Application of Cellulose and Cellulose Nanofibers in Oil Exploration

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Abstract: In this article, the application of cellulose and cellulose nanofibers in oil exploration was discussed, and the research status of using cellulose and cellulose nanofibers as oil displacement agents, oil-well cementing additives, and foam stabilizers were summarized.

Keywords: cellulose; cellulose nanofiber; oil exploration

1 Introduction

As a conventional and strategic energy resource, petroleum is called the “industrial blood”. Its output is directly related to the national economic development and national security. It has been predicted that by 2030, the global energy demand will continue to grow by more than 2% per year[1]. China is a big oil importing country, and more than 50% of the total oil used is imported. Under the current security situation in the world, excessive dependence on imports of oil seriously threatens the national economy and security. It is therefore important to improve the efficiency of oil production in Chinese oilfields[2].

Oilfield chemicals play a vital role in the process of oil exploitation. With the increasing global oil production, the types of oilfield chemicals are increasing, which include drilling chemicals, cementing chemicals, production chemicals, gathering and transporting chemicals, and oilfield water treatment chemicals[3].

Owing to the continuous exploitation of surface crude oil, oil drilling and production has moved towards the direction of deep wells and ultra-deep wells, and with the increase in the depth of oil wells, the salt concentration and temperature of oil wells have also increased. Therefore, the oil well environment with a high temperature

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and high salinity stipulates that oilfield chemicals have higher salt tolerance and thermal stability.

Partially hydrolyzed acrylamide (HPAM) is one of the most widely used oilfield chemicals\textsuperscript{4}; however, its temperature resistance, salt tolerance, and shear resistance are not satisfactory. For example, the maximum temperature HPAM can tolerate under reservoir conditions is 75°C; when the temperature approaches 75°C, the viscosity of HPAM decreases sharply\textsuperscript{4}. Moreover, the viscosity of HPAM decreases sharply in the presence of salt, especially, in the presence of divalent salts (Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, etc)\textsuperscript{5}. Under the condition of high shear rate, the molecular chain of HPAM breaks and its viscosity reduces. In high temperature as well as high salt concentration conditions, HPAM can easily decompose into acrylamide monomer, which pollutes the formation environment\textsuperscript{6}. These shortcomings of HPAM seriously limit its application in high-temperature oil wells with a high salt concentration.

In this context, researchers have been developing environmentally friendly oilfield chemicals, and cellulose and its derivatives have attracted researchers’ attention as environmentally friendly renewable materials. Cellulose is not only used in pulping and papermaking, medicine, films, and textiles\textsuperscript{7}, but also used as an environmental protection additive in the oil exploitation industry\textsuperscript{8}. This article mainly presented the application of cellulose and cellulose nanofibers in the exploitation of petroleum.

2 Cellulose and cellulose nanofibers

Cellulose is the most widely distributed and most abundant polysaccharide in nature. As it is lightweight, renewable, biodegradable, biocompatible, and has high hydrophilicity, high reactive activity, and other characteristics, it is applied in various industries\textsuperscript{9-12}. Moreover, cellulose and its derivatives are used as protective additives in the petroleum exploitation industry\textsuperscript{13}.

Cellulose nanofibers are derived from renewable natural cellulose. Because of their excellent physical and chemical properties, they have attracted great attention from researchers since their successful preparation. Cellulose nanofibers are ultra-fine fibers with diameter in the nanoscale and length generally in the nanoscale or micron scale. Cellulose nanofibers have not only the main properties of cellulose, but also the unique properties of nanomaterials, such as excellent mechanical properties and nanosize effects. They are applied in papermaking, coating, biomedicine, food, architecture, electronic products, energy storage products, petroleum exploitation, and many other fields\textsuperscript{14-16}. According to the morphology and preparation method, cellulose nanofibers can be divided into two categories: cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs)\textsuperscript{17}. The diameter of CNFs is in the nanometer scale and their length is in the micron scale. In recent years, many different definitions of CNCs and CNFs have been given in literature, and they are referred to as cellulose nanowhiskers, nanocrystalline cellulose, nano-fibrillated cellulose, and cellulose microfibers, and so on. Many different terms are misunderstood by the reader. In view of this, the Technical Association of Pulp and Paper Industry (TAPPI) redefined the cellulose nanomaterials (TAPPI WI 3021) based on the size of cellulose nanofibers\textsuperscript{18-19}. Designation, abbreviation, and size of cellulose nanomaterials are shown in Fig.1\textsuperscript{20}. The excellent rheological properties and nanosize effect of cellulose nanofibers provide the basis for their application in petroleum exploitation industry.

3 Application of cellulose-based materials in petroleum exploitation

3.1 Cellulose nanofiber-based oil displacement agent

With the increase in the drilling depth, the temperature and salinity of oil wells have increased. Ranka et al\textsuperscript{4} reported that the salinity range of general oil wells is 3.0 wt%~21.5 wt% (including monovalent salts and divalent salts), and the temperature range is 40~150°C. Therefore, modification of CNF hydrogels and imparting them with salt tolerance ability and
thermal stability has become a hot topic in recent years. The deterioration of the formation environment results in poor salt tolerance and thermal stability of some conventional polyacrylamides. In addition, the high temperature and high salinity of the formation environment makes polyacrylamide easily hydrolyze to acrylamide monomer, thus leading to pollution of the formation environment. This necessitates the petroleum exploitation industry to urgently develop a kind of “green” environment-friendly oilfield chemical. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) oxidized/carboxymethyl-modified CNF hydrogel has excellent properties such as good viscosity, non-Newtonian fluid characteristic and excellent viscoelastic properties and basic properties required for oilfield chemicals. However, the colloid stability of CNF with only carboxyl groups on the surface is poor in electrolyte solutions and high-temperature environment. Therefore, in order to improve its applicability in high-temperature and high-salt oil well environment, it is necessary to modify CNF through functionalization to endow it with salt tolerance and thermal stability.

Based on this, Wei et al\cite{21} used a TEMPO-oxidized CNF hydrogel as an oil displacement agent in oil displacement experiments. The results showed that a 0.2% CNF hydrogel could disperse well in 1% NaCl solution. Through oil recovery experiments, it has been proven that the main mechanism of CNF hydrogel flooding is that the CNF hydrogel can improve the recovery volume of the liquid and enhance emulsification and entrainment. In addition, the viscosity loss rate of the modified CNF hydrogel at high temperatures is obviously lower than that of HPAM, indicating that CNF hydrogel has potential as an oil displacement agent for oil recovery. Molnes et al\cite{22} studied the injectivity of CNC into the core of high-permeability sandstone. It was found that CNC could be used as an oil displacement agent in sandstone reservoirs to achieve improved oil recovery. Heggset et al\cite{23} reported that CNC has good thermal stability; they found that CNC maintained good colloid stability after heating at 140°C for 3 days. Li et al\cite{24} used 2-acrylamide-2-methylpropane sulfonic acid as a cross-linker to prepare CNF hydrogel.
acid (AMPS)- and hydrophobic group-modified CNF hydrogels (the structure of the compound is shown in Fig.2) as oil displacement agents. The results indicated that the modified CNF hydrogels maintained good gel properties in a complex salt solution (1% NaCl, 0.4% MgCl\textsubscript{2} and CaCl\textsubscript{2}), and the oil recovery ratio of modified CNF hydrogels increased by 6% as compared to that obtained with water flooding.

Further, Liu et al\cite{25} grafted N,N-dimethylacrylamide (DMA) and butyl acrylate (BA) onto the surface of CNF by radical copolymerization (as shown in Fig.3) and prepared the hydrogels of modified CNF (CNF-g-PDMA-PBA) by high-pressure homogenization. The salt tolerance of the CNF hydrogel increased from 1% to 8% after modification. The results of long-term thermal aging of the CNF hydrogels (before and after modification) revealed that upon aging them (the original CNF hydrogel and modified CNF hydrogel) at 105°C for 7 days, the viscosity loss rate of the original CNF hydrogel was 99%, while the viscosity loss rate of the modified CNF hydrogel was only 33% (as shown in Fig.4), indicating that the modified CNF hydrogel has significantly improved thermal stability. Moreover, the modified CNF hydrogels exhibited salt thickening phenomenon; when monovalent salt (2% NaCl) or combined salt (2% NaCl, 0.4% MgCl\textsubscript{2} and 0.4% CaCl\textsubscript{2}) was added to the hydrogel system, the viscosity of the hydrogel increased to 3.4 and 229 times that of the hydrogel without the salt. Overall, the modified CNF hydrogel showed good potential as an oil displacement...
agent for achieving enhanced oil recovery.

3.2 Cellulose-based oilfield cementing additives

Cellulose ether has been used in oilfield cementing for decades. As early as 1953, Kaveler added methyl cellulose ether as a retarder into drilling fluids at a dosage of 0.5% of the solid content of cement. The results showed that the rheological properties and filtration properties of the drilling fluid with methyl cellulose mixed ether were improved. Kaveler used sulfonated alkyl cellulose ether as a cement retarder, thickener, and water reducer in 1957. In addition, carboxymethyl hydroxyethyl cellulose (CMHEC) is also used as cement retarder, thickener, and water reducer in oilfield cementing.

To date, cellulose ethers including methyl cellulose, hydroxyethyl cellulose (HEC), CMHEC, and hydroxypropyl methyl cellulose have been widely used in oilfield cementing. Among them, HEC and CMHEC are the most widely used. Cellulose ethers are obtained by replacing the surface hydroxyl groups of cellulose fibers with methyl, hydroxypropyl, hydroxyethyl, and carboxymethyl groups. Etherification makes cellulose a water-soluble polymer. HEC is a very good filtrate reducer that can be used in different salinity conditions, but its thermal stability is poor. Generally, when the temperature exceeds 150°C, the ability of HEC to reduce filtration loss deteriorates. However, when HEC is used, a dispersant must be added to the cement slurry to restrain its thickening effect. Bülichen et al. also used HEC as a filter loss reducer. The results showed that when the dosage of HEC increased from 0.4% to 1% (relative to the cement slurry), the filtrate volume decreased from 318 mL to 36 mL.

Plank showed that adding CMHEC to a drilling fluid could reduce the filtration rate, because the introduction of carboxyl group was beneficial for delaying the filtration rate of water in cement slurry. Bülichen et al. used CMHEC as filter loss reducer; they reported that increasing the dosage of CMHEC from 0.1% (relative to the cement slurry) to 0.5%, resulted in a decrease in the filtrate volume from 1163 mL to 42 mL. The results indicated that CMHEC had excellent ability to reduce filtration loss at room temperature and in fresh water base drilling fluids.

3.3 Cellulose nanofiber-based cementing additives in oilfields

The application of cellulose nanofibers in oilfield cementing has the following advantages: ① the surfaces of CNF and CNC oxidized by TEMPO are usually highly negatively charged, and they easily adsorb onto the positively charged surface of bentonite particles. In order to maintain the colloid stability of a drilling fluid, it is beneficial to reduce the filtrate volume of the drilling fluid; ② both TEMPO oxidized CNF (TOCNF) and CNC have excellent rheological properties, which is beneficial for improving the rheological properties of the drilling fluid; ③ the nanosize effect of TOCNF and CNC is beneficial for filling the surface pores of the filter cake formed by the drilling fluid, to generate a more compact filter cake, which will then reduce the amount of the drilling fluid filtered; ④ cellulose nanofibers are composed of environmentally friendly, renewable, and easily degradable cellulose raw materials, and they can be added to the formulation as a filter loss reducing agent without causing pollution to the formation environment, thus having the advantage of environmental protection. In view of this, researchers have used cellulose nanofiber materials in drilling fluids, and have discussed the related properties of drilling fluids.

Hoyos et al. have shown that the addition of microcrystalline cellulose to cement-based materials can increase the content of hydration products, and increasing the hydration products is beneficial for filling the porous structure of cement, and thus improving the impermeability of cement. Further, Hoyos et al. studied the effect of CNFs on the rheological properties of a cement slurry from 25°C to 200°C by dynamic mechanical analysis. The results revealed that when the temperature is lower than 100°C, the storage modulus of the modified cement slurry is the same with that of the unmodified cement slurry, while at 200°C, the
storage modulus of the modified cement slurry is only 10% lower than that of the unmodified cement slurry. Scanning electron microscopy (SEM) analysis indicated that when 0.4% of CNF was added to the cement slurry, the surface porosity of the filter cake formed by the modified drilling fluid was the smallest.

Li et al. [35] demonstrated that microfibrillated cellulose (MFC) and CNC can effectively improve the rheological and filtration performance of a bentonite-water-based drilling fluid. Compared with MFC, CNC has a smaller size, higher negative surface charge, and higher stability in aqueous solutions. In addition, the water-based drilling fluid with CNC has better rheological properties, higher temperature stability, and less fluid filtration volume than that of the water-based drilling fluid with MFC.

Liu et al. [36] prepared CNF hydrogels by a Fe$^{3+}$ cross-linking method and studied the filtration reduction properties of the prepared hydrogels in a drilling fluid. First, poly-AMPS-DMA (PAD) was synthesized by the radical polymerization of AMPS and DMA, and then FeCl$_3$ and CNF were added to the PAD (as shown in Fig.5). The hydrogels with salt tolerance ability and thermal stability were synthesized by cross-linking Fe$^{3+}$ and the carboxyl group on the CNF surface and the sulfonic group on PAD surface. The salt tolerance and thermal stability of the obtained hydrogels were studied by rheometry. The results showed that the salt tolerance, high-temperature tolerance, and shear resistance of the cross-linked composite hydrogels with CNF were improved significantly compared with that of the non-crosslinked hydrogels. Because the composite hydrogels adsorbed on the surface of the filter cake with a positive charge, an adsorption layer was formed on the surface of the filter cake so as to reduce the filtration loss of the liquid. In addition, owing to the steric hindrance effect provided by the composite hydrogels, the stability of drilling fluid particles was maintained and particle aggregation was prevented, which led to reduced fluid filtration and formation of a denser filter cake (as shown in Fig.6). The filtration properties of the PAD-Fe$^{3+}$ (where the CNF dosage is 10% of the PAD) hydrogels are shown in Fig.6.

### 3.4 Cellulose nanofiber-based foam stabilizers

Foam flooding is a commonly used oil displacement...
The stability of the foam is a key factor determining the oil recovery rate during foam flooding. Therefore, in recent years, researchers have used nanoparticles to stabilize the foam, and nanoparticles play the role of skeletal support to improve the stability of the foam, and thus aid in the achievement of improved oil recovery. For example, Hu et al.\(^\text{[37]}\) have shown that adding CNCs to a foam solution containing methyl cellulose can significantly reduce the volume of bubbles, the initial density of the foam, and the drainage rate of the foam. Thus the stability of the foam was greatly improved. Cervin et al.\(^\text{[38]}\) explored the stabilization mechanism of CNFs in cellulose foam. The results showed that CNF formed intertwined networks and microgels in the solution. As a result, the complex viscoelastic modulus of the foam solution increased; a high complex viscous modulus was one of the important factors for maintaining the stability of foam. Thus, CNF can increase the stability of foam. In addition, increasing the negative charge density of CNF is also beneficial for increasing the complex viscoelastic modulus of the vapor-water interface of the foam solution.

Wei et al.\(^\text{[39]}\) used CNF hydrogel modified with AMPS and added a hydrophobic group to the foaming agent as a stabilizing agent. The results showed (as shown in Fig.7) that the addition of modified CNF hydrogels could make the foam smaller (as shown in Fig.7 and Fig.8), increase its stability, and then improve the oil recovery rate during foam flooding compared with that observed with only surfactant-added foam.

### 4 Conclusions

The trend in the development of the future oil recovery industry is to replace the traditional oil production chemicals that are harmful to the environment by environmental-friendly and green oilfield chemicals. This can not only improve the oil recovery efficiency but also reduce the environmental pollution. Improving the salt tolerance and thermal stability of cellulose-based materials is the most difficult issue hindering the expansion of their application in deep oil wells. For this, modification of cellulose materials to render them salt-resistant and heat-resistant is still being explored. At present, the most commonly used method is to graft...
functional groups onto the surface of cellulose-based materials by means of free-radical copolymerization, so as to improve their salt tolerance and thermal stability. In order to reduce the production cost, UV polymerization and metal ion crosslinking are applied to achieve this. In brief, the use of cellulose-based materials derived from environmental-friendly, non-toxic, renewable, easy-to-obtain raw materials with high reactivity as oilfield chemicals has very important economic and environmental benefits for the oil exploitation industry.

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