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Filter Loss Reducing Agent Polyanionic Cellulose

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Abstract
Poly anionic cellulose, as an upgraded product of sodium carboxymethyl cellulose, emerged in response to the market's demand for higher application performance of carboxymethyl cellulose. It has extensive applications in the field of oil drilling, and its key technical indicators include degree of substitution, viscosity and fluid loss, etc. At present, the production processes of polyanionic cellulose are divided into multiphase method and homogeneous method, and the multiphase method is generally adopted in industrial production. With the development of oil exploration and the increasing attention people pay to environmental pollution problems, the demand for PAC in the oil drilling industry is growing larger and larger. Therefore, the research on PAC is of great significance.

Key words: polyanionic cellulose；production process；synthesis principle

1 Introduction to PAC

Poly anionic cellulose (PAC for short) is essentially carboxymethyl cellulose (CMC), which is obtained as anionic cellulose ether with superior performance through solvent, formula and process adjustment and improvement of natural cellulose[1]. It is usually applied in its sodium salt form and plays an important role in many fields. The salient features in terms of physical properties, PAC include white or yellowish powder appearance, the appearance characteristics that PAC is easy to identify in the process of storage and transportation and operation. Its non-toxic and odorless properties ensure safety during use and also expand the application boundaries of PAC in fields with extremely high safety requirements such as food and medicine. The extremely strong hygroscopicity of PAC helps it rapidly swell and form a uniform solution when in contact with water. It can quickly dissolve in both cold and hot water and reach a certain viscosity. This characteristic provides convenience for the application of PAC in fields such as drilling mud and coating thickening.

From the perspective of chemical properties, the high degree of substitution of PAC is the cornerstone of its performance, with a substitution value ranging from 0.85 to 1.4. This means that more anionic groups are introduced into the cellulose molecular chain, enhancing its hydrophilicity and ion exchange capacity. This characteristic not only enhances the thermal stability of PAC, enabling it to maintain a stable structure and performance under high-temperature conditions, but also endows PAC with the ability to resist acids, alkalis and salts, allowing it to function in complex medium environments. PAC can remain stable within a wide pH range of 3 to 11, a characteristic that is particularly important for industrial applications that need to cope with variable environmental conditions[3]. PAC also demonstrates excellent compatibility and light stability, being able to coexist with a variety of substances. Meanwhile, it is not prone to degradation under light exposure, thus extending the product's service life.

2.3 Research Progress

In the increasingly developing field of materials science nowadays, polyanionic cellulose (PAC), as an important functional material, the innovation of its production process and the optimization of its performance have become the focus of industry attention. The following will provide a detailed analysis of the latest progress of PAC in production processes, environmental performance and the research and development of functional materials.

(1) production process optimization

In recent years, the production technology of PAC has experienced significant optimization process. With the introduction of advanced production equipment and the improvement of process control measures, the production efficiency of PAC has been greatly enhanced. These advanced devices possess a high level of automation and intelligence, capable of precisely controlling various parameters in the production process to ensure the stability and consistency of product quality. Meanwhile, the new production process reduces the waste of raw materials, lowers production costs and enhances the competitiveness of enterprises.

(2) environmental performance improvement:

With the increasing of global environmental protection consciousness, the environmental performance in the process of producing PAC also received widespread attention. At present, the production process of PAC has achieved significant environmental optimization. By improving the production process, reducing the discharge of pollutants such as wastewater and waste gas, and enhancing the utilization rate of raw materials [4], the production of PAC is more in line with the requirements of sustainable development. These environmental protection measures not only reduce environmental pollution during the production process, but also establish a good social image for the enterprise.

(3) functional materials research and development:

As a kind of functional material, PAC application fields are expanding. To meet the demands of different industries, the functional research and development of PAC has become an important direction for the development of the industry. At present, PAC products with special functions such as high temperature resistance, acid and alkali resistance, and high viscosity have been successfully developed. These products can meet the special demands of different industries for PAC, broadening the application scope of PAC. Meanwhile, the research and development of functional materials has also promoted the continuous progress and innovation of PAC production technology.

3The Application of PAC in Drilling Fluid

In the well excavation and drilling projects of oil and natural gas, the wellbore of deep Wells is prone to water loss, causing phenomena such as collapse and diameter reduction, which hinders the drilling machine and affects the smooth progress of the project. Therefore, it is necessary to prepare mud with appropriate values such as viscosity, water loss, acid resistance, salt resistance and thixotropy to ensure the normal operation of the drilling rig. However, the above-mentioned parameters of drilling mud vary with changes in conditions such as mud type, well depth and region. The use of PAC in the slurry can adjust these physical parameters to make it more suitable for the needs of various projects[5].

The PAC to join the mud, can make the wall form thin and firm, low permeability of filter cake, improve the coalescence stability of the system, reduce water loss; It can make the shearing force obtained by the drilling machine lower, facilitate the release of the gas embedded in the mud, and quickly discard the debris into the mud pit. It can make the drilling mud more stable and prolong its existence period. Mud containing PAC has good stability and can still reduce water loss at higher temperatures[6]. Using PAC as a treatment agent for drilling mud and well flushing fluid can resist the pollution of various soluble salts. With the development of petroleum exploration and the increasing attention paid by people to environmental pollution issues, the quality requirements for PAC have gradually increased, demanding that PAC have better resistance to calcium, temperature, salt and acid.

3.1The Application of PAC Viscosity in Drilling Fluid

The viscosity of PAC is the characteristic exhibited by the colloid solution formed after dissolving in water. The rheological behavior of PAC solution has an important influence on its application. The viscosity of PAC is related to the degree of polymerization, solution concentration and temperature to a certain extent. Generally speaking, the higher the degree of polymerization, the higher the viscosity. The viscosity increases with the increase of PAC concentration. The viscosity of the solution decreases with the increase of temperature[7]. The test of viscosity in the physical and chemical indicators of PAC products is usually conducted using the NDJ-79 or Brookfield viscometer[8]. The control of the viscosity of PAC products is determined based on application requirements. When PAC is used as a viscosity enhancer or rheological modifier, high-viscosity PAC is usually required (the product models are typically PAC-HV, PAC-R, etc.). When PAC is mainly used as a fluid loss reducer and does not increase the viscosity of the drilling fluid or change its rheological properties during use, Then low-viscosity PAC products are required (the product models are usually PAC-LV and PAC-L).

3.2The Application of PAC Substitution Degree in Drilling Fluid

When PAC is used as a fluid loss reducer, PAC can ionize to generate long-chain multivalent anions in drilling fluid. The hydroxyl and ethoxy groups on its molecular chain enable PAC to be adsorbed on clay by forming hydrogen bonds with oxygen on the surface of viscous particles or coordination bonds with Al^{3+} on the edge of broken bonds of clay particles. Multiple sodium carboxylate groups thicken the hydration film on the surface of the clay particles through hydration, preventing the clay particles from aggregating into large particles due to collision (protective effect). Moreover, multiple fine clay particles simultaneously adsorb onto one molecular chain of PAC, forming a mixed network structure covering the entire system, thereby enhancing the coalescation stability of the viscous particles. It is beneficial to protect the content of particles in the drilling fluid, form a dense mud cake and reduce the filtration loss [9]. The higher the degree of substitution of PAC products is, the higher the content of sodium carboxylate will be. The better the uniformity of substitution is, the more uniform the hydration film will be. This makes the protective effect of PAC in drilling fluid stronger, so the loss reduction effect is more obvious.

3.3 Application of PAC Purity in Drilling Fluid

Different drilling fluid systems require different amounts of drilling fluid treatment agents and treatment agents. Therefore, the dosage of PAC may vary in different drilling fluid systems. If the dosage of PAC in the drilling fluid is specified and it is ensured that the drilling fluid has good rheological properties and fluid loss reduction performance, it can be achieved by adjusting the purity.

The same conditions, if the PAC purity is high, the better the performance of the product. However, PAC with good product performance does not necessarily have high product purity. The balance between product performance and purity needs to be determined based on the actual situation.

4 Synthesis of PAC

4.1 The preparation principle of PAC

In the preparation of PAC, cellulose reacts with alkali to form alkali cellulose. Cellulose can react with NaOH solutions of different mass fractions to form alkaline cellulose. The composition of alkali cellulose is determined by the ratio of the binding reaction rate of alkali on cellulose to the hydrolysis reaction rate of alkali cellulose. With the differences in the mass fraction of the alkaline solution and the treatment temperature, alkaline cellulose has different NaOH and water contents, and generates different crystalline variants of alkaline cellulose [10]. Meanwhile, cellulose will dissolve to a certain extent in the alkaline solution. Alkaline solutions can dissolve cellulose with a relatively low degree of polymerization.

With the increase of the mass fraction of the alkali solution, the dissolution amount of cellulose first increases and then decreases, and the degree of polymerization (DP) of the dissolved cellulose is also different. Generally, when the temperature is relatively low, the degree of polymerization of dissolved cellulose is higher at the same mass fraction. Reacts with the chloroacetic acid, alkali cellulose get PAC products. During the etherification stage, if the content of dichloroacetic acid in chloroacetic acid is too high, it will cause gelation side reactions of the product[11]. The differences in the composition and structure of alkali cellulose will affect various subsequent chemical reactions. Therefore, increasing the content of chloroacetic acid in chloroacetic acid and reducing the content of dichloroacetic acid can improve the uniformity of etherifying agent substitution in PAC products.

In the process of the preparation, alkalization and etherification reaction must be fully, to restrain the adverse event, the utilization ratio of chloroacetic acid was improved.

4.2 Multiphase method

The multiphase method where water is commonly used as the medium is also called the water-medium method, and the method where the medium contains organic solvents is called the solvent-medium method.

Water medium method with water as medium. Due to the intense side reactions, the total etherification rate of the reaction was only 45% - 55%. Meanwhile, the product contained sodium hydroxyacetate glycolic acid and more salt impurities, which affected the purity and made the purification of the product difficult [12].

Solvent is often in the media system could be water - organic solvent mixture system. Practical research has found that in the preparation of polyanionic cellulose, the products obtained by using the water-organic solvent mixed system have better uniformity and purity than those obtained by using water alone and organic solvents alone. However, the ratio of water to organic solvents needs to be well controlled. The solvent method uses ethanol, isopropanol, butanol, etc. as the reaction medium[13]. During the reaction process, heat and mass transfer are rapid and uniform, the main reaction is accelerated, and the etherification rate can reach 60% to 80%. The reaction stability and uniformity are high, which greatly improves the substitution degree, substitution uniformity and application performance of the product. If the proportion of organic solvents is too large, it may lead to a relatively low degree of substitution in the final product.

Polyphase method depending on the amount of reaction in the process of using organic solvent, is divided into method and slurry method.

Pinched method is to use kneading reactor stirring blades to powerful shear at the same time, the reaction mass and to mixing of materials, so that the reaction reagent with good contact with cellulose, make the reaction of a kind of technological process. The advantage of this technological process lies in that the amount of organic solvent used in the reaction system is relatively small, and the mass ratio with cellulose raw materials is 1.1 to 2.5:1[14]. The mass and heat transfer in the reaction are relatively uniform. The solvent recovery in the process is simple. Under the condition of meeting the common requirements for materials, the material and energy consumption are relatively small.

Slurry method is to point to in the process of reaction, the use of organic dielectric quality for cellulose raw material 9 ~ 30 times, reaction system is porridge or state of suspension, cellulose raw materials with the aid of agitator under the condition of high bath ratio and reaction reagent

4.3 Homogeneous method

An important development direction of carboxymethylation of cellulose is to explore a solvent that can dissolve cellulose into a uniform and stable solution, so that the alkalization and etherification reactions of cellulose can be carried out in a homogeneous state to prepare CMC with an extremely high degree of substitution. This method is called the "solution method", that is, the homogeneous method[15].

In recent years, with ionic liquids to speed up the development process, especially the emergence of ionic liquid, can dissolve cellulose materials make cellulose ether derivative reaction in the homogeneous reaction in the solvent system possible. Homogeneous etherification provides the uniformity of the reaction and produces more uniformly distributed products than heterogeneous reactions. Meanwhile, it also provides a more sufficient basis for the equal-molar ratio of cellulose etherification reactions. However, during this process, due to the limited solubility of cellulose in the solvent system, the reaction takes place in a cellulose solution of a relatively low concentration, resulting in very unsatisfactory economic benefits. Moreover, in this process, the separation and purification of the product are rather difficult, and the cost of solvent recovery is too high. Currently, this method is still in the laboratory research stage. Therefore, it will be difficult to form an industrial scale for a considerable period of time.

7 Prospects

Polyanionic cellulose, as a fluid loss reduction agent, holds an important position in drilling engineering. Although there are some problems at present, with the continuous progress and innovation of technology, its future development potential is huge.

From the point of technology innovation, as the in-depth study of polyanionic cellulose structure and performance, the new preparation method will be constantly emerging. The raw material for preparing PAC is mainly refined cotton made from cotton linters, and the production cost is relatively high. In recent years, researchers have attempted to use various cellulose-rich biomass as alternatives to cotton linters, such as Zizania aquatica, bagasse, straw, bamboo, potato [16]. In addition, the modification research of PAC is also an important research direction. For example, cellulose is directionally modified by using genetic engineering technology to endow it with better filtration loss reduction performance and temperature resistance. Meanwhile, by integrating nanotechnology and intelligent materials technology, a polyanionic cellulose fluid loss reduction agent with self-adaptability and intelligent responsiveness has been developed. It can automatically adjust its performance according to changes in the drilling environment, improving drilling efficiency and safety.

In terms of market demand, with the growing global demand for energy, oil and gas exploration and development activities will continue to rise, the demand for high performance fluid loss agent also will continue to expand. Polyanionic cellulose is expected to occupy a larger share in the future market due to its excellent performance and environmental protection characteristics.

In addition, with the continuous improvement of environmental awareness, green environmental protection fluid loss agent will become the future development trend. Poly anionic cellulose, as a natural cellulose derivative, is biodegradable and environmentally friendly, meeting the requirements of green environmental protection. In the future, by further optimizing the preparation process, reducing the impact on the environment and enhancing the green and environmentally friendly performance of the product, it will contribute to the sustainable development of polyanionic cellulose in the field of filter loss reduction agents.

In conclusion, although polyanionic cellulose faces some problems in the field of filter loss reduction agents, with the further optimization of the production process of polyanionic cellulose and the expansion of its application performance, as well as the continuous promotion of its industrial production, polyanionic cellulose will have considerable market potential and development background. The future development prospects of polyanionic cellulose are worth looking forward to.

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