   – carboxymethyl cellulose
CMS   – carboxymethylated starch
CMCS   – carboxymethylated cornstarch
DLS   – dynamic light scattering;
DS   – degree of substitution
DSC   – differential scanning calorimeter
DP   – degree of polymerization
DTA   – differential thermal analyzer
EOR   – enhanced oil recovery
ORF   – oil recovery factor
PAM   – polyacrylamide
SEM   – scanning electron microscopy;
TGA   – thermogravimetric analyzer

INTRODUCTION

Assessment of the current state of the scientific or scientific-technological problems to be solved

The global demand for energy is constantly growing as the economy develops, and countries are consuming more and more energy to support growing industries. Much of the energy demand is provided by fossil energy, especially oil. Thus, in order to meet global energy demand, it is necessary to increase oil reserves and production capacity. When a new oil reservoir is discovered, the reservoir usually possesses the natural pressure to move the oil to the production well by expansion of its volatile components. This process is called primary oil recovery. When the natural pressure decreases, and the spontaneous flow of the oil diminishes, it is necessary to resort to secondary oil recovery techniques, which generally consist in increasing again the reservoir pressure by injection of water. This process, also called water flooding, is continued until the production cost becomes significant compared to the value of the produced oil. After these two stages, the total oil recovery is usually around 30-40% of the original oil in place. Therefore, the remaining oil is the target of the tertiary oil recovery [1]. Chemical flooding may displace more oil over conventional water flooding. However, chemicals used in such process may be harmful and required intensive treatment before discharging into the environment.

Polysaccharides offer eco-friendly and renewable alternatives for synthetic chemicals to be used in various applications in petroleum operations such as in the area of EOR. The use of carbohydrate polymer aqueous systems is fundamental in all process operations, from the crude oil extraction to the refined final product formulation [2].

Excessive water cut of oil reservoirs shortens the production life of wells and leads to intensive corrosion of equipment. High water cut (up to 90% and more) due to the geological heterogeneity of the reservoirs and long-continued water flooding process is the main reason behind low production rates at mature oilfields [3-4].

Injection of polymer solutions into the oil reservoir allows to increase considerably oil recovery in comparison with conventional water flooding. However, synthetic polymers such as polyacrylamide and hydrolyzed polyacrylamide in combination with chromium salts that are widely used in oil recovery may cause harmful effect to environment and require utilization according to ecological standards. While polysaccharides are eco-friendly and obtained from renewable resources and can be alternative to synthetic polymers. Polysaccharides that are characterized by gelation properties, stability to high mineralization and temperature are perspective reagents for oil recovery [5].

The analysis of literature sources shows that polymer clay-free and low-grade drilling fluids are most effective in modern drilling technologies for directional and horizontal wells that ensure the preservation of the productive properties of the bottomhole formation zone in the production process. The use of these solutions is especially important in the development of large depleted deposits with low-permeability reservoirs [6].

The basis and initial data for the development of the topic. Earlier, we [7] studied in detail the rheological properties of solutions of polysaccharide gellan in water and water-salt solutions, the conditions for their pseudoplastic flow and gelling are established.

Initial data: a) rheological properties of solutions of polysaccharides gellan and xanthan in water and water-salt solutions; b) the conditions for gelation of solutions of gellan in water and aqueous-salt solutions; c) biodegradability of gellan and xanthan in water and water-salt solutions.

Justification of the need for research on the topic. The special importance of biopolymer drilling fluids is caused by the need to introduce modern drilling technologies for directional and horizontal wells, while developing a significant number of low-yield and heavily watered deposits (Uzen, Kumkol, etc.) in Kazakhstan, as well as near and far aDMoad. In connection with this, the development of new environmentally friendly polymer drilling muds for the oil and gas extracting industry of the Republic of Kazakhstan on the basis of available domestic products (corn starch is produced in Almaty oblast, gellan is planned to be produced in Almaty, coal slag of Ekibastuz Power Plant), competing with foreign analogues, is a priority task of applied domestic scientific research.

Information about the planned scientific and technical level of development. The principal difference between our proposed concept of new drilling fluids and existing analogues is based on the ability of solutions of the gellan biopolymer to reversible conformation transitions of the sol-gel type under the influence of temperature and low molecular weight salts. Using these features of gellan will improve the filtration and caking properties of the drilling mud, reduce the chances of stuck drilling tools and other complications. The subsequent biodegradation of gellan ensures preservation of reservoir properties of the bottomhole formation zone at the production stage. Drilling fluids obtained under this project are expected to be tested in experimental industrial conditions and to develop technological regulations. Applications for security documents will be submitted. Thus, the basis for the introduction of developed drilling fluids into production will be prepared.

Conclusions of the patent research. An analysis of the research and patent literature carried out by us showed that clay-free and low-grade drilling fluids containing polysaccharides and modified polysaccharides (xanthan, starch, cellulose derivatives, etc.) are widely used in drilling in difficult mining and geological conditions, and also ensure maximum preservation reservoir properties of the formation. The analysis, as well as the results of experimental studies obtained by us in 2015 and 2016, have shown that the most promising for the introduction will be low-clay and clay-free drilling fluids for drilling in difficult mining and geological conditions, as well as the opening of reservoirs in normal conditions and low pressures.

Information about metrological provision of research. The Institute of Polymer Materials and Technologies and has certified, metrologically verified methods for carrying out scientific and applied research in the field of polymer colloid-disperse systems on a water basis, determining their structure, composition and properties, as well as other necessary characteristics. Certified precision equipment and instruments

were used: X-ray fluorescence analyzer Epsilon 3 (PANalytical, The Netherlands), RheolabQC rotational rheometer (AntonPaar, Austria), Nano-Z590 Malvern Zetasizer (UK), Eclipse LV150N polarization microscope (Nikon, Japan), Bruker Avance III 500 spectrometer, Carry 660 (Agilent, USA) DSC 131 EVO Setaram and TGA «Labsys EVO» Setaram (France), SEM (Jeol JSM-6490LA, Japan), texture analyser TA.XT plus, Stable Micro Systems, (UK), instrument SNS-2 (Russia), VM-6 (Russia), instrument WIKA IV-2 (Russia). The viscosity of aqueous gellan and CMCS solutions was measured using Ubbelohde viscometer at room temperature 25±0.1 °C (capillary length is 90 mm, capillary diameter is 0.86 mm, the diapason of viscosity measurement according to Interstate 40 Standard GOST 10028–81 is from 6 to 30 mm^2 ·s^{-1}).

The relevance of the research topic. Green chemistry approach is growing rapidly and the replacement of petroleum derived materials with bio-based materials is greatly enhanced for environmental and health concerns. Polymers from renewable vegetable feedstock attract an increasing interest of researchers predominantly due to environmentally friendliness, while synthetic polymers are mainly produced from non-renewable petroleum resources.

The impact of polysaccharides in industrial applications is enormous. The interest in natural polysaccharides has increased considerably in recent years, as they are candidates for many commercial applications in different industrial sectors like food, textile, bio nanotechnology, paper, petroleum, health and pharmaceuticals. The usefulness of natural polysaccharides in industry undoubtedly relies on the wide range of their functional properties. To solve the problems of drilling, oil recovery, oil treatment and transportation of oil the solutions and gels of natural and synthetic polymers possessing a high viscosity, ability to gelation, thixotropy and pseudoplasticity are widely applied.

Polysaccharides are widely applied for oil recovery as key components of water-based drilling fluids, workover substances and completion fluids. Wellbore instability problems significantly increase the cost of drilling and operations in the oil and gas industry. They are used as drill bit cooling, cleaning and protecting agents, and as drag reducing fluids intensifying drilling speeds. In these systems, all carbohydrate polymers employed possess the following features: high swelling at low polymer concentration, high efficiency as suspending agents, high pseudo plasticity and extreme compatibility with high concentrations of various salts and elevated temperatures [8].

Injection of polymer solutions into the oil reservoir allows to increase considerably oil recovery in comparison with conventional water flooding. However, synthetic polymers such as polyacrylamide and hydrolyzed polyacrylamide in combination with chromium salts that are widely used in oil recovery may cause harmful effect to environment and require utilization according to ecological standards. While polysaccharides are eco-friendly and obtained from renewable resources and can be alternative to synthetic polymers. Polysaccharides that are characterized by gelation properties, stability to high mineralization and temperature are perspective reagents for oil recovery [9].

The dissertation is devoted to investigation of solution properties and gelation of gellan, xanthan, carboxymethylated cornstarch, polyacrylamide as well as their mixtures for development of drilling fluid formulation and flow deviation or plugging reagents in oil recovery.

The novelty of the dissertation topic:

For the first time, the theme has been developed on the use of natural polymer gellan and domestic product – corn starch for the development of drilling fluids. Chemical modification of domestic product – corn starch from Zharkent corn syrup plant for preparation of high viscous water-soluble polymer as key component of drilling fluids.

Relationship of the investigation with other research works. The researches were carried out in the frame of the commercialization project (SSRG 161) of the Ministry of Education and Science of the Republic Kazakhstan and World Bank "Development and commercialization of polymer flooding technology for enhanced oil recovery" (2012-2015) and grant No.4410/GF4 of the Ministry of Education and Science of the Republic Kazakhstan «Justification of drilling technology by providing automatic stability of the wellbore under unfavorable geological conditions» for 2015-2017.

The purpose and tasks of the research. The aim of this dissertation is to study the solution properties and gelation process with participation of gellan, xanthan, carboxymethylated cornstarch, polyacrylamide as well as their mixtures for formulation of drilling fluids and development of reagents for oil recovery. To achieve this goal the following tasks were formulated:

- The literature survey on investigation of the polysaccharides – gellan, xanthan, carboxymethylated cornstarch, composition and properties of drilling fluids and technology gel-polymer flooding with participation of polysaccharides;

- Investigation of physicochemical, rheological, gelforming and mechanical properties of gellan in the presence of low-molecular -weight salts and oilfield water;

- Study of the behavior of aqueous solutions of gellan, xanthan, carboxymethylated cornstarch and polyacrylamide as well as their mixtures in oil reservoir conditions;

- Obtaining of water-soluble derivatives of corn starch by chemical modification, investigation of its physical chemical properties in aqueous and aqueous-salt solutions, formulation of drilling fluids;

- Selection of optimal drilling fluids formulation and reagents for oil recovery based on polysaccharides and analysis of the results of oilfield tests.

Objects of the research. Gellan, xanthan, carboxymethylated cornstarch and their physicochemical properties. Low molecular weight salts. Oilfield water. Mineral dispersed phases. Core samples. Sand packs models. Drilling fluids and reagents for oil recovery based on polysaccharides.

As a result of the conducted research the following theses are put forth to be defended:

- Development of new drilling fluids and oil production reagents based on natural and synthetic polymers;

- Development of the modification method of cornstarch – domestic product of Zharkent corn-syrup plant;

- Physical, chemical, rheological and conformational characteristics of CMCS, gellan and xathan solutions;

- Determination of the drilling muds compositions for drilling under different geological conditions. Water-based optimal drilling fluids composed of various polysaccharides, low-molecular-weight salts and bentonite were suggested to provide the oilfield tests.

1   LITERATURE REVIEW

Green chemistry approach is growing rapidly and the replacement of petroleum derived materials with bio-based materials is greatly enhanced for environmental and health concerns. Polymers from renewable vegetable feedstock attract an increasing interest of researchers predominantly due to environmentally friendliness, while synthetic polymers are mainly produced from non-renewable petroleum resources [3, p.125].

The interest in natural polysaccharides has increased considerably in recent years, as they are candidates for many commercial applications in different industrial sectors like food, textile, bionanotechnology paper, petroleum, health and pharmaceuticals [4, p.2]. Currently, many natural polysaccharides such as starch, cellulose, gellan and xanthan etc., and their derivatives have been adopted to prepare vast number of materials for different applications.

1.1   Polysaccharides, industrial applications of polysaccharides

Polysaccharides are natural, non-toxic, and biodegradable polymers. These polysaccharides are produced by a wide variety of microorganisms and are water soluble gums which have novel and unique physical properties. Polysaccharides are high molecular weight carbohydrates which, on hydrolysis, yield mainly monosaccharides or products related to monosaccharides [10]. They may also be regarded as polymeric anhydrides of simple sugars. D-glucose is the commonest component of polysaccharides. However, D-and L-galactose, D-mannose, D-xylose, L-arabinose as well as D-glucuronic, D-galacturonic, D-mannuronic acids, D-glucosamine, D-galactosamine and amino uronic acids also occur as constituents of polysaccharides. The various polysaccharides differ from one another not only in the composition of the constituent monosaccharide but also in the molecular weight, in the nature of the chain (whether linear or branched), in the type of glycosidic bond (whether α or β) and in the type of linkage (whether $1\rightarrow2$, $1\rightarrow3$, $1\rightarrow4$, or $10\rightarrow6$) involved in the respective monosaccharide units. The O-glycosidic linkage is formed by the condensation or dehydration reaction of the hemiacetal hydroxyl group of one sugar (glycosyl donor) and a hydroxyl group of another sugar unit(glycosyl acceptor) [11]. Due to the presence of multiple hydroxyl groups, one residue of a glycosyl acceptor may connect to more than one glycosyl donor through different O-glycosidic linkages (figure 1). Microbial polysaccharides are generally divided into three groups: exocellular, cell wall, and intercellular [12]. Microbial polysaccharides may be ionic or non-ionic and are primarily linear molecules to which side chains of varying length and complexity are attached at regular intervals. Consequently, polysaccharides may be linear or branched, and the branches of various structures can occur at different positions of sugar units on the polysaccharide backbones with different branching densities [13]. The degree of polymerization (DP) usually varies from a hundred to a few hundred thousands.
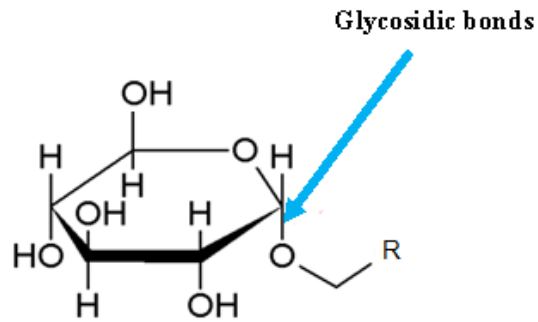
Figure 1 - Main structure of a polysaccharide.

The impact of polysaccharides in industrial applications is enormous. The usefulness of these water-soluble carbohydrate polymers in industry undoubtedly relies on the wide range of their functional properties. Chief among polysaccharide characteristics is their ability to modify the properties or" aqueous environments, that is their capacity to thicken, chelate, emulsify, stabilize, encapsulate, flocculate, swell and suspend, or to form gels, films and membranes. Polysaccharides are natural polymers from renewable sources; therefore, peculiar features like biocompatibility, biodegradability, bioadhesivity and nontoxicity, coupled with wide availability and usually low costs, account for their steadily increasing exploitation.

The use of carbohydrate polymer aqueous systems is fundamental in all process operations, from the crude oil extraction to the refined final product formulation [14].

Polysaccharides are present from the first step of the oil extraction process as essential components of water-based drilling fluids, workover substances and completion fluids. The drilling fluids are generally aqueous, oil, or emulsion (o/w or w/o) suspensions of clays, inert weighting agents and polymeric rheology modifiers. They are used as drill bit cooling, cleaning and protecting agents, and as drag reducing fluids allowing for faster drilling speeds. Workover and completion fluids are essential for achieving and maintaining a maximum well productivity by contributing to hole cleaning, rock cutting suspension and elimination, and friction reduction. In these systems, all carbohydrate polymers employed possess the following features: high swelling at low polymer concentration, high efficiency as suspending agents, high pseudo plasticity and extreme compatibility with high concentrations of various salts and elevated temperatures.

Some polymers are also used in the formulation of fracturing fluids. In close grained collector rocks of low permeability, the flow of oil to the production well sometimes is low despite very high pressure gradients being involved. In order to facilitate flow or increase intake capacity, the rocks in the bottom-hole zone of the reservoir can be subjected to artificial treatments designed to improve their permeability. There are several methods for this operation, and the choice depends on the formation conditions. However, one of the most effective is hydraulic fracturing. This technique consists of artificially creating or widening fractures in the oil-bearing rock formation by injecting a water-based fluid at high pressure. The resulting fractures extend towards the more remote productive parts of the sediment; thus, the productivity of the oil well is increased. In order to prevent fissures clogging or

collapsing after the pressure is relieved, a propping agent such as coarse-grained sand suspended in a gelling polysaccharide solution is injected with the fluid into the fracture.

When a new oil reservoir is discovered, the reservoir usually possesses the natural pressure to move the oil to the production well by expansion of its volatile components. This process is called primary oil recovery. When the natural pressure decreases, and the spontaneous flow of the oil diminishes, it is necessary to resort to secondary oil recovery techniques, which generally consist in increasing again the reservoir pressure by injection of water. This process, also called water flooding, is continued until the production cost becomes significant compared to the value of the produced oil. After these two stages, the total oil recovery is usually around 30-40% of the original oil in place. Therefore, the remaining oil is the target of the tertiary oil recovery.

It is known that major portion of fossil oil can be trapped in well rocks and therefore advanced methods of exploration need to be applied in order to recover it. Chemical flooding may displace more oil over conventional water flooding. However, chemicals used in such process may be harmful and required intensive treatment before discharging into the environment. Polysaccharides offer eco-friendly and renewable alternatives for synthetic chemicals to be used in various applications in petroleum operations such as in the area of EOR. Researchers have suggested several polysaccharides in the past as EOR agents. Of those polysaccharides xanthan and guar represent the majority. One of the disadvantages of utilizing polysaccharides in oil and gas filed is degradation especially in the harsh environment of high temperature and salinity.

Polymer flooding is the injection of a polymeric aqueous solution into an oil reservoir so that oil is displaced to production wells. Although hydrolyzed PAM have been employed for most commercial polymer floods, polysaccharides have now become popular, particularly under reservoir conditions where high salinity or hardness of formation water would substantially reduce the viscosity of PAM solutions [15].

1.1.1 PHPA/Cr^{+3} *in-situ* bulk gels

Application of aqueous solution of PHPA/Cr^{+3} for CCO and WST was proposed in 1972 [16]. Since that time this system along with its modified versions was numerously tested and implemented in field conditions throughout the world [15]. Later research allowed better control over the gelation time of PHPA/Cr^{+3} solutions within the temperature range between 60 and 135 ºC, making possible wider application of this system [17]. One of the first and the most successful field tests was conducted in 1980s by Maraphon oil company in naturally fractured carbonate and sandstone formations of Wyoming's Big Horn Basin [18]. This example may be considered as the most general case study since it has brought out merely all major requirements for successful application of polymer *in-situ* bulk gels concerning both CCO and WST. Conclusions drawn from this trial were proven to be correct later by

a number of other tests conducted throughout the world and are outlined along with supporting facts as the article proceeds.

There are some evidences from other field trials that the application of PHPA/Cr^{+3} and other in-situ bulk gels in producing wells may not increase oil productivity and in some cases even negatively affects it. It should be noted that some literature sources described PHPA/Cr^{+3} gels as being capable of providing disproportionate permeability reduction (DPR) effect. So, polymer bulk in-situ gelling agents may be successful only when the slug is properly placed inside of the reservoir. It should me mentioned that application of in-situ bulk gels in reservoirs without high permeability filtration paths may be complicated due to the injectivity restrictions. Manrique et al. [19] reported that some field projects failed because the injection of PHPA/Cr^{+3} gelling solutions was characterized by too high injection pressure values. The traditional in-situ bulk gel systems have another serious disadvantage related to certain drawbacks regarding the in-situ transport of chemicals [20]. The gelants are usually composed of high and low molecular components, while the application of single component formulations is most desirable because in this case there is no loss of reagent due to the precipitation or chromatographic separation [21]. Molecular weight of the polymer is significantly higher compared to that of the crosslinker, therefore during the injection process the crosslinker particles filtrate faster than polymer does, it leads to uneven distribution of the components at near wellbore zone. Some authors state that this phenomenon affects composition of gelling solution and gels with more inferior properties than it was originally intended are formed *in-situ* [22-24].

Strict requirements to the salinity of makeup water is also a limiting factor for PHPA/Cr^{+3} gelant application. At hydrolysis degree of PHPA between 30 and 90% and temperature range increasing from 20 to 200 °C the precipitation of PHPA from 1,000 ppm concentrated solution occurs within the range of divalent ions concentrations decreasing from 10,000 to 10 ppm [25-26]. For example, the precipitation of the polymer may occur when the concentration of divalent cations in makeup water is around 2,000 ppm at 75 °C [27].

It also should be mentioned that because of environmental protection concerns the inorganic (Cr^{+3}) and organic crosslinkers (phenol/formaldehyde and polyethyleneimine) used for the initiation of PHPA gelation after thorough revision were prohibited for application in some countries [28-29].

1.1.2 Gellan

Among the most important polysaccharides is gellan that has been extensively used in a wide range of applications due to its unique properties (table 1). It is widely used as a gelling agent, viscosity builder and texture modifier in food and pharmaceutical industry [30].

Besides xanthan, only gellan has gained industrial relevant application as a thickener, and because of the high tendency to form thermoreversible gels. It can produce thermoreversible transparent gels in aqueous solution even at a very low concentration, which depends on the kind and concentration of metallic ions.

Table 1 - Chemical and physical properties of gellan

Property	Description
Appearance	off-white powder
Types	native, deacetylated, clarified (i.e., filtered deacetylated gum)
Molecular weight	varies within a very wide range ~500,000 >70,000, with 95% above 500,000
Solubility	soluble in hot or cold deionized water soluble in water; insoluble in ethanol
Viscosity	can exhibit high viscosity in solution high-acyl gellan gum is viscous; deacylated gellan gum (treated with an alkali) has relatively low solution viscosity cold dispersions of native gellan gum provide extremely high viscosities, and the solutions are highly thiotropic; the viscosity decreases with heating as the gum hydrates; hot native gum solutions are more viscous than deacylated gellan gum solutions
Gelling property	forms a weak gel in water in its native state, but forms a rigid gel after treatment with an alkali
Ionic nature	anionic
Hydration	native (acylated) gellan gum will swell in deionized water forming a very thick particulate system, and the hydration temperature is reached at ~70°C; the swelling behavior and hydration temperature is altered in the presence of ions deacylated gum will only partially hydrate in cold deionized water, with hydration occurring with a heated deionized water temperature of ~70°C; also hydration is poor in mildly acidic conditions and in the presence of divalent ions

Gellan which is produced by the bacterium Pseudomonas elodea and consists of a tetrasaccharide repeating unit of D-glucose, D-glucuronic acid, D-glucose, and L-rhamnose [31-32]. The review by Morris et al. [33] comprehensively considers the structure, rheology, gelation, topology, and application aspects of gellan. The coil-helix conformational and sol-gel phase transitions of gellan gums induced by temperature, salt addition, pH change etc. were the main subject of many studies [34-37]. A series of publications cover formation of interpenetrating networks with participation of gellan and natural polymers [38-39]. Popa et al. [40] used gellan cross-linked with epichlorohydrin as a carrier for immobilization of catalase.

It is commonly accepted [41-46] that gellan gum exhibits a conformational change from the disordered state (single chain) to the ordered state (double helix) with decreasing of temperature, and the gelation is considered to be mediated by the

double-helix formation and the association of such helices, which is enhanced by the presence of mono- and divalent alkaline and alkaline earth cations [47]. As gellan molecules possess carboxyl groups in the repeating unit, the gelation of gellan is remarkably enhanced by the addition of cations in aqueous solutions. It has been established that the extent of aggregation and effectiveness in promoting gel formation by addition of ions follows this order: $Cs^+> Rb^+> K^+>Na^+> Li^+$. This sequence follows the Hofmeister series and agrees well with increasing of the ionic radius of cation species. The higher effectiveness of divalent cations in comparison with monovalent ones may be attributed to additional crosslinking of gellan chains due to cooperative binding (or "bridging") of the divalent cations between glucuronate residues according to their ionic radii. Divalent cations seem to bind directly to gellan macromolecules to form aggregates of gellan helices with the effectiveness of $Ca^{2+}>Mg^{2+}$ [48-50]. The main difference between the monovalent and divalent cations is that the monovalent cations shield the electrostatic repulsion between the COO^- while the divalent cations, rather than by suppressing electrostatic repulsion, form interchain ionic bonds with carboxylic groups of the glucuronic acid units resulting in the aggregation of the double helices [51-52]. As for the divalent cations, they do not appear to obey the Hofmeister series and the order among the divalent cations is more difficult to rationalize. Gellan salts with the monovalent cation, such as lithium or potassium, form stiff gels and that with divalent cation, Ca^{2+}, make a more rigid gel.

The most readily available gellan is a deacyled form with a tetrasaccharide repeating unit. After deacylation of the native gellan in alkaline conditions, it forms strong gels able to compete with agarose or gelatin. The L-glyceric groups stabilize the double helix and the acetyl groups located outside the double helix prevent their aggregation and gel formation [53-54].

The sol-gel technology is an effective tool to design materials with unique chemical, physical and mechanical properties. Transformation from sol to gel state proceeds with increasing of either concentration of disperse phase or under the action of external factors (concentration of polymer, temperature, time, pH medium, ionic strength etc.). The rheological properties of deacylated gellan gel are superior to those of other common polysaccharide gels such as agar, κ-carrageenan, and alginate at similar concentrations. The hardness, brittleness, and elasticity of gellan gel at 0.5% is comparable to, and its stiffness is much higher than, 1% K-carrageenan, 1.5% agar, or 4.0% gelatin gels [55-57].

In a physically crosslinked gellan gel, there are crosslinking regions called junction zones composed of aggregated helices which are interconnected by chains called network chains. However during gel formation, it is highly probable that some fraction of polymer chains remains uncrosslinked to the network and exists as free chains and dangling chains. They do not contribute effectively to the formation of the gel network and thus to the elasticity. This result suggests that comparatively shorter chains are releasing out to the external water. Results suggest that chain release become faster with increasing dimensions of the gel, however the concentration of released chain normalized by surface area and volume suggests that some additional

factors are responsible to control the chain release behavior. The network chains of the gellan gel become stiffer due to gel swelling leading to an increase in elastic modulus with time. Results suggests that the free chains release in shorter immersion time region and network chains release in longer time region when the gel is immersed in water. The unassociated gellan chains along with K^+ ions released out into pure water leading to gel erosion. The alkali-treated gellan has been widely utilized in food industry and biotechnology because it forms a transparent gel that is heat –resistant and its gel strength is less dependent on pH in comparison with polysaccharide gels [58-60].

1.1.3 Xanthan

Xanthan is one of the most extensively investigated polysaccharides produced by fermentation of a carbohydrate by naturally occurring bacterium *Xanthomonas compestris*. Xanthan is a polysaccharide consisting penta-saccharide units in form of glucose, mannose, and glucuronic acid [61]. Xanthan is completely soluble in hot or cold water (table 2), hydrates quickly once dispersed and provides water binding resulting in very high viscosity solutions at low concentration and encouraging its use as thickener, stabilizer, emulsifier and foaming agent. The industrial importance of xanthan is based upon its ability to control the rheology of water based systems [62]. Even at low concentrations xanthan gum solutions show a high viscosity in comparison with other polysaccharide solutions. Xanthan gum solutions are highly pseudoplastic, i.e. even after high shear rates the initial viscosity is rebuilt immediately. Xanthan gum is mainly considered to be non-gelling and used for the control of viscosity due to the tenuous associations endowing it with weak-gel shear-thinning properties.

Table 2 - Chemical and physical properties of xanthan

Property	Description
Appearance	cream-colored, odorless, free-flowing powder white/beige powder with a characteristic odor
Molecular weight	1,000,000 – 10,000,00 varies within a very wide range
Solubility	dissolves readily in water with stirring to give highly viscous solutions at low concentrations completely soluble in water, forming colloidal solution; insoluble in alcohol readily soluble in hot or cold water to form neutral, viscous, and nonthixotropic solutions that have relatively high viscosity
Stability	resistant to heat degradation
Ionic nature	anionic
pH	5.5-8.5 (1% solution, 25°C)

Xanthan gum in water fluidss provides non-Newtonian mud rheology, which is required for efficient cuttings lifting in lower density fluids. Xanthan is anionic polymer with the average molecular weight $(1-2) \cdot 10^6$ Dalton, tolerance for salinity and unaffected by pH (1-13). Temperature tolerance varies with water-phase components, but starts to degrade around from 93 to 121°C. Xanthan interacts with other polysaccharides giving a synergistic increase in solution viscosity, i.e. the observed viscosity is higher than the sum of viscosities of the pure components.

Xanthan gum is used in many fields such as petroleum production, pipeline cleaning, EOR, textile printing and dyeing, ceramic glazes, slurry explosives and in cosmetics, in the food and pharmaceutical industries [63]. In fossil oil or petroleum industry, xanthan may be used as a thickening agent for drilling mud that pushes the shattered rocks up to the surface. Xanthan is a good agent for polymer flooding of heavy oil recovery in high salinity reservoirs. It is also more mechanically stable than other EOR synthetic polymers such as PAM. Despite this fact, its adsorption on porous media was found to be superior over traditional EOR polymers such as hydrolyzed PAM. The ability of xanthan gum to adsorb on the surface of rocks is extremely important for reducing permeability of flooding agents, e.g. water, in porous media and hence force the oil to be recovered abundantly. Xanthan may be used as a good viscosifier for water flooding in high salinity reservoirs.

Another study conducted by Soudi et al. [64] verified the stability of xanthan solutions against heat, pH variation, and salinity. They reported that the reduction in its viscosity upon changing temperature and salinity was less than 20%. A minute reduction in viscosity of xanthan in a solution of 0.1 M NaCl was observed when compared to that of unsalted aqueous solution. The charged groups in xanthan chain are more likely to interact with the divalent cations such as Fe (II) and others which may lead to a decrease in solution viscosity [65].

1.1.4 Starch and its derivatives

Products made from starch have attracted the interest of researchers and companies due to the abundance of starch in nature, its low cost and biodegradability [66]. The carboxymethylation of starch in alkaline solution with sodium monochloroacetate was first carried out in 1924 [67]. Currently many papers concerning the carboxymethylation of starch were published with the aim to optimize the reaction conditions, to increase the yield of product and to increase the degree of substitution (DS) [68]. Starch is unique raw material resources due to high biocompatibility and annual renewability (potatoes (5%), corn (82%), wheat (8|%), etc.) that distinguish it from cellulose derived from wood, which period of maturing is 18-20 years for fast-growing wood [69]. Starch is a carbohydrate consisting of linear and helical amylose molecules and branched amylopectin molecules with general chemical formula $(C_6H_{10}O_5)_n$ [70-71].

Starch was the first polymer reagent used for the drilling fluids in 1939 [72]. However, with the introduction of polymer reagents based on cellulose ethers widespread use of starch started to reduce. This was primarily due to the need to use bactericides and low thermostable starch reagents [73].

Currently, the natural starch is not used in drilling fluids. Instead of it, the following types of modified starch such as carboxymethyl, hydroxyethyl, as well as oxidized starch are applied to regulate the filtration and rheological characteristics of drilling fluids. The chemical modification of cornstarch is performed to overcome the insolubility in water, hardly controlled viscosity after gelatinization, the turbidity of aqueous solutions [74]. Carboxymethylated starch (CMS) is the most commonly used material among the modified starch reagents. It is a starch derivative in which the –OH groups is partially substituted by ether group ($-O-CH_2COOH$) [75]. It is characterized by good resistance to high content of salt, high durability to thermal and bacteriological affect [76]. The CMS has a wide applicability due to water-solubility, high viscosity and stability as a fluid loss reducing agent in drilling fluid [77-78]. The application of CMS in EOR is also growing [80].

The main objective of this work is to synthesize and characterize CMCS with potential application as additives in water-based drilling fluids. These materials were also evaluated regarding their thermal resistance and rheological behavior in the presence of various salts. Starch is a perspective material from practical point of view because it is non-toxic, contains easily modifiable functional groups and is ecologically friendly [81].

This overview showed that limited number of polysaccharides have been investigated in the past as renewable and environmentally benign polymers for oil industry specifically as EOR agents. Xanthan is the most researched EOR polysaccharide followed by guar and other polysaccharides like starch and chitosan. Therefore, researchers may find this field, i.e. polysaccharides for oil industry, an attractive and premature research field that requires more exploration of unique benefits of existing and newly discovered polysaccharides as alternative to costly and non-environmentally friendly materials that are routinely used for various oil and gas recovery methods as in EOR processes. Earlier [82-84] we have demonstrated for the first time that the gellan solution can successfully be used for EOR. The remarkable property of gellan was plugging of high drainage channels in oil reservoirs. The application aspects of gellan in oil industry, to our knowledge, have not been described yet.

Natural polysaccharides like starch, carboxymethyl cellulose (CMC), xanthan and other widely used in the composition of a low-clay-content and clay-free polymer drilling fluid for drilling of vertical and lateral wells. The idea of using gellan to create drilling fluid based on the ability of its macromolecules to undergo through conformational and phase transition under the influence of temperature, low molecular salt concentration, pH medium and etc. This should ensure the effective capacity of gellan containing solutions to strengthen the walls of the well by forming a polymer or polymer-clay filter cake, to control the absorption of water and clean the down hole from cuttings.

1.2 Drilling fluids

The drilling fluid is one of the most important components of an oil-well drilling operation. It may in some cases represent the highest fraction of the overall cost of a

drilling operation. A drilling fluid is a specially designed fluid that is circulated through a wellbore as the wellbore is being drilled to facilitate the drilling operation.

The various functions of a drilling fluid include removing drill cuttings or solids from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation i accordance with the characteristics of a particular geological formation [85].

For a drilling fluid to perform its functions, it must have certain desirable physical properties. The fluid must have a viscosity that is readily pumpable and easily circulated by pumping at pressures ordinarily employed in drilling operations, without undue pressure differentials. The fluid must be sufficiently thixotropic to suspend the cuttings in the borehole when fluid circulation stops. The fluid must release cuttings from the suspension when agitating in the settling pits. It should preferably form a thin impervious filter cake on the borehole wall to prevent loss of liquid from the drilling fluid by filtration into the formations. Such a filter cake effectively seals the borehole wall to inhibit any tendencies of sloughing, heaving, or cave-in of rock into the borehole. The composition of the fluid should also preferably be such that cuttings formed during drilling the borehole can be suspended, assimilated, or dissolved in the fluid without affecting physical properties of the drilling fluid. Most drilling fluids used for drilling in the oil and gas industry are water based fluids [86].

Polymers are used as filtrate reducers because of their chemical composition and effects on viscosity. The filtration of a polymer fluid in a porous medium can be considerably reduced by increasing the elastic properties of the solution, achieved by controlling the distribution of molar mass of the polymer and keeping its viscosity and concentration constant. Various additives are used as filtrate reducers, among them: bentonite, due to its thixotropy and capacity for swelling and ion exchange; lignosulfonates, which are used to improve the performance of bentonite; starches, used to control fluid loss in situations where employing bentonite is impractical or undesirable [87].

1.2.1 Functions of the drilling fluids

Some functions of the drilling fluid can vary with the type of well or formation, but the basic functions remain the same for most oil-well drilling operations. Two of the most important functions are controlling the formation pressure and the transport of the cuttings from the bottom of the well up to the surface. The importance of a certain function of a drilling fluid will depend on the specific well being drilled.

The fluids serves a few primary function which are [88]:

Removes cutting from borehole and cleans the drill bit. As drilling is done , cuttings which are the drilled material build up within the hole. Therefore it is essential for the cuttings to be removed for drilling to proceed smoothly. Drilling fluids achieve this goal by bringing the drilled material to the surface by the use of

velocity or viscosity. The removal of cuttings also cleans the drill bit to avoid re-cut of cuttings [89].

Cool and lubricates the drill bit. Heat is generated by the friction between drill bits and the cuttings. The drilling fluids which are circulated in the well serve to transfer the heat from the drill bit back up to the surface thus cooling the drill bits. In addition to that, the presence of the fluid reduces the friction between the blades and the cuttings.

Lubricates the drill pipe. Friction can occur between the drill pipe and the formation as well as the cuttings. The presence of the drilling fluid serves as a barrier which reduces this friction and thus prolongs the life of the pipe [90].

Controls fluid loss. Fluids in the borehole have a tendency to move into the formation which could result in a loss of drilling fluids. Therefore it is necessary for a barrier known as a filter cake to prevent the fluid loss. This can be achieved through the deposition of clay particles on the borehole wall. A successful reduction in fluid loss can reduce well development time [91].

Stabilise the borehole. Boreholes can collapse if formation pressure gets too high. Therefore it is necessary to overcome this pressure with the use of drilling fluids' weight in order to maintain the structure of the borehole. In addition to that, drilling fluids also form an impermeable barrier to prevent the formation from swelling and close in on the drill pipes.

Suspend cuttings. Fluid velocity is essential in carrying cuttings out of the hole. However the drilling fluid also needs to be able to hold the cuttings in suspension when the pump stops and the fluid losses its velocity. This avoids cuttings from settling back into the bottom of the borehole [92].

1.2.2 Types of Drilling Fluids

Drilling fluids can be divided into various types according to their base fluids which are water based, oil based or synthetic based.

Water-based fluids can further be divided according to the additives into clay-based or polymer-based fluids.

Oil-based fluids generally use synthetic oil as a base fluid, but diesel-based drilling fluids may still be found in some parts of the world. The newer synthetic oils, also called mineral oils, are less harmful to the health of the drilling crew and therefore preferred [93].

When choosing a drilling fluid, one must always find a balance between the specific needs of the well and the cost of the fluid. The drilling fluids cost can vary quite substantially and may represent a big share of the total cost of the well.

1.2.3 Composition of drilling fluids

Modern drilling fluids may comprise of an extremely complicated chemistry depending on the application. The simplest type of drilling fluid used is probably the so called "spud mud", due to its use in top-hole sections. This fluid is usually constituted only of water and a viscosifier. As wells are drilled deeper and into more demanding formations, more additives are needed to control several properties, from

density to shale inhibition and lubricity. Many types of additives are used, some as simple as nutshells, used to seal fractures and stop fluid loss, others more complex such as advanced lubricants and polymer viscosifiers [94].

1.2.4 Properties of drilling fluids

During a normal drilling operation, the drilling fluid is tested at least twice per 12 hour shift to determine the values of a set of properties. The monitored properties depend mostly on the type of fluid being used, and can include the following:

The density of the drilling fluid is one of the most important properties and should always be adjusted to the specified value. Besides controlling the flow of formation fluids into the well, it also impacts hole cleaning. It is therefore a very important property to monitor and one of the two that we will focus on when designing an automated fluid property adjustment system.

After density, the viscosity of the drilling fluid is the next most important property to be monitored and corrected as it has influence in several of the functions that the fluid should provide during a normal drilling operation. For that reason, it is of great value to implement a system for automatic adjustment of this property, so that the efficiency of the operation can be maximized and not be conditioned by the attention or availability of the crew to treat the drilling fluid.

Shear dominates most of the viscosity-related aspects of drilling operations. Because of that, shear viscosity (or simply, "viscosity") of drilling fluids is the property that is most commonly monitored and controlled [95].

The fluid loss reveals the ability of the drilling fluid to form a barrier, called filter cake, which will prevent the loss of fluid into the area of the formation around the wellbore. This fluid is composed by the liquid fraction of the drilling fluid and is known as filtrate.

The filter cake should be thin and smooth, and the fluid loss should be low. The specification value for the fluid loss varies from well to well. Fluid loss is measured by placing the fluid in a cell, over a piece of filter paper and exerting back pressure, to simulate the situation found during drilling.

The pH of a drilling fluid is important for controlling corrosion and the development of bacteria that can consume polymer additives and produce H_2S gas. It also affects the efficiency of additives such as viscosifiers and may influence the lubricity of the fluid. The pH is usually specified as a range of values and is measure using a pH-meter or by titration, in oil-based fluids.

The salt content is also one factor that affects the efficiency of viscosifiers since is leaves less "free water" available for hydration. Its measurement enables the calculation of the water activity.

It is important to maintain a low level of sand content in the drilling fluid due to its abrasiveness on equipment such as pumps and pipes. The sand should be removed by the solids control equipment [96].

The total solids content of a drilling fluid is measured with the same test mentioned for the oil-water ratio, with the solids fraction being the volume of the

initial fluid not distilled in the retort. The data is usually introduced in computer software for calculating the low gravity solids (LGS) and high gravity solids (HGS).

The low gravity solids content should be kept at low levels and is usually one of the specified parameters in a fluid program. The amount and nature of these solids will affect the density and viscosity of the fluid, filter cake build up, hole cleaning, increase pressure losses due to friction and may also limit the solubility of viscosifiers [97].

1.3 Enhanced Oil Recovery

There are several different methods of EOR which can mostly be divided into the categories of thermal chemical, and gas. Thermal EOR is achieved in a variety of ways. This includes the injection of steam or hot water, and the process of in situ combustion where controlled ignitions occur inside the reservoir. The idea behind thermal EOR processes is that the added heat will reduce oil viscosity which improves the flow. Steam injection is quite effective with typical increased recovery between 50 and 65 percent of the original oil in place [98]. It is however a difficult method to employ as it requires boiling large quantities of water in the field. The water used of shore is typically the surrounding seawater which generates a less effective steam and the fuel used to generate the steam is the produced crude oil which leads to air pollution [99].

Chemical EOR includes the use of polymers, surfactants, and alkaline to assist in extraction. The chemicals alter the physical properties of the water, improving the displacement of oil. Polymer increases the viscosity of water which increases the volumetric sweep of the water flood. The result is that thief zones are no longer problematic and a larger portion of oil is displaced. The surfactants injected strive to lower the IFT between the water and oil phases. The surfactant is a monomer with hydrophilic and lyophilic ends. This duality causes the surfactant to accumulate at the interface of the two phases which reduces the IFT. Alkaline flooding seeks to create surfactants in situ to reduce IFT. A common practice is to combine these methods into alkaline surfactant polymer (ASP) flooding [100]. This method has the benefits of both increasing sweep and reducing IFT. Some of the main difficulties with employing chemical EOR are the logistics. For of shore platforms, the chemicals must first be delivered and then stored on a structure where limited space is already an issue.

While injecting a gas such as CO_2 in a reservoir is a secondary recovery technique, a combination of oil and gas is considered an enhanced technique. This can be performed simultaneously or in an alternating fashion. The advantages are that vertical sweep is improved as the dense water tends towards the bottom of the reservoir while gas tends towards the top. It also reduces the thief zone effect when compared with solely gas injection. This is because the presence of a mobile water phase effectively reduces the permeability for the gas. Consequently, alternating between injection types needs to follow a specific schedule to remain effective. This is a challenge as platform conditions may dictate that the physical switching of the injection type of a well is not a priority [101].

These three processes constitute the main effects and advantages of EOR. This is why there is such interest around MEOR, because it has the ability to achieve the same results when used effectively and properly.

Section summary

Green chemistry approach is growing rapidly and the replacement of petroleum derived materials with bio-based materials is greatly enhanced for environmental and health concerns. Polymers from renewable natural resources have attracted an increasing amount of attention over the last three decades, predominantly due to two main reasons: firstly environmental concerns, and secondly the realization that our petroleum resources are finite. The use of carbohydrate polymer aqueous systems is fundamental in all process operations, from the crude oil extraction to the refined final product formulation. The analysis of literature sources shows that polymer clay-free and low-grade drilling fluids are most effective in modern drilling technologies for directional and horizontal wells that ensure the preservation of the productive properties of the bottom hole formation zone in the production process.

2   EXPERIMENTAL PART

2.1 Materials

Food grade low acyl gellan (PubChem SID 135330201) purchased from "Zhejiang DSM Zhongken Biotechnology Co., Ltd.", China, was used without further purification. Gellan is an anionic extracellular bacterial polysaccharide discovered in 1978 [102]. Structural formula of gellan consisting of tetrasaccharide repeating units: 1,3-linked β-D-glucose, 1,4-linked β-D-glucoronic acid, 1,4-linked β-D-glucose, and 1,4-linked α-L-rhamnose is shown in figure 2.
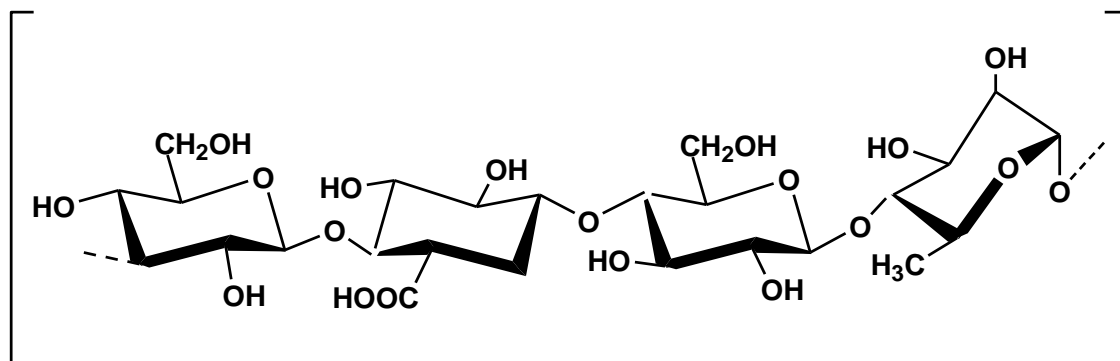
Figure 2 - Repeating monomeric unit of gellan gum

Xanthan gum purchased from "Xinjiang Fufeng Biotechnologies Co. Ltd", China, were used without further purification. Xanthan gum is also a microbial exopolysaccharide produced by bacterium *Xanthomonas campestis* [103-104]. It consists of repeated pentasaccharide units composed of two D-glucopyranosyl units, two mannopyrasonyl units and D-glucopyranosyluronic acid in the molar ratio 2.8:2.0:2.0 (figure 3). Xanthan is widely used in oil recovery, fracturing, pipeline cleaning and oil well drilling [105].

Figure 3 - The primary structure of xanthan

Gellan and xanthan were dispersed in distilled water at room temperature (25±1 °C) under vigorous magnetic stirring. Gellan and xanthan concentrations selected for experiments varied from 0.2 to1 wt.% on a dry weight basis.

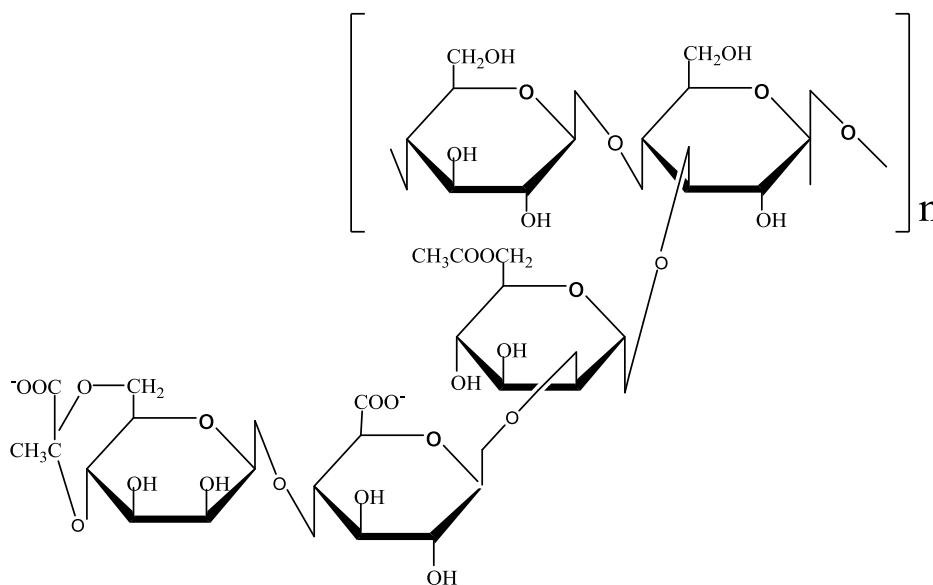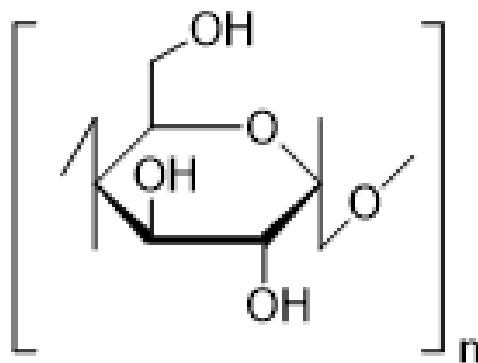Cornstarch was purchased from LLP "Zharkent Starch-Factory".

Figure 4 - Repeating monomeric unit of corn starch

Sodium monochloroacetate (Na-MCA) $ClCH_2COONa$ was obtained from Merck-Schuchardt (Hohenbrunn, Germany). The chemical reagents used in this investigation (NaOH, CH_3CH_2OH, HCl, LiBr, d_6-DMSO, and d_1-TFA were purchased from Sigma Aldrich (Finland) and used as received. Low molecular weight salts, NaCl, KCl, $CaCl_2$ $MgCl_2$, and $BaCl_2$ purchased from JSC "Reactive", Russia, were used without further purification. The bentonite $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$, montmorillonite $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$, montmorillinite SiO_2 9,2-34,42 %; Fe_2O_3 3,96-4,94 %; MgO 2,24-3,15 %; K_2O 40-57,0%, kaolinite $Al_2Si_2O_5(OH)_4$ purchased from JSC "Reactiv", Russia, were used without further purification.

The oilfield water and oil from "Kumkol" oilfield reservoir were used in the core and sand pack flooding tests. The oilfield water from "Kumkol" oil reservoir with density of 1.05 $g \cdot cm^{-3}$ and pH 6.68 was composed of 22.5 $g \cdot L^{-1}$ of Na^+ and K^+, 3.8 $g \cdot L^{-1}$ of Ca^{2+}, 0.85 $g \cdot L^{-1}$ of Mg^{2+}, and 43.9 $g \cdot L^{-1}$ of Cl^- ions with total salinity 73 $g \cdot L^{-1}$. The cations were determined by ICP analysis.

The filtration experiments were conducted by using core samples and sand from Kumkol field, strongly water wet river sand was used as well. In most experiments sand packs were used.

2.2 The preparation of 0.5 wt.% gellan solution in the mixture of distilled and oilfield water with salinity 73 $g \cdot L^{-1}$

The preparation procedure of gellan in the mixture of distilled and oilfield water is shown in table 3. The total volume (5 mL) and total concentration of gellan (0.5 wt.%) everywhere was kept constant, while the content of distilled and oilfield water changed respectively.

Table 3 **-** Preparation procedure of 0.5 wt.% gellan solution in the mixture of distilled and oilfield water with salinity 73 $g \cdot L^{-1}$

Sample No.		1	2	3	4	5	6	7	8	9	10
V_{total} =5 mL	Distilled water	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5
C_{total} = 0.5 wt.%	Oilfield water	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
*The phase state of gellan samples is demonstrated in figure 18.											

2.3 Synthesis of carboxymethylated cornstarch (CMCS)

Modification of cornstarch was carried out in two steps [106]. Firstly, alkalization was performed by mixing of 0.4 g cornstarch, 1.2 mL ethanol and 0.28 mL aqueous 11.5 M NaOH solution at 25ºC, the mixture was stirred for 20 min. In the second step, 0.28 g Na-MCA was added and the reaction mixture was heated to 58ºC and stirred during 100 min. The precipitated in ethanol CMCS was filtered and dried under vacuum at 50ºC.

2.4 The sand-packed model and filtration tests

The core flood experiments were performed on porous media obtained by packing of sand grains with an average granular size 0.125–0.25 mm into the cylindrical core holder (25 cm length and 4.3 cm diameter) made from steel (Figure 5a). Sand pack model with permeability of 2 and 20 Darcy respectively was selected to test the behavior of gellan solutions in porous media. All experiments with the sand pack model were carried out with UIC-C (2) (Russia) (figure 5b).

Filtration tests were conducted in the following order:

1) Measurement of the air permeability of the core or sand pack model;

2) Saturation of the porous media with water (brine);

3) Injection of several pore volumes of oil into the water saturated media until irreducible water saturation is reached;

4) Injection of several pore volumes of water into the media to model water flooding process until irreducible oil saturation is reached.

After the modeling of water flooding the models were subjected to the polymer treatment.
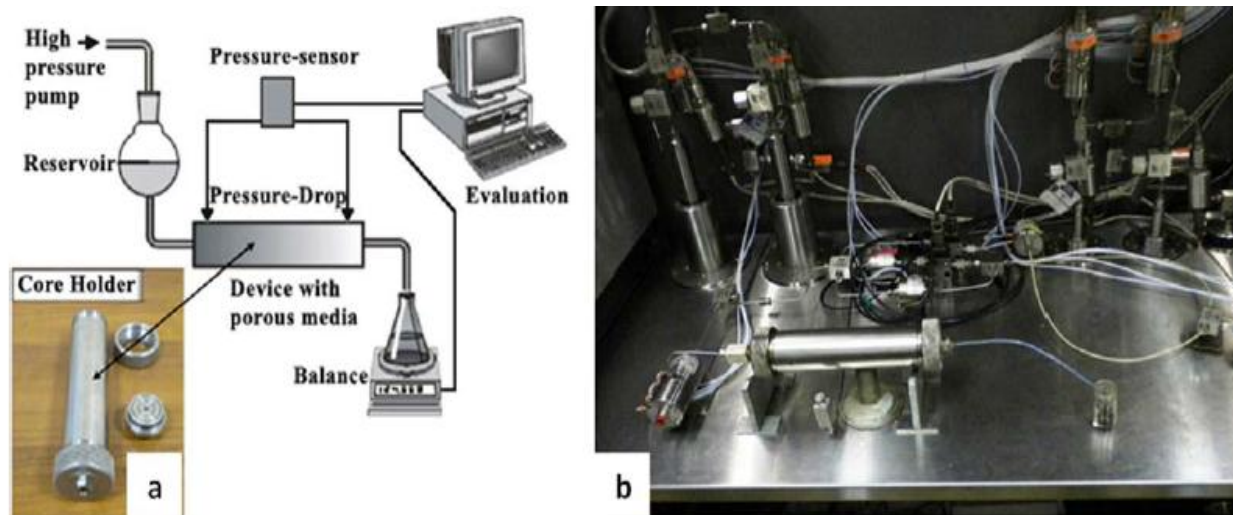
Figure 5 - The sand-packed model (a) and photo of UIC-C (2) equipment (b) for evaluation of the indepth propagation of polymer solution through the porous medium

2.5 Methods

The viscosity of aqueous gellan and CMCS solutions was measured using Ubbelohde viscometer at room temperature 25 ± 0.1 °C (capillary length is 90 mm, capillary diameter is 0.86 mm, the diapason of viscosity measurement according to Interstate 40 Standard GOST 10028–81 is from 6 to 30 mm^2 ·s^{-1}). The viscosity-average molecular weights of the cornstarch and CMCS were determined by Mark-Kuhn-Houwink equation, $[\eta]=K_\eta \cdot M^a$, where M_η is the viscosity-average molecular weight and the parameters K_η and *a* are related to local stiffness of the polymer and depend on the nature of polymer, solvent and temperature. The rheological behavior of aqueous gellan, xanthan and CMCS solutions was monitored with the help of Rheolab QC, Anton Paar (Austria) as a function of polymer concentration, salt types, pH and temperature. The rheological measurements were carried out by CDG42/SS/QC-LTD – Double Gap Cup compatible with LTD80. The approximation of results was performed by Ostwald–de Waele and Herschel–Bulkley models to find the rheological and conformational characteristics (shear stress - τ_0, plastic viscosity - η, consistency index – K and nonlinearity factor – n). Proton NMR spectra of 1 wt.% gellan solution were recorded using JNM-ECA 400 (JEOL) in D_2O at 30, 45 and 65 °C. ^{1}H NMR of cornstarch and CMCS were recorded on a Bruker Avance III 500 spectrometer at 70ºC according to procedure [107]. FTIR spectra of gellan, cornstarch and CMCS samples were recorded with the help of Carry 660 (Agilent, USA) in KBr pellets. The thermal characteristics of samples were determined with the help of DSC 131 EVO Setaram and TGA «Labsys EVO» Setaram (France). The average size and ζ-potential of CMSC was determined with the help of Dynamic Light Scattering (DLS) device Malvern Zetasizer Nano ZS90 (UK). Scanning electron micrographs were obtained with the help of SEM (Jeol JSM-6490LA, Japan). Mechanical testing of cylindrical gellan gel samples with diameter 20 mm and length of 30 mm was performed using texture analyser TA.XT plus, Stable Micro

Systems, (UK). The total salinity of oilfield water was determined on Seven Compact^{TM} S230 (Mettler-Toledo, Switzerland). The elemental composition of oil field water was analyzed with aX-ray fluorescence analyzer (Epsilon 3 SW LTU, PANalytical, The Netherlands). The elemental composition of oil field water was analyzed with a X-ray fluorescence analyzer (Epsilon 3 SW LTU, PANalytical, The Netherlan. Static shear stress (SSS) analysis was performed by means of the instrument SNS-2 (Russia). The fluid loss indicator (W) was measured with the help of BM-6 (Russia). The thickness of mud cake (δ) was measured by the instrument WIKA IV-2 (Russia).

Section summary

Preparation procedure of 0.5 wt.% gellan solution in the mixture of distilled and oilfield water was shown. A method of synthesis of carboxymethylated cornstarch was developed. Also described the sand-packed model and filtration tests.

3   RESULTS AND DISCUSSION

3.1   Gellan and Xanthan

3.1.1 H[1]NMR and FTIR spectra and DSC measurements of gellan

Proton spectra of gellan recorded in D_2O represent a set of resonance lines that are difficult to interpret comprehensively. Therefore, the proton signals belonging to each saccharide units were only identified. High frequency signal with 5.08 ppm corresponds to H-1 α-anomer of L-ramnose. The presence of ramnopiranosol residue is justified by signal at 1.25 ppm corresponding to protons of methyl radicals. Signals at δ = 4.66 and 4.48 ppm can correspond to 1,4-α- and 1,3-β-glucopiranosol units respectively. The presence of glucoronic acid is verified by downfield signal at δ = 4.64 ppm. Identification of proton signals of gellan is represented in figure 6 and table 4.
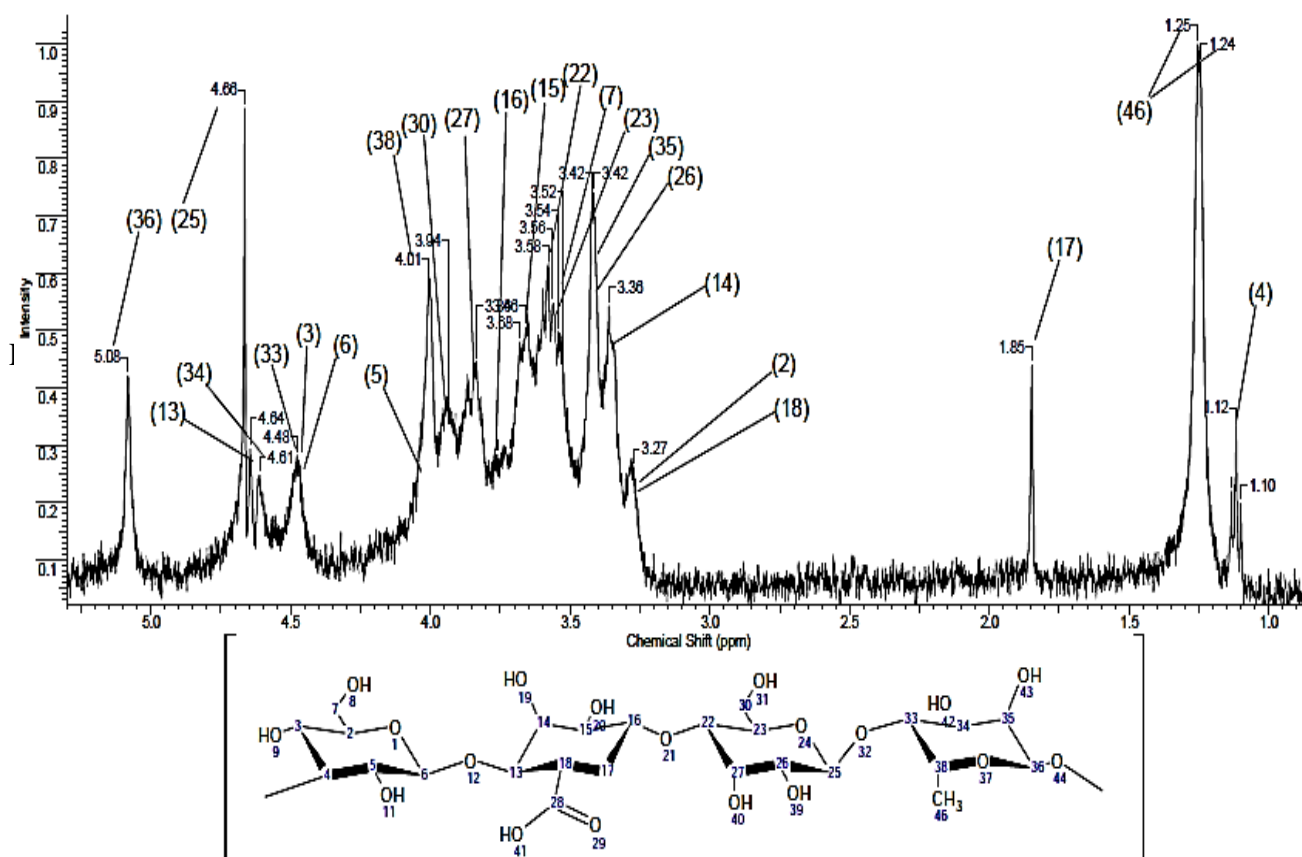

Figure 6 - Structural unit of gellan and its H[1] NMR spectra in D_2O at 30 °C

Table 4 - The characteristic chemical shifts of H[1] NMR spectra of gellan

Chemical shift, [ppm]	Fragment of saccharide
5.08; 1.25	1,4-α-L-ramnose
4.66	1,4-α-D-glucose
4.48	1,3-β-D-glucose
4.64	1,4-β-D-glucoronic acid

The temperature dependent H^{1}NMR spectra of gellan are shown in figure 7. According to the NMR signals of rigid polymers with ordered structure become so broad that they are effectively flattened into the baseline, and can hardly be detected.
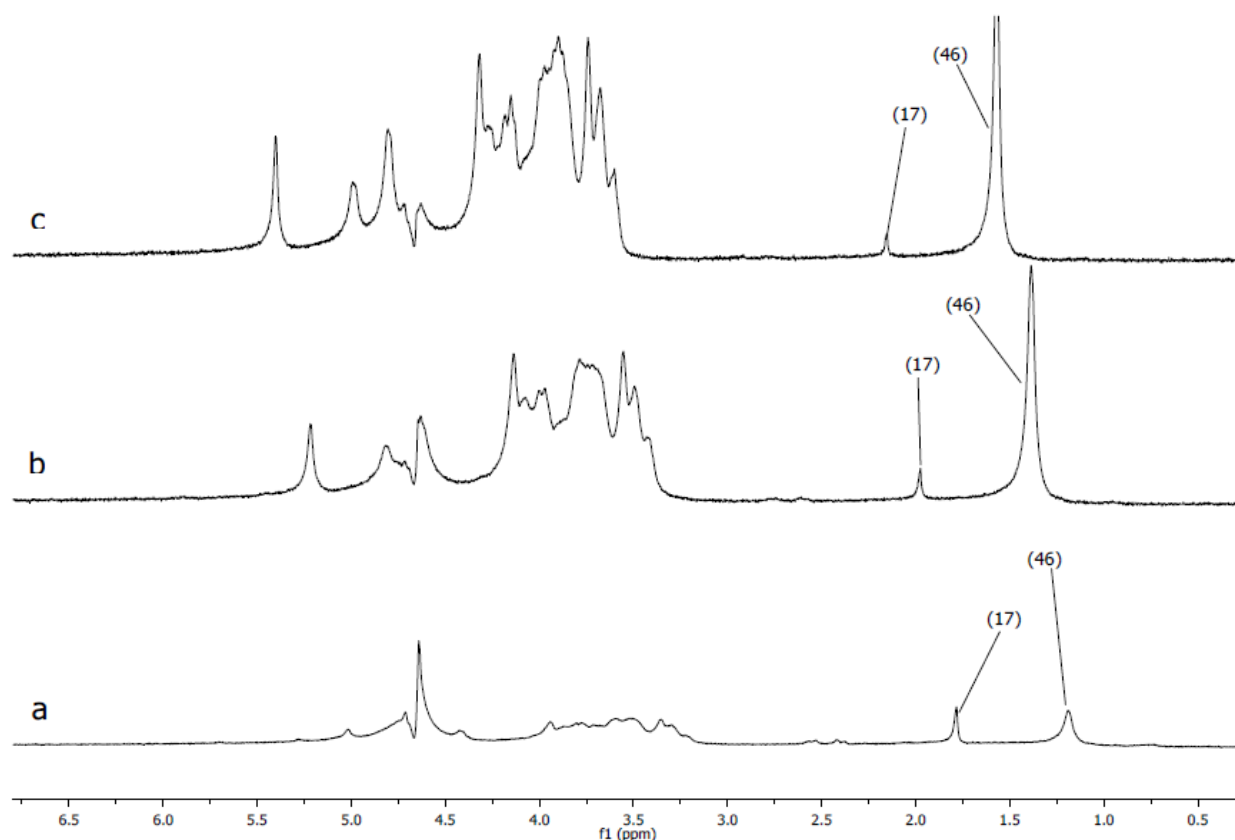
Figure 7 - H^1 NMR spectra of 1 wt.% gellan in D$_2$O at 30 (a), 45 (b) and 65 °C (c).

Heating of 1 wt.% gellan solution leads to downfield shift of proton signals and increases their intensity. Methyl protons of ramnopiranosol residue (H-46) appear at 1.19, 1.39 and 1.57 ppm at 30, 45 and 65 °C, respectively. Methylene groups of 1,4-β-D-glucoronic acid (H-17) are resonated at the frequency of 1.78, 1.98 and 2.15 ppm at 30, 45 and 65 °C, respectively. Opposite upfield shift of methyl protons of 1,4-α-L-ramnose and methylene protons of 1,4-β-D-glucoronic acid accompanied with decrease in their intensity is observed upon decrease of temperature from 65 to 25 °C. The thermal hysteresis was not detected for methyl and methylene protons of gellan. A reduction in intensity of proton spectra with decreasing temperature is consistent with the statement of authors [108] that gellan macromolecules are in disordered state at high temperature and in rigid conformation at low temperature.

Gellan spectra exhibited a broad band between 3266–3267 cm^{-1} due to O–H stretch vibrations of hydroxyl groups; C–H stretch vibrations of –CH$_2$ groups were recorded at around 2887-2926 cm^{-1}, the amide C=O strech at 1683; N-H bending vibrations at 1607-1575, asymmetric and symmetric carboxylate anions were recorded stretching at 1467 and 1455 cm-1, respectively, while C–O stretching occurred at 1020-1032 cm^{-1}.
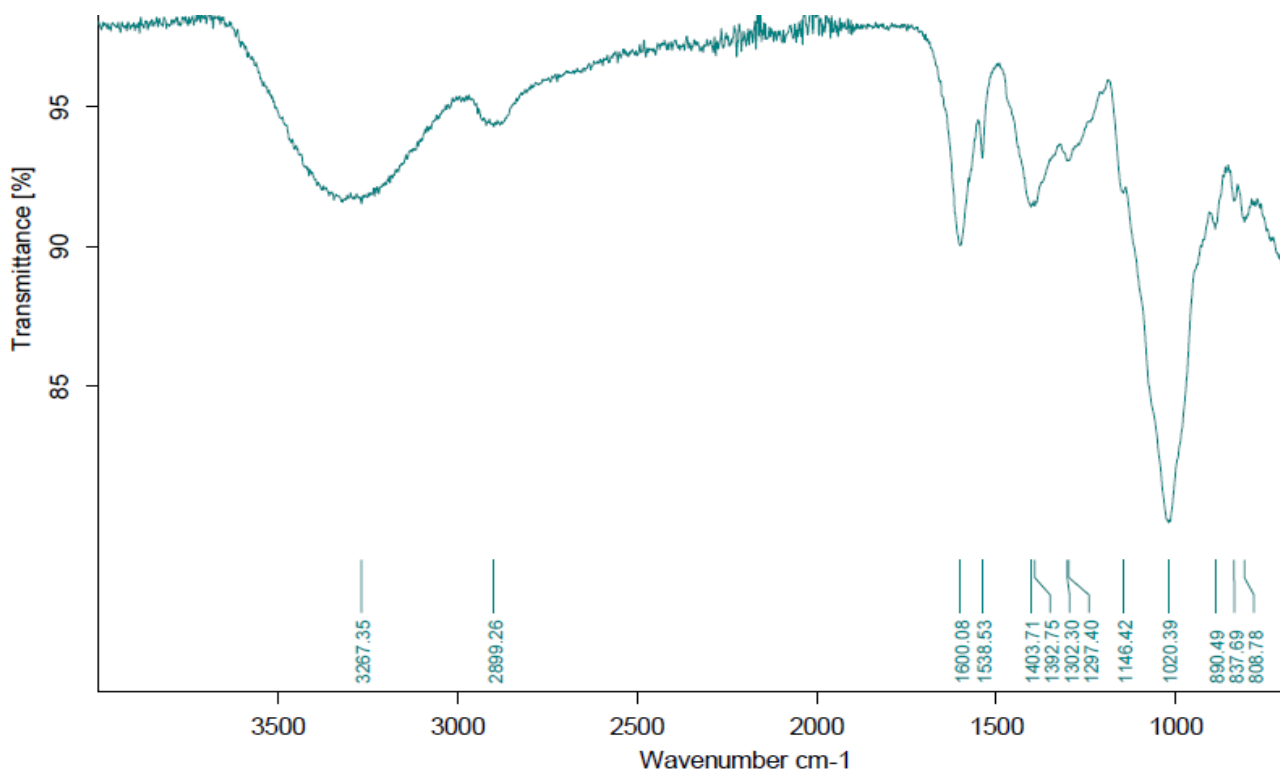
Figure 8 - FTIR-spectra of the powder gellan

FTIR spectra of pristine gellan and gellan gels isolated from NaCl, MgCl$_2$, CaCl$_2$ and oilfield water were compared (figures 9, 10). The pristine gellan has a broad band centered at 3430 cm^{-1}. It is attributed to the OH stretching vibration of saccharide units. The peak at 2923 cm^{-1} is related to the CH stretching vibration. The peaks at 1617 and 1419 cm^{-1} are typical for asymmetric and symmetric COO$^-$ stretching mode.
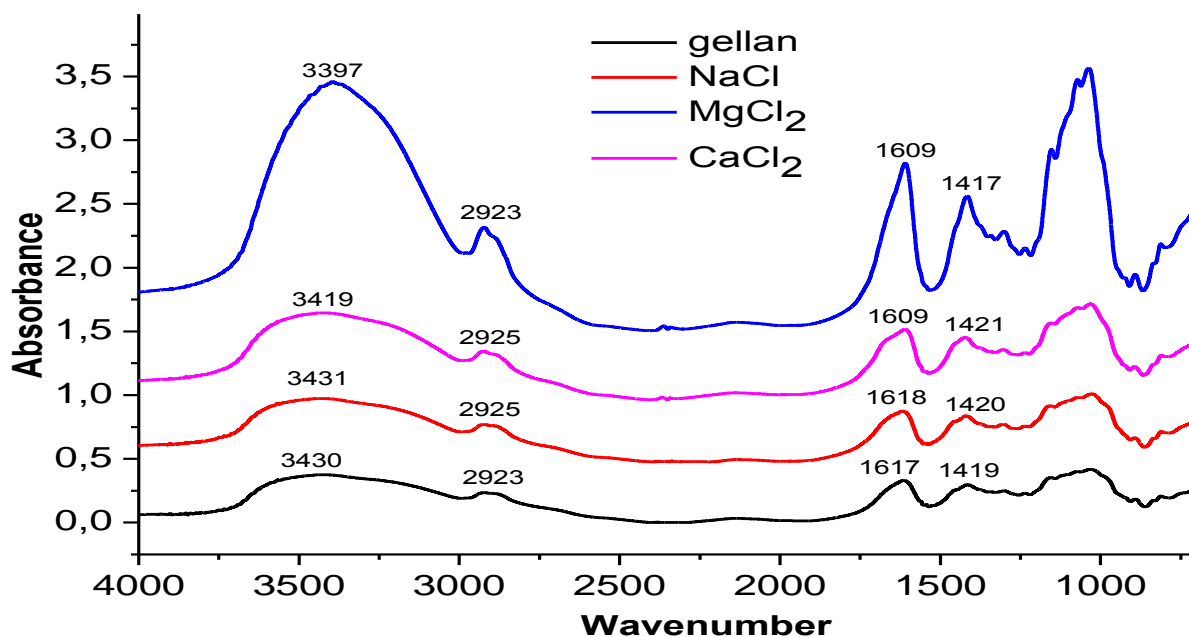
Figure 9 - FTIR spectra of gellan in the presence of MgCl$_2$, CaCl$_2$, NaCl, KCl
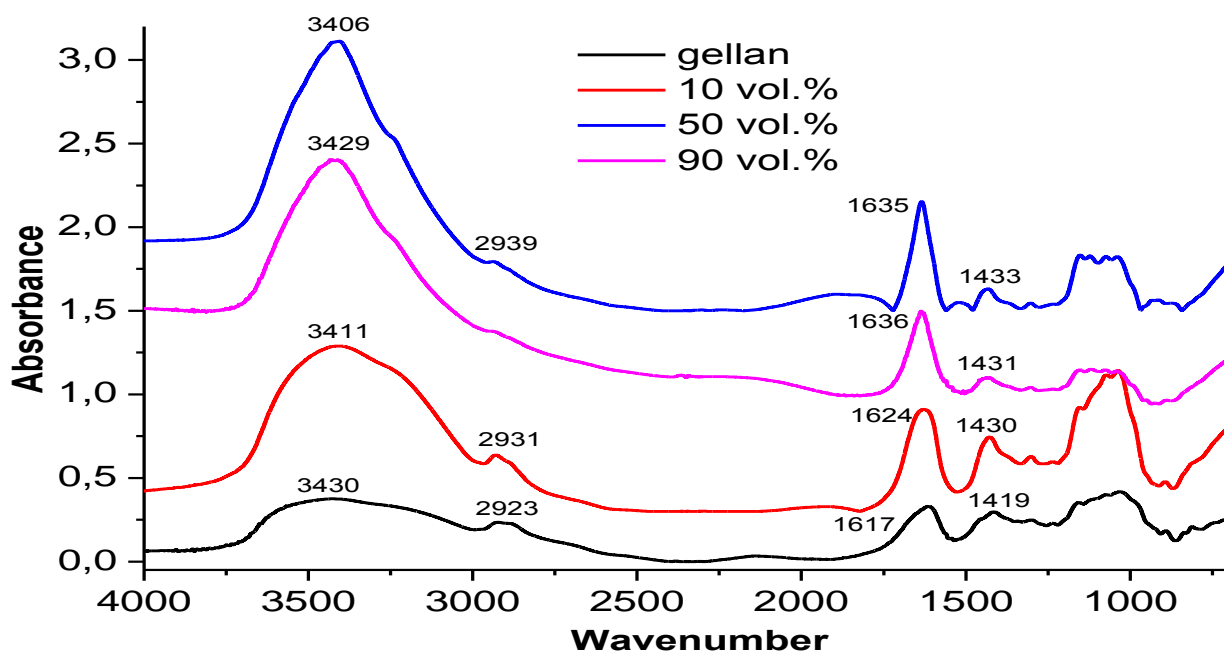
Figure 10 - FTIR spectra of gellan in the presence of 10, 50 and 90 vol.% oilfield water

The broad peaks replaced between 1000-1150 cm^{-1} are assigned to the C-O stretching vibrations. The OH stretching vibration of saccharide units at 3430 remains unchanged and is shifted to 3397 and 3419 cm^{-1} in the presence of NaCl, $MgCl_2$ and $CaCl_2$, respectively. The peak at 1617 cm^{-1} that belongs to asymmetric carboxylate groups does not change in the presence of NaCl but it appears at 1609 cm^{-1} in the presence of $MgCl_2$ and $CaCl_2$. Shifting of the vibrations of OH and asymmetric COO^- groups to low frequency regions can be explained by the complexation of these functional groups with divalent cations. Identification of FTIR spectrum of gellan precipitate isolated from the oilfield water is represented in table 5. The OH stretching vibration gradually shifts to lower, while CH stretching vibration shifts to higher frequency regions. The characteristic bands of both asymmetric and symmetric carboxylate groups are shifted to higher frequency regions. Shifting of the characteristic bands of gellan may be the result of effective surrounding of functional groups of gellan by mono- and divalent cations present in oilfield saline water.

Table 5 - The characteristic bands of precipitated solid gellan from the oilfield saline water

Oilfield water, [vol.%]	Wavenumber, [cm^{-1}]			
	Functional groups			
	δ (OH)	δ (CH)	ν_{asym} (COO$^-$)	ν_{sym} (COO$^-$)
0	3430	2923	1617	1419
10	3411	2931	1624	1430
50	3406	2939	1635	1433
90	3429	very weak	1636	1431

33

Figure 11 represents DSC and dDSC curves of gellan within temperature range from -30 to 300 °C. DSC curve shows the endothermic peak at 95 °C with melting enthalpy -264.5 J/g. The second endothermic peak corresponds to gellan decomposing or burning temperature – 251.1°C. Decomposing of gellan starts after 246 ^{0}C. Gellan decomposing enthalpy is equal to 98.99 J/g. Thus gellan is thermally stable polysaccharide, which in solid state melts within the temperature interval from 31.2 to 178 °C.
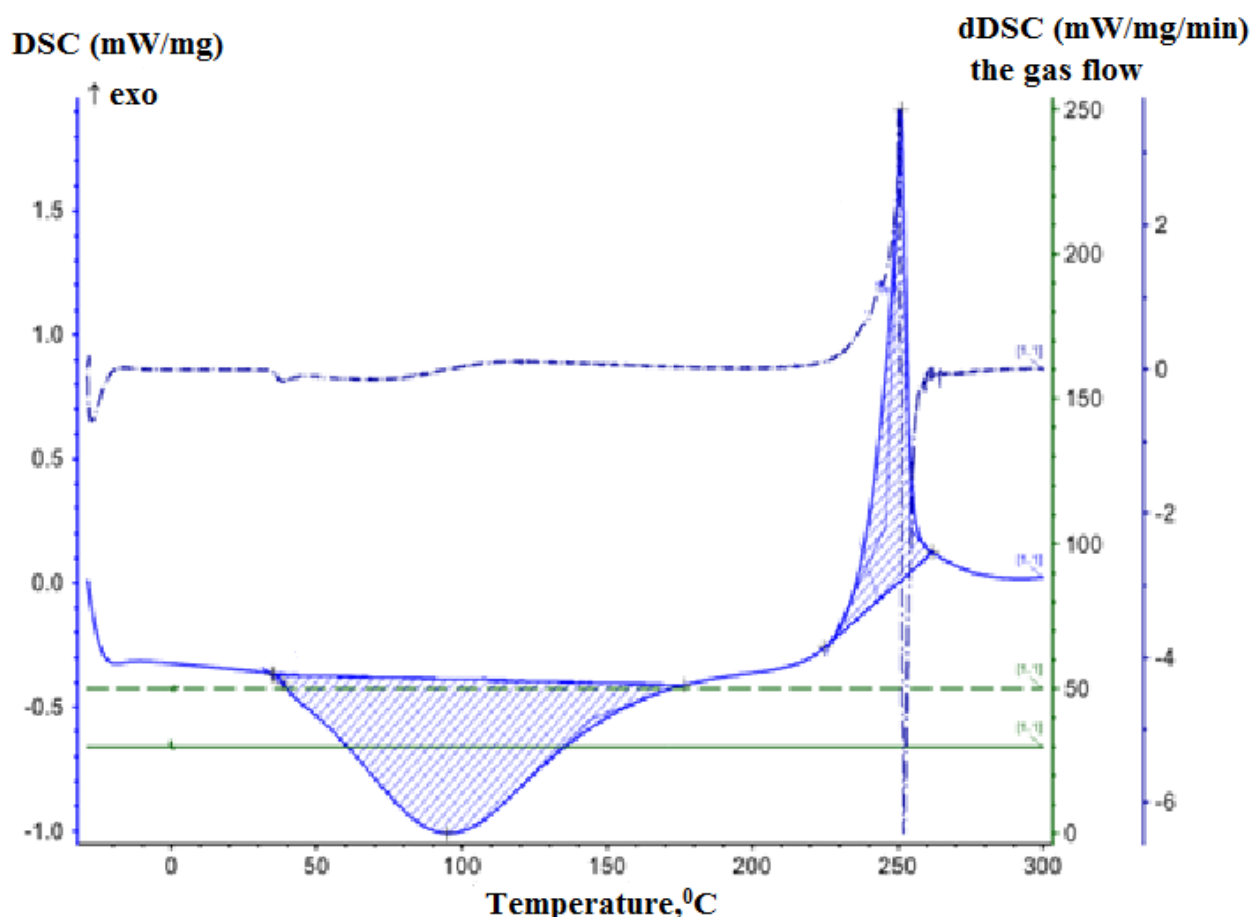
Figure 11 - The results of DSC and dDSC analysis of gellan

To evaluate the phase transition of gellan the aqueous solution at first it was cooled up to -5 °C and then heated up to 20 °C with the heating rate 0.5 °C·min^{-1}. As seen from the DSC curves (figure 12) the endothermic peak of pristine gellan at 5.5 °C gradually shifts to lower temperature up to 4.4 °C upon increasing the concentration of $CaCl_2$ (ΔT = 1.1 °C). In the presence of 0.1N NaCl the endothermic peak shifts up to 4.0 °C and the ΔT = 1.5 °C (figure 13). The DSC endothermic peaks are attributed to the dissociation of double helices to single macromolecular coils.[12] The difference in endothermic behavior of gellan solution in the presence of $CaCl_2$ and NaCl can be prescribed to dissociation of "bridged" and "shielded" macromolecular chains by two- and monovalent cations.
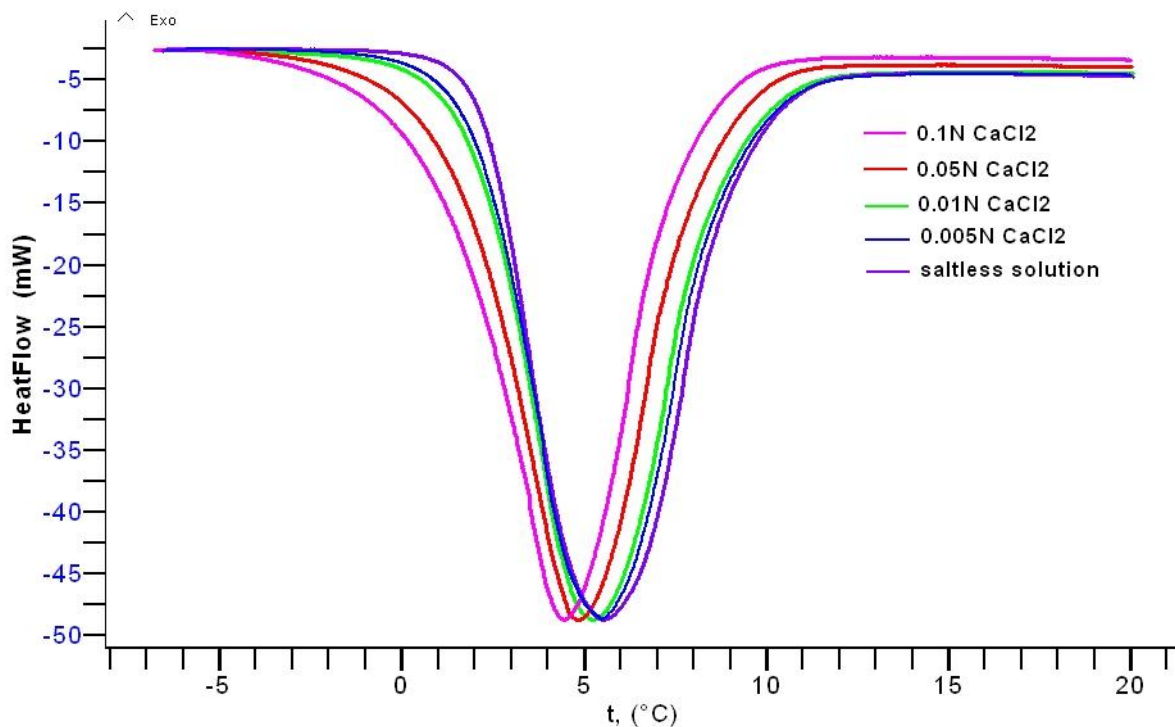
Figure 12 - DSC curves of 0.5 wt.% gellan in the presence of various concentration of CaCl$_2$ at heating rate 0.5 °C·min^{-1}
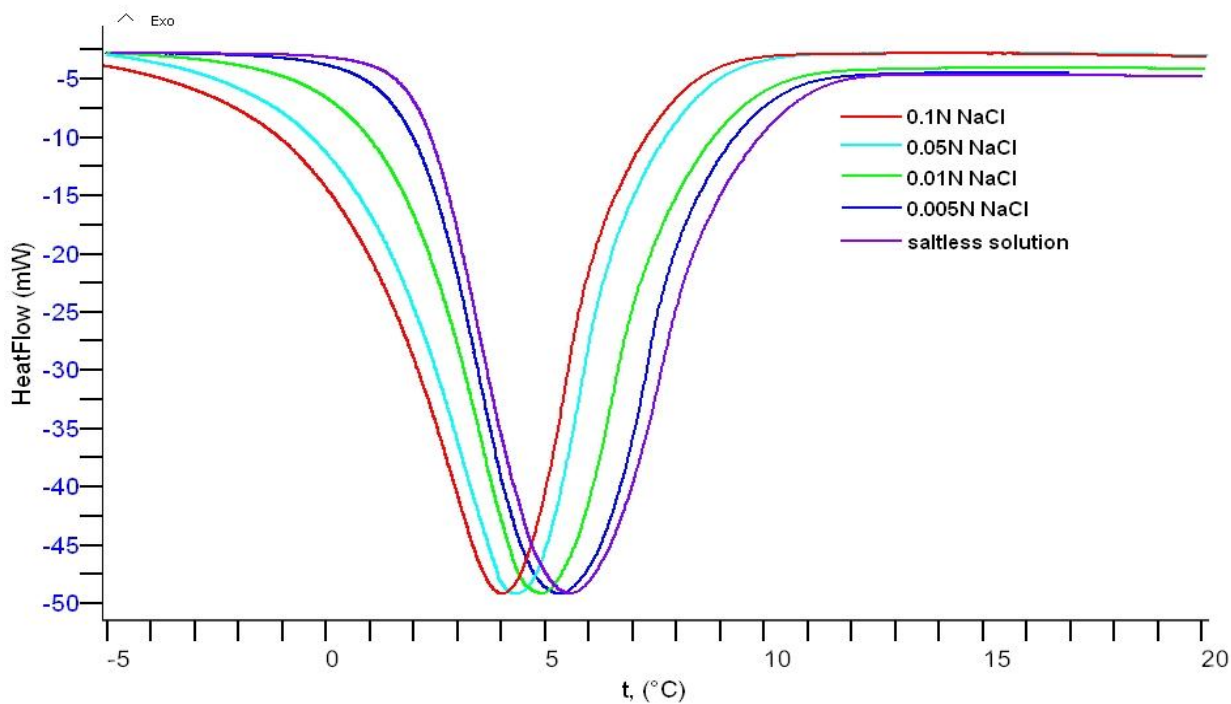
Figure 13 - DSC curves of 0.5 wt.% gellan in the presence of various concentration of NaCl at heating rate 0.5 °C·min^{-1}

Table 6 summarizes the specific heat capacity (ΔC) of 0.5 wt.% gellan solution calculated per 1 g of gellan in the presence of various salts. The values of ΔC have a tendency to decrease with increasing of salt concentration. While the ΔC increases in

the order of CaCl$_2$>MgCl$_2$>KCl>NaCl at the interval of salt concentration 0.005-0.01 mol·L^{-1}.

Table 6 - The specific heat capacity (ΔC) of 0.5 wt.% gellan solution with added salts

C$_{salt}$, N / Salt type	ΔC*, J·g^{-1}·K^{-1}			
	0.005	0.01	0.05	0.1
NaCl	107.63	95.58	66.33	59.93
KCl	111.75	105.70	103.23	96.07
CaCl$_2$	113.47	113.28	100.64	84.09
MgCl$_2$	118.90	117.38	96.50	92.38
*The specific heat capacities (ΔC) of 0.5 wt.% and 1.0 wt.% pristine gellan solutions are equal to129.71 and 121.73 J·g^{-1}·K^{-1}				

3.1.2 Influence of storage time, temperature, low-molecular-weight salts and oilfield water on the viscosity of gellan and xanthan

One of the main requirements to drilling fluids is the stability of their rheological characteristics versus time. Especially it concerns polysaccharides, which are able to undergo biodegradation. In this regard, dependence of viscosity of different concentrations of gellan and xanthan solutions was studied on storage time (figure 14, 15). The time dependent viscosity of gellan at the interval of concentration 0.2-0.5% is similar. At first the viscosity decreases, then insignificantly increases and further changes slightly. The viscosity has the minimal value on the fifth day's storage. Such time dependent change of the viscosity of gellan is probably related to the formation and destruction of gellan associates stabilized by hydrogen bonds.
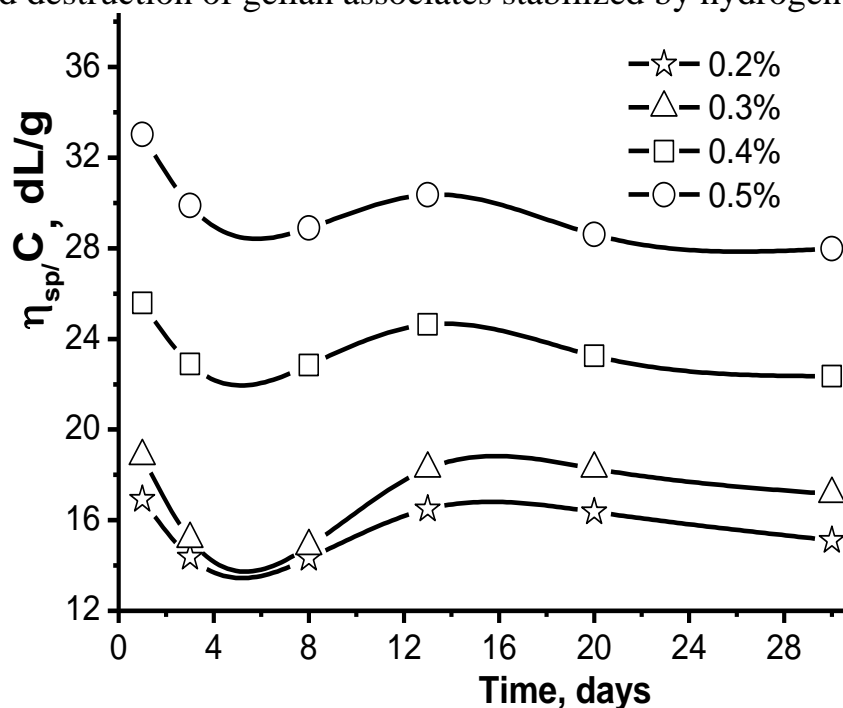
Figure 14 - Dependence of the viscosity of gellan on time storage

The viscosity of 0.05-0.2% xanthan solutions were measured for 30 days, where a slight change in viscosity was observed over time.
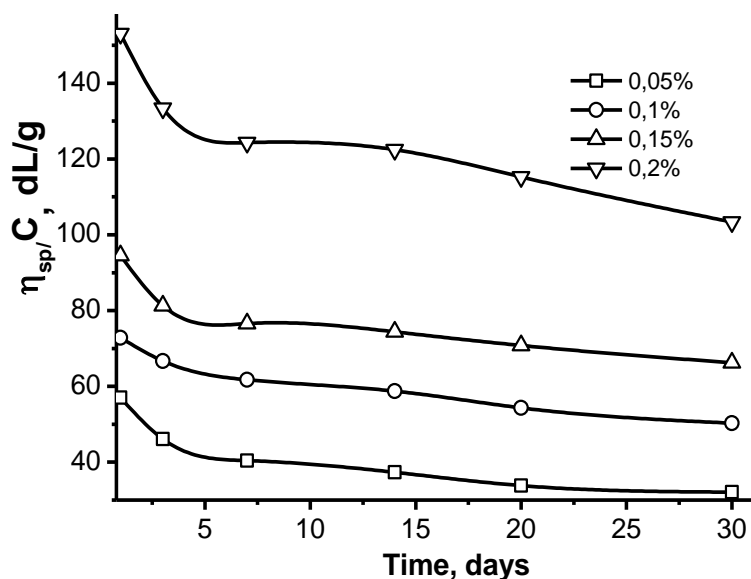
Figure 15 - Dependence of the viscosity of xanthan on time storage

The reduced viscosity of gellan solutions gradually decreases with increase in temperature (figure 16). Initial values of the viscosity considerably differ at 25 °C; however, they tend to fit together at 50 °C. This may be related to gradual disaggregation of macromolecular associates due to destruction of hydrogen bonds. One can suggest that in oil reservoir gellan solution may be stable to biodegradation during several months with lower viscosity at higher temperature.
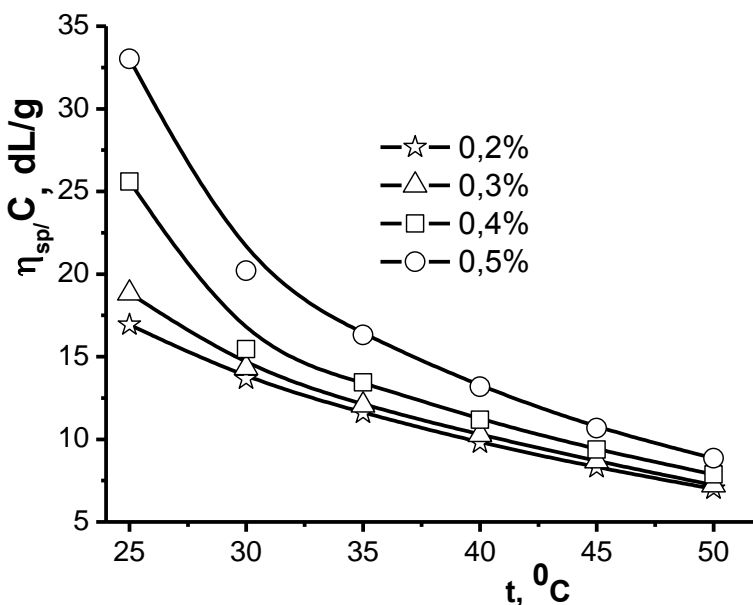
Figure 16 – Dependence of the viscosity of gellan on temperature

The viscosity of 0.05-0.15% xanthan solutions were studied at the interval of temperature 25-70 ° C (figure 17). Xanthan solutions were less affected by the temperature as compared with solutions of gellan.
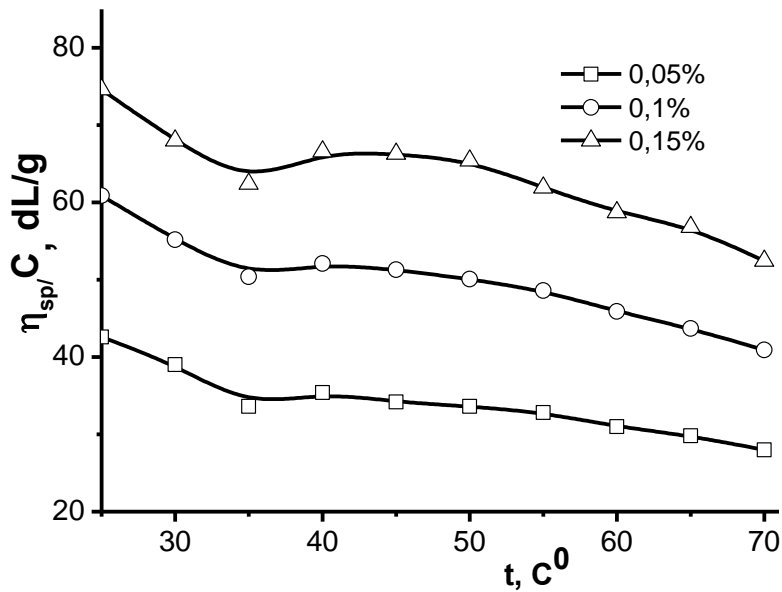
Figure 17 - Dependence of the viscosity of xanthan on temperature

The viscometric measurements were performed with 0.2 wt.% gellan because the reduced viscosity of 0.5 wt.% gellan solution is extremely high and difficult to measure. Dependence of the reduced viscosity of 0.2 wt.% gellan on the ionic strength of the solution adjusted by addition of NaCl, KCl, MgCl$_2$, CaCl$_2$, BaCl$_2$ and oilfield water with the salinity 73 g·L^{-1} is shown in figure 18. According to viscometric data the effectiveness of salts to enhance gelation changes in the following order: oilfield water > BaCl$_2$ > CaCl$_2$ ≈ MgCl$_2$ > KCl > NaCl [109]. This order is in good agreement with the results found for gellan by authors [110] however it is more difficult to rationalize.
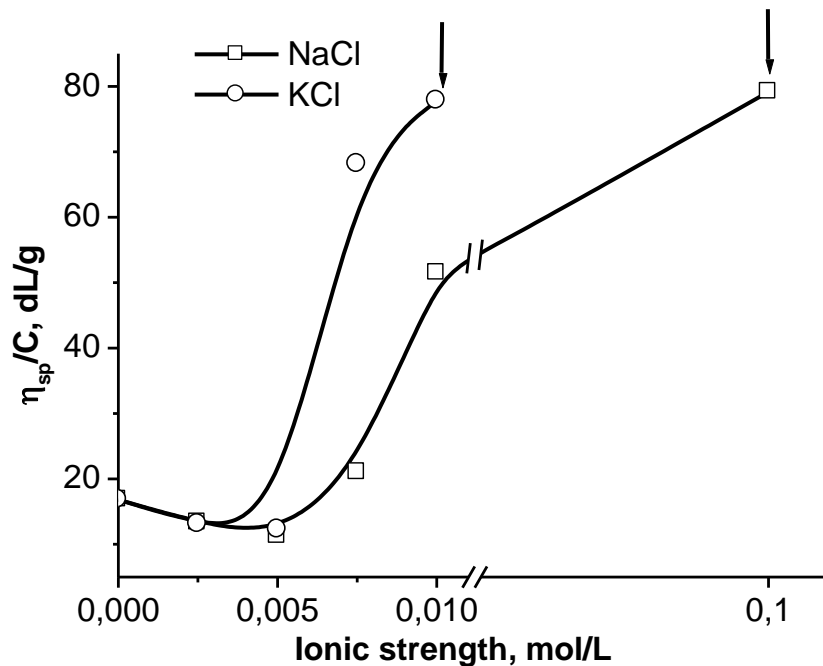
Figure 18 - Dependence of reduced viscosity of 0.2 wt.% gellan on the ionic strength of the solution adjusted by addition of NaCl and KCl. Arrows show the start of the gelation process. Temperature is 25 °C.
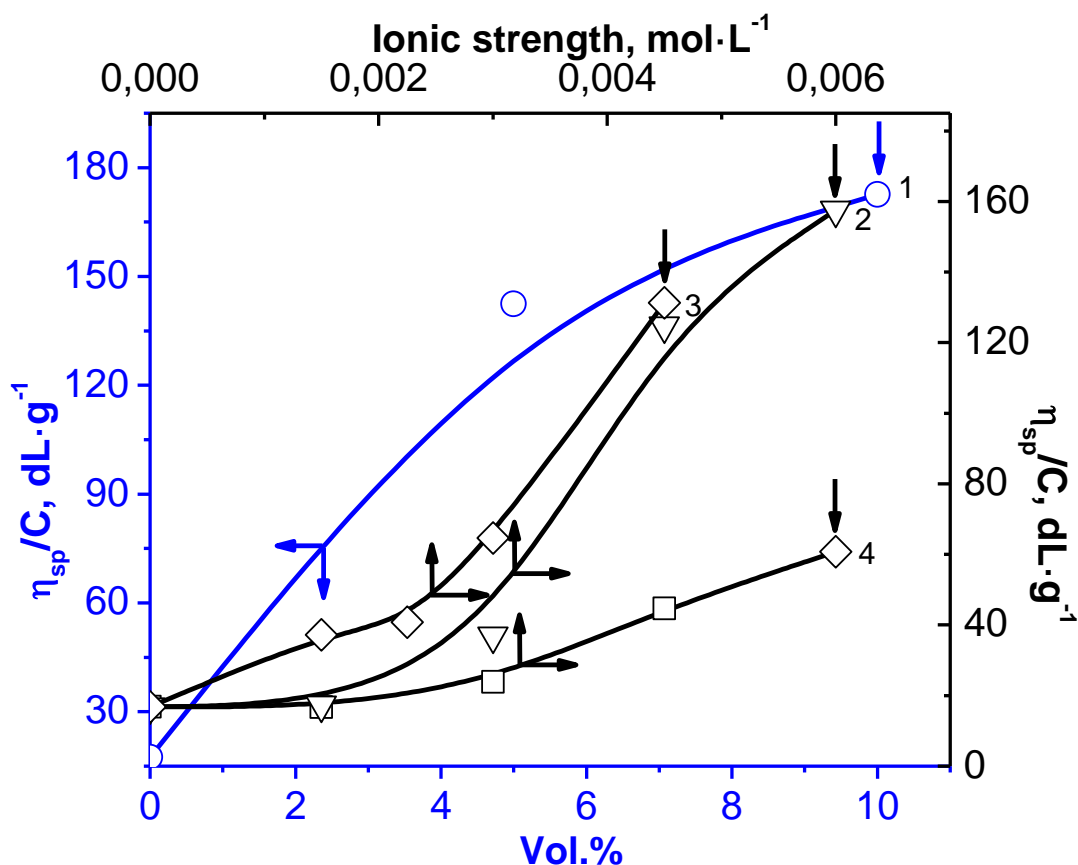
Figure 19- Dependence of reduced viscosity of 0.2 wt.% gellan on the ionic strength of the solution adjusted by addition of oilfield water with the salinity 73 g·L^{-1} (1), CaCl$_2$ (2), BaCl$_2$ (3), MgCl$_2$ (4). Arrows show the start of the gelation process. Temperature is 25 °C

The critical concentration of salts, expressed as the ionic strength of the solution, leading to sol-gel and liquid-solid phase transitions of 0.2 wt.% gellan solution are summarized in table 7.

Table 7 - The sol-gel and gel-sol phase transitions of 0.2 wt.% of gellan solution in the presence of various salts

Salt type	Critical value of the ionic strength inducing the sol-gel transition[a] (mol·L^{-1})	Critical value of the ionic strength inducing the liquid-solid transition[b] (mol·L^{-1})
BaCl$_2$	0.0045	0.036
CaCl$_2$	0.006	0.036
MgCl$_2$	0.006	0.036
KCl	0.01	0.15
NaCl	0.1	0.20
[a]According to viscometric data; [b]Visual observation		

According to the results, it can be noted that the xanthan solution is less sensitive to changes in the ionic strength of the solution compared to gellan solution, where gelation is pronounced with increasing salt concentration.
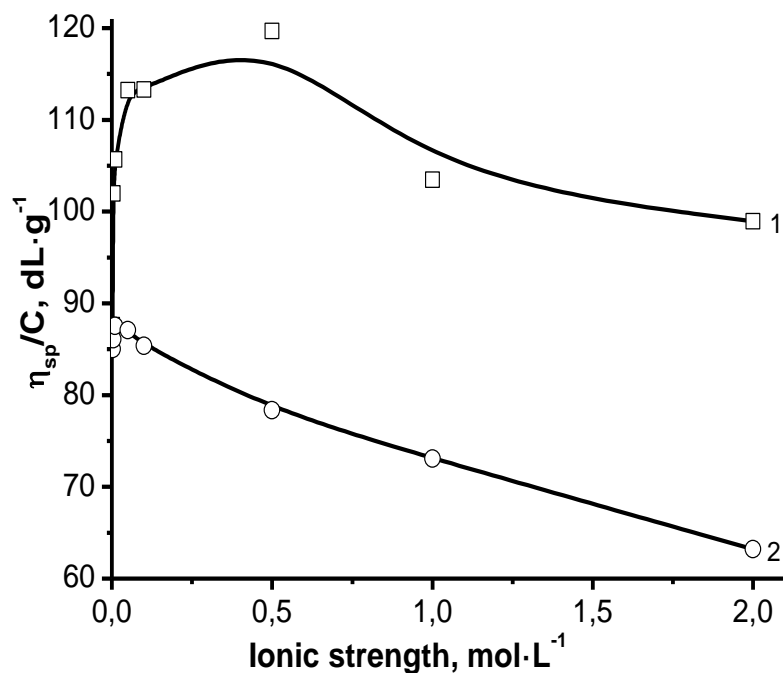
Figure 20 - Dependence of reduced viscosity of 0.2 wt.% xanthan on the ionic strength of the solution adjusted by addition of NaCl (1), KCl (2).
Temperature is 25 °C
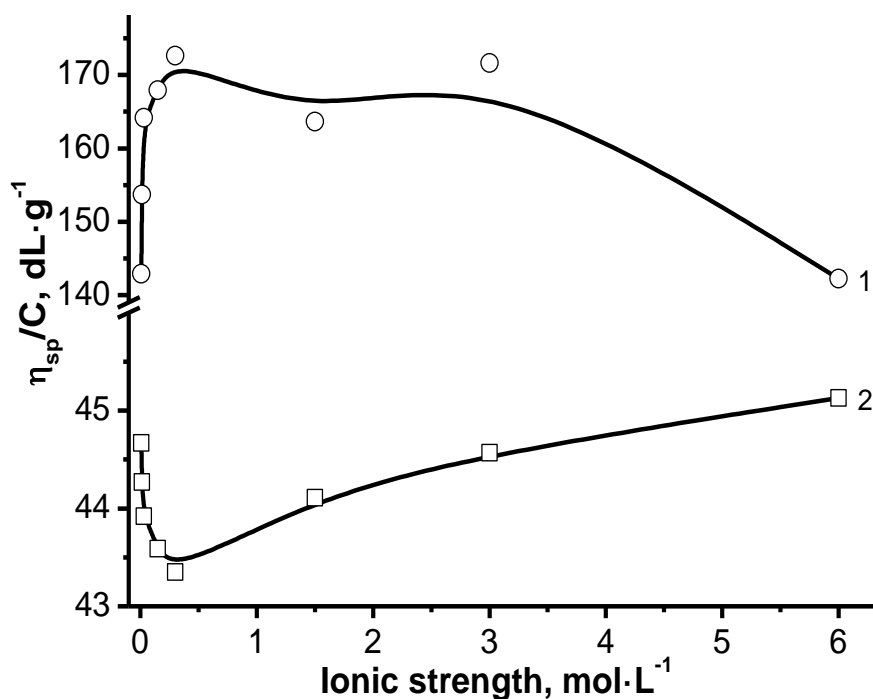
Figure 21 - Dependence of reduced viscosity of 0.2 wt.% xanthan on the ionic strength of the solution adjusted by addition of $CaCl_2$ (1), $MgCl_2$ (2).
Temperature is 25 °C

The viscosity of a 0.1% gellan solution in distilled water and in the presence of 5 and 10 vol.% of oilfield water was measured using an Ubbelohde viscometer with a capillary diameter of 0.86 mm at 25 ° C. When a oilfield water is added to a 0.1% gellan solution, the beginning of gelation occurs at 10 vol.% oilfield water (figure 22).
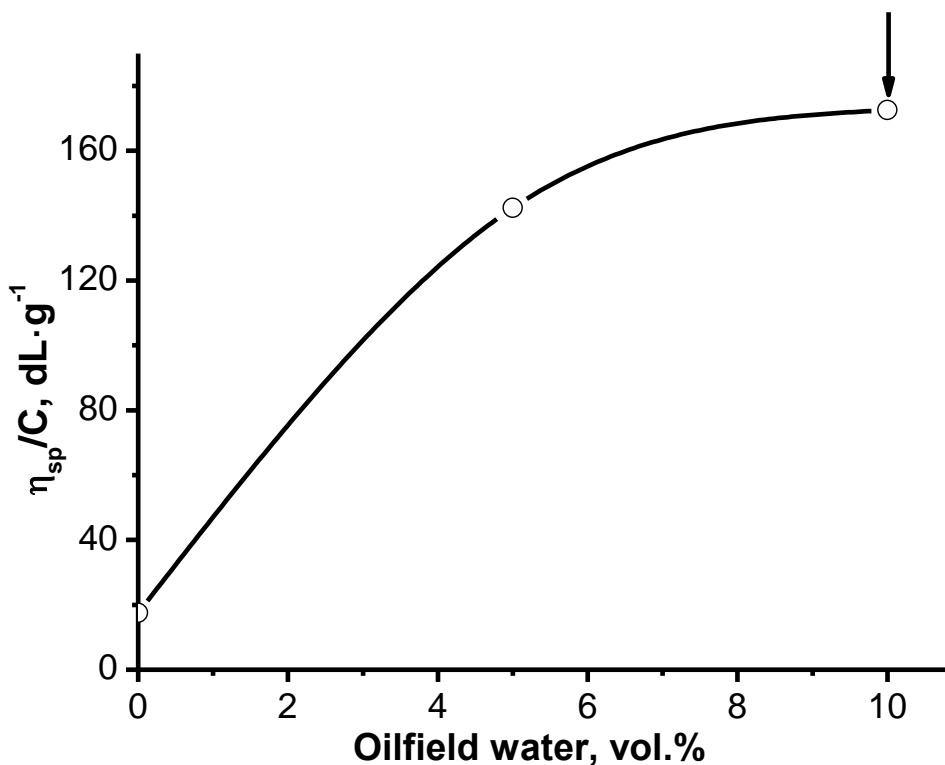
Figure 22 - Dependence of reduced viscosity of 0.1 wt.% gellan on the concentration of oilfield water with the salinity 73 $g·L^{-1}$. Arrows show the start of the gelation process.. Temperature is 25 °C

The tendency of 0.1% gellan solution to gelation and delamination is observed visually at a content of 80 and 90 vol.% of oilfield water (figure 23).
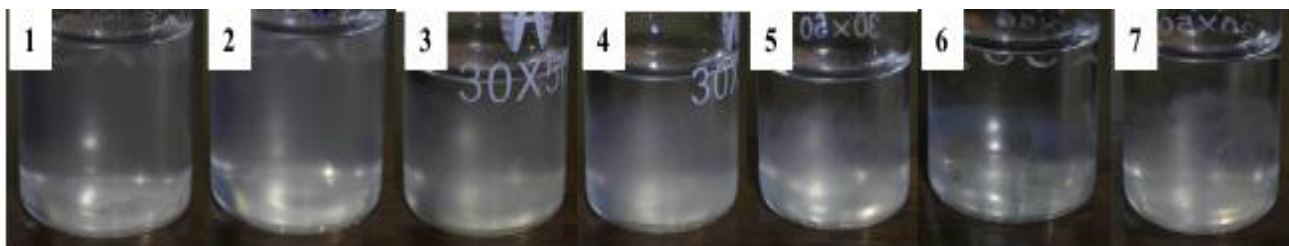
The oilfield water content is 10 (1), 30 (2),
50 (3), 60 (4), 70 (5), 80 (6) and 90 vol.% (7)

Figure 23 - Changes in the turbidity of a 0.1% gellan solution in the presence of oilfield water

The turbidity of gellan solutions at a content of oilfield water of 10, 30, 60, 80 and 90 vol.% were also measured on a JENWAY 6300 spectrophotometer (Germany) at wavelengths of 550, 580 and 620 nm. When measuring the turbidity of an aqueous solution in the presence of oilfield water, the gellan concentration was maintained constant and equal to 0.1%. The turbidity of a 0.1% gellan solution initially changes smoothly, then starting from 80 vol.% of oilfield water increases sharply (figure 24). This is due to the formation of colloidal particles, leading to greater dispersion of visible light.
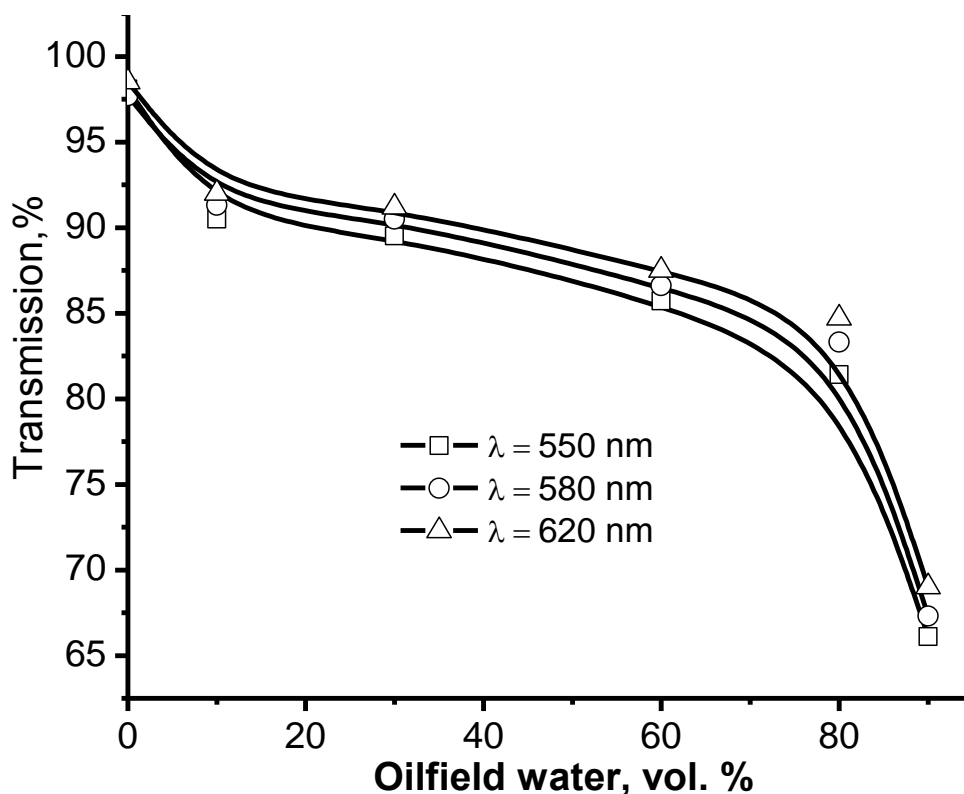
Figure 24 - Changes in the turbidity of 0.1% gellan solution
in the presence of oilfield water

One of the remarkable properties of gellan is its ability to undergo sol-gel and liquid-solid phase transitions in oilfield brine water of Kumkol oil reservoir containing mono- and divalent cations, such as Na^+, K^+, Ca^{2+} and Mg^{2+} with total salinity of 73 g·L^{-1}. In oilfield conditions the minimal concentration of gellan to be injected into the well is 0.5 wt.%. For this reason all experiments related to phase transition, rheological properties and hydrodynamic behavior in porous media were carried out with 0.5 wt.% gellan solution. Addition of 10-40 vol.% oilfield saline water to aqueous gellan solution causes the gel formation (sol-gel transition) while in the presence of ≥ 40 vol.% oilfield saline water a liquid and dense solid phases are formed (figure 18). Changing the amount of liquid and solid fractions of 0.5 wt.% gellan solution upon addition of oilfield water with salinity 73 g·L^{-1} is demonstrated in Figure 25.

The amount of solid fraction changes antibatically to the amount of liquid fraction. Analogous phase transitions are also observed for 0.3 wt.% gellan solution upon addition of oilfield water with salinity 73 $g \cdot L^{-1}$.
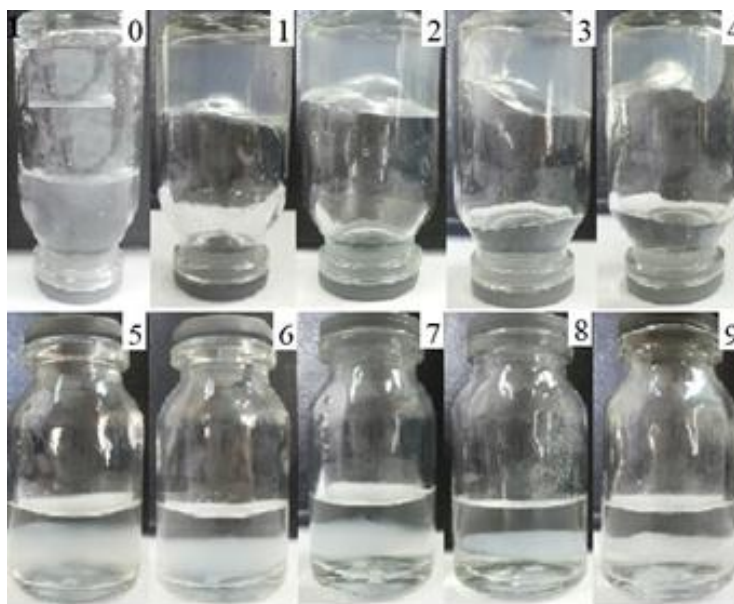
The content of oilfield water is 0 (0), 10 (1), 20 (2), 30 (3), 40 (4), 50 (5), 60 (6), 70 (7), 80 (8) and 90 wt.% (9). V_{total} = 5 mL, C_{total} = 0.5 wt.%

Figure 25 - Initial 0.5 wt.% aqueous solution of gellan (0), sol-gel transition (1-4) and formation of liquid and dense solid phases (5-9) in the presence of oilfield water with salinity 73 $g \cdot L^{-1}$
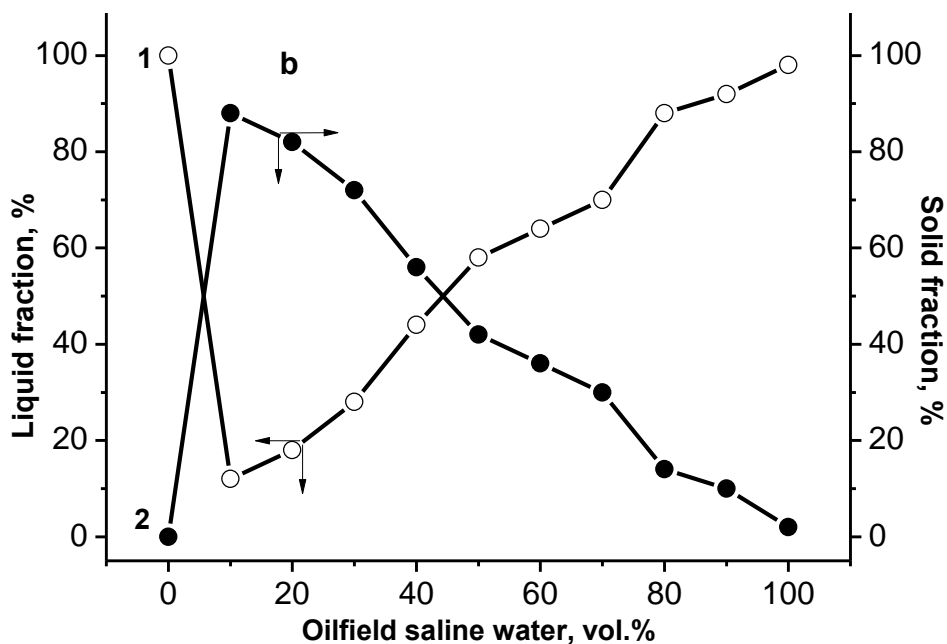
Figure 26 - Dependence of the amount of liquid (1) and solid (2) fractions of 0.5 wt.% gellan solution upon addition of oilfield water with salinity 73 $g \cdot L^{-1}$

To our knowledge the phase separation of gellan in extra high saline solution has not been described yet. In our opinion, the transformation of gel to liquid and further to dense precipitate in saline oilfield water may be due to synergistic "salting out" effect of mono- and divalent cations. The mechanism for the conformational change of gellan with salt concentration is proposed as shown in figure 27.
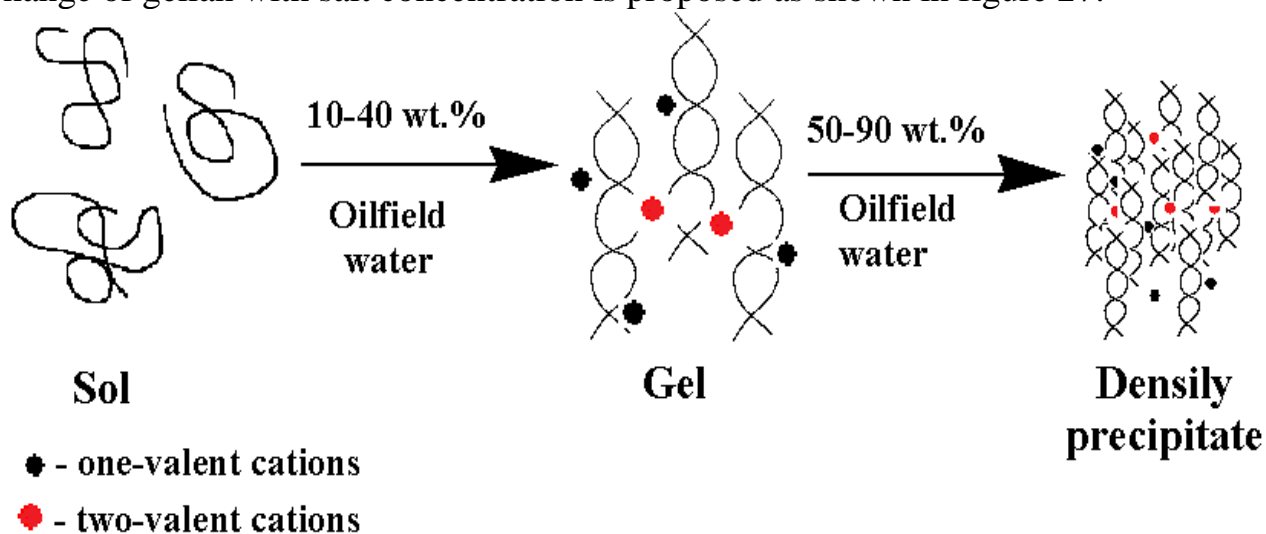
Figure 27 - The sol-gel phase transition of gellan and the "salting out" effect induced by oilfield water

Initial gelation of gellan is related to acceleration of charge-shielding effect by monovalent and of "bridging" effect by divalent ions. In combination, they give the double helix structure stabilized additionally by hydrogen bonds [111]. One can suggest that at high salt concentration due to "salting out" effect an aggregation of double stranded structure of gellan and its precipitation takes place. Both mono- and divalent cations present in oilfield water are associated with surface of double helix of gellan. Sol-gel transition of gellan in oilfield water may be of help for EOR from saline reservoirs. Initially, pumping of aqueous solution of gellan into the injection well will be easy because of low viscosity of polymer. Further, the gel slug that is formed after contacting with underground saline medium starts to plug the high-permeable channels without touching the less-permeable hydrocarbon-productive zones. Subsequently, the injected water (or water flooding) should penetrate as much as possible into the less-permeable zones so that oil can be displaced from these poorly swept zones.

3.1.3 Rheological properties of gellan, xanthan and gellan-xanthan mixture
Comprehensive information on the rheological properties of gellan, xanthan and gellan-xanthan mixture as a function of polymer concentration, salt content, pH, temperature and shear stress is necessary to predict the behavior of gellan solution in the oil reservoir as drilling fluids. The shear stress-shear rate curves of 0.5 wt.% gellan solution on temperature show the pseudo plastic behavior at temperature interval between 25 and 55 °C (figure 28). Newtonian flow of gellan solution is realized at 60-70 °C. Step-by-step transformation of gellan solution from

pseudoplastic behavior to Newtonian may be explained by "melting" of double stranded structure of gellan and formation of gellan macromolecules in random coil conformation at higher temperature.
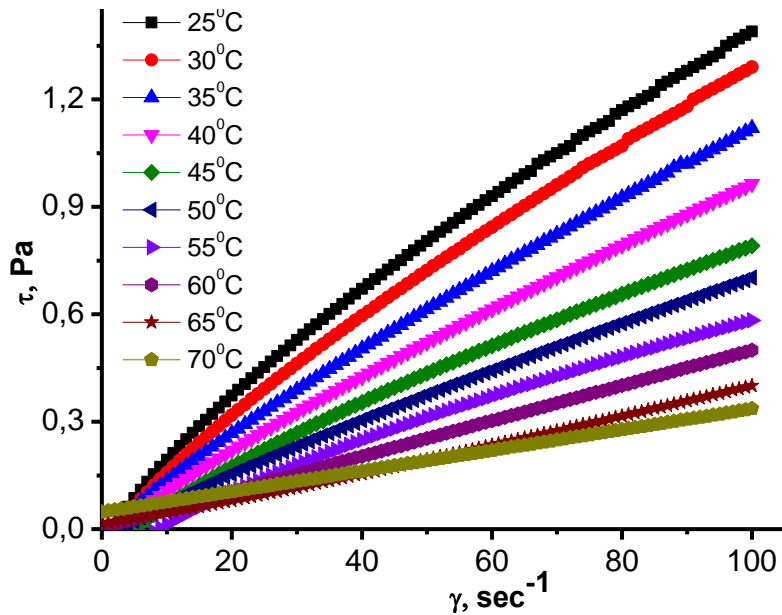
Figure 28 - The shear stress-shear rate curves of 0.5 wt.% gellan solutions at the interval of temperature 25-70 °C

The temperature dependent shear stress-shear rate curves for 0.2, 0.3 and 0.5 wt.% gellan solution are shown in figure 29. At 25 °C the gellan solution with the concentrations of 0.2 and 0.3 wt.% behave as Newtonian fluid while at C = 0.5 wt.% it exhibits pseudoplastic character.
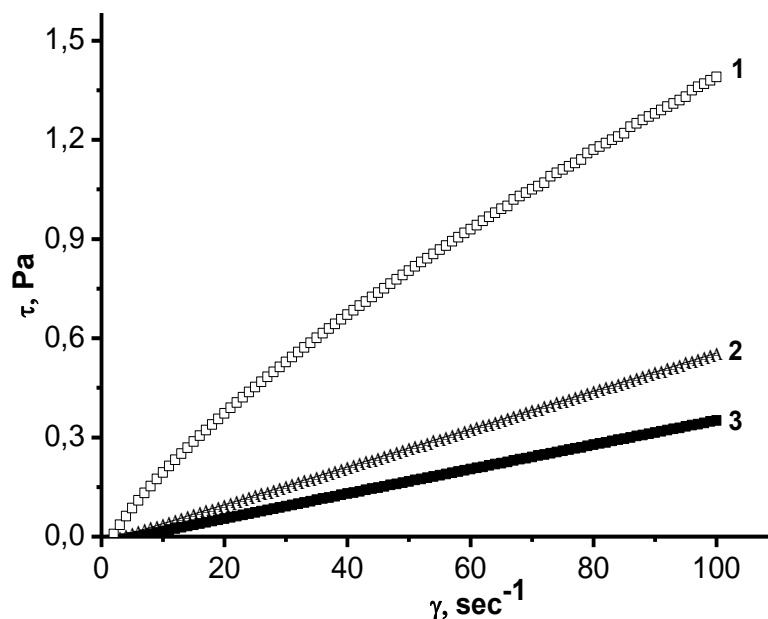
Figure 29 - The shear stress-shear rate curves of gellan solutions of 0.5 (1), 0.3 (2) 0.2 wt.% (3) at 25 °C

In contrast, at 70°C the diluted gellan solution with C = 0.2 and 0.3 wt.% shows the behavior of dilatant fluid, while the concentrated one with C = 0.5 wt.% falls within Newtonian fluid.
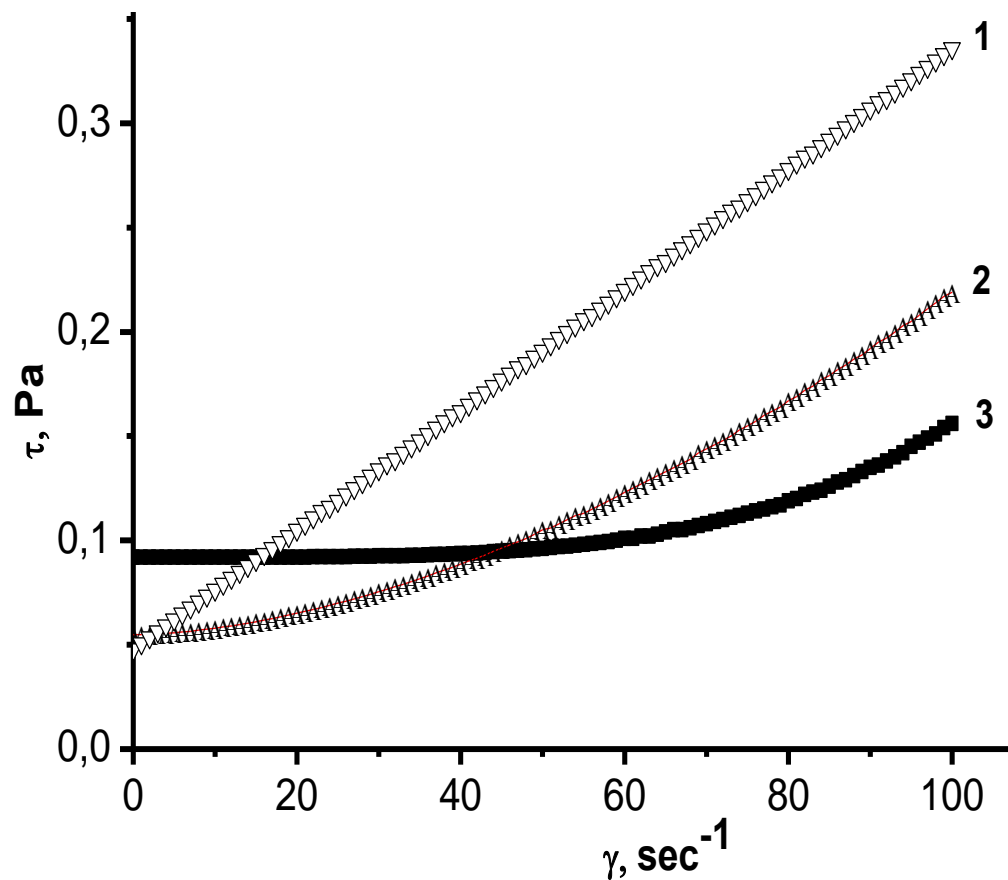
Figure 30 - The shear stress-shear rate curves of gellan solutions of
0.5 (1), 0.3 (2) 0.2 wt.% (3) at 70 °C

At lower concentrations (C = 0.2 or 0.3 wt.%) and lower temperature (25 °C) the macromolecules of gellan are in expanded conformation due to intermolecular electrostatic repulsions between carboxylic groups and behave like a Newtonian fluid. At temperature interval between 25 and 55 °C the 0.5 wt.% gellan solution exhibits the pseudoplastic property. This is due to conformational change of gellan from coiled to helical structure because the helix may be more easily orientated along the shear flow than the coil. At higher concentration (C = 0.5 wt.%) and higher temperature (70°C) the most of gellan molecules take a coil conformation and transforms to Newtonian fluid (figure 30).Temperature and concentration dependent flow behavior of gellan solution is summarized in table 8.

Table 8 - Temperature and concentration dependent flow behavior of gellan solution

Temperature, °C	Flow behavior of gellan at different concentrations, [wt.%]				
	0.2	0.3	0.5	1.0	2.0
5	Not measured	Not measured		Pseudoplastic	
10			Not measured		
20					
25	Newtonian	Newtonian	Pseudoplastic	Not measured	Not measured
30				Newtonian	
35	Dilatant				
40		Dilatant			Newtonian
45				Not measured	Not measured
50	Dilatant	Dilatant			
55					
60			Newtonian		
65					
70					

According to literature data [112] a behavior close to Newtonian flow was observed for the 1 and 2 wt.% gellan gum solution at 40 °C. At 20, 10 and 5 °C the 1 wt.% gellan gum solution changed to shear thinning behavior. Thus, a higher concentration of gellan gives more pronounced effect, if it is injected to oil reservoir possessing high salinity and temperature.

The 0.5% xanthan solution belongs to a typical viscoplastic liquid at temperature interval of 25-40 °C. However, it transforms to pseudoplastic liquid between 40 and 65 °C.
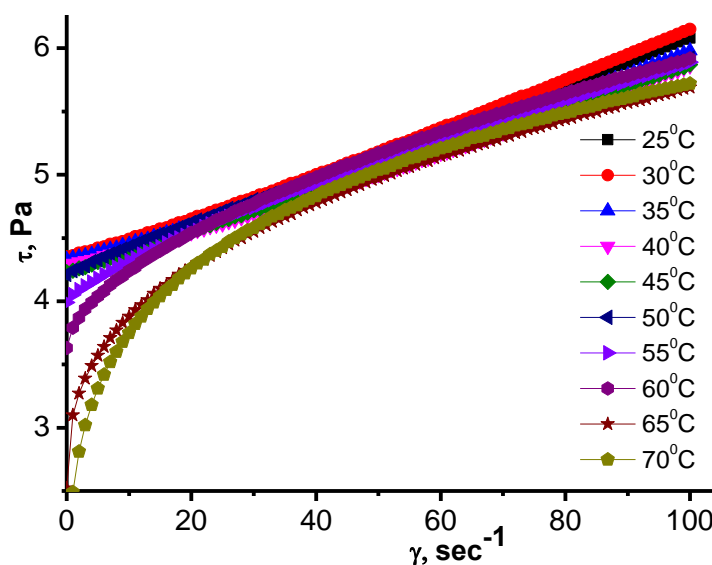
Figure 31 - The shear stress-shear rate curves of 0.5 wt.% xanthan solutions at the interval of temperature 25-70 °C
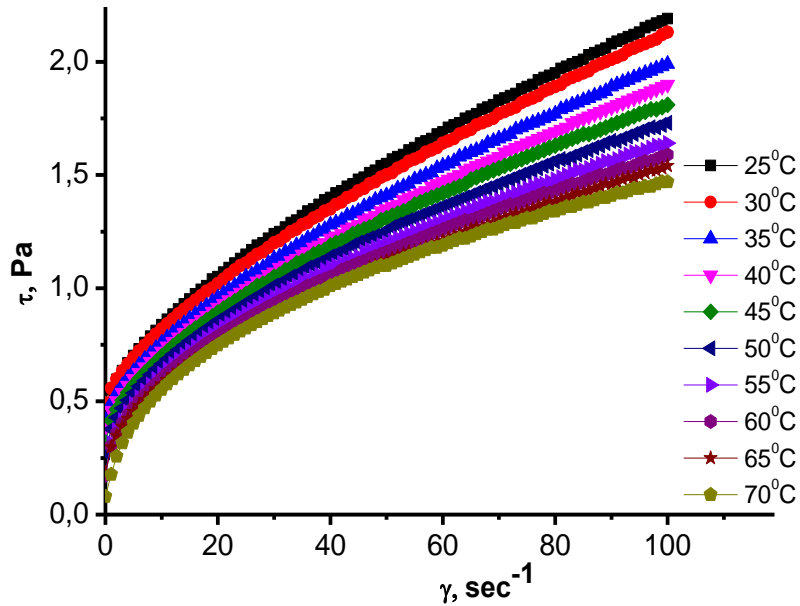
Figure 32 - The shear stress-shear rate curves of 0.5 wt.% gellan-xanthan (2:1) solutions at the interval of temperature 25-70 °C

The mixture of gellan-xanthan behave as pseudoplastic liquid at whole temperature interval 25-70 °C due to formation of interpolymer complexes between gellan and xanthan stabilized by hydrogen bonds.

Dependence of shear stress and effective viscosity of gellan and xanthan solutions on shear rate in the presence of NaCl, KCl, CaC1$_2$ and MgCl$_2$ and oilfield water are is shown in figures 33 and 34.
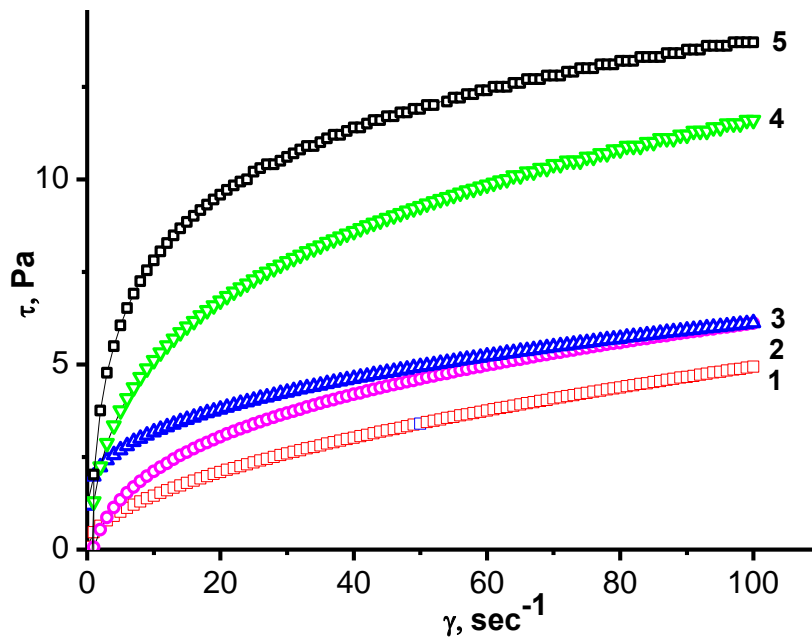
Figure 33 - Dependence of shear stress of 0.5 wt.% gellan solution on shear rate at the ionic strength $\mu = 0.01$ adjusted by addition of NaCl (1), KCl (2), MgCl$_2$ (3), CaC1$_2$ (4) and oilfield water (5)
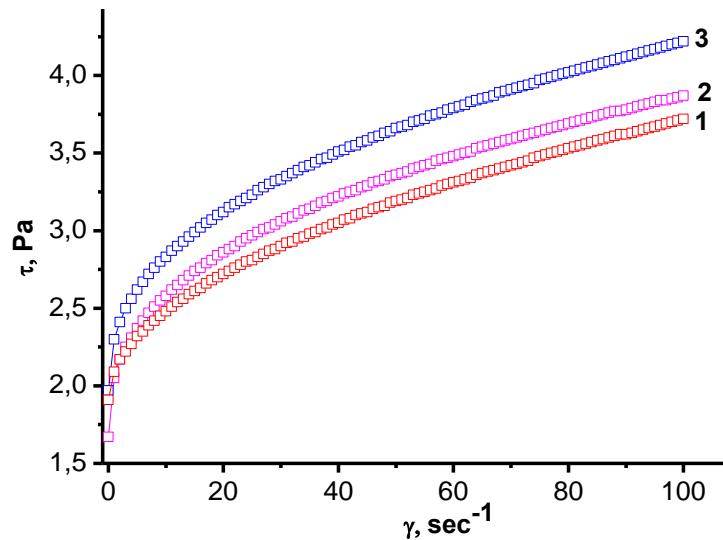
Figure 34 - The shear stress-shear rate curves of 0.5 wt.% xanthan
at the ionic strength μ = 0.01 adjusted by addition of
NaCl (1), KCl (2), MgCl$_2$ (3), CaC1$_2$ (4)

Increasing of shear stress and decreasing of the effective viscosity as a function of shear rate follows by the order: Oilfield water >CaC1$_2$>MgCl$_2$>KCl>NaCl. This sequence is in good agreement with the effectiveness of salts to enhance gellan gelation. It is seen that the effect of oilfield water is more substantial compared to solutions of individual salts. This may be due to combined effect of alkaline and alkaline earth metal ions with respect to coil-helix conformation of gellan.

In case of gellan-xanthan (2:1) mixture, the shear stress increases in the sequence: CaC1$_2$ > KCl > NaCl > MgCl$_2$ (figure 35). Gradually changing of gellan-xanthan mixture from pseudoplastic to viscoplastic liquid in the presence of salts is supposed the result of formation of ternary polymer metal complexes.
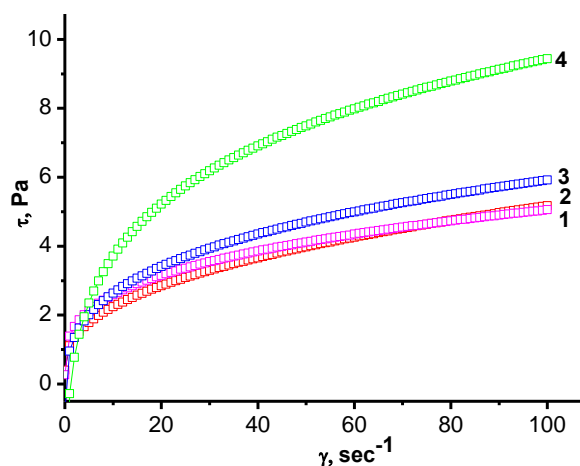
Figure 35 - The shear stress-shear rate curves of 0.5 wt.% gellan-xanthan (2:1)
solutions (c) at the ionic strength μ = 0.01 adjusted by addition of NaCl (1), KCl (2),
MgCl$_2$ (3), CaC1$_2$ (4)

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Influence of pH on the rheological behavior of gellan was studied for 0,5 and 1 wt. % gellan solutions. NaOH was used to increase pH of the medium. The curves for 1 wt.% gellan solution for different values of pH are shown in figure 36. The maximal value of shear stress are registered at pH = 7.5. The subsequent increase of pH leads to a decrease in the shear stress, which is caused by increasing of solution ionic strength [113]. All flow curves have the shape of pseudoplastic fluid, however, for some cases, there is yield stress. It is common for gel forming structures.
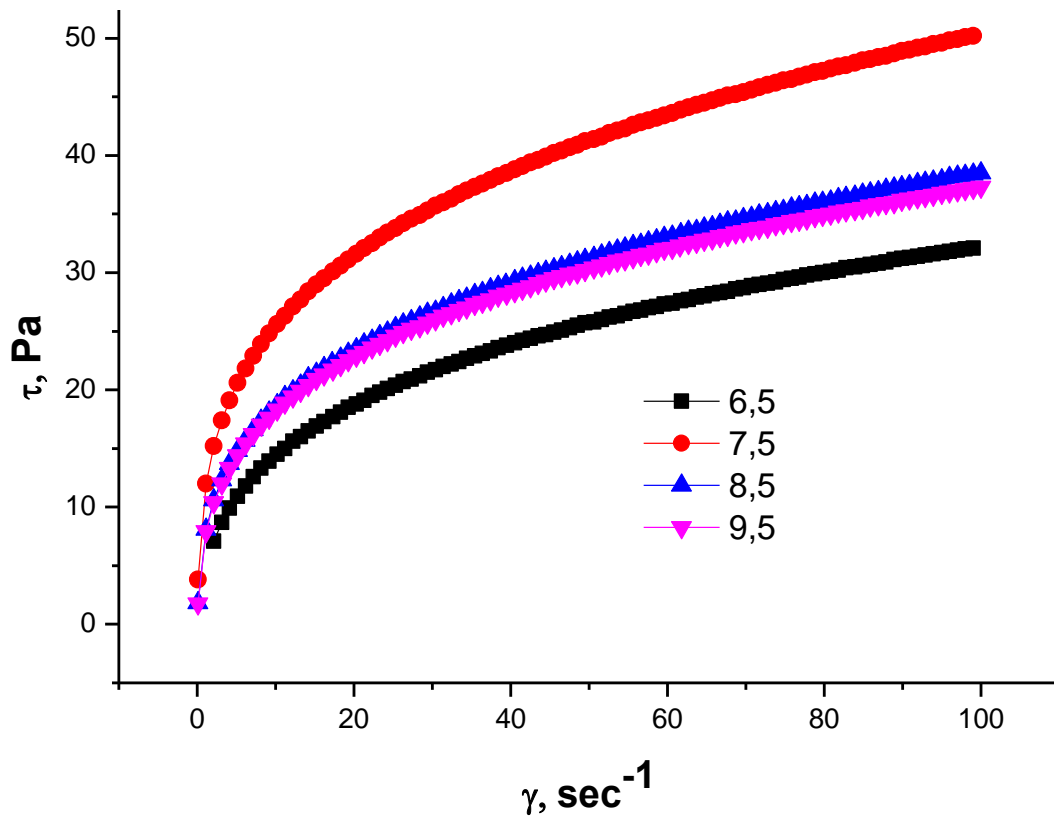
Figure 36 - Shear stress versus shear rate curves for 1.0 wt.% gellan solution at various pH values (before the registration the solutions were kept under static conditions for 1 minute)

Flow curves of gellan -xanthan solutions (figure 37) significantly differ from the corresponding flow curves of gellan (figure 36). All curves flow of gellan-xanthan solutions located in the area of anomalously low shear stress. Besides ionic strength effect at pH values above 7.5 is absent. These anomalies, apparently caused by the formation of interpolymer complexes (IPC) between macromolecules of gellan and xanthan.
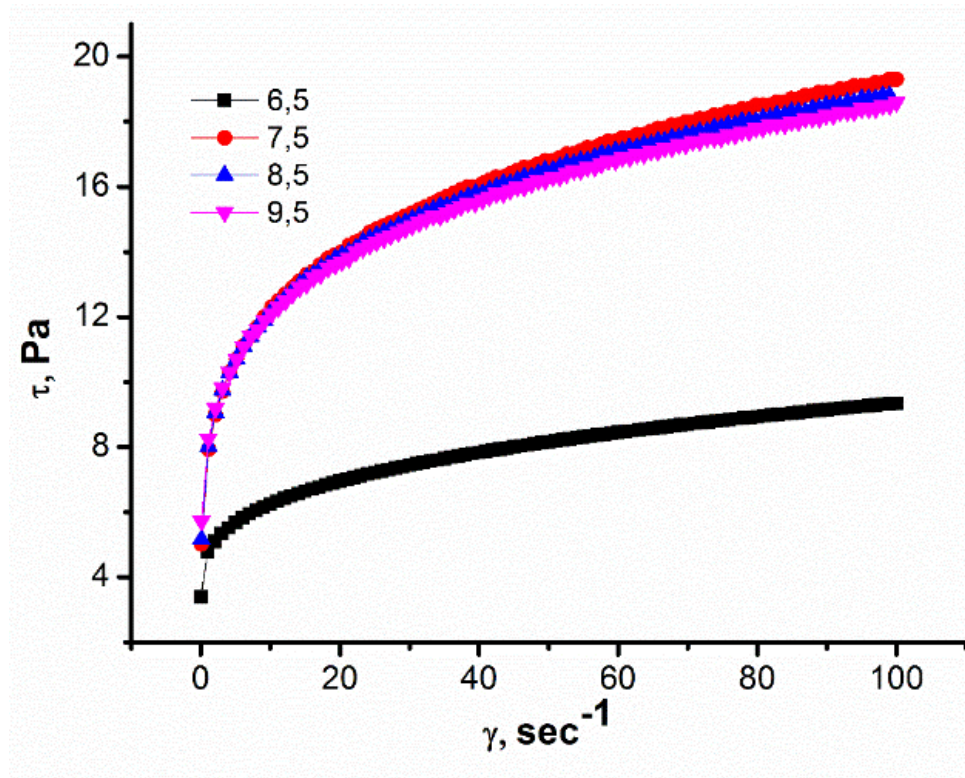
Figure 37 – Shear stress versus shear rate curves of 1 wt.% gellan-xanthan (1:1) solutions at different pH values; t=25^{0}C

The rheological parameters of 1.0 wt.% gellan solution were treated by Ostwald–de Waele model expressed as $\tau = K \times \gamma^n$ (where τ is shear stress, γ is shear rate, K is consistency index, n is nonlinearity factor). The values of correlation coefficient R^2 and K show that the model of Ostwald–de Waele is suitable for the description of rheological behavior of gellan solution (table 8). The rheological parameters of gellan solution exposed at static condition during 10 minutes are higher than that of 1 minute exposition at pH 7.5. This fact testifies that gellan solution exhibits the thixotropic property. The thixotropic behavior of drilling fluids determines the ability of suspended drilled rock particles to be in static conditions.

Table 9 - Dependence of rheological parameters of 1 wt.% gellan solution on pH at 25 °C after keeping of solutions during 1 and 10 minutes at static conditions

pH	Rheological parameters					
	Model of Ostwald–de Waele, 1 min			Model of Ostwald–de Waele, 10 min		
	K, c^{-1}	n	R^2	K, c^{-1}	n	R^2
9.5	5.654	0.411	0.968	7.241	0.367	0.970
8.5	4.605	0.448	0.991	7.420	0.368	0.970
7.5	7.50	0.394	0.988	11.359	0.330	0.984
6.5	0.053	0.768	0.982	0.012	0.983	0.708

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In order to establish the possibility of complexation the effect of the composition of polysaccharides mixtures on their rheological properties was studied in details. Figure 38 presents shear stress versus weight ratio of the gellan-xanthan mixture at shear rates varying between 10 and 100 sec^{-1}, with and without salt addition. The formed complexes are most probably stabilized by hydrogen bonds. The mentioned complexes may be stabilized not only by hydrogen bonds but also by electrostatic interactions between negatively charged carboxyl groups (–COO$^-$) and cations Ca^{2+}.

Identical ratio of gellan/xanthan in composition of IPC and PMC (2:1) allows to assume similarity in structure of these complexes. Therefore formation of 2:1 PMC realized by replacing the H-bonds to electrostatic interactions between negatively charged carboxyl groups (–COO$^-$) and Ca^{2+}ions.with the participation of the functional groups of the same polysaccharide units. In other words, the reaction of the conversion of IPC to PMC occurs by the mechanism of substitution.

IPC of gellan-xanthan, inriched with xanthan (weight ratio 2/3) in the presence of Ca^{2+}ions turns into two PMC of different compositions (weight rations 1/2 and 1/1). The formation of two PMCs apparently occurs by replacing of H-bonds on –COO$^-$ Ca^{2+} $^-$COO- bridges with participation of different polysaccharide units. Formation of these PMC occurs by the mechanism of disproportionation.

One IPC (1:1) and two PMC (2:3) form at t =50°C. The difference in compositions of IPC and PEC, which are obtained at 25 and 50°C, is due to sol I - sol II conformational transition in gellan solution at the temperature above 30°C. A transition from IPC to PMC apparently occurs by disproportionation mechanism.
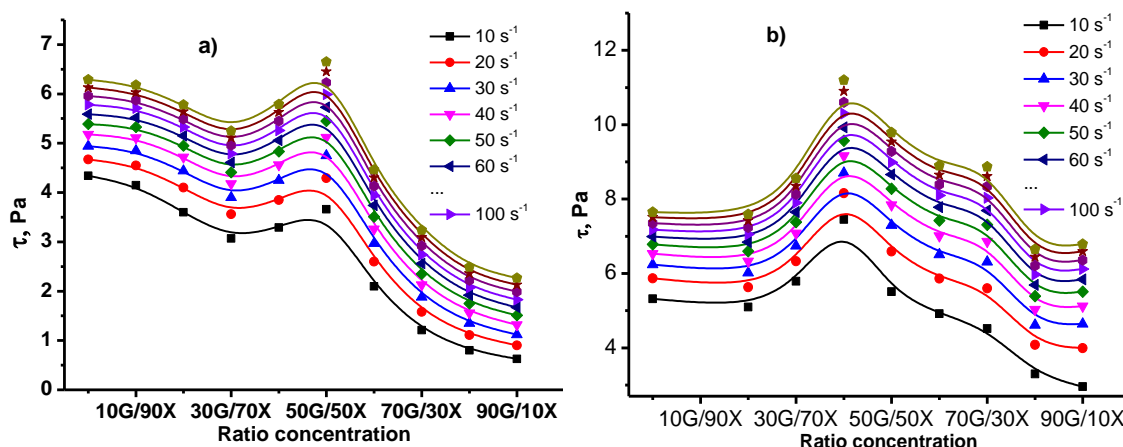
Figure 38 – Influence of weight ratios of gellan/xanthan mixture on the shear stress of 0.5 wt.% solutions; without salt addition - (a) and with the addition of 0.08% CaCl$_2$ - (b), at 50°C

3.1.4 Morphology of gellan gels

As mentioned above gellan gelation is related to acceleration of charge-shielding effect by monovalent and of "bridging" effect by divalent ions. In combination, they give the double helix structure stabilized additionally by hydrogen bonds [114]. Both mono- and divalent cations present in oilfield water are associated with the surface of

double helix of gellan. In our mind, the phase separation of gellan in high saline oilfield water may be due to synergistic "salting out" effect of mono- and divalent cations. Sol-gel transition of gellan in oilfield water may be of help for EOR from saline reservoirs. Morphology of gellan gels formed in the presence of NaCl, KCl, $MgCl_2$ and $CaCl_2$ represents micron-sized strands forming a continuous network (figure 39).
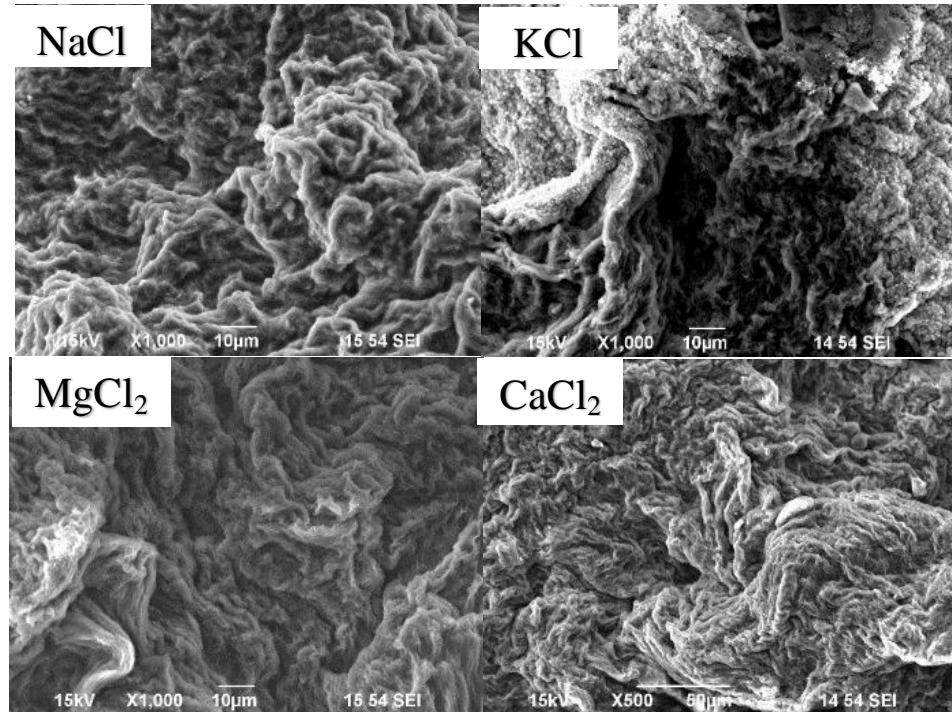
Figure 39 - SEM images of gellan gels formed in the presence of
NaCl, KCl, $MgCl_2$ and $CaCl_2$

3.1.5 Mechanical properties of gellan gels

When a formation water is added to a 2% gellan solution of the formation water, the opposite pattern of the sol – gel transition is observed; the initial gel formed at a content of 10% by volume of produced water, with an increase in its content, gradually passes into the state of a weak gel, then into the state of a sol (figure 40).
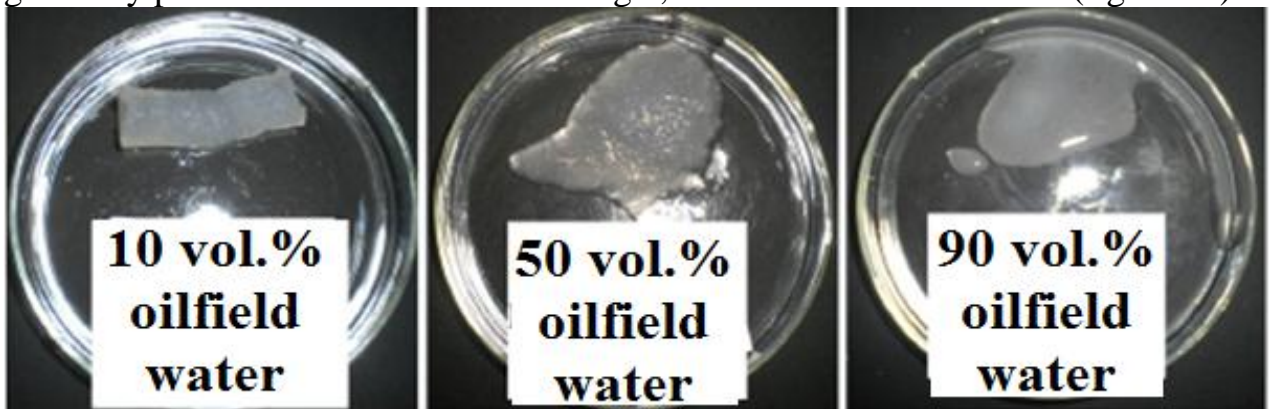
Figure 40 - Transformation of a gel into a sol state for a 2% gellan solution in the presence of various concentrations of oilfield water

Strain-stress curves from compression testing of gellan gels induced by addition of various salts including oilfield saline water. Data of Young's modulus and breaking stress (table 9). The mechanical parameters of gellan gel increase in the following order: Oilfield water > $CaCl_2$ > $MgCl_2$ > KCl > NaCl and coincide well with viscosity and rheology data.

Table 10 - Mechanical properties of gellan gel induced by addition of individual salts and oilfield saline water

Gellan gels induced by salt addition	Young's modulus, 10^{-2} $N \cdot m^{-2}$	Fracture stress, %
NaCl	7,84	26,1
KCl	8,45	31,7
$MgCl_2$	9,01	31,7
$CaCl_2$	9,36	32,0
Oilfield saline water	9,54	33,1

As seen from the data of table 5, the Young's modulus and breaking stress of gellan gel formed in oilfield water are higher than that of individual salts. This may be due to synergistic effect of both monovalent and divalent cations containing in saline water. The good mechanical properties of gellan gel in oilfield water are effective for plugging of the high permeable channels in oil reservoir.
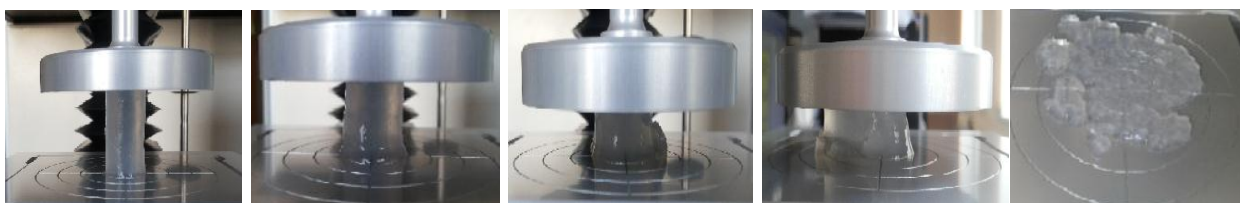
Figure 41 - Mechanical properties of gellan gel formed in oilfield water with salinity 73 g/L

An important function of drilling fluid is its ability to form a thin and strong film on the surface of the well. For this reason, on the basis of gellan and its mixtures with other polysaccharides samples of hydrogels were prepared. The mechanical characteristics of the obtained samples are shown in figure 42.
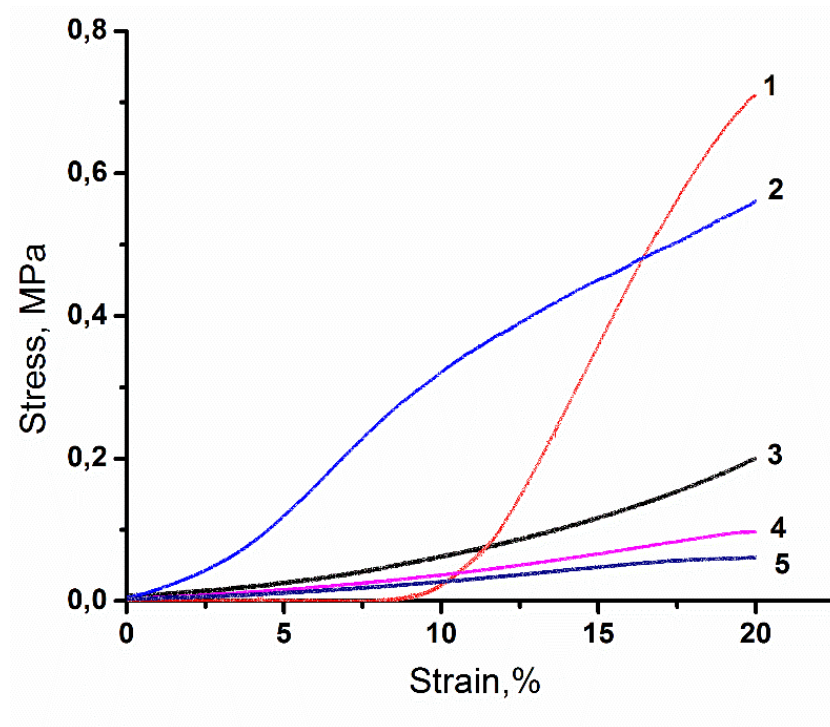
Figure 42 - The strain-stress curves of 2.0 wt.% polysaccharide-KCl gels at gellan/starch = 1/1 (curve 1), 2/1 (curve 2); gellan (curve 3) and gellan/xanthan= 3/1 (curve 4), 2/1 (curve 5)

The mechanical properties of gellan upon addition of xanthan and starch changes in the order of: gellan-starch > gellan > gellan-xanthan. Decreasing of gellan content in the mixture with other polysaccharides leads to lower mechanical strength of the gel samples.

3.2   Carboxymethylated corn starch
3.2.1 Modification of cornstarch
The carboxymethylation of cornstarch proceeds by two steps:
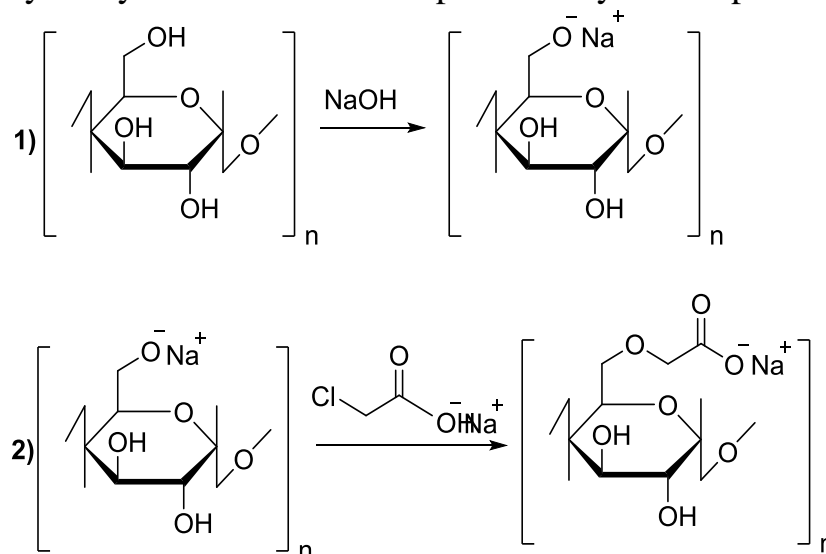
Figure 43 -Modification of corn starch with sodium monochloroacetate

In the first step (1) the OH groups are transformed to O^-Na^+, then on the second step (2) the Na^+ ions are eliminated by chlorine of sodium monochloroacetate by the following reaction:

$$—O^-Na^+ + Cl\text{-}CH_2COONa \rightarrow —O\text{-}CH_2COONa + NaCl$$
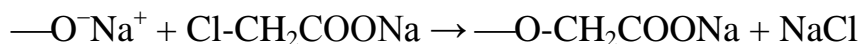
As a result a fully water-soluble carboxymethylated cornstarch (CMCS) with DS = 80% was obtsined.

3.2.2 Identification of the CMCS structure by H^1 NMR and FTIR spectroscopy
^1H NMR spectrum of CMCS registered at 70 ºC is shown in figure 44.
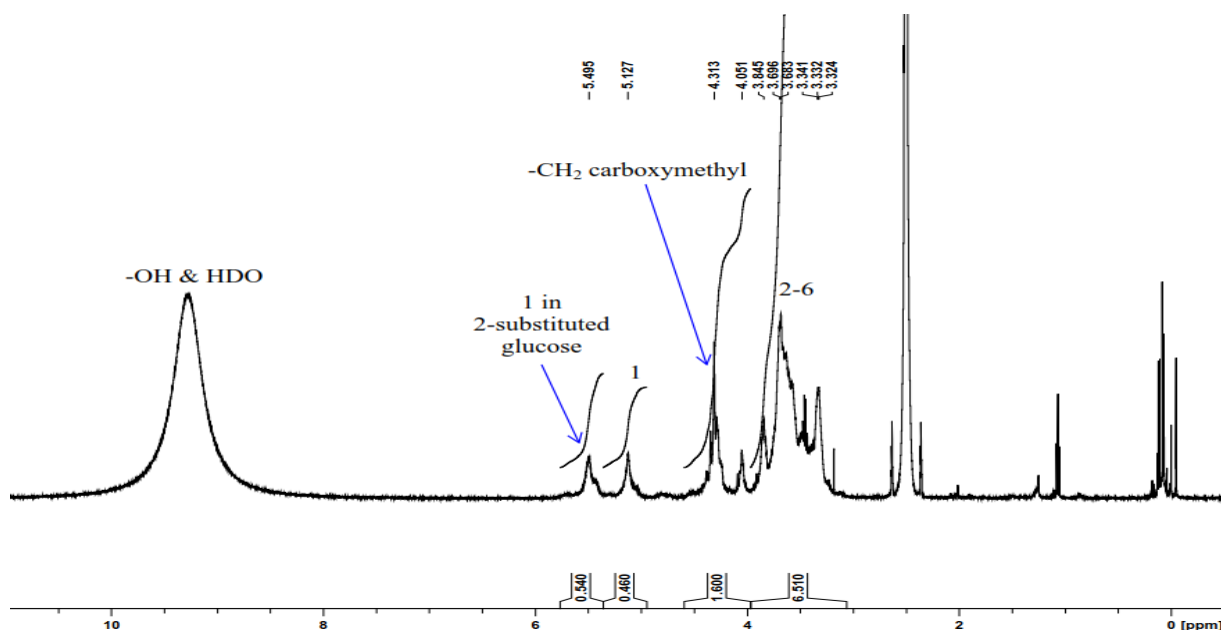
Figure 44 - ^1H NMR spectrum of CMCS in d_6-DMSO

The substitution degree of CMCS determined from the methylene signal of the carboxymethyl substituent (4.31 ppm) and the anomeric protons of glucose (5.13 and 5.50 ppm) was equal to 80%.

FTIR spectra of pristine and modified cornstarch are compared in figure 45.

The broad bands between 3336 and 3291 cm^{-1} is assigned to OH stretching vibrations due to hydrogen bonding between the hydroxyl groups. The band around of 2928 cm^{-1} belongs to CH_2 symmetrical stretching vibrations. A new peak at 1728 cm^{-1} is specific for ester groups, the bands at 1640 and 1400 cm^{-1} are related to asymmetric and symmetric vibrations of carboxylate ions (COO$^-$). At 1200-1360 cm^{-1} the vibrations of CH_2, CH, and C-OH groups are observed. An absorption band at 1009 cm^{-1} corresponds to stretching vibrations of ether groups -OCH-O-CH$_2$. Low intensive bands in the range of 860-760 cm^{-1} correspond to out-of-plane vibrations of OH-group of glucopyranose ring. Thus, both H^1 NMR and FTIR spectra of CMCS

reveal that the modification by Na-MCA takes place to obtain the water-soluble derivatives of cornstarch.
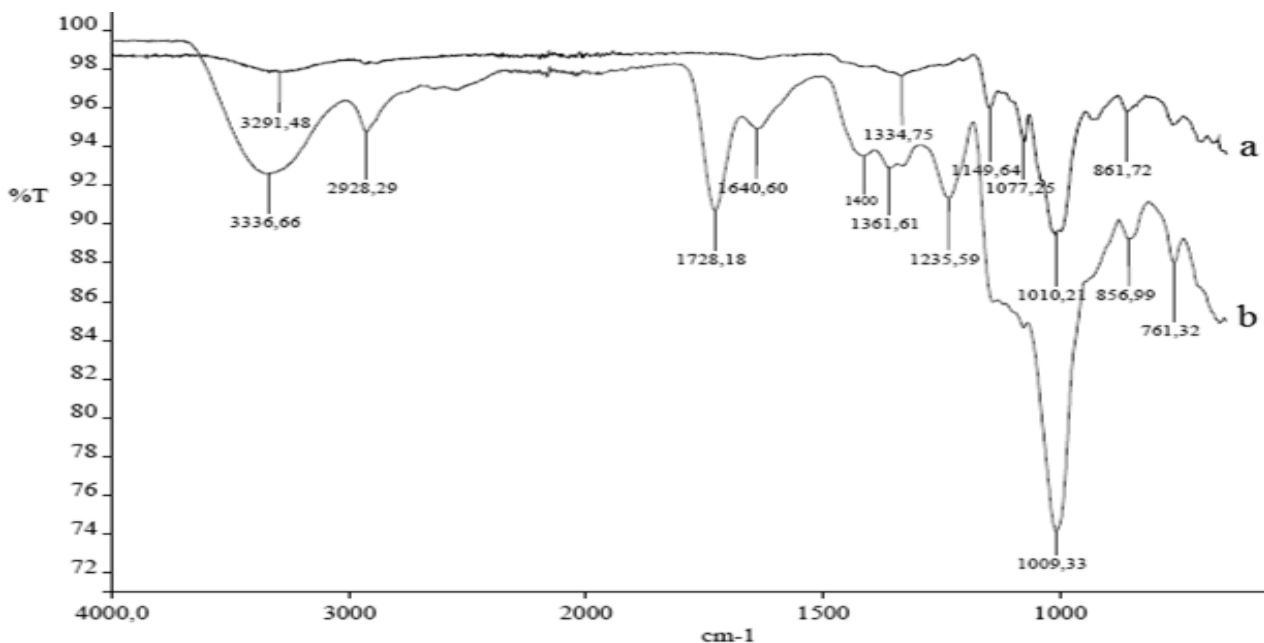
Figure 45 - FTIR spectra of cornstarch (a) and CMCS (b)

3.2.3 Viscosity measurements and viscosity-average molecular weight (M_η) of CMCS

The influence of temperature on solution behavior of CMCS is shown in figure 46.
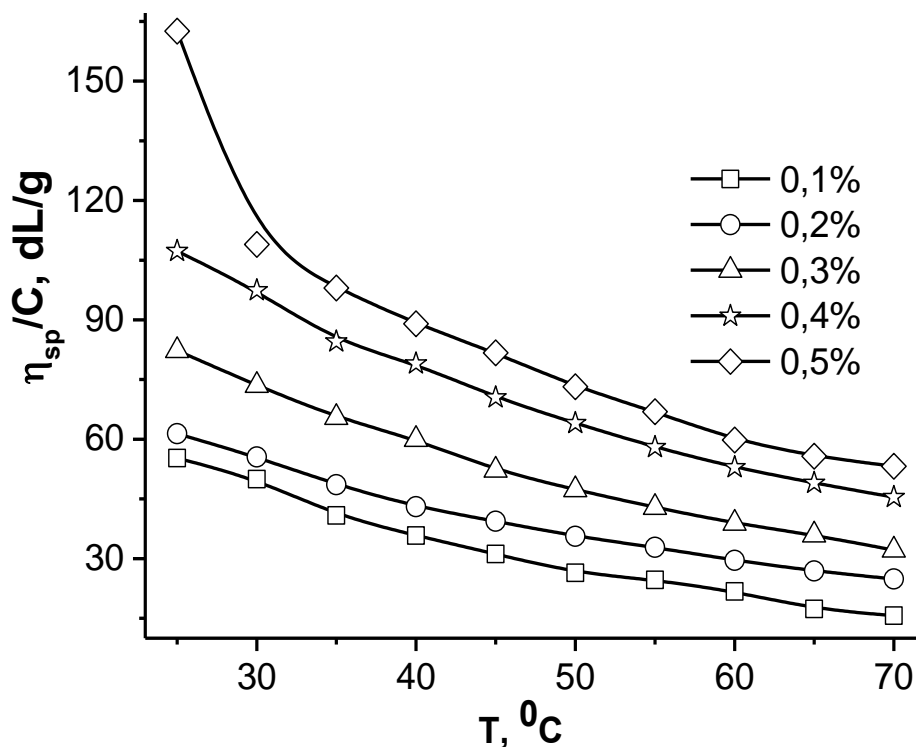
Figure 46 – Temperature dependent reduced viscosity of aqueous solutions of CMCS

The reduced viscosity of aqueous solutions of CMCS gradually decreases with increasing of the temperature. This may be connected with a gradual disaggregation of macromolecular associates due to destruction of hydrogen bonds.

The viscosity-average molecular weight (M_η) of the CMCS was calculated by the Mark-Kuhn-Houwink relationship $[\eta]=K_\eta \cdot M^a$ taking into account that $K_\eta = 2.0 \cdot 10^{-4}$ and $a=0.75$ for a standard starch in 0.1 M aqueous NaCl at $25^\circ C$ [115].

The viscosity-average molecular weights (M_η) of cornstarch and CMCS were found to be $2.15 \cdot 10^3$ g·mol^{-1} and $2.75 \cdot 10^5$ g·mol^{-1} respectively. A significant increase in the M_η of the cornstarch after carboxymethylation is due to the presence of bulkier carboxymethyl groups in modified cornstarch.

3.2.4 Rheological characteristics of CMCS solutions

Rheological properties are considered as important parameters to evaluate the applicability of the CMCS as drilling fluids. The CMCS solutions represent the pseudo plastic liquids and are suitable for the formulation of drilling fluids.
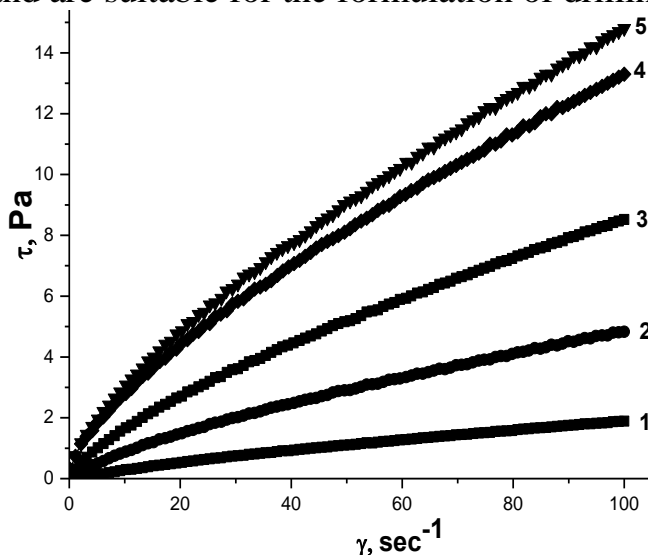
(1) 0.25, (2) 0.5, (3) 1, (4) 2, (5) 1.5 wt.%

Figure 47 – Concentration dependent shear stress-shear rate curves of aqueous solutions of CMCS

As the polymer concentration increases the solution viscosity increases as well. However, increasing of the polymer concentration higher than 1.5 wt.% is not efficient. Therefore it is expected that the optimal concentration of CMCS for shear rate is 1.5 wt.%.

Dependences of shear stress on shear rate for CMCS solutions in the presence of NaCl, KCl, MgCl$_2$ and CaCl$_2$ are shown in figure 48.
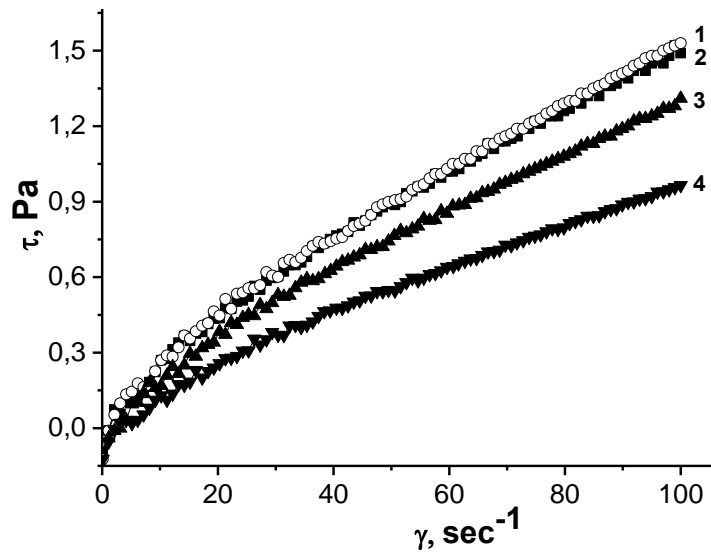
Figure 48 - The shear stress-shear rate curves of 0.5% wt.% CMCS solutions at the ionic strength of μ=0.01 adjusted by NaCl (1), KCl (2), $MgCl_2$ (3) and $CaCl_2$ (4)

Aqueous solutions of CMCS behave polyelectrolyte character that is suppressed upon addition of low-molecular-weight salts. The viscosity resistant behavior of CMCS in saline water provides the stability of drilling fluids in a wide range of salt concentrations.

3.2.5 Thermal characteristics of cornstarch and CMCS

Thermal properties of cornstarch and CMCS derived from DSC are shown in figure 50. The appearance of exothermic peaks at 80.2 and 83.3 ℃ is probably due to removal of residual moisture. The broad endothermic peaks at the interval of temperature 285.85-392.77 and 251.3-326.87 ℃ probably reflect the crystallization of cornstarch and CMCS, respectively.
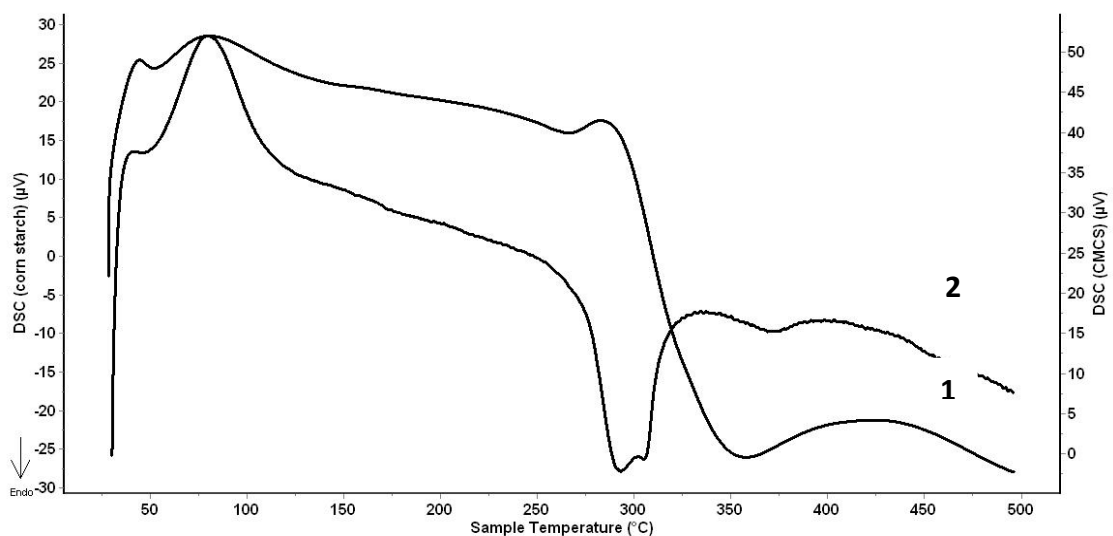
Figure 49 - DSC curves of cornstarch (1) and CMCS (2)

Mass loss percentages for cornstarch and CMCS were calculated from TGA data (Figure 50). TGA studies reveal high heat resistance for CMCS as compared to the cornstarch. CMCS loses 38.47 % of the mass, while cornstarch – 45.83
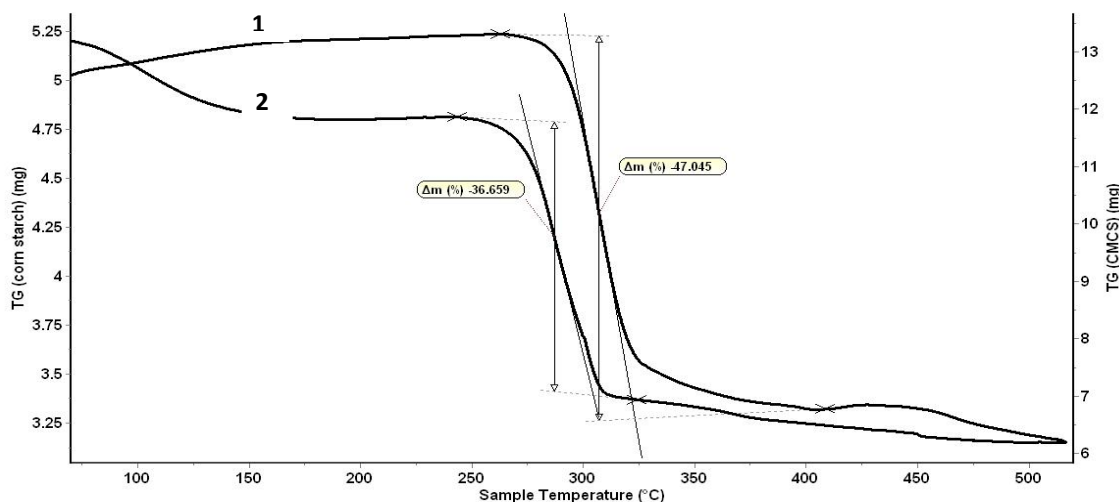
Figure 50 - TGA curves of cornstarch (1) and CMCS (2)

3.2.6 DLS measurements of CMCS

Table 11 shows the average sizes and ζ-potentials of CMCS. The size distribution of CMCS is varied from 235 nm to 1034 nm. The negative values of the ζ-potentials of CMCS in water confirm the substitution of hydroxyl groups of cornstarch by carboxymethyl moieties.

Table 11 – The average sizes and ζ-potentials of CMCS in water

C, wt.%	Size, nm	ζ-potential, mV
0.1	1034	-85
0.2	633	-60
0.3	235	-56
0.4	487	-50
0.5	552	-53

3.2.7 Morphology of cornstarch and CMCS

The SEM images of cornstarch and the CMCS are compared in figure 51. SEM showed the carboxymethylation to change the structure of starch granules, compared with native cornstarch. Cornstarch granules are smooth, round in shape with sizes ranging from 5 to 15 μm. After carboxymethylation the granules of cornstarch are bigger in size (400-500 μm) and the granular surface becomes rough and scaly. Probably these changes are due to modification of cornstarch affected by strong alkaline environment and heat treatment.
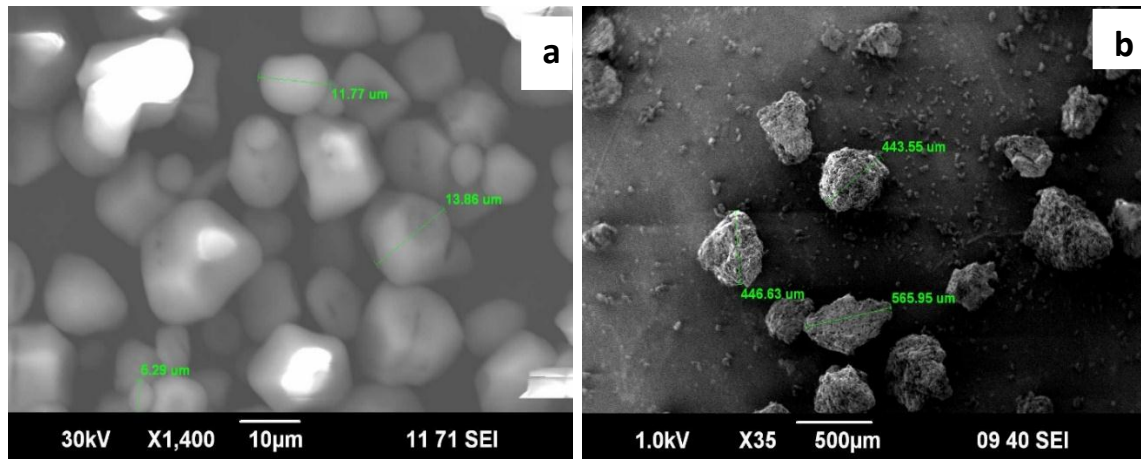
Figure 51 - SEM images of cornstarch (a) and CMCS (b)

3.3 Development of drilling fluids and polymer flooding reagents based on polysaccharides

Formulation of drilling fluids. The drilling fluids (DF) composed of gellan, xanthan, CMCS, Polyanionic cellulose (PAC), KCl and bentonite were formulated to obtain an appropriate DF with optimal solution density (ρ), relative viscosity (η_{rel}), dynamic shear stress (DSS), fluid loss indicator (W), thickness of mud cake (δ), and ratio of static shear stress (SSS_1/SSS_{10}).

3.3.1 Properties of drilling fluids based on CMCS

The structural-mechanical, filtration and filter cake forming properties of model system, consisting of 0.1% gellan, 0.2% xanthan, 0.25-0.35% CMCS at the interval of pH 9.2-10.0 are summarized in Table 12. Analysis shows that all drilling fluids based on CMCS possess good structural-mechanical and filtration characteristics. The thickness of filter cake may be increased by adding 4 wt.% of bentonite. The thixotropic characteristics of drilling fluids are improved with increasing of CMCS concentration. Moreover, the CMCS with high DS due to good water-solubility and high viscosity is more beneficial than industrial starch that is applied for formulation of drilling fluids.

Table 12 – Composition and characteristics of drilling fluids

№	Ratio DF*, %						pH	ρ, g/cm^3	η_{rel}, sec	DSS, Pa	W, cm^3	δ, mm	SSS_1/SSS_{10}, dPa
	gellan	xanthan	CMCS	PAC	KCl	bentonite							
1	0.1	0.2	1**	0.5	0	4	10	1.03	54	1.2	5	0.4	8/15
2	0.1	0.2	1**	0.5	1	4	9.8	1.04	52	1.4	5	0.4	7.5/14
3	0.1	0.2	1**	0.5	3	4	9.6	1.05	52	1.7	5	0.4	7/13
4	0.1	0.2	0.25	0.5	0	1	9.2	1.02	33.6	1.7	6	0.4	3.3/5.3
5	0.1	0.2	0.25	0.5	0	2	9.4	1.06	35.7	1.7	5.5	0.4	5/7
6	0.1	0.2	0.25	0.5	1	4	9.6	1.08	32.8	1.6	5	0.5	9.8/11.5
7	0.1	0.2	0.35	0.5	2	4	9.7	1.08	35.3	1.5	5	0.5	12.3/13.9
*The rest is water ** Industrial CMCS													

Samples No. 6 and 7 containing gellan, xanthan, CMCS and PAC in the presence of 4% bentonite exhibit the best SSS_1/SSS_{10} characteristics that are applicable as drilling fluids.

3.3.2 Low density drilling fluids

To prevent water absorption and the opening of productive reservoirs with low reservoir pressure, which include most of the low-yield and highly water-rich deposits of the RK and RF, low-density drilling muds should be used. In developing the formulation of these solutions, we used promising compositions of polysaccharides from gellan, modified starch and xanthan, which were obtained in 2016. To reduce the density of the drilling mud, it was additionally introduced aluminosilicate microspheres (ASM) with a bulk density of 0.60 g / cm^3 and an average a fraction size of about 100 μm.

Compositions and characteristics of the solutions obtained are given in tables 13 and 14. The proposed composition makes it possible to obtain a DM with a density of 0.94-0.98 g / cm^3 and technological parameters that provide prevention of absorption and allow to open productive strata with low reservoir pressures. Stability of the parameters of the drilling fluid in time, due to the absence of biodegradation, contributes to the quality of work on the wells and the opening of productive layers.

Table 13 - Composition of low- density drilling fluids based on biopolymers

| № | The composition of solutions in wt% | | | | | | |
	Gellan	Starch	Xanthan	ASM	Bactericide BIO 135	Hydrophobizer ОП-10	Water
1	0.1	2	0.32	4.0	0.3	0.05	93.23
2	0.1	1.7	0.32	3.0	0.3	0.01	94.87
3	0.1	1.7	0.35	3.0	0.3	0.01	94.54
4	0.1	1.7	0.37	3.0	0.3	0.01	94.52
5	0.1	2.4	0.33	3.0	0.3	0.1	93.77
6	0.1	2.4	0.32	6.0	0.3	0.1	90.78
7	0.1	2.4	0.32	8.0	0.3	0.1	88.78

In laboratory conditions, by impregnating the filter for the VM-6 device with $CaCl_2$ solutions of various concentrations, the process of supplying formation water to the well was simulated. In table 14, for example compositions 4 and 5, it is shown that the thickness of the filter cake increases with increasing $CaCl_2$ concentration and the filtration index decreases. This indicates the stability of the proposed solutions to the aggression of salts coming from the formation water, in particular the salts formed by cations of alkaline earth metals.

Table14 - Structural-mechanical and filtration characteristics of drilling muds of the compositions given in table 13

№	ρ, g / cm^3	pH	funnel viscosity , s	DSS, dPa	η_{PL}, мPa*c	SSS$_1$/ SSS$_{10}$, dPa	Φ, cm^3	δ, mm	The concentration of the CaCl$_2$
1	0.96	9.2	38.7	64	13	21/23	4	0.2	-
2	0.98	9.1	37	83.6	12.3	27/28	5	0.2	-
3	0.98	8.2	46	74.3	15.4	24/28	5	0.2	-
4	0.98	8.0	43	90	14.2	29/31	5.5	0.2	-
4	0.98	8.0	43	90	14.2	29/31	5	0.2	1
	0.98	8.0	43	90	14.2	29/31	5	0.2	2
	0.98	8.0	43	90	14.2	29/31	4.5	0.3	3
5	0.97	9.2	50	102	17	33/36	3.6	0.2	-
	0.97	9.2	50	102	17	33/36	3.5	0.3	1
	0.97	9.2	50	102	17	33/36	3.4	0.3	2
	0.97	9.2	50	102	17	33/36	3.2	0.4	3
6	0.96	9.4	58	106	19.3	35/40	3.5	0.3	-
7	0.94	9.2	56	77.8	18.7	24/26	3.0	0.3	-

Thus, the proposed low density biomass from biopolymers and ASM can find wide application in the oil industry of the Republic of Kazakhstan to prevent the absorption and opening of productive layers with low reservoir pressure.

Table 15 - Comparative characteristics of low-density drilling fluids

Patent	Composition, wt.%	Disadvantages
Patent RU 2330869 C1, IPC C09K 8/10, publ. 03/24/2009.	carboxymethylcellulose1.0-1.2; synthetic fatty acids with the number of hydrocarbon chains C16-C23 and with an acid number of not less than 100 1.0-2.0; Surfactant 0.1-0.2; aluminosilicate microspheres 5-20, and water else.	solution instability, high filtration rate at low concentrations of aluminosilicate microspheres, high values of dynamic shear stress at high concentrations of aluminosilicate microspheres.
Patent RU 2309970 C1, IPC C09K 8/24, published on 11/10/2007	bentonite-1.0-2.0, carboxymethylated starch (KMK) - 1.0-1.4, hydrolyzed polyacrylonitrile "uniflock" - 0.1-0.2, Xanthan biopolymer-0.08-0.1, water-repellent agent-0.05-0.1, aluminosilicate microspheres-5.0-20, water- the rest	increased values of conditional and plastic viscosities, dynamic shear stress and static shear stress. the solution contains a high content of the dispersed phase - aluminosilicate microspheres (AFM) and bentonite, which is unstable to the biodegradation of polysaccharides (KMK and xanthan biopolymer) during storage.

Low density drilling fluid. Patent 32905. 29.05.2018 Sigitov V.B., Shaikhymezhdenov Zh.G., Kudaibergenov S.E., Zh.A. Nurakhmetova	modified starch -1.7-2.4, Xanthan-0.32-0.37, gellan-0.1, aluminosilicate microspheres-3-8, water-repellent agent-0.01-0.1, bactericide BIO 135-0.3, water is the rest.	The proposed composition of the drilling fluid allows, in comparison with the prototype, to reduce the conditional viscosity to 37-58 s, dynamic shear stress to 64-106 dPa, plastic viscosity to 12.3-19.3 mPa · s, static shear stress to 21-35 / 23- 40 dPa, while the thickness of the filter cake is 0.2-0.4 mm, to maintain the operating parameters of the mud for at least 30 days. Drilling fluid with a density of 0.94-0.98 g / cm3i and technological parameters to prevent the absorption and opening of reservoirs with low reservoir pressure.

3.3.3 Selection of the composition of thin clay drilling fluids

Evaluation of the influence of bentonite on rheological characteristics of gellan solution is necessary for simulation of drilling mud ability to carry up drilled rock particles from the bottom hole of the well to the surface. Influence of dispersed phase on the rheological and conformational characteristics of 0.5 and 1 wt.% gellan solutions in the presence of bentonite was studied by rotational viscometry. Addition of bentonite leads to increase of pH value from 6.4 to 10.0. Shear stress versus shear rate curves of the colloid systems were processed by the models of Ostwald–de Waele. The Ostwald–de Waele equation $\tau=K\cdot y^{n}$ (where τ is shear stress, K is consistency index, n is nonlinearity index) gives two rheological parameters: K and n (n < 1). The low value of n is characteristic for high pseudoplasticity. It is commonly accepted that the pseudoplastic liquids with n < 0.3 are more effective as drilling fluids because they provide the effective borehole cleaning with minimal well pressure loss. The value of n depends on the ability of system to form the hydrogen bonds in solutions for evaluation of internal uniformity; the consistency index K indicates the strength of hydrogen bonds. The obtained results are summarized in table 16.

The values of correlation coefficient (R^2) show, that the model of Ostwald–de Waele better describes the rheological behavior of gellan solution and the colloid-dispersed systems gellan-bentonite excepting for 8 wt.% of bentonite concentration. When the bentonite concentration is equal to 8 wt. % or more the Ostwald–de Waele model cannot properly describe the rheological behavior of the systems due to formation of micro- and macro gels.

Table 16 - Rheological parameters of gellan solution in the presence of bentonite at 25 °C

$C_{bentonite}$, %	C_{gellan}, %	pH	Rheological parameters					
			Model of Ostwald–de Waele, 1 min			Model of Ostwald–de Waele, 10 min		
			K, Pa·s	n	R^2	K, Pa·s	n	R^2
0	1.0	6.37	0.810	0.829	0.943	1.109	0.789	0.964
2	1.0	9.84	20.038	0.243	0.996	20.67	0.262	0.989
4	1.0	9.86	18.54	0.217	0.999	23.35	0.166	0.958
6	1.0	9.89	13.781	0.307	0.967	15.38	0.286	0.764
8	1.0	9.91	15.445	0.267	0.932	30.50	0.062	0.093
0	0.5	6.34	0.371	0.829	0.958	0.43	0.739	0.968
2	0.5	9.94	8.038	0.243	0.997	9.69	0.242	0.999
4	0.5	9.97	9.754	0.218	0.992	11.36	0.263	0.986
6	0.5	10.01	10.781	0.288	0.989	12.38	0.247	0.964
8	0.5	10.05	11.445	0.298	0.972	9.50	0.192	0.693

For the mixture of gellan-xanthan the formation of strong hydrogen bonds between two macromolecules is expected leading to high values of K while the value of n is slightly changed (table 17).

Table 17 - Rheological parameters of gellan-xanthan (2:1) mixture in the presence of bentonite at 25 °C

$C_{bentonite}$, %	$C_{gellan-xanthan}$, %	Rheological parameters					
		Model of Ostwald–de Waele, after 1 min			Model of Ostwald–de Waele, after 10 min		
		K, Pa·s^n	n	R^2	K, Pa·s^n	n	R^2
0	0.5	0,985	0,324	0,986	0,619	0,416	0,989
2	0.5	1,556	0,390	0,979	2,125	0,347	0,986
4	0.5	2,569	0,348	0,985	2,481	0,396	0,965
6	0.5	2,749	0,341	0,983	4,032	0,289	0,993

Analysis of the results shows that all solutions form a good filter cake with the thickness δ = 0.5 mm but the best result was obtained for gellan-xanthan (2:1) mixture (the sample No.5) due to less fluid loss indicator (W) (table 18). The decrease of the filtration index and pseudoplastic behavior of the gellan-xanthan mixture (2:1) is probably connected with complexation of gellan with both xanthan and bentonite and stabilization of the formed structure by hydrogen bonds.

Table 18 - Composition and properties of drilling fluids based on gellan-xanthan mixtures

No.	Composition of drilling fluids*, %				Characteristics of drilling fluids			
	C_{total}	$C_{gellan}/C_{xanthan}$	$C_{bentonite}$	C_{KCl}	pH	Relative viscosity, s	W, cm^3	δ, mm
1	0,5	1:3	1	2	9,7	41	10	0,5
2	0,5	1:3	1.25	2	9,7	41	10	0,5
3	0,5	1:3	3	3	9,8	39	10	0,5
4	0,5	1:2	0,5	3	9,4	30	10	0,5
5	0,5	2:1	1,75	0,045	9,8	36	5,6	0,5
* The rest is water								

On the basis of a mixture of polysaccharides of different composition and concentration in the absence and presence of bentonite, as well as KCl, a number of drilling fluids were prepared and their structural-mechanical, filtration parameters were determined (table 19).

Table 19 - Composition and characteristics of drilling fluids based on mixture of polysaccharides with bentonite

№	Ratio DF*, %					Characteristics of drilling fluids							
	gellan	CMCS	xanthan	bentonite	KCl	pH	ρ, g/cm^3	η_{fun}, sec	DSS, dPa	η_{pl}, Pa·s	W, cm^3	δ, mm	SSS$_1$/SSS$_{10}$, dPa
1	0.2	0	0	1	1	9.0	1.01	14	2	0.5	>20	0.1	0.8/1.0
2	0.4	0	0	1	2	9.0	1.01	14	3	1	20	0.1	1.0/1.1
3	0.8	0	0	2	2	9.0	1.01	20	7	1.8	12	0.1	1.8/2.0
4	0.4	3	0	0	0	9.0	1.01	36	4	4	10	0.2	1.9/2.1
5	0.4	3	0	0	2	8.5	1.01	36	4	6	8	0.2	2.8/3.0
6	0.4	3	0	1	0	9.3	1.01	32	74	25	10	0.3	2/6
7	0.4	3	0	1	2	10	1.02	61	10.8	5.4	4	0.4	3.7/4.1
8	0.4	3	0	1	3	10	1.04	45	10	5	4	0.2	2.7/3.3
9	0.34	0	0.1	2.0	0.05	9.8	1.02	36	8	4	5.6	0.5	2.5/2.9
10	0.25	0.75	0.1	0.5	0	11	1.01	29	7	5	10	0.2	0.6/0.6
11	0.17	0	0.33	0.5	3	9.4	1.02	30	5	4.5	10	0.5	1.6/1.6
12	0.17	0.5	0.33	1	3	9.6	1.03	35	8	5.5	10	0.6	3.0/7.0
13	0.17	1	0.33	0.5	3	9.5	1.02	30	4.6	4	10	0.5	1.7/1.6
14	0.15	0	0.45	3	3	9.8	1.03	39	6.5	5	10	0.5	3.5/2.8
15	0.13	0	0.37	1	2	9.7	1.01	41	7	6	10	0.5	2.8/2.7
* The rest is water													

It can be seen that samples of DF № 1-3, containing gellan, bentonite and KCl, have low values of DSS, SSS, funnel and plastic viscosity which does not allow to use these solutions. Samples of DF № 4-8 show that solutions with a percentage ratio of gellan / starch 0.4: 3.0 have good structural-mechanical and filtration characteristics. Samples of DF №. 9, 11, 14, and 15, which include gellan xanthan and bentonite in different ratios, also have good structural-mechanical and filtration characteristics. Samples of DF №10, 12, 14, consisting of a four-component system gellan-starch-xanthan-bentonite in their structural-mechanical and filtration characteristics are superior to three-component systems.

To identify the causes of significant differences in the characteristics of drilling fluids containing different in nature clay minerals as a dispersed phase, they were characterized by composition, structure, average particle size in water, degree of dispersion D and ζ- potential.

The results of X-ray fluorescence analysis of dispersed phases of different nature (table 20) show that these minerals are aluminosilicates of potassium, sodium, calcium and iron.

Table 20 - The elemental analyzes of samples of the dispersed phase of different nature

Content,%	Bentonite	Kaolinite	Montmorillonite	Montmorillinite
Mg	0.587	4.359	0.936	1.756
Al	7.772	17.587	10.906	6.738
Si	22.254	60.585	55.266	24.035
P	0.43	1.215	0.969	0.451
Cl	0	0.767	0.11	0.326
K	0.913	0.379	4.997	0.149
Ca	1.504	3.992	0.927	1.807
Ti	0.916	0.76	0.971	0.319
V	0.03	0.018	0.019	0.007
Cr	0.026	0	0.019	0.002
Mn	0.045	0.062	0.017	0.027
Fe	10.008	10.105	4.854	4.279
Ni	0.011	0.005	0.003	0.002
Cu	0.008	0.006	0	0.004
Zn	0.013	0.045	0.006	0.019
Br	0	0.004	0	0.001
Ba	0	0.112	0	0.051

The average size of particle in water, the degree of dispersion D and ζ-potential, are given in Table 21, indicate a significant difference in the structure of minerals, which is due to their chemical composition.

Table 21 - Characteristics of 0.3wt.% clay minerals in water

Dispersed phase	d, nm	ζ-potential, mV	D, sm^{-1}
Bentonite	918,7-1593	-26	$6 \cdot 10^3$-$1 \cdot 10^4$
Kaolinite	997,9-1579	-22,1	$6 \cdot 10^3$-$1 \cdot 10^4$
Montmorillonite	2434-2782	-12,2	$3 \cdot 10^3$- $4 \cdot 10^3$
Montmorillinite	1664-2050	-24,9	$4 \cdot 10^3$- $6 \cdot 10^3$

Table 22 - Composition and characteristics of drilling fluids based on mixture of polysaccharides with different dispersed phase

№	Ratio DF*, %						Characteristics of drilling fluids							
	gellan	CMCS	xanthan	PAC	KCl	Dispersed phase, 4%	pH	ρ, g/cm^3	η_{fun}, sec	DSS, dPa	η_{pl}, Pa·s	W, cm^3	δ, mm	SSS$_1$/SSS$_{10}$, dPa
1	0.2	1	0.2	0.5	-	Montmorillinite	9.1	1.02	38	8.5	37	6	0.2	2/5
2	0.2	1	0.2	0.5	3	Montmorillinite	8.5	1.04	40	10.4	27	6	0.3	3/6
3	0.2	1	0.2	0.5	-	Montmorillonite	8.5	1.02	34	8.5	26	16	0.3	2/5
4	0.2	1	0.2	0.5	3	Montmorillonite	7.3	1.04	35	7.05	25	8	0.3	4/6
5	0.2	1	0.2	0.5	-	Kaolinite	9.4	1.03	33	8.1	22	16	0.3	1/0
6	0.2	1	0.2	0.5	3	Kaolinite	9.3	1.05	30	8.1	22	12	0.3	0/0
7	0.2	1	0.2	0.5	-	Bentonite	9.6	1.03	60	15	62	6	0.2	11/17
8	0.2	1	0.2	0.5	3	Bentonite	9.2	1.05	30	7.9	18	7	0.3	3/4
	* The rest is water													

Sample of DF № 7 has good filtration properties, but high values of funnel and plastic viscosity.

3.3.4 Assessment of the inhibiting firm ability of the drilling fluid to play the role of swelling by swelling cores of the values of various fields

To estimate the inhibitory capacity of a promising non-clay drilling mud, the swelling factors for 7 different cores in water and mud filtrate were determined. The core selection sites are indicated in table 23.

Table 23 - Core selection locations

Field	№ well.	Interval m	Composition	Colour	Structure	Texture
South-West Karabulak	21	1412-1415	aleuroargellite, 50/50 clay sand	gray	aleurolite	massif
South-West Karabulak	21	1421-1424	argillite, quartz, field shpaty, mica, clay minerals	gray	pelit	massif
South-West Karabulak	17	1408-1412	aleurolite, (concretion) sand siltstone quartz, field feldspar, mica, clay, Fe (OH)$_2$	DMick	aleurolite	psalitis
South-West Karabulak	17	1415-1418	80% clay minerals, 15% Fe(OH)$_2$ 5% quartz, field battles	gray	pelit	massif
South-West Karabulak	028-32 58	316-320 410- 447	sandy siltstone. Quartz, field spats, mica, clay minerals, Fe(OH)$_2$	reddish-DMown	aleurolite	massif
Uranium Field South Inkai	028-48	378-383	aleurolite. Quartzite, field feldspar, clay minerals, Fe(OH)$_2$.	reddish-DMown	aleurolite	massif
South-West Karabulak	028-41	351-358	clay aleurolite, Quartz, field shpaty, mica, hydromica, clay minerals.	light yellow	aleurolite	psalitis

The values τ of the core swelling factors presented in table 24 show a high inhibitory activity of DF especially for cores No. 2-6 with a high content of argellite, quartz, feldspar, mica and clay minerals.

Table 24 - Core swelling in distilled water and in the Composition drilling mud: (gellan -0.02%, starch -2.3%, xanthan-0.32%, KCl-3.0%, CaCO$_3$-10%)

№ Core	Field	№ well.	Interval, m	Composition	K in water	K in the drill. solution
1	South-West Karabulak	21	1412-1415	aleuroargellite, 50/50 clay-sand	11	6.15
2	South-West Karabulak	21	1421-1424	argillite, quartz, field shpaty, mica, clay minerals	6	0.85
3	South-West Karabulak	17	1408-1412	aleurolite, (concretion) sand aleurolite, quartz, field sticks, mica, clay, Fe (OH)$_2$	8.6	0.74
4	South-West Karabulak	17	1415-1418	80% clay minerals, 15% Fe (OH)$_2$, 5% quartz, field fuels	4.4	0.5
5	South-West Karabulak	028-32 58	316-320 410- 447	sand aleurolite, quartz, field feldspar, mica, clay minerals, Fe(OH)$_2$	24	2
6	Uranium Field South Inkai	028-48	378-383	Aleurolite, quartzite, field sprat, clay minerals, Fe(OH)$_2$.	7	0.95
7	South-West Karabulak	028-41	351-358	clay aleurolite, quartz, field scraps, mica, hydromica, clay minerals .	4	2.6

3.3.5 Conducting of DF tests in model conditions and pilot conditions

The compositions of two clayless and two low-density DFs for drilling the productive zone of the uranium deposit in the Suzaksky region of the South Kazakhstan region were determined. The choice of the DF formulation was based on geological and technical conditions for drilling the interval of the ore zone, as well as the need to maximize its reservoir properties for the subsequent extraction of uranium by the acid leaching method.

Geological and technical conditions of the productive zone: the Mesozoic group, the chalk system, the upper section, the Turon + Santon horizon, the depth of $340 \div 500$ m, the groundwater zone with a capacity of 5 to 40 m, the filtration coefficient from $9.5 \div 12.6$; characteristics of the rock: sand is heterogeneous with clay interlayers, sands with grain gravel and interbeds of gravel-pebble deposits, clay, sand grained with various grains, etc .; drillability category from III to V.

The investigations were carried out by selecting the DF compositions having optimal structural-mechanical (conditional viscosity, plastic viscosity, PDSs, SSS1 / SSS10), filtration and caking characteristics (δ и Φ), as well as swelling coefficients of 4 cores of the Inkai uranium deposit , obtained from different intervals of the ore zone.

The composition, structural-mechanical, filtration and caking properties of the proposed solutions are given in table 25. As can be seen from the presented data, clay-free DF (No. 1 and 2) have lower structural-mechanical, filtration and crustal characteristics in comparison with low-melting DF (No. 3 and 4). However, the cost of reagents for the preparation of DF in the latter case is less because of the higher price of starch, compared to bentonite.

Table 25 - Composition and properties of biopolymer drilling fluids

№	Composition of the drilling mud, wt.% *						Mud Parameters						
	Gellan	Starch	Xanthan	CaCO$_3$	Bentonite	BIO 135	pH	ρ, g / cm^3	η_{FUN}, c	CP, c^{-1}	ПDSS, dPa	η_{PL}, мPa·c	$\Phi_{30'}$, cm^3	SSS$_{1'}$/SSS$_{10'}$, dPa
1	0.02	2.0	0.3	7	0	0.03	9.6	1.05	38	1134	76	6.7	4	18/23
2	0.03	2.2	0.3	8	0	0.03	9.6	1.06	35	1012	85	8.4	5	20/26
3	0.02	1.8	0.3	6.5	1.0	0.03	9.8	1.05	40	873	69	7.9	5	24/28
4	0.03	2.0	0.3	5	1.5	0.03	10	1.06	42	848	73	8.6	7	29/32
* - the rest is water													

The analysis was carried out on 4 cores, obtained during the drilling of exploratory wells in the area of the prospective site for pilot-industrial tests (Inkai field). The characteristics of the core cores of the ore zone are shown in table 26.

Table 26 - The locations of core sampling at the uranium deposit

№ core	Interval , m	description of cores	Composition of the cores	Colour	Structure	Texture
1	340-380	sand grained with interbedded clay	aleurolite, quartz, field shpaty, clay minerals,	gray-DMown	aleurolite	massif
2	385-440	Sands with grain gravel and interbeds of gravel-pebble deposits	aleurolite, quartz, field	gray	aleurolite	massif
3	445-470	sand grained with grains	aleurolite, quartz, field	gray	aleurolite	massif
4	335-340, 380-385, 440-445, 470-480	clay	clay minerals	DMick	-	=

The values of the core swelling factors presented in table 27 indicate a low degree of swelling of the No. 1-3 cores in water and the average inhibitory activity of DF. Core number 4 has an average swelling in water and an average inhibitory activity of DF.

Table 27 - Core swelling in distilled water and in DF No. 1 (table 32)

№ core	K in water	K in the drill. solution
1	4	0.85
2	2.5	0.6
3	3	0.7
4	8	2.9

The proposed compositions of DF on structural mechanical, filtration and caking characteristics, as well as core swelling coefficients, correspond to the geological and technical conditions of drilling the ore zone of the Inkai uranium deposit.

In connection with the administrative problems that arose at the final stage of preparation for the PT, the place of testing was changed-the "Irkol" field, as well as the requirements for the composition of the DF. As the main component tested by DF by the management of JC. Volkovgeology, the Inbent reagent used by

Volkovgeologiya for the discovery of the ore zone of uranium deposits was proposed. It is a mixture of bentonite with low molecular weight polyacetylcellulose in a weight ratio of about 10: 1, as we established in the analysis.

A solution containing 1.5% by weight of "Inbent" according to the manufacturer's recommendations was modified with additives of gellan and xanthan. Its composition and characteristics are given in table 28. It can be seen that the modification of the DF with Inbent by the addition of 0.02% by weight of gellan and 0.15% by mass of xanthan allowed, with the preservation of the viscosity parameters, to significantly improve the coefficient of ductility (PC) characterizing the rock drillability, increase thixotropy, reduce the filtration index, stability. To increase the density of the DF, taking into account the technological conditions of drilling, and to prevent contamination of the ore zone, $CaCO_3$ was added to the solution in the form of marble chips (fraction 70 μm) in an amount of 5% by weight.

Table 28- Composition and characteristics of modified solutions with the reagent "Inbent"

№	Composition of mud,%				Drilling fluid characteristics								
	Inbent	Gellan	Xanthan	$CaCO_3$	pH	ρ, g/cm^3	η_{fun}, sec	CP	DSS, dPa	η_{PL}, mPa·s	Φ, cm^3	δ, mm	SSS_1/SSS_{10} dPa
1	1.5	-	-	-	10.6	1.02	19.3	449	30.1	6.7	4	0.3	2.4/3.6
2	1.5	0.01	-	-	10.3	1.02	19.8	451	30.2	6.7	3	0.3	3.6/3.6
3	1.5	0.02	-	-	10.3	1.02	20	455	30.9	6.8	3	0.3	4/4
4	1.5	0.02	0.1	-	10.2	1.02	21	500	34.5	6.9	2.5	0.3	4.4/8
5	1.5	0.02	0.15	-	10.2	1.02	22	840	54.9	6.53	2	0.3	6.8/10.8
6	1.5	0.02	0.15	5	10.2	1.05	23	744	56.8	7.63	2	0.3	6.8/10.8
Stability of the solution density through the day: No. 1 is unstable, No. 2-6 are stable													

The PT of the developed DF were conducted at Volkovgeology JSC (GRE-23 DManch) from July 14 to 20, 2017, 40 km from the city of Shieli (Kyzyl-Orda region) on the Irkol drilling site. The tests were carried out on three technological wells: No. 24-3-9-10A-2/1 (quenching), drilling unit No. 49; No. 81463 (downloadable), drilling unit No. 11; No. 81469 (downloadable), drilling unit No. 6.

Prior to the ore zone drilling was carried out using the natural spent DF. Drilling of the ore horizon was carried out using the tested DF. During the drilling process, the parameters of the drilling fluid and drilling regime were monitored.

Drilling was conducted on drilling units ZIF-1200a with a bit ø132mm. To carry out drilling, 20 m^3 of DF were prepared at each well. The solution was prepared in the drilling mud preparation workshop by means of a milling jet mill (FSM) in a capacity of 6 m^3, delivered to the drilling unit by a tank truck and poured into a storage tank for storage of DF-sump.

The parameters of the tested DF, measured during preparation:
- density of $1.05 \div 1.06$ g / cm3;
- conditional viscosity along the March funnel $36 \div 39$ sec;
- water loss $8 \div 11$cm3 for 30min.
- pH = $9.0 \div 9.3$ (additive 0.04 wt% Na_2CO_3);
- SSS1 / SSS10 8 seconds / 15 seconds;
- filter cake δ = 0.2 mm.

Drilling from the surface to the ore horizon $400 \div 420$ m was carried out using natural spent DF. Then it was replaced with the tested drilling mud. During the drilling, the density, conditional viscosity, pH of the medium and SSS were controlled.

Drilling of the ore horizon continued for $8.5 \div 10$ hours without failures and stops at all the above-mentioned wells.

During drilling, the following was observed:
- intensive removal of drill cuttings;
- Preservation of sedimentation stability and uniform consistency of drilling mud in the sump after completion of work;
- stability of drilling mud parameters;
- compatibility of the tested DF with the spent clay DF at substitution.

Important advantages of the tested DF is the simplicity and speed of its preparation on the FSM.

Upon completion of the PSI, an ACT was prepared on conducting joint field trials of Volkovgeology JSC (GRE-23 DFanch) and ChU "Institute of Polymer Materials and Technologies" drilling fluid developed by IMTM on July 20, 2017. (Appendix A).

3.3.6 Optimization of drilling formulations according to the results of laboratory and pilot-industrial tests. Development of technological regulations

The recipe for a new DF containing 1.4% by weight of bentonite, 0.1% by weight of polyacetylcellulose (PAC), 0.15% by weight of xanthan, 0.02% by weight of gellan and 5% by weight of $CaCO_3$, for drilling the ore zone of uranium deposits in difficult geological conditions was optimized based on the results of the PSI at the site of drilling operations "Irkol" JSC Volkovgeology. The composition of the DF was additionally introduced: $0.02 \div 0.06\%$ by weight Na_2CO_3 (to adjust the pH of the solution) and 0.03% by weight of BIO-135 bactericide (to increase the shelf life of the DF at elevated temperature). In addition, the PAC can be replaced with xanthan, with the concentration of the latter being 0.2-0.25% by weight. According to this recipe, an application for an innovative patent is being prepared.

The formulations of two clayless and two low-grade drilling mud containing, gellan, xanthan, modified starch, calcium carbonate and bentonite for drilling the ore zone of the Inkai uranium deposit in complex mining and geological conditions have already been optimized for laboratory results of core swelling.

Based on the results of the OPI, a technological regulation was prepared for the application of a new drilling fluid (Appendix A).

3.3.7 Economic evaluation of the developed compositions of drilling fluids

In the conditions of market competition, it is advisable to estimate the cost of all materials used for drilling a shallow clay-free and clay-free drilling mud. Table 29 presents the cost of drilling mud, proposed in this work and produced by Russian and foreign firms. The consumption of reagents, taking into account the depth of the drilled hole in the pilot test at 10 m^3.

Table 29 - Economic evaluation of the developed compositions of drilling fluids

Reagents	Quantity, kg		Price per kg, tg	Cost, tg	
	CDF	TCDF		CDF	TCDF
Gellan	0.2	0.2	1300	260	260
Xanthan	3	3	900	2700	2700
Starch	26	18	620	16120	11160
KCl	30	30	220	6600	6600
NaOH	0.12	0.12	300	36	36
Defoamer «OMEX»	3	3	1600	4800	4800
Bentonite	-	10	150	-	1500
Biocide «BIO 135»	1	1	750	750	750
TOTAL				31266	27806

3.3.8 Behavior of gellan and xanthan solutions in a sand pack model

The specific feature of gellan is its ability to viscosification and gelation in saline media. The advantages of gellan in comparison with poly(acrylamide) [116] that is traditionally used for EOR are: 1) manufacturing from renewable source of raw materials, for instance biomass, 2) low injectable concentration, 3) high effectiveness of oil recovery, 4) ecological friendliness due to biodegradability. It is also interesting to study the flow behavior of gellan solution in a sand pack model. It is expected that the gellan solution in the course of injection into oil reservoir will undergo coil-helix conformation and sol-gel phase transitions. Initially, pumping of aqueous solution of gellan into the injection well will be easy because of low viscosity of polymer solution. Further, the gel slug that is formed after contacting with underground saline medium starts to plug the high-permeable channels without touching the less-permeable hydrocarbon-productive zones (figure 52).
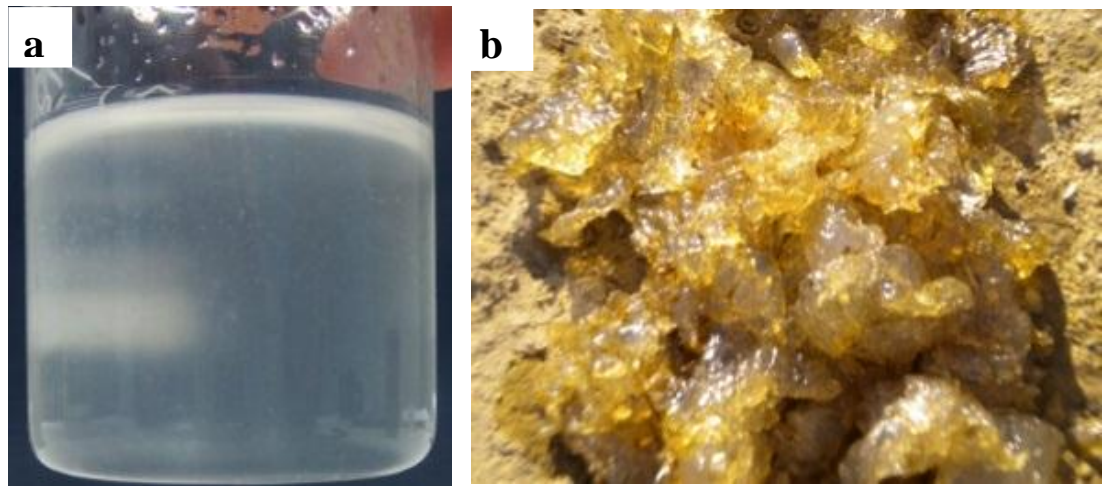
Figure 52 - Photos of aqueous solution of gellan before (a) and after (b) contacting with 73 g·L^{-1} salinity reservoir brine

The undeniable advantage of Gellan compared to polyacrylamide is the single component of the reagent, i.e. no need to add any chemical staplers to initiate the process of gelation. A schematic diagram of the treatment of injection and production wells with an aqueous solution of gellan is shown in figures 53, 54.
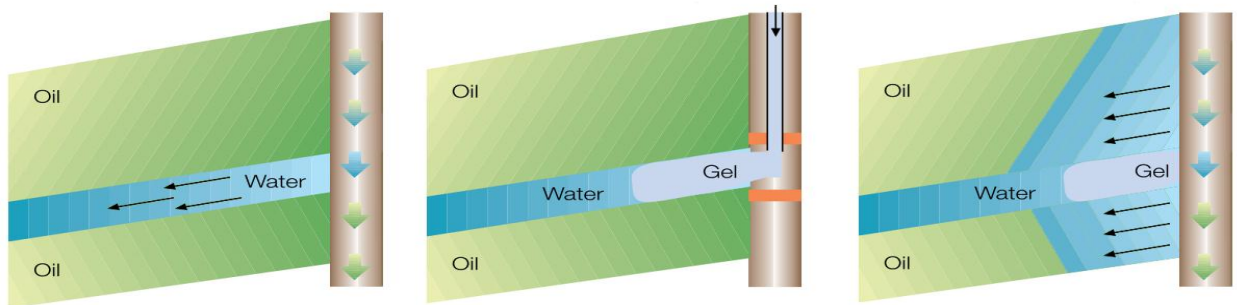
Figure 53 - Injection blocking scheme gellan solution
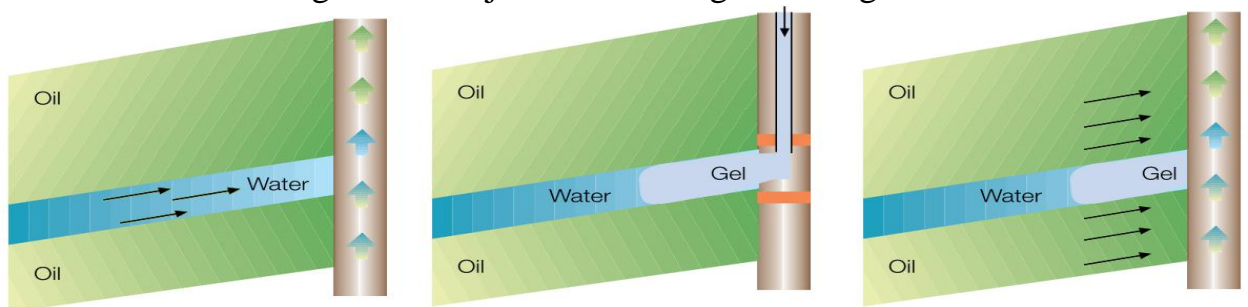
Figure 54 - Scheme of blocking production wells with gellan solution

Blocking (plugging) with the help of gellan gel highly permeable drainage and fractured formation channels in injection and production wells leads to a redistribution of the displacing agent into less permeable zones with a higher content of residual oil reserves, which leads to an increase in oil recovery factor (ORF).

Subsequently, the injected water (or water flooding) should penetrate as much as possible into the less permeable zones so that oil can be displaced from these poorly swept zones. The sand pack model with absolute gas permeability and pore volume that are equal to 20 d and 47 cm^3 (porosity – 38 %), respectively, was initially saturated with brine water with salinity of 73 g·L^{-1}. The brine saturated sand pack was flooded by crude oil with viscosity 1.218 mPa·s and density – 0.772 g· cm^{-3}. As a result, the initial oil and water saturation became equal to 73.2% and 26.7% respectively. The temperature of the sand pack model was kept at 62 °C during the whole filtration experiments. Water flooding was simulated by injection of brine into the sand pack model under the flow rate of 0.5 cm^3·min^{-1}. After pumping of 2 pore volumes (1 pore volume is equal to 50 cm^3) of water through the model, the oil displacement coefficient was equal to 49%. After completion of water flooding, the 0.5 wt.% gellan solution under the same flow rate was injected into the sand pack. The hydrodynamic behavior of gellan solution within the sand pack model is seen from the dependence of injection pressure on the pumped volume (figure 55).
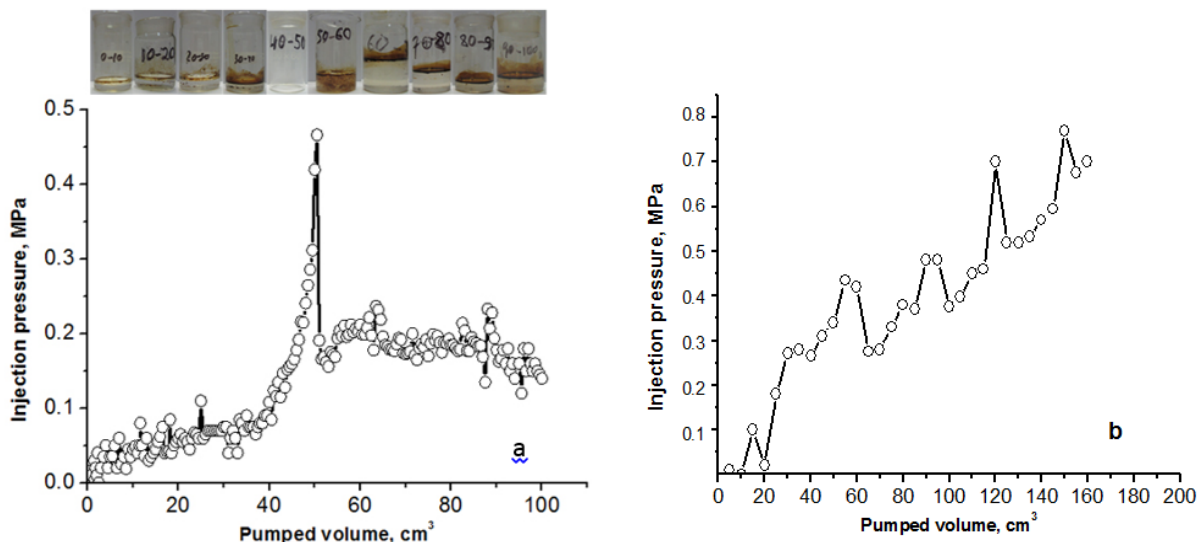
Figure 55 - Changing of injection pressure during the filtration of 0.5wt.% gellan solution through the sand pack model with permeability of 20(a) and 2 d (b); 1 pore volume is 50 cm^3; temperature is 55 °C, flow rate is 0.5 cm^3·min^{-1}

As seen from figure 55 a, the injection pressure sharply increases up to 0.47 MPa after injection of 40 cm^3 of gellan solution and it dramatically decreases down to 0.2 MPa after injection of 50 cm^3 of gellan solution. Such behavior of gellan is interpreted as follows. When the gellan solution penetrates into the high permeable channels (or pores) it contacts with brine and gelation process is enhanced. Formation of gel particles within the pores decreases the permeability and increases the injection pressure. Injection of 10-40 cm^3 of gellan solution into the sand pack saturated by brine and oil is accompanied by displacement of oil-containing liquid (no. 1-4 inset). Accumulation of gel particles inside of high permeable channels and severe plugging of the sand pack model takes place between 40 and 50 cm^3 of injected gellan solution. Plugging of high permeable zones of sand pack model by gellan gel is accompanied

by the absence of squeezed out liquid (no.5 inset). Some portion of gellan gel generated inside of the porous media is displaced out of the model after injection of 50-60 cm^3 gellan solution. The breakthrough of gel plug leads to sharp decrease of injection pressure together with continuous displacement of oil and water mixture from the sand pack model (no. 7-10 inset). The permeability of porous media and gellan concentration play a crucial role in plugging mechanism. When the permeability of porous media is extremely high (for instance, 20 d) the gelation of gellan takes place only once, causing sharp increase and decrease of pressure. Periodically increase and decrease of injection pressure (oscillation of pressure) is observed for the sand pack model with lower permeability (figure 55b). For example, the oscillation behavior of 0.5wt.% gellan solution was detected inside of the sand pack model with permeability 2d. The hydrodynamic behavior of 0.5 wt.% gellan solution presented in figure 55b may be explained in the following way. When 0.5 wt.% gellan solution penetrates into the brine saturated sand pack model, it preferentially occupies high permeable channels and plugs them (injection pressure increases). Accumulation of gel particles in high filtration channels leads to involvement of new channels to be plugged. When gellan solution finds such channels it flows into it (injection pressure decreases). Thus, permanent plugging of different channels by gellan gel leads to constant redirection of gellan solution to lower and lower permeable pores. Such step-by-step plugging of high and low permeable channels is responsible for periodic increase and decrease of injection pressure.

Injection of 0.5 % gellan-xanthan solution into sand pack model was conducted at the flow rate of 0.1 cm^3·min^{-1}. In the course of injection of 0.5 % solution of gellan and xanthan mixture into the core sample the injection pressure increases up to the maximal value – 1 MPa confirming the high ability of the gellan-xanthan mixture to plug the pore space (figure 55, curve 1). To simulate the water flow towards the producing well, the further injection of water into the core sample was conducted from the opposite side of the injected polymer. Curve 2 of the figure 53 shows that increasing of the water flow rate doesn't lead to the substantial increase of the injection pressure. During the last step at the flow rate of 1cm^3·min^{-1} the injection pressure increases up to 0.15 MPa. These results indicate on the ability of gellan-xanthan (2:1) mixture to plug the high permeable pore channels, however the mixture is less effective to create the high resistance to water filtration. The results of the polymer flooding experiment are summarized in table 26. The gellan-xanthan (2:1) mixture plugs pore space less effectively than gellan solution itself, so mixing of xanthan with gellan doesn't yield the improvement of oil displacement and doesn't increase the resistance to water flow. Moreover, the hydrodynamic behavior of gellan-xanthan mixture is not in favor of the passing of big volumes of the solution deeply into the reservoir. It is confirmed by gradually increasing of injection pressure up to 1 MPa during the injection of the mixture into the core sample whereas during the injection of gellan the pressure increases only up to 0.15 MPa. The subsequent water injection shows that the pure gellan plugs more effectively the high permeability channels.
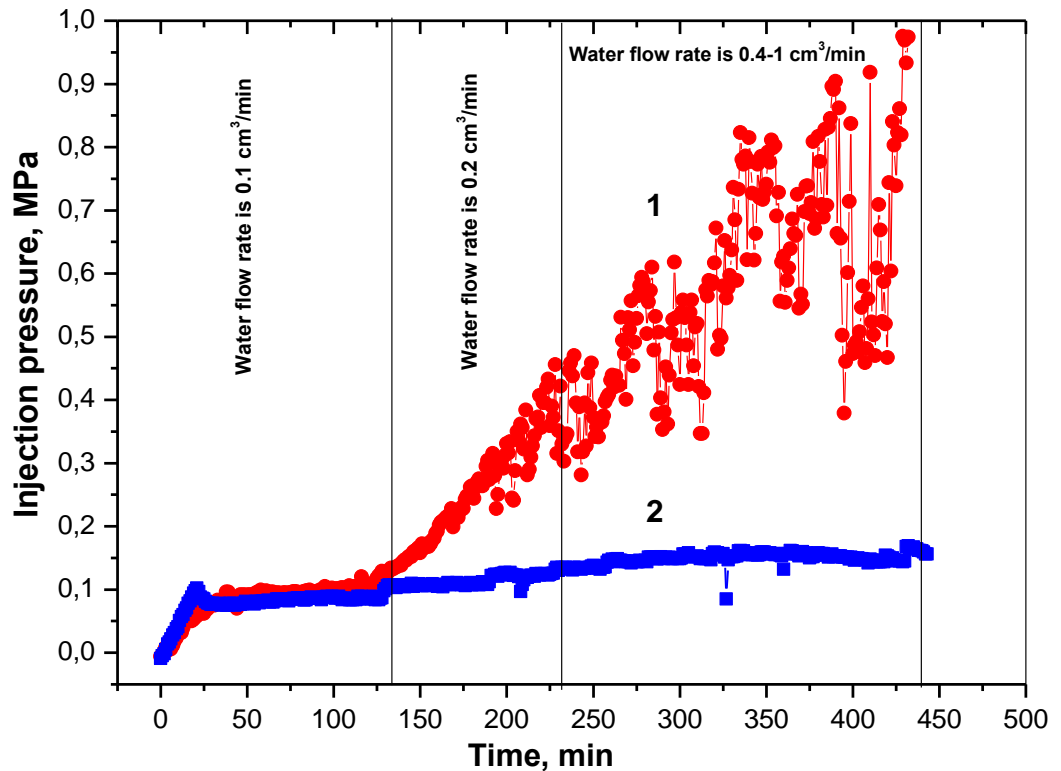
Figure 56 - Time dependent changing of injection pressure in the course of
injection of 0.5% gellan-xanthan (2:1) mixture (1) and reservoir water (2).

Table 30 - Oil displacement efficiency of water flooding and gellan-xanthan flooding

Step	Type of injection	Oil displacement coefficient, %
1	Water flooding	52
2	Injection of 0.5% gellan-xanthan (2:1)mixture	58 (increment 6%)*
3	Injection of water after injection of 0.5% gellan-xanthan (2:1) mixture	58 (increment 0%)
*Increment of oil displacement coefficient is equal to 6% obtained in lab conditions		

3.3.9 Experiments on sand pack model and comparison of the effectiveness of gellan and polyacrylamide

Model experiments to assess the effectiveness of reducing the permeability of the pore space after filtration of polymers were carried out for gellan and polyacrylamide. The experiments were carried out using saline water with a concentration of 75 g / L NaCl and aqueous solutions of gellan and polyacrylamide (PAA) with a concentration of 0.1%. The results of filtration of polymers through a porous medium, shown in figure 57 show that the discharge pressure does not change significantly when filtering 250 cm^3 of gellan solution (2.5 pore volumes).
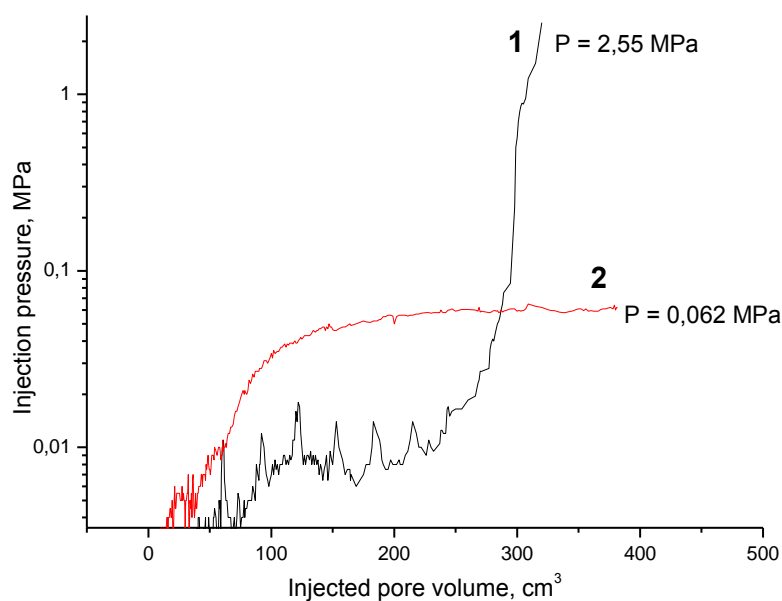
Figure 57 - Change in discharge pressure when pumping 0.1% solutions of gellan and PAA through a bulk model saturated with saline water

However, in this area, oscillatory pressure surges with an average amplitude of 0.006 MPa are observed. They are characteristic only of a gellan solution, which is filtered through a bulk model saturated with saline water. This behavior of gellan was discovered by us for the first time and it is associated with the phase sol – gel transition that takes place in a porous medium with high mineralization. This assumption is confirmed by the fact that the gellan solution undergoes a sol-gel transition upon contact with salt-saturated sand.

As can be seen from figure 57, after pumping 3 pore volumes of a 0.1% gellan solution, the pressure increases dramatically. At the time of pumping 315 cm3, the pressure rises to a value of 2.55 MPa. In the case of PAA, the curve monotonously increases to a pressure of 0.062 MPa and subsequently changes slightly. Thus, at very close values of medium permeability (permeability coefficient 3.7–3.8 Darcy) and the same polymer concentration (polymer concentration 0.1%), at the time of pumping three pore volumes of polymer through the model, gellan increases the discharge pressure 40 times more than PAA.

One of the main criteria for the successful application of flow-diverting technology is the ability to control the depth of penetration of the plugging solution into the formation. As follows from the two series of experiments, a sharp increase in the discharge pressure when filtering a gellan solution through the bulk model occurs after pumping several pore volumes of the solution. When using gellan solutions with a lower concentration, the amount of pumped pore volumes required to reduce the permeability of the rock increases. Thus, by changing the concentration of gellan

solution injected into the formation, it is possible to regulate the depth of its penetration into the formation.

Section summary

Physical, chemical, rheological and conformational characteristics of CMCS, gellan and xathan solutions were determined at the concentration of the polysaccharides varying from 0.1 to 1%, concentration of salts NaCl, KCl, $MgCl_2$, $CaCl_2$ и $BaCl_2$ varying between 0 and 1.5%, temperature range 25 – 70 ºC.

On the basis of the results of rheological measurements, drilling mud formulations were selected that are capable of carrying rock particles to the surface during the drilling of a well. Recipe of a new drilling fluid containing bentonite, polyacetylcellulose, xanthan, gellan and calcium carbonate was tested for drilling the ore zone of uranium deposits in difficult geological conditions. As a result of the pilot industrial test (PIT) at the Irkol drilling site of JSC Volkovgeology, it was shown that the drilling fluid has high performance characteristics. According to the results of the OPI, a test report was obtained and the technological regulations for the application of the new drilling mud were prepared.

The behavior of gellan and PAA in a water- and salt-saturated porous medium that simulates oil fields at a late stage of development has been studied. It is shown that when filtering dilute polymer solutions through a porous medium, an injection pressure increases as a result of the formation of a polymer rim in a certain part of the bulk model. The results of the PIT conducted in 2015 and 2017 at the Kumkol field with the participation of JSC Turgai-Petroleum and JSC NIPIneftegaz showed that the gepolymer injection of gellan into injection and production wells allowed additional extraction within 6 months 5805 tons of oil and reduce the water content of the production well over 3 years to 50-60% with a slight decrease in oil production.

CONCLUSION

1 The analysis of the literature on the study of polysaccharides - gellan, xanthan and starch, the composition and properties of drilling fluids and the technology of gel polymer polymer flooding with the participation of polyacrylamide and polysaccharides.

2 The physicochemical, rheological and conformational characteristics of solutions of gellan, xanthan, carboxymethylated corn starch were determined in the range of concentrations of polysaccharides (0.1 ÷ 1%), the nature of salts (NaCl, KCl, $MgCl_2$, $CaCl_2$ and $BaCl_2$) and the concentration of salts (0 ÷ 1.5 %), temperature (25 ÷ 70 ºC), pH of the medium (6.5 ÷ 9.5) and the content of the dispersed phase (0 ÷ 8%).

3 A sol-gel transition of gellan was established depending on the concentration of the polymer, the nature and concentration of low-molecular salts. It was shown that a 0.2% solution of gellan undergoes a sol-gel transition at concentrations of $CaCl_2$, $MgCl_2$, KCl and NaCl equal to $2 \cdot 10^{-2}$, $2 \cdot 10^{-2}$, $1 \cdot 10^{-2}$ and $1 \cdot 10^{-1}$ $mol \cdot L^{-1}$, respectively. A sol-gel transition of gellan was established in the presence of 10-40% by volume of produced water with a salinity of 73 g /L and a gel-sol transition at a concentration of formation water in the range of 50-90% by volume.

4 It is shown that aqueous solutions of gellan and xanthan are stable for 1 month and in the temperature range from 25 to 70 ° C, which correspond to the conditions of the formation and during drilling operations.

5 By the method of differential scanning calorimetry, a conformational transition of gellan in the presence of NaCl and $CaCl_2$ was established, associated with dissociation of double helices of gellan and its transition to a coil-shaped conformation. The specific heats of a 0.5% gellan solution were determined, which increase in the series $MgCl_2$> $CaCl_2$> KCl> NaCl in the salt concentration range of 0.005–0.01 $mol \cdot L^{-1}$.

6 It is shown that the strength of gellan gel increases in the following sequence: reservoir water> $CaCl_2$> $MgCl_2$> KCl> NaCl, and the strength of gels of a mixture of polysaccharides changes in the following order: gellan-starch> gellan> gellan-xanthan.

7 By chemical modification of corn starch, a domestic product produced by Zharkent Corn Factory, semi-water-soluble carboxymethylated starch, which has high viscosity and stability in salt solutions. The structure, degree of modification, average viscosity molecular mass, morphology, zeta potential and average hydrodynamic dimensions of macromolecules were determined by the methods of H1 NMR and FTIR spectroscopy, viscometry, scanning electron microscope and dynamic laser light scattering.

8 Rheological studies of aqueous solutions of gellan, xanthan and gellan-xanthan mixture were conducted depending on the ratio of polysaccharide components, the content of bentonite and salts, pH of the medium and temperature. It is shown that the rheological behavior of solutions of polysaccharides is described by

the Ostwald de Vaale and Herschel – Bulkley equations and corresponds to the model of a pseudo-plastic fluid.

9 On the basis of the results of rheological measurements, drilling mud formulations were selected that are capable of carrying rock particles to the surface during the drilling of a well. Formulations of new clayless drilling fluids in a wide range of density changes have been developed, consisting of gellan, modified starch, xanthan and aluminosilicate microspheres, which are recommended to prevent the absorption and opening of productive layers of oil fields with low reservoir pressures, as well as for opening productive layers of horizontal and inclined directional wells, represented by carbonate and terrigenous reservoirs. Drilling fluid formulations are protected by patents of the Republic of Kazakhstan.

10 Recipe of a new drilling fluid containing bentonite, polyacetylcellulose, xanthan, gellan and calcium carbonate was tested for drilling the ore zone of uranium deposits in difficult geological conditions. As a result of the pilot industrial test (PIT) at the Irkol drilling site of JSC Volkovgeology, it was shown that the drilling fluid has high performance characteristics. According to the results of the OPI, a test report was obtained and the technological regulations for the application of the new drilling mud were prepared.

11 The behavior of gellan and PAA in a water- and salt-saturated porous medium that simulates oil fields at a late stage of development has been studied. It is shown that when filtering dilute polymer solutions through a porous medium, an injection pressure increases as a result of the formation of a polymer rim in a certain part of the bulk model. It has been established that with the same permeability of the porous medium and the same polymer concentration, gellan increases the discharge pressure more than 40 times than the PAA. When filtering gellan through a porous medium saturated with saline water, an oscillatory change in pressure with a certain amplitude, associated with a phase sol-gel transition of a polymer in a salt solution, was first detected.

12 The results of the PIT conducted in 2015 and 2017 at the Kumkol field with the participation of JSC Turgai-Petroleum and JSC NIPIneftegaz showed that the gepolymer injection of gellan into injection and production wells allowed additional extraction within 6 months 5805 tons of oil and reduce the water content of the production well over 3 years to 50-60% with a slight decrease in oil production.

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APPENDIX A

The act of conducting experimental field trials

А К Т

о проведении совместных опытно-полевых испытаний АО «Волковгеология» (филиал ГРЭ-23) и ЧУ «Институт полимерных материалов и технологий» бурового раствора, разработанного ИПМТ

20 июля 2017г.   г. Шиели

Комиссия в составе: главного технолога ГРЭ-23 Корганбекулы К. и членов: ведущего технолога ПНТБиП АО «Волковгеология» Шалбаева Ж.С. и главного научного сотрудника ИПМТ Сигитова В.Б. составили настоящий акт, о том, что в период с 14.07.2017 по 20.07.2017 были проведены опытно-полевые испытания разработанной рецептуры бурового раствора на основе модифицированного интбента с добавками ксантановой смолы и полисахарида геллана для бурения рудного горизонта на участке буровых работ «Ирколь». Испытания проводилось на трех технологических скважинах. Буровой агрегат № 49 скважина № 24-3-9-10А-2/1 (закачная), буровой агрегат №11 скважина №81463 (закачная), буровой агрегат №6 скважина №81469 (закачная).

До рудной зоны бурение проводилось с применением естественного наработанного бурового раствора. Бурение рудного горизонта проводилось с использованием испытываемого бурового раствора. В процессе бурения и контролировали параметры раствора и режима бурения.

В процессе бурения наблюдалось:
- интенсивный вынос выбуренного шлама;
- сохранение седиментационной устойчивости и однородной консистенции бурового раствора в зумпфе по окончании работ;
- стабильность параметров бурового раствора;
- совместимость испытываемого раствора с наработанным глинистым раствором при замещении.

Параметры испытываемого бурового раствора:
Удельный вес 1.05 – 1.09 г/см^3;
Вязкость 39- 41 сек;
Водоотдача 8-11см^3/30мин.

Важными достоинствами испытываемого бурового раствора является простота и быстрота его приготовления на фрезерно-струйной мельнице.

По окончании работ на всех технологических скважинах был проведен комплекс исследований ГИС, при этом все приборы до проектной глубины дошли с первого раза без осложнений.

Члены комиссии   Корганбекулы К.

                                                       Шалбаев Ж.С.

                                                       Сигитов В.Б.

Geological data of the ore zone deposits JSC "Volkovgeology"

Филиал АО "Волковгеология"
"Геотехноцентр"

Предприятие:
Месторождение: Ирколь (коньяк)
Рудовмещающий горизонт, Залежь: 2
Дата каротажа: 20.07.2017 г.

Таблица
результатов интерпретации гамма-каротажа
Скважина № 24-3-9-10а-2_1

По Ra

№ п/п	Интервал, м от	Интервал, м до	Мощность m, м	Содержание с, %	Лин. запасы тс, м%
		Баланс			
1	417,90	419,00	1,10	0,047	0,0519
2	421,00	427,10	6,10	0,043	0,2601
3	427,90	431,40	3,50	0,144	0,5043
Итого: баланс			10,70	0,076	0,8163
		Забаланс			
1	432,30	433,50	1,20	0,013	0,0157
2	436,30	437,30	1,00	0,020	0,0195
Итого: забаланс			2,20	0,016	0,0352
Всего: баланс + забаланс			12,90	0,066	0,8515
		Технологический забаланс			
1	409,80	410,00	0,20	0,015	0,0031
2	427,30	427,90	0,60	0,058	0,0350
3	431,40	432,30	0,90	0,076	0,0685
Итого: тех. Забаланс					

По U

№ п/п	Интервал, м от	Интервал, м до	Мощность m, м	Содержание с, %	Лин. запасы тс, м%	Продуктив. Р, кг/м³
		Баланс				
1	417,90	419,00	1,10	0,059	0,0649	
2	421,00	427,10	6,10	0,053	0,3251	
3	427,90	431,40	3,50	0,180	0,6304	
Итого: баланс			10,70	0,095	1,0203	
		Забаланс				
1	432,30	433,50	1,20	0,016	0,0196	
2	436,30	437,30	1,00	0,024	0,0244	
Итого: забаланс			2,20	0,020	0,0440	
Всего: баланс + забаланс			12,90	0,083	1,0644	
		Технологический забаланс				
1	409,80	410,00	0,20	0,019	0,0039	
2	427,30	427,90	0,60	0,073	0,0438	
3	431,40	432,30	0,90	0,095	0,0856	
Итого: тех. Забаланс						

Предприятие:
Месторождение: Ирколь (коньяк)
Рудовмещающий горизонт, Залежь: 2
Дата каротажа: 20.07.2017 г.

Таблица

рудных интервалов по результатам интерпретации гамма-каротажа

Скважина № 24-3-9-10а-2_1

№ интер-вала	Интервал, м		Мощность	Среднее содерж.	Линейные запасы	Среднее содерж.	Линейные запасы	Крр	Литолого-фильтрационный тип (ЛФТ)	Тип руды
	от	до	m, м	c, %	mc, м%	c, %	mc, м%	доли ед.		
			По Ra-226					По U - 238		
1	409,80	410,00	0,20	0,015	0,0031	0,019	0,0039	0,80	непрониц.	тех.забаланс
2	417,90	419,00	1,10	0,047	0,0519	0,059	0,0649	0,80	прониц.	прониц.
3	421,00	427,10	6,10	0,043	0,2601	0,053	0,3251	0,80	прониц.	прониц.
4	427,30	427,90	0,60	0,058	0,0350	0,073	0,0438	0,80	непрониц.	тех.забаланс
5	427,90	431,40	3,50	0,144	0,5043	0,180	0,6304	0,80	прониц.	прониц.
6	431,40	432,30	0,90	0,076	0,0685	0,095	0,0856	0,80	непрониц.	тех.забаланс
7	432,30	433,50	1,20	0,013	0,0157	0,016	0,0196	0,80	прониц.	прониц.
8	436,30	437,30	1,00	0,020	0,0195	0,024	0,0244	0,80	прониц.	прониц.

Интерпретировала: Сарсембаева М. Т.

Дата интерпретации: 20.07.2017 г.
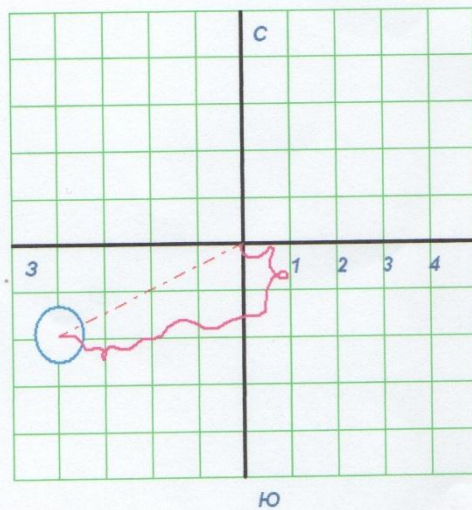
Инклинограмма
скв. 24-3-9-10а-2_1
Месторождение: Ирколь
Горизонтальное смещение забоя, м.4.4
Вертикальное смещение забоя, м. 457.4
Азимут смещения забоя, град. 244.1
Зенит смещения забоя, град. 0.6

Интерпретатор: Сарсембаева М.
Инклинограмма
Горизонтальное смещение забоя
Эллипс погрешностей

Результаты интерпретации инклинометрии скважины: 24-3-9-10а-2_1

N	Азимут	Зенит	Глубина	Коорд.X	Коорд.Y	Коорд.Z	Уход
1,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
2,0	228,8	0,9	0,7	0,0	-0,0	0,7	0,0
3,0	183,7	0,8	7,5	-0,1	-0,0	7,5	0,1
4,0	140,3	0,9	17,5	-0,2	-0,0	17,5	0,2
5,0	105,8	0,9	27,5	-0,3	0,1	27,5	0,3
6,0	70,7	1,2	37,5	-0,3	0,3	37,5	0,4
7,0	48,5	1,1	47,5	-0,2	0,5	47,5	0,5
8,0	28,7	0,7	57,5	-0,1	0,6	57,5	0,6
9,0	195,1	0,4	67,5	-0,1	0,7	67,5	0,7
10,0	214,0	0,8	77,5	-0,2	0,6	77,5	0,7
11,0	184,5	0,9	87,5	-0,4	0,6	87,5	0,7
12,0	167,1	1,1	97,5	-0,5	0,6	97,5	0,8
13,0	138,9	1,0	107,5	-0,7	0,7	107,5	1,0
14,0	102,5	0,9	117,5	-0,8	0,8	117,5	1,1
15,0	48,6	0,7	127,5	-0,7	1,0	127,5	1,2
16,0	294,5	0,6	137,5	-0,6	0,9	137,5	1,1
17,0	242,9	1,1	147,5	-0,6	0,8	147,5	1,0
18,0	223,2	1,5	157,5	-0,8	0,6	157,5	1,0
19,0	189,3	1,5	167,5	-1,0	0,5	167,5	1,1
20,0	174,6	1,3	177,5	-1,2	0,5	177,5	1,3
21,0	194,3	1,0	187,5	-1,4	0,5	187,5	1,5
22,0	284,7	1,3	197,5	-1,6	0,3	197,5	1,6
23,0	253,9	1,7	207,5	-1,6	0,0	207,5	1,6
24,0	251,7	2,0	217,5	-1,7	-0,3	217,5	1,7
25,0	234,6	1,7	227,5	-1,8	-0,6	227,5	1,9
26,0	292,5	1,4	237,5	-1,8	-0,8	237,5	2,0
27,0	307,1	1,0	247,5	-1,7	-1,0	247,4	2,0
28,0	287,2	1,2	257,5	-1,6	-1,2	257,4	2,0

95

29,0	249,9	1,4	267,5	-1,6	-1,4	267,4	2,2
30,0	231,6	1,5	277,5	-1,8	-1,6	277,4	2,4
31,0	203,9	1,3	287,5	-2,0	-1,8	287,4	2,6
32,0	294,0	1,1	297,5	-2,0	-2,0	297,4	2,8
33,0	251,8	1,6	307,5	-2,0	-2,2	307,4	3,0
34,0	206,9	1,3	317,5	-2,2	-2,4	317,4	3,3
35,0	278,9	0,2	327,5	-2,3	-2,5	327,4	3,4
36,0	260,5	0,6	337,5	-2,3	-2,6	337,4	3,4
37,0	300,5	0,7	347,5	-2,2	-2,7	347,4	3,5
38,0	282,2	1,2	357,5	-2,2	-2,9	357,4	3,6
39,0	201,3	1,0	367,5	-2,3	-3,0	367,4	3,8
40,0	212,0	0,4	377,5	-2,4	-3,1	377,4	3,9
41,0	75,5	0,7	387,5	-2,4	-3,0	387,4	3,9
42,0	319,1	1,3	397,5	-2,3	-3,0	397,4	3,7
43,0	266,7	1,3	407,5	-2,2	-3,2	407,4	3,9
44,0	226,3	0,4	417,5	-2,3	-3,3	417,4	4,0
45,0	341,1	0,8	427,5	-2,2	-3,4	427,4	4,1
46,0	318,3	1,0	437,5	-2,1	-3,5	437,4	4,1
47,0	307,5	1,1	447,5	-2,0	-3,6	447,4	4,1
48,0	249,5	2,7	457,5	-1,9	-4,0	457,4	4,4

Погрешность для координаты X   0.6

Погрешность для координаты Y   0.6

Погрешность для координаты Z   18.7

Горизонтальное смещение забоя, м.   4.4

Вертикальное смещение забоя, м.   457.4

Азимут смещения забоя, град.   244.1

Зенит смещения забоя, град.   0.6

Интерпретатор: Сарсембаева М.

ПАСПОРТ РУДНЫХ ИНТЕРВАЛОВ
по результатам комплексной интерпретации ГИС

Скважина № 24-3-9-10а-2_1

Тип скважины
(закачная)

Масштаб 1:200
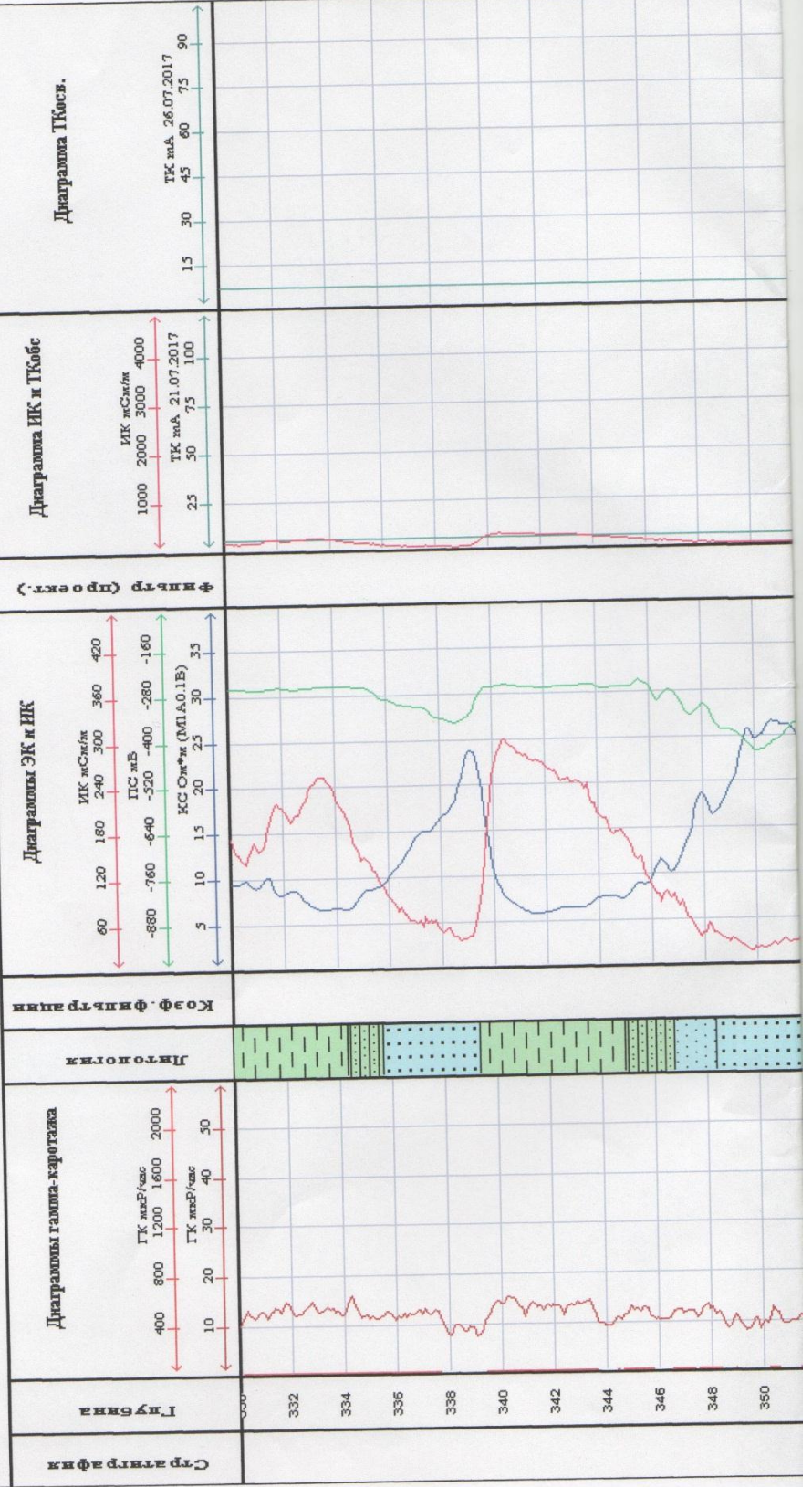
филиал АО "Волковгеология" "Геотехноцентр"
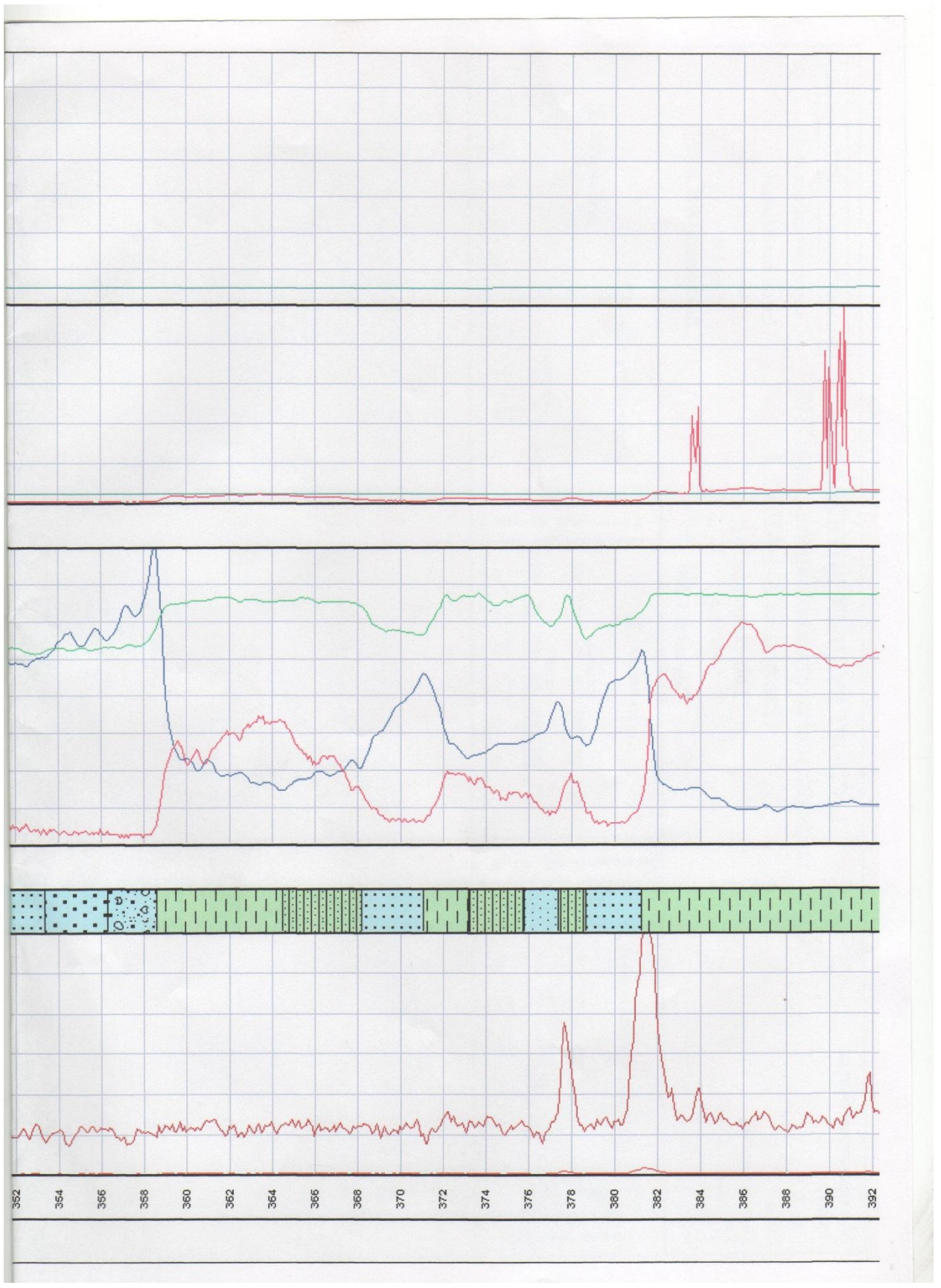
Геофизический цех № 3

Данные инклинометрии

A = 244.1 град

L = 4.4 м.

Дата каротажа: 20.07.2017 г.

Месторождение Иркол

Залежь 2

Блок № 24-3

Ряд №

Координаты устья:

X =

Y =

Z =

Диаграмма ТКосв.

ТК мА 26.07.2017

15   30   45   60   75   90

Диаграмма ИК и ТКобс

ИК мСм/м   1000 2000 3000 4000

ТК мА 21.07.2017   25   50   75   100

фильтр (проект.)

Диаграммы ЭК и ИК

ИК мСм/м   60   120   180   240   300   360   420

ПС мВ   −880   −760   −640   −520   −400   −280   −160

КС Ом*м (М1 А0.1В)   5   10   15   20   25   30   35

Коэф. фильтрации

Литология

Диаграммы гамма-каротажа

ГК мкР/час   400   800   1200   1600   2000

ГК мкР/час   10   20   30   40   50

Глубина

332   334   336   338   340   342   344   346   348   350

Стратиграфия

н. з. 458,9 м

433.60 m
439.40 m
450.80

427.90 - 431.40 3.50 0.180 0.6304
431.40 - 432.30 0.90 0.095 0.0856
432.30 - 433.50 1.20 0.016 0.0196
436.30 - 437.30 1.00 0.024 0.0244

430 432 434 436 438 440 442 444 445 448 450 452 454 455 458 460 462 464

Интерпретировала _____ Сарсембаева М. Т.

Проверил(а) _____ Когай И.И.

Принял: Инженер-маркшейдер _____ Жанекеев А.К.

Ведущий инженер-геолог _____ Досмагамбетова Н.Ж.

Главный геолог _____ Чебижов Г. А

Поправочные коэффициенты и зависимости при интерпретации ГК

БД-1: *Месторождение................* | Ирколь (коньяк) |

| 115 | K_o - пересчетный коэффициент, мкР/ч на 0,01% U |

| 0,80 | $П_{Rn}$ - поправка на отжатие Радона в относительных единицах |

| 14,0 | B - влажность руды, % |

| 0,000664 | q_o - эквивалентный по интенсивности гамма-излучения вклад Th и К |

где: $q_o = 0,43 \cdot q_{Th} + 1,8 \cdot 10^{-4} \, q_K$

| 5,40 | q_{Th} - содержание в рудах тория, 10^{-4}% | | 2,40 | q_K - содержание в рудах калия, % |

| 1,00 | - максимальная мощность безрудного пласта при объединении рудных интервалов |

| 0,0600 | - минимальные стволовые запасы для балансовых руд, м% |

БД-2: *Рудовмещающий горизонт, Залежь.....* | 2 |

| 1,80 | ρ - объемный вес сухой руды, г/см^3 |

| 0,80 | K_{pp} - коэф. радиактивного равновесия в отн. ед., вводится в зависимости от .... |

| 0,010 | C_3 - заданное значение содержания радия для выделения непроницаемых рудных интервалов, % |

Уравнение регрессии

$$c_\delta = a \bar{c}^{\,b}$$

Останец (с-ж)		**Мешок (с-с)**	
$a=$	0,0510	$a=$	0,0410
$b=$	0,3400	$b=$	0,3520

Крыло (с-ж)		**Крыло (с-с)**	
$a=$	0,0510	$a=$	0,0410
$b=$	0,3400	$b=$	0,3520

БД-3: *Скважина.........................* | 24-3-9-10а-2_1 |

| 132 | $2r_o$ - номинальный диаметр бурения, мм | | 132 | $2r$ - фактический диаметр бурения, мм |
(в интервале 0.0м-0.0м)

| 60 | $2R$ - диаметр скважинного прибора, мм | | 1,2 | ρ_o - плотность бурового раствора, г/см^3 |

| 0,8674805 | $П_\delta$ - поправка на поглощение гамма-излучения буровым раствором |

где: $П_\delta = 1 - 0,034931 \, T_\delta + 0,000985 \, T_\delta^2$

| 4,32 | $T_\delta = \rho_o * (r_o - R)$ - эквив. толщина слоя бур. раствора |

| 1,000 | $П_o$ - поправка за обсадные трубы |

где: $\Pi_o = 1 - 0,033 T_o + 0,00508 T_o^2 - 0,00321 \dfrac{r_o}{R} T_o + 0,0001 \dfrac{r_o}{R} T_o^2 + 0,000147 \left(\dfrac{r_o}{R}\right) T_o - 0,0000033 \left(\dfrac{r_o}{R}\right)^2 T_o^2$

| 0 | T_o - толщина обсадных труб, мм |

Филиал АО "Волковгеология"
"Геотехноцентр"

Предприятие:
Месторождение: Ирколь (коньяк)
Рудовмещающий горизонт, Залежь: 2
Дата каротажа: 20.07.2017 г.

Результаты интерпретации электрокаротажа

Скважина № 24-3-9-10а-2_1

L = 4,4 м
A = 244,1 град
гл.инкл. = 457,4 м

№ интервал	Глубина		Литотип
	от	до	
1	358,60	364,50	алевролит
2	364,50	368,20	песчаник глинистый
3	368,20	371,10	песок среднезернистый
4	371,10	373,20	алевролит
5	373,20	375,80	песчаник глинистый
6	375,80	377,40	песок мелкозернистый
7	377,40	378,70	песчаник глинистый
8	378,70	381,30	песок среднезернистый
9	381,30	394,30	алевролит
10	394,30	397,10	песок мелкозернистый
11	397,10	399,70	песчаник глинистый
12	399,70	401,90	песок среднезернистый
13	401,90	402,60	алевролит
14	402,60	404,80	песок мелкозернистый
15	404,80	407,10	песок среднезернистый
16	407,10	408,80	песок крупнозернистый
17	408,80	410,00	алевролит
18	410,00	411,80	песок среднезернистый
19	411,80	413,00	алевролит
20	413,00	419,30	технологическое закисление
21	419,30	419,80	алевролит
22	419,80	422,30	песок крупнозернистый
23	422,30	427,30	технологическое закисление
24	427,30	427,90	алевролит
25	427,90	431,40	технологическое закисление
26	431,40	432,30	алевролит
27	432,30	440,70	технологическое закисление
28	440,70	443,40	алевролит
29	443,40	446,10	песок среднезернистый
30	446,10	446,80	алевролит
31	446,80	447,60	песок мелкозернистый
32	447,60	449,60	песок среднезернистый
33	449,60	450,80	песок крупнозернистый
34	450,80	452,50	песок мелкозернистый
35	452,50	453,40	алевролит
36	453,40	455,30	песок мелкозернистый
37	455,30	458,90	песок среднезернистый
		2,00	

МИНИСТЕРСТВО ЮСТИЦИИ РЕСПУБЛИКИ КАЗАХСТАН

УДОСТОВЕРЕНИЕ АВТОРА

№ 102878

Настоящим удостоверяется, что **Нурахметова Жанар Ануарбековна (KZ)**

и **Сигитов Владимир Борисович (KZ); Шайхымежденов Жанибек Гинаятович (KZ); Кудайбергенов Саркыт Еликенович (KZ)**

является(ются) автором(ами) изобретения

(11) 32905

(54) Буровой раствор низкой плотности

(73) *Патентообладатель:* Частное учреждение "Институт полимерных материалов и технологий" (KZ)

(21) 2017/0139.1
(22) 23.02.2017

Вице-министр юстиции
Республики Казахстан

Н. Пан

APPENDIX C

Patent

2

Дата поступления заявки 31.03.2017

2 0 ДЕК 2018

47885

ЧУ "Институт полимерных материалов материалов и технологий"
ул. Сатпаева, 22а. г.Алматы. 050013
glmdai@gmail.com

ЗАКЛЮЧЕНИЕ
о выдаче патента на полезную модель

(21) Заявка № 2018/0922.2

(22) Дата подачи заявки 31.03.2017

ПРИОРИТЕТ УСТАНОВЛЕН:

☐ (22) по дате подачи заявки
☐ (23) по дате поступления
☐ дополнительных материалов от _____ к более ранней заявке №
☐ (66) по дате подачи ранее поданной заявки № _____ от
☐ (62) по дате подачи первоначальной заявки № _____ от
☐ по дате подачи первой заявки в государстве-участнике Парижской конвенции

(31) № приоритетной заявки   (32) Дата подачи приоритетной заявки   (32) Код страны приоритетной заявки

(85) Дата перевода международной заявки на национальную фазу _____ г.
(86) Регистрационные данные заявки РСТ

(71) Заявитель(и)   "Полимер материалдары және технологиялар институты" жеке меншік мекемесі (KZ)
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(73) Патентообладатель (и)   "Полимер материалдары және технологиялар институты" жеке меншік мекемесі (KZ)
Частное учреждение "Институт полимерных материалов и технологий" (KZ)

(51) МПК   *C09K 8/24* (2006.01)
C09K 8/528 (2006.01)
C09K 8/582 (2006.01)

(54) Название   Безглинистый буровой раствор
Сазсыз бұрғылау ерітіндісі

APPENDIX D

Technological effect of pilot tests

ТОРГАЙ ПЕТРОЛЕУМ акционерлік қоғамы
ТУРГАЙ ПЕТРОЛЕУМ акционерное общество
TURGAI PETROLEUM joint-stock company

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№ 463   " 11 "   05   201_8_ ж.
г.

Директору института полимерных
материалов и технологий
г-ну Кудайбергенову С.Е.

Уважаемый Саркыт Елекенович,

На Ваш запрос от 12.04.18г. №07 сообщаем, что общий технологический эффект проведенных ОПИ в 2017 году по выравниванию профиля приемистости с применением реагента «Геллан» составил 5805 т. Данная эффективность рассчитана за 6 месяцев после проведения мероприятия.

С уважением,
Директор по геологии и разработке   Ермаков А.В.

Исп.Мусиров М.
Тел: 262199

000366

ACKNOWLEDGEMENTS