The effect of a retarder on the early stages of the hydration of tricalcium silicate

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Abstract. Cement is used in the oil industry to line oil wells. The major component of oilwell cement is tricalcium silicate (C_3S), which is responsible for the initial thickening of the cement slurry. It is important to control the time that it takes for this slurry to thicken, and this is achieved in practice by the addition of chemical retarders, which delay the onset of thickening. In this paper, the action of a retarder whose main effect is to form a complex with calcium ions is investigated by use of a model for the hydration of C_3S previously investigated by Preece, Billingham and King (2001). It is found that such a retarder can significantly increase the thickening time of pure tricalcium silicate.

Key words: asymptotics, cement hydration, mathematical chemistry, modelling, oil wells

1. Introduction

Oilwell cement is used to secure a cylindrical metal liner in a newly drilled well, and thereby isolate the well from the surrounding formation. Accurate control of the thickening time, that is the time after initial mixing when the cement can no longer be pumped, is crucial in this process. If the thickening time is too short, the cement fails to reach its required placement, whilst too long a thickening time leads to costly delays [1, Chapter 2]. It is usual to control the thickening time using chemical additives, known as retarders, typically, phosphonates (see for example, [2]). The mechanism by which phosphonates and other chemicals act as retarders is not well understood, but it is known that they bind to calcium ions [3, Chapter 11]. Although other features of the chemistry of retarders may be important in their retarding action, for example the ability of phosphonates to inhibit the growth of ettringite crystals [4], we will focus on their action on calcium ions in this paper.

In an earlier paper [5], we argued that the early stages of cement hydration are dominated by the hydration of the main constituent of oilwell cement, tricalcium silicate (C_3S), to form hydrated calcium silicate gel (CSH) and calcium hydroxide (CH). Note that we are using the usual cement nomenclature where C represents calcium oxide, CaO, S represents silicate, SiO_2 and H represents water, H_2O. We showed that the representation of this process in terms of dissolution-precipitation reactions leads to a model that agrees well with experimental results, assuming that the thickening time is signalled by either the beginning of the precipitation of CH or by the formation of a sufficient amount of CSH gel.

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In this paper, we will consider the effect of including a retarder in the reaction scheme described by Preece, Billingham and King [5] for the hydration of pure C_3S. This retarder binds to calcium ions, making them unavailable for precipitation as either CSH gel or CH. We will see that the action of such a retarder is to significantly increase the thickening time of the system.
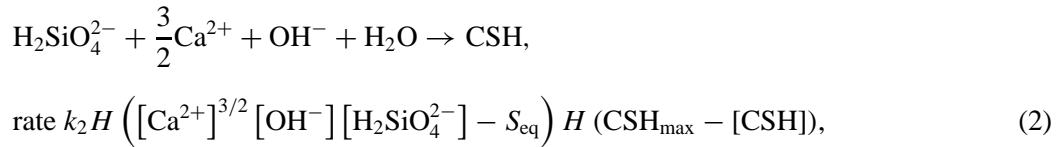
2. The mathematical model

We consider the dissolution of a spherical grain of C_3S that lies in $0 \le r \le r_0$. During the induction period, which we study here, only a small amount of this grain dissolves, so we assume that the boundary of the grain is fixed at $r = r_0$. We take into account the presence of other grains of C_3S by allowing no flux of chemicals through a spherical boundary at $r = r_1$. Initially, the grain is surrounded by water with a uniform initial concentration of the retarder alone. We assume that the chemical species react and diffuse in the region $r_0 < r < r_1$. Since the diffusivities of these ions differ only slightly, we assume equal diffusivities, D, for simplicity.

The three chemical reactions that we assume dominate the early stages of the hydration of C_3S are firstly, a surface reaction at $r = r_0$, the dissolution of C_3S,

$$C_3S + 3H_2O \rightarrow 3Ca^{2+} + 4OH^- + H_2SiO_4^{2-}, \quad \text{rate } k_1, \tag{1}$$
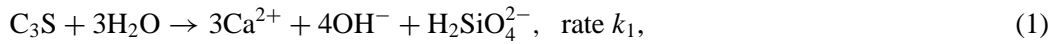
and secondly, two bulk reactions, the precipitation of CSH gel,

$$H_2SiO_4^{2-} + \frac{3}{2}Ca^{2+} + OH^- + H_2O \rightarrow CSH,$$

$$\text{rate } k_2 H \left(\left[Ca^{2+} \right]^{3/2} \left[OH^- \right] \left[H_2SiO_4^{2-} \right] - S_{eq} \right) H \left(CSH_{max} - [CSH] \right), \tag{2}$$

and the binding of calcium ions to the retarder,

$$Ca^{2+} + R \rightarrow CaR, \quad \text{rate } k_3 \left[Ca^{2+} \right] [R], \tag{3}$$

where CaR is a retarder/calcium ion complex, which remains in solution. In these rate laws, k_1, k_2 and k_3 are reaction-rate constants and H is the Heaviside step function. The dissolution of C_3S proceeds at a constant rate. The precipitation of CSH proceeds at a constant rate, provided that the solubility product exceeds its equilibrium value, S_{eq}, and the concentration of CSH is below CSH_{max}, a concentration that represents saturation with CSH. The binding of calcium ions to the retarder follows the law of mass action. Note that we have not explicitly included the precipitation of calcium hydroxide, $Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2 = CH$. Once the solubility product, $[Ca^{2+}][OH^-]^2$, reaches its saturated value, the precipitation of calcium hydroxide will occur. As we noted earlier, the end of the thickening period may be signalled either by this precipitation or by that of a sufficient quantity of CSH gel. For further discussion of the reaction scheme and the associated reaction rate laws, see [5].

Suitable scales with which to nondimensionalize the variables are $\left[S_{eq} \right]^{2/7}$, r_0 and r_0^2/D for concentrations, distance and time, respectively. This leads to the dimensionless initial/boundary value problem

$$\frac{\partial \alpha}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial \alpha}{\partial \rho} \right) - \frac{3}{2} \bar{k}_2 H \left(\alpha^{3/2} \beta \gamma - 1 \right) H \left(\delta_{max} - \delta \right) - \bar{k}_3 \alpha \theta, \tag{4}$$

$$\frac{\partial \beta}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial \beta}{\partial \rho} \right) - \bar{k}_2 H \left(\alpha^{3/2} \beta \gamma - 1 \right) H \left(\delta_{\max} - \delta \right), \tag{5}$$

$$\frac{\partial \gamma}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial \gamma}{\partial \rho} \right) - \bar{k}_2 H \left(\alpha^{3/2} \beta \gamma - 1 \right) H \left(\delta_{\max} - \delta \right), \tag{6}$$

$$\frac{\partial \delta}{\partial \tau} = \bar{k}_2 H \left(\alpha^{3/2} \beta \gamma - 1 \right) H \left(\delta_{\max} - \delta \right), \tag{7}$$

$$\frac{\partial \theta}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial \theta}{\partial \rho} \right) - \bar{k}_3 \alpha \theta, \tag{8}$$

to be solved subject to

$$\frac{\partial \alpha}{\partial \rho} = -3\bar{k}_1, \quad \frac{\partial \beta}{\partial \rho} = -4\bar{k}_1, \quad \frac{\partial \gamma}{\partial \rho} = -\bar{k}_1, \quad \frac{\partial \theta}{\partial \rho} = 0 \text{ at } \rho = 1, \tag{9}$$

$$\frac{\partial \alpha}{\partial \rho} = \frac{\partial \beta}{\partial \rho} = \frac{\partial \gamma}{\partial \rho} = \frac{\partial \theta}{\partial \rho} = 0 \text{ at } \rho = \rho_1, \tag{10}$$

$$\alpha = \beta = \gamma = \delta = 0, \quad \theta = \theta_0 \text{ when } \tau = 0 \text{ for } 1 < \rho < \rho_1. \tag{11}$$

The dimensionless chemical concentrations are

$$\alpha = \frac{\left[\mathrm{Ca}^{2+} \right]}{S_{\mathrm{eq}}^{2/7}}, \quad \beta = \frac{\left[\mathrm{OH}^- \right]}{S_{\mathrm{eq}}^{2/7}}, \quad \gamma = \frac{\left[\mathrm{H_2SiO_4^{2-}} \right]}{S_{\mathrm{eq}}^{2/7}}, \quad \delta = \frac{\left[\mathrm{CSH} \right]}{S_{\mathrm{eq}}^{2/7}}, \quad \theta = \frac{\left[\mathrm{R} \right]}{S_{\mathrm{eq}}^{2/7}}.$$

The dimensionless reaction rate constants are

$$\bar{k}_1 = \frac{k_1 r_0}{D S_{\mathrm{eq}}^{2/7}}, \quad \bar{k}_2 = \frac{k_2 r_0^2}{D S_{\mathrm{eq}}^{2/7}}, \quad \bar{k}_3 = \frac{k_3 r_0^2 S_{\mathrm{eq}}^{2/7}}{D};$$

$\delta_{\max} = \mathrm{CSH}_{\max} / S_{\mathrm{eq}}^{2/7}$ is the dimensionless maximum concentration of CSH gel, θ_0 is the dimensionless initial concentration of the retarder and $\rho_1 = r_1 / r_0$ is the dimensionless radius of the outer boundary. Note that the water/cement ratio, by mass, is $\left(\rho_1^3 - 1 \right) / \mu$, where $\mu \approx 3 \cdot 12$ is the relative density of C$_3$S.

3. Asymptotic solution

We are interested in the solution of (4) to (11) when the retarder reacts rapidly to bind with calcium ions, so we seek an asymptotic solution valid when $\bar{k}_3^{-1} \ll 1$. Since $\alpha = \beta = \gamma = 0$ when $\tau = 0$, we are mainly interested in the solution when $H \left(\alpha^{3/2} \beta \gamma - 1 \right) = 0$, and there is no precipitation of CSH gel ($\delta = 0$). In particular, if we write $\epsilon = \bar{k}_3^{-1}$ for notational convenience, we want to solve

$$\frac{\partial \alpha}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial \alpha}{\partial \rho} \right) - \epsilon^{-1} \alpha \theta, \tag{12}$$

$$\frac{\partial \theta}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial \theta}{\partial \rho} \right) - \epsilon^{-1} \alpha \theta, \tag{13}$$

subject to

$$\frac{\partial \alpha}{\partial \rho} = -3\bar{k}_1, \quad \frac{\partial \theta}{\partial \rho} = 0 \text{ at } \rho = 1, \tag{14}$$

$$\frac{\partial \alpha}{\partial \rho} = \frac{\partial \theta}{\partial \rho} = 0 \text{ at } \rho = \rho_1, \tag{15}$$

$$\alpha = 0, \quad \theta = \theta_0 \text{ when } \tau = 0 \text{ for } 1 < \rho < \rho_1, \tag{16}$$

with $\epsilon \ll 1$. The concentrations of hydroxide and silicate ions, β and γ, simply diffuse independently of α and θ until CSH gel begins to form.

3.1. INITIAL TRANSIENT, $\tau = O(\epsilon)$

Although (12) suggests that α is exponentially small, we know from (14) that $\partial \alpha / \partial \rho = O(1)$ at $\rho = 1$. This suggests that we require a boundary layer at $\rho = 1$. The richest balance of terms can be obtained by the rescaling

$$\rho = 1 + \epsilon^{1/2}\hat{\rho}, \quad \tau = \epsilon\hat{\tau}, \quad \alpha = \epsilon^{1/2}\hat{\alpha}, \quad \theta = \theta_0 + \epsilon^{1/2}\hat{\theta}, \tag{17}$$

with $\hat{\rho}, \hat{\tau}, \hat{\alpha}, \hat{\theta} = O(1)$ for $\epsilon \ll 1$. Note that when $\hat{\tau} = O(1)$, $\tau = O(\epsilon) \ll 1$, so that this scaling captures the initial transient behaviour of the solution. In terms of the variables (17), (12) to (16) become

$$\frac{\partial \hat{\alpha}}{\partial \hat{\tau}} = \frac{1}{\left(1 + \epsilon^{1/2}\hat{\rho}\right)^2} \frac{\partial}{\partial \hat{\rho}} \left\{ \left(1 + \epsilon^{1/2}\hat{\rho}\right)^2 \frac{\partial \hat{\alpha}}{\partial \hat{\rho}} \right\} - \hat{\alpha}\left(\theta_0 + \epsilon^{1/2}\hat{\theta}\right), \tag{18}$$

$$\frac{\partial \hat{\theta}}{\partial \hat{\tau}} = \frac{1}{\left(1 + \epsilon^{1/2}\hat{\rho}\right)^2} \frac{\partial}{\partial \hat{\rho}} \left\{ \left(1 + \epsilon^{1/2}\hat{\rho}\right)^2 \frac{\partial \hat{\theta}}{\partial \hat{\rho}} \right\} - \hat{\alpha}\left(\theta_0 + \epsilon^{1/2}\hat{\theta}\right), \tag{19}$$

subject to

$$\frac{\partial \hat{\alpha}}{\partial \hat{\rho}} = -3\bar{k}_1, \quad \frac{\partial \hat{\theta}}{\partial \hat{\rho}} = 0 \text{ at } \hat{\rho} = 0, \tag{20}$$

$$\frac{\partial \hat{\alpha}}{\partial \hat{\rho}} = \frac{\partial \hat{\theta}}{\partial \hat{\rho}} = 0 \text{ at } \hat{\rho} = \epsilon^{-1/2}(\rho_1 - 1), \tag{21}$$

$$\hat{\alpha} = \hat{\theta} = 0 \text{ when } \hat{\tau} = 0 \text{ for } 0 < \hat{\rho} < \epsilon^{-1/2}(\rho_1 - 1). \tag{22}$$

At leading order, we must therefore solve

$$\frac{\partial \hat{\alpha}}{\partial \hat{\tau}} = \frac{\partial^2 \hat{\alpha}}{\partial \hat{\rho}^2} - \theta_0\hat{\alpha}, \tag{23}$$

$$\frac{\partial \hat{\theta}}{\partial \hat{\tau}} = \frac{\partial^2 \hat{\theta}}{\partial \hat{\rho}^2} - \theta_0\hat{\alpha}, \tag{24}$$

subject to

$$\frac{\partial \hat{\alpha}}{\partial \hat{\rho}} = -3\bar{k}_1, \quad \frac{\partial \hat{\theta}}{\partial \hat{\rho}} = 0 \ \text{ at } \hat{\rho} = 0, \tag{25}$$

$$\hat{\alpha} \to 0, \ \hat{\theta} \to 0 \ \text{ as } \hat{\rho} \to \infty, \tag{26}$$

$$\hat{\alpha} = \hat{\theta} = 0 \ \text{ when } \hat{\tau} = 0 \text{ for } \hat{\rho} > 0. \tag{27}$$

By taking a Laplace transform of (23) we find that

$$\alpha = \frac{3\bar{k}_1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{e^{s\hat{\tau} - \sqrt{s+\theta_0}\hat{\rho}}}{s\sqrt{s+\theta_0}} \, ds,$$

where c is a strictly positive real constant. By closing this contour in the left half plane, we find that

$$\hat{\alpha} = \frac{3\bar{k}_1 e^{-\sqrt{\theta_0}\hat{\rho}}}{\sqrt{\theta_0}} - \frac{3\bar{k}_1 e^{-\theta_0\hat{\tau}}}{\pi} \int_0^\infty \frac{e^{-u\hat{\tau}} \cos\left(\hat{\rho}\sqrt{u}\right)}{u\,(u+\theta_0)} \, du. \tag{28}$$

As $\hat{\tau} \to \infty$, the second term tends to zero exponentially fast, and we conclude that this is an initial transient that allows the solution to adjust from its initial value of zero to the steady state solution, which is represented by the first term. As $\hat{\rho} \to \infty$, $\hat{\alpha} \to 0$ exponentially fast, and we conclude that $\hat{\alpha}$ is exponentially small outside this boundary layer.

We can solve for $\hat{\theta}$ by noting that $\partial(\hat{\alpha} - \hat{\theta})/\partial\hat{\rho}$ is a similarity solution of the diffusion equation. We find that

$$\hat{\theta} = \hat{\alpha} - 3\bar{k}_1 \left\{ \sqrt{\frac{4\hat{\tau}}{\pi}} \exp\left(-\frac{\hat{\rho}^2}{4\hat{\tau}}\right) - \hat{\rho}\,\text{erfc}\left(\frac{\hat{\rho}}{2\sqrt{\hat{\tau}}}\right) \right\}. \tag{29}$$

As $\hat{\rho} \to \infty$, $\hat{\theta}$ decays exponentially fast, and we conclude that $\hat{\theta}$ is also exponentially small outside the boundary layer. As $\hat{\tau} \to \infty$, $\hat{\theta} \sim -3\bar{k}_1\sqrt{4\hat{\tau}/\pi}$ for $\hat{\rho} = O(1)$, which gives

$$\theta \sim \theta_0 - \epsilon^{1/2} 3\bar{k}_1 \sqrt{\frac{4\hat{\tau}}{\pi}}.$$

This expansion is non-uniform when $\hat{\tau} = O(\epsilon^{-1})$, $\tau = O(1)$.

3.2. Steady consumption of calcium ions, $\tau = O(1)$

The structure that emerges from the initial transient is of a boundary layer with width of $O(\epsilon)$ and an outer region where α is exponentially small.

3.2.1. *Boundary layer*
In the boundary layer, when $\tau = O(1)$,

$$\frac{\partial^2 \hat{\alpha}}{\partial \hat{\rho}^2} - \hat{\alpha}\theta = O(\epsilon^{1/2}), \tag{30}$$

$$\frac{\partial^2 \theta}{\partial \hat{\rho}^2} - \epsilon^{1/2}\hat{\alpha}\theta = O(\epsilon), \tag{31}$$

subject to

$$\frac{\partial \hat{\alpha}}{\partial \hat{\rho}} = -3\bar{k}_1, \quad \frac{\partial \theta}{\partial \hat{\rho}} = 0 \text{ at } \hat{\rho} = 0, \tag{32}$$

and, from matching to the initial transient solution as $\tau \to 0$,

$$\hat{\alpha} = \frac{3\bar{k}_1 e^{-\sqrt{\theta_0}\hat{\rho}}}{\sqrt{\theta_0}}, \quad \theta = \theta_0 \text{ when } \tau = 0 \text{ for } \hat{\rho} > 0. \tag{33}$$

If we now expand

$$\theta = \bar{\theta}_0 + \epsilon^{1/2}\bar{\theta}_1 + O(\epsilon),$$

we find that θ is spatially-uniform at leading order, with $\bar{\theta}_0 \equiv \bar{\theta}_0(\tau)$. At leading order, this gives

$$\hat{\alpha} = \frac{3\bar{k}_1 e^{-\sqrt{\bar{\theta}_0(\tau)}\hat{\rho}}}{\sqrt{\bar{\theta}_0(\tau)}}, \tag{34}$$

which then shows that

$$\bar{\theta}_1 = A_1(\tau) + 3\bar{k}_1 \left(\hat{\rho} + \frac{e^{-\sqrt{\bar{\theta}_0}\hat{\rho}}}{\sqrt{\bar{\theta}_0}} \right), \tag{35}$$

where $A_1(\tau)$ is undetermined at this order. To complete the solution, we must determine $\bar{\theta}_0(\tau)$ by matching with the outer solution.

3.2.2. *Outer solution*
In the outer region, $O(\epsilon^{1/2}) < \rho < \rho_1$, α is exponentially small, so that, to all algebraic orders, the retarder simply diffuses in the bulk, with

$$\frac{\partial \theta}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial \theta}{\partial \rho} \right), \tag{36}$$

subject to

$$\frac{\partial \theta}{\partial \rho} = 0 \text{ at } \rho = \rho_1. \tag{37}$$

In order to match with the boundary-layer solution, we note that, as $\hat{\rho} \to \infty$, the boundary-layer solution has

$$\theta \sim \bar{\theta}_0(\tau) + 3\bar{k}_1 \epsilon^{1/2}\hat{\rho} = \bar{\theta}_0(\tau) + 3\bar{k}_1(\rho - 1),$$

and hence that the appropriate matching condition is

$$\frac{\partial \theta}{\partial \rho} = 3\bar{k}_1 \text{ at } \rho = 1. \tag{38}$$

There is therefore a flux of retarder into the boundary layer that exactly balances the flux of calcium ions into solution. These two species react rapidly in the boundary layer to form the complex CaR.

In this outer region, we must therefore solve (36) subject to (33), (37) and (38), which determines $\bar{\theta}_0(\tau) = \theta(1, \tau)$. We could solve this initial/boundary value problem using Laplace

transforms, but this would just lead to a complicated and impenetrable formula. Fortunately, we are only really interested in the solution at large times.

3.3. LARGE-TIME SOLUTION, $\tau \gg 1$

The initial/boundary-value problem given by (36) subject to (33), (37) and (38) represents a diffusion problem on a bounded domain with a constant rate of influx. After a long time, when diffusion has distributed the retarder uniformly across the domain, at leading order we therefore expect that the concentration θ grows linearly with time whilst being spatially uniform. We can verify this by looking for an asymptotic solution, valid for $\tau \gg 1$, of the form

$$\theta = f_0(\rho)\tau + f_1(\rho) + o(1). \tag{39}$$

In addition, by integrating (36) over $1 \le \rho \le \rho_1$ we obtain

$$\int_1^{\rho_1} \frac{\partial(\rho^2\theta)}{\partial\tau}\,\mathrm{d}\rho = \left[\rho^2\frac{\partial\theta}{\partial\rho}\right]_1^{\rho_1} = -3\bar{k}_1,$$

and hence, by integrating again with respect to τ,

$$\int_1^{\rho_1} \rho^2\theta(\rho,\tau)\,\mathrm{d}\rho = \frac{1}{3}\left(\rho_1^3 - 1\right)\theta_0 - 3\bar{k}_1\tau. \tag{40}$$

This simply states that the total amount of retarder in the system is equal to the initial amount less the amount that has diffused into the boundary layer and been bound to calcium ions. In particular, substituting (39) in (40) gives

$$\int_1^{\rho_1} \rho^2 f_0(\rho)\,\mathrm{d}\rho = -3\bar{k}_1, \quad \int_1^{\rho_1} \rho^2 f_1(\rho)\,\mathrm{d}\rho = \frac{1}{3}\left(\rho_1^3 - 1\right)\theta_0. \tag{41}$$

These formulae will enable us to fix two otherwise undetermined constants later.

On substituting the expansion (39) in (36), (33) and (37), we obtain, at $O(\tau)$,

$$\left(\rho^2 f_0'\right)' = 0, \quad \text{subject to } f_0' = 0 \text{ at } \rho = 1 \text{ and } \rho = \rho_1.$$

This means that f_0 is a constant and, using (41),

$$f_0 = -\frac{9\bar{k}_1}{\rho_1^3 - 1}.$$

At $O(1)$,

$$\left(\rho^2 f_1'\right)' = \rho^2 f_0, \quad \text{subject to } f_1' = 3\bar{k}_1 \text{ at } \rho = 1 \text{ and } f_1' = 0 \text{ at } \rho = \rho_1.$$

This has solution

$$f_1 = \frac{1}{3}f_0\left(\frac{1}{2}\rho^2 + \frac{\rho_1^3}{\rho}\right) + c_1,$$

which is monotone increasing with ρ, and satisfies both boundary conditions whatever the value of the constant c_1. However, on substituting this solution in (41), we can determine c_1 and arrive at
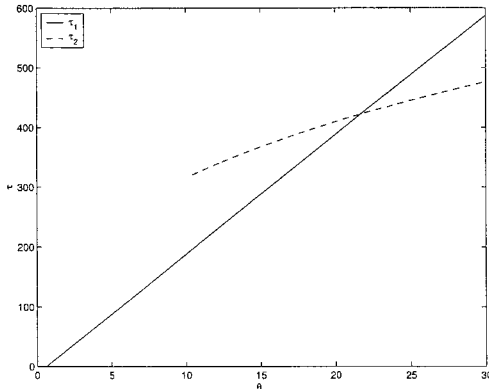
Figure 1. The times τ_1 and τ_2 (for $\theta_0 > \bar{k}^{3/5} \approx$ 10·5) when $\bar{k}_1 = 0\cdot35$, $\bar{k}_3 = 50$ and $\rho_1 = 4$.
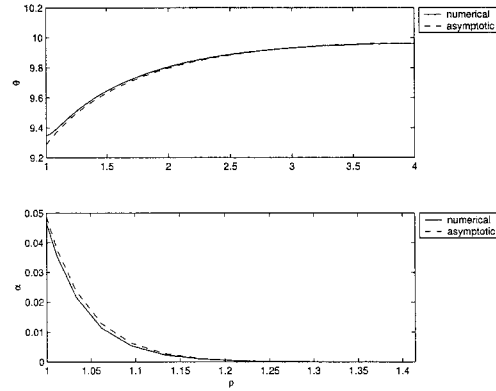
Figure 2. The numerical and asymptotic solutions for α and θ when $\tau = 2$, $\theta_0 = 10$, $\bar{k}_1 = 0\cdot35$, $\bar{k}_3 = 50$ and $\rho_1 = 4$.

$$f_1 = \theta_0 + \frac{9\bar{k}_1}{(\rho_1^3 - 1)^2}\left(\frac{3}{5}\rho_1^5 - \frac{1}{2}\rho_1^3 - \frac{1}{10}\right) - \frac{3\bar{k}_1}{\rho_1^3 - 1}\left(\frac{1}{2}\rho^2 + \frac{\rho_1^3}{\rho}\right),$$

and hence

$$
\begin{aligned}
\theta =\ & \theta_0 + \frac{9\bar{k}_1}{(\rho_1^3 - 1)^2}\left(\frac{3}{5}\rho_1^5 - \frac{1}{2}\rho_1^3 - \frac{1}{10}\right) - \frac{3\bar{k}_1}{\rho_1^3 - 1}\left(\frac{1}{2}\rho^2 + \frac{\rho_1^3}{\rho}\right) \\
& - \frac{9\bar{k}_1}{\rho_1^3 - 1}\tau + o(1)\ \text{ for } \tau \gg 1.
\end{aligned}
\tag{42}
$$

The minimum value of $\bar{\theta}_0$ is therefore

$$\bar{\theta}_0 = \theta(1, \tau) \sim \theta_0 - \frac{3\bar{k}_1\left(5\rho_1^6 - 9\rho_1^5 + 5\rho_1^3 - 1\right)}{5\left(\rho_1^3 - 1\right)^2} - \frac{9\bar{k}_1}{\rho_1^3 - 1}\tau \ \text{ as } \tau \to \infty. \tag{43}$$

We can use this value in (34) to determine how the calcium ion concentration behaves in the boundary layer for $\tau \gg 1$.

We are now in a position to ask when the solution that we have constructed becomes nonuniform. There are two possibilities. Firstly, if θ_0 is sufficiently large, we can use (43) to determine when the concentration of the retarder becomes small at $\rho = 1$. This occurs when $\tau \approx \tau_1$, where

$$\tau_1 = \frac{\rho_1^3 - 1}{9\bar{k}_1}\theta_0 - \frac{5\rho_1^6 - 9\rho_1^5 + 5\rho_1^3 - 1}{15\left(\rho_1^3 - 1\right)}. \tag{44}$$

In effect, we assume that (43) remains asymptotic, even though the two terms in the expansion for $\tau \gg 1$ may not be uniformly ordered when $\theta_0 \gg 1$.

Secondly, we have assumed that $\alpha^{3/2}\beta\gamma < 1$, so that CSH gel has yet to precipitate out of solution. We know from (34) that

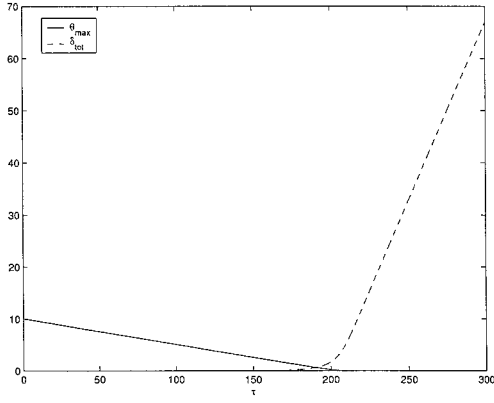$$\alpha(1, \tau) \sim \epsilon^{1/2}\frac{3\bar{k}_1}{\sqrt{\bar{\theta}_0}},$$

Figure 3. The total amount of CSH gel, δ_{tot} and the maximum concentration of retarder, θ_{max}, as functions of time, with $\theta_0 = 10$, $\bar{k}_1 = 0.35$, $\bar{k}_3 = 50$ and $\rho_1 = 4$.
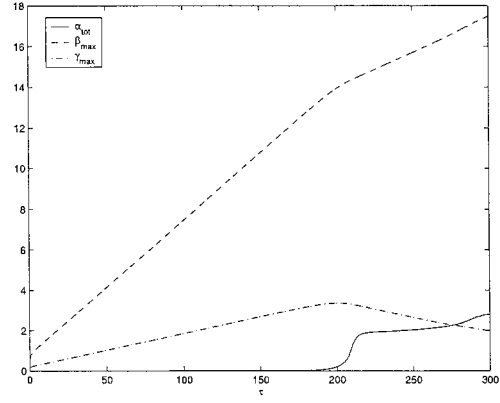

Figure 4. The total amount of calcium ion, α_{tot} and the maximum concentrations of hydroxide and silicate ions, β_{max} and γ_{max}, as functions of time, when $\tau = 2$, $\theta_0 = 10$, $\bar{k}_1 = 0.35$, $\bar{k}_3 = 50$ and $\rho_1 = 4$.

and that for $\theta_0 \gg 9\bar{k}_1\tau/(\rho_1^3 - 1)$, so that there is a sufficient initial concentration of the retarder that little has been consumed, $\bar{\theta}_0 \sim \theta_0$ and

$$\alpha(1, \tau) \sim \epsilon^{1/2}\frac{3\bar{k}_1}{\sqrt{\theta_0}}.$$

By determining the large time solutions for β and γ in the same way as we did for θ, we find that

$$\beta(1, \tau) \sim \frac{12\bar{k}_1}{\rho_1^3 - 1}\tau, \quad \gamma(1, \tau) \sim \frac{3\bar{k}_1}{\rho_1^3 - 1}\tau,$$

and hence

$$\alpha^{3/2}\beta\gamma \sim \epsilon^{3/4}\frac{96\sqrt{3}\bar{k}_1^{7/2}}{\left(\rho_1^3 - 1\right)^2 \theta_0^{3/4}}\tau^2 \quad \text{as } \tau \to \infty \text{ for } \theta_0 \gg \tau.$$

CSH gel therefore begins to precipitate when $\tau \approx \tau_2$, where

$$\tau_2 = \left(\frac{\theta_0}{\epsilon}\right)^{3/8}\frac{\rho_1^3 - 1}{\bar{k}_1^{7/4}\sqrt{96\sqrt{3}}}. \tag{45}$$

This is only true provided $\theta_0 \gg \tau_2$, and hence $\theta_0 \gg \epsilon^{-3/5} = \bar{k}_3^{3/5}$. The times τ_1 and τ_2 are shown in Figure 1 for the typical values $\bar{k}_1 = 0.35$, $\bar{k}_3 = 50$ and $\rho_1 = 4$. We can see that $\tau_1 = \tau_2$ when $\theta_0 = \theta_0^* \approx 21.7$. For $\theta_0 < \theta_0^*$, we would expect that the retarder will run out before any CSH gel is formed, whilst for $\theta_0 > \theta_0^*$, we expect that some CSH gel will be formed when $\tau > \tau_2$, because the concentrations of the OH$^-$ and H$_2$SiO$_4^{2-}$ ions become large enough for the solubility product to exceed S$_{eq}$, even though the concentration of Ca^{2+} ions is small.
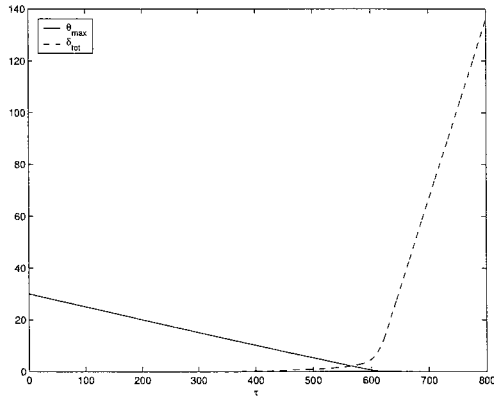
Figure 5. The total amount of CSH gel, δ_{tot} and the maximum concentration of retarder, θ_{max}, as functions of time, with $\theta_0 = 30$, $\bar{k}_1 = 0.35$, $\bar{k}_3 = 50$ and $\rho_1 = 4$.
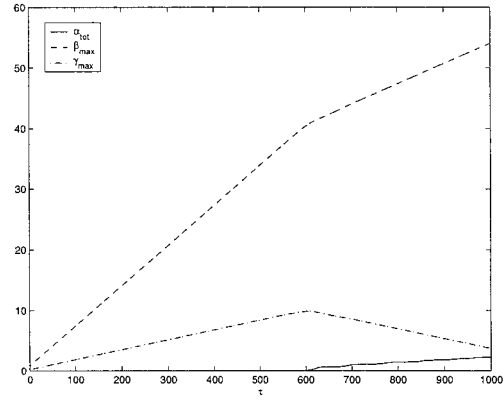

Figure 6. The total amount of calcium ion, α_{tot} and the maximum concentrations of hydroxide and silicate ions, β_{max} and γ_{max}, as functions of time, with $\theta_0 = 30$, $\bar{k}_1 = 0.35$, $\bar{k}_3 = 50$ and $\rho_1 = 4$.

4. Numerical solutions

In order to solve the initial/boundary-value problem (4) to (11) numerically, we use an explicit finite-difference scheme with a nonuniform spatial grid that clusters more points near to $\rho = 1$, where the steepest gradients occur. For more details, see [5]. We will focus our attention on the solution when $\bar{k}_1 = 0.35$, $\bar{k}_3 = 50$ and $\rho_1 = 4$. When $\theta_0 = 10 < \theta_0^*$, we expect that the retarder will be completely bound to calcium ions before any CSH gel is formed. Figure 2 shows α and θ when $\tau = 2$, calculated both numerically and using the asymptotic solutions, (34) and (42). Even though τ is not very large, the agreement is excellent. Figure 3 shows the total amount of CSH gel,

$$\delta_{tot} = \int_1^{\rho_1} \rho^2 \delta \, d\rho$$

and the maximum concentration of retarder, θ_{max}, as functions of time, τ. We can see that as $\tau \to \tau_1 \approx 187$, $\theta_{max} \to 0$ (the retarder runs out), and δ_{tot} starts to increase. Figure 4 shows that the calcium-ion concentration also starts to increase when $\tau \approx \tau_1$, since it is no longer immediately bound to the retarder, and also that the concentration of hydroxide ion starts to increase less rapidly, whilst that of silicate ion begins to fall, as they are consumed in the reaction that produces CSH gel.

We now consider what happens when we increase the initial amount of retarder to $\theta_0 = 30$, when $\tau_1 \approx 588 > \tau_2 \approx 476$. As $\tau \to \tau_2$, as predicted, CSH gel starts to form, as can be seen in Figure 5. However, there is no significant increase in the concentration of calcium ions, α, until $\tau \to \tau_1$, when the retarder is completely bound to calcium ions, as shown in Figure 6. In addition, the concentration of CSH gel grows significantly faster once $\tau > \tau_1$.

If we believe that the end of the induction period occurs when CSH gel starts to form, then the induction period has duration τ_1. If we believe that the end of the induction period occurs when calcium hydroxide starts to precipitate, then the induction period is longer than τ_1, and ends once $\alpha\beta^2$, the solubility product for $Ca(OH)_2$, reaches its saturated value. Note that the

precipitation of CSH gel follows the pattern, described in detail in [5], of forming in layers of successively increasing radius.

5. Conclusions

In this paper, we have studied how a retarder that binds to calcium ions can influence the hydration of tricalcium silicate, the major constituent of oilwell cement. We used a dissolution-precipitation mechanism introduced by Preece *et al.* [5], and showed that the action of such a retarder can significantly increase the length of the thickening time. We used asymptotic analysis, later verified by numerical integration, to quantify this effect. This allowed us to obtain analytical expressions for the time at which the retarder is completely bound to calcium ions, (44), and when CSH gel starts to form in the presence of uncomplexed retarder (45).

Although this mechanism provides a possible explanation for the retardation of the thickening of pure tricalcium silicate, the retardation of the thickening of an oilwell cement slurry is probably more complex. In particular, it seems likely that the interaction between phosphonate retarders and ettringite, the hydration product of tricalcium aluminate (C_3A) in the presence of sulphate ions provided by gypsum, is of crucial importance [4]. This is the focus of our current work [6].

Acknowledgement

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