$CaCO_3$ DISSOLUTION IN SO_2 SCRUBBING SOLUTION MASS TRANSFER ENHANCED BY CHEMICAL REACTIONS

BY

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ABSTRACT

The rate of $CaCO_3$ dissolution in slurry scrubbers for flue gas desulfurization affects SO_2 absorption, $CaSO_3$/$CaSO_4$ scaling, and ultimate $CaCO_3$ utilization. The dissolution rate of reagent $CaCO_3$ has been measured in 0.1 M $CaCl_2$ at constant pH and CO_2 partial pressure by batch titration with HCl. A mass transfer model has been developed assuming that the calcite particles behave as spheres in an infinite stagnant solution. The model incorporates the effects of several equilibrium acid/base reactions and also includes the finite rate reaction involving CO_2 and HCO_3^-. The cumulative rate of mass transfer is calculated by integrating over a particle size distribution obtained by a Coulter counter.

The results of this investigation show that $CaCO_3$ dissolution is controlled by mass transfer and not surface reaction kinetics. The measured dissolution rate was about 25% higher(but not less than)than the calculated rate of mass transfer, probably because of the effect of turbulence. The enhancement and inhibition effects of buffers on $CaCO_3$ dissolution are predicted by the general mass transfer model. Buffer additives such as adipic, acetic, acrylic, and sulfosuccinic acid tend to enhance the rate of dissolution by buffering the solution pH and

increasing acidity transport to the limestone surface. Dissolution is enhanced at low sulfite concentration but inhibited at high sulfite concentration, indicating some kind of surface adsorption or crystallization phenomenon. The rate of dissolution is a strong function of pH and temperature as predicted by mass transfer. At high CO_2 partial pressure, the rate of dissolution is enhanced due to the CO_2 hydrolysis reaction. CO_2 partial pressure also determines the equilibrium pH for $CaCO_3$ dissolution.

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CHAPTER I

INTRODUCTION

The dominant commercial technology for stack gas desulfurization is aqueous scrubbing using limestone ($CaCO_3$) to neutralize the SO_2 and produce $CaSO_3/CaSO_4$ waste solids. Such typical throwaway processes use either slurry scrubbing or clear solution scrubbing.

The typical slurry scrubbing process is represented by the flowsheet in Figure 1-1. It consists of a scrubber, a crystallizer, and a solid/liquid separator. The SO_2 waste gas ia absorbed with a slurry of product solids and unreacted limestone at pH 4 to 6. The alkalinity for SO_2 absorption is provided by $CaSO_3$ dissolution or by limited $CaCO_3$ dissolution in the scrubber. Slurry is recycled from the crystallizer to the scrubber and a small portion containing 10 to 15 wt.% suspended solids is withdrawn for solid/liquid separation(Rochelle and King, 1978). To avoid $CaSO_3$ and $CaSO_4$ crystallization and scaling in the scrubber, the crystallizer vessel must provide adequate residence time to control supersaturation of $CaSO_3$ and $CaSO_4$(Rochelle and King, 1978). Some of the $CaCO_3$ dissolution must also occur in the crystallizer to avoid $CaSO_3$ scaling in the scrubber. The $CaSO_3/CaSO_4$ solid product is disposed of as a solid waste in ponds

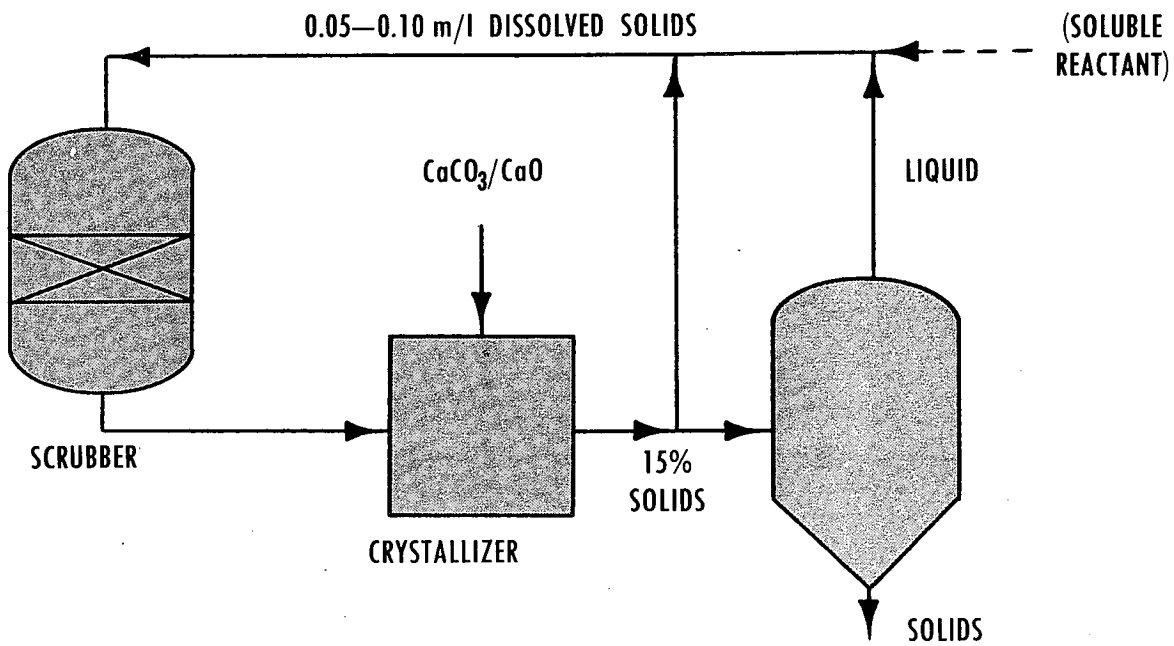

Figure 1-1. Simple Slurry Scrubbing

or landfills.

In the double-alkali processes(Figure 1-2) (Kaplan, 1973), SO_2 is absorbed into a clear solution of soluble alkali such as Na_2SO_3:

$$SO_3^{=} + SO_2 + H_2O \rightarrow 2HSO_3^{-}$$

The solution is reacted with $CaCO_3$ in a separate vessel to precipitate $CaSO_3$ and regenerate $SO_3^{=}$:

$$2HSO_3^{-} + CaCO_{3(s)} \rightarrow CaSO_{3(s)} + SO_3^{=} + H_2O + CO_2$$

The $CaSO_3$ solids are separated for disposal, and clear solution is recycled to the scrubber. The advantage of the double-alkali process over that of slurry scrubbing is that the problem of handling slurry in the scrubber are avoided. However, high levels of dissolved alkalinity are required to minimize the amount of liquid that must be processed for liquid/solid separation.

The use of additives such as soluble alkalis or buffering acids has been shown to enhance SO_2 removal efficiency of limestone slurry. Organic acids with pK_a values of 4.5 to 5.0 can accelerate the rate of SO_2 absorption at concentration as low as 3 to 10 mmoles/liter (Rochelle and King, 1977; Chang and Rochelle, 1980). These additives act as buffers to limit the drop in pH that normally occurs at the gas/liquid interface during SO_2 absorption.

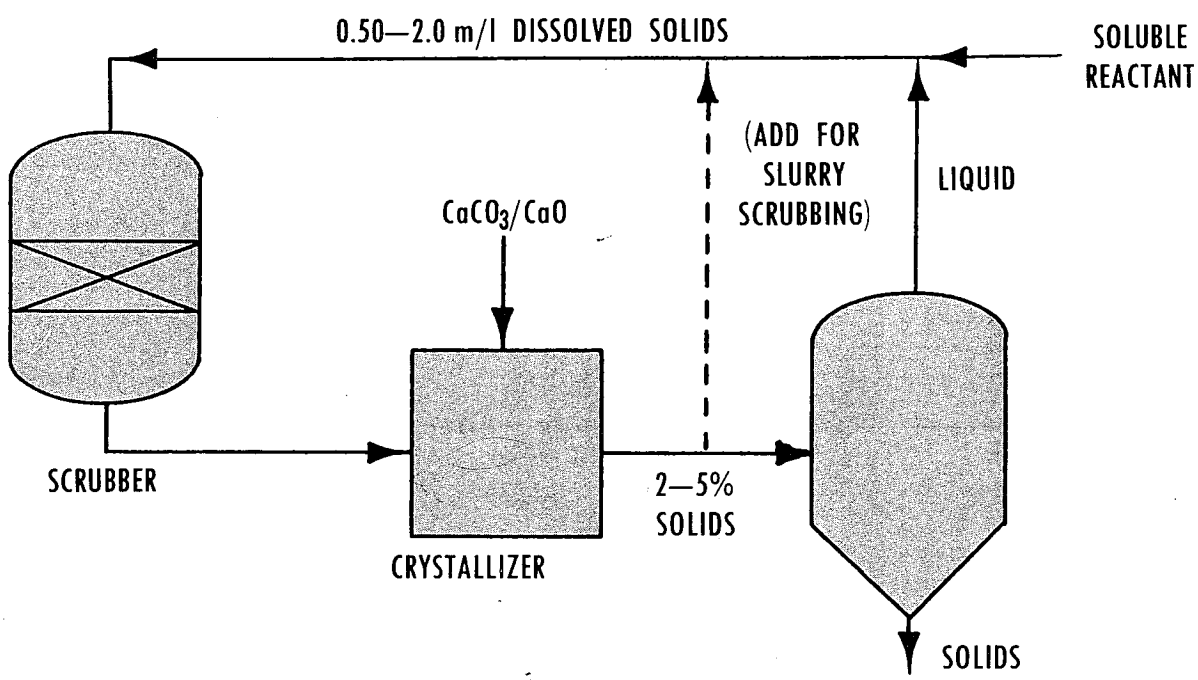

Figure 1-2. Double Alkali Process

The purpose of this investigation is to characterize limestone dissolution at conditions representative of slurry and double alkali scrubbers for stack gas desulfurization. The dissolution rate of reagent $CaCO_3$(calcite) has been measured. A mass transfer model assuming spherical $CaCO_3$ particles in an infinite stagnant medium is proposed to predictethe experimental rates. The results of this work should provide for more reliable, economic scrubber and reactor designs for both simple slurry and double-alkali processes.

CHAPTER II

LITERATURE REVIEW

$CaCO_3$ dissolution has been partially characterized by investigators interested in geochemistry, mine water disposal, and stack gas desulfurization. The most representative work being that of Berner and Morse (1974) and Plummer *et al.*(1978).

Berner and Morse (1974) used the pH-stat method to study the rate of dissolution of finely crystalline calcite(reagent or precipitated $CaCO_3$) in sea water. They report three regions of pH dependence. At pH less than 4, calcite dissolution appears to be controlled by diffusion of H^+ to the crystal surface. Near equilibrium, ΔpH(pH at equilibrium minus solution pH) of 0.0 to 0.4, the dissolution is sensitive to phosphate ion inhibition. At intermediate pH values the dissolution rate was a function of CO_2 partial pressure. At pH greater than 4, the dissolution rate was found to be distinctly less than that predicted for control by ionic diffusion.

Plummer *et al.* (1978) used the free drift and pH-stat method to study the dissolution of coarse Iceland spar. The pH-stat method identified three forward rate dependencies far from equilibrium: (1) linear dependence on the bulk fluid activity of H^+, (2) linear dependence on bulk

fluid P_{CO_2}, and (3) a constant forward rate in the near absence of H^+ and dissolved CO_2. Similar results were obtained when reaction approached equilibrium by the free drift method. In addition, the free drift method shows that the reverse reaction at constant p_{CO_2} and temperature is a linear function of the bulk fluid product activities of Ca^{++} and HCO_3^- in solution. A model of heterogeneous reaction in the adsorption layer was used and expanded by the authors to interpretate the rate expression.

Barton and Natanatham (1976) report a first order dependence on H^+ of the rate of dissolution of limestone in H_2SO_4 in the pH range of 2-6, indicating a mass transport reaction. Some investigators report dependence of dissolution on agitation which implies at least a certain degree of mass transfer resistance (Sjoberg, 1976; Erga and Terjesen, 1956; Ottmers et al., 1974). It appears that dissolved CO_2 does not participate in the mass transfer (Berner and Morse, 1974), probably because it does not react sufficiently fast at the limestone surface. Other buffering acidic components such as HSO_3^- or organic acids could substitute for H^+ by providing for mass transfer of acidity to the limestone surface (Rochelle, 1977).

Only limited work has been done on the temperature dependence of calcite dissolution. Sjöberg (1976)

measured an activation energy of 8.4 kcal/mol for dissolution at pH 8-10. Ottmers et al.(1974) found an activation energy of 14 kcal/mol at pH 5-6. Barton and Vatanatham (1976) reported a value of 3.6 kcal/mol for dissolution at pH 2-6. Plummer et al. (1978) gave values of 2.0 and 10.0 kcal/mol for dissolution at low and moderate pH. At high pH, an activation energy of 7.9 kcal/mol is reported for temperature greater than 25 °C and 1.5 kcal/mol for temperature less than 25 °C.

Particle size distribution and surface area are both important parameters for evaluating dissolution rate irrespective of the controlling mechanisms. Neglecting the surface area change during the experiment can lead to erroneous kinetics. It will also make the data incomparable for different runs and different limestone sources. Berner and Morse (1974) determined the initial particle size distribution by measuring several hundred individual crystal diameters under a high power microscope using a random sampling technique. Plummer et al. (1978) obtained the size distribution of coarse Iceland spar by wet sieving and estimated surface area by representing the particles as rhombohedra. Mean particle diameter was used to calculate the corresponding geometrical surface area. Sjöberg (1976) utilized the nitrogen adsorption method (BET) to

measure the reactive surface area. He found that the effective BET surface area was a factor of 2-3 times the area estimated from particle size assuming spherical shape.

CHAPTER III

THEORY

The dissolution of $CaCO_3$ in aqueous solution can be modeled by mass transfer assuming spherical particles suspended in an infinite stagnant medium. For spheres dissolving in a stagnant medium, the mass transfer coefficient is given by the asymptotic limit of a Sherwood number ($k_c d/D$) of 2 (Appendix A). A simplified mass transfer model integrated over the particle size distribution is used to calculate the theoretical dissolution constant k (cm^2/sec).

GENERAL MASS TRANSFER MODEL

A mass transfer model based on steady-state theory is proposed to describe limestone dissolution in aqueous solution. The calcite particles are assumed to be spheres suspended in an infinite stagnant medium. The model is limited to mass transfer with homogenous reaction rates and does not account for surface reaction rates. It usually assume liquid/solid equilibrium at the limestone surface.

When calcium carbonate is dissolved into aqueous solution of difunctional buffer(H_2A) in the pH range from 4 to 7, the following six reversible reaction should be considered:

$$CaCO_3^\circ + H^+ \rightleftharpoons Ca^{++} + HCO_3^- \qquad 3.1$$

$$CaCO_3^\circ \rightleftharpoons Ca^{++} + CO_3^= \qquad 3.2$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^= \qquad 3.3$$

$$H_2A \rightleftharpoons H^+ + HA^- \qquad 3.4$$

$$HA^- \rightleftharpoons H^+ + A^= \qquad 3.5$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad 3.6$$

All of the above reaction are essentially instantaneous (Weems, 1981). The values of the equilibrium constants for all but reaction 3.4 and 3.5 at 25 °C and infinite dilutions are:

$$K_1 = \frac{a_{Ca^{++}}\, a_{HCO_3^-}}{a_{CaCO_3^\circ}\, a_{H^+}} = 1.34\times10^{7}$$ (estimated from K_2 and K_3)

$$K_2 = \frac{a_{Ca^{++}}\, a_{CO_3^=}}{a_{CaCO_3^\circ}} = 6.3\times10^{-4}$$ (Garrels and Thompson, 1962)

$$K_3 = \frac{a_{H^+}\, a_{CO_3^=}}{a_{HCO_3^-}} = 4.69\times10^{-11}$$ (Harned and Scholes, 1941)

$$K_4 = \frac{a_{H^+}\, a_{SO_3^=}}{a_{HSO_3^-}} = 6.24\times10^{-8}$$ (Tartar and Garretson, 1941)

$$K_w = a_{H^+}\, a_{OH^-} = 1.008\times10^{-14}$$

At 55 °C, K_w was taken to be 7.26×10^{-14} and the other equilibrium constants were evaluated by relations given in Lowell et al.(1970). Activities of each species were calculated as the product of concentration and activity coefficient.

In order to account for $CaSO_3^\circ$ ion pair an effective K_4' is defined

$$K_4' = K_4\left(1 + \frac{a_{Ca^{++}}}{K_s}\right) \qquad 3.7$$

$$K_s = \frac{a_{Ca^{++}}\, a_{SO_3^=}}{a_{CaSO_3^\circ}} = 4.0\times10^{-4} \text{ (Lowell } \underline{\text{et al.}}\text{, 1970)}$$

at 25°C and infinite dilution.

For reactions 3.4 and 3.5

$$K_{A_1} = \frac{a_{H^+}\,[HA^-]}{[H_2A]} = 1.05\times10^{-4} \text{ M (Cavanaugh, 1978)}$$

$$K_{A_2} = \frac{a_{H^+}\,[A^=]}{[HA^-]} = 1.38\times10^{-5} \text{ M (Cavanaugh, 1978)}$$

These values are equilibrium constants in terms of concentrations for adipic acid in 0,1 M $CaCl_2$. For acetic and acrylic acids, K_{A_1} is estimated to be 3.55×10^{-5} and 9.54×10^{-5} M, respectively. The K_{A_1} and K_{A_2} values for sulfosuccinic acid are 7.94×10^{-4} and 3.98×10^{-5} M (Cavanaugh, 1978).

The material balance for CO_2 species at steady state in spherical coordinates gives:

$$\frac{1}{r^2}\left[D_{CO_2}\frac{\partial}{\partial r}\left(r^2\frac{\partial[CO_2]}{\partial r^2}\right)+D_{HCO_3^-}\frac{\partial}{\partial r}\left(r^2\frac{\partial[HCO_3^-]}{\partial r^2}\right)+\right.$$

$$\left.D_{CaCO_3^\circ}\frac{\partial}{\partial r}\left(r^2\frac{\partial[CaCO_3^\circ]}{\partial r^2}\right)+D_{CO_3^=}\frac{\partial}{\partial r}\left(r^2\frac{\partial[CO_3^=]}{\partial r^2}\right)\right] = 0 \qquad 3.8$$

Substituting $x = (1 - R_o/r)$ where R_o is the particle diameter and r the distance from the center of the sphere, equation 3.8 reduces to

$$D_{CO_2}\frac{\partial^2[CO_2]}{\partial x^2} + D_{HCO_3^-}\frac{\partial^2[HCO_3^-]}{\partial x^2} + D_{CaCO_3^\circ}\frac{\partial^2[CaCO_3^\circ]}{\partial x^2} +$$

$$D_{CO_3^=}\frac{\partial^2[CO_3^=]}{\partial x^2} = 0 \qquad 3.9$$

Integrating equation 3.9 with respect to x gives

$$D_{CO_2}[CO_2] + D_{HCO_3^-}[HCO_3^-] + D_{CaCO_3^\circ}[CaCO_3^\circ] +$$

$$D_{CO_3^=}[CO_3^=] = \alpha_1 + \beta_1 x \qquad 3.10$$

where α_1 (M cm^2 sec^{-1}) and β_1 (M cm^2 sec^{-1}) are constants of integration.

Similarly, other steady-state balances give for Ca^{++} species,

$$D_{Ca^{++}}[Ca^{++}] + D_{CaCO_3^\circ}[CaCO_3^\circ] = \alpha_2 + \beta_2 x \qquad 3.11$$

for a charge balance of diffusing species,

$$D_{H^+}[H^+] + 2D_{Ca^{++}}[Ca^{++}] - D_{HCO_3^-}[HCO_3^-] - 2D_{CO_3^=}[CO_3^=]$$
$$- D_{HA^-}[HA^-] - 2D_{A^=}[A^=] - D_{HSO_3^-}[HSO_3^-] - 2D_{SO_3^=}[SO_3^=]$$
$$- D_{OH^-}[OH^-] = \alpha_3 + \beta_3 x \qquad 3.12$$

for H_2A species,

$$D_{H_2A}[H_2A] + D_{HA^-}[HA^-] + D_{A^=}[A^=] = \alpha_4 + \beta_4 x \qquad 3.13$$

and for sulfite species,

$$D_{HSO_3^-}[HSO_3^-] + D_{SO_3^=}[SO_3^=] = \alpha_5 + \beta_5 x \qquad 3.14$$

By reaction stoichiometery, the flux of calcium must equal to the flux of CO_2:

$$\frac{\partial}{\partial x}\left(D_{Ca^{++}}[Ca^{++}] + D_{CaCO_3^\circ}[CaCO_3^\circ]\right) = \frac{\partial}{\partial x}\left(D_{CO_2}[CO_2] + D_{HCO_3^-}[HCO_3^-] + D_{CaCO_3^\circ}[CaCO_3^\circ]\right) \qquad 3.15$$

Therefore $\beta_1 = \beta_2 = \beta$. Since the net fluxes of H_2A species, sulfite species, and charge species are zero, β_3, β_4, and β_5 are zero. The constants α_1, α_2, α_3, α_4, and α_5 can be obtained from the compositions of the bulk solution (x = 1.0).

The finite-rate reversible CO_2 hydrolysis reaction

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^- \qquad 3.16$$

is also considered in the mass transfer model. The rate of this reaction is given by:

$$\frac{d[CO_2]}{dt} = k_f\left(\frac{\gamma_{H^+}[H^+]\gamma_{HCO_3^-}[HCO_3^-]}{K_5\,\gamma_{CO_2}} - [CO_2]\right) \qquad 3.17$$

where k_f is the forward rate constant and K_5 is the equilibrium constant for reaction 3.16. At 25°C and infinite dilution, the value of k_f and K_5 are 0.026 sec^{-1} (Pinsent et al., 1956) and 4.45×10^{-7} M (Harned and Bonner, 1954), respectively. The k_f and K_5 values at 55°C are 0.127 sec^{-1} (Pinsent et al., 1956) and 5.12×10^{-7} M (Lowell et al., 1970)

A steady-state differential material balance for CO_2 gives:

$$D_{CO_2} x^4 R_o^{-2} \frac{\partial^2[CO_2]}{\partial x} + k_f\left(\frac{\gamma_{H^+}[H^+]\cdot\gamma_{HCO_3^-}[HCO_3^-]}{K_5\,\gamma_{CO_2}} - [CO_2]\right) = 0 \qquad 3.18$$

The solubility of $CaCO_{3(s)}$ gives us the concentration of $CaCO_3$ at the limestone surface. The concentration of the

bulk species can be calculated from the pH, partial pressure of CO_2, total buffer and calcium concentrations, and the equilibrium relations 3.1 to 3.6. Therefore under slurry scrubbing conditions $CaCO_3$ dissolution becomes a process of simultaneous mass transfer with multiple equilibrium reactions and a single finite-rate reversible reaction.

Due to the non-linearity of the equilibrium equations, the concentration of chemical species at the limestone surface is calculated by trial and error using a modified interval halving method. If a value for β is guessed, the constants $\alpha_1, \alpha_2, \alpha_3, \alpha_4$, and α_5 can be calculated from the bulk composition(at x=1.0) and diffusivities by equations 3.10 to 3.14. The surface concentration of all species is calculated given the equilibrium solubility of $CaCO_3^\circ$ at the surface:

$$[CaCO_3^\circ]_s = 6.80 \times 10^{-6} \text{ M} \quad \text{(Lowell } \underline{\text{et al.}}\text{, 1970)}$$

Given CO_2 concentration at the surface (x=0.0) and a guess value for β, the CO_2 differential rate expression 3.17 is integrated numerically from x=0.0 to x=1.0 by the Simpson-Kutta method(Nielsen, 1964). A cubic equation fit of $[CO_2]$ from x=0.7 to x=0.85 is used to extrapolate the values of $[CO_2]$ from x=0.86 to x=1.0 as $r \to \infty$. If

$[CO_2]_b$ does not agree with its calculated value, a new value of β is guessed until the solution converges within 1% of CO_2. Due to the nonlinearity of the $[H^+][HCO_3^-]$ in equation 3.16, each step of the numerical integration requires numerical solution of equilibria and material balance equations. The interval numerical solution iterates on $[H^+]$ until it is known within 1%.

If the rate of the CO_2 hydrolysis reaction is negligible, the rate per unit radius is approximately constant and is given by β. The rate of limestone dissolved per unit surface area is given by

$$\text{Rate/unit area} = \frac{\beta}{(R_o \times 1000)} \left(\frac{\text{gmol}}{\text{cm}^2\text{sec}}\right) \quad 3.19$$

where β is in ($M\ cm^2\ sec^{-1}$) and R_o in cm. This mass transfer model can also be employed with other buffers by substituting the appropriate equilibrium constants and diffusivities.

A FORTRAN listing of the model is given in Appendix D.

MASS TRANSFER MODEL NEGLECTING CO_2 REACTION

For low P_{CO_2}, the CO_2 finite rate reaction is insignificant. Therefore the mass transfer model can be simplified by neglecting the CO_2 differential equation material balance. By specifying values for the dissolution flux(β), pH, P_{CO_2}, buffer concentration, and $[Ca^{++}]$ in the bulk, the constants α_1, α_2, α_3, α_4, and α_5 can be readily calculated. While applying the condition

$$[CO_2]_b = [CO_2]_s,$$

and specifying $[CaCO_3^\circ]$ at the surface, a trial and error calculation is made on $[H^+]$ until the following condition converges within 2% :

$$D_{H^+}[H^+] + D_{HCO_3^-}[HCO_3^-] + 2D_{CO_2}[CO_2] + D_{HA^-}[HA^-]$$
$$+ 2D_{H_2A}[H_2A] - D_{OH^-}[OH^-] - D_{SO_3^=}[SO_3^=] - \alpha_3 = 0$$

One can also calculate solution composition at the surface from a measured β (experimentally obtained rate data). Thus effects of surface kinetics or equilibria can be separated from mass transfer. We have used this mode of calculation to correlate $[CaCO_3^\circ]$ as a function of $[CaSO_3^\circ]$ at the surface.

A FORTRAN listing is given in Appendix D.

ACTIVITY COEFFICIENTS

Individual ion activity coefficients are calculated by a modified Debye-Hückel Limiting Law(Lowell *et al.*, 1970)

$$\log \gamma_j = AZ_j^2 \left(\frac{-I^{\frac{1}{2}}}{1 + Ba_j I^{\frac{1}{2}}} + b_j I \right) \qquad 3.20$$

where I is the ionic strength, Z_j is the charge on the jth ion, a_j and b_j are the characteristic parameters for each ion species. The values of the constants A and B in equation 3.20 are given by Hamer(1968):

$$A = \frac{1.8248 \times 10^6}{D_o \cdot T^{1.5}} \left(M^{-\frac{1}{2}} \right) \qquad 3.21$$

$$B = \frac{50.292}{D_o \cdot T^{1.5}} \left(M^{-\frac{1}{2}} \right) \qquad 3.22$$

where D_o is the dielectric constant of water(82.04, 68.30 at 25°and 55°C) and T is the absolute temperature in K. Values of a_j and b_j are given in Table 3-1.

The ionic strength I in equation 3.20 is given by

$$I = \frac{1}{2} \sum_i M_i Z_i^2 \qquad 3.23$$

Table 3-1 Activity Coefficient Parameters

Species	a_j	b_j
H^+	6.0	0.4
Ca^{++}	4.5	0.1
$SO_3^=$	4.5	0.0
$HSO_3^=$	4.5	0.0
$CO_3^=$	4.5	0.0
$HCO_3^=$	4.5	0.0
OH^-	3.0	0.0
Buffer species	3.0	0.0

The sum in equation 3.23 is over all charged species.

For uncharged species, the activity coefficients are given to a good approximation by the following equation (Harned and Owen, 1958)

$$\log \gamma_i = U_i I \qquad 3.24$$

in which U_i is an empirical constant taken to be 0.076.

DIFFUSIVITIES

Values of diffusivities used in the model are given in table 3-2 and 3-3. Interactions between ions are neglected, possibly resulting in errors as large as 40%.

Diffusivities for ions are taken to be those in absence of a potential gradient, since there is usually a large excess of $CaCl_2$ to disperse any potential gradient. At 25°C and infinite dilution, ionic diffusivities are given by:

$$D = \frac{RT\lambda_o}{n_j(Fa)^2} \qquad 3.25$$

where Fa is the Faraday number, n_j is the charge on the jth ion, and λ_o is the equivalent ionic conductivity at infinite dilution.

Diffusivities at 55°C were estimated by the Stokes-Einstein relationship:

Table 3-2 Self Diffusion Coefficients at 25° and 55°C

Species	Diffusivity x 10^5 (cm^2/sec) 25°C[a]	55°C
CO_2	2.00 [b]	3.89
HCO_3^-	1.20	2.33
$CO_3^=$	0.70	1.36
Ca^{++}	0.79	1.54
H^+	9.30	18.1
$CaCO_3^\circ$	0.75[c]	1.46
$SO_3^=$	0.70	1.36
HSO_3^-	1.33	2.59
OH^-	5.27	10.30

a Landolt-Bornstein, 1960

b Sherwood et al., 1975

c Estimated as average of $D_{Ca^{++}}$ and $D_{CO_3^=}$

Table 3-3 Diffusivities of Organic Acid additives at 25 °C

Organic Acids	Diffusivity x 10^5 (cm^2/sec) acid species	basic species
Adipic acid	0.736[a]	0.705[b]
Acetic acid	1.19[c]	1.09[d]

	H_2A^-	$HA^=$	$A^{\equiv}$
Sulfosuccinic acid	0.73[a]	0.53[e]	0.41[e]

a Albery et al.,1967

b Jeffrey and Vogel, 1935

c Lewis, 1955

d Landolt-Bornstein, 1960

e Weems, 1981

$$\frac{D_1 \eta_1}{T_1} = \frac{D_2 \eta_2}{T_2} \qquad 3.26$$

For the basic and monohydrogen species of sulfosuccinic acid, the diffusivities were reduced by 45% and 25% respectively to account for Ca^{++} interaction(Weems, 1981).

SIMULATED RESULTS BY THE MASS TRANSFER MODEL

The computer model of $CaCO_3$ dissolution limited by mass transfer has been used to calculate dissolution rates at 25°C and 0.3 ionic strength as a function of pH, P_{CO_2}, particle diameter(d), and dissolved Calcium($[Ca^{++}]$).

Figure 3-1 shows the effects of particle diameter on the dissolution flux. With small particles or low P_{CO_2} the dissolution flux varies inversely with particle diameter, because the CO_2 reaction with $CaCO_3$ is negligible. However, as shown in Figure 3-1, with larger particles(20 μm) and high P_{CO_2}(1 atm), the predicted dissolution flux is greater because the increased volume of solution around a single particle permits a greater amount of CO_2 reaction with $CaCO_3$.

Figure 3-2 shows the contributions of different species to the total dissolution rate at P_{CO_2} of 1 atm, d of 9 μm, and $[Ca^{++}]$ of 0.01 M. The relative contribution for each species is in (M cm^2 sec^{-1}. The total rate is

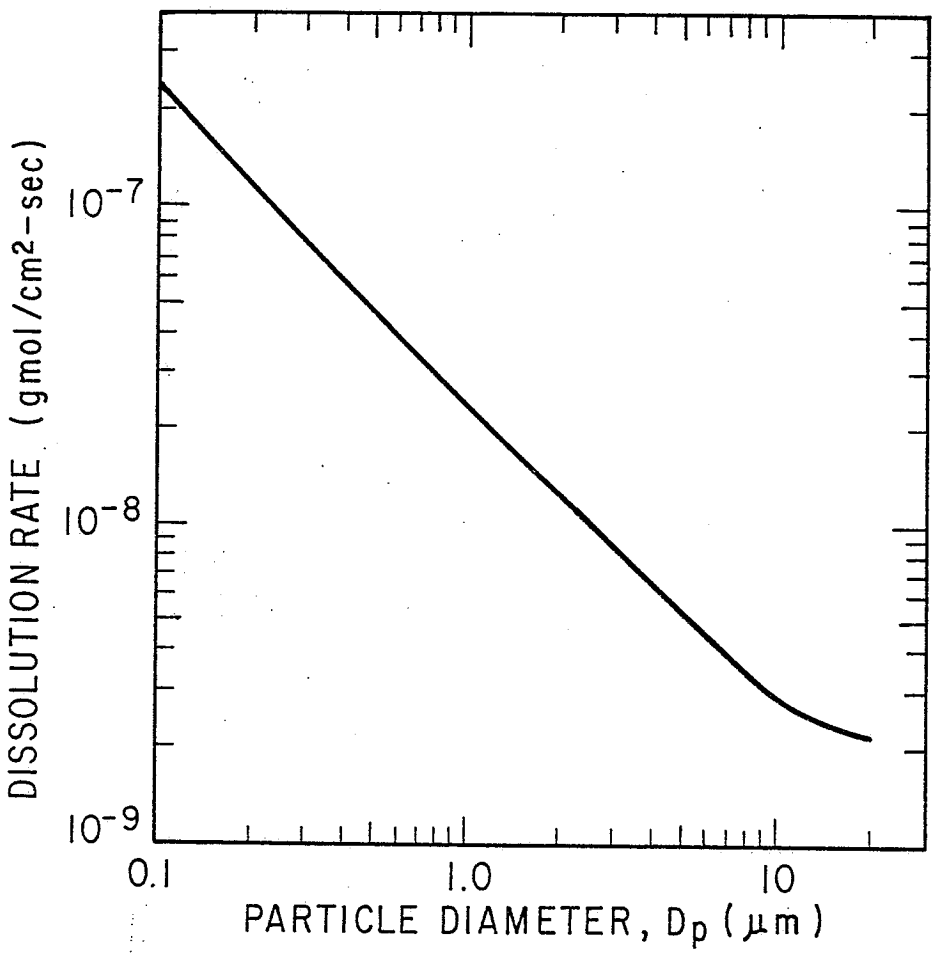

Figure 3-1. Effects of Particle Diameter on Dissolution Rate, pH 5.0, $[Ca^{++}] = 0.01M$, and $P_{CO_2} = 1$ atm

represented by $-\beta$:

$$-\beta = D_{CO_3^=}\Delta[CO_3^=] + D_{CaCO_3^\circ}\Delta[CaCO_3^\circ] - D_{H^+}\Delta[H^+] - D_{CO_2}\Delta[CO_2] \qquad 3.27$$

where $\Delta[\,_j\,]$ is the concentration difference (M) between the $CaCO_3$ surface and the bulk solution.

As shown in Figure 3-5, the contribution of $CaCO_3^\circ$ and $CO_3^=$ is small and nearly constant as a function of pH, but decreasing near equilibrium. The contribution of CO_2 diffusion dominates near equilibrium and increases to a maximum at pH 4.75. However, below pH 4.75 the CO_2 contribution decreases sharply and even becomes negative at pH 4.0. At low pH, the reverse reaction of HCO_3^- with H^+ reduces the availability of H^+ for $CaCO_3$ dissolution. The contribution of H^+ increases almost linearly with 10^{-pH} and dominates below pH 5.5. At pH 5.0, the total dissolution rate includes contributions of 66% from H^+, 28% from CO_2, and 7% from $CaCO_3^\circ$ and $CO_3^=$.

Figure 3-3 gives calculated data on the effects of pH and P_{CO_2}. At pH 4.5 to 5.5, P_{CO_2} of 1 atm increases the rate of dissolution by as much as 60% because of the indirect reaction of CO_2 with $CaCO_3$. However, at low pH(4.0) the effect of P_{CO_2} is significantly less. On the other hand, P_{CO_2} is dominant in determining the equilibrium pH at which dissolution stops.

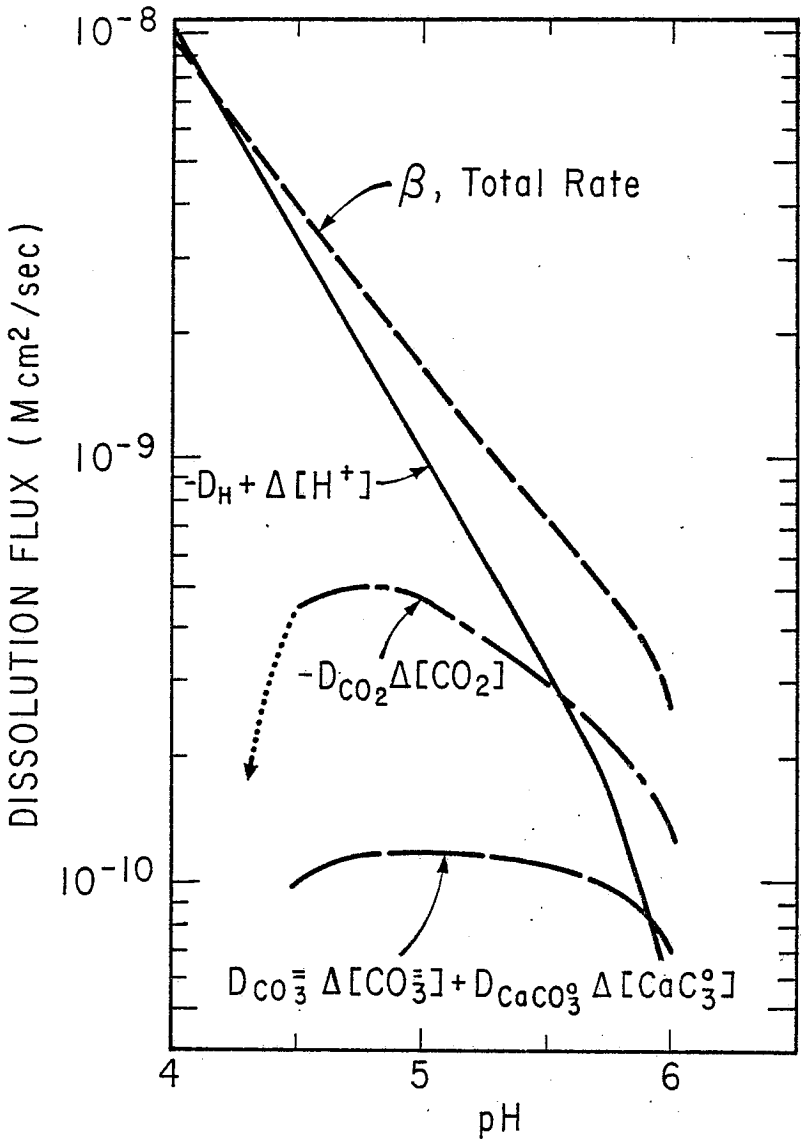

Figure 3-2. Flux Contribution to the Dissolution Rate with P_{CO_2} = 1 atm, $[Ca^{++}]$ = 0.01 M and 25°C

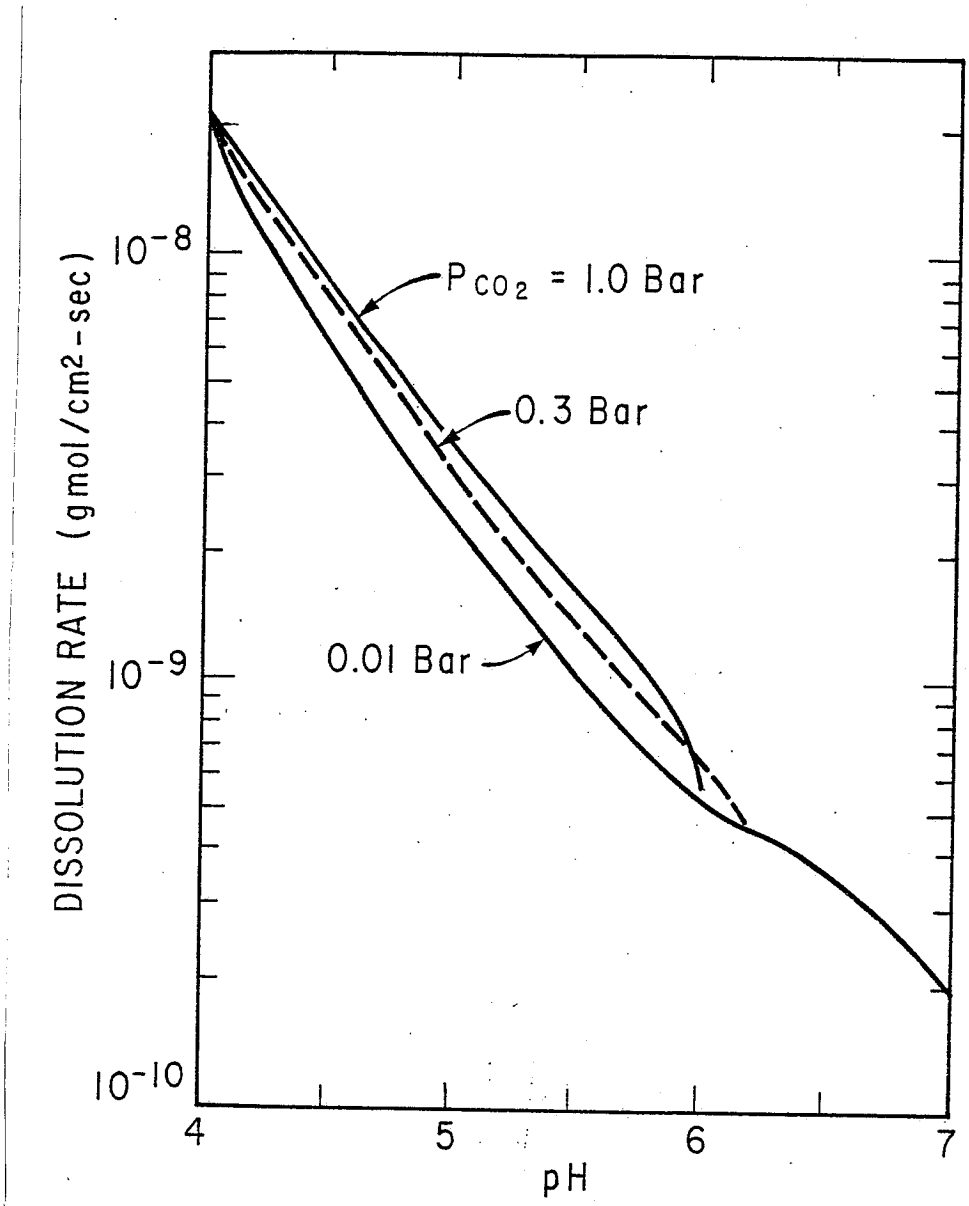

Figure 3-3. Effects of P_{CO_2} and pH on Dissolution Rate

PARTICLE SIZE DISTRIBUTION

If we neglect the finite-rate reaction involving CO_2, the rate of dissolution of a single spherical particle can be represented by the proportionality

$$\frac{dV}{dt} \cong d \cong V^{1/3} \qquad 3.28$$

where V is the volume of the particle and the proportionality constant varies with solution composition(pH) but is independent of particle diameter. This observation is confirmed by model simulation of rate of dissolution with different particle diameters. In order to account for the various particle size distributions, a simplified mass transfer model is used to integrate the size distribution of reagent grade $CaCO_3$ from Coulter counter measurement. The fraction remaining of a single particle after time t is given by integration of equation 3.28 to get

$$f = \frac{V}{V_o} = \left(1 - \frac{kt}{d^2}\right)^{1.5} \qquad 3.29$$

where k is the proportionality constant (cm^2/sec),
t is the time(sec) to dissolve a given fraction f,
and d is the particle diameter in cm.
The comprehensive mass transfer model gives k equal to 4.71×10^{-10} cm^2/sec at pH 5 for particles less than 10 to 20

μm. The proportionality constant, k, includes effects of solution composition, but is approximately independent of d.

With a polydisperse size distribution, the total fraction remaining, F, can be determined by summing over the differential size distribution ϕ where ϕ_i is the fraction of total particle mass with diameters from d_i to d_{i+1}:

$$F = \sum_{i=1}^{n} \phi_i \left(1 - \frac{kt}{d_i d_{i+1}}\right)^{1.5} \qquad 3.30$$

The fraction remaining of a given size range is taken to be zero when kt is greater than $d_i d_{i+1}$.

A FORTRAN program based on the above theory is written and listed in Appendix D. The program gives F as a function of kt or normalized time, t/t_{50}, where t_{50} is the time required for 50% of the limestone to dissolve. Figure 3-4 gives calculated values of total percent remaining (100·F) for reagent grade $CaCO_3$ based on the Coulter counter distribution in table 3-4. At 50% remaining the value of kt is 43.8×10^{-8} cm^2.

If a batch experiment gives the fraction remaining, FF, as a function of time at constant composition, the

Table 3-4 Size Distributions Determined by Coulter Counter for $CaCO_3$ (Reagent Grade)

Size (microns)	Volume % Differential[a]	Cumulative[b]
4.00	0.2	100.4
5.04	1.4	100.2
6.35	6.7	98.8
8.00	22.1	92.1
10.08	39.2	70.0
12.7	25.6	30.8
16.0	4.6	5.2
20.2	0.4	0.6
25.4	0.2	0.2
32.0	0.0	0.0

[a]Fraction of total volume between the given diameter and the next largest diameter.

[b]Fraction of total volume in sizes larger than the given diameter.

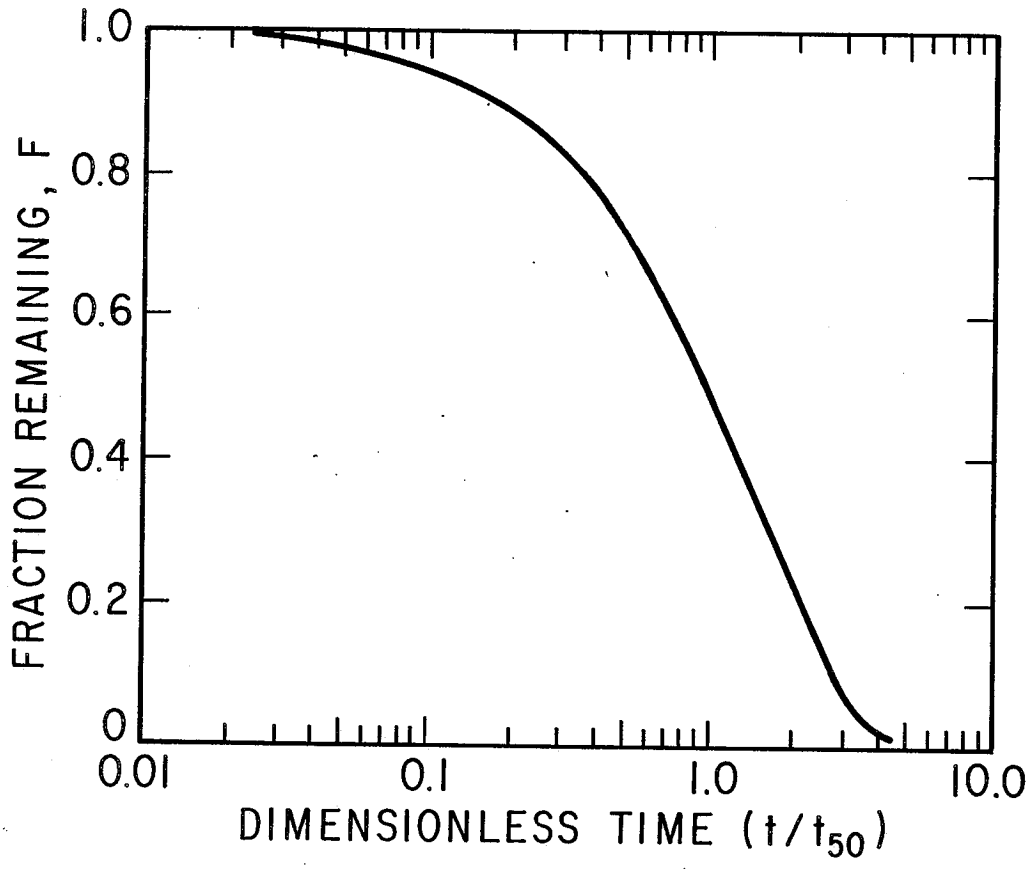

Figure 3-4. Calculated Dissolution Curve for Reagent Grade $CaCO_3$

rate constant, k, can be calculated from the experimental data and the mass transfer model. Two experimental data points (F_1, t_1) and (F_2, t_2) can be combined with two calculated data points at F_1 and F_2 with $[F_1, (kt)_1]$ and $[F_2, (kt)_2]$ to get the rate constant k_{exp}:

$$k_{exp} = \frac{(kt)_2 - (kt)_1}{t_2 - t_1} \qquad 3.31$$

If the experimental data at t=0.0 are reliable, k_{exp} can be obtained from a single data point of constant F:

$$k_{exp} = \frac{(kt)_2 - 0}{t_2 - 0} = \frac{(kt)_2}{t_2} \qquad 3.32$$

For example, with 50% remaining:

$$k_{exp} = \frac{(kt)_{50}}{t_{50}} \qquad 3.33$$

CHAPTER IV

APPARATUS AND PROCEDURE

METHODOLOGY

Rates were measured in a pH-stat with batch dissolution of $CaCO_3$ at constant pH and solution composition (Morse, 1974). The pH was controlled by HCl titration with the stoichiometry:

$$CaCO_{3(s)} + 2HCl \longrightarrow CaCl_2 + H_2O + CO_{2(g)}$$

Either CO_2 or N_2 were sparged into the solution to maintain a constant P_{CO_2} and HCO_3^- concentration. The relative change in calcium concentration was minimized by dissolving a small amount of $CaCO_3$ in solution with a high initial Ca^{++} concentration.

pH-STAT APPARATUS

A schematic representation of the pH-stat apparatus is shown in Figure 4-1. It consisted of a three-liter plexiglass batch reactor, an automatic burette/dispenser, an electrometer, and a titrate demand module. Nitrogen and carbon dioxide were supplied by two large gas cylinders.

The reactor was 15 cm in diameter and height with an o-ring sealed lid. It was baffled on four sides to eliminate vortex effects. The detail components of the reactor are shown in Figure 4-2. A variable speed agitator

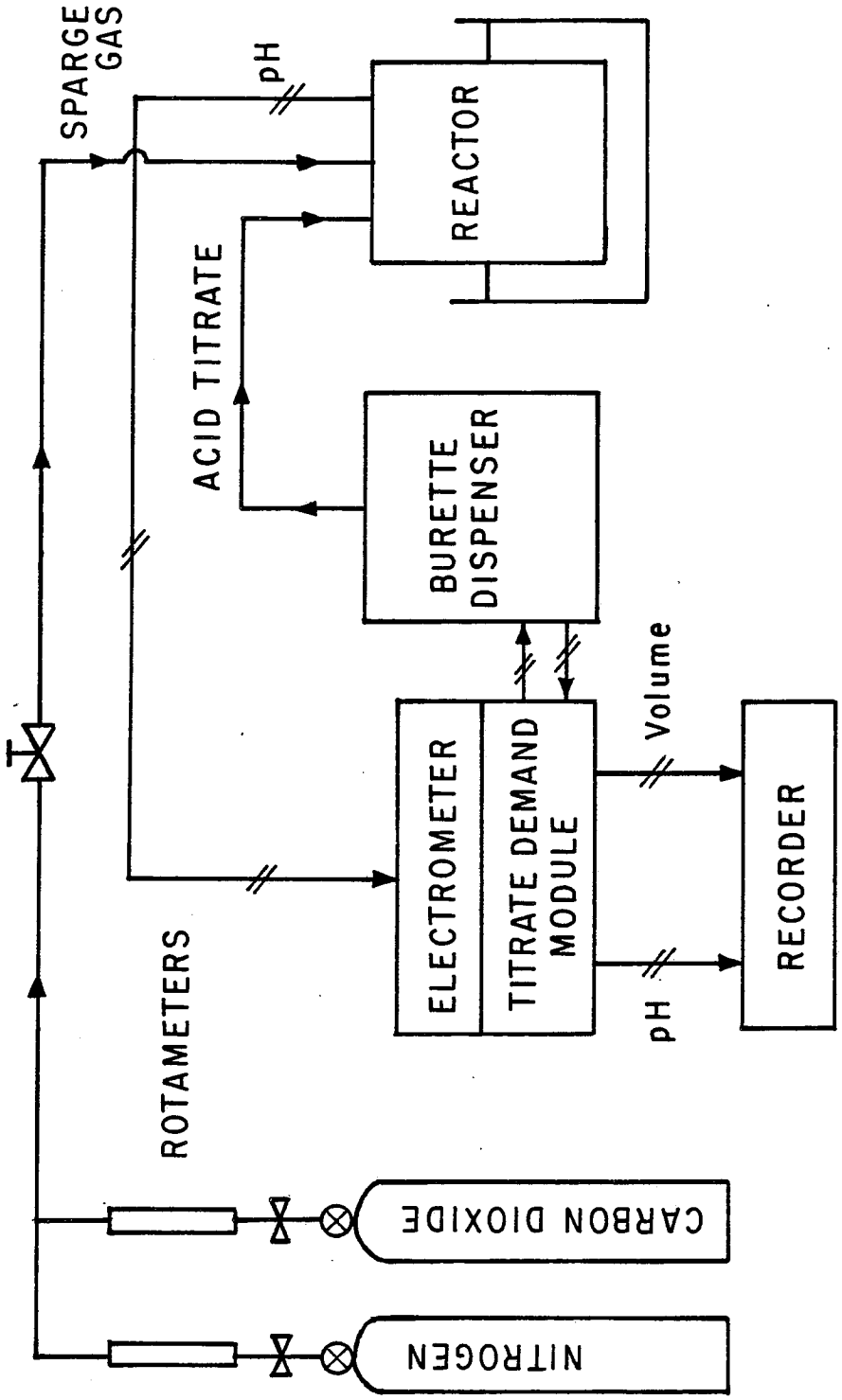

Figure 4-1. pH-Stat Apparatus

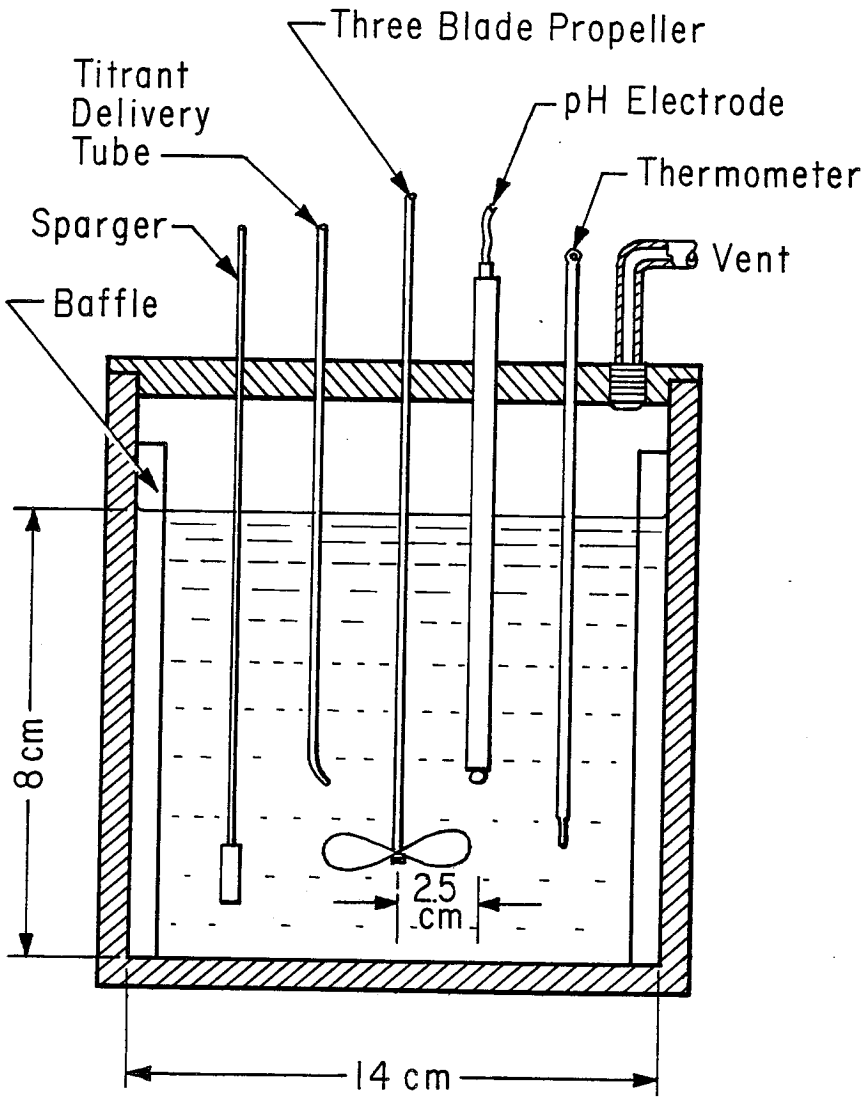

Figure 4-2. Detail Components of Reactor

with a three-bladed 2.5 cm marine propeller was used to keep the limestone in suspension. The variable speed agitator was kept constant at 720 rpm for all runs.

The pH of the solution was measured by a combination electrode calibrated with standardized pH 4 phthalate and pH 7 phosphate buffers. The acid titrant was added through a slanted glass-delivery tube.

Carbon dioxide or nitrogen was supplied to the reactor by fritted-glass tubing for better gas-liquid mass transfer. The flow rate of the gas was controlled by a needle valve and measured by a rotameter. The flow rate was maintained at about 1750 ml/min (at 1 atm and 70°F) for all experimental runs.

For runs at 55°C, the temperature of the reactor was kept constant within 2°C by a water bath with a mercury on/off thermoregulator. The heat was supplied by an electric heating coil submerged in the bath. The temperature of the solution in the reactor was measured by a thermometer. The cold gas was presaturated with water at 55°C to eliminate evaporation of water in the reactor.

Figure 4-3 shows the orientation of the various components in the reactor. All devices were fastened to reactor lid by means of number three and four rubber stoppers.

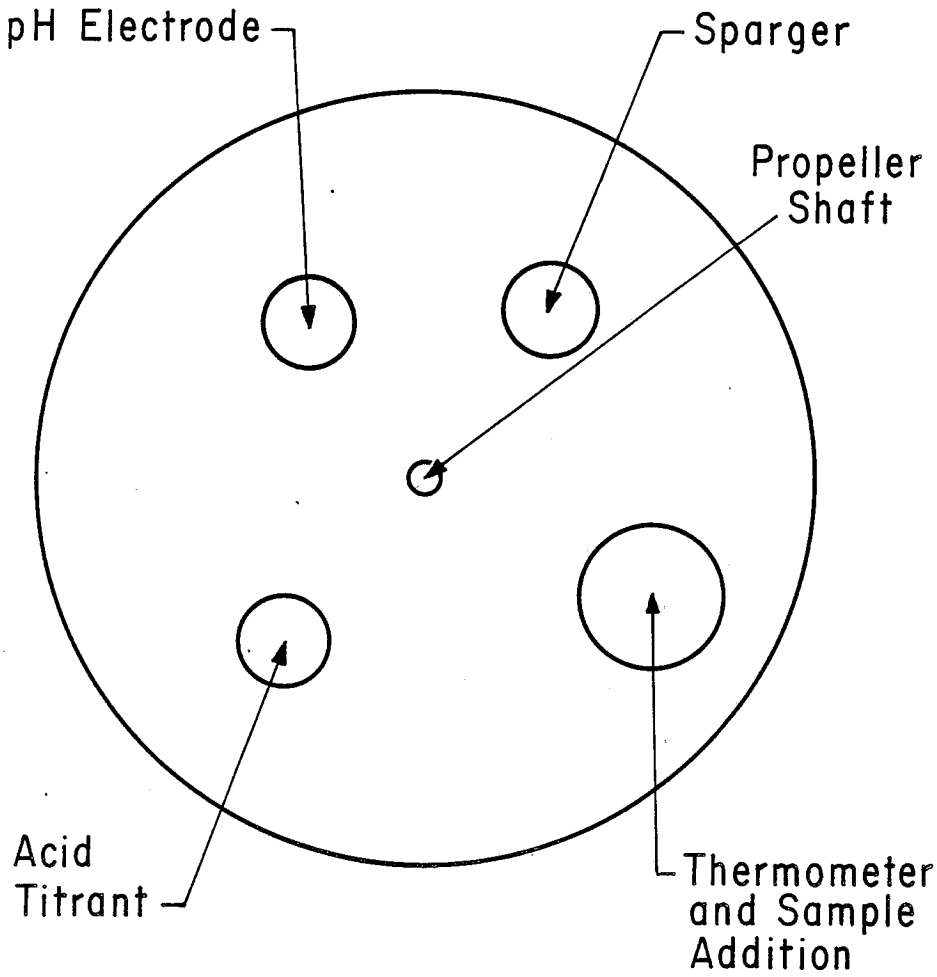

Figure 4-3. Top View of Reactor showing different orientations of each component

The Fisher Electrometer and Titrate Demand Module consisted of a pH controller with proportional or on/off functions. A 50 ml digital burette was used for acid addition with a 10 mv recorder output and a two-pen linear recorder for pH and cumulative volume versus time. A detailed description of the system is given in Appendix C.

PROCEDURE

The plexiglass reactor was filled with one liter of 0.1 M $CaCl_2$ solution. The solution was sparged by either CO_2 or N_2 depending on whether high or low P_{CO_2} was chosen for the experiment. The solution was sparged by either CO_2 or N_2 for about 20 minutes to presaturate the solution with the gas. During this time, the pH electrode was calibrated and a nominal pH was chosen. The agitator was turned on and 0.5±0.01 g of limestone was added to the reactor. The automatic burette/dispenser was started as soon as the limestone was added and the pH was controlled automatically within 0.02 pH. Cumulative titrant volume and pH were recorded versus time on a two pen linear chart recorder.

For CO_2 sparging, the pH controller was operated in the on/off mode (with a 0% proportioning band) since CO_2/HCO_3^- acts as a buffer for the solution. However, with N_2 sparging, on-off control gave cylic pH variations.

Therefore, the pH controller was used with a 50-60% proportioning band and a set point of almost one pH below the target value. The set point was adjusted manually to get the desired pH after the limestone was added and during the experiment. The use of the proportioning band eliminated the problem of pH fluctuating when a buffer is not present.

For runs at 55°C, the same procedures were followed except that the electrode was calibrated with standardized solutions preheated at 55°C. The 0.1 M $CaCl_2$ solution was preheated to about 57°C before adding to the reactor. The above procedure was necessary to reduce the time for reaching thermal equilibrium.

In experiments with buffers, an appropriate amount of organic acid or sodium salt was added to the 0.1 M $CaCl_2$ solution and the procedure for simple solutions was followed. With $HSO_3^-/SO_3^=$ buffer, a known sample of solution was drawn from the reactor before and after the run. The samples were quenched with excess iodine and backtitrated with thiosulfate to determine the amount of sulfite oxidized during the run.

PARTICLE SIZE DISTRIBUTION BY COULTER COUNTER

The Coulter counter determines the number and size of particles suspended in a conductive liquid by forcing the suspension to flow through a small aperture and monitoring an electrical current which also passes through the aperture. As a particle passes through the aperture, it changes the resistance between the electrodes. This produces a current pulse of short duration having a magnitude proportional to the particle volume. The measurements obtained from the Coulter counter are different percent volume versus volumetric size, and cumulative percent volume versus volumetric size. A single aperture can generate a size distribution with 14 fractions from 2 to 40% of the aperture diameter.

The particle size distribution of reagent $CaCO_3$ was measured with a 100 μm aperture in 0.18 M $CaCl_2$ electrolyte(Table 3-4). Preliminary measurements with NaCl electrolyte were unsuccessful because of $CaCO_3$ dissolution during size analysis. Dissolution was avoided by using $CaCl_2$ electrolyte or by using 1 mM Na_3PO_4 in 1 wt.% NaCl.

CHAPTER V

RESULTS AND DISCUSSION

The rate of calcite dissolution in 0.1 M $CaCl_2$ solution was measured and predicted by the general mass transfer model as a function of pH, P_{CO_2}, temperature, and buffer additives. The effect of P_{CO_2} is significant only in determing the equilibrium pH for dissolution due to buffer reaction. Acetic, adipic, acrylic, and sulfosuccinic acids enhance the rate of $CaCO_3$ dissolution at concentrations as low as 2 mM. However, sulfopropionic, hydroxypropionic, and polyacrylic acids inhibit the rate of $CaCO_3$ dissolution. Low sulfite concentrations enhance $CaCO_3$ dissolution. However, at high sulfite concentrations, crystallization or adsorption of $CaSO_3$ on the limestone surface tends to inhibit the rate. An equilibrium shift of $[CaCO_3^\circ]$ as a function of $[CaSO_3^\circ]$ on the limestone surface is used to model these effects. The enhancement of dissolution at low pH and high temperature is also observed.

The above results are modeled by mass transfer from a spherical particle to an infinite stagnant medium with enhancement by chemical reaction. This mass transfer model always predicts a rate that is about 25% lower than the experimental rate. Therefore, the model results in this chapter have been uniformly increased by 25% to

account for nonideality of the model. This nonideality may be the results of turbulence or non-spherical particles. Even for particles as small as 5 to 10 μm, the effect of turbulence may increase mass transfer as much as 25%. Furthermore, the model and Coulter counter measurement assume that the calcite particles are spheres instead of rhombehedra.

EFFECT OF PARTICLE SIZE

Figure 5-1 gives measured and calculated results of typical experiments as the fraction remaining versus dimensionless time. The integrated mass transfer model (polydisperse and monodisperse) is compared to that of runs at pH 4 and 5 with N_2 sparging. The results show that the integrated mass transfer model for polydisperse particles can predict the general dissolution shape for $CaCO_3$ dissolution at different solution compositions. The monodisperse (uniform particle size distribution) data also show that reagent grade $CaCO_3$ has a very uniform particle size distribution. However, for $t/t_{50} > 1.0$, the monodisperse model does not give as good a fit as the polydisperse model.

To obtain the experiment rate constant,k, equation 3.29 is used. From the general mass transfer model integrated over the size distribution (polydisperse),

$$kt_{56} - kt_{50} = 6.14 \times 10^{-8} \text{ cm}^2/\text{sec},$$

for the experimental run at pH 5, t_{50} = 11.3 min.

From Figure 5-1:

$$t_{50} - t_{56} = \left(1 - \frac{t_{56}}{t_{50}}\right) \cdot 11.3 \text{ min} = 96.8 \text{ sec}$$

Therefore $k_{exp} = 6.34 \times 10^{-10}$ cm^2/sec.

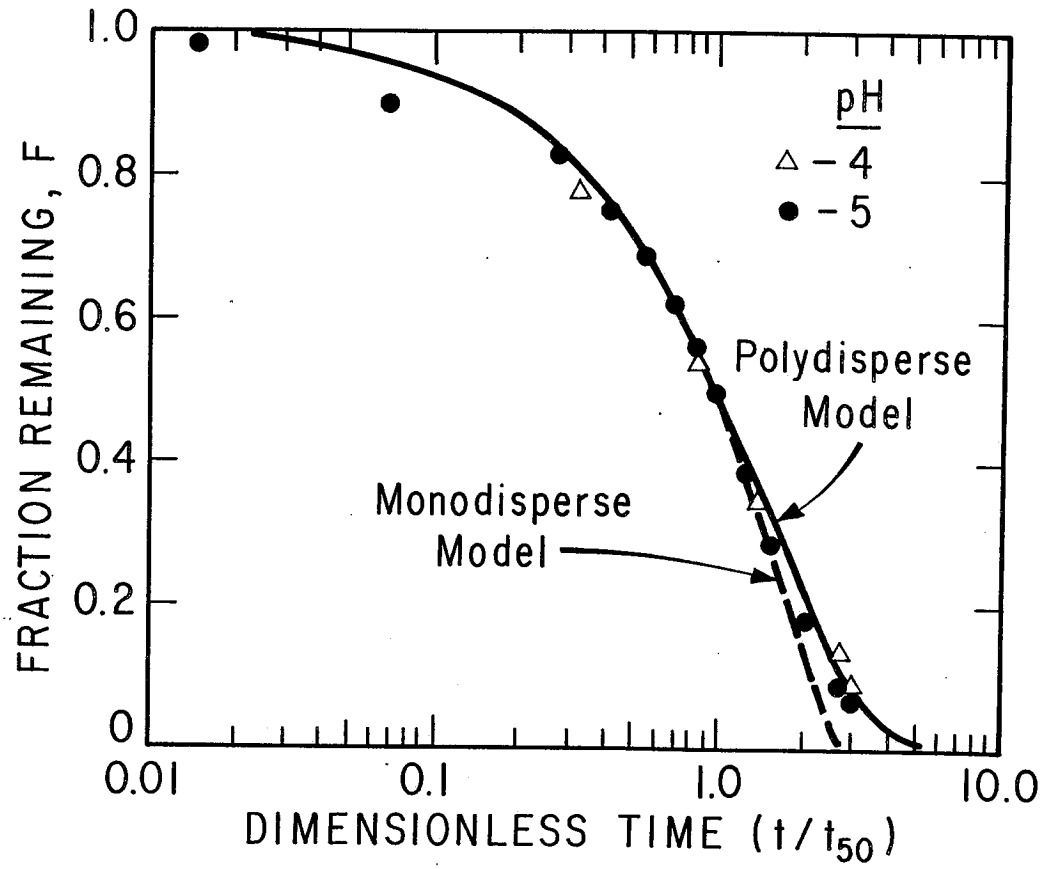

Figure 5-1. Dissolution Curves for Reagent Grade $CaCO_3$ at 25 °C with N_2 Sparging

EFFECT OF pH, P_{CO_2}, AND TEMPERATURE

Figure 5-2 and 5-3 give calculated and measured dissolution rates at 25 °C and 55 °C and pH 4 to 7 with CO_2 or N_2 sparging, respectively. Rates shown by the curves were calculated by the general mass transfer model assuming a particle diameter of 10 μm. The calculated rates were arbitrarily increased by 25% to account for nonideality of the model. The model works well for both CO_2 and N_2 sparging.

With CO_2 sparging, the model predicts a 6.7-fold increase in rate from pH 4 to 5. At 55 °C, the rates are 1.7 times than that at 25 °C for both high and low P_{CO_2}. The CO_2 reaction tends to increase the rate of dissolution 1.15 times below pH 5. With CO_2 sparging, the equilibrium pH is 5.6 at 25 °C and 5.4 at 55 °C.

With N_2 sparging, the model predicts rates at pH 7 which are 15% to 68% lower than experimental data at 25 °C and 55 °C respectively. These deviations are probably due to the sensitivity of the model to solution and surface equilibrium constants at high pH. At pH 6.5, the rate is three times higher at 55 °C than at 25 °C. However, at pH 5.0, the rate at 55 °C is about twice that at 25 °C. These effects were also predicted by the mass transfer model. The temperature dependence at high pH is probably due to the OH^- contribution to mass transfer.

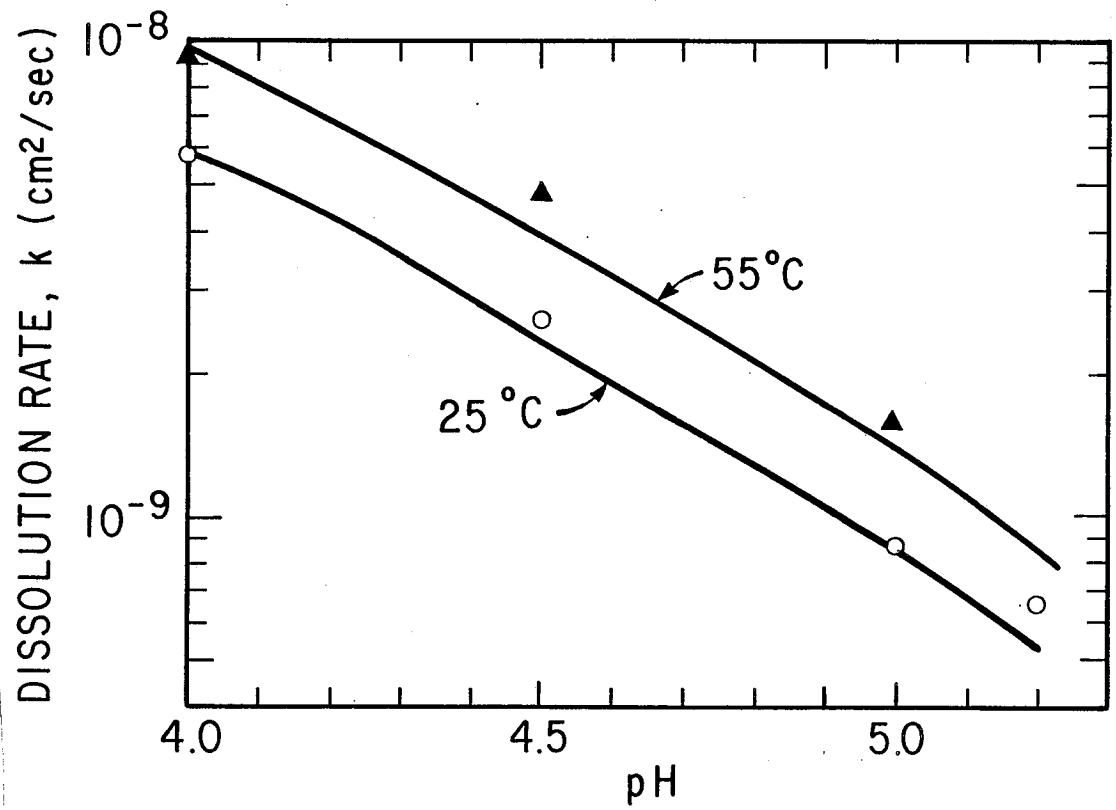

Figure 5-2. Dissolution Rate of Reagent $CaCO_3$ with CO_2 Sparging in 0.1 M $CaCl_2$. Curves Calculated by the General Mass Transfer Model

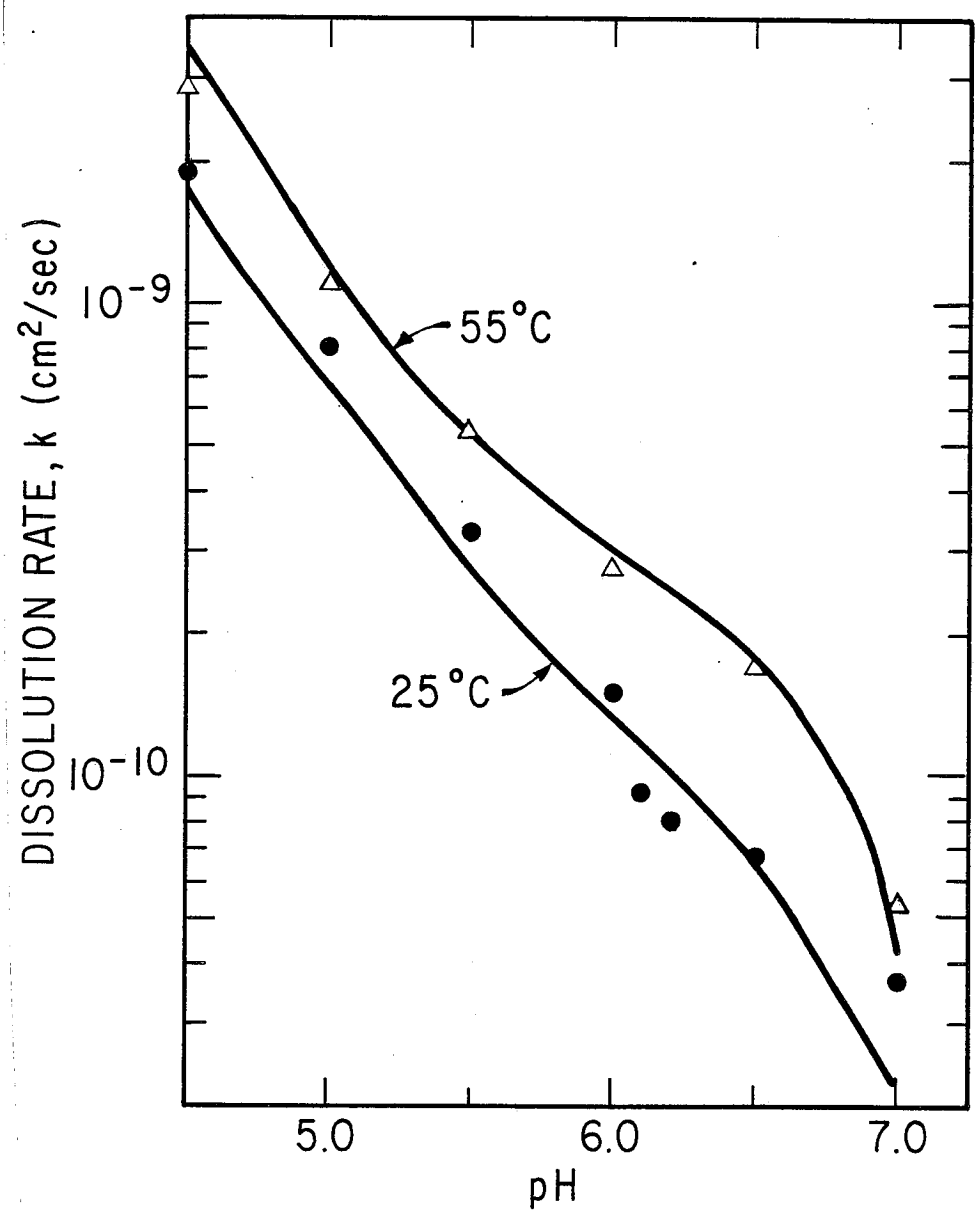

Figure 5-3. Dissolution Rate of Reagent Grade $CaCO_3$ with N_2 Sparging in 0.1 M $CaCl_2$. Curves Calculated by Mass Transfer Model Neglecting CO_2 Reaction

EFFECTS OF ORGANIC ACIDS

The rate constants for the various buffer systems were measured in 0.1 M $CaCl_2$ at 25 °C with N_2 and CO_2 sparging. Organic buffer additives such as acetic, adipic, acrylic, and sulfosuccinic acids enhance the rate of calcite dissolution by buffering the solution pH and providing for mass transfer of acidity to the limestone surface.

Acetic acid - The effects of 1, 3, and 10 mM acetic acid were measured at pH 4 to 6 with N_2 and CO_2 sparging. Figure 5-4 shows that the enhancing effects are predicted accurately by the mass transfer model. The enhancement of the dissolution rate with 1 mM acetic acid varies from 1.5 at pH 4 to 3.5 at pH 6. The buffer is more effective at high pH where H^+ diffusion has little effect on the rate. At pH 5 and 6, the dissolution rates are 2.8 and 3.5 times faster with 1 mM acetate than without acetate. At pH 5, the effect of CO_2 is insignificant in the presence of acetic acid.

Figure 5-4 shows results at pH 5.5 with CO_2 sparging. The calculated rates are 2-3 times higher than the measured rates. These deviations may due to the presence of impurities in the solution. Phosphate(Berner and Morse,1974) and certain metal ions (Terjesen et al.,1961)

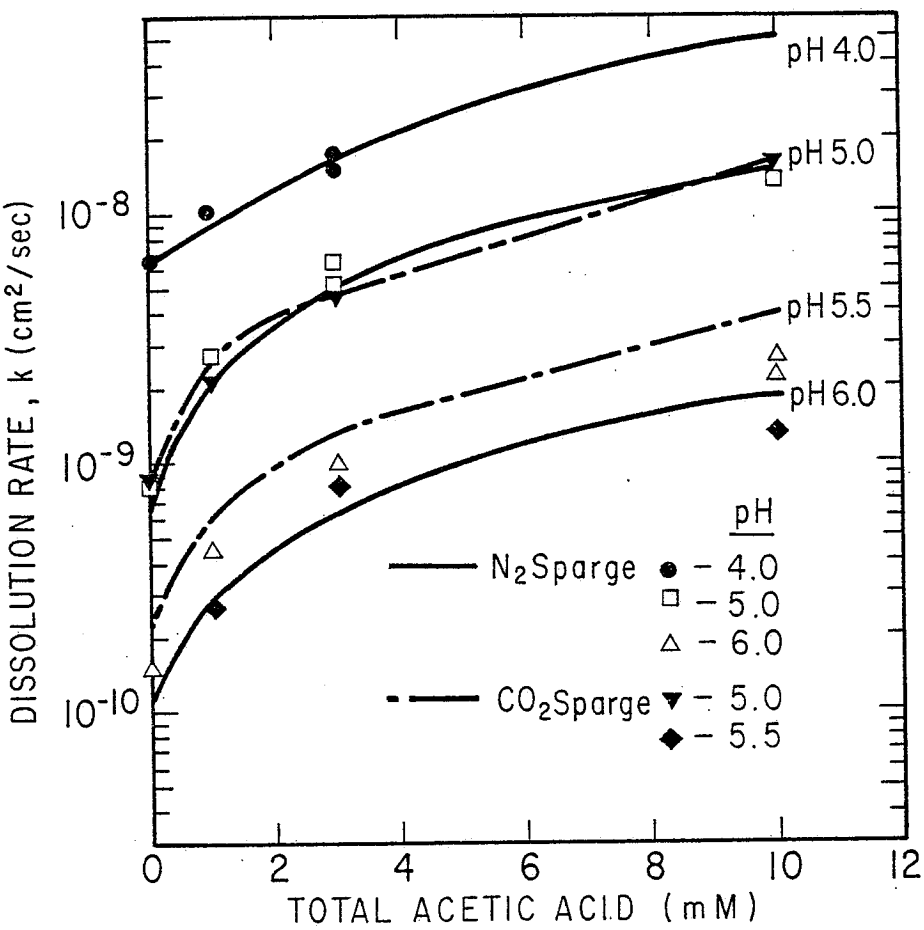

Figure 5-4. $CaCO_3$ Dissolution at 25°C in 0.1 M $CaCl_2$, Effect of Acetic Acid

shown some kind of inhibition by surface adsorption. Since the measured rates are extremely sensitive to pH near equilibrium, any inhibitors could cause a large deviation from the calculated rates. Furthermore, at pH close to equilibrium, the rates are very sensitive to the surface equilibrium and the values of the physical constants used in the mass transfer model.

Adipic acid - The effects of 3 mM adipic acid on the rate of dissolution are given in Figure 5-5. The calculated rate is within 5% of the experimental rate at pH 4 and 30% at pH 5 and 6. The rate data show that adipic acid is equivalent on a molar basis to acetic acid at pH 4, but gives 25% to 35% faster dissolution rates at pH 5 and 6.

Other buffers - The effects of acrylic, sulfosuccinic, hydroxypropionic, sulfopropionic and polyacrylic acids were measured at pH 5 with N_2 sparging(Figure 5-6). The acrylic and polyacrylic acids used were commercially available reagent grade materials. The other organic acids were synthesized from acrylic or maleic acid. Hydroxypropionic acid was synthesized from 2 M acrylic acid by heating with 1 M H_2SO_4 at 100 °C for 10-20 hours. Sulfopropionic acid was synthesized by reaction of Na_2SO_3 with

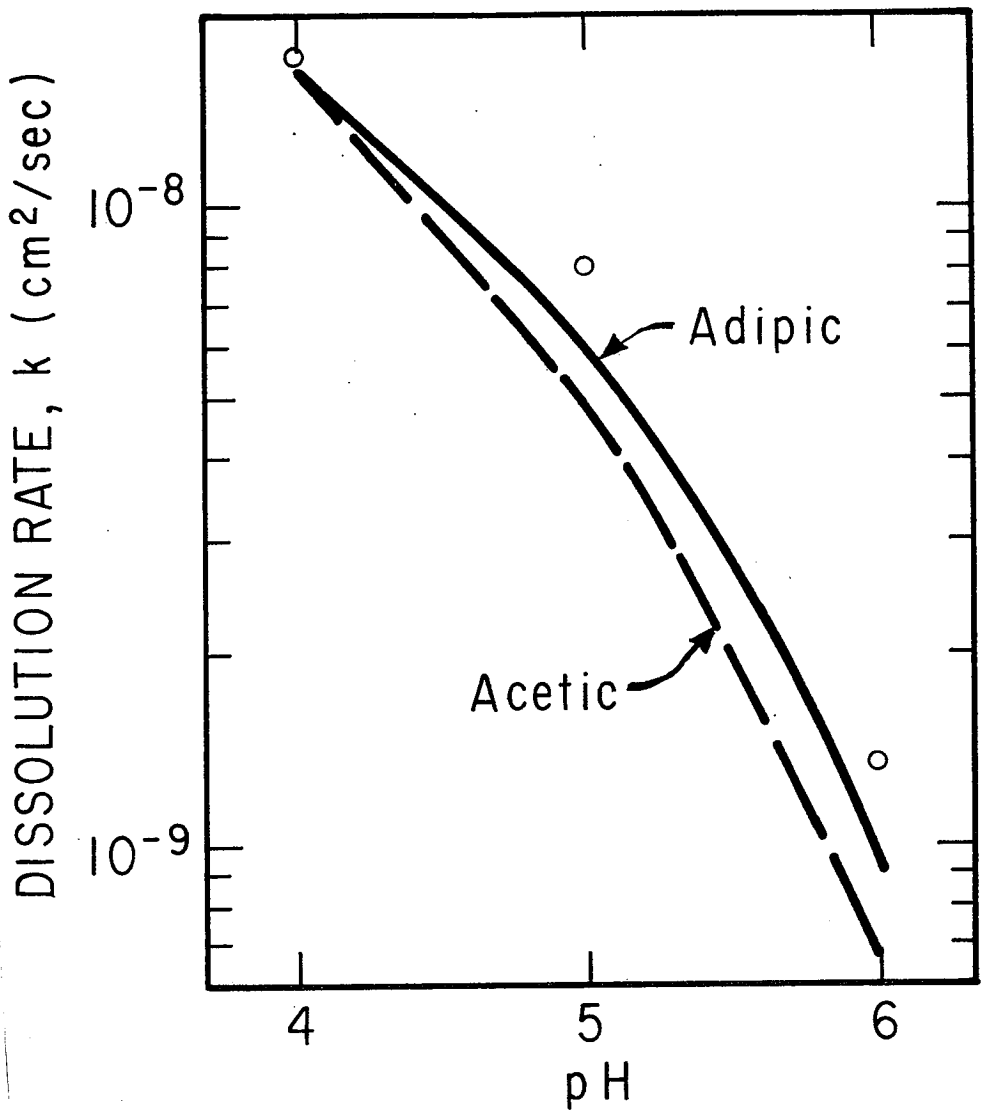

Figure 5-5. Dissolution Rate of $CaCO_3$ in 0.1 M $CaCl_2$ with N_2 Sparging at 25°C, and 3 mM Adipic Acid.
Curves Calculated by Mass Transfer Model Neglecting CO_2 Reaction

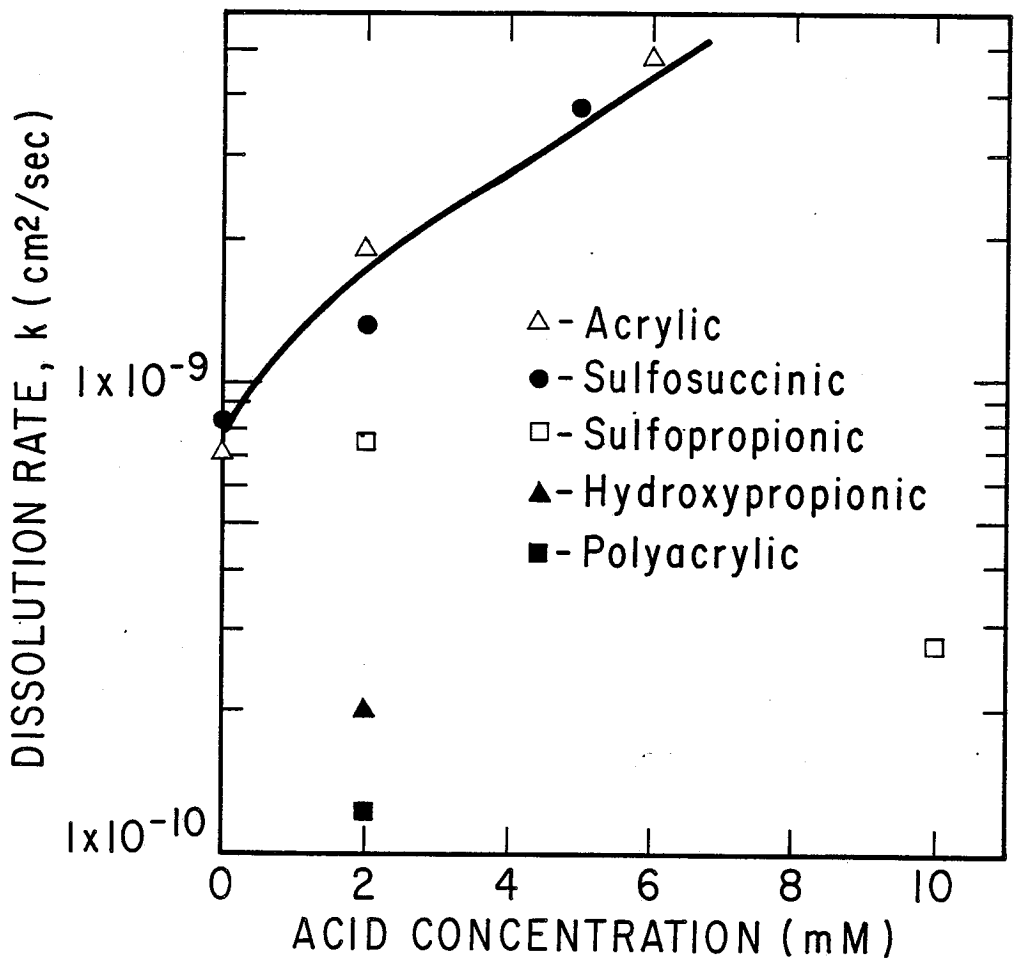

Figure 5-6. Effect of Organic Acids on Dissolution Rate in 0.1 M $CaCl_2$ with N_2 Sparging, 25°C and pH 5.
Curve for Acrylic and Sulfosuccinic Acid Calculated by Mass Transfer Model Neglecting CO_2 Reaction

acrylic acid at ambient temperature. Sulfosuccinic acid was synthesized by reaction of Na_2SO_3 with maleic anhydride at 25°C(Smith,1981).

The calculated rates for acrylic and sulfosuccinic acids happened to be about equal and agreed well with the measured data except at 2 mM sulfosuccinic acid. The diffusivity of acetic acid was used for acrylic acid. Polyacrylic acid(2 meq/liter) inhibited the dissolution rate probably by adsorption on the $CaCO_3$. Both sulfopropionic and hydroxypropionic acids also inhibited the rate, probably due to the presence of polyacrylic acid formed by the synthesis processes.

EFFECTS OF SULFITE/BISULFITE

The effects of sulfite/bisulfite on $CaCO_3$ dissolution were measured from pH 4.5 to 6.0 at 25°C. Rate data at pH 5 and 55°C were also measured. The experimental and calculated results are shown in Figure 5-7.

From the experimental data in Figure 5-7, one can see that sulfite enhances at low concentration but inhibits at high concentration. The inhibition starts at about 10 mM at pH 4.5 and at about 1 mM at pH 6.0. These concentrations correspond to those of calcium sulfite solubility at pH 4.5 and pH 6.0 respectively. The inhibition phenomenon suggests some sort of reversible blinding

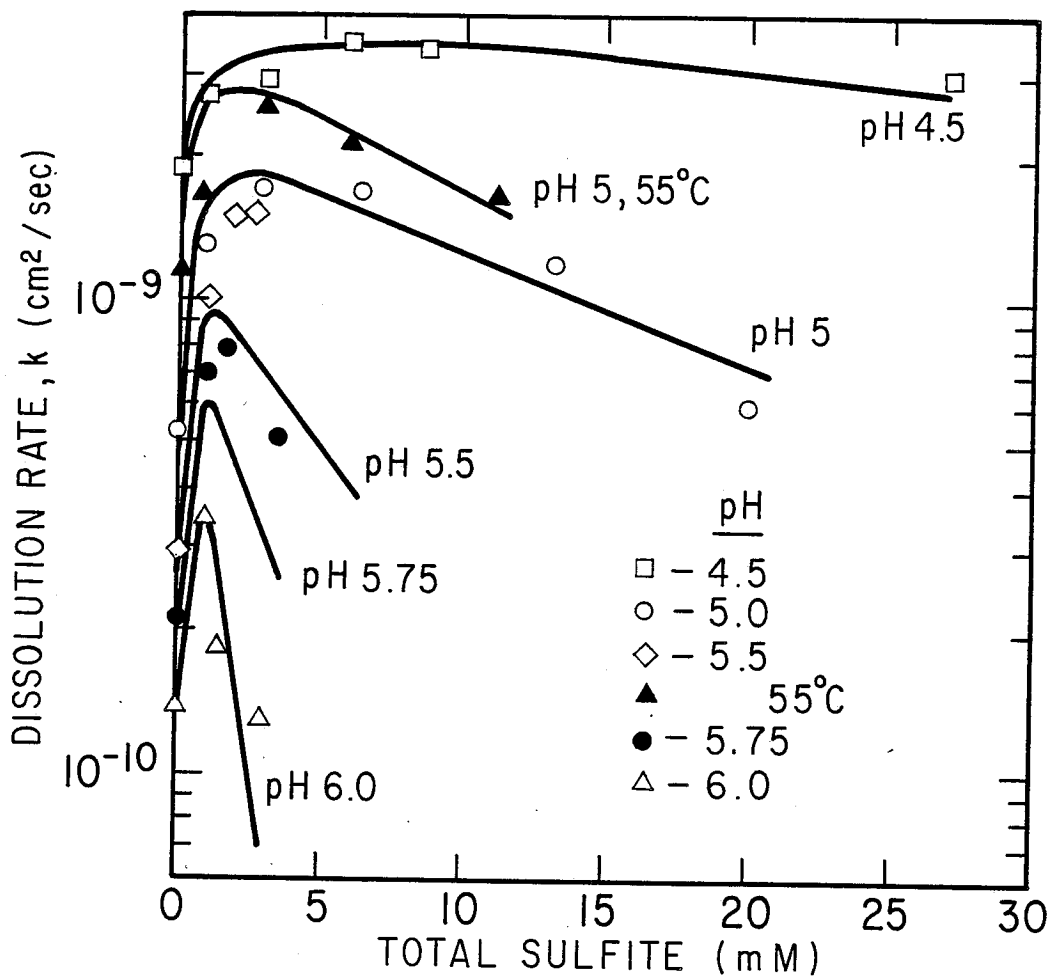

Figure 5-7. Effect of Sulfite, N_2 Sparging, 25° and 55°C. Curves Calculated from Mass Transfer Model Neglecting CO_2 Reaction and Including $CaCO_3^\circ$ /$CaSO_3^\circ$ Solid Solution

of the $CaCO_3$ surface by $CaSO_3$ adsorption or crystallization. Thus the present mass transfer model had to be modified to take into account the inhibition effect.

Figure 5-8 gives the combined effects of acetate and sulfite buffers on the rate of dissolution. The rates are enhanced from 0 to about 1.5 mM acetate with 3 mM sulfite but inhibited at higher acetate concentration.

The enhancing and inhibiting effect of sulfite in 0.1 M $CaCl_2$ solution can be modeled as a shift in equilibrium at the calcite surface. Thus the equilibrium $CaCO_3^\circ$ concentration is reduced by increased $CaSO_3^\circ$ concentration, much like a solid solution at the $CaCO_3$ surface. Using the simplified mass transfer model which neglects the CO_2/HCO_3^- reaction, the solution composition at the $CaCO_3$ surface was calculated from the experimental rate data.

Figure 5-9 shows a correlation of the surface concentration of $CaCO_3^\circ$ and $CaSO_3^\circ$ given by:

$$\log [CaCO_3^\circ] = -10.76 - 1.29 \log [CaSO_3^\circ]$$

Thus $CaSO_3^\circ$ concentration quantitatively reduces the equilibrium solubility of $CaCO_3^\circ$, probably by forming a solid solution at the calcite surface. For $[CaSO_3^\circ]$ less than 0.05 mM, $[CaCO_3^\circ]$ at the surface is equal to its normal equilibrium value, 6.80×10^{-7} M. The calculated rate is obtained by successive trial and error with β until the above solid solution equilibrium is satisfied.

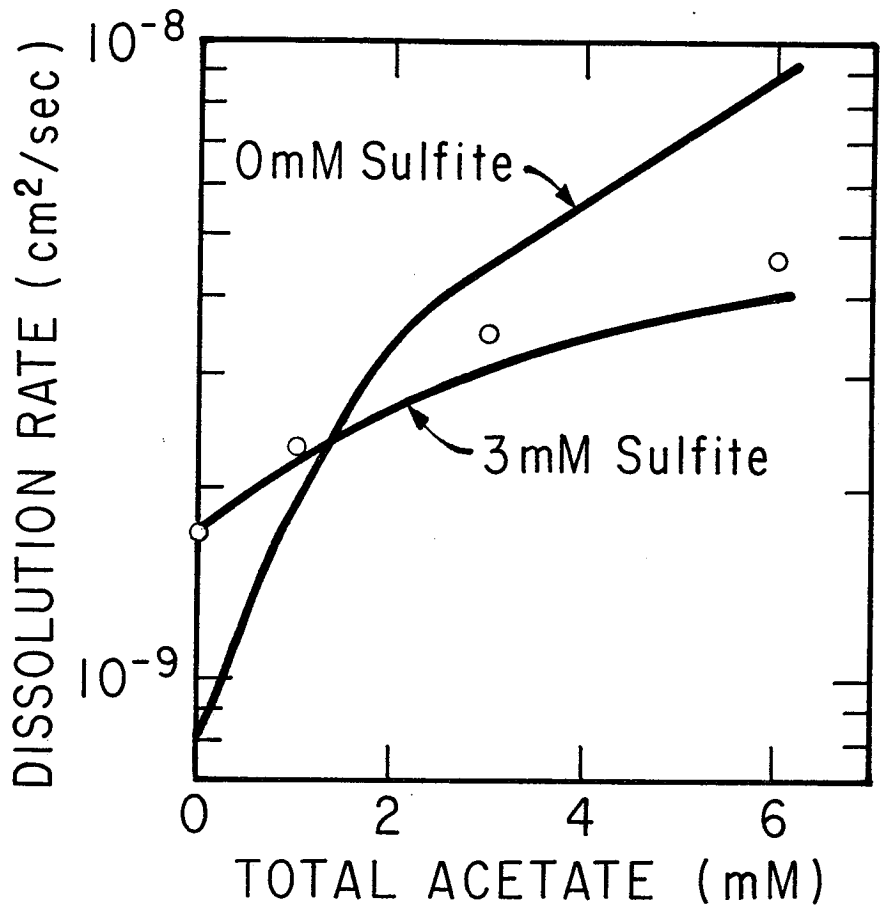

Figure 5-8. Effect of Acetate on Dissolution Rate with 3 mM of Total Sulfite, pH 5 and 25 °C.
Curves Calculated by Mass Transfer Model

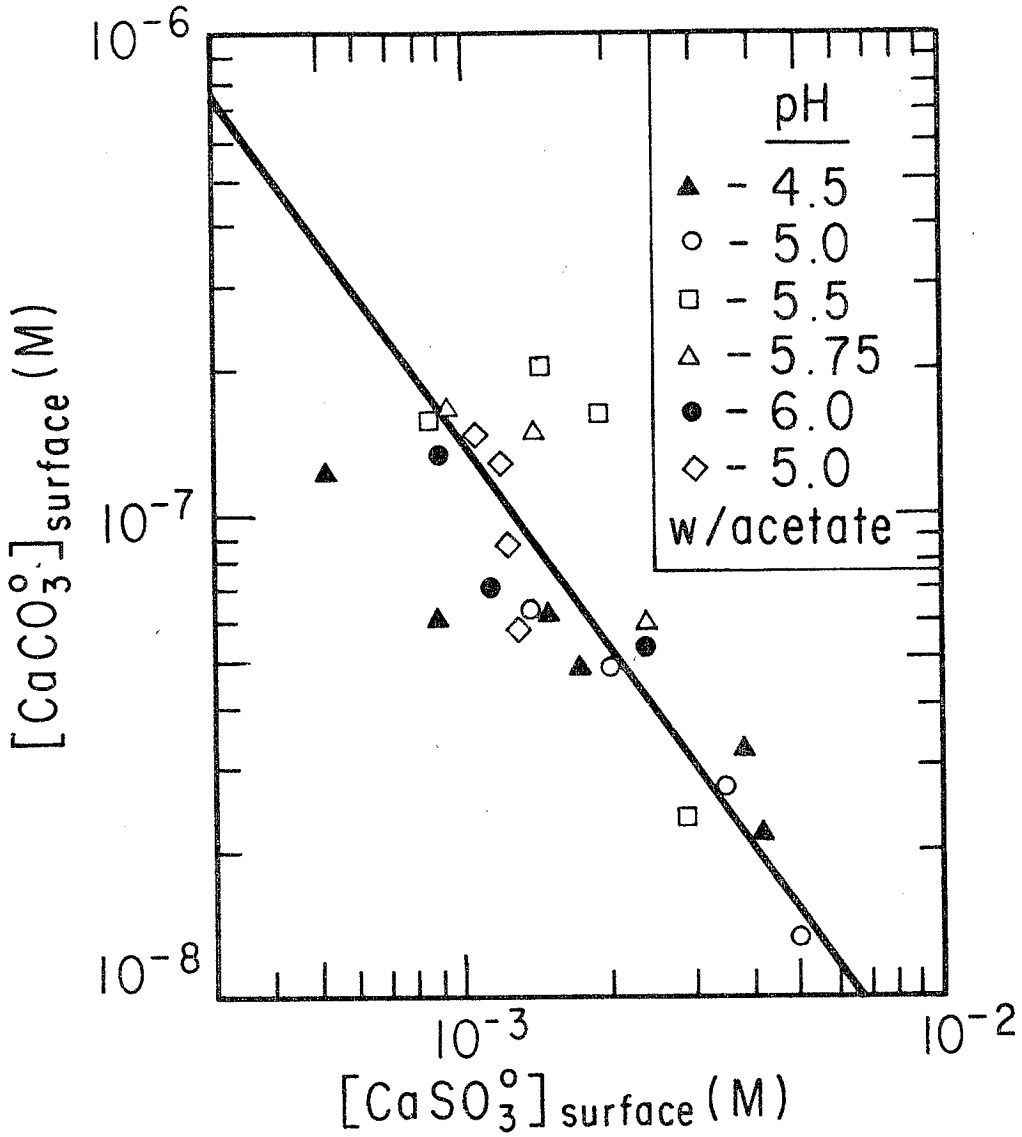

Figure 5-9. Calculated Solution Composition at $CaCO_3$ Surface, N_2 Sparging and 25°C

As shown in Figure 5-7, the modified mass transfer model predicts the measured rate well at pH 4.5, 5.0, and 6.0 but deviates significantly at pH 5.5 and 5.75. These deviations may result from the sensitivity of the calculated rates to the estimated equilibrium constants and diffusivities used in the model. The maximum dissolution rates at each pH correspond roughly to the $CaSO_3$ solubility, shifting to higher sulfite concentrations at lower pH. A higher dissolution rate was observed at 55°C, but the rates are still modeled well by mass transfer with the same $CaSO_3^\circ/CaCO_3^\circ$ equilibrium.

DISCUSSION

Several previous investigators(Plummer et al., 1978; Berner and Morse, 1974; Barton and Vatanatham, 1976; Sjoberg, 1976; Erga and Terjesen, 1956; and Ottmers et al., 1974) showed that $CaCO_3$ dissolution is controlled by H^+ diffusion at low pH. However, Plummer et al., (1978) and Berner and Morse(1974) found it necessary to model in terms of surface kinetics at moderate and high pH.

By using a more comprehensive mass transfer model than previous investigators, we have shown that the dissolution rate is modeled by mass transfer even at high pH. Berner neglected the effects of OH^- and the CO_2 reaction.

Our model has taken into account the effects of CO_2, OH^-, $CaOH^+$, and buffer additives. The general mass transfer model shows that at low pH, the diffusion of H^+ is the controlling mechanism for dissolution. At high pH, however, the contribution of OH^- dominates, especially at high temperature.

Present experimental work on limestone dissolution also goes beyond that of the previous investigators. The enhancement effect of buffer additives on $CaCO_3$ dissolution was observed as predicted by mass transfer. The buffer additives increase dissolution rate by providing acidity to the limestone surface. The inhibition of sulfite is analogous to inhibition by phosphate(Berner and Morse, 1974) and metal ions(Terjesen et al., 1961; Koss and Moller, 1974). Our results show that sulfite inhibits by surface adsorption, an equilibrium process, and not by an effect on surface kinetics. We also provide better particle size distribution data from Coulter counter than those determined optically(Berner and Morse, 1974) and by wet sieving(Plummer et al.,1978).

Finally, the effect of temperature can also be modeled by mass transfer as shown in this work. The temperature dependence shows an apparent ΔH of 4.4 kcal/gmol from pH 4.0 to 5.5. However at pH 6.0 to 6.5, an apparent ΔH of 7.1 kcal/gmol is observed. Berner and Morse did not report the effect of temperature on the rate of $CaCO_3$

dissolution. Plummer et al., however, reported high activation energy at pH close to equilibrium and proposed a surface kineticsmechanism. Our model enables the dissolution of calcite to be calculated even at high pH.

CONCLUSIONS AND RECOMMENDATIONS

1. Limestone dissolution in throwaway scrubbing can be modeled by mass transfer. For particles less than 10-20 μm, the mass transfer coefficient can be obtained by assuming a sphere in an infinite stagnant medium.

2. Organic buffer additives such as acetic, adipic, acrylic, and sulfosuccinic acid enhance the rate of calcite dissolution by buffering the solution pH and providing for mass transfer of acidity to the limestone surface.

3. At pH 4.5 to 5.5, P_{CO_2} of 1 atm increases the rate of dissolution by 15% because of the indirect reaction of CO_2 with $CaCO_3$. However, at low pH(4.0), the effect of P_{CO_2} is insignificant. High P_{CO_2} is also a dominant factor in determing the equilibrium pH at which dissolution stops.

4. The rate of dissolution is enhanced at low sulfite concentration and inhibited at high sulfite concentration. These phenomena are modeled by mass transfer with

a solid solution equilibrium of $CaSO_3^\circ$ and $CaCO_3^\circ$.

5. The dissolution of calcite is a function of the solution composition and particle size distribution. The rate should be independent of surface roughness, surface area,and shape.

6. The effects of temperature are predicted by the mass transfer model with appropriate physical constants. High temperature dependence at high pH results from the effect of temperature on OH^- equilibrium.

7. More experimental data are needed to establish the validity of the mass transfer model near equilibrium pH.

APPENDIX A

MASS TRANSFER FOR A SHERE IN AN INFINITE STAGNANT MEDIUM

The equation of continuity for mass transfer in spherical coordinates(Bird, Stewart, and Lightfoot, 1960) gives

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) = 0 \qquad \text{A-1}$$

where c is the concentration and r is the radius of particle.

Integrating equation A-1 gives

$$c = \frac{-A_1}{r} + A_2 \qquad \text{A-2}$$

where A_1 and A_2 are constants of integration.

For the dissolution of a sphere in a stagnant medium, the following B.C. apply:

$$\text{at } r = r_o \text{ ,} \qquad c = c_i$$

$$\text{and at } r = \infty \text{ ,} \qquad c = c_\infty$$

where r_o is the radius of the sphere, c_i is the surface concentration, and c_∞ is the bulk concentration.

Solving for A_1 and A_2 in equation A-2, one gets

$$c = \frac{-(c_i - c_\infty) r_o}{r} + c_\infty \qquad \text{A-3}$$

From Fick's first law

$$N = -D \left(\frac{\partial c}{\partial r}\right)_{r=r_o} \qquad \text{A-4}$$

where N is the flux at $r=r_o$ and D is the diffusivity.

Differentiating equation A-3 with respect to r and substituting in equation A-4 gives

$$N = \frac{D(c_i - c_\infty)}{r_o} \qquad \text{A-5}$$

Rearranging equation A-5 gives

$$\frac{N r_o}{D(c_i - c_\infty)} = 1 \qquad \text{A-6}$$

since $N = k_c(c_i - c_\infty)$ A-7

where k_c is the mass transfer coefficient.

Equation A-6 becomes

$$\frac{2Nr_o}{D(c_i - c_\infty)} = \frac{2k_c r_o}{D} = \frac{k_c d_p}{D} = 2 \qquad \text{A-8}$$

where d_p is the diameter of the sphere.

Thus for spheres dissolving in a stagnant medium the Sherwood number $(k_c d_p/D)$ is 2. This condition represents the asymptotic limit of small particles in an agitated vessel.

APPENDIX B

TABULATED DATA

Table B-1 Calculated Effects of Particle Diameter, 25°C at pH 5.0 $[Ca^{++}] = 0.01M$, $P_{CO_2} = 1$ atm, (Figure 3-1)

D_p (μm)	Dissolution Rate x 10^9 (gmol/cm^2-sec)
0.1	232.00
1.0	23.60
9.0	3.61
10.0	2.90
20.0	2.13

pH	$DCO_3^{=}$ $CO_3^{=}$ + $DCaCO_3^{\circ}$ $\Delta CaCO_3^{\circ}$	$-DH^+$ ΔH^+	$-DCO_2$ ΔCO_2	$-\beta$
	(M cm^2/sec)	(M cm^2/sec)	(M cm^2/sec)	(M cm^2/sec)
6.00	6.934×10^{-11}	6.429×10^{-11}	1.30×10^{-10}	2.636×10^{-10}
5.75	9.923×10^{-11}	1.639×10^{-10}	2.26×10^{-10}	4.890×10^{-10}
5.50	1.085×10^{-10}	3.194×10^{-10}	2.94×10^{-10}	7.221×10^{-10}
5.25	1.114×10^{-10}	5.839×10^{-10}	3.62×10^{-10}	1.058×10^{-9}
5.00	1.118×10^{-10}	1.047×10^{-9}	4.40×10^{-10}	1.598×10^{-9}
4.75	1.114×10^{-10}	1.867×10^{-9}	4.96×10^{-10}	2.476×10^{-9}
4.50	1.099×10^{-10}	3.324×10^{-9}	4.48×10^{-10}	3.881×10^{-9}
4.00	1.061×10^{-9}	1.052×10^{-8}	-7.06×10^{-10}	9.914×10^{-9}

Table B-2 Contribution to Dissolution by Individual Chemical Species (Figure 3-2)

Table B-3 Calculated effect of P_{CO_2}, 25 °C,
$[Ca^{++}]$ = 0.01 M, D_p = 8.856 μm
(Figure 3-3)

pH	Dissolution Rate x 10^{10} (gmol/cm^2sec)		
	P_{CO_2} = 1 atm	P_{CO_2} = 0.3 atm	P_{CO_2} = 0.1 atm
7.205	------	------	equil.
7.00	------	------	1.95
6.50	------	------	3.72
6.467	------	equil.	------
6.205	equil.	------	------
6.20	------	4.68	------
6.00	5.95	------	5.37
5.75	11.04	9.74	7.151
5.50	16.31	------	10.33
5.25	23.89	20.20	15.97
5.00	36.09	30.94	------
4.75	55.91	48.72	------
4.5	87.65	------	------
4.0	223.9	214.1	209.5

Table B-4 Values of kt/kt_{50} versus Percent Remaining Calculated by Simplified Mass Transfer Model (Figure 3-4)

kt/kt_{50}	Per Cent Remaining
.02283	99.04342
.04566	97.69510
.06849	96.35510
.09132	95.02351
.11416	93.70039
.13699	92.38583
.15982	91.07992
.18265	89.78275
.20548	88.49440
.22831	87.21498
.45662	74.94130
.68493	63.70998
.91324	53.64720
1.14155	44.69400
1.36986	37.07484
1.59817	30.28641
1.82648	24.58535
2.05479	20.26973
2.28311	16.36684
4.56621	1.44915
6.84932	.29189
9.13242	.11332
11.41553	.04919
13.69863	.02679
15.98174	.01034
18.26484	.00040
20.54795	0.00000
22.83105	0.00000

kt_{50}	Per Cent Remaining
43.80000	50.09767

Table B-5 Data from pH-Stat Experiments at 25°C in 0.1 M $CaCl_2$ Sparged with N_2 (Figure 5-1)

Reagent Grade 100% available $CaCO_3$

Run 1a pH 5 t_{50} = 11.27 min		Run 2a pH 4 t_{50} = 1.5 min	
Time (min)	Fraction $CaCO_3$ Remaining	Time (min)	Fraction $CaCO_3$ Remaining
0.13	0.985	0.50	0.78
0.80	0.900	1.30	0.538
3.20	0.825	2.10	0.344
4.80	0.755	3.70	0.136
6.40	0.688	4.50	0.095
8.00	0.624	5.30	0.072
9.60	0.562	6.10	0.064
11.27	0.500	6.90	0.056
12.80	0.450	7.70	0.055
14.4	0.390	9.70	0.045
16.00	0.340	11.30	0.036
17.60	0.294	14.50	0.030
20.00	0.240	18.10	0.022
23.20	0.180		
26.40	0.134		
30.40	0.094		
34.40	0.070		
37.60	0.060		
40.80	0.050		
44.00	0.040		
48.00	0.034		
52.80	0.028		
66.40	0.013		
74.40	0.010		

Table B-6 Integrated Mass Transfer Model data for Monodisperse Particle Size Distribution (Figure 5-1)

Fraction Remaining(F)	Dimensionless time(t/t_{50})
0.978	0.04
0.967	0.06
0.956	0.08
0.945	0.10
0.891	0.20
0.838	0.30
0.786	0.40
0.736	0.50
0.686	0.60
0.590	0.80
0.500	1.00
0.415	1.20
0.335	1.40
0.261	1.60
0.193	1.80
0.133	2.00
0.080	2.20
0.037	2.40
0.007	2.60

Table B-7 Calculated versus Measured Rate Constant for Reagent Grade Calcite at 25 °C and 55 °C with CO_2 Sparging (Figure 5-2)

Temperature(°C)	pH	$k(cm^2/sec) \times 10^9$	
		Calculated	Measured
25	4.0	5.8	5.8
25	4.5	2.3	2.6
25	5.0	0.86	0.87
25	5.2	0.53	0.65
55	4.0	9.8	9.3
55	4.5	3.9	4.9
55	5.0	1.4	1.6

Table B-8 Calculated versus Measured Rate Constant for Reagent Grade Calcite at 25° and 55°C with N_2 Sparging (Figure 5-3)

Temperature(°C)	pH	$k(cm^2/sec) \times 10^{10}$	
		Calculated	Measured
25	4.5	17.3	19.3
25	5.0	6.8	8.1
25	5.5	2.7	3.3
25	6.0	1.3	1.5
25	6.1	1.2	0.99
25	6.2	1.0	0.80
25	6.5	0.69	0.67
25	7.0	0.22	0.37
55	4.5	34.0	28.0
55	5.0	12.0	11.0
55	5.5	5.2	5.4
55	6.0	3.4	2.8
55	6.5	2.0	1.7
55	7.0	0.45	0.53

Table B-9 Dissolution of Reagent $CaCO_3$ at 25°C, 0.1 M $CaCl_2$, 5mM $CaCO_3$, and various Acetate Concentration (Figure 5-4)

pH	Total Acetate concentration (mM)	k(cm^2/sec) x 10^9 Calculated	Measured
N_2 sparge			
4	1	8.8	10.5
4	3	16.4	17.4 15.0
4	10	41.6	--
5	1	2.1	2.6
5	3	4.9	5.2 6.4
5	10	14.4	13.1
6	1	0.30	0.40
6	3	0.64	0.90
6	10	1.81	2.3 2.0
CO_2 sparge			
5	1	2.6	2.3
5	3	4.5	4.6
5	10	15.4	15.7
5.5	1	0.26	0.63
5.5	3	0.80	1.4
5.5	10	1.30	3.6

Table B-10 Calculated and Measured Rate $k(cm^2/sec)$ for 3 mM Total Adipate at Low P_{CO_2} and 25°C (Figure 5-5)

pH	$k(cm^2/sec) \times 10^9$	
	Calculated	Measured
4	16.7	17.4
5	6.2	8.1
6	0.89	1.3

Table B-11 Measured and Calculated Rate $k(cm^2/sec)$ for Reagent Grade $CaCO_3$ with Organic Acid Additives, pH 5, 25 °C, N_2 Sparging and 0.1 M $CaCl_2$ (Figure 5-6)

Organic Acid	Concentration (mM)	$k(cm^2/sec) \times 10^9$	
		Measured	Calculated
Acrylic Acid	0	0.69	0.77
	2	1.9	1.7
	6	4.8	4.4
Sulfosuccinic Acid	0	0.82	0.77
	2	1.3	1.7
	5	3.8	3.4

Table B-12 Experimental Rate of Dissolution k(cm^2/sec) of Reagent Grade $CaCO_3$ with Organic Acid Additives, pH 5, 25°C, N_2 Sparging, 0.1 M $CaCl_2$ (Figure 5-6)

Organic Acid	Concentration (mM)	Measured k x 10^9 (cm^2/sec)
Sulfopropionic	0	0.69
	2	0.72
	10	0.27
Hydroxypropionic	2	0.20
Polyacrylic	2(meq)	0.12

Table B-13 Reagent Grade $CaCO_3$ Dissolution in the Presence of Dissolved Sulfite (Figure 5-7)

N_2 sparging, 25 °C

pH	Total Sulfite Concentration(mM)	k(cm^2/sec) x 10^9 Measured	Calculated
4.5	0	1.9	1.9
4.5	0.9	2.7	2.9
4.5	3.0	2.9	3.3
4.5	5.8	3.5	3.4
4.5	8.7	3.4	3.4
4.5	27.0	3.5	2.8
4.5	38.0	2.8	2.4
5.0	0	0.53	0.46
5.0	0.9	1.3	1.7
5.0	3.2	1.7	1.8
5.0	6.3	1.7	1.6
5.0	13.2	1.2	1.1
5.0	20.0	0.60	0.73
5.5	0	0.29	0.26
5.5	1.0	1.0	0.93
5.5	1.8	1.5	0.86
5.5	2.6	1.5	0.75
5.5	5.8	0.33	0.40
5.75	0	0.14	0.18
5.75	1.0	0.35	0.61
5.75	1.7	0.18	0.51
5.75	3.5	0.13	0.27
6.0	0	0.14	0.13
6.0	1.0	0.35	0.34
6.0	1.4	0.18	0.27
6.0	3.1	0.13	0.07

N_2 sparging, 55°C

5.0	0	1.2	1.3
5.0	0.7	1.7	2.6
5.0	2.8	2.6	2.7
5.0	5.8	2.7	2.3
5.0	11.1	1.7	1.6

Table B-14 Effects of Total Acetate and Sulfite on Rate of Dissolution at 25 °C (Figure 5-8)

N_2 sparging 3.0 mM Total Sulfite

pH	Total Acetate Concentration(mM)	k(cm^2/sec) x 10^9 Measured	Calculated
5.0	0	1.7	1.7
5.0	1	2.3	2.2
5.0	3	3.5	3.1
5.0	6	4.6	3.9

APPENDIX C

THE FISHER TITRIMETER II TITRATION SYSTEM

The Fisher Titrimeter II Titration System consists of a burette/dispenser, an electrometer, and a titrate demand module. A linear two pen recorder is used to record the signals from the electrometer and burette/dispenser. The burette/dispenser is a 50 ml clear glass syringe which enables acid titrant to be added to the reactor at a continuous rate. The burette/dispenser refills after 50 ml is used.

The Fisher Electrometer Model 380 has controls for temperature 0/slope o, standardize 0/zero o, zero adjustment and mv/pH function. Four precision-calibrated scales are provided on the meter face for normal 0-14 pH measurements in the normal operating mode. The ± 5, ± 3.5, and $\pm$ 1 scales are employed for pH measurements in the expanded operating mode, and measure the pH deviation (± 5, ± 3.5, and ± 1 pH units full-scale, respectively) of a sample from a preset reference value.

The Fisher Titrate Demand Model 381 acts as a remote automatic proportional or on/off controller for the automatic dispenser system. Two end point settings which enable targets between zero and 19.99 be set to the closest 0.01 pH unit. The second endpoint setting is used only when dual-endpoint analysis are desired. A proportioning band control is used to set the endpoint deviation at

which proportioning will ensue. The rate of slow-down is always proportioning to the proximity of the endpoint target. The minimum delivery control places a lower limit on the extent to which the titrant delivery rate may be reduced by proportioning, and thus acts to enhance titration speed. The minimum delivery rate is maintained through approximately the final 5% of the proportioning band. When using the automatic demand module, the pH electrode act as a sensor for the titrate demand module. Acid titrant will be delivery if the pH is higher that the preset target endpoint. Acid delivery will be stopped once the target pH is reached. Signals from the burette/ dispenser and the electrometer are sent to a two pen recorder where the pH and acid titrant volume are recorded versus time.

APPENDIX D

NOMENCLATURE

A,B - constants defined by equation 3.21 and 3.22

a - activity, M

a_j, b_j - characteristic parameters for each ion species for estimation of activity coefficient

$\Delta[\ ]$ - concentration difference between the limestone surface and the bulk solution, M

D - diffusivity, cm^2/sec

D_o - dielectric constant of water

d - particle diameter, cm

Fa - Faraday Number, 23,062 cal/volt-equiv

f - fraction remaining of a given size fraction

F - total fraction remaining

ΔH - apparent heat of reaction, kcal/mol

I - ionic strength, M

k - dissolution rate constant, cm^2/sec

k_c - mass transfer coefficient, cm/sec

M - molar, gmol/liter

n_j - charge on the jth ion

P_{CO_2} - partial pressure of CO_2, bar

pH - negative logarithm of hydrogen ion activity

ΔpH - pH at equilibrium minus solution pH

R - universal gas constant, 0.08205 liter-atm/gmol-K

R_o - diameter of sphere, cm

r - distance from center of sphere, cm

T - temperature, K

t - time, sec

t_{50} - time for 50% of $CaCO_3$ remaining, sec

t_{56} - time for 50% of $CaCO_3$ remaining, sec

U - activity coefficient for uncharged species

V - volume of particle, cm^3

x - dimensionless distance $(1-R_o/r)$

Z_j - charge on the jth ion

β - rate of dissolution per unit radius, M cm^2 sec^{-1}

α_i, β_i - constants of integration, M cm^2 sec^{-1}

γ - activity coefficient

λ_o - equivalent ionic conductivity at infinite dilution $cm^2/gmol/ohm$

η - viscosity, poise

ϕ_i - the fraction of total particle mass with diameter from d_i to d_{i+1}

[ ] - concentration, M

SUPERSCRIPT

o - ion pair, degrees

SUBSCRIPTS

b - bulk

cal - calculated

exp - experimented

s - surface

(s) - solid

APPENDIX E

FORTRAN PROGRAM LISTINGS

PROGRAM I

MASS TRANSFER MODEL WITH CO_2 FINITE RATE REACTION

Program I calculates the rate of $CaCO_3$ dissolution with the reversible finite rate CO_2 differential equation and chemical equilibria relations given in Chapter III. The bulk solution compositions are calculated by specifying the solution pH, P_{co_2}, Ca^{++} concentration and particle diameter. By specifying a given range for β (the dissolution flux) and the $[CaCO_3^\circ]_s$, the CO_2 differential equation is solved numerically by a 4th-order Runge Kutta Method. Due to the nonlinearity of the equation, a trial and error on $[H^+]$ is made on each step size. The calculation stops when the $[CO_2]_{bulk}$ converges to the specified value.

Input Data

Diffusivities, equilibrium and rate constants, P_{co_2}, pH, particle diameter, $[CaCO_3^\circ]_{surface}$, and a guessed range for β.

Output Data

Echo prints input, β, rate of dissolution, and concentration profile of each chemical species versus the dimensionless distance, x.

```
      PROGRAM LIMSDIS(TTY,INPUT=TTY,OUTPUT)

C*************************************************************************
C*****THIS PROGRAM CALCULATE THE RATE OF LIMESTONE DISSOLUTION BY*******
C*****     A MASS TRANSFER MODEL USING SPHERICAL GEOMETRY***************
C*************************************************************************
      DIMENSION APH(10),APCO2(10)
      DIMENSION ACTP(10),BCTP(10),ZI(10),GAMMA(15)
      DIMENSION ACO2(120)
      DIMENSION CCO3(120),CCACO3(120),CCO2(120),CCA(120),CH(120)
      DIMENSION CHCO3(120),DX(120)
      DIMENSION COH(120),CSO3(120),CHSO3(120),CAA(120),CH2A(120)
      DIMENSION CHA(120)
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/RAD/RO,BETA
      COMMON/EPS/EPS1,EPS2
      COMMON/END/YO,YF
      COMMON/DKRATE/KA,KB,KC
      COMMON/COUNT/NJ
      COMMON/INDEX/NK
      COMMON/END2/YO1,YF1
      COMMON/SURF/CCO3,CCACO3,CCO2,CCA,CH,CHCO3,DX
      COMMON/SURF2/COH,CSO3,CHSO3,CAA,CH2A,CHA
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/BULK2/SO3B,HSO3B,OHB,AB,H2AB,HAB
      COMMON/ADD/KD
      REAL K1,K2,K3,KW,KF,KA1,KA2,KHSO3
      REAL KD,KS

C***************DIFFUSIVITIES IN CM2/SEC*********************************
C***************CACO3S SURFACE CONCENTRATION OF ION PAIR AT***************
C******************SOLID LIQUID INTERPHASE*********************************

      DATA DCO2,DHCO3,DCO3,DCA/2.0E-5,1.2E-5,7.0E-6,7.9E-6/
      DATA DH,DCACO3,CACO3S/9.3E-5,7.5E-6,6.204E-6/
      DATA DSO3,DHSO3,DOH,DA/7.E-6,1.19E-5,5.27E-5,7.05E-6/
      DATA DH2A,DHA/1.19E-5,1.09E-5/
      DATA KA1,KA2,KW,KHSO3/3.548E-5,0.0,1.0E-14,6.24E-8/
      DATA EPS1,EPS2/1.0E-6,1.0E-25/

C*********************ERROR CRITERIA FOR CONVERGENCE**********************
C********************     EPS1        EPS2         **********************


C******************ACTP,BCTP ACTIVITIES COEFFICIENT PARAMETERS***********
C******************FOR MODIFIED DEBYE-HUCKEL EQUATION*******************

      DATA(ACTP   (I),I=1,9)/6.0,4.5,4.5,4.5,4.5,4.5,3.,3.,3./
      DATA(BCTP   (I),I=1,9)/0.4,0.1,0.0,0.,0.,0.,0.3,0.3,0.3/

C*********HK       HENRY'S CONSTANT FOR CO2 IN WATER**********************
C********UI       EMPIRICAL CONSTANT FOR UNCHARGED SPECIES IN ***********
C********                    DEBYE-HUCKEL EQUATION             **********
C*********CI       IONIC STRENGTH OF SOLUTION      **********************
C*********ACONS,B TEMPERATURE CONSTANTS IN THE MODIFIED*******************
C*****************************DEBYE-HUCKEL EQUATION**********************
C**********ZI              IONIC VALENCIES          **********************
```

```
      DATA HK,UI,CI,ACONS,B/0.0305,0.076,0.3,0.512,0.312/
      DATA (ZI(I),I=1,9)/1.,2.,1.,2.,2.,1.,1.,2.,1./
      DATA K1,K2,K3,KF/1.34E7,4.45E-7,6.3E-4,2.6E-2/
      DATA KD/4.69E-11/
      DATA KS/4.0E-4/

C*****************************INPUT DATA*********************************
C******AT           TOTAL BUFFER CONCENTRATION(GMOLES/LITER)       ******
C******SO3T         TOTAL SULFITE CONCENTRATION(GMOLES/LITER)      ******
C******BETA1,BETA2 TRIAL INTERVALS FOR THE DISSOLUTION FLUX       ******
C******            (GMOLES-CM2/LITER-SEC)                         ******
C******NI           NUMBER OF PH AND PCO2 DATA PAIR                ******
C******APCO2,APH    PH & PARTIAL PRESSURE OF CO2(ATM)              ******
C******RO           PARTICLE DIAMETER(MICRO-METER)                 ******
C******CA           CALCIUM CONCENTRATION OF BULK SOLUTION         ******
C******                (GMOLES/LITER)                             ******
C*************************************************************************

      READ,AT,SO3T
      READ,BETA1,BETA2
      READ,   NI
      READ   ,CA,RO
      DO 2 K=1,NI
      READ   ,APCO2(K),APH(K)
  2   CONTINUE
      DO 21 I=1,9
      WA=ACONS*ZI(I)*ZI(I)
      WC=SQRT(CI)
      WB=1.+B*ACTP(I)*WC

C*************************************************************************
C*******ACTIVITY COEFFICIENTS**************COMPONENTS*****************
C            GAMMA(1)                                  H+
C            GAMMA(2)                                  CA++
C            GAMMA(3)                                  HCO3-
C            GAMMA(4)                                  CO3--
C            GAMMA(5)                                  SO3--
C            GAMMA(6)                                  HSO3-
C            GAMMA(7)                                  OH-
C            GAMMA(8)                                  A--
C            GAMMA(9)                                  HA-
C            GAMMA(10)                                 CO2
C            GAMMA(11)                                 H2A
C            GAMMA(12)                                 CACO3(ION PAIR)

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

  21  GAMMA(I)=10.**(WA*(-WC/WB+CI*BCTP(I)))
      DO 22 I=10,12
  22  GAMMA(I)=10.**(UI*CI)
      DO 3 J=1,NI
      PH=APH(J)
      PCO2=APCO2(J)
      AH=10.**(-PH)
      H=AH/GAMMA(1)
      CO2=HK*PCO2
      HB=H
      CO2B=CO2
      AACO2=CO2*GAMMA(10)
      AHCO3=K2*AACO2/AH
      HCO3=AHCO3/GAMMA(3)
      HCO3B=HCO3
      ACO3=KD*AHCO3/AH
      CO3=ACO3/GAMMA(4)
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```
      CO3B=CO3
      ACA=CA*GAMMA(2)
      CAB=CA
      ACACO3=ACA*ACO3/K3
      CACO3=ACACO3/GAMMA(12)
      CACO3B=CACO3
      SKF=KF
      SK1=K1
      SK2=K2
      SK3=K3
      SKA1=KA1
      SKD=KD
      SKA2=KA2
      SKHSO3=KHSO3
      BETA1S=BETA1
      BETA2S=BETA2

C*********REDEFINE EQUILIBRIUM AND RATE CONSTANT IN TERMS OF **********
C************************CONCENTRATIONS*****************************
C*******EQUILIBRIUM CONSTANT**************REACTION*********************
C            K1                  CACO3(ION PAIR) + H+ = CA++ + HCO3-
C            K2                  CO2 + H2O = H+ + HCO3-
C            K3                 CACO3(ION PAIR) = CA++ + CO3--
C            KHSO3              HSO3- = H+ + SO3--
C            KW                 H2O = H+ + OH-
C            KD                 HCO3- = H+ + CO3--
C            KS                 CASO3(ION PAIR) = CA++ + SO3--
C            KA1                H2A = H+ + HA-
C            KA2                HA- = H+ + A--

C********RATE CONSTANT**********************REACTION*******************
C            KF                 CO2 + H2O = H+ + HCO3-

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


      KF=KF*GAMMA(10)
      K1=(K1*GAMMA(1)*GAMMA(12))/(GAMMA(2)*GAMMA(3))
      K2=(K2*GAMMA(10))/(GAMMA(1)*GAMMA(3))
      K3=K3*GAMMA(12)/(GAMMA(2)*GAMMA(4))
      KHSO3=(KHSO3*GAMMA(6))/(GAMMA(5)*GAMMA(1))
      KHSO3=KHSO3*(1.+GAMMA(2)*GAMMA(5)*CA/(GAMMA(12)*KS))
      KW=KW/(GAMMA(1)*GAMMA(7))
      KD=KD*GAMMA(3)/(GAMMA(1)*GAMMA(4))
      OHB=KW/HB
      HAB=AT/(1.+HB/KA1+KA2/HB)
      H2AB=HAB*HB/KA1
      AB=AT-HAB-H2AB
      SO3B=KHSO3*SO3T/(HB+KHSO3)
      HSO3B=SO3T-SO3B
      PRINT 234
234   FORMAT(1H1,6X,*INPUT DATA*,//,6X,*DIFFUSIVITIES(CM2/SEC)*,/)
      PRINT 235
235   FORMAT(10X,*CO2*,11X,*HCO3-*,11X,*CO3--*,11X,*CA++*,13X,*H*,9X,
     1*CACO3(ION PAIR)*,/)
      PRINT 102,DCO2,DHCO3,DCO3,DCA,DH,DCACO3
      PRINT 236
236   FORMAT(10X,*OH-*,11X,*SO3--*,11X,*HSO3-*,11X,*A--*,11X,*H2A*,11X,
     1*HA-*,/)
      PRINT 102,DOH,DSO3,DHSO3,DA,DH2A,DHA
102   FORMAT(3X,6E15.3,/)
      PRINT 237
237   FORMAT(10X,*K1*,14X,*K2*,14X,*K3*,14X,*KF*,/)
      PRINT 103,K1,K2,K3,KF
      PRINT 238
```

```
238  FORMAT(10X,*KA1*,14X,*KA2*,14X,*KW*,/)
     PRINT 103,KA1,KA2,KW
103  FORMAT(3X,4E15.4,/)
     PRINT 251
 251  FORMAT(10X,*PH*,11X,*PCO2(ATM.)*,5X,*PARTICLE DIAMETER(CM)*,/)
     PRINT 105,PH,PCO2,RO
105  FORMAT(3X,3E15.3)
     BETA=BETA1
111  FORMAT(6X,E15.4)
     CALL CONVERG(S)
     PRINT 111,S
     S1=S
     BETA=BETA2
     CALL CONVERG(S)
     PRINT 111,S
     S2=S
     F1=S1-CO2B
     F2=S2-CO2B
     IF(F1*F2.GT.0.) GO TO 50
     FSAVE=F1
     DO 32 JJ=1,30
     TRUEB=BETA2-F2*(BETA2-BETA1)/(F2-F1)
     BETA=TRUEB
     CALL CONVERG(S)
     PRINT 111,S
     FW=S-CO2B
     ERR=ABS((BETA1-BETA2)/BETA1)/2.
     IF(ERR.LE.0.001) GO TO 60
     IF(ABS(FW).LE.1.0E-8) GO TO 60
     IF(FW*F1.LT.0.) GO TO 31
     BETA1=TRUEB
     F1=FW
     IF(FW*FSAVE.GT.0.) F2=F2/2.
     FSAVE=FW
     GO TO 32
 31  BETA2=TRUEB
     F2=FW
     IF(FW*FSAVE.GT.0.) F1=F1/2.
     FSAVE=FW
 32  CONTINUE
     GO TO 60
 50  PRINT 33
 33  FORMAT(1HO,10X,*NO CONVERGENCE*,/)
     GO TO 200
 60  CONTINUE
     PRINT 239
239  FORMAT(//,6X,*OUTPUT DATA*,/,1X,*1ST LINE*,4X,*X*,11X,*CO2*,11X,
    1*HCO3-*,11X,*CO3--*,11X,*CA++*,13X,*H+*,6X,*CACO3(ION PAIR)*)
     PRINT 240
240  FORMAT(/,1X,*2ND LINE*,15X,*OH-*,11X,*SO3--*,11X,*HSO3-*,11X,
    1*A--*,11X,*H2A*,11X,*HA-*,//)
     DO 34 I=1,101,5
     PRINT 35,DX(I),CCO2(I),CHCO3(I),CCO3(I),CCA(I),CH(I),CCACO3(I)
     PRINT 38,COH(I),CSO3(I),CHSO3(I),CAA(I),CH2A(I),CHA(I)
 38  FORMAT(21X,6E15.5)
 35  FORMAT(6X,7E15.5)
 34  CONTINUE
     PRINT 37,TRUEB
 37  FORMAT(3X,E15.4)
     RATED=-TRUEB/(1000.*RO)
     PRINT 36,RATED
 36  FORMAT(3X,*RATE OF DISSOLUTION=*,E15.5,*MOLE/SQ.CM.SEC*,/)
     DCCO2=CCO2(1)-CCO2(101)
     DCHCO3=CHCO3(1)-CHCO3(101)
     DCCA=CCA(1)-CCA(101)
     DCH=CH(1)-CH(101)
```

```
      DCCACO=CCACO3(1)-CCACO3(101)
      DCCO3=CCO3(1)-CCO3(101)
      DCOH=COH(1)-COH(101)
      DCSO3=CSO3(1)-CSO3(101)
      DCHSO3=CHSO3(1)-CHSO3(101)
      DCCAA=CAA(1)-CAA(101)
      DCH2A=CH2A(1)-CH2A(101)
      DCHA=CHA(1)-CHA(101)
      DICO2=DCO2*DCCO2
      DIHCO3=DHCO3*DCHCO3
      DICA=DCA*DCCA
      DIH=DH*DCH
      DICACO=DCCACO*DCACO3
      DICO3=DCO3*DCCO3
      DIOH=DOH*DCOH
      DISO3=DSO3*DCSO3
      DIHSO3=DHSO3*DCHSO3
      DIAA=DCCAA*DA
      DIH2A=DH2A*DCH2A
      DIHA=DHA*DCHA
      PRINT 11
 11   FORMAT(//,6X,*DIFFERENCE BETWEEN SURFACE & BULK CONCENTRATION
     1 FOR EACH SPECIES(GMOLE/LITER)*,/)
      PRINT 38,DCCO2,DCHCO3,DCCO3,DCCA,DCH,DCCACO
      PRINT 38,DCOH,DCSO3,DCHSO3,DCCAA,DCH2A,DCHA
      PRINT 12
 12   FORMAT(//,6X,*FLUX CONTRIBUTION FOR EACH SPECIES(GMOLE-CM2/LITER-S
     1EC)*,/)
      PRINT 38,DICO2,DIHCO3,DICO3,DICA,DIH,DICACO
      PRINT 38,DIOH,DISO3,DIHSO3,DIAA,DIH2A,DIHA
      CA=CAB
      KD=SKD
      K1=SK1
      K2=SK2
      K3=SK3
      KF=SKF
      KA1=SKA1
      KA2=SKA2
      KHSO3=SKHSO3
      BETA1=BETA1S
      BETA2=BETA2S
  3   CONTINUE
  200 STOP
      END
      SUBROUTINE SURCONE(BETA,HYS)

C*****SURCONE CALCULATE THE CONCENTRATION OF SPECIES AT THE LIMESTONE
C*****SURFACE
C*****BY THE SPECIFIED CACO3(ION PAIR) CONCENTRATION AT THE LIMESTONE
C*****INTERPHASE

      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/ADD/KD
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/BULK2/SO3B,HSO3B,OHB,AB,H2AB,HAB
      COMMON/EPS/EPS1,EPS2
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      REAL K1,K2,K3,KA1,KA2,KHSO3,KW
      ALPH1=DCO2*CO2B+DHCO3*HCO3B+DCACO3*CACO3B+DCO3*CO3B-BETA
      ALPH2=DCA*CAB+DCACO3*CACO3B-BETA
      ALPH3=DH*HB+DHCO3*HCO3B+2.*DCO2*CO2B+DHA*HAB+2.*DH2A*H2AB-DOH
```

```
     1*OHB-DSO3*SO3B
      ALPH4=DH2A*H2AB+DHA*HAB+DA*AB
      ALPH5=DHSO3*HSO3B+DSO3*SO3B
      CAS=(ALPH2-DCACO3*CACO3S)/DCA
      CO3S=K3*CACO3S/CAS
      W=DCO3*CO3S+DCACO3*CACO3S
      H1=HB
      H2=HB/1000.
      CALL CALC(H1,F1,W)
      CALL CALC(H2,F2,W)
      IF(F1*F2.GT.0.) GO TO 50
      FSAVE=F1
      DO 20 J=1,30
      H=H2-F2*(H2-H1)/(F2-F1)
      CALL CALC(H,FW,W)
      ERR=ABS((H1-H2)/H1)/2.
      IF(ERR.LE.EPS1) GO TO 60
      IF(ABS(FW).LE.EPS2) GO TO 60
      IF(FW*F1.LT.0.) GO TO 10
      H1=H
      F1=FW
      IF(FW*FSAVE.GT.0) F2=F2/2.
      FSAVE=FW
      GO TO 20
 10   H2=H
      F2=FW
      IF(FW*FSAVE.GT.0) F1=F1/2.
      FSAVE=FW
 20   CONTINUE
 50   PRINT 3
 3    FORMAT(1HO,10X,*SURCONE DO NOT CONVERGE*,/,)
 60   CALL CALC(H,F,W)
      HYS=H
      RETURN
      END
      SUBROUTINE CALC(HY,F,W)

C****THE SUBROUTINE CALC EVALUATE THE CO2 SURFACE CONCENTRATION

      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/RATEK/K1,K2,K3, KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/ADD/KD
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/RAD/RO,BETA
      REAL KA1,KA2,KHSO3,KW,K1,K2,K3
      REAL KD
      H=HY
      OH=KW/H
      H2A=ALPH4/(DH2A*(1.+DHA*KA1/(DH2A*H)+KA1*KA2*DA/(DH2A*H*H)))
      HA=KA1*H2A/H
      A=KA1*KA2*H2A/(H*H)
      HSO3=ALPH5/(DHSO3+DSO3*KHSO3/H)
      SO3=KHSO3*HSO3/H
      HCO3=K1*H*CACO3S/CAS
      CO3=KD*HCO3/H
      CO2=(ALPH1-W-DHCO3*HCO3)/DCO2
      CO2S=CO2
      F=DH*H+DHA*HA+2.*DH2A*H2A-DOH*OH-DSO3*SO3-2.*W-DHCO3*HCO3-ALPH3+
     12.*ALPH1
      RETURN
      END
      SUBROUTINE FIND(HYDO,X)
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C*****SUBROUTINE FIND CALCULATE THE CONCENTRATION OF SPECIES USING
C*****HYDROGEN CONCENTRATION CALCULATE IN SUBROUTINE CONVERG

      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/ADD/KD
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/RAD/RO,BETA
      REAL K1,K2,K3 ,KA1,KA2,KHSO3,KW
      REAL KD
      H=HYDO
      OH=KW/H
      H2A=ALPH4/(DH2A*( 1.+DHA*KA1/(DH2A*H)+KA1*KA2*DA/(DH2A*H*H)))
      A=KA1*KA2*H2A/(H*H)
      HA=KA1*H2A/H
      HSO3=ALPH5/(DHSO3+DSO3*KHSO3/H)
      SO3=KHSO3*HSO3/H
      HCO3=(ALPH3-DH*H-2.*DCO2*CO2-DHA*HA-2.*DH2A*H2A+DOH*OH+
     1DSO3*SO3)/DHCO3
      CO3=KD*HCO3/H
      CACO3=(ALPH2+BETA*X)/(DCA*K3/CO3+DCACO3)
      CA=(ALPH2+BETA*X-DCACO3*CACO3)/DCA

      RETURN
      END
      SUBROUTINE CONVERG(S)

C*****SUBROUTINE CONVERG EMPLOYS SUBROUTINES SURCONE,SIMPKUT,ROOT,& FIND
C*****UNTIL CONVERGENCE FOR BETA SATISFIED THE CALCULATED BULK
C*****CONCENTRATION OF CO2 IN THE SOLUTION

      DIMENSION ZA(15,4),ZB(15,1),T(4,1),WK(10)
      DIMENSION CCO3(120),CCACO3(120),CCO2(120),CCA(120),CH(120)
      DIMENSION CHCO3(120),DX(120)
      DIMENSION COH(120),CSO3(120),CHSO3(120),CAA(120),CH2A(120)
      DIMENSION CHA(120)
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/ADD/KD
      COMMON/SURF/CCO3,CCACO3,CCO2,CCA,CH,CHCO3,DX
      COMMON/COUNT/NJ
      COMMON/SURF2/COH,CSO3,CHSO3,CAA,CH2A,CHA
      COMMON/INDEX/NK
      COMMON/EPS/EPS1,EPS2
      COMMON/END/YO,YF
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/RAD/RO,BETA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/END2/YO1,YF1
      COMMON/DKRATE/KA,KB,KC
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      REAL KA,KB,KC
      REAL K1,K2,K3,KA1,KA2,KHSO3,KW
      CALL SURCONE(BETA,HS)
      YF=HS*3.
      YO=HS/3.
      AO=0.
      BO=CO2S
      CO=0.
      STEP=0.01
      I=0
```

```
   42 CALL SIMPKUT(AO,BO,CO,STEP,CONC,FLUX,A14,A11,B11,C11,I)
      NJ=NJ+1
      AO=A11+STEP
      BO=B11+CONC
      CO=C11+FLUX
      IF(A14.LE.0.87) GO TO 42
      DO 50 I=1,15
      ZA(I,1)=1.
      ZA(I,2)=DX(I+70)
      ZA(I,3)=DX(I+70)**2
      ZA(I,4)=DX(I+70)**3
      ZB(I,1)=CCO2(I+70)
   50 CONTINUE
      CALL OFIMA3(ZA,15,ZB,15,15,1,4,T,4,WK,IER)
      DIST=0.84
      DO 10 J=86,101
      DX(J)=DIST+0.01
      DIST=DX(J)
      CCO2(J)=((T(4,1)*DX(J)+T(3,1))*DX(J)+T(2,1))*DX(J)+T(1,1)
      X=DX(J)
      CO2=CCO2(J)
      CALL ROOT(X,CO2)
      CCO3(J)=CO3
      CCACO3(J)=CACO3
      CHCO3(J)=HCO3
      CH(J)=H
      CCA(J)=CA
      COH(J)=OH
      CSO3(J)=SO3
      CHSO3(J)=HSO3
      CAA(J)=A
      CH2A(J)=H2A
      CHA(J)=HA
      S=CCO2(101)
   10 CONTINUE
      RETURN
      END
      SUBROUTINE SIMPKUT(AO,BO,CO,STEP,CONC,FLUX,A14,A11,B11,C11,I)

C****SIMPKUT APPLY THE 4TH-ORDER RUNGE KUTTA METHOD TO SOLVE THE 2ND
CC****ORDER CO2 DIFFERENTIAL RATE EQUATION

      DIMENSION CCO3(120),CCACO3(120),CCO2(120),CCA(120),CH(120)
      DIMENSION CHCO3(120),DX(120)
      DIMENSION COH(120),CSO3(120),CHSO3(120),CAA(120),CH2A(120)
      DIMENSION CHA(120)
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/RAD/RO,BETA
      COMMON/END/YO,YF
      COMMON/COUNT/NJ
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/SURF/CCO3,CCACO3,CCO2,CCA,CH,CHCO3,DX
      COMMON/SURF2/COH,CSO3,CHSO3,CAA,CH2A,CHA
      COMMON/ADD/KD
      REAL K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      A11=AO
      A12=A11+STEP/2.
      A13=A12
      A14=A11+STEP
      B11=BO
      C11=CO
      CALL ROOT(A11,B11)
```

```
      D11=-KF*(H*HCO3/K2-B11)/(DCO2*(1.-A11)**4/(RO*RO))
      I=I+1
      DX(I)=A11
      CCO2(I)=B11
      CHCO3(I)=HCO3
      CCO3(I)=CO3
      CCA(I)=CA
      CH(I)=H
      CCACO3(I)=CACO3
      COH(I)=OH
      CSO3(I)=SO3
      CHSO3(I)=HSO3
      CAA(I)=A
      CH2A(I)=H2A
      CHA(I)=HA
      B12=B11+C11*STEP/2.
      C12=C11+D11*STEP/2.
      CALL ROOT(A11,B11)
      D12=-KF*(H*HCO3/K2-B12)/(DCO2*(1.-A12)**4/(RO*RO))
      B13=B11+C12*STEP/2.
      C13=C11+D12*STEP/2.
      CALL ROOT(A11,B11)
      D13=-KF*(H*HCO3/K2-B13)/(DCO2*(1.-A13)**4/(RO*RO))
      B14=B11+C13*STEP
      C14=C11+D13*STEP
      CALL ROOT(A11,B11)
      D14=-KF*(H*HCO3/K2-B14)/(DCO2*(1.-A14)**4/(RO*RO))
      CONC=STEP/6.*(C11+C12*2.+2.*C13+C14)
      FLUX=STEP/6.*(D11+2.*D12+2.*D13+D14)
      RETURN
      END
      SUBROUTINE ROOT(X,CABO)

C****ROOT IS A MODIFIED HALVE-INTERVAL METHOD USE TO EVALUATED THE
C****SOLUTION COMPOSITON ONCE A CO2 COMPOSITION IS CALCULATE BY
C****SIMPKUT
C****THE INTERVAL OF H+ CONCENTRATION BETWEEN THE BULK & SURFACE
C****ARE USED

      COMMON/END/YO,YF
      COMMON/EPS/EPS1,EPS2
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/RAD/RO,BETA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/ADD/KD
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      REAL K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      REAL KD
      CO2=CABO
      E=ALPH3-ALPH1-BETA*X
      H1=YO
      CALL FIND(H1,X)
      F1=DH*H1+DCO2*CO2+DHA*HA+2.*DH2A*H2A-DOH*OH-DSO3*SO3-DCACO3*CACO3-
     1DCO3*CO3-E
      H2=YF
      CALL FIND(H2,X)
      F2=DH*H2+DCO2*CO2+DHA*HA+2.*DH2A*H2A-DOH*OH-DSO3*SO3-DCACO3*CACO3-
     1DCO3*CO3-E

      IF(F1*F2.GT.0.) GO TO 50
      FSAVE=F1
      DO 20 J=1,30
      H=H2-F2*(H2-H1)/(F2-F1)
```

```
      H3=H
      CALL FIND(H3,X)
      FW=DH*H+DCO2*CO2+DHA*HA+2.*DH2A*H2A-DOH*OH-DSO3*SO3-DCACO3*CACO3
     1-DCO3*CO3-E
      ERR=ABS((H1-H2)/H1)/2.
      IF(ERR.LE.EPS1) GO TO 60
      IF(ABS(FW).LE.EPS2) GO TO 60
      IF(FW*F1.LT.0.) GO TO 10
      H1=H
      F1=FW
      IF(FW*FSAVE.GT.0.) F2=F2/2.
      FSAVE=FW
      GO TO 20
 10   H2=H
      F2=FW
      IF(FW*FSAVE.GT.0.) F1=F1/2.
      FSAVE=FW
 20   CONTINUE
  50  PRINT 3
 3    FORMAT(1HO,10X,*NO SOLUTION IN THE RANGE FOR ROOT*,/)
      GO TO 63
 60   HNG=H
      CALL FIND(HNG,X)
      YO=H/2.
      YF=H*2.
 63    RETURN
      END
```

PROGRAM II

MASS TRANSFER MODEL NEGLECTING CO_2 REACTION

Program II is a modification of program I. It neglects the CO_2 finite rate reaction by assuming $[CO_2]_{surface} = [CO_2]_{bulk}$. This program simulates rate data at low P_{CO_2} since CO_2 reaction is insignificant. It also saves computer time and has better convergence.

Input and output as in program I

```
      PROGRAM LIMSDIS(TTY,INPUT=TTY,OUTPUT)

C*********************************************************************
C*****THIS PROGRAM CALCULATE THE RATE OF LIMESTONE DISSOLUTION BY******
C*****     A MASS TRANSFER MODEL USING SPHERICAL GEOMETRY**************
C*********************************************************************
      DIMENSION APH(10),APCO2(10)
      DIMENSION ACTP(10),BCTP(10),ZI(10),GAMMA(15)
      DIMENSION ACO2(120)
      DIMENSION CCO3(120),CCACO3(120),CCO2(120),CCA(120),CH(120)
      DIMENSION CHCO3(120),DX(120)
      DIMENSION COH(120),CSO3(120),CHSO3(120),CAA(120),CH2A(120)
      DIMENSION CHA(120)
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/RAD/RO,BETA
      COMMON/EPS/EPS1,EPS2
      COMMON/END/YO,YF
      COMMON/DKRATE/KA,KB,KC
      COMMON/COUNT/NJ
      COMMON/INDEX/NK
      COMMON/END2/YO1,YF1
      COMMON/SURF/CCO3,CCACO3,CCO2,CCA,CH,CHCO3,DX
      COMMON/SURF2/COH,CSO3,CHSO3,CAA,CH2A,CHA
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/BULK2/SO3B,HSO3B,OHB,AB,H2AB,HAB
      COMMON/ADD/KD
      REAL K1,K2,K3,KW,KF,KA1,KA2,KHSO3
      REAL KD,KS

C**************DIFFUSIVITIES IN CM2/SEC*********************************
C**************CACO3S SURFACE CONCENTRATION OF ION PAIR AT**************
C****************SOLID LIQUID INTERPHASE*********************************

      DATA DCO2,DHCO3,DCO3,DCA/2.0E-5,1.2E-5,7.0E-6,7.9E-6/
      DATA DH,DCACO3,CACO3S/9.3E-5,7.5E-6,6.204E-6/
      DATA DSO3,DHSO3,DOH,DA/3.85E-6,1.19E-5,5.27E-5,7.05E-6/
      DATA DH2A,DHA/1.19E-5,1.09E-5/
      DATA KA1,KA2,KW,KHSO3/4.02E-5,0.0,1.0E-14,6.24E-8/
      DATA EPS1,EPS2/1.0E-6,1.0E-25/

C*********************ERROR CRITERIA FOR CONVERGENCE**********************
C********************     EPS1        EPS2          **********************


C******************ACTP,BCTP ACTIVITIES COEFFICIENT PARAMETERS***********
C******************FOR MODIFIED DEBYE-HUCKEL EQUATION*******************

      DATA(ACTP   (I),I=1,9)/6.0,4.5,4.5,4.5,4.5,4.5,3.,3.,3./
      DATA(BCTP   (I),I=1,9)/0.4,0.1,0.0,0.,0.,0.,0.3,0.3,0.3/

C********HK       HENRY'S CONSTANT FOR CO2 IN WATER**********************
C********UI       EMPIRICAL CONSTANT FOR UNCHARGED SPECIES IN **********
C********                    DEBYE-HUCKEL EQUATION            **********
C********CI       IONIC STRENGTH OF SOLUTION      **********************
C********ACONS,B TEMPERATURE CONSTANTS IN THE MODIFIED*****************
C****************************DEBYE-HUCKEL EQUATION**********************
```

```
C*********ZI              IONIC VALENCIES          **********************

      DATA HK,UI,CI,ACONS,B/0.0305,0.076,0.3,0.512,0.312/
      DATA (ZI(I),I=1,9)/1.,2.,1.,2.,2.,1.,1.,2.,1./
      DATA K1,K2,K3,KF/1.34E7,4.45E-7,6.3E-4,2.6E-2/
      DATA KD/4.69E-11/
      DATA KS/4.0E-4/

C*****************************INPUT DATA*********************************
C******AT           TOTAL BUFFER CONCENTRATION(GMOLES/LITER)       ******
C******SO3T         TOTAL SULFITE CONCENTRATION(GMOLES/LITER)      ******
C******BETA1,BETA2 TRIAL INTERVALS FOR THE DISSOLUTION FLUX       ******
C******            (GMOLES-CM2/LITER-SEC)                         ******
C******NI           NUMBER OF PH AND PCO2 DATA PAIR                ******
C******APCO2,APH    PH & PARTIAL PRESSURE OF CO2(ATM)              ******
C******RO           PARTICLE DIAMETER(MICRO-METER)                 ******
C******CA           CALCIUM CONCENTRATION OF BULK SOLUTION         ******
C******                (GMOLES/LITER)                             ******
C***********************************************************************


      READ,AT,SO3T
      READ,BETA1,BETA2
      READ,   NI
      READ   ,CA,RO
      DO 2 K=1,NI
      READ   ,APCO2(K),APH(K)
  2   CONTINUE
      DO 21 I=1,9
      WA=ACONS*ZI(I)*ZI(I)
      WC=SQRT(CI)
      WB=1.+B*ACTP(I)*WC

C***********************************************************************
C********ACTIVITY COEFFICIENTS**************COMPONENTS*****************
C             GAMMA(1)                                  H+
C             GAMMA(2)                                  CA++
C             GAMMA(3)                                  HCO3-
C             GAMMA(4)                                  CO3--
C             GAMMA(5)                                  SO3--
C             GAMMA(6)                                  HSO3-
C             GAMMA(7)                                  OH-
C             GAMMA(8)                                  A--
C             GAMMA(9)                                  HA-
C             GAMMA(10)                                 CO2
C             GAMMA(11)                                 H2A
C             GAMMA(12)                                 CACO3(ION PAIR)

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

  21  GAMMA(I)=10.**(WA*(-WC/WB+CI*BCTP(I)))
      DO 22 I=10,12
  22  GAMMA(I)=10.**(UI*CI)
      DO 3 J=1,NI
      PH=APH(J)
      PCO2=APCO2(J)
   3  CONTINUE
      AH=10.**(-PH)
      H=AH/GAMMA(1)
      CO2=HK*PCO2
      HB=H
      CO2B=CO2
      AACO2=CO2*GAMMA(10)
      AHCO3=K2*AACO2/AH
      HCO3=AHCO3/GAMMA(3)
      HCO3B=HCO3
```

```
      ACO3=KD*AHCO3/AH
      CO3=ACO3/GAMMA(4)
      CO3B=CO3
      ACA=CA*GAMMA(2)
      CAB=CA
      ACACO3=ACA*ACO3/K3
      CACO3=ACACO3/GAMMA(12)
      CACO3B=CACO3

C*********REDEFINE EQUILIBRIUM AND RATE CONSTANT IN TERMS OF **********
C************************CONCENTRATIONS*****************************
C*******EQUILIBRIUM CONSTANT**************REACTION*********************
C             K1                   CACO3(ION PAIR) + H+ = CA++ + HCO3-
C             K2                   CO2 + H2O = H+ + HCO3-
C             K3                  CACO3(ION PAIR) = CA++ + CO3--
C             KHSO3               HSO3- = H+ + SO3--
C             KW                  H2O = H+ + OH-
C             KD                  HCO3- = H+ + CO3--
C             KS                  CASO3(ION PAIR) = CA++ + SO3--
C             KA1                 H2A = H+ + HA-
C             KA2                 HA- = H+ + A--

C********RATE CONSTANT*********************REACTION********************
C             KF                  CO2 + H2O = H+ + HCO3-

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



      KF=KF*GAMMA(10)
      K1=(K1*GAMMA(1)*GAMMA(12))/(GAMMA(2)*GAMMA(3))
      K2=(K2*GAMMA(10))/(GAMMA(1)*GAMMA(3))
      K3=K3*GAMMA(12)/(GAMMA(2)*GAMMA(4))
      RKHSO3=(KHSO3*GAMMA(6))/(GAMMA(5)*GAMMA(1))
      KHSO3=RKHSO3*(1.+GAMMA(2)*GAMMA(5)*CA/(GAMMA(12)*KS))
      KW=KW/(GAMMA(1)*GAMMA(7))
      KD=KD*GAMMA(3)/(GAMMA(1)*GAMMA(4))
      OHB=KW/HB
      HAB=AT/(1.+HB/KA1+KA2/HB)
      H2AB=HAB*HB/KA1
      AB=AT-HAB-H2AB
      SO3B=KHSO3*SO3T/(HB+KHSO3)
      HSO3B=SO3T-SO3B
      PRINT 234
 234  FORMAT(1H1,6X,*INPUT DATA*,//,6X,*DIFFUSIVITIES(CM2/SEC)*,/)
      PRINT 235
 235  FORMAT(10X,*CO2*,11X,*HCO3-*,11X,*CO3--*,11X,*CA++*,13X,*H*,9X,
     1*CACO3(ION PAIR)*,/)
      PRINT 102,DCO2,DHCO3,DCO3,DCA,DH,DCACO3
      PRINT 236
 236  FORMAT(10X,*OH-*,11X,*SO3--*,11X,*HSO3-*,11X,*A--*,11X,*H2A*,11X,
     1*HA-*,/)
      PRINT 102,DOH,DSO3,DHSO3,DA,DH2A,DHA
 102  FORMAT(3X,6E15.3,/)
      PRINT 237
 237  FORMAT(10X,*K1*,14X,*K2*,14X,*K3*,14X,*KF*,/)
      PRINT 103,K1,K2,K3,KF
      PRINT 238
 238  FORMAT(10X,*KA1*,14X,*KA2*,14X,*KW*,12X,*KHSO3*,/)
      PRINT 103,KA1,KA2,KW,KHSO3
 103  FORMAT(3X,4E15.4,/)
      PRINT 251
  251  FORMAT(10X,*PH*,11X,*PCO2(ATM.)*,5X,*PARTICLE DIAMETER(CM)*,/)
      PRINT 105,PH,PCO2,RO
 105  FORMAT(3X,3E15.3)
      PRINT 239
```

```
239 FORMAT(7X,*OUTPUT*,//,6X,*BULK CONCENTRATIONS(G-MOLE/L)*,/)
    PRINT 235
    PRINT 102,CO2B,HCO3B,CO3B,CAB,HB,CACO3B
    PRINT 236
    PRINT 102,OHB,SO3B,HSO3B,AB,H2AB,HAB
    CALL SURCONE(BETA1)
    CALL PHI(CACO3,CACO3S,SIDE1)
    CALL SURCONE(BETA2)
    CALL PHI(CACO3,CACO3S,SIDE2)
    IF(SIDE1*SIDE2.GT.1.) GO TO 187
    M=0
120 BETA=(BETA2+BETA1)/2.
    CALL SURCONE(BETA)
    CALL PHI(CACO3,CACO3S,SIDEN)
    IF(SIDE1*SIDEN.LT.1.) BETA2=BETA
    IF(SIDE2*SIDEN.LT.1.) BETA1=BETA
    DELT=ABS((BETA1-BETA2)/BETA1)
    IF(DELT.LT.0.0003) GO TO 188
    IF (M.EQ.25) GO TO 187
    M=M+1
    GO TO 120
188 PRINT 241
241 FORMAT(13X,*SURFACE CONCENTRATION(G-MOLE/L)*,//)
    PRINT 235
    PRINT 102,CO2,HCO3,CO3,CA,H,CACO3
    PRINT 236
    PRINT 102,OH,SO3,HSO3,A,H2A,HA
    PRINT 37,BETA
 37 FORMAT(//,3X,E15.4)
    RATED=-BETA/(1000.*RO)
    PRINT 36,RATED
 36 FORMAT(/,3X,*RATE OF DISSOLUTION=*,E15.5,*G-MOLE/SQ.CM.SEC*,/)
    DCCO2=CO2-CO2B
    DCHCO3=HCO3-HCO3B
    DCCA=CA-CAB
    DCH=H-HB
    DCCACO=CACO3-CACO3B
    DCCO3=CO3-CO3B
    DCOH=OH-OHB
    DCSO3=SO3-SO3B
    DCHSO3=HSO3-HSO3B
    DCCAA=A-AB
    DCH2A=H2A-H2AB
    DCHA=HA-HAB
    DICO2=DCO2*DCCO2
    DIHCO3=DHCO3*DCHCO3
    DICA=DCA*DCCA
    DIH=DH*DCH
    DICACO=DCCACO*DCACO3
    DICO3=DCO3*DCCO3
    DIOH=DOH*DCOH
    DISO3=DSO3*DCSO3
    DIHSO3=DHSO3*DCHSO3
    DIAA=DCCAA*DA
    DIH2A=DH2A*DCH2A
    DIHA=DHA*DCHA
    PRINT 11
 11 FORMAT(//,6X,*DIFFERENCE BETWEEN SURFACE AND BULK CONCENTRATION
   1FOR EACH CHEMICAL SPECIES*,//)
    PRINT 235
    PRINT 102,DCCO2,DCHCO3,DCCO3,DCCA,DCH,DCCACO
    PRINT 236
    PRINT 102,DCOH,DCSO3,DCHSO3,DCCAA,DCH2A,DCHA
    PRINT 12
 12 FORMAT(//,6X,*FLUX CONTRIBUTION FOR EACH SPECIES*,/)
    PRINT 235
```

```
      PRINT 102,DICO2,DIHCO3,DICO3,DICA,DIH,DICACO
      PRINT 236
      PRINT 102,DIOH,DISO3,DIHSO3,DIAA,DIH2A,DIHA
  187 STOP
      END


      SUBROUTINE PHI(CACO3,CACO3S,SIDE)
      IF(CACO3.LT.CACO3S) SIDE=1
      IF(CACO3.GT.CACO3S) SIDE=-1
      RETURN
      END
      SUBROUTINE SURCONE(BETA)
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/BULK2/SO3B,HSO3B,OHB,AB,H2AB,HAB
      COMMON/EPS/EPS1,EPS2
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/ADD/KD
      REAL KD
      REAL K1,K2,K3,KA1,KA2,KHSO3,KW
      ALPH1=DCO2*CO2B+DHCO3*HCO3B+DCACO3*CACO3B+DCO3*CO3B-BETA
      ALPH2=DCA*CAB+DCACO3*CACO3B-BETA
      ALPH3=DH*HB+DHCO3*HCO3B+2.*DCO2*CO2B+DHA*HAB+2.*DH2A*H2AB-DOH
     1*OHB-DSO3*SO3B
      ALPH4=DH2A*H2AB+DHA*HAB+DA*AB
      ALPH5=DHSO3*HSO3B+DSO3*SO3B
      H1=HB
      H2=HB/1.0E4
      CALL FIND(BETA,H1,F1)
      CALL FIND(BETA,H2,F2)
      IF(F1*F2.GT.0.) GO TO 50
      FSAVE=F1
      DO 20 J=1,25
      H=H2-F2*(H2-H1)/(F2-F1)
      CALL FIND(CO2,H,FW)
      ERR=ABS((H1-H2)/H1)/2.
      IF(ERR.LE.EPS1) GO TO 60
      IF(ABS(FW).LE.EPS2) GO TO 60
      IF(FW*F1.LT.0.) GO TO 10
      H1=H
      F1=FW
      IF(FW*FSAVE.GT.0.) F2=F2/2.
      FSAVE=FW
      GO TO 20
   10 H2=H
      F2=FW
      IF(FW*FSAVE.GT.0.) F1=F1/2.
      FSAVE=FW
   20 CONTINUE
   50 PRINT 3
    3 FORMAT(1HO,10X,*FIND DO NOT CONVERGE*,/)
   60 CALL FIND(BETA,H,F)
      CACO3=CA*HCO3/(K1*H)
      CO3=KD*HCO3/H
      RETURN
      END

      SUBROUTINE FIND(BETA,HYS,F)
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
```

```
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/ADD/KD
      REAL K1,K2,K3,KD
      REAL KA1,KA2,KHSO3,KW
      H=HYS
      OH=KW/H
      H2A=ALPH4/(DH2A*(1.+DHA*KA1/(DH2A*H)+KA1*KA2*DA/(DH2A*H*H)))
      HA=KA1*H2A/H
      A=KA1*KA2*H2A/(H*H)
      HSO3=ALPH5/(DHSO3+DSO3*KHSO3/H)
      SO3=KHSO3*HSO3/H
      HCO3=(ALPH1-DCO2*CO2)/(DHCO3+DCACO3*CA*KD/(H*K3)+DCO3*KD/H)
      F=DH*H+DHCO3*HCO3+2.*DCO2*CO2+DHA*HA+2.*DH2A*H2A-DOH*OH-DSO3*SO3
     1-ALPH3
      RETURN
      END
```

PROGRAM III

MASS TRANSFER MODEL FOR CALCULATING SURFACE $CaCO_3^\circ$ and $CaSO_3^\circ$ CONCENTRATIONS

Program III is the same as program II, except that an experimental β is used to backcalculate the $[CaCO_3^\circ]$ and $[CaSO_3^\circ]$ at the limestone surface.

Input and output same as in program II

```
      PROGRAM LIMSDIS(TTY,INPUT=TTY,OUTPUT)
C*********************************************************************
*
C*****THIS PROGRAM CALCULATE THE RATE OF LIMESTONE DISSOLUTION BY*****
*
C*****     A MASS TRANSFER MODEL USING SPHERICAL GEOMETRY*************
*
C*********************************************************************
*
      DIMENSION APH(10),APCO2(10)
      DIMENSION ACTP(10),BCTP(10),ZI(10),GAMMA(15)
      DIMENSION ACO2(120)
      DIMENSION CCO3(120),CCACO3(120),CCO2(120),CCA(120),CH(120)
      DIMENSION CHCO3(120),DX(120)
      DIMENSION COH(120),CSO3(120),CHSO3(120),CAA(120),CH2A(120)
      DIMENSION CHA(120)
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/RAD/RO,BETA
      COMMON/EPS/EPS1,EPS2
      COMMON/END/YO,YF
      COMMON/DKRATE/KA,KB,KC
      COMMON/COUNT/NJ
      COMMON/INDEX/NK
      COMMON/END2/YO1,YF1
      COMMON/SURF/CCO3,CCACO3,CCO2,CCA,CH,CHCO3,DX
      COMMON/SURF2/COH,CSO3,CHSO3,CAA,CH2A,CHA
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/BULK2/SO3B,HSO3B,OHB,AB,H2AB,HAB
      COMMON/ADD/KD
      REAL K1,K2,K3,KW,KF,KA1,KA2,KHSO3
      REAL KD,KS
C*************DIFFUSIVITIES IN CM2/SEC*******************************
*
C*************CACO3S SURFACE CONCENTRATION OF ION PAIR AT*************
*
C*****************SOLID LIQUID INTERPHASE*****************************
*
      DATA DCO2,DHCO3,DCO3,DCA/2.0E-5,1.2E-5,7.0E-6,7.9E-6/
      DATA DH,DCACO3,CACO3S/9.3E-5,7.5E-6,6.204E-6/
      DATA DSO3,DHSO3,DOH,DA/3.85E-6,1.19E-5,5.27E-5,7.05E-6/
      DATA DH2A,DHA/1.19E-5,1.09E-5/
      DATA KA1,KA2,KW,KHSO3/3.548E-5,0.0,1.0E-14,6.24E-8/
      DATA EPS1,EPS2/1.0E-6,1.0E-25/
C*********************ERROR CRITERIA FOR CONVERGENCE*******************
*
C********************     EPS1        EPS2          *********************
*
C*****************ACTP,BCTP ACTIVITIES COEFFICIENT PARAMETERS*********
*
C*****************FOR MODIFIED DEBYE-HUCKEL EQUATION*****************
*
      DATA(ACTP   (I),I=1,9)/6.0,4.5,4.5,4.5,4.5,4.5,3.,3.,3./
      DATA(BCTP   (I),I=1,9)/0.4,0.1,0.0,0.,0.,0.,0.3,0.3,0.3/
```

```
C********HK       HENRY'S CONSTANT FOR CO2 IN WATER**********************
*
C********UI       EMPIRICAL CONSTANT FOR UNCHARGED SPECIES IN *********
*
C********                      DEBYE-HUCKEL EQUATION            *********
*
C********CI       IONIC STRENGTH OF SOLUTION       **********************
*
C********ACONS,B TEMPERATURE CONSTANTS IN THE MODIFIED*****************
*
C**************************DEBYE-HUCKEL EQUATION**********************
*
C**********ZI              IONIC VALENCIES           ********************
*

      DATA HK,UI,CI,ACONS,B/0.0305,0.076,0.3,0.512,0.312/
      DATA (ZI(I),I=1,9)/1.,2.,1.,2.,2.,1.,1.,2.,1./
      DATA K1,K2,K3,KF/1.34E7,4.45E-7,6.3E-4,2.6E-2/
      DATA KD/4.69E-11/
      DATA KS/4.0E-4/

C*****************************INPUT DATA*********************************
*
C******AT           TOTAL BUFFER CONCENTRATION(GMOLES/LITER)       *****
*
C******SO3T         TOTAL SULFITE CONCENTRATION(GMOLES/LITER)      *****
*
C******BETA1,BETA2 TRIAL INTERVALS FOR THE DISSOLUTION FLUX       *****
*
C******             (GMOLES-CM2/LITER-SEC)                        *****
*
C******NI            NUMBER OF PH AND PCO2 DATA PAIR               *****
*
C******APCO2,APH    PH & PARTIAL PRESSURE OF CO2(ATM)             *****
*
C******RO           PARTICLE DIAMETER(MICRO-METER)                *****
*
C******CA           CALCIUM CONCENTRATION OF BULK SOLUTION        *****
*
C******                 (GMOLES/LITER)                           *****
*
C*******************************************************************
*

      READ,AT,SO3T
      READ,BETA
      READ,   NI
      READ   ,CA,RO
      DO 2 K=1,NI
      READ   ,APCO2(K),APH(K)
  2   CONTINUE
      DO 21 I=1,9
      WA=ACONS*ZI(I)*ZI(I)
      WC=SQRT(CI)
      WB=1.+B*ACTP(I)*WC

C*******************************************************************
**
C********ACTIVITY COEFFICIENTS**************COMPONENTS***************
**
C             GAMMA(1)                              H+
C             GAMMA(2)                              CA++
C             GAMMA(3)                              HCO3-
C             GAMMA(4)                              CO3--
```

```
C            GAMMA(5)                          SO3--
C            GAMMA(6)                          HSO3-
C            GAMMA(7)                          OH-
C            GAMMA(8)                          A--
C            GAMMA(9)                          HA-
C            GAMMA(10)                         CO2
C            GAMMA(11)                         H2A
C            GAMMA(12)                         CACO3(ION PAIR)

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

  21  GAMMA(I)=10.**(WA*(-WC/WB+CI*BCTP(I)))
      DO 22 I=10,12
  22  GAMMA(I)=10.**(UI*CI)
      DO 3 J=1,NI
      PH=APH(J)
      PCO2=APCO2(J)
   3  CONTINUE
      AH=10.**(-PH)
      H=AH/GAMMA(1)
      CO2=HK*PCO2
      HB=H
      CO2B=CO2
      AACO2=CO2*GAMMA(10)
      AHCO3=K2*AACO2/AH
      HCO3=AHCO3/GAMMA(3)
      HCO3B=HCO3
      ACO3=KD*AHCO3/AH
      CO3=ACO3/GAMMA(4)
      CO3B=CO3
      ACA=CA*GAMMA(2)
      CAB=CA
      ACACO3=ACA*ACO3/K3
      CACO3=ACACO3/GAMMA(12)
      CACO3B=CACO3

C*********REDEFINE EQUILIBRIUM AND RATE CONSTANT IN TERMS OF *********
*
C***************************CONCENTRATIONS*******************************
*
C*******EQUILIBRIUM CONSTANT**************REACTION**********************
*
C            K1                    CACO3(ION PAIR) + H+ = CA++ + HCO3-
C            K2                    CO2 + H2O = H+ + HCO3-
C            K3                   CACO3(ION PAIR) = CA++ + CO3--
C            KHSO3                HSO3- = H+ + SO3--
C            KW                   H2O = H+ + OH-
C            KD                   HCO3- = H+ + CO3--
C            KS                   CASO3(ION PAIR) = CA++ + SO3--
C            KA1                  H2A = H+ + HA-
C            KA2                  HA- = H+ + A--

C********RATE CONSTANT**********************REACTION********************
*
C            KF                   CO2 + H2O = H+ + HCO3-

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



      KF=KF*GAMMA(10)
      K1=(K1*GAMMA(1)*GAMMA(12))/(GAMMA(2)*GAMMA(3))
      K2=(K2*GAMMA(10))/(GAMMA(1)*GAMMA(3))
      K3=K3*GAMMA(12)/(GAMMA(2)*GAMMA(4))
```

```
      RKHSO3=(KHSO3*GAMMA(6))/(GAMMA(5)*GAMMA(1))
      KHSO3=RKHSO3*(1.+GAMMA(2)*GAMMA(5)*CA/(GAMMA(12)*KS))
      KW=KW/(GAMMA(1)*GAMMA(7))
      KD=KD*GAMMA(3)/(GAMMA(1)*GAMMA(4))
      OHB=KW/HB
      HAB=AT/(1.+HB/KA1+KA2/HB)
      H2AB=HAB*HB/KA1
      AB=AT-HAB-H2AB
      SO3B=KHSO3*SO3T/(HB+KHSO3)
      HSO3B=SO3T-SO3B
      PRINT 234
  234 FORMAT(1H1,6X,*INPUT DATA*,//,6X,*DIFFUSIVITIES(CM2/SEC)*,/)
      PRINT 235
  235 FORMAT(10X,*CO2*,11X,*HCO3-*,11X,*CO3--*,11X,*CA++*,13X,*H*,9X,
     1*CACO3(ION PAIR)*,/)
      PRINT 102,DCO2,DHCO3,DCO3,DCA,DH,DCACO3
      PRINT 236
  236 FORMAT(10X,*OH-*,11X,*SO3--*,11X,*HSO3-*,11X,*A--*,11X,*H2A*,11X
     ,
     1*HA-*,/)
      PRINT 102,DOH,DSO3,DHSO3,DA,DH2A,DHA
  102 FORMAT(3X,6E15.3,/)
      PRINT 237
  237 FORMAT(10X,*K1*,14X,*K2*,14X,*K3*,14X,*KF*,/)
      PRINT 103,K1,K2,K3,KF
      PRINT 238
  238 FORMAT(10X,*KA1*,14X,*KA2*,14X,*KW*,12X,*KHSO3*,/)
      PRINT 103,KA1,KA2,KW,KHSO3
  103 FORMAT(3X,4E15.4,/)
      PRINT 251
  251  FORMAT(10X,*PH*,11X,*PCO2(ATM.)*,5X,*PARTICLE DIAMETER(CM)*,/)

      PRINT 105,PH,PCO2,RO
  105 FORMAT(3X,3E15.3)
      PRINT 239
  239 FORMAT(7X,*OUTPUT*,//,6X,*BULK CONCENTRATIONS(G-MOLE/L)*,/)
      PRINT 235
      PRINT 102,CO2B,HCO3B,CO3B,CAB,HB,CACO3B
      PRINT 236
      PRINT 102,OHB,SO3B,HSO3B,AB,H2AB,HAB
      CALL SURCONE(BETA)
      PRINT 241
  241 FORMAT(13X,*SURFACE CONCENTRATION(G-MOLE/L)*,//)
      PRINT 235
      PRINT 102,CO2,HCO3,CO3,CA,H,CACO3
      PRINT 236
      PRINT 102,OH,SO3,HSO3,A,H2A,HA
      PRINT 37,BETA
   37 FORMAT(//,3X,E15.4)
      RATED=-BETA/(1000.*RO)
      PRINT 36,RATED
   36 FORMAT(/,3X,*RATE OF DISSOLUTION=*,E15.5,*G-MOLE/SQ.CM.SEC*,/)
      DCCO2=CO2-CO2B
      DCHCO3=HCO3-HCO3B
      DCCA=CA-CAB
      DCH=H-HB
      DCCACO=CACO3-CACO3B
      DCCO3=CO3-CO3B
      DCOH=OH-OHB
      DCSO3=SO3-SO3B
      DCHSO3=HSO3-HSO3B
      DCCAA=A-AB
      DCH2A=H2A-H2AB
      DCHA=HA-HAB
      DICO2=DCO2*DCCO2
```

```
      DIHCO3=DHCO3*DCHCO3
      DICA=DCA*DCCA
      DIH=DH*DCH
      DICACO=DCCACO*DCACO3
      DICO3=DCO3*DCCO3
      DIOH=DOH*DCOH
      DISO3=DSO3*DCSO3
      DIHSO3=DHSO3*DCHSO3
      DIAA=DCCAA*DA
      DIH2A=DH2A*DCH2A
      DIHA=DHA*DCHA
      PRINT 11
   11 FORMAT(//,6X,*DIFFERENCE BETWEEN SURFACE AND BULK CONCENTRATION
     1FOR EACH CHEMICAL SPECIES*,//)
      PRINT 235
      PRINT 102,DCCO2,DCHCO3,DCCO3,DCCA,DCH,DCCACO
      PRINT 236
      PRINT 102,DCOH,DCSO3,DCHSO3,DCCAA,DCH2A,DCHA
      PRINT 12
   12 FORMAT(//,6X,*FLUX CONTRIBUTION FOR EACH SPECIES*,/)
      PRINT 235
      PRINT 102,DICO2,DIHCO3,DICO3,DICA,DIH,DICACO
      PRINT 236
      PRINT 102,DIOH,DISO3,DIHSO3,DIAA,DIH2A,DIHA
      STOP
      END

      SUBROUTINE SURCONE(BETA)
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/BULK2/SO3B,HSO3B,OHB,AB,H2AB,HAB
      COMMON/EPS/EPS1,EPS2
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/ADD/KD
      REAL KD
      REAL K1,K2,K3,KA1,KA2,KHSO3,KW
      ALPH1=DCO2*CO2B+DHCO3*HCO3B+DCACO3*CACO3B+DCO3*CO3B-BETA
      ALPH2=DCA*CAB+DCACO3*CACO3B-BETA
      ALPH3=DH*HB+DHCO3*HCO3B+2.*DCO2*CO2B+DHA*HAB+2.*DH2A*H2AB-DOH
     1*OHB-DSO3*SO3B
      ALPH4=DH2A*H2AB+DHA*HAB+DA*AB
      ALPH5=DHSO3*HSO3B+DSO3*SO3B
      H1=HB
      H2=HB/1.0E4
      CALL FIND(BETA,H1,F1)
      CALL FIND(BETA,H2,F2)
      IF(F1*F2.GT.0.) GO TO 50
      FSAVE=F1
      DO 20 J=1,25
      H=H2-F2*(H2-H1)/(F2-F1)
      CALL FIND(CO2,H,FW)
      ERR=ABS((H1-H2)/H1)/2.
      IF(ERR.LE.EPS1) GO TO 60
      IF(ABS(FW).LE.EPS2) GO TO 60
      IF(FW*F1.LT.0.) GO TO 10
      H1=H
      F1=FW
      IF(FW*FSAVE.GT.0.) F2=F2/2.
      FSAVE=FW
      GO TO 20
   10 H2=H
```

```
      F2=FW
      IF(FW*FSAVE.GT.0.) F1=F1/2.
      FSAVE=FW
   20 CONTINUE
   50 PRINT 3
    3 FORMAT(1H0,10X,*FIND DO NOT CONVERGE*,/)
   60 CALL FIND(BETA,H,F)
      CACO3=CA*HCO3/(K1*H)
      CO3=KD*HCO3/H
      RETURN
      END

      SUBROUTINE FIND(BETA,HYS,F)
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/ADD/KD
      REAL K1,K2,K3,KD
      REAL KA1,KA2,KHSO3,KW
      H=HYS
      OH=KW/H
      H2A=ALPH4/(DH2A*(1.+DHA*KA1/(DH2A*H)+KA1*KA2*DA/(DH2A*H*H)))
      HA=KA1*H2A/H
      A=KA1*KA2*H2A/(H*H)
      HSO3=ALPH5/(DHSO3+DSO3*KHSO3/H)
      SO3=KHSO3*HSO3/H
      HCO3=(ALPH1-DCO2*CO2)/(DHCO3+DCACO3*CA*KD/(H*K3)+DCO3*KD/H)
      F=DH*H+DHCO3*HCO3+2.*DCO2*CO2+DHA*HA+2.*DH2A*H2A-DOH*OH-DSO3*SO3
     1-ALPH3
      PRINT 10,F
   10 FORMAT(3X,E15.3)
      RETURN
      END

CC:
```

PROGRAM IV

MASS TRANSFER MODEL WITH EQUILIBRIUM SHIFT OF $CaSO_3^\circ$ ON $CaCO_3^\circ$

Program IV is similar to program II with the addition of $[CaCO_3^\circ]$ as a function of $[CaSO_3^\circ]$ at the limestone surface.

Input and output is the same as in program II

```
      PROGRAM LIMSDIS(TTY,INPUT=TTY,OUTPUT)

C*****************************************************************
*
C THE PHYSICAL CONSTANTS USED IN THIS PROGRAM IS AT 55 DEGREE C
C*****************************************************************
*
C*****************************************************************
*
C*****THIS PROGRAM CALCULATE THE RATE OF LIMESTONE DISSOLUTION BY*****
*
C*****     A MASS TRANSFER MODEL USING SPHERICAL GEOMETRY*************
*
C*****************************************************************
*
      DIMENSION APH(10),APCO2(10)
      DIMENSION ACTP(10),BCTP(10),ZI(10),GAMMA(15)
      DIMENSION ACO2(120)
      DIMENSION CCO3(120),CCACO3(120),CCO2(120),CCA(120),CH(120)
      DIMENSION CHCO3(120),DX(120)
      DIMENSION COH(120),CSO3(120),CHSO3(120),CAA(120),CH2A(120)
      DIMENSION CHA(120)
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/RAD/RO,BETA
      COMMON/EPS/EPS1,EPS2
      COMMON/END/YO,YF
      COMMON/DKRATE/KA,KB,KC
      COMMON/COUNT/NJ
      COMMON/INDEX/NK
      COMMON/END2/YO1,YF1
      COMMON/SURF/CCO3,CCACO3,CCO2,CCA,CH,CHCO3,DX
      COMMON/SURF2/COH,CSO3,CHSO3,CAA,CH2A,CHA
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/BULK2/SO3B,HSO3B,OHB,AB,H2AB,HAB
      COMMON/ADD/KD
      REAL K1,K2,K3,KW,KF,KA1,KA2,KHSO3
      REAL KD,KS

C**************DIFFUSIVITIES IN CM2/SEC*******************************
*
C**************CACO3S SURFACE CONCENTRATION OF ION PAIR AT*************
*
C*****************SOLID LIQUID INTERPHASE*****************************
*

      DATA DCO2,DHCO3,DCO3,DCA/3.89E-5,2.33E-5,1.36E-5,1.54E-5/
      DATA DH,DCACO3/1.81E-4,1.46E-5/
      DATA DSO3,DHSO3,DOH,DA/7.49E-6,1.46E-5,1.03E-4,1.37E-5/
      DATA DH2A,DHA/2.32E-5,2.12E-5/
      DATA KA1,KA2,KW,KHSO3/0.,0.,7.26E-14,3.99E-8/
      DATA EPS1,EPS2/1.0E-6,1.0E-25/

C*********************ERROR CRITERIA FOR CONVERGENCE*******************
*
C*******************     EPS1        EPS2          ********************
*


C*****************ACTP,BCTP ACTIVITIES COEFFICIENT PARAMETERS*********
*
```

```
C******************FOR MODIFIED DEBYE-HUCKEL EQUATION*****************
*
      DATA(ACTP   (I),I=1,9)/6.0,4.5,4.5,4.5,4.5,4.5,3.,3.,3./
      DATA(BCTP   (I),I=1,9)/0.4,0.1,0.0,0.,0.,0.,0.3,0.3,0.3/

C********HK       HENRY'S CONSTANT FOR CO2 IN WATER*********************
*
C********UI       EMPIRICAL CONSTANT FOR UNCHARGED SPECIES IN *********
*
C********                     DEBYE-HUCKEL EQUATION             *********
*
C********CI       IONIC STRENGTH OF SOLUTION      **********************
*
C********ACONS,B TEMPERATURE CONSTANTS IN THE MODIFIED*****************
*
C*************************DEBYE-HUCKEL EQUATION**********************
*
C**********ZI              IONIC VALENCIES          *********************
*
      DATA HK,UI,CI,ACONS,B/0.0168,0.076,0.3,0.543,0.336/
      DATA (ZI(I),I=1,9)/1.,2.,1.,2.,2.,1.,1.,2.,1./
      DATA K1,K2,K3,KF/6.43E6,5.12E-7,4.51E-4,0.127/
      DATA KD/7.02E-11/
      DATA KS/2.81E-4/

C*****************************INPUT DATA*******************************
*
C******AT           TOTAL BUFFER CONCENTRATION(GMOLES/LITER)       *****
*
C******SO3T         TOTAL SULFITE CONCENTRATION(GMOLES/LITER)      *****
*
C******BETA1,BETA2 TRIAL INTERVALS FOR THE DISSOLUTION FLUX       *****
*
C******            (GMOLES-CM2/LITER-SEC)                         *****
*
C******NI           NUMBER OF PH AND PCO2 DATA PAIR                *****
*
C******APCO2,APH    PH & PARTIAL PRESSURE OF CO2(ATM)              *****
*
C******RO           PARTICLE DIAMETER(MICRO-METER)                 *****
*
C******CA           CALCIUM CONCENTRATION OF BULK SOLUTION         *****
*
C******                (GMOLES/LITER)                             *****
*
C*************************************************************************
*

      READ,AT,SO3T
      READ,BETA1,BETA2
      READ,   NI
      READ   ,CA,RO
      DO 2 K=1,NI
      READ   ,APCO2(K),APH(K)
  2   CONTINUE
      DO 21 I=1,9
      WA=ACONS*ZI(I)*ZI(I)
      WC=SQRT(CI)
      WB=1.+B*ACTP(I)*WC

C*************************************************************************
**
C********ACTIVITY COEFFICIENTS***************COMPONENTS****************
```

```
**
C             GAMMA(1)                          H+
C             GAMMA(2)                          CA++
C             GAMMA(3)                          HCO3-
C             GAMMA(4)                          CO3--
C             GAMMA(5)                          SO3--
C             GAMMA(6)                          HSO3-
C             GAMMA(7)                          OH-
C             GAMMA(8)                          A--
C             GAMMA(9)                          HA-
C             GAMMA(10)                         CO2
C             GAMMA(11)                         H2A
C             GAMMA(12)                         CACO3(ION PAIR)

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

  21  GAMMA(I)=10.**(WA*(-WC/WB+CI*BCTP(I)))
      DO 22 I=10,12
  22  GAMMA(I)=10.**(UI*CI)
      DO 3 J=1,NI
      PH=APH(J)
      PCO2=APCO2(J)
   3  CONTINUE
      AH=10.**(-PH)
      H=AH/GAMMA(1)
      CO2=HK*PCO2
      HB=H
      CO2B=CO2
      AACO2=CO2*GAMMA(10)
      AHCO3=K2*AACO2/AH
      HCO3=AHCO3/GAMMA(3)
      HCO3B=HCO3
      ACO3=KD*AHCO3/AH
      CO3=ACO3/GAMMA(4)
      CO3B=CO3
      ACA=CA*GAMMA(2)
      CAB=CA
      ACACO3=ACA*ACO3/K3
      CACO3=ACACO3/GAMMA(12)
      CACO3B=CACO3

C*********REDEFINE EQUILIBRIUM AND RATE CONSTANT IN TERMS OF *********
*
C*************************CONCENTRATIONS*****************************
*
C*******EQUILIBRIUM CONSTANT*************REACTION*********************
*
C             K1                  CACO3(ION PAIR) + H+ = CA++ + HCO3-
C             K2                  CO2 + H2O = H+ + HCO3-
C             K3                CACO3(ION PAIR) = CA++ + CO3--
C             KHSO3             HSO3- = H+ + SO3--
C             KW                H2O = H+ + OH-
C             KD                HCO3- = H+ + CO3--
C             KS                CASO3(ION PAIR) = CA++ + SO3--
C             KA1               H2A = H+ + HA-
C             KA2               HA- = H+ + A--

C********RATE CONSTANT*********************REACTION*******************
*
C             KF                CO2 + H2O = H+ + HCO3-

C*************************************************************************
*
```

```
      KF=KF*GAMMA(10)
      K1=(K1*GAMMA(1)*GAMMA(12))/(GAMMA(2)*GAMMA(3))
      K2=(K2*GAMMA(10))/(GAMMA(1)*GAMMA(3))
      K3=K3*GAMMA(12)/(GAMMA(2)*GAMMA(4))
      RKHSO3=(KHSO3*GAMMA(6))/(GAMMA(5)*GAMMA(1))
      KHSO3=RKHSO3*(1.+GAMMA(2)*GAMMA(5)*CA/(GAMMA(12)*KS))
      KW=KW/(GAMMA(1)*GAMMA(7))
      KD=KD*GAMMA(3)/(GAMMA(1)*GAMMA(4))
      OHB=KW/HB
      HAB=AT/(1.+HB/KA1+KA2/HB)
      H2AB=HAB*HB/KA1
      AB=AT-HAB-H2AB
      SO3B=KHSO3*SO3T/(HB+KHSO3)
      HSO3B=SO3T-SO3B
      PRINT 234
  234 FORMAT(1H1,6X,*INPUT DATA*,//,6X,*DIFFUSIVITIES(CM2/SEC)*,/)
      PRINT 235
  235 FORMAT(10X,*CO2*,11X,*HCO3-*,11X,*CO3--*,11X,*CA++*,13X,*H*,9X,
     1*CACO3(ION PAIR)*,/)
      PRINT 102,DCO2,DHCO3,DCO3,DCA,DH,DCACO3
      PRINT 236
  236 FORMAT(10X,*OH-*,11X,*SO3--*,11X,*HSO3-*,11X,*A--*,11X,*H2A*,11X
     ,
     1*HA-*,/)
      PRINT 102,DOH,DSO3,DHSO3,DA,DH2A,DHA
  102 FORMAT(3X,6E15.3,/)
      PRINT 237
  237 FORMAT(10X,*K1*,14X,*K2*,14X,*K3*,14X,*KF*,/)
      PRINT 103,K1,K2,K3,KF
      PRINT 238
  238 FORMAT(10X,*KA1*,14X,*KA2*,14X,*KW*,12X,*KHSO3*,/)
      PRINT 103,KA1,KA2,KW,KHSO3
  103 FORMAT(3X,4E15.4,/)
      PRINT 251
  251  FORMAT(10X,*PH*,11X,*PCO2(ATM.)*,5X,*PARTICLE DIAMETER(CM)*,/)
      PRINT 105,PH,PCO2,RO
  105 FORMAT(3X,3E15.3)
      PRINT 239
  239 FORMAT(7X,*OUTPUT*,//,6X,*BULK CONCENTRATIONS(G-MOLE/L)*,/)
      PRINT 235
      PRINT 102,CO2B,HCO3B,CO3B,CAB,HB,CACO3B
      PRINT 236
      PRINT 102,OHB,SO3B,HSO3B,AB,H2AB,HAB
      CALL SURCONE(BETA1)
      CALL PHI(SO3,CACO3,SIDE1)
      CALL SURCONE(BETA2)
      CALL PHI(SO3,CACO3,SIDE2)
      IF(SIDE1*SIDE2.GT.1.) GO TO 187
      M=0
  120 BETA=(BETA2+BETA1)/2.
      CALL SURCONE(BETA)
      PRINT 660,SO3,CACO3
  660 FORMAT(4X,2E15.4)
      CALL PHI(SO3,CACO3,SIDEN)
      IF(SIDE1*SIDEN.LT.0.) BETA2=BETA
      IF(SIDE2*SIDEN.LT.0.) BETA1=BETA
      DELT=ABS((BETA1-BETA2)/BETA1)
      IF(DELT.LT.0.0003) GO TO 188
      IF (M.EQ.25) GO TO 187
      M=M+1
      GO TO 120
  188 PRINT 241
  241 FORMAT(13X,*SURFACE CONCENTRATION(G-MOLE/L)*,//)
```

```
      PRINT 235
      PRINT 102,CO2,HCO3,CO3,CA,H,CACO3
      PRINT 236
      PRINT 102,OH,SO3,HSO3,A,H2A,HA
      PRINT 37,BETA
   37 FORMAT(//,3X,E15.4)
      RATED=-BETA/(1000.*RO)
      PRINT 36,RATED
   36 FORMAT(/,3X,*RATE OF DISSOLUTION=*,E15.5,*G-MOLE/SQ.CM.SEC*,/)
      DCCO2=CO2-CO2B
      DCHCO3=HCO3-HCO3B
      DCCA=CA-CAB
      DCH=H-HB
      DCCACO=CACO3-CACO3B
      DCCO3=CO3-CO3B
      DCOH=OH-OHB
      DCSO3=SO3-SO3B
      DCHSO3=HSO3-HSO3B
      DCCAA=A-AB
      DCH2A=H2A-H2AB
      DCHA=HA-HAB
      DICO2=DCO2*DCCO2
      DIHCO3=DHCO3*DCHCO3
      DICA=DCA*DCCA
      DIH=DH*DCH
      DICACO=DCCACO*DCACO3
      DICO3=DCO3*DCCO3
      DIOH=DOH*DCOH
      DISO3=DSO3*DCSO3
      DIHSO3=DHSO3*DCHSO3
      DIAA=DCCAA*DA
      DIH2A=DH2A*DCH2A
      DIHA=DHA*DCHA
      PRINT 11
   11 FORMAT(//,6X,*DIFFERENCE BETWEEN SURFACE AND BULK CONCENTRATION
     1FOR EACH CHEMICAL SPECIES*,//)
      PRINT 235
      PRINT 102,DCCO2,DCHCO3,DCCO3,DCCA,DCH,DCCACO
      PRINT 236
      PRINT 102,DCOH,DCSO3,DCHSO3,DCCAA,DCH2A,DCHA
      PRINT 12
   12 FORMAT(//,6X,*FLUX CONTRIBUTION FOR EACH SPECIES*,/)
      PRINT 235
      PRINT 102,DICO2,DIHCO3,DICO3,DICA,DIH,DICACO
      PRINT 236
      PRINT 102,DIOH,DISO3,DIHSO3,DIAA,DIH2A,DIHA
  187 STOP
      END


      SUBROUTINE PHI(SO3,CACO3,SIDE)
      IF(SO3.LT.4.96E-5.AND.CACO3.LT.6.2E-6) SIDE=-1.
      IF(SO3.LT.4.96E-5.AND.CACO3.GT.6.2E-6) SIDE=1.
      IF(SO3.GE.4.96E-5) SIDE=ALOG10(CACO3)+10.76+1.29*ALOG10(SO3)
      RETURN
      END
      SUBROUTINE SURCONE(BETA)
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/CONSUR/HCO3S,CO3S,CAS,HS,CO2S
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/BULK/CO2B,CO3B,HCO3B,CACO3B,HB,CAB
      COMMON/BULK2/SO3B,HSO3B,OHB,AB,H2AB,HAB
```

```
      COMMON/EPS/EPS1,EPS2
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/ADD/KD
      REAL KD
      REAL K1,K2,K3,KA1,KA2,KHSO3,KW
      ALPH1=DCO2*CO2B+DHCO3*HCO3B+DCACO3*CACO3B+DCO3*CO3B-BETA
      ALPH2=DCA*CAB+DCACO3*CACO3B-BETA
      ALPH3=DH*HB+DHCO3*HCO3B+2.*DCO2*CO2B+DHA*HAB+2.*DH2A*H2AB-DOH
     1*OHB-DSO3*SO3B
      ALPH4=DH2A*H2AB+DHA*HAB+DA*AB
      ALPH5=DHSO3*HSO3B+DSO3*SO3B
      H1=HB
      H2=HB/1.0E4
      CALL FIND(BETA,H1,F1)
      CALL FIND(BETA,H2,F2)
      IF(F1*F2.GT.0.) GO TO 50
      FSAVE=F1
      DO 20 J=1,25
      H=H2-F2*(H2-H1)/(F2-F1)
      CALL FIND(CO2,H,FW)
      ERR=ABS((H1-H2)/H1)/2.
      IF(ERR.LE.EPS1) GO TO 60
      IF(ABS(FW).LE.EPS2) GO TO 60
      IF(FW*F1.LT.0.) GO TO 10
      H1=H
      F1=FW
      IF(FW*FSAVE.GT.0.) F2=F2/2.
      FSAVE=FW
      GO TO 20
 10   H2=H
      F2=FW
      IF(FW*FSAVE.GT.0.) F1=F1/2.
      FSAVE=FW
 20   CONTINUE
 50   PRINT 3
3     FORMAT(1H0,10X,*FIND DO NOT CONVERGE*,/)
 60   CALL FIND(BETA,H,F)
      CACO3=CA*HCO3/(K1*H)
      CO3=KD*HCO3/H
      RETURN
      END

      SUBROUTINE FIND(BETA,HYS,F)
      COMMON/DIFF2/DSO3,DHSO3,DOH,DA,DH2A,DHA
      COMMON/DIFF/DHCO3,DCO3,DH,DCO2,DCA,DCACO3
      COMMON/CANC/CO2,CO3,HCO3,CACO3,H,CA,CACO3S
      COMMON/CANC2/SO3,HSO3,OH,A,H2A,HA
      COMMON/RATEK/K1,K2,K3,KF,KA1,KA2,KHSO3,KW
      COMMON/CONST/ALPH1,ALPH2,ALPH3,ALPH4,ALPH5
      COMMON/ADD/KD
      REAL K1,K2,K3,KD
      REAL KA1,KA2,KHSO3,KW
      H=HYS
      OH=KW/H
      H2A=ALPH4/(DH2A*(1.+DHA*KA1/(DH2A*H)+KA1*KA2*DA/(DH2A*H*H)))
      HA=KA1*H2A/H
      A=KA1*KA2*H2A/(H*H)
      HSO3=ALPH5/(DHSO3+DSO3*KHSO3/H)
      SO3=KHSO3*HSO3/H
      HCO3=(ALPH1-DCO2*CO2)/(DHCO3+DCACO3*CA*KD/(H*K3)+DCO3*KD/H)
      F=DH*H+DHCO3*HCO3+2.*DCO2*CO2+DHA*HA+2.*DH2A*H2A-DOH*OH-DSO3*SO3

     1-ALPH3
      RETURN
      END
```

PROGRAM V

SIMPLIFIED MASS TRANSFER MODEL SUMMING DISSOLUTION RATE OVER PARTICLE SIZE DISTRIBUTION

Program V calculates kt versus fraction remaining F by the following equation:

$$F = \sum_{i=1}^{n} \phi_i \left(1 - \frac{kt}{d_i d_{i+1}}\right)^{1.5}$$

For values of $\left(1 - \frac{kt}{d_i d_{i+1}}\right) < 1$, set F = 0.

Input

ϕ_i particle size distribution and

d_i particle diameter from Coulter counter data

and values of kt

Output

Values of fraction remaining and kt

```
      PROGRAM   MASS(TTY,INPUT=TTY,OUTPUT)
      DIMENSION PHI(50),DP(50),DPSQ(50),F(50),KT(50),FR(100),DIFF(100)
      DIMENSION D(50)
      REAL KTL,KTH
      REAL MN,KT
      INTEGER TYPE(2)
      DATA(KT(I),I=1,9)/.1,.2,.3,.4,.5,.6,.7,.8,.9/
      DATA(KT(I),I=10,18)/1.,2.,3.,4.,5.,6.,7.,8.,9./
      DATA(KT(I),I=19,27)/10.,20.,30.,40.,50.,60.,70.,80.,90./
      DATA(KT(I),I=28,36)/100.,200.,300.,400.,500.,600.,700.,800.,900./
      DATA(KT(I),I=37,45)/1000.,2000.,3000.,4000.,5000.,6000.,7000.,
     18000.,9000./
      READ 999,(TYPE(I),I=1,2)
999   FORMAT(2A10)
      READ,N,DO2
      READ,(PHI(I),I=1, N)
C
C
      PRINT 888,((TYPE(I),I=1,2),DO2)
888   FORMAT(1H1,2X,*LIMESTONE TYPE *,2A10,5X,*GEOM MEAN DIAM FO FIRST
     1COULTER INTERVAL*,E10.3,//,2X ,*COULTER DISTRIBUTION*,/)
      PRINT 666
666   FORMAT(2X,*MEAN SQUARE DIAM*,9X,*WGT PER CENT*)
      DO 555 I=1,N
      DPSQ(I)=DO2*(1.58740)**(I-1)
      PRINT 777,DPSQ(I),PHI(I)
777   FORMAT(2X,F15.3,20X,F8.3)
555   CONTINUE
      SUM=0.
      KTL=0.
      KTH=0.
      T50=1.0
      PRINT 111
      DO 3 J=1,45
      DO 20 I=1, N
C     EVALUATE THE PRODUCT OF PARTICLE DIAMETERS AT A SPECIFIED
C     DIFFERENTIAL PARTICLE SIZE DISTRIBUTION
      DP(I)=1.-KT(J)/DPSQ(I)
      IF(DP(I).GT.0.) GO TO 30
      GO TO 20
  30  F(I)=DP(I)**1.5*PHI(I)
C     THE ABOVE EXPRESSION CALCULATE THE FRACTION REMAINING FOR A SPECIFY KT
      SUMF=F(I)
      SUM=SUM+SUMF
      IF (I.LT. N) GO TO 20
      PRINT 5,KT(J),SUM
      FR(J)=SUM
      SUM=0.
  20  CONTINUE
3     CONTINUE
111   FORMAT(1H1,9X,*KT*,20X,*PER CENT REMAINING*,//)
5     FORMAT(6X,F10.5,22X,F10.5)
      DO 40 I=1,45
        DIFF(I)=50.-FR(I)
        IF(DIFF(I) .GT.-15. .AND. DIFF(I) .LT. 0.) GO TO 32
           GO TO 99
32         KTL=KT(I)
99      IF(DIFF(I) .LT.15. .AND. DIFF(I) .GT. 0.) GO TO 31
           GO TO 40
31         KTH=KT(I)
```

```
      GO TO 96
40    CONTINUE
96    CONTINUE
      IF(KTH .LT. 1.0) GO TO 50
      RKT=KTL
      DO 60 J=1,100
        RINCR=(KTH-KTL)/100.
        RKT=RKT+RINCR
        SUM=0.
        DO 70 I=1, N
          DP(I)=1.-RKT/DPSQ(I)
          IF(DP(I).GT.0.) GO TO 33
          GO TO 70
33        F(I)=DP(I)**1.5*PHI(I)
         SUMF=F(I)
          SUM=SUM+SUMF
         IF (I .LT.  N) GO TO 70
          ROD=SUM-50.
         IF(ROD .LT.0.1 .AND. ROD .GT.-0.1) GO TO 34
           GO TO 60
34         T50=RKT
           GO TO 80
70       CONTINUE
60    CONTINUE
      IF(T50 .LT. 1.0) GO TO 50
80    PRINT 6
6     FORMAT(//,8X,*KT/KT50*,21X,*FRACTION REMAINING*,//)
      DO 90 I=1,45
      DIFF(I)=KT(I)/T50
      PRINT 7,DIFF(I),FR(I)
7     FORMAT(6X,F10.5,22X,F10.5)
90    CONTINUE
      PRINT 8
8     FORMAT(//,8X,*KT50*,21X,*PER CENT REMAINING*,//)
      PRINT 9,T50,SUM
9     FORMAT(6X,F10.5,22X,F10.5)
      GO TO 100
50    CONTINUE
      PRINT 212
212   FORMAT(/,5X,*NO CONVERGENCE FOR KT50*)
100   STOP
      END
```

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VITA

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This thesis was typed by the author

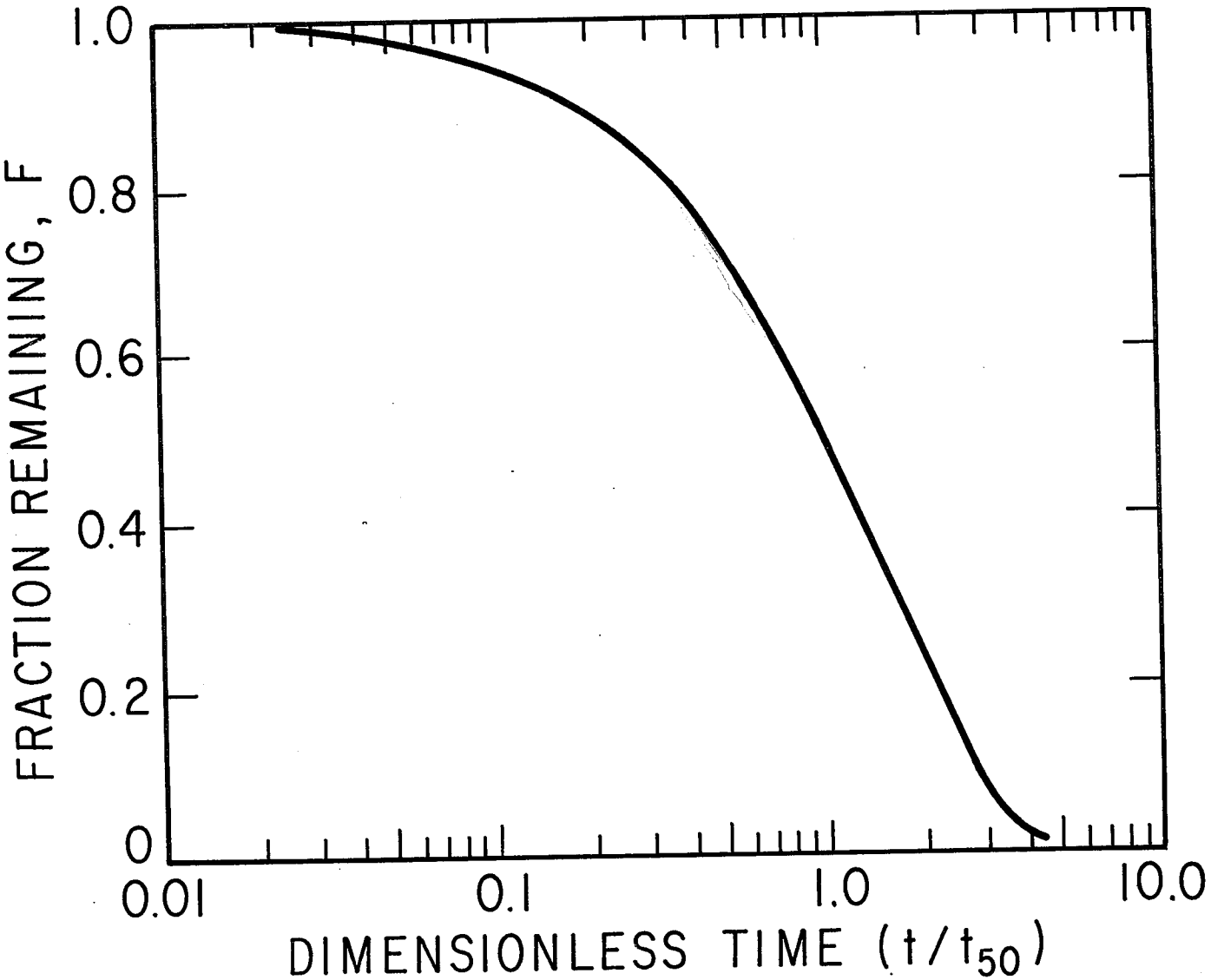
$CaCO_3$ DISSOLUTION IN SO_2 SCRUBBING SOLUTION MASS TRANSFER ENHANCED BY CHEMICAL REACTIONS

APPROVED:

_____

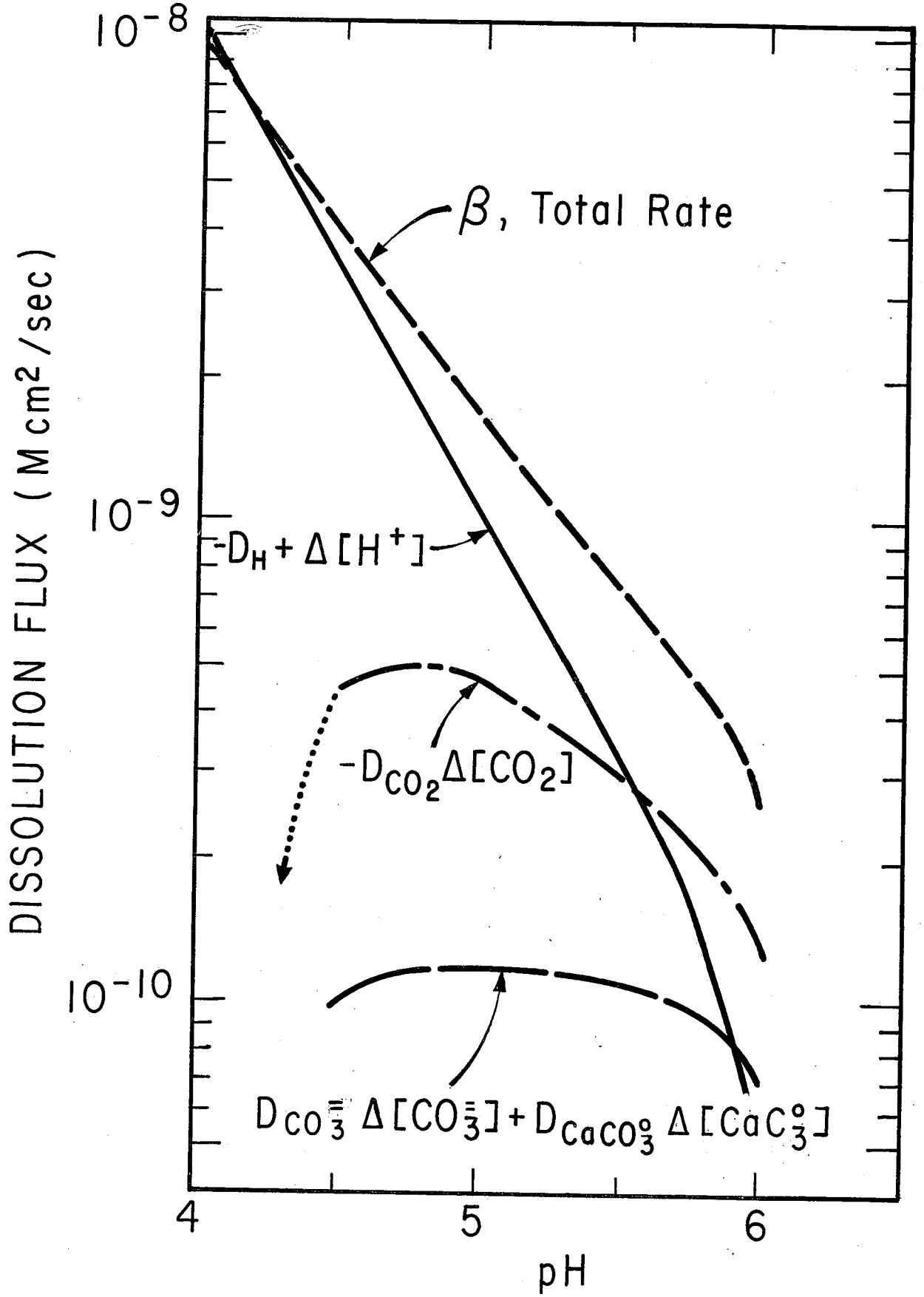
_____

To my mother and in memory of my father


1.0
0.8
0.6
0.4
0.2
0
FRACTION REMAINING, F
0.01
0.1
1.0
10.0
DIMENSIONLESS TIME (t/t50)

PARTICLE DIAMETER, D_p (μm)
0.1
1.0
10
DISSOLUTION RATE (gmol/cm^2-sec)
10^{-9}
10^{-8}
10^{-7}

pH
4
5
6
7
DISSOLUTION RATE (gmol/cm²-sec)
10⁻⁸
10⁻⁹
10⁻¹⁰
P_{CO_2} = 1.0 Bar
0.3 Bar
0.01 Bar


10^{-8}
10^{-9}
10^{-10}
DISSOLUTION FLUX (M cm^2 /sec)
β, Total Rate
$-D_H + \Delta[H^+]$
$-D_{CO_2}\Delta[CO_2]$
$D_{CO_3^{=}}\Delta[CO_3^{=}] + D_{CaCO_3^o}\Delta[CaC_3^o]$
4
5
6
pH

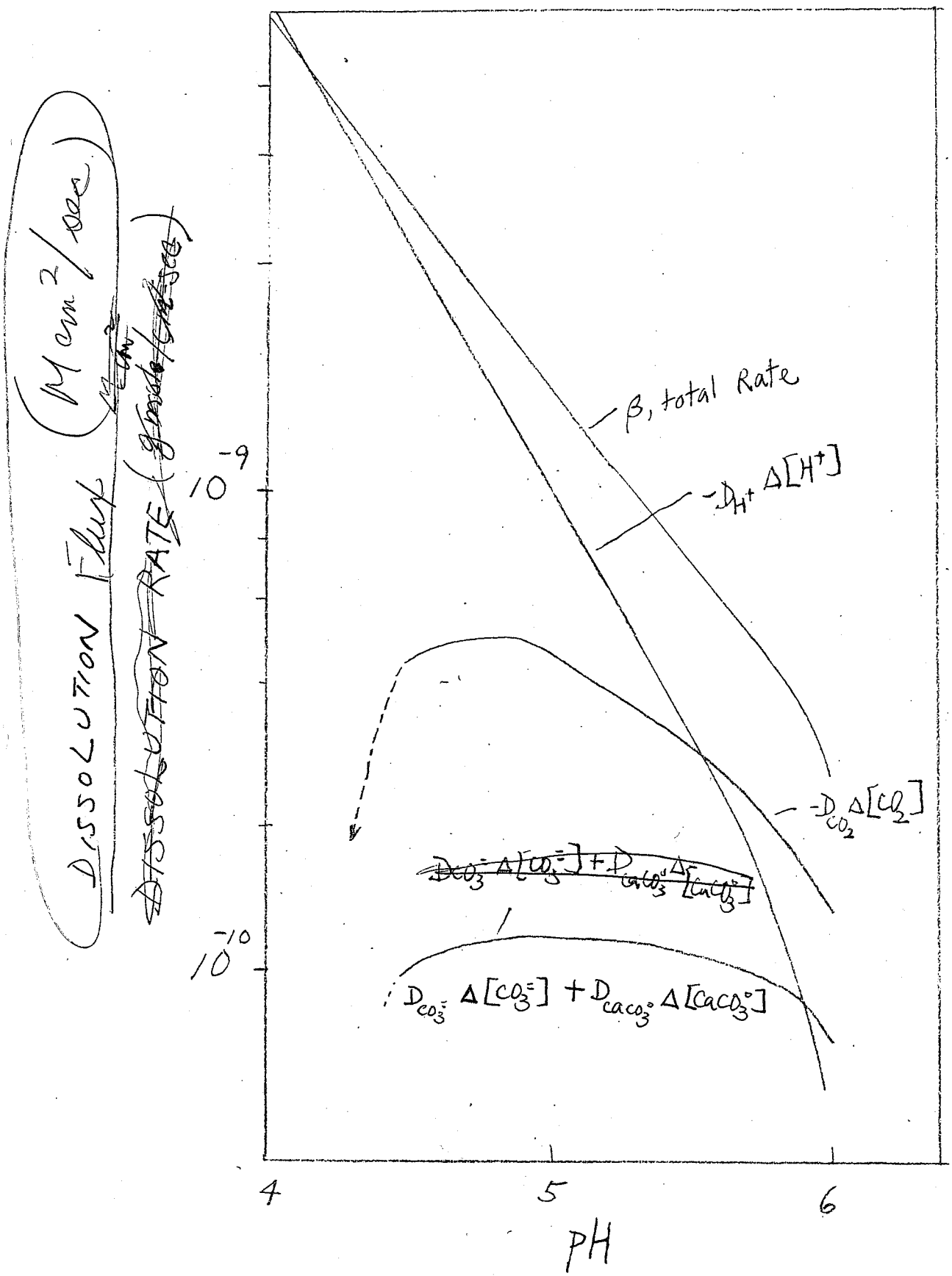


FIGURE 3-2: DISSOLUTION RATE CONTRIBUTION From various chemical Species
P_{CO_2} = 1 atm, $[Ca^{++}]$ = 0.01 M. pH = 2.8 -

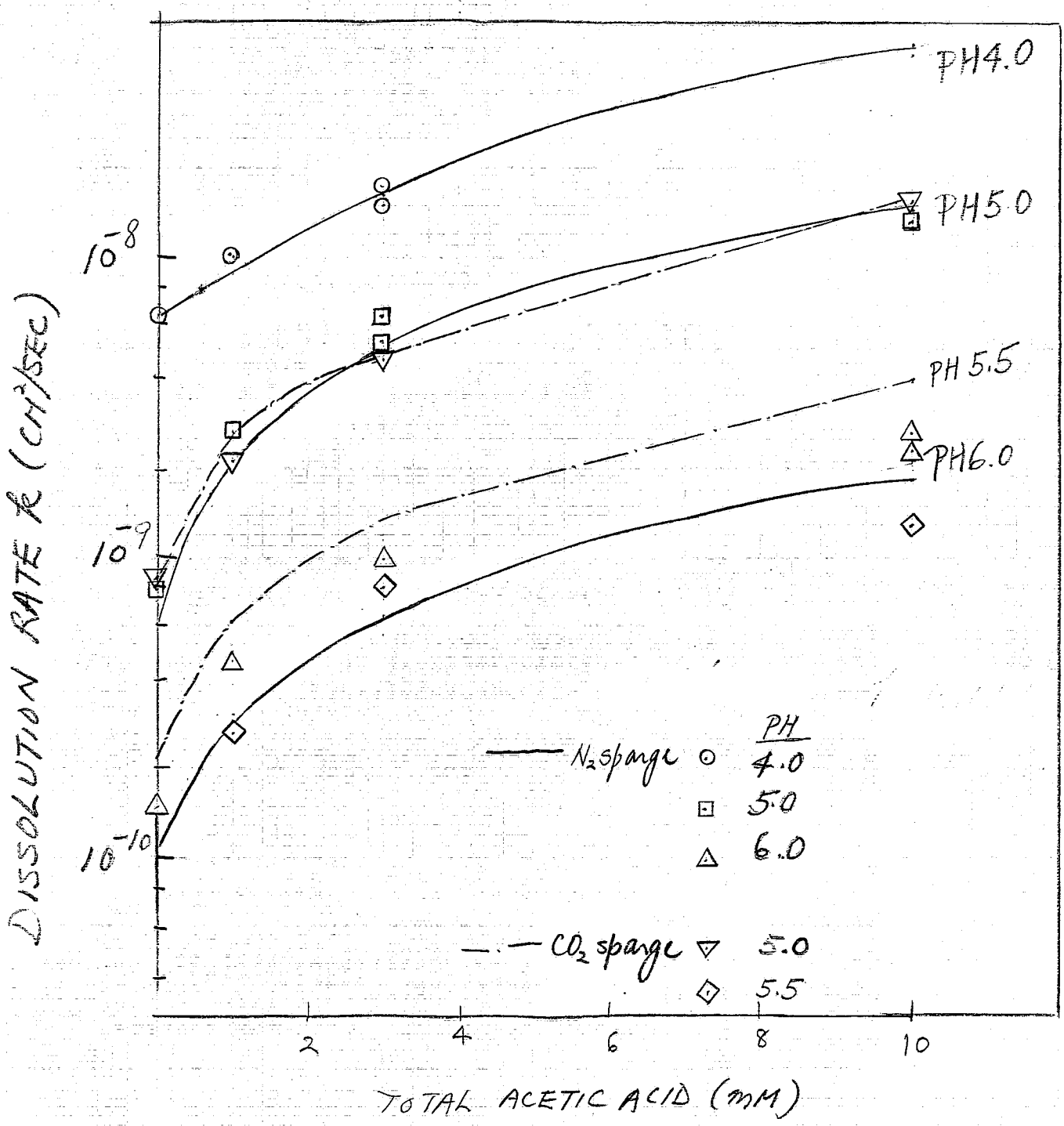
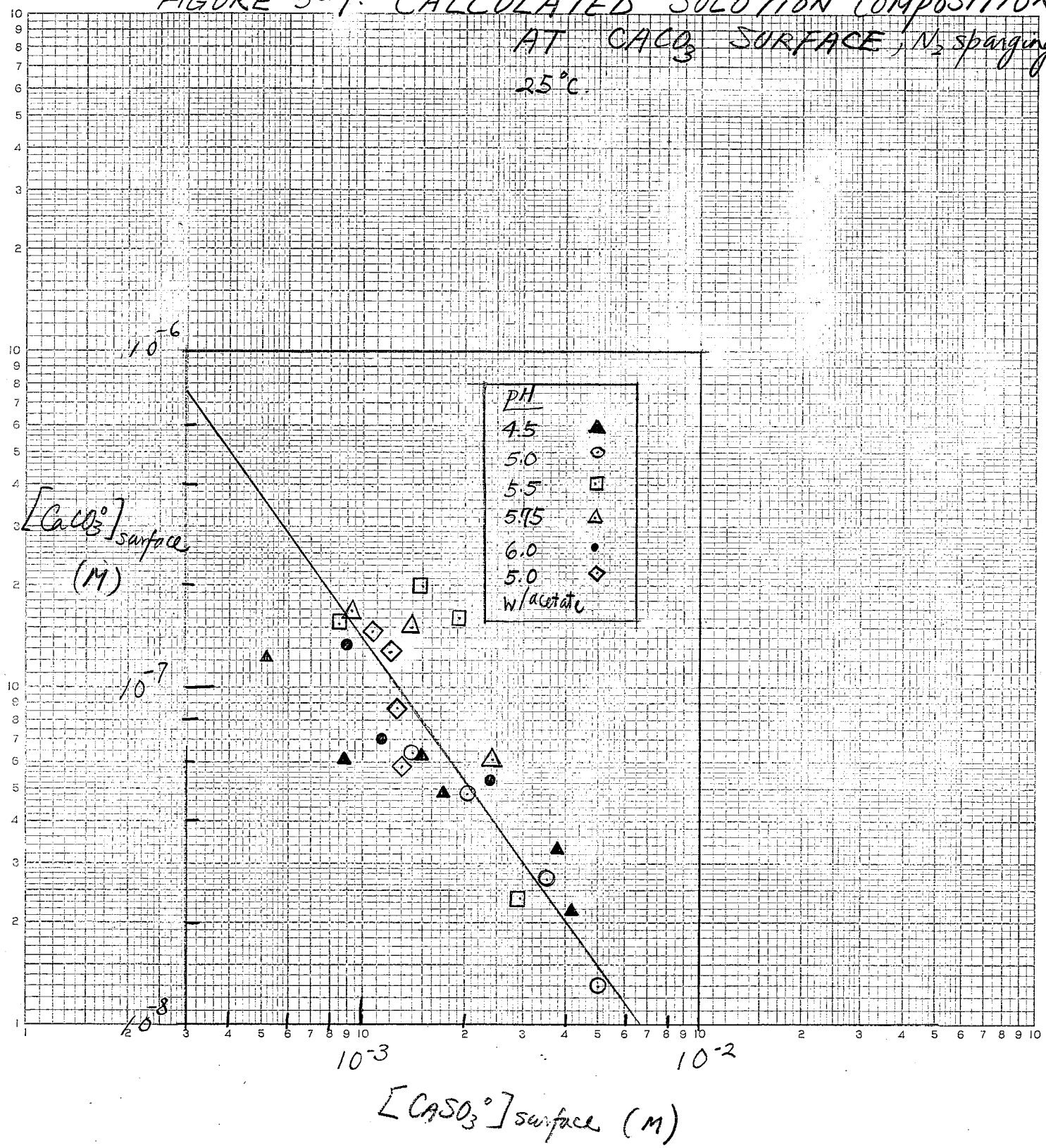


FIGURE 5-4 $CaCO_3$ DISSOLUTION at 25°C in 0.1M $CaCl_2$. effect of Acetic acid.

FIGURE 5-9: CALCULATED SOLUTION COMPOSITION AT $CaCO_3$ SURFACE, N_2 sparging, 25°C.



Full Logarithmic, 3 × 3 Cycles