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Effects of chitosan treatment on strength and thickening properties of oil well cement

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HIGHLIGHTS

- We study the influence of chitosan on cement under downhole temperature condition.
- Chitosan has negative effects on oil well cement due to active group.
- Chelating pretreatment will weaken the retarding effect of chitosan.
- Effects of LMW chitosan on cement are more acute than that of HMW chitosan.
- HMW chitosan is fit for using as coating material in oil well cement.

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ABSTRACT

The research objectives were to investigate the influence of chitosan on strength and thickening properties of oil well cement under the downhole temperature condition. The results showed that the chitosan has the ability to increase the thickening time, but due to chelating Ca^{2+} ion, it may cause consistency wave at initial stage, and shorten thickening time at higher dosage and higher temperature. Chelating pretreatment will weaken the retarding effect of chitosan. Effects of LMW chitosan on strength and thickening properties are more acute than that of HMW chitosan. Because of increasing induction period, the pre-chelating LMW chitosan extends thickening time.

1. Introduction

Self-healing cement-based materials have received much attention in recent years [1–6]. Due to the special downhole conditions, many self-healing methods in construction industry are not suitable for oil well cement slurry system [7–9]. A self-healing oil well cement system including cement, water and super-adsorbent polymers (SAP) that swells in contact with water from reservoir or from formation was proposed [10]. This cement slurry can prevent formation fluids from entering the water table and polluting drinking water, or prevent water from passing into the well instead of oil or gas. Since it is highly reactive with water, if the concentration of superabsorbent added to the blend is too much, the slurry may typically have a too high viscosity for pumping in favorable conditions; but if the dosage is too small, the self healing may not be effective. Therefore, avoiding the above mentioned two issues is a key problem.

Encapsulation has numerous applications to immobilize, isolate, protect and control the rate of transfer of many substances like acids, drugs, nutrients, perfumes [11]. So it can control the initial water absorption rate of superabsorbent. The control effect mainly depends on the coating material. Chitosan produced by the deacetylation of chitin is a nontoxic biopolymer with the ability to form films [12–14], and it is insoluble in cement slurry whose pH is 12–13 [15]. So chitosan has the potential to wrap superabsorbent which will be used in cement slurry. Further, because of the hydrophilicity of hydroxyl group which exists in the molecular chain of chitosan, the coated superabsorbent will be well dispersed in slurry.

Before the coated superabsorbent being used, the effects of chitosan on properties of oil well cement should be definite. In construction industry, chitosan was proved to act as a thickener

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in cement mixtures, and have a set-retarding role due to the consequence of an interaction of the molecule chains with the cement particles [16,17]. However, the effects of chitosan on properties of oil well cement need further research because of high temperatures in the underground.

Thickener affects thickening performance, thereby affecting pumping performance of oil well cement slurry. Retarder affects the compressive strength, thereby affecting the ability of set cement to provide zonal isolation, and to protect and support the pipe [18]. Therefore, in this paper, the effects of different molecular weights chitosans on strength and thickening properties of oil well cement are experimentally investigated.

2. Experimental

2.1. Materials

Glacial acetic acid (Analytical Reagent), glutaraldehyde (Analytical Reagent, 25%) and $CaCO_3$ (Analytical Reagent) were provided by Sinopharm Chemical Reagent Co., Ltd.; polyacrylamide microspheres were prepared by inverse suspension polymerization.

Class G oil well cement was used in our experiments. The typical mineral composition and physical properties of class G oil well cement are given in Table 1. The typical chemical composition is given in Table 2. Chitosans with different molecular weights (low molecular weight (LMW), 8–15 kDa; and high molecular weight (HMW), 150–200 kDa) and 90–92% deacetylation degree used in this study are commercial products from Naijin industry (Shanghai, China). The MW and deacetylation degree were supplied by the manufacturer. Chitosans were added in three different dosages (0.25%, 0.50%, and 1.00% of the cement weight) with the purpose of evaluating the influence of dosage on the properties of slurries. Seven pastes were prepared as shown in Table 3. The first paste was prepared to provide the standard values of thickening time of cement sample without chitosan.

In addition, chitosan can chelate Ca^{2+} ions [16], which may influence the properties of cement. In order to analyze the effects on cement slurry properties, chitosans were added into the $Ca(OH)_2$ suspension to chelate the Ca^{2+} ion for 3 h at the same temperature with the compressive strength or thickening time experiment in advance. Six another pastes were prepared as shown in Table 4.

2.2. Method

2.2.1. The coated superabsorbent

The chitosan was dissolved in the acetic acid solution of which the concentration was 3%, and then polyacrylamide microspheres were added into the solution. After microspheres being mixed uniformly, the $CaCO_3$ was used to make the chitosan separate out. The chitosan was immobilized on microsphere's surface with glutaraldehyde as crosslinking agent.

2.2.2. Water absorption testing

Due to cement slurry system is alkaline (pH = 12–13) with a certain temperature surroundings in downhole, the water absorption was tested under the condition of 75 °C and pH = 13. The testing procedure was as follows: microspheres(1 g) was placed into a nylon bag; the total quantity of microspheres and nylon bag was weighed which was denoted as *M*1; the nylon bag was then placed in the sodium hydroxide solution (pH = 13) under the condition of 75 °C; the nylon bag was taken out after a certain time which as follows: 5 min, 10 min, 15 min, 20 min, 30 min, 40 min, 50 min, 120 min, 200 min; after the bag being hanged to no liquid drop, the total quantity was tested again which was denoted as *M*2. The water absorption of microspheres at different time is given by:

$$\eta = M2 - M1 \tag{1}$$

where η is the water absorption of microspheres, g/g.

2.2.3. Chitosan chelation amount of Ca^{2+}

EDTA titration is used to measure the amount of residual Ca^{2+}, which can prove the chelation of Ca^{2+}. Due to the pore solution of cement slurry consists of many other ions which may influence the titration result, the $CaCl_2$ solution was prepared. The testing method was given as follows. The tests were performed at room temperature (20 ± 2 °C). EDTA·2Na (4.65 g) was dissolved in 500 ml distilled water to prepare the standard solution (0.0250 mol/L). $CaCl_2$ (0.694 g) was dissolved in 250 ml distilled water. And the $CaCl_2$ solution was then poured in a 500 ml beaker. Chitosan (0.5 g) was dropped into the beaker with stirring. After stirring for two hours, centrifugal separation was carried out. 10 ml supernatant was removed to a 250 ml conical flask, and then was diluted with distilled water to 50 ml. 4 ml NaOH solution whose concentration is 2 mol/L was dropped into the conical flask, and then the calcium indicator was added to the solution. Shake up the solution, and then the EDTA·2Na standard solution was used to titration. When the color of the solution change from red wine to pure blue, record the consumption volume of the EDTA·2Na standard solution. The chelating capacity of Ca^{2+} is given by:

$$q = 12.5 - 1.25V_{EDTA} \tag{2}$$

where q is the chelating capacity of Ca^{2+}, mmol/g; V_{EDTA} is the consumption volume of the EDTA·2Na standard solution, ml.

2.2.4. Preparation of pre-chelating chitosan

The $Ca(OH)_2$ whose weight was 0.3% of cement was added into water whose weight was identified according to the pastes in Table 3 to prepare $Ca(OH)_2$ suspension. Then added chitosan, and stirred the suspension at the speed of 150 r/min for 3 h at the same temperature with the compressive strength or thickening time experiment to form a mixed system. This system was directly blended with cement and other addictives for preparing cement slurry.

2.2.5. Manufacturing process

Cement slurry was mixed according to API Spec. 10B-3-2004. After being prepared, cement slurry was placed into compressive-strength molds (5 cm × 5 cm × 5 cm) and consistometer which measures the consistency of the test slurry contained in a rotating cup.

2.2.6. Thickening time

Thickening time tests are designed to determine the length of time which slurry remains in a pumpable fluid state. The pumpability or consistency of the slurry is measured in Bearden units (Bc), a dimensionless quantity with no direct conversion factor to more common units of viscosity such as the poise. The end of a thickening time test is defined when the cement slurry reaches a consistency of 100 Bc; however, 70 Bc is generally considered to be the maximum pumpable consistency.

There is a rotating cup with a fixed blade in consistometer. The cup which driven by the motor is counter clockwise rotation at the speed of 150 r/min. The cement slurry in cup gives the blade a certain resistance which is proportional to the consistency of cement slurry. This resistance torque and potentiometer spring torque are in balance. Therefore, the consistency signal can be imported to the recorder through the potentiometer. Considering the temperature conditions in downhole, in our research, the consistency was tested at 75 °C or 98 °C and 0.1 MPa.

2.2.7. Compressive strength

Considering the temperature circumstance in downhole, the device and molds were put into high temperature curing chamber, and cement slurries were cured for different time periods at 75 °C or 98 °C which was choice to simulate the downhole temperature. After being cured, the set cement cubes were removed from the molds, and placed in hydraulic compression test equipment and loaded to failure. The compressive strength is recorded as the maximum compressive stress.

2.2.8. X-ray diffraction

XRD analyses were conducted in the State Key Laboratory of Heavy Oil Research using a PANalytical X'Pert MPD X-ray diffractometer. The data acquisition was carried out within the range of well-known cement minerals 2–70° at a grade of 0.02° increments with Cu Kα radiation.

2.2.9. Adsorption of chitosan on cement particle surface

Prepare the cement slurry which consists of water, cement and chitosan (0.50% of the cement weight). In order to observe clearly, the W/C is 6.0. Optical microscopy was used to describe for cement particle distribution. For comparison, the slurry which consists of water and cement was also prepared.

2.2.10. Hydration of chitosan

Chitosan is insolubility in cement slurry alkaline environment. Hydration can make the molecular chain of chitosan extend. The hydration degree of chitosan was characterized by the water retention ability. The same quantity which was recorded as *M* of different molecular weight chitosans (100–200 mesh) were separately placed into different nylon bags. The quantity of nylon bag with chitosan was

Table 1
Phase composition and physical properties of class G oil well cement.

C_3S (wt%)	C_2S (wt%)	C_3AC (wt%)	C_3AF (wt%)	Specific density (kg/L)	Specific surface area (m^2/kg)
53.7	30.46	2.8	8.0	3.17	332