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Towards establishing a combined rate law of nucleation and crystal growth – The case study of gypsum precipitation

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ABSTRACT

The main obstacle in the formulation of a quantitative rate-model for mineral precipitation is the absence of a rigorous method for coupling nucleation and growth processes. In order to link both processes, we conducted a series of batch experiments in which gypsum nucleation was followed by crystal growth. Experiments were carried out using various stirring methods in several batch vessels made of different materials. In the experiments, the initial degree of supersaturation of the solution with respect to gypsum (Ω_{gyp}) was set between 1.58 and 1.82. Under these conditions, heterogeneous nucleation is the dominant nucleation mode. Based on changes in SO_4^{2-} concentration with time, the induction time of gypsum nucleation and the following rate of crystal growth were calculated for each experiment. The induction time (6–104 h) was found to be a function of the vessel material, while the rates of crystal growth, which varied over three orders of magnitude, were strongly affected by the stirring speed and its mode (i.e. rocking, shaking, magnetic stirrer, and magnetic impeller). The SO_4^{2-} concentration data were then used to formulate a forward model that couples the simple rate laws for nucleation and crystal growth of gypsum into a single kinetic model. Accordingly, the obtained rate law is based on classical nucleation theory and heterogeneous crystal growth.

1. Introduction

The precipitation of minerals from solution in general, and of gypsum ($CaSO_4{\cdot}2H_2O$) in particular, is a common phenomenon in nature. Evidence for gypsum precipitation can be found in the geological record [22,26,44,8], as well as in contemporary natural environments [10,38,15]. Gypsum is also widespread as a side product during environmental remediation such as treatment of mine tailings [11], as well as during various industrial processes, such as in the petroleum industry [12,46,40,2], during the course of forward and reverse osmosis [34,45,4,50], in the processes of nano filtration of agricultural drainage water [16] and as scaling in pipes during the flow of reject solutions [21,39].

Due to its abundant occurrence, gypsum precipitation has been extensively studied over the last decades. Most of the studies present rate equations for mineral precipitation which separately describe nucleation and crystal growth rates [41,25,23,18,20,33,45,37]. The few studies that did propose combined rate equations were not based on experimental data (e.g., [19,32]).

The present study presents a simple empirical precipitation rate law based on experimental results, which combines nucleation and growth. The overall aim is to improve our understanding of gypsum precipitation mechanisms. Accordingly, the specific goals are to: (1) formulate a coupled nucleation and crystal growth forward model; (2) examine and interpret the changes in the precipitation rates derived from a wide range of batch reactors made of different materials; (3) examine and interpret the changes in the precipitation rates with various stirring devices and speeds.

2. Scientific background

Two basic processes control mineral precipitation: (a) nucleation, by which a new phase is formed and (b) crystal growth, during which the formed nuclei and crystals continue to grow. Crystal growth from a solution involves both a solid and a liquid phase and thus depends on the properties of both phases and the interface between them. Since crystal growth is a surface reaction, the heterogeneous precipitation rate is a function of the reactive surface area of the mineral. The degree of supersaturation of the

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Nomenclature

A	pre-exponential rate coefficient
a	proportionality coefficient
a_i	activity of species i
b	solubility-independent pre exponential rate coefficient
b_{het}	heterogeneous solubility-independent pre exponential rate coefficient
b_{hom}	homogeneous solubility-independent pre exponential rate coefficient
C_s	solubility
$C_{j\ ini}$	initial concentration (mol kg^{-1})
$C_{j\ p}$	concentration consumed by precipitation (mol kgs^{-1})
$C_{j\ t}$	concentration of component j at time t (mol kgs^{-1})
eq	chemical equilibrium
$f(\theta)$	correction factor for heterogeneous nucleation
IAP	ion activity product
J_s	nucleation rate (mol nuclei m^{-3} s^{-1}, also as, mol nuclei kg^{-1} s^{-1})
K	proportionality coefficient (number of nuclei m^{-3})
k_{het}	heterogeneous rate coefficient (mol s^{-1} m^{-2})
K_{sp}	ion activity product at equilibrium
k'	apparent rate coefficient (mol s^{-1} g^{-1})
k''	larger apparent crystal growth rate coefficient (mol s^{-1} g^{-1})
n	apparent reaction order
N_A	Avogadro number
N_0	concentration of the growth units
N_t	number of crystals at time t
m_i	initial mass of the growing crystals (g)
$M_{nuc\ j}$	stable nucleus of component j (#molecules $nuclei^{-1}$)
m_t	mass of the growing crystals at time t (g)
$\bar{m}_t$	average mass of the growing crystals at time t (g)
p	crystal growth habit coefficient
R	gas constant (J K^{-1} mol^{-1})
$Rate_{het}$	heterogeneous crystal growth rate (mol s^{-1})
S_A	mineral surface area (m^2)
$S_{A(i)}$	initial surface area (m^2)
T	temperature (K)
t	time (s)
T_{ind}	induction time (s)
V	solution volume (m^3)
V_m	mineral molar volume (m^3 mol^{-1})
β	geometric shape factor
ΔG_r	reaction's Gibbs free energy
ν	number of ions in the crystal formula unit
ρ	solution density (kg m^{-3})
σ	solution-mineral interfacial energy (J m^{-2})
υ	frequency factor
Ω	degree of supersaturation of the solution
Ω_{gyp}	degree of supersaturation of the solution with respect to gypsum
Ω_{ini}	initial degree of supersaturation of the solution

solution with respect to the growing crystal is another key parameter in determining the growth rate.

Eq. (1) is a typical rate law describing the dependence of crystal growth rate on the deviation from equilibrium [29]:

$$\frac{Rate_{het}}{S_A} = k_{het}\cdot\left(\Omega^{1/\nu}-1\right)^n \tag{1}$$

where Ω is the degree of supersaturation of the solution, $Rate_{het}$ is the observed heterogeneous crystal growth rate (mol s^{-1}), S_A is the mineral surface area (m^2), k_{het} is a heterogeneous rate coefficient (mol s^{-1} m^{-2}), ν is the number of ions in the crystal formula unit other than the solvent (two in the case of gypsum) and n is the apparent reaction order with respect to the deviation from equilibrium ($\Omega - 1$).

The surface area following dissolution or precipitation may be empirically related to the initial surface area ($S_{A(i)}$) [9,48,49,18]:

$$S_A = S_{A(i)}\cdot\left(\frac{m_t}{m_i}\right)^p \tag{2}$$

where m_i and m_t are the masses (g) of the initial and the growing crystals at time t, respectively, and p is a coefficient that depends on the crystal growth habit. p is equal to 2/3 if the surface proportions of the growing crystal remain invariant during the growth process [41].

While the rate of crystal growth may be monitored by following the decrease in concentrations of the dissolved lattice ions, this cannot be done for nucleation, due to the slow rate of consumption of lattice ions. In the absence of crystallization seeds, a time period elapses before the detection of the formation of a new phase in the supersaturated system. This time is known as the "induction period" or "induction time" (T_{ind}) [43]. It should be noted that the induction time is generally longer than the time required for the actual nucleation, and includes also a period of crystal growth that takes place prior to the detection of the new phase. The induction time is not a fundamental property of a system since the term "new phase detection" depends on the observation method, such as the first "appearance" of crystals or the onset of an identifiable change in solution property [43]. The definition and duration of the induction time therefore depend on the experimental and analytical set-ups.

Nevertheless, it is widely accepted that the induction time is inversely proportional to the nucleation rate [27]:

$$T_{ind} = \frac{K}{J_s} \tag{3}$$

where J_s is the nucleation rate (number of nuclei m^{-3} s^{-1}) and K is a proportionality coefficient.

The main parameters affecting the rate of nucleation (and therefore the induction time) include [28,7,48,49,6]: (a) The degree of supersaturation of the solution with respect to the nucleating mineral; (b) interfacial energy between the mineral and the solution; (c) presence (or absence) of catalysts and inhibitors (such as antiscalants), (d) temperature; and (e) solubility of the mineral in solution, defined as the molal concentration of the mineral at saturation state. In stoichiometric solutions, the solubility is equal to the molal concentration of any of the lattice ions, divided by its stoichiometric coefficient in the mineral formula. In non-stoichiometric solutions the solubility is equal to the lowest amongst these quotients.

According to the classic nucleation theory [28,47,13], the nucleation rate (J_s) depends on the solution-mineral interfacial energy (σ, J m^{-2}), the molar volume of the mineral (V_m, m^3 mol^{-1}), the temperature (T, K) and the supersaturation degree of the solution (Ω):

$$J_s = A\cdot\exp\left\{-\frac{\beta V_m^2\sigma^3 N_A f(\theta)}{(RT)^3\ln^2\Omega}\right\} \tag{4}$$

where A is a pre-exponential rate coefficient, β is a geometric shape factor, N_A is Avogadro number, $f(\theta)$ is a correction factor for heterogeneous nucleation and R is the gas constant (J K^{-1} mol^{-1}).