Pore-scale Modelling of Nucleation and Growth in Porous Media

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ABSTRACT

During the chemical interactions between fluid and minerals in different geological processes, it is of high importance to predict where the secondary precipitates form in the porous rocks as it helps to correctly predict the hydrodynamic properties of the porous media. The reactive transport models developed for this purpose need to account for the nucleation process which is probabilistic by nature. To our knowledge, probabilistic nature of nucleation based on classical nucleation theory has not been accounted for previously in reactive transport models. In this study, we develop a new probabilistic nucleation model and incorporate it into a pore-scale reactive transport solver to simulate the mineral nucleation and growth in the porous media. Simulations are done for different supersaturations, growth rates, and flow rates using single component mineral reaction. Simulations show initial supersaturations strongly affect the pattern of secondary precipitate formation. Higher initial supersaturations lead to more uniformly dispersed nucleation on all the grains while the lower initial supersaturations result in more isolated patterns. Decreasing the growth rate favors the formation of uniformly dispersed nuclei whereas higher growth rates cause more isolated nucleation. Injection of fluid with higher velocity gives rise to more precipitation. Moreover, comparison of probabilistic and deterministic nucleation showed that the isolated nucleation patterns cannot be modelled using the deterministic approach. Results showed that permeability for the porous media is influenced by the pattern of secondary precipitates growth and it is demonstrated that generally the permeability has a direct relation with the initial supersaturation and an inverse relation with the growth rate and the flow rate. Finally, the model was applied for simulation of calcite nucleation and growth on quartz grains. The calcite nucleation and growth exhibit similar behavior to what observed for the single-species simulations.

1. INTRODUCTION

Precipitation occurs in many different geological processes such as CO₂ sequestration, sediment diagenesis, and hydrothermal circulation to name a few¹⁻⁴. Precipitation might be or might not be of interest depending on the geological process in which the precipitation occurs. For instance, in geological CO₂ sequestration, precipitation can occur at different stages as CO₂ is flowing through the porous media. It can happen in areas near the wellbore or minerals might precipitate in the cracks and fractures inside well casing cement or caprock. Precipitation in the first case is unwanted because it clogs the available pore space that could be used for sequestration and therefore it reduces the injectivity of the storage reservoir. However, precipitation in the latter case is favorable since it can prevent leakage of CO₂ by sealing the open fractures in the casing cement or seals. In all these cases, precipitation of minerals affects the hydrodynamic properties of the porous media such as permeability. The change in permeability affects the fluid flow in the porous media which subsequently impacts the transport of chemical species and also the reaction rate. The pore-scale reactive transport models can help better understand this coupled process in the porous media. When modeling the precipitation of a mineral phase using the reactive transport models, it is important to take into account the nucleation which is the first step in the precipitation process. During nucleation, a nucleus forms from a supersaturated solution which then undergoes processes of growth, ripening, phase transformation, and crystallization⁵. The nucleation can occur in the bulk of a fluid, called homogeneous nucleation, or it can occur at the interface of a liquid and solid, called heterogeneous nucleation. There are few reactive transport models which have taken into account the nucleation process where nucleation occurs when species concentrations reach a certain threshold value^{6, 7}. While these models were well-developed, approximation of the nucleation in the reactive transport models can be further improved by implementing the classical

exponential nucleation rate equation suggested by the classical nucleation theory (CNT)^{8, 9}. In CNT the nucleation rate depends on parameters such as supersaturation and interfacial free energies. Recently attempts have been made to incorporate CNT into the reactive transport simulators. Li et al.¹⁰ incorporated CNT in a continuum-scale reactive transport simulator to model precipitation of calcite while simulating the chemical alterations of wellbore cement in the context of wellbore integrity of CO₂ storage processes. Prasianakis et al.¹¹ coupled a pore-scale reactive transport solver with CNT to show how the homogeneous and heterogeneous precipitation kinetics can affect the evolution of a porous media. Their results demonstrated that micro-scale processes such as nucleation should be included in the reactive transport models¹¹ in order to reproduce the experimental observations.

It is believed that the nucleation is a probabilistic process¹²⁻¹⁴ meaning that the nucleation can occur anywhere in the domain even if all physical conditions are the same (such as supersaturation, temperature). Probabilistic nucleation leads to different spatial distribution of the precipitates which consequently influences the permeability of the system. A more sophisticated reactive transport model should include the probabilistic behavior of the nucleation process in order to produce more reliable results such as better porosity-permeability relations. In this study we propose a new model for incorporation of nucleation into the pore-scale reactive transport models. The novelty of our approach is appropriate consideration of the probabilistic nature of the nucleation process based on the classical nucleation theory. The proposed probabilistic nucleation model has been implemented in a pore-scale Lattice Boltzmann (LB)-based reactive transport simulator (Yantra)¹⁵. Using this simulator, parametric studies are done on the effects of different parameters such as different supersaturations, growth rates, and different injection flow rates on the nucleation and growth of minerals in the porous media which to our knowledge were missing

in the previous pore-scale reactive transport models. To this end, we use this pore-scale reactive transport model to simulate the nucleation and growth of a single component mineral. Finally, simulations are performed to study the nucleation of calcite on quartz grains using experimentally-measured nucleation parameters, such as interfacial energy.

2. MODEL DESCRIPTION

2.1. Probabilistic nucleation theory

The induction time can be defined as the time it takes before the first stable crystals are observed in nucleation rate experiments. This time will vary statistically and is the basis for the probabilistic model. The mathematical expression for the induction time, τ_N , is defined based on the CNT¹⁶

$$\ln \tau_N = \frac{\hat{\Gamma} \sigma^3}{T^3 (\ln \Omega)^2} - \ln k_N \quad (1)$$

where T [K] is absolute temperature, Ω is the saturation ratio providing the thermodynamic driving force for the nucleation, σ [J.m⁻²] is the interfacial free energy between nucleating phase and the substrate, k_N [nuclei.m⁻².s⁻¹] is the nucleation rate constant. $\hat{\Gamma}$ is a lumped parameter expressed as:

$$\hat{\Gamma} = B v^2 k_B^{-3} \quad (2)$$

where B is a geometry factor, v [m³/molecule] is molecular volume of the nucleating phase, and k_B is Boltzmann constant, 1.38×10^{-23} [J.K⁻¹]^{11, 16}.

To calculate the induction time using Equation 1, one needs the values of σ and k_N which can be obtained from experiments where nucleation rates are measured at different supersaturations and then the rates are incorporated into the CNT to calculate the σ and k_N (see works done by Li et al^{5, 17}). Another parameter is the geometry factor B . It can be calculated based on the shape of the nucleus; for example for a spherical nucleus, it is estimated as $16\pi/3$ for homogeneous nucleation but for heterogeneous nucleation, B is no longer $16\pi/3$ ⁵. In previous works, where determination of the

geometry factor has been complex, the effect of the nuclei shape and their contact angle on the substrates are accounted for in the effective interfacial free energy⁵.

In the probabilistic nucleation method presented in this study, the induction time is considered as the variate (random variable) and the statistical spread of induction times around the measured or reported induction time, τ_N , is expressed through the cumulative distribution function $F(x)$ of the normal distribution with mean and standard deviation assumed to be one. Although the probability distribution of the induction times might not necessarily be normal, assuming a normal distribution for induction times could be a good approximation because of an important result known as central limit theorem stating that other distributions can be approximated using the normal distribution^{18, 19}. The probability distribution function, $P(x)$, and cumulative distribution function, $F(x)$, of the normal distribution are given by¹⁸

$$F'(x) = P(x) \quad (3)$$

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}, \quad -\infty \leq x \leq +\infty \quad (4)$$

Where σ is standard deviation, and μ is the mean of the random variable x . Considering the σ and μ values used in this study, the range of x in the normal distribution is considered as $-3 \leq x \leq 5$ (the values for probability distribution function are approximately zero for x values smaller than -3 and greater than 5). Since the random variable is the induction time, the x -axis in the normal distribution is transformed from $-3 \leq x \leq 5$ to $0 \leq \tau_p \leq 2\tau_N$, where τ_p is the probabilistic induction time which takes a value between 0 and $2\tau_N$. τ_N is the induction time which can be obtained from experiments or it may be calculated using Equation 1 (in the present work, τ_N is calculated using Equation 1). To find τ_p , a random number $0 < p < 1$ is generated and then a τ_p (between 0 and $2\tau_N$) is found such that the value of the normalized cumulative distribution function, $F_n(x)$, at τ_p is equal to p i.e. $F_n(x = \tau_p) = p$. During the reactive transport simulations, this procedure of finding τ_p is repeated at

every time-step and it is assumed that one stable nucleus is formed for each τ_p . Therefore, the number of crystals formed, N , can be calculated using relation $N = \frac{\Delta t}{\sum \tau_p}$. In this relation, Δt , is the time interval during which the number of crystals are calculated. Having calculated the number of crystals in each time-step, then we are able to calculate the reactive area that these crystals provide for the growth. This reactive area is then used as an input parameter for the calculation of the growth rate. In the rest of this paper when we mention nucleation, we refer to the probabilistic nucleation.

2.2.Pore-scale Lattice Boltzmann-based reactive transport model

The simulator used in this study to perform the reactive transport simulations builds upon the pore-scale LB-based reactive transport simulator developed and validated in our previous works^{15, 20, 21}. The details of the model development can be found in our previous publications^{15, 20, 21} and we here present the overview of the model. In the pore-scale reactive transport simulations, the advection-diffusion-reaction equation is solved to obtain the concentration of different species

$$\frac{\partial C_j}{\partial t} + \nabla \cdot (-D_j \nabla C_j + \mathbf{u} C_j) = R_j \quad (5)$$

Where C_j [NL^{-3}] is the aqueous concentration of species j , D_j [L^2T^{-1}] is the diffusion coefficient of species j , and R_j [$\text{NL}^{-3}\text{T}^{-1}$] represents the source or sink term due to reactions for species j . In Equation 5, R_j represents the homogeneous reactions while heterogeneous reactions at the interface between solid and liquid are usually treated as boundary conditions.

In Equation 5, the velocity can be obtained by solving the Navier-Stokes and continuity equations

$$\nabla \cdot \mathbf{u} = 0 \quad (6)$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla P + \mu \nabla^2 \mathbf{u} + \mathbf{F} \quad (7)$$

154 where ρ [ML^{-3}] is density, u [LT^{-1}] is velocity, P [$\text{M}^1\text{L}^{-1}\text{T}^{-2}$] is pressure, μ [$\text{M}^1\text{L}^{-1}\text{T}^{-1}$] is dynamic
155 viscosity and F [$\text{M}^1\text{L}^{-2}\text{T}^{-2}$] is body force.

156 The Navier-Stokes and advection-diffusion-reaction equations in the pore-scale model are solved
157 using the LB method in this study. In the LB method, the discretized Boltzmann equation, which
158 describes the behavior of a collection of particles, is solved to obtain the properties such as flow
159 velocity and concentrations of different species. The discretized LB equation used to solve for the
160 velocity reads²²

$$161 \quad f_i(\mathbf{x} + \mathbf{c}_i\Delta t, t + \Delta t) = f_i(\mathbf{x}, t) + \Omega^{SRT}_i(f) + \mathbf{F}_i\Delta t \quad (8)$$

162 Where

$$163 \quad \Omega^{SRT}_i(f) = \frac{-\Delta t}{\tau}(f_i - f_i^{\text{eq}}) \quad (9)$$

$$164 \quad f_i^{\text{eq}} = w_i\rho \left(1 + \frac{\mathbf{u}\cdot\mathbf{c}_i}{c_s^2} + \frac{(\mathbf{u}\cdot\mathbf{c}_i)^2}{2c_s^4} - \frac{\mathbf{u}\cdot\mathbf{u}}{2c_s^2} \right) \quad (10)$$

$$165 \quad \mathbf{F}_i = w_i \frac{c_{i\alpha}}{c_s^2} F_\alpha \quad (11)$$

$$166 \quad c_s^2 = \frac{1}{3} \cdot \left(\frac{\Delta x}{\Delta t} \right)^2 \quad (12)$$

167 In above equations, Δx and Δt are space and time resolutions. f_i is discrete distribution function,
168 f_i^{eq} is equilibrium distribution function, Ω^{SRT}_i is collision operator, $\mathbf{F}_i$ is body force, c_s is lattice
169 speed of sound, $\mathbf{u}$ is velocity, ρ is density, τ is relaxation time, c_i is discrete velocity, and w_i is the
170 weighing coefficients. In the LB method for flow, the D2Q9 lattices are used where 2 is the number
171 of spatial dimensions (x and y) and 9 is set's number of velocities²². In the LB scheme, when the
172 Equation 8 is solved, the $\mathbf{u}$ and $\mathbf{p}$ can be computed from the following²²

$$173 \quad \mathbf{u} = \frac{1}{\rho} \sum_{i=0}^8 f_i \mathbf{c}_i + \frac{\mathbf{F}\Delta t}{2\rho} \quad (13)$$

$$\rho = \sum_{i=0}^8 f_i \quad (14)$$

To show that the Equation 8 can recover the Navier-Stokes equation an analysis called Chapman-Enskog can be done. Using this analysis, demonstrates that the dynamic viscosity of fluid, ν , can be related to the relaxation parameter through the following relation²²

$$\nu = c_s^2 \left(\tau - \frac{\Delta t}{2} \right) \quad (15)$$

The LB equation used to solve the mass transport, advection-diffusion-reaction, equation reads²³

$$g_i^j(\mathbf{x} + \mathbf{c}_i \Delta t, t + \Delta t) = g_i^j(\mathbf{x}, t) + \Delta t \Omega_i^{\text{TRT},j}(\mathbf{x}, t) + \Delta t \Omega_i^{\text{rxn},j}(\mathbf{x}, t) \quad (16)$$

Where

$$\Omega_i^{\text{TRT},j}(\mathbf{x}, t) = \frac{-1}{\tau_{+g}} (g_i^{+j} - g_i^{\text{eq},+j}) + \frac{-1}{\tau_{-g}} (g_i^{-j} - g_i^{\text{eq},-j}) \quad (17)$$

$$g_i^+ = \frac{g_i + g_{-i}}{2}, \quad g_i^- = \frac{g_i - g_{-i}}{2} \quad (18)$$

$$g_i^{\text{eq},+} = \frac{g_i^{\text{eq}} + g_{-i}^{\text{eq}}}{2}, \quad g_i^{\text{eq},-} = \frac{g_i^{\text{eq}} - g_{-i}^{\text{eq}}}{2} \quad (19)$$

$$\Omega_i^{\text{rxn},j}(\mathbf{x}, t) = w_i R_{\text{total}}^j \quad (20)$$

$$g_i^{\text{eq},j} = w_i C^j \left(1 + \frac{\mathbf{u} \cdot \mathbf{c}_i}{c_s^2} \right) \quad (21)$$

Where g_i^j is discrete distribution function for species j , $g_i^{\text{eq},j}$ is equilibrium distribution function of species j , and C^j is concentration of species j . $\Omega_i^{\text{TRT},j}$ is a two-relaxation-time collision operator in which the symmetric, g_i^{+j} , and antisymmetric, g_i^{-j} , distribution functions are used. In above equations, subscript i is related to the direction with velocity $\mathbf{c}_i$ and $-i$ shows the direction with velocity $-\mathbf{c}_i$. The lattice structure used for this LB scheme is D2Q5. The contribution of the

reactions to the concentration of j th species can be added to the discretized LB equation through the term R_{total}^j which includes both reactions in the bulk of the fluid and also the reactions at the fluid-mineral interface and is obtained by the following

$$R_{\text{total}}^j = \frac{C_{\text{reaction}}^j - C_{\text{transport}}^j}{\Delta t} \quad (22)$$

Where $C_{\text{transport}}^j$ is the concentration of species j after the transport step. This concentration is then given to the chemical solver. The pore-scale reactive transport solver uses the geochemical solver PHREEQC²⁴ to perform the reaction calculations and to compute the new concentration of species j which is C_{reaction}^j . The Sequential Non-iterative Approach (SNIA) has been used to couple PHREEQC and the transport solver.

After solving the Equation 16, the concentration of species j can be computed using the following

$$C^j = \sum_{i=0}^4 g_i^j \quad (23)$$

As with LB method for flow, Chapman-Enskog analysis can be used to show that Equation 16 can recover the advection-diffusion-reaction equation²⁵. Performing this analysis also shows that the following relation exists between diffusion coefficient and the relaxation parameter

$$D = c_s^2 \left(\tau - \frac{\Delta t}{2} \right) \quad (24)$$

It should be mentioned that the reactive transport solver can also track the geometry changes due to the precipitation and/or dissolution of minerals which helps better simulate the processes in which the geometry evolution affects the flow and mass transport processes.

3. RESULTS AND DISCUSSION

The pore-scale reactive transport simulations are presented for two cases. The first case is related to the precipitation of a single-component idealized mineral system. In the latter case calcite nucleation and growth in the porous media, considering experimentally-measured parameters for

CNT, is investigated. Figure 1 shows the artificially generated porous media containing non-reactive grains used as the substrates for the simulations. The simulation domain is $2 \text{ mm} \times 1 \text{ mm}$ with the grid resolution of $10 \text{ }\mu\text{m}$.

3.1. Single-species simulations

In the single-species simulations, it is assumed that the domain is initially oversaturated with respect to mineral $A_{(s)}$ and the concentrations of species $A_{(aq)}$, C_A , at the inlet and in the domain are the same. During the simulations, the solution containing species $A_{(aq)}$ enters the domain through the inlet, left side. The fluid flow is driven by applying a constant pressure gradient across the domain (using the force term in LB method). In the simulations it is assumed that the kinematic viscosity of the solution is $10^{-6} [\text{m}^2.\text{s}^{-1}]$.

Figure 1. The input geometry used for the simulations. The light grey colour represents the non-reactive substrates on which nucleation occurs.

The C_A at the inlet solution is kept constant. The top and bottom boundary conditions for C_A are no-flux and the boundary condition at the domain outlet is zero diffusive-flux. In the domain, species $A_{(aq)}$ starts nucleating on the substrates where the nucleation rate, or induction time, can

be estimated using the CNT equation, Equation 1. Once the nucleation occurs the growth rate of the mineral $A_{(s)}$ can be calculated using the following expression

$$R = kS\left(1 - \frac{C_A}{C_{eq}}\right) \quad (25)$$

which is related to the reaction $A_{(s)} \rightleftharpoons A_{(aq)}$. In Equation 25, R [mol.s^{-1}] is the rate of reaction, k [$\text{mol.m}^{-2}.\text{s}^{-1}$] is reaction rate constant, S [m^2] is the reactive surface area, C_A [mol.L^{-1}] is the aqueous concentration of species A, and C_{eq} [mol.L^{-1}] is the equilibrium aqueous concentration of species A. It should be mentioned that this reaction rate is included in the PHREEQC input file during the simulations.

In the following we study the effect of solution supersaturation, growth rate, and flow velocity on the pattern of precipitation of mineral $A_{(s)}$ in the porous media. We also compare the probabilistic vs deterministic approaches for nucleation.

3.1.1. Effect of solution supersaturation and growth rate

To investigate what nucleation and growth patterns look like under different supersaturation conditions, simulations are performed with the initial average flow velocity of $\sim 4.6 \times 10^{-7}$ [m.s^{-1}] and with three different supersaturations where saturation ratios, defined as $\Omega = \frac{C_A}{C_{eq}}$, are equal to 80, 73, and 69. Although these supersaturations are rather close, they create different deterministic induction times. Therefore, the selected supersaturations are able to indicate the effect of supersaturation on the nucleation pattern. In the simulations C_{eq} is equal to 10^{-5} [mol.L^{-1}] and it is assumed that initial and inlet concentrations are the same. This means that the inlet and initial concentrations for the three supersaturation conditions are equal to 80×10^{-5} , 73×10^{-5} , and 69×10^{-5} [mol.L^{-1}]. Figures 2-4 show the changes in the amount of precipitated $A_{(s)}$ over time when initial Ω in the domain is equal to 69, 73, and 80. For each Ω , the deterministic induction time is estimated using Equation 1. For the single-species simulations, the values used for $\hat{\Gamma}$, σ , T , and k_N are 5×10^{14}

$[J^3.m^{-6}.k^{-3}]$, $39 \times 10^{-3} [J.m^{-2}]$, $40 [^{\circ}C]$, and $6 \times 10^{29} [nuclei.m^{-2}.s^{-1}]$, respectively. Using these values the initial (deterministic) induction times for the saturation ratios of 69, 73 and 80 are calculated as 69.4, 17, and 1.9 minutes, respectively. Once first nuclei form, they start growing with the growth rate calculated using Equation 25. The results shown in figures 2-4 are related to the simulations where the kinetic rate constant used in Equation 25 is $5 \times 10^{-5} [mol.m^{-2}.s]$. As is evident from figures 2-4, for each Ω , the amount of precipitates increases over time. The growth of nuclei formed on the substrates near the inlet is higher than the growth of nuclei formed further down the domain. This is clearer when comparing the growth patterns of the nuclei at 90 and 135 minutes, for a given $\Omega_{initial}$ (compare figures 3 and 4). For example, In figures 3 and 4, the amount of porosity change for $\Omega_{initial} = 69, 73$, and 80 is equal to 0.77%, 1.97%, and 1.65%, respectively, for areas near the inlet (length $< 1.2mm$), while the porosity change for the downstream areas (length $> 1.2 mm$) is 0.65%, 0.26%, and 0.19% for $\Omega_{initial} = 69, 73$, and 80 , respectively. This is due to the presence of solution with higher Ω in regions near the inlet. The concentration profiles at 90 and 135 minutes can be seen in figures S.2 and S.3 showing that, at a given $\Omega_{initial}$, the concentration of the A(aq) near the domain outlet is getting lower because the growth of minerals near the inlet clogs the available pathways and therefore the solution with higher Ω cannot reach the downstream regions. This causes the concentrations at the outlet areas to approach the equilibrium concentration which leads to the lower growth rate while the solution near the inlet is fresh and has higher Ω resulting in higher growth rate. Figures 2-4 also indicate the difference in the growth patterns for different $\Omega_{initial}$. For $\Omega_{initial} = 80$, the nucleation occurs almost everywhere on the substrates whereas for the lower initial supersaturations, 69 and 73, the nuclei form only in some locations on the substrates. When saturation ratio is 80, the induction time is 1.9 minutes and this causes the nuclei to form faster

273 than the other cases with initial supersaturation of 73 and 69 which have longer induction times of
274 17 and 69.4 minutes, respectively. When nuclei first form on the substrates, the supersaturation at
275 the nucleation site decreases because of the nucleation. The produced low Ω solutions are then
276 transported to the other areas around the substrates. Formation of the low Ω regions around the
277 substrates and their transport to the areas without any nucleus increases the induction time in these
278 areas because the supersaturation decreases (Figure S.4 shows an example of the low Ω layer
279 formed around the nucleation sites on the substrates and how this layer extends during the early
280 times of the simulation). This shows that if the induction time required for the nucleation in a
281 region without nucleus is shorter than the transport time of the low Ω solutions (i.e. the low Ω
282 solutions which are transported from the sites where nuclei have previously formed to the region
283 without nucleus), there is then higher probability for formation of nuclei in this region. Therefore,
284 when comparing a case with a higher Ω_{initial} , such as 80, with a case having a lower Ω_{initial} , such as
285 69, while the transport time is approximately the same, there is a higher possibility to see more
286 nucleation for the case of $\Omega_{\text{initial}} = 80$ because of its shorter induction time. This can explain why
287 more parts of the substrates have been covered by the precipitates for higher Ω_{initial} . It should also
288 be mentioned that in comparison to the case with the lower Ω_{initial} , a higher Ω_{initial} in the domain
289 might result in a solution with a lower Ω after first nuclei start growing (because of the higher Ω
290 in Equation 25). Transport of this lower Ω to the regions without nucleus can then lead to the
291 longer induction times for these regions (i.e. the regions without nucleus), thus meaning rare
292 nucleation for higher Ω_{initial} ; however, as mentioned before, in figures 2-4 we do not observe rare
293 nucleation for higher Ω_{initial} and we see the opposite which is formation of more nuclei for the
294 higher Ω_{initial} . One reason to explain this could be the same as before meaning that if the transport
295 time around the substrates is very long, then the amount of the decrease in initial Ω is not very

important since it takes so long for the produced low Ω solution to move to the regions with higher Ω and without nucleus. This means that in the regions around the substrates where there is not any nucleus, Ω is still high and induction time is low leading to higher nucleation probability. Apart from this, looking at the amount of decrease in Ω in a specific part of the domain, near the inlet, showed that one minute after first nuclei form, Ω decreases from 80 to ~67 and from 69 to ~62 for the cases with Ω_{initial} equals to 80 and 69, respectively. This indicates that although the decrease for the higher Ω_{initial} is more than that of the lower Ω_{initial} within the same time period, still $\Omega = 67$ leads to shorter induction time compared to the induction time related to the $\Omega = 62$ which again translates into more possibility for the nucleation events for $\Omega_{\text{initial}} = 80$.

As mentioned before, the results in figures 2-4 were related to the case where the kinetic rate constant in Equation 25 is 5×10^{-5} [mol.m⁻².s]. To see the pattern of nucleation and growth at the lower growth rates, simulations were performed with kinetic rate constant equals to 5×10^{-6} [mol.m⁻².s]. Figures 5-7 show the amount of precipitated mineral at 45, 90, and 135 minutes. Comparison of figures 2-4 with figures 5-7, at the same time and saturation ratio, shows that for the case with lower growth rate, i.e. figures 5-7, the extent of mineral growth is less than that of higher growth rate which is clearly due to the lower kinetic growth rate constant. The other observed characteristic from the results is that for the lower growth rate, i.e. the results in figures 5-7, the precipitated minerals have covered more parts of the substrate surface. Table 1 shows the percentages of the substrate areas covered by the precipitates (to calculate these percentages, a computational grid is considered as *covered* when volume of its neighbor is completely filled with a mineral). As shown in the Table 1, generally, when the growth rate is lower (corresponding to Figures 5-7), the percentage of the covered substrate surface is higher. At T=45 minutes, however, the percentages of the covered area for higher growth rate are larger, because in the case of lower

growth rate it takes more time for a grid to be completely filled with the precipitating mineral. Lower growth rate case shows higher percentages for covered substrate areas because for the case of low kinetic rate constant, after first nuclei are formed, the saturation ratio of the solution around the substrates does not decrease as much as the case with high kinetic rate constant. For example, figures S.5-S.7 demonstrate that the concentrations around the substrates are higher than the ones in figures S.1-S.3 because of the lower growth rates. Therefore, in lower growth rate case the induction times are shorter leading to the higher nucleation probability. Also, in case the produced low Ω solution around substrates is transported to the sites without any nucleus, because of the higher Ω values, still probability of the nucleation will be higher in comparison to the higher growth rate case. In Figures 5-7 one can see that the growth pattern is uniform (i.e. precipitates form uniformly on all parts of the substrates) compared to the higher growth rates (figures 2-4) where the growth patterns are like dendritic growth patterns.

Table 1. The percentages of the covered substrate surface (the substrates are the grains with light grey colour in Figure 1) when minerals precipitate on the substrates.

	T=45 minutes			T=90 minutes			T=135 minutes		
	$\Omega_{\text{initial}} =$ 69	$\Omega_{\text{initial}} =$ 73	$\Omega_{\text{initial}} =$ 80	$\Omega_{\text{initial}} =$ 69	$\Omega_{\text{initial}} =$ 73	$\Omega_{\text{initial}} =$ 80	$\Omega_{\text{initial}} =$ 69	$\Omega_{\text{initial}} =$ 73	$\Omega_{\text{initial}} =$ 80
HGR*	14%	35%	69%	23%	38%	75%	24%	40%	75%
LGR**	0%	0%	3%	42%	86%	95%	74%	97%	97%

*HGR: high growth rate ($k=5 \times 10^{-5} [\text{mol.m}^{-2}.\text{s}^{-1}]$)

**LGR: low growth rate ($k=5 \times 10^{-6} [\text{mol.m}^{-2}.\text{s}^{-1}]$)

Figure 2. The amount of precipitated mineral in mol.L^{-1} for $\Omega = 69, 73$, and 80 at $t = 45$ minutes. The kinetic rate constant for this case is $5 \times 10^{-5} [\text{mol.m}^{-2}.\text{s}^{-1}]$. The initial average flow velocity is $4.6 \times 10^{-7} [\text{m.s}^{-1}]$ for this scenario.

Figure 3. The amount of precipitated mineral in mol.L^{-1} for $\Omega = 69, 73$, and 80 at $t = 90$ minutes. The kinetic rate constant for this case is $5 \times 10^{-5} [\text{mol.m}^{-2}.\text{s}^{-1}]$. The initial average flow velocity is $4.6 \times 10^{-7} [\text{m.s}^{-1}]$ for this scenario.

Figure 4. The amount of precipitated mineral in mol.L^{-1} for $\Omega = 69, 73$, and 80 at $t = 135$ minutes. The kinetic rate constant for this case is $5 \times 10^{-5} [\text{mol.m}^{-2}.\text{s}^{-1}]$. The initial average flow velocity is $4.6 \times 10^{-7} [\text{m.s}^{-1}]$ for this scenario.

Figure 5. The amount of precipitated mineral in mol.L^{-1} for $\Omega = 69, 73$, and 80 at $t = 45$ minutes. The kinetic rate constant for this case is $5 \times 10^{-6} [\text{mol.m}^{-2}.\text{s}^{-1}]$. The initial average flow velocity is $4.6 \times 10^{-7} [\text{m.s}^{-1}]$ for this scenario.

Figure 6. The amount of precipitated mineral in mol.L^{-1} for $\Omega = 69, 73$, and 80 at $t = 90$ minutes. The kinetic rate constant for this case is $5 \times 10^{-6} [\text{mol.m}^{-2}.\text{s}^{-1}]$. The initial average flow velocity is $4.6 \times 10^{-7} [\text{m.s}^{-1}]$ for this scenario.

Figure 7. The amount of precipitated mineral in mol.L^{-1} for $\Omega = 69, 73$, and 80 at $t = 135$ minutes. The kinetic rate constant for this case is $5 \times 10^{-6} [\text{mol.m}^{-2}.\text{s}^{-1}]$. The initial average flow velocity is $4.6 \times 10^{-7} [\text{m.s}^{-1}]$ for this scenario.

3.1.2. Effect of flow velocity

To study the effect of flow velocity on the precipitation pattern, simulations are also done with higher flow velocities. In this scenario the initial average flow velocity is $\sim 2.3 \times 10^{-6}$ [m.s⁻¹]. To compare the results from higher flow rate with the results of lower flow rate, patterns of precipitated mineral at 45, 90, and 135 minutes are plotted in figure 8 for Ω_{initial} equals to 69. Figure 8 is related to the case with higher kinetic rate constant, 5×10^{-5} [mol.m⁻².s⁻¹] (See figures S.8-S.12 for precipitation patterns of $\Omega_{\text{initial}} = 69, 73$, and 80 at different times and for kinetic rate constant $= 5 \times 10^{-5}$ and 5×10^{-6} [mol.m⁻².s⁻¹]). As can be seen, the results related to the higher injection rate case, figures 8 and S.8-S.12, show greater precipitation in comparison to the lower flow rate, figures 2-7, especially in the regions near the inlet. The reason is that the growth in these simulations are mainly controlled by transport (See figures S.13-S.18 for concentration profiles of the $\Omega_{\text{initial}} = 69, 73$, and 80 for high injection rate and low and high kinetic rate constants). Table 2 indicates the percentages of the covered substrate surface for different Ω_{initial} and at different times. As Table 2 shows, generally (except for $\Omega_{\text{initial}} = 69$), the substrate surface is a bit more covered when the flow rate is lower. This could be because, for the higher flow rate case, a low Ω solution is produced around the substrates and transported faster to the regions without any nucleus. (Compare Figure S.4 and S.19). This therefore indicates that the regions without any nucleus have lower Ω and longer induction times which gives rise to lower nucleation probability for the case of higher injection rate. For the case of $\Omega_{\text{initial}} = 69$, one can also observe that the produced low Ω solution around the substrates is transported faster (compare Figure S.4 and S.19), but it seems due to the probabilistic nucleation, nuclei have formed sooner for the case of higher flow rate (Figure S.19) compared to the low flow rate (Figure S.4) and this has led to a bit more covered area for the high flow rate case when $\Omega_{\text{initial}} = 69$.

Table 2. The percentages of the covered substrate surface (the substrates are the grains with light grey colour in Figure 1) when minerals precipitates on the substrates.

	T=45 minutes			T=90 minutes			T=135 minutes		
	$\Omega_{\text{initial}} =$ 69	$\Omega_{\text{initial}} =$ 73	$\Omega_{\text{initial}} =$ 80	$\Omega_{\text{initial}} =$ 69	$\Omega_{\text{initial}} =$ 73	$\Omega_{\text{initial}} =$ 80	$\Omega_{\text{initial}} =$ 69	$\Omega_{\text{initial}} =$ 73	$\Omega_{\text{initial}} =$ 80
HF*	20.12%	33.71%	65.3%	23.94%	36.48%	68.24%	25.08%	36.97%	68.40%
LF**	14%	34.85%	69.38%	22.96%	38.27%	74.59%	24.42%	39.73%	75.4%

*HF: higher flow rate

**LF: lower flow rate

3.1.3. Probabilistic vs deterministic nucleation

Figure 9 shows the precipitation pattern when the deterministic approach is utilized to calculate the induction time. The results in figure 9 are related to the case with $\Omega_{\text{initial}} = 69$, kinetic rate constant = $5 \times 10^{-5} [\text{mol.m}^{-2}.\text{s}^{-1}]$ and for the lower flow rate. As can be observed in figure 9, there is no nucleation until 45 minutes of simulation time because the deterministic induction time for $\Omega_{\text{initial}} = 69$ is around 69.4 minutes so there is no nucleation event at 45 minutes. At times = 90 and 135 minutes, there are less precipitation in comparison to figures 3 and 4, for $\Omega_{\text{initial}} = 69$. The reason is that in the probabilistic case the nucleation might form at a time much sooner than the deterministic induction time because of the probabilistic nature of the process. For instance for the case of $\Omega_{\text{initial}} = 69$, kinetic rate constant = $5 \times 10^{-5} [\text{mol.m}^{-2}.\text{s}^{-1}]$ and low flow rate, first nuclei form around time = 12 minutes while for the deterministic case nuclei first form at 69.4 minutes. It is clear that for the probabilistic nucleation case since the nuclei form sooner, the extent of mineral growth will be greater than the deterministic scenario.

Figure 8. Temporal evolution of the amount of precipitated mineral in $mol.L^{-1}$ for $\Omega = 69$ at $t = 45, 90$, and 135 minutes. The kinetic rate constant for this case is $5 \times 10^{-5} [mol.m^{-2}.s^{-1}]$. The initial average flow velocity is $2.3 \times 10^{-6} [m.s^{-1}]$ for this scenario.

Another difference between deterministic and probabilistic cases is that in the deterministic nucleation the nuclei have covered all parts of the substrates (see figure 9) which is not the case for the probabilistic nucleation (see figure 2-4 at $\Omega_{\text{initial}} = 69$). For deterministic case when the simulation time approaches when nucleation should occur, i.e. induction time = 69.4 minutes, nuclei form equally everywhere on the substrates and nuclei therefore cover all substrate surfaces. Moreover, since the nuclei first form everywhere on the substrates, a low Ω region form around all the substrate and this layer is developed during the simulation, see figure S.20 in SI. Formation of this layer everywhere around the substrates causes a more uniform growth for the precipitates. In the probabilistic approach however, since nuclei form at different times, the formation of the low Ω layer is not uniform, hence affecting the induction times and nucleation events around the substrates. This subsequently causes more non-uniform growth patterns for the probabilistic approach.

3.1.4. Porosity and permeability evolution

Effects of different nucleation and growth patterns simulated in the previous sections on porosity-permeability relationship for the porous media are discussed in this part. The normalized permeability vs normalized porosity, during 161 minutes of the simulations, for the initial $\Omega = 69$, 73, and 80 are plotted in figure 10. The data are related to the cases with lower and higher kinetic rate constants (i.e. lower and higher growth rates) and also lower and higher flow rates. The lower and higher growth rates in figure 10 are designated as LG and HG, respectively. The lower and higher injection flow rates are also designated as LF and HF, respectively. For the sake of brevity, we use these designations to refer to the normalized permeability of the different cases.

Figure 9. Temporal evolution of the amount of precipitated mineral in mol.L^{-1} for $\Omega = 69$ at $t = 45, 90$, and 135 minutes where deterministic approach is used for the nucleation calculations. The kinetic rate constant for this case is $5 \times 10^{-5} [\text{mol.m}^{-2}.\text{s}^{-1}]$. The initial average flow velocity is $4.6 \times 10^{-7} [\text{m.s}^{-1}]$ for this scenario.

590 For example, K_{HG_HF} refers to the normalized permeability for the case with high kinetic rate
 591 constant (growth rate) and high injection flow rate. As can be seen in figure 10, for each saturation
 592 ratio and at a given porosity, $K_{HG-LF/HF} < K_{LG-LF/HF}$, '/' in the subscript means 'or', which is because
 593 higher kinetic rate constant leads to higher growth rate which consequently results in more
 594 dendritic growth pattern which quickly clogs the pathways in the porous media. The other
 595 characteristic from figure 10 is that if we take one saturation ratio, at a given porosity, $K_{HG-HF} <$
 596 K_{HG-LF} and $K_{LG-HF} < K_{LG-LF}$. The reason being that a higher flow rate causes the precipitates to be
 597 accessible to the solution with higher Ω which translates into a higher growth rate, thus restricting
 598 the flow paths and reducing the permeability. The other characteristic observed in figure 10 is that
 599 at a given porosity and for the same flow rate and kinetic rate constants, the permeability for $\Omega_{initial}$
 600 $= 69$ is less than $\Omega_{initial} = 73$ and the permeability for $\Omega_{initial} = 73$ is less than that of $\Omega_{initial} = 80$.
 601 For example if we take HG-HF scenario, we see that at the normalized porosity $= 0.94$, K_{HG-HF}
 602 values for $\Omega_{initial} = 69, 73$, and 80 are equal to $0.108, 0.186$, and 0.311 , respectively. The time it
 603 takes to reach to a given porosity is longer when the $\Omega_{initial}$ is smaller. In previous example, it takes
 604 approximately 111 minutes for the porosity in the case with $\Omega_{initial} = 69$ to approach the normalized
 605 porosity of 0.94 while this time for the case of $\Omega_{initial} = 80$ is ~ 57 minutes. It is clear that the extent
 606 of growth is higher for $\Omega_{initial} = 69$ in comparison to the cases of $\Omega_{initial} = 73$ and 80 which is also
 607 shown in figure S.21. The greater precipitation occurred for the case of $\Omega_{initial} = 69$ creates more
 608 restrictions for the flow as can be seen in figure S.22 demonstrating the velocity profiles for $\Omega_{initial}$
 609 $= 69, 73$, and 80 . Figure 10 also compares the $K_{HG_LF_deterministic}$ with K_{HG_LF} when $\Omega_{initial} = 69$. As
 610 is evident $K_{HG_LF_deterministic} > K_{HG_LF}$. This is because for the case of probabilistic nucleation, it
 611 started to nucleate sooner than the deterministic case and also the pattern of precipitation for

probabilistic case is more non-uniform (compare figures 2-4 for $\Omega_{\text{initial}} = 69$ and figure 9) which leads to more limitations for flow and lower permeability.

Figure 10. The normalized permeability vs normalized porosity for different scenarios. HG refers to the case with $k=5 \times 10^{-5}$ [mol.m⁻².s⁻¹] and LG represent the case with $k=5 \times 10^{-6}$ [mol.m⁻².s⁻¹]. Also, HF refers to the scenario with higher average initial velocity (2.3×10^{-6} [m.s⁻¹]) while LF is related to the lower average initial flow velocity (4.6×10^{-7} [m.s⁻¹]) scenario. Data are plotted for different $\Omega_{\text{initial}}=69, 73$, and 80.

3.2. Multispecies simulations

To demonstrate the applicability of the proposed pore-scale model for more realistic scenarios, in this section simulation results on the nucleation and growth of calcite which is of relevance for different geological systems are presented. The simulation are done within the same geometry used for single-species simulations and for only two different supersaturations for calcite. The type of

boundary conditions for mass transport and flow equations are also the same as single-species simulations. The diffusion coefficient for different chemical species are considered the same and equal to $10^{-9} \text{ [m}^2\text{.s}^{-1}\text{]}$. The system is initially oversaturated with respect to calcite and the simulations are performed for two different supersaturations where saturation index, $SI = \log\left(\frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{K_{\text{eq}}}\right)$, equals to 1.23 and 1.13 (the fluid compositions are given in table S1). In SI definition, $a_{\text{Ca}^{2+}}$, $a_{\text{CO}_3^{2-}}$ are activities of Ca^{2+} and CO_3^{2-} .

The calcite reaction pathways is given by²⁶:

The growth rate of calcite, $R \text{ [mol.s}^{-1}\text{]}$, is described by the following equation²⁶

$$R = -kS(\Omega - 1) \quad (29)$$

where reaction rate constant, k , is $1.58 \times 10^{-9} \text{ [mol.m}^{-2}\text{.s}^{-1}\text{]}$, and $S \text{ [m}^2\text{]}$ is the reactive surface area.

The parameters used for calcite nucleation in the CNT equation, Equation 1, are $\sigma = 48 \times 10^{-3} \text{ [J.m}^{-2}\text{]}$, $\hat{\Gamma} = 2.4 \times 10^{13}$, $J_0 = 2.1 \times 10^{13} \text{ [nuclei.m}^{-2}\text{.s}^{-1}\text{]}$, and $T = 25 \text{ }^\circ\text{C}$. The values of σ and J_0 are based on the experimentally-measured data by Li and Jun⁵.

Figure 11 shows the precipitated calcite at 4.2, 12.2, and 24.5 minutes where $SI = 1.23$. As is evident from Figure 11, the precipitates have formed everywhere on the substrates. In this case the induction time of calcite nucleation process is around 2 minutes and nuclei form rather quickly on all the grains. Moreover, since the growth rate is very low, the growth pattern is uniform. Figure 12 shows the calcite precipitation pattern for a lower $SI=1.13$. As explained for the single-species simulations, a lower SI leads to rare nucleation on the grains. In this case, however, lower SI does

not show rare nucleation events on the grains. This is due to the very low growth rate of the calcite which causes the SI in the regions around the grains not to dramatically decrease, thus leading to more nucleation probability. The rare calcite nucleation on the grains can be observed if the growth rate of the calcite increases. We repeated the simulations with very high kinetic rate constants for the calcite growth equation, Equation 25. For these cases, figure S.23 and S.24, it can be seen that the high growth rate has prevented the nucleation at some regions on the substrates which is because the layers around grains have lower SI which reduces the probability of the calcite nucleation, similar to what observed for the single-species simulations.

4. Implications

Predicting the effect of precipitation reactions on fluid flow in different geological environments such as soils, sediments, and aquifers is of prime importance in wide range of applications. Precipitation reactions can impact the fluid flow by changing the volume of the void spaces in the porous media. While predicting the porosity changes triggered by the precipitation reactions is important, the prediction of the changes in permeability of the system might even be more crucial due to the high effect of permeability on the fluid flow. To predict permeability changes during the precipitation reactions, one has to know the spatial distribution of the secondary precipitates. For this, accounting for nucleation, a probabilistic process, is important because such consideration has significant impact on porosity-permeability relationship as demonstrated in this study. An example of a system where consideration of probabilistic nucleation is essential is the column experiments performed to study the spatial distribution of the secondary mineral precipitates while the CO₂-acidified brine reacts with the basalt rocks²⁷. The result of this experimental work demonstrated that only few but large crystals form in random locations along the column where the authors claim that such an observation can only be modeled with a reactive transport model in

which a probabilistic approach for nucleation is used²⁷. The model proposed in this study can help get the overall kinetics and distribution of the secondary precipitates seen in the column experiments and also other similar studies.

Figure 11. Temporal evolution of the amount of precipitated mineral in mol.L⁻¹ for SI = 1.23 at t = 4.2, 12.2, and 24.5 minutes. The initial average flow velocity is 4.6×10^{-7} [m.s⁻¹].

Figure 12. Temporal evolution of the amount of precipitated mineral in mol.L⁻¹ for SI = 1.13 at t = 4.2, 12.2, and 24.5 minutes. The initial average flow velocity is 4.6×10^{-7} [m.s⁻¹].

Conclusions

A LB-based pore-scale reactive transport model was developed in this work to simulate the mineral nucleation and growth in the porous media. A probabilistic nucleation step, based on the CNT, was added to the reactive transport simulator so it can be used to simulate the systems in which the nucleation occur in random locations. The model was used to simulate the nucleation and growth of a single-species mineral under different supersaturations, growth rates, and flow conditions. Results showed that for the lower supersaturation conditions, the precipitates form only in some parts of the substrates and then they grow while for the higher supersaturations the nucleation appears to occur in more parts of the substrates. Decreasing the reaction rate constant in the kinetic growth rate equation indicated that if the growth rate becomes low, the precipitation pattern then change from ‘few isolated-pocket structures’ to ‘more uniformly dispersed-structures’. These observations demonstrate that the most uniform nucleation and growth occur for the high supersaturation and low growth rate conditions and the isolated kind of nucleation and growth patterns can be observed for lower supersaturations and higher growth rates. Also, simulations with higher flow rates showed that the extent of growth is higher when flow rate is higher.

The deterministic nucleation approach was also compared with the probabilistic one. The comparison showed that the isolated pocket pattern seen in the case of the probabilistic nucleation approach cannot be seen when deterministic approach is used for the nucleation which confirms that the deterministic approach might not always be used for simulation of the real cases where the minerals are nucleated in random locations in the media.

Looking at the permeability and porosity evolutions of the porous media for different scenarios with different supersaturations, growth rates, and flow velocities showed that, for a given kinetic

rate constant and flow velocity, the normalized permeability is lower for the lower initial supersaturations, at a given normalized porosity. Also, at a constant initial supersaturation and growth rate, higher flow velocity leads to the lower normalized permeability for a given normalized porosity. Moreover, for a given normalized porosity, flow velocity, and initial supersaturation, higher kinetic growth rate constant (growth rate) results in a lower normalized permeability.

The model developed in this study was also used for the simulation of a more realistic case of calcite nucleation and growth where the results showed similar trends as those seen for single-species simulations. Calcite nucleation and growth simulations also showed that the developed model can be used for more real cases indicating random calcite nucleation such as the calcite precipitation in basalt column in previous experimental works²⁷.

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SUPPORTING INFORMATION

The supporting information is available free of charge.

Plots showing the temporal evolution of A(aq) concentration for lower and higher kinetic rate constants and lower and higher flow rates; Figures indicating temporal evolution of precipitated A(s) for lower and higher kinetic rate constants and higher flow rate; Figure demonstrating the temporal evolution of A(aq) concentration when deterministic nucleation approach is used for $\Omega_{\text{initial}} = 69$; Figure showing the velocity profile for high flow rate and kinetic rate constant and when normalized porosity is 0.94; Figures showing the temporal evolution of precipitated calcite when a high kinetic rate constant is used.

REFERENCES

1. Noiriél, C.; Steefel, C. I.; Yang, L.; Bernard, D., Effects of pore-scale precipitation on permeability and flow. *Advances in water resources* **2016**, *95*, 125-137.
2. Tenthorey, E.; Scholz, C. H.; Aharonov, E.; Léger, A., Precipitation sealing and diagenesis: 1. Experimental results. *Journal of Geophysical Research: Solid Earth* **1998**, *103* (B10), 23951-23967.
3. Lackner, K. S., A guide to CO₂ sequestration. *Science* **2003**, *300* (5626), 1677-1678.
4. Hilgers, C.; Urai, J. L., Experimental study of syntaxial vein growth during lateral fluid flow in transmitted light: first results. *Journal of Structural Geology* **2002**, *24* (6-7), 1029-1043.
5. Li, Q.; Jun, Y.-S., The apparent activation energy and pre-exponential kinetic factor for heterogeneous calcium carbonate nucleation on quartz. *Communications Chemistry* **2018**, *1* (1), 56.
6. Chen, L.; Kang, Q.; He, Y.-L.; Tao, W.-Q., Mesoscopic study of the effects of gel concentration and materials on the formation of precipitation patterns. *Langmuir* **2012**, *28* (32), 11745-11754.
7. Chen, L.; Kang, Q.; Carey, B.; Tao, W.-Q., Pore-scale study of diffusion–reaction processes involving dissolution and precipitation using the lattice Boltzmann method. *International Journal of Heat and Mass Transfer* **2014**, *75*, 483-496.
8. Kelton, K.; Greer, A. L., *Nucleation in condensed matter: applications in materials and biology*. Elsevier: 2010; Vol. 15.
9. Kalikmanov, V. I., Classical nucleation theory. In *Nucleation theory*, Springer: 2013; pp 17-41.
10. Li, Q.; Steefel, C. I.; Jun, Y.-S., Incorporating nanoscale effects into a continuum-scale reactive transport model for CO₂-deteriorated cement. *Environmental science & technology* **2017**, *51* (18), 10861-10871.

11. Prasianakis, N.; Curti, E.; Kosakowski, G.; Poonoosamy, J.; Churakov, S., Deciphering pore-level precipitation mechanisms. *Scientific reports* **2017**, 7 (1), 13765.
12. Sosso, G. C.; Chen, J.; Cox, S. J.; Fitzner, M.; Pedevilla, P.; Zen, A.; Michaelides, A., Crystal nucleation in liquids: Open questions and future challenges in molecular dynamics simulations. *Chemical reviews* **2016**, 116 (12), 7078-7116.
13. Dimitrov, I. L.; Hodzhaoglu, F. V.; Koleva, D. P., Probabilistic approach to lysozyme crystal nucleation kinetics. *Journal of biological physics* **2015**, 41 (4), 327-338.
14. De Yoreo, J. J.; Vekilov, P. G., Principles of crystal nucleation and growth. *Reviews in mineralogy and geochemistry* **2003**, 54 (1), 57-93.
15. Patel, R. A.; Perko, J.; Jacques, D.; De Schutter, G.; Van Breugel, K.; Ye, G., A versatile pore-scale multicomponent reactive transport approach based on lattice Boltzmann method: Application to portlandite dissolution. *Physics and Chemistry of the Earth, Parts A/B/C* **2014**, 70, 127-137.
16. Pham, V.; Lu, P.; Aagaard, P.; Zhu, C.; Hellevang, H., On the potential of CO₂-water-rock interactions for CO₂ storage using a modified kinetic model. *International Journal of Greenhouse Gas Control* **2011**, 5 (4), 1002-1015.
17. Li, Q.; Fernandez-Martinez, A.; Lee, B.; Waychunas, G. A.; Jun, Y.-S., Interfacial energies for heterogeneous nucleation of calcium carbonate on mica and quartz. *Environmental science & technology* **2014**, 48 (10), 5745-5753.
18. Weisstein, E. W., Normal distribution. **2002**.
19. Evans, M. J.; Rosenthal, J. S., *Probability and statistics: The science of uncertainty*. Macmillan: 2004.
20. Fazeli, H.; Patel, R. A.; Ellis, B. R.; Hellevang, H., Three-Dimensional Pore-Scale Modeling of Fracture Evolution in Heterogeneous Carbonate Caprock Subjected to CO₂-Enriched Brine. *Environmental science & technology* **2019**, 53 (8), 4630-4639.
21. Fazeli, H.; Patel, R.; Hellevang, H., Effect of Pore-Scale Mineral Spatial Heterogeneity on Chemically Induced Alterations of Fractured Rock: A Lattice Boltzmann Study. *Geofluids* **2018**, 2018.
22. Krüger, T., *The Lattice Boltzmann Method: Principles and Practice*. sl: Springer International Publishing. **2017**.
23. Patel, R. A.; Perko, J.; Jacques, D.; De Schutter, G.; Ye, G.; Van Bruegel, K., Effective diffusivity of cement pastes from virtual microstructures: Role of gel porosity and capillary pore percolation. *Construction and Building Materials* **2018**, 165, 833-845.
24. Charlton, S. R.; Parkhurst, D. L., Modules based on the geochemical model PHREEQC for use in scripting and programming languages. *Computers & Geosciences* **2011**, 37 (10), 1653-1663.
25. Patel, R. A. Lattice Boltzmann method based framework for simulating physico-chemical processes in heterogeneous porous media and its application to cement paste. Ghent University, 2016.
26. Molins, S.; Trebotich, D.; Steefel, C. I.; Shen, C., An investigation of the effect of pore scale flow on average geochemical reaction rates using direct numerical simulation. *Water Resources Research* **2012**, 48 (3).
27. Hellevang, H.; Wolff-Boenisch, D.; Nooraiepour, M. In *Kinetic control on the distribution of secondary precipitates during CO₂-basalt interactions*, E3S Web of Conferences, EDP Sciences: 2019; p 04006.