The effect of preferential nucleation sites on the distribution of secondary mineral precipitates

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Introduction

Nucleation and growth of secondary mineral phases is of great importance in a variety of processes in different fields. Some examples are:

- precipitation of clay and carbonate minerals due to an increase in acidity of the formation water the injection of CO_2 into an aquifer [Pham et al., 2011],
- accumulation of salt in the near wellbore area because of evaporation of formation water into the CO_2 stream during CO_2 storage [Miri and Hellevang, 2016; Parvin et al., 2020],
- deposition of mineral scales caused by the incompatibility of injected water in the secondary and tertiary water-based enhanced oil recovery [Manzari Tavakoli et al., 2018],
- scale formation resulting from thermal, chemical, and mechanical disturbance of the reservoir in geothermal systems [Pandey et al., 2018],
- calcium carbonate precipitation due to calcium leaching in deep geological disposal sites or tunnels [Patel et al., 2021].

In each of these cases as well as many more, mineral precipitation alters the morphology and hydrodynamics of the porous media by blocking the pore and throats and changing the tortuosity and permeability of flow paths. Even reaction rates are affected by the reshaping of available reactive surfaces. Thus, a deeper understanding of the mineral nucleation and growth process is essential.

Any mineral precipitation process begins with the nucleation. Nucleation, which is a probabilistic phenomenon [Hellevang et al., 2019], controls the distribution of the precipitated minerals in the porous media. Therefore, it is necessary to develop a new probabilistic nucleation approach that could produce more reliable results. Therefore, in our previous works, we have developed a new probabilistic nucleation model and investigated the effect of various factors such as saturation ratio, flow rate, temperature, nucleation rate, and growth rates on the distribution of precipitated secondary minerals [Fazeli et al., 2020; Masoudi, 2021; Masoudi et al., 2021; Nooraiepour et al., 2021].

The nucleation of a secondary mineral on a primary substrate depends on the thermodynamic conditions (temperature and saturation ratio), type of the nucleating phase and the substrate, and the physical condition of the substrate (geometry and surface roughness). We have also conducted microfluidic experiments on calcium carbonate crystals precipitating on heterogeneous sandstone substrates to determine the effect of the interplay of thermodynamic conditions and the characteristic of primary and secondary substrates on mineral nucleation and growth [Nooraiepour et al., 2021]. The results demonstrated that substrate surface properties and substrate types introduce favorable areas where nucleation events are more likely to occur. The carbonate cement between sandstone grains, the hollows and indented surfaces, and the edges of grains are favorable environments for nucleation and growth of secondary minerals. The preferential sites for mineral nucleation exist because of the lower interfacial free energy between the precipitating phase and the substrate. The lower interfacial energy may be attributed to the type of nucleating phase and the substrate or the surface characteristics of the substrate, such as its roughness and geometry.

In this work, we used the developed probabilistic nucleation model in our previous works to carry out sensitivity analysis on the interfacial free energy between the nucleating phase and the substrate. We also used Shannon entropy to assess the spatial randomness and the evolution path of the systems as solid phases form. The main objective is to investigate the role of interfacial free energy on the nucleation and growth of secondary minerals.

Theory and Methods

In our newly developed probabilistic nucleation model, the probabilistic induction time (τ_P) is treated as a random variable that is statistically distributed around the deterministic mean induction time (τ_N). τ_N is calculated by the nucleation rate equation of the classical nucleation theory (CNT):

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

where σ [J·m^{-2}] is interfacial free energy between the substrate and the nucleating mineral, T [K] is absolute temperature, Ω is the saturation ratio (C/C$_{eq}$), which is the thermodynamic driving force for nucleation, k_N [nuclei·m^{-2}·s^{-1}] is nucleation rate constant, and $\hat{\Gamma}$ is a lumped parameter expressed as:

$$\hat{\Gamma} = \beta\upsilon^2 K_B^{-3} \quad (2)$$

where β is a geometry factor, υ [m^3/molecule] is the molecular volume of the nucleating phase, and k_B is the Boltzmann constant, 1.38 × 10^{-23} [J·K^{-1}]. More about probabilistic nucleation and how to implement it into pore-scale reactive transport models can be found in our previous works [Masoudi et al., 2021; Nooraiepour et al., 2021].

We implemented the probabilistic nucleation model into a pore-scale Lattice Boltzmann (LB)-based reactive transport model to simulate the formation of secondary minerals on a dual substrate (Figure1.a).

The simulation domain is 400×400 μm with a grid resolution of 4 μm. All boundaries are subject to periodic boundary conditions. The domain is initially oversaturated with mineral A (Ω_0 = 60). Using a source term, an infinite supply of this solution is introduced on top of the domain. The simple ideal reaction, {A$_{(aq)}$ ⇄ A$_{(s)}$} is modeled.

As it is shown by Nooraiepour et al. (2021), the nucleation and growth of the secondary phase on the initial substrate will create a new substrate in which nucleation will be more likely to occur. This is implemented into the model by using weighted arithmetic averaging based on the surface area:

$$\overline{\sigma} = \frac{\sum_i S_i\sigma_i}{\sum_i S_i}, \qquad \text{i = type of substrates} \quad (3)$$

where S is the surface area of different substrates in a grid cell. More about the reactive transport model, numerical implementations, and assumptions can be found in our previous works [Fazeli et al., 2020; Masoudi et al., 2021; Nooraiepour et al., 2021].

Four different simulations are performed to analyze the effect of interfacial free energy on the distribution of precipitated minerals on the simulation domain: σ2/σ1={0.1, 0.5, 1, 1.6}. As shown in Figure 1a, the interfacial free energy of the bottom-left and top-right parts of the domain is different from the rest.

Results and Discussions

Figure 1 shows the sensitivity analysis results of the interfacial free energy between the nucleating phase and the substrate. In Figure 1b and 1c, the bottom-left and top-right portions have smaller interfacial free energy than the rest of the domain (σ2 < σ1). The figures show that more minerals formed in the areas with lower interfacial free energy. According to Equation (1), the lower the interfacial free energy, the shorter the deterministic induction time (τ_N). The search for the probabilistic induction time (τ_P) takes place in an area expressed by a Gauss-Laplace (normal) probability density function with the mean value of τ_N (m = τ_N) [Masoudi et al., 2021; Nooraiepour et al., 2021]. As a result, the probability of

nucleation events is higher in the areas with shorter induction times (here due to lower interfacial free energy). Nucleation is necessary for growth, so a combination of more nucleation events and earlier nucleation events will result in more accumulation of mineral precipitation in favorable areas.

In Figure 1d, the secondary mineral precipitates are distributed in the same pattern all around the substrate since all the areas have the same interfacial free energy (no favorable nucleation region exists).

On the other hand, in Figure 1e, where the bottom-left and top-right portions have larger interfacial free energy than the rest of the domain ($\sigma 2 > \sigma 1$), less accumulation of secondary minerals happened in those areas. However, nucleation still occurred at high interfacial free energy regions due to the probabilistic nature of the nucleation model.

Comparing the bottom-left and top-right areas of figures 1b to 1e, we can see how probabilistic mineral nucleation controls the evolution of the porous medium. In these areas, the differences in interfacial free energy led to different amounts of precipitation, different nucleation locations, and different growth patterns. Using the Shannon entropy of mineral distributions during the simulation time, we quantified the degree of disorder within the simulated scenarios. Figure 2b illustrates the changes in Shannon entropy of the top-right and bottom-left areas in Figures 1b to 1e (the favorable areas with interfacial free energy of σ_2). Clearly, all of the simulation scenarios follow a Gaussian path. The path begins with a fully ordered system without solid precipitation on the surface. The entropy increases as minerals start precipitating on the substrate until it reaches its maximum value (1). Following that, the disorder decreases as more and more surface areas are covered. Eventually, the entropy approaches zero when the surface is fully covered.

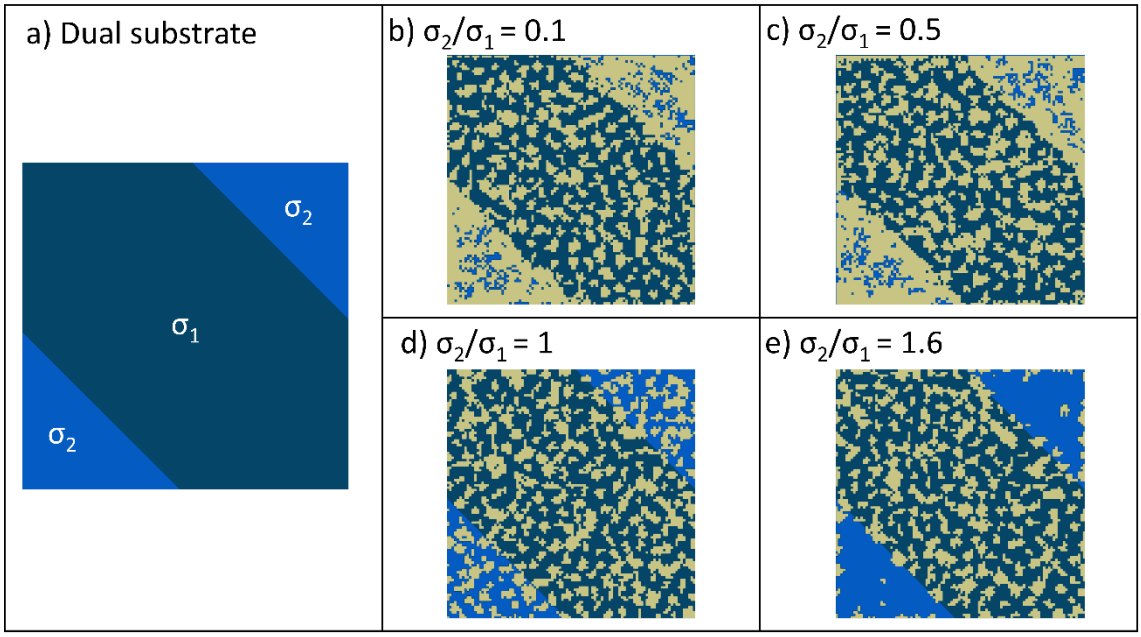

Figure 1 *The results of the sensitivity analysis of the interfacial free energy between the nucleating phase and the substrate.*

As it is shown and discussed by Nooraiepour et al. (2021), a system can follow the Gaussian path in countless ways, hence we call it the "probabilistic window." After the probabilistic region, the system moves into the deterministic region when it evolves to a certain extent. In deterministic regions, the probabilistic model is no longer needed to be implemented and the nucleation process can be handled in a traditional deterministic manner without violating mineral nucleation and growth physics. Nevertheless, it should be stressed that, even within the deterministic regimes, the nucleation phenomenon is still probabilistic. However, from a stochastic point of view, the probability of nucleation after such a long time is high enough that using a probabilistic model is no longer relevant. Since the areas with low interfacial

free energy (longer induction time) have larger probabilistic windows, in environments with long induction times, the probabilistic model becomes more relevant.

The size of probabilistic windows in a system is not solely determined by induction time (or nucleation rate). Reaction rate also plays an important role. To demonstrate the effect of reaction rate on the probabilistic windows, three simulations have been performed for a system with no favarable areas (σ_2/σ_1=1) and different growth rate constants. Figure 2b shows the Shannon entropy during simulation time for these three simulation scenarios. Reaction rate has a major effect on the evolution of the systems. The faster the growth, the narrower the standard deviation of the Gaussian bell. The higher the growth rate, the narrower the probabilistic window. Faster growth leads to faster coverage of the substrate, and as a result, the system evolves faster into the deterministic region.

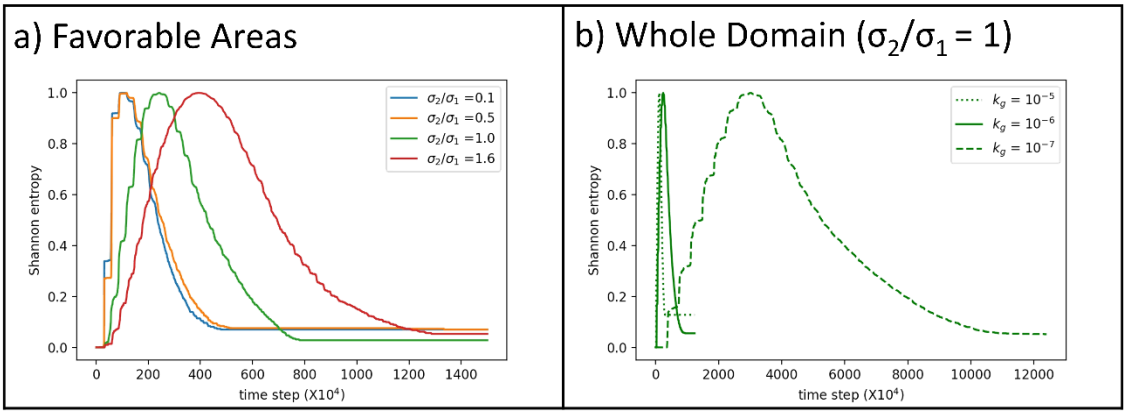

Figure 2 *The Shannon entropy during simulation time for a) the favorable areas (top-right and bottom-left areas with interfacial free energy of σ_2) and b) the whole domain for three scenarios with no favarable areas ($\sigma 2/\sigma 1=1$) and different growth rate constants.*

It should be noted that the most favorable area for new nucleation events still remains the new substrates formed by the nucleation and growth of the secondary phase. Nevertheless, the new substrates in early times have a relatively small surface area, so they cannot significantly influence precipitation patterns. The reverse is also true when the growth is swift. In this case, the location of the very first nucleation event determines the outcome.

Conclusions

In this study, a pore-scale Lattice Boltzmann (LB)-based reactive transport model incorporating a probabilistic nucleation model has been used to assess the role of interfacial free energy on the nucleation and growth of secondary minerals. Performing four sets of simulations on a dual substrate, the following conclusions have been reached:

- In the presence of preferential sites, the developed model can accurately capture the selective behavior of nucleation processes. The simulation results demonstrate the importance of using a probabilistic nucleation model to capture the correct physics of this phenomenon.
- Probabilistic models are more relevant in environments with longer induction times.

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