CALCIUM CARBONATE PRECIPITATION KINETICS

By

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Declaration

I hereby declare that this thesis is my own work and has not been submitted for a degree at any other university.

PETER STURROCK

September 1975
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1.

SYNOPSIS

A modified equation from that of Nancollas and Reddy is presented to describe the rate of calcium removed from water in CaCO₃ precipitation. The mass of CaCO₃ precipitated at any moment was obtained by monitoring pH and utilizing this in the equilibrium equations for the Ca - H₂CO₃ system including ion pairing and ionic strength effects. Both batch and back mixing steady state conditions were studied. The precipitation rate constant was found to be independent of pH, and functionally related to the state of initial supersaturation in the batch tests and the state of supersaturation in the steady state tests. Both steady state and batch tests gave the same dependence of the precipitation rate constant with supersaturation.
2.

Introduction

Calcium and magnesium ions are the predominant contributors to hardness in water. They are present in varying concentrations in all natural waters but are particularly evident in underground and surface waters derived from dolomitic areas. In water reclamation, addition of Ca(OH)$_2$ as a flocculating agent is widely used. The effluent pH is high (>10.5) and subsequently the pH of the water must be reduced and the residual calcium removed. The Ca$^{++}$ ions are usually removed from solution by the precipitation of calcium carbonate.

In 1973 Loewenthal and Marais developed the modified Caldwell-Lawrence diagram (→). This diagram relates the pH, alkalinity, acidity and calcium concentration of a water. If a water is supersaturated with respect to Ca$^{++}$ the amount of CaCO$_3$ that will eventually precipitate can be estimated. However, the Caldwell-Lawrence diagram gives no indication of the time required for the estimated precipitation to take place.

To design a water-softening plant it is necessary to know the rate of CaCO$_3$ precipitation under different conditions so that the hydraulic retention time and hence the volume of the reactor can be calculated.

In water reclamation the same situation applies. However, experimental data on water reclamation plants indicate that the residual calcium concentration in effluents is higher than the solubility product for CaCO$_3$, $K_{sp}$, would appear to indicate. This observation could be due to three factors:

/ (1) The $K_{sp}$ ...
(1) The Ksp value has changed.

(2) The Ksp value is the same as for the pure system but complexing of Ca$^{++}$ with organic and phosphorous compounds occurs or,

(3) Poisoning of the crystal surface occurs. Before the removal of calcium in water reclamation can be quantified in a theoretical model, it is necessary, as a first step, to determine the rate of CaCO$_3$ removal from pure systems (where Ksp is known) to serve as a criterion against which the real life system can be compared.

Reddy and Nancollas (1971) proposed a model for the kinetics of calcium carbonate precipitation as follows:

$$ -d \left[ \text{Ca}^{++} \right]_T / dt = K_S f \left( \left[ \text{Ca}^{++} \right]_F \left[ \text{CO}_3^- \right]_F - \text{Ksp} / f_D \right)^2 $$

where:

- $K$ = rate constant.

- $S_f$ = surface area of CaCO$_3$ crystals

- $\left[ \text{Ca}^{++} \right]_T$ = total concentration of calcium in solution.

- $\left[ \text{Ca}^{++} \right]_F$, $\left[ \text{CO}_3^- \right]_F$ = concentration of free Ca$^{++}$ and CO$_3^-$ ions respectively.

- Ksp = solubility product for CaCO$_3$.

- $f_D$ = activity coefficient for a divalent ion.

To test the validity of Eq. (1) Reddy et al monitored the changes in calcium and pH in supersaturated solutions of CaCO$_3$ seeded with calcite crystals of known surface area. They determined the parameters $\left[ \text{Ca}^{++} \right]_F$ and $\left[ \text{CO}_3^- \right]_F$ from the theory of the carbonic system taking due account of all possible ion pairs. Supersaturated solutions with concentrations of Ca$^{++}$ 15 - 45
and CO$_3$ 20 - 40 ppm as CaCO$_3$ were inoculated with calcite seed crystals at concentrations from 340 to 2 800 ppm as CaCO$_3$. After an initial surge of growth a value of $K$ was obtained which was independent of the seed mass and initial Ca$^{++}$ and CO$_3^-$ concentrations. They concluded that within the ranges of ionic and seed concentration Eq. (1) applied.

Wiechers (1973) critically examined the work of Reddy et al. He concluded that the concentration and supersaturation used by Reddy et al were very low compared with the concentration which might be encountered in water treatment plants and that the model should therefore be tested at higher supersaturations. Also, the concentration and size of CaCO$_3$ crystals in solution could vary considerably under different conditions. Wiechers proposed that Eq. (1) be modified in terms of the mass, $M$, instead of the surface area, $S_f$, of CaCO$_3$ seed crystals, i.e.

$$- \frac{d}{dt} \left[\text{Ca}^{++}\right]_T = KM\left(\left[\text{Ca}^{++}\right]_F \left[\text{CO}_3^-\right]_F - Ksp/f_D^2\right) \quad (2)$$

This modification has the disadvantage of limiting the model, and any data obtained, to the particular size, type and brand of CaCO$_3$ seed crystals used. However by doing an investigation using one batch of seed crystal it is still possible to determine the laws relating the parameters of precipitation.

To test if Eq. (2) described the precipitation reaction at practical CaCO$_3$ concentrations, Wiechers did experiments at Ca$^{++}$ and CO$_3^-$ concentrations each up to about 400 ppm measured as CaCO$_3$. He showed theoretically that by neglecting the CaOH ion pair, which is low at pH 9.5 and below, he could
determine each of the parameters in Eq. (2) by measuring the pH only. In contrast Reddy et al had to measure both the pH and calcium concentration. The measurement of calcium is possible when the rate of crystallization is slow as in the case studied by Reddy et al but when the rate of precipitation is high it is difficult to do this measurement accurately.

The value of K was determined by plotting \(- \frac{d[Ca^{++}]}{dt}\) against \(M([Ca^{++}]_F, [CO_3^{--}]_F - K_{sp}/f_D^2)\). This plot yielded a straight line for any particular experiment, as did the results of Reddy et al. In this respect the model described the precipitation reaction.

Wiechers, Sturrock and Marais (1975) then investigated the effects of (1) seed crystal concentration, (2) temperature, (3) stirring speed and (4) concentration of CO\(_3^{--}\) and Ca\(^{++}\) ions on the rate constant, K :

(1) To determine the effect of seed crystal concentration the Ca\(^{++}\) concentration (72 ppm as CaCO\(_3\)), the CO\(_3^{--}\) concentration (38 ppm as CaCO\(_3\)), temperature (25\(^\circ\)C) and stirring speed (500 r.p.m.) were all kept constant while the seed crystal mass was varied from 100 to 1 000 ppm as CaCO\(_3\). At seed crystal concentration less than 400 ppm as CaCO\(_3\) an initial growth surge was observed and thereafter for each experiment the value of K became steady at a similar value to that obtained for experiments with seed crystal concentrations greater than 400 ppm as CaCO\(_3\). It was therefore concluded that, provided sufficient area or growth sites are supplied by the inoculated seed mass, the value of the rate constant, K, is independent of the seed mass.

/ (2) To determine ...
(2) To determine the effect of temperature experiments were done at 10, 20, 30 and 40°C while the stirring speed (500 rpm), Ca⁺⁺ concentration (80 ppm as CaCO₃) and CO₃⁻ concentration (33 ppm as CaCO₃) were kept constant. The van't Hoff-Arrhenius equation was used to describe the relationship between K and temperature:

\[ K_T = K_{20} \theta^{(T-20)} \]  

or \[ \log K_T = \log K_{20} + (T-20) \log \theta \]

where \( T \) = temperature °C.

\( K_T, K_{20} = K \) at temperature \( T°C \) and 20°C respectively.

\( \theta = \) constant.

The plot of \( \log K_T \) versus \( T°C \) approximated to a straight line yielding:

\[ K_T = 1,53*1,053^{(T-20)}(1.\text{mol}^{-1}.\text{min}^{-1})/(\text{mg seed}^{-1}) \]

(3) With regard to stirring energy, it was found that provided the stirring speed was sufficient to keep the CaCO₃ crystals in suspension, it had no marked effect on the rate constant K.

(4) To determine the effect of Ca⁺⁺ and CO₃⁻ concentrations the seed mass (700 ppm as CaCO₃), temperature (25°C) and stirring speed (500 rpm), were kept constant while the concentration of the reagents were varied (Ca⁺⁺ 330-70 ppm as CaCO₃, CO₃⁻ 18-54 ppm as CaCO₃). As the concentration varied, different values of K were obtained. A plot of K versus pH showed that K was apparently related to the initial equilibrium pH. However, in any particular experiment...
experiment, as the reaction proceeded and the $\text{pH}$ decreased, the value of $K$ remained constant, whereas one would expect the value of $K$ to change concurrently with the change in $\text{pH}$. Wiechers et al. could give no satisfactory explanation for this apparently inconsistent behaviour.

In this thesis Eq. (2) is modified and in the light of this modification further experimental data are analysed in an attempt to gain insight into the kinetics of $\text{CaCO}_3$ precipitation. Also, a calculation procedure to determine the parameters in Eq. (2) is developed. This procedure requires the measurement of $\text{pH}$ and alkalinity at the start of each test, thereafter only the $\text{pH}$ need be measured. It takes account of all ion pairs; therefore the limitation $\text{pH} < 9.5$ falls away.
CaCO$_3$ crystal growth and precipitation model

Calcium carbonate crystal growth occurs in four sequential steps (Stumm and Morgan 1970):

1) The reaction takes place whereby the hydrated CaCO$_3$ ion pair is formed:
   \[ \text{Ca}^{++} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \]
2) The hydrated CaCO$_3$ ion pair is transported to the crystal/solution interface.
3) At the crystal/solution interface the ion pair is dehydrated and adsorbed onto the crystal surface, i.e.
   \[ \text{CaCO}_3 \rightarrow \text{CaCO}_3 \]  This reaction takes place in both directions. The forward reaction, whereby the \[ \text{CaCO}_3 \] is dehydrated, is called precipitation and the reverse reaction whereby the \[ \text{CaCO}_3 \] is hydrated is called dissolution.
4) The CaCO$_3$ adsorbed onto the crystal is incorporated into the crystal lattice - a process called ripening.

At low turbulence the rate of transportation of CaCO$_3$ ion pairs to the crystal face is the controlling factor in crystal growth, i.e. growth is controlled by the diffusion rate of CaCO$_3$ ion pairs to the crystal face - called diffusion controlled growth. At high turbulence levels CaCO$_3$ transportation to the crystal face is adequate and the rate of crystal growth becomes limited by the rate at which the CaCO$_3$ ion pairs are adsorbed and incorporated into the crystal lattice - called interface controlled growth. The experiments reported by Wiechers et al indicate that, provided the stirring speed is sufficient to keep the seed crystal...
seed crystal in suspension, variation in stirring speed (i.e. turbulence) has no effect. This suggests that the CaCO₃ crystal growth is interface controlled.

The rate of precipitation in any seeded solution (either supersaturated, saturated or undersaturated with respect to CaCO₃) is assumed proportional to the surface area of seed and the concentration of the zero ion pair, CaCO₃ₒ, in the bulk solution, thus

\[
\text{Rate of precipitation} = K_p S(CaCO₃ₒ)
\] (5)

where \( K_p \) = the rate constant for precipitation.

Note that the ion pair has zero charge so that its active and molar concentrations in solution are equal.

Dissolution is assumed to occur simultaneously with precipitation and to be proportional only to the surface area of seed, \( S_f \)

\[
\text{Rate of dissolution} = K_d S_f
\] (6)

where \( K_d \) = the rate constant for dissolution.

Eq. (4) implies that the rate of dissolution is independent of the saturation state, i.e. it is constant per unit surface area of the crystal irrespective of over- or undersaturation. For a solution just saturated with respect to CaCO₃ the rates of precipitation and dissolution are equal, thus from Eqs. (3) and (4):

\[
K_p S(CaCO₃ₒ)_s = K_d S_f
\]

i.e.

\[
K_d = K_p (CaCO₃ₒ)_s
\] (7)

where the subscript, \( s \), refers to a saturated solution.

Substituting for \( K_d \) from Eq. (7) into Eq. (6):

\[
\text{Rate of dissolution} = K_p S(CaCO₃ₒ)_s
\] (8)

/ As the rate ...
As the rate of dissolution, Eq. (8), is constant per unit surface area, the rate of precipitation from a supersaturated solution is given by the difference in the rates of precipitation and dissolution:

\[
\text{Net rate of precipitation} = -\frac{\delta \mathcal{J}_{\text{CaCO}_3}}{\delta t} = k_p s \left\{ \mathcal{J}_{\text{CaCO}_3} - \mathcal{J}_{\text{CaCO}_3}^s \right\} \quad (9)
\]

The negative sign arises as the equations refer to the species in the bulk solution.

Irrespective of the saturation state of the water, the ion pair \( \text{CaCO}_3^0 \) must be in equilibrium with the free ions \( \text{Ca}^{++} \) and \( \text{CO}_3^{-} \) in the aqueous phase, i.e.

\[
(Ca^{++})_F (CO_3^-)_F / (CaCO_3^0) = K_3 \quad (10)
\]

where \( K_3 \) = thermodynamic equilibrium constant for the ion pair \( \text{CaCO}_3^0 \).

Taking ionic strength effects into account Eq. (10) is written in the molar form:

\[
\mathcal{J}_{\text{CaCO}_3} = f_D^2 \mathcal{J}_{\text{Ca}^{++}} \mathcal{J}_{\text{CO}_3^{-}} / K_3 \quad (11)
\]

i.e.

\[
\mathcal{J}_{\text{Ca}^{++}} \mathcal{J}_{\text{CO}_3^{-}} / f_D^2 = \mathcal{J}_{\text{CaCO}_3} / K_3 \quad (12)
\]

For a saturated solution:

\[
\mathcal{J}_{\text{Ca}^{++}} \mathcal{J}_{\text{CO}_3^{-}} / f_D^2 = K_{sp} / f_D^2 \quad (13)
\]

where \( K_{sp} \) = solubility product constant for \( \text{CaCO}_3 \).

Substituting Eq. (13) into Eq. (10) and simplifying:

\[
\mathcal{J}_{\text{CaCO}_3}^s = K_{sp} / K_3 \quad (14)
\]

Substituting Eqs. (11) and (14) into Eq. (9):

\[
-\delta \mathcal{J}_{\text{CaCO}_3} / \delta t = k_p s f_D^2 K_3 \left\{ \mathcal{J}_{\text{Ca}^{++}} \mathcal{J}_{\text{CO}_3^{-}} - K_{sp} / f_D^2 \right\} \quad (15)
\]

/ and defining ...
Eq. (16) differs from Eq. (1) proposed by Reddy and Nancollas in that an activity coefficient term is included outside the bracket on the right-hand side of Eq. (16).

Replacing $S_f$ in Eq. (16) by $M$, the mass concentration of a particular brand of crystal seed:

$$- \frac{d[CaCO_3]}{dt} = KS_f f_D^2 \left\{ \left[ Ca^{++} \right] F \left[ CO_3^- \right] F^{-Ksp/f_D^2} \right\}$$ (17)

Eq. (17) can also be derived as follows:

A general equation for interface controlled growth is given by Stumm and Morgan (1970):

$$\frac{dC}{dt} = K S_f (C - Co)^n$$ (18)

where $S_f$ = surface area of crystals in solution

$C$ = concentration of solution

$Co$ = concentration of solution immediately surrounding the crystals

The term $(C - Co)$ defines the supersaturation with respect to $C$. Making the modification proposed by Wiechers (i.e. substituting mass of seed crystals, $M$, for surface area, $S_f$)

Eq. (18) becomes:

$$- \frac{dC}{dt} = KM (C - Co)^n$$ (19)

Applying Eq. (19) specifically to CaCO$_3$ precipitation:

$$- \frac{d[Ca^{++}]}{dt} = KM \left\{ (CaCO_3^0) - (CaCO_3)_s \right\}^n$$ (20)

The equilibrium equation for the CaCO$_3^0$ ion pair is:

$$f_{Ca} \left[ Ca^{++} \right] f_{CO_3} \left[ CO_3^- \right] / \left[ CaCO_3 \right] = K_{CaCO_3} = K_{13}$$ (21)

which can be written

$$\left[ CaCO_3 \right] = \left[ Ca^{++} \right] \left[ CO_3^- \right] f_{Ca} f_{CO_3} / K_{13}$$ (22)

/ At saturated ...
At saturated equilibrium:

\[ \left[ CaCO_3 \right]_s = \left[ Ca^{++} \right] \left[ CO_3^{-} \right] f_{Ca} f_{CO_3} / K_{13} \quad (23) \]

Also at saturation the solubility product equilibrium for CaCO\(_3\) must be satisfied, i.e.

\[ \left[ Ca^{++} \right] \left[ CO_3^{-} \right] = K_{sp} / f_{Ca} f_{CO_3} \quad (24) \]

Substituting Eqs. (22), (23) and (24) in Eq. (20):

\[ -d[Ca^{++}]_T / dt = K \cdot M \left\{ \left[ Ca^{++} \right] F \left[ CO_3^{-} \right] F f_{Ca} f_{CO_3} / K_{13} - K_{sp} / K_{13} \right\}^n \quad (25) \]

Since \( K = K' / K_{13} \)

\[ -d[Ca^{++}]_T / dt = KM \left( f_{Ca} f_{CO_3} \left[ Ca^{++} \right] F \left[ CO_3^{-} \right] F - K_{sp} / f_{Ca} f_{CO_3} \right)^n \quad (26) \]

Eq. (26) is proposed as an improved model for CaCO\(_3\) precipitation.
Apparatus

Chemical reagents
Analytical reagent grade chemicals were used throughout. Calcium carbonate crystals (Hopkins and Williams, Analar grade) were used as seed. The solutions were made up using carbon dioxide free distilled water with a conductivity less than 5μS. Stock solutions (0.01M) of sodium bicarbonate, sodium hydroxide and calcium chloride were made up and standardized before each series of tests. The NaHCO₃ and NaOH were standardized against hydrochloric acid (0.01N) with borax as a primary standard. The CaCl₂ solution was standardized by the EDTA method (see Standard Methods).

Reactor
A reactor, designed by Wiechers (1973) was used for the study of the reaction kinetics with the minimal solution - atmosphere contact to minimise CO₂ transfer with the air. The reactor (see Figs. 1, 2, 3, 4, and 5) consists of a cylindrical vessel, constructed of thin perspex, with its interior sealed from the atmosphere by an O-ring sealed lid. It has four circular openings in the lid, lined with O-rings, to allow easy air-tight insertion of three probes, i.e. glass and calamel electrodes and a thermometer. The fourth hole is very small and allows air-solution pressure equalization. Two perspex cylinders are fitted to the reactor through a joint connection for the purpose of injecting the reactants. The reactants are well mixed within a period of two to three seconds. The temperature of the reactor is controlled by means of a

/ waterbath ...
and a Haake E51 thermostat. The reactants and buffers are placed in the waterbath to attain a constant temperature before use. The reaction solution is completely insulated (electrically) from its surroundings by using perspex screws and rubber O-rings, to prevent stray electric currents from affecting measuring probes. The solution is stirred by magnetic stirrer using a Teflon coated stirring bar.

**pH Meter**

The radiometer pH meter, type PHM 26, has the following specifications which make it suitable for measuring pH changes which occur as calcium carbonate is precipitated from solution:

- **Read out:**
  1.4 pH for full-scale detection.

- **Smallest scale div:**
  0.01 pH.

- **Repeatability:**
  ± 0.002 pH.

- **Relative accuracy:**
  ± 0.002 pH at buffer point.
  ± 0.005 pH sample in the range as buffer.
  ± 0.007 pH typical with buffer and sample in different ranges.

- **Amplifier drift:**
  ± 0.002 pH/day non-accumulative.

- **Temperature compensation:**
  0 to 100°C

- **Recorder output:**
  10 mV/pH.

The pH meter has a built-in device to correct for loss of electrode sensitivity. The meter has an iso pH adjustment device with which the electrical zero of the output voltage can be set at any convenient value, for recorder purposes.

The glass electrode, G202C, is made of glass which responds very rapidly to pH changes.

/ NBS - standard buffers ...
NBS Standard buffers

NBS standard buffers, in the pH range of interest, were used to calibrate the electrode system. Borax and phosphate buffer solutions were made up as follows: The borax buffer (0.01M) is prepared by dissolving 3.81 g. borax in fresh carbon dioxide free distilled water and making it up to one litre. The phosphate buffer is prepared by dissolving the following quantities of salts in distilled water and making it up to one litre:

\[
\begin{align*}
K_2HPO_4 & \quad 3.44 \text{ g.} \\
Na_2HPO_4 & \quad 3.55 \text{ g.}
\end{align*}
\]

The phosphates must be dried in an oven at 110°C for one to two hours and left to cool in a desiccator.

The pH of these NBS standard buffers as a function of temperature is described by Bates (6), and is as follows:

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>20.0</th>
<th>21.0</th>
<th>22.0</th>
<th>23.0</th>
<th>24.0</th>
</tr>
</thead>
</table>

The accuracy of the pH of the buffers is given as $\pm 0.01$ pH.

Strip chart recorder

The Hewlett Packard strip chart recorder type 7100B with amplifier module type 17501A has a chart speed range which covers all the speeds necessary to study the calcium carbonate precipitation reactions. Its specifications are:

Recorder mechanism: Servo activated electro-burning pen drive.

Response time: One half second for full scale.

/ Chart speeds ...
16.

Chart speeds:

1;2 in/hour: 0,1; 0,2; 0,5;
1;2 in/minute: 0,1; 0,2; 0,5
1;2 in/second
Experimental method

The volume of the reactor was 500 ml. Two 250 ml. flasks one containing the sodium bicarbonate and sodium hydroxide solutions and the other containing the calcium chloride solution, were made up and placed in the waterbath to attain the required temperature. The pH meter and recorder were calibrated using NBS standard buffers. The carbonate solution, together with the required mass of seed, was poured into the reactor and the pH electrodes and thermometer were positioned in their respective holes in the reactor. The calcium solution was poured into the injecting cylinder. The stirrer in the reactor was switched on. When the valve of the injecting cylinder was opened (i.e. when mixing of the Ca$^{++}$ and CO$_3^-$ solutions began) CaCO$_3$ ion pairs were immediately formed which resulted in an instantaneous decrease in pH (see Fig. 6) due to the removal of free CO$_3^-$ ions from solution. Thereafter as the reaction proceeded and CaCO$_3$ precipitated, the pH dropped, and a graph of pH versus time was recorded. As the CaCO$_3$ precipitates the acidity remains constant and the pH and alkalinity decrease. Therefore, since the initial alkalinity was known and the change of pH was recorded, the change in alkalinity (and hence the rate of CO$_3^-$ removal) could be calculated (see Appendix A). For each part of CO$_3^-$ that is removed one part of CaCO$_3$ is precipitated. Therefore if the rate of CO$_3^-$ removal is known, then the rate of calcium removal can be calculated.

Back mix reactors

The method of running the precipitation tests described above is unlikely to be duplicated in practical processes. In water
treatment works it is more probable that back mix reactors will be used in preference to batch reactors. Therefore in order to establish whether the data obtained under batch conditions also applied to backmix reactors, a series of steady state experiments were done. The experimental apparatus was similar to that used for batch tests but modified as follows: Two CO₂ free feed tanks are connected to the reactor. The one tank contains a carbonate solution and the other a calcium solution together with CaCO₃ seed crystals (Hopkins and Williams Analar brand) at a concentration of 1800 ppm (see Fig. 7). The seed is kept in suspension in the feed tank by means of a magnetic stirrer. Solutions from each tank are pumped at equal ratios into the reactor and the pH of the reactor contents is monitored.

For any given hydraulic retention time, the flow is maintained until the pH attains a steady reading and remains steady for a period of two retention times. The influent feeds are then stopped and the decrease in pH with time is recorded for a period until the pH shows no significant change. The feed flows are then restarted to give a different hydraulic retention time in the reactor.

At any particular steady state, knowing only the pH, temperature, alkalinity and concentration of Ca⁺⁺ of the influent feeds, it is possible to determine each of the parameters in Eq. (17) (exactly as was done for the batch tests described previously). Consequently the CaCO₃ supersaturation at steady state can be calculated. Also, when the feed flow is stopped the rate of precipitation can be calculated, the initial rate giving an
estimate of the rate at that particular steady state. By this means a value for the reaction constant, \( K \), is determined for each steady state condition (see Table 2).

By comparing the values of \( K \) obtained for batch tests (Table 1) and those for completely mixed tests (Table 2) it can be seen that they are very similar. Therefore batch tests, which are simpler and less time-consuming to run, can be used to establish data for completely mixed conditions. The work reported here, on both batch and completely mixed reactors utilised pure solutions and pure seed masses. The absolute value of \( K \) is very sensitive to the type of seed. This was verified by using the same brand of CaCO\(_3\) crystals, but from a different manufactured batch, when the \( K \) values were notably different (see Fig. 9). Therefore it is very likely that the absolute value of \( K \) will differ between laboratory and full scale works where the seed crystals are self-generated.

Specifically to separate the effects of pH and supersaturation on the rate constant \( K \), in a proportion of tests the supersaturation was kept constant but the initial pH varied and vice versa. The initial pH of the experiments covering a range from 8.6 to 10.3 was controlled by varying the relative concentration of the hydroxide and bicarbonate solutions. The initial CaCO\(_3\) supersaturation* was varied from 100 to 2500 ppm (as CaCO\(_3\)) by adding different concentrations of calcium and carbonate solutions.

* "Supersaturation" refers to the parameter \((\text{CaCO}_3^0 - (\text{CaCO}_3^0)_s)\) which is the apparent instantaneous supersaturation; this parameter will not equal the mass concentration of CaCO\(_3\) to be precipitated because with precipitation there is a resultant decrease in pH which decreases the concentration of CO\(_3^2\) in solution.
Analysis

In Eq. (26) to determine the variation in the rate constant, $K$, an analysis must first be carried out to establish the reaction order, $n$. By taking the log of Eq. (26):

$$\log \left( \frac{d[L(Sa++_T)]}{Mdt} \right) = \log K + n \log (f_{Ca^2+} f_{CO_3^-} f_{Ca^2+} f_{CO_3^-} - K_{sp}/f_{Ca^2+} f_{CO_3^-})$$

(27)

The value of $n$ is determined by plotting:

$$\log \left( \frac{d[L(Sa++_T)]}{Mdt} \right) \text{versus} \log (f_{Ca^2+} f_{CO_3^-} f_{Ca^2+} f_{CO_3^-} - K_{sp}/f_{Ca^2+} f_{CO_3^-})$$

The slope of the plot gives the value of the reaction order, $n$.

The values of $n$ are listed (see Table 1). The mean value of $n = 0.98 \pm 0.09$ indicates an apparent first order reaction (i.e. $n=1$) with respect to Ca$^{2+}$ supersaturation. If $n$ equals unity, the value of $K$ can be determined either by substituting $n = 1$ in Eq. (27) or by plotting Eq. (26), i.e.:

$$d[L(Sa++_T)]/dt \text{versus} Mf_{Ca^2+} f_{CO_3^-} \left\{ f_{Ca^2+} f_{CO_3^-} - K_{sp}/f_{Ca^2+} f_{CO_3^-} \right\}$$

The slope of the plot above gives the value of $K$ (see Fig. 9). Both methods will yield the same results. Note in Fig. 8 that the plots for seed concentrations equal to 900 ppm approximate to straight lines, i.e. in these experiments the value of $K$ remained constant throughout the precipitation period even though the pH and Ca$^{2+}$ supersaturation were steadily decreasing. The dependence of $K$ on initial pH and/or initial super saturation was determined by plotting $K$ versus pH (Fig. 10) and $K$ versus initial supersaturation (Fig. 8). From Fig. 10 it would appear that there is no decided relationship between pH and $K$. At any particular pH a range of $K$ values can be obtained. This data tends to show that the conclusion of Wiechers et al. — that the rate constant depends on initial pH — is not sustained.

/ From Fig. 13 ...
From Fig. 8 there appears to be a decided relationship between K and the initial CaCO$_3$ supersaturation. A functional relationship between K and the initial CaCO$_3^0$ supersaturation was identified from various plots assuming different basic relationships. A basic relationship of the kind expressed by Eq. (28) was found to give excellent correlation:

$$K = K_0 + (K_m - K_0) (1 - e^{c'S})$$  \hspace{1cm} (28)

where $K = \text{rate constant (ppm Ca}^{++}\text{ precipitated as CaCO}_3^{3}) (\text{min})^{-1}$

$$K_m = \text{maximum value of } K$$

$$K_0 = \text{value of } K \text{ at zero supersaturation}$$

$c' = \text{constant}$

$S = \text{initial CaCO}_3^{3} \text{ supersaturation (ppm as CaCO}_3^{3})$

The functional relationship was established as follows. A value of $K_m$ was assumed and for each experimental $K$ value the function $(K_m - K)$ was found and plotted against initial supersaturation on semi-log paper (Fig. 11). By trial and error a value of $K_m$ was found that gives a straight line plot ($K_m=3.25 \times 10^{-5}$). The difference between $K_m$ and the $K$ values given by the intersection of the straight line plot with the abscissa provides an estimate of the rate constant at zero supersaturation

$$(K_0 = (3.25-2.65) \times 10^{-5} = 0.60 \times 10^{-5}), (\text{see Fig. 11})$$

The slope of the plot gives an estimate of $c' = 0.00162$. Substituting numerical values, Eq. (15) becomes:

$$K \times 10^5 = 0.60 + (2.65 \times 10^{-5} - e^{-0.00162S}) (\text{min. ppm. as CaCO}_3^{3})^{-1}$$  \hspace{1cm} (29)

The fact that $K$ is a function of the initial supersaturation (Eq. 29) leads to a contradiction:

/ From Eq. (26) ...
From Eq. (26)
\[ \frac{d[\text{Ca}^{++}]_T}{dt} = KM \text{ (supersaturation)} \]
and at the initial state this must be:
\[ \frac{d[\text{Ca}^{++}]_T}{dt} = KM(\text{initial supersaturation}) \]

But \( K = \text{function (initial supersaturation)} \)

Substituting for \( K \) at the initial state:
\[ \frac{d[\text{Ca}^{++}]_T}{dt} = \text{function (initial supersaturation)}M(\text{initial supersaturation}) \]

From this contradiction it would appear that the precipitation model is wrongly formulated, i.e. that the equation of Reddy and Nancollas and the one proposed in this thesis do not adequately explain the precipitation phenomena.

A number of practical consequences are exposed in this investigation. In back mix reactors in water softening plants where the CaCO\(_3\) supersaturation is low, the rate of precipitation is very slow. This means that either there must be a long hydraulic retention time or else the mass of crystals in the reactor must be large to speed up the precipitation. Also the rate of precipitation will be slow in pipes in water supply systems where the supersaturation is usually very low.
Summary and Conclusion

1. The equation proposed by Nancollas and Reddy, to describe CaCO₃ precipitation rate, was modified to:

\[
\frac{d[Ca^{++}]}{dt} = k M \left( f_{Ca} f_{CO_3} \left( \frac{Ca^{++}}{F^2} \frac{CO_3^-}{F} f_{sp} / f_{Ca} f_{CO_3} \right) \right)
\]

2. It was established that batch tests give similar values for k to the back mix reactions.

3. The reaction approximates to a first order reaction with \( n = 0.98 \pm 0.09 \)

4. The rate constant, k, appears to be independent of pH.

5. In both batch and steady state tests the value of k is very sensitive to the type of seed mass.

6. For batch and back mix reactions k varies with initial CaCO₃ supersaturation according to the expression:

\[
k \times 10^5 = 0.60 + 2.65 \left( 1 - e^{-0.00162S} \right) (\text{min. ppm. as CaCO₃})^{-1}
\]

The fact that k is a function of initial supersaturation leads to a contradiction since, at the initial state, both the rate and k are functions of the initial CaCO₃ supersaturation. Therefore it would appear that the formulation of Reddy and Nancollas is not sustained.

From this investigation the following practical conclusions can be drawn:

a) In back mix reactors in water softening plants the supersaturation is usually very low and hence the rate of precipitation is slow. In order to speed up the precipitation a large seed mass is required.

b) Precipitation will be slow in water supply systems where the supersaturation is usually very low.
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<tr>
<th>Expt. No.</th>
<th>Initial pH</th>
<th>Initial CaCO$_3^\circ$ Supersaturation ppm as CaCO$_3$</th>
<th>Seed mass mg/l</th>
<th>Reaction Order $n$</th>
<th>Reaction Constant $K(min)^{-1}(ppm as \text{CaCO}_3)^{-1}$</th>
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* Batch B of seed crystals
TABLE 2.

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<th>Expt. No.</th>
<th>Steady State Supersaturation ppm as CaCO₃</th>
<th>Seed Mass mg/l</th>
<th>Reaction constant K (min⁻¹.(ppm as CaCO₃)⁻¹)</th>
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* Batch B of seed crystals
LIST OF SYMBOLS

\( C \) = concentration of solution (mass. unit vol\(^{-1}\))

\( S_f \) = surface area of crystals in solution

\( S \) = initial \( \text{CaCO}_3 \) supersaturation (ppm as \( \text{CaCO}_3 \))

\( C_0 \) = concentration of solution immediately surrounding crystals (mass. unit vol\(^{-1}\))

\([ \]_T\) = total concentration of solution (ppm as \( \text{CaCO}_3 \))

\([ \]_F\) = concentration of free solution (ppm as \( \text{CaCO}_3 \))

\( K_{sp} \) = solubility product for Calcite

\( f_D \) = activity coefficient for divalent ion

\( f_{Ca} \) = activity coefficient for Calcium ions

\( F_{CO_3} \) = activity coefficient for Carbonate ions

\( t \) = time (min)

\( M \) = Mass concentration of seed crystals (ppm as \( \text{CaCO}_3 \))

\( K \) = rate constant (ppm Ca precipitated as \( \text{CaCO}_3 \)).

\( \frac{(\text{min})^{-1}\times(\text{ppm} \text{ CaCO}_3 \text{ seed}\times\text{ppm} \text{ CaCO}_3 \text{ supersaturation as } \text{CaCO}_3)^{-1}}{\text{(min.ppm as } \text{CaCO}_3)^{-1}} \)

\( K_m \) = maximum value of \( K \)

\( K_0 \) = value of \( K \) at zero \( \text{CaCO}_3 \) supersaturation
Fig. 1  Front elevation of water bath, supporting frame and reactor vessel.
Fig. 2  Side elevation of water bath, supporting frame and reactor vessel.
Fig. 3 Plan of water bath, supporting frame and reactor vessel.
Fig. 4  Elevation of reactor vessel.
Fig. 5 Plan of reactor vessel.
Fig. 6  Relationship between time and pH. The pH drops instantaneously at start of reaction due to pairing of Ca\(^{++}\) and CO\(_3^{2-}\) ions and thereafter decreases steadily as CO\(_3^{2-}\) is removed from solution.
Fig. 7 Schematic diagram of apparatus for steady state tests.
Fig. 8 Relationship between rate constant, $K$, and initial $\text{CaCO}_3$ supersaturation.
Fig. 9. Relationship between the rate of Ca$^{2+}$ precipitation and the function $M^2_D\{[Ca^{2+}]_F[CO_3^{2-}]_F - \frac{K_{sp}}{f^2_D}\} \times 10^5$. 

Rate (ppm as CaCO$_3$.min$^{-1}$)

- Expt. 15, 900 ppm seed
  Init. Supersat = 656
- Expt. 9, 900 ppm seed
  Init. Supersat = 320

$K = 2.40 \times 10^{-5}$

$K = 1.65 \times 10^{-5}$

Zero seed crystal - $K$ varies
Fig. 10 No apparent relationship between rate constant, $K$, and initial pH.
Fig. 11 Method of plotting the relationship $K = K_0 + (K_m - K_0)(1 - e^{CS})$ on a semi-log scale.

$K = K_0 + (K_m - K_0)(1 - e^{CS})$

- $K_m = 3.25 \times 10^{-5}$
- $(K_m - K_0) = 2.65 \times 10^{-5}$

- $900$ ppm CaCO$_3$ seed crystals
- $1500$ ppm
- $300$ ppm
References


The procedure for calculating the parameters that influence Eq. (26) is described below. The method utilizes the relationship between Alkalinity, Acidity and pH (Loewenthal and Marais, 1973). The method is not restricted to any pH range.

The pH in a water containing only carbonic species and associated cations is governed by equilibria reactions between the carbonic species \( \text{H}_2\text{CO}_3^* \), \( \text{HCO}_3^- \), and \( \text{CO}_3^{--} \) and water species \( \text{H}^+ \) and \( \text{OH}^- \). These equilibria are:

\[
\begin{align*}
\frac{(\text{HCO}_3^-)}{(\text{H}^+)/\text{H}_2\text{CO}_3^*} &= K_1 \\
\frac{(\text{CO}_3^{--})}{(\text{H}^+)/\text{HCO}_3^-} &= K_2 \\
\frac{(\text{OH}^-)}{(\text{H}^+)} &= K_w
\end{align*}
\] (A1)

where ( ) indicate active concentrations

\( K_1, K_2 \) and \( K_w \) = thermodynamic equilibrium constants

Subscript 'F' refers to free ion species

If \( \text{Ca}^{++} \) and \( \text{Na}^+ \) are in the water ion pairing will occur between these cations and the anions \( \text{CO}_3^{--}, \text{HCO}_3^- \) and \( \text{OH}^- \). Equilibria equations for these ion pairing reactions are:

\[
\begin{align*}
\frac{(\text{Ca}^{++})}{(\text{CO}_3^{--})} &= K_{\text{CaCO}_3} \\
\frac{(\text{Ca}^{++})}{(\text{HCO}_3^-)} &= K_{\text{CaHCO}_3} \\
\frac{(\text{Ca}^{++})}{(\text{OH}^-)} &= K_{\text{CaOH}} \\
\frac{(\text{Na}^+)}{(\text{CO}_3^{--})} &= K_{\text{NaCO}_3} \\
\frac{(\text{Na}^+)}{(\text{HCO}_3^-)} &= K_{\text{NaHCO}_3} \\
\frac{(\text{Na}^+)}{(\text{OH}^-)} &= K_{\text{NaOH}}
\end{align*}
\] (A4)

/ For equilibrium
For equilibrium, Eqs. (A1 to A9) must be simultaneously satisfied. The following mass balance expression must also be satisfied:

\[
\begin{align*}
\sqrt{\text{Na}^+}_T &= \sqrt{\text{Na}^+}_F + \sqrt{\text{NaHCO}_3^-}_F + \sqrt{\text{NaOH}^0}_T \\
\sqrt{\text{Ca}^{++}}_T &= \sqrt{\text{Ca}^{++}}_F + \sqrt{\text{CaHCO}_3^+}_F + \sqrt{\text{CaCO}_3^0}_T + \sqrt{\text{CaOH}^+}_T \\
\text{Alkalinity} &= 2\sqrt{\text{CO}_3^{--}}_T + \sqrt{\text{HCO}_3^-}_T + \sqrt{\text{OH}^-}_T - \sqrt{\text{H}^+}_T \\
\text{Acidity} &= 2\sqrt{\text{H}_2\text{CO}_3^*}_F + \sqrt{\text{HCO}_3^-}_T + \sqrt{\text{H}^+}_T - \sqrt{\text{OH}^-}_T \\
\sqrt{\text{HCO}_3^-}_T &= \sqrt{\text{HCO}_3^-}_F + \sqrt{\text{CaHCO}_3^+}_F + \sqrt{\text{NaHCO}_3^0}_T \\
\sqrt{\text{CO}_3^{--}}_T &= \sqrt{\text{CO}_3^{--}}_F + \sqrt{\text{CaCO}_3^0}_F + \sqrt{\text{NaCO}_3^-}_T \\
\sqrt{\text{OH}^-}_T &= \sqrt{\text{OH}^-}_F + \sqrt{\text{CaOH}^+}_F + \sqrt{\text{NaOH}^0}_T \\
\end{align*}
\]

where \( \sqrt{\_} \) indicates molar concentrations, and subscript \( T \) indicates the sum of free and ion paired species.

In the sixteen Eqs. (A1) to (A6) there are eighteen unknown parameters (i.e. \( \text{H}_2\text{CO}_3^* \), \( \text{HCO}_3^- \), \( \text{CO}_3^{--} \), \( \text{OH}^- \), \( \text{H}^+ \), \( \text{Ca}^{++} \), \( \text{CaHCO}_3^+ \), \( \text{CO}_3^{--} \), \( \text{Ca}_T^{++} \), \( \text{CaOH}^+ \), \( \text{CaCO}_3^0 \), \( \text{Na}^+ \), \( \text{NaHCO}_3^0 \), \( \text{NaCO}_3^- \), \( \text{NaOH}^0 \), \( \text{OH}^-_T \), Alkalinity and Acidity). To determine each of the parameters at least two must be measured.

In the method of solution described below, to initiate the solution theoretically only the initial \( \text{pH} \) and initial alkalinity need be measured and thereafter as \( \text{CaCO}_3 \) precipitation proceeds only \( \text{pH} \) needs to be measured for an additional condition applies i.e. the Acidity remains constant during precipitation and equals the initial value.

/Initially ...
Initially Alkalinity and Acidity were determined as follows:

Solutions of NaHCO\textsubscript{3} and NaOH were standardized against a strong acid of known concentration. The standardized solutions of NaHCO\textsubscript{3} and NaOH were then used as the source of Alkalinity and Acidity for a particular test, thus

Initial Alkalinity \[ = \sqrt{\text{NaHCO}_3} \text{added} + \sqrt{\text{NaOH}} \text{added} \]

Initial Acidity \[ = \sqrt{\text{NaHCO}_3} \text{added} - \sqrt{\text{NaOH}} \text{added} \]

Initial pH was measured using a glass electrode.

However, CO\textsubscript{2} exchange between the solution and atmosphere may occur during the experimental preparation. Such CO\textsubscript{2} exchange would alter the initial Acidity (estimated from the known masses of standard solutions used); the Alkalinity would not be affected. Thus, the best estimate of initial Acidity is calculated from the initial measured Alkalinity and the observed initial pH using Eqs. (Al) to (Al6). Usually the Acidity based on the measured pH was about 2 ppm as CaCO\textsubscript{3} greater than the observed Acidity. A theoretical check was carried out for each experiment as follows: Using the initial Alkalinity and Acidity values (based on the masses of standard solutions used) a theoretical value of initial pH was calculated using Eqs. (Al) to (Al6) and compared with the initial observed pH.

**Determination of initial Acidity from known Alkalinity and pH**

1. Calculate an initial approximate value for ionic strength, \( \mu \), from the mass concentrations of NaOH, NaHCO\textsubscript{3} and CaCl\textsubscript{2} used in an experiment.

2. Using the extended Debye-Hückel equation calculate the activity coefficients for each of the charged species from the value of \( \ldots \).
from the value of $\mu$ above. (The ionic radius for monovalent hydrated ion pairs was assumed equal to that for $\text{HCO}_3^-$).

3. Calculate activity coefficients for neutral species from the relationship $-\log_{10} f_N = k_s \cdot \mu$ (Garrels and Christ, 1965,) where $f_N$ = activity coefficient for neutral species $k_s$ = salting out coefficient for neutral species in water.

4. Calculate thermodynamic equilibrium constants, at the experimental temperature from the enthalpy and entropy for the reaction using the equation proposed by Helgesson (1969).

5. Adjust equilibrium constants for ionic strength effects to give $K'$.

6. Calculate $\sum H^+$ from the measured pH and the approximate value for the activity coefficient, $f_{\text{H}^+}$, determined in step (2), i.e. $\sum H^+ = (10^{-\text{pH}})/f_{\text{H}^+}$.

7. Calculate an approximate initial value for $\sum \text{HCO}_3^-$ from measured Alkalinity and pH assuming no ion pairing, i.e. $\sum \text{HCO}_3^- = (\text{Alk} - K'_\text{W} )/(\sum H^+ + \sum H^+ + \sum H^+)/\sum H^+ + 2K'_\text{H}^+ / \sum H^+)$

8. Calculate values for $\sum H_2\text{CO}_3^-$, $\sum \text{CO}_3^-$ and $\sum \text{OH}^-$ from equilibrium equations, Eqs. (A1) to (A3), and the assumed values for $\sum H^+$ and $\sum \text{HCO}_3^-$, i.e. $\sum H_2\text{CO}_3^- = \sum H^+ \cdot \sum \text{HCO}_3^- / K'_1$ and $\sum \text{CO}_3^- = K'_2 \cdot \sum \text{HCO}_3^- / \sum H^+$

9. Calculate ion paired species $\sum \text{NaCO}_3^-$, $\sum \text{NaHCO}_3^-$, $\sum \text{NaOH}^-$, $\sum \text{CaCO}_3^-$, $\sum \text{CaHCO}_3^-$ and $\sum \text{CaOH}^+$ from equilibrium equations, Eqs. (A4) to (A9). (In the first iteration the species concentrations $\sum \text{Ca}^{2+}$ and $\sum \text{Na}^+$ are assumed equal to the total ...
total analytical concentrations of these species
\[ \frac{[Ca^{++}]}{T} \text{ and } \frac{[Na^+]}{T} \].

In all subsequent iterations the values for \[ \frac{[Ca^{++}]}{F} \] and \[ \frac{[Na^+]}{F} \] used are those calculated from the previous iteration, i.e. those values calculated in step 10.

10. Calculate adjusted values for \[ \frac{[Na^+]}{F} \] and \[ \frac{[Ca^{++}]}{F} \] e.g.
\[ \frac{[Na^+]}{F} = \frac{[Na^+]}{T} - [NaOH^O] - [NaHCO_3] - [NaCO_3] \]

11. (i) Calculate values for Alkalinity and Acidity from the values for individual species determined above using Eqs. (A12) and (A13), i.e.
Alk. (calculated) = \( 2(\frac{[CO_3^2]}{F} + [NaCO_3] + [CaCO_3]) + (\frac{[HCO_3^-]}{F} + [NaHCO_3] + [NaCO_3]) + (\frac{[OH^-]}{F} + [CaOH^+] + [NaOH^O]) - \frac{[H^+]}{\mathcal{M}} \)

Acidity (calculated) = \( 2\frac{[H_2CO_3]}{F} + (\frac{[HCO_3^-]}{F} + [NaHCO_3] + [CaHCO_3] + [H^+] - (\frac{[OH^-]}{F} + [CaOH^+] + [NaOH^O]) \)

(ii) Calculate an adjusted value for ionic strength, \( \mathcal{M} \), from the individual species concentrations determined in steps 8 and 9.

(iii) Recalculate the activity coefficients, and adjust the equilibrium constants accordingly.

(iv) Recalculate \( \frac{[H^+]}{\mathcal{M}} \) from the measured pH and adjusted activity coefficient \( f_H \).

12. Steps 7 to 11 are then reiterated until the calculated value for Alkalinity remains constant.
13. Compare the calculated value for Alkalinity, Alk. (calculated) with the known initial Alkalinity.

14. Steps 8. to 13. are repeated with an adjusted value for $\left[ HCO_3^- \right]_F$ until the calculated value for Alkalinity agrees with the true Alkalinity to within $10^{-10}$ moles/l. When this condition is satisfied, Acidity is given by acidity value calculated in step 11. (i). This calculated value usually will be $\pm 4.10^{-5}$ moles/l greater than the Acidity value based on mass of chemicals used in solution and is due to CO$_2$ contamination. The calculated value is now assumed constant for the remaining calculations in the particular experiment.

Determination of Alkalinity from known pH and Acidity

During a precipitation experiment pH is monitored with time. Alkalinity values corresponding to the observed pH values are determined using a similar method to that set out above, except that the parameter Alkalinity is now replaced by a known Acidity value in steps 7, 13 and 14. These calculated Alkalinity values can be used to give a plot of Alkalinity with time for a particular experiment. From this plot the change in Alkalinity with time can be estimated which equals the rate of CaCO$_3$ precipitation.
Appendix B

Listing of Computer Programmes PRECIP. MAIN with sub-routines IONP and SG 13 used for doing the calculations described in Appendix A.
*PRECIP:MAIN
1 C*********************************************************************
2 C PROGRAM PRECIP
3 C*********************************************************************
4 C THIS PROGRAM CALCULATES THE DISTRIBUTION OF IONIC SPECIES.
5 C THE RATE OF REMOVAL OF CA++ FROM SOLUTION (DCA++/DT)/M
6 C AND THE FUNCTION CAF*CC3F*(CA+CO3-KSP/CAF*CC3F)
7 C*********************************************************************

C DATA SET

C FIRST DATA CARD: IDENT IS THE EXPERIMENTAL NUMBER

C SECOND DATA CARD: NAHCO3,NAOH,CAACL2,MGCL2 ARE THE CONCENTRATIONS
C IN MOLES/L OF THE REACTANTS

C THIRD DATA CARD: T IS THE TEMPERATURE IN DEGREES CELSIUS

C FOURTH DATA CARD: SEED IS THE CACO3 SEED CRYSTAL CONC.
C IN PPM AS CACO3

C FIFTH DATA CARD: NUM IS THE NUMBER OF PH VALUES READ
C DT IS THE TIME DIFFERENCE BETWEEN PH READINGS

C THE NEXT DATA CARDS ARE THE EXPERIMENTAL PH VALUES
C FOLLOWED BY THE ENTROPY(USR) AND ENTHALPY(DHR) DATA FOR
C THE REACTIONS

C*********************************************************************

REAL K1,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,K12,K13,K14,K15,K16
REAL NAHC03,NAOH,CAACL2
DOUBLE PRECISION TALK,TS04,FSC4,HCC3,FRACT,SACID,OH,
H*COH*COC*HCC*CTCC
CCMHCN TS04,FSC4,TALK,HC03*FSC*OH*Tm0,TS04,CH4,CClC1,K1,K2,K3,K4,
K5,K6,K7,K8,K9,K10,K11,K12,K13,K14,K15,K16
狈i2HCC3*OH*COHC*HCC
DIMENSION PKK(30),CSR(30),SUR(30),PH1300),PK(30),SFUN(1000),
TICAS(1000),SEED(1000)
DIMENSION PHS(1000)
DIMENSION X(1000),Y(1000)*Z(1000),TIM(1000)
DIMENSION TFUNC(1000)

C 15 CONTINUE
READ(*,91) IDENT
91 FORMAT(16,31)
WRITE(5,92) IDENT
92 FORMAT(16,31)"EXPERIMENT NO."
READ(*,3) NAHC03,NAOH,CAACL2,MGCL2
3 FORMAT(4E10.4)
WRITE(5,4) NAHC03,NAOH,CAACL2,MGCL2
4 FORMAT(1H1,*NAHC03=**E10.4,**NAOH=*E10.4,**CAACL2=**E10.4,**
1*MGCL2=**E10.4,**MOLES/L**)
READ(8,5) T
5 FORMAT(F10.4)
WRITE(5,6) T
6 FORMAT(1H1,*TEMPERATURE=*F10.4,*DEGREES CELSIUS**)
READ(8,7) SEED
7 FORMAT(F10.4)
WRITE*(5,8) SEED
9 FORMAT(1H*CACO3 SEED CRYSTAL CONC.=*F10.4,*PPM AS CACO3*///)
10 READ(8,1011) NUM,DT
11 FORMAT(10F5.3)
12 IM 11 I=1,16
13 READ(8,12) DSRI(I),DHR(I)
14 FORMAT(2F10.3)
15 CONTINUE
16 TIM(I)=0
17 IM 113 I=2*NUM
18 CONTINUE
19 PHI=PHI(I)
20 FORMAT*(5F2.1)
21 WRITE*(5,102)PHI
22 IM 102, FFORMAT(1H*EXPERIMENTAL INITIAL PH=*,F6.4///)
23 IM 111 I=1*NUM
24 X(I)=TIM(I)
25 Y(I)=PH(I)
26 CONTINUE
27 NDIM=NUM
28 CALL SG13(X,Y,Z,NDIM,IER)
29 LDIM=NDIM-1
30 IM 112 I=2*LDIM
31 PHS(I)=Z(I)
32 CONTINUE
33 DALK=NAHCO3+NAGH
34 Dacid=NAHCO3-NAGH
35 TNA=NAHCO3+NADH
36 TMG=MGCL2
37 TCL=2*(CACL2+MGCL2)
38 TCA=CACL2
39 U=2*(TCA+TMG)+0.5*(TNA*TCL)
40 WRITE*(5,F10.3)
41 FORMAT*(14HCONVERT CONC. IN MOLES/L TO PPM AS CACO3///)
42 CALL SG13(X,Y,Z,NDIM,IER)
43 LDIM=NDIM-1
44 IM 112 I=2*LDIM
45 PHS(I)=Z(I)
46 CONTINUE
47 DALK=5*(10.**4.)
48 DACID=5*(10.**4.)
49 TNA=5*(10.**4.)
50 TMG=5*(10.**5.)
51 TCL=5*(10.**4.)
52 TCA=5*(10.**5.)
53 TTC=5
54 WRITE*(5,16) DALK.TNA.TMG.TCL.TTC
55 FORMAT(1H*TCT ALK=*,F10.4,*3X,*TNA=*,F10.4,*3X,*TMG=*,F10.4,*3X,*
56 TCL=*,F10.4,*3X,*TCA=*,F10.4,*PPM AS CACO3*///)
57 CALL SG13(X,Y,Z,NDIM,IER)
58 LDIM=NDIM-1
59 IM 112 I=2*LDIM
60 PHS(I)=Z(I)
61 CONTINUE
62 R=1.987
63 IM 17 TA=273.15+T
64 TR=298.15
65 IM 13 I=1,16
66 YY=EXP(-12.741+0.01875*TA)-EXP(784*(TA-TR)/219.
67 XX=TR/(1.00322)*(1.-EXP(YY))
68 PKK(I)=(DSRI(I)*XX/(2.303*R*TA)-DHR(I)/(2.303*R*TA))
69 PK(I)=-PKK(I)
B 4

14 PKK(1) = 9.153 - 0.02195 * TA - 2382.3 / TA
15 PKK(2) = 5.388 - 0.0219 * TA - 2730.7 / TA
16 PK(1) = PKK(1)
17 PK(2) = PKK(2)
18 WRTE (5, 14) PK(1) * PK(2) * PK(3) * PK(4) * PK(5) * PK(6) * PK(7) * PK(8)
19 FORMAT 1H * PKH2CO3 = F6.4 * 2X * FKHCO3 = F7.4 * 2X * PKS4 = F6.4 * 2X
20 1 * PKNASO4 = F6.4 * 2X * PKMGSO4 = F6.4 * 2X * PKNAHCO3 = F6.4 * 2X
21 2 * PKH2ACC3 = F6.4 * 2X * PKMGGHCO3 = F6.4 * 2X
23 FORMAT 1H * FKHCO3 = F6.4 * 2X * PKCAHCO3 = F6.4 * 2X
24 1 * PKCAOH = F6.4 * 2X * PKCAOH2 = F10.4
25 2 * PKW = F6.4 * 2X * PKS = F6.4 * 2X * PKMG0H2 = F10.4

17 PK1 = PK(1)
18 PK2 = PK(2)
19 PK3 = PK(3)
20 PK4 = PK(4)
21 PK5 = PK(5)
22 PK6 = PK(6)
23 PK7 = PK(7)
24 PK8 = PK(8)
25 PK9 = PK(9)
26 PK10 = PK(10)
27 PK11 = PK(11)
28 PK12 = PK(12)
29 PK13 = PK(13)
30 PK14 = PK(14)
31 PK15 = PK(15)
32 PK16 = PK(16)
33 LX = 0
34 LICN = 1
35 NN = 1
36 NUMM = NUM - 2
37 DO 10 1 = 1 * LDIM
38 44 U1 = U**0.9
39 C CONVERT BACK TO MCLES/L
40 C******************************************************************************
41 IF (LION = 1) 42, 42, 43
42 43 K1 = K1 * HF * ANF / (2.5 * ANH * 10.0 * 4.)
43 K2 = K2 * HF * CO3F / (ANF * 10.0 * 5.)
43 K3 = K3 * CAF * SO4F / (ANH * 10.0 * 5.)
43 K4 = K4 * SO4F / (10.0 * 5.)
43 K5 = K5 * GMF * SO4F / (ANM * 10.0 * 5.)
43 K6 = K6 * ANF * 2.0 / (ANM * 5.0 * 10.0 * 5.)
43 K7 = K7 * CO3F / (10.0 * 5.)
43 K8 = K8 * GMF / (10.0 * 5.)
43 K9 = K9 * GMF * CO3F / (ANM * 10.0 * 5.)
43 K10 = K10 * CAF / (10.0 * 5.)
43 K11 = K11 * OHF * GMF / (10.0 * 5.)
43 K12 = K12 * OHF * CAF / (10.0 * 5.)
43 K13 = K13 * CAF * CO3F / (10.0 * 5.)
43 KH = KH * OHF * HF / (2.5 * 10.0 * 9.)
43 KS = KS * CAF * CO3F / (10.0 * 10.0)
43 KMGM = KMGM * GMF / (OHF * 2.0 / (2.5 * 10.0 * 14.0)
43 C CALCULATE ACTIVITY COEFFS. FOR INDIVIDUAL SPECIES
44 C******************************************************************************
45 ARSF = 0.585 * 4.0 / (U1 / (1.0 * 0.328 * 1.0 * U1))
ACAF = -0.5094*(U1/(1.0+0.3286*U1))

ASOF = -0.5094*(U1/(1.0+0.3284*U1))

ANAF = -0.5094*(U1/(1.0+0.3284*U1))

AHF = -0.5094*(U1/(1.0+0.3284*U1))

ACOF = -0.5094*(U1/(1.0+0.3285*U1))

AOGF = -0.5094*(U1/(1.0+0.3283*U1))

GMF = 10.0**AMGF

CAF = 10.0**ACAF

SO4F = 10.0**ASOF

ANF = 10.0**ANAF

HF = 10.0**AHF

CO3F = 10.0**ACOF

OHF = 10.0**AOGF

CALCULATE ACTIVITY COEFF. FOR NEUTRAL SPECIES (ANH)

SALTING OUT COEFF. = SK = 0.75

LOG(ANH) = SK = 0

ANM = 0.75

ADJUST K VALUES TO INCORPORATE ACTIVITY COEFFS.

K1 = (10.0**(-1.*PK1))*ANM/(HF*ANF)

K2 = (10.0**(-1.*PK2))*ANF/(HF*CO3F)

K3 = (10.0**(-1.*PK3))*ANM/(CAF*SO4F)

K4 = (10.0**(-1.*PK4))/(SO4F)

K5 = (10.0**(-1.*PK5))*ANM/(GMF*SO4F)

K6 = (10.0**(-1.*PK6))*ANM/(ANF**2)

K7 = (10.0**(-1.*PK7))/(CO3F)

K8 = (10.0**(-1.*PK8))/GMF

K9 = (10.0**(-1.*PK9))*ANM/(GMF*CO3F)

K10 = (10.0**(-1.*PK10))/CAF

K11 = (10.0**(-1.*PK11))/(CHF*GMF)

K12 = (10.0**(-1.*PK12))/CHF*CAF

K13 = (10.0**(-1.*PK13))*ANM/(CAF*CO3F)

K14 = (10.0**(-1.*PK14))/CHF

K15 = (10.0**(-1.*PK15))/CAF*CO3F

KMG = (10.0**(-1.*PKMG))/(GMF*(CHF**2))

ADJUST K VALUES TO EXPRESS CONC. OF SPECIES IN PPM AS CACO3

K1 = K1*2.5*(10.0**4.)

K2 = K2*(10.0**5.)

K3 = K3*(10.0**5.)

K4 = K4*(10.0**5.)

K5 = K5*(10.0**5.)

K6 = K6*5.0*(10.0**4.)

K7 = K7*(10.0**5.)

K8 = K8*(10.0**5.)

K9 = K9*(10.0**5.)

K10 = K10*(10.0**5.)

K11 = K11*(10.0**5.)

K12 = K12*(10.0**5.)

K13 = K13*(10.0**5.)

K14 = K14*(10.0**5.)

K15 = K15*(10.0**5.)

KMG = KMG*2.5*(10.0**14.)

IF (NN-1) 306*306*496

IF (LION-4) 201*201*219
CALCULATE EXACT IONIC STRENGTH

H = 1.0/(10.0**PHI)/HF
H = H**5.0/(10.0**4.)
CH = Kw/H
KK = 1
HC03 = (CALK-OH+H)/(K2/H+1)
C03 = (HC03*K2/H)
H2CO3 = (HC03+H)/K1
CALL IONP
IF (TALK-DALK) 204, 205, 203
HC03 = HC03*0.9
GO TO 202
FRACT = 0.1*HC03
HC03 = HC03 + FRACT
C03 = C03/K2/H
H2CO3 = (HC03+H)/K1
CALL IONP
IF (TALK-DALK) 206, 209, 207
KK = KK + 1
IF (4-KK) 203, 205, 208
HC03 = HC03 - FRACT
FRACT = 0.1*FRACT
GO TO 206
END

CALCULATE INITIAL PH

LX = LX + 1
A = DALK
CH = D*95*A
LM = 0
H = Kw/CH
C03 = (A-CH+H)/(11.0+H/K2)
GO TO 270
C03 = (A-CH+H)/(C03+C*HC03/K2)
HC03 = H*C03/K2
H2CO3 = (HC03+H)/K1
KK = 1
CALL IONP
LM = LM + 1
IF (LM-3) 265, 265, 925
IF (SAC1D-CAC1O) 930, 930, 940
OH = 0.1-OH
LM = 0
H = Kw/CH
C03 = (A-CH+COH+H)/(C03+C*HC03/K2)
IF (C03) 930, 930, 935
GO TO 270
FRACT = OH
OH = CH + FRACT
LM = 0
H = Kw/CH
C03 = (A-CH+COH+H)/(C03+C*HC03/K2)
IF (C03) 947, 947, 948
OH = OH - FRACT
FRACT = 0.9*FRACT
GO TO 341
HCO3=H+CO3/K2
H2CO3=H+HCC3/K1
FCA=KS/CO3
CALL ICNP
LM=LM+1
IF(LM-3)<5.5, 550
IF(SACID-DACID)<555.990, 941
KKK=KKK+1
IF(5-KKK)=990, 980, 980
OH=OH-FRACT
FRACT=O.1*FRACT
GO TO 541
IF(LX-2)=44991, 991
H=H/(5.1*10.**4.)
CPHI=1.*ALOG1(H*HF)
WRITE(5,*70) CPHI
FORMAT(1H **CALCULATED INITIAL PH=*, F6.4, '///)
CALCULATE PH AND CORRESPONDING SPECIES CONCENTRATION VALUES
ACID=SACID
PHN=PHS(I)
TIMN=TIM(I)
NN=2
ALKD=0,0
ALK2=ALK
GO TO 600
KKK=1
PHN=PHS(I)
TIMN=TIM(I)
H=1./(10.**PHN)/HF
H=H+5.1*10.**4.
OH=Kw/H
HCO3=(ACID-H+OH)/(1.+H/K1)
H2CO3=H+HCO3/K1
CALL ICNP
IF(SACID-ACID)<510, 550, 580
HCC3=0.9*HCO3
GO TO 499
FRACT=0.1*HCC3
HCO3=HCO3+FRACT
CC3=HCC3*K2/H
H2CO3=(HCO3*H)/K1
CALL ICNP
IF(SACID-ACID)<520, 550, 530
KKK=KKK+1
IF(5-KKK)=550, 550, 540
HCO3=HCC3-FRACT
FRACT=O.1*FRACT
GO TO 520
LION=LION+1
IF(LION-9)=560, 560, 553
GO TO 44
ALK1=ALK
ALKD=ALK2-ALK1
ALK2=ALK1
TCA = TCA - ALKD
TCAS(I) = TCA
DCA = TCA - TCA
SSEEED(I) = SEEED + DCA
FUNC = CAF * C03F * (FCA * C03 - KS)
SFUNC(I) = FUNC
FUNCA = SSEEED(I) * FUNC
TFUNC(I) = FUNCA

WRITE(6, 610) TIMN, PHN, FCA, C03, TCA, DCA, C03F, CAF, ALKD
FORMAT(9E10.4)
NN = 2
LION = 2
1010 CONTINUE
DO 586 I = 3, NUMM
730 RATE = (TCAS(I-2) - 8 * TCAS(I-1) + 8 * TCAS(I+1) - TCAS(I+2)) / (12 * DT)
WRITE(5, 743) PHS(I) * RATE, SFUNC(I) * SSEEED(I) * TFUNC(I)
743 FORMAT(4F10.4, 4E10.4)
586 CONTINUE
200 CONTINUE
IF (LZ = 10) STOP, 820, 820
800 LZ = LZ + 1
GO TO 515
320 CONTINUE
STOP
ENC
SUBROUTINE ICNP

REAL K1,K2,K3,K4,K5,K6,K7,K8,K9,K10,K11,K12,K13,KW,K5

DOUBLE PRECISION TALK,TSO4,FSO4,HCO3,FRACT,SACID,OH,

1H+COH+CO3C+HCO3+CO3

COMMON TSO4,FSO4,TALK,HCO3,FMG,CH,H,THG,TCA,TNA,CO3,K1,K2,K3,K4,

K5,K6,K7,K8,K9,K10,K11,K12,K13,KW,KG,KS,FCA,FNA,TCL,U,SACIC,

2H2CO3+COH+CO3C+HCO3

LN=1

FSO4=TSO4

20 FMG=TMG/(1.*HCO3/K8+C03/K9+FSO4/K5+OH/K11)

FNA=TNA/(1.+FSO4/K4+HCO3/K6+C03/K7)

FCA=TCA/(1.+HCO3/K10+FSO4/K3+CH/K12+C03/K13)

Y=TSO4-FSO4*(1.+FNA/K4+FCA/K3+FMG/K5)

IF(Y) 30 100

30 FSO4=9.9*FSO4

GO TO 20

40 FRACT=0.1*FSO4

60 FSO4=FSO4+FRACT

80 LN=LN+1

FSO4=FSO4-FRACT

100 CONTINUE:

TALK=C03*(1.+2.*FNA/K7+FMG/K5)+HCO3*(1.+FNA/K6+FCA/K11+FMG/K8)+

10H*(1.+FCA/K12+FMG/K11)-H+CO3+FCA/K13

SACID=H2CO3+HCO3*(1.+FNA/K6+FCA/K11+FMG/K8)+H-CH*(1.+FCA/K12+FMG/1K11)

C03C=1.+2.*FNA/K7+FMG/K5+FCA/K13

HC03=1.+FNA/K6+FCA/K11+FMG/K8

COH=1.+FCA/K12+FMG/K11

FNACO=(FNA+FSO4)/(K4*5.*10.*4.)

FMGHNC=(FMG+HCO3)/(K8*5.*10.*4.)

FCACO=(FCA+HCO3)/(K10*5.*10.*4.)

FNACO=(FNA+C03)/(K7*5.*10.*4.)

1

HCO3=HCO3/(S.*10.*4.)

2

FC03=CC3/(10.*5.)

3

FFSO4=FSO4/(10.*5.)

4

FFCL=TCL/(5.*10.*4.)

5

FFNA=FNA/(5.*10.*4.)

6

FMG=FMC/(10.*5.)

7

FCA=FCA/(10.*5.)

8

U=2.*(FFSO4+FFCA+FFMG+FC03)+U.5.*(FFNA+FFCL+FNACO+FM6HC+FCJHC

1+FNA+FC03)

RETURN

END
SUBROUTINE SG13

PURPOSE
VECTORS OF ARGUMENT VALUES AND CORRESPONDING FUNCTION VALUES.

USAGE
CALL SG13(X,Y,Z,NDIM,IER)

DESCRIPTION OF PARAMETERS
X - GIVEN VECTOR OF ARGUMENT VALUES (DIMENSION NDIM)
Y - GIVEN VECTOR OF FUNCTION VALUES CORRESPONDING TO X
Z - RESULTING VECTOR OF SMOOTHED FUNCTION VALUES
NDIM - DIMENSION OF VECTORS X,Y AND Z
IER - RESULTING ERROR PARAMETER
IER = -1 - NDIM IS LESS THAN 3
IER = 0 - NO ERROR

REMARKS
1) IF IER=-1 THERE HAS BEEN NO COMPUTATION.
2) Z CAN HAVE THE SAME STORAGE ALLOCATION AS X OR Y. IF X OR Y IS DISTINCT FROM Z, THEN IT IS NOT DESTROYED.

SUBROUTINES AND SUBPROGRAMS REQUIRED
NONE

METHOD
EXCEPT AT THE ENDPOINTS X(1) AND X(NDIM), EACH SMOOTHED VALUE Z(I) IS OBTAINED BY EVALUATING AT X(I) THE LEAST-
SQUARES POLYNOMIAL OF DEGREE 1 RELEVANT TO THE 3 SUCCESSIVE
POINTS (X(I-K)+Y(I-K)) K = -1,0,1. (SEE HILDEBRAND, F.B.,
INTRODUCTION TO NUMERICAL ANALYSIS, MC GRAW-HILL, NEW YORK/
TORONTO/LONDON, 1956, PP.258-311.)

SUBROUTINE SG13(X,Y,Z,NDIM,IER)

DIMENSION X(1),Y(1),Z(1)

TEST OF DIMENSION
IF(NDIM=3)7*1*1

START LCOP
1 00 6 I=1:NDIM
2 XM=44333333*(X(I-2)+X(I-1)+X(I))
3 YM=44333333*(Y(I-2)+Y(I-1)+Y(I))
4 T1=X(I-2)-XM
5 T2=X(I-1)-XM
6 T3=X(I)-XM
7 XM=T1*T1+T2*T2+T3*T3
8 IF(XM)3*2
9 XM=(T1*(Y(I-2)-YM)+T2*(Y(I-1)-YM)+T3*(Y(I)-YM))/XM

10 STOP
11 END
CHECK FIRST POINT

3 IF((I-3)4*5
4 H=X*M*T1+Y*M
5 Z(I-2)=H
6 H=X*M*T2+Y*M
7 END OF LOC

UPDATE LAST TWO COMPONENTS

8 Z(NDIM-1)=H
9 Z(NDIM)=X*M*T3+Y*M
10 IER=0
11 RETURN

ERROR EXIT IN CASE NDIM IS LESS THAN 3

12 IER=-1
13 RETURN
14 END

PRINTS