



Isothermal calorimetry study of the effect of chloride accelerators on the hydration kinetics of oil well cement



Xueyu Pang^{*}, Peter Boul, Walmy Cuello Jimenez

Halliburton, 3000 N Sam Houston Pkwy E, Houston, TX 77032, United States

HIGHLIGHTS

- A cement hydration mechanism profile is defined in this study.
- The hydration mechanism profile is useful in studying cement additive chemistry.
- Overall hydration rate increases linearly with CaCl_2 concentration.
- Overall hydration rate increases linearly with the logarithm of NaCl concentration.
- Overall hydration rate increases linearly with the logarithm of KCl concentration.

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ABSTRACT

The hydration kinetics of Class H oil well cement with and without chloride accelerators were evaluated via isothermal calorimetry. A series of tests were conducted with two different water-to-cement (w/c) ratios (0.38 and 0.91) at two different temperatures (15 °C and 25 °C). The test results indicate that the effect of different chlorides on the overall cement hydration rate is primarily determined by the molar concentration of the chloride in water and can be simulated by a generalized scale factor model. At concentrations up to 0.9 M Cl^- , the overall hydration rate increases approximately linearly with the CaCl_2 concentration and shows virtually no dependence on temperature and w/c ratio. In contrast, when NaCl or KCl is used at similar concentrations (up to 0.9 M Cl^-), the hydration rate increases linearly with the logarithm of the chloride concentration and the correlation varies slightly with temperature and w/c ratio.

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1. Introduction

Portland cement set accelerators are primarily used to decrease setting time and increase early strength gain of cement-based materials, especially at low temperature conditions. Calcium chloride is the most common and most widely used inorganic salt accelerator, primarily due to its wide availability and cost-effectiveness [1,2]. ACI 212.3R [2] recommends a dosage of 1–2% by weight of cement (bwoc) for applications that permit the use of CaCl_2 . Several studies have similarly reported that maximum acceleration on the hydration of tricalcium silicate (C_3S) and Portland cement by CaCl_2 is achieved at about 2% dosage bwoc [3,4]. Further additions appear to have very little effect on the degree of hydration and the mechanical properties of set cement (≥ 24 h) [4,5].

The effect of CaCl_2 at higher dosages ($\geq 2\%$) on the hydration of C_3S and Portland cement during the first hours seems to be more complex and strongly dependent on the cement composition [4,6] and sometimes curing temperature [7]. Other chlorides, such as NaCl and KCl, are also known to accelerate the hydration of Portland cement. However, the effectiveness of acceleration by NaCl and KCl is significantly less than that by CaCl_2 [8]. Correspondingly, studies of these less common accelerators are relatively rare in the open literature. It has been reported that the addition of KCl may slightly increase the setting time of ordinary Portland cement [9]. In oil well cementing, NaCl is known to accelerate cement hydration at lower dosages and retard the hydration at higher dosages [10].

The accelerating effect of calcium chloride on Portland cement hydration has been recognized since over a century ago [11]. However, due to the complex hydration process of Portland cement, the mechanism through which such acceleration takes place is still not

^{*} Corresponding author.

E-mail address: Xueyu.Pang@halliburton.com (X. Pang).

fully understood today. Some earlier investigations [12,13] suggested that the acceleration effect of CaCl_2 is due to the higher diffusion rate of Cl^- relative to OH^- . More recent studies [8,14,15] often attributed the acceleration to the ability of CaCl_2 to flocculate hydrophilic colloids, such as calcium-silicate-hydrate (C-S-H) gel, which increases the permeability of the C-S-H layer formed around the cement grains and allows a higher rate of diffusion. By fitting cement hydration models to C_3S and Portland cement hydration kinetics test data, other studies suggested that the acceleration may be due to higher nucleation rate [16] or higher growth rate [17] of C-S-H nuclei in the presence of CaCl_2 , which are particularly intriguing considering that both the nucleation and the growth behaviors of C-S-H were shown to be dependent on the Ca^{2+} concentration in the solution during C_3S hydration in dilute suspensions [18].

In this work, a comprehensive evaluation of different chloride accelerators (CaCl_2 , NaCl and KCl) on the hydration kinetics of oil well cement is performed based on isothermal calorimetry tests. The main variables studied include water-to-cement (w/c) ratio, dosage of the accelerator, mixing method, curing temperature and cement composition. An empirical scale factor model is proposed to quantify the relative strength of acceleration of different chlorides for different cements.

2. Theory

The reaction rate of cement hydration is strongly dependent on the total extent of reaction that has been reached. For the convenience of discussion during this study, cement hydration mechanism profile is defined as the plot of the normalized rate of hydration (against the main peak) as a function of total degree of hydration. In isothermal calorimetry tests, the rate of hydration is represented by the heat flow rate while the total degree of hydration is represented by the cumulative heat evolution [19]. It is well known that the hydration rate of Portland cement is strongly dependent on its curing condition. In the range between 5 and 60 °C, curing temperature is known to slightly change the properties of cement hydration products and affect the microstructure development of the set cement [20]. However, it appears that the cement hydration mechanism profile is not significantly affected by these changes and can be assumed to be invariant at different curing conditions, especially for relatively small temperature changes [19,21,22]. It has been shown that the effect of curing temperature and pressure on cement hydration kinetics can be approximately simulated by a scale factor that represents the overall hydration rate change as a function of total degree of hydration. For curing condition change from a reference temperature T_r (K) to a new temperature T (K), the scale factor C can be expressed as [21]:

$$C(T_r - T) = \exp\left(\frac{E_a}{R}\left(\frac{1}{T_r} - \frac{1}{T}\right)\right) \quad (1)$$

where E_a is the apparent activation energy (J/mol) and R is the gas constant (8.314 J/(mol K)). The proposed scale factor model has been previously validated for different neat oil well cement systems consisting of cement and water only in the temperature range from 25 °C to 60 °C [19,21,22]. This study will extend the applicability of the model to a lower temperature of 15 °C both with and without chloride accelerators.

Although the mechanism of acceleration induced by different chloride admixtures is not yet clear, it is observed in this study that the overall effect of these accelerators on cement hydration kinetics is somewhat similar to that produced by increasing curing temperature and pressure, especially at relatively low dosages. Therefore, the scale factor model can be generalized to model the

effect of chloride admixtures on cement hydration at different dosages. When the neat slurry (i.e. with no admixtures) is used as a reference, the change in hydration rate (represented by a scale factor C) introduced by a certain amount of admixtures can be expressed as a function of the molar concentration of the admixture:

$$C(\text{admixture}, c) = f(c) \quad (2)$$

where $f(c)$ is an empirical function that can be obtained from the experimental test data. When the test results at a given molar concentration (c_r) of admixture is used as a reference, the scale factor associated with an arbitrary molar concentration (c) can be expressed as,

$$C(\text{admixture}, c_r - c) = \frac{f(c)}{f(c_r)} \quad (3)$$

The generalized scale factor model proposed in this study assumes that cement hydration always follows the same mechanism profile despite the overall rate changes caused by different factors (such as the addition of accelerators). Correspondingly, the overall hydration rate change from a reference test to an arbitrary test can be represented by a scale factor that equals the ratio of their peak hydration rates. The model can be utilized to simulate the hydration kinetics of the cement with an arbitrary dosage of an accelerator based on the results of a reference test and a calculated scale factor from Eqs. (2) or (3). As in the previous studies [19,21,22], application of the scale factor model involves representing hydration kinetics of cement with functions whose exact expressions are not defined. For example, if the functions for the reference condition are represented by:

$$\text{Integral curve : } \alpha = \alpha_r(t), \text{ Derivative curve : } d\alpha/dt = \alpha'_r(t) \quad (4)$$

Then the transformed functions for the condition to be predicted are,

$$\begin{aligned} \text{Integral curve : } \alpha &= \alpha(t) = \alpha_r[C(t - t_0)], \\ \text{Derivative curve : } d\alpha/dt &= \alpha'(t) = C \cdot \alpha'_r[C(t - t_0)] \end{aligned} \quad (5)$$

where t_0 is a small offset time that is often necessary to obtain the best agreements between the experimental results and the model simulation, which may be determined to be 0 sometimes. The existence of such offset is probably due to the different mechanism of hydration of cement between the initial reaction period and the main hydration period.

3. Experimental program

3.1. Materials

An API high-sulfate-resistant (HSR) grade Class H cement (by Joppa Plant of Lafarge Co.) as provided by the manufacture was used to study the effect of different chlorides, including CaCl_2 , NaCl and KCl , on cement hydration kinetics. All chlorides were obtained from Fisher scientific. Anhydrous CaCl_2 was provided in a powder form with more than 96% purity. NaCl and KCl were provided in a crystalline powder form with more than 99% purity. Another API Class H cement (by Texas Lehigh Cement Co.) was also tested with different dosages of CaCl_2 to study the cement composition effect on test results. The oxide analysis results of the cement and the correspondingly estimated clinker phase compositions based on Bogue calculation method [23] are presented in Table 1. Phase compositions estimated by Rietveld refinement method using X-ray diffraction test data are also included in the table for comparison purposes. The calculated specific surface areas of the Lafarge H and the Lehigh H cements were 303 m^2/kg and 254 m^2/kg , respectively, based on particle size distribution measurement (assuming spherical particles and a density of 3150 kg/m^3 for cement).

3.2. Methods

Tests were performed in a TAM Air microcalorimeter (TA Instruments) following standard test procedures [24]. A majority of slurries were mixed at room temperature (approximately 21 °C) in a Waring® laboratory blender using deionized water and following standard mixing procedures described in API RP 10B-2 [25].

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