Plugging Behavior of Gellan in Porous Saline Media

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ABSTRACT: In this article, the hydrodynamic behavior of dilute aqueous solutions of a natural polysaccharide—gellan in the porous media under the modeled oilfield conditions is described. The hydrodynamic properties of gellan and poly(acrylamide) solutions in saline porous media are compared. The influence of inorganic salts NaCl, KCl, $CaCl_2$, $MgCl_2$, and $BaCl_2$ on sol–gel and gel–sol transitions of dilute gellan solutions was evaluated. The mechanism of sol–gel transition in the presence of individual alkaline and alkaline-earth metal salts is described on the basis of literature data. The viscometric measurements revealed that the effectiveness of salts to enhance gelation of gellan changes in the following order: $BaCl_2 > CaCl_2 \approx MgCl_2 > KCl > NaCl$. The sol–gel and gel–sol phase transitions of gellan solution were also observed upon addition of oil field water containing 73 g L^{-1} of alkaline and alkaline earth metal ions. During the injection of gellan solutions into the porous media saturated by saline water an oscillation of the injection pressure was observed. Such behavior of gellan is explained by either the sol-to-gel and the gel-to-sol transitions of the polymer taking place in saline water or the step-by-step plugging of high permeable channels until all high permeable channels of sand packs are plugged due to gellan invasion. The application of brine-initiated gelation of gellan for water shutoff operations (WSO) in field conditions was demonstrated. Higher technological effectiveness of gellan injection in comparison with existing gelation systems was shown. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2015, 132, 41256.

INTRODUCTION

Understanding the fundamental and applied aspects of using water-soluble and water-swelling polymers for enhanced oil recovery (EOR) is a challenging task for both academic and industrial purposes.[1,2] One particular technology within this area of EOR intends to reduce water production and is called *water shut-off or conformance control operations*. Development and use of "green" polymers for water shutoff, conformance, and mobility control operations is important for the oil industry.[3] The most applicable polymers for EOR are flexible synthetic polymers—poly(acrylamide) (PAAm) or partially hydrolyzed PAAm (HPAAm) and semirigid natural polymers—polysaccharides[4,5] or cellulose derivatives.[6] They are used in two ways: (1) to plug high permeability zones adjacent to the wells and (2) to cause *in situ* 3D gelation of the polymer and thus form a complete shut off. However, the most widely used polymers for EOR, PAAm, and HPAAm, suffer excessive hydrolysis

under harsh reservoir conditions of high salinity and temperature. They may also precipitate in the presence of bivalent cations located in the reservoirs.[7] While polysaccharides, for instance, xanthan and gellan gum display robustness at high temperatures. It has been demonstrated[8] that the solution viscosity of commercial xanthan gum remains relatively constant for more than 2 years at 80°C. More recent study showed that gellan gum maintains its strength at 90°C, whereas xanthan gum looses 74% of its original strength only after heating up to 90°C.[9] However, a disadvantage of the polysaccharides is their susceptibility to bacterial degradation. Sorbie et al.[5] presented experimental results and theoretical analysis on the effect of pH on the rheology and transport of xanthan biopolymer solution through porous media.

A successful shut-off treatment requires the knowledge of the reservoir structures and the control of polymer displacement. Important issues for the latter are polymer rheology (i.e., its
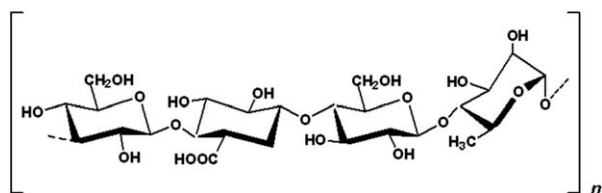
Figure 1. Structure of the repeating monomer unit of gellan.

flow behavior) and its retention behavior upon injection in porous rocks. A brief literature survey on flow of polymer solutions through porous media shows that the relationship between polymer rheology and polymer retention is complex and depends strongly on the porous medium structure and is often very different from bulk behavior. The shear thickening behavior in porous media arises due to coil-stretched conformational or sol sol–gel phase transitions of the polymer chains. The polymer/porous media relationships, such as adsorption, mechanical entrapment, and inaccessible pore volumes, have a direct effect on both the transport and *in situ* rheology of a polymer solution.[10] Laboratory and field studies[11] have been conducted on some polymers, including partially hydrolyzed polyacrylamide, polyethylene oxide, hydroxyethyl cellulose, and a biopolymer to improve oil displacement by reducing both water mobilities and water flow through high-permeability channels. The influence of rock composition, formation heterogeneity, water salinity, and polymer flow rate on oil recovery was estimated. Polymer flooding characteristics of HPAAm solution with the addition of NaOH were examined previously in homogeneous glass-bead packs[12]. Flood tests showed an increase in oil recovery by 30% over water-flooding when the water-cut reached 95%, indicating that an alkali-polymer could be more effective in improving sweep efficiency than a polymer flood. Both inorganic[13,14] and organic polymer gels[15–17] are suitable to shut-off (or prevent) the water flow into the wellbore. Temperature-induced *in situ* formation of inorganic gels has been developed.[18] The multicomponent system for EOR is based on the mixture of aluminum salt-carbamide-water-surfactant that generates a gel and releases ammonia and carbon dioxide gases. This technology has been successfully applied in West Siberia oil fields. The gel system based on a copolymer of polyacrylamide tertiary butyl acrylate crosslinked with polyethyleneimine[19] has been widely applied in the field for conformance control (gas shut off) worldwide[20] particularly in southern Mexico[21], the Middle East,[22] and the North Sea.[23] The behavior of microgels based on colloidal particles of PAAm in porous media has been thoroughly studied.[3] It was shown that their propagation distance is only limited by the volume injected; injectivity is facilitated by a shear-thinning behavior; and water permeability reduction can be achieved by controlling the thickness of the adsorbed layer. These new microgels are available at the industrial scale and can be applied not only for water shutoff but also for conformance control in a heterogeneous reservoir. The possibility of using micro-capsules consisting of hydroxypropyl cellulose in the core and poly (lactic-*co*-glycolic) acid in the shell during EOR has been investigated.[24] Experiments in the field with two permeability regions showed that the micro-capsules clogged up the high permeability layer more than the low permeability

region. A numerical model of *in situ* gelation for polyacrylamide/chromium (III)/thiourea, xanthan/Cr(III), and xanthan/borax systems in porous media has been made.[25] Diffusion of polymer chains in porous media was studied by means of the Monte Carlo method.[26]

Earlier, we studied the efficiency of gellan as an oil displacement agent in comparison with water and PAAm.[27–29] In case of injection of 0.1% gellan and 0.1% PAAm solutions, the oil displacement coefficient from the cores and sand packs varied from 60 to 65%, which is two times higher than water injection. The aim of the work presented herein was to study the flow behavior of dilute aqueous solutions of gellan in porous saline media in comparison with PAAm. Gellan, a water soluble polysaccharide, is an anionic extracellular bacterial polysaccharide discovered in 1978. Structural formula of gellan consisting of tetrasaccharide repeating units: 1,3-linked β-D-glucose, 1,4-linked β-D-glucoronic acid, 1,4-linked β-D-glucose, and 1,4-linked α-L-rhamnose is shown in Figure 1.

EXPERIMENTAL

Materials

Gellan was purchased from Zhejiang DSM Zhongken Biotechnology and they produced it from the biomass resulting from the aerobic fermentation of the micro-organism *Sphingomonas elodea*.

PAAm with molecular weight 1×10^6 (Polysciences) and reagent-grade salts (NaCl, KCl, CaCl$_2$, MgCl$_2$, and BaCl$_2$) were used. The polymer and salt solutions were prepared in distilled water. Distilled water, model saline water containing 75 g L^{-1} NaCl and oil field water containing 73 g L^{-1} of alkaline and alkaline earth metal ions were used for testing the saturation of the sand pack model. The oil field water with density of 1.05 g cm^3 and pH 6.68 was composed of 22.5 g L^{-1} of Na$^+$ and K$^+$, 3.8 g L^{-1} of Ca^{2+}, 0.85 g L^{-1} of Mg^{2+}, and 43.9 g L^{-1} of Cl$^-$ ions. The core samples from the Kumkol oilfield (Kyzylorda region, Kazakhstan) were used for propagation experiments (Table I).

Methods

The coreflood experiments were performed on porous media obtained by packing of sand grains with an average granular size 0.125–0.25 mm into the cylindrical core holder (25 cm length and 4.3 cm diameter) made from steel [Figure 2(a)]. Permeability of these models varied from 0.2 to 4 Darcy. All experiments with the sand pack model were carried out with UIC-C (2)(Russia) [Figure 2(b)].

Under the coreflood set-up accurate pressure drop measurements were performed under a wide range of flow rates. In all

Table I. Some Petrophysical Characteristics of Core Samples

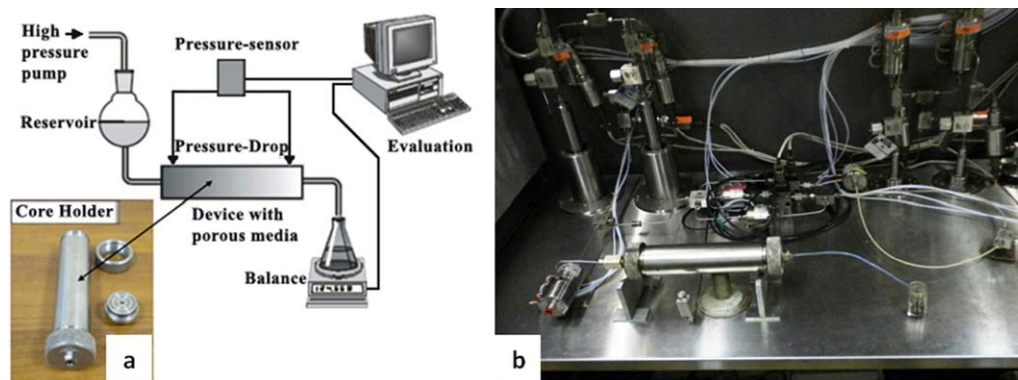| Core length (cm)	Core diameter (cm)	Air permeability (mDarcy)	Porosity (%)	Pore volume (cm^3)
5.08	2.54	5506	27.66	7.12
4.68	2.40	5254	30.02	6.35

Figure 2. The sand-packed model (a) and photo of UIC-C (2) equipment (b) for evaluation of the indepth propagation of polymer solution through the porous medium. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

experiments the injection rate was 1 cm^3 min^{-1}. Filtration experiments on core samples were conducted by means of two modern facilities "BRP-350" and "RPS-700" (VINCI Technologies, France), which allow determination of all required parameters under the simulated conditions with the best approximation to real-world conditions. The viscosity of polymer solutions and oil samples was measured on the Ubbelohde and Ostwald viscometers at $25 \pm 0.1°C$, respectively. The total salinity of oilfield water was determined on SevenCompact^{TM} S230 (Mettler-Toledo, Switzerland). The elemental composition of oil field water was analyzed with a X-ray fluorescence analyzer (Epsilon 3 SW LTU, PANalytical, The Netherlands).

RESULTS AND DISCUSSION

Sol–Gel and Gel–Sol Transition of Gellan

Aqueous solution of gellan behaves polyelectrolyte character due to intra- and intermacromolecular electrostatic repulsions between the negatively charged glucuronate groups.[30] Gellan gels are considered to result from association of double helical stretches. Gellan undergoes a sol–gel transition at a particular temperature, pH, and level of salinity.[9,30] It has been established that the extent of aggregation and effectiveness in promoting gel formation by addition of ions follows this order: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. This sequence coin-

cides well with increasing of the ionic radius of cation species.[31,32] A cation species with a larger ionic radius aggregates the gellan chains more effectively. Cation species that have a larger ionic radius have a higher 'effective' shielding ability for electrostatic repulsions between intramolecular segments and intermolecular chains. One specific property of gellan is that its type of rheology-solution, "weak gel" and "strong gel" depends on the salt concentrations.[30] According to our viscometric measurements the effectiveness of salts to enhance gelation changes in the following order: $BaCl_2 > CaCl_2 \approx MgCl_2 > KCl > NaCl$ (Figure 3; Table II). This order is in good agreement with the results of authors[33] found for gellan. The higher effectiveness of divalent cations in comparison with monovalent cations may be attributed to additional crosslinking of gellan chains due to cooperative binding (or "bridging") of the divalent cations between glucuronate residues according to their ionic radii.[34,35]

The critical concentration of salts, expressed as the ionic strength of the solution, leading to sol–gel and gel–sol phase transitions of 0.2% gellan solution are summarized in Table II.

As seen from Table II, the concentration of divalent cations required to induce gelation of gellan is far lower than for monovalent cations. Gelation of gellan in the presence of
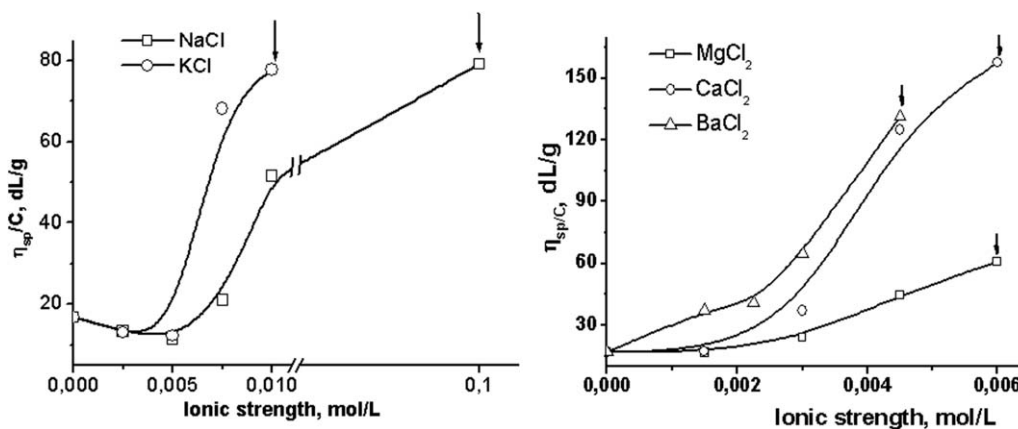

Figure 3. Dependence of reduced viscosity of 0.2% gellan on the ionic strength of the solution adjusted by addition of NaCl and KCl (left), BaCl$_2$, CaCl$_2$, and MgCl$_2$ (right). Arrows show the start of the gelation process. Temperature is 25°C.

Table II. The Sol–Gel and Gel–Sol Phase Transitions of Gellan in the Presence of Various Salts

Salt type	Critical value of the ionic strength inducing the sol–gel transition[a] (mol L^{-1})	Critical value of the ionic strength inducing the gel–sol transition[b] (mol L^{-1})
BaCl$_2$	0.0045	0.036
CaCl$_2$	0.006	0.036
MgCl$_2$	0.006	0.036
KCl	0.01	0.15
NaCl	0.1	0.20

[a] According to viscometric data.
[b] Visual observation.

mono- and divalent cations is connected with coil-helix conformational transition of gellan chains while the gel–sol transition of gellan at higher concentration of added salts may be attributed to the "salting out" effect and dissociation of double helices to single coils.

One of the remarkable properties of gellan is its ability to undergo sol–gel and gel–sol transitions in oilfield brine water of Kumkol oil reservoir containing mono- and divalent cations, such as Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+}. However, it should be noted that when divalent and monovalent cations are present together (as would occur in case of oilfield brine water), the gelation and properties of the gels can be complex and difficult to interpret.[30]

For example, 0.1% aqueous solution of gellan upon addition of 10–30% oilfield saline water with the salinity 73 g L^{-1} is transformed to the gel (sol–gel transition) (Figure 4). However, in the presence of $\geq$50% oilfield saline water, transformation of gellan from the gel-to-sol (gel–sol transition) takes place.

The reduced viscosity of a 0.2% aqueous solution of gellan gradually increases upon addition of oilfield saline water [Figure 5(2)]. Addition of more than 10 vol % of oilfield water causes gelation of gellan. While addition 10 vol % of oilfield saline water to a 0.2% aqueous solution of PAAm causes sharp decrease of the viscosity [Figure 5(1)]. Considering that PAAm contains at least 0.1% degree of hydrolysis, it is hypothesized

that intrachain complexation between COO$^-$ and the Ca^{2+} or Mg^{2+} ions in oilfield water is responsible for the shielding of PAAm chains[2] in addition to the "salting out" effect that takes place with respect to hydrophilic groups of macromolecules.

Addition of 10 vol % of oilfield water to 2% aqueous solution of gellan also leads to gel formation. However, transformation of gellan from the "strong gel" to "weak gel" takes place in the presence of 50 and 90% oil field water (Figure 6).

The behavior of gellan upon contact with sand granules saturated by oil-field water with salinity of 73 g L^{-1} containing various amounts of NaCl, KCl, MgCl$_2$, and CaCl$_2$ was studied. As seen from Figure 7, the aqueous solutions of gellan are immediately transformed to gel when the gellan sol is contacted with the sand surface saturated by oil field water.

Gelation of gellan in saline water may be one of the key factors for extraction of oil from saline reservoirs containing both monovalent and divalent cations. The sol–gel transition of gellan in oilfield water may be beneficial from several points of view. Firstly, pumping an aqueous solution of gellan into the injection well will be easy due to the low viscosity of the polymer. Secondly, the gel slug that is formed after contacting the underground saline medium can move to the deep stratum and can plug or reduce the flow capacity of high-permeability channels without damaging less-permeable hydrocarbon-productive zones. Consequently, injecting water (water flooding) should penetrate as much as possible into the less-permeable zones so that oil can be displaced from these poorly swept zones.

Flow Behavior of Gellan in Saline Porous Media

Flow behavior of polymers within porous media depends on the molecular structure of macromolecules and the microscopic structure of the porous medium itself, and also on such *in situ* factors as pH, salinity, and temperature.[5] A series of experiments was conducted to estimate the permeability reduction of pore space after polymer filtration through the sand pack model saturated by distilled, saline, and oil field water. Figure 8 shows the filtration behavior of 0.05% gellan and 0.05% PAAm solutions through the sand packed model with permeability of 4.2 Darcy saturated by distilled water.

Injection of 0.05% gellan solution with viscosity 1.5–2.0 mPa·s leads at first to more or less a linear increase of pressure. This

Figure 4. Gelation of 0.1% gellan solution in the presence of 10–90 vol % oilfield saline water at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
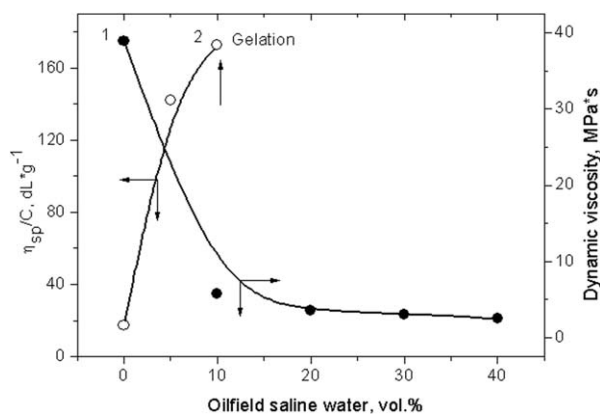
Figure 5. Changing of the dynamic viscosity of 0.2% PAAm (1) and the reduced viscosity of 0.2% gellan solution (2) upon addition of oilfield water with salinity 73 g L^{-1}. Arrow shows on starting of gelation process. Temperature is 25°C.

is probably a result of the displacement of distilled water by a polymer solution with a higher viscosity and polymer adsorption, which induces a permeability reduction. However, after injection of 3.5 pore volumes of gellan solution (1 pore volume is equal to 100 cm^3 of injected liquid) a sharp increase of injection pressure takes place. The final pressure after injection of 450 cm^3 gellan solution is 2.75 MPa. This is probably due to a coil-helix conformational or sol–gel phase transition of gellan caused by shear thickening in porous media. Under analog conditions, injection of 0.05% aqueous solution of PAAm increases the injection pressure and plateaus at 0.084 MPa when adsorption of PAAm is fully accomplished and thermodynamic equilibrium is reached. A similar mobility reduction (R_m) as a function of injected pore volume (PV) for PAAm at different polymer concentrations was observed previously.[36] Thus, due to the ability to plug ability of pore space addition of a 0.05% gellan solution increases the injection pressure (flow resistance) 40 times as that of the equivalent addition of a 0.05% PAAm solution. Decreased permeability caused by adsorption, and the hydrodynamic, or mechanical retention of polymer chains in the course of filtration in porous medium is characterized by the residual retention factor (RRF). This is calculated as K_b/K_f, where K_b is the initial water permeability before polymer filtration and K_f is water permeability after polymer filtration. For determination of RRF before and after filtration of polymer solutions, distilled water through the sand pack model sample was injected (Figure 9).

As seen from Figure 9, the injection pressure of distilled water after injection of gellan solution sharply increases and levels off at 2.37 MPa. The value of initial permeability decreases 128 times, which indicates the plugging of some parts of pores. Pumping of distilled water after injection of PAAm increases the injection pressure to 0.034 MPa and decreases the permeability 4.5 times. The RRF of gellan is 28 times higher than that of PAAm. This confirms the effective plugging of pore space by gellan rather than PAAm.

The next series of experiments was conducted with model saline water containing 75 g L^{-1} NaCl and aqueous solutions of gellan and PAAm both with a concentration of 0.1%. The injection pressure as a function of injected volume of gellan and PAAm solutions added to the sand pack model sample saturated by saline water is presented in Fig. 10. After injection of three pore volumes of 0.1% gellan solution the injection pressure increases very sharply. After injection of 315 cm^3 gellan solution the pressure increases up to 2.55 MPa. In the case of injecting PAAm, the pressure increases monotonically until leveling off at 0.062 MPa. The addition of the gellan solution plugs the sand pack and increases the pressure 40 times as compared to PAAm addition.

Oscillation of the injection pressure was observed while injecting 0.1% gellan solution through the porous media saturated by model saline water (Figures 10, 11). The amplitude of oscillation was dependent on the permeability of the sand pack model. The oscillating peaks appear strictly after injection of 1/3 of pore volume (30–35 cm^3 of gellan solution). Such behavior of gellan is likely explained by sol-to-gel and gel-to-sol transitions. When the front edge of injected gellan solution meets the saline water, it turns to gel (sol-to-gel transition) and the injection pressure sharply increases. Here the association of gellan double helices into stable aggregates is responsible for formation of true gels. As the gradient of salt concentration increases within the sand pack model sample, the gel-to-sol transition of gellan (or more probably "strong gel"-to-"weak gel") can take place, and the injection pressure decreases. Previously, it has been shown[37,38] that the gel strength decreases after addition of salt, and at higher salt concentrations there is a tendency of "weak gel" formation. The gel systems which are not able to support their own weight and can be stirred and poured like normal
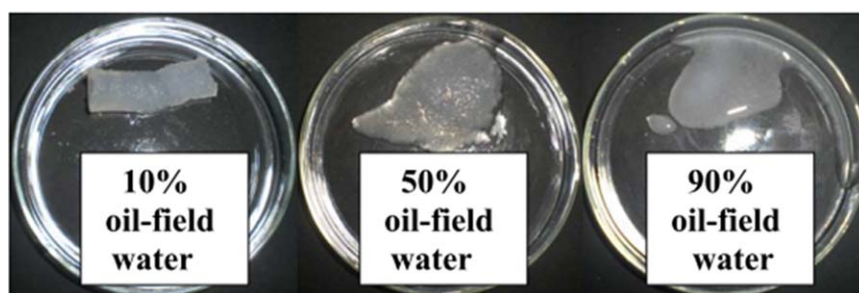

Figure 6. The state of gellan (2 wt %) in the presence of 10, 50, and 90% of oilfield saline water at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
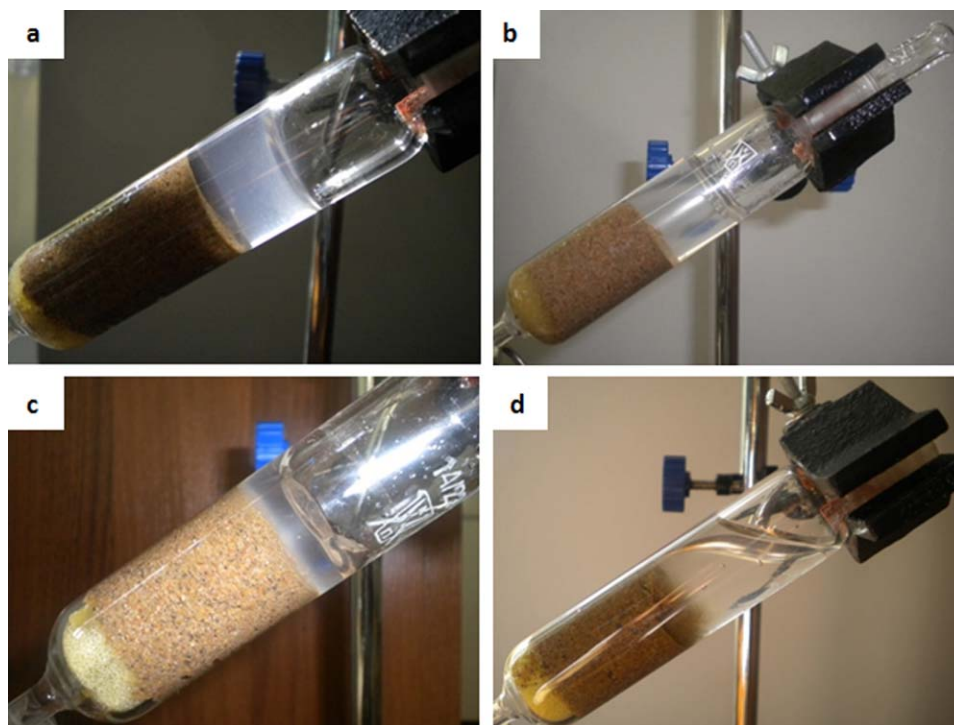
Figure 7. Gelation of aqueous solution of gellan after contacting with sand saturated with oilfield saline water (73 g L^{-1}) at room temperature. [Gellan] = 1.0 (a), 0.5 (b), 0.25 (c), and 0.1% (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solutions, are identified as "weak gels" as shown in Figure 6. The further permanent sol-to-gel and gel-to-sol transitions of gellan is probably responsible for the periodic oscillation phenomenon of gellan. Sol-to-gel and gel-to-sol transitions occur with only some polymers. For instance, the sol–gel–sol transitions caused by intermacromolecular interaction of α-cyclodextrin with polymer side chains have been demonstrated.[39] An aqueous solution of a diblock copolymer consisting of methoxy polyethylene glycol and poly(ε-caprolactone)

exhibited two phase transitions: a sol-to-gel transition and a gel-to-sol transition as a function of temperature (thermoresponsive sol–gel–sol phase transition).[40]

An alternative explanation of the oscillation behavior of the injection pressure during the filtration of gellan may also be step-by-step plugging of the high permeability channels by the "strong gel". The injection pressure increases when gellan solution penetrates into the high permeable channels and meets with salty water transforming into the gel. The next injected
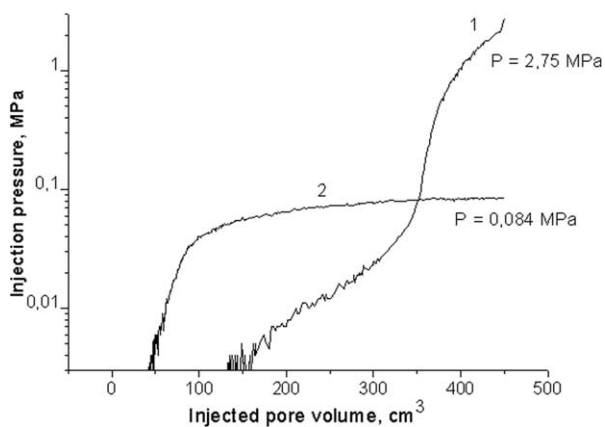

Figure 8. Changing of pressure upon injecting of 0.05% aqueous solutions of gellan (1) and PAAm (2) through the sand pack model saturated by distilled water. The permeability of the sand pack model is 4.2 Darcy. Temperature is 25°C, flow rate is 1 cm^3 min^{-1}. For comparison of experimental results, the values of injection pressure are expressed in logarithmic scale.
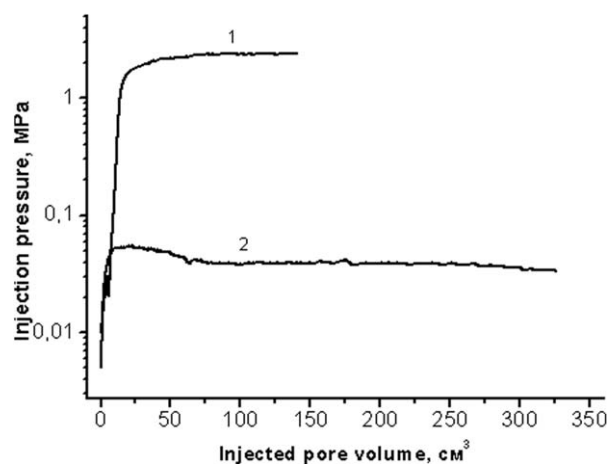

Figure 9. Injection pressure of distilled water within the sand pack model sample while injecting 0.05% aqueous solutions of gellan (1) and PAAm (2). The permeability of the sand pack model is 4.2 Darcy. Temperature is 25°C, flow rate is 1 cm^3 min^{-1}.
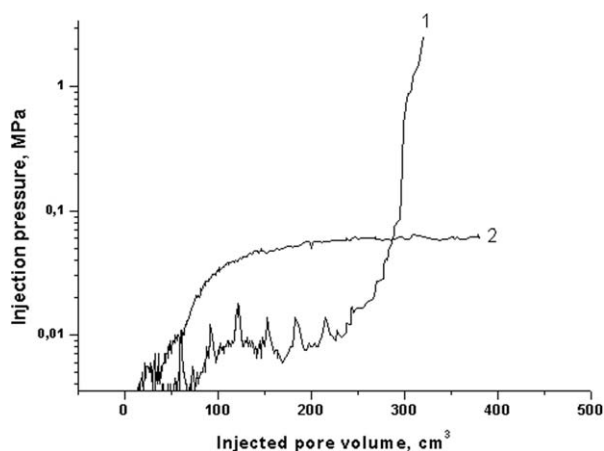
Figure 10. Injection pressure versus injected pore volume with 0.1% gellan (1) and 0.1% PAAm (2) solutions through the sand pack model sample saturated by saline water. The permeability of the sand pack is 3.7–3.8 Darcy. Temperature is 25°C, flow rate is 1 cm^3 min^{-1}.

Figure 12. Changing of injection pressure of saline water through the sand pack model after injecting 0.1% aqueous solutions of gellan (1) and PAAm (2). The permeability of the sand pack is 3.7–3.8 Darcy. Temperature is 25°C, flow rate is 1 cm^3 min^{-1}.

solution finds another high permeable flow path and breaks through it and as a result the injection pressure decreases, but inside of the same flow path the formation of new gel species takes place resulting in the increase of the pressure. This process is repeated until all high permeable channels that are available to gellan invasion are plugged, leading to sharp increase of the injection pressure (Figure 11).

After pumping 0.1% gellan solution, saline water was injected to the sand pack model sample. As seen from Figure 12, the injection pressure of brine water through the sand pack model after filtration of 0.1% gellan solution is about 0.036 MPa and the RRF is 14.42. In comparison, the injection pressure of brine water after filtration of 0.1% PAAm solution is equal to 0.023 MPa and the RRF is equal to 4.11. Under these conditions, the value of RRF after filtration of gellan is three times higher than that of PAAm.
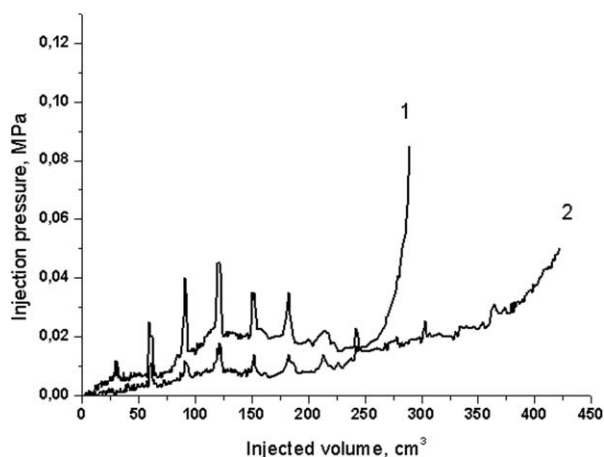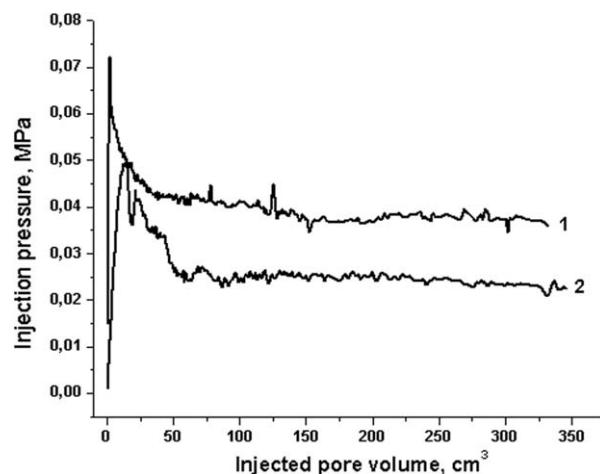
Brine-initiated gelation of gellan may be used as a shut-off agent in polymer flooding. Flow behavior of 0.1% gellan solution through the sand pack model sample saturated by oilfield water containing 73 g L^{-1} mono- and divalent cations, such as Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+} from Kumkol oil reservoir was also tested (Figure 13). While there is an overall exponential increase in injection pressure, there is also oscillation of pressure observed while injecting 0.1% gellan solution through the sand pack model sample saturated by oil field water with salinity of 73 g L^{-1}. The smeared oscillating behavior of 0.1% gellan solution within the saline sand pack is probably due to the presence of a mixture of mono- and divalent cations that make the gelation of gellan more complex.[30]
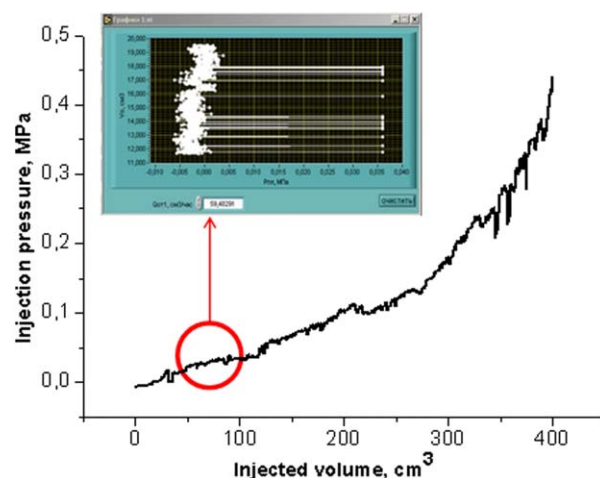

Figure 11. Oscillation of injection pressure upon injecting of 0.1% gellan solution through porous media of permeability coefficients (K_{perm}). $K_{perm} = 3.80$ (1) and 3.18 Darcy (2). Temperature is 25°C, flow rate is 1 cm^3 min^{-1}.

Figure 13. Flow behavior of 0.1% gellan solution through the sand pack saturated by oilfield water with salinity of 73 g L^{-1}. The permeability of the sand pack is 3.7 Darcy, and the Inset figure shows an oscillation of injection pressure with second interval. Temperature is 25°C, flow rate is 1 cm^3 min^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
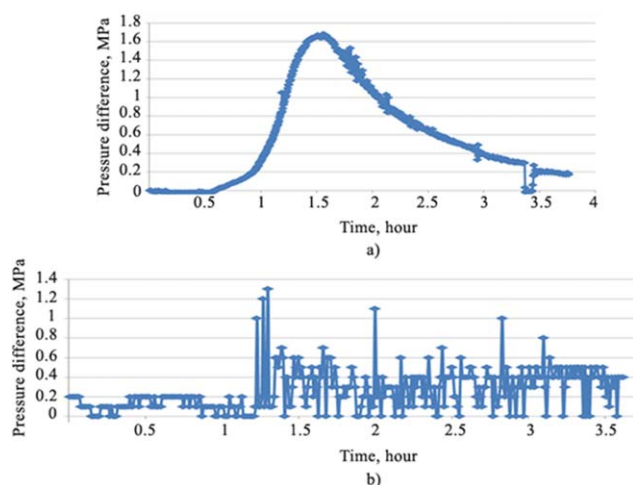
Figure 14. Pressure difference over time upon filtration of 0.1% aqueous solutions of PAAm (a) and gellan through the core samples (b). Temperature is 70°C, flow rate is 0.1 cm^{3}min^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The results obtained from the sand packs saturated by reservoir water with salinity of 73 g L^{-1} are in good agreement with additional experiments conducted with two core samples of Kumkol oilfield. Presented in Figure 14 is the differential pressure change in the course of filtration of 0.1% aqueous solutions of PAAm and gellan through the core samples saturated by saline water. In the case of injecting 0.1% PAAm solution through the core sample, the pressure difference passes through a maximum [Figure 14(a)]. The gradual increase in pressure difference, which shows a certain plugging effect, may be explained by the replacement of saline water by a polymer solution with a higher viscosity and the adsorption and entrapment of PAAm macromolecules within the pore openings. Since PAAm macromolecules are shielded in a high salinity environment and are sensitive to shear degradation, the viscosity of PAAm is considerably reduced, and with the extreme salinity and shearing at a high flow rate through the sandstone core, the viscosity becomes closer to the viscosity of the brine. All these factors decrease the pressure difference at longer times. In the case of injecting a 0.1% gellan solution through the saline

core sample, the pressure difference changes slightly at first then it starts to oscillate with time [Figure 14(b)].

A reasonable explanation of this phenomenon may be the sol-to-gel and gel-to-sol phase change of gellan within core sample saturated by saline water. It should be noted[9] that gellan, unlike PAAm, is less subjected to high shear stress. Comparison of the results obtained in the sand pack model and core samples allows one to conclude that when the sand pack is filled up by relatively homogeneous sand grains (average granular size is 0.125–0.25 mm) and homogeneous brine solution (such as NaCl) the oscillating behavior of gellan solution in porous media is well realized (see Figures 10, 11). In the case of gellan filtration through homogeneously distributed sand grains saturated by inhomogeneous oilfield brine solution (composed of NaCl, KCl, MgCl$_2$, and CaCl$_2$), the smooth oscillatory behavior of gellan solution is observed (see Figure 13). In the case of core samples that have a heterogeneous structure saturated by a heterogeneous oil field brine solution (composed of NaCl, KCl, MgCl$_2$, and CaCl$_2$), the oscillating behavior of gellan solution in porous media is also realized but to less of an extent.

Results of Pilot Tests at "Kumkol" Oilfield

It is expected that the reservoir conditions are complex and considerably influence the sol–gel and gel-sol transitions of gellan. The porosity and permeability of core materials, viscosity and density of oil, total salinity of oilfield water, elemental composition of brine solution, and temperature regime are key factors to evaluate the efficiency and behavior of gellan in oil reservoir. More salinity is beneficial for gellan to undergo to gel state because the lower concentration of gellan can be injected into oil reservoir. At the same time, the more salinity will cause the gel–sol transition of gellan (or formation of "weak gel"). Also taking into account that gellan gum maintains its strength at 90°C in our mind for each oil reservoir the thorough laboratory experiments should be conducted and optimal concentration of gellan solution for field conditions should be defined.

Aqueous solutions of gellan in the concentrations range of 0.2–0.5% were injected into 2 injection wells (Nos. 3383 and 3065) of Kumkol oil field (Kyzylorda region, Kazakhstan). The total volumes of injected polymer solution into well Nos. 3383 and 3065 were equal to 234 and 160 m^3, respectively. As seen from
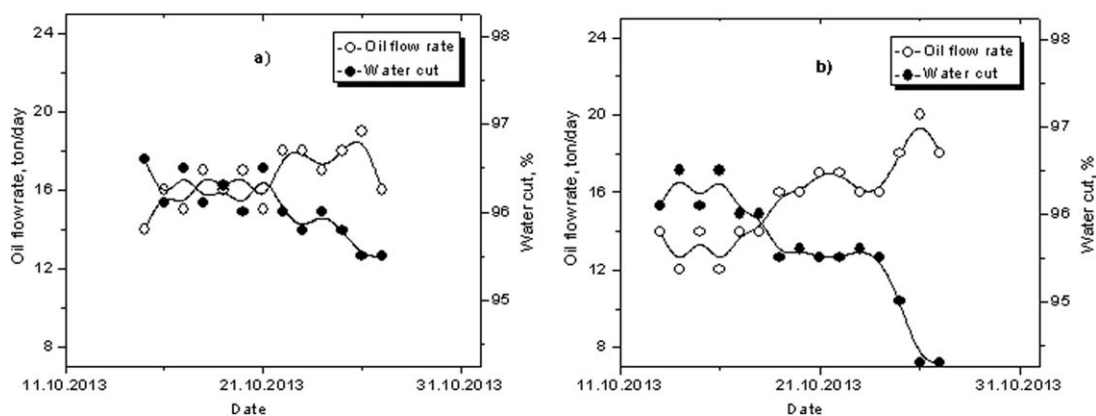

Figure 15. Response of the production wells No. 2315 (a) and No. 3064 (b) to injection of gellan solutions in field conditions over time.
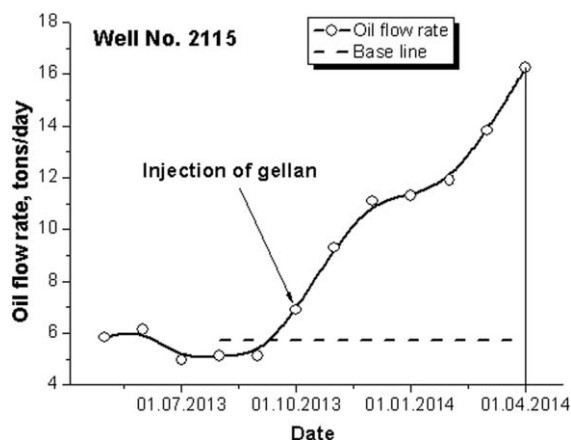
Figure 16. Response of the production well No. 2115 to the injection of gellan solution.

Figure 15, pumping gellan solutions into the injection wells leads to decrease of water cut and increase of oil flow rate in the production wells (Nos. 2315 and 3064) that are in the vicinity of injection well No. 3065. It is proposed that the injection of gellan solutions plugs the high permeable zones of oil reservoir, redirects the filtration streams and affects new oil deposits that were not exploited before by water flooding.

The effective plugging of high permeable channels of the oil reservoir, formation of solid gel structure, and increased filtration resistivity is confirmed by increasing the injection pressure from 55 atm to 90–95 atm. The oil flow rate in production wells increases up to 8 tons per day during 25 days after the injection of gellan solution. In comparison, the water cut in production wells decreases up to 2–3% over the same period of time.

After injection of 2 tons of gellan into 2 injection wells totally 3790 tons of additional oil was produced during the 6 months. In particular the well 2115 showed the most optimistic response to the treatment compared to the prehistory of oil flow rate (water flooding) (Figure 16).

Efficiency of gellan was compared with existing polymer gel systems used in oil industry (Table III). Comparative analysis demonstrates that the effectiveness of gellan is 5–21 times higher than the tested polymer flooding technologies.

As seen from Table III injection of 1 ton of dry gellan into oil reservoir allowed to produce 1 895 tons of incremental oil while for the other reagents this value varies from 88 to 380 tons of

incremental oil per 1 ton of dry powder. The technological efficiency of PAAm tested at North Buzachi (West Kazakhstan) oil field is 380 tons/ton in 2009 was considered as the best result.[36] However, the efficiency of gellan is five times higher than PAAm in spite of the fact that its cost is 2–3 times higher than PAAm. Thus, the pilot test results on Kumkol oilfield (Kyzylorda region, Kazakhstan) confirmed that the solution to major challenge facing water shut off effectiveness is the excellent gelation ability of gellan in high saline oilfield water and plugging of high drainage channels.

CONCLUSIONS

Flow behavior of dilute solutions of gellan and PAAm was studied in porous media saturated by distilled, model saline, and oil field water. It was shown that the effectiveness of salts to enhance gelation follows this order: $BaCl_2 > CaCl_2 \approx MgCl_2 > KCl > NaCl$. The sol-to-gel and gel-to-sol phase transitions of gellan in oilfield brine water containing mono- and divalent cations, such as Na^+, K^+, Ca^{2+}, and Mg^{2+}, were demonstrated. Quick gelation of gellan solution upon contact with sand granules saturated by oil field water with salinity of 73 g L^{-1} was shown. Injection of 0.05 and 0.1% gellan solution to a sand pack led to plugging of pore space and increased the injection pressure (flow resistance) 40 times in comparison with 0.05 and 0.1% PAAm solution. While injecting 0.1% gellan solution through the porous media saturated by model saline water (75 g L^{-1} NaCl), an oscillation of injection pressure was observed. This oscillatory behavior of gellan solution in saline medium was explained by two ways: (1) sol-to-gel and gel-to-sol transitions and (2) step-by-step plugging of high permeable zones until the next injected gellan solution finds another high permeable flow path and breaks through it. The flow behavior of a 0.1% gellan solution through the sand pack model sample saturated by oil field water containing 73 g L^{-1} mono- and divalent cations, including Na^+, K^+, Ca^{2+}, and Mg^{2+}, from the Kumkol oil reservoir was also tested. The pressure surge within seconds was observed when 0.1% gellan solution was injected through the sand pack saturated by oilfield water. The results obtained with the help of sand packs were confirmed by additional experiments conducted with core samples from the Kumkol oilfield. It was concluded that the realization of the oscillatory regime takes place when the sand pack is filled by more or less homogeneous sand grains (average granular size is 0.125–0.25 mm) and saturated by a homogeneous brine solution (such as NaCl). The oscillating behavior of gellan solution in porous media was also

Table III. Comparative Analysis of the Effectiveness of Gellan with Tested Polymer Flooding Technology

Oil field/used reagent	Type of rock	Salinity of brine, (g L^{-1})	Temperature (°C)	Number of injection wells	Amount of reagent (tons)	Incremental oil recovery (tons)	Technological efficiency[a] (tons/ton)	Time (months)
Kumkol/Gellan	Sand	73	55	2	2	3,790	1895	6
Buzachi/PAAm[41]	Sand	58.8	29.7	1	42	16,000	380	12
Daqing/ PPG[42]	Sand	4	40	4	134	15,000	113	10
Usinskoe/Galka[43]	No data	No data	82	No data	117	10,316	88	6

[a] Technological efficiency is a ratio between the amount of incremental oil recovery and the amount of reagent used.

realized with core samples that have a heterogeneous structure and were saturated by heterogeneous oil field brine solution (composed of NaCl, KCl, MgCl$_2$, and CaCl$_2$). The brine-initiated gelation effect from adding gellan was employed to shut-off high permeability channels in oilfield conditions. The decreased water cut up to 2–3% and increased oil flow rate up to 8 tons per day was observed during 25 days. Efficiency of gellan in oilfield conditions was compared with existing polymer gel systems used in oil industry. Injection of 1 ton of dry gellan into oil reservoir produced 1895 tons of incremental oil that is 5–21 times higher than the tested polymer flooding technologies.

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