

REVIEW

to the PhD dissertation of Nurakhmetova Zhanara entitled «Synthetic and natural polymers for oil production and development of drilling fluids» submitted for the degree of Doctor of Philosophy (PhD), on the specialty of «6D073900 - Petrochemicals»

1. Thematic justification of the research topic and its link to general scientific and National programs.

The dissertation is dedicated to investigation of properties and gelation of gellan, xanthan, carboxymethylated cornstarch, polyacrylamide solution as well as their mixtures for development of drilling fluid formulation and flow deviation or plugging reagents in oil recovery. This is the task of current interest for the oil production fields in the Republic of Kazakhstan.

Polymers from renewable plant feedstock attract an increasing interest of researchers predominantly due to environmentally friendliness, while synthetic polymers are mainly produced from non-renewable petroleum resources. To solve the problems of drilling, oil recovery, oil treatment and transportation of oil, the solutions and gels based on natural and synthetic polymers and possessing a high viscosity, ability to gelation, thixotropy and pseudoplasticity, are widely applied.

Polysaccharides are generally applied for oil recovery as key component of water-based drilling fluids, and fluids for well repairmen and completion. 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.

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.

Injection of polymer solutions into the oil reservoir allows to increase considerably oil recovery in comparison with conventional water flooding.

The PhD dissertation of Nurakhmetova Zhanara performed 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.

2. The scientific results within the framework of the requirements for thesis (according to points 127 from 31.03.2011, Rules of awarding of scientific degrees).

The thesis has the integrity to the unity of scientific arguments. The scientific data have been described concisely and consistently. Most of results are new and were validated by using modern methods and equipment. The main parts of the research results were published in 32 papers, among them 2 in the international journals with impact factor, 2 in the journals which are included into Scopus database, 4 papers are

in the journals that are in the list of the Committee of Science of Ministry of Education and Sciences of RK, and 12 abstracts in the proceedings of the international conferences.

The thesis is well organized with logical appearance of each chapter. It is illustrated with 57 figures and 30 tables. The literature survey has been written using modern scientific information and it reflects the current state and role of synthetic and natural polymers in the oil and petrol industry. Materials, methods of research, results and their discussion show that the actual performance of work is made by the author. Overall, the work corresponds to requirements for the PhD theses.

3. The degree of validity and reliability of each outcome (scientific position), the findings and conclusions of the applicant made in the dissertation.

The scientific results are presented in the following hierarchy: i) physicochemical properties of gellan and xanthan polysaccharides, ii) modification of cornstarch, identification of structure and investigation of properties of the CMCS, iii) development of drilling fluids based on polysaccharides, iv) development of polymer flooding reagents based on polysaccharides, v) economical evaluation of the developed drilling fluids, vi) behavior of gellan and xanthan solutions in a sand pack model and comparison of their effectiveness with polyacrylamide.

Each described section represents a comprehensive research study. The obtained results are interpreted based on the data of the literature survey on the selected subject. In dissertation author develops the clayless and clay containing formulations for drilling fluids with high economic benefit. In conclusion part the author studied the application of gelpolymer injections of gellan for EOR resulting in additional oil extraction and reducing the water content in production well. This result is very important for development of drilling fluids and polymer flooding reagents based on polysaccharides. The results of work has widely been discussed at the International conferences and published in International journals, which reflects the importance of the scientific work and the originality of the research.

4. The degree of novelty of every scientific result (position) and the withdrawal of the applicant made in the dissertation.

- For the first time it was studied the sol-gel and gel-sol phase transitions in gellan and gellan-xanthan solutions in the presence of low-molecular-weight salts and oilfield brine water for development of drilling fluids and gel-polymer reagents for injection into low-permeable reservoir;

- For the first time it was developed the novel drilling fluids and oil recovery reagents based on polysaccharides that are produced in Kazakhstan to provide wellbore strengthening during drilling of unstable rocks and to produce additional oil.

- For the first time it was conducted 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.

5. The practical and theoretical importance of the obtained results.

The sol-gel phase transition of gellan in model aqueous-salt solutions and in oilfield saline water is unique for application in EOR.

The rheology of 0.5 wt.% gellan solution at temperature interval of 25 – 55 °C is pseudoplastic. The Newtonian flow of 0.5 wt.% gellan solution is realized at 60–70

°C. The 0.5% xanthan solution is typical viscoplastic liquid at temperature interval of 25-40 °C. However, it transforms to pseudoplastic liquid between 40 and 65 °C. The mixture of gellan-xanthan behaves as a pseudoplastic liquid at whole temperature interval 25-70 °C due to formation of interpolymer complexes between gellan and xanthan stabilized by hydrogen bonds. Gradually changing of gellan-xanthan mixture from pseudoplastic to viscoplastic liquid in the presence of salts is supposed to be the result of formation of ternary polymer metal complexes. The brine-initiated gelation of gellan may be used for plugging of the high-permeable channels of oil reservoir and as a shut-off agent in polymer flooding technology.

Water-soluble CMCS were prepared by carboxymethylation of cornstarch. Aqueous solutions of CMCS show high viscosity which reduces upon increasing of temperature and presence of salt. Water-based optimal drilling fluids composed of various polysaccharides, salt and bentonite have been formulated and suggested for application.

The influence of bentonite on rheological characteristics of gellan solution was evaluated to carry up drilled rock particles from the bottom hole of the well to the surface. The gellan-xanthan and gellan-xanthan-bentonite systems represent the pseudoplastic liquids and are suitable for the formulation of drilling fluids.

It should be highlighted that the work contains not only the results of laboratory experiments but also the results of field pilot tests in which the author has participated together with her colleagues.

The drilling fluids were tested in the field conditions by JSC "Volkovgeology" at the Irkol drilling site (Shieli, Kyzyl-Ordinsk region). In the positive Test Report it is outlined that the main advantage of suggested drilling fluids in comparison with traditionally used drilling fluids the simplicity and quickness of preparation.

Also the gellan solution was injected to oil reservoirs of "Kumkol" with participation of JSC "Turgay-Petroleum" and JSC "NIPIneftegaz". The common technological efficiency was equal to 5805 tons of additional oil recovery during 6 months.

6. The comments, propositions on the thesis.

There are some minor comments and propositions concerning this PhD thesis:

1. In dissertation the interpretation of CH stretching vibration shifts in IR spectra of solid precipitated gellan from oilfield saline water as a result of the effective surrounding of functional groups of gellan by mono- and divalent cations of saline water is not entirely clear. This shift can be caused by intermolecular interactions of gellan macromolecules due to gel formation.

2. Author explains the viscosity change at the first 10 days of gellan solutions storage by the h-bonds formation and destruction in polymer structure but there is no explanation of such behavior.

3. What is the basis of the assumption that oil reservoir gellan solution may be stable to biodegradation during several months? There is no any evidence of this suggestion.

4. In the dissertation the author not give a sufficient explanation of the temperature impact on viscosity of xanthan solutions.

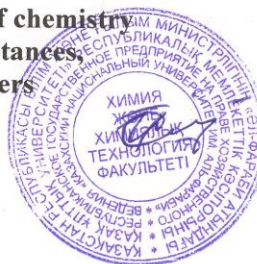
5. Why the rheological study of gellan-xanthan was conducted only for solutions of NaCl, KCl, MgCl₂ and CaCl₂ and not for oilfield water?

In spite of these comments the PhD thesis of Nurakhmetova Zhanara has been performed in high level, contains a valuable results that are discussed in good manner, all elements are in logic sequence to accept the main idea of the dissertation. The minor remarks are not influenced on the dissertation level.

7. The conformity of the dissertation to the requirements of “Regulation of the attribution scientific degree”

Taking into account the valuable contribution of the dissertation for formulation of drilling fluids and development of reagents for oil recovery it is recommended that the dissertation of Nurakhmetova Zhanara entitled: “Synthetic and natural polymers for oil production and development of drilling fluids” completely meets the requirements of the Ministry of Education and Science of Republic of Kazakhstan "Regulation of the attribution of scientific degrees" for the degree of Doctor of Philosophy (PhD) on specialty 6D073900 – Petrochemicals and the applicant can be awarded by this degree.

**Deputy Head of Department of chemistry
and technology of organic substances,
natural compounds and polymers,
PhD, assoc. prof.**



Galiya Irmukhametova