Early-Age Stress and Pressure Developments in a Wellbore Cement Liner: Application to Eccentric Geometries

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Early-Age Stress and Pressure Developments in a Wellbore Cement Liner: Application to Eccentric Geometries

This paper introduces a predictive model for the stress and pressure evolutions in a wellbore cement liner at early ages. A pressure state equation is derived that observes the coupling of the elastic changes of the solid matrix, the eigenstress developments in the solid and porespaces, and the mass consumption of water in course of the reaction. Here, the transient constitution of the solid volume necessitates advancing the mechanical state of the poroelastic cement skeleton incrementally and at constant hydration degree. Next, analytic function theory is employed to assess the localization of stresses along the steel–cement (SC) and rock–cement (RC) interfaces by placing the casing eccentrically with respect to the wellbore hole. Though the energy release rate due to complete debonding of either interface is only marginally influenced by the eccentricity, the risk of evolving a microcrack along the thick portion of the sheath is substantially increased. Additionally, it is observed that the risk of microannulus formation is principally affected by the pressure rebound, which is engendered by the slowing reaction rate and amplified for rock boundaries with low permeability. [DOI: 10.1115/1.4034013]

1 Introduction

To maintain the benefits of natural gas as a safe transition energy source, drilling contractors must ensure that wells remain sealed during construction and operation. Accordingly, a cement barrier is placed into the annular region between the steel production casing and the wellbore hole. Nonetheless, Ingraffea et al. note that in Pennsylvania 6.2% (1.0%) of unconventional (conventional) wells drilled between 2000 and 2012 have compromised cement liners [1]. Moreover, it is known that early-age shrinkage phenomena and pore pressure developments are primary contributors to sheath failure: After placement, the curing cement undergoes pore pressure changes, chemical shrinkage phenomena, and eigenstress developments in the calcium–silicate–hydrate (CSH) gel—the binding phase of cement—that cause bulk volume changes [2,3]. Under restraint of the steel and rock boundaries, these volume changes can lead to stresses that impair the integrity of the sheath. A diagram of a typical wellbore system is presented in Fig. 1.

Current work at the molecular and mesoscales is revealing the fundamental driving forces of the cement volume changes and their relation to the CSH packing density [2]. Here, the construction of CSH gel as a system of colloidal particles has evinced net-attractive forces that follow the out-of-equilibrium dynamics of cement hydration. When left unconstrained, this eigenstress $\sigma^*$—a loading that produces no mechanical work—engenders a volume shrinkage of the gel. Additionally, the classification of confined water into free, constrained, and chemically bound water molecules [4] has elucidated the details of the H$_2$O kinetics during hydration and lends opportunity for improvements in modeling the hydrating cement phase morphology. Specifically, the hydration reaction produces a water sink in the paste that is driven by the stoichiometric demand of the cement chemical reaction and the adsorption of H$_2$O molecules onto the CSH gel pore surfaces [5]. This causes a drop in pore pressure $\Delta p$ and, at the engineering scale, incites a fluid exchange between cement and rock formation.

An important design parameter, yet to be studied in connection with the early-age driving forces of cement volume change, is the eccentricity of the production casing with respect to the wellbore hole. In an experimental setup, Albawi investigated the fraction of interfacial debonding due to thermal cycling of specimens containing a centrically and an eccentrically located casing [4]. Using computer tomography, the eccentric casing (with a degree of eccentricity of $\mathcal{E} = 0.5$; at its thinnest portion, the sheath thickness is half the thickness of an equivalent concentric sheath) showed a greater fraction of debonding and subsequent creation of fluid channels. Related finite element simulations show that casing eccentricity can significantly enhance the risk of cement sheath failure [6], and it was noted that the added contribution of shear stress along the interfaces plays an acute role in crack initiation [7]. To the best of our knowledge, no analytic or semi-analytic model is available for the stress and pressure evolutions in a wellbore cement liner at early ages.
solution exists for the boundary value problem of a material domain confined by two eccentric, elastically deforming circular contours. The present work offers sophistication in the design of wellbore cement liners: Section 2 develops a pressure state equation that balances the chemical and mechanical changes of the porosity with the external water supply from the adjacent rock formation. Section 3 is devoted to the derivation of an analytic solution of the stress state of the sheath, where the well-known complex variable method for plane elasticity is employed when the boundary contours are positioned eccentrically. The paper concludes in Sec. 4 by connecting the bulk stress calculations of the coupled chemoporomechanics model to the risk of fracture due to microannulus formation along the SC interface or the RC interface.

2 Incremental State Equations of Stress and Pressure in a Hydrating Cement Sheath

The incremental constitutive relations for the steel, cement paste, and rock are written, in order of appearance, as

\[ d\Sigma(z) = \left(K_c - \frac{2}{3}G_c\right)\text{tr}(dE(z)) + 2G_c\,dE(z) \quad (1a) \]

\[ d\Sigma(z) = \left(K_c - \frac{2}{3}G_c\right)\text{tr}(dE(z)) + 2G_c\,dE(z) + dE^s(z)I \quad (1b) \]

\[ d\Sigma(z) = \left(K_c - \frac{2}{3}G_c\right)\text{tr}(dE(z)) + 2G_c\,dE(z) - b\,dp(z)I \quad (1c) \]

where \( z = x + iy = r e^{i\theta} \) is the position vector in the complex plane, and \( K_d \) and \( G_d \) denote the drained bulk and shear moduli, respectively. The concentric geometry is depicted in Fig. 1, where the material domains are rigidly connected along the surfaces \( \{z\} = r_1 \) and \( \{z\} = r_2 \). The internal loading of the cement paste drives the bulk stress development of the system, where \( dE^s = [(1 - b)\,d\sigma^s - b\,dp] \) is the incremental change in the bulk eigenstress. Specifically, \( d\sigma^s \) accounts for the eigenstress in the solid phase and \( dp \) accounts for the pressure in the porespace, which are connected to the macroscale via the Biot coefficient, \( b \) [8]. It should further be noted that the growth of the solid volume during the cement hydration stiffens the material, such that \( K_c, G_c, \) and \( b \) are functions of the hydration degree \( \xi \) (see Fig. 2). As the pressure in the cement drops, the pressure in the rock in proximity to RC experiences a similar change. As a consequence, \( dp \) has been accounted for in Eq. (1c), where \( b \) is the Biot coefficient of the rock, herein assumed to be 1.

In the paragraphs to follow, we describe the origin of the pressure drop and connect it to the exchange of water with the rock formation.

2.1 Mass Balance of Water. The porespace of cement may broadly be categorized into macro pores (capillary pores) and gel pores (formed in the CSH gel). Using the Lagrangian porosity \( \phi \), the total pore volume at a given hydration degree \( \xi \) and incremental loading \( d(p, \sigma^s, E_c) \) per unit initial reference volume, the fluid mass content is defined as \( m = \rho_o \phi \), where \( \rho_o \) denotes the fluid mass density [9]. Under drained and saturated conditions, the mass content of a representative elementary volume (REV) obeys

\[ \frac{dm}{dr} = M_0 - (\delta m_{hyd} + \delta m_{surf}) \quad (2) \]

where the temporal change in fluid mass \( dm/dr \) is driven by the difference in the external water supply, \( M_0 \), and the use of \( \text{H}_2\text{O} \) molecules in the creation of CSH \((\delta m_{hyd} + \delta m_{surf})\). To elaborate:

(i) The stoichiometric sink term \( \delta m_{hyd} \), also termed water of constitution or structural water [10], refers to the observation that 1 g of cement requires between \( \approx 0.20-0.25 \) g of water to produce CSH and calcium hydroxide products. Translated into volume fractions, this stoichiometric term thus reads

\[ \frac{\delta m_{hyd}}{\rho_o} = \rho_c \frac{\rho_o}{\rho_l} \frac{\xi}{\delta t} \frac{\frac{\delta \xi}{\delta t}}{\delta t} = \beta_{hyd} \frac{\delta \xi}{\delta t} \quad (3) \]

where \( \rho_c / \rho_l = 3.15 \) is the cement-to-liquid mass density ratio, and \( \beta_{hyd} \) is the initial cement volume content. \( \delta z/\delta t \) is the reaction rate, which is described by a hydration kinetics law (e.g., Ref. [11], see Appendix B). For \( w/c = 0.45 \), the stoichiometric sink term is on the order of \( \beta_{hyd} \approx 0.27-0.33 \).

(ii) The adsorption sink term \( \delta m_{surf} \) was discovered by Powers [12] and has recently been quantified by reactive molecular simulations that traced the state of water in CSH [13]. The driving force of the adsorption sink term is the interaction potential, that is, the interparticle potential between the water adsorbed on the CSH gel pore surface and the bulk water in the gel pores, which in good approximation can be viewed as constant over the hydration process. Given the surface nature of the adsorption phenomena, the rate of water adsorption is scaled by the change of the surface area of the gel porosity, or more generally, by the specific surface area

\[ \frac{\delta m_{surf}}{\rho_o} = 2\xi w_{\text{c.-w}} n_{\text{H}_2\text{O}} M_w \left( \frac{\delta S_{\text{gel}}}{\delta t} \frac{\delta \xi}{\delta t} \right) = \beta_{surf} \frac{\delta \xi}{\delta t} \quad (4) \]

where \( w_{\text{c.-w}} \) is the number of C–w bonds per surface, approximated at 2.4 bonds/mm²; \( n_{\text{H}_2\text{O}} = \text{number of water molecules per bond} \approx 10 \text{H}_2\text{O} \); \( M_w = 18 \text{ g/mol} \) is the molar mass of water; and \( S_{\text{gel}} \) is the gel pore surface, which has been shown to increase almost linearly with the hydration degree [14,15]. A rough estimate of this term is provided by considering that the specific surface of cement paste \( S_{\text{gel}} / \beta \approx 168 \text{ m}^2 / \text{g} \), as calculated from a colloidal mesoscale simulation for \( w/c = 0.45 \) paste [16], where \( \beta \approx 2 \text{ g/cm}^3 \) is the average paste density. Thus, \( \beta_{surf} \approx 0.12-0.43 \), which means that the surface adsorption term is of the same order of magnitude as the stoichiometric sink term.

The change in the mass content accounted for in Eq. (2) is likewise obtained by considering the differential variation in the porosity and the fluid compressibility.
Development. Once the pressure state equation (Eq. (6)) is across the cement domain. This is not the case for an eccentrically concentric annular geometry results in a uniform volumetric strain produces gradients in strain. Nonetheless, a uniform loading of a of the steel and the rock interfaces. As the cement contracts or of water to the gelpore surfaces, and the growth of the solid skele-
cement system: the stoichiometric water demand, the adsorption water consumption by the reaction. The effective sink term quan-

d = \frac{d\phi}{dt} \bigg|_{p, \sigma, E_c} + \frac{d\phi}{dt} \bigg|_{\xi} + \frac{d\rho_b}{dt} \phi \tag{5}

(i) The first term, \(d\phi|_{p, \sigma, E_c}\), measures the change in the porosity due to the morphology of the REV phases—calculated at constant pressure \(p\), eigenstress \(\sigma^e\), and volumetric strain \(E_c\). In poromechanics literature, this term is coined the chemical porosity \([9,17]\). Both the changes in the capillary and the gel pores contribute to this term, such that the evolution of \(\phi|_{p, \sigma, E_c}\) in function of \(\xi\) is depicted by the dashed contour in the inset of Fig. 2.

(ii) The second term, \(d\phi|_{\xi}\), measures, at constant hydration degree, the change in porosity due to the loading of the pore–solid system. More specifically, it measures the deformation of the solid skeleton due to an infinitesimal increment of volume strain, pressure, and eigenstress loading \((d\sigma, p, \sigma^e)\) \([9]\).

(iii) The final term \((d\rho_b/\rho_b)\phi\) quantifies the mass change due to the compressibility of the fluid, where, under iso-
ternal conditions, \(d\rho_b/\rho_b = dp/\rho_b\) with \(1/\rho_b\) being the fluid compressibility, i.e., the inverse of the fluid bulk modulus, \(k_b\).

Equating the mass balances described by Eqs. (2) and (5), one can write the state equation for the fluid mass content in cement paste under isothermal hydration as

\[
\frac{dE_c}{dt} + \frac{1}{N} \frac{d\sigma}{dt} + \frac{1}{M} \frac{dp}{dt} = k_c \frac{\rho_b N}{\eta_h} \frac{\sqrt{\rho_p}}{M} \frac{1}{\tau_{hyd}} \beta_{eff} \tag{6}
\]

where \(\xi\) has passed the solid percolation threshold \(\xi_0\), and \(dp/dt = 0\) otherwise. The first term on the left-hand side (l.h.s.) of the equation quantifies the effect on the porespace due to an incre-
mental bulk volume strain \(dE_c\), of the REV as per definition of the Biot coefficient \(b(\xi)\). The second term on the l.h.s. models the effect of the eigenstress development in the CSH gel, where \(N(\xi)\) is the corresponding Biot modulus of the solid matrix. The third

term on the l.h.s. accounts for the change in pore pressure and its influence in compressing both the solid matrix and the fluid in the macro- and gel pores, \(1/M(\xi) = 1/N + \phi/k_b\). Finally, the terms on the right-hand side of the equation quantify, in order of appearance, the Laplacian \((\nabla^2)\) of the pore pressure and the effective water sink. Here, \(k_c\), \(\rho_b\), and \(\eta_h\) are the cement permeability, fluid density, and fluid viscosity, respectively, while \(\tau_{hyd} = (d\xi/dt)^{-1}\) is the characteristic time of cement hydration, dictating the rate of water consumption by the reaction. The effective sink term quanti-
tifies the combined effect of the physicochemical changes to the cement system: the stoichiometric water demand, the adsorption of water to the gel pore surfaces, and the growth of the solid skeleton; \(\beta_{eff} = \beta_{hyd} + \beta_{surf} + d\phi|_{p, \sigma, E_c}/d\xi_c\).

2.2 Simplifying Assumption of Uniform Bulk Eigenstress Development. Once the pressure state equation (Eq. (6)) is applied to the boundary value problem of the cement sheath, the pore pressure varies according to the restraints and flux conditions of the steel and the rock interfaces. As the cement contracts or expands, the difference in the resistance of the steel and the rock produces gradients in strain. Nonetheless, a uniform loading of a concentric annular geometry results in a uniform volumetric strain across the cement domain. This is not the case for an eccentrically placed casing, where a gradient in \(E_c\) develops due to the nonuni-
form distribution of hydrating matter around the casing. Additional-
ly, the no-flux boundary condition along the steel and permeable boundary of the soil causes fluid to travel into the cement sheath only along the outer interface upon water consumption by the reaction. Thus, a gradient in pressure is necessitated along RC.

Yet, the coupling of Eq. (6) to the macroscopic stress field is vastly simplified without loss of predictive power, if, in good approximation, the solid eigenstress and pressure developments can be assumed to develop uniformly. More precisely, we are enabled to apply the effective bulk eigenstress \(\sigma^e(\xi) = (1-b)\sigma^e(\xi) - b dp(\xi)\) directly along the boundary contours to calculate the equivalent stress field of the domain.

Small-to-moderate eccentricities of the casing maintain a mean stress field that is approximately uniform. By inspecting the stress state in the cement due to a uniform increment \(d\Sigma^e\) and \(D_c = 0.8\), where the derivation of the stress state is presented in Sec. 3 and input parameters are presented in Table 1, the radial and tangential stresses varied by \(\sim 25\%\) of the applied load, while the mean stress varied by less than \(2\%\) over the cement body. Though the stiffness of the cement and rock may differ from the values chosen, model results by varying these parameters showed no appreciable growth in the mean stress gradient relative to the radial gradients of \(\Sigma_r\) and \(\Sigma_0\). Consequently, \(E_c\) may reasonably be considered uniform without incurring error beyond the uncertain-
ty posed by the model parameters.

Because the eigenstress development of the CSH gel phase is an intrinsic property of the cement and the mix design is assumed homogeneous, it remains only to outline the conditions that render the spatial variations in the pressure negligible to solve \((\sigma^e, p, E_c)\) as approximately uniform.

2.2.1 Two Key Time Scales. Isolating the pressure components of Eq. (6) and nondimensionalizing, the normalized diffusion length of the pressure within the sheath is revealed as \(\delta_p(\xi) = \sqrt{\xi_0/\eta_h} \left( r_2 - r_1 \right) \). Here, \(\lambda_p(\xi) = k_c(\xi)\rho_b/\eta_h\) is the hydraulic conductivity of the cement, \(\tau_{hyd}(\xi)\) is the characteristic time of hydration, and \(\delta_p \geq 1\) allows the pressure to be modeled as uniform in good estimation. It must be remembered that the perme-
ability of the sheath \(k_c\) changes with the microtexture of the cement and is directly related to the capillary porosity \([18–20]\). Thus, near the beginning of the hydration reaction \(\lambda_p\) is large, rapidly equilibrating the pressure in the sheath. At later stages of the reaction when \(\lambda_p\) decreases, the hydration kinetics slow (i.e., \(\tau_{hyd}\) becomes large) to further minimize developments of the pressure variations.

Instead of resolving the pressure field explicitly, the dynamics are further investigated by discretizing Darcy’s law to model the flow of water between the formation and the sheath

\[
\frac{d\rho_o}{dt} = \frac{\rho_o}{\eta_h} \left( \frac{k_r}{k_c} + \frac{l_s}{k_r} \right)^{-1} - p_0 \tag{7}
\]

where \(p_0\) is the far-field formation pressure, and the above Newton coefficient depends on the flow characteristics of the cement and the rock via

\[
\lambda_B = \frac{\rho_o}{\eta_h} \left( \frac{k_r}{k_c} + \frac{l_s}{k_r} \right) \tag{8}
\]

where \(k_r\) is the permeability of the rock, and \(l_s (\lambda_c)\) is the character-

<table>
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<th>Geometry (cm)</th>
<th>Elastic constants (GPa)</th>
<th>Newton coeff. (s⁻¹)</th>
<th>Eigenstress (MPa)</th>
<th>Eff. sink term</th>
<th>Ref. pressure (MPa)</th>
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<td>15.4</td>
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Table 1 Model input parameters

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(cement). Moreover, the discretized expression for the fluid velocity allows us to relate the volume of the water consumed during the reaction \(d\Omega_{\text{link}}/dt \sim \pi(r_2^2 - r_1^2)/\tau_{\text{hyd}}\) and the volume of water entering along the RC boundary \(d\Omega_{\text{link}}/dt \sim \lambda_0 M r_2^2/\rho_0\). Comparison of these two quantities shows that the pressure dynamics depend on two characteristic time scales

\[
\frac{d\Omega_{\text{link}}}{d\Omega_{\text{link}}} \sim \frac{2M\Omega_{\text{hyd}}}{\rho_0 r_2 (1 - r_1^2/r_2^2)} = \frac{\tau_{\text{hyd}}}{\tau_1}
\]

such that the characteristic time of hydration \(\tau_{\text{hyd}} = \frac{dt}{d\xi}\) competes with the characteristic time of fluid influx \(\tau_0 = \rho_0 r_2 (1 - r_1^2/r_2^2)/(2M\lambda_0)\) to change the pressure. Considering the parameters governing the fluid mobility in the cement and the formation and the hydration kinetics, several regimes of the pressure development emerge.

2.2.2 Sample Pressure Output of the Poromechanics Model. Table 1 and Fig. 2 provide the input parameters for the sample simulations presented in this paper; additional information on the calculation of the poroelastic constants is given in Appendix C. We chose to restrict ourselves to typical conditions encountered during primary cementing operations. In doing so, the parameters \(\lambda_0, \rho_0, \) and \(\zeta_0\) were adjusted within the range of observable values to allow model resemblance with the pressure evolution of typical wellbore measurements. Figure 3 demonstrates the dependence of the pressure changes within the sheath on the ratio between the characteristic time of hydration and the characteristic time of mass exchange (\(\tau_{\text{hyd}}/\tau_0\)):

(I) At early curing times, the rate of the hydration reaction is fast compared to the rate of recharge \(\tau_{\text{hyd}}/\tau_0 \sim 10^{-100}\), producing a rapid decrease in the cement pressure. Here, \(\kappa_s\) is large and the water entering the cement sheath moves rapidly to equilibrate the pressure in the cement. It is thus the rock permeability that limits influx of water to the sheath, and the exchange coefficient in Eq. (8) tends toward \(\lambda_0 \to \left(\rho_0/\eta_h\right)\left(k_s/l_i\right)\). Because \(\tau_{\text{hyd}}\) is small, the initial, rapid decrease in pressure is the dominant mechanism of the bulk eigenstress development. This is well exhibited by comparing the driving forces in Fig. 3(a) to the pressure changes in Fig. 3(b).

(II) At a degree of hydration of \(\zeta \approx 0.35\), the water demand of the reaction and the changes in the porespace are balanced by the Darcy flux into the annulus, such that a pressure minimum is realized. It is at this transition stage and during the early recovery of the pressure toward the equilibrium value of the far-field formation pressure that the uniformity of the pressure is most approximate. Nonetheless, the pressure has passed its minimum value, and hence, the local extremum in the loading conditions has expired. The percolation of a dense solid matrix decreases \(k_s\), such that the pressure gradients are expected to evolve as a fringe along RC.

(III) For a more mature paste, the rate of the hydration reaction slows, and the pressure changes in the cement are principally affected by the influx of water. \(\tau_{\text{hyd}}/\tau_0 \sim 10^{-1}\). As a consequence, the decreased permeability of the cement drives variations in pressure. However, as the hydration reaction progresses, the incremental bulk eigenstress \(d\Sigma^*\) is dominated by \(d\pi\) in the CSH gel phase. Again, we assume \(l_s\) to be small and limited by the dimension of the sheath and \(l_i\) to be large and controlled by the pressure drop in (I), such that the Newton coefficient is approximated as \(\lambda_0 \to \left(\rho_0/\eta_h\right)\left(k_s/l_i\right)\).

For a low-to-moderately eccentric geometry, it is remarked that any pressure gradient in the radial direction far exceeds the gradient in the tangential direction: The distance over which the pressure varies is larger, \(2\pi r_2 > r_3 - r_1\), and gradients develop principally due to the radial influx of water. As a consequence, an assumption of uniform radial pressure similarly implies tangential uniformity. Accepting the conditions for the uniform treatment of the pressure and the CSH eigenstress development, the state equation in Eq. (6) can be simplified to the discrete form

\[
M_b \frac{d(E_h)}{d\xi} = \frac{M d\Sigma^*}{N d\xi} + \frac{dp}{d\xi} = \frac{\tau_{\text{hyd}}}{\tau_0} (1 - \bar{\rho}) - \frac{M}{\rho_0} \bar{\rho}_{\text{eff}}
\]

where \(\xi > \zeta_0\) and \(dp/d\xi = 0\) otherwise. The variables \(\bar{\rho} = \rho/\rho_0\) and \(\bar{\sigma} = \sigma/\rho_0\) are the normalized quantities of the pressure and solid eigenstress, and the brackets around \(E_h\) indicate its mean field value.

3 Stress and Pressure Elevations

In the next segment of the paper, we couple the discrete version of pressure state equation (Eq. (10)) to the loading incurred by the boundary restraints. Though the solution assumes a linear elastic material behavior, nonlinearity arises due to the growth of the system volume, which is delineated by the boundary of the REV and the interface between solid and porespace. Hence, the out-of-equilibrium calculation of the mass growth is separated from the incremental loading of the solid (see Appendix of Ref. [5] for a more detailed thermodynamic reasoning).

3.1 The Case of a Concentrically Placed Casing. In a concentric geometry and for plane strain, the displacement solution, evaluated at a constant degree of hydration, is of the well-known form

\[
du_r = du_r e_r = d\Sigma^* \left( C_{11}^r + \frac{C_{22}^r}{r} \right) + dp \left( C_{1}^r + \frac{C_{2}^r}{r} \right)
\]

where \(C_{11}^r\), \(C_{22}^r\), \(C_{1}^r\), and \(C_{2}^r\) are constants determined by the boundary conditions and are given in Appendix A. Moreover, we have separated the mechanical response due to the
loading increments of the bulk eigenstress and pressure, because the SC and RC interfaces differ in their drainage. Substituting the volumetric strain, $δε_{vol} = 6(δΣ_{C1}^+ + p δC_1^+)$, into the pressure equation (Eq. (10)) allows the incremental change in pressure to be calculated as

$$dp|_z = \frac{dε_z}{D^p} + \frac{1}{\eta} \left( \frac{\nu_{hyd}}{\rho} (1 - p) - \frac{M}{p_F} \beta_{ef} \right) - \left( D^r + \frac{M}{N} \right) \frac{dσ_z}{dε_z}$$  \hspace{0.5cm} (12)$$

where $D^r = (C_1^+ - 6h^2MC_1^+)$ and $D^r = (6h(1-h)MC_1^+)$. The results of iteratively updating first $p$ and $Σ$, and then the solid mass are displayed for the pressure in Fig. 3 and for the interfacial radial and tangential stresses in Fig. 4. The simulations were run for a more or less liberal exchange of water between rock and cement ($λ_0 = 1.0 \times 10^{-5} \text{ s}^{-1}$ and $λ_0 = 1.0 \times 10^{-6} \text{ s}^{-1}$).

The effective radial stress (Figs. 4(a) and 4(b)) in the sheath shows particular sensitivity to the dynamics of the pressure. Initially, during the period of accelerated hydration, a pressure drop is imposed on a relatively incompressible slurry; much of the system is still composed of a fluid mixture of water and cinder grains. As the matter hydrates, the growth of porous CH gel increases the percolation and compressibility of the system. Finally, as the reaction rate slows and upon repressurization, the compressible cement matrix is placed into a state of residual tension. This phenomenon further increases the effective radial tensile stress beyond effects purely due to the eigenstress in the solid and pore space. In fact, if the system were to remain incompressible in course of the pressure evolution, no additional Cauchy stresses would be created. Instead, the hardening sheath is most vulnerable to microannulus percolation and compressibility of the system. Finally, as the reaction rate slows and upon repressurization, the compressible cement matrix is placed into a state of residual tension. This phenomenon further increases the effective radial tensile stress beyond effects purely due to the eigenstress in the solid and pore space. In fact, if the system were to remain incompressible in course of the pressure evolution, no additional Cauchy stresses would be created. Instead, the hardening sheath is most vulnerable to microannulus percolation and compressibility of the system. Finally, as the reaction rate slows and upon repressurization, the compressible cement matrix is placed into a state of residual tension. This phenomenon further increases the effective radial tensile stress beyond effects purely due to the eigenstress in the solid and pore space.

Fig. 4 Bulk effective radial ((a) and (b)) and tangential ((c) and (d)) stress development along the SC interface ((a) and (c)) and the RC interface ((b) and (d)). At complete hydration, a residual $Δp$ remains in the system. Thus, the dashed contours show the asymptotic values of the effective stress, once the pressure has fully recovered to the reference value $p = p_0$.

3.2 The Case of an Eccentrically Placed Casing. The boundary value problem of the cement sheath is complicated when casing eccentricity admits a loss of axisymmetry to the equilibrium equations. Jeffrey [21] is the first to have thoroughly treated the problem of a two-dimensional elastic solid bounded by eccentric circular contours, and his solution admits any prescriptions of traction along the boundaries so long as they are known and can be expressed as analytic functions of the polar argument. The difficulty in the elastic interface continuity conditions of the sheath is that they do not permit an a priori knowledge of the tractions. In the paragraphs to follow, we adopt the approach of seeking $Σ$ and $u$ as series representations, where added care is made to satisfy the elastic response of the bonded steel and rock.

3.2.1 Stress and Displacement Under Conformal Mapping. In our two-dimensional analysis of the sheath, we resort to the well-known Muskhelishvili representation of the incremental stress field [22]

$$dΣ : \begin{cases} dΣ_{rr} - idΣ_{θθ} = \mathcal{Q}(z) + \phi(z) - z\mathcal{Ω}(z) - z\mathcal{Ω}(z) \\ dΣ_{θθ} + idΣ_{rr} = \mathcal{Q}(z) + \phi(z) + z\mathcal{Ω}(z) + z\mathcal{Ω}(z) \end{cases}$$  \hspace{0.5cm} (13)$$

where $κ = 3 - 4ν$ in plane strain, $ϕ$ and $ψ$ are complex potentials holomorphic in the domain of interest, and an overbar denotes complex conjugation. The change in displacement in Cartesian coordinates is given by

$$du : 2G(du_x + idu_y) = \kappa(ϕ(z) - z\mathcal{Ω}(z) - \mathcal{Ω}(z))$$  \hspace{0.5cm} (14)$$

where $ϕ(z) = Ψ(z)$ and $ψ(z) = Ψ(z)$, and it is often more convenient to work with the differentiated form.
Fig. 5 Contour plots of the influence of the shear modulus ratio between rock and cement $G_i / G_c$ and the Newton coefficient $\lambda_0$ on the effective radial stress along SC (left column of panel) and RC (right column) at complete hydration (top row) and once the pressure has completely recovered (bottom row). The casing placement is assumed concentric with the borehole.

\[
\frac{2G}{-iz} \frac{\partial}{\partial \theta} (du_i - idu_s) = \kappa \overline{\phi}(z) - \phi(z) + z \psi(z) + \frac{\bar{z}}{2} \psi(z) \quad (15)
\]

We map the cement interfaces onto circular contours centered at the origin. This allows for the complete description of the contours by their radial coordinate. In doing so, it is necessary to evaluate the stress and displacement of the steel, cement, and rock in separate coordinate systems, the $z$-, $s$-, and $\bar{z}$-planes.

- The steel casing is placed at the center of the physical system in the $z$-plane. This defines the inner and outer surfaces of the casing by $|z| = r_0$ and $|z| = r_1$, respectively.
- The eccentric boundaries of the cement annulus are mapped onto concentric circles in the $s$-plane, defined by $|s| = \rho_1$ and $|s| = \rho_2$, where $s = re^{i\theta}$.
- The wellbore hole is mapped to the $\bar{z}$-plane by translating the $z$-plane in the direction opposite the eccentricity, $d$, such that its surface is described by $|\bar{z}| = r_2$ and $\bar{z} = z - d = re^{i\theta}$.

Movement between the reference and transformed domains of the cement is defined by

\[
s = w(z) = \frac{x + z}{\gamma + \beta z} \quad (16a)
\]
\[
z = w(s) = -\frac{x - \gamma s}{1 - \beta s} \quad (16b)
\]

and shown in Fig. 6. The radii of the transformed interfaces are calculated from the geometry of the physical system by

\[
r_i \rightarrow \rho_j = \frac{\sqrt{1 + (2\beta r_i)^2 - 1}}{2\beta r_i} \quad i, j = 1, 2
\]

where $\beta = d/\sqrt{(r_1^2 - r_0^2)^2 - 2d(r_1^2 + r_2^2) + d^2}$, $x = \beta r_1^2 / (1 - \beta^2 r_1^2)$, $\gamma = (1 + x \beta)$, and $d$ is the eccentricity. Inserting the transformation into Eqs. (13) and (15) allows for the evaluation of stress and displacement in the $s$-plane

\[
d\Sigma_{\rho i} + i d\Sigma_{\rho i} = \overline{\phi}(s) + \phi(s) - \Gamma(s)\phi'(s) - H(s)\chi(s) \quad (18a)
\]
\[
d\Sigma_{\rho i} + i d\Sigma_{\rho i} = \overline{\phi}(s) + \phi(s) + \Gamma(s)\phi'(s) + H(s)\chi(s) \quad (18b)
\]

\[
2G \frac{\partial}{-ic(x)} \frac{\partial}{\partial \theta} (du_i - idu_s) = \overline{\phi}(s) + \phi(s) - \Gamma(s)\phi'(s) - H(s)\chi(s) \quad (18c)
\]

where $\Gamma = s^2 \omega / \rho^2 c^2 = \frac{\gamma}{2} \rho^2 / \chi + (2\gamma - 1) e^{i\theta} - x e^{2i\theta}$ and $H = s^2 \omega / \rho^2 c^2 = \sum_{n=0}^\infty H_n e^{in\theta}$ and

\[
H_n = \begin{cases} 
\beta \rho^2 & \text{if } n = 0 \\
(-2n \rho^2 + (n - 1) \rho^{2n - 2} - 2 + (n + 1) \rho^{2n + 2}) \rho^n & \text{if } n > 0
\end{cases}
\]

\[
\chi(s) = \frac{1}{2} \left[ \frac{d}{ds} \left( \frac{\kappa}{\gamma + \beta s} \right) \right] \quad (19)
\]
where the positive powers of the potentials defining the rock stress remain constant.

The potentials of the Muskhelishvili formalism are sought as Laurent series

\[ \phi_1(z) = \sum_{n=-\infty}^{\infty} A_n^1 z^n, \quad \psi_1(z) = \sum_{n=-\infty}^{\infty} B_n^1 z^n \quad \text{where} \quad z \in S \quad (20a) \]

\[ \varphi(s) = \sum_{n=-\infty}^{\infty} A_n^s s^n, \quad \chi(s) = \sum_{n=-\infty}^{\infty} B_n^s s^n \quad \text{where} \quad \omega(s) = z \in C \quad (20b) \]

\[ \phi_2(\bar{z}) = \sum_{n=-1}^{-3} A_n^2 \bar{z}^n, \quad \psi_2(\bar{z}) = \sum_{n=-3}^{\infty} B_n^2 \bar{z}^n \quad \text{where} \quad \bar{z} - d = \bar{z} \in R \quad (20c) \]

where the positive powers of the potentials defining the rock stress have been truncated to keep the solution bounded as \( z \to \infty \). We may further set \( A_{-1}^1 = 0 \) and \( B_{-3}^1 = 0 \) on account that the far-field stress remains constant.

The total stress in the sheath is calculated by linearly superposing the real-valued stress \( \Sigma^e \) in \( \rho_1 < |s| < \rho_2 \) onto the boundary value problem. Complete continuity of traction and displacement ensures that both the normal and shear stresses generated by the shrinking cement specimen are transferred to the steel and rock. Solving for a divergence-free stress field, the boundary conditions are summarized as follows:

1. The inner surface of the steel casing is assumed traction-free \((0 < \theta < 2\pi)\)

\[ \overline{\phi_1} + \phi_1 - z \phi_1' - \frac{z}{2} \psi_1 = 0 \quad r = r_0 \quad (21) \]

2. A rigid connection between steel and cement implies traction and displacement continuity along SC \((r = r_1, 0 < \theta < 2\pi)\) and \( \rho = \rho_1, 0 < \vartheta < \theta < 2\pi)\)

\[ \overline{\phi_1} + \phi_1 - z \phi_1' - \frac{z}{2} \psi_1 = \overline{\psi_1} + \phi_1 - \frac{z}{2} \psi_1 = \frac{z}{2} \psi_1 = \frac{z}{2} \psi_1 = G_1/G_2 [\overline{\sigma} - \phi_1 - \Gamma \phi - H_f] \quad (22a) \]

\[ \overline{\phi} - \phi_1 - z \phi_1' - \frac{z}{2} \psi_1 = G_1/G_2 [\overline{\sigma} - \phi_1 - \Gamma \phi - H_f] \quad (22b) \]

3. A rigid bond of the cement to the wellbore hole implies traction and displacement continuity along RC \((\bar{r} = \bar{r}_2; 0 < \theta < 2\pi)\) and \( \rho = \rho_2, 0 < \vartheta < 2\pi)\)

\[ \overline{\phi_2} + \phi_2 - (\bar{z} + d e^{i\theta}) \phi_2' - \frac{\bar{z}}{2} \psi_2 - dp = \overline{\psi_2} + \phi_2 - \frac{z}{2} \psi_2 = G_1/G_2 [\overline{\sigma} - \phi_1 - \Gamma \phi - H_f] \quad (23a) \]

\[ \overline{\phi_2} - \phi_2 - (\bar{z} + d e^{i\theta}) \phi_2' - \frac{\bar{z}}{2} \psi_2 = G_1/G_2 [\overline{\sigma} - \phi_1 - \Gamma \phi - H_f] \quad (23b) \]

3.2.3 Matching the Boundary Arguments. It is readily noticed that the boundary conditions above are expressed as mutually non-orthogonal modes of \( e^{i\theta} \), \( e^{i\theta/2} \), and \( e^{i\theta/3} \). With the help of Eq. (16b), the arguments along SC and RC are connected by

\[ f(\theta) + if(\theta + \pi/2) = \begin{cases} e^{i\theta} = \sigma(s = \rho_1 e^{i\theta}/r_1) & \text{if } r = r_1 \to \rho = \rho_1 \\ e^{i\theta} = (\sigma(s = \rho_2 e^{i\theta}) - d)/r_2 & \text{if } r = r_2 \to \rho = \rho_2 \end{cases} \quad (24) \]

Furthermore, the analytic mapping of \( s \to \bar{z} \) along \( z \in SC \) allows the mode \( e^{i\theta/3} \) to be evaluated as a power series

\[ e^{i\theta/3} = \sum_{n=1}^{\infty} k_n \eta_n e^{i\theta/3} \quad (25) \]

In evaluating the coefficients \( k_n \eta_n \), the Chebyshev polynomials of the first kind \( T_n \) allow higher modes \( e^{i\theta/3} \) to be calculated from the relation in Eq. (24), such that the orthogonality condition of the polynomials gives

\[ k_n \eta_n = \frac{2}{\pi} \int_0^\pi \cos(k \theta) T_n(f(\theta)) \frac{d\theta}{d\theta} \quad (26) \]

Here, the discrete approximation is evaluated at the abscissas \( \vartheta_m = \pi(m - 1/2)/N \), and \( k < N \) is required to achieve an accurate result. The same procedure is used to match modes of the \( \bar{z} \) and \( \psi \) coordinate systems along RC (i.e., \( e^{i\theta/3} = \sum_{m=1}^{N} k_n \eta_n e^{i\theta/3} \)).

The remaining calculation of the stress proceeds in the usual manner, where the series relations of the boundary conditions—now expressed solely using the modes \( e^{i\theta/3} \)—are truncated upon convergence to produce a system of equations that determine the coefficients in Eqs. (20a)–(20c).
4 Energy Release Rate Due to the Formation of a Microannulus

For common rock-to-cement stiffness ratios, the eccentricity of the boundaries will produce an increase (decrease) in the effective stress along the thick (thin) portion of the liner for an increment of loading. Here, the increase along the thick portion generally ranges between 10% and 20%, and is spread across a large fraction of the interface, whereas the drop in stress along the thin portion is more significant and spatially concentrated. Additionally, the loss of axisymmetry entails the creation of shear stresses that concentrate near the rock boundary; the rigid body displacement of the steel casing with respect to the wellbore hole reduces $R$ along SC.

The design of wellbore liners has traditionally been framed in the context of stress–strength-based failure criteria [6,23,24]. However, a recent spurt in research is shifting the design paradigm for liners toward predictive poromechanical fracture models [5,7,25,26]. Wang et al. [26], for instance, analyzed crack tunneling by loading the inner surface of the steel casing, and Petersen and Ulm [27] analyzed the early-age radial fracture in a cement sheath. A fracture design of setting cement requires the energy release rate $G$ to be compared to the fracture energy $G_{cr}$, for which the rate of evolution depends on the hydration degree as $\frac{dG_{cr}}{d\xi} \sim 1/\xi$ [28] and we expect the interfacial fracture energy along SC and RC to show a similar trend.

Using Clapeyron’s formula, the risk of failure of the liner due to microannulus formation is stated using the following fracture criterion:

$$G = \frac{\partial \varepsilon_{pot}}{\partial \Gamma} = \frac{\partial W}{\partial \Gamma} = \int_{\Omega} \frac{dG}{ds} \, ds \leq G_{cr} \quad (27)$$

In the above equation, the release of potential energy $\partial \varepsilon_{pot}$ in creating new crack surface area $\partial \Gamma$ may equivalently be regarded as the work done on the crack surfaces $\partial W$ to reverse the infinitesimal fracture process. Hence, $\frac{dG}{ds}$ is the distribution of work done along the boundary $\partial \Omega$ to bring the two fractured surfaces back together. Fracture is substantiated when $G$ equals the interface toughness $G_{cr}$.

Therefore, with the requirement that the interfaces are in tension $(\Sigma(r_{1}) + \Delta P I) > 0$, we obtain for a drained fracture process

$$G = \left\{ \begin{array}{ll}
\frac{1}{2} \int_{\Omega} (\Sigma(r) + \Delta P I) \cdot e_{r} \cdot e_{r} \, ds & \text{if } r = r_{1} \\
\frac{1}{2} \int_{\Omega} (\Sigma(r) + \Delta P I) \cdot e_{r} \cdot e_{r} \, ds & \text{if } r = r_{2}
\end{array} \right. \quad (28)$$

where the term in the absolute value brackets measures the crack opening displacement. Hence, $u_{i}(u_{j})$ is the displacement of the debonded inner (outer) sheath boundary with respect to the position before setting. The displacement must also account for the effects of a fluid pressure $p$ acting on the newly created surfaces, such that the fractured steel (rock) interface displaces by $\Delta r_{1}/\xi_{1} (\Delta r_{2}/\xi_{2})$.

In Fig. 7(a), we display the progression of $G$ corresponding to the evolution of $\Sigma_{r} + p$ in Fig. 4 for $\lambda_{0} = 1 \times 10^{-3} \text{s}^{-1}$ and we have adopted the normalization, $G = G_{r}^{\infty}/2\pi \Sigma_{r}^{\infty}$, where $G_{r}^{\infty}$ and $\Sigma_{r}^{\infty}$ are the terminal values ($t \to \infty$; $\Delta P = 0$) of the cement sheath modulus and the effective radial stress, respectively, and $2\pi r_{i} (i = 1, 2)$ is a measure of the crack length. In the plot, $G$ increases rapidly upon entering the tensile stress regime and achieves normalized values $\sim 0.1$–1.4 upon recovery to the formation pressure (indicated by the dashed lines). Here, it is remarked that the pressure recovery more drastically amplifies the energy release rate along SC. Next, Fig. 7(b) shows $G$ at $t \to \infty$ in function of $G_{cr}/G_{r}$, where a low rock stiffness increases the system’s compliance and, as a consequence, the normalized energy release rate. This must be contrasted with the reduced effective stresses entailed by the soft system (displayed in Fig. 5), such that the dimensional quantity $G$ typically increases for larger $G_{cr}$.

To quantify the increased risk posed by casing eccentricity, Fig. 8 shows the distribution of work done along SC and RC to reverse a microannulus, i.e., the integrands written in Eq. (28), which have been normalized with respect to the uniform distribution of the concentric geometry. While the $\sim 10\%$ increase in work done along the thicker portion of the annulus along RC (Fig. 8(b)) coincides with the increase in the radial stress distribution, it is counterintuitive to observe a reduction of $dG/d\theta$ along the entirety of SC for large eccentricities (Fig. 8(a)). In other words, casing eccentricity can reduce the risk of complete debonding along SC. Next, the increased risk of crack initiation is aptly quantified by considering the presence of a small flaw or microcrack along either interface, where the crack length is much smaller than the thicknesses of the casing and the sheath, $l \ll r_{1} - r_{0} < r_{2} - r_{1}$. For such a crack, we can neglect the influence of the curvature of the boundaries, such that the condition of a crack between two semi-infinite material half-spaces can be assumed. The analytic behavior of such interface cracks is well
understood [30], where the energy release rate for crack initiation scales as 

\[ G_i = \frac{1}{2} R_{rr} \left( h \right)^2 + \frac{R_{r} h \left( h \right)^2}{C_1}, \]

and \( R_{rr} + D_p > 0 \). The \( \theta \)-dependence of crack initiation is plotted in Figs. 8(c) and 8(d) for SC and RC for the terminal stress states of our sample simulation. Normalized by the value of the concentric geometry, \( G_i \) increases for both SC and RC along the thick portion of the sheath, reaching maxima of \( \sim 1.08 \) and \( \sim 1.30 \), respectively. Hence, the introduction of casing eccentricity universally amplifies the prospect of crack formation.

To conclude, we display the relation between the maximum value of \( G_i \) along the interfaces and the rock-to-cement stiffness ratio in Fig. 9. The plot shows that an eccentrically placed casing increases the risk of crack initiation most drastically for soft formations, and it is noted that the normalized values for the low and high permeability scenarios differ due to the effects of their incremental loading histories. Interestingly, in decreasing the stiffness of the rock, the curve displaying \( G_i \) along SC for the highly permeable formation decreases to 1. This marks the ratio \( G_i/G_c \) at which the loading along SC transitions from tensile to compressive. Conversely, the increased repressurization at the end of hydration prevents a similar transition for \( k_{fs} = 1.0 \times 10^{-6} \text{ s}^{-1} \).

5 Conclusions

An analysis of the early-age pressure and stress evolution in a wellbore cement sheath has been conducted. We derived a pressure state equation by balancing the chemical and mechanical changes of the capillary porespace. Tracing the morphology of the phase volume fractions, and incorporating the loading due to eigenstress and pressure, we calculated the exchange of fluid with the adjacent rock formation. Though the model acts under the assumption of saturated, creep-free deformation, it nonetheless captures the underlying physics of the pressure and stress evolution. For a growing solid volume, the stress and pressure were advanced incrementally, which elucidated a critical phenomenon: the increase in cement compressibility in a lowered pressure environment poses a grave risk of microannulus formation upon repressurization. This highlights the system’s permeability as the primary predictor of the final state of the radial effective stress.

Second, an analytic solution for the stress state of the sheath hydrating between two elastic eccentric boundaries was derived and used to infer the added risk of fracture. For a concentric geometry, it was found that high rock stiffness increases the effective radial stress along the boundaries, where \( G \propto (\Sigma_{rr} + \Delta p)^2 \).
though the simultaneous reduction in the system’s compliance curbs the boundary displacement and consequently $G$ upon fracture. Next, the effect of casing eccentricity was inspected in the context of fracture. It was found that $G$ for complete debonding of the interfaces is typically not substantially increased and in some cases even decreases along SC. Instead, there is a higher risk of crack initiation due to the localization of stresses and addition of the shear traction.

By shifting from stress–strength-based failure criteria toward fracture modeling and incorporating the chemoporous nature of the cement paste, the design of cement liners is progressed toward predictive, physics-based tools.

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Table 2: Phase volume fractions and homogenized poroelastic constants for an REV at the characteristic length scales, levels I–III. The Biot coefficients and Biot moduli at the three scales are derived in Refs. [5] and [32].

<table>
<thead>
<tr>
<th>Level I (CSH solid + gelpores)</th>
<th>Level II (CSH gel + macropores)</th>
<th>Level III (hydrating matrix, CSH gel, macropores, and nonreactive inclusions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference volume $V_i = V_{hp}$</td>
<td>$V_{III} = V_i + V_c + V_{ac}$</td>
<td>$V_{III} = V_i + V_k + V_{ac}$</td>
</tr>
<tr>
<td>Matrix fraction $n_i = \eta$</td>
<td>$n_{III} = V_i / V_{III}$</td>
<td>$n_{III} = V_i / V_{III}$</td>
</tr>
<tr>
<td>Inclusion fraction $\phi = 1 - \eta$</td>
<td>$\phi_{III} = V_c / V_{III}$</td>
<td>$f_{inc} = (V_c + V_{ac})/V_{III}$</td>
</tr>
<tr>
<td>Total porosity $\phi_i^0 = \phi$</td>
<td>$\phi_{III}^0 = \phi_{III}^0 + n_i \phi$</td>
<td>$\phi_{III}^0 = \phi_{III}^0 + \phi_{acc}$</td>
</tr>
<tr>
<td>Biot coefficient $b_i = 1 - k_i \eta_i$</td>
<td>$b_{III} = 1 - k_{III} \eta_{III}$</td>
<td>$b_{III} = \eta_{III}$</td>
</tr>
<tr>
<td>Solid Biot modulus</td>
<td>$\frac{n_i}{k_{III}} = \phi_i^0 / \eta_i$</td>
<td>$\frac{n_{III}}{k_{III}} = \phi_{III}^0 / \eta_{III} + \phi_{acc}$</td>
</tr>
</tbody>
</table>

Appendix A: Parameters Defining the Cement Stress Field in a Concentric Geometry

Defining the effective stiffnesses of the steel casing $K_i$ and rock formation $K_s$ as the uniform pressure acting along the outer and inner boundaries, respectively, to produce a unit of radial displacement, we write

$$K_i = 2G_i \left( G_i + 3K_i \right) (\sigma_i^2 - 1) / G_i (3\sigma_i^2 + 1) + 3K_i$$

where $\sigma_i = R_i / R_0$. Hence, the constants defining the stress in the concentric geometry of the sheath are given as

$$C_1 = - \frac{2G_i (1 - \sigma_i^2) + K_s \sigma_i + \sigma_s^2 \sigma_i}{\sigma_s K_s + \sigma_s^2 \sigma_i}$$

$$C_2 = \frac{3(\sigma_s K_s + \sigma_s^2 \sigma_i)}{\Lambda}$$

$$C_3 = - \frac{\Lambda}{\sigma_s K_s + \sigma_s^2 \sigma_i}$$

$$C_4 = \frac{\Lambda}{\sigma_s K_s + \sigma_s^2 \sigma_i}$$

where $\sigma_s = R_s / R_1$ and $\Lambda = 2(4G + 3K)(\sigma_s K_s + \sigma_s^2 \sigma_i) + (1 - \sigma_s^2) (3\sigma_s (\sigma_s^2 - 2K) - 2G (3\sigma_s + \sigma_s) + 4G (3K + G))$.

Appendix B: Arrhenius Law

The hydration reaction is advanced using an Arrhenius type law of the form [31]

$$\frac{dG}{dt} = A(\xi) e^{-Ea/RT} = a \left( \xi \right) \left( 1 - e^{-b \xi} \right)$$

where $a$, $b$, $c$, and $d$ are parameters to be determined by fitting the above functional form to cement calorimetry data. The packing density—the volume ratio between hydrated cement and the hydration products—of the CSH gel is given by

$$\frac{G_s}{G_{sc}} = \frac{G_{sc}}{G_{sc}} = \frac{G_{sc}}{G_{sc}} = \frac{G_{sc}}{G_{sc}} = \frac{G_{sc}}{G_{sc}}$$

Appendix C: Upscaling Procedure of a Three-Level Cement System

The elastic constants of the CSH gel, a granular, colloidal composite, are upcaled via a self-consistent scheme [33], where $K_i / k_i = (4\eta G / g_s) (4G / g_s + 3(1 - \eta) r_s)$

$$\frac{G_i}{K_s} = \frac{5}{4} (1 - \eta) \frac{r_s (2 + \eta)}{16} + \frac{1}{16}$$

where $r_s = K_i / k_s = 2(1 + v_s) / 3(1 - 2v_s) > 0$. Next, the Mori–Tanaka scheme homogenizes the constants for a CSH gel matrix with capillary porosity using $K_{III}/K_1 = (4(1 - \phi_{III}^0) / (4 + 3 \phi_{III}^0 r_1))$ and $G_{III}/G_1 = (8 + 9 r_1 (1 - \phi_{III}^0)) / (8 + 9 r_1 + 6 \phi_{III}^0 r_1)$, where $r_1 = G_1 / G_1$ and $G_1 = (V_s + V_{ac}) / V_{III}$ [27]. Finally, we access the macroscale by incorporating rigid, slippy inclusions (representative of, e.g., silica flour), and the unhydrated clinker grains in a self-consistent scheme: The bulk and shear moduli are calculated as $K_{III}/K_{II} = [3r_s + 4(G_{III}/G_{III}) r_s] / [3(1 - \eta) r_s]$, and

$G_{III} / G_{III} = \frac{1}{24} \frac{1}{(2 - 3\eta_{III})} \left( 8(3 - 2\eta_{III}) - (15 - 24\eta_{III}) r_s \right)$

where $r_{III} = K_{III} / G_{III}$ [34]. Herein, the bulk properties of the CSH solid were assumed $K_s = 49$ GPa and $G_s = 23.5$ GPa [35]. The
remaining relations are found in Table 2, where \( w \) = water, \( c \) = cement clinker, \( hp \) = hydration products, and \( nr \) = nonreactive inclusions.

References


