



Amphoteric ion polymer as fluid loss additive for phosphoaluminate cement in the presence of sodium hexametaphosphate



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ARTICLE INFO

Article history:

Received 19 January 2016

Received in revised form

29 February 2016

Accepted 20 March 2016

Available online 24 March 2016

Keywords:

Phosphoaluminate cement

Sodium hexametaphosphate

Amphoteric ion polymer

Fluid loss additive

ABSTRACT

The fluid loss of modified aluminate phosphate cement system with excellent CO₂ resistant ability cannot meet the demand of cementing engineering and the conventional fluid loss additive lose effectiveness in this cement system. The aim of this paper is to reveal the failure mechanisms of the conventional fluid loss additive and develop one kind of amphoteric ion polymer to control the fluid loss. Results showed that massive of sodium hexametaphosphate exists in cement system limits the hydration and expansive degree of hydrophilic group of fluid loss additive and succeeds in the competition with fluid loss additive for adsorbing on the surface of cement particle. Using 2-acrylamido-2-methyl propane sulfonic acid, acrylamide, diallyl dimethyl ammonium chloride, and itaconic acid, a new fluid loss additive which has excellent ability to control fluid loss is synthesized by free radical aqueous solution copolymerization. The reducing fluid loss function of this kind of fluid loss additive is achieved by the cationic groups adsorbing on the surface of cement particle and anionic groups absorbing water to achieve hydration expansion to plug the flow passages between the cement particles. However, the dosage of this kind of fluid loss additive is limited by the negative retarding effect.

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1. Introduction

Oil well cementing is very important to the construction of a well bore, and the sealing ability of the cement sheath is very crucial to affect the life time of the well and the environmental safety (Garnier et al., 2007; Liu et al., 2016; Shahvali et al., 2014; Velayati et al., 2015). Conventionally, the cement used to seal the oil well is Portland cement, which is known to degrade under the attack of CO₂ (Barlet-Gouedard et al., 2006, 2009, 2012; Nasvi et al., 2014). After being attacked by the CO₂ for some time, the cement sheath will lose its sealing capability. Therefore, many wells integrity are threatened by the carbon dioxide, such as the natural gas wells with high concentration of carbon dioxide, miscible gas injection well (Kaydani et al., 2014), and carbon dioxide storage

wells (Kutchko et al., 2007). To avoid these problems, many cementing systems with corrosion resistance to CO₂ were developed (Barlet-Gouedard et al., 2009; Barlet-Gouedard et al., 2012; Bengel, 2005, 2009; Papadakis, 2000; Santra et al., 2009). One of the most promising systems is CAPC (Bengel, 2009), which could not react with CO₂ at a temperature of 320 °C. CAPC consists of four main components: calcium aluminates cement, sodium polyphosphate, ASTM Class fly ash and water. MAPC which also showed excellent CO₂ resistant ability was developed by using sintered phosphoaluminate cement and sodium hexametaphosphate (SHP), in which SHP is necessary for improving the strength properties of phosphoaluminate cement (Ma et al., 2014).

However, the APIf of the MAPC without the FLA could reach 1500 mL/30 min, which does not meet the demand of cementing operation. Therefore, the FLA must be introduced to the MAPC to control the fluid loss. However, just like the CAPC, due to the special mineral composition, the conventional FLA does not work in MAPC. Furthermore, because of the high dosage of SHP, the excellent FLA of poly (2-Acrylamido-2-Methyl Propane Sulfonic Acid/Acrylamide/N, N-Dimethyl Acrylamide/Maleic Anhydride) (Guo and Bu, 2013) used in Portland cement and CaATBS-co-NNDMA (Bilic et al., 2011)

Abbreviations: CAPC, calcium aluminate phosphate cement system; MAPC, modified aluminate phosphate cement system; APIf, American Petroleum Institute fluid loss; FLA, fluid loss additive.

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<http://dx.doi.org/10.1016/j.jngse.2016.03.062>

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used in CAPC also do not show good fluid loss control ability in MAPC, which makes the MAPC still be in research and have not been applied in the oil field. Therefore, the development of FLA with excellent fluid loss control ability for the MAPC is very necessary.

The monomer used to synthesize the FLA for the Portland cement mainly contains the anionic and nonionic monomer. 2-acrylamido-2-methyl propane sulfonic acid (AMPS), acrylic acid (AA), maleic acid (MA) and itaconic acid (IA) (Zhang et al., 2015) are commonly used anionic monomer, in which AMPS with outstanding thermal resistant and salt-tolerant properties was used extensively to synthesize the FLA (Paneva et al., 2003; Tolstov et al., 2012; Zhiyu et al., 2007). The nonionic monomer which is generally used to develop FLA includes Acrylamide (AM) and N, N-Dimethyl acrylamide (NNDMA) (Plank et al., 2006, 2007). However, The FLA containing cationic monomer was used rarely in Portland cement. Polyethylene imine (PEI) which is cationic polymer was reported to be used as FLA (Plank et al., 2006, 2007, 2009). However, the fluid loss control ability of PEI was very poor when used in Portland cement alone, and the fluid loss could be controlled only when the PEI was used with the dispersant which is one kind of anionic polymer (Plank et al., 2009 SPE). The FLAs synthesized by conventional kinds of monomer cannot control the fluid loss in MAPC; therefore, the introduction of new type monomer is the key point.

In this paper, the failure mechanism of conventional FLA was analyzed first. Based on the failure mechanism, a new amphoteric ion polymer (DAAI) which showed excellent fluid loss control ability in MAPC was developed by using diallyl dimethyl ammonium chloride (DMAAC), AM, AMPS and IA via free radical aqueous solution copolymerization, and the mechanism of reducing fluid loss was analyzed. At last, the compressive strength of MAPC with DAAI was also tested.

2. Experimental

2.1. Materials

AMPS, AM, IA, DMAAC, sodium hydroxide (NaOH), ammonium persulfate (APS), SHP and sodium bisulfite (SS) were obtained from SINOPHARM CHEMICAL REAGENT CO. (Shanghai, China). The lignin sulfonate and sodium borate complex system which was used as retarder was obtained from BO-XING ENGINEERING SCIENCE AND TECHNOLOGY CO. OF CNPC (Tianjin, China). Phosphoaluminate cement was obtained from ZIBO SPECIAL CEMENT CO. (Zibo, China), and the phase composition of the phosphoaluminate cement is shown in Table 1. PANM (Guo and Bu, 2013) and CaATBS-co-NNDMA (Bilic et al., 2011) were synthesized by free radical aqueous solution copolymerization. Twelve cement samples in which S1 is a plain slurry system were prepared as shown in Table 2. S1 and S2 were used to reveal the influence of SHP on the filtrate of cement mixture.

2.2. Method

2.2.1. The testing of basic properties of oil well cement

(1) Cement slurry preparation

Table 2

Mix proportions of cement slurry.

Sample ^a	Fluid loss additive		S/C (%)	R/C (%)	De/C (%)	W/C
	Type	F/C (%)				
S1	—	0	0	1.2	0.5	0.5
S2	—	0	15	1.2	0.5	0.5
S3	PANM	2.0	15	1.2	0.5	0.5
S4	PANM	2.5	15	1.2	0.5	0.5
S5	CaATBS-co-NNDMA	2.0	15	1.2	0.5	0.5
S6	CaATBS-co-NNDMA	3.0	15	1.2	0.5	0.5
S7	DAAI	0.5	15	1.2	0.5	0.5
S8	DAAI	1.0	15	1.2	0.5	0.5
S9	DAAI	1.5	15	1.2	0.5	0.5
S10	DAAI	1.8	15	1.2	0.5	0.5
S11	DAAI	2.0	15	1.2	0.5	0.5
S12	DAAI	2.5	15	1.2	0.5	0.5

^a C, F, S, R, De and W are, respectively, the weight of Phosphoaluminate cement, Fluid loss additive, sodium hexametaphosphate, retarder and defoamer.

Cement slurry was mixed based on API RP 10B-2002. After being prepared, the basic properties of cement were tested as follows.

(2) API static fluid loss

According to API RP 10B-2002, the stirred fluid loss cell was used to obtain the API fluid loss. The slurry was stirred continually at the speed of 150 ± 15 rpm before it reached the final temperature. Filtration was obtained by passing through a 325 mesh metal sieve (3.5-in. (88.9 mm)). 1000 psi (6.895 MPa) differential pressure was applied to the fluid loss cell. The filtrate produced by the differential pressure was collected for 30 min. The fluid loss was twice as much as the collected filtrate volume. After testing, the filter cake was formed on the sieve.

(3) Compressive strength

Cement slurries were placed into compressive-strength moulds (50 mm × 50 mm × 50 mm). Considering the temperature circumstance in downhole, cement slurries were cured for different time periods at 75 °C in high temperature curing chamber. The curing temperature was chosen to simulate the downhole temperature. After curing, the hardened cement was removed from the moulds, placed in hydraulic compression test equipment and loaded to failure. The compressive strength was recorded as the maximum compressive stress.

2.2.2. Determination of mineralized degree

Gravimetric method was used to test mineralized degree of filtrate which was obtained from the test of API static fluid loss. After the floating debris and precipitated solids being removed by filtration, hydrogen peroxide was used to get rid of organics contained in filtrate. Take 100 mL of filtrate and dry the filtrate in evaporating dish at 105–110 °C. After the filtrate was dried, the residue was weighed, which was noted as M. The mineralized degree of filtrate (Mc) whose unit is g/L was given by Eq. (1).

$$M_c = 10 \times M \quad (1)$$

Table 1

Phase composition of aluminate phosphate cement.

CaO (wt %)	Al ₂ O ₃ (wt %)	SiO ₂ (wt %)	P ₂ O ₅ (wt %)	Fe ₂ O ₃ (wt %)	MgO (wt %)
45.61	25.74	8.76	3.02	2.61	12.6

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