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Study on the performance and mechanism of accelerators LSA-1 and LSA-2 for deepwater well cementing at low temperatures

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ABSTRACT

There are abundant hydrocarbon resources in the deepwater region, so the exploration and development of deepwater oil and gas has become an important strategy for the Chinese petroleum industry. However, well cementing in deepwater, especially the cementing of the surface casing, is challenged due to the low temperature, which requires proper cementing accelerators to make the cement have certain strength at the early stage. Aiming to enhance the cementing quality of the surface casing, two kinds of lithium salt accelerators named LSA-1 and LSA-2 were developed in our early works based on the effects of different salts on oil well cement at low temperatures. In this paper, a comprehensive set of experiments was designed to test the effects of LSA-1 and LAS-2 on the Class-G oil well cement, including observations and measurements of the cement hydration products, the hydration heat and the developments of the static gel strength and the compressive strength. Based on these experiments, we discussed the mechanisms and performances of these two lithium salt accelerators at low temperatures. The experiment results indicate that both LSA-1 and LSA-2 can accelerate the hydration rate by advancing the hydration acceleration period and result in the earlier generation of $Ca(OH)_2$ and AFt. They can also induce the cement hydration products to form regular and compact gel structures, which contributes to the development of the static gel strength and the compressive strength of cement slurry at the early stage. Moreover, the two lithium salt accelerators have the characteristic of low hydration heat. This is helpful to reconcile the contradiction between the development of cement early compressive strength and the hydration heat, which can help to avoid channeling and hydrate decomposition in the strata containing gas hydrate. In general, LSA-2 has a stronger effect on accelerating hydration of oil well cement, while LSA-1 has less impact on cement hydration heat. Therefore, both LSA-1 and LSA-2 are qualified to serve as low-temperature accelerators for deepwater cementing, which are able to meet the diverse requirements of the deepwater low-temperature environment and the field cementing operation.

1. Introduction

It is urgent to exploit the deepwater hydrocarbons for China as the consumption of oil and gas is progressively increasing. The South China Sea is one of the four largest hydrocarbon accumulation regions in the world and known as the "Second Persian Gulf" (Chen et al., 2007). But the hydrocarbon resources of South China Sea are mostly buried in deepwater. The oil and gas exploration in deepwater is much more complicated due to its special environment, such as water depth, stratigraphic structure, weather conditions, lack of oilfield facilities, and so on (Chita and Cordeiro, 1988; Feng et al., 2015). The deepwater well cementing is also confronted with various challenges such as low temperature, low fracture gradient, shallow flow hazard and gas hydrate, which directly influence the safety of drilling and the quality of cementing (Ravi et al., 1999). Among these harsh factors, low temperature is the most formidable challenge for deepwater cementing. The low-temperature environment of deepwater will greatly delay the hydration process of cement, which hinders the development of cement compressive strength and weakens the cementation (Biezen and Ravi, 1999). And the extension of the curing time and the slowed development of compressive strength can induce fluid migrations along the cement sheath (Velayati et al., 2015). In addition, the heat generated by cement hydration reaction can cause the instability of gas hydrate in deepwater, which leads to

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channeling and even more serious accidents (Gupta et al., 2014).

Therefore, some chemical accelerators are added into the cement slurry to speed up the formation of early strength. Calcium chloride is the most widely used accelerator for onshore well cementing. Unfortunately, it is not applicable in deepwater cementing because of its large hydration heat, which can cause the dissolution of natural gas hydrate. Some new accelerators for offshore cementing have been developed in recent years, such as $Al(OH)_x(R)_y$ (R is a basic anion which is not sulfate and $x + y = 3$, Salvatore, 1998), hydrophobic silica powder (Baireddy et al., 2002) and nanosilicas (Pang et al., 2014). But their accelerating effects on oil well cement at low temperatures are still weak, which constrain their further application in deepwater cementing. As a result, it is necessary to develop more suitable accelerators for deepwater well cementing, especially for the cementing of the surface casing at low-temperature.

Some of alkaline salts have proved to effectively accelerate the cement hydration, such as sodium and potassium salts (Teodoriu and Asamba, 2015). Lithium also belongs to the alkaline metal, which is widely known in the application of batteries. However, there are limited studies about the effect of lithium on cement, which mostly concentrate on the suppression of alkali-silica reaction (Demir and Arslan, 2013). Some papers investigated the manufacture of cement using lithium slag and lithium salt as set accelerator for high alumina cement (Matusinović and Čurlin, 1993). Lithium salt can also be used as accelerator for oil well cement because of its special chemical and physical properties (Wang et al., 2011). But the such research is still in the primary stage.

Nowadays, one single chemical is hard to satisfy the requests of well cementing under complicated conditions. The accelerators which contain a variety of components are increasingly developed and applied, such as the mixture of amorphous aluminium hydroxide and/or aluminium hydroxysulphate, and amine and the mixture of $CaCl_2$, phosphate and silica (Viveros et al., 2011).

There are two kinds of lithium salt accelerators have been developed in our laboratory named LSA-1 and LSA-2. LSA-1 is essentially made of lithium chloride, and LSA-2 comprises the well-mixed lithium chloride and sodium sulfate with the ratio of weight 1:1.5. In this paper, we designed a comprehensive set of experiments and measured the hydration heat, the development of the static gel strength, and the compressive strength at low temperatures. And then we compared the effects of LSA-1 and LSA-2 on oil well cement, and try to reveal the accelerating mechanism of lithium salt accelerators.

2. Experimental materials and methods

2.1. Experimental materials

The experimental materials included "Sheng Wei" brand Class-G oil well cement (produced by the Shengli Huanghe Cementing Corp., China, its clinker compositions are given in Table 1), lithium salt accelerators LSA-1, LSA-2 (self-made), calcium chloride, potassium chloride and anhydrous alcohol (analytic pure, produced by Shanghai Branch of China Pharmaceutical Group).

Table 1
Chemical and mineral composition of Class-G oil well cement used.

Chemical composition (wt%)					
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
23.05	2.86	3.52	65.2	1.79	2.12
Mineralogical composition (wt%)					
C_3S	C_2S	C_4AF	C_3A		
59.89	16.75	10.7	1.63		

2.2. Experimental methods

The cement slurry was prepared after adding certain accelerator by weight of cement (BWOC %) with a water-to-cement ratio of 0.44 according to the API 10B-3-2004 standards "Recommended practice on testing of deepwater well cement formulations". Based on the previous studies and experimental results, the optimal dosage of LSA-1 and LSA-2 is 3% for the accelerating effects on cement and economic considerations.

The prepared cement slurry was cured at 7 °C for different periods of times, and then the hydration reaction of slurry was terminated by alcohol. Next, some of cement was ground into powder with the size about 75 μm after being dried at the vacuum condition. The prepared cement powder was characterized by X-ray diffraction (XRD, conducted by an X'pert PRO MPD X-ray diffractometer, produced by Panalytical Co., Netherlands), infrared spectroscopy (IR, conducted by a Fourier transformation infrared spectrometer, produced by Nicolet Co., America), scanning electron microscope (SEM, conducted by the S4800 field emission scanning electron microscope, produced by Hitachi Co., Japan) and transmission electron microscope (TEM, conducted by the JEM-2100UHR transmission electron microscope, produced by Japanese Electronics Co.), to investigate the hydration products and the microstructures of different cement samples at low temperatures.

The hydration heats of different cement slurries were measured by a self-made adiabatic temperature-rise tester, respectively. The temperature changes in the process of hydration were recorded through the automatic temperature measurement system.

The static gel strength and the compressive strength development of one set cement slurry could be simultaneously measured by the static gel strength analyzer (Model 5265U with UCA functionality, produced by American Chandler Corp.), and all data acquisition was performed with the Chandler 5270 DACS system.

3. Acceleration mechanism of LSA-1 and LSA-2

The hydration of tricalcium silicate (C_3S) can be defined into five successive periods according to the hydration rate and heat, including preinduction period, induction period, acceleration period, deceleration period, and diffusion period. Relatively little hydration activity is observed during the induction period. The acceleration and deceleration periods, also collectively known as the "setting period", represent the interval of most rapid hydration. During the acceleration period, solid calcium hydroxide ($Ca(OH)_2$) crystallizes from solution and the C–S–H gel deposits into the available water-filled space to form a cohesive network. The low temperature will prolong the induction period and inhibit the cement slurry from further hydration (Wang et al., 2009). And the generation of calcium hydroxide is the indicator for the end of C_3S induction period. Similarly, the generation of ettringite (AFt) suggests the acceleration of aluminate hydration reaction. In order to reveal the acceleration mechanism of LSA-1 and LSA-2 on oil well cement, in this study, a series of tests were designed to observe the changes of cement hydration products and micro morphology at different curing times, and then compared the results with those of neat cement slurries.

3.1. XRD analysis of the low-temperature hydration products

The neat oil well cement slurry, slurries with 3% LSA-1 and 3% LSA-2, respectively, were analyzed by XRD after being cured for 8, 10 and 20 h at 7 °C. In order to obtain convincing conclusions, each