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**Study of the possibility of gel forming polymers application for the
productivity increase of oil wells**

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Abbreviations

CCO – Conformance control operations;
CDGs – Colloidal Dispersion Gels;
CSGs - Colloidal Silica Gels;
DPR – Disproportionate Permeability Reduction;
DW – Distilled water;
FOT – Fall-off Test;
GOR – Gas Oil Ratio;
HCPV – Hydrocarbon Pore Volume;
ICP - Inductively coupled plasma mass spectrometry;
IOR – Incremental Oil Recovery;
 N_{Da} - Damkohler Number;
PHPA – Partially Hydrolyzed Polyacrylamide;
PPGs – Preformed Partial Gels;
PV – Pore Volume;
RF – Resistance Factor;
RRF – Residual Resistance Factor;
RRFo - RRF to oil;
RRFw – RRF to water;
SG – Silicate Gels;
Sor – Residual oil saturation;
TAPs – Thermally Activated Particles;
TDS – Total dissolved solids;
WOR – Water Oil Ratio;
WST – Water Shut-off Operations.

1 Introduction

Excessive water production from oil reservoirs shortens production life of wells [1] and leads to intensive corrosion of equipment [2, 3], moreover, disposal of produced water costs tens of billions of dollars annually [4]. Early excessive water production as a result of premature water breakthrough *via* high permeability channels of the reservoir [5] is an indication of poor reservoir sweep efficiency and oil displacement [6]. This problem is more pronounced for mature reservoirs in which the formation of super high permeability thief zones induced by long-continued intensive water flooding is common [7]. Thus, control of water production in mature water flooded reservoirs may be considered as one of the most important priorities in the process of oil field development [8].

It was proven that *in-situ* redirection of water flow through the modification of reservoir permeability gives the second productive life to mature oilfields [9]. Permeability reduction treatments are referred as conformance control operations (CCO) when applied in injectors and water shutoff treatments (WST) when applied in producers [10, 11]. The invention of these methods dates back to the first half of the 20th century [12], but the real era of permeability modification treatments began in the 1970s [13] after the first discovered big oilfields had matured as a result of several decades long water flooding operations [14]. Since that time a number of technologies were proposed among which gel systems have gained the widest application [15].

Despite wide chose of plugging materials water production control is still an urgent problem for most oil producing companies. As the matter of fact, in 2000 around \$40 billion are spent annually to dispose excessively produced water [16]. Today the production of unwanted water still means substantial additional costs and environmental impact since 300-400 million barrels of water are produced per day along with 75 barrels of oil [17].

In Kazakhstan, more than half of produced oil comes from mature oilfields like Uzen, Karazhanbas, Buzachi, Kumkol, Kalamkas, and others. High water cut (up to 90% and more) due to the geological heterogeneity of the reservoirs and several decades long water flooding process is the main reason behind low production rates at mature oilfields [18]. Mainly polyacrylamide and silicate gels have been applied at some of the Kazakhstani oilfields in order to reduce water cut and boost oil production rate. However, practical experience has already proved that despite their effectiveness polyacrylamide and silicate gels possess a number of drawbacks (described in the literature review) and are not recommended to be used under the high salinity conditions [14 p.2, 19-21]. So it is worth to consider the applicability of other plugging materials which may demonstrate better performance at the conditions of Kazakhstani oilfields.

There are a number of polymer materials which were not thoroughly screened and accessed in spite of the potential to become routinely applied for CCO and WST. Polymers with good gelling properties tolerant to high salinity and temperature are the main candidates for COO and WST in oil reservoirs. For example, polymers like

gellan gum and different types of carrageenan gum are used for gel preparation in food industry [22]. The application of these polymers for EOR has been studied before [23], however, the previous works did not account for the behavior of gellan at different permeabilities, water salinities and temperatures.

The aim of this work is to examine the applicability of gellan gum for water shut off operations and productivity increase treatments in oil wells.

The object of the study is plugging materials used for permeability reduction treatments in oil reservoirs and their application features.

The subject of the study is the biopolymer gellan gum and its hydrodynamic behavior in brine and oil saturated porous media.

In the course of performing this research the author realized the following aims:

- 1) The literature review of the existing permeability reduction technologies and plugging materials invented and applied worldwide in light of their advantages and drawbacks.

- 2) The extensive laboratory analysis of the biopolymer gellan as plugging material in order to determine the range of reservoir conditions at which this polymer can be successfully applied.

- 3) The study of the hydrodynamic behavior of gellan gum aqueous solution inside of brine and oil saturated porous media.

- 4) The field pilot tests of gellan gum.

- 5) The comparative analysis between gellan gum and its alternatives.

It should also be stressed that this dissertation presents extensive literature review that summarizes the most popular versions of *in-situ* bulk gels and microgels including partially hydrolyzed polyacrylamide (HPHA) crosslinked with chromium acetate (HPHA/Cr⁺³), colloidal dispersion gels (CDGs), preformed particle gels (PPGs), Bright Water, silicate gels and etc., in light of their advantages and drawbacks revealed after laboratory studies and pilot tests. So the dissertation may be also considered as a guideline on the selection of gel treatment technology suitable for certain.

The studied biopolymer gellan transforms into gel phase upon the contact with salty water (brine) this feature makes gellan distinguishable among other polymer plugging materials since no extra chemicals are required to initiate the gelation process. Though there have been other developments like an aqueous solution of hydroxypropyl cellulose (HPS)/sodium dodecyl sulfate (SDS) and self-thickening polymer (STP), the literature review showed that due to the instability in the presence of divalent cations or too rapid gelation none of these brine initiated gels were applied in field conditions [24-27].

Thus the current dissertation is considered as relevant since it focuses on the full range of laboratory studies of gellan gum as an agent for permeability reduction in oil reservoirs. The conducted research covered bulk rheology tests, bulk gel strength tests, sand pack and core filtration tests, field pilot tests conducted in injection and production wells of Kumkol and Karabulak oilfields. The obtained

results prove the suitability of gellan gum application under the range of reservoir conditions which also has been determined by this study.

The practical significance of the work. The conducted laboratory works determined the range of reservoir conditions within which the effective application of polymer gellan is possible. As a result, the recommendations on the application of gellan for the treatment of injectors and producers have been given. The interpretation of the results of the field pilot tests suggests high efficiency of gellan gum for the isolation of discrete high permeability fractures and channels.

The scientific novelty of this work consists in the following:

- 1) The hydrodynamic behavior of the gellan aqueous solution inside of salt saturated porous space with different permeabilities has been studied for the first time (fig.37).
- 2) The ability of gellan gel to decrease permeability of the porous media depending on the salinity of saturating water and temperature has been investigated (fig.41, 43, 44).
- 3) The effect of gellan solution on the reduction of oil permeability has been demonstrated (fig.51).

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

1) A unique feature of gellan gum makes it convenient one-component gelant that can be used for the isolation of watered out thief layers. Exceptional stability of gellan gel in the presence of divalent cations (fig.28) is an advantage of this polymer over its counterparts.

2) Taking into account the properties of aqueous gellan solution, alternating injection of gellan and brine slugs is recommended for the near wellbore treatments (fig.39). It has been demonstrated that the alternated injection regime allows the reduction of the amount of polymer used at least in 2 times. However, for the in-depth treatments, the continuous injection of gellan solution after sufficient pre-flush is the best choice (fig.49).

3) The results provided by JSC “Turgai Petroleum” prove the efficiency of gellan for the treatment of injection wells. According to the report, the injection of 2 tons of dry gellan powder into the injectors 3383 and 3065 allowed the incremental production of 5,890 tons (43108 bbls) of oil during 11 months after the treatment (table 8). At oil price 50 USD per barrel and gellan cost 4.5 USD/kg the net profit turns out to be around 2 million USD excluding the cost of the equipment rental.

4) The efficiency of gellan for the treatment of producing wells has been proved by the results presented by LLP “Soth-Oil” (see the Appendix). According to the report, the injection of 120 m³ of 1% concentrated gellan solution into the production well K-34 resulted in the reduction of water cut from 80 down to 40% (fig.60). The comparison of the well performance before and after the treatment proves the high efficiency of gellan gum for the plugging of discrete high permeability channels and fractures.

The results of this research are represented by graphical and numerical data obtained by rheological, liquid filtration as well as analytical chemistry experimenting methods. Also, sufficient amount of data were obtained through the monitoring of the production wells' performance at the tested sites of Kumkol and Karabulak oilfields.

2 Literature review

This section contains the review of the most popular materials (technologies) used for WST and CCO worldwide. As a result of the reviewing not only laboratory developments but also field trials results each of the reviewed technology was summarized according to its application range at different rock type, permeability, temperature, as well as brine and makeup water salinity conditions. The ability of each material to provide disproportionate permeability reduction (DPR) and in-depth propagation was also accessed. The table 3 presents the summary of the conducted review.

Since each of the currently applied materials (technologies) was introduced to solve the problem of excessive water production within the certain range of reservoir conditions, the conducted review helped to justify the necessity of introducing one-component gellan gum solution as a gelant that allows effective bulk gelation at high salinity conditions without the need for the addition of crosslinking agent and in-situ transportation problems associated with its stripping from the bulk solution.

The completion of this review also allowed proper design of laboratory and field tests.

2.1 PHPA/Cr⁺³ *in-situ* bulk gels

Application of aqueous solution of PHPA/Cr⁺³ for CCO and WST was proposed in 1972 [28]. Since that time this system along with its modified versions was numerously tested and implemented throughout the world [13 p.44-51, 29-33]. Later research allowed the application of this gelant at temperatures up to 135 °C [34-36].

In 1980s 17 injectors and 18 producers located in carbonate and sandstone formations of Wyoming's Big Horn Basin have been treated by PHPA/Cr⁺³ [37]. It is worth to note that 98.3% of the total IOR (128,000 bbls) was attributed solely to the injectors' treatment. While the producers demonstrated the decrease of oil flow rates along with the reduction of water cut [13 p.44-51, 33 p.15-17]. Liao (2014) [9] and Perdomo et al. (2007) [38] mentioned that such result is a common outcome of WST. This is partly due to the complex geology that makes the selective plugging of watered out zones difficult to achieve [39-41].

At low permeability contrasts between oil and water zones or high vertical permeability the viscous gelant solution tends to invade into both zones [42-48]. Since high permeability channels usually occupy less than 10% of the whole formation volume [49], large portion of the gelant may leak-off into oil-bearing zones. In one field treatment, it has been shown, that the volume of the leaked-off viscous plugging agent exceeded the volume of the thief zones in 10 times [39 p.226, 50]. In this respect, identifying the extent to which PHPA/Cr⁺³ gel can decrease permeability to water more than to oil is of high importance.

In the laboratory tests of Liang et al. (1992) the treatment of Berea sand cores by some traditional *in-situ* bulk gels, including PHPA/Cr⁺³, resulted in 2-100 fold

reduction of water permeability, whereas oil permeability decreased in 2-15 times [51]. Seright et al. (2004) demonstrated that PHPA/Cr⁺³ gel regardless of rock wettability nature reduced permeability to water in 80-90 times more than that to oil [52]. In the study of Willhite et al. (2002) this value varied between 100 and 1000 [53]. It was revealed that depending on the wettability of the porous space different mechanisms of DPR effect are activated [52 p.1-11, 54]. X-ray computed microtomography analysis demonstrated that after the filtration of oil through the gel treated Berea core the size of the gel reduced by 55%, resulting in the coalescence of discrete oil droplets and therefore partial recovery of oil permeability [52 p.5, 53]. In oil-wet porous media, the improvement of oil phase connectivity was not observed and DPR effect was explained by the ability of oil to slip along the interface between the oil-wet pore walls and the gel [52 p.1-11].

The extent to which PHPA/Cr⁺³ can provide DPR effect heavily depends on permeability contrast between oil and water zones. As Fig.1 shows the gel containing

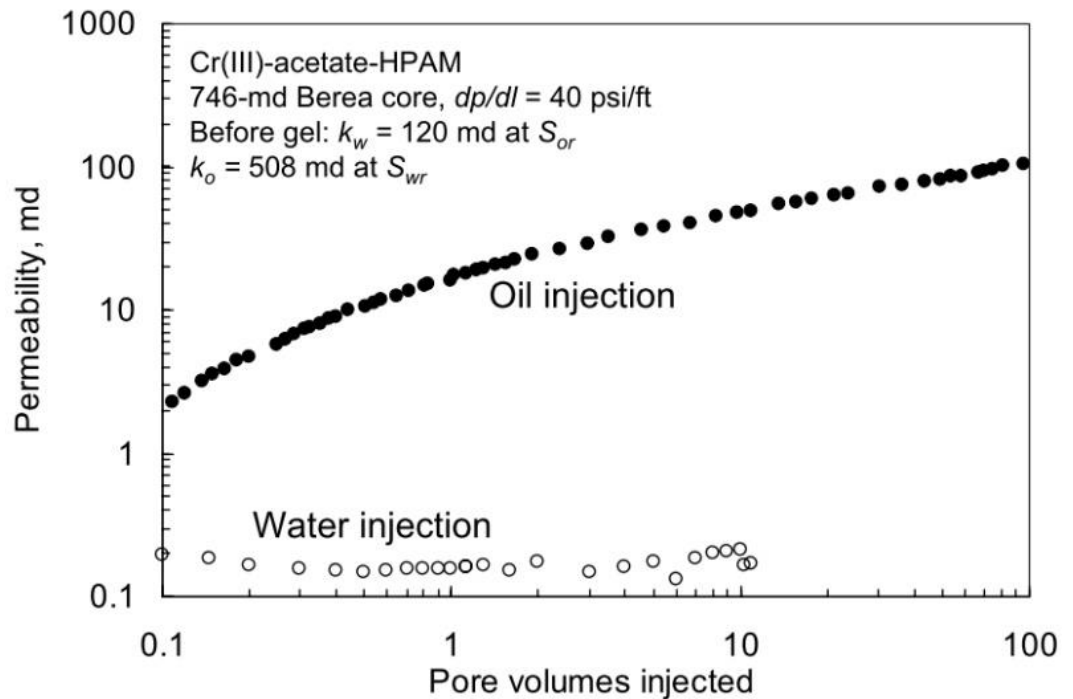


Figure 1 - Permeability to oil and water versus injected volume in Berea sand core sample [55].

5,000 ppm of PHPA and 417 ppm of Cr⁺³ decreased water and oil permeabilities of hydrophilic Berea core in 700 and 4.8 times respectively. However, it required 100 PVs of oil to be pumped through the core until the oil permeability reached its highest value. The author argued that this suggests the necessity of limited gel penetration (less than few feet) into oil-bearing zones in order to provide such kind of DPR effect. Moreover, the decrease of oil permeability in more than 2 times may be considered as unacceptable in some cases [55 p.1-10]. In fact, the plugging agent formulations that may decrease water permeability by a factor of 10 are not recommended for the treatment of multilayered matrix reservoirs with vertical cross-flows [41 p.2].

However, for fractured formations the risk of oil permeability damage might not be so high [56]. Seright and Liang (1994) concluded that during the 1970s and 1980s the most successful production well treatments have been conducted in naturally fractured carbonates [39 p.223]. However, the permeability of fractures should be high enough to provide the intake and prevent the invasion of the gelling agent into oil saturated matrix. In addition, the existing system of fractures should not connect between oil and water zones. In fact, core and well test data helped to find out that the few successful WST at the mentioned above Big Horn Basin have been conducted in producers that intersected high permeability fractures connected with the aquifer. Whereas failed WST have been conducted in areas intersected by fractures that connected oil and watered out zones, so even relatively small volumes of plugging agent (6-920 bbls), at polymer concentration and the [polymer]:[crosslinker] ratio equal to 2,000 - 2,200 ppm and 88:1 respectively, caused the reduction of both water and oil rates [33 p.8].

Sydansk and Seright (2006) provided a guidance on the application of permeability modification treatments in both injectors and producers with regard to different geological conditions of the reservoir and some more detailed explanation of pre- and post-treatment hydrodynamic processes [57].

In the case of injection wells treatment, near wellbore geology is less critical, since oil permeability damage occurs far away from the producers. CCT conducted in 2008 at Guarda oilfield in Colombia and other examples described below support this claim. As the mechanical isolation of the thief zone failed to correct the injection profiles inside of two-layered fractured reservoir, 25,736 bbls of PHPA/Cr⁺³ solution at polymer concentration increasing from 2,000 to 8,000 ppm has been injected, aiming deeper plugging of the upper layer. Despite severe vertical cross-flows, no zonal isolation of the lower layer has been undertaken. The payout was achieved within 6 months after the treatment, while IOR calculated in 2011 was equal to 172,600 bbls [58]. During April-August of 2009 at the mentioned above Big Horn Basin, 7 producers were aggressively treated with 8,200-11,400 bbls of PHPA/Cr⁺³ gelant at polymer concentration increasing from 3,000 to 10,000 ppm. Despite the isolation of the oil-bearing zone by the packer, it was damaged and resulting decrease of water cut on 72% was accompanied with oil rate reduction on 56%. However, the treatment changed fluid dynamics of the reservoir and increased the average oil flow rate of 22 surrounding wells from 1,270 to 1,340 bbls/day [59], showing that treatment of the injectors would have been a better choice at the existing geological conditions. In August 1997 fractured dolomite reservoir at McElroy field (Texas) with matrix permeability of 3 mD have been subjected to the injection of 113 bbls of PHPA/Cr⁺³ gelant through the injector 23 in order to plug the thief conduit connecting it with the producer 6. As a result, water production decreased from 230 to 45 bbls/day. By October 1997 oil production increased from 0 to 5 bbls/day. In March and October 1998 five additional treatments were conducted in neighbor wells, the injected volumes of gelling solutions ranged between 500 and 2,000 bbls per treatment. By October 1999 36,000 bbls of incremental oil were produced at the cost \$1-3.6 per barrel. At oil price \$10 per barrel the project's costs were paid off

during ten months after the treatment. This example showed that when applied right the bulk gels may be effective even at low oil prices [60].

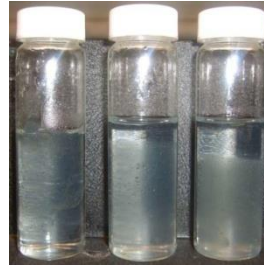
Application of high concentrated PHPA/Cr⁺³ gelling solutions in producers is often necessary to ensure that gel will not be washed out after the placement. However, in the mentioned above field test at Big Horn Basin high concentration of PHPA (20,000-22,000 ppm) caused injectivity and cost restrictions. As a result, only small portion of the reservoir has been treated and most probably, it was the reason why the increase of oil production in few producers was followed by its rapid decline [33 p.15-18]. Manrique et al. (2014) also reported on this problem [61].

Since PHPA/Cr⁺³ gelling solution is composed of high and low molecular weight components, precipitation and chromatographic separation may cause uneven distribution of PHPA and Cr⁺³ within near wellbore zone [62-66]. In fact, Ganguly et al. (2002) evidenced the decrease of Cr⁺³ concentration from 100 to 20 ppm inside of the fracture due to the diffusion of chromium to the Berea core matrix during 17 hours shut-in period, while the concentration of PHPA did not change significantly [67]. As a result, no gel has been formed. It should be noted that in the experiments of Ganguly et al. (2002) PHPA/Cr⁺³ was placed as a gelant - not as a formed gel. If it had been placed as a formed gel, there may not have been a problem. Ganguly et al. (2002) also mentioned that pH increase due to the dissolution of carbonates by polymer solution may induce chromium precipitation, however, this phenomenon needs to be investigated further.

The effect of shear stress on the gelation time and final gel strength of PHPA/Cr⁺³ formulations should always be considered. Combined interpretation of the results of Broseta et al. (2000) [68], Aslam et al. (1984) and Huang et al. (1986) suggests that depending on the molecular weight and concentration of the polymer, the applied shear rate may accelerate, delay or not affect the gelation time [69, 70]. However, a study that would cover a wide range of temperatures, polymer concentrations, and molecular weights, as well as the duration of shearing periods, has not been found in the literature.

Shear stress may also induce the syneresis of PHPA gels. McCool et al. (2007) exposed the gelants containing 5,000 ppm of high molecular weight ($6 \cdot 10^6$) PHPA and 100 ppm of Cr⁺³ with bulk gelation time around 5 hours to shearing for 20 hours [71]. As it may be seen from Fig.2 the gels exposed to higher shear rates demonstrated more pronounced syneresis. Thus, the effect of shearing on the dehydration of the gel should be always taken into account. This is especially important when dealing with production well treatments, since the effect of the treatment may be considerably shortened in time due to the reservoir water breaking through the syneresis induced voidages in gel structure.

Salinity and chemical composition of makeup water may be a limiting factor for PHPA/Cr⁺³ gelant application. In fact, 2,000 ppm content of divalent cations in



a) b) c)

Figure 2 - PHPA/Cr⁺³ gels after being sheared at 1 s⁻¹ (a), 10 s⁻¹ (b) and 100 s⁻¹ (c) during the gelation and aged for 130 days [71].

makeup brine is enough to cause the precipitation of the polymer at 75 °C [72]. Moradi-Araghi and Doe (1987) conducted a detailed study on the solubility of PHPA at a wide range of hydrolysis degrees, divalent ions concentrations and water temperatures [73]. It should be also noted that the difference between the salinities of makeup water and water which will come in contact with the gel inside of the reservoir may influence the plugging efficiency of PHPA/Cr⁺³ gels [74]. Brattekås et al. (2015) proved that low salinity water is more preferable for chase flooding, since unlike 79 ppm brine it does not cause the rupture of the gel [19 p.15].

It also should be mentioned that because of environmental protection concerns the inorganic (Cr⁺³) and organic (phenol/formaldehyde and polyethyleneimine) crosslinkers have been prohibited in some countries [75].

The next chapters review several popular technologies invented to overcome some of the disadvantages inherent for the PHPA/Cr⁺³ gels.

2.2 Colloidal dispersion gels (CDGs)

From the above section, it is clear that traditional in-situ bulk gels are not the right choice for multi-layered formations with ordinary permeability and sufficient cross-flows between the layers [76, 77]. Even mechanical isolation of oil zones may be useless if high vertical permeability is present [78, 79], in such case regular polymer flooding might be a better choice [80].

Seright and Liang (1994) mentioned that a gelant which in its activated state would propagate through the reservoir is a good variant for the treatment of multi-layered formations. The introduction of such gelant system would have allowed the same sweep improvement at a smaller volume of injected slug, as compared to regular polymer flooding. However, the authors highlighted that regrettably such gelant does not exist [39 p.6]. Remarkably the propagation of gels through matrix strata was claimed to be impossible at normal permeabilities (less than 1 D) [81]. However, this goal may be achievable in fractured reservoirs. For example, Sydansk and Moore (1990) suggested that the application of PHPA/Cr⁺³ gels, which were formulated to flow in fractures, for the treatment of the injectors at the fractured reservoir of Big Horn Basin most probably resulted in the increase of the treated reservoir volume to the size of the whole interwell pattern. The fact that the profiles of the injection wells did not change after the injection of relatively large volumes

(640-37,000 bbls per treatment) of PHPA/Cr³⁺ at moderate polymer concentrations (around 5,000 ppm) and the [polymer]:[crosslinker] ratio varying between 44:1 and 88:1 indicates in-depth propagation of the formed gel. As a result, 128,000 bbls of incremental oil have been produced [33 p.1, 18].

Later on the formulations with lower concentrations of PHPA (100-1,200 ppm) at the [polymer]:[crosslinker] ratio ranging between 20:1 and 100:1 were screened and claimed to provide the described above effect of flowing gels in matrix strata [82-84]. Due to the low concentration of polymer and crosslinker the slug does not turn into a bulk gel form, but separated gel particles with the size of 1-150 nm are formed instead [85, 86].

Mack and Smith (1994) stated that low concentration of the crosslinker should prevent the chromatographic separation of low and high molecular weight components, because at high ratio of anionic PHPA to cationic crosslinker the later tends to be more associated with polymer chains rather than with cationic rock [82 p.527-534]. On the contrary Ranganathan et al. (1998) found out that during the injection of 2 PVs of freshly prepared 300 ppm PHPA/15 ppm aluminum citrate solution into 4 ft long sandpack model with permeability 3-4 D the concentration of aluminum in effluents was varying between 0-10 ppm, due to this fact the effluent samples never formed gel (Fig.3) [87]. Results of Ranganathan et al. (1998) suggest that at reservoir conditions the retention of aluminum will reduce the gel treatment process to a regular polymer flooding operation [88].

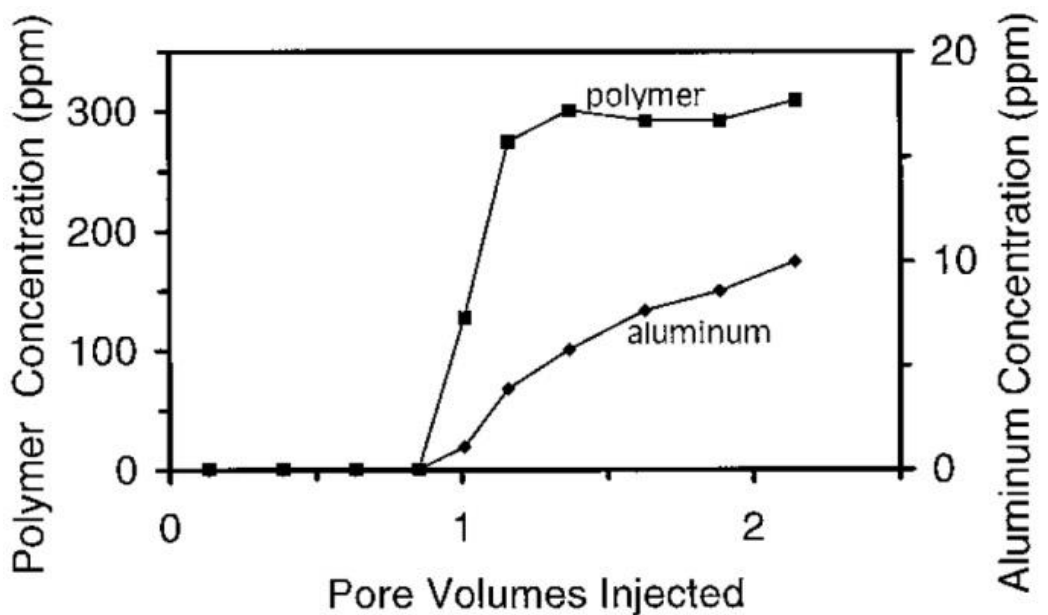


Figure 3 - Concentration of polymer and aluminum in the effluent samples [87 p.340].

It was claimed that due to the low polymer and crosslinker concentration, the application CDGs, unlike traditional bulk gels, is not restricted by injectivity problems [82 p.527-534]. Mack and Smith (1994) reported that in lab conditions at differential pressure (transition pressure) varying between 0.017 and 0.13 MPa the gel particles start to propagate through the pack of 100-mesh screens experiencing the

shear thinning effect. This property of CDGs was claimed to provide the possibility of deeper placement - beyond the vicinity of the injector [82 p.538]. However, since the differential pressure tends to decrease with distance from the injection well, in-depth propagation of large CDGs volumes should be accompanied with the uniform rise of injection pressure and may be problematic [89]. Experimental works of Seright (1994) and Al-Assi et al. (2009) are among those that question CDGs' ability of in-depth propagation in reservoirs without super high permeability features. In fact, Al-Assi et al. (2009) concluded that in-depth propagation of the tested CDGs formulation inside of 10 D permeability matrix media at the interstitial velocity of $5 \text{ ft}\cdot\text{day}^{-1}$ is limited to as low as 12 feet [90, 91].

In his review on CDGs Seright (2015) has examined 24 papers advocating and questioning the validity of this technology, as a result he stated that there is no evidence that CDG's can propagate through conventional matrix rock [88 p.63]. Based on these results it was concluded that high injection rates reported in the descriptions of the successful CDGs treatments [61 p.1-13] would have been impossible if the injection wells had not been connected with super high permeability features [87 p.337]. In the same time, Chang et al. (2004) reported on the failed CDGs treatment of an injector which was unsuccessful because of severe polymer and crosslinker breakthrough caused by 30 years of water flooding. So the range of permeabilities within which the successful application of CDGs is possible is still has to be determined [92].

Low tolerance to brine salinity is another serious limitation of CDGs, it was reported that CDGs could not be used at the salinity of makeup water higher than $30 \text{ g}\cdot\text{L}^{-1}$. In fact, some oil field trials were unsuccessful because of this problem [82 p.527-534]. Experimental results showed that the salinity increase decreases gel strength and retards the gelation of the system [92 p.2]. According to Ranganathan et al. (1998), the presence of chlorine at 0.25 ppm in water caused the gel's deterioration during 24 hours after the moment it was formed [87 p.338]. Even if CDGs formulation has been prepared in fresh water the contact with reservoir brine may significantly affect the properties of in-situ formed gel particles [82 p.527-534].

Number of papers was published, describing the success of CDGs and presenting them as being superior over regular polymer flooding and traditional gels [82 p.527-534; 93, 94]. Seright (2015) questioned the validity of the technology by pointing out some contradictions and obscurities in these papers and provided other plausible explanations for the mechanism of oil recovery increase by CDGs. The findings of Seright (2015) may encourage new interest for the investigation of CDGs validity [88 p.1-63].

Thus, the *pro at contra* evidences of CDGs' ability of in-depth propagation are not enough and additional research is required to clarify the uncertainties. The following chapter describes a technology, which significantly differs from traditional bulk gels and was designed especially for more effective treatment of super high permeability zones.

2.3 Preformed particle gels (PPGs)

The invention of PPGs was motivated by the inability of bulk and colloidal dispersion gels to operate under the conditions of severe channeling, high temperature and brine salinity [95].

The PPGs are dried and sieved millimeter-sized gel particles able to form stable suspensions in water [95 p.1-3]. The particles expand in size up to 200 times by absorbing brine [96]. Unlike PHPA/Cr⁺³ the PPGs are effective for all types of brines and salt concentrations, the gel particles were reported to be thermally stable under 110 °C at least during one year [42 p.3]. However, PPGs studied by Tongwa and Bai (2014) were stable at 80 °C only for several days. Therefore, the results of the laboratory investigations of the thermal stability of PPGs may seem controversial at this point [97]. Nevertheless, the treatment of 2 injectors at Zhongyuan field (China) by 20.5 tons of dry PPGs proved their effectiveness at high temperature (107 °C) and salinity (150 g·L⁻¹) conditions as 3,239 tons of IOR were produced during 3 months after the treatment [42 p. 1-7, 98].

Unquestionable advantage of PPGs over PHPA/Cr⁺³ is the absence of the separation between low and high molecular weight components inside of a reservoir [83 p.8]. However, according to Suk Kyoon et al. (2006), mechanical trapping may complicate in-depth placement of PPGs [66 p.1]. Sang et al. (2014) reported that one millimeter-sized PPG particles cannot be injected into a porous media unless its permeability is equal to several Darcy [99]. In fact, such high conductive filtration paths are not unusual for fractured reservoirs or formations that have been water flooded for several decades [83 p.1-10]. Goudarzi et al. (2016) injected 5,000 ppm concentrated suspension of swollen PPGs into fractured Berea rock sample. As a result, 24% of IOR was achieved. In field conditions, high effectiveness of the PPGs for the treatment of severely drained zones was demonstrated at one block of Lamadian reservoir in Daqing. The block was in operation for more than 30 years, resulting in average water cut around 95.4%, at reservoir temperature and brine salinity equal to 40 °C and 4 g·L⁻¹ respectively [100]. Since 2003 to 2004 four injection wells were treated with 356,120 bbls of the suspension containing 132 tons of 0.06-3.0 millimeter-sized PPGs. During 10 months after the treatment, 15,000 tons of oil were produced incrementally [42 p.1-18].

It is remarkable that no well plugging had been reported after a number of field applications of PPGs in China. These treatments covered sandstone and naturally fractured carbonate reservoirs with reservoir temperature and brine salinity varying in the range of 20-100 °C and 2-280 g·L⁻¹ respectively [42 p.1-18; 98 p.1-10; 101]. Also, Qiu et al. (2014) summarized the treatments of 655 wells mostly located in unfractured reservoirs and have reported no injectivity problems even though 11.5-20.6 tons of PPGs have been injected per each well [102].

The absence of injectivity problems may be partly attributed to the deformability of the particles [103, 104]. The shear-thinning behavior of PPGs as a result of flow rate increase was evidenced experimentally [105]. For example, it was shown that RF decreased from 15.29 to 9.13 as a result of flow rate increase from 100

to 400 cm³/hr during the filtration of 30,000 ppm concentrated PPGs suspension through sand pack model [106]. Another lab study demonstrated that the filtration of water through the PPGs packs at increased flow rates causes elastic deformation of the gel pack and forces its propagation through the filtration channels of the model [96 p.178-185]. Similar results were obtained by Hamid et al. (2016) (Fig.4) [107].

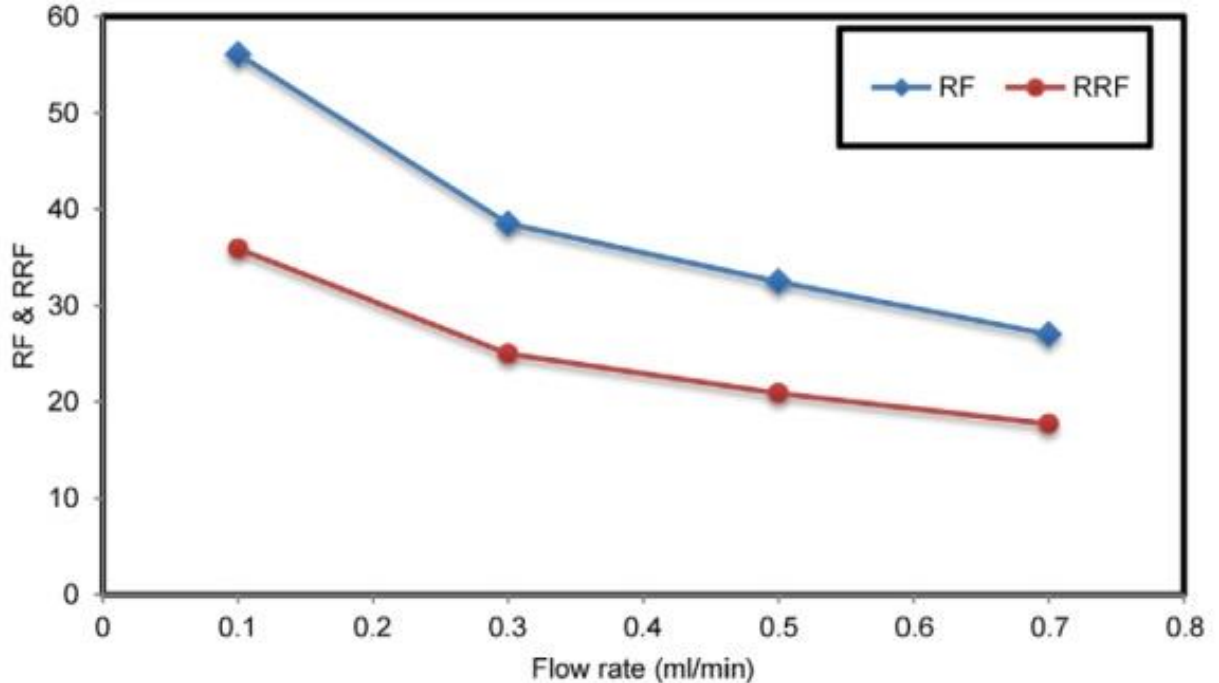


Figure 4 - RF & RRF versus flow rate for 3,000 ppm PPGs suspension at 20 °C and permeability of the porous media around 137 D, PPG swollen particle to pore size diameter ratio is 1.4 [107 p.175-189].

The results of Al-Ibadi and Civan (2012) [106]; Hamid et al. (2016) [107]; Muhammed et al. (2014) [103]; Zhang and Bai (2010) [105] suggest that the swollen PPGs cannot propagate through the porous media unless the applied pressure is high enough to cause the shrinkage of their size below the pore throat diameters [95]. In fact, the filtration of stronger and less deformable PPGs is characterized by higher injection pressure values [103]. For example, Coste et al. (2000) demonstrated that the injection of 1,000 ppm concentrated suspension of strong PPG particles (8# 250 mesh (G gel)) into the core sample with permeability 9.5 D at 2 ml·min⁻¹ was characterized by high amplitude irregular injection pressure fluctuations, indicating repeated formation and distraction of gel cake. While the injection of medium strength PPGs (4# 250 mesh (D gel)) into the sample with similar properties demonstrated propagation of the particles through the pore space without any gel cake accumulation (Fig.5) [95; 106]. However there still no experimental data evidencing that PPGs are able to propagate through low permeability matrix strata, except one laboratory study which determined the lowest permeability limit for the injection of PPGs to be around 0.3 D [108], what seems to be highly unlikely, taking into account large size of the particles. Thus, additional studies are required in order

to determine the exact permeability range within which the application of PPGs is possible.

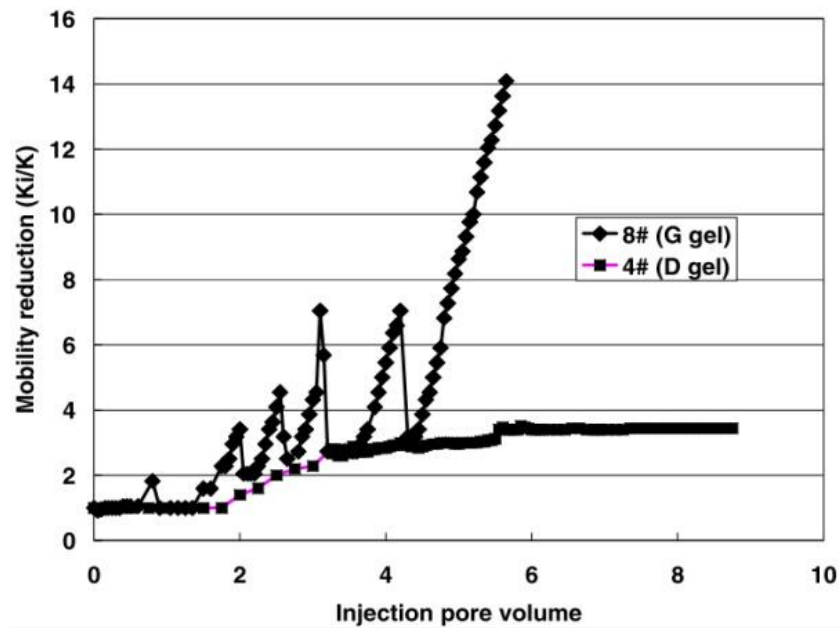


Figure 5 - Effect of PPG particles strength on the injectivity of the suspension. 8# 250 mesh (G gel) – strong PPGs; 4# 250 mesh (D gel) – moderately strong PPGs [95].

The possibility of minimizing the penetration of pre-gelled particles into lower permeability oil-bearing zones by varying their size may be considered as another advantage over traditional liquid gelants [47, 109]. In this context Elsharafi and Bai (2015) have shown that small (100-120 meshes) size PPGs suspended in low salinity (500 ppm NaCl) brine create a permeable gel cake on the surfaces of 3-15 mD cores and decrease their original permeability on 24-65%, while large size PPGs (30-80 meshes) don't damage matrix rock within this range of permeabilities. Imqam et al. (2014b) found that the extent of DPR in modeled fracture filled with PPGs depends on water/oil injection flow rates and gel strength. It was shown that since each cycle of oil filtration through the gel plug caused its shrinkage and dehydration the softer gels provided better DPR effect. As a result, permeability to water has been reduced in 10-100 times higher than that to oil [110].

Imqam and Bai (2015) showed that the gel particles swollen in low salinity brine exhibited less strength and bigger swelling ratio than the particles activated by brine with higher salinity (Table 1). They also have measured the permeability of swollen and packed PPGs versus applied load pressure. Slight permeability increase as a result of the weakest gel particles compression from 150 to 200 psi suggested the formation of micro-channels inside of the pack (Fig.6. (a), 0.05 wt.% NaCl curve). It was concluded that for better plugging of high permeability channels suspensions consisting of particles with a larger pre-activated size and higher make-up brine salinity are preferred (Fig.6) [96].

Table 1 - Measurements of 30-mesh PPGs' swelling ratio and strength [96].

No.	Brine concentration, wt.% NaCl	PPGs concentration (wt.%)	Swelling ratio	Gel strength (Pa)
1	0.05	0.60	165	515
2	1	2.0	50	870
3	10	4.0	25	1300

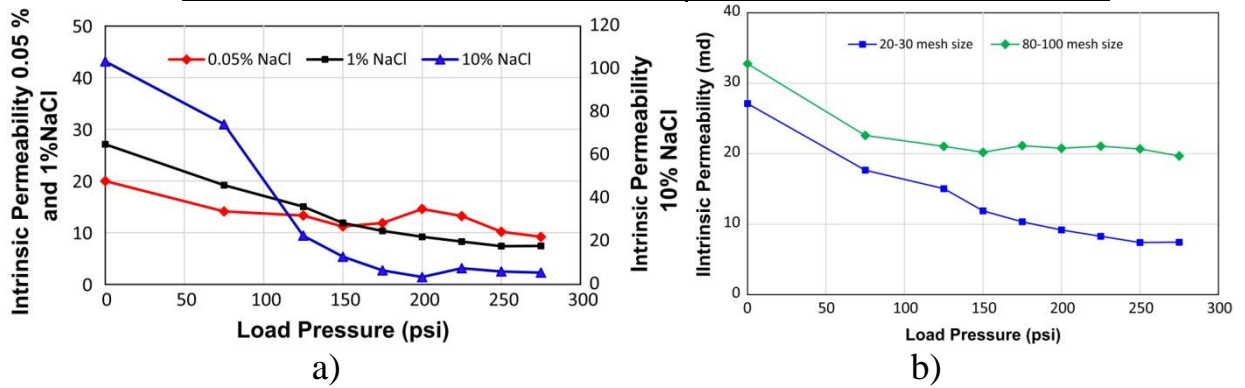


Figure 6 - Permeability of swollen and packed PPGs versus load pressure and a) make-up brine salinity for 30-mesh sized particles; b) size of non-activated particles for 10,000 ppm make-up brine salinity [96].

The accuracy of the conclusions made by Imqam and Bai (2015) was supported by Hamid et al. (2016), who have filtrated 3,000 ppm PPGs suspension through 137 D limestone at 0.1 ml/min and 20 °C. As a result, it was shown that the increase in the size of the pre-activated particles from 37-44 up to 74-105 μm resulted in the increase of RF and RRF values from 50 and 29 up to 118 and 79 respectively. The increase of dry PPGs' size to pore throat diameter ratio was suggested to be the reason behind the increase of RF and RRFs. In the same time, it was shown that the gels with higher swelling ratio due to the lower make-up brine salinity or lower crosslinker concentration demonstrate lower RF and RRFs [96, 107].

In recent time, several researches have been conducted aiming the improvement of PPGs' properties. Tongwa and Bai (2014) showed that the incorporation of laponite XLG nanoclay into the structure of PPGs allowed substantial improvement of gel strength, the swelling ratio of dry particles as well as long-term thermal stability. Tongwa and Bai (2014) see the improvement of thermal stability of nanocomposite PPGs as the most important advantage over conventional PPGs. Similar research has been conducted by Saghafi et al. (2016) who have introduced nano-clay montmorillonite Na^+ into the structure of PPGs in order to make them applicable to the conditions of Persian gulf reservoirs (145 °C and 225 $\text{g}\cdot\text{L}^{-1}$ brine salinity) [97]. However long-term stability of the gels under these conditions have not been studied [111].

To make PPG particles applicable in matrix reservoirs micro- and nano-meter sized particles has become a new drift in the development of the technology [99]. For example, Qiu et al., (2016) have reported successful application of preformed gels with particle size varying between 28 and 1000 μm in the reservoir with temperature

around 125 °C. However, the fact that the permeability of the watered-out zones was more than 1 D does not allow us to suggest that the formulated suspensions would have been successful in regular matrix rock [112].

Below some technologies based on the usage of micro- and submicron-sized polymer particles for matrix treatments are reviewed.

2.4 STARPOL microgels

STARPOL – soft, size-controlled, nontoxic and insensitive to reservoir conditions microgels were proposed in 1999 [113]. The microgels were synthesized by crosslinking of polyacrylamide solution with ZrO_2 under shear stress [114]. Non-toxic microgels based on acrylamide and sulfonate (neutral non-toxic organic crosslinker) have also been known since 2004 [109, 115]. Imqam and Bai (2015) reported that by varying the conditions of crosslinking process the size of gel particles can be adjusted to the range between 10 and 1,000 nm. In the described below lab studies and filed cases 2 μm sized particles were used [96].

The microgels can be produced to be repulsive or attractive to each other. Thus propagation of the microgels through porous media may be accompanied by their monolayer or multilayer adsorption [109]. The character of the interactions between the microgels is expressed through Huggins Constant (K_H): when $K_H < 0.3$ the dispersed colloids are repulsive and when $K_H > 0.3$ the colloids are attractive. As seen from Fig.7, the depth of the microgels penetration increases with the decrease of K_H [116]. Thus by varying K_H any desired penetration depth can be achieved [109].

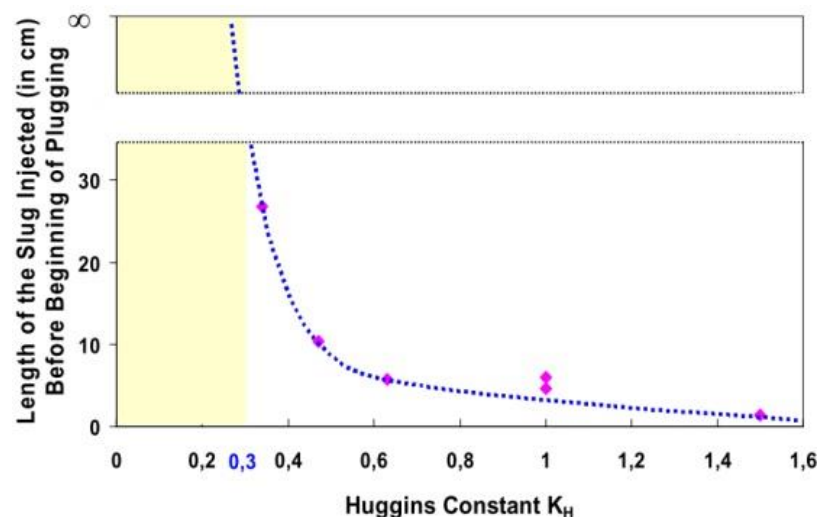


Figure 7 - Effect of Huggins Constant on the propagation of microgels [116].

One example of the microgels' application for in-depth treatment through an injection well was published recently [117]. The well located in the heterogeneous sandstone with permeability ranging from 0.01 to 1 D. Reservoir temperature and brine salinity were measured to be around 50 °C and 8,000 ppm. During 3 months 57,000 bbls (0.1 PV) of 500 ppm concentrated suspension of 2 μm sized microgels were injected into the formation. As a result, 9,900 bbls of additional oil were

produced during one year after the treatment while water production was reduced on 150,000 bbls.

It should also be added that the increase of the injection flow rate reduces RF of the microgels propagation. For example, RFs registered during the filtration of 3,000 ppm concentrated microgels suspension through 0.205 D core sample at 200 and $20 \text{ cm}^3 \cdot \text{h}^{-1}$ were equal to 30 and 50 respectively. While at flow rate of $2 \text{ cm}^3 \cdot \text{h}^{-1}$ the core was plugged by the gels [118]. Similar results were obtained in the work [119].

Dupuis et al. (2013) tested mechanical and thermal stabilities of microgels with different internal cross-linking densities. It was shown that the microgels are stable under shear rates up to $1.2 \cdot 10^6 \text{ s}^{-1}$, whereas other traditionally used polymers lose 50% of their viscosity at shear rates equal to 10^4 to 10^5 s^{-1} . It also was shown that after the aging for one month at $140 \text{ }^\circ\text{C}$ the microgels undergo minimal thermal degradation [109, 120].

Cozic et al. (2008) studied the influence of high saline environment on the properties of the microgels and showed that the salinity has no effect on the hydrodynamic thickness of microgels adsorbed on the surface of rock sample. Even at brine salinity equal to $200 \text{ g} \cdot \text{L}^{-1}$ of mono and divalent ions the adsorbed layers were found to be stable and shear-controlled over-adsorption was detected [121].

Due to low viscosity (2-15 mPa·sec for 0.1-0.3 wt.% concentrated suspensions at $60 \text{ }^\circ\text{C}$), steric effect and possibility of size regulation the microgels were claimed to exhibit the quasi-ideal selective water permeability reduction even under the conditions of bullhead injection [119, 121]. For example, Chauveteau et al. (2004) on the basis of laboratory experiments mathematically simulated bullhead injection of $1.5 \text{ }\mu\text{m}$ microgels suspension into three layered model with cross-flows, permeability of each layer was set to be 1,000, 100 and 75 mD. The results showed that 98% of the suspension volume was placed in the most permeable layer, demonstrating almost ideal selective placement [109]. Rousseau et al. (2005) claimed that the microgels are able to shrink under the impact of oil-water capillary pressure, preventing oil permeability impairment. Comparison of relative permeability curves before and after the treatment of 0.3 D Berea core with $3 \text{ g} \cdot \text{L}^{-1}$ concentrated suspension of the microgels showed that water permeability was severely reduced while oil permeability was not damaged (Fig.8) [115]. Similar results were obtained by Dupuis et al. (2015), who showed that the treatment of 3.8 Darcy core sample with $2 \text{ }\mu\text{m}$ sized microgels resulted in two times reduction of permeability to water while oil permeability was not damaged at all [119].

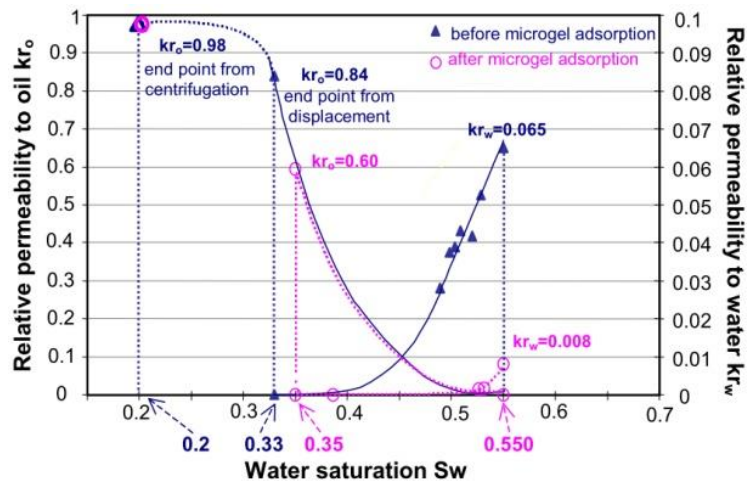


Figure 8 - Relative permeability to oil and water before and after high crosslink density microgels adsorption in Berea core sample [115].

The ability of the microgels to provide DPR was proved in field conditions. In 2005 the technology was used for water shut-off operation in the underground gas storage reservoir [109, 121]. The suspension of 2 μm sized microgels was bullheaded (injected without zonal isolation) into open hole well completed with a liner aiming the isolation of a thin high permeable layer located in the lower part of the interval. According to the core analysis, the permeability of the thief layer was around 6 D while the permeability of the rest of the interval was 0.2 D. Thus, the reservoir conditions were very suitable to test the microgels' ability to provide the selective self-placement and DPR. Due to the intensive increase of the injection pressure, only 160 bbls of the suspension were injected. As a result, water cut reduced in 5 times allowing the operators to increase gas production by 25% during 6 months after the treatment. Besides that sand production was also considerably reduced [118]. Similar results were obtained after the treatment of 100% watered out producer at one of the Omani heavy oil reservoirs. The precise identification of the thief layers was not possible due to the gravel pack. The average permeability of the productive interval and reservoir temperature were 0.5 D and 60 $^{\circ}\text{C}$ respectively. In September 600 kg of 2 μm sized microgels suspended in 500 bbls of tap water (7,000 ppm) containing 3 wt.% of KCl were injected into the reservoir followed by 150 bbls of 0.625 wt.% concentrated bulk gelling solution at [polymer]:[crosslinker] ratio equal to 6:1. As a result, water cut was reduced to 85% and sand production stopped for more than 1 year. During this period of time, 9,000 bbls of oil were produced incrementally. The cost of the work-over was paid-off during 6 months. The decrease of sand production was related to rock surface consolidation as a result of the adsorption of the microgels on it [119]. However, this statement needs to be proven by laboratory experiments.

Excellent stability of the microgels under harsh reservoir conditions, their self-placement ability together with a good DPR properties as well as the possibility to regulate the plugging intensity make them a promising technology not only for near wellbore and in-depth permeability modification treatments but also as an alternative for polymer flooding in reservoirs where the regular linear polymers are less effective

[115]. However, the results of field and laboratory tests of this technology are still scant.

2.5 pH-triggered polymer microgels

pH dependent rheological behavior of some anionic polymers was used to produce the pH-triggered polymeric microgels. The microgels swell and expand thousand times upon the inevitable increase in pH (from ~ 1 up to 3-5) as a result of the interaction between rock minerals and water [122-124]. Expansion of the particles is accompanied by dramatic increase of the viscosity from 2-5 cp up to more than 1,000 cp [125]. It is remarkable that the dependence of the particles' size and the suspension's viscosity on pH is reversible (Fig.9) [123]. Therefore, in field conditions, the formed plug is always can be removed by an acid flush.

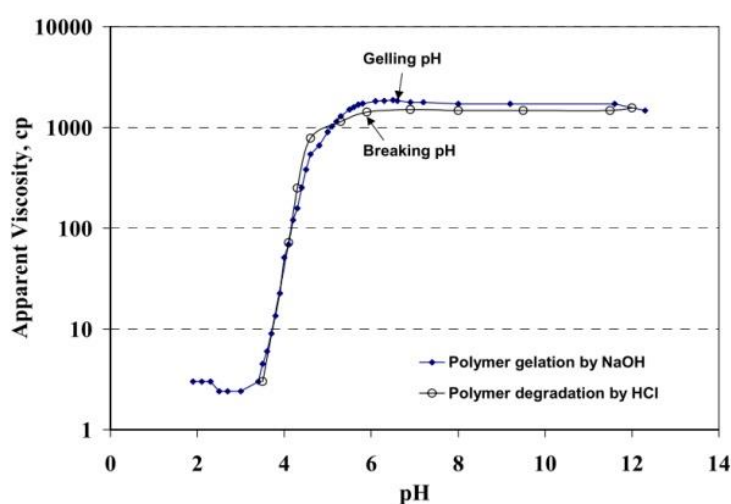


Figure 9 - Gelation and degradation of 3 wt.% pH-triggered microgels' suspension prepared in 3 wt.% NaCl brine [126].

As seen from the above figure, at acidic conditions the suspension exhibits low viscosity and thus is expected to provide the injection of big volumes at acceptable injection pressure. However, the injection of the suspensions may be complicated by intensive adsorption at low pH and viscosity increase at high pH. Lalehrokh et al. (2008) recycled the suspension of 3 wt.% concentrated pH-sensitive microgels through 11 inches long fractured sandstone and carbonate cores saturated with 3 wt.% NaCl brine at low ambient temperature, without acid pre-flush. 45 PVs of the suspension were recycled through the sandstone until pH of the effluent sample raised up to 3.5 - gelation point (Fig.10). In carbonate rocks pH increased much faster than in sandstones and the gel particles formed after just 3.5 PVs of the suspension had been recycled through the core. On the basis of these results, Lalehrokh et al. (2008) suggested that in field conditions the suspension of the microgels may propagate at a distance of 1,000-2,300 ft in sandstone and 40-130 ft in carbonate fractured rock before the gelation starts. However, such estimation seems incorrect because of unrealistic assumption that during each cycle the core acts as a fresh rock even after contacting with polymer. Invalidity of this assumption is supported by the

fact that the adsorption and retention of the microgels induced by low pH should significantly reduce the contact area between newly injected polymer and rock minerals. The intensive adsorption of the microgels was indicated by 10 times permeability decrease of the core after 5 PVs of the suspension have been filtrated through it (Fig.10) [127]. The similar results were got by Al-Anazi and Sharma, (2002), who have filtrated 3 wt.% concentrated suspension of microgels through low permeability (120 mD) 6 inches long Berea sand cores saturated with 3 wt.% NaCl brine and pre-flushed with 2 wt.% HCl (Fig.11). The comparison of bulk viscosity versus pH (Fig.9) with pH of effluent samples and pressure drop versus injected volume (Fig.11) curves proves that the permeability reduction of the cores before the pH reached 4 (swelling point) was induced by the adsorption of the particles rather than by the viscosity increase. Since the viscosity increase is instantaneous and takes place only at pH reaching 4 (Fig.9).

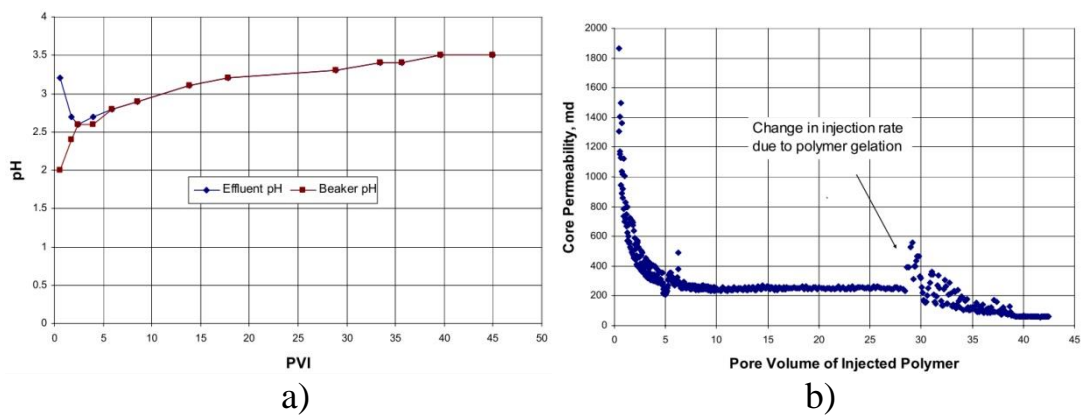


Figure 10 - a) Beaker and effluent pH and b) fractured Berea sandstone core permeability (mD) versus pore volume of injected gelling solution [127].

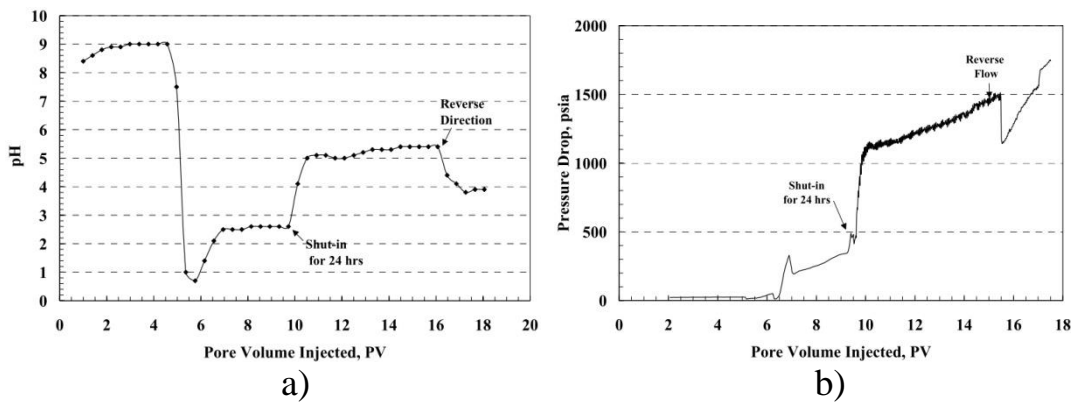


Figure 11 - pH of effluent samples (a) and pressure drop (b) versus injected pore volume of 3 wt.% NaCl (0-4 PVs), 2wt% HCl (4-6 PVs), 3 wt.% pH sensitive microgels (6-9.3 PVs), 3 wt.% NaCl (9.3-18 PVs) [126].

It was shown that in-depth propagation of the microgels depends on the mentioned in the previous section Huggins constant (K_H). The microgels with high crosslinking density (low K_H values) exhibit less particle interaction than those with lower crosslink density (high K_H values). Anionic surfactant sodium dodecyl sulfate (SDS) were used to reduce the attraction between the particles and improve their in-

depth propagation [66]. Some additional studies are required for proper assessment of the pH-sensitive microgels' ability of in-depth propagation.

Al-Anazi and Sharma in 2001 and 2002 studied the compatibility of pH-triggered microgels with various salts and showed that multivalent cations Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{2+} cause precipitation of the gelled particles (at high pH values). However, when pH is less than 3 no precipitation is observed. In field conditions, the pre-flush may be required in order to exclude the negative influence of multivalent cations on gel properties. It should be taken into account that high salinity of base brine is not suitable for preparation of the suspension because it may negatively affect the viscosity of the activated microgels' suspension (Fig.12 (a)). The effect of salinity may be eliminated by increasing the concentration of polymer constituent (Fig.12 (b)) [123, 126].

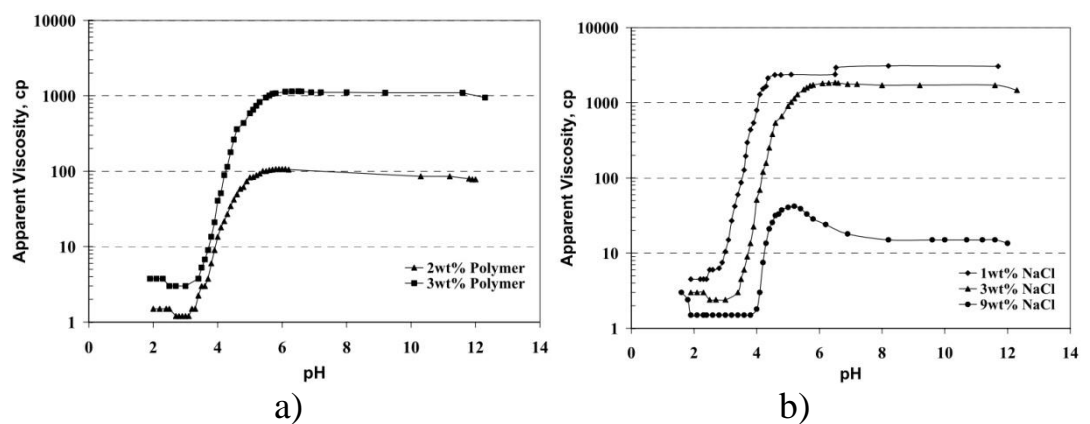


Figure 12 - Apparent viscosity versus pH for a) 3 wt.% concentrated microgels' suspension in different brines at shear rate of 170.348 sec^{-1} and b) 2 wt.% and 3 wt.% microgels suspension in 3 wt.% NaCl brine at shear rate of 340.697 sec^{-1} [126].

The effect of temperature was also studied. It was demonstrated that temperature variations below $80 \text{ }^\circ\text{C}$ do not significantly affect the rheology of the suspensions [126].

As far as the literature survey shows, pH-triggered microgels were not applied in any field project, a possible reason for that is the uncertainty of their in-depth placement possibility. Besides that high polymer adsorption at low-pH conditions, gel's precipitation by multivalent cations and necessity of fresh water and acid pre-flush may negatively affect the project's economy [66]. Nevertheless, the pH-triggered microgels have high potential as non-damaging carrier fluid for gravel packing because they can easily be removed by mild acid before the well will be put on production [123]. The microgels also they can be used as sealing agent to plug fractures in cement annulus with small openings that cannot be plugged with usual cement due to its high viscosity [128].

2.6 Thermally activated particles (TAPs)

Thermally activated particles (TAPs) known under the trade name of “Bright Water” are the sulfonate-containing 0.1-3 μm sized particles which may increase their size (“pop”) in 10 times by adsorbing brine after being exposed to sufficient heating [129]. The popping time can be regulated by controlling pH and changing the molecular properties of the particles [130]. TAPs can be applied at injection water salinity below 70,000 ppm and reservoir temperature between 50 and 150 $^{\circ}\text{C}$. Another demand is the existence of thermal front at some distance from the injector, this requires some sufficient positive difference between the reservoir and injected water temperatures [64, 89, 131-133]. Suspension of TAPs in non-activated state exhibits low viscosity (around 1.4 cp), this is favorable for the deep propagation of the solution [134]. For example, at Salema Field (Brazil) the TAPs were chosen as an easy injectable gelling solution for in-depth permeability modification [135].

Due to their small size TAPs can be applied only within the range of permeabilities between 0.1 D [89] and 4 D [129], whereas fractures are better to be isolated by bulk gels [129, 132, 136].

The in-depth propagation of TAPs was proved by a number of lab and field tests and generally is not subject to debates. In-depth propagation of non-activated TAPs and permeability reduction ability of activated TAPs have been tested by different authors for a variety of conditions [89]. The following figure shows the increased flow resistance measured at different sections of 40 ft long sand pack model during 200 days after the injection of 0.5 PVs of 3,000 ppm concentrated TAPs’ suspension overflushed by 0.3 PVs of water at 80 $^{\circ}\text{C}$. It is clearly seen that unlike the rest part of the model the inlet section was not subjected to intensive permeability reduction (Fig.13) [131, 132].

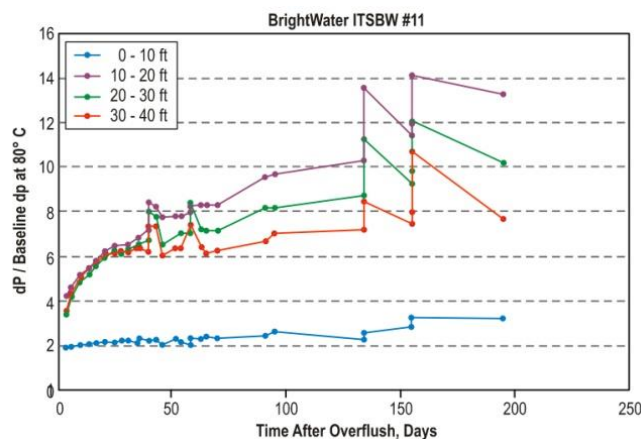


Figure 13 - Pressure drop versus time after the overflush [132].

Lab studies have shown that 1,500-7,500 ppm concentrated suspensions of TAPs generate RRFs which in general tend to decrease from several hundred to 1.5 as permeability increases from 0.29 to 7.5 D [136-138]. It was also demonstrated that activated TAP slugs may be partly washed out by chase water [137]. As an example, Garmeh et al. (2011) treated 20 inches long 0.29 Darcy sand pack with 5,000 ppm

concentrated suspension of TAPs. To activate the swelling the model was aged for 50 days at 30 °C and then subjected to chase water injection. As seen from Fig.14 RRFs determined in the beginning of the chase water filtration process are higher than those registered after sufficient amount of water had been pumped through the model, washing out non-adsorbed particles. This is explained by relatively small viscosities of the activated suspensions (20-35 cp) [134].

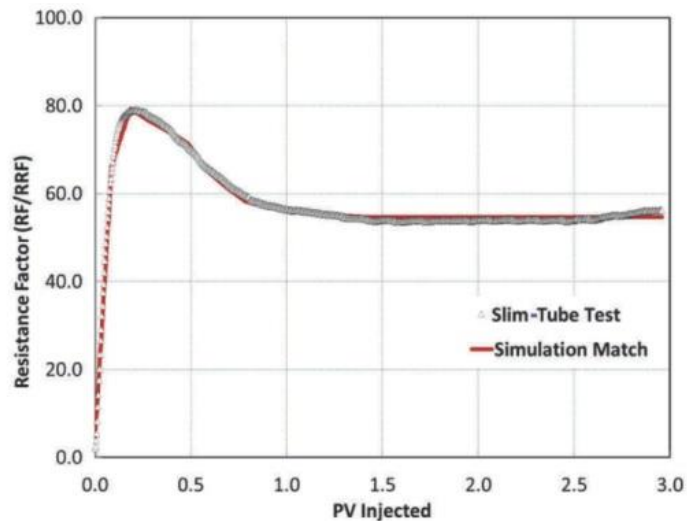


Figure 14 - RRF versus injected pore volume [134].

Thus, TAPs' ability to create high RRFs is considerably limited in comparison with traditional bulk gels. However Frampton et al. (2004) stated that high RRFs are required only for near wellbore treatments, whereas in-depth permeability modification may be achieved by much lower RRF values. However, during designing of TAPs treatments it should be kept in mind that the susceptibility of the slug to the dilution and washing out by chase water injection as well as high adsorption (130 $\mu\text{g/g}$ rock) in fully water saturated regions may cause the initial concentration to be decreased in 1.3-2 times before the placement at predetermined location [131]. In this respect, numerical simulation showed that high flow rates should be applied during the injection of TAP suspension in order to achieve deepest possible placement, whereas low rates are preferable during the process of chase water injection in order to maximally prevent the slug washing out effect and achieve highest possible oil recovery increment by in-depth fluid diversion [136].

In stratified reservoirs with sufficient cross-flows TAPs have been proved to be more effective than technologies adapted for near wellbore treatments. For example at Prudhoe Bay oilfield in Alaska in-depth treatment was required after the failed water shutoff operation in the stratified reservoir with permeability varying between 50 and 1,500 mD. Between November 2004 and February 2005 all 3 injectors of the treated segment were subjected to the injection of 630-645 bbls of TAPs' suspension. The suspension was mixed with 310-335 bbls of surfactant along with the injected water so that the concentration of the particles was at 3,000 ppm. Reservoir and injected water temperatures were 92 and 63 °C respectively. The injectivity reduction occurred only seven months after the treatment (May 2005) and kept to decrease over

the following years. Between May 2005 and October 2007 around 500,000 bbls of oil were produced incrementally. On average water cut decreased on 4% [139].

TAPs were successfully used for in-depth treatment at Tunisian mature oilfield El-Borma in sandstone reservoir with shale interlayering. The temperature of the pilot segment was equal to 75 °C, reservoir brine salinity 26 g·L⁻¹, injection and production water salinity 0.4 and 4.5 g·L⁻¹ respectively. The producer was surrounded with 6 injectors but had strong connectivity with only one of them and operated at 98% of water cut. The logging conducted in the injector indicated a thief zone in the bottom of the interval 2411,3-2412,7 m which took 90% of the injected water. Average permeability between the wells and near wellbore permeability were calculated to be around 0.5-0.7 and 1.4 D respectively. RRFs measured on core samples with the initial permeability of 0.7 D were around 20. 330 bbls of TAPs' suspension were dissolved in 33,100 bbls of injected water and injected during 9-23 of January 2010 at flow rate 95 bbls/h. During the injection process, the pressure rose up from 49 to 84 bar. Taking into account that polymer reaction was expected to appear only after 7-8 months the increase of injection pressure cannot be attributed to initial polymer swelling. Post-treatment logging conducted in the injector after TAPs' activation showed no change in the injection profile. After about 5 months reduction of water cut and the increase of oil recovery were observed. During the period between June 2010 and January 2012 total oil production rate was raised from 44 up to 76 bbls/d on average (70% increase) [136].

During the injection of a plugging agent, RF must be equal to 1 in order to provide ideal selective placement in matrix reservoirs [42]. RFs between 1 and 4 were registered during the injection of 4,400-5,000 ppm concentrated TAPs' suspensions into sand packs with permeabilities between 1.3 and 0.29 D [134, 138]. Thus at low permeability contrast, oil permeability damage by TAPs should be concerned.

Numerical simulation has shown that at high TAPs concentration (>10,000 ppm) or big slug volume (>10% of channel volume (CV)) or low permeability contrast (<10) or high Kv/Kh values (>0.9), the injected TAPs suspension tends to invade into low permeability oil saturated strata decreasing the IOR [134]. However, 10,000 ppm concentrated TAPs' suspensions were successfully applied in 6 injectors at permeability contrast around 5 (450 mD/80 mD) at mature water flooded San Jorge Basin (Argentina). As a result, 60,000 bbls of oil were produced incrementally during 7 months after the treatment. The average water cut decreased on 16% [132].

The numerical simulations also have shown that at noticeable cross-flows higher IOR is achieved if the slug is placed closer to the producer, TAPs with longer swelling time are preferred for this purpose [130, 134]. In this context, it is worth to mention failed TAPs treatment at Minas oilfield. The treated area contained 1 injector and 3 producers with well spacing varying between 1014 and 1140 feet and average reservoir permeability equal to 0.4-0.6 D. High permeability thief zone located at the bottom of the injection interval and absorbed 96% of the injected water. During November 11-20 of 2001, 42,000 bbls were injected at 4,500 ppm and 1,500 ppm of TAPs and surfactant (dispersant) concentration respectively. The injected slug was

followed by 68,800 bbls of field water during two weeks and three weeks long shut-in period. After the injector was returned to water flooding 60% of injectivity reduction was detected. Post-treatment tracer test showed the increase of transition time on 72 days without detection of polymer production. According to pressure fall-off test, the water permeability was considerably reduced within the radius of 125 feet around the injection point. Overall oil recovery increment was too insufficient and lasted for less than 12 months [89]. In comparison with successful applications of TAPs, it is obvious that low IOR at Minas oilfield most probably is related to the placement of the slug at the too short distance from the injector. The case study described below is an example of successful TAPs treatment where the slug was placed at the distance beyond 300 feet from the injection point.

In 2004 TAPs were used at the unit HU 152 of Milne Point field for the isolation of the thief layer (B7U) that was sandwiched between two low permeability layers (B7L and C) and was absorbing 100% of the injected water. It required 4-6 months for the transition of the particles from cooled to heated zone, located 300 feet away from the injector, so the TAPs with the swelling time of 4 months were selected. 370 bbls of TAPs' suspension were dispersed by adding 190 bbls of surfactant into 38,000 bbls of injected water. Since 28 June to 19 July 2004 38,000 bbls of the suspension at TAP's concentration equal to 3,300 ppm have been injected. The well tests indicated in-depth permeability reduction without affecting near-wellbore zone. The treatment yielded more than 60,000 bbls of incremental oil produced by the end of 2007. The cost of one incrementally produced barrel was estimated to be less than 5 USD [138].

As was mentioned 4 D was set as the highest permeability limit for the application of TAPs [129], however in 2011 48,000 bbls of 15,000 ppm concentrated TAPs' suspension has been used for the isolation of 25 D permeability thief layer at Ebano field. IOR increase was not reported, however, it was mentioned that water production declined from 4,500 bbls/d to 3,500 bbls/d and became stable for one year after TAPs treatment [140].

Mustoni et al. (2010) reported that until 2010 around 80% of TAPs pilot treatments have been successful, however, the dependence of TAPs' slug right placement and the magnitude of generated RRFs on many inter-related variables does not let bullheaded application of the technology and requires thorough well testing, lab and computer simulation verification [132, 141].

2.7 Silicate gels

An aqueous solution of alkaline silicate as a gelling agent and HCl or other acids as activators of the gelation has been studied and applied for permeability modification treatments [142]. This system was patented in 1922 [143], but due to not fully explicable reasons was not used as often as polymer gels [14]. Since silicate gels are environmentally friendly inorganic chemicals tolerant to biological degradation they can substitute some currently used materials listed by REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) as harmful [142]. As a

matter of fact, sodium silicate was recognized to be safer than any chemicals currently used for permeability modification treatments [144].

Water-like viscosity of sodium silicate solution should guarantee its selective placement in watered out zones [44]. However, divalent cations cause rapid gelation of sodium silicate and the precipitation of $Mg(OH)_2$. Stavland et al. (2011a) have experimentally shown that due to the cation exchange effect some sufficient pre-flush is required to precondition the reservoir for sodium silicate treatment [21]. The pilot test conducted at Snorre field (offshore Norway) is a good example to back up this conclusion. In June 2011 4,800 bbls of 40,000 ppm concentrated sodium silicate solution containing 4,300 ppm of HCl were injected in the injector P07. The volume of the pre-flush was equal to 2,530 bbls of 0.5 wt.% KCl brine. In the end of the injection of the sodium silicate solution, RF increased in 10 times. According to the authors, RF rose because the injected pre-flush was not enough to prevent the mixing of sodium silicate with divalent ions and the precipitation of $Mg(OH)_2$. As a result, 100 times permeability reduction was observed within 70 m away from the injector. Results of production wells monitoring have not been published yet [144].

The single injection well treatment at Snorre field was followed by large scale project. During June-October of 2013 1,520,000 bbls of 4 wt.% sodium silicate and 0.2 wt.% HCl solution were injected into the reservoir [144]. Though the post-treatment field data were not published yet this example proves that silicate gelants with low concentrations of HCl are more suitable for deep placements [142]. Apart from HCl concentration, the injection flow rate also influences the depth of gelant's penetration. In fact, at high injection rates *in-situ* and bulk gelation times are the same, while at low flow rates premature plugging may take place because of the increased rate of silicate particles deposition [21]. So sodium silicate gelants are difficult to be placed at large distances from the injection point [145]. However, near wellbore treatments may also reanimate the well in case if high water cut is caused by poor cementing [11]. For example, in Alberta (Canada) in 1996 the injection of silicate-based polymer slurries into 200 producers with water cut increased from 10 up to 98% due to poor cementation resulted in the decrease of water production from 24,850 to 400 bbls/day and increase of oil production by 660 bbls/day [146].

Acidic silicate gels were described as rigid and not tolerant to high shear stresses in fractured reservoirs [142]. In 1994 at Gullfaks oilfield (North Sea) 25,300 bbls of 5 wt.% concentrated sodium silicate gelant were injected into the producer with zonal isolation aiming the plugging of the lower intervals. Untimely plugging in the end of the injection process caused the fracturing of the formation negatively affecting the result of the treatment. Therefore, the actual RRF in the gel plug zone was 40 instead of anticipated 100, as a result later back production of silicate gel was detected. Nevertheless, eventually water cut decreased from around 60 to below 50% after the treatment, and became less dependent on total liquid rate. 164,560 bbls of the oil produced in 1995 were attributed to the gel treatment [147].

The increase of silicate concentration may improve the plugging in fractures, as Hatziagnatiou et al. (2015) have shown 85 wt.% sodium silicate gelant allowed 20,000 fold permeability decrease of 5 mm width and $2.1 \cdot 10^6$ D hole made inside of the

carbonate core. On the other hand, the increase of silicate concentration may cause severe syneresis of the gel [148]. In fact, in the study of Vinot et al., (1989) 9.8% SiO₂ gel shrunk on 80% of its original size after it had been aged for 2 months at 60 °C [149]. However, in the experiments of Hatzignatiou et al. (2015) the aging of the treated core at 60 °C during three weeks did not cause any syneresis of the gel [148]. Thus, more research is required in this context.

The low viscosity of silicate gelants even at high concentrations (1.5-2 cp) complicates its firm placement in fractured reservoirs with uneven pressure distribution. In this context, Hatzignatiou et al. (2015) have shown that the combined use of sodium silicate with xanthan may result not only in more reliable placement but also should improve the plugging efficiency of fractures because of gel's expansion upon the increase of chase water flow rate [148]. Lakatos et al. (2011) reported on the sequential bullheaded injection of 13 wt.% sodium ortho-silicate/0.4 wt.% PHPA solution and crosslinkers carrying liquid (0.2 wt.% of aluminum sulfate and 1.25 wt.% of HCl) at the ratio of 1:1 for the treatment of the injection well A-60 located in a faulted multilayered reservoir. Average increase of oil and decrease of water production on 400 and 1,800 bbls/day respectively had been achieved, demonstrating high efficiency of the method [150].

Since the addition of polymers may complicate the placement of silicate solutions their replacement with SiO₂ and Al₂O₃ nanoparticles has been suggested. Lakatos et al. (2012) have shown that unlike SiO₂ the Al₂O₃ nanoparticles tend to sediment in a liquid phase and thus are not compatible with silicate solution, while the concentration of SiO₂ nanoparticles should be below 5 g·L⁻¹ [151]. In 2014 two producers of the largest Hungarian oilfield were subjected to the injection of 2,530 bbls of gelant containing 50 g·L⁻¹ of the soluble silicate, 1 g·L⁻¹ of polymer, and 1 g·L⁻¹ of nanosilica. Preliminary results showed the decrease of water cut on 10-50% (initially 95%) [14].

Several papers were dedicated to the problem of gelation time control of silicate solutions. Vinot et al. (1989) suggested to substitute HCl for diesters which can be introduced into sodium silicate solution in the form of microemulsion and hydrolyze, producing acid and alcohol at temperatures below 90 °C [149]. Bauer et al. (2005) described the system which contains sodium silicate and the activator encapsulated in temperature sensitive shell in order to delay the activation of silicate hydration process. The system was tested in the temperature range between 80 and 300 °C and was proposed to solve the problem of lost-circulation during geothermal drilling process [152].

In order to make silicate gelants nontoxic, the usage of urea instead of HCl was suggested. However, it is possible only at temperatures above 70 °C since the gelation is initiated by the byproducts of urea heat induced decomposition. Core flooding experiments showed excellent gel stability at pressure gradients reaching 56.6 MPa/m. Unfortunately, the gelation time of silicate/urea gelants is also accelerated by divalent cations, 0.8 g·L⁻¹ is the maximal acceptable CaCl₂ concentration [153]. In 2007 at CO₂ storage field Becej (Serbia) 10,760 bbls of the solution consisting mainly of silicate (9.4 wt.% of 25 wt.% SiO₂), PHPA (0.06 wt.%)

and urea (1 wt.%) were injected through directional well to create plug around collapsed well (which blew up in 1968) and prevent vertical gas flow. The reservoir temperature was equal to 87.2 °C. As a result annual reservoir pressure decline rate decreased from 0.9 to 0.03 bar/year. Monitoring of post-treatment reservoir performance confirmed significant restriction of vertical CO₂ migration [154].

Herring et al. (1984) provided another example of successful application of sodium silicate/HCl gelant for gas shut-off treatment [155].

There are a few papers that were dedicated to the DPR effect provided by silicate gels. Askarinezhad et al. (2016) have shown that in order to provide sufficient DPR effect the sodium silicate solution should be injected along with oil otherwise full blockage of 0.7-0.8 D Berea cores may occur. Also, Askarinezhad et al. (2016) concluded that simultaneous oil and sodium silicate injection provides a pronounced DPR effect in oil-wet rocks ($RRF_w=129$ and $RRF_o=20$ at 78% water cut), while in water-wet media at similar conditions it may not be effective at all ($RRF_w=100$ and $RRF_o=460$). Thompson and Fogler (1997) developed a new system based on oil-soluble organic compound Si(OCH₃)₄ - tetramethyl orthosilicate (TMOS). The gel is formed as a result of the partitioning of TMOS from oil into aqueous phase upon the contact with water [156]. Since the gelling component is carried by oil the disruption of oil phase continuity by gel placement should not occur. That is how DPR effect was planned to be achieved [157]. However, the experiments conducted on two-dimensional transparent micromodel visually showed that the formation of gel decreases oil phase continuity. RRF to oil and water filtration after the treatment with 10 wt.% concentrated TMOS were equal to 3.91 and 4.66 respectively. The experiment conducted on Berea sandstone with permeability equal to 0.66 D confirmed this result [158]. It is remarkable that in field operations described by Herring et al. (1984) and Boreng and Svendsen (1997) temporary bridging agent - “salt weighted polymer gel” and 2 wt.% KCl brine were used to prevent the invasion of silicate gelants into oil zones [155, 159]. It should be noted that some silicate gels were reported to be not stable when contacting with alkaline fluids [160]. This may be beneficial for the removal of the plug after improper placement or unacceptable oil permeability reduction.

For more detailed information on sodium silicate gelation and gel behavior one may refer to the work of Aly and Hossien, (2014) [161].

2.8 Temperature triggered inorganic and organic bulk gels

As it was mentioned above, PHPA/Cr⁺³ bulk gels cannot be applied at temperatures above about 120 °C. In 1990s two bulk gel systems applicable at the temperature range between 20 and 320 °C were developed in Russia and tested on Siberian oilfields. Later on, these gels were successfully applied at Chinese, Vietnamese and Omani reservoirs [162]. As the published data shows, the gelants were applied only for the near wellbore treatments, most of the pilot tests were conducted in injectors by using volumes varying between 80 and 1,250 bbls. The average incremental oil recovery was equal to 800-1,600 tons per treatment [163].

The inorganic gel system named “GALKA” consists of aluminate, carbamide, and surfactant dissolved in water. Heating of carbamide produces CO₂ and ammonia leading to the increase of pH, the latter initiates the hydrolysis of alumina ions. Finally, the whole volume of the solution immediately turns into gel phase. The system can be applied at temperatures from 20 to 320 °C independently on the salinity of brine. The ability of “GALKA” gelant to divert the fluid flow was proven by comparison of well log data registered in the steam injector before and after the treatment. The injection of 760 bbls of “GALKA” caused the increase of reservoir sweep efficiency from 10 to 38% [162, 164].

Between 1989 and 2014 “GALKA” was tested in different Siberian reservoirs including those subjected to steam injection. The injected volumes varied between 80 and 1,000 bbls as a result 3-45% water cut reductions and substantial increases of oil flow rates in up to 4.8 times were detected [164, 165].

The organic gel system is based on the application of cellulose ethers (CE), which exhibit viscosity increase at elevated temperatures and salinities (Fig.16).

According to the laboratory studies, the gels are stable at temperatures below 220 °C and the gelation temperature may be regulated in the range between 40 and 120 °C by inorganic and organic additives. Moreover, the gelation was found to be reversible at 20-30 °C below the gelation temperature [164]. This gel system composed of CE aqueous solution with electrolytes and nonelectrolytes complexes added to it was named “METKA”.

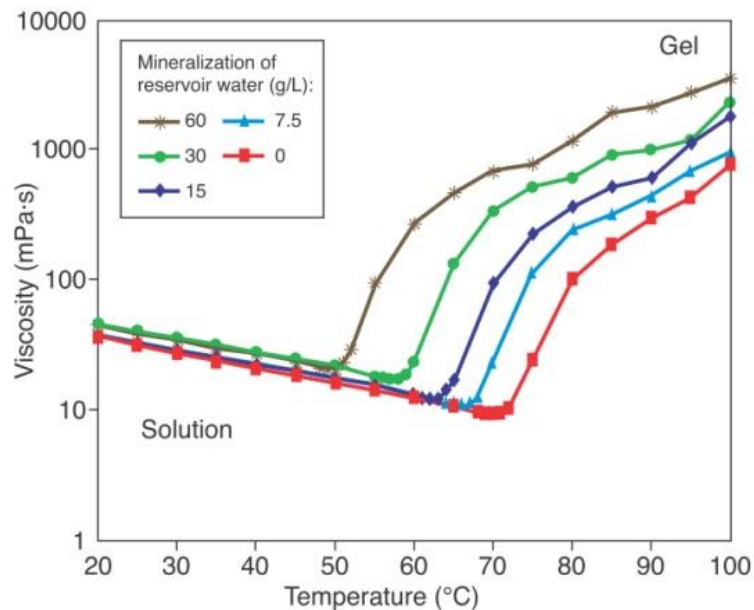


Figure 16 - Dependence of 1 wt.% concentrated CE solution on temperature for various salinity of brine, g·L⁻¹: 60 (1), 30 (2), 15 (3), 7.5 (4), 0 (5) [164].

It was proven that “METKA” gels provide the effect of DPR. 11 D sample has been treated with “METKA” and was subjected to the alternated injection of water and oil. The results clearly showed that the filtration resistance to oil was 2-3 times lower than that to water [164].

“METKA” gels were tested many times in field conditions. Russian oil company “Lukoil” applies “METKA” since 1998. During 1998-2000 158 wells were

treated including steam injectors on average one treatment allowed to produce 1,630 tons of IOR. One of the most successful pilots has been conducted at Uryevskoye oilfield in 2001, 320-1,270 bbls of the gelant were injected into each well, the total size of the slug was 3,900 bbls, during 7 months after the treatment 6,542 tons of oil were produced incrementally [165].

The unique ability of “METKA” system to sustain high pressure gradients in gel form and the possibility of 100% permeability recovery by cooling down the plugged area makes this gelant a good candidate for wide variety of applications [166], like temporary bridging agent to be used in drilling, directed injection, fracturing and other well operations [155].

It is remarkable that small slug volumes (not bigger than 1,300 bbls) were injected in all “GALKA” and “METKA” applications. The suitability of the systems for in-depth fluid diversion and bullhead injection into multilayered reservoirs is difficult to be accessed due to the lack of published information. It may be supposed that small slugs injected in all pilot tests are not a part of the treatment design but rather a necessity imposed by rapid *in-situ* gelation and plugging.

2.9 Comparison of the discussed technologies

The table 2 provides quick overview of the discussed technologies.

Table 2 - Comparison of the discussed gel treatment technologies.

Name	Reservoir rock	Temperature	Brine salinity	Effect of DPR	Ability of in-depth permeability treatment
PHPA/Cr⁺³	Effective for the treatment of fractured formations and reservoirs with super high permeability filtration paths. Application in matrix reservoirs may be restricted due to the injectivity problems (Manrique et al., 2014; Sydansk and Moore, 1990).	Up to 135 °C (Lockhart and Albonico, 1994).	Not tolerant to the presence of divalent cations, at hydrolysis degree of PHPA between 30 and 90% and temperature 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 (Moradi-Araghi and Doe, 1987). Moreover, high salinity of reservoir brine negatively affects plugging efficiency of PHPA gels (Brattekaas et al., 2015).	The gel is able to reduce permeability to water in 100-1000 times higher than that to oil, while oil permeability is reduced by a factor of 1.2-4.8, what is still a substantial decrease (Seright, 2006; Willhite et al., 2002). Treatment of multilayered matrix reservoirs with PHPA/Cr ⁺³ formulations that may decrease water permeability by a factor of 10 is not recommended (Zaitoun, 1999).	In naturally fractured reservoirs the deep placement of 640-37,000 bbls of PHPA/Cr ⁺³ gellant with polymer concentration varying between 0.2 and 0.8 wt.% and [polymer]:[crosslinker] ratio equal to 44:1 – 88:1 was possible (Montoya Moreno et al., 2014; Sydansk and Moore, 1990).
CDGs	The application in mature long water flooded and fractured reservoirs may be complicated due to the gelant breakthrough (Mack and Smith, 1994; Zhidong et al., 2011).	Was not found in the literature.	Taking into account low concentration of PHPA (around 300 ppm) the gels are more susceptible to brine salinity. Ranganathan et al. (1998) demonstrated that the presence of 0.25 ppm of chlorine in makeup water caused the gel to deteriorate during 24 hours after it was formed.	Results of laboratory tests of CDGs' ability to provide DPR have not been found in literature.	Despite of numerous field trials confirming the injection of CDGs slugs as large as 550,000-600,000 bbls into reservoirs with permeability varying between 10 and 1,200 mD (Manrique et al., 2014; Smith et al., 1996), the deep propagation ability of CDGs is still uncertain and is debated in literature (Al-Assi et al., 2009; Castro et al., 2013; Liu et al., 2006; Ranganathan et al., 1998; Seright, 1994; Seright, 2015; Smith et al., 2000; Spildo et al., 2010).

Continuation of the table 2.

<p>PPGs</p>	<p>Due to large particle size the gels are not applicable in matrix reservoirs with permeability lower than 0.3-1 Darcy (Elsharafi and Bai, 2015; Sang et al., 2014).</p>	<p>The gels are stable under 110-120 °C (Bai et al., 2008; Mazen et al., 2014).</p>	<p>The gels are stable at all types of brine and any salinity (Bai et al., 2008).</p>	<p>Oil filtration through the PPG plug causes gel's dehydration and shrinkage contributing to the recovery of post gel treatment oil permeability (Imqam et al., 2014b). Depending on gel strength and injection flow rate the particles exhibit shear-thinning behavior, what may improve the injectivity and prevent matrix plugging (Al-Ibadi and Civan, 2012; Coste et al., 2000; Imqam et al., 2014b; Muhammed et al., 2014; Seright, 1997; Zhang and Bai, 2010). In one experiment it was even possible to achieve zero oil permeability reduction while water permeability was reduced by a factor of 6 (Imqam et al., 2014b).</p>	<p>Due to particle nature of the gel it's in-depth placement is not influenced by those <i>in-situ</i> transport problems inherent to PHPA/Cr⁺³ and CDGs (Liu et al., 2006). Moreover, the deformability of PPGs may be advantageous for the injection of large slugs (as large as 1,265,000 bbls) into unfractured formations (Bai et al., 2008; Imqam et al., 2014a; Muhammed et al., 2014).</p>
<p>STARPOL microgels</p>	<p>Due to small size (10-1000 nm) the gel particles are not suitable for the treatment of fractured reservoirs and formations with super high permeability streaks (Bai et al., 2008; Imqam and Bai, 2015).</p>	<p>Can be applied under 140 °C (Chauveteau et al., 2004; Dupuis et al., 2013).</p>	<p>In the reported lab studies the microgels were prepared in 300-20,000 ppm brine (Chauveteau et al., 2003; Rousseau et al., 2005). The adsorbed layers were found to be stable under the salinity of 200 g·L⁻¹ (Cozic et al., 2008).</p>	<p>Lab and field tests confirmed that due to low viscosity, the possibility of size regulation and shrinkage under the impact of oil-water capillary pressure the microgels are able of selective self-placement and exhibit excellent DPR properties (Rousseau et al., 2005; Zaitoun et al., 2007).</p>	<p>The propagation of the microgels is improved at higher flow rates (Zaitoun et al., 2007). Besides that it was experimentally proved that the depth of the treatment can be regulated by changing the microgel's chemistry, which determines the character of the interaction between separated particles (Chauveteau et al., 2003; Rousseau et al., 2005).</p>

Continuation of the table 2.

<p>pH-triggered polymer microgels</p>	<p>The technology was tested only at lab conditions for the treatment of both carbonate and sandstone cores (Lalehrokh et al., 2008; Suk Kyoong et al., 2006). The examples of treatments of porous media with permeability higher than 2.3 D were not found in literature</p>	<p>Below 80 °C the rheology of the suspension is not affected by temperature (Al-Anazi and Sharma, 2001; Al-Anazi and Sharma, 2002)</p>	<p>The suspensions of pH-sensitive microgels prepared in 1-3 wt.% NaCl brine are stable, but the further increase of brine salinity causes significant decrease of the viscosity of the activated microgels' suspension (Al-Anazi and Sharma, 2002). At pH>3 the multivalent cations cause precipitation of the gelled polymer (Al-Anazi and Sharma, 2001), thus in field conditions pre-flush may be required.</p>	<p>Was not found in the literature.</p>	<p>The conducted experiments demonstrated that in-depth propagation of pH-sensitive microgels is significantly restricted due to the intensive adsorption at low-pH values (Lalehrokh et al., 2008) and attraction between the particles. The addition of an anionic surfactant allowed to decrease RFs from 14-30 to 6-9 (Suk Kyoong et al., 2006), what is still enough to cause invasion into low permeability oil-bearing strata as it was demonstrated by numerical simulation (Benson et al., 2007).</p>
<p>TAP (Bright Water)</p>	<p>According to many authors, the technology is applicable in matrix reservoirs with permeability varying from 0.1 up to 7.5 D (Fabbri et al., 2015; Fethi et al., 2010; Garmeh et al., 2011; Ohms et al., 2010; Pritchett et al., 2003; Towns et al., 2013). However, in one field trial TAPs were successfully applied for the treatment of the thief zone with permeability equal to 25 D (Choudhary et al., 2014), thus the maximal permeability limit at which the technology may be successful is still unclear.</p>	<p>TAPs are applicable in temperature range from 50 to 150 °C (Pritchett, et al., 2003).</p>	<p>Acceptable brine salinity is under 70 g·L⁻¹ (Pritchett, et al., 2003).</p>	<p>Reports on the investigation of TAPs DPR ability were not found in the literature.</p>	<p>The ability of TAPs deep propagation was demonstrated on 40 ft long sand pack (Mustoni et al., 2010). TAPs were successfully used for in-depth permeability modification of multilayered formations where near wellbore treatment technologies failed due to the sufficient cross-flows between the layers (Fethi et al., 2010; Husband et al., 2010).</p>

Continuation of the table 2.

Silicate Gels	<p>Since the silicate gels do not possess high shear rate stability their application in fractured reservoirs may be complicated due to the back production of the gel (Krumrine and Boyce, 1985; Rolfsvag et al., 1996). Lab tests proved that high concentrated (85 wt.%) sodium silicate gelants can be effectively applied for the plugging of fractures (Hatzignatiou et al., 2015). However, due to the low viscosity of the gelant it may leak off into more severely drained zones, especially when static gelation mechanism is exploited (Hatzignatiou et al., 2015; Sandiford, 1979).</p>	<p>The silicate gels can be applied at temperatures as high as 300 °C (Bauer et al., 2005).</p>	<p>Presence of divalent cations cause the precipitation of Mg(OH)₂ from the silicate solution, thus in field conditions pre-flush is required in order to precondition the reservoir (Lakatos et al., 2015; Skrettingland et al., 2012; Stavland et al., 2011a).</p>	<p>Very few researchers studied DPR effect of silicate gels. Askarinezhad et al. (2016) showed that in order for sodium silicate to provide DPR the gelant should be injected simultaneously with oil, otherwise total blockage may take place. Also, it was shown that sodium silicate provides better DPR effect in oil-wet (RRF_w=129 and RRF_o=20) rather than in water-wet rock (RRF_w=100 and RRF_o=460). The modified system based on the application of Si(OCH₃)₄ was developed in order to overcome this drawback, however provided only moderate DPR effect (Askarinezhad et al., 2016; Grattoni et al., 2001; Thompson and Fogler, 1997).</p>	<p>Despite of all obstacles like precipitation of Mg(OH)₂, increased rate of silicate particles deposition at low injection rates and poor control over the gelation time, one field trial proved that at low HCl concentrations it is possible to achieve in-depth placement of silicate gelant slug without damaging near wellbore zone (Skrettingland et al., 2014; Skrettingland et al., 2012).</p>
Inorganic (“GALKA”) and organic (“METKA”) bulk gels	<p>Both systems are applicable in carbonates and sandstones. The permeability range at which the gelants may be successful was claimed to be 1 mD - 10-20 D for “GALKA” and 10-20 mD – 10-20 D for “METKA” (Altunina and Kuvshinov, 2008). Upon contacting with rock, the GALKA solution can dissolve the carbonate minerals and prevent clay swelling (Altunina et al., 2015b).</p>	<p>“GALKA” – 20-320 °C (Altunina et al., 2013; Altunina et al., 2015a). “METKA” – 30-200 °C (Altunina et al., 2011). Gelation temperature of METKA may be regulated in the range between 40 and 120 °C (Altunina et al., 2001).</p>	<p>In the case with “GALKA” salinity of base brine is not limited, while “METKA” can be prepared only under 200 g·L⁻¹ of brine salinity (Altunina et al., 2015b).</p>	<p>Injection of “METKA” gelant into the core sample with permeability equal to 11 D showed that permeability to water was decreased in 2-3 times higher than that to oil (Altunina et al., 2011).</p>	<p>It may be suggested that the injection of small volumes of the slugs (not bigger than 1,300 bbls) inherent for all filed trials (Altunina et al., 2015a) were dictated by the lack of control over the gelation time rather than was predetermined at the design stage of the treatments. The laboratory studies on long sand packs were not found in literature.</p>

3 Experimental study of gellan gum as an agent for WST and CCO

This section contains the results and discussion of the experimental work dedicated to the study of polymer gellan gum as a candidate for the treatment of injection and production wells in watered out zones.

3.1 Materials and methods

Food grade gellan was purchased from “Zhejiang DSM Zhongken Biotechnology Co., Ltd.”. The polymer was dissolved in DW at a required concentration, in some tests technical water from Kumkol oilfield containing $0.96 \text{ g}\cdot\text{L}^{-1}$ of TDS was used instead of DW. Kumkol technical water contained the following cations $0.244 \text{ g}\cdot\text{L}^{-1}$ of Na^+ , $0.00336 \text{ g}\cdot\text{L}^{-1}$ of Ca^+ and $0.004251 \text{ g}\cdot\text{L}^{-1}$ of Mg^+ , as was determined by ICP analysis.

Reservoir brine and oil from Kumkol, Karabulak, Kenlyk, Karazhanbas and Uzen oilfields were used in the core and sand pack flooding tests. Kumkol brine was composed of $22.5 \text{ g}\cdot\text{L}^{-1}$ of Na^+ and K^+ , $3.8 \text{ g}\cdot\text{L}^{-1}$ of Ca^{2+} , $0.85 \text{ g}\cdot\text{L}^{-1}$ of Mg^{2+} , and $43.9 \text{ g}\cdot\text{L}^{-1}$ of Cl^- ions with total salinity $73 \text{ g}\cdot\text{L}^{-1}$. Karabulak brine (total salinity is $90 \text{ g}\cdot\text{L}^{-1}$) chemical composition was not determined, however the cation content of the near located Kenlyk oilfield brine ($18.37 \text{ g}\cdot\text{L}^{-1}$ of Na^+ , $2.46 \text{ g}\cdot\text{L}^{-1}$ of Ca^{2+} , $0.64 \text{ g}\cdot\text{L}^{-1}$ of Mg^{2+} , with total salinity around $90\text{-}120 \text{ g}\cdot\text{L}^{-1}$, depending on the formation) is likely to be similar with that of Karabulak. Karazhanbas brine was synthesized in the laboratory by dissolving 63.24 g of NaCl , 12.34 g of CaCl_2 and 17.57 g of MgCl_2 per 1 L of DW (total salinity is $93 \text{ g}\cdot\text{L}^{-1}$). TDS of Uzen brine was equal to $110 \text{ g}\cdot\text{L}^{-1}$.

The table 3 below presents the densities and viscosities of the oil samples measured at the corresponding reservoir temperatures by Viscometer of Stabinger SVM 3000 (Fig.16).



Figure 16 - Viscometer of Stabinger SVM 3000.

Table 3 – The densities and viscosities of the oil samples used in this study.

Oil field	Density, $\text{g}\cdot\text{cm}^{-3}$	Viscosity, $\text{mPa}\cdot\text{sec}$	Reservoir temperature, $^{\circ}\text{C}$
Kumkol	0.795	2.68	55
Karabulak	0.785	1.683	57.7
Kenlyk	0.772	1.2	62
Karazhanbas	0.926	346	30
Uzen	0.829	10.5	50

The filtration experiments were conducted by using core samples and sand from Kumkol and Karabulak fields (Fig.17), strongly water wet river sand was used as well (Fig.18). The information about the permeabilities of the core samples and sand pack models can be found below. In some tests polystyrol spheres with diameter of 1 mm were used to model oil wet rock. In most experiments sand packs (Fig.19) were used.



Figure 17 – Core samples.



Figure 18 – Water-wet river sand.



Figure 19 – Sand pack model.

The viscosity of aqueous gellan solutions was measured using Ubbelohde viscometer at room temperature 25 ± 0.1 $^{\circ}\text{C}$ (capillary length is 90mm, capillary diameter is 0.86mm, the diapason of viscosity measurement according to Interstate

Standard GOST 10028–81 is from 6 to 30 mm²·s⁻¹). The rheological behavior of aqueous gellan solutions was monitored with the help of Rheolab QC, Anton Paar (Austria) (Fig.20). The rheological measurements were carried out by C-DG42/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.



Figure 20 – Rheological viscometer Rheolab QC, Anton Paar (Austria).

Mechanical testing of cylindrical gellan gel samples was performed by using texture analyser TA.XT plus, Stable Micro Systems, (UK) (Fig.21).



Figure 21 - Texture analyser TA.XT plus, Stable Micro Systems, (UK).

Filtration tests were conducted on the apparatus for the investigation of core samples УИК-C(2) (Fig.22).



a)



b)

Figure 22 – Core holder (a) and core flooding set up (b) used in this work.

Most filtration tests except those in which the polymer solution was injected into brine saturated porous media 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. The details of the polymer solution injection process and the following steps are discussed below. The information about flow rates, ambient pressure and temperature set in each experiment can be found below as well.

3.2 Main chemical and physical properties of gellan gum and its aqueous solution. Comparison with counterparts and analogies

Gellan – a water soluble polysaccharide produced from the biomass by the aerobic fermentation of the microorganism *Sphingomonas elodea* – is produced as food product by Chinese company “Zhejiang DSM Zhongken Biotechnology Co., Ltd.”. Figure 23 presents the gellan’s molecular structure.

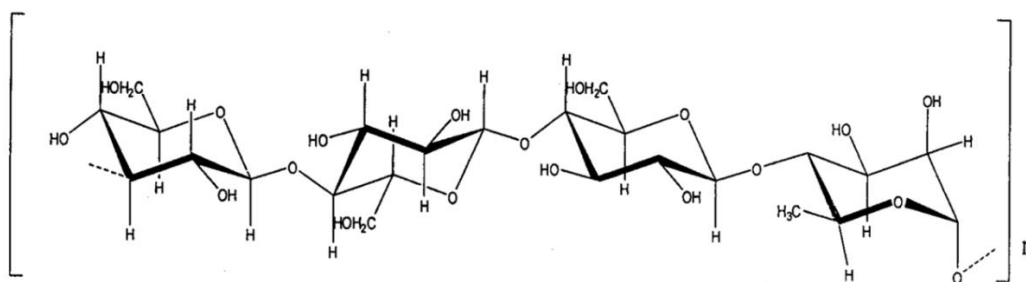


Figure 23 – Molecular structure of gellan.

The unique ability of the aqueous solution of gellan gum to transform into gel phase (Fig.24) upon the contact with salt or salt containing water as well as due to the change of pH and decrease of temperature was discussed and studied by different authors (Kudaibergenov et al., 2016).



Figure 24 – Gellan solution after contacting with Kumkol ($73 \text{ g}\cdot\text{L}^{-1}$) brine.

The figure 25 demonstrates the viscosity of gellan aqueous solution versus time, concentration and temperature. The influence of storage time on the gellan solution behavior is shown in fig.25 (a). At first the viscosity decreases, then insignificantly increases and further changes slightly. Such time dependent change of

the viscosity of gellan is probably related to the formation and destruction of gellan associates stabilized by hydrogen bonds. The reduced viscosity of gellan solutions gradually decreases with increase in temperature (Fig. 25 (b)). 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

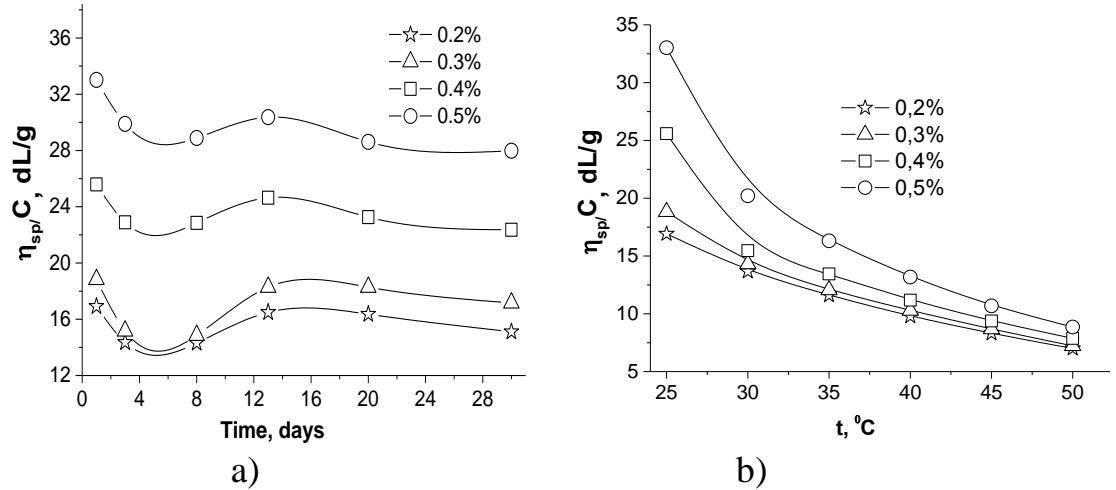


Figure 25 - Dependence of the viscosity of gellan on time storage (a) and temperature (b) (Kudaibergenov et al., 2016).

the 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 (Kudaibergenov et al., 2016). Moreover, the reduction of gellan solution's viscosity upon the increase of temperature may be beneficial for the selective placement of the solution inside of watered out layers of the oil reservoir without invasion into oil saturated channels. However, as it will be shown in the section 3.3, at elevated temperatures (around 90 °C) the gellan loses its ability to plug the pore space, as bulk elastic gel is not formed. Nevertheless, as it is seen from the fig. 26 (b) the gellan solution is still able to form bulk gel at temperature of 60 °C. Thus reservoir temperature can positively impact the placement of the solution only when it is below 90 °C.

Figure 26 demonstrates the phase behavior of 1.5 wt.% concentrated gellan gum aqueous solution in presence of 10-90 vol.% of Karabulak brine ($90 \text{ g}\cdot\text{L}^{-1}$) at 30 and 60 °C. The visual demonstration of gellan aqueous solution gelation upon the contact with brine saturated rock is presented by the figure 27.



a)



b)

Figure 26 - Gelation of 1.5 % gellan solution in the presence of 10-90 vol.% of Karabulak brine ($90 \text{ g}\cdot\text{L}^{-1}$), a) $30 \text{ }^\circ\text{C}$, b) $60 \text{ }^\circ\text{C}$.

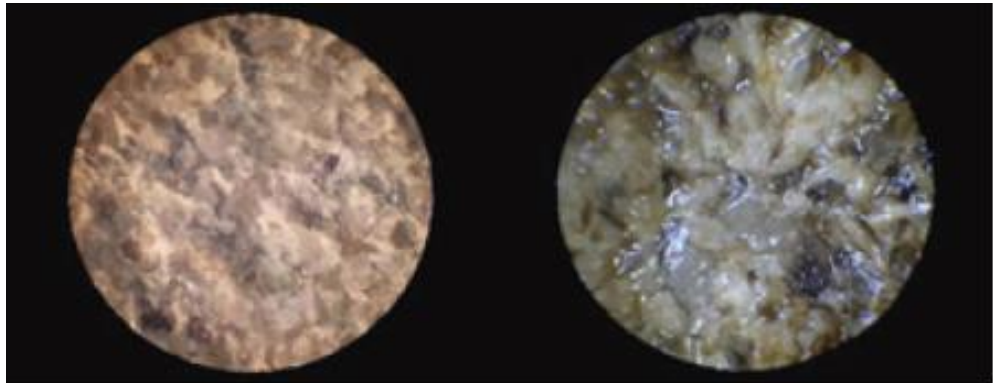


Figure 27 – The face side of core sample before (left) and after the injection of gellan solution (right).

The unique property of gellan gum aqueous solution to transform into gel phase upon the contact with saline water makes it a promising candidate for WST and CCO in watered out oil reservoirs. In this context it should be stressed that polyacrylamide - the most widely used polymer for WST and CCO is not tolerant to the presence of salt, as its viscosity decreases upon the addition of brine (Fig.28 (1)). On the contrary, in case with gellan the addition of brine causes dramatic viscosity increase and gelation (Fig.28 (2)).

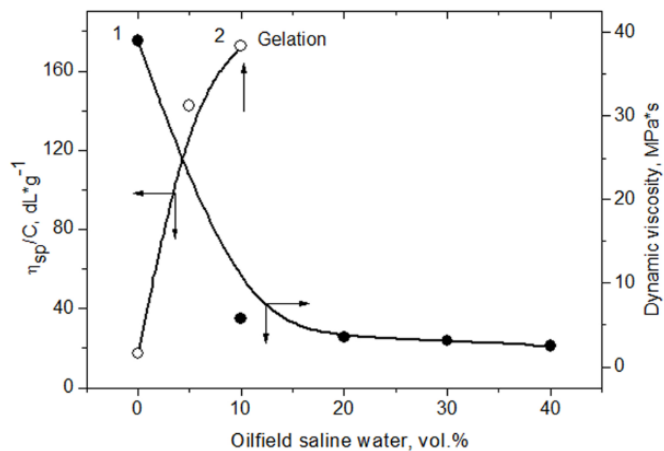


Figure 28 – Changing of the dynamic viscosity of 0.2% PAAm (1) and the reduced viscosity of 0.2% gellan solution (2) upon the addition of Kumkol brine ($73 \text{ g}\cdot\text{L}^{-1}$).

Comprehensive information on the rheological properties of gellan as a function of polymer concentration, salt content, temperature and shear stress is necessary to predict the behavior of gellan solution in the oil reservoir. 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 (Fig.29). Newtonian flow of gellan solution is realized after 65 °C. Step-by-step transformation of gellan solution from pseudo plastic 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.

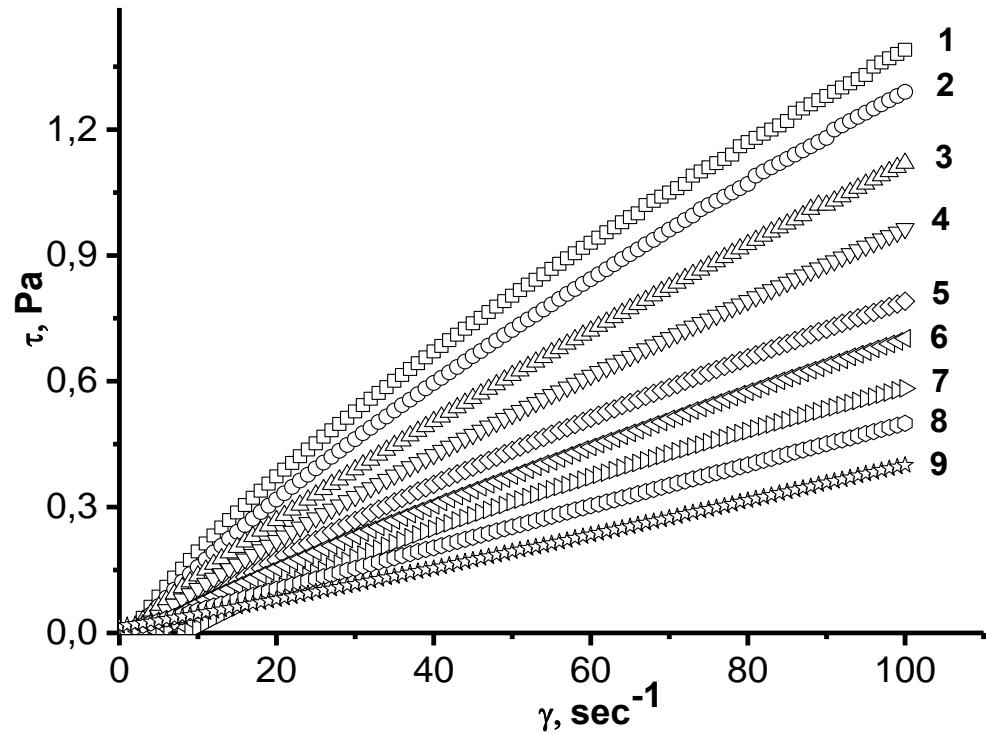


Figure 29 - The shear stress-shear rate curves of 0.5 wt.% gellan solution at 25 (1), 30 (2), 35 (3), 40 (4), 45 (5), 50 (6), 55 (7), 60 (8) and 65 °C (9) (Kudaibergenov et al., 2016).

Determination of mechanical properties of gellan gel and their comparison with those of other polymer gels is of high importance for proper screening of the polysaccharide as a plugging agent. The measurement of Young’s modulus of gellan gel sample generated by the contact with Kumkol brine ($73 \text{ g}\cdot\text{L}^{-1}$) resulted in $9.54\cdot 10^{-2} \text{ N}\cdot\text{m}^{-2}$ (Kudaibergenov et al., 2016). Previously it has been proved that mechanical properties of polyacrylamide and gellan gels are surprisingly similar in spite the difference in molecular structure. Both polymers demonstrate similar form of the stress strain curves when their gels are compressed (Giulio G. Ferruzzi et al., 2000). Figure 30 below presents the stress versus strain curves detected during the compression of gellan gels generated by contacting 9 ml of 0.5% gellan solution and 1 ml of Karabulak brine ($90 \text{ g}\cdot\text{L}^{-1}$). From the fig. 30 it is seen that the breaking stress for the gels varied between 20 and 27 kPa. This is in agreement with the results of

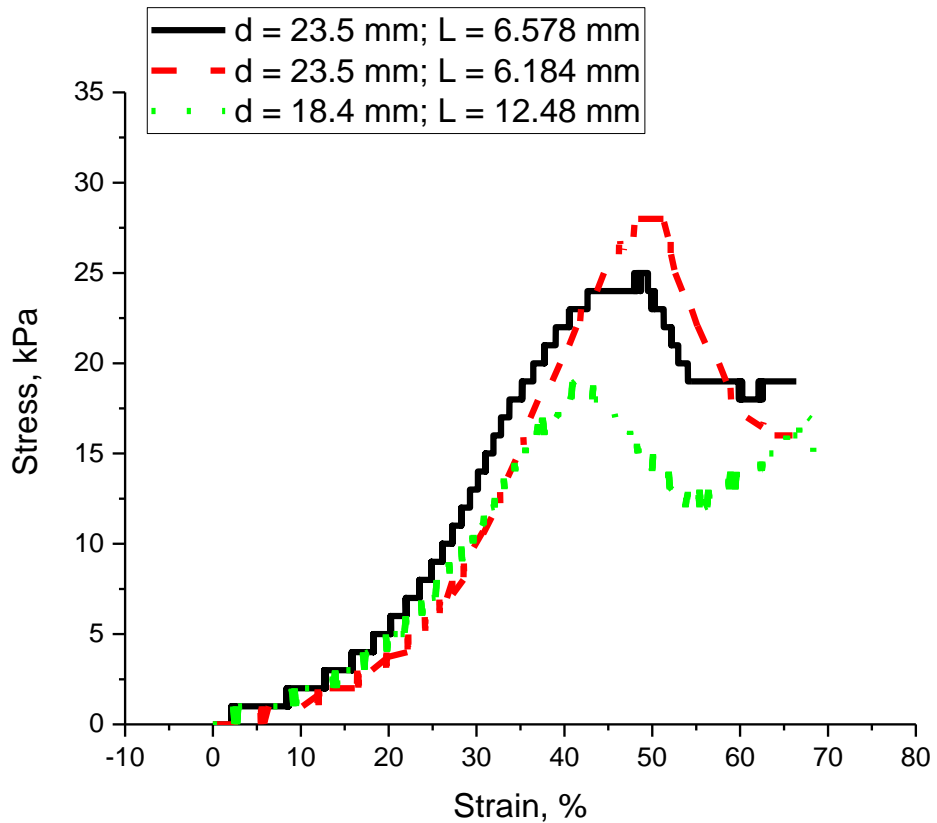


Figure 30 - Stress versus strain curve of gellan gels generated by contacting 9 ml of 0.5% gellan solution and 1 ml of Karabulak brine ($90 \text{ g}\cdot\text{L}^{-1}$).

other authors, though depending on the gellan concentration and gelation conditions much higher breaking stresses can be obtained as well. For example, Giulio G. Ferruzzi et al., (2000) summarized the results of different authors in order to compare the breaking stresses of different polymer gels (Table 4).

Table 4 - Breaking stresses with corresponding breaking strains from different works reviewed by Giulio G. Ferruzzi et al., (2000) [167].

Gel	Breaking stress, kPa	Breaking strain, %
Agar	18-90	16-27
Carrageenan	8-96	22-38
Gellan	25-130	16-25
Gellan	6-130	22-300
Gellan	9-351	70-262
Polyacrylamide	9-340	10-160
Polyacrylamide	12.5-883	0.42-249

As it can be seen from the above table gellan gel's mechanical properties are comparable with those of polyacrylamide and carrageenan as well as agar. The similarity between their mechanical stability and that of gellan gel credits gellan as

suitable agent for WST and CCO, since polyacrylamide gels have been numerously applied for this purpose.

3.3 Hydrodynamic behavior of gellan gum aqueous solution in homogeneous porous media

Firstly, a series of experiments has been conducted in order to investigate plugging behavior of gellan aqueous solution inside of brine and oil saturated porous media. Pressure response as well as the analysis of the effluent samples helped to determine the plugging behavior of gellan solution at a certain range of reservoir conditions.

In all experiments the injection of gellan was accompanied with the increase of injection pressure above the base line obtained during the previous water filtration through the same model (core sample). The increase of the injection pressure is associated with the gelation of gellan solution upon the contact with brine. Residual resistance factor (RRF) values were registered during the further water filtration. RRF is the ration between water injection pressure registered before and after the injection of polymer solution. RRF shows how much the permeability has been reduced as a result of the treatment of pore space with polymer solution. These data are of high importance for the prediction of a gelant behavior inside of a real reservoir and are necessary for the proper design of the treatment.

The below figure 31 demonstrates the time dependent change of the injection pressure during the injection of 0.5% concentrated gellan solution into 25 cm long sand pack model with permeability of 2 Darcy and pore volume of 100 cm³.

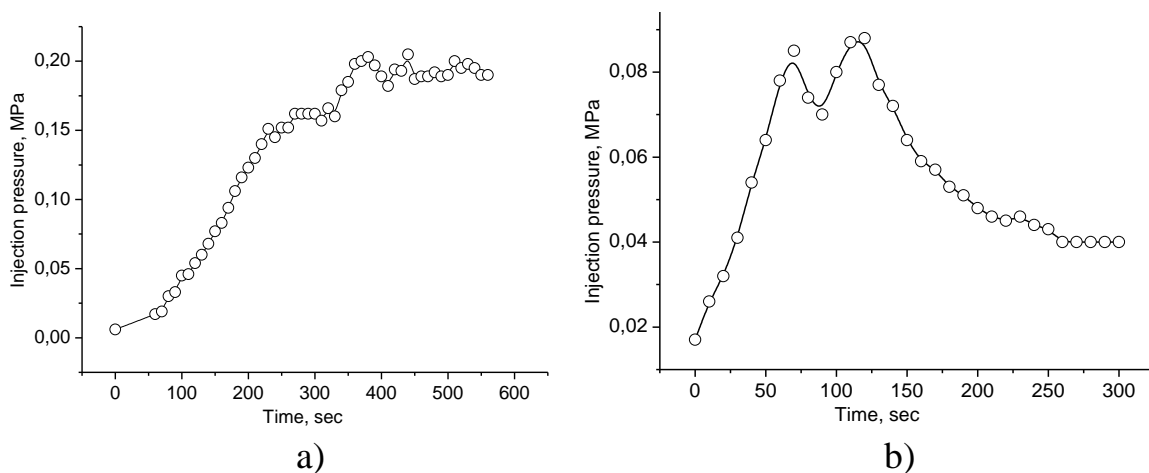


Figure 31 – Time dependent changing of the injection pressure inside of Kumkol brine (73 g·L⁻¹) saturated sand pack model upon the injection of a) 10 cm³ of 0.5% gellan solution and b) 10 cm³ of brine after the polymer.

As it can be seen from the fig. 31 (a) above the injection pressure at first linearly increases and then levels off to a plateau. Gradual gel formation inside of the sand pack model is responsible for the linear increase of the injection pressure due to the plugging of the pore space. The injection of brine after gellan (Fig.31 (b)) causes the gelation of the rear edge of the placed gellan slug indicated by dramatic pressure

increase enough for the breakthrough of water. As a result the portions of newly injected water bypass the gel plug. This experiment proved the possibility of permeability reduction by gellan solution. However, it is also worth to observe the injection pressure responses registered during the injection of larger gellan solution slugs (1-3 PV) instead of the injection of separated small (0.1 PV) slug.

It was shown that continuous injection of large slugs of gellan solutions into the core samples and sand packs is characterized by pressure oscillation behavior. In some experiments injection pressure value keeps oscillating until it reaches its highest point (Fig.32).

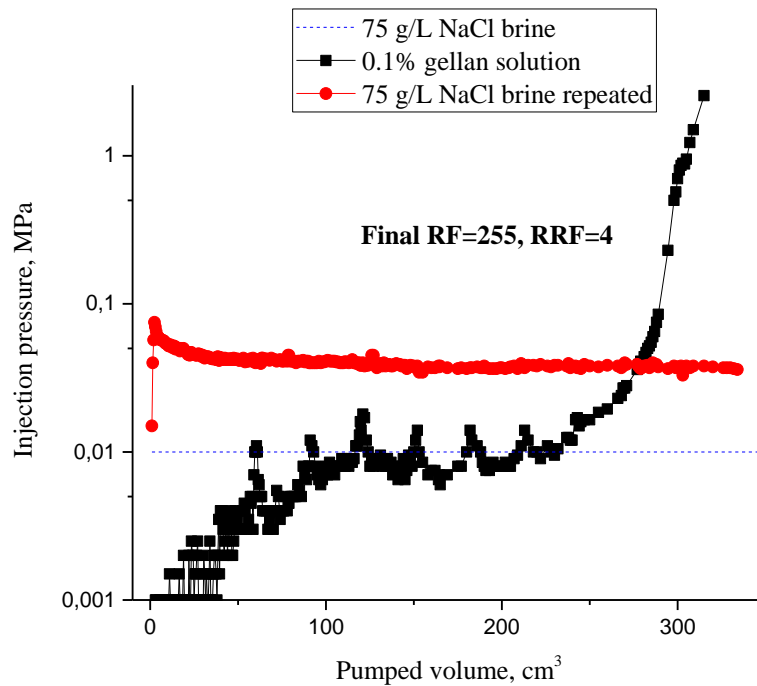


Figure 32 – The injection of 0.1% concentrated gellan solution and brine into 20 cm long water-wet sand pack model saturated with 75 g·L⁻¹ NaCl brine. Permeability is 3.7 Darcy, temperature is around 25 °C and flow rate is 1 cm³/min.

The evidence of the presence of the gel plug inside of the pore space was provided by the tests described below in which the gel plug was partly displaced from the model under the influence of increased pressure. Fig. 33 presents the results of the injection of 0.5% gellan solution and brine into 20 cm long water-wet sand pack model initially saturated with Kenlyk brine (120 g·L⁻¹) and having permeability of 5.7 Darcy. This experiment has been conducted at 60 °C. As it can be seen at fig. 33 (a) the injection of gellan solution at constant mode resulted in the accumulation of gel inside of the model and its breakthrough when the injection pressure reached 0.6 MPa. High temperature (60 °C) as compared with the previous test (25 °C) was the reason behind better flowability of the formed gel in this experiment.

Another experiment has been at the conditions similar with the previous test (Fig.33 below), however the permeability was above 20 Darcy and Kenlyk oil (1.2 mP·sec) was used to create initial oil saturation inside of the 8.6 cm long water-wet

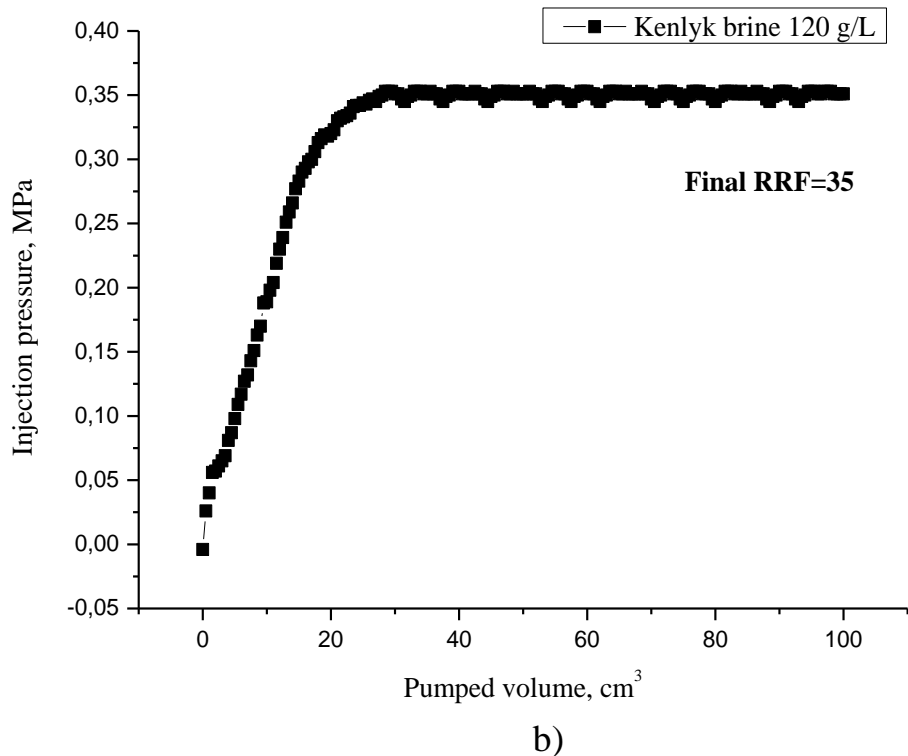
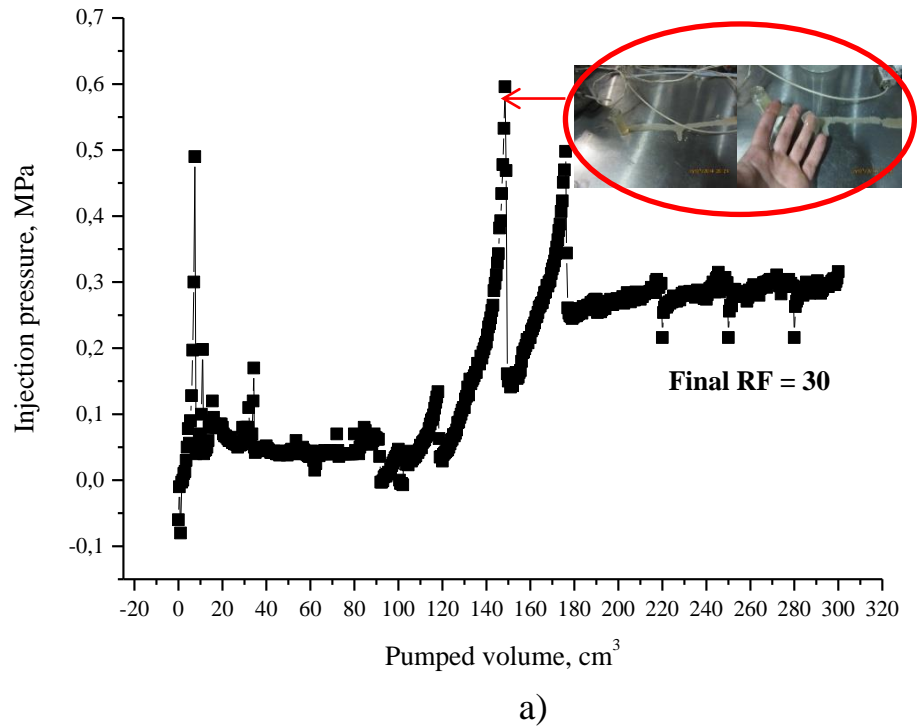


Figure 33 – Injection pressure versus pumped volume of 0.5% gellan solution (a) and Kenlyk brine (120 g·L⁻¹) (b) into 20 cm long water-wet sand pack model saturated with Kenlyk brine. Permeability is 5.7 Darcy, temperature is around 60 °C and flow rate is 1 cm³/min.

sand pack model. The injection of water into the model containing 27% of initial water and 74% of initial oil saturation resulted in the recovery of 50% of oil, the

following injection of gellan allowed the additional recovery of 5.4% of oil. However, the main purpose of the experiment was to observe the pressure responses.

It is clearly seen that the injection of 0.5% concentrated gellan solution into 20 Darcy sand pack caused only 5.6 fold permeability reduction (Fig. 34 below), while the injection of the same solution into 5.7 Darcy model reduced permeability in 35 times (Fig. 33 above). The reason for that is higher flowability of gellan gel in high permeability channels. The figure 35 below demonstrates the photo of the effluent samples superimposed on the curve of injection pressure registered during the injection of gellan into the model with permeability of 20 Darcy (Fig. 34 below). As it is seen, during the injection of gellan solution from 40 to 50 cm³ no effluent was collected since the plugging of the model was taking place. However, after the injection pressure reached its critical value breakthrough of the gel plug occurred. As a result, the effluent sample collected between 50 and 60 cm³ contained the gel aggregates.

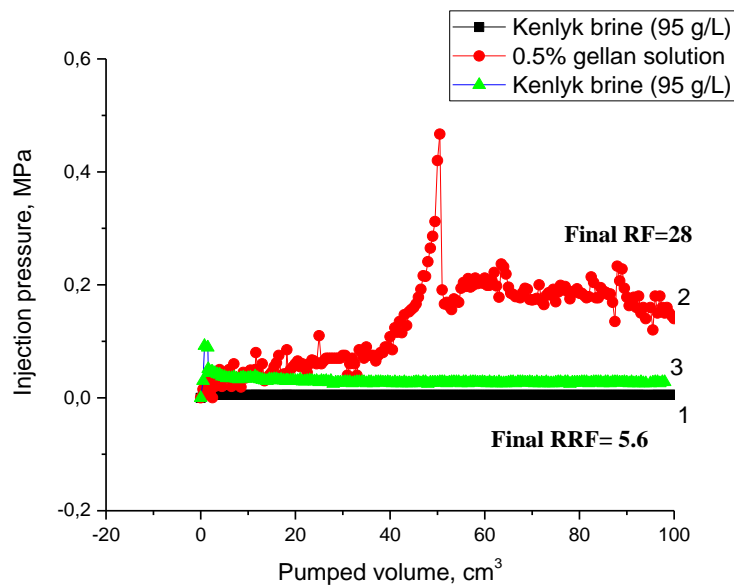


Figure 34 – Injection pressure versus pumped volume of Kenlyk brine (95 g·L⁻¹) (1), 0.5% gellan solution (2) and repeated injection of Kenlyk brine into 8.6 cm long water-wet sand pack model saturated with Kenlyk oil and brine. Permeability is 20 Darcy, temperature is around 60 °C and flow rate is 0.5 cm³/min.

Similar results were obtained during the injection of 0.5% gellan solution into 6 cm long water-wet sand pack model with permeability of 2 Darcy after the oil saturation and water flooding at 60 °C and 0.25 cm³/min. The breakthrough of the gel plug was observed at 0.2 MPa, again transport of gellan through the model was detected by its presence in the effluent samples (Fig.36).

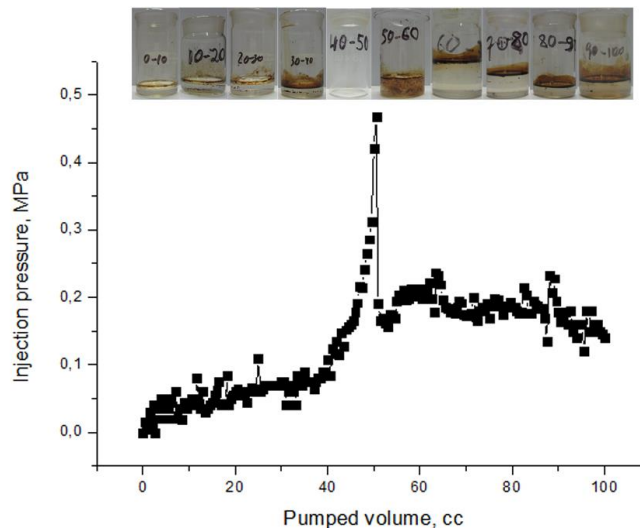
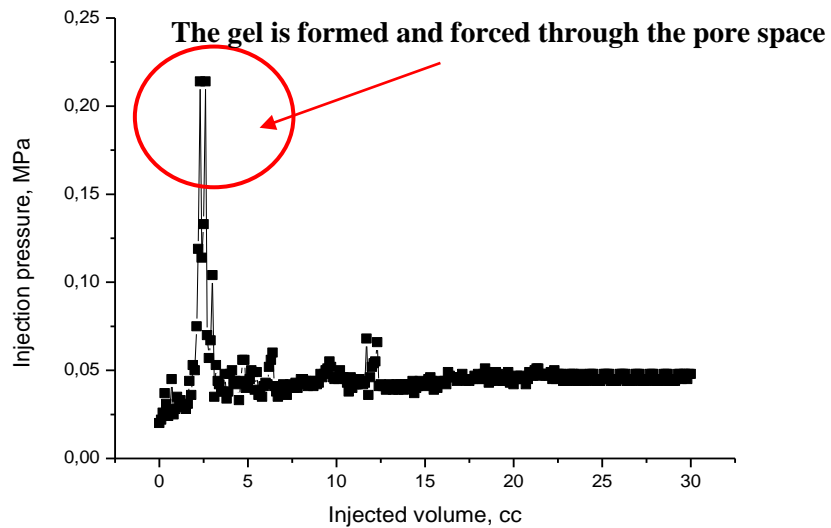
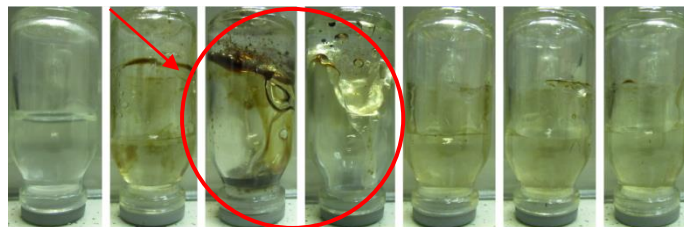


Figure 35 – The photo of effluent samples superimposed on the curve of injection pressure registered during the injection of gellan into the model with permeability of 20 Darcy (Fig. 34 above).



a)

Gel formed only once at the contact of gellan and brine

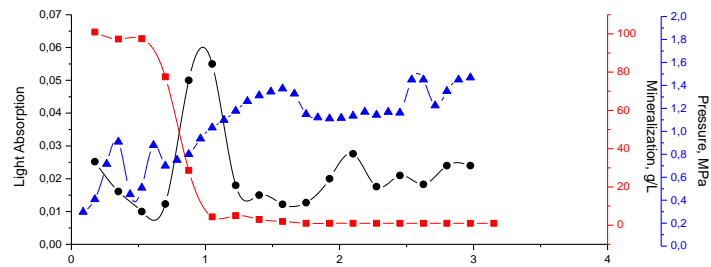


Pure gellan 5cc 10 cc 15cc 20 cc 25cc 30 cc

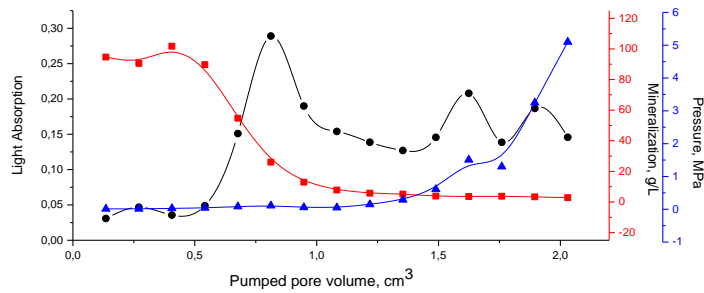
b)

Figure 36 – The injection of 0.5% gellan solution into 2,3 Darcy permeability water-wet sand pack. Length of the model is 6 cm, diameter is 3 cm. Kenlyk brine ($120 \text{ g}\cdot\text{L}^{-1}$). Oil viscosity is $1.22 \text{ mPa}\cdot\text{sec}$. Temperature is $60 \text{ }^\circ\text{C}$ and flow rate is $0.25 \text{ cm}^3/\text{min}$.

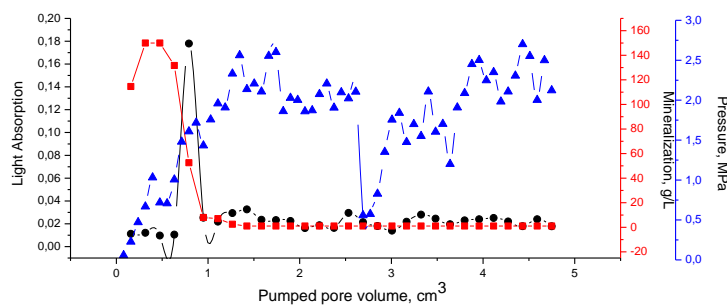
In order to get more insights on gellan plugging behavior in homogeneous sand packs, a series of tests have been conducted on sand packs composed of water-wet sand with an average granular size of 0.125-0.25 mm. In the course of gellan solution injection the inlet injection pressure, salinity, and turbidity of the effluent samples were measured. 0.2 and 0.5% concentrated solutions were injected into oil saturated and water flooded models at 55 °C and 0.5 cm³/min. Kumkol brine (73 g·L⁻¹) and oil (2.6 mP·sec at 55 °C) were used. The results of these tests are presented by the below curves (Fig.37).



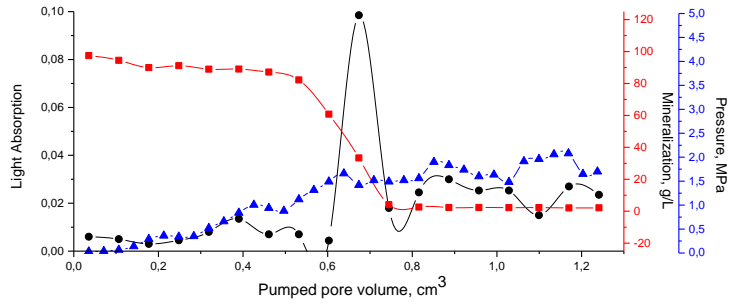
a) Permeability 0,33 Darcy, 0,5 % gellan solution;



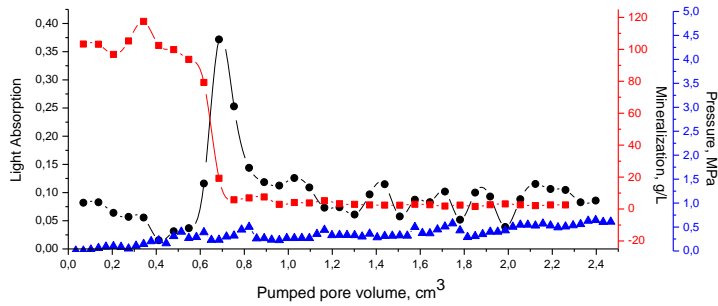
b) Permeability 0,75 Darcy, 0,5 % gellan solution;



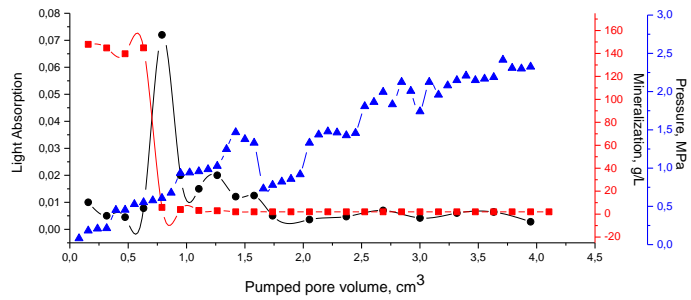
c) Permeability 1,7 Darcy, 0,5 % gellan solution;



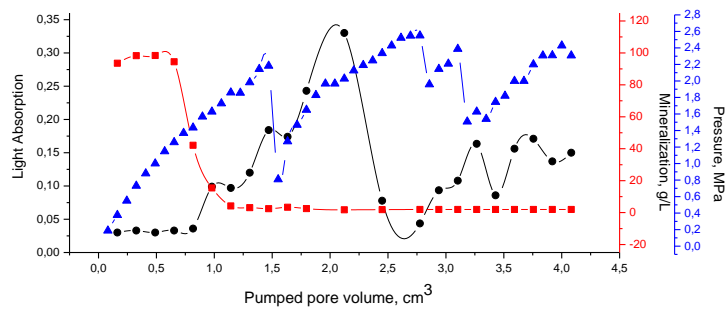
d) Permeability 3,2 Darcy, 0,5 % gellan solution;



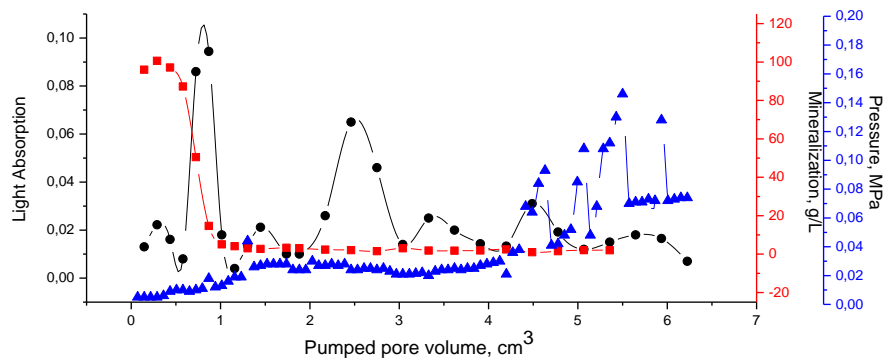
e) Permeability 10 Darcy, 0,5 % gellan solution;



f) Permeability 0,5 Darcy, 0,2 % gellan solution;



g) Permeability 1,122 Darcy, 0,2 % gellan solution;



h) Permeability 7 Darcy, 0,2 % gellan solution in technical water;

Figure 37 - Experimental results of the modeling of Gellan's injection into the oil formation of Kumkol oilfield.

Salt concentration in the effluent fraction is marked by the red curve. In all experiments after pumping of ≈ 0.6 pore volumes of the polymer solution, a sharp decrease of salt concentration in the effluents was observed indicating the decrease of salt content in the sand pack. It happens because brine water is washed out from the model by injection of the polymer solution. In fact, the decrease of salt content inside of the sand pack constrains gellan's gelation which is initiated by salt.

The black curve represents the light absorption of the effluent samples. In all experiments, the highest value of this parameter was observed after pumping of ≈ 0.6 pore volumes of the polymer. In this case, the formation of gel particles is observed by unaided eye. After the withdrawal of gel from the model, the light absorption curve levels down and the gel formation is not observed because of the lack of salt inside of the sand pack. Comparison of salt concentration and light absorption curves shows that gelation process takes place at the interface between polymer solution and salted water. Thus inside of the sand pack model, there is only one zone which contains the gel and after pumping of ≈ 0.6 pore volumes of the polymer solution, a portion of this gel is found in the effluent fraction indicated by the peak in light absorption curve. Authors assume that another portion of this gel is retained in the porous media which leads to the decrease in permeability.

Injection pressure is marked by blue curve. All experiments showed that injection pressure has a tendency to increase gradually while gellan solution is injected. It is seen that almost in all experiments the final value of pressure exceeds 2 MPa. This is direct evidence that injection of gellan solution into the pore space leads to the decrease of permeability.

From the fig. 38 below it is seen that less concentrated gellan solutions should be able of deeper propagation inside of the reservoir. Therefore it is suggested that 0.2% gellan solution is better to be used for in-depth permeability modification. While the 0.5% gellan solution is better to be used as a permeability modifier in the vicinity of a well.

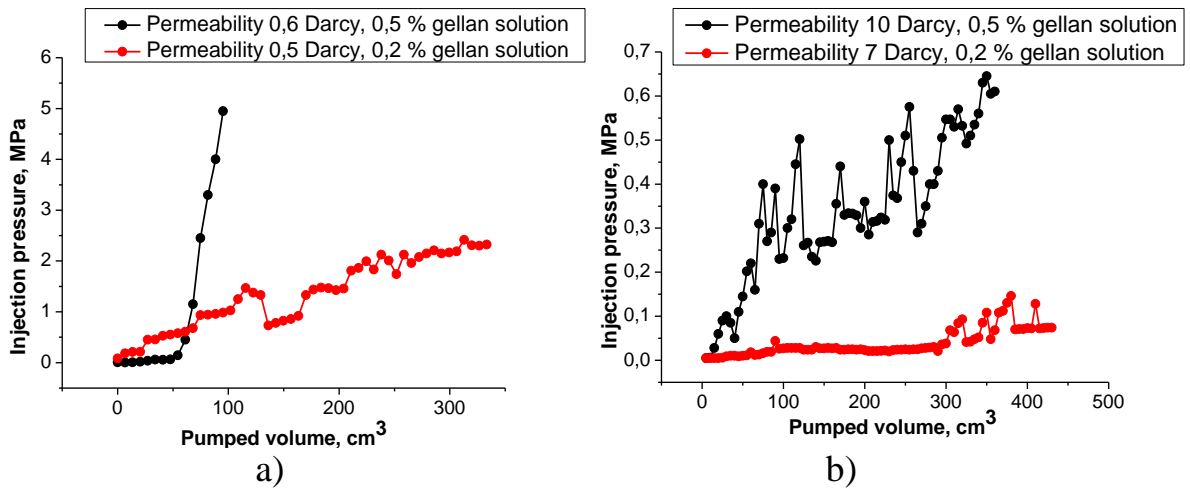


Figure 38 – The injection of 0.2 and 0.5 % gellan solutions into oil saturated and water flooded sand pack models at 0.5 cm³/min and 55 °C. Kumkol brine (73 g·L⁻¹) and oil (2.679 mPa·sec).

In-depth propagation of gel is advantageous for the treatment of the injection wells. However, in the case of producers, it is often necessary to create a firm stable plug right in the vicinity of the well.

Since gellan powder is dissolved in technical water with low salinity, the constant injection of its solution leads to the washing out of salt from the vicinity of the well. As it has been proved above, the gel formation takes place when the front edge of injected gellan solution meets the saline water (so called sol-gel transition). Due to permanent injection of gellan solution into the well, the salinity of oil reservoir gradually decreases. In its turn, this causes the formation of the flowable weak gel that is not suitable for the plugging in the near wellbore region of a producer where high pressure drops are common and may cause the gel to be produced back. It is expected that alternating injection of gellan and brine solutions will overcome this problem. To check this point a series of filtration experiments were conducted on sand pack models with permeabilities of 2 Darcy. Experiments consisted of alternating injection of 10 cm³ of 0.5 % gellan solution and brine water into the water flooded sand packs. The dependence of injection pressure on pumped volume was compared with constant injection of gellan (Fig.39).

It is clearly seen from fig. 39 that each portion of the injected gellan solution is followed by the injection of brine water portion. Alternate injection of gellan and brine solutions leads to the gradual increase of the injection pressure. The reasonable explanation of this phenomenon is the permanent formation of gel slug inside of the sand pack.

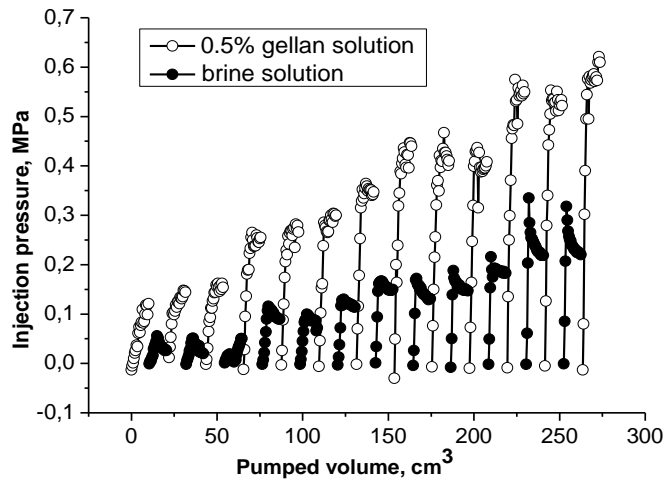


Figure 39 - Alternated injection of 0.5% gellan and brine solutions into water flooded sand pack (2 Darcy), $0.5 \text{ cm}^3 \cdot \text{min}^{-1}$ (100 cc – 1PV), temperature 55 C, Kumkol brine ($73 \text{ g} \cdot \text{L}^{-1}$) and oil ($2.679 \text{ mPa} \cdot \text{sec}$).

Fig. 40 clearly demonstrates that alternated injection of gellan and brine gives the same effect if only gellan solution will be injected. The difference between the constant injection of gellan and alternating injection of gellan and brine is small in the context of pore space plugging.

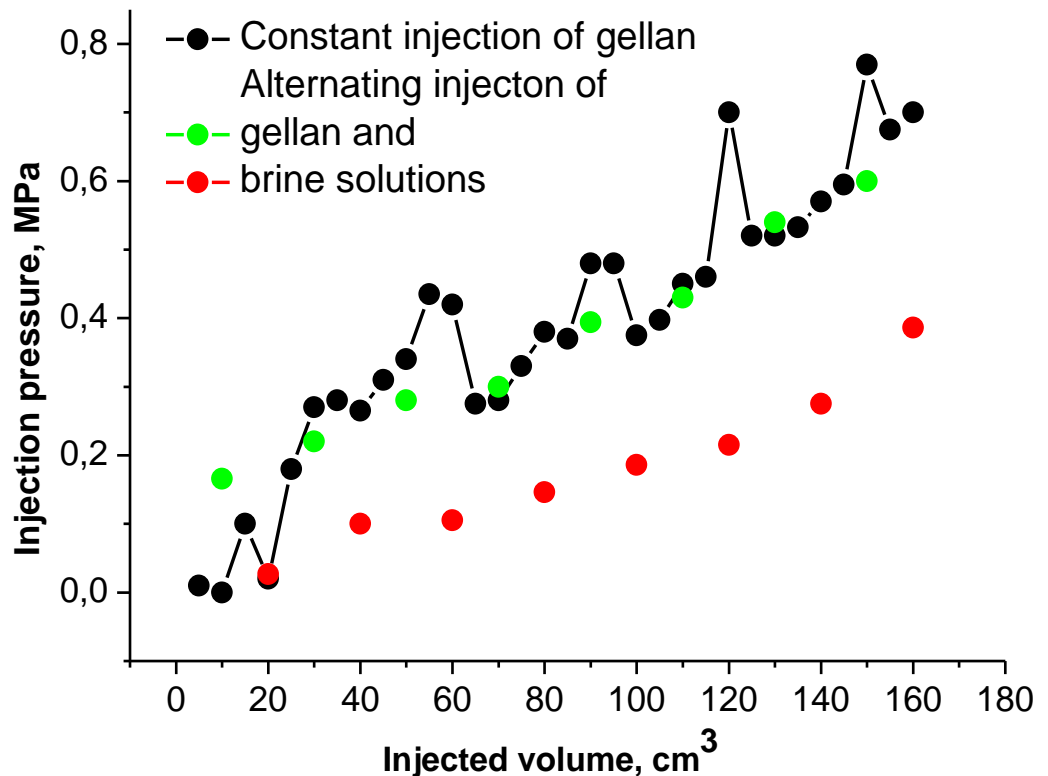
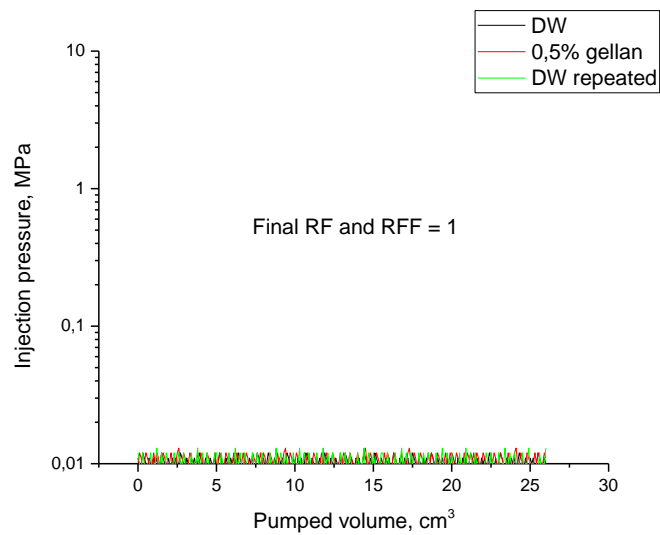


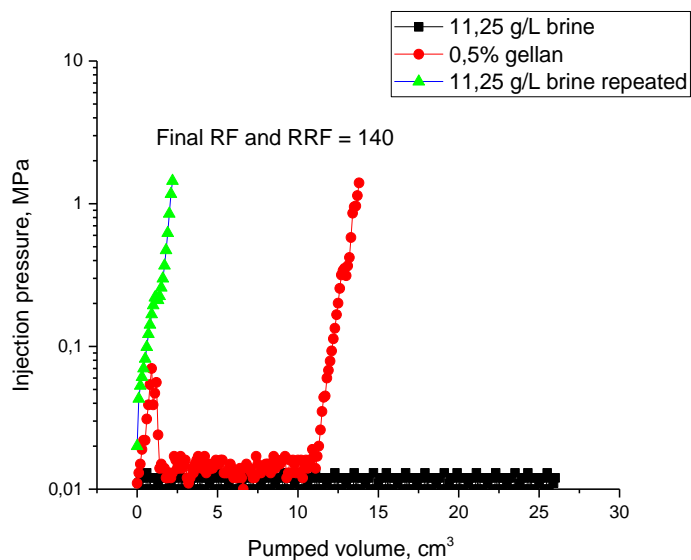
Figure 40 – Comparison between separate injection of gellan solution and alternating injection of gellan and brine solutions into the sand pack model.

Thus by the alternating injection of gellan and brine, it is possible to reduce the amount of injecting reagent at least in two times without detriment to the efficiency of the technology. This approach will considerably reduce the cost of the project.

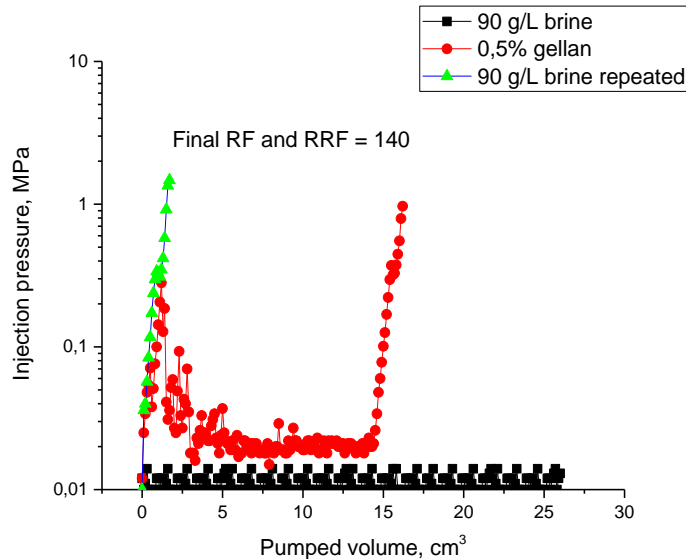
Another important factor that should be considered at the design stage of a well treatment by gellan solution is the effect of brine salinity on the plugging efficiency of the solution. In order to determine the relationship between the efficiency of plugging and brine salinity a series of tests have been conducted on 6 cm long polystyrol packs with diameter of 3 cm. In the first experiment, 0.5% concentrated gellan solution was injected into the polystyrol pack saturated with DW. In the second test pure Karazhanbas brine ($90 \text{ g}\cdot\text{L}^{-1}$) was used. The third experiment was conducted with the same brine diluted by DW in 8 times to make the total salinity equal to $11.25 \text{ g}\cdot\text{L}^{-1}$. All tests have been conducted at room temperature. The curves at the fig.41 below present the results of these experiments.



a)



b)



c)

Figure 41 – The injection of 0.5% concentrated gellan solution into polystyrol pack model at $1 \text{ cm}^3/\text{min}$ and $25 \text{ }^\circ\text{C}$. The pack was saturated with a) distilled water, b) $11.25 \text{ g}\cdot\text{L}^{-1}$ diluted Karazhanbas brine and c) $90 \text{ g}\cdot\text{L}^{-1}$ pure Karazhanbas brine. The length of the model is 6 cm, the diameter is 3 cm. Permeability is 14 Darcy.

As it is seen from the above figure 41 (a), the injection of gellan into polysterol pack saturated with distilled water did not cause any permeability reduction. This is due to the absence of salt inside of the model. Also, it should be noted that there was no substantial difference between the experiments conducted at 90 and $11.25 \text{ g}\cdot\text{L}^{-1}$ brine salinities. This suggests that even at low salinities gellan solution is still able to operate effectively.

The effect of temperature will be discussed in the following section.

3.4 Hydrodynamic behavior of gellan gum aqueous solution in heterogeneous porous media

Experiments on homogeneous sand pack models did not show significant tertiary oil recovery increment. It was reported that the filtration experiments should be conducted on heterogeneous models in order to clarify the effect of polymer gel treatment on oil recovery as a result of sweep efficiency improvement (Qian Sang et al., 2014). Moreover, the filtration experiments on heterogeneous models are necessary for the assessment of selective plugging ability of gellan solution, because due to high viscosity of gelant solutions many polymer gel systems fail to provide the selective plugging in multilayered reservoirs with low permeability ratio between the layers (below 10) (Garmeh et al., 2011; Bai et al., 2008). Thus, gellan treatment of two-layered sand pack model with permeabilities of layers around 2.8 and 7 Darcy (the permeability ratio is 1:2.5) (Fig.42) was conducted for more complete characterization of the technology. 500 and 125 mkm sand particles of Karabulak sand were used to fill the model.

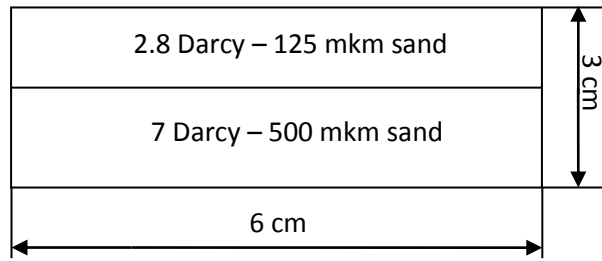


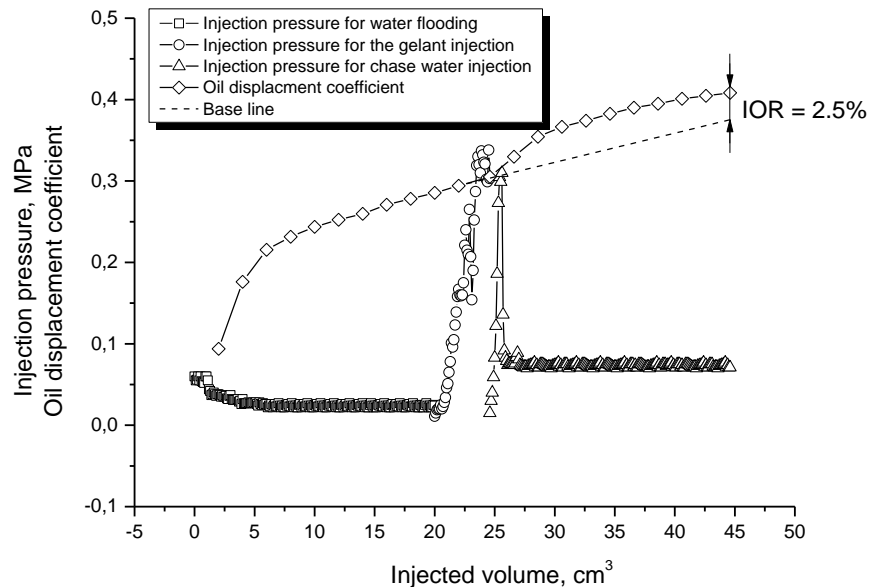
Figure 42 – Heterogeneous two-layered model used for the study of gellan solution behavior.

The experiments were conducted in the following order:

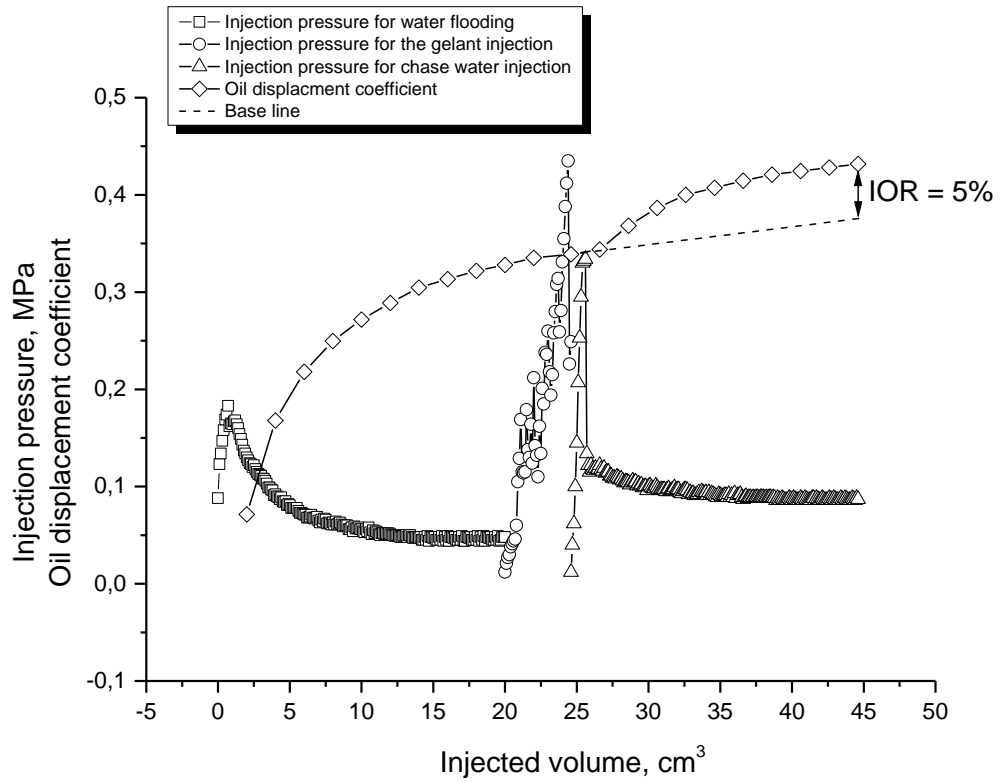
- 1) Packing the sand and permeability measurements;
- 2) Model saturation with Karazhanbas brine ($90 \text{ g}\cdot\text{L}^{-1}$);
- 3) Injection of Karazhanbas oil ($346 \text{ mPa}\cdot\text{sec}$) to displace brine until irreducible water saturation is reached;
- 4) Injection of two pore volumes of the same brine to model water flooding;
- 5) Injection of 0.5 PV of gellan solution to plug the high permeability channel;
- 6) Repeated injection of two pore volumes of the same brine to model chase water flooding and observe the extent to which the redirection of water flow occurred.

All filtration procedures have been conducted at $0.1 \text{ cm}^3/\text{min}$. Ambient temperature varied between 30, 60 and $90 \text{ }^\circ\text{C}$. Ambient pressure was set at 2 MPa.

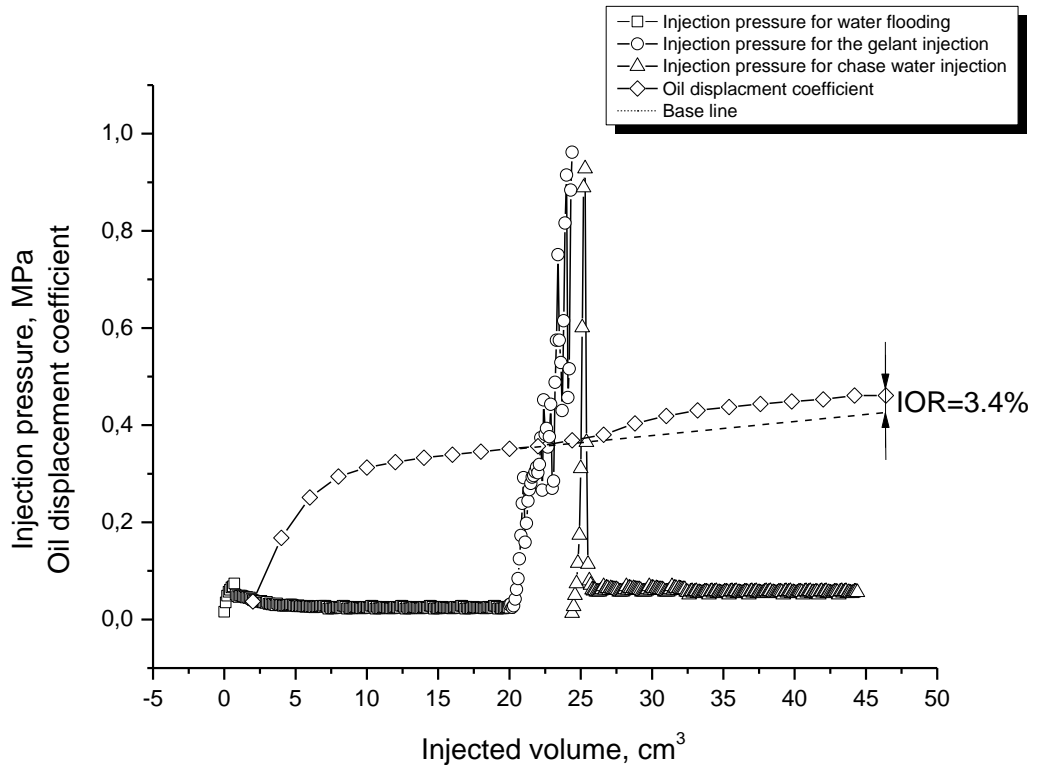
The fig. 43 demonstrates the results of the tests conducted at $30 \text{ }^\circ\text{C}$ and different gellan concentrations.



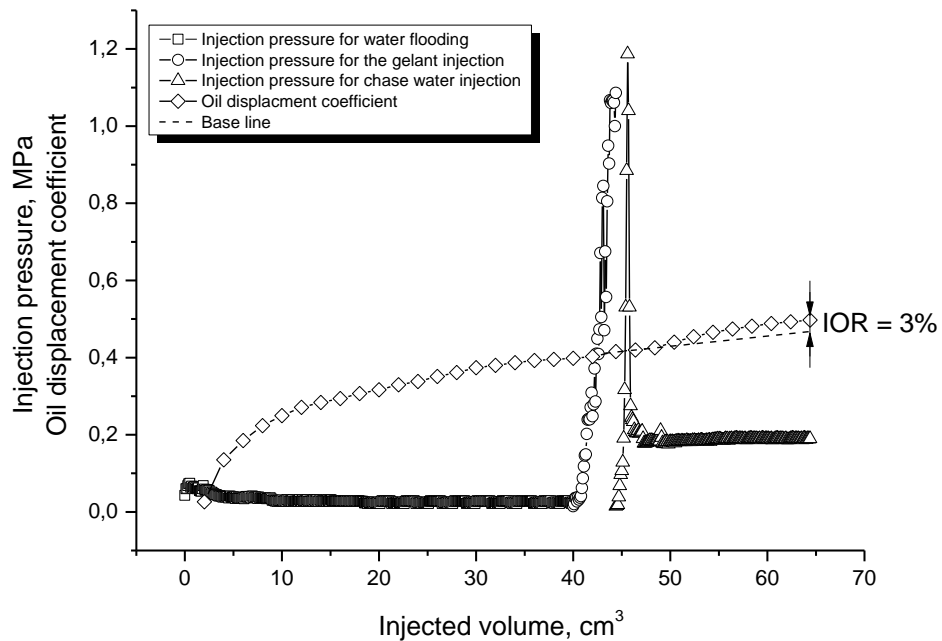
a) 0.1% gellan, two-layered model, ambient temperature is $30 \text{ }^\circ\text{C}$;



b) 0.25% gellan, two-layered model, ambient temperature is 30 °C;



c) 0.5% gellan, two-layered model, ambient temperature is 30 °C (2PV of water were pumped in the beginning);



d) 0.5% gellan, two-layered model, ambient temperature is 30 °C (4PV of water were pumped in the beginning);

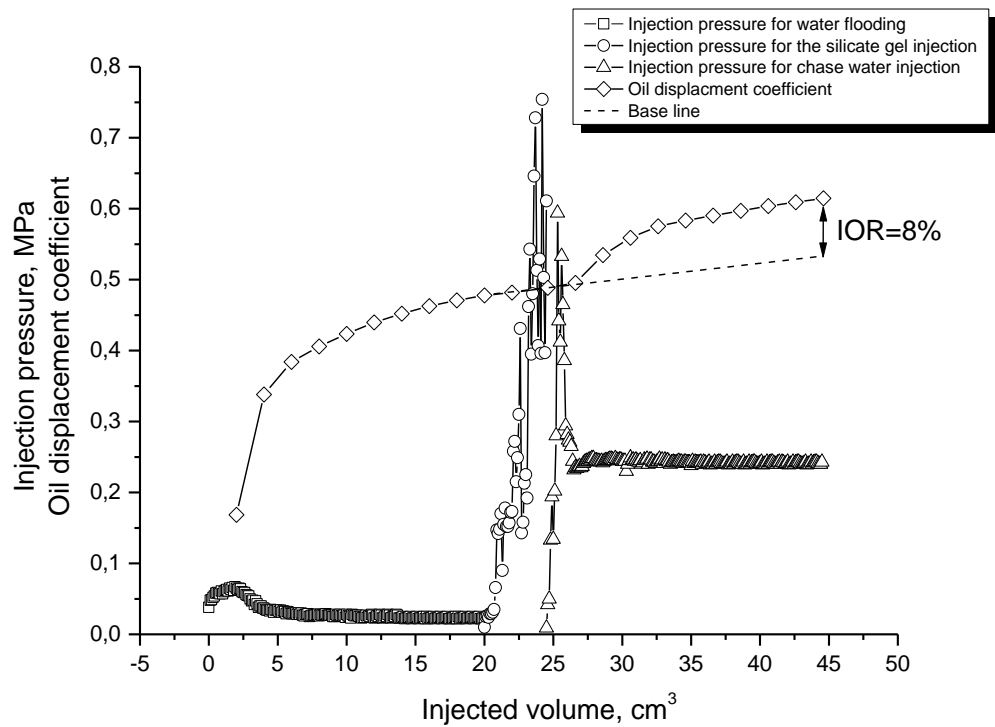
Figure 43 – Injection of gellan solutions into the two-layered sand pack model.

The shown above injection pressure and oil displacement coefficient curves demonstrate that gellan solution can be successfully applied in two-layered heterogeneous models. It is seen that the injection of water is not characterized by severe pressure increase, since water preferentially filtrates through high permeability layer. On the other hand, the injection of 0.5PV of gellan solution is associated with dramatic increase of pressure due to the gelation and plugging of the model with the formed gel. The repeated water injection shows severe pressure increase followed by water breakthrough as the injection pressure falls down. The further filtration of water occurs at pressure values higher than those registered during the initial water injection (before polymer).

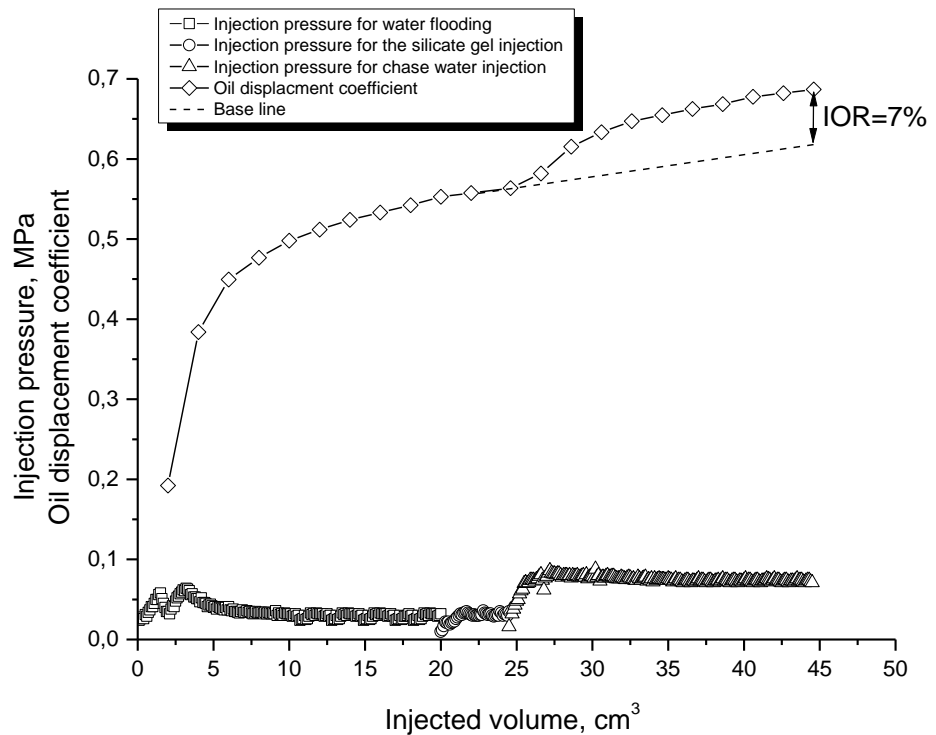
Another two tests were conducted at ambient temperature of 60 and 90 °C (Fig.44 a, b).

As it may be seen from the below figure 44, the increase of temperature negatively affects the plugging efficiency of gellan. At 90 °C the plugging effect is not observed due to the instability of gellan gel at elevated temperatures. The increase of oil recovery observed at 90 °C is likely due to the temperature increase.

The fact that no gel tracers were observed in the effluent samples of any of the above described experiments ensures the stability of gellan plug and its contribution to the observed effect of IOR. However, it is still not clear whether the observed oil recovery increase is due to the redirection of water flow from high to low permeability layer or just a consequence of polymer flooding effect. Also, since the



a) 0.5% gellan, two-layered model, ambient temperature is 60 °C;



b) 0.5% gellan, two-layered model, ambient temperature is 90 °C;

Figure 44 – Injection of gellan solutions into two-layered sand pack model.

permeability contrast between the layers is around 2.5 and the viscosity of gellan is higher than that of water (Fig.28, 29), especially when it is in gelled form, it cannot

be stated that the gel penetrates only into high permeability zone. X-ray computed microtomography analysis should be applied in order to get broader understanding of gellan behavior in two-layered models.

Similar experiments were conducted with Karabulak sand and fluids from Uzen oil field. Ambient temperature and pressure were set at 50 °C and 6 MPa. The flow rate was set at 0.1 cc/min. The length of the sand packs was 6 cm and the diameter was 3 cm. The first two experiments were conducted on homogeneous models made of 125 and 250 mkm sized sand particles with permeability 4.8 and 8.23 Darcy respectively. The third test has been conducted on two layered model composed of 4.8 and 8.23 D permeability layers (Fig.45).

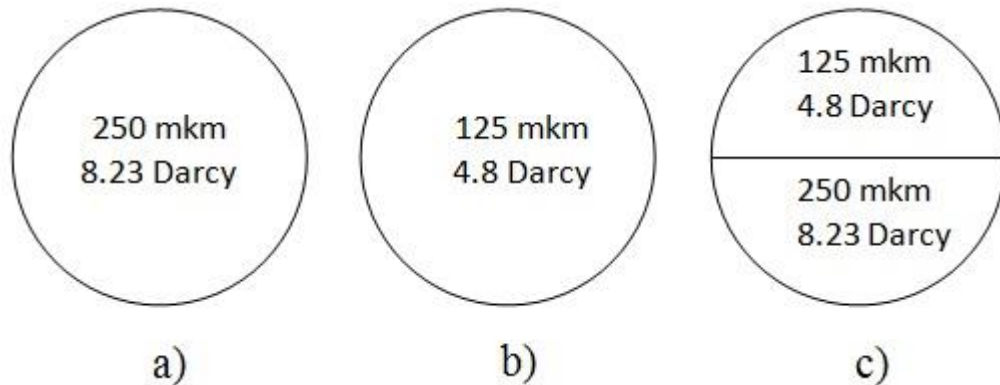


Figure 45 - Cross sectional area of the homogeneous (a, b) and heterogeneous (c) models.

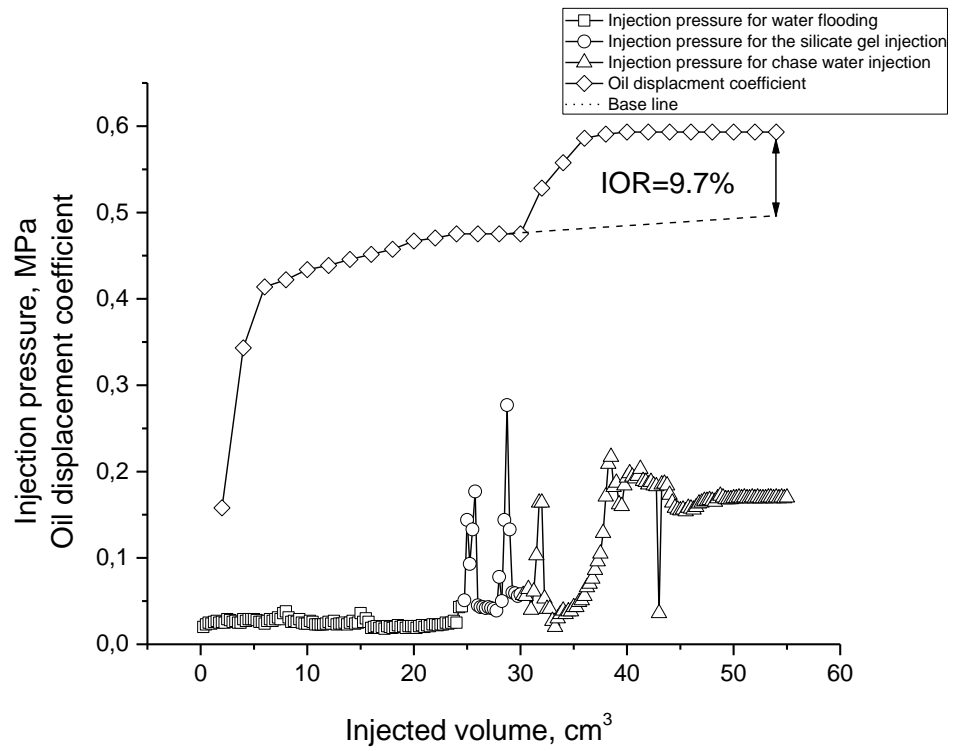
It should be kept in mind that the cross-sectional area of low and high permeability layers inside of the heterogeneous model is two times smaller than that of the homogeneous models. Thus, the injection pressure registered during the filtration of water or gellan solution through high or low permeability layer of the two-layered model should be two times bigger than that observed in homogeneous models.

The experiments were conducted in the following order:

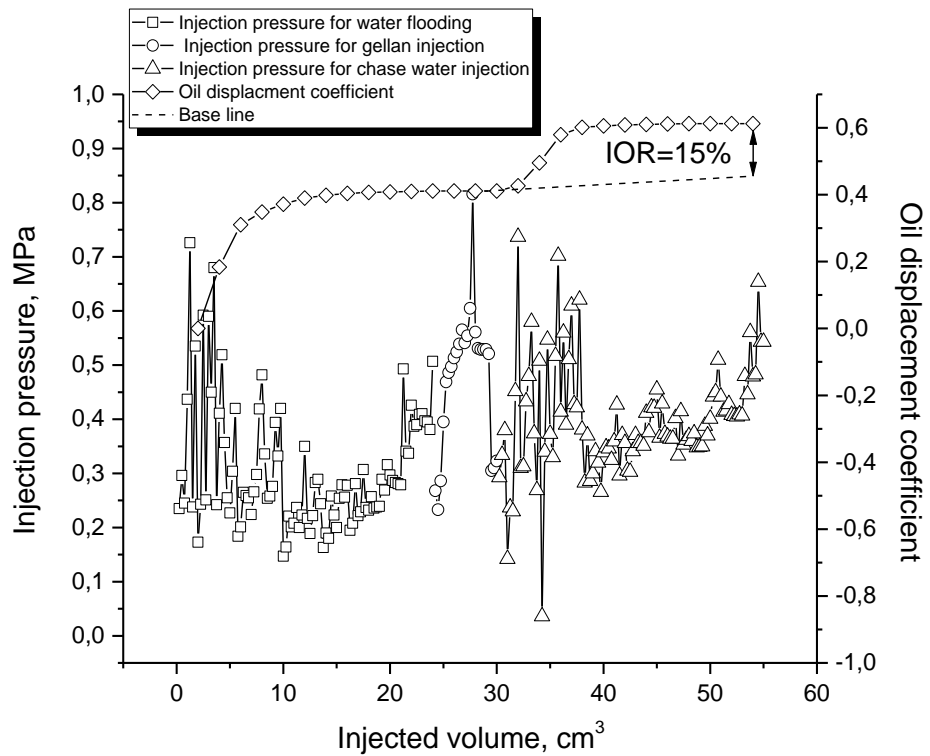
- 1) Packing the sand and permeability measurements;
- 2) Model saturation with Uzen brine ($110 \text{ g}\cdot\text{L}^{-1}$);
- 3) Injection of Uzen oil ($10.5 \text{ mPa}\cdot\text{sec}$) to displace brine until irreducible water saturation is reached;
- 4) Injection of two pore volumes of the same brine to model water flooding;
- 5) Injection of 0.5 PV of gellan solution to plug the high permeability channel;
- 6) Repeated injection of two pore volumes of the same brine to model chase water flooding and observe the extent to which the redirection of water flow occurred.

The comparison of the filtration tests conducted on homogeneous and two-layered models was necessary to get broader understanding of gellan's behavior in heterogeneous model.

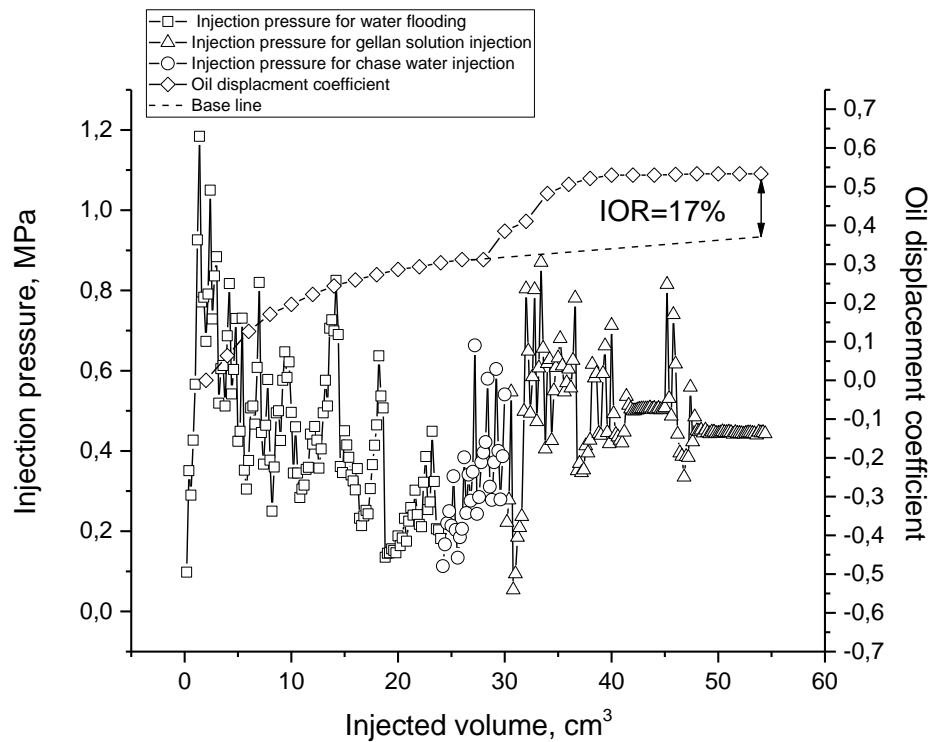
The below figure 46 presents the results of these tests.



a) 250 mkm, 8.23 Darcy, 0.5% gellan solution;



b) 125 mkm, 4.88 Darcy, 0.5% gellan solution;



c) Two-layered model, 0.5% gellan solution;

Figure 46 – Injection of water and gellan into homogeneous and heterogeneous models.

As it can be seen from the above figure 46 (c) the injection of water into the two-layered model is accompanied with the monotonic decrease of the injection pressure from 1.2 down to 0.18-0.2 MPa. This implies that 0.5 cp water monotonically displaces 10 cp oil. If water was filtrating only through the high permeability channel the stabilized injection pressure would be equal to 0.06 MPa, as this value in homogeneous high permeability channel was around 0.03 MPa (Fig.46 (a)). Another important detail is that we see such large pressure fluctuations (see Fig.46 b and c) even during brine injection. For such high permeabilities, one would have expected very smooth pressures. The reason for that is perhaps the movement of the sand particles which adjust their positions inside of the pack under the influence of water flow. Also, the pressure fluctuations may be associated with clay swelling and as a consequence fine migration. Thus, the next research should be conducted on smooth river sand or polysterol spheres.

However, the fact that only 30% of oil were recovered after initial water flooding indicates poor sweep efficiency of the two-layered model, as in homogeneous models 47% (Fig.46 (a)) and 40% (Fig.46 (b)) of oil were recovered after the initial water floods. Further comparison of homogeneous and heterogeneous sand pack floods reveals that the injection pressure during the placement of 0.5 PV of gellan solution preferentially inside of the high permeability channel should be around 0.3-0.6 MPa, as this value was equal to 0.15-0.3 MPa in homogeneous high permeability model (Fig.46 (a)). It is also seen that if the solution invaded

preferentially into low permeability channels the injection pressure would be around 1.2-1.6 MPa (compare Fig.46 (b, c)). Since gellan injection pressure did not increase above 0.6 MPa (Fig.46 (c)) one may suggest that high permeability channel was plugged more severely than the low permeability one. The repeated injection of water inside of the two-layered model was conducted at 0.5 MPa. Taking into account that the water filtration through low permeability homogeneous channel was characterized by stabilized injection pressure around 0.25 MPa (Fig.46 (b) initial water flood), it may be suggested that complete redirection of water flow from high to low permeability channel took place after the injection of 0.5 PV of 0.5% gellan solution into the two-layered model. Once again, the X-ray computed microtomography analysis is required to determine the depth of gellan penetration into the layers of the model.

Anyway, the presented above results prove that in the two-layered model with permeability contrast between the layers as low as 1.7 gellan solution still may be effective and provide additional oil recovery (17% as a result of 0.5PV 0.5% gellan solution injection at $S_{or} = 40\%$). As no gel particles were found in the effluents and since oil recovery increase was accompanied with substantial permeability decrease, it is more likely that the observed IORs were due to the pore space plugging rather than due to the “polymer flooding effect”.

3.5 Comparison of gellan gum aqueous solution plugging behavior with that of counterparts and analogies

This section contains both the results of literature search and laboratory tests conducted in order to compare the efficiency of gellan gum with that of other salt or brine sensitive gels.

Some gelants like the solution of hydroxypropylcellulose (HPS)/sodium dodecyl sulfate (SDS) immediately form gels upon their contact with brine (Naae and Whittington, 1991). As laboratory studies showed, the injection of 1 wt.% of HPC/1 wt.% of SDS solution with viscosity around 80 cp into 0.3-0.4 D Berea sandstones resulted in 95% permeability reduction after 0.36 PVs of the solution had been alternately injected with brine in 0.05 PV slugs at 54 °C. No sever syneresis was detected by both bulk tests and the aging of the treated core sample. However, it was shown that when the concentration of divalent cations in brine reaches 5,000 ppm HPC/SDS gel becomes phase unstable. Stabilization of the gel requires partial substitution of SDS by sodium lauryl ether sulfate (SLES). Addition of SLES in ratio 1:1 with SDS is a necessary condition for the gelation reaction in the presence of divalent cations, whereas complete substitution of SLES for the SDS prevents the gelation (Naae and Whittington, 1991; Whittington and Naae, 1992; Whittington et al., 1994). Both core flood tests and field application of the HPC/(SDS+SLES) gel were not found in literature. HPC/SDS system also was not applied in field conditions most likely because of its intolerance towards the presence of divalent cations in brine.

Iglauer et al. (2011) suggested the application of ι -carrageenan gels instead of PHPA/Cr³⁺ gels for near-wellbore treatments in high salinity reservoirs. The viscosity of ι -carrageenan solutions was found to increase not only in the presence of monovalent cations but also in the presence of multivalent cations like Mg²⁺ and Ca²⁺ (Iglauer et al., 2011). However, filtration experiments with carrageenan solutions were not reported so far. The presented below results of the laboratory tests allow us to compare the efficiency of plugging effect provided by gellan gum and κ - and ι -carrageenan solutions.

The photos presented in the figure 47 below demonstrate gelation of κ - and ι -carrageenan solutions upon the contact with brine in different proportions. From the comparison of the gellan and carrageenan gels formed at 60 °C (Fig. 26(b) and 48), it is visually seen that gellan gels are more stable at this temperature.

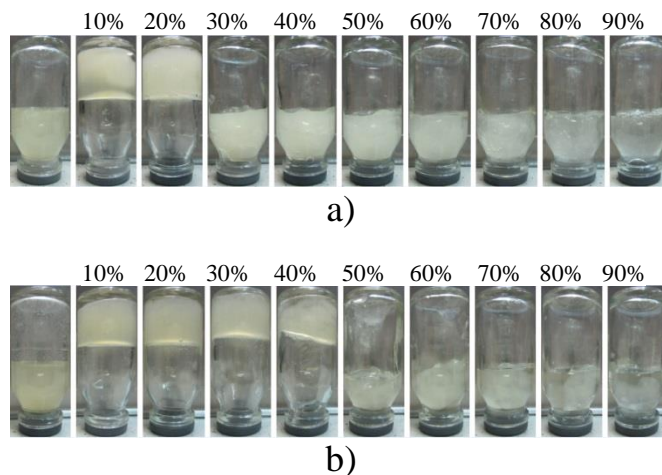


Figure 47 - Gelation of 1.5 % ι - (a) and κ -carrageenan (b) solution in the presence of 10-90 vol.% oilfield saline water 30 °C.

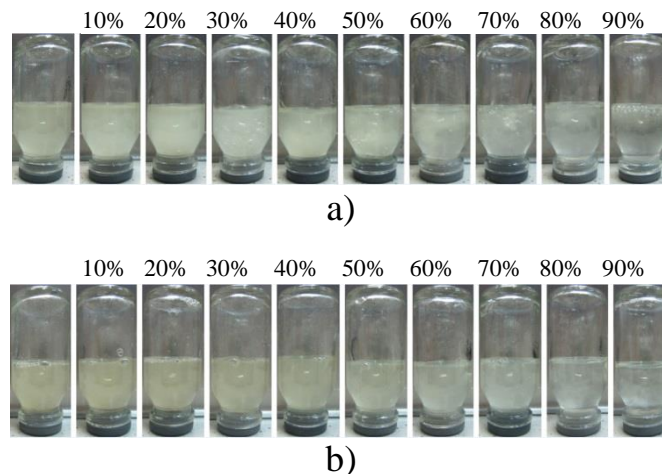
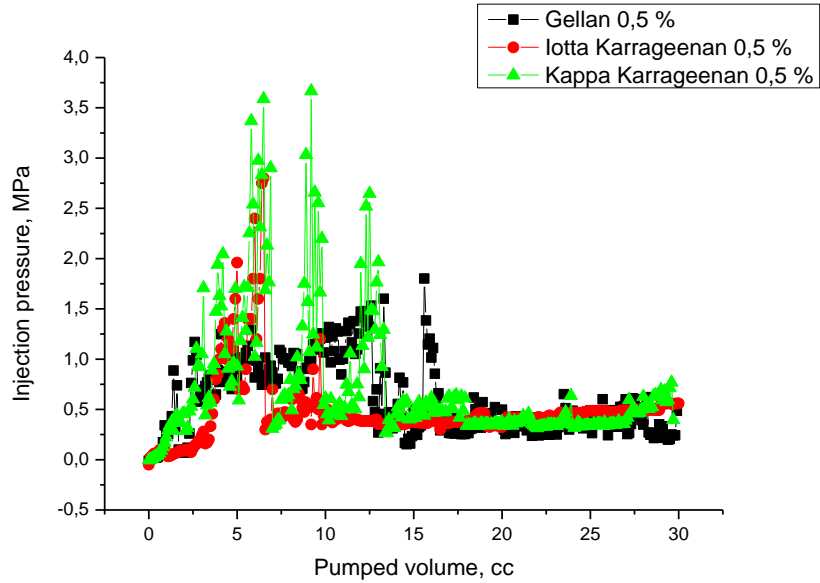
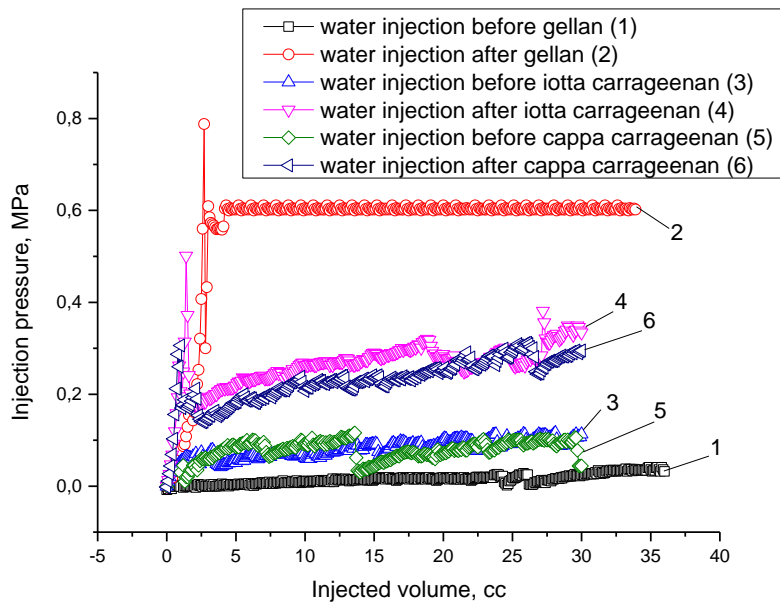


Figure 48 - Gelation of 1.5 % ι - (a) and κ -carrageenan (b) solution in the presence of 10-90 vol.% oilfield saline water 60 °C.

The below fig. 49 demonstrates injection pressure versus pumped volume for the injection of κ - and ι -Carrageenan as well as gellan solutions through sand packs with permeability of 2-2.3 Darcy.



a) Polymer injection into water flooded sand packs;



b) Chase water injection after polymer;

Figure 49 - The treatment of water flooded sand pack models (6 cm long; 2 cm in diameter) by gellan, κ - and ι -carrageenan solutions. The permeability of the packs is around 2-2.3 Darcy. Brine salinity is $120 \text{ g}\cdot\text{L}^{-1}$. Temperature $62 \text{ }^\circ\text{C}$. Flow rate $0.25 \text{ cc}/\text{min}$. Low viscosity oil – 1.2 cp (Kenlyk field).

As it may be seen from the above fig. 49, gellan decreased permeability of the packs in 17 times ($\text{RRF}=17$), while the carrageenans decreased it in 3 times ($\text{RRF}=3$). Thus carrageenan gels are less effective than gellan gels in the context of pore space plugging. Nevertheless, it was demonstrated that high RRFs are required only for

near wellbore treatments whereas in-depth permeability modification may be achieved by much lower RRF values (Frampton et al., 2004).

The disadvantage of ι -carrageenan as well as gellan gum is the necessity of applying fresh water as a solvent (Kudaibergenov et al., 2015). In this context, it is worth to mention so called novel self-thickening polymer (STP). STP was proposed by Qing You et al. (2015) and is one-component gelant which forms bulk gel only when there is enough salt in makeup water (Fig.50). The optimal salinity of makeup water was determined between 4 and 8 wt.%. Whereas the optimal concentration of the STP should be around 0.25-0.3 wt.%. However, the gelation is very rapid and the viscosity of freshly prepared STP solution may reach several hundred mPa·sec. This fact disqualifies the application of this polymer for the treatments of low and medium permeability reservoirs. In fact, STP is not recommended to be applied below 4 D permeability, whereas the maximal temperature limit is 70 °C. Moreover 0.5 g·L⁻¹ is the maximal concentration of CaCl₂ (Qing You et al., 2015). No field tests of STP have been reported so far.

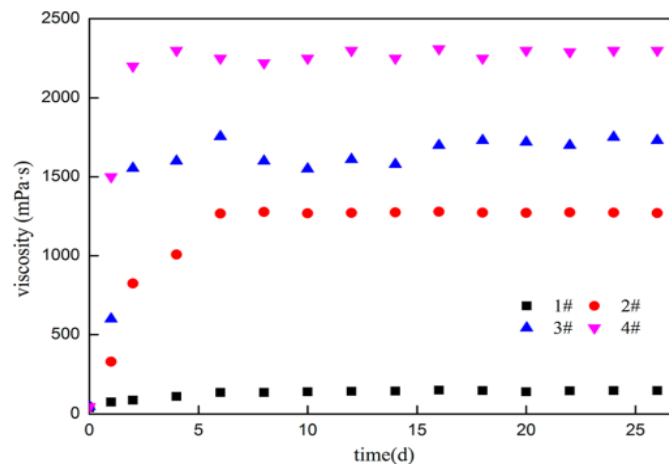


Figure 50 - Viscosity of 0.275% STP solution versus time at salinities of makeup brine between 1.95-7.95% of NaCl and 0.05% of CaCl₂ (Qing You et al., 2015).

In reservoir conditions the injection of big STP slugs is possible only into super high permeability cannels. The influence of divalent cations is still not clear.

Concerning brine initiated gels, additional laboratory and field tests are required to get more advanced idea of their application for permeability reduction treatments. Anyway, the opportunity of exploiting brine as an activator of gelation process might be considered at the design stage of many treatments. Especially those which have to be conducted in high salinity conditions.

Constant search for materials that may generate gel upon the contact with brine should be continued. Taking into account the above discussed drawbacks of the currently used bulk gels it is obvious that these newly introduced brine initiated gels preferably should be one-component (to avoid *in-situ* transport problems) and tolerant to the high divalent ion concentration in brines. The presented in this work biopolymer gellan gum is claimed to suit these requirements.

3.6 Disproportionate permeability reduction (DPR) by gellan solution

In order to study the effect of gellan gel on the deterioration of oil filtration efficiency one experiment has been done. In the experiment 2PV of Karazhanbas oil were injected into the 6 cm long sand pack model saturated with brine (Fig.51 (initial oil filtration)). In the end of the filtration process connate water saturation was around 30%. The injection pressure versus pumped volume curve allowed us to access the initial oil filtration capacity of the model. The next step was to inject 0.5PV of 0.1% gellan solution in order to model the invasion of gellan into oil saturated channel. As we see from fig.51 (red curve), the injection pressure did not rise substantially. Most probably due to the lack of salty water inside of the model insignificant gelation took place. The repeated injection of oil after gellan was characterized with the increase of injection pressure values up to 0.7 MPa so that the final RRF was around 3 (Fig.51).

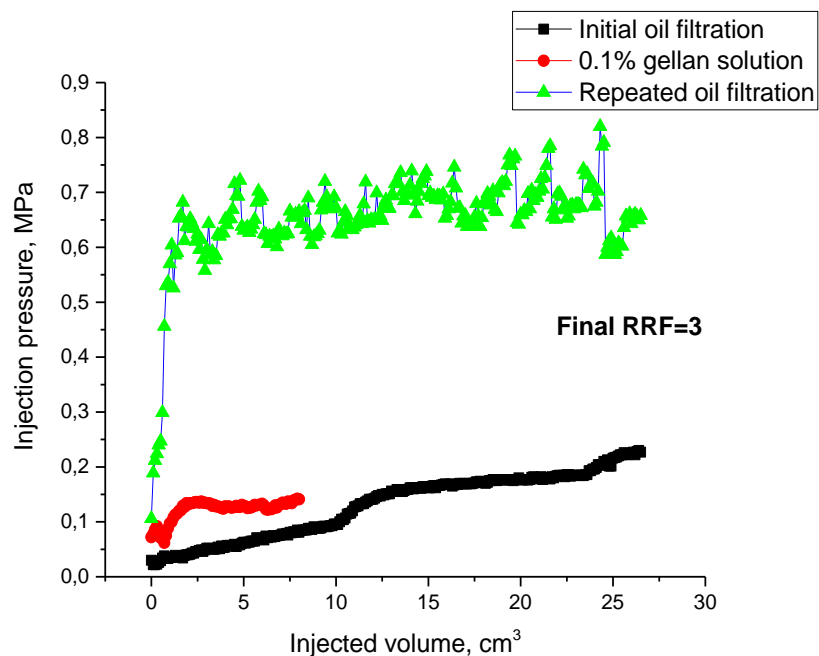


Figure 51 - Injection pressure versus injected volume for the injection of Karazhanbas oil and 0.1% gellan solution into the sand pack model with the following parameters: permeability 2.5 Darcy, 6 cm length, 3 cm diameter, 125 mkm sand particles size. Ambient temperature and pressure are 30 °C and 2 MPa.

As it may be concluded from the results presented by the above figure 51, the invasion of gellan solution into oil saturated channels is not desired especially at low permeabilities since the decrease of permeability in several times may cause a serious decrease of oil flow rates.

Additional research should be conducted in order to determine the effect of gellan gel on the deterioration of oil filtration capacity of a rock at different conditions and permeabilities.

4 Field pilot tests

The current section is dedicated to the description of two pilot tests conducted in 2013 and 2015 in injection and production wells at Kumkol and Karabulak oilfields.

4.1 Injection wells treatment at Kumkol oilfield

4.1.1 Materials, equipment and methods

In October 2013 pilot test directed on the injection of gellan's solution into the U-III oil formation of Kumkol oilfield was conducted. In the conducting of the pilot test the following organizations were involved: CJSC "Turgai Petroleum", JSC "LUKOIL", JSC "NIPIneftegaz", JSC "Institute of petroleum chemistry", PI "Institute of polymer materials and technology" and South-East serves group (IOBCГ) (Appendix 1).

Pilot test on Kumkol oilfield was conducted in two injection wells 3383 and 3065 (Fig.52), geological and technical characteristics of these wells are presented in the tables 5 and 6.

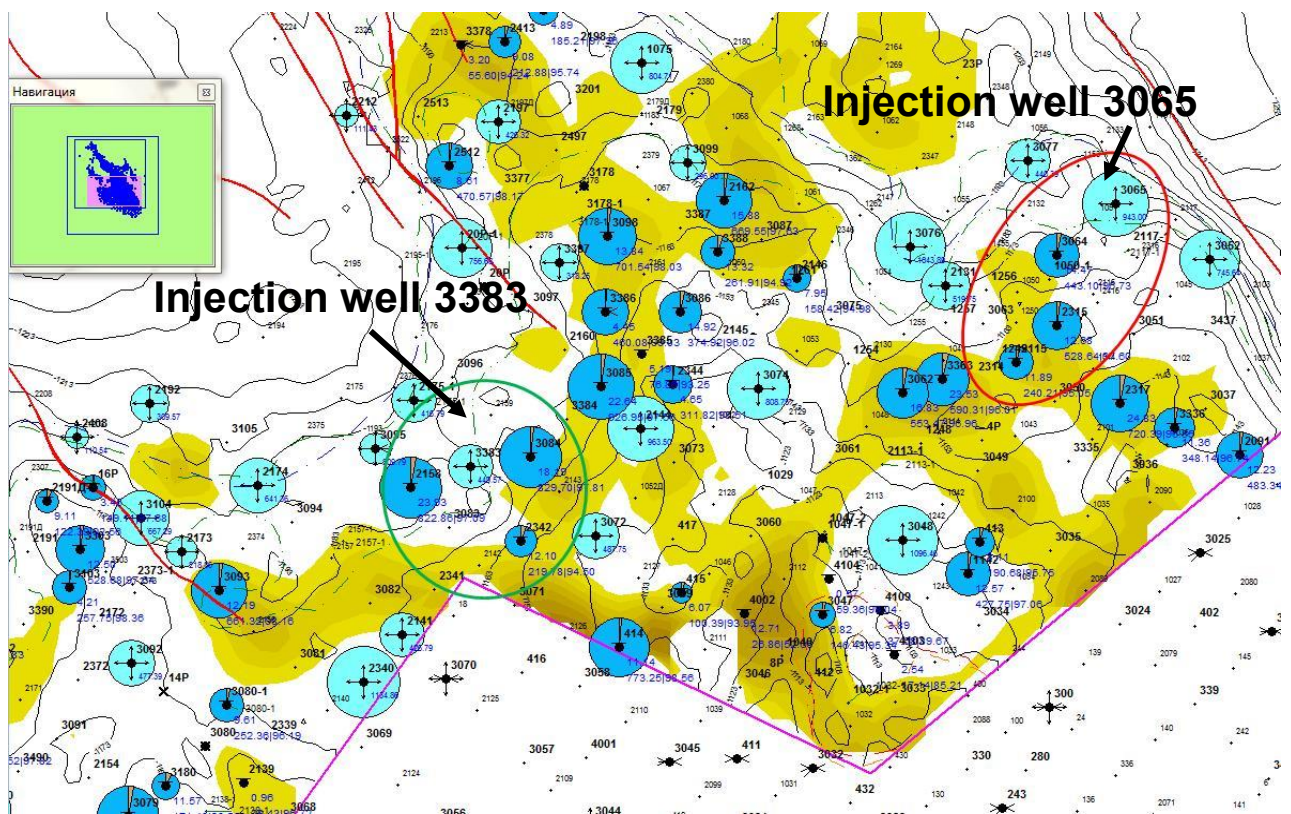


Figure 52 - Map of the Kumkol oilfield.

Table 5 - Geological and technical characteristics of the well 3383.

Parameters	Well 3383
Formation	U-III
Purpose	Injection
Injection pressure, MPa	10
Diameter of the injection tubes, mm	73
Perforation interval, U- III	1305.5-1308.5, 1312-1315, 1317-1318
Perforated formation thickness, m	8.6
Formation pressure, MPa	7.71
Well head pressure, MPa	10
Current deliverability, m ³ /day	1300

Table 6 - Geological and technical characteristics of the well 3065.

Parameters	Well 3065
Formation	U-III
Purpose	Injection
Injection pressure, MPa	10
Diameter of the injection tubes, mm	73
Perforation interval, U- III	1303-1310, 1311.5-1313, 1314-1317
Perforated formation thickness, m	11.5
Formation pressure, MPa	7.4
Well head pressure, MPa	10
Current deliverability, m ³ /day	944

Table 7 presents the list of chemicals that have been used to conduct the pilot test, and concentrations that were set in plan with respect to the possibility to be changed according to the injection wells deliverability on the date of the pilot test.

Table 7 - Water volume, concentration and dosage of chemicals for the polymer injection test.

N ^o Step	Chemicals	Volume of fresh water, m ³	Concentration, %	Dosage, kg/m ³	Total mass, kg
1	Biocide	36	0.05	0.50	18
2	Polymer Gellan	100	0.2	2.00	200
3	Polymer Gellan	160	0.5	5.00	800

The preparation of gellan solution has been done by means of dosage apparatus demonstrated at the below figure 53.



Figure 53 - КУДР - complex equipment for dosage of chemicals.

To ensure continuous pumping warmed up to 60 °C fresh water was delivered by several water carriers fig.54.



Figure 54 - Providing of fresh water for the well №3065.

Scheme of the arrangement of surface equipment used for gellan's injection is illustrated on the fig.55.

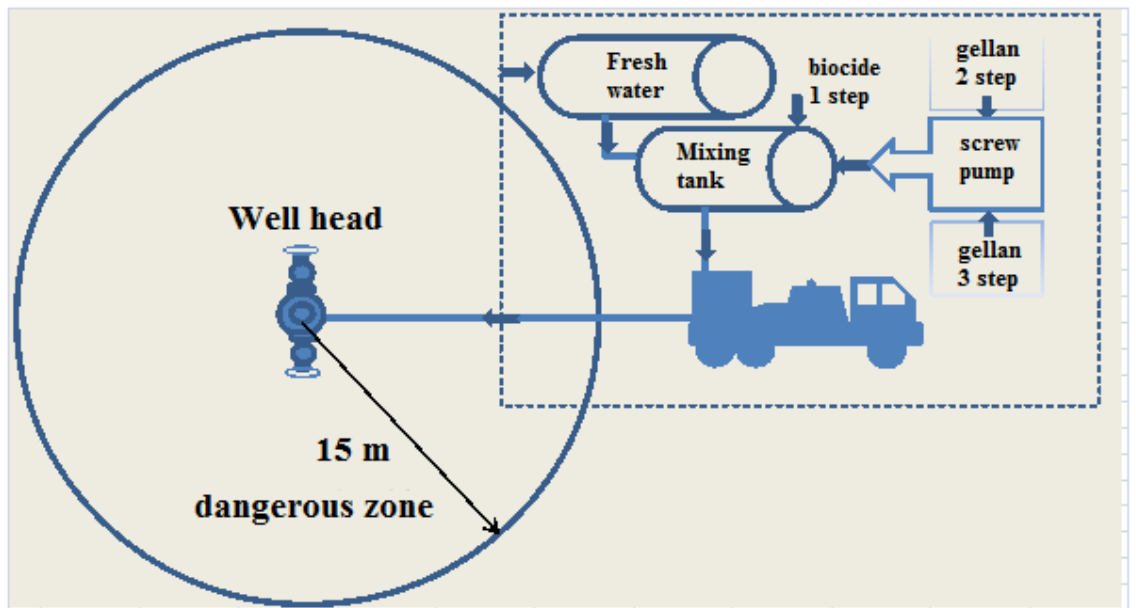
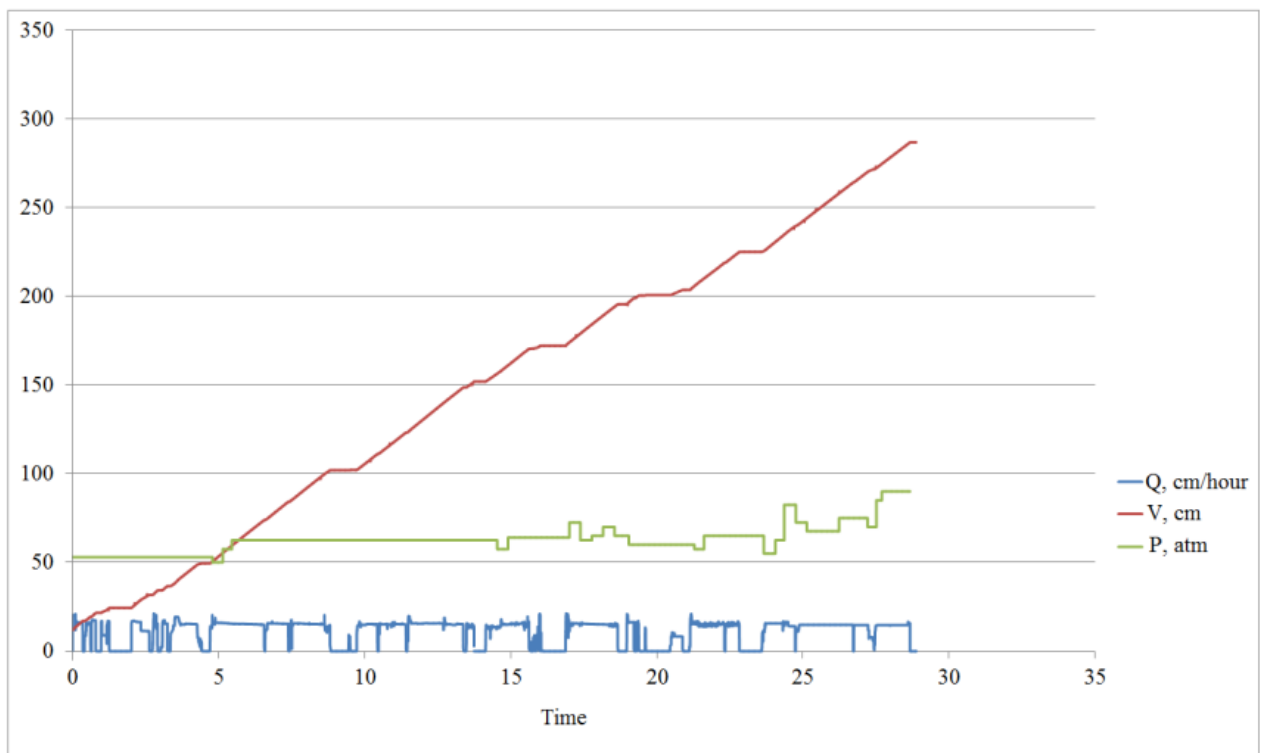
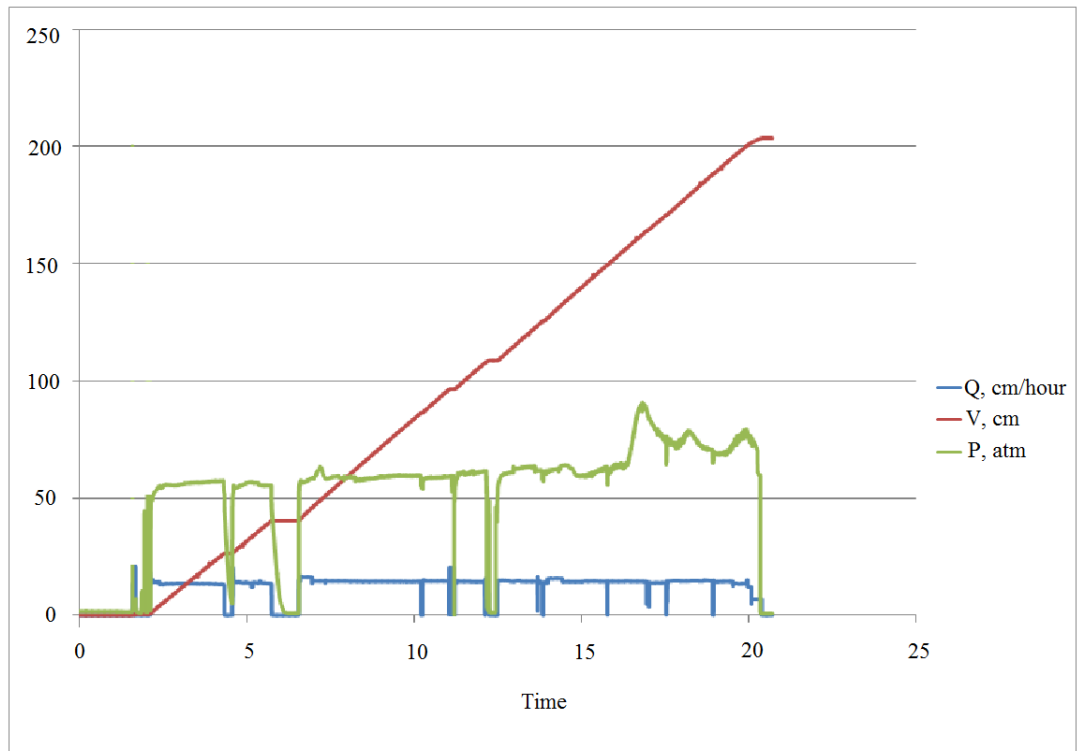


Figure 55 - Arrangement of surface equipment used for gellan's injection.

In total 234 m³ and 160 m³ of 0.2-1% concentrated polymer solution were injected into the two injection wells 3383 and 3065 respectively. Successfulness of this operation is illustrated by the following plots fig. 56.



a)



b)

Figure 56 - Dependence of the instantaneous rate (Q cm/hour), cumulative volume (V cm) and injection pressure (P atm) on time for wells a) 3083 and b) 3065.

Gellan's solution was injected into the formation with the aim to increase oil flow rates and to decrease water cut in the production wells located in the vicinity of the injection wells 3383 and 3065. Calculation of incremental oil recovery value for the last 11 months after the injection of gellan is presented below.

4.1.2 Results of the test

Incremental oil recovery due to well treatment operations is the amount of oil that was produced after the treatment minus the amount of oil that might have been produced or expected if the treatment has not been done.

Oil flow rate values obtained after the treatments and extrapolation of the previously stable trend of oil flow rate values or extrapolation of the average value during the last several months before the treatments outline the area on the plot which has to be calculated in order to find out the value of incremental oil recovery. Such methodology is well known and accepted by oil producing companies throughout the world and consequently was used in our case.

Fig.57 shows the oil flow rate versus time for each of the six producing wells located in the vicinity of the two injectors through which gellan was pumped into the reservoir in October 6-8, 2013.

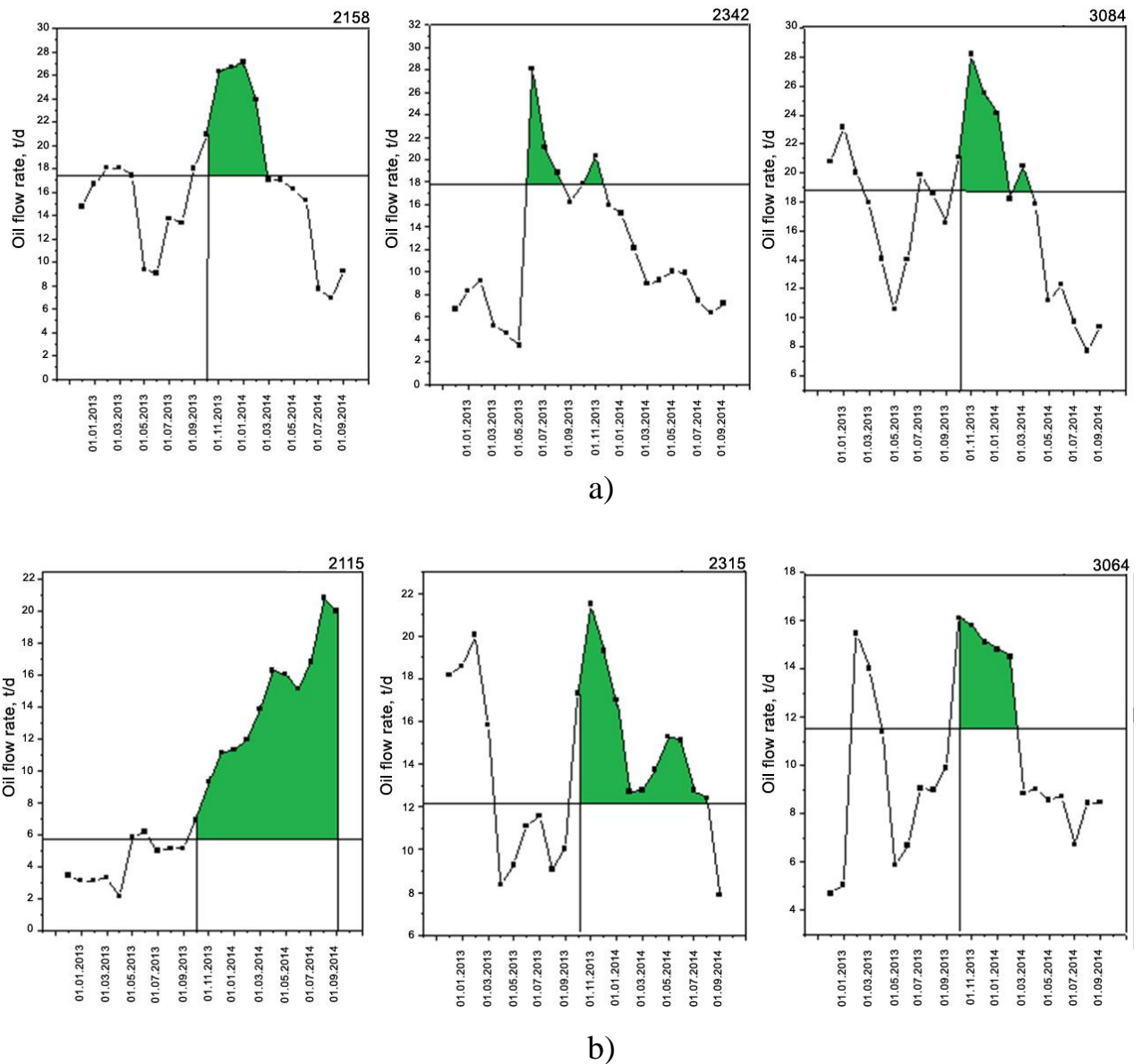


Figure 57 - Oil flow rate history from the wells No. 2158, 2342, 3084, 3064, 2315 and 2115 during 11 months.

Green colored area on the each plot represents incremental oil recovery produced during the last 11 months after the treatment was performed. The area on each plot is outlined by the real oil flow rate curve and the baseline which is an average of the value during the last 3 months before the treatment. The areas are found by the integration of the curves in Origin 8.1 software. The values are presented in the following Table 8.

Table 8 - Incremental and total oil recovery values from the producing wells.

Number of the wells	Incremental oil recovery (tons)
2158	1,063
2342	84.24

Continuation of the table 8.

3084	720
3064	470
2315	780
2115	2,790
Total	5,890

Thus the total incremental oil recovery is considered to be 5,890 tons of oil, which is 6,811 m³ (the density of oil is 865 kg·m⁻³) or 43,108 barrels of oil.

4.2 Production well treatment at Karabulak oilfield

23 May 2015 field works at producing well Karabulak - 34 have been started (Appendix 2). The producer was perforated in the intervals – 1,395-1,397 m, 1,398.5-1,405 m, 1,408.5-1,412 m. The following figure 58 shows that during the last 5 months after the well was put on production the water cut has increased from 16 up to 77 % while the well was produced under the constant liquid flow rate 80 tons/day. It was planned that the injection of 2 tons of dry gellan powder in the form of aqueous solution into the Karabulak-34 producing well would decrease water cut and increase oil recovery rate.

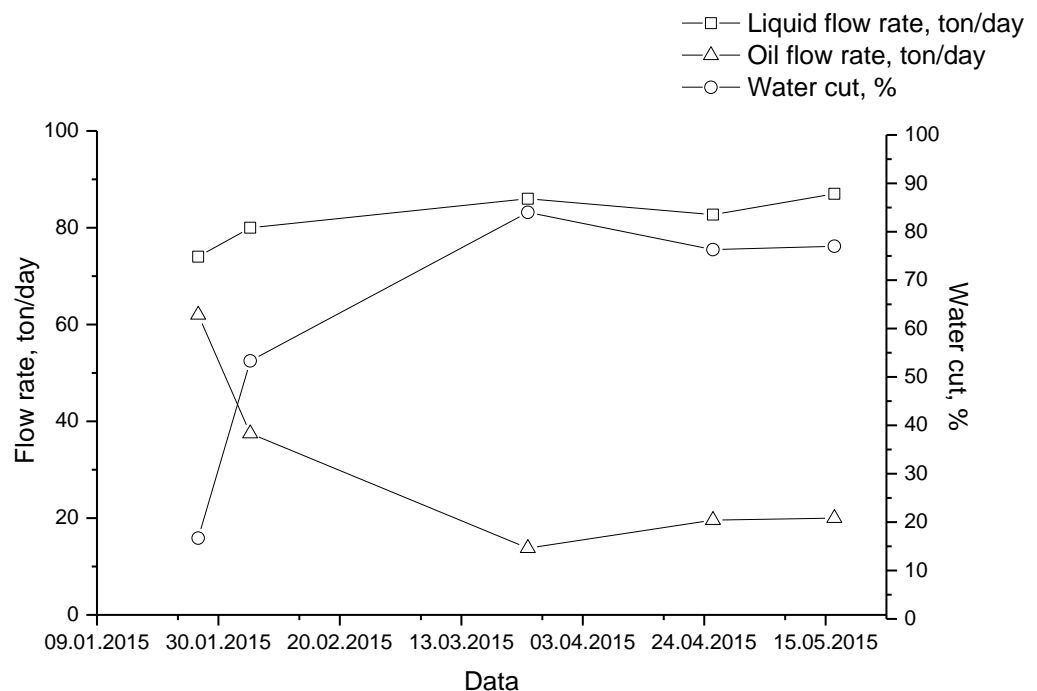


Figure 58 - Production history of the well K-34.

All works were conducted in the following steps:

1) Identification of water bearing layers. In order to direct injected gellan solution into the water bearing formations geophysical survey has been conducted aiming identification of watered out layers (Fig.59).

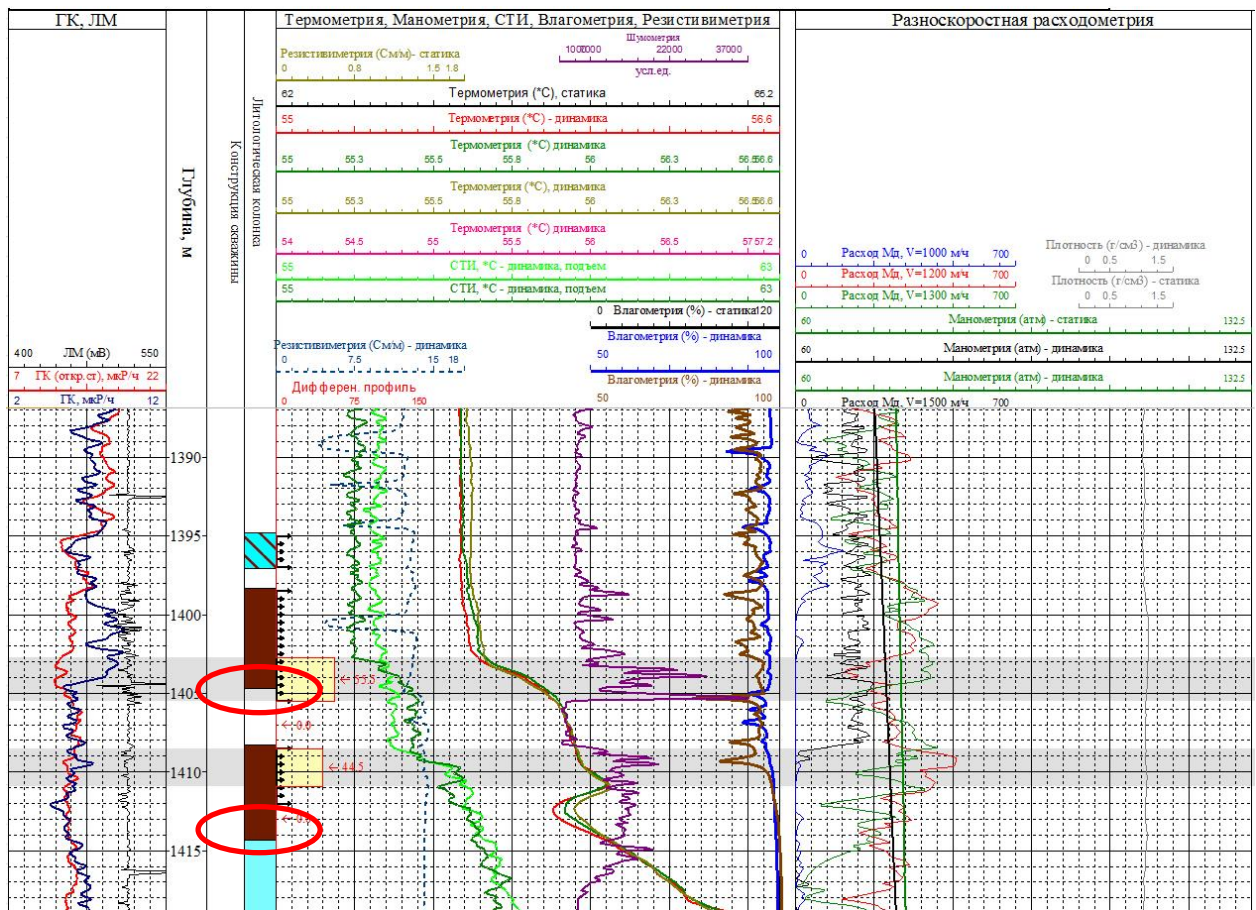


Figure 59 - Geophysical log data for the well K-34; - watered out layers.

2) Connection of the well with water bearing layers and its isolation from oil saturated strata.

Watered out layers were disjoined with oil bearing formations by injection of concrete into the well that was drilled through and layers that mainly contribute to the water production were perforated for consequent injection of gellan solution. Perforations specified for the injection of gellan solution were made in the following intervals 1404,5-1405,5 m, 1413-1414 m.

3) Increasing deliverability of the well for the injection of gellan solution.

Water injection capacity of upper and lower perforation intervals was measured and equal 173 tons/day and 43 tons/day respectively, thus total deliverability of the well was equal to 216 tons/day. In order to increase this value the well was subjected to acid treatment, 2,2 cubical meters of acid solution were injected into the well followed by the injection of 4,6 m³ of technical water. After the acid treatment deliverability of the well was measured again and showed to be increased at least in two times – 480 tons/day.

4) Injection of gellan solution.

After what injection of 1 % concentrated gellan solution has begun. Since 01.06.2015 to 02.06.2015 120 m³ of 1 % concentrated gellan solution was injected

into the well K-34, the injection process was characterized by initial and final injection pressure values equal to 70 and 100 bar respectively.

5) Reconnection of the well with oil saturated strata.

After the injection of gellan the well was washed by technical water and filled with concrete solution in the interval between 1390-1415 m. The following operations should include drilling of concrete cement plug, perforation of intervals 1395-1397 m, 1398,5-1403 m, 1408,5-1411m through which the well will be exploited by using electrical submersible pump unit.

All conducted works are confirmed by the certificate presented in the appendix and signed by the employees of LLP “South-Oil”, “Smart-Oil” and LLP research and development center “Vostokneftegas 2050”.

Currently first obtained results from the treatment are presented by the following plot (Fig.60).

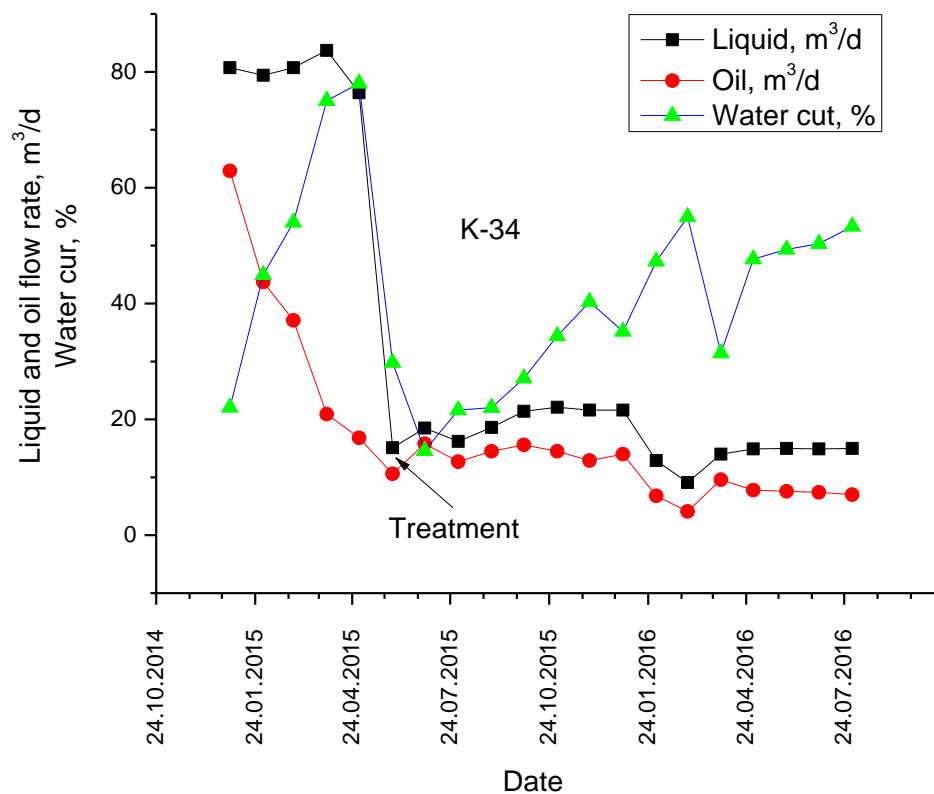


Figure 60 – Production history of the well K-34.

From the above plot, it is directly seen that after the treatment had been done the amount of produced water has decreased in about 16 times while oil flow rate did not change considerably. Tremendous decrease in water cut will allow the oil company to save a considerable amount of money that otherwise would have been spent on water transportation and separation. The stability of oil flow rate after the treatment implies that the polymer gel placement was successful and did not decrease permeability to oil in the bottom-hole zone. And the last but not least is that decrease of water production has a positive impact on environmental protection.

From the above fig. 60 it also may be noted that water cut increased during 150 days after the well was put on production. As a result oil rate has decreased as well. Such fast watering out of the well implies the existence of a fracture or super high permeability streak inside of the reservoir. Moreover, the fact that only 120 m³ of gellan solution, which is relatively small volume, was enough to cause the plugging of the watered out zones also suggests the existence of a fracture. Since in comparison with fractures, the matrix layers usually require bigger volumes of plugging materials. This observation may encourage the future research of gellan solution and gel behavior in fractured rocks.

5 Conclusions

As an outcome of this work the following conclusions may be made:

1) The ability of gellan solution to form gel upon the contact with brine allows its application for the isolation of watered out channels inside of oil reservoirs. The important advantage of gellan gum solution over other gelants is that no additional chemicals are required in order to initiate the gelation process. Moreover, exceptional stability of gellan gel in the presence of divalent cations is another advantage of this polymer.

2) Taking into account the features of gellan solution hydrodynamic behavior, the alternated injection of gellan and brine is recommended for the plugging of super high permeability thief layers in near wellbore zones. This injection regime allows the reduction of the amount of polymer used at least in 2 times.

3) The continuous injection of gellan solution after sufficient pre-flush with fresh water is recommended for the in-depth treatments.

4) The experiments conducted on two-layered sand packs demonstrated modest oil recovery factor increase (around 5-6%), however the fact that unrealistically high pressure gradients (25 MPa/m) were required for 0.5PV gellan slug placement and subsequent water injection leaves lots of doubts concerning the possibility of successful application of this polymer for the treatment of multilayered reservoirs.

5) It has been demonstrated that the penetration of 0.1% concentrated gellan solution into oil bearing zones may result at least in 3 times permeability reduction to oil.

6) The decrease of brine salinity from 90 to 11.25 g·L⁻¹ did not cause significant deterioration of gellan solution plugging properties. However, no plugging was detected when distilled water was used to saturate the model.

7) It has been demonstrated that gellan solution can be effectively used at temperature 60 °C. The experiments conducted at 90 °C did not show positive result. Thus, the maximal temperature allowed for gellan application is between 60 and 90 °C.

8) The data provided by JSC “Turgai Petroleum” and LLP “South-Oil” demonstrated the efficiency of aqueous gellan solution for the treatment of injection and production wells. As a result of the injection of 2 tons of dry gellan powder in the form of aqueous solution into 2 injectors at Kumkol oilfield, 5,890 tons (43,108 bbls) of oil were produced incrementally during 11 months. Taking into account the oil price (50 USD/bbl) and gellan cost (4.5 USD/kg) the net profit was calculated to be around 2 million USD. The injection of 120 m³ of 1% concentrated gellan solution into the production well at Karabulak oilfield resulted in the decrease of water cut from 80 to 40%.

9) The interpretation of the results of gellan field pilot tests suggests high its efficiency for the isolation of high permeability fractures and streaks.

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APPENDIX A
Reports on the treatments conducted at Kumkol oilfield

09.10.2013

м/р Кумколь

Акт
выполненных работ
по выравниванию профиля приёмистости нагнетательных скважин 3383 и 3065

Мы, нижеподписавшиеся Аскарбеков Т.С., Абилхаиров Д. Т., Прапорщиков В.И., Статура А.А., Крысенко А.П., Кудайбергенов С.Е., Сагиндыков А.А., составили настоящий акт о том, что в период с 6.10.13 – 8.10.13 согласно утверждённому плану работ по выравниванию профиля приёмистости нагнетательных скважин 3383 и 3065 на месторождении Кумколь успешно и в полном объёме выполнили запланированные работы.

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Директор

Сагиндыков А.А.

АКТ
на проведение обработки пласта Ю - 3
на скважине 3383 месторождения Кумколь

Дата и время начала работ на скважине 06.10.2013 г., 14-00

Дата и время окончания работ на скважине 07.10.2013 г., 18-00

1. Состояние скважины:

Рабочее давление: $P_{\text{мн.}} = 2,0$ МПа. $P_{\text{кон.}} = 8,5$ МПа.

2. Состояние по фонду: в работе.

3. Порядок проведения работ: Объем:

1. Закачка раствора «Биоцид»	36	(м ³)
2. Закачка раствора «Геллан»	<u>234</u>	(м ³)
3. Объем продавки	<u>36</u>	(м ³)

4. Количество спец. техники:

1. ЦА - 320	(ед.) 2	<u>60</u> часов.
3. АЦ - 25 м3	(ед.) 1	<u>26</u> часов
2. КУДР 33	(ед.) 1	<u>24</u> часа.

Примечание:

5. Материалы и хим. реагенты:

1. Геллан	(тн) <u>1,00</u>	<u>АО «ТУРГАЙ-ПЕТРОЛЕУМ»</u>
4. Биоцид «Биолан»	(тн) <u>0,02</u>	<u>АО «ТУРГАЙ-ПЕТРОЛЕУМ»</u>

Примечание:

6. Незапланированный объем работ, прочие условия при проведении обработки:

Заместитель начальника отдела разработки
АО «ТУРГАЙ-ПЕТРОЛЕУМ»


Д.Т. Абиляиров

Заместитель начальника ЦДНГ по геологии
и добыче АО «ТУРГАЙ-ПЕТРОЛЕУМ»


М. Сыдык

Ведущий технолог по добыче
и КПС ЦДНГ АО «ТУРГАЙ-ПЕТРОЛЕУМ»


Б. Рыспаев

Руководитель направления ПНП и ППД
АО «НИПИнефтегаз»


В.И. Прапорщикова

мастер ПНП ТОО «ЮВСТ»


А.П. Крысенко

АКТ
на проведение обработки пласта Ю - 3
на скважине 3065 месторождения Кумколь

Дата и время начала работ на скважине 08.10.2013 г., 4-00

Дата и время окончания работ на скважине 08.10.2013 г., 20-00

1. Состояние скважины:

Рабочее давление: $P_{изв.} = \underline{5,5}$ МПа. $P_{кон.} = \underline{7,4}$ МПа.

2. Состояние по фонду: в работе.

3. Порядок проведения работ:

Объем:

- | | | |
|------------------------------|-----|-------------------|
| 1. Закачка раствора «Биоцид» | 36 | (м ³) |
| 2. Закачка раствора «Геллан» | 160 | (м ³) |
| 3. Объем продавки | 24 | (м ³) |

4. Количество спец. техники:

Примечание:

- | | | |
|---------------|---------|-----------|
| 1. ЦА - 320 | (ед.) 2 | 28 часов. |
| 3. АЦ – 25 м3 | (ед.) 1 | 30 часов |
| 2. КУДР 33 | (ед.) 1 | 16 часа. |

5. Материалы и хим. реагенты:

Примечание:

- | | | |
|--------------------|-----------|-----------------------|
| 1. Геллан | (тн) 1,00 | АО «ТУРГАЙ-ПЕТРОЛЕУМ» |
| 4. Биоцид «Биолан» | (тн) 0,02 | АО «ТУРГАЙ-ПЕТРОЛЕУМ» |

6. Незапланированный объем работ, прочие условия при проведении обработки:

Заместитель начальника отдела разработки
АО «ТУРГАЙ-ПЕТРОЛЕУМ»

 Д.Т. Абилхайров

Заместитель начальника ЦДНГ по геологии
и добыче АО «ТУРГАЙ-ПЕТРОЛЕУМ»

 М. Сыдык

Ведущий технолог по добыче
и КИРС ЦДНГ АО «ТУРГАЙ-ПЕТРОЛЕУМ»

 Б. Рыспаев

Руководитель направления ПНП и ПЦД
АО «НИПИнефтегаз»

 В.И. Прилорциков

мастер ПНП ТОО «ЮВСТ»

 А.П. Крысенко

APPENDIX B
Report on the treatment conducted at Karabulak oilfield
Report from LLP "South-Oil"

ТОО «САУТС – ОЙЛ»

Месторождение
Юго-Западный Карабулак
Скважина К-34

Акт

Мы нижеподписавшиеся подтверждаем, что в период с 01.06.2015 по 02.06.2015 на месторождение Юго-Западный Карабулак в скважину К-34 было закачено 120 м³ водного раствора «Полисаха». Начальное и конечное давление закачки 70 и 100 атм., соответственно.

Директор по ЭМ ТОО «САУТС – ОЙЛ»

 Н.М. Усембаев

«02» июня 2015

Начальник отдела разработки ТОО «САУТС – ОЙЛ»

 Д.Т. Абилхайров

«02» июля 2015

Инженер по КРС ТОО «САУТС-ОЙЛ»

 Р. Ниязбаев

«02» июля 2015

Мастер по КРС ТОО «SMART - OIL»

 А. Серикбаев

«02» июня 2015

Инженер ТОО НТЦ «Востокнефтегаз 2050»

 И. Гусенов

«02» июня 2015

№ 16/50- *1130*
30 / *09* 2016 г.

ОТЗЫВ

На месторождении Юго-Западный Карабулак ТОО «САУТС-ОЙЛ» были проведены работы по ограничению водопритоков с применением технологии ТОО «НТЦ «Востокнефтегаз-2050» закачки полисахарида и рисовой шелухи на двух скважинах Юго-Западный Карабулак-34 и Юго-Западный Карабулак -5.

Скважина Юго-Западный Карабулак-34:

Параметры скважины до РИР: добыча жидкости составляла – 85 м³/сут, нефти – 19 м³/сут при обводненности – 78%.

Параметры скважины после РИР: добыча жидкости составила – 18 м³/сут, нефти – 16 м³/сут, при обводненности – 15%. По истечении 15 месяцев добыча жидкости составляет – 14,9 м³/сут, нефти – 7,3 м³/сут при обводненности 51%.

Юго-Западный Карабулак-5:

Параметры скважины до РИР: добыча жидкости составляла – 60 м³/сут, нефти – 4 м³/сут при обводненности – 93%.

Параметры скважины после РИР: добыча жидкости составила – 22 м³/сут, нефти – 21 м³/сут, при обводненности – 5%. По истечении 6 месяцев добыча жидкости составляет – 16 м³/сут, нефти – 8 м³/сут при обводненности 49%.

Проведенные работы по ограничению водопритоков с применением технологии ТОО «НТЦ «Востокнефтегаз-2050» закачки полисахарида и рисовой шелухи на двух скважинах месторождения Юго-Западный Карабулак ТОО «САУТС-ОЙЛ» доказали эффективность применения данной технологии на добывающих скважинах.

Главный геолог



М.Маманов