A generalised chemical precipitation modelling approach in wastewater treatment applied to calcite

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Highlights (for review)

- A general kinetic-based model for precipitation has been identified and validated.
- The model is first order in mineral state and \( n \)th order in supersaturation.
- The model is tolerant to a fast kinetic coefficient, but not a slow coefficient.
- The kinetic effect of temperature can be corrected with Arrhenius-relationships.
- This base model can be applied to multiple simultaneous precipitation reactions.
\[ R_{\text{cryst}} = k_{\text{cryst}} X_{\text{cryst}} \sigma^n \]
A generalised chemical precipitation modelling approach
in wastewater treatment applied to calcite

Christian Kazadi Mbamba a, Damien Batstone a, Xavier Flores-Alsina b, Stephan Tait a

a Advanced Water Management Centre, The University of Queensland, St Lucia, Brisbane, QLD 4072, Australia
b CAPEC-PROCESS, Department of Chemical and Biochemical Engineering, Technical University of Denmark,
Building 229, DK-2800 Lyngby, Denmark.

ABSTRACT

Process simulation models used across the wastewater industry have inherent limitations due
to over-simplistic descriptions of important physico-chemical reactions, especially for
mineral solids precipitation. As part of the efforts towards a larger Generalized
Physicochemical Modelling Framework, the present study aims to identify a broadly
applicable precipitation modelling approach. The study uses two experimental platforms
applied to calcite precipitating from synthetic aqueous solutions to identify and validate the
model approach. Firstly, dynamic pH titration tests are performed to define the baseline
model approach. Constant Composition Method (CCM) experiments are then used to
examine influence of environmental factors on the baseline approach. Results show that the
baseline model should include precipitation kinetics (not be quasi-equilibrium), should
include a 1st order effect of the mineral particulate state (X_{cryst}) and, for calcite, have a 2nd
order dependency (exponent n=2.05±0.29) on thermodynamic supersaturation (σ). Parameter
analysis on the kinetic coefficient k_{cryst}, indicated that the model was more tolerant to a fast
kinetic coefficient (k_{cryst}) and so, in general, it is recommended that a large k_{cryst} value be
nominally selected where insufficient process data is available. Zero seed (self nucleating)
conditions could be effectively represented by including arbitrarily small amounts of mineral phase in the initial condition. Both of these aspects are important for wastewater modelling, where knowledge of kinetic coefficients, and precipitates present, are not usually known. The CCM experiments confirmed the baseline model, particularly the dependency on supersaturation. Temperature was also identified as an influential factor that should be corrected for via an Arrhenius-style correction of $k_{\text{cryst}}$. The influence of magnesium (a common and representative added impurity) on $k_{\text{cryst}}$ was found to be significant but was considered an optional correction because of a lesser influence as compared to that of temperature. Other variables such as ionic strength and pH were adequately captured by the quasi-equilibrium description of the aqueous-phase and no further kinetic corrections were required. The baseline model is readily expandable to include other precipitation reactions. For simple representations, large values for $k_{\text{cryst}}$ with $n=2$ (or $n=2$ or 3 for other minerals) should be selected without corrections to $k_{\text{cryst}}$, and, where accuracy is required (e.g., in mechanistic studies), machine estimation of $k_{\text{cryst}}$ should be performed with robust process data and $k_{\text{cryst}}$ should at least be corrected for temperature.

**Keywords**

Physico-chemical modelling, minerals precipitation, calcite, acid-base titration, equilibrium, kinetics

**1. Introduction**

In recent years, mathematical process modelling of wastewater processes has become an increasingly active field, with models being successfully used for research, process design, training, control and optimization of physical, chemical and biological processes. However,
to date the focus of model development has largely been on the biological reactions that 
occur during wastewater treatment (Henze et al., 2000; Batstone et al., 2002). Much less 
attention has been given to the many non-biological chemical reactions that occur in 
wastewater treatment, even though such reactions are essential to achieve effective treatment 
(Batstone et al., 2012). Process simulation models used across the industry currently have 
inherent limitations due to simplistic and situation-specific representations of important 
physico-chemical reactions (Batstone, 2009). A key neglected area is liquid-solid chemical 
precipitation modelling, due to its widespread occurrence in wastewater treatment processes 
(Doyle and Parsons, 2002; Chen et al., 2008; Batstone and Keller, 2003; van Langerak et al., 2000) and a general under-representation in existing standardised models (Batstone et al., 2012). Chemical precipitation is also particularly significant from a modelling perspective, because of heavy interactions with other physico-chemical reactions in the wastewater such 
as the weak acid-base system and ion complexation. A model containing chemical 
precipitation therefore automatically requires representation of other physico-chemical 
reactions, which is a key limitation of (for example) the ASM2d (Henze et al., 2000) which 
models precipitation without considering pH.

Several studies have used mathematical modelling to improve the understanding of chemical 
precipitation mechanisms in wastewater treatment (Barat et al., 2009; Maurer et al., 1999; 
Musvoto et al., 2000; Smith et al., 2008; Szabó et al., 2008; Tait et al., 2009; van Rensburg et 
al., 2003). Typically, unique modelling approaches have been applied to specific 
experimental datasets. Key differences between the various modelling approaches have 
included:

(a) an assumption that precipitation reactions are occurring at sufficiently rapid rates to be 
effectively at equilibrium (Smith et al., 2008; Hanhoun et al., 2011; Loewenthal et al., 1995;
Ohlinger et al., 1998; Scott et al., 1991; Wrigley et al., 1992) or instead treating them as kinetic reactions in the dynamic state equation set (Maurer et al., 1999; Musvoto et al., 2000; van Rensburg et al., 2003);

(b) accounting for the effect of the available mineral surface area on the overall rate of precipitation (Smith et al., 2008; Tait et al., 2009) or not (Musvoto et al., 2000); and

(c) assuming competitive or synergistic interactions are occurring between multiple chemical precipitation reactions occurring in parallel (Barat et al., 2011) or not (Musvoto et al., 2000).

In particular, more complex models that include multi-step precipitation with a broad range of controlling mechanisms tend to focus on specific applications, with generalised approaches being simplified to equilibrium and simple kinetics. To date, there has not been substantial experimental-based work focussed on systematically developing a general precipitation modelling approach. With increasing interest in correctly predicting precipitation such as struvite for phosphorus resource recovery (Rahaman et al., 2014; Galbraith et al. 2014), and with the rise in plant-wide model descriptions (Gernaey et al., 2011) to develop new control strategies that consider nutrient recovery, a generally applicable and robust model approach is required for both detailed mechanistic descriptions and broader engineering analysis.

In this paper, a baseline precipitation model approach is developed in the context of calcite precipitation and further analysis then focuses on clarifying key environmental factors that influence precipitation modelling. The model approach is intended to form part of a larger Generalized Physicochemical Modelling Framework (Batstone et al., 2012) but is also intended for use across a wider range of wastewater applications. The paper is structured to first present the baseline precipitation model validated via dynamic pH titration tests, after which Constant Composition Method (CCM) experiments and robust statistics are used to examine the influence of environmental factors.
2. Materials and methods

Experiments investigated the precipitation of calcite (a crystalline form of calcium carbonate) from synthetic aqueous solutions. Two experimental platforms were used, namely, dynamic pH titration tests with precipitation, and the Constant Composition Method (CCM). Titration was used to identify the baseline model approach across a range of pH values, and CCM tests investigated the influence of environmental factors on the baseline model approach. In continuous pH titration the aqueous solution is titrated from a low pH to a high pH with precipitation or dissolution of minerals occurring along the way. The Constant Composition Method maintains a constant chemical composition while precipitation occurs, by continuously adding a titrant to replenish soluble ingredients that are being sequestered by the precipitating mineral (Tomson and Nancollas 1978). The rate of precipitation for a CCM test can then be directly quantified from the amount of titrant added over time.

2.1 Materials

Analytical reagent-grade chemicals and de-ionised water were used in all cases. Metastable (no spontaneous nucleation) supersaturated test solutions were prepared by adding an aqueous solution of calcium chloride (CaCl$_2$) at a known concentration, drop-wise over 20-30 minutes, to an aqueous solution of sodium bicarbonate (NaHCO$_3$) at a known concentration. The ionic strength of test solutions was altered with dissolved potassium chloride. The inorganic carbon reagent solution was always prepared fresh. Synthetic calcite seed crystals were prepared similarly in a 50:50 mix of CaCl$_2$ and sodium carbonate (Na$_2$CO$_3$) solutions at 25°C, but at a much higher dissolved calcium carbonate concentration of 0.4 M to induce
spontaneous nucleation. The addition of CaCl$_2$ was much slower for the seed preparation (dropwise over about 2-3 hours). Freshly precipitated seed crystals were aged for 2 days in their mother liquor and were subsequently extensively washed with distilled water. The washed seed crystals were aged for at least 3 weeks in a 0.02 M aqueous solution of NaHCO$_3$, then filtered and again washed with distilled water. Adhering water was displaced with absolute ethanol which in-turn was evaporated off at 18-20°C in a desiccator to minimize re-exposure to moisture. The crystals were examined using X-ray diffraction analysis as per the method below and only peaks for calcite were detected. Specific surface area and crystal morphology were examined by nitrogen adsorption and scanning electron microscopy, respectively, as described below.

### 2.2 Apparatus

The dynamic titration experiments used an auto-titrator (T50, Mettler-Toledo, Greifensee, Switzerland) with a pH sensor (Model DGi115-SC, Mettler-Toledo, Greifensee, Switzerland). The titrator was equipped with a 10 mL burette to add titrant to the test solutions. Titration vessels used were (a) 100 mL beakers, with working volumes of 75 mL or b) a 1 L stirred glass crystallizer. During a titration, the test sample to which titrant was added was stirred with a 25 mm teflon-coated magnetic bar stirrer at 300 rpm. The volume of each titrant added, the pH and the temperature were recorded over time through a LabX Light Titration Software interface (Mettler-Toledo, Greifensee, Switzerland).

The CCM experiments used a crystallizer (See schematic in Supporting Information) which was a 1.0 L (working volume = 900 mL) Pyrex glass vessel with a glass heating/cooling jacket and a sealed lid with crimp-sealed ports for sensors to minimize atmospheric gas-
exchange. The crystallizer, positioned over a magnetic stirrer plate, was stirred with a 40 mm
teflon-coated magnetic bar stirrer at 350 rpm. Water was circulated from a temperature-
controlled water bath through the jacket to maintain the temperature inside the crystallizer to
within ±0.5°C. A change in the continuously measured pH (S900C, Sensorex, Garden Grove,
USA) triggered the simultaneous addition of two titrants by high-accuracy self-priming
micropumps (120SP, 130SP, Bio-Chem Valve, New Jersey, USA), which replaced the
dissolved calcium and inorganic carbon and maintained a constant pH (to within 0.1%) and
aqueous phase composition (to within 1.5% of the set concentrations). The volume of each
titrant added was recorded over time through a LABVIEW VI Software interface (v. 11.0,
National Instruments, Austin, USA) via a multifunction data acquisition card (iUSBDAQ
U120816, Hytek Automation, Ontario, Canada). Calcium ion activity was also monitored
with an ion selective electrode (Model 361-75, Sentek, Essex, UK) and was recorded.

2.3 Experimental protocol

For the dynamic titration tests, the pH of a 1 L aliquot of test solution with known
composition (actual volume known accurately) was adjusted to a desired initial value with
concentrated sodium hydroxide (NaOH) or hydrochloric acid (HCl) solution, with the amount
of added acid or caustic recorded. A 2M aqueous solution of NaOH (5-10 mL total) was then
quantitatively added at a predetermined fixed rate and pH was continuously measured. For
each experiment, pH and the rate and volume of titrant added were continuously recorded
with the control software as was the volume of the original test solution. For chemical
analysis, 1.1 mL samples of the titration vessel contents were collected at specified time
intervals, immediately filtered through 0.2 µm cut-off syringe filters (PES), diluted with
deionized water to prevent post-precipitation and stored at 4°C until analysis by Inductively
Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and a Total Carbon Analyser as detailed below. The experimental conditions were as follows:

a) 2.6M NaOH added at a rate of $2.5 \times 10^{-5}$ mL.min$^{-1}$ to a synthetic aqueous solution with 4.95mM sodium bicarbonate (NaHCO$_3$) and 1.96mM calcium chloride (CaCl$_2$) with initial pH decreased by adding a small quantity of concentrated HCl.

b) 2.35M NaOH added at a rate of $2.5 \times 10^{-5}$ mL.min$^{-1}$ to a synthetic aqueous solution with 4.86mM NaHCO$_3$ and 1.95mM CaCl$_2$ (initial pH was also decreased with concentrated HCl) and 50 mg.L$^{-1}$ of calcite seed added when the saturation index (SI) value was estimated to be near zero (See below).

c) 2.6M NaOH added at a rate of $2.5 \times 10^{-5}$ mL.min$^{-1}$ to a synthetic aqueous solution with 4.87mM NaHCO$_3$ and 1.98mM CaCl$_2$ (initial pH was decreased with concentrated HCl) and 200 mg.L$^{-1}$ of calcite seed material when the SI value was estimated to be near zero (See below).

For the CCM tests, metastable test solutions were added to the crystallizer and while stirring, the initial pH was adjusted by drop-wise addition of 1M NaOH or HCl as required. Once the measured pH was stable, precipitation was initiated by adding a weighed amount of calcite seed crystals. Usually, this seed addition immediately triggered titrant dosing. Separate sets of experiments were performed to assess the effect of various environmental factors (See Table 1 for test conditions). Measured calcite precipitation rate ($R_{\text{calcite}}$, moles.L$^{-1}$.min$^{-1}$) for each CCM experiment was determined as follows:

$$R_{\text{calcite}} = C_{\text{eff}}q_t$$  

where $q_t$ is the titrant flow rate (L.min$^{-1}$) and $C_{\text{eff}}$ is the equivalent number of moles precipitated per litre of added titrant per L of reactor vessel (moles.L$^{-1}$.L$^{-1}$). Values of $q_t$ were determined by linear regression fits of the cumulative volume of titrant added over time.
2.4 Analytical techniques

X-ray diffraction analysis (Bruker D8, Bruker, Massachusetts, USA) of the seed crystals, only detected peaks for calcite and had a clear background. The specific surface area of the seed crystals was measured by nitrogen adsorption (Tristar II 3020, Micromeritics, Norcross, GA) and is given in Table 1. Seed crystal morphology was examined with scanning electron microscopy (JEOL 2100, JEOL Ltd, Tokyo, Japan) and was found to resemble the typical morphology of calcite with reasonably uniform particle size.

The major elements (Ca, Na) in the synthetic aqueous solution were analysed with ICP-OES (Perkin Elmer Optima 7300DV, Waltham, MA, USA). Total Inorganic Carbon (TIC) concentrations were quantified using a Total Carbon Analyser (Shimadzu TOC-L CSH Total Organic Carbon Analyser, Kyoto, Japan).

2.5 Data and model analysis

A reduced form of the draft generalised physicochemical model (See Supplementary Material) was used with states that were not being utilised, deactivated in the code for the sake of speed and simplicity. The baseline precipitation model approach applies an algebraic equation set for fast aqueous-phase reactions such as weak acid-base and ion pairing, and simple kinetics for mineral precipitation reactions.

2.5.1 Aqueous-phase reactions: Algebraic equation set
Weak acid-base reactions and ion pairing were mathematically described with a set of non-linear algebraic equations as is commonly done in geochemical reference models (Allison et al., 1991; Parkhurst and Appelo, 1999). The equation set included one law of mass-action (see Eq. (2)) for each aqueous phase reaction and a number of molar contribution balances (see Eq. (4)) to satisfy the required degrees of freedom for the calculation. In general form, the mass action laws were:

\[ K_i = \prod_{j=1}^{N} S_{(j)}^{v_{ij}} \quad i = 1, 2 \ldots, N \]  

(2)

where \( K_i \) is the equilibrium constant for aqueous phase reaction \( i \), \( v_{ij} \) is the stoichiometric coefficient of the reactant or product \( j \) for aqueous phase reaction \( i \), and \( S_{(j)} \) is soluble concentrations expressed in terms of chemical activities, applied as corrections due to deviations from ideality. Chemical activities are equal to the actual physical soluble concentrations \( S_j \) multiplied by a correction factor \( \gamma_j \) as follows (Eq. (3)):

\[ S_{(j)} = \gamma_j S_j \]  

(3)

where \( S_{(j)} \) is the chemical activity and \( \gamma_j \) is activity coefficient describing how interactions among charged ions influence chemical behaviour. The extent of correction for non-ideal behavior depends on the ionic strength of the wastewater, with increasing corrections required for a higher ionic strength. In this work, the Davies approximation to activity coefficients was used with temperature correction. Equilibrium constants (\( K_i \)) were also adjusted for temperature using the constant-enthalpy form of the van’t Hoff equation.

In general form, the molar contribution balances were:

\[ S_{\text{tot}} = \sum_{i=1}^{N} S_i \]  

(4)
where $S_{i,\text{tot}}$ is the total measurable concentration of an aqueous phase ingredient which is the sum contribution of that ingredient in various chemical forms in the aqueous phase.

In this work, a reactive proton balance (a molar contribution balance) was used for pH calculations as done by others (Serralta et al, 2004). The reactive proton balance (TotH) approach is noted to be fully compatible with the alternative charge balance/electroneutrality approach. Indeed, a charge balance model was also run and the results were identical to that of the TotH model. As is commonly done, the mass action laws were substituted into the molar contribution balances until all the remaining substituted equations were linearly independent (the most reduced form of the algebraic equation set). The Tableau method (Morel and Morgan, 1972) was used to guide this substitution of equations which reduced the number of equilibrium variables from 25 ($H^+, Na^+, K^+, Cl^-, CO_3^{2-}, Ca^{2+}, Mg^{2+}, CaCl^+, CaCO_3,$ $CaHCO_3^+, CaOH^+, H_2CO_3, HCO_3^-, KCl, KOH, Mg_2CO_3^{4+}, MgCl^+, MgCO_3, MgHCO_3^+, MgOH+, NaCl, NaCO_3^-, NaHCO_3, NaOH, OH^$) down to seven ($H^+, Na^+, K^+, Cl^-, CO_3^{2-}, Ca^{2+}, Mg^{2+}$). The former are commonly called chemical species and the latter are called chemical components. The chemical species were calculated from the mass action laws and the solved chemical components.

The implicit algebraic equation set was iteratively solved by the Newton-Raphson (NR) method as follows:

$$Z_{i+1} = Z_i - \nabla G(Z_i)^{-1} G(Z_i)$$

where $Z_i$ is the vector of equilibrium variables ($z_{1,i}, ..., x_{n,i}$) obtained from the previous iteration step $i$, $G(Z_i)$ is a vector containing the values of the set of implicit algebraic equations ($g_1(z_1, ..., z_n), ..., g_n(z_1, ..., z_n)$) which has to be zero in order to satisfy equilibrium and $\nabla G(Z_i)$ is the function gradient for step $i$. The iteration was repeated as long as the elements
of the error function are larger than a predefined value, which in this case was set to $10^{-12}$. A reduced analytical 1-D gradient ($\nabla G = \left[ \frac{\partial g_1}{\partial z_1}, \ldots, \frac{\partial g_n}{\partial z_n} \right]$) considering only the identity elements was used in this case due to its convergent nature and to increase speed, but the full gradient could also be used for a more complex system. The aqueous phase model results were verified against Visual MINTEQ (Version 3.0, Royal Institute of Technology (KTH)) and thermodynamic parameters were also sourced from the Visual MINTEQ database. The set of algebraic equations were solved for each time step with precipitation implemented as rate equations (ordinary differential equations). The method used solves the differential equations separately with an ODE solver in SIMULINK, and then iterates at each time step the accompanying nonlinear algebraic system using an iterative solver (Newton-Raphson method). As a result, the pH and aqueous species concentration were calculated as a function of time through a series of differential algebraic equations (DAEs).

The species and components were also used to determine precipitation or dissolution, by calculating the well-known indicator, the Saturation Index ($SI$ value):

$$SI = \log_{10} \left( \frac{S_{(Ca^{2+})} S_{(CO_3^{2-})}}{K_{SP,\text{calcite}}} \right)$$

(6)

where $S_{(Ca^{2+})}$ and $S_{(CO_3^{2-})}$ are the chemical activities of calcium and carbonate ions in the aqueous phase and the solubility product constant for pure calcite ($K_{SP,\text{calcite}}$) was taken to be $10^{-8.48}$ at 25$^\circ$C (Nordstrom et al., 1990; Plummer and Busenberg, 1982). For a given aqueous phase, three conditions exist:

- $SI < 0$, the aqueous phase is undersaturated and a mineral solid phase can dissolve into the aqueous phase;
- $SI = 0$, the aqueous phase is saturated or at equilibrium; or
• $SI > 0$, the aqueous phase is supersaturated or oversaturated with respect to the mineral and chemical precipitation can occur.

In general, the $SI$ value can help a model developer to select relevant mineral precipitation reactions for inclusion in the model (if $SI > 0$, or if $SI < 0$ and mineral phase is present).

2.5.2 Precipitation: Simple kinetics

Calcium carbonate precipitation was modelled with three dynamic state equations for total dissolved calcium, total dissolved inorganic carbon and the particulate calcite mineral phase. The baseline model proposed in this paper, used a semi-empirical kinetic rate law (Nielsen and Toft 1984, Stumm and Morgan 1996):

$$ R_{calcite} = k_{cryst} X_{CaCO_3} \sigma^n $$

with $n=2$  \hspace{1cm} (7)

where $R_{calcite}$ is the calcite precipitation rate (moles.L^{-1}.min^{-1}), $k_{cryst}$ is an empirical kinetic rate coefficient (min^{-1}), $X_{CaCO_3}$ (moles.L^{-1}) is the concentration of calcium carbonate precipitate at any time $t$ (a dynamic state variable) (similar to the approach of (Wiechers et al., 1975)) and $n$ is the order of the precipitation reaction with respect to supersaturation, $\sigma$, calculated as follows (Nielsen, 1984):

$$ \sigma = \left( \frac{S_{(Ca^{2+})} \times S_{(CO_3^{2-})}}{K_{sp,calcite}} \right)^{\frac{1}{2}} - 1 $$

A non-zero initial condition of $X_{CaCO_3}$ of $1\times10^{-6}$ M (which is 0.1 mg.L^{-1}) was used to model the dynamic titration experiment that had no seed crystals added (self-nucleating).

The gaseous species carbon dioxide (CO$_2$) is not considered in this model (only dissolved H$_2$CO$_3$), because prevailing low concentrations of inorganic carbon and pH adjustment with sodium hydroxide (rather than by aeration), caused little to no stripping of CO$_2$ during the
experiment. In cases where CO$_2$ mass transfer would be important, a model could readily include the gas stripping or dissolution as a kinetic or quasi-equilibrium process as per Batstone et al. (2002).

2.5.2 Model analysis

The only adjustable parameter in the baseline model (Eq. (7)) was $k_{\text{cryst}}$, because the algebraic equation set was entirely resolved by thermodynamics with no adjustable parameters. The best fit value of $k_{\text{cryst}}$ was estimated by simultaneously fitting pH titration data from three separate experiments with very different experimental conditions, using a non-linear parameter estimation technique, *lsqcurvefit*, in MATLAB. Calcium concentration was selected as the fitted output and the residual sum of squares was selected as the objective function ($J=\text{RSS}$). The model was implemented in MATLAB S-Function/SIMULINK (Version 8.1, MathWorks Inc.) and the complete model code is also included in the Supplementary Material. Errors in parameters were generally estimated by two-tailed $t$-tests based on linear estimates of standard error, but where necessary, true confidence intervals were estimated based on an F-test in $J$ as follows:

$$J_{\text{crit}} = J_{\text{opt}} \left(1 + \frac{p}{n_{\text{data}}-p}\right) F_{0.95,p,n_{\text{data}}-p}$$

(9)

where $J_{\text{crit}}$ is the 95% confidence objective function (where $p=p_{95}$), $p$ is the number of parameters (1), $n_{\text{data}}$ is the number of data points, and $F_{0.95,p,n_{\text{data}}-p}$ is the cumulative F distribution value.

Further model analysis tested the importance of various optional corrections to $k_{\text{cryst}}$ for the influence of environmental factors, and sought to validate the linear dependency of precipitation rate on $X_{\text{CaCO}_3}$ and the exponent $n=2$ in Eq. (7). For this purpose, an Analysis of
Variance (ANOVA) first identified significant singular and interaction effects of environmental factors on calcite precipitation rates measured in the CCM experiments. Other CCM tests (Lin and Singer, 2005) typically examine normalized precipitation rates (precipitation rate divided by mineral surface area) instead of raw precipitation rates (not normalized) as determined by Eq. (1), but in the present study, raw precipitation rates were preferred as a more applicable approach. ANOVA was carried out with the software package R (Version 3.0.1, 2013-05-16, The R Foundation for Statistical Computing) with a significance threshold of 5%. Non-linear regression analysis was then performed with the nlinfit function in MATLAB to assess the significant environmental effects, either as kinetic corrections to \( k_{\text{cryst}} \) or by parameter estimating the exponent \( n \) on supersaturation. The regression analysis also clarified the effect of \( X_{\text{CaCO}_3} \) in Eq. (7) by determining a power-law dependency (\( y \)) of the precipitation rates on \( X_{\text{CaCO}_3} \) as follows:

\[
R_{\text{calcite, measured}} = k_{\text{cryst}} (X_{\text{CaCO}_3})^y \sigma^n
\]

\( k_{\text{cryst}}, y \) and \( n \) = estimated parameters \hspace{1cm} (10)

The correction for added magnesium impurity was approximated with an adsorption style relationship as follows:

\[
k_{\text{cryst, corrected Mg}} = k_{\text{cryst}} \times \left(1 - \frac{K_{\text{ads}} \times S_{\text{Mg}^{2+}}}{K_{\text{ads}} \times S_{\text{Mg}^{2+}} + 1}\right)
\]

\( k_{\text{cryst, corrected Mg}} \) = \( k_{\text{cryst}} \) \hspace{1cm} (11)

where \( S_{\text{Mg}^{2+}} \) is the free dissolved magnesium ion concentration and \( K_{\text{ads}} \) is an empirical adsorption coefficient (L.mole\(^{-1}\)). The form of Eq. (11) was selected because magnesium is said to adsorb and block growth sites on the calcite crystal lattice instead of calcium ions due to chemical similarity between calcium and magnesium (Reddy and Wang, 1980; Lin and Singer, 2009; Chen et al., 2006; (Ferguson and McCarty, 1971)). The kinetic effect of temperature (in degrees Kelvin) was corrected for with the correction form of the Arrhenius-style relationship:
where $k_{\text{cryst,25}}$ is the reference value of $k_{\text{cryst}}$ at 25°C (298K), $R$ is the ideal gas constant (8.314×10^-3 kJ.mol^-1.K^-1) and $E_a$ is an empirical activation energy (kJ.mol^-1).

3. Experimental results

3.1 Dynamic titration experiments

Three titration experiments under very different conditions (200 mg.L^-1 added seed, 50 mg.L^-1 added seed, 0 mg.L^-1 added seed) were fitted with the baseline model of Eq. (7), giving an estimated value for $k_{\text{cryst}}$ of 0.0025±0.0004 min^-1 (±linear estimate of 95% confidence interval). Fig. 1 presents the fit together with the experimental data and shows that the baseline model fit all three experiments qualitatively well. The model fit of the experiment with 0 mg.L^-1 added seed was found to be insensitive to nominated concentrations below 1×10^-5 M.

The objective function $J$ (residual sum of squares) is presented in Fig. 2 and shows that the true 95% confidence region for $k_{\text{cryst}}$ was 0.0018-0.0038 min^-1 ($J_{\text{crit},95}=2764.8$). Fig. 2 also shows strong asymmetry which suggests that the model is more tolerant of high values of $k_{\text{cryst}}$ as opposed to low values of $k_{\text{cryst}}$ and thus a quasi-equilibrium approach (arbitrary high value of $k_{\text{cryst}}$) may be a valid approach where insufficient process data exists (see Discussion). However, Fig. 3 presents simulated and calculated saturation index values ($SI$), and clearly shows that $SI$ values were never zero during precipitation between 30-200 minutes (never at equilibrium). These results suggest that the precipitation was still
kinetically limited, albeit that the SI values were generally less positive for a larger amount of added seed (see Discussion).

3.2 Constant composition experiments

The constant composition (CCM) experiments sought to clarify the influence of environmental factors on the baseline model approach of Eq. (7). Fig. 4 presents typical results from CCM experiments and shows that the rate of titrant addition \( q_t = \frac{dV}{dt} \) was stable. This translates to a single constant value of \( R_{\text{calcite}} \) measured for each experiment. Table 2 presents results for the Analysis of Variance which indicated a very strong influence of supersaturation, \( \sigma \) (P<0.0001), in agreement with the baseline modelling approach of Eq. (7). Water temperature (\( T \)) was also found to have strong influence (P<0.001). The effect of added magnesium impurity (\( S_{\text{Mg}^{2+}} \)) was noted to be significant (P<0.05), but was much weaker than the influence of \( T \). Higher order effects of magnesium, temperature and supersaturation was also found to be statistically significant (Table 2). However, the impact of these higher order effects on \( k_{\text{cryst}} \) is expected to be too small to justify a more complex model that accounts for these influences. The effects of ionic strength (\( \mu \)) and \( pH \) were found to be not significant (Table 2, P>0.05) or have low effect, and indicates that their influence on kinetics has been appropriately resolved via calculations of supersaturation (\( \sigma \)) with the algebraic equation set.

To show the performance of the baseline model approach of Eq. (7) with and without optional corrections for magnesium and temperature, Fig. 5 presents a comparison of measured precipitation rates from the CCM Test 1 (Table 1) vs. fitted precipitation rates via the non-linear regression analysis. Fig. 5A presents the baseline model fits of Eq. (7) without
optional corrections, Fig. 5B presents the baseline model fits with $k_{\text{cryst}}$ corrected only for
temperature and Fig. 5C presents the baseline model fits with $k_{\text{cryst}}$ corrected for both
magnesium and temperature. In general, the model fit appears to be qualitatively good only if
a temperature correction is applied with Eq. (12) (then $R^2$ is $>0.9$). The $R^2$ values in Figs. 5B
and C show that corrections for the influence of magnesium on $k_{\text{cryst}}$ (Eq. (11)) and
temperature on $k_{\text{cryst}}$ (Eq. (12)) were significant and appropriate.

A regression analysis was also used to confirm the effects of $X_{\text{CaCO}_3}$ and supersaturation in
Eq. (7), by determining power-law exponents $y$ (Eq. (10)) and $n$ (Eqs. (7) and (10)). This
analysis identified that $y=1$ (linear dependence in crystal mass $X_{\text{CaCO}_3}$) and $n=2$ (2nd order
dependence in supersaturation, $\sigma$), in support of Eq. (7) (see below). Table 3 presents the
estimated values for $y$ and $n$ together with fitting parameters for Eqs. (11) and (12), namely,
$K_{\text{ads}}$, $k_{\text{cryst},25}$ and $E_a$. Precipitation rates were found to generally increase with increasing
supersaturation and increasing added seed concentration ($X_{\text{CaCO}_3}(0)$), and the value of $k_{\text{cryst}}$
and precipitation rates generally increased with increasing temperature and decreased with
increasing magnesium concentration. Most importantly, the exponent $y$ on $X_{\text{CaCO}_3}$ was found
to be $0.96 \pm 0.2$ (given $\pm 95\%$ confidence interval), which indicates a linear relationship as per
Eq. (7), and the exponent $n$ was found to be $2.05(\pm 0.29)$ for experiments with added
magnesium and $1.3-1.6(\pm 0.2)$ for experiments without added magnesium.

4. Discussion

4.1 Baseline modelling approach
A number of environmental factors can influence minerals precipitation in a wastewater. However, results in this paper suggest that a model may only need to consider a limited number of key effects, including supersaturation, the amount of mineral phase present in the wastewater and wastewater temperature (Table 2, Table 3). The findings lead to the simple and robust baseline approach in Eq. (7), with a linear dependency on the mineral solid state $X_{\text{CaCO}_3}$, a 2nd order dependency on supersaturation and a single adjustable parameter $k_{\text{cryst}}$.

This approach has the major advantage of not requiring detailed analysis of mineral surface area present in the wastewater, while still being able to model induction where very low seed concentrations exist. This is important because the amount of mineral surface area is one of the most influential factors for precipitation reactions (Wiechers et al., 1975). Larger amounts of mineral phase forces the precipitation or dissolving of a mineral in a wastewater towards equilibrium, and equilibrium is achieved much faster. This is seen in Fig. 3, where an experiment with a larger amount of added calcite seed had lower $SI$ values between 30 and 100 minutes, because of more rapid precipitation. Solids precipitation is driven by the mineral surface area available in the wastewater. However, it is difficult or impossible to reliably estimate the amount of mineral surface area in a wastewater. Consequently, a lumped growth rate parameter has been common with no separate treatment of mineral phase or mineral surface area (Batstone et al., 2002; van Langerak et al., 2000; Musvoto et al., 2000).

The results of the dynamic titration experiments (Fig. 1) indicated that the baseline model approach of Eq. (7) with $X_{\text{CaCO}_3}$ provided reasonable flexibility and model prediction capability. The constant composition experiments provided further support of this baseline model approach by validating the linear dependency of precipitation rates on $X_{\text{CaCO}_3}$ (Table 3) and by confirming the second-order dependency of precipitation rate on supersaturation $\sigma$ (Table 3).
Parameter estimation (Fig. 2) indicated that the baseline modelling approach was tolerant to quasi-equilibrium (high value of $k_{\text{cryst}}$) but not to slow kinetics (low value of $k_{\text{cryst}}$), so the default approach should adopt a high value for $k_{\text{cryst}}$. This is shown in Fig. 2 which has strong asymmetry with a sharper increase in the value of the objective function $J$ for lower values of $k_{\text{cryst}}$ (below 0.0018 min$^{-1}$) and a very gradual increase in the value of $J$ at higher values of $k_{\text{cryst}}$ (above 0.0038 min$^{-1}$). Having some minimal quantities of mineral seed in a system is not a problem, since the parameter fit was relatively insensitive to seed concentration below 1 mg.L$^{-1}$ and hence this can be used as a default initial condition where the amount of mineral phase present is nil or unknown but small. While the model was more tolerant to high values of $k_{\text{cryst}}$ (indicating that it is equilibrium-limited), it is noted from Fig. 3 and a survey of the wastewater modelling literature (Barat et al., 2011; Joss et al., 2011; van Langerak et al., 1999) that $SI$ values for calcite/aragonite are either significantly positive or negative in wastewater, so precipitation or dissolution have not usually attained strict equilibrium, even within the timeframe of biological processes. Accordingly, it is suggested that, although the model is more tolerant to high values of $k_{\text{cryst}}$, it remains kinetically limited as indicated by the non-zero $SI$ values (Fig. 3).

Eq. (7) is a general approach to simulate precipitation processes from a reaction-based mechanistic standpoint and is designed to be easily coupled with biological models. Such a kinetic-based model allows chemical precipitation reactions to occur with each model timestep to achieve a resulting solution composition which may still have a significant supersaturation state. Although the validation is based on calcite precipitation, the model structure can be easily expanded to include precipitation of many other minerals of interest in wastewater treatment, with appropriate selection of $n$. As the approach is general, it is possible to implement the precipitation model to calculate the pH for precipitating systems.
and to simulate precipitation in whole-of-plant models. In full-scale facilities, it is expected that mineral precipitates would be continuously recycled, such that the linkage of rate to precipitate is implicitly included. The presence of and recycling of heterogeneous surfaces (e.g. grit or particulate organics) in wastewater can and probably does induce heterogeneous nucleation and thus minerals precipitation. Nevertheless, it is expected that this would not greatly influence the model approach proposed in Eq. (7), for two reasons: (1) nucleation (whether homogeneous, or more likely heterogeneous) is allowed for in Eq. (7) by seed crystal for each relevant mineral, which accounts for induction kinetics and (2) heterogeneous nucleation is likely to speed up overall precipitation, which is consistent with the default selection of a fast $k_{\text{cryst}}$ in cases where kinetics cannot be fully defined by available data.

Minerals that can precipitate in a wastewater treatment plant include phosphate minerals, carbonate minerals, magnesium ammonium phosphate (struvite), sulfide minerals (at anaerobic conditions) and hydroxides of aluminium and iron (Batstone et al. 2012). Not all of these precipitating reactions take place at all wastewater conditions. Some of these minerals, in particular calcium carbonate and calcium phosphate, are capable of crystallizing out of solution in a variety of different mineral forms (crystalline vs. amorphous, and/or various crystalline polymorphs). It is suggested that the kinetics of transformation from a less to more stable mineral phase can be described by the baseline model approach proposed in Eq. (7), by implementing both polymorphs/phases as parallel competitive reactions with dedicated rate laws. The less stable polymorph/phase can then initially form and ultimately redissolve (via the use of a reversible precipitation reaction) while the more stable polymorph/phase forms over long process times. As precipitation mechanisms in wastewater become clearer (e.g., polymorphs) or where kinetic performance is more important, the proposed model can be
readily expanded with additional rate processes (e.g., stable polymorphs in parallel with a slow $k_{\text{cryst}}$ and high $K_{\text{sp}}$).

4.2 Optional model corrections

The model analysis using data from the constant composition experiments (Table 2) highlighted wastewater temperature as an important environmental factor and a need for temperature corrections of $k_{\text{cryst}}$. This is also shown in Fig. 5 where the model fit is only deemed statistically acceptable ($R^2>0.9$) when temperature correction of $k_{\text{cryst}}$ was applied. Water temperature was observed to be a highly influential environmental factor (Table 2) with the rate of precipitation approximately tripling with a 10°C increase in temperature. A relevant temperature range for wastewater treatment might be 10-50°C, particularly where temperature is artificially manipulated (e.g., in digesters and stripping). Both to account for seasonality and for artificial temperature variations in a plant-wide model, temperature correction of kinetics should be applied and an Arrhenius-style kinetic correction of $k_{\text{cryst}}$ is suggested (Eq. (11)). There is still a general lack of activation energy ($E_a$) values for all the relevant minerals in wastewater (Batstone et al., 2012), although some values are available for relevant minerals (Harmandas and Koutsoukos, 1996; Boskey and Posner, 1973; Inskeep and Silvertooth, 1988). An estimate of $E_a$ for calcite from the present work ($E_a \approx 52 \text{ kJ.mole}^{-1}$, Table 3) agrees well with values of 40-60 kJ.mole$^{-1}$ previously reported by others (Wiechers et al., 1975; Mullin, 2001; Kazmierczak et al., 1982; Nancollas and Reddy, 1973; Nancollas, 1979; Nancollas and Reddy, 1971).

Magnesium impurity showed a significant effect on calcite precipitation rates (Table 2). The presence or absence of magnesium impurity also significantly altered the power law exponent
for the effect of supersaturation on precipitation rates (Table 3). However, the influence of magnesium was much weaker than supersaturation, the concentration of mineral phase and temperature. Accordingly, correction of precipitation kinetics with dedicated inhibition-style terms such as Eq. (11) may be considered as optional, and may depend on the level of model application. Three basic levels of application can be considered:

i. Mainly equilibrium driven – dilute systems (e.g., main line). Aqueous phase via algebraic equation set and precipitation kinetics with a high $k_{\text{cryst}}$ without corrections for temperature and impurities.

ii. Higher wastewater strengths – e.g., digesters. Aqueous phase via algebraic equation set and precipitation kinetics with an order of magnitude estimate of $k_{\text{cryst}}$ based on prior knowledge. Furthermore the model should at least implement kinetic temperature correction of $k_{\text{cryst}}$.

iii. Mission critical modelling (e.g., crystallisers, scaling, mechanistic studies). Aqueous phase via algebraic equation set, precipitation kinetics with the use of reliable kinetic information (very important to this implementation) to estimate $k_{\text{cryst}}$ and kinetic corrections to $k_{\text{cryst}}$ for both temperature and impurities.

The influence of other ions in wastewater such as copper, zinc, and calcium in the case of magnesium-based minerals, may have a similar effect to that observed for magnesium in the present study. It would be possible to include their complexation reactions in the algebraic equation set. Finally, where required for mission critical modelling, the kinetic effects of other ions can be accounted for via an inhibition-style correction of $k_{\text{cryst}}$ such as is implemented for magnesium via Eq. (11).

5. Conclusions
Calcite precipitation could be effectively modelled in both extended pH titration experiments, as well as constant composition experiments using a single-parameter rate equation that was first-order in mineral solid state concentration, and $n$th order in thermodynamic supersaturation ($n=2$ for calcite). This was effective both with and without seed crystal, with no-seed experiments being simulated with a residual (<1 mg.L$^{-1}$) seed mass which effectively replicated induction kinetics. The effect of temperature in precipitation rate kinetics could be corrected for by an Arrhenius-style relationship, while competing ions ($\text{Mg}^{2+}$) could be corrected for by a Langmuir adsorption isotherm. The pH and ionic strength of the aqueous phase did not show substantial additional effects beyond those already accounted for in the base model. Where the kinetic coefficient $k_{\text{cryst}}$ is unknown, it should be preferentially selected as a high value, since the model is tolerant to a high coefficient, but not a low coefficient. Due to its general applicability, the use of this model is recommended for generalised precipitation modelling in wastewater systems.

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Water Association (IWA) is acknowledged for their promotion of this collaboration through their sponsorship of the IWA Task Group on Generalized Physicochemical Modelling Framework (PCM).

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Plummer, L.N., Busenberg, E., 1982. The solubilities of calcite, aragonite and vaterite in CO$_2$-H$_2$O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO$_3$-CO$_2$-H$_2$O. Geochimica et Cosmochimica Acta 46(6), 1011-1040.


Fig. 1 - Data from three titration tests with calcite precipitation (A (0mg.L\(^{-1}\) of calcite seed), B (50mg.L\(^{-1}\) of calcite seed) and C (100mg.L\(^{-1}\) of calcite seed)) for which a model fit of Eq. (7) gave \( k_{\text{calcite}} = 0.0025 \text{ min}^{-1} \). The lines show the model fit of Eq. (7).
Fig. 2 – Objective function (residual sum of squares) for the kinetic rate coefficient $k_{\text{cryst}}$ from the parameter estimation on the dynamic titration test data. The optimum $k_{\text{cryst}}$ was observed to be $0.0025 \text{ min}^{-1}$. 
Fig. 3 – Saturation index (SI) values which were calculated (from experimental composition measurements) and simulated ($k_{cryst} = 0.0025 \text{ min}^{-1}$) for the dynamic titration tests with precipitation for 0 mg.L$^{-1}$ added calcite seed (stars, solid lines), 50 mg.L$^{-1}$ added calcite seed (circles, dashed lines) and 200 mg.L$^{-1}$ added calcite seed (diamonds, dot-dash lines).
Fig. 4 – Typical titrant volume data from the Constant Composition Experiments at a solution pH of 8.2 (black symbols), 8.5 (dark grey symbols), 8.7 (light grey symbols) and 8.9 (white symbols). The lines are linear regression fits from which a constant slope was obtained for the volumetric rate of titrant added ($q_t$ for Eq. (1)).
Fig. 5 – Comparison of measured and fitted calcite precipitation rates: Full-factorial design test set (A: baseline precipitation model fit (Eq. (7)); B: baseline model fit corrected for temperature only with Eq. (12)); C: baseline model fit corrected for temperature and adsorption with Eq. (11)). The line shown in each plot is y=1x.
Table 1 – Test conditions and analyses for Constant Composition Method Experiments (CCM)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test set 1 (full-factorial)a</th>
<th>Test set 2 (pH, Temperature and supersaturation)b</th>
<th>Test set 3 (Crystal seed mass and supersaturation)c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Added NaHCO₃ (M)</td>
<td>0.004</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Added CaCl₂ (M)</td>
<td>0.002 or 0.004</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Added MgCl₂ (M)</td>
<td>0.00075 or 0.0015</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seed surface area (m²/g)</td>
<td>0.46</td>
<td>0.46</td>
<td>0.59</td>
</tr>
<tr>
<td>Added seed concentration (mg.L⁻¹)</td>
<td>525</td>
<td>525</td>
<td>25, 42, 62.5 or 78</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>15 or 30</td>
<td>20, 25, 30, 35, 40</td>
<td>25</td>
</tr>
<tr>
<td>Ionic strength (M)</td>
<td>0.1 or 0.2</td>
<td>0.1</td>
<td>0.01 – 0.2</td>
</tr>
<tr>
<td>pH</td>
<td>8.2</td>
<td>8.9</td>
<td>8.5</td>
</tr>
<tr>
<td>Relative supersaturation, σ</td>
<td>0.81-2.16</td>
<td>0.87-2.30</td>
<td>0.87-2.30</td>
</tr>
<tr>
<td>Number of experiments</td>
<td>16</td>
<td>30</td>
<td>25</td>
</tr>
</tbody>
</table>

a Full-factorial experimental design testing the effects of ionic strength, supersaturation, added magnesium (impurity) and temperature

b To further evaluate the effects of temperature, pH and supersaturation

c To further evaluate the effects of supersaturation and added seed crystal mass per Eq. (7)
Table 2 – ANOVA results for the analysis of environmental effects on CCM test results for CCM Tests 1 and 2 in Table 1.

Response – Measured calcite precipitation rate ($R_{\text{calcite}}$) with units of moles.L$^{-1}$.min$^{-1}$

<table>
<thead>
<tr>
<th>Effect $^a$</th>
<th>p (Test 1, $n_1 = 16$)</th>
<th>p (Test 2, $n_2 = 30$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{Mg}^+2}$</td>
<td>0.01339</td>
<td>-</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.00005</td>
<td>2.20E-16</td>
</tr>
<tr>
<td>$T$</td>
<td>0.00049</td>
<td>2.70E-12</td>
</tr>
<tr>
<td>$\mu$</td>
<td>0.82200</td>
<td>-</td>
</tr>
<tr>
<td>$pH$</td>
<td>-</td>
<td>0.0884</td>
</tr>
<tr>
<td>$S_{\text{Mg}^+2} \times \sigma$</td>
<td>0.06852</td>
<td>-</td>
</tr>
<tr>
<td>$S_{\text{Mg}^+2} \times T$</td>
<td>0.17843</td>
<td>-</td>
</tr>
<tr>
<td>$\sigma \times T$</td>
<td>0.00318</td>
<td>0.0015</td>
</tr>
<tr>
<td>$S_{\text{Mg}^+2} \times \mu, S_{\text{Mg}^+2} \times pH, \sigma \times \mu, \sigma \times pH, \mu \times pH, pH \times T$</td>
<td>&gt; 0.1</td>
<td>&gt; 0.1</td>
</tr>
<tr>
<td>DOF $_{\text{resid}}$</td>
<td>5</td>
<td>23</td>
</tr>
</tbody>
</table>

$^a$ $S_{\text{Mg}^+2}$ – free dissolved magnesium concentration; $\sigma$ – supersaturation; $T$ – temperature (Kelvin); $\mu$ – ionic strength (M); Variable 1*Variable 2 – second order interaction effect; $pH$ – pH of test solution

$^b$ All tested at 95% confidence level, p (>F); not significant (0.05 < p < 0.1); just significant (0.01 < p < 0.05); significant (0.001<p<0.01); highly significant (p<0.001)
### Table 3 – Model parameter estimation values for the CCM tests (±95% confidence intervals)

<table>
<thead>
<tr>
<th>Fitted parameters</th>
<th>CCM1 - Full-factorial design experiment</th>
<th>CCM2 - Test of effects of supersaturation, temperature and pH</th>
<th>CCM3 – Crystal seed mass and supersaturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supersaturation exponent, ( n )</td>
<td>2.05(±0.29)</td>
<td>1.3(±0.17)</td>
<td>1.6(±0.2)</td>
</tr>
<tr>
<td>( X_{\text{Caco}_2(\alpha)} ) exponent, ( y )</td>
<td>-</td>
<td>-</td>
<td>0.96(±0.2)</td>
</tr>
<tr>
<td>Activation energy, ( E_a ), kJ.mole(^{-1} )</td>
<td>52.7(±11.8)</td>
<td>51.68 (±7.9)</td>
<td>-</td>
</tr>
<tr>
<td>Adsorption coefficient, ( K_{\text{ads}} ), L.moles(^{-1} )</td>
<td>1,829(±1,473)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( k_{\text{cryst},25^\circ C} ), min(^{-1} )</td>
<td>0.0043(±0.0013)</td>
<td>0.0017(±0.0002)</td>
<td>0.0014(±0.0011)</td>
</tr>
</tbody>
</table>