

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 devoted to the study of of gellan, xanthan, carboxymethylated cornstarch and their mixtures as drilling fluids and polymer flooding reagents. Green chemistry approach is growing quickly and the substitution of petroleum derived materials with bio-based materials is greatly enhanced for environmental and health concerns. The affect of polysaccharides in industrial applications is colossal. 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 convenience of polysaccharides in industry without a doubt depends on the wide range of their functional properties. 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.

Excessive water cut of oil reservoirs shortens the exploitation life of wells and leads to seriously corrosion of equipment.

Injection of polymer solutions into the oil reservoir permits to extend considerably oil recovery in comparison with conventional water flooding. Polysaccharides that are characterized by gelation properties, stability to high mineralization and temperature are perspective reagents for oil recovery.

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 scientific data have been described concisely and consistently, fully show the position for the defense. Most of results are new and the scientific data were validated by author. The main parts of the research results were published in 32 papers, among them 2 is in International journal with impact factor, 2 is in the journal that is included into database of Scopus, 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 of papers and materials are in International Conferences.

The thesis has the integrity to the unity of scientific arguments. The thesis 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 petrol industry. Materials, methods and results 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, iii) identification structure and investigation properties of the CMCS, iv) development of drilling fluids and polymer flooding reagents based on polysaccharides, v) behavior of gellan and xanthan solutions in a sand pack model, vi) comparison of the effectiveness of gellan and polyacrylamide.

Each described section represents a comprehensive research study. The obtained results are discussed attracting the results of the literature survey on the selected subject. In conclusion part of the dissertation the author outlines that the gel formation of gellan depends on the concentration of the polymer, the nature and concentration of low-molecular salts. 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.

- Conformational, sol-gel and gel-sol phase transitions of gellan and gellan-xanthan mixture in the presence of low-molecular-weight salts and oilfield brine water for application and development of drilling fluids and flow deviation technology – gel-polymer injection of polymer reagents into low-permeable reservoir;

- Formulation of 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.

- 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.

In order to model the behavior of aqueous solutions of gellan, xanthan, carboxymethylated cornstarch and their mixture in oil reservoir conditions and as drilling fluids, Nurakhmetova Zhanara has studied the viscosity, rheology, sol-gel phase transitions of polysaccharides in the presence of low molecular weight salts and oilfield saline water. The main attention was paid to solution behavior of gellan because it possesses excellent gelling property in the presence of low molecular weight salts. The mechanical properties of gellan gels were studied in the presence of alkaline, alkaline earth metal salts and in oilfield water. As a result, the Young

modules and breaking stresses were found. Sol-gel transition of gellan and gellan-xanthan solutions inside of sand pack model was demonstrated.

By chemical modification of cornstarch – domestic product of Zharkent corn-syrup plant – the water-soluble carboxymethylated cornstarch possessing a high modification degree, viscosity and hydrodynamic size has been synthesised. Carboxymethylated cornstarch is one of the key component of drilling fluids.

The influence of gellan, carboxymethylated cornstarch and xanthan mixture together with bentonite on the rheological characteristics of drilling fluids was evaluated for simulation of drilling mud ability to carry up the drilled rock particles from the bottom hole of the well to the surface. The structural-mechanical, filtration and filter cake forming properties of drilling fluids and fluid loss indicators of CMCS were found. The obtained results will be useful to select the optimal concentrations of polysaccharides to be injected into the oil reservoir for application in EOR and as drilling fluids.

The drilling fluids were tested in the field conditions by JSC “Volkovgeology” from July 14 to July 20, 2017 at the Irkol drilling site (Shieli, Kyzyl-Ordinsk region). In the positive ACT of tests it is outlined that the main advantage of suggested drilling fluids in comparison with traditionally used drilling fluids the simple and quick preparation.

In July 2017 the gellan was injected to oil reservoirs of “Kumkol” with participation of JSC “Turgay-Petroleum” and JSC “NIPIneftegaz”. The common technological efficiency during 6 months was equal to 5805 tons of additional oil recovery.

6. The comments, propositions on the thesis.

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

1. For formulation of drilling fluids and development of reagents for oil recovery author uses gellan, xanthan, carboxymethylated cornstarch, and polyacrylamide. However, information on the price of natural and synthetic polymers is absent to evaluate the economic feasibility of used polymers.

2. In Experimental part the molecular weights of gellan and xanthan are not given. How the molecular weights of natural polymers influence on the properties of drilling fluids and reagents for EOR?

3. It is stated that aqueous solution of carboxymethylated corn starch behave polyelectrolyte character. However, there is no any viscometric justification of this fact.

4. The results of the polymer flooding experiment summarized in Table 2 show that the gellan-xanthan (2:1) mixture plugs pore space less effectively than gellan solution itself. Moreover, mixing of xanthan with gellan doesn't yield the improvement of oil displacement and doesn't increase the resistance to water flow. In that case, what is the reason of preparation of gellan-xanthan (2:1) mixture and injection of this mixture into oil reservoir?

5. The list of abbreviation is too short and does not reflect some terminology like IFT, ASP, DSC, TGA, DTA, IPC etc.

6. There is some stylistic and grammatical mistakes. The English language of the dissertation might considerably be improved. It would be better to attract the native English speaker (co-advisor) for proofreading.

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" fully corresponds to the requirements of the Ministry of Education and Science of Republic of Kazakhstan "Regulation of the attribution scientific degrees" for the degree of Doctor of Philosophy (PhD) on specialty 6D073900 – Petrochemicals and the applicant can be awarded by this degree.

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