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A two-fluid model for calcium carbonate precipitation in highly supersaturated solutions

M.C. Reis^{a,*}, M.F.B. Sousa^a, F. Alobaid^b, C.A. Bertran^a, Y. Wang^c^a University of Campinas, Institute of Chemistry, Campinas 13083970, Brazil^b Technische Universität Darmstadt, Institute of Energy Systems and Technology, Darmstadt 64287, Germany^c Technische Universität Darmstadt, Institute of Fluid Dynamics, Darmstadt 64287, Germany

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ABSTRACT

Precipitation of calcium carbonate is a common phenomenon in nature, which has attracted attention from researchers due to its importance in biomineralization processes, climatic changes, and especially incrustations in pipelines. In this work, a two-fluid model is proposed for homogeneous crystallization of calcium carbonate in highly supersaturated solutions. By making an analogy between the dynamics of a granular gas and the dynamics of a solid dispersion, the proposed model not only accounts for the interaction forces between the solid particles and dispersion medium, but also for the mass transfer and changes in the particles size during the precipitation reaction. Moreover, by using a numerical scheme based on an iterative algorithm, 3D numerical simulations are performed for the homogeneous crystallization of calcium carbonate, and the results are compared with experimental particles size distributions and curves of pH versus time. The good agreement between theoretical and experimental results indicates that the two-fluid model can be successfully used to evaluate the growth kinetics of calcium carbonate nuclei.

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1. Introduction

The physico-chemical properties of calcium carbonate have always attracted attention from numerous researchers due to its importance in many bio and geological processes. Of particular interest is the study of calcium carbonate precipitation in highly supersaturated solutions since crystallization of $\text{CaCO}_3(\text{s})$ is the most common and important source of mineral scales in petroleum industries. In fact, petroleum industries invest millions of dollars every year in order to develop powerful inhibitors, and new methodologies to prevent the adherence and growth of scale on metal surfaces. However, *in loco* studies about the inhibitors' performance, and efficiencies of scale-removal techniques are not always possible owing to the large pipelines dimensions, the fluid flow regimes, and technical difficulties for the simultaneous analysis of chemical and hydrodynamic processes. Consequently, many experimental investigations [1–4] on scale prevention are carried out in laboratories, by simulating some of the conditions that favor the formation of deposits in pipelines.

In the literature, one can find several experimental studies [5–8] about $\text{CaCO}_3(\text{s})$ precipitation kinetics in high salinity water, but unfortunately little is known about the thermodynamics of the process of calcium carbonate homogeneous crystallization in highly supersaturated solutions. Basically, supersaturated solutions are non-equilibrium systems, which have a greater concentration of dissolved solute than would exist at equilibrium. For many of these solutions, precipitation of sparingly soluble salts is not observed, although the solutions present a high supersaturation ratio. Since such a behavior is unexplainable according to equilibrium thermodynamics, researchers have developed new physico-chemical models that permit to better understand the dynamics of the crystallization process in supersaturated solutions [9]. In this context, molecular dynamics [10–12] and Monte Carlo simulations [13] have played an important role as they help to elucidate the influence of some parameters— ionic strength, alkalinity, interaction forces between clusters, concentration *etc.*— on the mechanisms of nucleation and growth of calcium carbonate crystals.

Nevertheless, despite the evident theoretical advances provided by works based on molecular dynamics and Monte Carlo simulations, many phenomenological aspects of homogeneous crystallization of calcium carbonate remain untouched, especially those related to mass transfer during the precipitation reaction and

* Corresponding author.

E-mail address: marreis@iqm.unicamp.br (M.C. Reis).<https://doi.org/10.1016/j.apt.2018.03.022>

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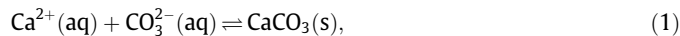
interaction forces between solid particles and dispersion medium. Regarding this matter, the two-fluid model presents a great capability since it provides a general framework for the macroscopic description of non-equilibrium processes without requiring knowledge of several molecular parameters that sometimes are hardly obtainable. Indeed, from the two-fluid model one may develop large-scale simulations under different experimental conditions without prohibitive computational effort.

According to the two-fluid approach, physical quantities experience mathematical discontinuities and fluctuations as a natural result of the motions of solid-liquid interfaces in a solid dispersion. The dynamics of each phase is treated separately, so that each phase of the dispersion has its own governing equations and phenomenological laws. However, since each phase does not evolve independently, interfacial interaction terms appear in the balance equations in order to couple the exchange of physical properties between phases. At this point, the governing equations can be directly obtained from the exploitation of averaging operations by which the discrete distribution of phases is smoothed over a representative volume element, such as presented in the recent work developed by Reis and Wang [14].

Even though molecular dynamics and Monte Carlo simulations provide valuable microscopic information about the nucleation process, there still is no account of phenomenological models in the literature that provide fundamental information about precipitation of $\text{CaCO}_3(\text{s})$ in high ionic strength solutions. Therefore, in view of this, a two-fluid model is proposed in this manuscript for calcium carbonate homogeneous crystallization in highly supersaturated solutions, by applying some ideas of the kinetic theory of granular gases to a solid dispersion. Particularly, the model offers a phenomenological insight into the mass transfer process during the precipitation reaction of calcium carbonate. In order to verify the adequacy of the proposed model, 3D numerical simulations are performed for an experiment of homogeneous crystallization, by coupling the population balance equations to the set of non-linear partial differential equations that govern the mass and linear momentum balances of the solid dispersion. With this approach, one can simultaneously follow the temporal changes in the concentration of $\text{Ca}^{2+}(\text{aq})$, $\text{CO}_3^{2-}(\text{aq})$, and $\text{H}_3\text{O}^+(\text{aq})$ ions during the precipitation, and the changes in the particle size distribution. The good agreement between theoretical results and experimental data indicates that the two-fluid model presented in this work may be successfully used in studies of homogeneous crystallization, especially in those studies whose focus is on large-scale processes.

2. Model equations

Let a solid dispersion be a collection of small solid particles that can exchange mass, linear and angular momenta, energy, etc. through solid-fluid interfaces. Because precipitation of calcium carbonate in highly supersaturated solutions is the result of a heterogeneous chemical reaction that involves ions dissolved in the liquid phase, it is convenient to follow the physico-chemical behavior of both solid and liquid phases. For this purpose, one considers the simplest chemical composition of an aqueous solution of high ionic strength in which precipitation of calcium carbonate may happen. Thus, the liquid phase is regarded as an aqueous solution containing dissolved $\text{Ca}^{2+}(\text{aq})$, $\text{Na}^+(\text{aq})$, $\text{CO}_3^{2-}(\text{aq})$, and $\text{Cl}^-(\text{aq})$ ions, such that the concentration of $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ is much larger than the concentration of other ions as they are in large part responsible for the elevated ionic strength of the solution. At a certain time, when the solution can no longer hold the state of supersaturation because thermal, chemical, and/or mechanical perturbations are introduced into the system, $\text{Ca}^{2+}(\text{aq})$ and $\text{CO}_3^{2-}(\text{aq})$ ions react according to the chemical reaction,



to form crystals of calcium carbonate.

A supersaturated solution containing particles of calcium carbonate must obey the following equations [14],

$$\frac{\partial \rho_1^v \alpha_1^v}{\partial t} + \text{div}(\rho_1^v \alpha_1^v \mathbf{v}_1) + \text{div}(\mathbf{j}_1^v) - \gamma \dot{m}_1^v = 0, \quad (2)$$

$$\frac{\partial \rho_1 \alpha_1}{\partial t} + \rho_1 \text{div}(\alpha_1 \mathbf{v}_1) - \gamma \dot{m}_1 = 0, \quad (3)$$

$$\frac{\partial \rho_2 \alpha_2}{\partial t} + \rho_2 \text{div}(\alpha_2 \mathbf{v}_2) - \gamma \dot{m}_2 = 0, \quad (4)$$

$$\begin{aligned} \frac{\partial \rho_1 \alpha_1 \mathbf{v}_1}{\partial t} + \text{div}(\rho_1 \alpha_1 \mathbf{v}_1 \otimes \mathbf{v}_1) + \alpha_1 \nabla p_1 - \text{div} \mathbf{T}_1 - \alpha_1 \rho_1 \mathbf{g} \\ - c_{12}(\mathbf{v}_2 - \mathbf{v}_1) + \gamma \dot{m}_1 \mathbf{v}_1 = \mathbf{0}, \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{\partial \rho_2 \alpha_2 \mathbf{v}_2}{\partial t} + \text{div}(\rho_2 \alpha_2 \mathbf{v}_2 \otimes \mathbf{v}_2) \\ + \nabla p_2 + \alpha_2 \nabla p_1 - \text{div} \mathbf{T}_2 - \alpha_2 \rho_2 \mathbf{g} - c_{12}(\mathbf{v}_1 - \mathbf{v}_2) + \gamma \dot{m}_2 \mathbf{v}_2 = \mathbf{0}, \end{aligned} \quad (6)$$

where $\alpha_1 = \sum_{v=1}^n \alpha_1^v$, $\rho_1 \alpha_1 \mathbf{v}_1 = \sum_{v=1}^n \rho_1^v \alpha_1^v \mathbf{v}_1^v$, and $\dot{m}_1 = \sum_{v=1}^n \dot{m}_1^v$. In the above equations, the indexes $k = 1$ and $k = 2$ respectively refer to quantities of the liquid and solid phases, and the index $v = 1, \dots, n$ denotes the ionic constituents present in solution. Moreover, α_k stands for the volume fraction of phase k , such that $\alpha_1 + \alpha_2 = 1$, ρ_k is the true mass density, \mathbf{j}_1^v is the diffusive flux, \dot{m}_k is the mass transfer rate per unit area of interface, such that \dot{m}_k is subject to the constraint $\dot{m}_1 + \dot{m}_2 = 0$, γ is the surface area of the solid-liquid interface per unit volume of mixture, \mathbf{v}_k is the partial velocity, p_1 is the hydrostatic pressure, p_2 is the solid pressure, \mathbf{T}_k is the stress tensor, \mathbf{g} is the gravity field, and c_{12} is a coefficient related to the drag force.

Although Eqs. (2)–(6) have been applied for a calcium carbonate dispersion, they are balance equations that any supersaturated solution with particles of sparingly soluble salts must obey. In addition, it is worth mentioning that the proposed model is not appropriate for the case in which precipitation of solid particles is induced by fluctuations of temperature. For this case, the mass transfer rate is greatly dependent on temperature fluxes, and the set of basic governing equations is no longer given by Eqs. (2)–(6), but rather by a set of equations that encompasses the balances of mass, linear momentum, and enthalpy. Thus, since one is not interested in the influence of temperature on the nucleation of particles, the enthalpy balance equation may be omitted in the model.

Eqs. (3) and (4) express the mass balance for a phase of the dispersion in terms of the convective flux of mass $\alpha_k \mathbf{v}_k$, and the mass transfer across the solid-liquid interfaces. An analogous interpretation can also be made for Eq. (2), which gives the mass balance for the ionic constituents. On the other hand, Eqs. (5) and (6) represent the linear momentum balances for the liquid and solid phases, respectively. These equations state that the change rate of linear momentum depends on the convective flux $\alpha_k \mathbf{v}_k \otimes \mathbf{v}_k$, internal stress forces, body forces that act throughout the volume of the phases, and, of course, contact forces that account for the transport of linear momentum across the solid-liquid interfaces. The stress forces that act in the liquid phase are the pressure-gradient force and the viscous forces that are respectively given by the gradient of hydrostatic pressure and divergence of stress tensor \mathbf{T}_1 . Likewise, the operating stress forces in the solid phase are the elastic forces and the interaction forces between solid particles that are given by the divergence of stress tensor \mathbf{T}_2 and the gradient of solid pressure, respectively. In turn, the body forces existing in both solid and liquid phases are exclusively due to the gravitational force, if external electromagnetic fields are absent. To complete

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