Remineralization of desalinated water by limestone dissolution in a packed bed

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Abstract

Distilled waters or highly soft waters produced by desalination plants cannot be directly used as they are unpalatable, corrosive and unhealthy. Remineralization is necessary in order to overcome these problems.

A commonly used operation in the remineralization process is to contact $CO_2$ acidified desalinated water with a bed of domestic limestone. Limestone dissolution provides two essential ingredients to the water – bicarbonate alkalinity and calcium content:

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^{-}$$

Limestone dissolution is a slow rate-controlling step. Prediction of the limestone rate of dissolution as a function of the water composition is essential for reliable design and operation of the limestone contactor. A critical comparison of various kinetic expressions proposed in the literature carried out in this study reveals major differences in results evaluated from different dissolution models.

An experimental study was conducted in order to identify the most reliable kinetic dissolution model. Two series of experiments were carried out – one involving remineralization of distilled water containing low initial $CO_2$ concentrations (0.5 to 2 mM) and the other, remineralization of soft water, having high initial $CO_2$ concentrations (1.5 to 15 mM). The $CO_2$ acidified water was contacted in a 2 m high vertical column (32 mm I.D.), packed with 2.85 mm calcite particles. The change in water composition along the column was monitored to provide both differential and integral dissolution data.

Analysis of the data showed that none of the available models fitted the experimental results. The closest agreement was with the rather complex model of Plummer et al but this agreement was rather mediocre. In the high $CO_2$ content range, the model predicted dissolution rates higher by a factor of 2 to 4 in the high $CO_2$ range and by a factor of 10 to 20 in the low $CO_2$ range.

Based on the experimental results, two models were developed for the design of limestone dissolution column contactors. When the final composition of the remineralized water has a $CO_2$ content above 2 mM, the limestone bed can be designed by a very simple integral expression. However, if the dissolution depletes the $CO_2$ concentration to low values, well below 2 mM, the bed design requires numerical integration of the more general dissolution rate expression derived in this work.
Introduction

The lack of dissolved minerals in the high purity waters produced by desalination processes raises some problems. High purity water tends to be highly reactive and unless treated, it can create severe corrosion difficulties during its transport in conventional pipelines. For example, the cement mortar lining of water pipes deteriorates by the corrosive attack of soft waters. Also, untreated desalinated water cannot be used directly as a source of drinking water. A certain degree of remineralisation is necessary in order to make the water palatable and for re-introducing some essential ions required from health considerations. According to Gabbrielli and Geroﬁ [1], the optimal ranges of TDS, hardness and specific ion content of remineralized water in mg/L are 200-400 for TDS, 50-75 for $Ca$, 0-10 for $Mg$, 0-100 for $Na$, 30-150 for $Cl$ and 0-200 for sulfate – all in units of mg/L. The bicarbonate content recommendation is to have a concentration equivalent to the hardness content.

The main processes for the remineralization of desalinated water are as follows:

A. Dosage of chemical solutions (based on calcium chloride and sodium bicarbonate).

Large scale preparation and dosage of such mineralizing solutions is costly and impractical. This remineralization method is a viable option only for small capacity plants.

B. Lime dissolution by carbon dioxide.

This process involves treatment of milk of lime with $CO_2$ acidified desalinated water. The reaction involved is:

$$Ca(OH)_2 + 2CO_2 \rightarrow Ca^{+2} + 2HCO_3^{-1}$$  \hspace{1cm} (1)

C. Limestone dissolution by carbon dioxide.

Contacting limestone with $CO_2$ acidified desalinated water mineralizes the solution according to:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{+2} + 2HCO_3^{-1}$$  \hspace{1cm} (2)

Limestone dissolution is the simplest and most widely used process. Limestone is cheaper than lime and half the $CO_2$ amount is consumed in the formation of the same minerals. Moreover, the equipment for handling limestone is much cheaper compared with the system required for preparing and dosing lime slurries. The only advantage of the lime process is that the reaction proceeds almost to completion whereas in the limestone process, the reaction is much slower and does not reach completion so that residual excess $CO_2$ has to be neutralized by addition of $NaOH$ or $Na_2CO_3$. In large capacity plants, it is more economical to recover the excess $CO_2$ by degasification.

A difficulty in the design of limestone dissolution beds is the lack of reliable data on the kinetics of dissolution of limestone by $CO_2$ acidified water. The objective of the present study was to measure dissolution rates in a well controlled laboratory system and to confront the experimental data with the conflicting kinetic expressions published in the literature.
Characterization Of The Dissolution Process

Thermodynamic equilibria.

The solubility in water, \([CO_2] \text{ mol/L}\), of carbon dioxide in contact with a gaseous atmosphere having a partial pressure \(p_{CO2}\) is dictated by Henry’s law:

\[
p_{CO2} = H \times [CO_2] \quad (3)
\]

The equilibrium maintained in solution by the various carbonate species is given by:

\[
CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^{-1} \\
\downarrow \uparrow \\
H^+ + CO_3^{2-} \quad (4)
\]

The total concentration of the carbonate species maintained in solution is:

\[
C_T = CO_2 + HCO_3^{-1} + CO_3^{2-} \quad (5)
\]

The distribution of the species is governed by the first and second dissociation equilibria of carbonic acid:

\[
[H^+] \times [HCO_3^{-1}] / [CO_2] = K_1' \quad (6)
\]

\[
[H^+] \times [CO_3^{2-}] / [HCO_3^{-1}] = K_2' \quad (7)
\]

where \(K_1'\) and \(K_2'\) are the dissociation constants, adjusted for the ionic strength of the solution. The water dissociation equilibrium is given by:

\[
[H^+] \times [OH^-] = K_w' \quad (8)
\]

Eqs [5] to [7] show that the carbonate species distribution is governed by the pH (Fig. 1). Note that at the pH range of about 4.5 to 8.5, which is of practical interest for water remineralization, the \(CO_3^{2-}\) concentration is negligibly small and only the \(CO_2\) and \(HCO_3^{-1}\) species need be considered.

Dissolution of limestone requires that the water composition be such that:

\[
[Ca^{2+}] \times [CO_3^{2-}] < K_{sp}' \quad (9)
\]

where \(K_{sp}'\) is the solubility product of the limestone crystals. The stable crystallographic form of limestone is calcite.

Dissolution path in a closed system

A closed system consists of a single phase liquid solution, not in contact with a gaseous phase. Here, the carbon dioxide concentration is depleted by the dissolution reaction [Eq. 2]. The changes in solution composition accompanying dissolution are constrained by material and electric balances. Let the initial known composition of an aggressive water be denoted by \([Ca]_o, [CO_2]_o, [HCO_3]_o, [CO_3]_o, [H^+]_o, [OH^-]_o\).

The change in the concentration of each species is denoted by \(\Delta = C - C_o\), where \(C\) is a final condition. The mass balance constraint shows that:

\[
\Delta[Ca] = \Delta[C_T] = \Delta[CO_2] + \Delta[HCO_3] + \Delta[CO_3] \equiv \Delta[CO_2] + \Delta[HCO_3] \quad (10)
\]
The electrical balance shows that:

$$2\Delta[Ca] = \Delta[HCO_3^-] + 2\Delta[CO_3^{2-}] + \Delta[OH^-] - \Delta[H^+] \equiv \Delta[HCO_3^-]$$  \hfill (11)

Combining Eqs. [10] and [11], it is seen that:

$$\Delta[Ca] = \frac{1}{2} \Delta[HCO_3^-] = -\Delta[CO_2]$$ \hfill (12)

Thus, in the usual situation of negligibly small concentrations of the carbonate, hydrogen and hydroxyl ions, the dissolution path can be conveniently described (Fig. 2) by a simple linear relation between $[CO_2]$ and $[HCO_3^-]$ having a slope of -(1/2):

$$[CO_2] = ([CO_2]_o + [HCO_3^-]_o) - \frac{1}{2} [HCO_3^-]$$ \hfill (13)

The $Ca$ concentration is linearly related to the $HCO_3^-$ concentration by:

$$[Ca] = \frac{1}{2} [HCO_3^-] + ([Ca]_o - \frac{1}{2} [HCO_3^-]_o)$$ \hfill (14)

Inspection of the above system shows that in a dissolution process there are 6 unknown concentrations $([Ca], [CO_2], [HCO_3^-], [CO_3^{2-}], [H^+], [OH^-])$ and 5 equations [Eqs. 6, 7, 8, 13 and 14]. Thus in order to follow composition changes occurring in a remineralization process, it is sufficient to measure only one of the six concentrations. The other 5 concentrations are readily determined by solution of the set of equilibria and balance constraints.

**Open system**

In an open system, in which there is a gaseous atmosphere held at a constant $CO_2$ partial pressure, the dissolved $CO_2$ concentration is constant. Here the total carbon in the dissolution path is not constant and replaces the $CO_2$ concentrations as an unknown variable. Dissolution acts to increase the pH of the solution. In the widely used pH-stat technique [2] for studying the kinetics of $CaCO_3$ dissolution, the pH is held constant by automatic acid titration which neutralizes the alkalinity increase accompanying dissolution. Under these conditions, all the parameters affecting the rate of dissolution are constant and the rate of acid dosage represents the rate of dissolution corresponding to the solution composition.

**Equilibrium composition**

The dissolution process in a closed system terminates when the system reaches equilibrium conditions, characterized by:

$$[Ca^{2+}]_e \cdot [CO_3^{2-}]_e = K_{sp}'$$ \hfill (15)

where the subscript e denotes equilibrium conditions. Eliminating the $CO_3^{2-}$ concentration from Eqs. [6,7]:

$$[CO_2]_e = K_2 \cdot \frac{[Ca]_e \cdot [HCO_3^-]_e}{K_{sp}'}$$ \hfill (16)

Denoting the final conversion by $X = \Delta[Ca]$, the amount of Ca released by dissolution is given by:

$$\frac{[Ca]_o + X}{[CO_2]_o - X} \cdot \frac{[HCO_3^-]_o + 2X}{[CO_3^{2-}]_o + X} = K_{sp}' \cdot K_i \quad K_2$$ \hfill (17)
The final carbon species equilibrium concentrations, obtained in limestone dissolution of soft water containing some initial calcium bicarbonate, are related by:

\[
[CO_2]_e = \frac{K_2}{2K_j \cdot K_{sp}} \cdot [HCO_3]_e \cdot \left\{ 1 - \frac{[HCO_3]_o - 2[Ca]_o}{[HCO_3]_o} \right\} \tag{18}
\]

If dissolution occurs in distilled water, or in soft waters in which \([2Ca]_o = [HCO_3]_o\) the equilibrium concentrations are related by:

\[
[CO_2]_e = \frac{K_2}{2K_j \cdot K_{sp}} \cdot [HCO_3]_e \tag{19}
\]

Fig. 2 depicts graphically the dissolution path with \(CO_2\) and \(HCO_3\) coordinates. For a closed system, the dissolution path is the “operating line” of slope of \(-(1/2)\), given by Eq. 13. Plots of the \([CO_2]_e-[HCO_3]_e\) equilibria, expressed by Eqs. [18,19], are also shown. The intersection of the dissolution line with the equilibrium curve indicates the final equilibrium composition achieved in the system.

The driving force for the dissolution process is a difference between the actual water composition and its final equilibrium solubility. Fig. 2 illustrates two different driving forces that have been used in the literature in the development of kinetic expressions:

Driving force based on the equilibrium \(CO_2\) concentration:

\[
[CO_2] - [CO_2]_e
\]

Driving force based on a pseudo-equilibrium \(CO_2\) concentration:

\[
[CO_2] - [CO_2]^*\]

The pseudo-equilibrium concentration \([CO_2]^*\) is an equilibrium concentration based on the prevailing \(Ca\) and \(HCO_3\) concentrations:

\[
[CO_2]^* = \frac{K_2}{K_j \cdot K_{sp}} \cdot \{[Ca] \cdot [HCO_3]\} \tag{20}
\]

**Review of Dissolution Models**

Table 1 summarizes the main features of various dissolution kinetic studies. Only papers dealing with dissolution of calcite in the absence of metallic impurities are considered here. Commonly encountered metallic impurities such as \(Zn^{+2}\) and \(Cu^{+2}\) can slow down significantly the dissolution of limestone. Available data on the effect of metallic impurities will be reviewed in a future publication.

As illustrated below, there are considerable differences in the experimental set-ups, in the methods adopted for measuring the dissolution rate and in the models used for correlating the dissolution rate data. The different dissolution paths in the various investigations are displayed in Fig. 3. Open systems, in which dissolution of powdered \(CaCO_3\) particles occurred in the presence of a constant pressure gaseous \(CO_2\) atmosphere, were used by Erga and Terjesen [3], Plummer et al [4,5] and Chan and Rochelle [6]. Dissolution rates were determined by either the free drift method [3] or the more accurate pH-stat method [4-6].
Dissolution in continuous flow of either distilled or soft water over a bed of \( \text{CaCO}_3 \) particles was investigated by Yamauchi et al [7], Letterman et al [8] and in this study.

A major difference can be noted in the modeling of the dissolution process. Some authors [3, 4, 5, 7] assume that the dissolution process is controlled by surface chemical reactions and that diffusional mass transport processes are fast and need not be considered. On the other hand, Chan and Rochelle [5] and Letterman et al [8] correlate the dissolution data assuming a mass transfer controlled process. A different mass transfer model was adopted in each of these studies.

The most comprehensive investigation is, undoubtedly, that carried out by Plummer et al [4, 5]. The most convenient formulation for limestone bed design is that presented by Yamauchi et al [7].

According to Yamauchi et al, the basic dissolution rate expression is:

\[
R = \frac{Q \cdot d[\text{CO}_2]}{dS} = k \left( [\text{CO}_2] - [\text{CO}_2]_e \right)
\]  

(21)

where \( Q \) is the flow rate of the water and \( S \) is surface area of limestone particles. Integration of Eq. 21 gives:

\[
\ln \frac{[\text{CO}_2] - [\text{CO}_2]_e}{[\text{CO}_2]_o - [\text{CO}_2]_e} = k \cdot \frac{S_o V (1 - \varepsilon)}{Q} = k \cdot \frac{6(1 - \varepsilon)}{d_p \phi} \cdot \frac{L}{u_{app}}
\]

(22)

where \( \varepsilon \) is the bed fractional porosity, \( d_p \) is the particle size, \( \phi \) is the particle shape factor (\( \phi=1 \) for a sphere, \(<1 \) for irregular shapes), \( L \) is the bed length and \( u_{app} \) is the superficial flow velocity (flow rate/column cross sectional area). Eq. 22 predicts a linear relationship between \( \ln \frac{[\text{CO}_2] - [\text{CO}_2]_e}{[\text{CO}_2]_o - [\text{CO}_2]_e} \) and the apparent residence time \( (L/u_{app}) \). Note that the slope \( k' \) of this straight line depends on bed properties \( (\varepsilon, d_p, \text{ and } \phi) \).

**Comparison of Dissolution Rate Correlations**

A comparison of results predicted by the various dissolution rate correlations was made by calculating dissolution rates along the dissolution paths of waters having different initial compositions. The dissolution paths examined are shown in Fig. 4. In 6 cases denoted by the letters A to F, dissolution was carried out by distilled water having an initial \( \text{CO}_2 \) content in the range of 0.005 mM \( (pH=5.8) \) to 16.2 mM \( (pH=4.0) \). In 6 other cases denoted by the letters G to L, dissolution was carried out by soft water having a fixed initial total alkalinity of 3.8 mM and an initial \( \text{CO}_2 \) content varying from 0.05 mM \( (pH=8.15) \) to 25.0 mM \( (pH=5.5) \).

Fig. 5 shows a comparison of dissolution rates calculated from the correlations of Plummer et al [4, 5] and Yamauchi et al [7] for a temperature of 40 °C along the dissolution paths of the distilled water cases A to F. The initial dissolution rate calculated from Plummer’s correlations is much higher than that calculated from Yamauchi’s correlation. However, over a considerable medium alkalinity range, there is reasonable agreement in the results evaluated from the two correlations. At very low alkalinitities, there is a wider disagreement. Fig 6 shows a similar comparison for the soft water cases G to L. Agreement is mediocre in most cases.
It should be noted that Fig. 5 and 6 are based differential dissolution rates which accentuate differences. In a practical water remineralization column, the terminal water composition is governed by integration of the rate equation along the dissolution path. Differences in the exit water composition predicted by the above correlations will be less accentuated. Thus, designs of a remineralization column calculated from the two correlations will give results of the same order of magnitude.

Fig. 6 shows a comparison of dissolution rates calculated from the correlations of Plummer et al [4,5] and Letterman et al [7]. Here, there is a very wide discrepancy. The correlation of Letterman et al predicts considerably higher dissolution rates. Designs based on these two correlations will differ widely.

**Experimental**

In view of the considerable uncertainty in the choice of a rate expression on which to base the design of a remineralization column, an experimental study was carried out to provide first hand dissolution rate data. The functional parts of the experimental system (Fig. 8) were:

- Water supply lines providing either distilled water (prepared by condensing steam) or soft water (prepared by a water softening column)
- A water feed vessel equipped with a stirrer, a thermostatically controlled heating element and a CO$_2$ gas sparger, connected to pH controlled CO$_2$ cylinder
- A Perspex column, 32 mm internal diameter, 2 m high, packed with limestone particles (“Hydro-carbonat 00 Grade”), supplied by Akdolit Co., Germany. Crystallographic analysis confirmed that the particles consisted of pure calcite. Particles were sized by sieving and the fraction in the size range of 2.4 to 3.4 mm 2.85 mm average) was packed in the column. The limestone particles density was 2640 kg/m$^3$, bed porosity was 38%, the shape factor of the particles was in the range of 0.6 to 0.8 and the specific surface of the particles, measured by the pressure drop method, was $4000 \pm 200$ m$^2$/m$^3$.

The limestone dissolution path along the packed bed was followed by monitoring the composition of water extracted from sampling points located at distances of 14, 34, 64, 104, 170 cm down the column. The pH at the various sampling points was directly read from pH probe inserted in the column wall. Each sample was analyzed to determine its alkalinity and Ca content.

All experiments were carried out at a water temperature of 30±1°C. The nominal water flow rate in the various runs was either 0.1 or 0.2 or 0.3 L/min, corresponding to superficial velocities of 2, 4.1 and 6.2 mm/sec respectively. Since velocity had no apparent effect on the dissolution rate, most runs were carried out at the intermediate flow rate.

Two run series were carried out – Series I with soft water (17 experiments) and Series II with distilled water (7 experiments). The dissolution paths of the various runs are depicted in Fig. 9. The initial alkalinity in Series I runs varied in the range of 2.6 to 6.6 mequiv/L, the initial CO$_2$ content was in the range of 1.5 to 15 mM and the initial pH, in the range of 7.3 to 5.5. In
Series II runs, initial alkalinity was in the range of 5 to 10 mequiv/L, initial $CO_2$ content was in the range of 0.5 to 2 mM and the initial pH, in the range of 6.2 to 5.2.

Results

Differential analysis of the dissolution rate data

Experimental values of the dissolution rates were obtained by a differential analysis of the composition profile along the length of the column. Fig. 10 compares experimental dissolution rates with dissolution rates predicted by the correlation of Plummer et al [4,5] as a function of the driving force potential $\{[CO_2]-[CO_2]^e\}$ proposed by Yamauchi et al [7].

Close examination of the data shows that in runs of high initial $CO_2$ content $\{[CO_2]^o > 2$ mM or $[CO_2]^o-[CO_2]^e > 0.5$ mM}, the Plummer-predicted dissolution rates are higher by a factor of 3 to 4 at the inlet region and by a factor of 1.5 to 2 at the outlet region. In the low $CO_2$ runs, the deviations are higher and increase progressively with the decrease in $CO_2$ concentration, reaching deviation factors as high as 10 to 20.

Integral analysis of the data

Eq. 22, proposed by Yamauchi et al [7], enables simple analysis of the experimental data. Plots of $\ln \frac{[CO_2]-[CO_2]^e}{[CO_2]^e-[CO_2]^o}$ versus column depth $L$ (Fig. 11) displayed the predicted linear relationship, with regression coefficients close to unity. The slope of these straight lines were used to determine values of $k'$, defined by:

$$k' = k \cdot \frac{6(1-\varepsilon)}{d_p \phi}$$  \hspace{1cm} (23)

Fig. 12 shows values of the coefficient $k'$ derived from the various runs, plotted as a function of the $CO_2$ concentration. It is seen that above a $CO_2$ concentration of 2 mM, the kinetic coefficient is essentially constant, and has the value of $(5.5 \pm 0.5) \times 10^{-3}$ sec$^{-1}$. Inserting values of the bed porosity and particle size, it is found that for dissolutions carried out at 30 °C, $6k/\phi = 0.025$ mm/sec. This result is in very good agreement with the value $6k/\phi = 0.025 = 0.031$ mm/sec measured by Yamauchi et al at 40 °C.

Thus, design of a limestone bed contactor in which the final $CO_2$ concentration is above 2mM can be readily designed according to Eq. 22.

Further analysis of the data was carried out in the search of a model which gives a concentration independent kinetic coefficient at $CO_2$ concentrations below 2 mM. The best results were obtained by adopting the following rate expression:

$$R = \frac{Q \cdot d[CO_2]}{dS} = k \cdot \frac{\{[CO_2]-[CO_2]^e\}}{\{Ca\}^e}$$  \hspace{1cm} (24)
According to this model, \( k' = k''/[Ca]_e \). Hence values of \( k'/[Ca]_e \) should be independent of concentration. A test of this assumption is shown in Fig. 13. The average value of the kinetic coefficient, based on molar \( CO_2 \) concentrations and units of PPM as \( CaCO_3 \) for \( Ca_e \) is:

\[
   k'' = 0.69 \text{ PPM as } CaCO_3/\text{sec} \quad (25)
\]

The scatter in the data is moderate, the standard deviation in the value of \( k'' \) amounting to 24%. Design of a limestone bed in which the final \( CO_2 \) content is well below 2mM can be made by numerical integration of Eq. 24.

**Conclusion**

Rational design of a limestone bed contactor for remineralizing desalinated water rests on the availability of a reliable kinetic expression relating dissolution rate with water composition. The critical literature review presented in this paper highlights the difficulty that there is substantial disagreement among the various dissolution models published in the literature.

The results of the present investigation show that a limestone dissolution bed can be simply designed according to Eq. 22 if the terminal \( CO_2 \) concentration is sufficiently high. In the low \( CO_2 \) concentration region, dissolution rates can be roughly approximated by Eq. 24, which can only be numerically integrated to provide design dimensions.

Further research is called for in order to extend available data, to investigate the effect of temperature and to refine the low \( CO_2 \) dissolution rate model.

**Acknowledgments**

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4. L. N. Plummer, T. M. L. Wigley and D. L. Pakhurst, “The kinetics of calcite dissolution in \( CO_2 \) -water system at 5 °C to 60 °C and 0.0 to 1.0 Atm. \( CO_2 \)”, Amer. J. Science, 278 (1978) 179-216
Table 1. Summary of limestone dissolution rate studies

<table>
<thead>
<tr>
<th>Authors</th>
<th>System</th>
<th>Dissolution Rate Expressions</th>
</tr>
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<tbody>
<tr>
<td>Erga and Terjesen (1956)</td>
<td>Dissolution of 0.3 to 0.4 mm CaCO$_3$ powder in stirred vessel</td>
<td>Mass transfer resistance neglected</td>
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<tr>
<td></td>
<td>in contact with constant pressure CO$_2$ gas at 25 °C</td>
<td>$R = k\cdot[Ca]_e\cdot[Ca]_o$</td>
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<tr>
<td></td>
<td>Initial solution - distilled water</td>
<td>$= k'\cdot[HCO_3^-]_e\cdot[CO_2]_o$</td>
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<td>[CO$_2$]$_o$ = 9 to 60 mM</td>
<td>Rate determined by free drift expts.</td>
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<td>Dissolution rates determined by</td>
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<td>both free drift and pH-stat expts.</td>
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</table>
| Plummer et al (1978, 1979) | Dissolution of 0.3 to 0.6 mm CaCO$_3$ powder in stirred vessel         | Dissolution occurs by 3 simultaneous reactions involving attacks by H$^+$, CO$_2$ and H$_2$O.
|                          | in contact with constant pressure CO$_2$ gas at temperatures of 5 to 60 | The CO$_2$ rate expression is: $R_2 = k\cdot[CO_2]_o - k'\cdot[Ca][HCO_3^-][HCO_3^-]$        |
|                          | °C                                                                      | where [HCO$_3^-$]$_s$ is the adsorbed surface concentration, assumed to be at equilibrium with |
|                          | Initial solution – 100mM CaCl$_2$                                      | bulk CO$_2$ concentration                                                                    |
|                          | [CO$_2$]$_o$ = 0 to 60 mM                                              |                                                                                             |
|                          | Dissolution rate determined by                                        |                                                                                             |
|                          | pH-stat expts.                                                         |                                                                                             |
| Chan and Rochelle (1982) | Dissolution of 0.01 mm CaCO$_3$ powder in stirred vessel               | Limited experimental data.                                                                 |
|                          | in contact with constant pressure CO$_2$ gas at temperatures of 25 and | Dissolution assumed to be controlled by mass transfer and not by surface reactions. Dissociation of |
|                          | 55 °C                                                                  | carbonic acid is considered to be a slow rate controlling reaction given by: $R = k\cdot[CO_2]_o - k'\cdot[HCO_3^-][H^+]$ |
|                          | Initial solution – 100mM CaCl$_2$                                      |                                                                                             |
|                          | [CO$_2$]$_o$ = 0 to 60 mM                                              |                                                                                             |
|                          | Dissolution rate determined by                                        |                                                                                             |
|                          | pH-stat expts.                                                         |                                                                                             |
| Yamuchi et al (1987)     | Dissolution by flow of CO$_2$ acidified distilled water at 40 °C in a   | Dissolution rate expression: $R = k\cdot[CO_2]_o - [CO_2]_e$                               |
|                          | 100 mm diameter column, packed with CaCO$_3$ particles                  | Design equation derived by integration: $ln \left[ \frac{[CO_2]}{[CO_2]_e} \right] = -k \cdot \frac{6(1-\varepsilon)}{d_p\phi \cdot u_{app}} \cdot \frac{L}{d_p}$ |
|                          | Packing length = 0.5 to 2.4 m                                          | $6k/\phi = 0.03125$ mm/sec; $T = 40 ^\circ$ C                                               |
|                          | Particle sizes = 1.4 to 10 mm                                          | $\varepsilon$ = fractional bed porosity; $L$ = bed length, mm                               |
|                          | [CO$_2$]$_o$ = 2.4 to 5 mM                                             | $d_p$ = particle diameter, mm; $\phi$ = shape factor                                        |
|                          | Superficial vel. = 2.5 to 9 mm/ sec                                     | $u_{app}$ = Superficial flow velocity, mm/sec                                               |
|                          | Retention time = 55 to 270 sec                                         |                                                                                             |
|                          | Dissolution by flow of HCl acidified soft water at 9-22 °C in four     |                                                                                             |
|                          | 150-380 mm diameter columns.                                           |                                                                                             |
|                          | Packing lengths = 2.1 to 3.5 m                                         |                                                                                             |
|                          | Initial CO$_2$ and HCl acidity = 0.002 to 0.4 mM                       |                                                                                             |
|                          | Particle sizes = 9.6 to 32 mm                                          |                                                                                             |
|                          | Superficial vel. = 0.15 to 12 mm/sec                                    |                                                                                             |
|                          | Retention time = 230 – 3800 sec                                        |                                                                                             |
|                          | 150-380 mm diameter columns.                                           |                                                                                             |
|                          | Packing lengths = 2.1 to 3.5 m                                         |                                                                                             |
|                          | Initial CO$_2$ and HCl acidity = 0.002 to 0.4 mM                       |                                                                                             |
|                          | Superficial vel. = 0.15 to 12 mm/sec                                    |                                                                                             |
|                          | Retention time = 230 – 3800 sec                                        |                                                                                             |
|                          | Dissolution assumed to be controlled by mass transfer and a first order |                                                                                             |
|                          | surface reaction. Overall rate given by: $R = k\cdot[Ca]_o - [Ca]_e$  |                                                                                             |
|                          | Integration based on dispersion model. Data show that dispersion term is |                                                                                             |
|                          | negligible. Form of design equation identical to Yamuchi’s except that  |                                                                                             |
|                          | Ca replaces CO$_2$.                                                     |                                                                                             |
|                          | Correlation of $k$ values are given, in terms of the Reynolds number.  |                                                                                             |
Figure 1. Distribution of carbonate species at 25 °C

Figure 2. Graphical illustration of dissolution paths and dissolution driving forces
Figure 3. Dissolution systems investigated in various studies

Figure 4. Dissolution paths in simulation study
Figure 5. Comparison of dissolution rates predicted by Yamuchi et al and Plummer et al (distilled water simulations)

Figure 6. Comparison of dissolution rates predicted by Yamuchi et al and Plummer et al
Figure 7. Comparison of dissolution rates predicted by Plummer et al and Letterman et al

Figure 8. Experimental system
Figure 9. Dissolution paths of experimental runs

Figure 10. Comparison of experimental dissolution rates with values predicted by Plummer et al.’s model
Figure 11. Linear correlation of the CO$_2$ depletion along the bed

Figure 12. Effect of the CO$_2$ concentration on the magnitude of the kinetic coefficient $k'$
Figure 13. Effect of the CO$_2$ concentration on the magnitude of the adjusted kinetic coefficient $k'' = k'[Ca]_e$