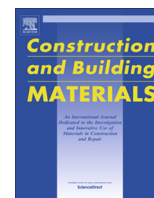




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## Do chlorides qualify as accelerators for the cement of deepwater oil wells at low temperature?

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### HIGHLIGHTS

- Accelerating ability of chlorides follows the order of  $\text{CaCl}_2 > \text{LiCl} > \text{KCl}$ .
- LiCl has the most excellent comprehensive performance.
- $\text{CaCl}_2$  increases the adiabatic temperature most and causes “flash set”.
- Cement containing 3% LiCl generates the strip-like and the spherical particle CSH gels.

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### ABSTRACT

In this paper, the acceleration performances and mechanisms of chlorides ( $\text{CaCl}_2$ , LiCl and KCl) on oil well cement at low temperatures were studied. The results indicated that their accelerating ability follows the order of  $\text{CaCl}_2 > \text{LiCl} > \text{KCl}$ .  $\text{CaCl}_2$  has some unfavorable effects on the performance of cement, such as increasing the adiabatic temperature, causing bad rheology and thixotropy of cement slurry, and thickening the slurry, which may cause a “flash set”. LiCl can significantly enhance the compressive strength development of oil well cement stone at low temperatures like  $\text{CaCl}_2$ , but do not have the disadvantages of  $\text{CaCl}_2$ . Besides, LiCl can effectively shorten the static gel strength from 48 Pa to 240 Pa and also have much smaller adiabatic temperature. Based on the micro-test analyses, it was found that LiCl can accelerate the hydration rate of oil well cement under low temperatures. The hydration products of cement slurry include the ettringite (Aft), strip-shaped CSH gel (250–350 nm) and strip-shaped CSH gel (50–70 nm). The small spherical CSH gel fills in the pores of strip-shaped CSH gel to form a dense spatial structure. On contrast, the CSH gel forms a network structure in the cement containing  $\text{CaCl}_2$  or KCl.  $\text{CaCl}_2$  also inhibits the generation of Aft.

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## 1. Introduction

Temperature has a critical influence on the hydration process of Portland cement [1,2]. The slow growth of cement strength at low temperatures is one of the worldwide and arduous challenges. Under the condition of exterior winter, high altitudes or the polar regions, low temperature produces negative effects on the building and construction. In deepwater ocean regions, the well cementing is faced with severe difficulties such as the low temperature, low fracture gradient, shallow flow hazard and gas hydrate. Definition of deepwater may vary with operators and researchers. In general, the deepwater region is specified as the sea area with the water depth of more than 500 m [3,4]. On the deepwater seafloor, the

temperature is typically no more than 4 °C. When cementing the surface casing in deepwater, the circulating temperature in surface cementing is normally about 15 °C because of the inversion of thermal gradient and the heat transfer between riser and sea water. Besides, the bottom hole pressure will increase with water depth, and the increase is about 1 MPa per hundred meters. The temperature is a key factor directly controlling the hydration rate of cement slurry. Low temperature will dramatically reduce the cement hydration rate, which can cause the longer thickening time, the slow development of compressive strength of the set cement and the insufficient shear stress of annular cement sheath to support the casing within a short period. So this will inevitably prolong the waiting-on-cement (WOC) time and increase the well construction cost [5–9].

Accelerator is a kind of cement additive that is used to shorten the thickening time and enhance the early compressive strength. The mostly used accelerators are classified as soluble inorganic

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salts (e.g. chlorides, nitrates and alkali metal salts) and soluble organic compounds (e.g. triethanolamine and triisopropanolamine) [10]. Besides, the accelerating effects of nanosilica, silica fume and calcium formate have been demonstrated [11–13]. In order to obtain better performance, the accelerators which contain a variety of components are increasingly developed and applied, such as catalytic cracking catalyst residue combined with metakaolin, a mixture of sodium thiocyanate, diethanolamine and glycerol [14,15].

The chlorides are the best known accelerator of oil well cement. Previously, cementing crew often use  $\text{CaCl}_2$  as an accelerator to shorten the thickening time of cement at low temperatures and enhance the early strength of cement stone.  $\text{CaCl}_2$  has the advantages of low-cost and obvious development of early strength, but it will shorten the initial setting time and cause a bad rheology of cement slurry. It can even cause a “flash set” that the cement slurry quickly loses its fluidity and probably leads to a serious cementing accident [16,6,17,18]. Recently, some new types of chlorides have been applied in the cement, and the chlorides still play an indispensable role in accelerating the hydration of oil well cement at low temperatures [19].

Alkali metal salts, such as sodium salt and potash salt, have been used as set-accelerating materials on cement.  $\text{NaCl}$  is known to accelerate cement hydration at lower dosages and retard the hydration at higher dosages. In 2015, Pang et al. investigated the effect of  $\text{NaCl}$  and  $\text{KCl}$  on cement by isothermal calorimetry [18]. In 2008, Millard et al. studied the effects of  $\text{LiNO}_3$  on early-age cement hydration [20]. Until now, there are still limited comprehensive studies about the accelerating effects of potassium and lithium salt at low temperatures. Theoretically, lithium has a small atomic radius but strong polarization and large radius of hydrated ions. Therefore, lithium salts should have different chemical properties from sodium and potassium. The previous related researches have been concentrated on the acceleration of aluminate cement and the inhibition of alkali-silica reaction by lithium salt [21–27]. Thus,  $\text{LiCl}$  is a promising accelerator to solve the deepwater cementing challenges at low temperatures.

Previous studies have evaluated the acceleration performances of many accelerators, but due to the special technical requirements of well cementing in deepwater, such as low hydration heat, good rheology and thixotropy, we still need to reappraise available accelerators and develop some newtype accelerators [28]. Besides, the hydration of Class-G oil well cement at low temperatures is still not fully understood. Although some papers have introduced the accelerating effects of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{TiO}_2$ ,  $\text{CaCO}_3$  and so on [6,19,29], there is a lack in the detailed explanation for the acceleration mechanisms of chlorides at low temperatures.

In this study, we tested and compared the effects of the three chlorides ( $\text{LiCl}$ ,  $\text{KCl}$  and  $\text{CaCl}_2$ ) on Class-G oil well cements' properties, including hydration heat, rheology, thixotropy, compressive strength and static gel strength. And then we explored the acceleration mechanisms of these chlorides through micro-test analyses, aiming to clarify the reasons for their different performances.

## 2. Experimental materials and methods

### 2.1. Materials

Lithium chloride ( $\text{LiCl}$ , 97.0% purity), potassium chloride ( $\text{KCl}$ , 99.5% purity) and calcium chloride ( $\text{CaCl}_2$ , 96.0% purity) were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received.

An API Class-G oil well cement (“Jiahua label” from Jiahua cement company, Sichuan, China) corresponding to API Specifica-

tion 10A was used. Its clinker composition was determined through powder XRD technique (see Table 1).

### 2.2. Cement slurry preparation

Chloride ( $\text{LiCl}$ ,  $\text{KCl}$  or  $\text{CaCl}_2$ ) was added into the Class-G oil well cement slurry at a certain mass fraction by weight of cement (% bwoc). The cement slurry was prepared with a water-to-cement ratio of 0.44 by following the API 10B-3-2004 standards “Recommended practice on testing of deepwater well cement formulations” [30].

### 2.3. Measurements of hydration heat

We used a house-made adiabatic temperature-rise tester to determine the adiabatic temperature of the cement slurry. The prepared oil well cement slurry was poured into a constant-volume container. A temperature probe was submerged in the center of the cement slurry for measuring the slurry temperature. Then the temperatures in the process of hydration were recorded through the automatic temperature measurement system. By measuring the changes of temperature in the process of hydration, we could calculate adiabatic temperature rises of different slurries prepared with  $\text{LiCl}$ ,  $\text{KCl}$  and  $\text{CaCl}_2$ , and then analyze the different influences of the three chlorides on cement hydration heat.

### 2.4. Determination of rheological and thixotropic properties

According to the standard of “Evaluation method for well cement additives-Part 3: Dispersant” (SY/T 5504.3-2008), we used a ZNN-D6 rotational viscometer (produced by Qingdao Haitongda Instrument Factory) to obtain the readings under different shear rates for a given oil well cement slurry. We could calculate the fluidity index  $n$  and consistency coefficient  $K$  of the slurry by

$$n = 2.0961g \left( \frac{\theta_{300}}{\theta_{100}} \right) \quad (1)$$

$$K = \frac{0.511\theta_{300}}{511^n} \quad (2)$$

where  $\theta_{300}$  is the reading at the shear rate of 300 r/min, and  $\theta_{100}$  is the reading at the shear rate of 100 r/min. A larger  $n$  indicates a better slurry fluidity, while a larger  $K$  indicates a thicker slurry.

In the study of thixotropy, the prepared slurry was poured into the outer cylinder of the rotational viscometer. At first the cement slurry was sheared with a high velocity of 600 r/min for 10 s under room temperature (20 °C), and then sheared with a low rotational speed of 3 r/min. The maximum scale readings under the rotational velocity of 3 r/min were recorded for 10 s, 1 min and 10 min, respectively. These readings were referred to as “early-gel-strength  $\tau_{10sec}$ ”, “1 min-gel-strength  $\tau_{1min}$ ” and “10 min-gel-strength  $\tau_{10min}$ ”, respectively. The ratio of  $\tau_{10min}/\tau_{10sec}$  reflects the degree of the slurry thixotropy.

### 2.5. Determination of thickening time, static gel strength and compressive strength

The thickening time of set cement slurry was determined by a pressurized consistometer equipped with a temperature controlling system (OWC-2000A, Shenyang Petroleum Instrument Research Institute). Static gel strength was measured with a Static Gel Strength Analyzer (5265U, American Chandler Corporation). All the data were collected with the Chandler 5270DACS system, and the measured static gel strength was plotted as a function of time with the Origin software. The compressive strength of set cement was tested after the prepared cement slurry was poured into a

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