Journal of Natural Gas Science and Engineering 38 (2017) 582–589

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

Synthesis and performance evaluation of a novel biodegradable dispersant for offshore cementing

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A R T I C L E I N F O

Article history:
Received 14 June 2016
Received in revised form
7 January 2017
Accepted 10 January 2017
Available online 11 January 2017

Keywords:
Dispersant
Biodegradation
Offshore cementing
Gelatin grafted polymer

A B S T R A C T

We developed a novel biodegradable oil-well dispersant, gelatin grafted acetone formaldehyde sulphonates (GAFS). This dispersant was prepared based on the chemical modification of naturally biodegradable products: gelatin. GAFS was synthesized through aldehyde ketone addition, hydroxyl condensation and Mannich amine methylation reaction. Functional groups and molecular structure of GAFS were characterized by *FTIR* (Fourier Transform Infrared Spectroscopy) and *NMR* (Nuclear Magnetic Resonance). Lab tests were conducted to determine the biodegradation rate, rheological properties, thickening time, compressive strength and dispersing property of GAFS in Class-G cement slurry. It is found that GAFS exhibits no retarding by-effect on oil well cement and can be considered biodegradable based on the biodegradation test results. The measured adsorption capacity and zeta potential of GAFS in Class-G well cement slurry show that: GAFS can be adsorbed greatly onto the surface of cement particles, resulting in strong electrostatic repulsion between cement particles and consequently generating an excellent dispersion performance.

1. Introduction

Oil or gas well cementing is routinely utilized to build a stable and safe wellbore as well as achieve zonal isolation. Normally, various chemical admixtures need to be added into the cement slurry for fine-tuning or optimizing cement-slurry properties. For example, when the cement powder and water are mixed, patches with positive or negative charges appear on the cement grain surfaces, which interact with each other to create a continuous structural network. This network must be broken to make the cement slurry pumpable. Cement dispersants, also known as "superplasticizers" in the construction industry, help to adjust the particle surface charges to obtain desirable rheological properties of the cement slurry. Dispersants are commonly added to the cement slurry to ensure its pumpability over several kilometers. An adequate rheological characterization of cement slurry is critical for designing and executing a successful primary cementing job (Nelson and Guillot, 2006; Velayati et al., 2015).

Dispersants reduce the apparent viscosity of cement slurry so that the cement slurry can be pumped with less friction pressure and fewer pump horse powers. In addition, the lower viscosity can more easily induce a turbulent flow during the pumping of cement slurry. Turbulent flows are more desirable when pumping cement slurry downhole because drilling fluid can be more efficiently replaced from the wellbore surfaces by a turbulent displacement.

A number of dispersants have been utilized previously to prepare oil-well cement slurry, for example, polynapthylene sulfonate, poly-B-naphthol sulfonate, polymelamine sulfonate, the condensation product of formaldehyde, acetone and an alkali metal sulfite (Lou et al., 2012; Sebök et al., 2001). Although these dispersants function very well in most cases, they are often environmentally unacceptable in offshore well-drilling operations in that they cannot undergo complete biodegradation in the offshore environment and pose potential hazards to various ocean lives. Certain organic acids such as citric acid and gluconic acid are also often recognized as versatile well-cement dispersants. However, the use of these organic acids also brings about some undesirable side effects, such as retarding the setting of cement slurry (Burgos-Montes et al., 2012; Hou et al., 2010; Zhang et al., 2015; Zingg et al., 2009).

With the petroleum industry paying more attention to offshore petroleum development, the use of these difficult-to-degrade substances fails to meet the increasingly stringent environmental

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http://dx.doi.org/10.1016/j.jngse.2017.01.016
1875-5100/

protection in offshore oil exploration and development (Haheim et al., 2007; Rae et al., 2001; Wang et al., 2011). This is because they are poisonous to the marine animals, plants and other life. In 2007, several environmental incidents related to offshore oil and gas development occurred, including some incidents happening during the exploitation of oil resources in the Arctic region (Reddy and Eoff, 2007; Vieira et al., 2005). Consequently, the development of new oil-well cement dispersant, which has excellent dispersing property and biodegradable characteristics, has become one of the industry's priorities, but meanwhile a very challenging task.

The biodegradability of material is closely related to its molecular structure. The material can be easily biodegraded if it contains hydrolysable groups, such as hydroxyl (-OH), carboxyl (-COOH), carboxylic acid ester [C (O) OR], amide [C (O) NR_2], aldehyde (-CHO), anhydride or organic phosphate (Qiu et al., 2015; Sadeghi and Moradi, 2012; Swift and Baciu, 2006), etc. Gelatin is a kind of natural protein substance with a polypeptide chains formed by various amino acids. These various amino acids are mutually connected by carboxyl group and amino group. It is rich in 18 kinds of amino acids and its molecular chain contains many free functional groups such as hydroxyl, carboxyl and amino groups. Overall, gelatin is demonstrated in previous studies to own an excellent biodegradability.

The aim of this research is to develop one biodegradable oil-well cement dispersant and subsequently perform a thorough evaluation of its properties. The animal gelatin material with excellent biodegradation property was used as the raw material to synthesize this new dispersant. Through the Mannich amine methylation reaction, sulfo-acid basic groups could be introduced into the side chain of gelatin molecules (Mi, 2005). Eventually a new-type of oil well cement dispersant, gelatin grafted acetone formaldehyde sulfite (GAFS), were synthesized.

2. Experimental section

2.1. Materials

Gelatin is purchased from Huaxuan company (Xiamen, China) and used as received. Formaldehyde (37 wt% aqueous solution), sodium pyrosulfite (99.0% purity), acetone (99.0% purity), hydrochloric acid (36 wt% aqueous solution) and solid sodium hydroxide are all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further treatment. An API Class-G oil well cement (Jiahua Cement Company, Sichuan, China) corresponding to API Specification 10A is used. Its clinker composition is determined through powder XRD technique (see Table 1).

2.2. Synthesis of GAFS [gelatin grafted acetone formaldehyde sulfite]

200 mL distilled water, 59 mL formaldehyde, 45.6 g sodium metabisulfite and 120 g gelatin were added successively into a reaction flask equipped with a reflux cooling device, a mixer, a thermometer and a drop liquid funnel. The mixture was heated to 30 °C while being stirred. Then, 20% aqueous NaOH solution was gradually added into the mixture until the pH is adjusted to 14. 75 mL acetone was added with a suitable dropping speed to make the reaction fluid's temperature drop down to 40 °C. Subsequently, the reaction fluid was heated to 60 °C and maintained at such a temperature. The reaction fluid was refluxed for 1.5 h at 60 °C. Next, the pH of the reaction fluid was adjusted to 6.5 by subtly adding 10% aqueous HCl solution. 65 mL formaldehyde was again added into the mixture. The mixture was heated to 85 °C and the reaction fluid was refluxed for 3 h at 85 °C. Eventually, the resultant product is a kind of red brown viscous liquid. Impurities such as methanol were removed from the product by vacuum distillation, and the pH of the remaining product was adjusted to 7 by adding 20% aqueous NaOH solution. Afterwards, the final product-gelatin grafted acetone formaldehyde sulfite (GAFS) - was synthesized. Fig. 1 shows the synthesis routes of GAFS as well as its molecular structure. The molecular weight was measured by gel permeation chromatography (Waters Alliance 2695, USA). The molecular weight measurement employs ultrahydrogel liner columns; 0.10 mol/L of sodium chloride was used as a mobile phase with a flow rate of 0.50 mL/min, and polysaccharide was used as a standard fluid. The physical properties of the GAFS solution, such as pH, color, viscosity, solid content, molecular weight and polydispersity (ration between number-average molecular weight (*Mn*) and weight-average molecular weight (*Mw*)), are shown in Table 2.

Table 1
Chemical and mineral composition of Class-G well cement used in this study.

Chemical composition (wt%)						Mineralogical composition (wt%)			
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	C_3S	C_2S	C_4AF	C_3A
23.05	2.86	3.52	65.20	1.79	2.12	59.89	16.75	10.70	1.63

2.3. Biodegradability assessment of GAFS

According to the standard "*Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium*" (GB/T 22047-2008), the percentage of the biological decomposition of the GAFS samples could be calculated by the amount of the released CO_2. The ingredients of the test medium are shown in Table 3, while the test devices used are shown in Fig. 2. Besides, the concentration of KOH solution used was 10 mol/L and the concentration of $Ba(OH)_2$ solution was 0.0125 mol/L. The initial concentration of GAFS dispersant was calculated to be 100 mg/L with the dissolved organic carbon (DOC). The inoculated sludge was the activated sludge from a sewage treatment plant, and the inoculation concentration of the sludge was 500 mg/L. The total reaction fluid volume in the reaction bottle was 2000 mL. The air flow rate was held constant at 80 mL/min and monitored by a flow meter. The reaction times were selected to be 3 d, 7 d, 10 d, 14 d, and 28 d.

Using phenolphthalein as an indicator, the residual $Ba(OH)_2$ was gradually titrated by 0.05 mol/L^{-1} HCl standard solution to determine the released amount of CO_2, and the biodegradation degree D_T (%) can be calculated by the following equation:

$$D_T = \frac{\sum (co_2)_T - \sum (co_2)_B}{ThCO_2} \times 100 \quad (1)$$

where $\sum (CO_2)_T$ represents the amount of CO_2 (mg) released from the reaction bottle from start to time *t*, $\sum (CO_2)_B$ represents the amount of CO_2 (mg) released from an empty reaction bottle from start to time *t*, $ThCO_2$ represents the released amount of CO_2 (mg) from the sample, which is theoretically calculated from the

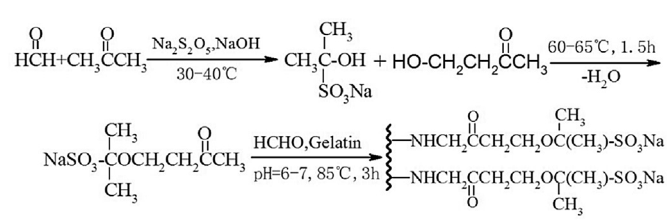

Fig. 1. Synthetic routes and molecular structure of GAFS dispersant.