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Suitability of polyacrylamide superabsorbent polymers as the internal curing agent of well cement

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HIGHLIGHTS

- We research the internal curing agent of well cement at some certain temperature.
- Poly acrylamide is unstable in alkaline circumstance of well cement.
- Modified polyacrylamide mitigates autogenous shrinkage of well cement significantly.

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ABSTRACT

The research objectives were designed to investigate polyacrylamide superabsorbent polymers as internal curing agent to mitigate autogenous shrinkage of well cement. Results show that poly acrylamide superabsorbent polymer hydrolyzes in alkaline circumstance of cement slurry at high temperature, which causes water absorption increase and then has negative effects on thickening and compressive strength. Due to steric hindrance effect and carrying negative charge, poly acrylamide/bentonite/N,N-dimethyl acrylamide superabsorbent polymer has ability to prevent the addition reaction between hydroxyl ion and acylamino to stably exist in well cement and reduce autogenous shrinkage significantly when the dosage is 0.3 wt%.

1. Introduction

Cement has been used in underground for sealing oil and gas well for many years [1,2]. One of the major requirements for well cement is to create a very low permeability barrier for fluids [3], especially in the natural gas well [4], underground gas storage well [5,6] and CO_2 sequestration and storage well [7]. However, autogenous shrinkage increases the risk of cracking the hardened cement [8] and debonding the interface between cement and formation to induce well sealing failure. Autogenous shrinkage is caused by self-desiccation of cementitious materials with low water/cement (W/C) or low water/binder (W/B) ratios [9]. The conventional value of W/C of well cement slurry is 0.38–0.56, which has been set by API (American Petroleum Institute) Spec. 10B. In general, when the value is smaller than 0.4, the autogenous shrinkage begins to occur [10]. Furthermore, the cement slurries with corrosion resistant ability used in CO_2 (carbon dioxide) injection wells [11] and high density cement slurry used in high pressure well [12–14] have much lower W/C. Therefore, it is necessary to pay more attention to the autogenous shrinkage of well cement.

Superabsorbent polymers (SAP) have been used in cement for many functions [15–19]. One of the major actions is to mitigate autogenous shrinkage [20]. SAP with a high water storing capacity would supply water to the surrounding matrix as soon as self-desiccation begins to occur. Data obtained in previous studies [10] indicated that SAP with high density of anionic functional groups absorbed the cement pore solution quickly, but greatly released it subsequently due to the presence of Ca^{2+} ions in the alkaline solution; SAP with lower density of anionic groups could remain the mitigation of autogenous shrinkage even during the deceleration period and had no negative effects on the compressive strength of the hardened cement. Polyacrylamide superabsorbent polymer (A-SAP) of which the synthesis and modification technology are simple has no anionic functional groups. Therefore, it could be predicted that polyacrylamide superabsorbent polymers or modified polyacrylamide superabsorbent polymers are likely to be suitable for using as an internal curing agent of well cement.

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In cementing industry, it is well known that, the temperature of downhole can reach to a certain value (geothermal gradient general is about 3 °C/100 m), which is different from the construction industry. The temperature could influence the water absorption properties of SAP. Therefore, the effects of SAP on properties of well cement should be identified first. Due to the ability of absorbing water, SAP can affect thickening performance which affects pumping performance of well cement slurry and compressive strength which affects the ability of hardened cement to provide zonal isolation. Therefore, in this paper, the effects of polyacrylamide superabsorbent polymers and modified polyacrylamide superabsorbent polymers on strength and thickening properties of well cement are experimentally investigated, and then the mitigation of autogenous shrinkage is tested.

2. Experimental

2.1. Materials

Acrylamide (AM) and N,N-dimethyl acrylamide (NNDMA) which have no anionic groups were choice to synthetic SAP. AM, N,N-methylene bisacrylamide (MBA), sodium bisulfite ($NaHSO_3$), potassium peroxydisulfate ($K_2S_2O_8$), water paraffin, calcium chloride ($CaCl_2$), sodium hydrate (NaOH), ethylene diamine tetraacetic acid disodium (EDTA·2Na), calcium indicator (NN) and Span-80 were provided by Sinopharm Chemical Reagent Co., Ltd. NNDMA was obtained from RBL Chemicals (Beijing, China). Bentonite which is commercial product was provided by Bentonite Co., Ltd. Weifang SOAR (Shandong, China). 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. Nine cement samples in which P1 is the basic cement slurry were prepared as shown in Table 3. Because of water absorption of SAP, if there is no extra water, the cement slurry consistency will become significantly stiffer. Therefore, the cement samples of P4–P9 were modified by the addition of SAP and an extra amount of water. P2 and P3 were prepared to research the influence of extra amount of water on the properties of cement slurry.

2.2. Method

2.2.1. Polyacrylamide superabsorbent polymers

SAP was prepared by inverse suspension polymerization in the laboratory [21]. A procedure and selected experimental conditions were given as follows. Span-80 (0.5 g) was dissolved in 100 ml water paraffin at 50 °C for 30 min to prepare the continuous medium. And then the medium was carried out in a 250 ml three-necked flask equipped with a stirrer at the speed of 550 r/min. AM (10 g), MBA (0.02 g), $K_2S_2O_8$ (0.08 g) and $NaHSO_3$ (0.02 g) were mixed in 50 g distilled water at room temperature (20 ± 2 °C) to obtain the aqueous solution. And then the mixture was added to continuous medium with stirring in a water bath of 50 °C. After the polymerization proceeded for 3.5 h, the poly acrylamide superabsorbent polymers (A-SAP) beads were obtained. After being dried in vacuum at 50 °C, the A-SAP was used in oil well cement directly.

2.2.2. Modified polyacrylamide superabsorbent polymers

Before the synthesis, NNDMA was exposed over calcium hydride ($Ca(OH)_2$) for about 24 h and then distilled under vacuum to remove the stabilizers, and bentonite was immersed in distilled water with a stirrer at the speed of 200 r/min for 12 h to hydrate. Pre-hydration bentonite (1.5 g) and the aqueous solution of $K_2S_2O_8$ (0.08 g) and $NaHSO_3$ (0.02 g) were dropped into the solution which was prepared by mixing AM (7.5 g), NNDMA (2.5 g) and MBA (0.02 g) in 50 g distilled water. And then the mixture was added to continuous medium which was prepared referring to "2.2.1 Polyacrylamide superabsorbent polymers" with stirring at the speed of 550 r/min in a water bath of 50 °C. After reacted for 3.5 h, the poly (acrylamide/bentonite/N,N-dimethyl acrylamide) superabsorbent polymers (ABNN-SAP) were obtained. The ABNN-SAP which was dried in vacuum at 50 °C was used to prepare cement mixture directly.

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

Table 2
The main chemical composition of class G oil well cement.

SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	CaO (wt%)	SO_3 (wt%)	MgO (wt%)	K_2O (wt%)	Loss on ignition (wt%)
22.70	3.39	4.81	65.60	1.21	0.90	0.37	0.49

Table 3
Mix proportions of cement slurries.

Paste [a]	SAP		D/C (%)	De/C (%)	W/C
	TYPE	S/C (%)			
P1	–	0	0.5	0.5	0.36
P2	–	0	0.5	0.5	0.42
P3	–	0	0.5	0.5	0.54
P4	A-SAP	0.30	0.5	0.5	0.36
P5	A-SAP	0.30	0.5	0.5	0.42
P6	A-SAP	0.30	0.5	0.5	0.54
P7	ABNN-SAP	0.30	0.5	0.5	0.36
P8	ABNN-SAP	0.30	0.5	0.5	0.42
P9	ABNN-SAP	0.50	0.5	0.5	0. 54

[a] S, C, D, De and W are, respectively, the weight of SAP, cement, dispersant (sulfonated ketone/aldehyde polycondensates), defoamer and water. For identifying the influence of SAP, the dosages of dispersant and defoamer will not be changed in each paste. A-SAP is the poly acrylamide superabsorbent polymers. ABNN-SAP is the poly (acrylamide/bentonite/N,N-dimethyl acrylamide) superabsorbent polymers.

2.2.3. Copolymer characterization

Fourier Transform infrared spectroscopy (FTIR) spectra of SAP were recorded using a NEXUS Fourier Transform Interferometer. HITACHI S-4800 Field-emission Scanning Electron Microscope was choice to observe the appearance of SAP bead.

2.2.4. Manufacturing process

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

2.2.5. Thickening time

Thickening time tests are designed to determine the length of time when 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 balance. Therefore, the consistency signal can be imported to the recorder through the potentiometer. Considering the temperature circumstance in downhole, in this research, the consistency was tested at 20 °C, 50 °C, 80 °C and 0.1 MPa.

2.2.6. Cement slurry filtrate

The cement slurry filtrate was prepared by using the fluid loss cell following API Spec. 10B-3-2004. Firstly, slurry was stirred in consistometer for 30 min. And then the slurry was poured into the filter cell. Filtration was produced through a 3.5-in.^{2} mesh metal sieve placed at the bottom of the cell. 1000 psig differential pressure was applied to the fluid loss cell.

2.2.7. Water absorption testing

The water absorption of SAP in cement pore fluid was tested in previous study, but the study was carried out at 20 °C [22]. Considering the certain temperature surrounding in downhole, in this research, the water absorption testing was carried out at 20 °C, 50 °C, 80 °C. The testing procedure was as follows. Put 1 g microspheres into a nylon bag. Weigh the total quantity of microspheres and nylon bag, which was denoted as *M1*, then placed the nylon bag in the cement slurry filtrate. Take out the nylon bag after a certain time. After the bag being hanged to no water drop, the total quantity which was denoted as *M2* was tested again. The water absorption of microspheres at different time is given by:

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

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