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APPLICATION PROGRESS OF INSITU POLYMER GEL IN OILFIELD CONFORMANCE CONTROL TREATMENT

Abstract

Many oilfields around the world are using enhanced oil recovery methods to maximize oil production. Long-term water flooding processes have led to water channeling in mature reservoirs, which is a severe problem in oilfields. Polymer gel is widely used as a plugging agent to reduce water production. Previously, the conventional polymer gel is extensively used for blocking the thief zones, but the performance of conventional polymer gel is not satisfactory in high salinity and high temperature conditions due to rapid syneresis and thermal degradation. The amphiphilic polymer is taking much attention for polymer gel formulation because they are more salt resistant in low concentration compared to high concentration conventional HPAM polymer. In this paper, the crosslinking mechanism of insitu polymer gel is reviewed. The related difficulties and development prospects of polymer gels are presented. It provides a basis for the application of polymer gel in oilfield conformance control treatment. This will help researchers to develop polymer gels to improve oil recovery under economic conditions to meet the requirements of oilfields.

Key words: insitu polymer gel, amphiphilic polymer, crosslinking mechanism, high salinity, high temperature.

Introduction

Excessive water production in mature reservoirs is a major concern recently. During the water flooding, water overflows in the heterogeneous reservoirs, cause mineral dissolution. The production water together with hydrocarbon is undesirable by product, the total produced water consists of the formation and the injected water during the flooding, that increases production cost for proper disposal of produced water that affects overall project economics. According to the recent statistical analysis, 40 billion dollars per year is spent on the treatment of unwanted water. Therefore, proper, stable and economical treatment is needed for the disposal of this produced water [1–4].

Weak gels are very effective when they cross-linked under the reservoir condition as a plugging agent and for the fluid diversion conformance improvement. The gel treatment is a function of placement and size of the gel slug. The most important restrictions as discussed is a slow gelatin rate, effectiveness of pH, low retention, high mobility of the gallant, effective water diversity, stability of gel and effect of temperature and salinity [5].

The insitu gel system consists of hydrolyzed poly-acrylamide (HPAM) named as conventional polymer, that consist of hydroxyl group. Due to thermal hydrolysis under high salinity and high temperature, some of the amide groups (–$CONH_2$) on polymer backbone convert to carboxylate groups that crosslink under excessive brine, resulting in syneresis or precipitation of polymer gel, which is not very useful for high salinity and temperature application. HPAM is a straight-chain polymer that has acrylamide (AM) molecule as monomer, hydrolysis of conventional polymer increases with the increase of temperature and as a result, the amount of polyacrylic acid increases in the backbone, which is sensitive to hardness. The hydrolysis degree determines the properties of these monomers. If the hydrolysis is less, polymer will not be water-soluble and if the degree of hydrolysis is too large, its properties will be more sensitive to salinity and hardness [6, 7]. Polymer gels are unstable above a certain temperature and salinity limit. Efforts are made to increase the upper salinity and temperature limit. Crosslinkers, such as metallic, organic and inorganic commonly used for viscosity enhancement. Polymer gel can form three dimensional network structure that traps water and thus will increase the viscosity of water by ionic or covalent bond depends on the type of crosslinkers and polymer selected, as the ionic and covalent bond have different structure so that the stability. Covalent bond usually formed with the organic crosslinkers has high thermodynamically stable, at elevated temperature as compared to ionic bond [8, 9].

Crosslinking mechanism of insitu polymer gels

A lot of progress has been done in polymer gel technology, some new kind of materials synthesized that makes polymer gel technology beneficial as a permeability reduction in the heterogeneous reservoir. The Reservoirs between the temperature ranges greater than 80˚C, conventional polymer system was not so effective for excessive water treatment, the addition of temperature resistance monomer like, N-vinyl pyrrolidon (NVP) and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) can enhance the temperature resistance ability of a polymer gel, on the other hand for harsh reservoirs there is a great progress for insitu polymer gel formulated by the addition of surfactant, nano materials with the polymer and crosslinker, named as nano composite gels, which gives better performance in the harsh reservoir condition, but it's an expensive technology [10, 11].

The double crosslinking techniques also used recently to enhance the effectiveness of insitu polymer gel for high temperature conditions. The conventional polymer HPAM has two functional groups amide and carboxylate that react with crosslinker to form polymer gel with high mechanical strength, but the concentration for conventional polymer used is too high and due to high viscosity one group of the polymer is reacted with the cross linker and other groups remain unreacted due to which strength of polymer gel is not so good that's why concept double crosslinking will introduced so that both groups of the polymer will react with cross linkers, the result showed that the double crosslinked polymer gel system can easily to inject in the deep reservoir and have high temperature and salt resultant [12].

Due to unsatisfactory performance of conventional polymer the modified functional polymer also used recently to formulate polymer gel for high temperature and high salinity reservoirs, like amphiphilic polymer, hydrophobic associative polymer (HAP), salt-resistant comb-type acrylamide polymers (KYPAM), and AMPS/AM copolymer are used, their chemical structure is shown in Figure 1 **(p. 161)** [13, 14].

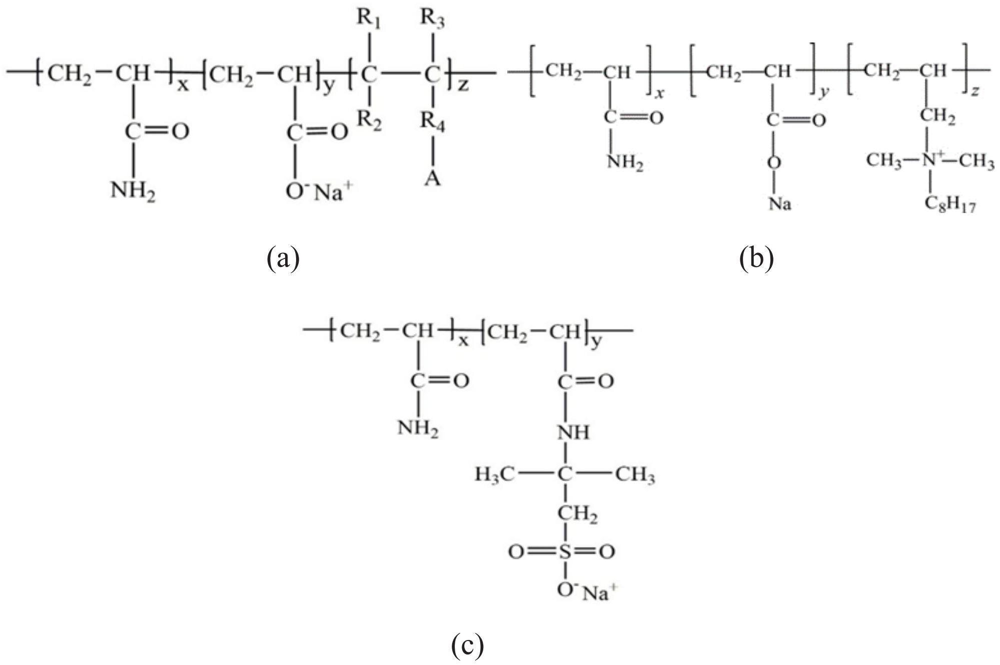

Figure 1 – Chemical structure of recently used polymer for gel formulation (a) KYPAM (b) AMPS/AM copolymer (c) HAP

The HAP has good performance but there is a difference of gelation time and gel strength in dynamic and static experiments. Dynamic experiment means the sand pack core flooding experiment and static method mean the most commonly used bottle test method. The double crosslinking system of Crl/WPF crosslinked with conventional polymer gives extremely high temperature and high salinity resistant polymer gel. Associative polymer gel under high salinity and Temperature have good performance in laboratory and the oil field [15, 16].

For the high temperature reservoir, the performance of inorganic cross-linked polymer gel is unsatisfactory. However, the organic crosslinker has better performance for high temperature reservoir condition but the crosslinking reaction is too fast at elevated temperature. To avoid the problem of low gelation time some retardant and delaying agent can be used to enhance the gelation time of organic crosslinkers [17, 18]. For the metallic cross linker like Cr^{3+}, Al^{3+} and Zr^{4+} etc. the gelation time is also very low even less than 2 hours at the temperature greater than 90˚C, the gelation time of HPAM/Cr^{3+} is extended by sodium lactate [19]. However, it is difficult to set the criteria between high temperature and higher temperature, the different researcher gives the different criteria for the temperature ranges for organic and inorganic cross linkers.

However, there are no suitable criteria found for temperature ranges of high temperature reservoirs but usually in enhanced oil recovery (EOR) process the reservoir with temperature greater than 80˚C is considered as high temperature reservoir and the reservoir with temperature greater than 120˚C is consider extremely high temperature reservoir, and the reservoir with temperature ranges in between 60˚C to 80˚C will consider low temperature reservoirs [20].

During the process of water flooding the produced water from the production well is unnecessary, because of this the water flooding is not so much effective. Therefore, the conformance control treatment method is required to increase the effectiveness of water flooding and decrease the unnecessary water production. Weak gels are most widely used as a conformance control treatment and their performance is very satisfactory and to decrease the unwanted water production.

For in-depth fluid diversion in the heterogeneous reservoir, week gel is used because their viscosity is very low before injection, so they can easily inject in large volume into the deep formation to block the thief zones of the heterogeneous reservoirs. Secondly, weak gels are very effective under the condition of high salinity and high temperature. Some weak gels have low gelation time but they are very effective, it is difficult to inject this kind of gels in the deep formation, some delaying agent is always required to increase the gelation time so that they can be injected into the deep formation.

For insitu gel, the gellant is prepared at the surface by mixing the different chemicals like polymer, cross linker, and other additives to form a gellant solution. After the formulation of gallant solution, the gallant is injected into the target reservoir and the gel will form under the reservoir conditions after the specific gelling time.

The performance of insitu polymer gel is effected by many factors like degradation of gallant when injected into the reservoir by the pump, the condition of the formation water like some kind of gel will not perform well in the high salinity formation water, the temperature of the reservoir, pH and chemical composition. The first time the insitu gel system was applied in 1970, for in-depth conformance control insitu gel system is used previously [21]. In Figure 2 shown the formulation of insitu polymer gel system.

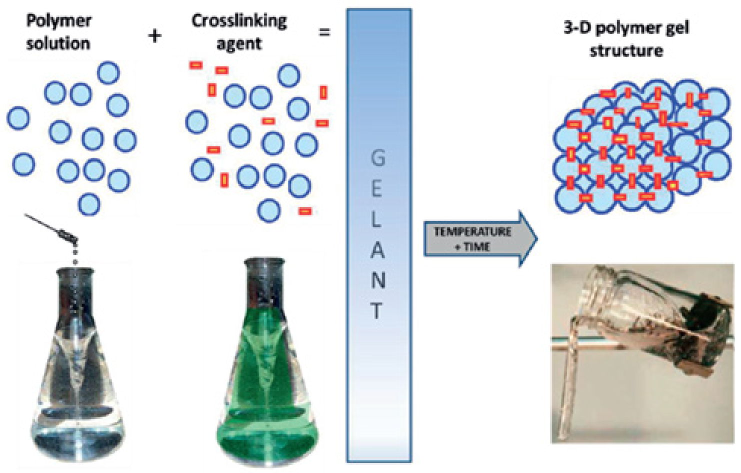

Figure 2 – Formulation of insitu polymer gel

During the polymer gel operation, for the most part, either by diverting fluid flow from high permeability, low permeability zones, insitu polymer gel have been used for water shut off and profile modification across injection and production well, as shown in Figure 3, after formation of gel the flow part of the fluid is diverting to the low permeability layer [22].

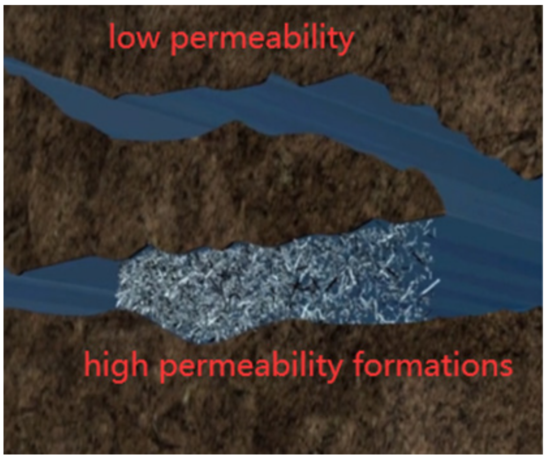

Figure 3 – Plugging of thief zones with polymer gel

Weak gels have low gellant viscosity before forming the three dimensional polymer gel, actually the weak gels are portion of the bulk gel system, these gels are effective in the wide range of salinity and temperature and they can be injected in the deep reservoirs to plug the high permeability region in the subsequent water flooding, but some of the weak gel has very low gelation time, such kind of gels are very effective with delaying agent.

The bulk gel used previously have some drawbacks such has their plugging radius is very insignificant, and because of this their injection is not effective, due to this reason they have poor plugging rate and fluid diversion properties. So, the weak gel is preferred because of their low viscosity they can easily penetrate into fractured and high permeability reservoirs and gives better plugging properties. Weak gels are multifunctional they can be used as oil displacement agent [23, 24]

Gel formulations

For gel formulation, polymer play a vital role, a different type of polymers are used for the gel formulation have benefits and draw backs according to the condition of the reservoirs. So, it is important to choose a polymer that has better performance under high salt and temperature conditions. For gel formulation, various polymers have been studied such as HPAM, HAP, and salt tolerant KYPAM polymer.

Development of salt and temperature resistant polymer

Many developments take place for the synthesization of salt and temperature resistant polymers. Amphiphilic polymers are a new class of polymers that have been synthesized by the addition of a small number of hydrophobic groups into the HPAM molecular chain. These polymers are generally utilized in different fields in oil field development. At the point when the concentration of the amphiphilic polymer is higher than the critical association concentration, the hydrophobic group is for the most part made of inter molecular association, developing a spatial network structure. Due to the association between the hydrophobic groups, the amphiphilic polymer has good temperature resistance, salt resistance and mechanical shear resistance in aqueous solution compared with the partially hydrolyzed polyacrylamide, amphiphilic polymers are unique in relation to the established water-soluble polymers as in the measure of hydrophobic monomers suitable for making physical relationship with one another is low [25, 26].

Despite the fact that their molecular weight is high, but still, they depend on excessive hydrophobic collaborations between various polymer chains for the thickness impacts. The hydrophobic groups interrelate and form an intermolecular polymer network in the aqueous solution as shown in Figure 4 [27].

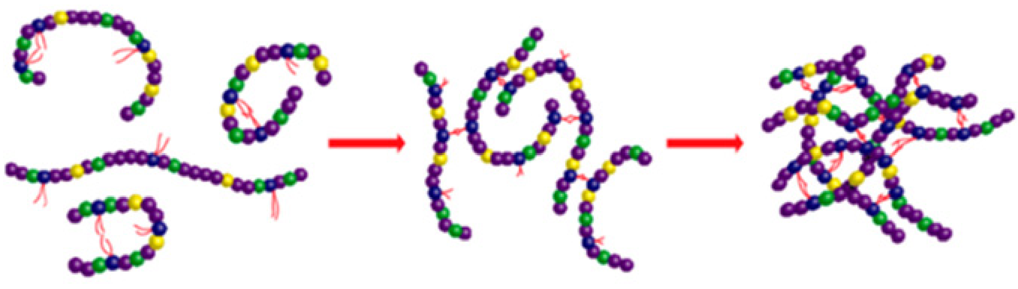

Figure 4 – Association process of amphiphilic polymers

If the visualization of the network structure of polymer is taken randomly it will exhibit the network similar to the gel, indicating a viscoelastic property, but with the passage of time flow occurs due to the Brownian movement breaks the end-gather relationship for a short duration of time before the other association of same group on a similar chain. These polymers have not been tried for conformance control treatment, yet the lab results demonstrate that with some specific crosslinkers, they can be utilized for particular water-shutoff applications. Progressively more research is required to utilize this hypothesis. In this thesis, the purpose is to change the current profile of the main agent and make full utilization of the amphiphilic polymer.

Types of crosslinkers

Inorganic crosslinkers

Wide range of inorganic crosslinkers is used previously, formed strong polymer gel. The different kinds of cross-linker prompt to divergences in the rheological properties, salt, and temperature resistance. Gels synthesized with metallic cross-linker such as Cr^{3+}, Al^{3+} or Zr^{4+} has inferior stability at high temperature and their small gelation time avoids appropriate placement in deep high temperature reservoirs, however with a delayed gelation mechanism their gelation time can be enhanced and, this kind of cross linkers can be used for deep conformance control treatment, Al crosslinker has low gelation time and is suitable for low temperature but by chelating the aluminum with citrate, its gelation time can be enhanced [28].

The chromium cross-linked with polyacrylamide polymer to complexion of Cr ions with carboxylate groups on the polymer chain, this cross linker also shows the syneresis problem under the high salinity and high temperature condition and not thermally stable. Others type are polyacrylamide/Cr^{3+} carboxylate system and Xanthan/Cr^{3+} system. Titanium crosslinker has also been developed due to the bad environmental impact of some metallic crosslinkers. The inorganic crosslinkers linked through ionic bonding among the negatively charged carboxylate groups on the polymer chain and multivalent cation. Inorganic cross-linked polymer gel usually used at low temperature (<70˚C) reservoirs, since high temperature and high salinity will be the reason for syneresis of inorganic polymer gel [29,30].

Organic crosslinkers

There has been an enduring demand within the oil industry to develop active conformance improvement polymer gel technologies by using the organic chemical crosslinking agents that would impart carbon-carbon-bond chemical crosslinking between the gel polymer molecules [31]. This would avoid the use of metal crosslinking agents, and would outcome in remarkably strong and stable polymer gels. These gels are suitable for high temperature application (>70˚C). Organic cross-linked polymer gel results in the formation of a covalent bond between amide group of polymer and crosslinker which can form a good temperature resistance gel [32].

For example, the commonly used organically cross-linked polymer-gel technologies developed are based on, hydroquinone (HQ), hexamethylene (HMTA), organic chromium, phenol formaldehyde chemistries. The organic cross linker of phenol/formaldehyde is used widely but due to the high content of its toxicity, that limit its use. There is a covalent bond formation among organic crosslinkers and the amide group of the polymer and stabilize under high salinity and high temperature conditions.

Polymer gel application in China

The conformance control treatment technology has been applied on site since the 1950s and has a history of nearly 40 years. In most of the oil fields currently developed, water flooding is a conventional means of enhancing oil recovery. However, after some long-term water injection in some old oil fields, the water content of the oilfield has reached a limit. At the same time, due to the heterogeneity of the reservoir, the distribution of remaining oil is relatively more dispersed, but in the local but relatively concentrated. According to statistics, the current average oil recovery rate in China is about 29.8%. However, due to technical means and economic factors, a large part of crude oil is still stuck in the stratum. Therefore, it is urgent to explore various new technical means for underground complex areas, carrying out reasonable research on enhanced oil recovery to meet the demand for oil in daily production [33, 34].

In the 1970s, the successful application of polymer weak gels to reduce produced water made the petroleum industry very interested in this technology. Injecting polymer gel into the wellbore can effectively block the formation in the near-well zone, thereby reducing the water yield of the well. After the 1990s, along with the continuous updating of technology, polymer weak gels are gradually used in the deep migration of reservoirs, mainly for reservoirs with serious reservoir heterogeneity. In addition, they are often used for cracks and large an oil layer with a very poor permeability in the tunnel or layer. This method can not only block the large pores and high permeability layers in the reservoir but also improve the oil-water mobility ratio in the layer. Compared with pure polymer flooding, this system uses a low polymer concentration and is more applicable [35].

The TP-910 conformance control treatment technology researched by the Petroleum Exploration and Development Research Institute has been widely used in oil fields such as Liaohe, Shengli, and Henan, and also seen obvious effects in Bohai Oil Company. During this period, various research units have successively developed PIA series conformance control treatment technology, BD-861 conformance control treatment technology, and three-phase foam. Since the 1990s, oil wells in the eastern oil fields of China have entered a period of high water cut, and the technology of conformance control treatment and water shutoff has been fully developed. As a particle-moving conformance control treatment agent for blocking large holes, it has been widely used in oil fields such as Shengli, Jianghan and Zhongyuan due to its low cost and easy operation. At the same time, polymer gel conformance control treatment and water shutoff technology have also been fully developed [36, 37].

Recently the major oil fields in the country (including Shengli, Liaohe, Dagang, Zhongyuan, Yumen, Daqing, Jilin, North China, Xinjiang, Qinghai, Jianghan and other oil fields) have carried out water injection well conformance control treatment and production well water shutoff work with water injection wells as the unit. Daqing Oilfield has carried out comprehensive management of "stable oil control and water control" with the main content of "regulating water, increasing production and extracting liquid" in the Saraji oil area, and achieved remarkable results. The conformance control treatment and water shutoff technology have been widely used in China [38].

Problems associated with insitu polymer gel during conformance control treatment

Although polymer gel treatment is widely used technique for conformance control there are still many problems that affect the performance of polymer gel which limits its use in the oilfields operations. Some of the major problems related to the polymer gel are given below.

Mechanical degradation

When an external force act on the polymer solution its structure is destroyed this phenomenon is called shear degradation. As many water shuts off polymers have a high molecular weight due to which they have high viscosity when this polymer mix with a cross linker that makes its injection difficult [39].

The pump will induce the mechanical force on a gellant solution, caused the mechanical degradation of polymer structure and may affect its performance. HPAM named as the conventional polymer used most commonly but their viscosity is declining with an increase of mechanical force and limits its use under the influence of high mechanical force.

Chemical degradation and precipitation

During the precipitation, solid particles will be deposited on the surface of polymer solution. The formation water contains many divalent cations like Ca^{2+} and $Mg^{2+}$when the carboxylate group of hydrolyzed polymer is interacting with these divalent cations, with the increase of these carboxylate groups the solubility of these cations will decrease and precipitation occurs due to which polymer is unavailable for polymer gel formulation [40].

Syneresis

Extraction of water from the polymer gel under the influence of high temperature, salinity, divalent cations is called syneresis, due to this the polymer gel structure is decompose with the passage of time, numerous polymer gel system has this issue as appeared in Figure 5 (p. 156) [41]. Syneresis is described by a decrease in volume, ejection of water and stickiness loses. Conceivable causes are polymer hydrolysis, excessive cross linkage, NaCl and divalent cations.

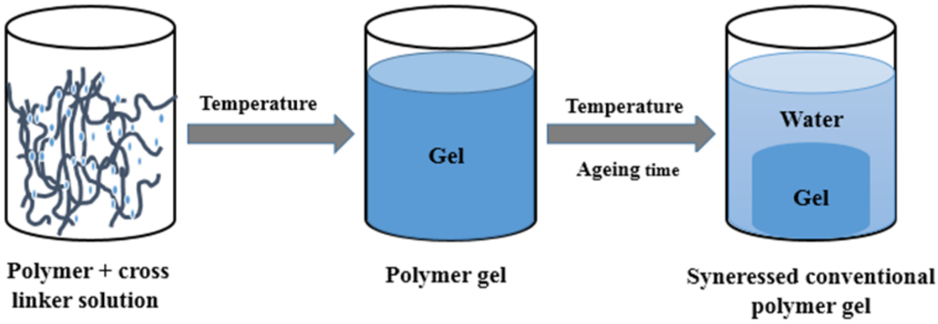

Figure 5 – Syneresis of conventional polymer gel in high salinity and temperature and reservoirs

Polymer gel with syneresis may involve 5% of the initial gel volume. Under high temperature conditions, conventional polymers (HPAM) hydrolyze to acrylate groups, which gives more sites for crosslinking and conceivable syneresis. In the formation water concentration of divalent cations is higher that cause the reason for over crosslinking as compared to metal crosslinker injection. Even with low syneresis (%), the polymer gel is still effective for the permeability reduction applications. For matrix applications, it is not so significant but for fractured reservoirs, it is very important [42].

Future development of polymer gels

In recent years, reservoir exploitation has developed towards deeper wells. At the same time, great progress has been made in polymer gel research, but there are still deficiencies. In order to meet the requirements of reservoir consistency control treatment to improve oil recovery, it is necessary to improve the performance of polymer gel, which can start from the following points:

(1) Strengthen and improve the existing process, use polymers with good temperature and salt resistance to improve the deficiencies of the system.

(2) By controlling the gelling time and strength of the polymer gel, the polymer gel is gelled in the deep part of the core, and the deep consistency control treatment of the oilfield is realized.

(3) Synergist is added to the polymer gel system to reduce the cost by reducing the amount of polymer gel.

(4) In order to make up for the shortcomings of poor stability and shear resistance of a single polymer gel system, the polymer gel system is combined with inorganic particles, polymer microspheres, surfactants and other systems to achieve the complementary advantages of each system.

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МҰНАЙ КЕН ОРЫНДАРЫНДАҒЫ ҚАБЫЛДАУ ПРОФИЛІН БАҚЫЛАУ ҮШІН ПОЛИМЕРЛІ ГЕЛДЕРДІ ҚОЛДАНУДАҒЫ ПРОГРЕСС

Аңдатпа

Дүние жүзіндегі көптеген мұнай кен орындарында мұнай өндіруді барынша арттыру үшін мұнай өндірудің жетілдірілген әдістері қолданылады. Ұзақ мерзімді су басу процестері судың жетілген қабаттарға қайта бағытталуына әкеліп соқты, бұл мұнай кен орындарындағы күрделі мәселе. Полимерлі гель сұйықтықтың жоғалуын азайту үшін бітеу агенті ретінде кеңінен қолданылады. Бұрын қарапайым полимерлі гель абсорбция аймақтарын блоктау үшін кеңінен қолданылған, бірақ тез синерезс және термиялық ыдырау салдарынан қарапайым полимерлі гельдің тиімділігі жоғары тұздылық пен жоғары температура жағдайында қанағаттанарлық емес. Амфифилді полимерлер полимер гельдерін жасауда басты назарға алынады, өйткені олар әдеттегі жоғары концентрациядағы ГПАМ полимерімен салыстырғанда төмен концентрацияда және тұзға төзімді. Бұл мақалада полимерлі гельді өзара байланыстыру механизмі қарастырылады. Осыған байланысты қиындықтар және полимер гельдердің даму перспективалары ұсынылған. Бұл мұнай кен орындарының қабылдау профилін бақылауда полимер гельді қолданудың негізін құрайды. Бұл зерттеушілерге мұнай кен орындарының талаптарына сәйкес келетін экономикалық жағдайларда мұнайды жақсарту үшін полимер гельдерін жасауға көмектеседі.

Тірек сөздер: полимер гелі, амфифильді полимер, тігілу механизмі, жоғары тұздылық, жоғары температура.

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ПРОГРЕСС В ПРИМЕНЕНИИ ПОЛИМЕРНОГО ГЕЛЯ ДЛЯ РЕГУЛИРОВАНИЯ ПРОФИЛЯ ПРИЕМИСТОСТИ НЕФТЯНЫХ МЕСТОРОЖДЕНИЙ

Аннотация

Многие нефтяные месторождения по всему миру используют методы повышения нефтеотдачи для максимизации добычи нефти. Длительные процессы заводнения привели к перенаправлению воды в зрелые пласты, что является серьезной проблемой на нефтяных месторождениях. Полимерный гель широко используется в качестве закупоривающего агента для снижения водоотдачи. Ранее обычный полимерный гель широко использовался для блокировки зон поглощения, но эффективность обычного полимерного геля не является удовлетворительной в условиях высокой солености и высоких температур из-за быстрого синерезиса и термического разложения. Амфифильным полимерам уделяется большое внимание при разработке полимерных гелей, поскольку они более устойчивы к соли при низкой концентрации по сравнению с обычным полимером ГПАМ с высокой концентрацией. В этой статье рассматривается механизм сшивания полимерного геля. Представлены связанные с этим трудности и перспективы развития полимерных гелей. Это обеспечивает основу для применения полимерного геля при проведении регулирования профиля приемистости нефтяных месторождений. Это поможет исследователям разработать полимерные гели для повышения нефтеотдачи в экономических условиях, отвечающих требованиям нефтяных месторождений.

Ключевые слова: полимерный гель, амфифильный полимер, механизм сшивки, высокая соленость, высокая температура.