SIMULATION OF POZZOLAN BLENDED CEMENT HYDRATION

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ABSTRACT:
Pozzolan blended cement hydration reactions, the most promising route towards the sustainability of cementitious materials, have been simulated by Hymostruc, a numerical model for cement hydration and microstructure development. The 3D model calculates the progress of the hydration process as a function of the particle size distribution, water cement ratio, morphological development and chemistry. The paper presents a comparison of numerical results with systematic literature experimental data and demonstrates the potential to use particle-based numerical simulation models (growing spheres) to simulate hydration reactions in blended cement systems.

Keywords: pozzolanic reaction, hydration kinetics, blended cement, numerical modeling.

1. INTRODUCTION

Blending clinker with supplementary cementitious materials (SCM) has been recognized as the most promising route towards the sustainability of cementitious materials [1,2]. The effect of pozzolanic materials on hydration reaction kinetics is complicated with many interactions among the clinker minerals and the pozzolanic additions, and currently there is a large interest in understanding these intricate interactions. The development of numerical models has provided advanced methods to describe the hydration reactions based on the 3D microstructure evolution algorithms. There are two main modelling approaches for such implementations: 1) cellular automata rules applied to digital images (CEMHYD3D [3]) and 2) resolution free growing spheres approach (e.g. Hymostruc [4,5], µic [6]). NIST’s 3D model already includes the description of pozzolanic materials [3]. In this paper, it is presented how the pozzolanic reactions of blended cements is modeled explicitly in Hymostruc. The 3D model simulates the progress of the hydration process as a function of cement replacement ratio, particle size distribution, water-cement ratio, temperature, morphological development and chemistry. The chemical reactions as well as the relation with the morphological changes will be discussed and results of the potential modelling approach will be shown. The validation of such an intricate multi-component hydration kinetics model coupled with the evolving 3-D microstructure incorporating pozzolanic fillers calls for a comparison of the evolution of the component fractions, i.e. reactants and hydration products, over time, with the equivalent experimental data. The paper presents a comparison of numerical results with literature experimental data and demonstrates the potential to use particle-based (growing spheres) numerical simulation models to simulate hydration reactions in blended cement systems. Besides, the implemented SCM module enables the possibility to assess the corresponding microstructural changes as well.

2. MODELING APPROACH

The vision behind the modelling approach is that the primary silicate reactions produce CH and that the secondary reaction uses the SiO₂ content of the pozzolans to react and produce pozzolanic CSH. Here the results are presented only for C₃S blended hydration system. The modeling approach can be also applied for the simulation of the real clinker blended system by employing the multi-component (C₃S, C₂S, C₃A, C₄AF) model of the Portland cement (PC) hydration reactions already implemented within the Hymostruc platform [4-6]. Both the clinker and the pozzolanic fractions follow a certain particle size distribution (PSD) and are taken into account in the modelling approach. According to the Rosin-Ramler equation, the grading of the particles can be calculated per single fraction. A 3D impression of a virtual microstructure is provided in Fig 1 (for simulation parameters please see Sect. 4).
From 3D particle structure, the inter-particle spacing and the paste density can be calculated for each fraction individually. Based on this, the geometrical structure of the paste is available for the hydration simulation. In Hymostruc, the placement and hydration of the individual particles is modeled explicitly following two approaches: 1) a statistically-based cell concept [4], and 2) a full 3D approach [5]. A cell is an elementary paste volume that contains the volume of water and the volume of (blended) cement grains up to a certain fraction, namely one central particle with diameter $x$ and smaller particles ($<x$) assuming homogenous distribution. The rib size of the cell is equal to the mean particle spacing (for details please see [4]). Based on the cell concept, the rate of growth of hydration products (represented by the inner and outer shell, Fig. 2) is followed for each individual fraction. In the full 3D approach these rates are calculated for each individual particle, having random locations. The outer expansion of the particles is calculated according to the so-called particle expansion mechanism (Fig 2) [4]. The expansion mechanism describes the outer growth of a spherical central particle $x$, while embedding the cement and pozzolanic particles. Statistical approach assumes that only particles smaller than the central particle of the cell are embedded in its expanding shell.

The progress of the hydration process is associated by expansion of the particles that fall into the discrete diameter size $x$. At time $t = t_i$, the degree of hydration of particle $x$ is $\alpha_{x}$. The volume of the reacted anhydrous particle is equal to the inner hydration product volume. A particle has a dual entity: $E = c$ for cement and $E = p$ for pozzolan. Therefore, the volume of the outer product $v^E_{\text{outer},x,j}$ is related to the volume of the initial particle $v^E_x$ and its degree of hydration by:

$$v^E_{\text{outer},x,j} = (v^E_{x} - 1)\alpha_{x,j} v^E_{x}$$

(1)

Absence of particles embedded in the shell surrounding particle $x$ would lead to free expansion of this particle.

However, with increasing degree of hydration the outer shell is more and more filled with embedded cement and pozzolan particles. To account for this we calculate the corrected volumetric outer expansion of the particles $v^E_{\text{outer},x,j}$ (with diameter $x$ at time $j$ and an outer volume $v^E_{\text{outer},x,j}$) separately for cement (sup. $E=c$) and pozzolan (sup. $E=p$) particle entities according to statistical approach [4].

$$v^{E}_{\text{outer},x,j} = \frac{v^{E}_{\text{outer},x,j}}{1 - \zeta_{a} (f(\alpha_{c,x,j}) + f(\alpha_{p,x,j})))}$$

(2)

where $\zeta_{a}$ is the shell density (vol. fraction) of particles with a shell surrounding a central particle (for derivation please see [4]). The factors $f(\alpha_{c,x,j})$ are the contributions accounting for the volumetric effect due to the individual potential particle expansion $\nu^j$ ($E=c$ or $p$, for cement or pozzolanic particle entity, respectively), and the degree of hydration for cement grains $\alpha_{c,x,j}$ and for pozzolanic grains $\alpha_{p,x,j}$ according to:

$$f(\alpha_{c,x,j}) = \nu_{c,x,j} \left\{ 1 + (v^E_{c} - 1) \cdot \alpha_{c,x,j} \right\}$$

(3)

and where $\nu_{c,j}$ and $\nu_{p,j}$ are the volumetric contributions of both cementitious materials. With these equations the basis for expansion of the cementitious (here only C$_3$S) and the pozzolanic fraction of SiO$_2$ can be calculated forming the morphology of the developing microstructure. From the individual hydrating phases, (e.g. C$_3$S and SiO$_2$), the molar volumes per gram can be calculated for each fraction. This algorithm implicitly accounts for the effect that smaller particles will hydrate faster than the bigger particles and show a much more rapid increase of the degree of hydration in comparison with the coarser cement particles. However, in terms of mass, the finer pozzolanic fractions contribute less, which also holds for the development of the degree of hydration of the blended system. In the model the degree of hydration of the blended system $\alpha_{x}$ is calculated according to:

$$\alpha_{x}(t) = \alpha_{x,j} = m_{c} \cdot \alpha_{x,j} + m_{p} \cdot \alpha_{p}$$

(4)

where $m_{c}$ is the mass fraction of the cement and $m_{p}$ the
mass fraction of the pozzolan. The virtual microstructure development during hydration is iteratively followed up in order to obtain the basic kinetic equation parameters. For C/S particle the incremental degree of reaction is calculated as:

\[
\Delta \alpha_{C/S} = \left[1 - \frac{\delta_{x,j}^{C/S}}{r'_s}\right] - \left[1 - \frac{\delta_{x,j}^{C/S} + \Delta \delta_{x,j}^{C/S}}{r'_s}\right]
\]

where, \(\delta_x\) is the actual depth of the reaction penetration front, \(\Delta \delta_x\) is the incremental increase of the penetration front within a particular period of hydration time and \(r_s\) the radius of the clinker particle. For the pozzolanic particles the degree of hydration can be calculated analogue to the approach described above. Therefore, for the pozzolanic particles in the system the degree of hydration is calculated according to:

\[
\Delta \alpha_{S/O} = \left[1 - \frac{\delta_{x,j}^{S/O}}{r'_p}\right] - \left[1 - \frac{\delta_{x,j}^{S/O} + \Delta \delta_{x,j}^{S/O}}{r'_p}\right]
\]

where \(r_p\) is the radius of a pozzolanic particle. With these set of equations and with the formulations of the clinker reactions the amount of phases consumed (e.g. C_3S, SiO_2 and H_2O), and the amount of phases produced (CSH and CH) during hydration of a blended system can be calculated as a function of time (degree of hydration), particle size distribution, mineralogical composition, morphological development and temperature.

### 2.1 Pozzolanic Reactions

Modelling of the reactions in the pozzolanic blended cementitious systems is a complex piece of work. Many processes that run at the same time have to be considered and included in the schematization in order to end up with a feasible algorithm. Processes that run during the pozzolanic reaction can be distinguished into different classes, i.e. morphological, physical, and chemical. In terms of the development of the cementitious microstructure, all classes have their own particular characteristic and affect the pozzolanic reaction in a certain way. Within the Hymostruc model Portland cement was the primary starting point for hydration modeling, the results showing good agreement with experimental data for Portland cement based mixtures [4-6]. However, in order to extend the model and to make it suitable for the simulation of blended cement based the silicate reactions are considered together with the pozzolanic reaction as defined by Bentz et al. [3]. Reactions of the C_3S mineral can be summarized as:

\[
C_3S + (3-C/S)H \rightarrow C_{3S}SH_y + (3-C/S)CH
\]

For the numerical calculations in this paper C/S = 1.8 [8] and \(y = 4\) is adopted. Designing a matrix with a blend of Portland cement (PC) and pozzolanic material leads to a hydration process where the secondary pozzolanic reaction is causing a lowering of the calcium hydroxide (CH) content according to:

\[
z\cdot CH + S + (y-z)H \rightarrow C_{3S}SH_y
\]

Pozzolanic reactions generally lower the CSH gels Ca/Si ratio. In the simulation, CH produced by PC hydration reactions is considered to enter the pozzolanic (SF) reaction just in the amount to maintain the Ca/Si ratio of the pozzolanic hydration product (Eq. 8) to \(z = 1.1\) [3]. If there is not enough CH produced by the PC hydration, to satisfy this demand, the pozzolanic reaction will start to consume CSH product obtained by the PC hydration (Eq. 7), thus lowering Ca/Si ratio.

\[
C_{C/S}SH + S \rightarrow C_uSH
\]

Reactions Eqs. 8 and 9 are coupled with the PC hydration reactions of calcium silicates (e.g. Eq. 7) to give a final Eq. 10.

\[
n_{\text{alite}} C_3S + n_S + n_H \rightarrow n_{\text{alite}} C_{3S}SH_{(HS)} + (n_{CH, PC} - n_{CH, pozz})CH
\]

where, \(n_{\text{alite}} \) represents moles of consumed C_3S by the PC reaction; \(n_{CH,PC} \) moles of produced CH by PC hydration; and \(n_S \) and \(n_{CH,pozz}\) moles of consumed S and CH by the pozzolanic reaction, respectively. The moles of produced CH by PC hydration are calculated following the reactions of C_3S mineral (Eq. 7):

\[
n_{CH,PC} = (3 - C/S)n_{\text{alite}}
\]

If there is enough CH in the system the moles of consumed CH by pozzolanic reaction are calculated as \(n_{CH,pozz} = 1.1 \cdot n_S\) [3]. If the demand for CH by the pozzolanic reaction is more than there is CH available, the remaining CH is consumed according to reaction Eq. 8, while the missing C is obtained from Ca rich CSH according to reaction Eq. 9. From the coupled chemical reaction Eq 10, the Ca/Si ratios of CSH gel can be calculated as an equilibrated value (11), \(\overline{\chi}\), considering the compositional equilibrium in CSH from both PC and SF hydration reactions.

\[
\overline{\chi} = \frac{3n_{\text{alite}} + 2n_{\text{belite}} - n_{CH,PC} - n_{CH,pozz}}{n_{\text{alite}} + n_{\text{belite}} + n_S}
\]

In the hydration model Hymostruc, these chemical reaction equations are explicitly modeled enabling the evolution of primary and secondary hydration reactions and the associated evolution of the microstructure. Particle size distributions of both the cementitious and the pozzolanic materials are modeled explicitly enabling the possibility to handle both materials as individual phases.
2.2 Reaction Kinetics

Yajun and Cahyadi [9] considered a Jander diffusion to describe the SF reaction kinetics. They investigated the influence of particle size of SF on the reaction kinetics using only mono-sized sphere model simulations. However, Jander’s diffusion model does not account for the time dependency of the diffusion coefficient and thickness of a diffusing layer (i.e. morphology changes during hydration) nor does it account for the reduction of the amount of water in the system. The microstructure development is the central part of the model, from which the microstructural properties and reaction kinetics are calculated. In the Hymostruc model, hydration kinetics is coupled to the microstructural evolution via the basic reaction rate equation, BRE shown in a reduced form by Eq. (13), and accounts for the actual state of water in the system and the changes in morphology.

\[
\frac{\Delta \delta^E_{\text{m,n,j+1}}}{\Delta t_{j+1}} = K_0^E \cdot F_1^E \cdot \Omega_1 \cdot \Omega_2 \cdot \Omega_3 \cdot \left( \frac{\delta^E_p}{\delta^E_{n,j}} \right)^{\beta_1}
\]

where the rate of penetration of the reaction front in an individual cement particle \( x \) at time \( t \) is calculated, \( K_0 \) is the basic rate factor (\( \mu m/h \)), \( \delta_\text{t} \) the transition thickness (\( \mu m \)) of a hydration product layer \( \delta_{\text{tr,j}} \) at which the reaction for the individual particle changes from a phase boundary (\( \lambda = 0 \)) to a diffusion controlled mechanism (\( \lambda = 1 \)). The rate of the reaction process is driven by the initial rate of penetration (phase boundary reaction mechanism) which is reduced by three so-called reduction coefficients, \( \Omega_1, \Omega_2 \) and \( \Omega_3 \), representing the reduction of water withdrawal of particles in the shell of a central cement particle, the reduction of the available water while emptying of the capillary pores, and the water shortage of the overall system, respectively. A detailed description of the original Hymostruc model is given in [4,5]. The BRE Eq. 13 assumes that the reaction rate is immediately controlled with a phase boundary reaction kinetic mechanism, i.e. starts with the highest possible reaction rate which eventually decreases due to change in surface area, water reduction effects (\( \Omega_3 \)) as well as switch to the diffusion controlled mechanism due to the increasing thickness and densification of the shell of hydration products formed around the dissolving particle. Such a kinetic model is satisfactory only for predicting long term hydration. However, it is not capable of capturing the very early age kinetic behavior, when the rate is governed by a nucleation mechanism.

Therefore, the kinetic model needed improvement by considering the initial increase in reaction rate due to the nucleation of hydration products. An increase of the rate of hydration during nucleation controlled reaction mechanism, is implemented numerically in the BRE by assuming that the hydration rate constant \( K_0 \) is a linear function of the hydration degree of the C3S phase:

\[
K_0^E = K_{\text{m,n}}^E \cdot \alpha^E
\]

The rate constant is recalculated according to Eq. 14 as long as the new improved value is lower than the initial input value for the phase boundary constant \( K_0 \). Otherwise, if the recalculated value of \( K_0 \) (by Eq. 14) exceeds the initial input value for \( K_0 \) this value will be adopted in the BRE and the kinetics is switched to the phase boundary controlled mechanism (i.e. then Eq. 14 is not valid anymore and the user input value for constant \( K_0 \) is used).

For the pozzolanic particles, a similar kinetic modelling methodology has been adopted as for cement particles (therefore \( E = p \) in Eq. 13). The only difference is that the start of the pozzolanic reaction can also depend on the pH threshold parameter (pH evolution is calculated following the approach in [10]).

### 4. SIMULATION

In order to test the potential of the model to simulate the hydration of blended pozzolanic systems the output results are compared with literature [8] experimental data for C3S blended system with 25% of silica fume (SF) addition. The reactive (amorphous) constituent of the SF is assumed to be 95% of the SiO₂ content. Each individual hydration reaction kinetics for C3S and SiO₂ was modeled according to BRE (Eq. 13) with a corresponding set of kinetic input parameters \( K_{\text{m,n}}, \delta_\text{tr}, \) and \( \beta_1 \). Kinetic parameters used for reference C3S and blended hydration system employed for hydration simulation are given in Table 1. The free outer growth of the particle expansion can be calculated according to stoichiometry and densities of components in the reaction equation. The expansion factor for C3S reaction, in this first approach, was considered to be \( \psi = 2.2 \), thus assuming both CSH and CH reaction products to grow in the shell around the C3S particles. Recently, in the 3D kernel, separate nucleation and growth of CH particles in a free capillary pore space was implemented, thus allowing a more realistic microstructural description, however with a high price on computational efficiency. For the pozzolanic reaction the expansion factor of \( \varphi = 3.77 \) is used [3].

#### Table 1 Reaction kinetic parameters

<table>
<thead>
<tr>
<th>System</th>
<th>Phase</th>
<th>( K_{\text{m,n}} ), ( \mu m/h )</th>
<th>( K_0 ), ( \mu m/h )</th>
<th>( \delta_\text{tr} ), ( \mu m )</th>
<th>( \beta_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>C3S</td>
<td>8.0</td>
<td>0.07</td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td>Blended</td>
<td>C3S</td>
<td>8.0</td>
<td>0.45</td>
<td>6.0</td>
<td>7</td>
</tr>
<tr>
<td>Blended</td>
<td>SF</td>
<td>3.0</td>
<td>0.016</td>
<td>0.66</td>
<td>7</td>
</tr>
</tbody>
</table>

#### Table 2 PSD input values for C3S and SF particle

<table>
<thead>
<tr>
<th>Phase</th>
<th>( n )</th>
<th>( b )</th>
<th>Blaine, ( m^3 \text{kg}^{-1} )</th>
<th>Range, ( \mu m )</th>
<th>Fraction width, ( \mu m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3S</td>
<td>1.08</td>
<td>0.04</td>
<td>400</td>
<td>1 - 90</td>
<td>1</td>
</tr>
<tr>
<td>SF</td>
<td>2.00</td>
<td>0.04</td>
<td>1 - 10</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
In the blended model the volumetric expansion of the C3S reaction is effected by the pozzolanic reaction due to the consumption of CH, and therefore the value 2.2 must be corrected in each time increment in order to consider the interaction with the pozzolanic reaction.

4.1 Particle Size Distribution: SF Agglomeration
Both Portland cement and pozzolanic material have their own particle size distribution (PSD). When replacing a percentage of the mass fraction of Portland cement by pozzolanic material, the fineness and packing of the blended material will be affected as well.

In this particular simulation case, the PC with a grain size range of 1 – 90 µm is replaced for 25 % by SF with a grain size range of around 1 – 10 µm (assuming agglomeration of very small SF particles, as discussed later) causing an implicit densification of the particle packing and leading to a denser microstructure. In Hymostruc the PSD of both the Portland cement and the pozzolanic material are taken into account as independent phases and modeled according to the Rosin-Rammler equation. From this, the hydration and the microstructure development can be modeled taking into account the two grain phases: including their particle fractions, chemical and physical interaction.

Silica fume dispersion in cement paste and the impact of undispersed (agglomerated) silica fume on the reaction kinetics and hence on the short and long-term concrete properties still needs a lot of research. The effect of agglomerates of silica fume can be investigated by the developed model by changing the actual PSD of SF material in the simulations. The simulation parameters for the particle size distribution are given in Table 2. The agglomeration of SF was considered by assuming the PSD curve starting from 1µm towards bigger (agglomerated) sizes (Table 1).

5. RESULTS AND DISCUSSION
The presented modeling approach is a valuable tool that can be employed to test hypothesis on fundamental mechanisms involved in hydration of pozzolanic blended cement systems. It can be used to investigate the effects of parameters, such as particle size distribution, agglomeration effects, distribution of hydration products on particles, thickness of the diffusing layer, etc., onto the hydration process. Here the model was tested against the literature experimental data on influence of silica fume (SF) addition (25 %) on C3S hydration. The validation of the multicomponent kinetic model coupled with the evolving 3D microstructure incorporating pozzolans requires experimental data about the evolution of the reactants and hydration products, over time. For crystalline phases, quantitative X-ray diffraction appears to be the most straightforward method for obtaining phase quantification. This would be particularly useful for the PC minerals and crystalline hydration products such as CH. Microscopic (e.g. bse-SEM with EDX microanalysis) image analysis is also a useful technique for analyzing real microstructures at various hydration ages. Thermogravimetric analysis (TGA) provides data on the water released at different temperatures, from which one can quantitatively estimate the CH content of pozzolanic pastes. However, 29Si NMR [8,11] is the only direct method for obtaining the reactivity of amorphous silica and evolution of the CSH gel formation. A combination of all these techniques should be used in order to validate and test the modeling approach.

In Hymostruc, the parking and hydration of the individual particles are modeled explicitly in two ways: 1) an original statistically-based cell concept [4] and a full 3D random based approach [5]. These two approaches differ in positioning of the particles in the system and hence also in the calculation of the particle interactions during hydration. In the first part of the statistically-based approach, to determine the amount of particles found in a fictitious shell around an arbitrary particle $x^r$, a homogeneous (periodic) distribution is assumed, i.e. particles of the same size are assumed to be located at equal (average) distances from each other. In the second part of the calculations, the position of the particles in the paste is not defined explicitly. This second part includes both the calculation of the degree of hydration of the particles present in the shell (i.e. embedded particles) and determination of the physical interaction between the central particle and adjacent particles in this shell. The number of particles involved in the interaction process is thus obtained, in a relatively computationally cheap way, considering the concept of free and embedded particles (for details please see [4]). With a random distribution of particles in the 3D kernel, each particle of the poly-sized cement, as well as of the pozzolana, has a unique position relative to its neighbouring particles. Consequently, also the interaction with the neighbour particles during hydration and microstructure development is unique and so is the effect of the interaction on the rate of hydration of individual particle. Accounting for the different rates of hydration of the individual particles, results in a much higher computational cost. The computation time largely depends on the number of particles that has to be considered. The number of particles increases exponentially with increase of the smallest diameter of the particles, since the smallest fractions (although representing only a relatively small amount of a blended sample) accommodate a huge number of particles. Ignoring the smallest fraction, however, will adversely affect the reliability and consistency of the model [6]. The importance of small particles (and thus computation time limitations) is even more pronounced in the silica fume or fly ash blended systems due to the possibility of extremely fine particle dimensions of such supplementary materials in blended paste. The blended hydration model is implemented in both kernels, statistical and full 3D random. However in this paper only the statistical approach results are presented. Modeling results are validated against the systematic experimental measurements taken from the work of Dobson et al. [8]. They investigated the influence of silica fume (SF) addition (25 %) on C3S hydration, obtained by 29Si NMR and TGA techniques. The results are presented in
in reference cement, to 7 in blended system. Also it is interesting to compare, in Table 1, the influence of SF addition on the transition thickness $\delta_0$ of a hydration product layer at which the reaction for the individual particle changes from a phase boundary ($\lambda = 0$ in Eq. 13) to a diffusion controlled mechanism ($\lambda = 1$). The $\delta_0$ changes from 2.5 $\mu$m to 6 $\mu$m. This could be attributed to the preferential precipitation of the hydration products on the SF particles. The fine particles of SF provide additional surfaces for the growth of CSH precipitating from the pore solution, thus resulting in a reduction of the thickness of CSH around the C3S particles. This effect can be further studied by using the proposed modeling methodology to test hypothesis on fundamental mechanisms involved in pozzolanic blended cement hydration systems and compare the simulation results with the available experimental data. For example, currently we are studying the effect of preferential precipitation of hydration products on SF particles.

Fig. 4 also shows that the kinetic rate Eq. 13 seems to satisfactorily describe the SF reaction curve as obtained by $^{29}$Si NMR quantification. In the presented simulation the diffusion controlled mechanism starts after achieving the shell thickness of $\delta_0 = 1.1$ $\mu$m, while the nature of densification of the diffusion layer is the same as for hydration of C3S particles (same $\beta_1$ values for blended system, in Table 1). The pozzolanic reaction kinetics can also be coupled to the pH evolution of pore solution. The pH evolution is calculated following the approach in [10]. Here, as a first approach, the pH information was used only to determine the commencement of the pozzolanic reaction. The pozzolanic reaction is triggered by reaching a certain pH threshold value set by the user as an input parameter (in this case the nucleation mechanism, i.e. Eq. 14 is not considered). In another approach the nucleation mechanism (Eq. 14) is considered to describe the kinetics of pozzolana (setting the pH threshold to low values so the pozzolana are activated as soon as the water is added in the mix). In future developments the pH calculation will be used to describe the catalytic effect of alkalis onto the dissolution of pozzolana [2,3,10].
When considering the development of the chemical phases the mass of calcium hydroxide (CH) per gram of cement can be calculated with the numerical model and the results compared with experimental data. Fig. 5 shows the development of CH as a function of time for both the reference and blended paste and the results are compared with TGA experiments. For the reference C₃S hydration the quantity of CH produced increases continually with the hydration degree. In blended system, however, the CH quantity reaches a maximum, which is still much lower than the final quantity reached by reference C₃S hydration, and begins to decrease within the first 2 days of hydration (Fig. 5). These results are consistent with the reaction of SF with CH produced by the C₃S hydration (Eqs. 7 and 8). Calcium hydroxide is consumed and used for the formation of pozzolanic CSH. This chemical process affects, therefore, also the amount of CSH formed as well as the microstructure development. The measured CH evolution for both systems is higher than predicted ones, and this difference is increasing with hydration for blended system.

From the simulated and experimental results it can also be observed that for blended system the amount of CH in system reduces after 1 day of hydration. Justnes [11] and Yajun and Cahyadi [9] show for different silica fume blended systems that the CH content may even reduce to zero amounts (depending on amount of replacement and w/c ratios) indicating the potential influence of pozzolanic reactions. The proposed model is also capable to describe this scenario of CH deficiency as well as further lowering of C/S ratio according to reaction Eq. 14, as shown in Fig. 6. By combining the direct measurement of the SF degree of hydration determined by NMR and TG measurements, Dobson et al. [8] calculated the overall (averaged) C/S ratio of the CSH in the system. For hydration of the C₃S reference paste the average C/S ratio of the CSH is maintained in the range 1.6-1.8 (Dobson). Results on C/S evolution during the hydration of blended paste are plotted in Fig. 6. In blended paste the average C/S ratio decreases with the hydration degree and after 28 days reaches a value of 1.5 (in agreement with data of Wu and Young, as cited in [8]).

Fig. 6 Simulated vs. experimental averaged Ca/Si molar ratio of the overall CSH hydration product

Fig. 7 Comparison of hydration simulation with ²⁹Si NMR experimental results [8] for CSH evolution

Fig. 8 shows a virtual 3D microstructure after obtained by a numerical model after 40 days of hydration for the blended system. Fig. 9 depicts the corresponding simulated capillary pore morphology with 20% porosity. The effect of SCM’s on the virtual evolution of the simulated averaged Ca/Si molar ratio of the overall CSH hydration product with hydration time. The Ca/Si molar ratio starts to decrease when the pozzolanic reaction is activated (by pH threshold input parameter) at about 5 h. This first decrease (Fig. 6) is due to the precipitation of C₁₇SH (Eq. 7) while PC precipitates C₃₀SH (Eq. 6), thus lowering the average C/S value. The experimental results suggest that the C/S ratio starts to decrease only after the C₃S hydration has ceased. Moreover, the model is capable of simulating the further decrease in Ca/Si ratio according to reaction (8) that could happen when there is no more CH available in the system, which describes the sharp change in C/S ratio after 400 h of hydration in Fig 6. Fig. 7 shows a comparison of hydration simulation with ²⁹Si NMR experimental results [8] for the CSH evolution. An interesting correlation can be observed between the calculated type of CSH formed (i.e. from C₃S or SF) and quantity of different Si environments in CSH (i.e. end SiO₄-groups in CSH chain or inner SiO₄-groups). There is an excellent agreement between predicted and experimental total quantity of CSH.

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6. CONCLUSION

The pozzolanic model described in this paper demonstrates the potential to use growing spheres numerical models to simulate pozzolanic reactions in blended cement systems. The model is implemented in the original Hymostruc platform, both in the statistical and the full 3D kernel. Only numerical results obtained by the statistical kernel are presented here. The validation of the multi-component hydration kinetics model incorporating pozzolanic fillers requires a comparison of the simultaneous evolution of the reactants and associated hydration products, with the systematic experimental data. The simulated results show good agreement with literature experimental data [8] obtained by combining TGA and NMR laboratory experiments to investigate the influence of silica fume addition on hydration of C3S.

The numerical model includes the improvement in the Hymostruc basic kinetic model by considering the nucleation and growth mechanism, which is now able to predict the very early age hydration as well. Excellent agreements could be achieved with experimental data for reaction kinetics.

The implemented SCM module also enables the possibility to assess the effect of SCM’s on the corresponding microstructural changes and morphology. In our future work this will be done by employing the recently implemented Hymostruc 3D module for transport property analysis of the simulated microstructures [12].

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