Characterization of early hydration and setting of oil well cement by a multifaceted approach

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Abstract

A broad experimental study has been performed on characterization of early hydration and setting of cement pastes prepared with Class H oil well cement with different water to cement ratio (w/c), cured at various temperatures, and mixed with different chemical additives. Chemical shrinkage during the hydration was measured by a newly developed chemical shrinkage measurement system, degree of the cement hydration was determined by the thermogravimetric analysis (TGA), and setting time was tested by Vicat method and ultrasonic measurement. A mathematical nucleation and growth model, Avrami-Cahn-Thomas (ACT) model, was used to approximate the hydration.

Background

In oil well cementing, a cement slurry is pumped down the steel casting of the well and up the annular space between it and the surrounding rock. The main objectives are to restrict movement of fluids between formations at different levels and to support and protect the casing. Pumping can take several hours, retarders and dispersants are widely employed. To avoid damage to the pumping equipment used to place the cement slurry, the cement must remain a fluid state for several hours while it is pumped into place; to avoid wasting valuable rig time, the cement should set shortly after being placed. So, prediction of oil well cement setting is desirable.

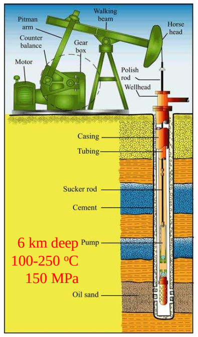

Fig. 1 An illustration of an oil well

Objective

- Characterize the early hydration and predict the setting of cement paste by multiple techniques.
- Verify the assumption that the amount of product formed at the point of setting is a constant at a given w/c. So the following equation can be used to predict the cement setting under various temperature and pressure histories.

$$\ln\left(\frac{t_{set}(T_1,p_1)}{t_{set}(T_0,p_0)}\right)=\frac{\Delta E+p_1\Delta V}{RT_1}-\frac{\Delta E+p_0\Delta V}{RT_0}$$

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Methods

This study focused on the effect of temperature (10-60ºC), w/c (0.25-0.40) and additives (retarder Maltodextrin (MD), accelerator $CaCl_2$, water reducer Hydroxyethylcellulose (HEC) and Diutan (DT)) on the hydration kinetics of Class H oil well cement.

Table 1 Compound composition and fineness of cements

Cements	C_3S	C_2S	C_3A	C_4AF	Gypsum	Fineness (m^2/kg)
Type I OPC	54	18	10	8	~5	369
Class H	64	16	0.7	11	1.8	200

The early hydration leading to setting is dominated by alite (tricalcium silicate, C_3S). ACT model can be reasonably used in Class H cement.

A chemical shrinkage measurement is used and the results are analyzed by the Avrami-Cahn-Thomas (ACT) model to interpret the initial hydration. Vicat method and ultrasonic transmission measurements identify the setting time. Degree of the cement hydration is determined by TGA. To obtain sufficient time resolution, a freeze-drying procedure is used to instantaneously cease the hydration at setting time for TGA measurement.

Results and discussions

Ultrasonic and Vicat

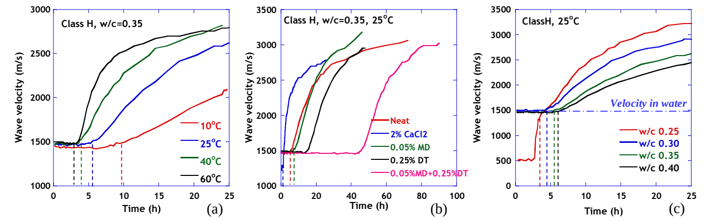

Fig. 2 Ultrasonic wave velocity of Class H cement paste during hydration, (a) at different temperatures; (b) with additives; and (c) at different w/c. In the suspension period at early hydration, the pore solution acts as the dominant influencing factor that determines the ultrasonic wave velocity. As cement hydrates, the ultrasonic velocity shows a significant increase after the appearance of the solid percolation threshold, indicating the setting. Dashed lines show the initial setting points determined by Vicat needle penetration test.

Chemical Shrinkage

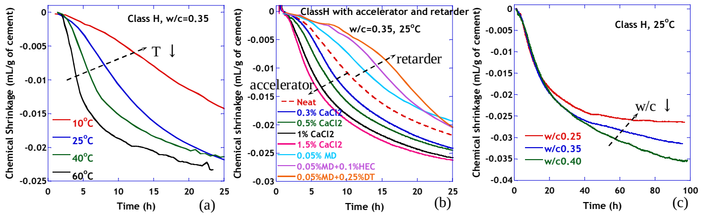

Fig. 3 Chemical shrinkage of Class H cement paste during hydration, (a) at different temperatures; (b) with additives; and (c) at different w/c. The chemical shrinkage value is computed as the measured volume (mL) of sorbed water per gram of cement in the paste specimen. The method is based on ASTM C1608 standard, and the volume of sorbed water is automatically recorded by a pressure sensor. Our study also find there is linear relationship between chemical shrinkage and the degree of hydration. Chemical shrinkage is initially independent of w/c, but the later divergence in the curves may occur from the diffusion-control period.

Avrami-Cahn-Thomas model

$$X(t)=\frac{F(t)}{A}=1-\exp\left[-2k_G t\left(1-\int_0^1\exp\left[-\frac{\pi}{3}\frac{k_B^4}{k_G}t^3\left(1-3x^2+2x^3\right)\right]dx\right)\right]$$

$$\approx 2k_G t\int_0^1\frac{\pi}{3}\frac{k_B^4}{k_G}t^3\left(1-3x^2+2x^3\right)dx$$

$$=\frac{\pi}{3}k_B^4t^4 \quad\rightarrow\quad t_{set}=\left(\frac{3}{\pi}X_{set}\right)^{1/4}k_B^{-1}$$

Where,

$$k_B=\left(I_B O_V^B\right)^{1/4}G^{3/4},\quad k_G=O_V^B G$$

X(t): volume fraction transformed at time *t*.
F(t): measured quantity (heat release or volume change) with reaction time
A: total change (heat or shrinkage) per unit mass of reactant
I_B: nucleation rate per unit area of untransformed boundary
G: linear growth rate
O_V^B: boundary area per unit volume

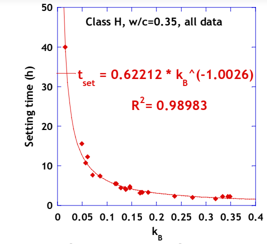

Fig. 4 Nucleation parameter k_B vs. setting time of all the samples with various temperatures and additives at a given w/c=0.35. Setting time and k_B has a certain relationship which confirms that the amount of hydration product at setting is a constant in the left equation from ACT model.

Degree of hydration @ setting time

Degree of hydration is determined by TGA. The amount of product that is burned allows to calculate the degree of hydration. Cement at initial setting time was quenched and dried by a freeze-drying method.

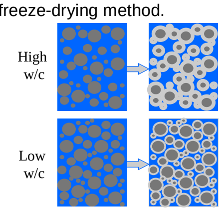

Fig. 5 An illustration of solid phase percolation at setting at different w/c. High w/c needs more product to cause percolation.

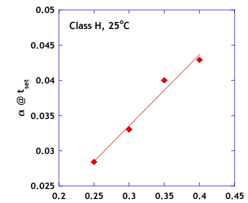

Fig. 6 Degree of hydration at setting time at various w/c.

Table 2 Setting time and the degree of hydration at setting time, w/c=0.35

Sample	t_{set} (h)	α @ t_{set}
10ºC	10.75	0.033
25ºC	5.5	0.040
40ºC	3.33	0.042
60ºC	2.25	0.037
0.05% MD	7.4	0.037
0.25% DT	7.67	0.034
0.05%MD+0.1%HEC	12.3	0.038
0.05%MD+0.25%DT	15.55	0.043
0.5%CaCl2	3.18	0.045
Average	~	**0.0388**
Standard Derivation	~	0.0038

Conclusions

- Temperature increase and calcium chloride expedite the rate of cement hydration, causing more rapid production of hydration products and earlier setting; conversely, retarder maltodextrin, and the dispersants hydroxyethylcellulose and diutan delay cement hydration, causing later setting times.
- The low w/c paste needs less amount of hydration product (lower degree of hydration) to form a percolating solid network (setting), however at a given w/c the degree of hydration at setting is a constant regardless of the effects of ambient temperature or presence of additives.
- The initial hydration of cement follows the Avrami-Cahn-Thomas model. There is a certain relationship between its parameter k_B and the setting time.

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