THE EFFECTS OF PRECIPITATION OF CALCIUM CARBONATE ON SOIL pH FOLLOWING UREA APPLICATION

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ABSTRACT

This thesis describes a series of experiments both in solution systems and soil systems to study the precipitation of calcium carbonate in soils and the effects of the precipitation on soil pH after urea had been applied.

(1) A gas bubbling system has been established which introduces ammonia at a steady rate to the reaction solution and keeps it equilibrated at 0.00484 atm partial pressure of carbon dioxide.

(2) In a non-seeded system, the effects of calcium, urea, Mg (magnesium), P (phosphate), and DOC (water-dissolved organic matter) on the precipitation were examined individually and in various combinations.

Calcite and vaterite were found in the 10 mM $CaCl_2$ solutions with and without the addition of urea. When the solutions contained Mg, P, and DOC, vaterite was not found. Aragonite was found in the reaction solution containing 5 mM Mg.

In high initial concentration of P (5×10^{-4} M), the formation of calcium phosphate (amorphous by X-ray analysis) catalysed the formation of calcite. The effects of urea and Mg on the precipitation are negligible compared with the effects of P and DOC.

(3) In a seeded system, 16 sets of experiments with four sizes of calcite-seeds were carried out to study the precipitation rate of calcium carbonate. This was described by the equation

$$LR = -4.113 \pm 0.132 + 0.379 \pm 0.029\ LWA + LSI$$

where LR=log(precipitation rate, PR, in mole litre^{-1} min^{-1}), LWA= log(newly formed calcium carbonate, g ml^{-1}), and LSI=log(degree of supersaturation of calcium carbonate, SI).

(4) A wide range of concentrations of urea (0.05, 0.1, 0.3, 0.5, 0.7, and 1 M) were added to three soils (Beg., Uni., and VWH) with or without the addition of 5 per cent of calcite (10-15 μm) to establish a rate model for the precipitation of calcium carbonate in soils. The precipitation model (in logarithmic form) in soils is

$$\ln PR = -9.47 \pm 0.30 + \ln K_{SOIL} + 0.379 \pm 0.029\ \ln WA + \ln SI - 1686 \pm 703\ P - 6.13 \pm 3.02\ DOC + 3854 \pm 1775\ (P\ DOC)$$

where P and DOC are the concentrations in soil solutions, and $\ln K_{SOIL}$ is the effect of soils on the precipitation, which is -1.98, 0.43, and -0.10 for Beg., Uni., and VWH soils respectively.

The amount of newly formed calcium carbonate is about a third to a half of the amount of ammoniacal-N released by urea hydrolysis. It was able to reduce the increase of soil pH by more than 0.6 pH units in some circumstances.

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Symbols and Definitions

AADR	Apparent ammonia dissolution rate, in mol. litre^{-1} min^{-1}.
B_{CaCO3}	The concentration of base in solution dissolved from calcite-seeds.
Beg.	Begbroke soil, Sutton series.
B_{NH3}	The concentration of base in solution dissolved from ammonia.
CEC	Cation exchange capacity, in me/100 g of oven-dry soil.
DOC	Water-dissolved organic matter, in mol. litre^{-1} of carbon.
1.) K_{CIAP}	The ion activity product of calcite.
K_{SOIL}	The effect of soil on the rate of precipitation of calcium carbonate in soil.
NT	The total concentration of ammoniacal-N, in mol. litre^{-1}.
P	Phosphate, in mol. litre^{-1}.
P_{CO2}	The partial pressure of carbon dioxide, in atm.
pH_p	The peak pH of reaction solutions.
pK_{CIAP}	$pK_{CIAP}=-\log(K_{CIAP})$.
P_{NH3}	The partial pressure of ammonia, in atm.
2.) PR	The rate of precipitation of calcium carbonate, in mol. litre^{-1} min^{-1}.
PVT	PVC tubing.
RE	The replication of experiment.
3.) SI	The degree of supersaturation of calcium carbonate with respect to calcite, i.e. $SI=(Ca^{2+})(CO_3^{2-})/K_{CIAP}$.
SGGB	Sintered glass gas bubbler.
Uni.	University Parks soil, Sutton series.
VWH	The soil of the Vale of White Horse, Denchworth series.
WA	The newly formed calcium carbonate.

1. K — Rate constant of calcium carbonate precipitation.
2. ppm — Part per million.
3. S — Surface area of precipitates, cm^2/ml.

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CHAPTER 1

INTRODUCTION

Modernization of agriculture is essential to meet the challenge of the increasing demand for food as a consequence of the demographic explosion of the world's population. Modern methods of cropping, mechanization, more productive breeding practices and highly efficient use of fertilizers are necessary not only from the economic point of view but from the ecological viewpoint also. It is increasingly important to avoid depleting and polluting the world's natural resources with inappropriate use of fertilizers.

The large amount of nitrogen fertilizers required by most agricultural crops and the complex transformations (e.g. nitrification, denitrification, and ammonia volatilization) between different forms of nitrogen in soils, make nitrogen unique among the fertilizer nutrients. Urea is becoming a major solid nitrogen fertilizer because of the unlimited supplies of nitrogen in the air for factory production, low cost, high nitrogen content and good physical characteristics for storage, distribution and application (Engelstad and Hauck, 1974; and Sharratt, 1983).

Ammonia volatilization is strongly related to high concentrations of ammoniacal-N and to pH. It has been recognized as one of the major processes that cause nitrogen loss from soils. The urease activity of most arable soils is high and most of the applied urea is hydrolysed within a few days. This results in a rapid rise of soil pH and the rise of pH favours ammonia volatilization, especially when urea is applied to the surface of neutral and alkaline soils.

The addition of calcium carbonate to soils increases soil

pH and increases ammonia volatilization (Ryan et al., 1981). However, many workers (Terman and Hunt 1964; Boateng and Ballard, 1978; Terman, 1979; Fenn and his co-workers, 1973; 1981[abc]; 1982[ab]; and 1986) have suggested that if urea plus soluble salts of calcium or other cations are applied to soil the precipitation of further calcium carbonate may lead to a reduction in the rise of soil pH and hence in the loss of ammonia. The theoretical equilibrium solution pH is 7.12 when calcite is added to a 10 mM calcium chloride solution at a temperature of 25^0 C and a partial pressure of carbon dioxide of 0.00484 atm. However when urea is applied to soil, soil pH could rise to 9.0 (Rachhpal-Singh, 1984); thus calcium carbonate may precipitate after urea is added to soil.

The precipitation of calcium carbonate has been studied widely in geochemistry, oceanography, physiology, and pedogenetic chemistry. Initially its rate is controlled by the nucleation reaction, which may be homogeneous (on old or new calcium carbonate) or heterogeneous (on other materials), and then controlled by crystal growth (Johnson and O'Rourke, 1954; Nanchollas and Reddy, 1971; Kamiyar et al., 1977; House, 1981).

It is recognised that certain inhibitors were able to retard the precipitation of calcium carbonate, which may encourage the formation of polymorphs. Their inhibitory mechanisms are, however, not fully understood.

The aim of this project was to study the effects of the precipitation of calcium carbonate on soil pH, particularly after urea application. Presumably the results from this study can be extended to other forms of ammoniacal-N fertilizers. The study concentrated on the effects of certain soil factors (e.g. precipitation inhibitors) on the precipitation processes rather

than on the mechanisms of calcium carbonate precipitation as such. It is necessary to know the magnitude of the effective components that significantly affect the rate of precipitation of calcium carbonate in soils in order that soil pH may be predicted following treatments which tend to raise soil pH to high levels. This information could have important applications, for example, in developing a comprehensive model to predict the extent of ammonia volatilization. However, the development of an ammonia volatilization model is beyond the scope of this thesis.

Sadeghi et al (1988) assume that calcium carbonate in soil solution enabled equilibrium to remain at the ion activity product of calcite, $K_{CIAP}=5x10^{-9}$, whenever calcium carbonate precipitates or dissolves. However, inhibitors such as magnesium, phosphates, and DOC (water-dissolved organic matter) may be in sufficient concentrations in soil solutions to alter the equilibrium and to affect calcium carbonate precipitation significantly.

When urea is added to soils, its hydrolysis will yield ammonium bicarbonate, and increase soil pH and the activities of bicarbonate and carbonate ions. This will increase the product of Ca^{2+} and CO_3^{2-} in the soil solution and potentially increase calcium carbonate precipitation. In order to study the effects of soil factors on calcium carbonate precipitation, it is necessary to simulate conditions in the laboratory that resemble those when urea is added to soil, but it is difficult to establish reproducible systems that release ammonia at a constant rate from solutions containing urease because :

(1) urease activity in the soil is strongly affected by environmental factors, such as soil pH and urea concentration (Rachhpal-Singh and Nye, 1984[a]).

(2) preliminary experiments show that the activity of commercial urease (from BDH) decreased quickly after it was added to aqueous solution.

For these reasons a bubbling system was developed to obtain a reproducible experimental system which introduces ammonia gas to the reaction solution at a steady rate which is referred to as the constant apparent ammonia dissolution rate, AADR.

This thesis falls into six chapters, each chapter has a literature survey and related experiments. Basic information (e.g. thermodynamic constants), the chemical reactions, the technique of the determination of DOC in soil solutions using a UV spectrophotometer, the determination of soil buffer capacity, and some related data are given in appendices.

Chapter 2 describes the development of the bubbling experimental system for adding ammonia steadily to the reaction solution and controlling the reaction system under a constant P_{CO2} (the partial pressure of carbon dioxide).

Chapter 3 describes the precipitation of calcium carbonate, with and without the addition of calcite-seeds, using the bubbling system. A concept is developed which uses the "peak pH" (the peak of pH in the reaction solution) to compare the effects of different inhibitors on the precipitation of calcium carbonate. At the "peak pH" the release rate of acidity from calcium carbonate precipitation is equal to AADR. Experiments seeded with calcite-seeds were used to determine the effects of the degree of supersaturation (SI) of calcium carbonate with respect to the ion activity product of calcite (K_{CIAP}) in the reaction solution, and the effects of the presence of particles (initial seeds and newly formed calcium carbonate) on the precipitation. A technique

was developed to estimate the quantity of calcium carbonate precipitated from the measured solution pH and AADR using the bubbling system.

Chapter 4 uses measurements of the "peak pH" in a non-seeded system, to examine the effects of urea, magnesium, phosphate and DOC singly or together, on the precipitation and the formation of polymorphs of calcium carbonate.

Chapter 5 extends the results from chapters 3 and 4 to three soils (Begbroke, University Parks, and the Vale of White Horse) and describes :

(1) changes in soil chemical properties, including soil pH, the concentrations of phosphate and DOC in soil solutions, and the quantity of calcium carbonate precipitated, following urea application.

(2) the development of a model to describe the precipitation of calcium carbonate in soil systems.

Chapter 6 summarizes the extent to which urea, magnesium, phosphate, and DOC affect calcium carbonate precipitation.

CHAPTER 2

DEVELOPMENT OF THE EXPERIMENTAL SYSTEM

2.1 INTRODUCTION

In order to investigate the effects of precipitation of calcium carbonate on soil pH after the application of urea, an understanding of the process of precipitation is crucial. It has been reported that oversaturation with respect to calcite ranges from 3 to 5 times the equilibrium solubility in naturally occurring water (Levy, 1981[ab]) to 30 to 40 times in soil solutions (Suarez and Rhoades, 1982; and Inskeep and Bloom, 1986[a]). It ranges from 2 to 5 in well waters (Suarez, 1977), to 10 to 100 in lake waters, and is near 4 in typical sea water (Berner et al., 1978). Although intensive studies have been carried out to examine this oversaturation, and much effort has been devoted to investigating the mechanisms which cause the build-up of such oversaturation, many questions remain unanswered.

The problem has been examined using thermodynamic and kinetic techniques. It has been examined in homogeneous and heterogeneous systems; with or without seeds of various forms of calcium carbonate or other crystals; and under conditions of dissolution or precipitation, with or without inhibitors. Most of the work has involved the precipitation of calcium carbonate from initial conditions of high supersaturation, rather than from a gradual increase in saturation. However, the development of oversaturation of calcium carbonate in natural environments from natural causes is unlikely to start from a highly supersaturated condition. Highly supersaturated solutions were prepared by mixing solutions of calcium chloride and sodium bicarbonate (Reddy and Nancollas, 1971) or sodium carbonate (deBoer, 1977),

or by dissolving calcite in a solution with pure carbon dioxide and then outgassing carbon dioxide by flushing the system with carbon dioxide free nitrogen gas (House, 1981[b]; House and Tutton, 1982; and Reddy et al, 1981). The precipitation was started by adding calcite seeds. Under such experimental conditions, there were several problems :

(1) One probably cannot assume a constant value for the partial pressure of carbon dioxide (P_{CO2}), which is assumed to be involved in the precipitation reaction (Plummer et al, 1978), and in the state of equilibrium of carbon dioxide between the gas, liquid, and solid phases.

(2) Since calcium and carbonate ions were added into the reaction solution stepwise to keep one or both of them at a desired concentration, the volume of the reaction solution and the ratio between seeds and solution in the seeded systems were changing all the time. This made the system very complex.

Furthermore, the aim of this research is not only to improve our understanding but also to provide a basis for tackling environmental problems. If the experimental system is too far removed from the natural conditions, the application of the achieved results may be limited and unreliable, and may need careful modification. Therefore, it is of great importance to develop a suitable experimental system.

When urea is added to soils, the source of base in solution is NH_4HCO_3 which is released during the hydrolysis of urea, as in reaction 2.1 (Blakely et al., 1969).

$$CO(NH_2)_2 + 3H_2O + CO_2 \text{ <=> } 2NH_4HCO_3 \qquad (2.1)$$

It is important to supply a stable and constant addition of NH_4HCO_3 to the reaction solution. The method most consistent with natural situations is one which generates NH_4HCO_3 in the reaction

medium. It is, however, very difficult to achieve a constant rate of hydrolysis using commercial urease, as urease activity is strongly affected by factors such as urea concentration, solution pH, and temperature. Preliminary experiments showed that urease activity was unstable in laboratory experiments unless extreme care was taken. An inorganic procedure is probably easier to control than a biological procedure such as the urease hydrolysis of urea. Therefore, a bubbling system with a mixture of ammonia and carbon dioxide gases might be a better alternative.

The bubbling system should satisfy the following requirements :

(1) Ammonia should be added to the aqueous solution steadily in order that the amount of added base could be simply calculated by reaction time.

(2) The P_{CO2} in the reaction solution should be kept constant, i.e. the P_{NH3} (the partial pressure of ammonia) and other chemical reactions such as the formation of calcium carbonate, which may release carbon dioxide, should not affect the initial P_{CO2} significantly. If P_{CO2} in the reaction solution is not constant the experimental system would be more complicated.

This chapter is divided into three sections. Section 2.2 describes the standard set-up of the bubbling experimental system, and the dissolution of ammonia and carbon dioxide gases and following reactions in aqueous solutions. Section 2.3 presents some preliminary experiments without (section 2.3.1) or with (section 2.3.2) precipitation inhibitor (phosphate) to check the application of the bubbling system to studying the precipitation of calcium carbonate.

2.2 The dissolution of carbon dioxide and ammonia and their

reactions in aqueous solutions

This section is divided into five subsections :

(1) Section 2.2.1 describes the standard set-up and experimental procedures of the bubbling system.

(2) Section 2.2.2 presents experiments which were carried out to determine the effect of gas flow rate on the dissolution of carbon dioxide in a bubbling system.

(3) Section 2.2.3 examines the effect of the use of a magnetic stirrer on the dissolution of carbon dioxide in aqueous solution.

(4) Section 2.2.4 describes how to estimate solution pH from the partial pressure of carbon dioxide and the total concentration of ammoniacal-N dissolved from ammonia in the aqueous solution.

(5) Section 2.2.5 presents experiments which were carried out to establish a suitable concentration of ammonium bicarbonate, the "source solution", which would yield an appropriate mixture of ammonia and carbon dioxide gases, and also to determine a convenient gas flow rate.

2.2.1 The standard set-up and experimental procedures of the bubbling system

Figure 2.1 shows the standard set-up of the bubbling system used in all experiments carried out in chapters 2, 3, and 4; except that necessary adjustments were required for special treatments. The steps in experimental procedures were as follows :

(1) A mixed gas (containing 0.5 % of carbon dioxide and 99.5 % of nitrogen, purchased from British Gas Company) from a compressed cylinder (a) was led to pass a gas regulator (b).

(2) It was bubbled through a 2 litre flask (c) containing double distilled water. This flask was used to saturate the gases with

water vapour (23.8 mm Hg at 25^0 C), and as a pressure buffer vessel for controlling the gas flow rate.

(3) The mixed gas was bubbled through another 2 litre flask (d). This vessel contained ammonium bicarbonate solution and is referred to as the "source solution" because when the mixed gas came out of the vessel it carried ammonia gas. By controlling the gas flow rates and ammonium bicarbonate concentrations, a steady flow of ammonia was produced. The change in concentration of total ammoniacal-N in the "source solution" was negligible even after being bubbled for over 24 hours.

(4) The mixed gas passed a sensitive gas regulator (e1) and a calibrated gas flow meter (e2).

(5) Then the mixed gas was led into a 100 ml pyrex beaker containing 60 ml of reaction solution (f). Different solution components (such as precipitation inhibitors) were added into the reaction vessel according to different treatments. The reaction vessel was stopped with a rubber bung with holes for holding electrodes (a combined pH electrode (Philips CE8, or Pye Unicam Ingold) and sometimes with calcium-sensitive electrodes (Philips ISE 310)) and gas supply tubes, and a small hole (j) left for releasing gas pressure. In the calcite-seeded experiments the reaction vessel was a tube (described in chapter 3).

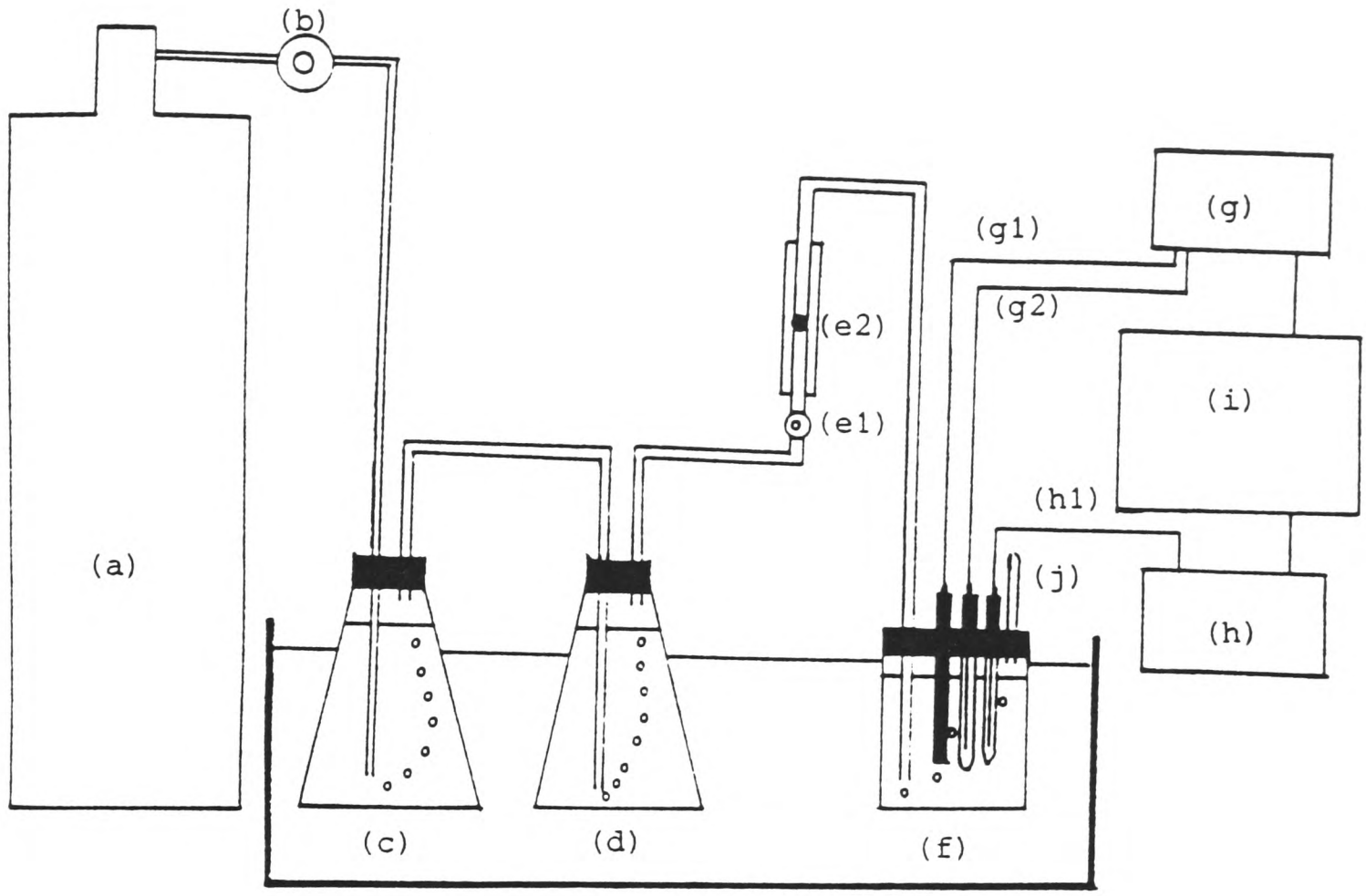
(6) Finally the reaction solutions were monitored by pH (h1) and calcium-sensitive electrodes (g1 and g2) with meters Orion 701A (g) and Philips PW 9418 (h), and a double pen recorder/Kelvin (i).

(7) All experiments in this study were carried out in a water bath (k) with temperature kept at 25.0 ± 0.1^0 C.

(8) At varying periods a 2 ml syringe was used to take 1 ml of reaction solution for determining the concentration of ammonia-

cal-N using the indophenol blue method (Page et al, 1982) and for determining other components when it was necessary.

Figure 2.1 THE LAYOUT OF THE EXPERIMENTAL SYSTEM.



(k)

(a) gas cylinder. (b) gas regulator.
(c) double distilled water container (2 litre flask).
(d) "source solution" container (2 litre flask).
(e1) and (e2) gas regulator and gas flow metre.
(f) reaction solution vessel (100 ml pyrex beaker).
(g), (g1), and (g2) mV metre, calcium-sensitive electrode, and calomel reference electrode.
(h) and (h1) pH metre and combined pH electrode.
(i) double pen recorder.
(j) pressure release hole.
(k) water bath.

(9) Precipitates were collected by putting a cover slip into the reaction solutions and examined by light microscope (Swift), SEM scanning electron microscope (Cambridge Steroscan 150), and X-ray diffractometer (Philips). Surplus solution was removed with a tissue immediately after the slip was taken out of the reaction solution.

(10) The pH electrode was calibrated with standard buffer

solutions (pH 4.00, 7.00, and 9.00 from BDH) before it was put into the reaction solution and at the end of each experiment. The calcium-sensitive electrode was also calibrated with standard solutions containing concentrations of $CaCl_2$ at 10, 1, 0.1, and 0.01 mM before and after each measurement.

2.2.2 The effects of gas flow rate on the equilibrium time for dissolution of carbon dioxide

The dissolution rate of gas is proportional to the magnitude of disequilibrium, the surface area of the interface between gas and liquid phases, and agitation. In a bubbling system, gas flow rate affects the gas dissolution rate, thus it is necessary to ensure that the fluctuation of gas flow rate does not affect the dissolution of gas significantly.

The dissolution of ammonia and carbon dioxide from the gas phase into aqueous solutions and their corresponding dissociation reactions have been clearly outlined elsewhere, both in terms of kinetics and thermodynamics, and so it is unnecessary to present a detailed discussion here. The hydration rate of ammonia in aqueous solution is very rapid. Equilibrium is closely approached in a few microseconds to milliseconds, and is much faster than that of carbon dioxide, whose hydration equilibrium needs a few minutes (Stumm and Morgan, 1981). The dissolution of carbon dioxide will be the rate-limiting step for a solution containing ammonia and carbon dioxide to reach equilibrium at given partial pressures of ammonia and carbon dioxide. Thus carbon dioxide was used to determine the effects of gas flow rate on the dissolution of gas in the bubbling system.

<u>The pH and activities of carbonic ions in a H_2O-CO_2 system</u>

When an aqueous solution is equilibrated under a partial

pressure of carbon dioxide (P_{CO2}), the composition is determined by solution pH, P_{CO2}, and temperature. A compressed gas mixture containing 99.5 % nitrogen and 0.5 % carbon dioxide by volume was used throughout this study. The initial P_{CO2} of the gaseous mixture is 0.005 atm at ambient pressure and the saturated water vapour pressure is 23.8 mm Hg at 25^0 C, therefore

P_{CO2}=0.005x((760 mmHg - 23.8 mmHg)/760 mmHg)=0.00484 (atm)

after equilibration in aqueous solution.

The dissolution of carbon dioxide from the gas phase into the aqueous phase is described by equations 2.2 and 2.3,

$$CO_{2(g)} \Leftrightarrow CO_{2(aq)} \qquad (2.2)$$

$$CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_{3(aq)} \qquad (2.3)$$

where (g) represents the gas phase, and (aq) represents the aqueous phase. The equilibrium constants for equations 2.2 (Henry's constant : H_{CO2}) and 2.3 (hydration constant) are quoted in Table A.2.1 of appendix 2. According to the reaction constant of equation 2.3 (1/650 : Table A.2.1), the concentration of $H_2CO_{3(aq)}$ is much lower than of $CO_{2(aq)}$, so their combined concentration H_2CO_3*, where H_2CO_3*=$H_2CO_{3(aq)}$ + $CO_{2(aq)}$, is commonly used to describe the first dissociation reaction of carbonic acid (2.4).

$$H_2CO_3^* \Leftrightarrow HCO_3^- + H^+ \qquad (2.4)$$

The second dissociation equation is described in equation 2.5.

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \qquad (2.5)$$

If H_2CO_3* is used instead of $H_2CO_{3(aq)}$, and equations 2.2 and 2.3 are combined, the concentration of H_2CO_3* can be calculated directly from P_{CO2},

$$H_2CO_3^* = H_{CO2}\ P_{CO2} \qquad (2.6)$$

where H_{CO2} is Henry's constant. After rearranging equations 2.4 and 2.5, the activities of the bicarbonate and carbonate ions can be calculated from H_2CO_3*,

$$(HCO_3^-) = k1\ (H_2CO_3^*)/(H^+) \qquad (2.7)$$

$$(CO_3^{2-}) = k1\ k2\ (H_2CO_3^*)/(H^+)^2 \qquad (2.8)$$

where k1 and k2 are the first and second dissociation constants of carbonic acid, and round brackets represent ion activities. At low ionic strength, the activities of solution components are assumed to be equal to their concentrations. Thus the terms for activity in equations 2.7 and 2.8 can be used to denote concentration. In the solutions of higher ionic strength, equations 2.7 and 2.8 can be used to calculate the concentrations of bicarbonate and carbonate ions if they are divided by their ion activity coefficients, in the form

$$[HCO_3^-] = (HCO_3^-)/f_{HCO3} \qquad (2.9)$$

$$[CO_3^{2-}] = (CO_3^{2-})/f_{CO3} \qquad (2.10)$$

where square brackets represent concentrations and f_{HCO3} and f_{CO3} are the activity coefficients of bicarbonate and carbonate ions respectively, calculated by the Debye-HÜckel equation.

An actual calculation will make this clearer. In the experimental system P_{CO2} is 0.00484 atm, hence

$$H_2CO_3^* = 0.0339 \times 0.00484 = 1.64\times10^{-4}\ M \qquad (2.11)$$

where 0.0339 is Henry's constant (H_{CO2}). Then, with $H_2CO_3^* = 1.64\times10^{-4}$ M k1=4.446×10^{-7}, and k2=4.688×10^{-11}, the activities of bicarbonate and carbonate ions at any solution pH can be calculated.

$$(HCO_3^-) = 4.446\times10^{-7} \times 1.641\times10^{-4}/(H^+) \qquad (2.12)$$

$$(CO_3^{2-}) = 4.446\times10^{-7} \times 4.688\times10^{-11} \times 1.641\times10^{-4}/(H^+)^2 \qquad (2.13).$$

The negative logarithms of equations 2.12 and 2.13, produce two simple equations(2.14 and 2.15)

$$p(HCO_3^-) = 10.14 - pH \qquad (2.14)$$

$$p(CO_3^{2-}) = 20.47 - 2pH \qquad (2.15)$$

where pH is the solution pH. In the H_2O-CO_2 system without other solutes, the charge balance is

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{-2}] \quad (2.16)$$

At low solution pH, the concentrations of $[OH^-]$ and $[CO_3^{-2}]$ are negligible compared to that of $[HCO_3^-]$, so the concentration of $[H^+]$ is nearly equal to the concentration of $[HCO_3^-]$. At low concentrations of solutes, the activities of (H^+) and (HCO_3^-) are almost equal to their corresponding concentrations, so $p(HCO_3^-)$ is almost equal to pH. With pH substituting for $p(HCO_3^-)$ and rearranging equation 2.14, the equilibrium solution pH will be 5.07 when P_{CO2} is 0.00484 atm and temperature is 25^0 C.

Equations 2.14 and 2.15 are useful for describing the relationships between the activities of bicarbonate and carbonate ions and solution pH.

It is well established that the increase of interface area increases the dissolution rate of gas. Increase of gas flow rate and/or a decrease of bubble size increases the interface area per unit of time, and increases the dissolution rate, therefore it decreases the reaction time. Two types of gas bubblers were used, one was PVT (PVC tubing) and the other was SGGB (Sintered glass gas bubbler P160). In this experimental system, the SGGB tube has a perforated plate producing a number of streams of small bubbles, while the PVT just has one hole (0.3 cm diameter) producing a stream of bubbles. The apparent interface area of the bubbles produced from SGGB bubbler is certainly greater than that from PVT. The dissolution rate from SGGB bubbler should be, therefore, greater than that from the PVT tube at the same gas flow rate. The aim of this section was to study whether the effect of gas flow rates on the dissolution of carbon dioxide from these two bubblers was different.

2.2.2.1 Materials and Methods

The standard set-up (page 9) of the bubbling system was used under the following conditions : -

(1) The "source solution" was double-distilled water.

(2) The reaction solution was double-distilled water.

(3) The gas flow meters were calibrated before use by measuring release volume. Different gas flow rates, varying from 15 to 231 cm^3 min^{-1} were used for this study.

(4) Experiments were terminated when the solution pH was equilibrated (steady at about pH 5.07).

(5) Four replications were run for each gas flow rate.

The lapse of time from the beginning of each run to the state of equilibrium was referred to as the "reaction time". The "reaction time" should reflect the dissolution rate of gas. The shorter the "reaction time", the greater the dissolution rate of gas will be. The aim of this part was to study the effect of the gas flow rate on the dissolution of gas (carbon dioxide). The relationship between the gas flow rate and "reaction time" was used to examine the effect so it did not seem necessary to show individual values for changes in solution pH. The flat part of the curve of solution pH against time shown on the chart was used to determine the "reaction time" for each run and to measure the equilibrium time in minutes.

2.2.2.2 Results and Discussion

The pattern of the change in solution pH after carbon dioxide gas was bubbled into the reaction solution (double distilled water) was similar for all gas flow rates. At the beginning the solution pH decreased abruptly, then less sharply, and finally remained steady. The average value of solution pH of all runs was 5.05±0.05. Considering that the experimental data

were determined with two type of pH electrodes, the variation of pH is acceptable, and it agrees with the calculated value pH 5.07.

Figure 2.2 illustrates the relationship between the "reaction times" and gas flow rates (the standard deviation was 10 percent for both gas flow rate and "reaction time"). In the graphs the points ("reaction time"), which represent data using the SGGB bubbler, are all lower than those points which represent the data using the PVT tube. This may show that the experimental results agreed with the hypothesis that the "reaction times" from the experiments with the SGGB bubbler were shorter than those from the PVT tube at the same flow rate.

Figure 2.2 THE EFFECTS OF GAS FLOW RATES ON THE EQUILIBRIUM TIME OF THE DISSOLUTION OF CARBON DIOXIDE, 0.00484 atm, IN DOUBLE DISTILLED WATER WITH PVT TUBE AND SGGT PERFORATED PLATE.

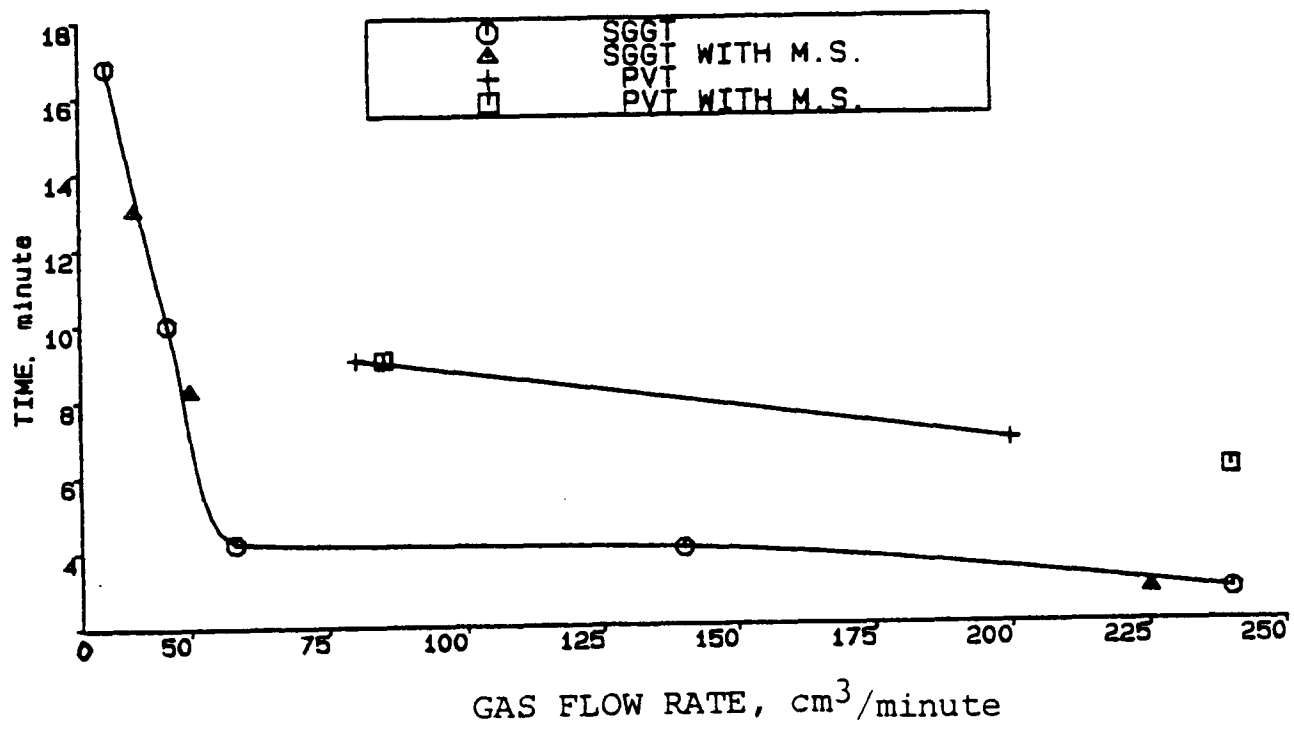


Figure 2.2 also shows that the "reaction time" needed for the dissolution reaction to reach equilibrium was inversely proportional to the gas flow rate over the low range (< 60 cm^3 min^{-1}) of flow rates in the SGGB series. An abrupt change of the "reaction time" was observed when the rate of gas flow was around

60 cm^3 min^{-1}. Above 60 cm^3 min^{-1} further increase of the gas flow rate did not decrease the "reaction time" greatly, so it was assumed that the further increase of gas flow rate did not greatly affect the dissolution rate of carbon dioxide. For example, when the flow rate was increased by about 200 per cent (from 80 to 231 cm^3 min^{-1}) the reaction time did not change significantly (from 4.2±0.5 minutes to 4.0±0.5 minutes). The results from the experiments using the PVT tube also had the similar response pattern of gas flow rate against reaction time as that of the SGGB. Therefore, if the gas flow rate is set at the high range, the variability of the dissolution of carbon dioxide caused by small fluctuations in the gas flow rate should be negligible.

2.2.3 The effect of agitation on the dissolution of gas

Stirring systems are widely used in laboratory experiments. In the experimental system in section 2.2.2, the gas bubbles are the only stirring force in reaction solutions. One may doubt whether this stirring force is enough to mix components from the interface between gas and aqueous phases into bulk solution. It was necessary to determine whether an extra stirring force was needed in the bubbling system. Thus a magnetic stirrer was introduced to the bubbling system to check whether the additional stirring force would affect the dissolution rate of carbon dioxide.

2.2.3.1 Materials and Methods

Using the experimental system and methods in the above section, a magnetic stirrer (Gallenkhamp) was used in the reaction solution with the stirring speed set at about 200 rpm.

Four replications were completed for each treatment.

2.2.3.2 Results and Discussion

The pattern of changes in solution pH in the experimental system using a magnetic stirrer was similar to that without it (above section). Figure 2.2 also shows that the correlations of the "reaction time" against gas flow rate in experiments with the magnetic stirrer were equal or close to the relationships of the results without stirrer for both bubblers SGGB and PVT. This suggests that the use of the magnetic stirrer had not increased the diffusion of carbon dioxide and carbonic acids from the interface between gas and aqueous phases into the bulk solution in the experimental system. Hence it is not necessary to employ the extra stirring equipment.

So far we know that both bubblers SGGB and PVT in this experimental system could effect steady gas dissolution, and the dissolution rate using SGGB is significantly quicker than using PVT. However since the perforated plate of the SGGB bubbler may affect the precipitation of calcium carbonate, the PVT tube was used in the following experiments.

2.2.4 The calculation of theoretical pH of ammonium bicarbonate solution equilibrated at P_{CO2} 0.00484 atm

When a quantity of ammonia is dissolved in an aqueous solution it will increase the solution pH as ammonia is basic. The pH will be predictable provided all the reactions attain equilibrium. In order to examine whether ammonium bicarbonate solution was equilibrated under a constant P_{CO2}, a technique was used to calculate the theoretical solution pH using the total concentration of ammoniacal-N (NT) and P_{CO2}. An assumption was

made that if the measured solution pH in reaction solutions agreed with the values for theoretical pH corresponding to the concentration of NT, the reaction solutions would be assumed to be in equilibrium at the P_{CO2} (0.00484 atm). Then simple equations can be used to predict the relationships between the activities of bicarbonate and carbonate ions and solution pH such as equations 2.14 and 2.15.

In addition to the dissolution equations of carbon dioxide (equations 2.2 and 2.3) and dissociation equations of carbonic acids (equations 2.4 and 2.5), the chemical reactions in the solution now include the dissociation of water (2.17) and ammonium (2.18) and the formation of ion pairs of ammonium bicarbonate ($NH_4HCO_3^0$) (2.19) and ammonium carbonate ($NH_4CO_3^-$) (2.20).

$$H_2O \text{ <=> } H^+ + OH^- \qquad (2.17)$$

$$NH_4^+ \text{ <=> } NH_3 + H^+ \qquad (2.18)$$

$$NH_4HCO_3^0 \text{ <=> } NH_4^+ + HCO_3^- \qquad (2.19)$$

$$NH_4CO_3^- \text{ <=> } NH_4^+ + CO_3^{2-} \qquad (2.20)$$

Their reaction constants are listed in Table A.2.1 of appendix 2. In a low concentration of ammoniacal-N solution, the formation of complexes $NH_4HCO_3^-$ (equation 2.20) and $NH_4CO_3^0$ (equation 2.19) can be ignored, but in order to widen the application in cases where solutions contain high concentration of ammoniacal-N (e.g. in some soil conditions) these two complexes are taken into consideration.

In order to calculate the concentration and activity of each component of the solution in this system, their chemical reaction equations are expressed as a mass balance equation.

<u>The estimation of the concentrations of carbonic ions</u>

The concentration of carbonic acids is controlled by P_{CO2} and solution pH, as described in section 2.2.2. P_{CO2} was assumed to

be constant at 0.00484 atm, so equations 2.14 and 2.15 were used to describe the relationship between solution pH and the activities of bicarbonate and carbonate ions in reaction solutions.

Calculating the concentrations of forms of ammoniacal-N

In this thesis, the total concentration of ammoniacal-N (NT) is defined as the sum of free ammonia, ammonium ion, ammonium bicarbonate complex, and ammonium carbonate complex as described by the mass balance equation,

$$NT=[NH_4^+]+[NH_4CO_3^-]+[NH_3]+[NH_4HCO_3^0] \qquad (2.21)$$

Equations 2.18 to 2.20 are all interrelated. So once the concentration or activity of one component has been calculated, the other equations can be solved simultaneously. Since ammonium is the common ion in these equations, the concentrations of other components are expressed in the terms of the ammonium ion.

The activity of ammonia is calculated from the ammonium activity derived from the ammonium dissociation equation 2.18 as

$$(NH_3)=(NH_4^+)\,k_{NH4}/(H^+) \qquad (2.22)$$

where k_{NH4} is the ammonium dissociation constant. The activity of ammonium is its concentration multiplied by its activity coefficient, f_{NH4},

$$(NH_4^+)=[NH_4^+]\,f_{NH4} \qquad (2.23)$$

Thus by substituting terms from equations 2.22 and 2.23 into 2.21, the concentration of ammonia is

$$[NH_3]=(NH_3)/f_{NH3}=[NH_4^+]\,f_{NH4}k_{NH4}/(f_{NH3}(H^+)) \qquad (2.24)$$

By a similar process the concentration of ammonium bicarbonate is

$$[NH_4HCO_3^0]=[NH_4^+]\,f_{NH4}\,(HCO_3^-)/(f_{NH3}k_{NH4HCO3}) \qquad (2.25)$$

where $k_{NH4HCO3}$ is the dissociation constant, and f_{NH3} is used instead of $f_{NH4HCO3}$. Since the ammonium bicarbonate complex is neutral its

activity coefficient is assumed to be the same as that of ammonia. The concentration of the ammonium carbonate complex is derived from 2.26.

$$[NH_4CO_3^-] = [NH_4^+] f_{NH4} (CO_3^{2-}) / (f_{HCO3} k_{NH4CO3}) \qquad (2.26)$$

where k_{NH4CO3} is its dissociation constant, and f_{HCO3} is used for $f_{NH4HCO3}$ because both of them carry a single negative charge.

Substituting the concentrations of ammonia, ammonium bicarbonate, and ammonium carbonate from equations 2.24, 2.25, and 2.26 into equation 2.21, and rearranging

$$[NH_4^+] = NT f_{NH3} f_{HCO3} (H^+) k_{NH4HCO3} k_{NH4CO3} / (f_{NH3} f_{HCO3} (H^+) k_{NH4HCO3} k_{NHCO3} + f_{NH4} f_{HCO3} k_{NH4} \times k_{NH4HCO3} k_{NH4CO3} + f_{NH4} f_{HCO3} (H^+) (HCO_3^-) k_{NH4CO3} + f_{NH4} f_{NH3} (H^+) (CO_3^{2-}) k_{NH4HCO3}) \qquad (2.27)$$

where the activity coefficients of the ions or complexes but not ammonia were calculated by the Debye-Hückel equation,

$$\log(fi) = -A\ Zi^2\ I^{1/2} / (1 + B\ ai\ I^{1/2}) \qquad (2.28)$$

where A=0.509, B=0.329, Zi is the charge of ion, ai is an adjustable parameter (in angstroms) corresponding to the size of ion (see Table A.2.2 of appendix.2), and I is the ionic strength which is defined as,

$$I = 1/2\ \Sigma(Ci\ Zi^2) \qquad (2.29)$$

where Ci is the concentration of ion.

The activity coefficient of ammonia, f_{NH3}, was calculated by an approach offered by Koelliker and Kissel (1988), quoting Bulter (1964),

$$\log f_{NH3} = 0.12\ I.$$

The concentration of ammonia is equal to the activity of ammonia divided by its activity coefficient f_{NH3} which is calculated as below

$$[NH_3] = (NH_3) / f_{NH3} \qquad (2.30)$$

<u>Balancing ionic charges</u>

The total charge of the cations in aqueous solution must be equal to that of the anions, as in equation 2.31.

$$\Sigma(Zi\ Cci)=\Sigma(Zi\ Cai) \qquad (2.31)$$

where Cci is the concentrations of the cations and Cai is the concentrations of the anions. In this system the charge balance is

$$[H^+] + [NH_4^+]=[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [NH_4CO_3^-] \qquad (2.32)$$

Procedures for calculating the theoretical solution pH and concentrations of solution components at 0.00484 atm P_{CO2}

The chemical reactions, mass balance, and charge balance equations have been expressed above, so that when the concentration of NT is known, solution pH can be calculated by the following iterative procedure :

(1) The concentration of bicarbonate ions is almost equal to that of ammonium ions which is lower than the total ammoniacal-N (NT) if solution pH is below 9.3. Thus at the start of the calculating program, the concentration of bicarbonate was taken to be $[HCO_3^-]=0.95NT$.

The concentration of $CaCl_2$ in the future experiments is 10 mM. In the solution with no calcium chloride, 30 mM KCl solution was added to match the ionic strength and to widen the usefulness of the calculating program, so I=0.03 + 0.95NT was taken as a starting value for ionic strength.

(2) Given this initial value of I, the value of (HCO_3^-) was calculated from the approximate values of $[HCO_3^-]$ and f_{NH3}, then the first approximation to the solution pH was calculated by equation 2.14. Using this value of pH and equation 2.15, the approximate values of activities, (CO_3^{2-}), and concentrations, $[CO_3^{2-}]$, of carbonate were determined.

(3) Having calculated the values of pH, NT, (HCO_3^-), and (CO_3^{2-}) the concentration of ammonium was calculated by equation 2.27,

and then the concentrations of ammonia, ammonium bicarbonate, and ammonium carbonate were calculated from equations 2.24, 2.25, and 2.26, respectively.

To check whether these calculated parameters were acceptable, a comparison was made between the total positive ion charge (CC, the left side of equation 2.32) and the total negative charge (AC, the right side). If the absolute value of DC, where DC=CC-AC, was less than 0.0001NT, it was assumed that the calculated pH was the equilibrium pH (theoretical pH) of the reaction solution, and all the other calculated quantities were acceptable too. If DC was greater than 0.0001NT, it was assumed that the predicted pH for the reaction solution was too low. On other hand, if DC was less than -0.0001NT the predicted pH was too high. The concentration of bicarbonate is proportional to solution pH and *vice versa*. Therefore when CC was too high the concentration of bicarbonate was increased by a thousandth of the previous concentrations and a new value of I was calculated by equation 2.33.

$$I=0.5([H^+] + [NH_4^+] + [OH^-] + [HCO_3^-] + 4[CO_3^{2-}] + [NH_4CO_3^-]) \quad (2.33)$$

The new values of bicarbonate and I were used in a new iterative run, repeating steps (2) and (3). These two steps were repeated until the absolute value of DC was less than 0.0001NT.

These calculating procedures were written in FORTRAN for programming iteratively until all parameters were acceptable, or 1000 runs had been completed.

The calculating procedures taking P_{CO2} and P_{NH3} into account

When there is ammoniacal-N in the aqueous solution, the gas phase will nevertheless contain free ammonia, with a partial pressure of P_{NH3}. In the presence of P_{NH3} the partial pressure of other components (i.e. N_2 and CO_2) will be diluted, but whether the

be great enough to
change of P_{CO2} will alter solution pH is not known. However, the partial pressure of ammonia can be calculated from the concentration of free ammonia (equation 2.34) which also can be calculated from solution pH and the concentration of ammonium ions as described in equation 2.24.

$$P_{NH3}=[NH_3]f_{NH3}/H_{NH3} \qquad (2.34)$$

where H_{NH3} is Henry's constant of ammonia (Table A.2.1 of appendix 2). P_{CO2} can be determined by equation 2.35.

$$P_{CO2i}=0.00484\ (1 - P_{NH3})\ (atm) \qquad (2.35)$$

where P_{CO2i} is the partial pressure of carbon dioxide after taking into account the dilution effect from P_{NH3}.

The procedures for calculating solution pH and the concentrations of all other components were as above, except that the relationship between (HCO_3^-) and pH was directly calculated by equation 2.7 instead of equation 2.14, and P_{CO2i} was used instead of P_{CO2} in the calculating program.

Table 2.1 THE EQUILIBRIUM SOLUTION pH AND P_{NH3} IN REACTION SOLUTIONS CONTAINING DIFFERENT CONCENTRATIONS OF AMMONIUM BICARBONATE AND 0.03 M KCl.

NT, M	0.1	0.05	0.02	0.01	0.005	0.001
pH*	8.85	8.61	8.29	8.03	7.74	7.06
pH**	8.85	8.61	8.29	8.03	7.74	7.06
P_{CO2}, $x10^2$ atm	0.484	0.484	0.484	0.484	0.484	0.484
P_{NH3}, $x10^4$ atm	3.18	1.13	0.25	0.072	0.019	0.000

NT, total concentration of ammoniacal-N.
pH*, theoretical pHs estimated without taking P_{NH3} into account.
pH**, theoretical pHs taking P_{NH3} into account.
P_{CO2} and P_{NH3} the partial pressures of carbon dioxide and ammonia, in atm, in the reaction solution.

The theoretical solution pH calculated in H_2O-CO_2-NH_3 system

The thermodynamic equilibrium data calculated by P_{CO2} and NT

from the two previous sections are shown in Table 2.1 (above). Comparing the theoretical solution pHs (1) ignoring the dilution effect of P_{NH3} on P_{CO2} (pH*) and (2) taking the dilution effect into account (pH**), demonstrates that the presence of P_{NH3} has no significant effect on P_{CO2}, even in 0.1 M ammonium bicarbonate solution. For example, the calculated values of P_{NH3} of solutions containing 0.1 M and 0.05 M NT (Table 2.1) are 3.18×10^{-4} and 1.13×10^{-4} atm respectively; these values are far too low to have a dilution effect on P_{CO2} (0.00484 atm) or to affect the calculated values of solution pH.

2.2.5 The reaction between ammonia and carbon dioxide in 0.03 M KCl solution

It is important to understand the dissolution behaviour of ammonia and carbon dioxide in the reaction solutions when a gaseous mixture was produced from different concentrations of ammonium bicarbonate solutions and introduced to reaction solutions.

A series of experiments using different concentrations of ammonium bicarbonate in the "source solution" and various gas flow rates were undertaken to look for useful combinations of gas flow rate and concentration of ammonium bicarbonate in order to produce suitable mixtures of ammonia and carbon dioxide gases, which can meet the requirements mentioned in section 2.1, i.e. keeping P_{CO2} constant while adding ammonia into reaction solution at a steady rate.

Most experiments in this thesis started with 0.01 M $CaCl_2$ solution. Potassium chloride (0.03 M) was used in this section to prevent precipitation of carbonate (which will release acidity and affect solution pH) and to compensate for the effects of

ionic strength.

2.2.5.1 Materials and Methods

The standard experimental procedures (p. 9) were used under the following conditions : -

(1) Potassium chloride ($3x10^{-2}$ M) was used for the reaction solution.

(2) The concentrations of ammonium bicarbonate in "source solution" were prepared at 0.01, 0.02, 0.05 and 0.1 M. In order to stabilize the partial pressures of ammonia and carbon dioxide produced from the "source solution", solution pH was adjusted to the corresponding theoretical pHs, 8.03, 8.29, 8.61, and 8.85 (Table 2.1). These theoretical values of solution pH were based on the assumption that the ammonium bicarbonate solutions are at equilibrium under P_{CO2} at 0.00484 atm (the calculation is described in section 2.2.4). pHs were adjusted using 2 M NaOH and equilibrated with carbon dioxide.

(3) Gas flow rates were set at 56, 118, and 231 cm^3 min^{-1} after calibration by measuring gas volumes.

Four replications were performed for each treatment.

2.2.5.2 Results and Discussion

If the measured pH in a reaction solution agrees with the theoretical pH calculated according to a given NT, all chemical reactions including dissolution and neutralization between ammonia and carbonic acids in the reaction solution were assumed to be at equilibrium under the P_{CO2} at 0.00484 atm. In Figure 2.3, the solid line denotes the relationship between NT and the theoretical solution pH. Data are also shown in Table 2.1.

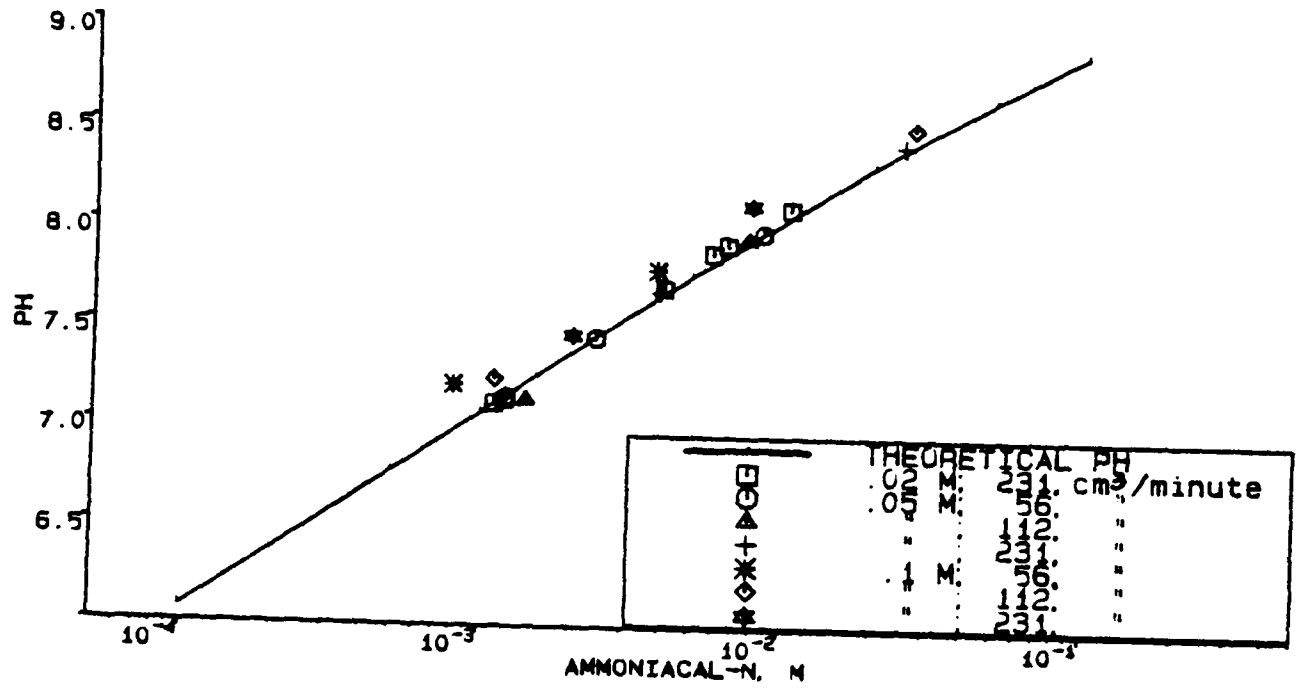
Table 2.2 shows that AADR (the apparent ammonia dissolution

rate) which was the quotient of NT over t (the reaction period) in reaction solutions increased with the increase of gas flow rate from both 0.05 M and 0.1 M ammonium bicarbonate source solutions. Using a mixture of gases produced from 0.05 M ammonia-cal-N sources, the pHs of the reaction solutions followed the solid line (Figure 2.3) in spite of an increase of gas flow rate from low (56 cm^3 min^{-1}) to high (231 cm^3 min^{-1}) and AADR being increased about three times (from 6.3±0.1 to 20.4±1.3, in μ mol $litre^{-1}$ min^{-1}). The consistency between the measured and the theoretical pHs suggests that the dissolution of ammonia and carbon dioxide and the neutralization reaction between carbonic acids and ammonia in the reaction solutions, are controlled by P_{CO2} at 0.00484 atm. The results with 0.02 M source solution also followed the solid line. Therefore, both 0.02 M and 0.05 M ammonium bicarbonate solutions are suitable "source solutions" for producing mixtures of ammonia and carbon dioxide gases for reaction solutions. However, the pH of the reaction solutions using gaseous mixture produced from 0.1 M ammonium bicarbonate "source solution" was significantly higher than that of the solid line at corresponding NT in the reaction solution. This suggests that the reaction solution is not at equilibrium under P_{CO2} 0.00484 atm. Therefore, 0.1 M ammonium bicarbonate "source solution" is not suitable for subsequent experiments.

The results in Table 2.2 show that the values of AADR are nearly constant throughout the whole reaction period in each treatment with varying gas flow rates and "source solutions". Even though the experiment was continued for about two days, the AADR of the 0.02 M source treatment remains fairly constant, and the mean values of AADR are 4.1, 3.2, 3.5, and 3.8 $x10^{-6}$ mole $litre^{-1}$ min^{-1} measured after 260, 1242, 1652, and 2747 minutes of

bubbling. The standard deviations of all determined data throughout each reaction period were all less than a tenth of AADR. Variations in the values of determined AADR were mainly due to the limits of the analytical method for the higher concentration of ammoniacal-N which required high magnitudes of dilution (some of up to 500 times).

Figure 2.3 THE EFFECTS OF THE CONCENTRATION OF AMMONIUM BICARBONATE IN "SOURCE SOLUTION" AND GAS FLOW RATES ON pH IN THE REACTION SOLUTION.



Solution pH increased with the addition of base from the dissolution of ammonia. If the rate of addition of base is stable, the solution pH can be calculated from the addition rate of base by multiplying it by the reaction time. The results so far show that the bubbling system could introduce the mixed gase containing ammonia and carbon dioxide steadily and constantly to the reaction solution. Thus, the value of AADR in this bubbling system could be used to calculate the concentration of ammoniacal-N, and could be used in turn to calculate the theoretical solution pH in the reaction period.

AADRs of reaction solutions increased with the increase of gas flow rates and the concentrations of ammonium bicarbonate in "source solutions". They were 6.3±0.1, 10.2±0.6, and 20.4±1.3 $x10^{-6}$ mol litre^{-1} min^{-1} with gas flow rates at 56, 112, and 231 cm^3 min^{-1} through 0.05 M ammonium bicarbonate "source solution", and 13.0±1.3, 24.6±4.0, and 47.6±1.5 $x10^{-6}$ mol litre^{-1} min^{-1} through 0.1 M ammonium bicarbonate "source solution".

Table 2.2 THE EFFECTS OF GAS FLOW RATES AND CONCENTRATIONS OF AMMONIUM BICARBONATE IN THE SOURCE SOLUTION ON THE DISSOLUTION OF AMMONIA IN KCl (0.03 M) SOLUTIONS.

	AMMONIUM BICARBONATE, M								
	0.02				0.05			0.1	
GF, 231 cm^3 min^{-1}									
t	260	1242	1652	2747	60	180	1310	41	166
pH	7.10	7.69	7.87	8.10	7.13	7.67	8.41	7.44	8.11
NT	1.09	4.00	5.80	10.5	1.25	3.88	25.0	2.00	7.75
AADR	4.1	3.2	3.5	3.8	20.8	21.5	19.0	48.7	46.6
		(3.6±0.3)			(20.4±1.3)			(47.6±15)	
GF, 112 cm^3 min^{-1}									
t					132	780		40	1237
pH					7.12	7.94		7.22	8.50
NT					1.40	7.58		1.10	27.0
AADR					10.6	9.70		27.5	21.8
					(10.2±0.6)			(24.6±4.0)	
GF, 56 cm^3 min^{-1}									
t					194	372	1355	79	234
pH					7.13	7.43	7.97	7.19	7.78
NT					1.25	2.40	8.50	0.85	3.75
AADR					6.4	6.4	6.2	10.7	15.4
					(6.3±0.1)			(13.0±3.3)	

GF, gas flow rate.
t, Reaction time in minutes.
NT, Concentration of total ammoniacal-N in mM.
AADR, Apparent ammonia dissolution rate was calculated by NT/t. 10^{-6} mol litre^{-1} min^{-1}. Their average values with standard deviation throughout the whole reaction period are shown in brackets.

2.2.6 Conclusion

The relationship between pH and NT in the reaction solution agrees very well with the thermodynamic equilibrium value under constant P_{CO2} 0.00484 atm, when the gaseous mixture was produced using a "source solution" whose NT was 0.05 M or less. This does not hold for the 0.1 M "source solution".

2.3 THE PRECIPITATION OF CALCIUM CARBONATE IN A BUBBLING SYSTEM

In a solution containing calcium ions, the rise of solution pH during bubbling with the mixture of gases of ammonia and carbon dioxide will increase the degree of supersaturation (SI) of calcium carbonate in the reaction solution with respect to calcite. When SI reaches a critical level, nuclei of calcium carbonate will be formed, and precipitates will develop. Thus in this reaction solution, the rise of solution pH will stimulate the precipitation of calcium carbonate ($CaCO_{3(s)}$); in turn the precipitation will affect solution pH. When one mole of $CaCO_{3(s)}$ precipitates, it consumes one mole of CO_3^{2-} and releases two moles of H^+ as

$$Ca^{2+} + H_2CO_3^* \iff CaCO_{3(s)} + 2\ H^+.$$

However, when a molecule of ammonia is dissolved into reaction solutions, it will release a molecule of OH^- ; this in turn will neutralize a molecule of H^+ from carbonic acid as

$$OH^{-1} + H^+ \iff H_2O.$$

In the system, we may define the addition rate of base in solution as AADR (mol. $litre^{-1}$ min^{-1}). If we define the rate of precipitation of calcium carbonate (PR) in mol. $litre^{-1}$ min^{-1}, then the release rate of acidity (mol. $litre^{-1}$ min^{-1} of H^+) is 2PR. Generally, at the early stage solution pH is mainly controlled by AADR until the onset of precipitation. As the number and size of the particles increase PR will increase and the rise of

solution pH will be slowed down. The changes of solution pH may then follow one of three pathways :

(1) The pH will continue to increase if AADR>2PR.

(2) The pH remains constant if AADR=2PR.

(3) The pH decreases if AADR<2PR.

Later there will be a decrease of precipitation rate due to the decrease in supersaturation, accompanied by reduction in the concentration of calcium ions, as calcium carbonate is formed. When the solution pH decreases the concentration of the carbonate ion decreases and the degree of supersaturation will decrease more sharply, although the crystals may continue to grow in surface area. The precipitation processes of calcium carbonate will be discussed in chapter 3.

The pH at the peak (AADR=2PR) before it begins to fall will be referred to as "peak pH" (seen in Figure 3.5 (p.76)). In this study, it will be used to assess the precipitation of calcium carbonate in reaction solutions. If the release rate of acidity (2PR) from the precipitation of calcium carbonate in a reaction solution is never greater than the addition rate of base (AADR), the solution pH will never decrease and there will be no "peak pH" point to be found in that solution. Since in this study the concentration of calcium ions started at the same level, 10 mM, and remained fairly steady during the experimental period, the higher the value of solution pH attained, with subsequent increase in activity of carbonate ions, the greater the SI in the reaction solution.

The precipitation rate of calcium carbonate is related to SI. The greater the rate of the addition of base (i.e. the higher AADR), the higher the solution pH necessary to raise SI to increase the calcium carbonate precipitation (PR) sufficiently to increase the

rate of release of acidity enough to counteract the base, so a higher "peak pH" is attained in the reaction solution.

The relationship between the addition of ammonia (base) to reaction solution, the changes in pH and base in solution also are shown in Figure 3.5 (p.76), where base 3 represents the total base added and base 4 represents the base remaining in solutions after calcium carbonate precipitation had occurred, the difference between them is assumed to be due to the precipitation of calcium carbonate; the "peak pH" also indicates that AADR equals 2PR.

The "peak pH" of reaction solution can also be used to compare the effects of different inhibitors on calcium carbonate precipitation. When there is a precipitation inhibitor in the reaction solution it may decrease nucleation and/or crystal growth and will be observed as an increase of solution pH with the continuing addition of ammonia. The greater the degree of supersaturation, the greater will be the competitive ability of the carbonate and bicarbonate ions relative to inhibitors. Meanwhile the inhibitory effect can be decreased, as the concentration of inhibitor is decreased, due to adsorption on or co-precipitation with newly formed calcium carbonate. If so PR will increase, increasing the release of acidity (2PR), and eventually 2PR=AADR; then 2PR>AADR and solution pH falls. Therefore, the stronger the inhibitor in the reaction solution, the greater the "peak pH" attained. Moreover if the effect of the inhibitor is too strong the "peak pH" will never be reached.

The results so far showed (1) that the bubbling system could add ammoniacal-N to reaction solution steadily, (2) the P_{CO2} could be kept constant when the concentration of ammonium bicarbonate in the "source solution" was 0.05 M or less. This system seemed to have satisfied the requirements for studying the precipitation

of calcium carbonate. Some further preliminary experiments without (section 2.3.1) and with (section 2.3.2) addition of precipitation inhibitor, therefore, were carried out to check the effectiveness of the bubbling system and the applicability of the "peak pH".

2.3.1 The effect of gas flow rate on the precipitation of calcium carbonate

It has been shown in section 2.2.5 that AADR increased with the increase of flow rate of the mixture of ammonia and carbon dioxide gases. It will be useful to know how far AADR affects the precipitation of calcium carbonate, and whether its effect on the "peak pH" would be noticeable, and whether the "peak pH" could be used as a standard of comparison to indicate that the calcium carbonate precipitation is actually occurring. Results (section 2.2.5) showed that the open experimental system could be assumed to be in equilibrium thermodynamically if the concentration of the ammonium bicarbonate in the "source solution" was 0.05 M or less. Thus experiments were carried out with 0.05 M of ammonium bicarbonate as the "source solution".

2.3.1.1 Materials and Methods

The standard experimental procedures (p. 9) were used under the following conditions :-

(1) The calcium-sensitive electrode (Philips ISE 310) was placed in the reaction solution.

(2) The reaction solution contained 0.01 M $CaCl_2$ solution.

(3) Gas flow rates were set at 56, 112, and 231 $cm^3\ min^{-1}$.

(4) Replications are shown in Table 2.3

(5) The "peak pH" of each run was directly read from pH meters

or from the chart recorder.

2.3.1.2 Results and Discussion

The values for "peak pH" recorded are 8.09±0.03, 8.00±0.03, and 7.90±0.02 (pH_p in Table 2.3) corresponding to gas flow rates at 231, 112, and 56 cm^3 min^{-1} from the 0.05 M source solution. These results confirm the prediction that the higher the AADR, the higher will be the value of the "peak pH".

An increase of one unit of pH in the reaction solution will increase the activity of bicarbonate and carbonate ions by one and two logarithmic units, respectively (according to equations 2.14 (i.e. $p(HCO_3^{-1})=10.14 - pH$) and 2.15 (i.e. $p(CO_3^{2-})=20.47 - 2pH$)). Thus increases of 0.10 and 0.19 pH units will raise carbonate ion activities by x 1.58 and x 2.40 that of the 56 cm^3 min^{-1} flow rate for 112 and 231 cm^3 min^{-1} flow rates, respectively. The corresponding activities of bicarbonate ions in 112 and 231 cm^3 min^{-1} gas flow rates solutions are x 1.26 and x 1.55 times that of 56 cm^3 min^{-1} treatment. Their respective AADR at 112 and 231 cm^3 min^{-1} gas flow rates are x 1.62 and x 3.24 that of the 56 cm^3 min^{-1} flow rate in potassium chloride solution (Table 2.2). The consistency of this comparison of relative ratios of AADR and carbonate ion activities brings further support to the hypothesis that the increase of solution pH increases SI with a subsequent increase in precipitation rate. The details of the effect of SI on the rate of precipitation of calcium carbonate will be discussed in chapter 3.

Measurements documenting the changes in calcium ion activity (related to the changes in millivoltage (mV) of calcium-sensitive electrode) in the reaction period after the "peak pH" also show similar tendencies, in that the higher the gas flow rate, the

greater the reduction in calcium activity. The precipitation rates (PRM, mean of decrease rate of mV in Table 2.3, below) were 0.46, 0.82, and 2.1 mV h^{-1} for corresponding gas flow rates at 56, 112, and 231 cm^3 min^{-1}. The reduction of calcium ion activity in the reaction solution is associated with the precipitation of calcium carbonate. Unfortunately, the poor reproducibility of measurements with the calcium-sensitive electrode (if it is retained in the reaction solution all the time) makes it extremely difficult to obtain accurate values for calcium ion activity. The measurement of solution pH, however, is known to be accurate and stable. The "peak pH" of the reaction solution can, therefore, be used to mark that the rate of precipitation of calcium carbonate is equal to half of AADR. Reaction solutions were extracted with a 2 ml syringe to measure the activity of calcium ions with the electrode instead of keeping the electrode in the reaction vessel throughout the experimental period.

Table 2.3 THE EFFECTS OF GAS FLOW RATES AND PHOSPHATE CONCENTRATIONS ON THE PRECIPITATION OF CALCIUM CARBONATE.

GF	phosphate	pH_p	PRM	RE	crystal form
56	0	7.90±0.02	0.46	2	single hexagonal and rhombohedral
118	0	8.00±0.03	0.82	2	"
231	0	8.09±0.03	2.1	6	"
118	0.5	8.23±0.04	1.8	2	clumping rhombohedral
231	0.5	8.32±0.03	1.3	2	"

GF, Gas flow rate in cm^3 min^{-1}.
P, The concentration of phosphate in ppm.
pH_p, "The peak pH".
PRM, Precipitation rate in mV per hour (mV h^{-1}).
RE, Replications.

2.3.2 The effect of phosphate on the precipitation of calcium carbonate in the bubbling system

The results in section 2.3.1 already demonstrate that the "peak pH" of a reaction solution responds to the AADR. Here we want to examine whether the "peak pH" could respond to the inhibitory effects of inhibitors on calcium carbonate precipitation. Phosphate is well known as a strong inhibitor on the precipitation of calcite (Reddy and Nancollas, 1973; Griffin and Jurinak, 1973; Reddy, 1977; De Kanel and Morse, 1978; and Mucci, 1986), and was therefore employed to examine the applicability of the experimental system.

2.3.2.1 Materials and Methods

The standard procedures (p. 9) were used under the following conditions :-

(1) The reaction solution contained 0.5 ppm Na_2HPO_4 and 0.01 M $CaCl_2$.

(2) 112 and 231 cm^3 min^{-1} gas flow rates were used.

2.3.2.2 Results and Discussion

When reaction solutions contained 0.5 ppm phosphate, the "peak pHs" of the reaction solutions increased significantly by approximately 0.23 units from 8.00±0.03 to 8.23±0.04, and from 8.09±0.03 to 8.32±0.03, at 112 and 231 cm^3 min^{-1} gas flow rates, respectively (Table 2.3). The results confirm that the presence of precipitation inhibitor in reaction solution will retard the precipitation and cause an increase of "peak pH".

The difference between the "peak pH" of the reaction solutions with gas flow rates of 118 and 231 cm^3 min^{-1} were the same, 0.09 pH units, in spite of the addition of phosphate,

suggesting that the AADR and the phosphate inhibitory potential may have a additive effect on the precipitation of calcium carbonate. Their combined effects effectively demonstrate that the experimental system is suitable for investigating the effects of inhibitors on the precipitation.

The inhibitory effect of phosphate on the precipitation, is evident not only from the increase of the "peak pH", but also by the change in the appearance of the crystals viewed under a light microscope. The deposited particles from solution without phosphate were in single fine rhombohedral, and hexagonal spherulite (SEM photo shown in Figure 3.3), whereas clumps of rhombohedral crystals (SEM photo shown in Figure 4.9) formed in the solution where phosphate was present. This confirms that the inhibitor could influence the crystal growth behaviour.

These results definitely confirm that phosphate is a strong inhibitor on calcium carbonate precipitation.

2.3.3 Conclusion

Three conclusions can be drawn from the above results:

(1) At the "peak pH" of reaction solutions in the experimental system, the rate of precipitation of calcium carbonate (as measured by the release of H^+) is equal to the rate of dissolution of ammonia; therefore the "peak pH" provides a useful standard of comparison between different reaction solutions.

(2) The "peak pH" of a reaction solution is positively correlated with AADR, whether it is increased by increasing the concentration of ammonium bicarbonate in the source solution or by increasing the gas flow rate.

(3) The presence of phosphate in the reaction solutions not only inhibits the precipitation of calcium carbonate causing an

increase in the "peak pH", but also affects the appearance of crystals formed.

The preliminary experiments of sections 2.3.1 and 2.3.2 suggest that the processes of calcium carbonate precipitation may be investigated through the use of precipitation inhibitors. This, in turn, can further the understanding of the precipitation and supersaturation of calcium carbonate in soils and other natural environments.

CHAPTER 3

THE PRECIPITATION OF CALCIUM CARBONATE

Mineralogical research on carbonate minerals has provided detailed basic descriptions of the structures of anhydrous and hydrated calcium carbonates. Petrological research has investigated the formation of carbonates in detail in the field. Many problems still exist and the mechanism of calcium carbonate precipitation is not known in detail.

In this chapter a review of relevant literature is given first, concerned with the properties of calcium carbonates and the mechanisms of nucleation and crystal growth of calcium carbonate. Non-seeded experiments were carried out to identify the species formed under varying initial calcium ion concentrations, and calcite-seeded experiments were carried out to examine the factors (such as degree of supersaturation(SI)and deposited calcium carbonate) that control the processes of calcium carbonate precipitation. A method was developed in the calcite-seeded system for using the measured solution pH and AADR to estimate the amount of calcium carbonate precipitated during th reaction period. The bubbling experimental system which was described in chapter 2, was used in this study.

3.1 REVIEW OF LITERATURE

3.1.1 The properties of calcium carbonates

Polymorphs of calcium carbonate

Five different forms of calcium carbonate (calcite, aragonite, vaterite, monohydrate, and hexahydrate) were described by Brooks et al. in 1950. Thermodynamically, calcite is the most stable phase of calcium carbonate in natural environments.

Staveley and Linford (1969) have measured the entropy of the formation of aragonite, finding it to be 0.89 cal K^{-1} mol^{-1} less than that of calcite. Turnbull (1973) reported that vaterite would have a higher entropy than calcite since it has a lower density and more lattice disorder as revealed by line broadening using an X-ray diffractometer.

The conditions required for their formation can occur in natural soils, so it should be possible to find all five forms in soil systems. The last three however, have rarely been reported from soils.

Vaterite has not been reported in soils so far; it has been found in metamorphic rocks (McConnell, 1959), sediments (Bentor et al., 1963; Rowland and Webster, 1971), and in biological materials such as mollusc shells, otolith of fish, and human gallstones (Hall and Taylor, 1971). Cole (1957), however, observed that vaterite has formed when calcium carbonate was precipitated from a soil extract containing calcium, magnesium, and organic matter. Meyer (1965) also reported that vaterite could be precipitated in the laboratory from an aqueous solution of calcium salts under favourable conditions (cited from Turnbull, 1973). Wray and Daniel (1957) and Ogino et al (1987) reported that vaterite was precipitated at relatively low temperatures (< 30^0 C). Turnbull (1973) also prepared extremely pure vaterite by passing a rapid stream of carbon dioxide through a stirred solution of 1 M calcium chloride and 2 M ammonia at 20^0 C.

Palache et al. (1949) reported that the crystallization of aragonite is favoured by small amounts of Ba, Sr, Mg, or Pb salts or of calcium sulphate in the solution, and by relatively high temperatures. He also reported that rapid precipitation and

relatively high concentrations of reactants also encourage aragonite formation. Wray and Daniel (1957) and Ogino et al. (1987) reported that aragonite formed predominantly at high temperature (70^0 C).

Correlation between polymorphs

Nancollas et al (1983) outlined the processes involved in the crystallization of calcium carbonate. In an unseeded highly supersaturated solution a number of precursor phases are formed which may subsequently dissolve as the thermodynamically more stable phases appear. Johnston et al. (1916) assumed that the first formed calcium carbonate would be amorphous. This has been verified by experimental evidence of its synthesis from ethanolic calcium carbonate solutions (Yasue et al., 1984) or from highly supersaturated calcium carbonate solutions (cited from Ogino et al., 1987).

Ogino et al. (1987) carried out a series of experiments to study the transformation of calcium carbonate from its amorphous form to vaterite, aragonite, and calcite. They found that the relative abundance of vaterite was greater at 25^0 C than at 30^0 C and 70^0 C. The relative abundance of vaterite was also greater as the concentrations of calcium and carbonate ions in the reaction solutions increased. They also suggested that vaterite might be precipitated directly when the initial supersaturation of the reaction solution was lower than the ion solubility product of amorphous calcium carbonate. In a similar experimental system a slow rate of precipitation yielded the stable calcite form and a rapid rate yielded the thermodynamically unstable forms, aragonite or vaterite (Kitano, 1962 in Kitano and Hood, 1965).

The transformation of vaterite to calcite required hours (Ogino et al., 1987) and that from aragonite to calcite, months

(Taft, 1967, cited from deBoer, 1977). However, the processes of transformation of calcium carbonate polymorphs are not fully understood and conflicting mechanisms have been presented.

Transformation by a direct solid phase transition (Nakahara et al., 1976, cited from Ogino et al., 1987) is different from a recrystallization (i.e. dissolution and reprecipitation) mechanism (Turnbull, 1973). The review of Ogino et al. (1987) reports that Yamaguchi and Murakawa (1981) proposed that the dissolution of vaterite was the rate-determining reaction in the transformation from vaterite to calcite; but Matsuda et al. (1968) said that the dissolution of vaterite and the growth of calcite were both involved. However, Ogino et al. (1987) concluded that the growth of calcite was the rate-determining step in the aragonite to calcite, and vaterite to calcite transformation processes. (The coexistence of these polymorphs will be discussed later)

Solubility of calcium carbonates

Table 3.1 summaries the ion activity products (in negative logarithms) of these calcium carbonates. The solubility of aragonite is about 1.3 times that of calcite, (Garrels et al., 1960; and Hull and Turnbull, 1973), vaterite 5.6 times, carbonate hexahydrate between 2 to 3 times (Brooks et al, 1950), and amorphous calcium carbonate is approx. 300 times (Ogino et al., 1987).

Most research on the solubility of calcium carbonates has concentrated on calcite as it is the dominant form at normal temperatures and pressure. Consequently the majority of published reports are concerned with calcite. Table 3.1 shows that once the concept of ion-pairing (Nakayama, 1968; and Adams, 1971) was accepted, the value of the ion activity product (K_{CIAP}) of calcite

after correcting for the presence of ion pairs (such as $CaCO_3^0$, $CaHCO_3^+$, $CaCl^+$, and $Ca(OH)^+$) reported from different sources, was close to a constant value (pK_{CIAP}=8.48, Pk_{CIAP}=-log(K_{CIAP})). This is lower than previous values. Earlier reports on solubility values must be assumed to have been referring to an ion concentration product rather than to the ion activity product.

The Pk_{CIAP} of calcite will be taken as 8.48 and as the reference point for the measurement of the degree of supersaturation ($SI=(Ca^{2+})(CO_3^{2-})/K_{CIAP}$) of calcium carbonate in a reaction solution.

Table 3.1 THE ION ACTIVITY PRODUCTS OF CALCIUM CARBONATES, NEGATIVE LOGARITHMS AT 25° C.

Calcite	8.30 (Akin and Lagerwerff, 1965[a]), 8.31 (Nakayama, 1968), 8.32 (Frear and Johnston, 1929), 8.35 (Garrel et al., 1960), 8.37 (Truesdale and Jones, 1974), 8.41 (Lindsay, 1979), 8.47 (Hull and Turnbull, 1973), 8.48 (Plummer and Busenberg, 1982; Sass et al., 1983; Inskeep and Bloom, 1986[b]).
Aragonite	7.82 (Suarez and Rhoades, 1982), 8.18 (Lindsay, 1979), 8.22 (Garrel et al., 1960), 8.30 (Hull and Turnbull, 1973; Sass et al., 1983).
Vaterite	7.72 (Turnbull, 1973)
$CaCO_3.H_2O$	7.6 (Hull and Turnbull, 1973)
Amorphous	6.0 (Ogino et al., 1987)

The properties of calcite

The rhombohedral unit $Ca_2(CO_3)_2$ is the basic cell unit of the crystal. Calcite shows a greater variety of crystal habits than any other mineral. These include hexagonal prisms, basal pinacoid, acute, unit and obtuse rhombohedral, and a very characteristic "general form" the scalenohedron (cited from Palache et al, 1949). Except in the hexagonal prisms and basal

pinacoids, these may occur in their simple forms or in parallel growths, and more or less interpenetrating individual crystals are frequent. The name "dog-tooth spar" has been given to the crystal formed mainly of scalenohedron units. A crystal combination capped by an obtuse rhombohedron has been termed "nail-head spar". Subparallel aggregates are occasionally formed which have characteristic saddle-shaped crystals with strongly curved and composite faces.

The properties of vaterite

The unit cell of vaterite is like that of calcite, $Ca_2(CO_3)_2$. Its main crystal shape is hexagonal. Laboratory preparation produces microscopic hexagonal plates or lens-shaped skeletal crystals resembling snowflakes. It may also be spherulitic with a radial fibrous structure (e.g. in Figure 3.3).

The properties of aragonite

Aragonite has orthorhombic and dipyramidal crystal forms; its cell composition is $Ca_4(CO_3)_4$. Single crystals are very rare. Its formation usually results in pseudohexagonal aggregates both of the contact and penetration types.

3.1.2 The mechanism of calcium carbonate precipitation

The precipitation of calcium carbonate in aqueous solution under a variety of experimental conditions has been much researched. The mechanism, however, is still somewhat obscure because it is greatly affected by a variety of environmental factors.

In general, the precipitation process is initially controlled by the nucleation reaction and finally controlled by the growth reaction (Johnson and O'Rourke, 1954). The nucleation reaction is determined by the degree of supersaturation (Davies

and Jones, 1949; and Mott, 1949) and the size of the nuclei (Oster, 1978; and Stumm and Morgan, 1981). Even in seeded experiments homogeneous or heterogeneous nucleation may both still occur (House and Tutton, 1982). Therefore two routes, seeded and non-seeded systems, may be used to approach the formation of crystals from a supersaturated system (Stumm and Morgan, 1981). The precipitation rate of any crystal depends on the magnitude of disequilibrium between the concentration of the reaction solution and the equilibrium solubility of the crystal, the surface area of the seeds, and other conditions, such as temperature, and the presence of impurities.

3.1.2.1 Nucleation of calcium carbonate

Nucleation in a non-seeded system

Johnson and O'Rourke (1954) postulated the steps of nucleation. The nucleation starts from the build-up of clusters, which are the mother phase and tend to dissociate. When these clusters have reached a critical size beyond which a stable configuration is established, the particles tend to grow. The particles which have attained critical size are called nuclei and are a new phase. A certain critical degree of supersaturation must be attained to overcome the energy barrier to the formation of stable nuclei (Nielsen, 1964). The critical value of the degree of supersaturation, SI, for nucleation ranges from 1.01 to 10 up to the compositions of calcium and carbonate ions in reaction solutions and increases with the disparity in the concentrations of cations and anions (Davies and Jones, 1949; Reddy, 1983). The small (<1 μm) homogeneous nuclei were assumed to be amorphous calcium carbonate. They were visible for a few minutes but

gradually redissolved and then grew on other crystals or on the glass walls of the vessel (Kamiya et al., 1977). Laboratory studies on calcite crystallization have shown that the ion activity product can be as much as 10 times (SI=10) that of the equilibrium calcite solubility (Reddy, 1983). House (1981[a]) found that calcium bicarbonate solutions, with an initial supersaturation SI less than 5, remained metastable even upon the addition of calcite seeds. However the composition of these solutions gradually changed with the loss of dissolved carbon dioxide until the SI reached 5 and precipitation occurred. Furthermore when the SI of the reaction solution reached 32 a very slow calcium loss was observed. It was assumed that this was a result of heterogeneous nucleation on impurity particles or on the glass walls of the vessel.

House and Tutton (1982) found that nucleation occurred in highly supersaturated solutions (SI=25.5). Duke and Brown (1954) studied the reaction order of nucleation during the induction period, and of the rates of crystal growth after the induction period. They found the order of the nucleation reaction was higher than that of crystal growth by a factor of 2. Packter (1968) examined the effect of the ion concentration product of calcium and carbonate on the reaction rates of nucleation and crystal growth and found their reaction orders to be 4.2 and 1.3, respectively.

Nucleation in a seeded system

In a seeded system, solutes became adsorbed onto particle surfaces (Davies and Nancollas, 1955) and initially formed the more soluble (Zahaby and Chien, 1982) or metastable forms (Egli and Zerfoss, 1949; and Hull and Turnbull, 1973). Then crystal growth continued up to the equilibrium size. An initial surge in

the crystal growth curves appears to result from additional nucleation occurring on the surfaces of the pre-existing calcite crystals and in the bulk of the supersaturated solution. Observations have shown that the precipitation takes place at a lower degree of supersaturation than that needed for a non-seeded system and there is photomicrographic evidence for the presence of newly formed particles (Nancollas and Reddy ,1971). Bischoff and Fyfe (1968) found calcite nucleation occurred on the surface of aragonite. Growth developed on point or line defects. deBoer (1977) reported that crystal breeding - the formation of new nuclei on the surface of the seeds - was caused by mechanical agitation.

Heterogeneous nucleation on materials other than calcium carbonate

The precipitation of calcite may also occur on surfaces other than calcium carbonate. This may be investigated by following changes in the ionic composition of supersaturated solutions of calcium carbonate. In the process of heterogeneous nucleation calcium loss occurs at a SI that is much lower than the critical SI needed for homogeneous nucleation. This can be attributed to the heterogeneous nucleation of calcite on to the vessel wall or on to impure particles within the solution (House and Tutton, 1982). Nielsen (1964) suggested that extra caution is necessary in cleaning apparatus for crystal growth experiments.

Inskeep and Bloom (1986[c]), using X-ray energy-dispersive analysis and scanning electron microscope observation of soil carbonates, found that the larger calcite particles (0.5-20 μm) were irregularly shaped and did not exist as independent crystals. They were always found to be associated with alumino-

silicate solid phases (Levy, 1981[a]). However, as several authors have shown, the kinetics of heterogeneous reactions in geochemical systems are not well defined (Berner, 1978; Nancollas et al., 1979; Plummer et al., 1979).

Mechanism of nucleation

Nielsen (1964) suggested that both mono-nuclear and poly-nuclear nucleation can be identified in the seeded system. During mono-nuclear nucleation a single nucleus forms on the seed and spreads to the crystal edge. During poly-nuclear nucleation several nuclei form and spread before the spreading from any one nucleus completes a layer of growth. Reynolds (1978) reported that in the presence of polyphenols calcite almost certainly precipitates by a reaction that includes surface nucleation as a rate-limiting step. He noted that the growth mechanism may be by polynuclear growth.

3.1.2.2 The crystal growth of calcium carbonate

The mechanism of calcium carbonate precipitation

Five mechanisms (equations 3.1 to 3.5) of the reaction have been mentioned in the literature :

$$Ca^{2+} + CO_{2(g)} + H_2O \;<=>\; CaCO_{3(s)} + 2H^+ \qquad (3.1)$$

$$Ca^{2+} + 2HCO_3^- \;<=>\; CaCO_{3(s)} + H_2CO_3^* \qquad (3.2)$$

$$Ca^{2+} + 2HCO_3^- \;<=>\; CaCO_{3(s)} + H_2O + CO_{2(g)} \qquad (3.3)$$

$$Ca^{2+} + HCO_3^- \;<=>\; CaCO_{3(s)} + H^+ \qquad (3.4)$$

$$Ca^{2+} + CO_3^{2-} + CaCO_3^0 \;<=>\; ACC_{(s)} \qquad (3.5)$$

where $CaCO_3^0$ is the complex compound of calcium carbonate, ACC is the amorphous calcium carbonate.

Inskeep and Bloom (1985) used the three equations 3.1, 3.4, and 3.5. to describe the reaction mechanism. Suarez (1983) used equation 3.2, and Kitano and Hood (1965), Jacboson and Usdowski

(1975), and House (1981[ab]) used equation 3.3.

$$Ca^{2+} + CO_3^{2-} \leftrightarrows CaCO_{3(s)} \quad (3.6)$$

$$CO_{2(g)} + H_2O \leftrightarrows H_2CO_3^* \quad (3.7)$$

$$H_2CO_3^* \leftrightarrows HCO_3^- + H^+ \quad (3.8)$$

$$HCO_3^- \leftrightarrows CO_3^{2-} + H^+ \quad (3.9)$$

Equation 3.6, the stoichiometric equation, is commonly used to describe the precipitation and dissolution of calcium carbonate. A decrease in carbonate ions, as precipitation occurs, will provoke a change in the composition of the reaction solution in the H_2O-CO_2-$CaCO_{3(s)}$ system. The dissociation reactions of carbonic acids (equations 3.7 to 3.9) will be affected and these reactions will proceed to their right hand sides. The summing of equations 3.6 to 3.9 will be equivalent to equation 3.1. This suggests that when a molecule of $CaCO_{3(s)}$ precipitates and a molecule of each of Ca^{2+}, $CO_{2(g)}$, and H_2O is consumed, two molecules of H^+ (acidity) are released to the reaction solution. This is the reason that in section 2.3 of chapter 2 we assumed that the release rate of acidity (2PR) was twice that of the calcium carbonate precipitation rate (PR). In a closed system, a calcium bicarbonate reaction solution will follow equation 3.2, 3.3, or 3.4. Equation 3.5 describes the reaction beginning with calcium carbonate solution.

This summary shows that authors who tried to utilise reaction rate equations to explain the mechanism of the precipitation of calcite had to adapt equations to suit their experimental data. Kitano and Hood (1965) described equation 3.3 : "If the reaction rate is controlled by calcium and bicarbonate ion concentrations, then third order kinetics will fit the situation. If the escape of carbon dioxide gas alone controls, then first order kinetics should apply." They found that most

reactions in their experimental treatments were first order, but the precipitation inhibitors, citrate, malate, and glycylglycine led to third order reactions.

The rate law of calcium carbonate precipitation

A rate law is an equation expressing an instantaneous reaction rate in terms of the concentrations of the substances taking part in the reaction. A number of models have been developed to describe the precipitation rate of calcium carbonate (most of them relating to calcite precipitation). The models can be categorized into four groups:

(1) Davies and Jones (1955) and Reddy and Nancollas (1971) :

Both of these two models predict the growth rate or reduced growth rate (Leeuwen and Blomen, 1979) as a unique function of ß, the growth affinity,

$$ß=\ln((Ca^{2+})(CO_3^{2-})/K_{CIAP})=2.303 \log (SI)$$

where K_{CIAP} is the ion activity product of calcium carbonate at equilibrium.

The model of Davies and Jones (1955) has been widely adopted . . . Leeuwen and Blomen, 1979; . 1979; House, 1981[a,b]; House and Tutton, 1982; Inskeep and Bloom, 1985). It is based on a double layer model that allows a difference between the concentrations of constituent ions which exist in adsorbed layer and in bulk solution (House and Tutton, 1982). The monolayer concentrations of calcium and carbonate ions are assumed to be equal in supersaturated and also in equilibrium solutions. When the general equation, 3.10, is adapted to express the precipitation of calcium carbonate, it becomes equation 3.11 (cited from Inskeep and Bloom, 1985).

$$PR=K_{(1)}S([A]-[A]_{eq})([B]-[B]_{eq}) \qquad (3.10)$$

$$PR=K_{(2)}S([Ca^{2+}]-[Ca^{2+}]_{eq})([CO_3^{2-}]-[CO_3^{2-}]_{eq}) \qquad (3.11)$$

* R, net rate in mol litre^{-1} min^{-1}, is determined by the difference in dissolution and precipitation rates,

$K_{(1)}$ and $K_{(2)}$ are precipitation rate constants,

where PR represents the precipitation rate,

S surface area, eq at equilibrium, and square brackets represent molar concentrations.

The model of Reddy and Nancollas (1971) is based on equation 3.12. Inskeep and Bloom (1985) found that it was necessary to include the divalent ion activity coefficient f_2 in equation 3.12 in order to account for ionic strength dependence and developed equation 3.13. Using equation 3.13, the dependence of precipitation rates on ionic strength has a theoretical justification.

$$PR=K_{(3)}S([Ca^{2+}][CO_3^{2-}] - K_{CIAP}/f_2^2) \qquad (3.12)$$

$$PR=f_2^2K_{(4)}S([Ca^{2+}][CO_3^{2-}] - K_{CIAP}/f_2^2) \qquad (3.13)$$

where $K_{(3)}$ and $K_{(4)}$ are precipitation rate constants.

House (1981[b]) found that the growth model of Davies and Jones led to good agreement with experimental data when the extent of precipitation was between 0.1 and 0.45 of the total amount of calcium carbonate deposited. The model has been found unsuitable at high growth rates (House, 1981[b]), low P_{CO2} conditions (House and Tutton, 1982; and Inskeep and Bloom, 1985), and at pH greater than 8.

Inskeep and Bloom (1985) adapted the model to describe their experiments and calculated a precipitation rate constant of 118.±13.9 $dm^6\ mol^{-1}\ m^{-2}\ s^{-1}$ with an apparent Arrhenius activation energy of 11.5 kcal mol^{-1}. House (1981[b]), however, found the model cannot cover a wide range of solution conditions.

(2) Plummer et al. (1978) :

The model of equation 3.14 can describe both dissolution and precipitation of calcite at all pH and P_{CO2} values (Inskeep and Bloom, 1985).

$$R=K_1(H^+) + K_2(H_2CO_3^*) + K_3(H_2O) - K_4(Ca^{2+})(HCO_3^-) \qquad (3.14)$$

where K_1^*, K_2, and K_3 are dissolution rate constants, and K_4 is the precipitation rate constant, and brackets represent the ion acti-

vities. It suggests that the (H^+) on the surface of calcite is different from that in the bulk solution (House, 1981[b]), and is consistent with the presence of an adsorbed layer of carbon dioxide which reduces the precipitation rate (House, 1981[a]). Plummer et al. (1979) and House (1981[a,b]) found good agreement between observed crystallization rates and those predicted by this model. Reddy et al. (1981) carried out experiments varying over three orders of magnitude of SI, and P_{CO2} values, and found a considerable agreement with the calculated rates leaving an "uncertainty factor" of 2 from the model. The differences between observed and predicted rates were most pronounced at high P_{CO2} values and low SI. Suarez (1983) applied this model to his experimental work with natural and synthetic Colorado river water at pH values of 8.2 and 8.5 and P_{CO2} near atmospheric levels. The largest error between observed and predicted rates was at high pH's where the model underestimated the rates of precipitation, however, by not more than a factor of 2. The model also underestimated precipitation rates when solution pH's were greater than 8.35. (Inskeep and Bloom, 1985)

(3) deBoer model (1977) :

deBoer (1977) developed a model based on the assumption of crystal breeding to describe his experimental results. It describes an exponential increase of the amount of precipitate with time according to equation 3.15,

$$PR=K_{(5)} \exp(vSt) \qquad (3.15)$$

$K_{(5)}$ is the precipitation rate constant,

where v is the linear growth rate of the crystals, S the specific surface area (based on Bischoff's data, 1968), and t the reaction time. The model predicts that the precipitated particles will reach a constant size distribution after a certain period of time.

(4) Empirical model :

The assumption that a reaction rate is controlled by the extent of disequilibrium has been used to develop empirical rate equations of precipitation.

$$PR=SK_{(6)}(SI-1)^{n} \qquad (3.16)$$

$$PR=K_{(7)}(SI-1)^{n} \qquad (3.17)$$

where $K_{(6)}$ and $K_{(7)}$ are precipitation rate constants, n represents the reaction order. Reddy et al. (1981) found that the empirical model (equation 3.16) successfully described calcite growth at low p_{CO2} (less than 10^{-3} atm), however their results, from 0.03-0.3 atm P_{CO2}, were not consistent. Mucci and Morse (1983) modified equation 3.16 into equation 3.17 and measured the n value, 2.8, for calcite precipitation.

The rate-determining step of calcium carbonate precipitation

Both diffusion and surface-controlled processes have been proposed as the rate determining step in crystal growth (Nancollas, 1968).

Nancollas and Reddy (1971), Reddy and Nancollas (1971), Nancollas (1973), and Wiechers et al. (1975) agree that at moderate to low precipitation rates from simple solutions, the crystal growth of calcite is controlled by a surface-controlled process, such as spiral dislocation growth. This is based on the following facts :

(1) The precipitation rate is proportional to the product of the calcium and carbonate ion concentrations.

(2) Stirring has no effect on the precipitation rate.

(3) The measured activation energy of precipitation is high compared with that for a diffusion-controlled process.

Although there are differences between the values of the activation energy from different sources, e.g. 11.0±1.0 (Nancollas and Reddy, 1971), 10.3±0.9 (Wiechers et al. 1975), and

9.4±0.9 kcal mol^{-1} (Kazmierza* et al., 1982), they are still significantly higher than that of 4.2 kcal mol^{-1} for a diffusion controlled mechanism (Howard et al., 1960).

However Goodarz-Nia and Motamedi (1980) reported that the crystal growth of calcium carbonate in an unstirred solution was diffusion controlled up to about 35 and 60 per cent of the crystallization, for calcium concentrations of 1.2 mM and 3.7 mM, respectively.

Reynolds (1978) noted that the carbonate ion, not the calcium ion, seemed to be involved in the rate-limiting step for nucleation and except at low concentrations of calcium ion, the level of this ion would be rate-controlling. However deBoer (1977) suggested that crystal growth depended mainly on the dehydration rate of calcium ionsadsorbed on the calcite surface.

Surface characteristics of calcium carbonate

Douglas and Walker (1950) reported that a negative potential would accumulate on the surface of the calcite, since the Ca^{2+} ion has a higher hydration energy than CO_3^{2-}, so that it goes into solution leaving a surplus of negative charge on the calcite surface. However, Thompson and Pownall (1989) found that the zeta potential on calcite varies from positive to negative with increasing solution pH. They found, in general, the zeta potential developed in aqueous $CaCl_2$ was significantly more positive than that developed in NaCl and in $NaCl/NaHCO_3$ solutions. Recently Compton and Unwin (1990) reported that the dissolution reaction of calcite changed its topography and roughened its surface.

The determination of surface area of particles

Different methods have been used to estimate the surface area of particles. BET (i.e. Brunauer, Emmett, and Teller, 1938;

Reddy et al (1981), and Inskeep and Bloom (1985)), optical microscopic (House, 1981[ab]; House and Tutton, 1982; and Packter, 1968), and isotope exchange (House and Tutton, 1982) methods. None of these methods are perfect. House and Tutton (1982) reported that the nitrogen BET method was not reliable for determinations of area below 1 m^2 g^{-1}. Plummer et al (1979) reported that they had to halve the surface area data from Erga and Terjesen (1956) to incorporate it into their simulation model describing the dissolution of calcite. Therefore, some workers used more than one method to check the accuracy of their measurements. Packter (1968) used sedimentation and optical microscopic methods. House and Tutton (1982) used isotope exchange and optical microscopic methods.

The majority of workers who have studied the calcium carbonate precipitation rate used a calcite-seeded system. They have exploited the advantages of the seeded system, such as the utilization of a well defined surface of a known polymorph, of a known surface area, to characterize calcite crystal growth. However not one of the models developed can successfully describe precipitation in a variety of experimental conditions (as reviewed above). Also well crystallized calcium carbonate is rarely found in natural environments, and especially not in supersaturated solutions which supposedly contain precipitation inhibitors. Furthermore the possibility of the co-existence of polymorphs of calcium carbonate in natural systems will make the precipitation behaviour different to that of the calcite-seeded system. The non-seeded system (3.2.1), which was developed, and has been demonstrated to work well (chapter 2), will be used in this work. Using this method, one can obtain more useful information from experimental results. The effects of inhibitors,

for example, may significantly affect not only the reaction rate, but also the forms of the precipitates. A series of seeded experiments were also carried out in section 3.2.2 to examine the roles of SI and seeds of calcite on calcium carbonate precipitation.

3.2 EXPERIMENTS

3.2.1 The precipitation of calcium carbonate in a non-seeded system

The effect of the concentration, or activity, of calcium ions on the precipitation was examined with initial concentrations of calcium ions within the range encountered in most soils (mM levels).

3.2.1.1 Materials and Methods

Standard experimental procedures (p. 9) were used, under the following conditions : -

(1) The gas flow rate was set at 231 cm^3 min^{-1}.

(2) Initial reaction solutions contained 1, 2, 5, 7.5, or 10 mM $CaCl_2$, and were filtered through an 0.2 μm filter (Millipore) in order to reduce the influence of impurities.

(3) The activity of calcium ions in the reaction solution was determined with a calcium-sensitive electrode immediately after samples (2 ml) were withdrawn with a 2 ml syringe. Samples were taken twice, at "peak pH" and one hour later, for measuring the activity of calcium ions and the concentration of ammoniacal-N.

(4) Precipitates were examined by X-ray diffractometer (Philips, by Dr. Atkins a Geologist of the Department of Earth Science Oxford), light microscope (Swift), and SEM (scanning electron microscope, Cambridge Steroscan 150).

3.2.1.2 Results and Discussion

Only the relevant data at the "peak pH" are shown in Table 3.2. [Ca] and (Ca) are the concentration and activity of calcium ions in mM, respectively. NT is the total concentration of ammoniacal-N in mM. $CaCO_{3(s)}$ the amount of calcium carbonate precipitated, in mM, was estimated by the amount of decrease of concentration of calcium ions in the reaction solution from the initial concentration (10 mM). PR, the precipitation rate of calcium carbonate, in $\frac{mol\ litre^{-1}\ min^{-1}}{\wedge}$, was calculated by dividing the amount of decrease of calcium concentration between the two sampling times by the interval of time. PRH the rate of decrease of solution pH after the "peak pH" in pH units h^{-1} (pH per hour) was calculated by dividing the decrease of solution pH by the interval of time. PH_p is the "peak pH" of reaction solutions. SI is the degree of supersaturation of calcium carbonate with respect to calcite. RE is the number of replications.

Table 3.2 THE EFFECTS OF CALCIUM CONCENTRATIONS ON THE PRECIPITATION OF CALCIUM CARBONATE.

$[CaCl_2]$, mM	2	5	7.5	10
pH_p	8.42±0.06	8.23±0.01	8.17±0.02	8.09±0.03
NT, mM	15.8±0.9	9.80±0.80	8.44±0.65	7.32±0.89
[Ca], mM	0.94±0.49	2.57±0.64	5.25±0.47	7.81±0.26
(Ca), mM	0.39±0.17	1.28±0.31	2.61±0.17	3.87±0.09
$CaCO_{3(s)}$, mM	1.06±0.49	2.43±0.64	2.25±0.47	2.19±0.26
PR, $x10^5$ $mol\ litre^{-1}\ min^{-1}$	0.22±0.06	0.74±0.15	1.01±0.18	0.93±0.20
PRH, pH units h^{-1}	0.01	0.015±.005	0.025±.005	0.030±.017
SI	28.4±11.6	34.2±9.2	50.8±11.4	50.6±8.5
RE	4	4	4	6

Data in Table 3.2 show that the "peak pH" was higher the

lower the initial concentration of calcium ions. For example, the "peak pH" in 10 mM reaction solution was 8.09±0.03, and 8.42±0.06 in 2.0 mM reaction solution. The rise of solution pH in the lower initial calcium concentration solutions may provide an explanation for the rise in carbonate ion activities to meet the requirement of the critical degree of supersaturation for nucleation and precipitation. However, the "peak pH" point was not easy to distinguish in the more dilute reaction solutions. In the 2 mM treatment the fall of the solution pH after the peak pH point is only 0.01 units and this small difference is very hard to detect on the chart recorder. No "peak pH" could be determined in experiments with the initial concentration at 1 mM.

At "peak pH" the release rate of acidity from the precipitation of calcium carbonate is equal to the ammonia dissolution rate. Thus the "peak pH" provides a standard of comparison between reaction solutions.

The relationships between the "peak pHs" and the initial concentrations or activities of calcium ions in the reaction solution, are shown in Figures 3.1 and 3.2, and described by equations below,

$$pH_p = 8.57 \pm 0.01 \; ([Ca] \times 10^3)^{-0.025 \pm 0.001} \qquad (3.18)$$

$$pH_p = 8.52 \pm 0.02 \; ((Ca) \times 10^3)^{-0.030 \pm 0.002} \qquad (3.19)$$

where pH_p is the "peak pH", and [Ca] and (Ca) are the initial concentration and activity of calcium ions. Equation 3.19 is more useful than equation 3.18 because solutions which have the same activity of calcium ions do not necessarily have the same concentration (Leeuwen and Blomen, 1979).

As expected the concentration of total ammoniacal-N, NT, in the reaction solutions with lower initial calcium concentration was higher because more ammonia was dissolved in it at a constant

AADR and a longer reaction time. It also corresponds to the higher "peak pH".

Figure 3.1 THE RELATIONSHIP BETWEEN THE INITIAL CONCENTRATION OF CALCIUM IONS AND THE PEAK pH IN REACTION SOLUTION.

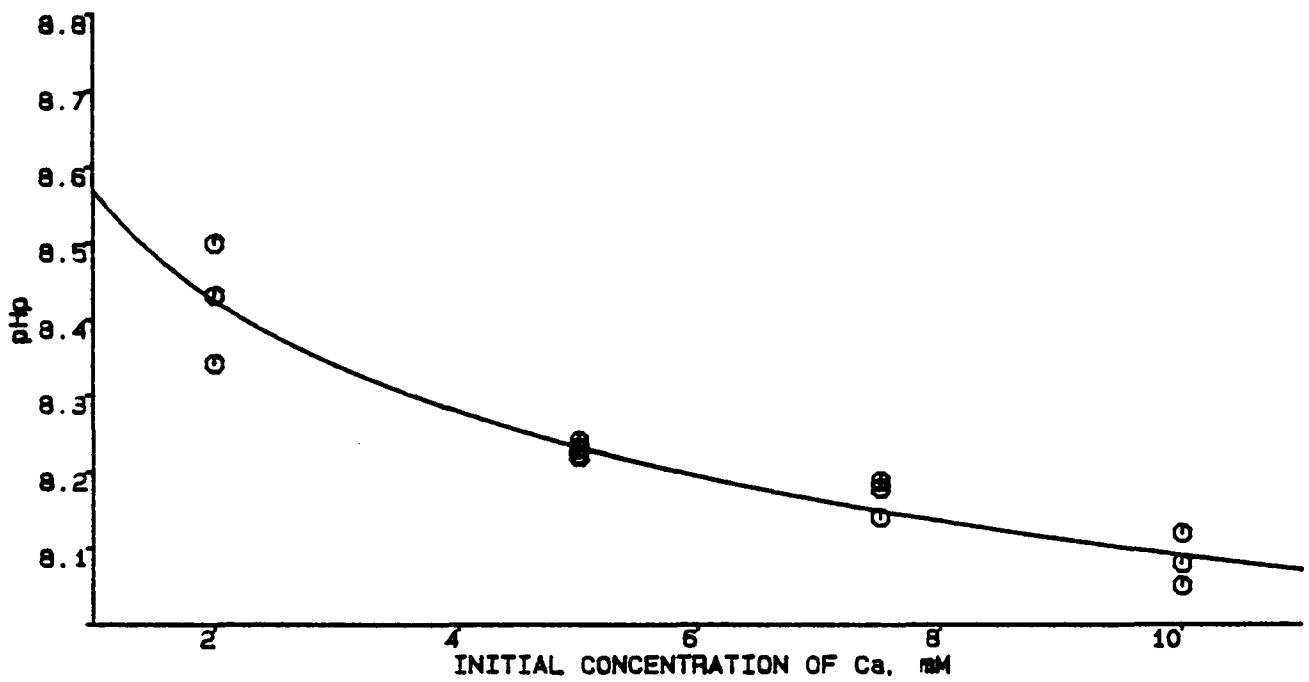
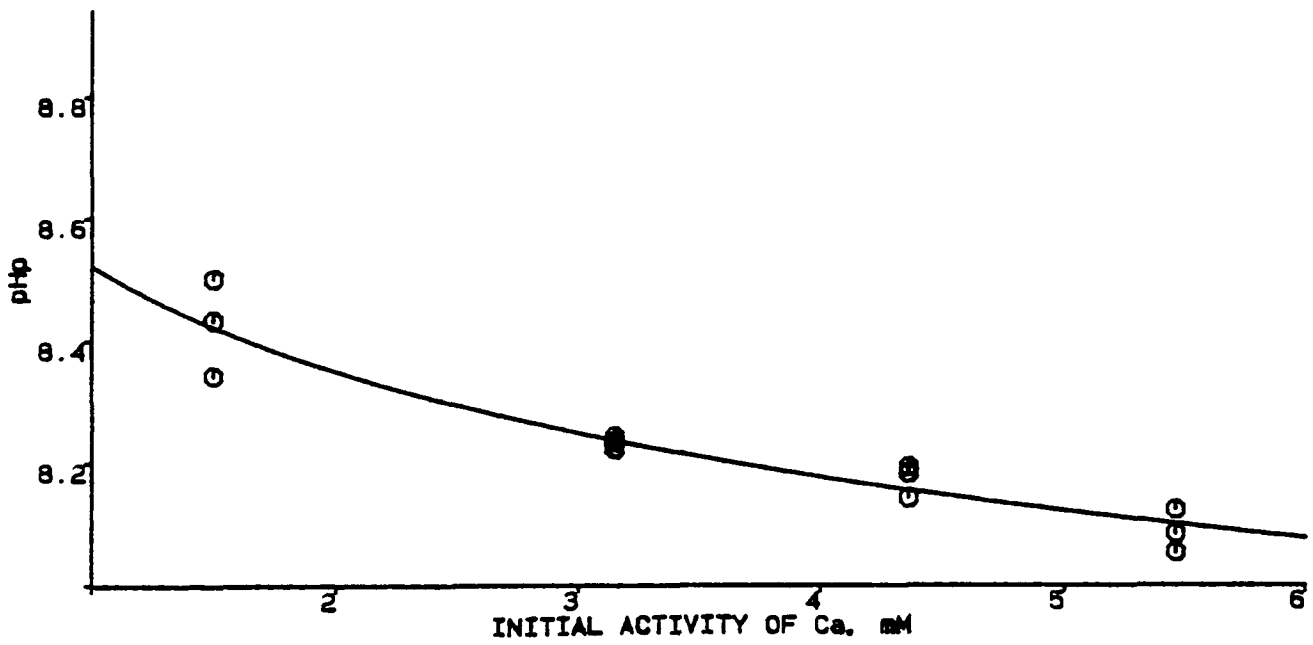


Figure 3.2 THE RELATIONSHIP BETWEEN THE INITIAL ACTIVITY OF CALCIUM IONS AND THE PEAK pH IN REACTION SOLUTION.



The amount of calcium carbonate $CaCO_{3(s)}$ precipitated in each reaction solution was calculated from the decrease of the concentration of calcium ions after correcting for the presence of ion pairs and is expressed in mM. There is no significant

difference in $CaCO_{3(s)}$ near the "peak pH" between the treatments with 5, 7.5, and 10 mM initial concentrations, but the amount is significantly lower for the 2 mM treatment than the others.

X-ray diffraction analysis showed that calcite (dominant) and vaterite were formed in the reaction solution with 10 mM calcium chloride, but only calcite was formed in the reaction solution with 2 mM calcium chloride. The SEM photos show that there were rhombohedral particles, the typical shape of calcite, and hexagonal plates, the typical shape of vaterite, with the 10 mM treatment (Figure 3.3); however there were only rhombohedral particles in the 2 mM reaction solution (Figure 3.4). The absence of vaterite with the 2 mM treatment cannot be attributed to the transformation of vaterite to calcite during the period of reaction. This transformation requires hours (Yamaguchi and Murakawa, 1981, cited from Ogino et al., 1987), but the precipitation in this study was terminated within two hours after attaining the "peak pH".

These results are somewhat different from the results of Ogino et al. (1987), who found that vaterite was relatively abundant in higher concentrations of both calcium and carbonate ions. In this study, at the "peak pH" (Table 3.2) the activity of calcium ions in the 10 mM calcium chloride solution (3.87 mM) is nearly 10 times that (0.39 mM) in the 2 mM solution, but the corresponding activity of carbonate ions in the 10 mM calcium chloride solution is 0.22 times that in the 10 mM solution according to the pH_p of the 10 mM reaction solution (8.09±0.03), which is 0.33 pH units lower than that of the 2 mM reaction solution (8.42±0.06). Thus the formation of vaterite seems to be associated with the high concentration of calcium ions rather than carbonate ions.

Figure 3.3 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION STARTED WITH 10 mM $CaCl_2$.

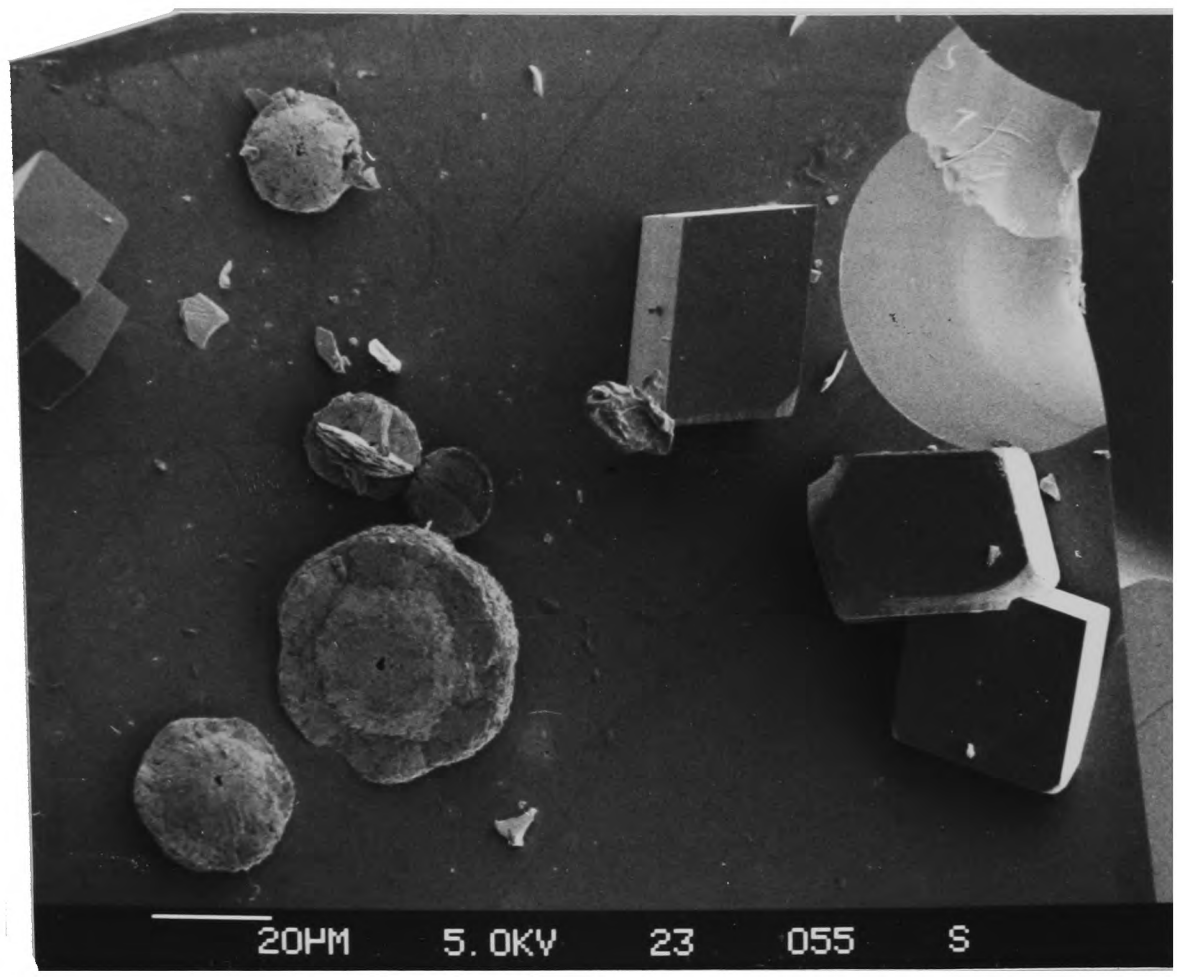
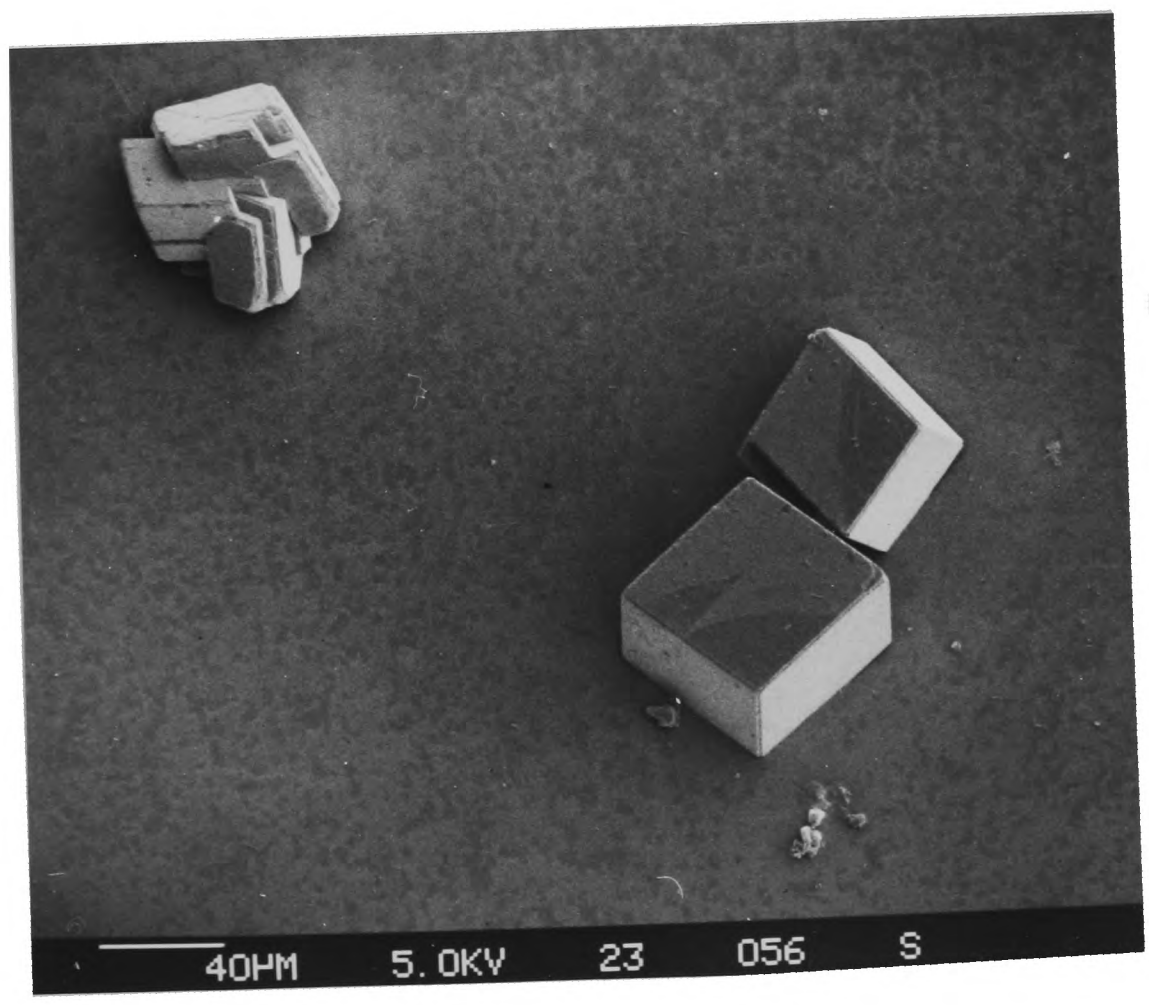


Figure 3.4 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION STARTED WITH 2 mM $CaCl_2$.



The effect of calcium concentrations on the precipitation rates, both PR (precipitation rate expressed as the rate of decrease in concentration of calcium ions) and PRH (expressed as the rate of decrease of solution pH), in 5 to 10 mM calcium chloride solutions were significantly higher than that in 2 mM solution. The low precipitation rate (both of PR and PRH, Table 3.2) in 2 mM calcium chloride solution may be another reason why vaterite did not precipitate. Kitano (1962) suggested that a rapid precipitation rate tends to yield the unstable forms.

In general, rapid precipitation rate is associated with high supersaturation, i.e. high SI. The SI of the 2 mM treatment is a little lower than that of other treatments, and there are no significant differences between those of 5 to 10 mM treatments (Table 3.2). The results of this study suggest that the formation of vaterite is related to the concentration of the calcium ions in reaction solutions rather than to precipitation rate.

3.2.1.3 Conclusion

(1) The lower the initial concentration of calcium ions in reaction solutions, the higher the "peak pH" attained. However if the concentration is too low, no "peak pH" occurrs .

(2) The precipitation of vaterite seems to be correlated with a high concentration of calcium ions rather than a high concentration of carbonate ions.

3.2.2 The precipitation of calcium carbonate in a seeded system

Previous studies (Reddy and Nancollas, 1971; deBoer, 1977; House, 1981[b]; Inskeep and Bloom, 1985) confirm that the precipitation rate of calcium carbonate (calcite) is related to surface area (S) and degree of supersaturation (SI); although different

reaction powers of the two factors have been used. Since we want to develop a model to describe the precipitation of calcium carbonate in soil, it is important to study the reaction model. Most workers, who study the precipitation model have only used a special batch of seeds. In this study we want to use varying sizes of calcite-seeds to develop a universal model of calcium carbonate precipitation to determine the reaction orders of S and SI. However, most of the precipitates of calcium carbonate crystals in soil systems are shapeless so it seems impossible to calculate the surface area. It would be useful to investigate whether another factor could be used instead of surface area. For instance, the results in chapter 4 show that in a reaction solution containing a strong inhibitor the precipitates of calcium carbonate develop as clumps of small particles, the weight of which is correlated with their surface area.

Since the calcium-sensitive electrode tends to be unstable over a long period, it was not possible to monitor the changes in calcium ion activity throughout the reaction. A technique was developed in this study that used the measured solution pH and NT (estimated from AADR) to estimate the amount of $CaCO_{3(s)}$ precipitated from the reaction solution during reaction. Two samples (near the "peak pH" and one hour later) for each run of each treatment were taken for determining the calcium ion activities by the calcium-sensitive electrode to check the reliability of the technique. A best-fit regression equation (a polynomial) through 15 data points was used to describe the relationship between $CaCO_{3(s)}$ and time for each treatment. Then the first differential of each equation was used to describe the reaction rate of calcium carbonate precipitation. Finally different solution parameters such as S (surface area), SI, and

W0 (the initial weight of particles), and WA (the amount of newly formed $CaCO_{3(s)}$), were tested on various models to find the most effective variables which could be used to describe the precipitation rate.

In this section, varied weights of calcite-seeds grouped according to diameter, were treated in order to examine the effects of surface area, supersaturation degree, and the newly formed calcium carbonate, on rate of precipitation.

3.2.2.1 Materials and Methods

Seeds of calcite

Details of the separations of calcite-seeds are described in appendix 2.

Two groups (10-15 and 30-35 μm) of seeds were separated from a commercial calcite (purchased from BDH) by a sedimentation method. The seeds of calcite were examined (50 seeds from each group) and the lengths of two sides per particle were measured under light microscope. The average width of edge for the 10-15 μm group was 12.16±1.97 μm, and for the 30-35 μm group it was 30.59±3.52 μm. All the seeds were rhombic, almost cubic, but most of them had a rough surface with a layered appearance. Since these two groups of seeds had been separated using Stokes' law, they were treated as round particles to calculate their particle surface area and particle weight. On this basis the surface areas of a single seed were 4.91×10^{-6} and 3.32×10^{-5} cm^2 for the 10-15 and 30-35 μm groups respectively, and their corresponding weights were 2.77×10^{-9} and 4.87×10^{-8} g.

The other two groups (75-150 and 150-212 μm) were obtained from natural particles after grinding fine natural crystals and dry sieving. These two groups of calcite seeds were examined

under a light microscope in the same way as the finer groups. They all had a rhombohedral appearance and smooth surfaces. The average width of edge for the 75-150 μm group was 118.4±46.2 μm and for the 150-212 μm group it was 186.9±66.2 μm. These rhombohedral particles had angles near 90^0 so their particle surface was treated as rectangular and the width of the edges were taken as 112.5, and 181 μm instead of 118.4 and 186.9 μm. Their corresponding surface areas were 7.59×10^{-4} and 1.96×10^{-3} cm^2, and their weights were 3.86×10^{-6} and 1.61×10^{-5} g per particle.

Estimation of particle surface area during the experimental period

No newly formed nuclei were found by examining the crystals before the experiments started and at the end of experiments under a light microscope. The change of surface area of a particle is estimated from the decrease or increase of its weight, whether by addition or dissolution, and is assumed that the addition or loss is evenly distributed over all of its surface. Once the change of particle weight has been calculated, the new surface area is simply obtained by multiplying it by a factor that was referred to as ri,

$$ri=(pw1/pw)^{2/3}$$

where pw is the initial weight of a single particle, pw1 is the new weight, 2/3 is the algebraic factor that transfers the change of particle weight into the change of particle surface area. For example, when the length of the edge of a particle doubles, its surface area will be squared and its weight and volume will be the cube of their corresponding initial values.

For each treatment, the total weight of seeds, the volume of reaction solution, and the surface area for each particle was estimated, giving the average initial particle surface area, S0,

expressed in cm^2/ml . The particle surface area (Si) of particles after the change of weight was estimated by

Si=S0 ri.

Treatments

Table 3.3 shows the 16 treatments with different weights of these four groups of seeds, where "+" denotes treatments done and "-" denotes no treatment.

Table 3.3 TREATMENTS WITH DIFFERENT WEIGHTS AND SIZES OF CALCITE-SEEDS.

size, μm	weight of seeds, g						
	0.01	0.025	0.05	0.1	0.3	0.5	1.0
10-15	+	+	-	+	-	+	+
30-35	-	+	+	+	-	+	+
75-150	-	-	+	+	+	+	+
150-212	-	-	-	+	-	-	-

Procedures

Standard procedures (p. 9) were used under the following conditions : -

(1) A 20 cm test tube with a diameter of 2.5 cm was used instead of the 100 ml beaker.

(2) The PVT used as a bubbler was led to the bottom of the test tube to make bubbles to stir up the seeds and to distribute them evenly throughout the reaction solution.

(3) 65 ml of 0.01 M $CaCl_2$ solution was used.

(4) At least four replications of each treatment were performed, except for the treatment with 0.1 g of 150-212 μm seeds which had two replications.

Technique for estimating the amount of $CaCO_{3(s)}$ precipitated by the measured solution pH and AADR

In a calcite-seeded experimental system, the changes of

solution pH depended on the addition rate of base from the dissolution both of ammonia (B_{NH3}) and calcite-seeds (B_{CaCO3}), and on the release rate of acidity from calcium carbonate precipitation. In this experimental system with a constant AADR (ammonia dissolution rate) and at constant P_{CO2} (0.00484 atm) and temperature (25^0 C), we may distinguish the part of base B_{NH3} from that of base B_{CaCO3}, and may estimate the amount of calcium carbonate precipitated by measured solution pH.

It has been discussed in section 2.2.4 of chapter 2 that in a $H_2O-CO_2-NH_3$ system with constant P_{CO2} and temperature, solution pH (here referred to as theoretical solution pH) can be estimated when NT, the total concentration of ammoniacal-N, is given. Consequently the concentration of base (B_{NH3}) can be estimated. NT also can be estimated by multiplying AADR by time. Presumably the principles used in the $H_2O-CO_2-NH_3$ system also can be used in the $H_2O-CO_2-NH_3-CaCO_{3(s)}$ system, in that, whenever the amount of source of base (B_{NH3} and B_{CaCO3}) is given, both the theoretical solution pH and the equilibrium concentration of base can be predicted.

In order to separate the sources of base, i.e., B_{NH3} from B_{CaCO3}, and to estimate the amount of calcium carbonate precipitated, constant AADR, P_{CO2}, and temperature are needed, as well as two further conditions, viz. : - (1) When solution pH is at 7.12 the ion activity product of calcium carbonate in the reaction solution will be equal to the equilibrium ion activity product of calcite, i.e. SI=1. When calcite ($-\log(K_{CIAP})=8.48$) is in equilibrium in aqueous solution at pressure 1 atm, temperature 25^0 C, and P_{CO2} 0.00484 atm, the solution pH will be 7.12. (2) When solution pH is higher than 7.12 (pH > 7.12), B_{CaCO3} will increase no further (i.e. there will be no further dissolution).

Using the assumptions made above, the calculation was performed in stages A and B :

(A) This stage was used to estimate the amount of B_{CaCO3} when solution pH <= 7.12. The calculation of the theoretical concentration of base in solution using NT is described in A1 and referred to as Base 1 (i.e. B_{NH3}). The real concentration of base in solution calculated using NT and the measured solution pH is described in A2 and referred to as Base 2. The difference between the real base concentration and the theoretical base concentration is taken as the part of base dissolved from calcite (i.e. B_{CaCO3}). The amount of B_{CaCO3} at pH=7.12 is the maximum amount of B_{CaCO3} dissolved from calcite in each treatment.

(B) This stage was used to estimate the amount of calcium carbonate precipitated when solution pH was >7.12. In B1, the maximum amount of B_{CaCO3} calculated from stage (A) was added to the total amount of base in solution to calculate the theoretical value of solution pH and concentration of base and referred to as base 3. B2 describes the method used to calculate the real concentration of base (referred to as base 4) in solution using NT and measured solution pH. The shortfall of base in base 4 compared to base 3 is due to the amount of calcium carbonate precipitated.

The calculation programs are detailed in appendix 2, a brief description follows :

(A) The amount of base dissolved from calcite-seeds at pH <= 7.12

The method of estimating the amount of B_{CaCO3} when pH < 7.12 is the same as that when pH = 7.12, therefore only the method used to estimate the maximum amount of B_{CaCO3} is presented here.

(A1) The amount of base in solution was calculated based on the assumption that the solution base was only added to the reaction

solution from ammonia dissolution as in a CO_2-NH_3-H_2O system without calcite-seeds. The total concentration of base was defined as,

$$\underline{\text{Base 1}}=[OH^-] + [HCO_3^-] + 2[CO_3 2-] + [NH_4HCO_3^0] + 2[NH_4CO_3^-] \quad (3.20)$$

The calculating program was described in section 2.2.4 of chapter 2.

In this experimental system, NT was estimated by multiplying AADR by the time taken for the solution pH to reach 7.12, since AADR was stable throughout the whole reaction time. The theoretical solution pH was calculated from NT and P_{CO2}, then the concentration of hydroxide, bicarbonate, and carbonate ions were calculated, and finally the theoretical concentration of <u>Base 1</u> was calculated.

(A2) We will consider the reaction solution in a H_2O-CO_2-NH_3-$CaCO_3$ system. The chemical reactions in the system will include the reactions mentioned in the H_2O-CO_2-NH_3 system (section 2.2.4 of chapter 2), and the dissociation reactions of the complex ion pairs, calcium bicarbonate $CaHCO_3^+$ (equation 3.21) and calcium carbonate $CaCO_3^0$ (equation 3.22),

$$CaHCO_3^+ \text{ <=> } Ca^{2+} + HCO_3^- \quad (3.21)$$

$$CaCO_3^0 \text{ <=> } Ca^{2+} + CO_3^{2-} \quad (3.22)$$

where k_{cahco3} (dissociation constant of $CaHCO_3^+$), and k_{CaCO3} (dissociation constant of $CaCO_3^0$) are quoted in Table A.2.1 of appendix 2. The ionic strength was calculated as

$$I=0.5(4[Ca^{2+}] + [CaHCO_3^+] + [H^+] + [NH_4^+] + [OH^-] + [HCO_3^-] + 4[CO_3^{2-}] + [NH_4CO_3^-]) \quad (3.23)$$

The principle of the program was the same as in section 2.2.4 of chapter 2. On this basis the concentration of NT and solution pH are measured. The iterative calculating procedure was as follows :

(1) An approximate value of I from (A1) was estimated.

(2) The ion activity coefficients of all components were calculated using the approximate values of I. The activity coefficient of $CaCO_3^0$ was taken as 1 and the activity coefficient of $CaHCO_3^+$ was taken to be the same as that for bicarbonate.

(3) The concentrations and activities of all components were calculated.

(4) Since the dissolution of calcite-seeds would occur in this system, the concentration of calcium ions in this system would be higher than the initial concentration of 10 mM. So the concentration of calcium ions, $[Ca^{2+}]$, was calculated as half of the shortfall of positive charge in the reaction solution as

$$[Ca^{2+}]=0.5(0.02 + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [NH_4CO_3^-]) - ([CaHCO_3^+] + [H^+] + [NH_4^+]) \quad (3.24)$$

(5) The new concentrations of all solution components were used to calculate a new value of I using equation 3.23.

(6) When the calculating program reached the control requirement, i.e. the difference of I between two successive runs was less than 1.0×10^{-6}, base 2 was calculated by

$$\underline{\text{Base 2}}=[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [NH_4HCO_3^0] + 2[NH_4CO_3^-] + [CaHCO_3^+] + 2[CaCO_3^0] \quad (3.25)$$

The difference between base 2 and base 1 then was taken as maximum amount of B_{CaCO3},

$$B_{CaCO3}=\underline{\text{base 2}} - \underline{\text{base 1}} \quad (3.26)$$

(B) The amount of calcium carbonate precipitated

The total concentration of calcium carbonate precipitated in the reaction solution was estimated by the difference between the theoretical concentration of base (base 3, described in (B1)) and the real concentration of base (base 4, described in (B2)).

(B1) This part was used to calculate the theoretical concentra-

tion of base (referred to as base 3) from NT and the maximum amount of B_{CaCO3} (from (A)) assuming that no calcium carbonate was precipitated during the experiment period even when the solution pH was far greater than 7.12 (i.e. SI>1). The programming procedures were similar to those of (A2) with the following exceptions : -

(1) The approximate starting value of I was estimated as

$$I=0.03 + 0.95NT + B_{CaCO3}.$$

(2) An approximate value of bicarbonate activity was estimated using the concentrations of NT and B_{CaCO3} as

$$(HCO_3^-)=f_{HCO3}(0.95NT + B_{CaCO3}).$$

(3) Equation 2.14 was used to estimate an approximate value of solution pH.

(4) The activity of the calcium ion in (A2) was used as the approximate starting value.

(5) The concentration of calcium ionswas estimated by subtracting the concentration of calcium complex from the total potential calcium concentration including the initial 0.01 M and the part dissolved from calcite 0.5 B_{CaCO3} (half of B_{CaCO3}).

$$[Ca^{2+}]=0.01 + 0.5B_{CaCO3} - [CaHCO_3^+] - [CaCO_3^0] \quad (3.27)$$

(6) Base 3 was calculated by

$$\text{base 3}=[OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [NH_4HCO_3^0] + 2[NH_4CO_3^-] + [CaHCO_3^+] + 2[CaCO_3^0]. \quad (3.28)$$

(B2) This part was used to calculate the real concentration of base in solution (referred to as base 4) using NT and the measured solution pH. The calculating procedures in this part were similar to those in above (A2) with the following exceptions : -

(1) At the beginning approximate values of I and (Ca^{2+}) were adopted from the results of (B1).

(2) The concentration of calcium ion was calculated from the shortfall of positive charge using the charge balance equation 3.24.

(3) The concentration of base 4 was calculated as

$$\underline{\text{base 4}} = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + [NH_4HCO_3^0] + 2[NH_4CO_3^-] + [CaHCO_3^+] + 2[CaCO_3^0] \quad (3.29)$$

The amount of newly formed calcium carbonate was calculated as

$$[CaCO_{3(s)}] = 0.5(\underline{\text{base 3}} - \underline{\text{base 4}}) \quad (3.30)$$

A positive value of $[CaCO_{3(s)}]$ indicates that precipitation of calcium carbonate took place. On the other hand a negative value would signify the dissolution of calcite seeds. This would conflict with the assumption that there would be no further dissolution of calcite-seeds when solution pH was higher 7.12. Some low negative values (seen in Figures 3.5) were calculated from this program during the early part of the experimental period, but, in view of the errors associated with variations in pH measurements, they were considered to be acceptable.

Calcium carbonate precipitation rate

A best-fit regression equation of polynomial was fitted to $[CaCO_{3(s)}]$ and time to describe the precipitation of calcium carbonate throughout the reaction period (by SAS program). In each treatment, the solution pH (the mean of replications) at 15 reaction times were entered into the program (written in Fortran 77 described in appendix 2) to calculate the values of $[CaCO_{3(s)}]$ and concentrations of solution components. The first differentiation at that value of time of the best-fit regression equation was, therefore, used to describe the precipitation rate throughout the reaction period.

3.2.2.2 Results and Discussion

The results of this section are rather complicated, so they have been divided into several parts for easier understanding. Part (A) describes the changes in pH and the quantity of base in solution. Part (B) describes the estimation of the amount of newly formed calcium carbonate. Part (C) describes the factors that control calcium carbonate precipitation rate.

(A) The changes in pH and concentration of base in solutions during reaction period

<u>The changes in solution pH</u>

As mentioned above, in the calcite seeded system, the reaction solution received base not only from ammonia introduced into the bubbling system, but also base added by the dissolution of calcite-seeds during the initial stages of the reaction when the solution pH was still low and SI less than 1.0.

Table 3.4 SOLUTION pH 20 MINUTES AFTER THE START OF THE EXPERIMENTS, THE LARGEST STANDARD DEVIATION OF DATA IS 0.02 pH UNITS.

size, μm	weight of seeds, g						
	0.01	0.025	0.05	0.1	0.3	0.5	1.0
10-15	6.76	6.97	-	7.15	-	7.17	7.16
30-35	-	6.80	6.86	6.94	-	7.12	7.15
75-150	-	-	6.60	6.63	6.84	6.88	7.06
150-212	-	-	-	6.58	-	-	-

The detailed data are presented in Tables A.3.1 to A.3.16 of appendix 3; only part of the data are quoted for this discussion. Figure 3.5 gives brief pictures of the changes of solution pH during the reaction period for the 16 treatments. It shows that the greater the amount of seeds added to each group of seeds and the finer the seeds used, the higher the solution

pH reached in the early stages. Table 3.4 (above) which shows the pH of the reaction solutions 20 minutes after the start of the experiments, also allow these comparisons to be made.

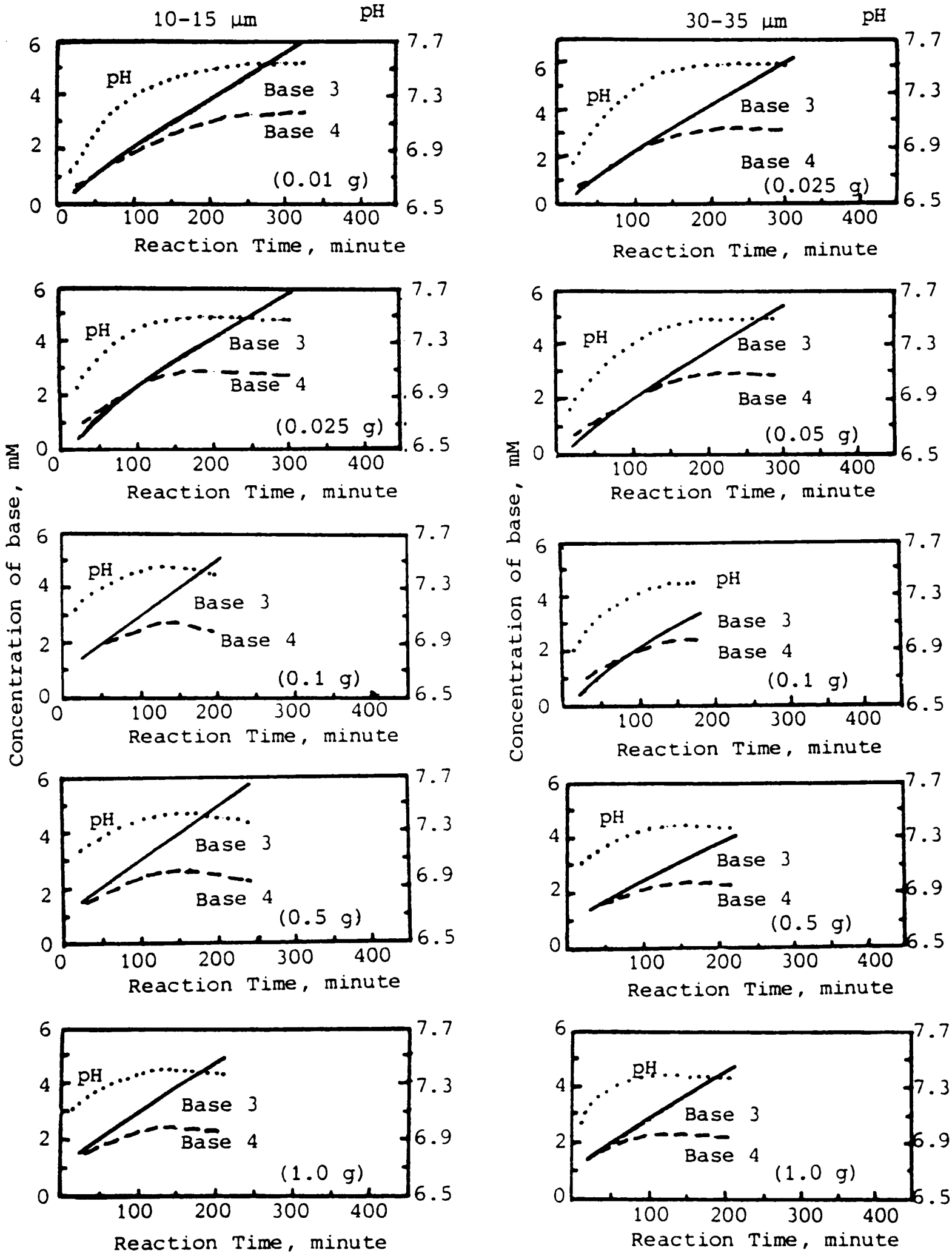
In this experimental system, at the early stage, with the same bubbling period, variations of the part of base from NT (B_{NH3}) between treatments will be negligible because the variation of AADR between treatments is negligible. Thus the differences in concentration of base and their corresponding pH value between different treatments may be due to the differences in the additional amount of base from dissolved calcite-seeds (B_{CaCO3}). Presumably this is reflected in the greater surface area exposed in the solution by the greater number or the smaller sizes of seeds used. Plummer et al (1979) confirm that the rate of dissolution is related to surface area. This is supported by observations of the solution pH during the early stages.

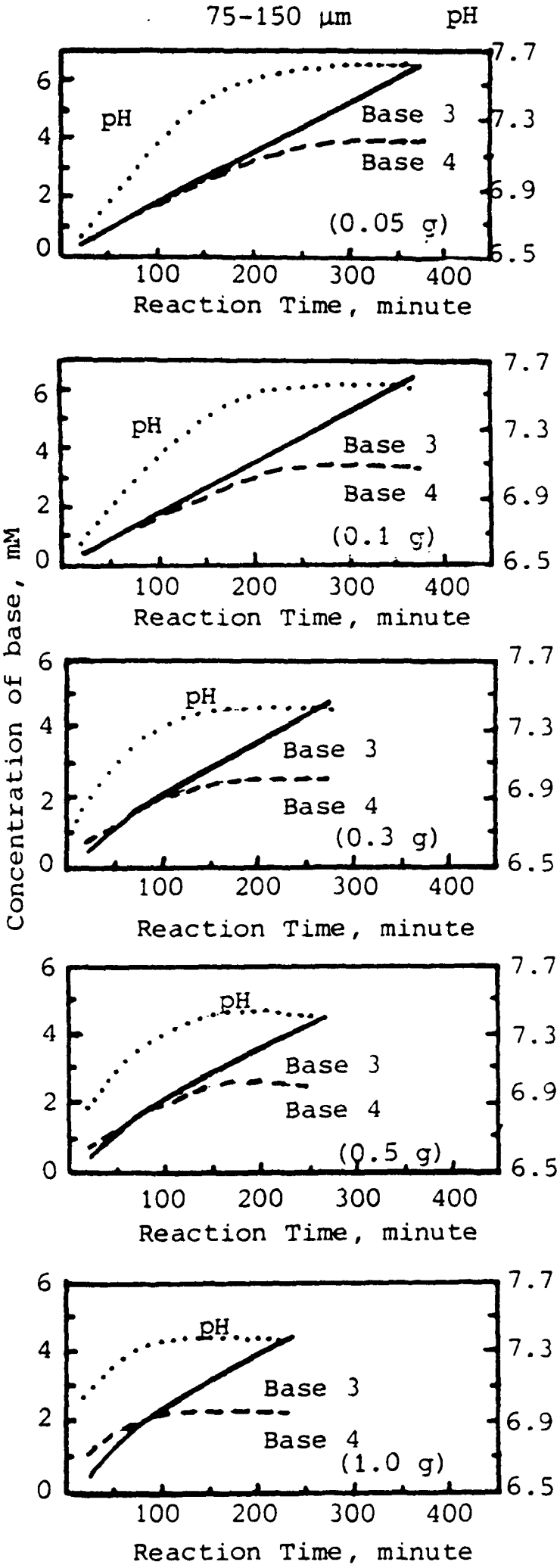
The calculation of the concentration of B_{CaCO3} is presented in parts (A) and (B) in the section on materials and methods (p.67), and results are presented later (in part (C) (p.80)).

Table 3.5 THE "PEAK pH" of 16 TREATMENTS, THE LARGEST STANDARD DEVIATION OF DATA IS 0.04 pH UNITS.

size, μm	weight of seeds, g						
	0.01	0.025	0.05	0.1	0.3	0.5	1.0
10-15	7.55	7.49	-	7.47	-	7.45	7.40
30-35	-	7.52	7.49	7.40	-	7.39	7.38
75-150	-	-	7.62	7.56	7.44	7.44	7.38
150-212	-	-	-	7.63	-	-	-

Figure 3.5 THE CHANGES OF SOLUTION BASE WITHOUT (SOLID LINE) AND WITH (BROKEN LINE) TAKING ACCOUNT OF THE EFFECT OF CALCIUM CARBONATE PRECIPITATION, AND SOLUTION pH (DOTTED LINE) IN THE REACTION SOLUTIONS OF 16 TREATMENTS.




75-150 μm
pH
Base 3
Base 4
(0.05 g)
(0.1 g)
(0.3 g)
(0.5 g)
(1.0 g)
Concentration of base, mM
Reaction Time, minute
150-212 μm

As mentioned before, Figure 3.5 shows that at the early stages of reaction the smaller the weight of calcite-seeds used, the lower the solution pH measured. As reaction proceeded the solution pH for the lower amounts of calcite-seeds increased and eventually became higher than that found for the higher amounts of calcite-seeds. It appeared that, although the dissolution rate for higher amounts of calcite-seeds was initially higher, the SI of the reaction solution quickly reached the value that allowed calcium carbonate precipitation to start, so that solution pH remained at a relatively low level. Comparison of "peak pH" values for each treatment, given in Table 3.5 (above), makes this evident. More details are available in Table A.3.1-16 of appendix 3.

The changes of concentration of base

Estimates of the amount of calcium carbonate precipitated were based on the difference between the theoretical concentration (base 3) and the real concentration (base 4) of base in reaction solutions. It is important to examine the changes of the two bases before speculating on the calcium carbonate precipitation.

Figure 3.5 depicts the changes in solution pH and concentrations of base 3 and base 4 of all 16 treatments. It is found in Figure 3.5 that the greater the weight of calcite-seeds, and the finer the particles, the higher the solution pH in the early stages of the reaction, but the lower the "peak pH" during the whole of the reaction.

Actually, when the theoretical base (base 3), assuming no precipitation is compared with the real base (base 4), the effect of the addition of seeds on solution base is very marked. In the early stages of the reaction, the concentration of base in the

reaction solutions that contained larger amounts of added seeds increased more quickly than those containing small amounts of seeds. Table 3.6 shows the concentration of base 4 in reaction solutions 20 minutes after initiating the reaction.

Table 3.6 THE CONCENTRATION OF BASE (mM) IN REACTION SOLUTION 20 MINUTES AFTER THE START OF THE EXPERIMENTS.

size, μm	weight of seeds, g						
	0.01	0.025	0.05	0.1	0.3	0.5	1.0
10-15	0.54	0.89	-	1.35	-	1.41	1.38
30-35	-	0.60	0.69	0.83	-	1.26	1.35
75-150	-	-	0.38	0.40	0.66	0.72	1.09
150-212	-	-	-	0.36	-	-	-

(B) The estimation of the newly formed calcium carbonate

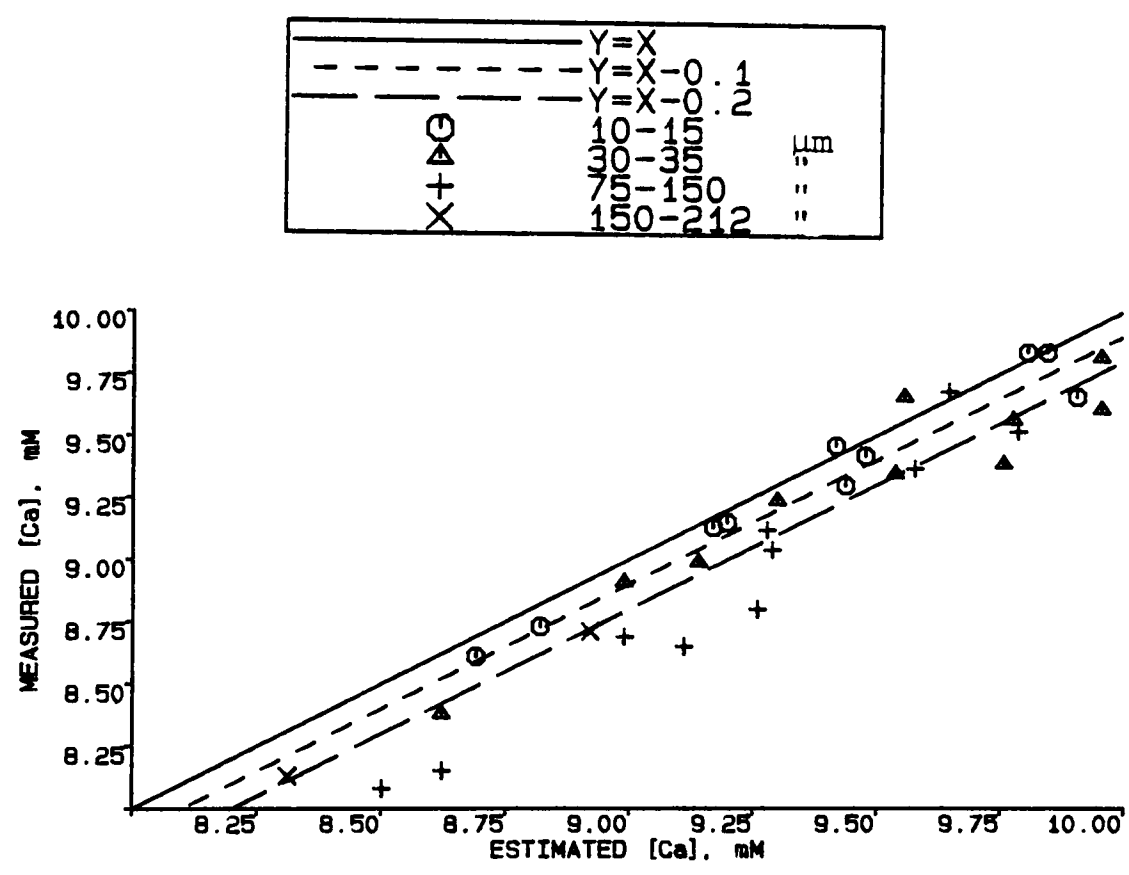
The reliability of the estimation of calcium carbonate precipitated

Before generating models of calcium carbonate precipitation using the results estimated from solution pH and NT, the reliability of the results was examined.

Since the quantity of calcium carbonate precipitated is related to the concentration of calcium ions remaining in reaction solutions, the reliability of the estimate of concentration of calcium ions can be used to calculate the error in the estimate of the amount of calcium carbonate precipitated. Figure 3.6 shows the comparison of concentration of calcium ions in reaction solutions between the estimated and the measured values. In general, the estimated values were greater than the measured values. The lower values of the measured concentration of calcium ions remaining in reaction solutions can be explained by the fact that some calcium carbonate may precipitate during the measurement of the activity of calcium ions in the extracted

solutions using a calcium-sensitive electrode. It is likely that the P_{CO2} in the reaction solution decreased after the reaction solution was taken out of the reaction vessel. If so, the decrease of P_{CO2} would cause the solution pH and SI to increase, which in turn would have enhanced the precipitation during the operation measuring calcium activity. In practice the differences between estimated and measured data are less than 0.2 mM. They are therefore negligible and acceptable, and the estimated data are reliable.

Figure 3.6 COMPARISON OF THE CONCENTRATIONS OF CALCIUM IONS IN THE REACTION SOLUTIONS MEASURED USING CALCIUM-SENSITIVE ELECTRODE AND ESTIMATED BY CALCULATION FROM SOLUTION pH AND BASE.



(C) The precipitation of calcium carbonate

As Inskeep and Bloom (1985) reported, there are two important criteria in evaluating fundamental or empirical models. First, the model should fit the data, or the model should describe why there is a lack of fit. Second, if the model is based on certain assumptions or fundamental relationships, then

these assumptions should be theoretically sound. It is not enough that a model fit the data if there are flaws in its theoretical foundation. Therefore all possible factors which might control the precipitation must be examined to determine which of them are critical.

Table 3.7 COEFFICIENTS USED IN THE BEST-FIT EQUATIONS FOR THE AMOUNT OF CALCIUM CARBONATE PRECIPITATED ($CaCO_{3(s)}$) WITH REACTION TIME (t), $[CaCO_{3(s)}]=a + bt + ct^2 + dt^3$.

Weight g	a x10^4	b x10^5	c x10^8	d x10^{10}	F	R^2
10-15 µm seeds						
0.01	12.49 ±2.28	-1.215 ±0.299	2.554 ±1.00	0.415 ±0.00	17557	0.999
0.025	10.27 ±0.20	-2.283 ±0.038	14.49 ±0.0	-2.117 ±0.00	99999	0.999
0.1	0.290 ±0.156	0.072 ±0.054	0.144 ±0.100	1.486 ±0.00	11153	0.999
0.5	0.143 ±0.174	-0.163 ±0.048	1.378 ±0.00	0.472 ±0.00	24487	0.999
1.0	-0.261 ±0.060	0.267 ±0.023	0.166 ±0.236	0.856 ±0.070	33388	0.999
30-35 µm seeds						
0.025	14.20 ±0.60	-2.896 ±0.100	17.30 ±0.01	-2.507 ±0.00	34144	0.999
0.05	6.945 ±0.533	-1.548 ±0.098	9.523 ±1.00	-1.246 ±0.00	12320	0.999
0.1	7.595 ±0.820	-1.605 ±0.167	9.242 ±1.00	-0.629 ±0.00	21252	0.999
0.5	0.195 ±0.078	0.091 ±0.024	0.257 ±0.218	0.645 ±0.058	35016	0.999
1.0	2.532 ±0.714	-1.099 ±0.190	13.68 ±2.00	-2.917 ±0.00	3499	0.999
75-150 µm seeds						
0.05	27.80 ±1.72	-3.199 ±0.197	10.77 ±1.00	-0.858 ±0.00	31182	0.999
0.1	15.84 ±1.28	-2.262 ±0.169	9.636 ±1.00	-0.973 ±0.00	8926	0.999
0.3	10.28 ±0.45	-2.180 ±0.077	13.60 ±0.00	-2.030 ±0.00	47877	0.999
0.5	4.224 ±0.410	-0.859 ±0.056	4.035 ±0.00	0.114 ±0.00	1716	0.999
1.0	3.848 ±0.200	-1.367 ±0.046	13.02 ±0.00	-2.492 ±0.00	56963	0.999
150-212 µm seeds						
0.1	26.00 ±1.65	-2.826 ±0.166	9.000 ±1.00	-0.686 ±0.00	14683	0.999

Precipitation rate of calcium carbonate in reaction solutions

In order to estimate the precipitation rate of calcium carbonate during the reaction period, the changes of the amount of precipitated calcium carbonate ($[CaCO_{3(s)}]$) during the reaction was described by regression equations. The best-fit regression equation for each treatment was fitted to $[CaCO_{3(s)}]$ and time, to describe the precipitation of calcium carbonate throughout the reaction period (by SAS program). Table 3.7 (above) shows that the best-fit third order equations with respect to time all have high values of F test (significant probability greater than 0.0001) and R^2 (0.999). Thus the equations and the first differentiated equations can be used to describe the amount of calcium carbonate precipitated and the precipitation rate during the reaction period.

The growth of particles during calcium carbonate precipitation

According to the literature survey, the surface character of calcite is affected by the change of composition in the solution and uncertainty exists in the estimation of surface area. Therefore the role of particle surface area on the precipitation rate must be examined. In this study the calcite seeds were examined under light microscope before and after each reaction. It could be seen that the surface of the particles became smoother after the reaction. This implies that a newly deposited layer may modify the initial surfaces of particle and change their character, which might affect further precipitation; although the growth of the particle in the experimental system seems to agree with the assumption that the newly precipitated calcium carbonate is evenly spread over the existing particles. Two observations support this assumption : -

(1) In an experiment with 0.01 g of 10-15 μm seeds, the growth

of particles was examined. When 1.3 mM of calcium carbonate was deposited, the total weight (WAt) of the newly formed calcium carbonate in the reaction solution (65 ml) is

WAt=1.3 mM x 65 ml x 100 g/mole=0.0084 g.

The total weight of particles becomes 0.0184 g, and becomes 1.84 times that of initial weight (0.01 g). If the specific density of the newly formed part is the same as the seed, the volume of the particle will become 1.84 times that of the initial volume, and the width of particle edge will become 1.22 (i.e $(1.84)^{1/3}$) times that of the initial width. When the initial mean of width of edge is 12.16±1.97 μm, its width will be 14.84 μm which is close to the observed value 14.60±3.74 μm (the mean of 50 particles with two sides of each are measured).

(2) In an experiment with 0.025 g of 30-35 μm size of seed, when 1.53 mM of calcium carbonate precipitated, the total weight (WAt) of the newly formed calcium carbonate in the reaction solution (65 ml) is

WAt=1.53 mM x 65 ml x 100 g/mole=0.0099 g.

The total weight of particles becomes 0.0349 g, i.e., 1.40 times that of initial weight (0.025 g). The volume of the particles becomes 1.40 times that of the initial volume, and the width of particle edge becomes 1.12 times that of the initial width. When the initial mean of width of edge is 30.59±3.52 μm, its width will be 34.26 μm. This value is close to the observed value, 33.92±2.06 μm, that is the mean of 50 particles measuring two sides of each.

Although the variation of size of calcite-seeds is high, the growth in size is consistent. Thus the surface area of calcium carbonate can be predicted if it is assumed that the newly deposited calcium carbonate was evenly spread over the initial

surface. Therefore, whenever the changes of calcium carbonate is estimated, the surface area of precipitates (Si) will be estimated by $Si=S0\ (pw1/pw)^{2/3}$.

The model of the rate of precipitation of calcium carbonate

The precipitation rate of calcium carbonate is related to surface area (S) and degree of supersaturation (SI),

$$PR=f(S, SI).$$

When the reaction orders of S and SI to the precipitation rate are not pre-set, the rate equation will be

$$LR=LK + a1\ LS + a2\ LSI \qquad (3.31)$$

where LK=log(precipitation rate constant K), LR=log(PR), LS=log(S), LSI=log(SI), and a1 and a2 the reaction powers of S and SI respectively. So far we have discussed the method to estimate the values of the precipitation rate, the surface area, and the degree of supersaturation during the reaction period. With data collected from the 16 treatments (the available data points are over 210), after regressing LR on LS and LSI, the best-fit equation is

$$LR=-5.948\pm0.104 + 0.228\pm0.046\ LS + 1.161\pm0.167\ LSI,$$

and the standard deviation of each coefficient is very small, the F test (24.13) is very significant, though the $R^2=0.19$ is low. The coefficient of surface area (S) 0.228±0.046 is significantly different from 1, this may be due to the changes of topography of particle surface, or because of the uncertainty associated with the values of surface area calculated. Since the coefficient of the degree of supersaturation (SI) 1.161±0.167 is not significantly different to 1.0, it is suggested that precipitation rate is directly proportional to SI. Mucci and Morse (1983) and Mucci (1986) reported that the reaction power of supersaturation degree on the rate of calcium carbonate precipi-

tation is 2.8 when inhibitors are absent and increases when inhibitors are present; this value is questionable because : (i) they assumed that the rate of precipitation is proportional to the total surface area, but they did not calculate the growth in surface area. (ii) they used the average value of rate of precipitation, over at least six hours, instead of measuring precipitation rate at frequent intervals. However, results from previous reports support the assumption that the precipitation rate of calcium carbonate is proportional to the supersaturation degree. Nancollas and Reddy (1971) found that the precipitation rate of calcite is directly proportional to the concentration product of calcium and carbonate ions. Inskeep and Bloom (1985) reported that the initial precipitation rate of calcite is proportional to the supersaturation degree. House (1981[b]) also found that, when the extent of precipitation is between 0.1 and 0.45 of the total amount of calcium carbonate precipitated, the rate of precipitation is proportional to the degree of supersaturation. Thus we will accept that the precipitation rate of calcium carbonate is proportional to SI.

It is very difficult to have a precise estimation of the surface area of calcium carbonate in soils. However the observation in chapter 4 shows that the precipitates of calcium carbonate in a solution containing strong inhibitor are clumps of small particles, and the weight of newly formed calcium carbonate (WA, g ml^{-1}) may have a similar effect on precipitation rate to that of surface area. Hence we may approach a precipitation model (in logarithmic form) as

$$LR - LSI = LK' + a1' \, LWA \qquad (3.32)$$

where LWA is log(WA). The best-fit equation when (LR - LSI) regresses on LWA is

$$LR - LSI = -4.113 \pm 0.132 + 0.379 \pm 0.029\ LWA,$$

where the value of F test is 204 and R^2 is 0.508. The value of R^2 of equation 3.32 is much greater than that of equation 3.21. This is due to the range of SI values in the experimental system being quite narrow; the highest SI is only about 10. When the WA is used as an independent variable, it changes along with the changes in precipitation rate, hence a better R^2 is obtained.

Statistically the application of an empirical equation is limited to its data range. In this experimental system, the narrow ranges of changes in SI and the small change of weight of WA in reaction solution may restrict the application of the model. Therefore when the model

$$LR = -4.113 \pm 0.132 + 0.379 \pm 0.029\ LWA + LSI \qquad (3.33)$$

is applied to soil systems, some correction may be needed.

3.2.2.3 Conclusion

(1) Results suggest that the reaction order of SI is 1.0 in the calcite precipitation model.

(2) Measurement of the weight of the newly formed calcium carbonate in the precipitation model is effective for estimating the rate of precipitation of calcium carbonate.

CHAPTER 4

THE INHIBITORY EFFECTS OF UREA, MAGNESIUM, PHOSPHATE, AND WATER-DISSOLVED ORGANIC MATTER ON THE PRECIPITATION OF CALCIUM CARBONATE

When urea is applied to soil by spreading it on the surface or by banding, the concentration of urea in soil solution may reach a high level (its saturation concentration is about 10 M, according to Rachhpal-Singh, 1984). However, there is no report so far examining the effect of urea on calcium carbonate precipitation. Magnesium, phosphate, and water-dissolved organic matter (DOC) are important soil components from the viewpoint of soil chemistry and have been reported as strong inhibitors on the precipitation of calcium carbonate. Therefore, in addition to urea the effects of these inhibitors on calcium carbonate precipitation were also examined singly (sections 4.1 to 4.4) and in various combinations (section 4.5) in this chapter. A comprehensive review of literature about the inhibitors will be given in individual sections.

A number of workers (Reddy and Nancollas, 1973; Reddy, 1977; Reddy and Wang, 1980; and Inskeep and Bloom, 1986[bc]) have claimed that it is possible to make reliable measurements of crystal growth rate in the presence and absence of inhibitors by means of a seeded experimental system. However, some results (from literature and previous study) show that a seeded experimental system may not be applicable to conditions found in nature for the following reasons :

(1) Well-defined crystals of calcium carbonates are not common in soils (Inskeep and Bloom 1986[c]).

(2) Polymorphs of calcium carbonate may be formed in natural environments (Brooks et al., 1950).

However, it has been shown that the bubbling experimental system with no seeds added (developed in chapter 2) can be used to examine the effects of inhibitors on the precipitation of calcium carbonate, not only by their inhibitory potential as expressed by the "peak pH" of reaction solutions, but also by the formation of polymorphs. Thus the bubbling experimental system described in section 2.2.1 was used for the studies in chapter 3 and was used in this chapter as well.

Solution pH in this study was monitored with a pH meter and recorded by a double-pen chart recorder; other parameters (e.g. activity of calcium ions and the concentration of ammoniacal-N) were measured twice, once at the "peak pH" and the other at about one hour after the "peak pH". However in order to concentrate on the aim of this chapter, only the values of related parameters at "peak pH" and some at one hour later are shown in Tables.

4.1 THE EFFECT OF UREA ON THE PRECIPITATION OF CALCIUM CARBONATE

Since the Debye-Hückel equation cannot be used to calculate ionic activities of non-ionic solutes in aqueous solution, the effect of urea concentrations in aqueous solutions on calcium ion activities have to be measured directly with a calcium-sensitive electrode.

In preliminary experiments, urea reduced calcium ion activities when urea concentrations were higher than 0.1 M. The activities of calcium ions in 0.01 M $CaCl_2$ solution decreased 11 and 62 per cent with the addition of 1 M and 5 M urea, respectively (Table A.1.1 of appendix 1). The contributing effects of urea at 1 M and 5 M on ionic strength (I) are equivalent to monovalent electrolytes at 0.05 and 0.96 M, respectively. When

urea is applied to soil its concentration in the surrounding solution may reach these levels (Rachhpal-Singh, 1984). Experiments with varying concentrations of urea were carried out to examine the effect of urea on the precipitation of calcium carbonate.

4.1.1 Materials and Methods

Except for the addition of urea (0.01, 0.1, 1, or 5 M) to the 0.01 M calcium chloride reaction solution all of the experimental processes here were similar to those in the standard system in section 2.2.1 (p. 9).

4.1.2 Results and Discussion

As previously described, solution pH increased along with the dissolution of ammonia in the bubbling system until solution pH was high enough to raise the degree of supersaturation of calcium carbonate for the precipitation of calcium carbonate to occur. The increase of solution pH then slowed down and began to decrease when the rate of release of acidity from calcium carbonate precipitation was higher than the addition rate of base from ammonia dissolution, i.e. 2PR>AADR.

The results in Table 4.1 show that when urea concentrations were 0.01 and 0.1 M there were no differences in the all measured parameters, e.g., pH_p (the "peak pH"), NT (total ammoniacal-N concentration excluding urea-N), [Ca] (concentration of calcium ions), $CaCO_{3(s)}$ (calcium carbonate precipitated), SI (degree of supersaturation of calcium carbonate), and PR (average rate of precipitation of calcium carbonate between two sampling times), compared with those from experiments without urea. The differences of these parameters between treatments are within the

standard deviation of replications. However at 1 M and 5 M the values of pH_p and SI, and the value of NT at 5 M, were significantly higher than those in other treatments.

Table 4.1 THE EFFECT OF UREA CONCENTRATIONS ON THE PRECIPITATION OF CALCIUM CARBONATE.

Urea, M	0.0	0.01	0.1	1.0	5.0
pH_p	8.09±0.03	8.06±0.02	8.08±0.04	8.14±0.03	8.41±0.00
NT, mM	7.32±0.89	8.3±0.2	8.3±0.1	8.0±0.2	14.2±1.7
[Ca], mM	7.81±0.26	7.89±0.59	8.74±0.02	8.03±0.03	7.54±0.62
(Ca), mM	3.87±0.09	3.78±0.21	4.10±0.06	3.44±0.08	1.58±0.12
f_{Ca}	0.50	0.48	0.47	0.43	0.21
$CaCO_{3(s)}$, mM	2.19±0.26	2.11±0.51	1.25±0.00	1.98±0.03	2.46±0.62
PR, ($x10^5$ mol litre^{-1} min^{-1}	0.93±0.20	1.12±0.59	1.36±0.05	0.94±0.34	1.68±0.01
SI	50.6±8.5	45.9±9.7	55.6±9.5	62.1±9.4	98.3±12.8
RE	6	4	4	4	4

f_{Ca}, activity coefficient of calcium ion; f_{Ca}=(Ca)/[Ca].
PR, Precipitation rate calculated by the formation of calcium carbonate after the peak pH point.

The results may be due to the effect of urea concentration on the calcium ion activity. If it is true that the effect of urea concentration on the calcium activities is only due to the effects on ionic strength, calcium ion activity in solution may be measured by a calcium-sensitive electrode. Then the empirical equation 3.19 (p.59) (which describes the relationship between the pH_p of the reaction solution and its initial calcium ion activity) could be used to estimate the pH_p in solutions containing urea. In 0.01 M $CaCl_2$ solution the activity of calcium ions is 5.46 mM calculated by the Debye-Hückel equation. The activity of calcium ions became 4.84 mM determined by the calcium-sensitive electrode when the solution contained 1 M of urea, and became 2.09 mM with

5 M of urea. The value for pH_p estimated by equation 3.19 is 8.13, which is reasonably in agreement with the experimental value, 8.14±0.03, in 1 M urea. However the predicted value, 8.33, in 5 M is lower than the experimental value of 8.41±0.00. This shows that the influence of high concentration of urea on the precipitation of calcium carbonate is greater than that due to its effects on calcium activity, and/or that the measurements of ionic strength with the calcium-sensitive electrode were affected by urea concentration above a critical level. It is beyond the purpose of this study to determine this critical concentration.

The relation between urea concentration and pH_p is shown in Figure 4.1 and can be described by equation 4.1.

$$pH_p = 8.07 \pm 0.01 + 0.062 \pm 0.023\ [U] + 0.0011 \pm 0.0004\ [U]^2 \quad (4.1)$$

where pH_p is the "peak pH" of the reaction solution, [U] is the concentration of urea, and r=0.99. Using equation 4.1, when [U] is zero, the estimated "peak pH", 8.07, agrees with the experimental value, 8.09±0.03. When [U] is 10 M the estimated "peak pH" will be 8.81, however this high urea concentration condition will rarely occur or will not remain long in arable soils.

The crystals of calcium carbonate precipitated from reaction solutions containing 1 M (Figure 4.2; from SEM) and 5 M urea show rhombohedral and plate-like shapes. They are similar to the crystals precipitated in the 0.01 M $CaCl_2$ solution without urea (Figure 3.3 (p.62)), and were identified as calcite and vaterite by X-ray diffraction. The increase of SI due to 1 M and 5 M urea suggests that the high concentration of urea may delay the nucleation of calcite and vaterite but does not affect their crystal growth once it has started, or it may only show that the calcium-sensitive electrode cannot reflect calcium activity properly at such a high concentration of urea.

Figure 4.1 THE RELATIONSHIP BETWEEN THE INITIAL CONCENTRATION OF UREA AND THE PEAK pH IN 10 mM $CaCl_2$ REACTION SOLUTION.

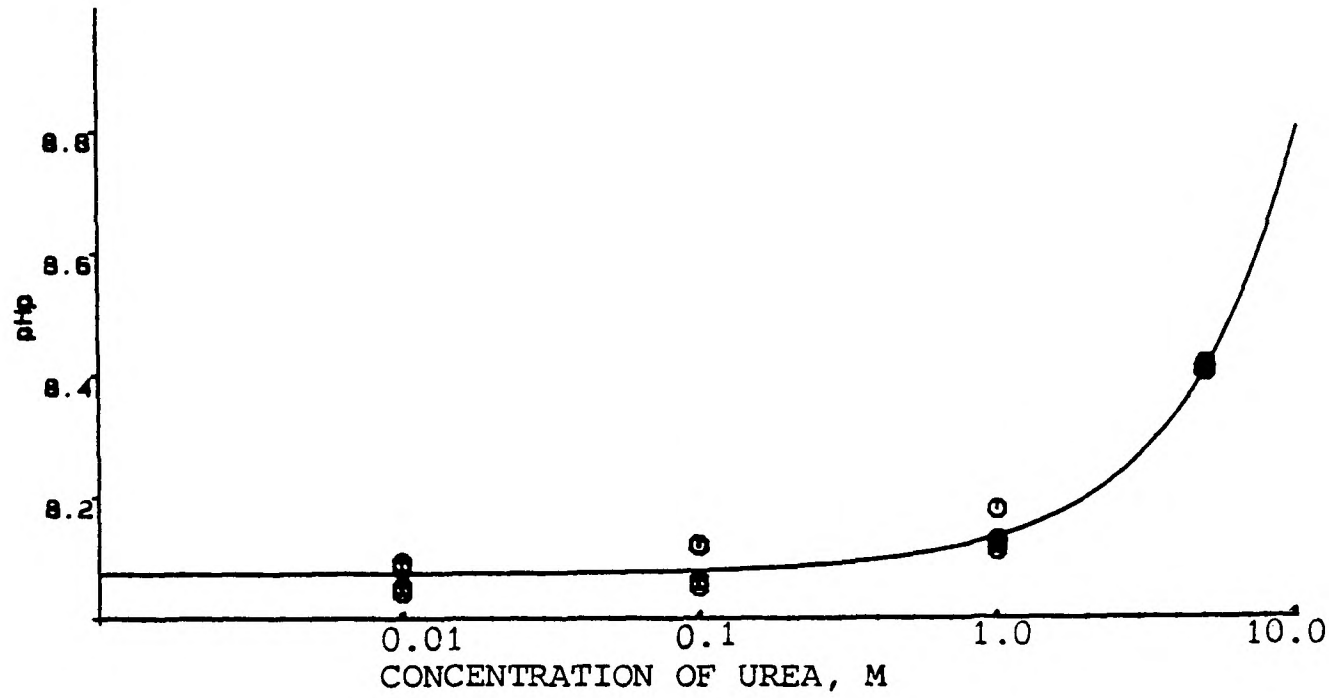
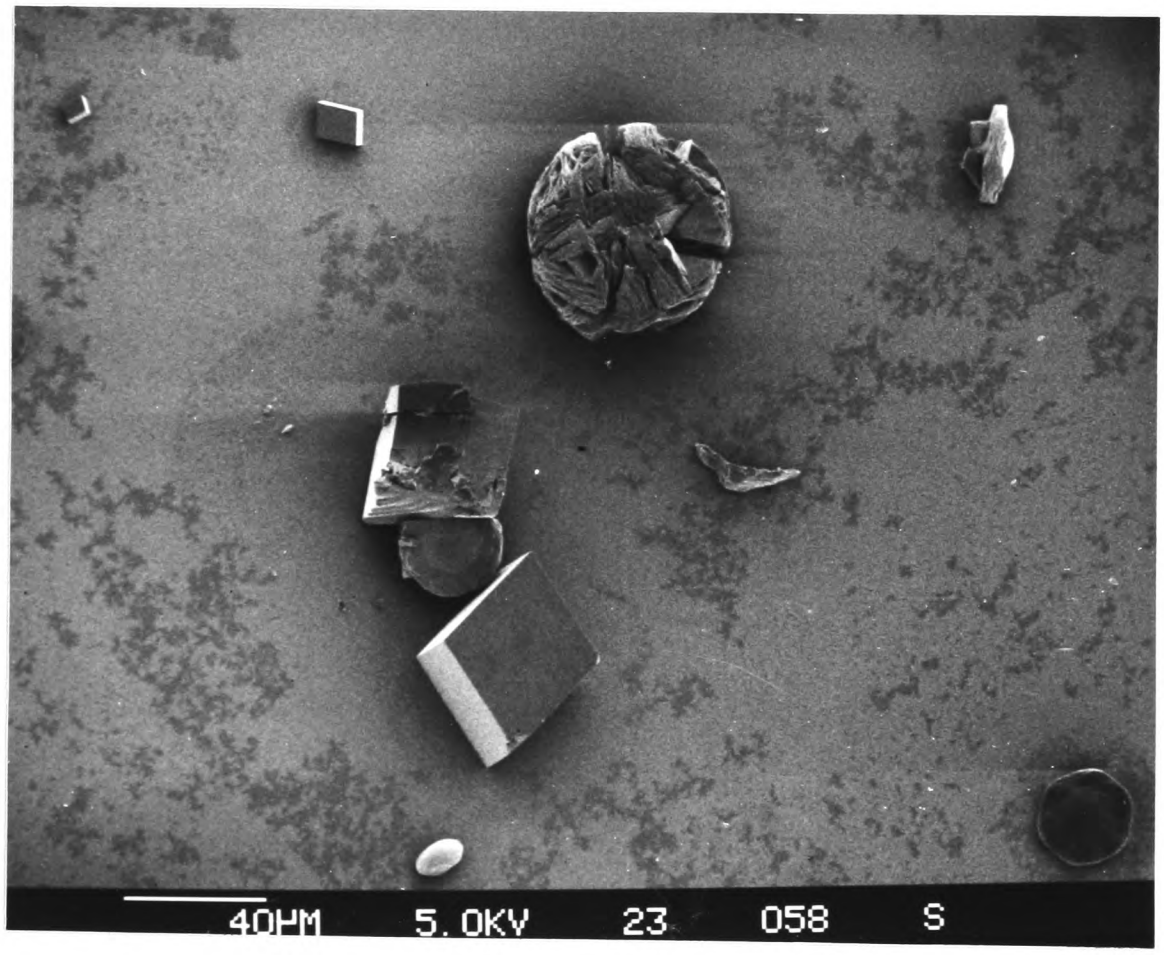


Figure 4.2 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING UREA AT 1 M.



4.1.3 Conclusion

The results suggest that urea does not affect the appearance of the calcite and vaterite. At high concentrations, urea affects calcium ion activity. This effect can be observed by the increase of the "peak pH" of solution, but the effect tends to be underestimated by the calcium ion activities measured with a calcium-sensitive electrode.

4.2 THE EFFECT OF MAGNESIUM ON THE PRECIPITATION OF CALCIUM CARBONATE

It is well-known that Mg ions influence the solubility, kinetics of precipitation and dissolution, crystal morphology, and diagenesis of calcium carbonate. Numerous reports have given contradictory observations, so it is necessary to have a brief review before describing further experiments.

The formation of magnesian calcite and its effect on the solubility of calcite

Levy (1981[b]) suggested that it is a magnesian calcite that usually precipitates from supersaturated solutions of sea water. She also reported that some Mg was precipitated along with calcium carbonate, but that most of the Mg remained in solution. Mucci and Morse (1983) and Mucci et al. (1985) reported that the proportion of magnesium incorporated in magnesian calcite was determined by the concentration ratio of Mg/Ca in the reaction solution, and was independent of the precipitation rate over a wide range of degree of supersaturation. However, Doner and Pratt (1969) pointed out that variable amounts of Mg were precipitated with calcium carbonate, but their X-ray diffraction data did not prove that the precipitate was a magnesian calcite or any other well-defined crystalline magnesium carbonate.

Berner (1975), Marion and Babcock (1977), Mucci and Morse (1984), and Walter and Morse (1984) reported that the solubility of magnesian calcite generally increases as the amount of Mg substitution increases. Mackenzie et al. (1983) reported that in some soils and marine environments the extent of Mg substitution reached 10 to 15 mole per cent. Marion and Babcock (1977) have reported that the solubility of soil carbonate was apparently controlled by magnesian calcite.

Mucci and Morse (1984) and Walter and Morse (1984) pointed out that the solubility of calcite containing 0.1 mole fraction of Mg substitution is nearly 1.2 times that of pure calcite, and with a 0.2 mole fraction of Mg substitution the solubility is nearly 3 times more. Reddy and Wang (1980) found that for solutions with Mg/Ca ratios of 1.2, 2.9 and 5.0 their ion activity products of calcium and carbonate ions were 2, 3, and 4 times oversaturated with respect to pure calcite. However, Suarez (1977), Levy (1981[b]), and Mucci and Morse (1984) failed to find a correlation between the concentration of Mg in solution and the solubility of calcite in their experiments. Walter and Morse (1984) suggested that the wide range of solubilities of the magnesian calcite may be the result of the differences of sample preparation procedures. Inskeep and Bloom (1986[a]) also noted that the effect of Mg substitution cannot fully explain the oversaturation observed in experimental soil solutions.

The inhibition mechanisms of magnesium ions on the precipitation of calcium carbonate

Reddy and Wang (1980) reported that magnesium ions greatly decreased the calcite crystallization rate at 1 mM, but had almost no effect at 0.01 mM. Berner (1975) found magnesium concentration at sea water levels (54 mM) retarded calcite

precipitation, but at 2.7 mM no inhibition was evident. However, Katz (1973) noted that if the Mg/Ca ratio in solution was sufficiently low, the Mg ion did not prevent calcite crystallization, even in concentrations at the level of sea water.

Pytkowicz (1965) reported that the nucleation rate of calcium carbonate was second order with respect to the concentration of carbonate ions in the absence of magnesium, but it was sixth order in its presence. Mucci and Morse (1983) found that the logarithmic form of rate constant for the precipitation of calcium carbonate was a linear function of the ratio of Mg/Ca in the solution. They found that the empirical reaction order with respect to the concentration of carbonate ions increased from 3.07 to 3.70 as the Mg/Ca ratio increased from 1.0 to 10.3.

Sjöberg (1978), and Reddy and Wang (1980) suggested that the inhibition of calcite precipitation by Mg was due to surface adsorption. Mucci and Morse (1985) noted that the Mg/Ca ratio in the surface region of calcite (about 10 A^0) followed the Langmuir adsorption isotherm profile. Akin and Lagerweff (1965^{ab}) also used Langmuir adsorption theory to describe the adsorption of Mg on calcite, and postulated that the crystal surface consists of calcite with a modified lattice.

Dehydration of Ca and Mg ions

It has been reported that the inhibitory effect of Mg ions on calcite crystal growth is due, at least in part, to the slower dehydration of magnesium ions, relative to calcium ions, on the surface of calcite as the ions are incorporated into the crystal lattice (deBoer, 1977; Lahann, 1978; and Mucci and Morse, 1983).

Ion exchange on crystal surfaces

Experiments involving rapid precipitation from highly supersaturated solutions tend to yield calcite higher in

magnesium content (Berner, 1978) than that formed in natural sediments. On the other hand, the precipitation of magnesian calcite in natural conditions should be a slow process, and exchange equilibrium of magnesium between aqueous and solid phases may be more closely approximated (Lafon, 1978). This proposition is also supported by Mucci and Morse (1985). However, the Mg content of marine calcite ranges from 6 to 21 mole per cent (Milliman, 1974). A possible explanation is that the content of Mg in marine calcite is kinetically controlled by the rate or rate mechanisms by which they are precipitated (Berner, 1975, 1978; Thorstenson and Plummer, 1977, 1978).

The surface character of calcite

Ionic radius, lattice type (carbonates), polarizability, and heat of hydration of Mg and Ca ions fail to explain the difference of the adsorption of these ions on calcite. Douglas and Walker (1950) suggested that the net magnitude of the specific crystal and Coulombic forces acting on the hydrated ions near the crystal surface can explain it. They also reported that in calcium chloride solution at mM levels the zeta-potential of Iceland spar is positive, but it is negative in magnesium chloride solutions of the same concentration range. However, Thompson and Pownall (1989) found variable values of zeta potential ranging from positive to negative. These are more difficult to explain, since they showed no systematic dependence on solution pH, dissolved calcium, or total dissolved carbonate concentrations.

The effect of magnesium on the formation of Polymorphs

The aragonite form of calcium carbonate did not precipitate until the concentration of Mg in the reaction solution increased to 8.1 mM (Doner and Pratt, 1969). Kitano (1962, cited from

Kitano and Hood, 1965) stated that in calcium bicarbonate solutions with temperatures ranging from 10^0 to 39^0 C, the forms of precipitated calcium carbonate were calcite and aragonite, with 0 to 10 per cent of aragonite in reaction solutions containing no magnesium, and 70 to 90 per cent of aragonite when the reaction solutions contained 6 mM magnesium. He concluded that the Mg ion influenced the crystal forms but was not incorporated since no magnesian calcite was found. Chave and Suess (1970) found that the Mg ion affected calcium carbonate nucleation. However, Berner (1975) reported that magnesium affected the crystallization of calcite but not that of aragonite.

Although so much effort has been put into studies of the effect of magnesium on the precipitation of calcium carbonate, the mechanism of its effects is still uncertain. This study examined the effect of magnesium ions on the precipitation of calcium carbonate within the limits of magnesium concentration normally occurring in soil.

4.2.1 Materials and Methods.

All experimental processes and methods were similar to those of section 2.2.1 with the following exceptions :

(1) Reaction solutions contained magnesium chloride with concentrations at 0.01, 0.1, 1, and 5 mM.

(2) The concentration of magnesium in reaction solutions was determined using an atomic absorption spectrophotometer (Unicam, sp1900). The solutions were filtered through 0.2 μm filter (Millipore) before they were diluted with acid solutions of lanthanum ions (1000 ppm).

The decrease in concentration of magnesium ions in reaction

solutions was used to estimate the amount of magnesium precipitated along with the precipitation of calcium carbonate.

4.2.2 Results and Discussion

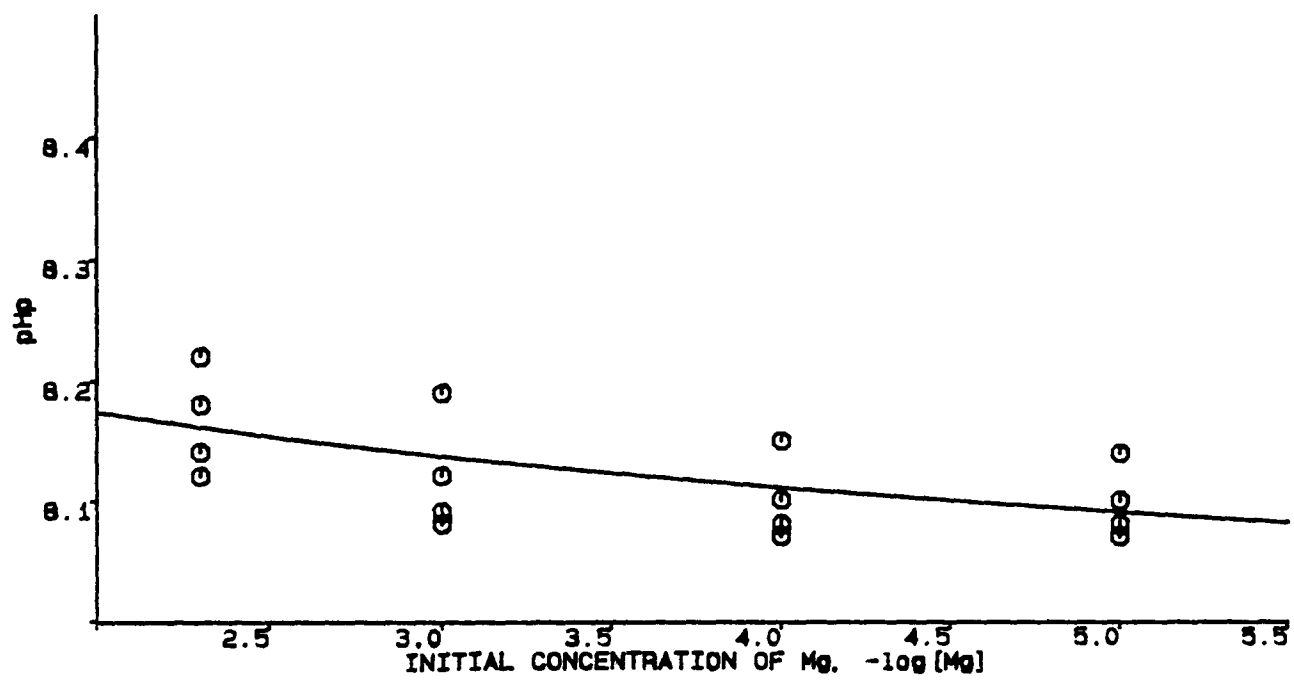
The "peak pHs" (pH_p, in Table 4.2, below) were 8.10±0.03, 8.10±0.03, and 8.12±0.06 in reaction solutions which contained 0.01, 0.1, and 1 mM magnesium, respectively. They are not significantly different from that with no magnesium (8.09±0.03). Even when the reaction solution contained 5 mM magnesium, the "peak pH" (8.16±0.04) was only raised by 0.07 pH units. As mentioned in section 4.1, if the addition of inhibitors did not affect the precipitation of calcium carbonate, then the "peak pH" of the reaction solutions could be estimated by equation 3.19 using the measured calcium activity. The values calculated by this equation according to their effect on the ionic strength were 8.09, 8.09, 8.10, 8.11, and 8.12, respectively. All of the estimated values were close to the measured values. The discrepancy between the measured and estimated "peak pH" increased with the increase of concentration of magnesium. The increase of the "peak pH" value in solutions with the greatest amount of added magnesium (5 mM) confirms that the magnesium ion has an inhibitory effect on the precipitation of calcium carbonate; but the effect is not as great as claimed by Reddy and Wang (1980). The potential effect of magnesium on the "peak pH" of the reaction solutions can be described by an empirical equation (equation 4.2) as shown in Figure 4.3 (solid line).

$$pH_p = 8.24 \pm 0.04 \; pMg^{-0.011 \pm 0.004} \qquad (4.2)$$

where pMg is -log(the initial concentration of magnesium). The correlation coefficient (r) of the equation is 0.99. From a practical point of view, this expression is more useful than the

Langmuir equation . However, the low value of the power (0.011) of the magnesium concentration on "peak pH" indicates that magnesium ions have only a small effect on the formation of calcium carbonate in soil situations.

Figure 4.3 THE RELATIONSHIP BETWEEN THE INITIAL CONCENTRATION OF MAGNESIUM AND THE "PEAK pH" IN 10 mM $CaCl_2$ REACTION SOLUTION.



The presence of magnesium may inhibit the precipitation of some forms of calcium carbonate and stimulate growth of other forms of calcium carbonate. Examining the collected crystals should help to demonstrate this effect. The results from X-ray diffraction show that only calcite was formed in a reaction solution containing 1 mM magnesium; but both aragonite and calcite were found in 5 mM experiments. No vaterite was found in either of them. This differs from Cole's results (1957). He found vaterite was precipitated in soil extracts containing magnesium. The presence of the magnesium ion stimulated the formation of vaterite in his study but it inhibited its formation in this study. The SEM photos confirm the results from X-ray diffraction, i.e. only rhombohedral particles were found in the reaction

solution containing 1 mM magnesium (Figure 4.4), but deformed rhombohedral and coral shaped particles (aragonite) were found in the reaction solution containing 5 mM magnesium (Figure 4.5). These results suggest that magnesium at 1 mM does not retard the formation of calcite but prevents the formation of vaterite. Magnesium not only inhibits the crystallization of calcite and the formation of vaterite but encourages the formation of aragonite at the 5 mM level. This agrees with the results of Doner and Pratt (1969), and Kitano (1962). However, the formation of aragonite in solutions without magnesium and the greater proportion of aragonite in magnesium enriched solutions in Kitano's experiments (cited from Kitano and Hood, 1965) seem unlikely to occur under the conditions of this study.

Table 4.2 THE EFFECT OF MAGNESIUM CONCENTRATIONS ON THE PRECIPITATION OF CALCIUM CARBONATE.

Mg, mM	0.0	0.01	0.1	1.0	5
pH_p	8.09±0.03	8.10±0.03	8.10±0.03	8.12±0.06	8.16±0.04
NT, mM	7.32±0.89	7.6±0.6	7.1±0.8	7.7±0.7	9.8±0.7
[Ca], mM	7.81±0.26	7.95±0.42	8.10±0.44	8.01±0.18	7.88±0.10
[Mg], mM	0.0	0.01±0.00	0.10±0.00	0.91±0.00	4.88±0.03
$CaCO_{3(s)}$, mM	2.19±0.26	1.66±0.34	1.48±0.28	1.56±0.12	1.66±0.08
$MgCO_{3(s)}$, $x10^4$ M	0.0	0.01±0.01	-	0.90±0.10	0.80±0.2
PR, $x10^5$ mol litre^{-1} min^{-1}	0.93±0.20	0.99±0.10	0.83±0.23	0.55±0.36	1.00±0.14
Mg♥, %	0.0	0.07±0.07	-	5.8±1.4	4.2±0.2
Mg♥♥, %	0.0	0.04±0.06	-	2.4±0.9	2.3±0.9
SI	50.6±8.5	64.6±5.9	58.8±5.7	69.0±20.4	79.1±16.1
RE	6	4	4	4	4

Mg♥, The ratio of $MgCO_{3(s)}$ to $CaCO_{3(s)}$ at the "peak pH".
Mg♥♥, The ratio of $MgCO_{3(s)}$ to $CaCO_{3(s)}$ one hour later than Mg♥.

The well formed crystals of calcite (Figure 4.4) in the 1 mM reaction solution suggests that magnesium at 1 mM may inhibit nucleation of calcium carbonate but does not affect the crystal growth once it has started. This agrees with the observations of Pytkowicz (1965), and Chave and Suess (1977). Berner (1975) claimed that magnesium only affects the crystallization of calcite, but the results from this study show that magnesium in high concentration (5 mM) inhibits calcite and aragonite growth as well, since no perfect crystal forms were found in the SEM photos (Figure 4.5) of the reaction solution with 5 mM magnesium.

In the reaction solution containing 1 mM magnesium (Table 4.2), the mole ratios of Mg/Ca in the deposited calcium carbonate were 5.8±1.4 and 2.4±0.9 per cent at the "peak pH" and one hour later, respectively. In reaction solution containing 5 mM magnesium, the corresponding values were 4.2±0.2 and 2.3±0.9 per cent. Comparing the proportion of magnesium in the deposited calcium carbonate for solutions with different concentrations, there is no difference in the ratio of Mg/Ca between 1 mM and 5 mM magnesium treatments both at the "peak pH" period and one hour later, though the ratio of concentrations of Mg/Ca increased from 1:10 to 5:10. However, in the reaction solution containing 0.01 M magnesium, the corresponding values were 0.07±0.07 and 0.04±0.06 per cent, which is much lower than those in 1 mM and 5 mM treatments. The results of this study did not fully agree with the results from Mucci and Morse (1983) and Mucci et al. (1985). They reported that the contents of magnesium in precipitated calcium carbonate were determined by the concentration ratio of Mg to Ca in the reaction solution; however the results in Table 4.2 suggest that when the ratio of Mg/Ca increased to a critical level it had no further effect.

Figure 4.4 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING 1 mM $MgCl_2$.

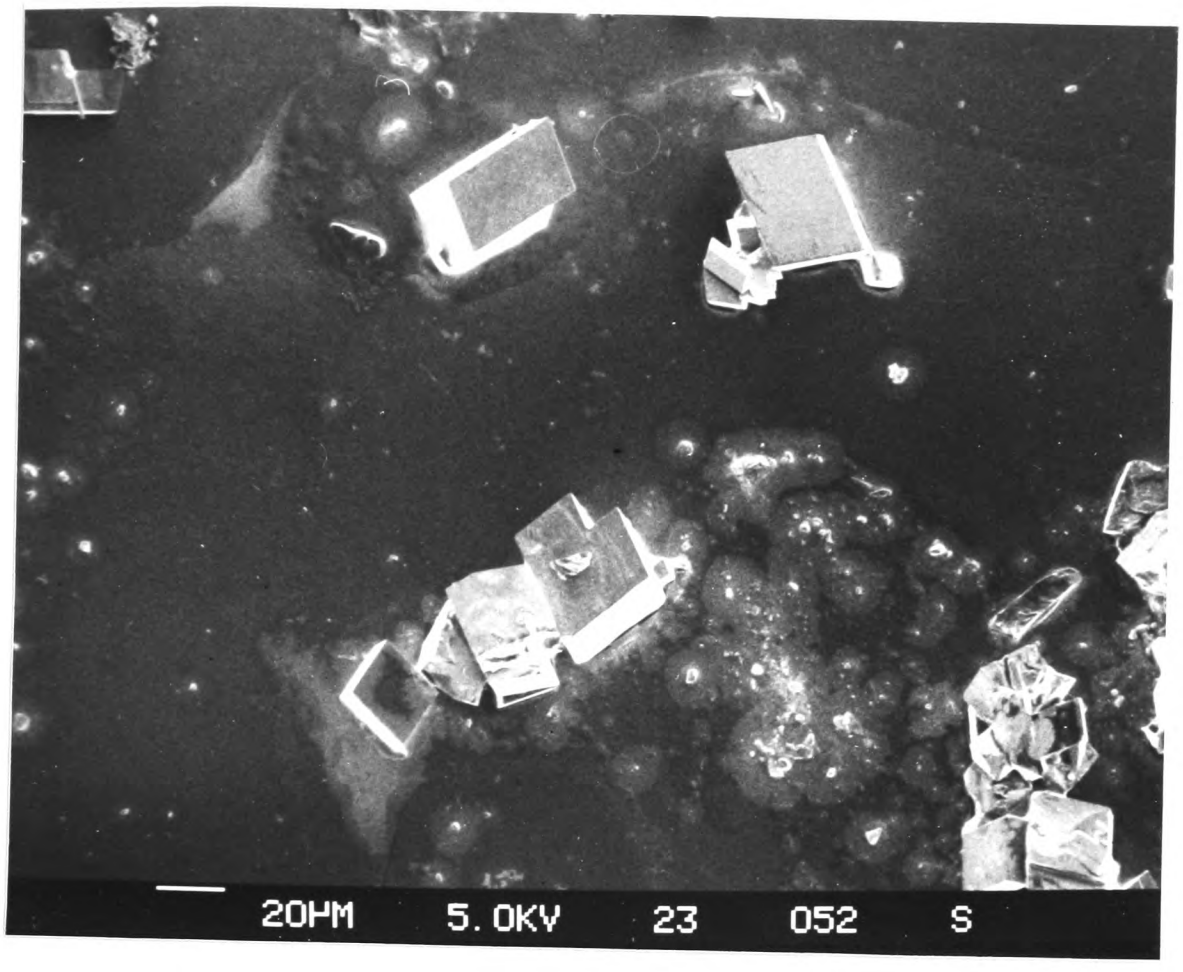
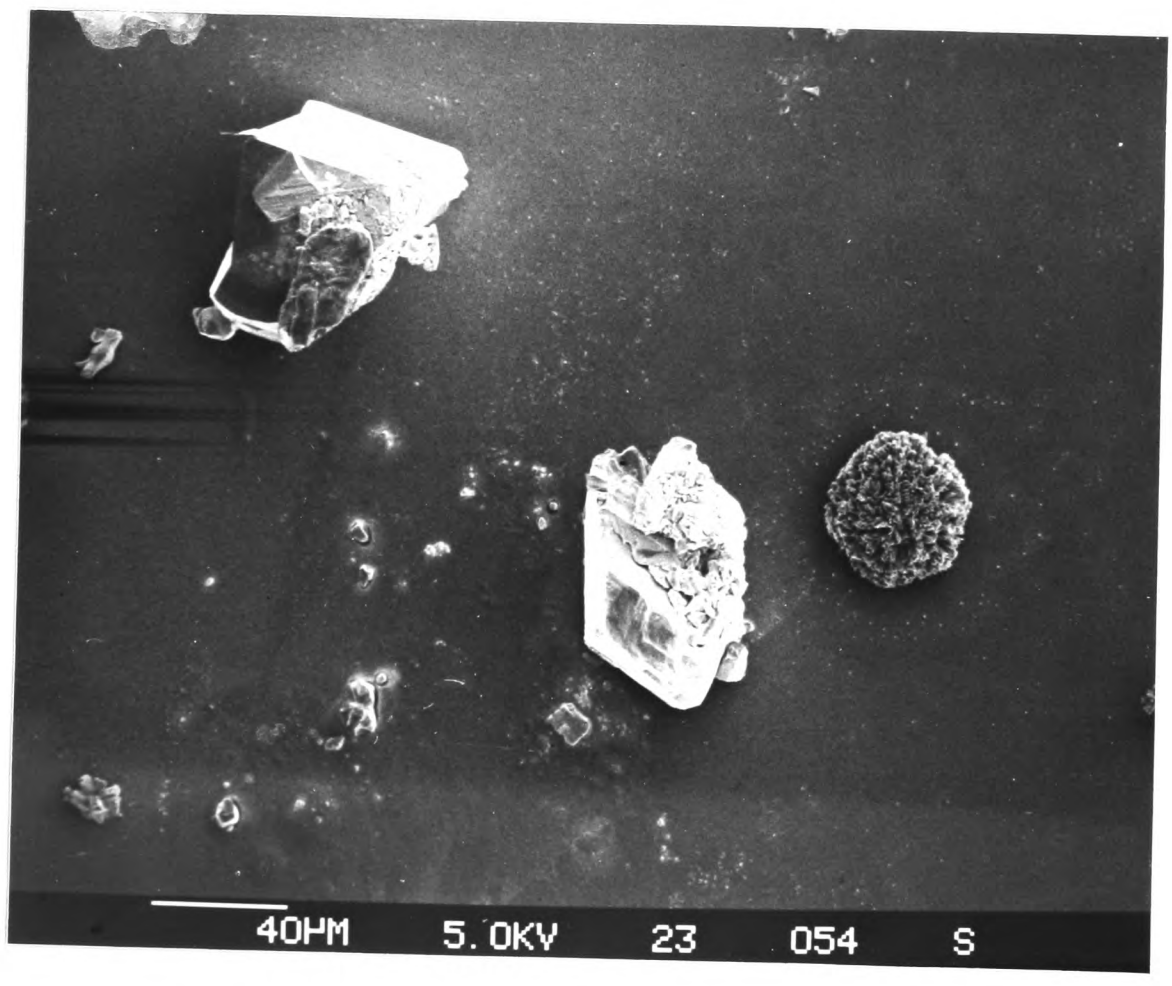


Figure 4.5 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING 5 mM $MgCl_2$.



Comparing the results between the two sampling times, the magnesium contents significantly decreased with the reaction time in all three treatments. The decrease of the magnesium contents in deposited precipitates (the content decreased nearly 50 per cent) suggests that the coprecipitation of magnesium with calcium carbonate in this study system may occur only on the crystal surfaces and is probably not due to the formation of magnesian calcite. It seems that if the ratio of Mg/Ca in the solution only affects the ratio on the surface region of deposited calcium carbonate, the relative amount of coprecipitated magnesium will decrease with the increase of size of precipitates, since the specific surface area of particles decreases as particle size increases. This explanation and results agree with the observations of Mucci et al (1985) that magnesium content was concentrated on the surface region of calcium carbonate.

This model may explain the conclusion of Suarez (1977), Levy (1981^{b}), and Mucci and Morse (1984) that there is no correlation between the concentration of magnesium and the solubility of calcite. It also could explain the conclusion drawn by Walter and Morse (1984) that the solubility of magnesian calcite varies widely with sample preparation procedures.

4.2.3 Conclusion

(1) The presence of magnesium at 1 mM concentration inhibits the formation of vaterite, but has no effect on the crystal growth of calcite.

(2) The presence of magnesium at 5 mM concentration encourages the formation of aragonite and inhibits the crystal growth both of calcite and aragonite by surface poisoning.

(3) Magnesium coprecipitates with calcium carbonate on the

surfaces of precipitates, but does not form a magnesian calcite.

4.3 THE EFFECT OF PHOSPHATE ON THE PRECIPITATION OF CALCIUM CARBONATE.

It is widely reported that phosphate is a strong inhibitor on the precipitation of calcium carbonate.

The mechanism of the inhibition of phosphate on the precipitation of calcium carbonate has been related to the adsorption of phosphate on the crystals (Simkiss, 1964). The adsorption of phosphate on the calcite surface is a low energy adsorption compared with its adsorption on dithionite-soluble Fe (Holford and Mattingly, 1975). Miura et al. (1964) found that phosphate even at a thousandth of the concentration of calcium ions in solution could prevent the spontaneous precipitation of calcium carbonate. Reddy (1977) pointed out that the concentrations of phosphate and glycerophosphate which halved the rate constant of the precipitation of calcium carbonate were 1.96±0.1 μM and 16.2±1.1 μM, respectively. Griffin and Jurinak (1973) reported that a monolayer capacity of phosphate per gram of calcium carbonate was 8.43 μg/g, while 25 μg/g was reported by Kuo and Lotse (1972). Therefore, in comparison with the experimentally determined specific surface area of the calcite, it seems that not more than 5 per cent of the surface is involved in phosphate adsorption (Griffin and Jurinak, 1973). The solution concentration of phosphate (6 μM) required to fill the monolayer specific sites is higher than that (<1 μM) in natural environments (Suarez, 1977). A comprehensive survey of the literature concerning the effect of phosphate on calcium carbonate precipitation is necessary for clearer understanding.

Active phosphate ion species

De Kanel and Morse (1978) postulated that either the HPO_4^{3-} or the PO_4^{3-} ion was the species active in the retardation; while Mucci (1986) assumed that it was the concentration of PO_4^{3-} ions rather than the reactive phosphate concentration that was the determining factor.

Adsorption isotherm

The kinetics of phosphate interaction with calcite may be described by two simultaneous reactions. One is second order and describes the adsorption of phosphate on the calcite surface. The other one is first order, and is thought to describe the surface rearrangement of phosphate clusters into calcium phosphate heteronuclei Griffin and Jurinak, 1974).

Reddy (1973, 1975, and 1977) and Reddy and Nancollas (1973) observed that the Langmuir equation can be used to describe the inhibitory effect of phosphate ions on calcite growth satisfactorily in low ionic strength solutions. The reactive adsorption sites for phosphate on calcite have been assumed to be the exposed surface Ca^{2+} ions. In an aqueous suspension of the solid it is assumed that the vacant coordinate positions may be occupied by water molecules, bicarbonate ions or hydroxyl ions. Phosphate ions may replace these molecules or ions in a chemical adsorption process. Douglas and Walker (1950) reported that even when a negative potential would accumulate on the surface of the calcite, phosphate ions can overcome the electrostatic energy barrier and be chemisorbed on the surface.

Freeman and Rowell (1981) reported that the exchangeability of phosphate adsorbted on calcite with isotope ^{32}P falls from 100 per cent for small amounts (0 to 10 μg phosphate per g of calcite) to a constant 30 per cent when larger amounts are present (200 to 1000 μg g^{-1}).

De Kanel and Morse (1978) reported that their data could not be described by Langmuir and Freundlich adsorption isotherms, but that it was satisfactorily described by Elovichian chemisorption theory and this was consistent with a heterogeneous growth.

Morse and Berner (1979) reported that when the reaction solution contained 10 μM of orthophosphate, the reaction order of calcite precipitation rate with respect to saturation state increased by approximately a factor of 6. Mucci (1986) noted that the precipitation rate of magnesium calcite was negatively related to the concentration of phosphate ions.

Dissolution

It has been reported that phosphate inhibits the dissolution of calcite (Morse, 1974[b]; Berner and Morse, 1974; and Sjöber, 1978) and of aragonite (Walter,1983, cited from Walter and Morse, 1984). However Morse et al. (1979) found that phosphate catalyses aragonite dissolution.

Stumm and Leckie (1971, cited from Avnimelech (1980)) suggested that the solubility of phosphate in calcareous soils may be controlled by the chemisorption of phosphate on calcium carbonate particles, with the formation of amorphous calcium phosphates or of surface complexes.

Coprecipitation of calcium phosphate and calcium carbonate

It has been reported that phosphate ions coprecipitate with calcium carbonate in lake water and stream water (Larsen and Widdowson, 1970; Otsuki and Wetzel, 1972; Hargreaves, 1983; and Murphy et al, 1983). The fall in phosphate concentration during the formation of particulate carbonate from the solution suggests that phosphate ions are incorporated into rapidly growing particulate carbonate, rather than adsorbed on particulate carbonate after it has formed crystals (Otsuki and Wetzel, 1972).

Avnimelech (1980) supported the formation of a surface compound ($Ca_3(HCO_3)_3PO_4$) on calcite, and quoted from Grimshow's (1971) assumption that this surface compound has a crystal structure like that of calcite or aragonite. In both crystals (calcium carbonate and calcium phosphate) three calcium ions are located on the surface of each cell unit. This is consistent with Rastrick's (1949) suggestion that the strong inhibitory effect of metaphosphate on the crystal growth of calcium carbonate is due to the orientation of the calcium atoms in the 111 faces of calcite being similar to that of the oxygen atoms in the metaphosphate chain.

Polymorphs

Brooks et al. (1950) found that 9 ppm Calgon (molar ratio of Na_2O/P_2O_5 is 1.12/1.0) prevented the nucleation of calcite, and 200 ppm prevented the precipitation of calcite, but did not affect the formation of vaterite.

The potential inhibitory effects of phosphate ions on the precipitation of calcium carbonates is examined in this study.

4.3.1 Materials and Methods

All the experimental processes and methods were similar to those in the standard system (section 2.2.1) under the following conditions : -

(1) Reaction solutions contained 0.01 M $CaCl_2$ and $2x10^{-7}$, $5x10^{-7}$, $1x10^{-6}$, $5x10^{-6}$, $1x10^{-5}$, $5x10^{-5}$, $1x10^{-4}$, and $5x10^{-4}$ M Na_2HPO_4.

(2) Calcium ion activities were measured using a calcium-sensitive electrode after the withdrawn reaction solutions had been diluted 25 times.

(3) The concentration of phosphate in reaction solutions was determined using the method developed by Watanabe and Olsen in

1965.

4.3.2 Results and Discussion

The "peak pH" of the reaction solution increased with the increase of phosphate concentration up to a phosphate concentration of $5x10^{-5}$ M. At higher phosphate concentrations the "peak pH" did not increase, but decreased (Table 4.3 and Figure 4.6). It is suggested that the decrease of the "peak pH" in $5x10^{-4}$ M phosphate was due to the formation of calcium phosphate which in turn became the catalyst of the nucleation of calcium carbonate. This may be explained by the assumption from Avnimelech (1980), and Rastrick (1949) that calcium carbonate and calcium phosphate have a similar crystal structure.

The increases of the "peak pH" with the increase of phosphate concentration demonstrated that the phosphate ion inhibited the precipitation of calcium carbonate (Table 4.3). Although the rise of "peak pH" was not significant when the concentration of phosphate in reaction solutions was less than 10^{-6} M levels, the inhibitory effect could be inferred by observing the appearance of crystals. Only rhombohedral particles were seen under a light microscope and a SEM (Figure 4.7), and only calcite was identified by X-ray diffractometer. Vaterite was found in the reaction solution with no phosphates added (mentioned before), but was not found in the reaction solution containing phosphate. This may suggest that phosphate retards the formation of vaterite rather than that of calcite. At these concentration levels, the inhibitory effect of phosphate on calcite formation presumably retards nucleation rather than crystal growth. The perfect rhombohedral shape of the crystals provides evidence to support this. Some authors reported that the

inhibitory effect is through a surface adsorption mechanism (Simkiss, 1964). However, at these low phosphate concentrations (<= 1 μM), it is reasonable to consider that the low energy adsorption (Holford and Mattingly, 1975) of phosphate through ion exchange (Kuo and Lotse, 1972) could be overcome by the increase of the activity of carbonate ions accompanied with the rise of solution pH.

Table 4.3 THE EFFECT OF PHOSPHATE CONCENTRATIONS ON THE PRECIPITATION OF CALCIUM CARBONATE.

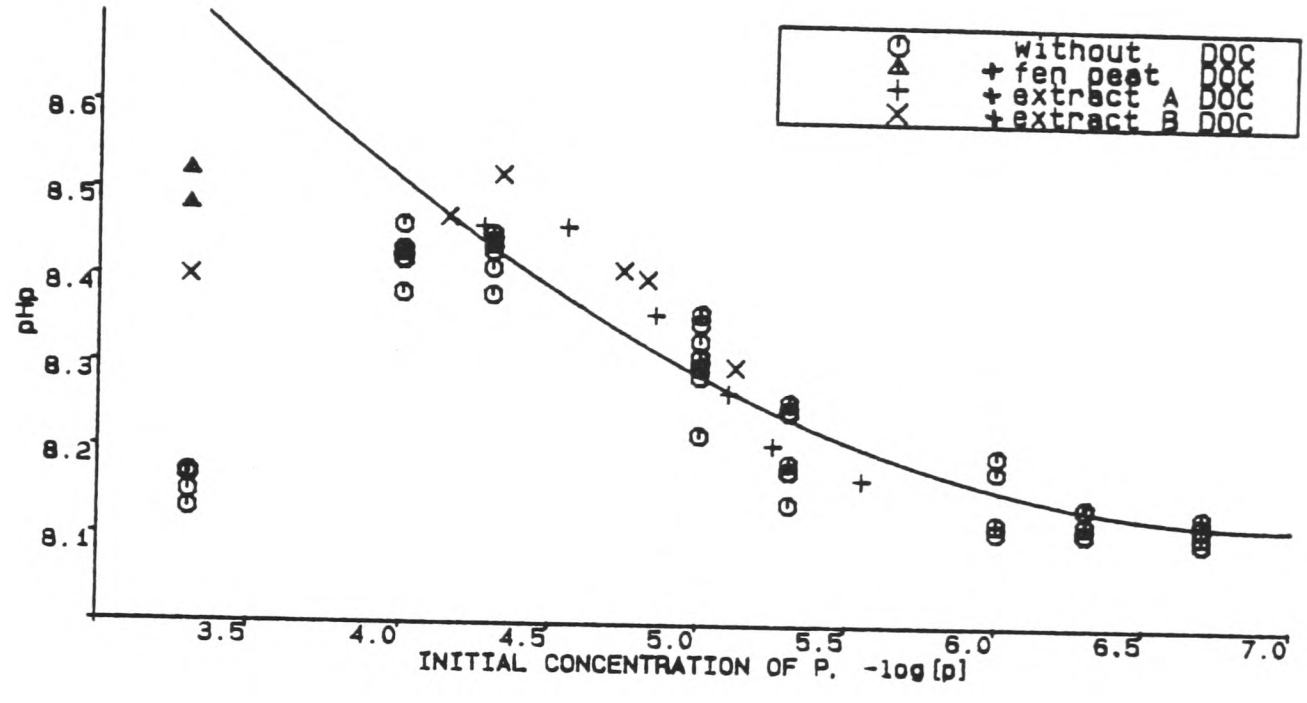
Phosph., M	0.0	$2x10^{-7}$	$5x10^{-7}$	$1x10^{-6}$	$5x10^{-6}$	$1x10^{-5}$	$5x10^{-5}$	$1x10^{-4}$	$5x10^{-4}$
pH_p	8.09 ±0.03	8.12 ±0.04	8.13 ±0.02	8.15 ±0.04	8.21 ±0.05	8.31 ±0.05	8.42 ±0.02	8.42 ±0.03	8.15 ±0.03
NT, mM	7.32 ±0.89	8.0 ±0.4	9.1 ±0.6	10.0 ±0.8	11.6 ±1.1	14.5 ±1.0	21.5 ±2.8	19.4 ±1.7	12.6 ±0.6
[Ca], mM	7.81 ±0.26	8.56 ±0.20	8.67 ±0.04	8.29 ±0.28	8.27 ±0.08	8.31 ±0.56	7.74 ±0.40	7.31 ±0.57	7.42 ±0.51
$CaCO_{3(s)}$, mM	2.19 ±0.26	0.91 ±0.22	1.16 ±0.03	1.50 ±0.26	1.48 ±0.29	1.59 ±0.15	1.47 ±0.10	1.66 ±0.15	1.04 ±0.55
SI	50.6 ±8.5	68.8 ±4.2	72.6 ±6.9	87.2 ±21.6	104.0 ±17.7	159.1 ±31.8	228.4 ±30.4	233.8 ±24.7	66.5 ±9.5
P♥, μM	-	-	0.23 ±0.15	0.62 ±0.45	0.39 ±0.40	7.8 ±0.60	10.3 ±2.7	18.7 ±1.7	3.25 ±0.00
P♥♥, μM	-	-	-	0.50 ±0.13	0.29 ±0.30	5.9 ±0.90	7.7 ±1.3	12.6 ±1.6	2.91 ±0.30
RE	6	4	4	4	6	7	6	6	5

p♥ and P♥♥ represent the total concentrations of phosphate in the reaction solution withdrawn at the peak pH point and one hour later, respectively, reaction solution being filtered through a 0.2 μm filter.

The precipitation of dicalcium phosphate and octa-calcium phosphate on calcite (Cole et al., 1953; Larsen and Widdowson, 1970; and Freeman and Rowell, 1981) and the assumption of a heterogeneous nucleation mechanism (Griffin and Jurinak, 1973, 1974) suggest that the presence of calcium phosphates might be a catalyst for the nucleation of calcium carbonate and vice versa. With high phosphate concentration (>0.1 mM) in 0.01 M $CaCl_2$, when pH increases to a certain level, the solution becomes

oversaturated with calcium phosphate; therefore, the formation of calcium phosphate is expected, in turn, to be the catalyst for the heterogenous nucleation of calcium carbonate.

Figure 4.6 THE RELATIONSHIP BETWEEN THE INITIAL CONCENTRATION OF PHOSPHATE (WITH OR WITHOUT DOC) AND THE PEAK pH IN 10 mM $CaCl_2$ REACTION SOLUTION.



This model can be used to explain the fact that the "peak pH" of the reaction solutions did not increase further when initial concentrations of phosphate were higher than $5x10^{-5}$ M. The "peak pH" (8.42±0.03) of 10^{-4} M phosphate treatment was the same as that (8.42±0.02) of $5x10^{-5}$ M phosphate. Moreover, the "peak pH" in $5x10^{-4}$ M phosphate treatment had significantly decreased to 8.15±0.03.

The failure to discover crystallized calcium phosphate by X-ray diffraction suggests that these deposits (Figure 4.10) are amorphous. The SEM photo of the $5x10^{-4}$ M phosphate treatment shows only calcite crystals and some amorphous deposits. The mechanism of the formation of calcium phosphate is beyond the scope of this thesis so it will not be discussed here.

In the reaction solution containing $1x10^{-5}$ M phosphate, the

surface of the calcite particles were etched and most particles were single crystals (Figure 4.8). In the $5x10^{-5}$ M phosphate reaction solution, most particles were in clumps of rhombohedral crystals with deformed surfaces (Figure 4.9). However in $5x10^{-4}$ M phosphate reaction solution, crystals were clearly identified as single "dog-tooth spar" particles with surfaces partially destroyed (Figure 4.10). This series of SEM photos of calcium carbonate crystals suggest that the inhibitory effects of phosphate ions on calcite precipitation were evident as etching of the crystal surfaces and modification of the crystal growth behaviour.

Examining the changes of phosphate concentration at the "peak pH" (Table 4.3), the phosphate concentrations were significantly decreased from their initial concentration in all treatments at "peak pH" time. This suggests that phosphate could coprecipitate (at least in part) with calcium carbonate. Comparing the changes of phosphate concentration between the "peak pH" time and one hour later (comparing the values of P♥ and P♥♥ in Table 4.3), there is a consistent tendency for a further decrease of phosphate concentration in all the reaction solutions. This also supports the case for coprecipitation.

Although most of the added phosphate was deposited, the higher the initial concentration of phosphate, the higher the phosphate concentration remaining in the reaction solution except for the $5x10^{-4}$ M phosphate treatment, in which the phosphate concentration in reaction solution was even lower than that in the treatment with initial phosphate concentration $1x10^{-5}$ M. Just as the precipitation of calcium carbonate needs a critical degree of supersaturation, the precipitation of calcium phosphate needs a critical degree of supersaturation for precipitation to

commence.

In the treatments containing initial concentrations of phosphate at $1x10^{-5}$, $5x10^{-5}$, and $1x10^{-4}$ M, the phosphate concentration in the reaction solutions at the "peak pH" was 7.8, 10.3, and 18.7 μM, respectively. The concentrations of phosphate remaining in the reaction solutions were all higher than 6 μM, which as Griffin and Jurinak (1973) claimed was a necessary phosphate concentration to produce a monolayer adsorption on calcite and to inhibit its further precipitation. However, in this study the occurrence of the "peak pH" has been associated with the precipitation rate of calcium carbonate equals to half of ammonia dissolution rate (AADR). Although the formation of calcium phosphate may also affect the changes of solution pH, it can be ignored in this study, since the amount of formation of calcium phosphate was much less than that of calcium carbonate. Apparently the results of this study did not agree with the conclusion of Griffin and Jurinak (1973). Hence the results of this study may suggest that in a reaction solution the concentration of an inhibitor is not the only determining factor.

Considering the effect of solution pH on the distribution of phosphate ions, the results may suggest that the species of phosphate ions active in the inhibitory effect was $H_2PO_4^{-1}$ rather than HPO_4^{2-} (Kanel and Morse, 1978) or PO_4^{3-} ions (Mucci, 1986), since the dominant concentration of $H_2PO_4^-$ ion will decrease with the increase of solution pH, but it is the opposite for HPO_4^{2-} and PO_4^{3-} ions. When HPO_4^{2-} and PO_4^{3-} ions act as strong inhibitors, the release rate of acidity from calcium carbonate precipitation will never be greater than ammonia dissolution rate.

Figure 4.7 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING Na_2HPO_4 AT $1X10^{-6}$ M.

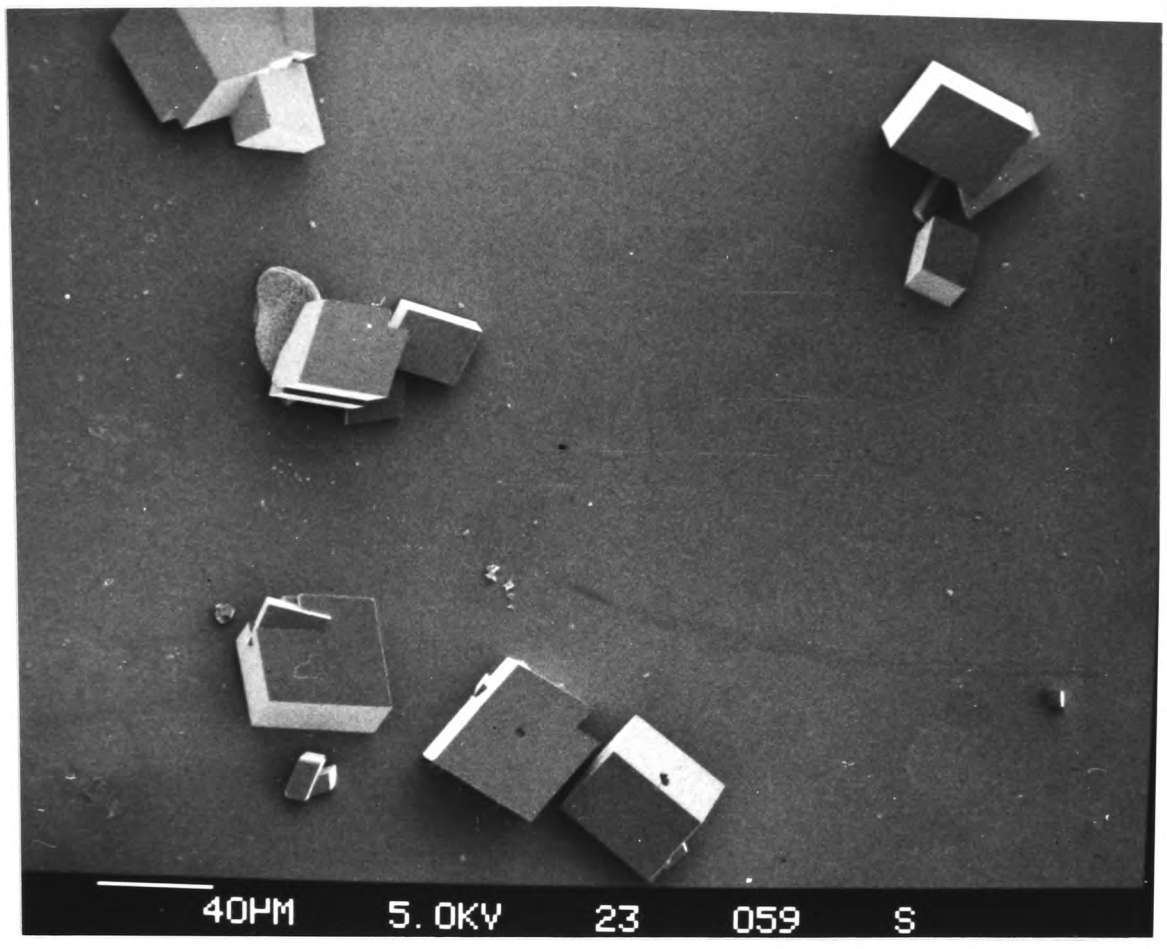


Figure 4.8 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING Na_2HPO_4 AT $1X10^{-5}$ M.

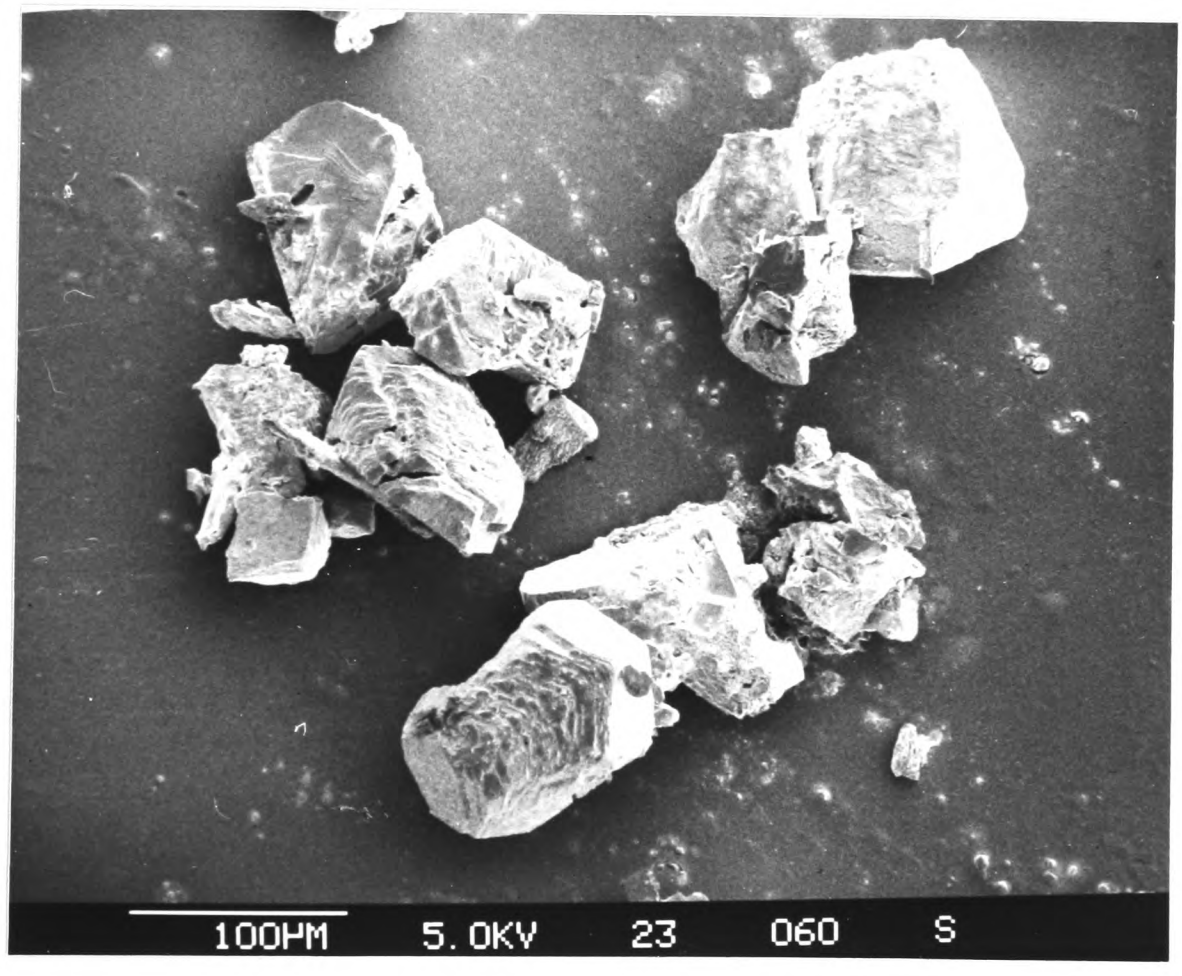


Figure 4.9 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING Na_2HPO_4 AT $5x10^{-5}$ M.

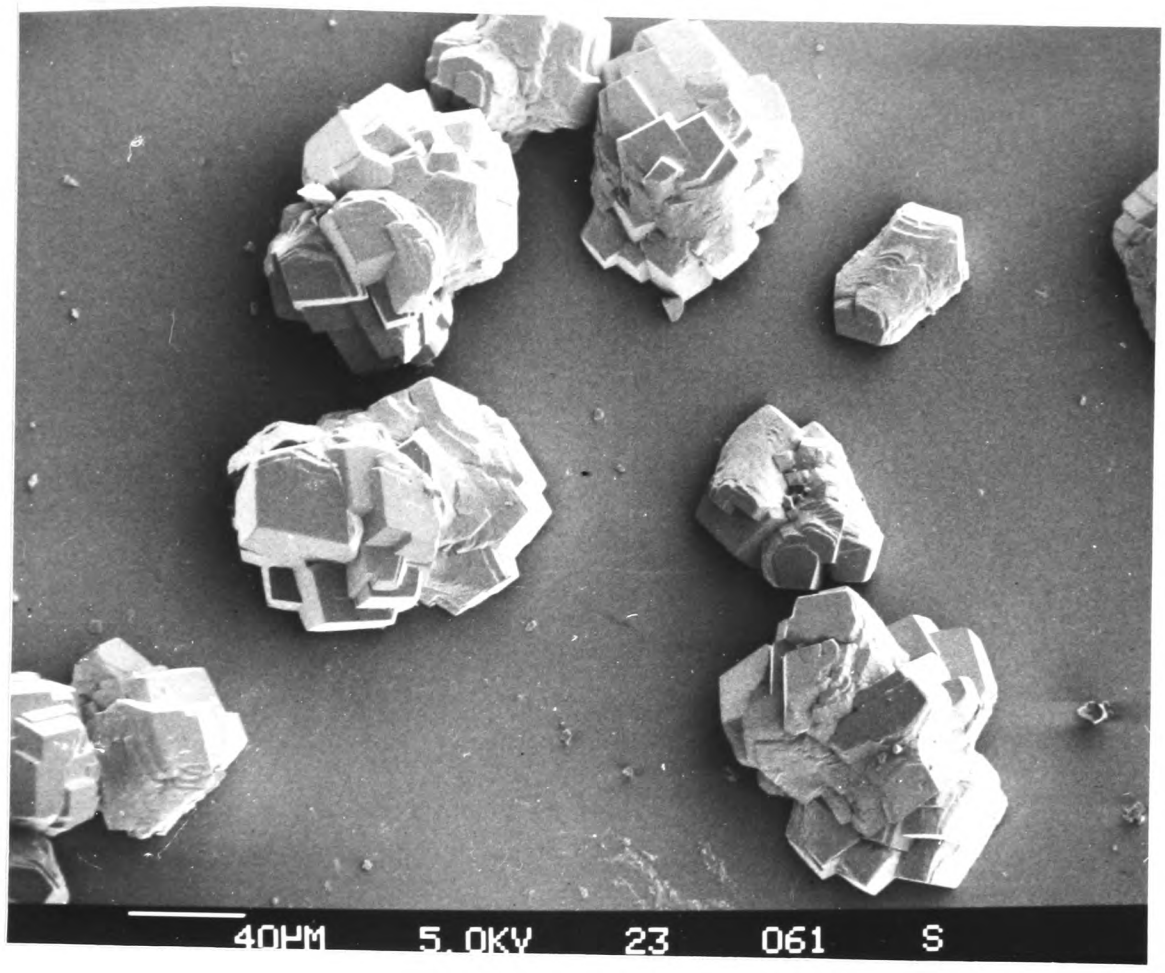
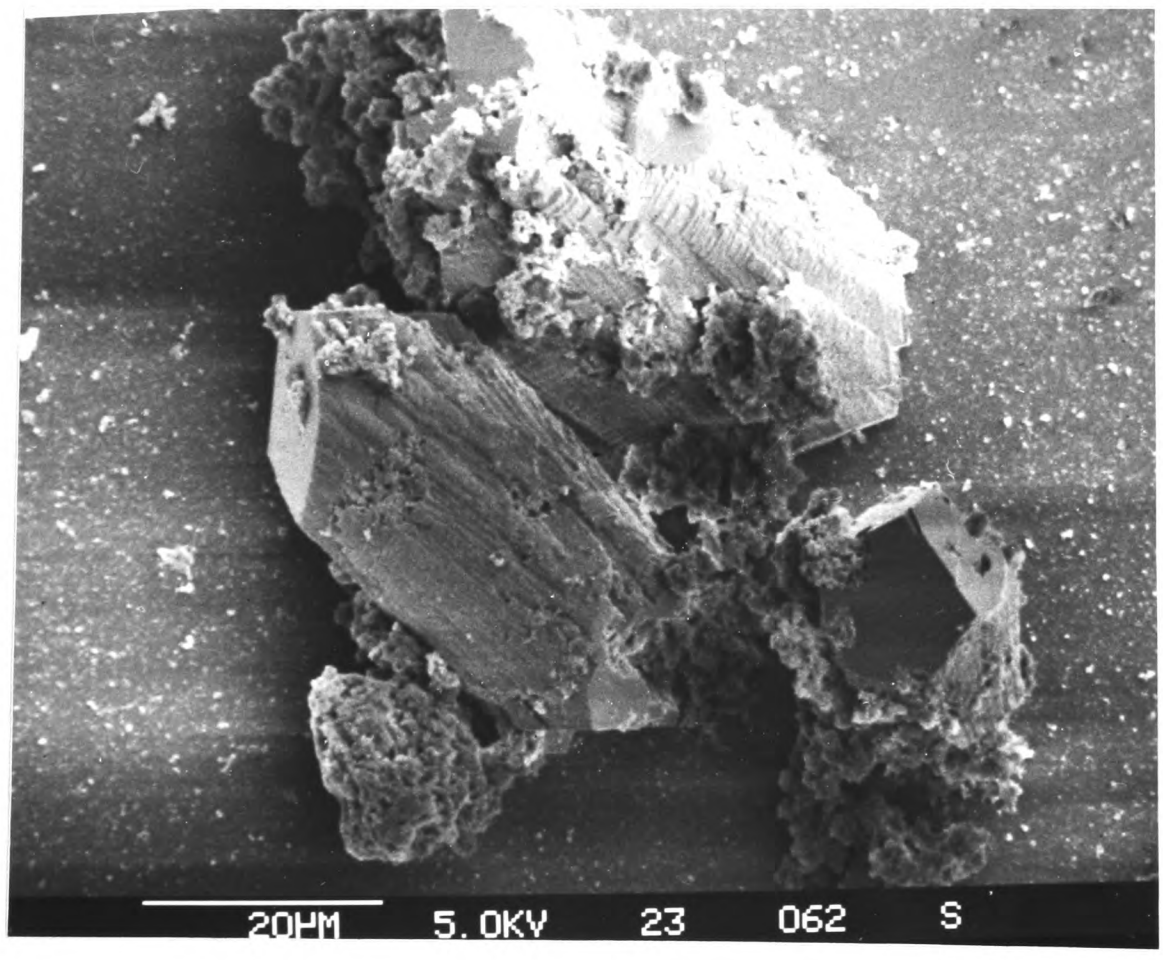


Figure 4.10 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING Na_2HPO_4 AT $5x10^{-4}$ M.



The good correlation, shown in Figure 4.6 (P.110), between the "peak pH" (pH_p) and the initial phosphate concentration can be described by an empirical equation,

$$pH_p = 10.30 \pm 0.36 - 0.63 \pm 0.14\ pP + 0.045 \pm 0.012\ pP^2 \qquad (4.3)$$

where pP is -log(initial concentration of total phosphate). In order to exclude the possible effect of the formation of calcium phosphate on the calcium carbonate precipitation, equation 4.3 was established with the data from the experiments in which the initial concentration of phosphate was $<= 5 \times 10^{-5}$ M. With the high correlation coefficient (r=0.99), equation 4.3 can be used to predict the precipitation potential of calcium carbonate in any high phosphate concentration solution when no calcium phosphate is formed.

The catalyst effect of calcium phosphate on the formation of calcium carbonate may occur in arable soils following the application of urea or ammonia-N fertilizers since most soils contain calcium phosphates.

4.3.3 Conclusion

(1) Phosphate prevents the precipitation of vaterite.

(2) Phosphate coprecipitates with calcite and is not just adsorbed on the surface.

(3) At concentrations of less than 1 μM, phosphate does not affect calcite crystal growth.

(4) Phosphate changes calcite crystal growth habits and alters calcite surfaces.

(5) Amorphous calcium phosphate formed in solutions with high amounts of added phosphate acts as a catalyst for the precipitation of calcite.

(6) The "peak pH" of reaction solutions containing phosphate can

be predicted by an empirical equation.

4.4 THE EFFECT OF WATER-DISSOLVED ORGANIC MATTER ON THE PRECIPITATION OF CALCIUM CARBONATE

Since the supersaturation of calcite in soil solution cannot be explained by the effects of magnesium concentration, phosphate concentration, or small calcite particle size, it has been suggested that the effects of water-dissolved organic compounds have to be considered to explain the phenomenon (Inskeep and Bloom, 1986[bc]; and Amrhein and Suarez, 1987).

Chave (1965) found that the calcium carbonate grains have brownish coating which presumably contain organic material. Chave and Suess (1970) also reported that water-dissolved organic matter was rapidly precipitated at the beginning of the precipitation of calcium carbonate, and nearly 10 per cent of the total organic carbon was associated with the calcium carbonate nuclei. Meanwhile Suess (1970) reported that calcite absorbed 10-14 per cent of total organic carbon, 30 percent of total phosphorus, 44 to 60 percent of lipids, 71-76 per cent of chloroform-extractable phosphorus, and 75 per cent of amino acid-containing substances. He also estimated that 18.6 per cent of the calcite surface is covered by steric acid.

Chemical characters

Soil organic matter has been categorized in three parts, humin (insoluble both in acid and alkali solutions), humic acid (soluble in alkali but insoluble in acid), and fulvic acid (soluble both in alkali and acid) according to their dissolution chemistry. Generally, 50 to 80 per cent of the organic matter in soils can be recovered as brown to black colloidal pigments by alkali extraction (Fairbridge and Finkl, 1983).

Soil organic matter is a mixture of an enormous number of organic compounds; the major compounds are alkanes, fatty acids, phthalate, phenolic acid, and benzenecarboxylic acids.

The titration curves of the humic acids show three to six inflection points, while curves of the dioxane extracts show three or four inflection points (McLaren and Skujins, 1971).

Generally fulvic acid is more phenolic in character, and it appears that oxidation of humic substances produces phenolic and benzenecarboxylic acids as major products in addition to smaller amounts of aliphatic dicarboxylic acids. Titration curves of humic and fulvic acids with alkali metal and alkaline earth salts show the inflection point between pH 7 and 8 for chelation of the COOH group. Gamble (1972) found that fulvic acid has one of the carboxyl groups in the ortho- position to a phenolic OH group. Perdue (1978) pointed out that at least one third of the COOH groups are not ortho- to the OH group (cited from Bloom, 1981).

The relation between pH and soil organic matter

It is well established that the change of soil pH with the application of urea is similar to that with ammonia. The increase of soil pH following the application of ammonia can disperse (Schnitzer, 1978) and solubilize soil organic matter (Inskeep and Baham, 1983; Tomasiewicz and Henry, 1985; and Myers and Thien, 1988). However, the increase of dissolution of soil organic matter resulting from applications of monoammonium phosphate must be due to factors other than pH, since the pH was decreased by this addition (Myers and Thien, 1988).

The micelle weight of humic acids changes with changes of pH (Paul and McLaren, 1975), so the pH may affect the character of soil organic matter. The adsorption of dissolved organic carbon on r-Al_2O_3 reaches a maximum at pH 5, then decreases

monotonically with the increase of pH and approaches zero at pH>10 (Davis, 1980). Reynolds (1978) found that polyphenol had a strong inhibitory effect on the precipitation of calcite at low pH. Low concentration of metallic ions, except Al^{3+} and Fe^{3+}, do not precipitate humic acid; Al^{3+} and $Fe3^{+}$ humus complexes will break down at pH greater than 8 (Khan, 1969). In the range of solution pH 7 to pH 9, the amounts of malate and glycine-Ca complexes in solution decrease with the increase of pH (Kitano and Hood, 1965).

Inhibitory mechanisms

The effects of organic matter on kinetic reaction of calcium carbonate is due to its physical coating rather than chemisorption according to Morse, 1974[b]; and Sjöberg, 1978. The most widely distributed functional groups in humic substances that have been shown to participate in metal-complexing are COOH, phenolic OH, and possibly C=O and NH_2 groups (Schnitzer and Khan, 1972). In most soil (pH <8.0) the binding behaviour of cations with organic matter can be modelled well by means of COOH groups on nonadjacent carbons.

Chave and Suess (1967) reported that the adsorption of DOC from seawater on to carbonate surfaces was faster than the precipitation of calcium carbonate on to the same surfaces. They (1970) also suggested that a rapid calcium carbonate precipitation could only occur after most DOC had been removed from solution.

Inskeep and Bloom (1986[b]) reported that the rate constants of calcite precipitation decreased to zero with WSE (water soil extract) and FA (fulvic acid) at 0.15 mM and 0.028 mM DOC, respectively. The organic surface coverages of WSE and FA on the calcite seeds corresponding to complete retardation of calcite

precipitation were 90 and 30 atoms C nm^{-2}, respectively. These levels of DOC are very common in soil solutions, surface seawaters, lake waters, and stream waters (Suarez, 1977; Inskeep and Baham, 1983; Thurman, 1985; and Inskeep and Bloom, 1986[b]).

Berner et al. (1978) found that fulvic acid and aromatic carboxylic acid (mellitic, gallic, and tannic) are relatively strong inhibitors of aragonite precipitation; and amino acids, sodium sterate, and EDTA have little or no effect. Reynolds (1978) stated that tannic acid and plant polyphenols are strong inhibitors, but at 2 ppm pyrogallic, gallic, acetic, citric, tartaric, or glycolic acids are not. Kitano and Hood (1965) found that the rate of calcium carbonate precipitation was most reduced by citrate, malate, pyruvate, glycylglycine, and glycogen; but galactose, dextrose, alanine and acetate ions have little effect; and chondroitinsulfate, succinate, lactate, arginine, taurine, glutamate, glycine, and serine have a moderate effect. Inskeep and Bloom (1986[b]) suggested that it is the larger aromatic acids and polymeric constituents that are probably responsible for the inhibition.

Jackson and Bischoff (1971) found that basic and neutral amino acids accelerated the recrystallization of calcite from aragonite, while acidic amino acids inhibited it. They suggested that the carboxyl group in proxying for CO_3^{2-} caused the inhibition. Berner et al. (1978) suggested that the power of humic substances to inhibit precipitation must reside in the structural properties of the molecules and the way in which the compounds are attached to the surface of aragonite, although the presence of benzenecarboxyl groups might be a necessary (but not sufficient) prerequisite.

Reynolds (1978) indicated that a surface polynuclear growth

process became effective when polyphenol adsorption blocked spiral dislocation growth sites of calcite, and the blocking effect reduced the precipitation rate.

Polymorphs

Data on the effects of organic materials on polymorphic crystal formation are few and most of these experiments were not conducted with soil organic matter.

Kitano and Hood (1965) reported that citrate, malate, pyruvate, glycycogen, lactate, chondroitinsulfate, and arginine favoured the formation of calcite; glutamate stimulated vaterite and calcite precipitation; glycine and serine favoured precipitation of vaterite and aragonite; taurine encouraged aragonite to precipitate; galactose, dextrose, alanine, and acetate did not influence the form of the precipitates.

4.4.1 Materials and Methods

All experiments were carried out with the standard procedures shown in section 2.2.1 apart that reaction solutions contained 0.01 M $CaCl_2$ and $2.5x10^{-4}$, $x10^{-3}$, and $x10^{-2}$ M DOC (water-dissolved organic matter).

In order to extract DOC that did not contain phosphate, a fen peat soil, collected at Oxford University field No. 13, was used in this study. The procedures used for extracting DOC were as follows : -

(1) Soil was air dried and sieved through a 2 mm sieve.

(2) 1.8 Kilograms of soil were added to three litres of double distilled water containing 0.5 M urea.

(3) This was shaken on a reciprocal shaker at about 120 rpm in 25^0C temperature room for one week.

(4) The extract was collected after centrifuging at 10,000 rpm

for one hour.

(5) It was allowed to stand so that ammonia could volatilize for two weeks to reduce ammonium content, from about 1.0 to 0.025 M, and to decrease solution pH, from 8.72 to 6.65.

(6) It was then filtered through 0.2 μm filter and stored at 4^0C.

The extract contained $2.5x10^{-1}$ M DOC (expressed in the concentration of organic carbon and determined using the Walkley-Black modified method, Page et al, 1982), $3.0x10^{-6}$ M inorganic phosphate, $1.84x10^{-4}$ M organic phosphate (Page et al, 1982), and $1.1x10^{-3}$ M calcium (using a calcium-sensitive electrode).

4.4.2 Results and Discussion

The "peak pH" of reaction solutions increased with the increase of DOC concentrations (Table 4.4 and Figure 4.11). It increases from pH 8.22±0.01 in $2.5x10^{-4}$ M DOC reaction solution to 8.58±0.06 in $2.5x10^{-2}$ M DOC. The correlation is represented by an empirical equation,

$$pH_p = 8.89\pm0.05 - 0.18\pm0.02\ pDOC \qquad (4.4)$$

where pDOC=-log([DOC]). The correlation coefficient, r, is -0.98 in the experimental concentration ranges. The inhibitory effect in the experiments is due to the presence of DOC, since with the presence of the low concentration of inorganic phosphate (< 0.2 μM), the inhibitory effect from orthophosphate can be disregarded. The linear relationship may suggest that the inhibitory potential of DOC rises with its concentration until the precipitation of calcium carbonate is totally prevented.

Calcite was the only calcium carbonate identified by X-ray diffraction in all the experiments with addition of DOC. The crystals (Figure 4.12) in $2.5x10^{-4}$ M DOC have hexagonal and rhombohedral surfaces. Most of the particles are twins or clumped

together, but hexagonal and rhombohedral surfaces are still obvious. However the degree of deformation on the surface of single particles is similar to that from the $5x10^{-5}$ M phosphate experiment. The particles (Figure 4.13) in $2.5x10^{-3}$ M DOC solution are like massive rhombohedron stacked together. Moreover the particles (Figure 4.14) in $2.5x10^{-2}$ M have curved surfaces, like a mass of amorphous material, and are not easily recognized as calcite. These SEM photos show that DOC strongly affects the appearance of precipitates of calcite. At high DOC concentration it destroys calcite's normal appearance. The results help to explain why soil calcium carbonate is irregularly shaped (Inskeep and Bloom 1986[c]).

Table 4.4 THE EFFECT OF DOC CONCENTRATIONS ON THE PRECIPITATION OF CALCIUM CARBONATE WITH OR WITHOUT AN EXTRA ADDITION OF PHOSPHATE.

Phosphate, M	0				$5x10^{-4}$ M	
DOC♦, M	0	$2.5x10^{-4}$	$2.5x10^{-3}$	$2.5x10^{-2}$	$2.5x10^{-3}$	$2.5x10^{-2}$
pH_p	8.09 ±0.03	8.22 ±0.01	8.42 ±0.02	8.58 ±0.06	8.48 ±0.02	8.52 ±0.02
NT, mM	7.32 ±0.89	11.0 ±0.5	16.7 ±0.8	40.3 ±0.4	23.1 ±0.8	35.8 ±4.8
[Ca], mM	7.81 ±0.26	6.39 ±0.60	6.50 ±0.70	4.11 ±0.35	6.64 ±0.37	3.84 ±0.65
$CaCO_{3(s)}$, mM	2.19 ±0.26	2.46 ±0.23	2.07 ±0.21	3.61 ±0.11	1.48 ±0.16	4.25 ±0.85
(Ca), mM	3.87 ±0.09	3.35 ±0.25	3.22 ±0.32	1.94 ±0.18	3.19 ±0.35	1.86 ±0.33
SI	50.6 ±8.5	100 ±10	195 ±26	254 ±42	259.6 ±26.2	200.6 ±21.5
PRH, pH units h^{-1}	0.03 ±0.02	0.07 ±0.01	0.05 ±0.00	0.10 ±0.01	0.14 ±0.01	0.02 ±0.00
RE	6	4	4	4	4	4

4.4.3 Conclusion

(1) DOC prevents the precipitation of vaterite.

(2) The inhibitory effect of DOC on calcite precipitation is linearly correlated with its concentration.

(3) DOC deforms the crystal surfaces of calcite.

Figure 4.11 THE RELATIONSHIP BETWEEN THE INITIAL CONCENTRATION OF DOC AND THE PEAK pH IN 10 mM $CaCl_2$ REACTION SOLUTION.

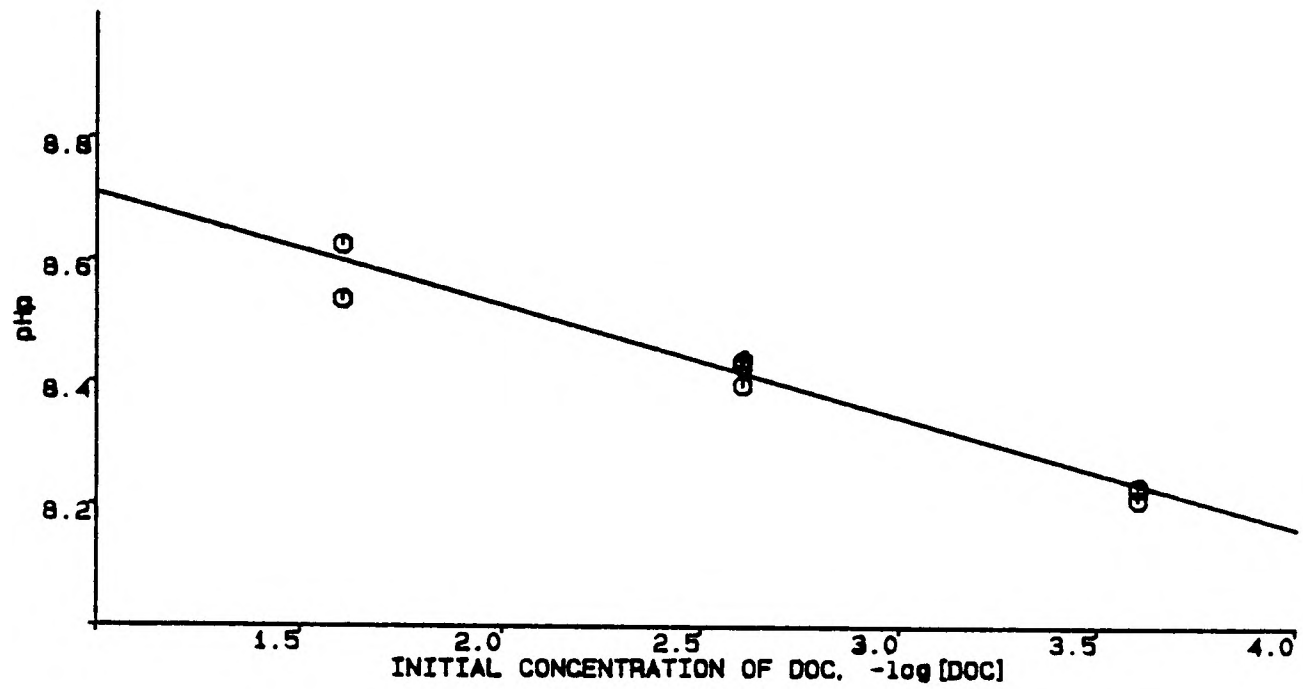


Figure 4.12 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING DOC AT 0.25 mM.

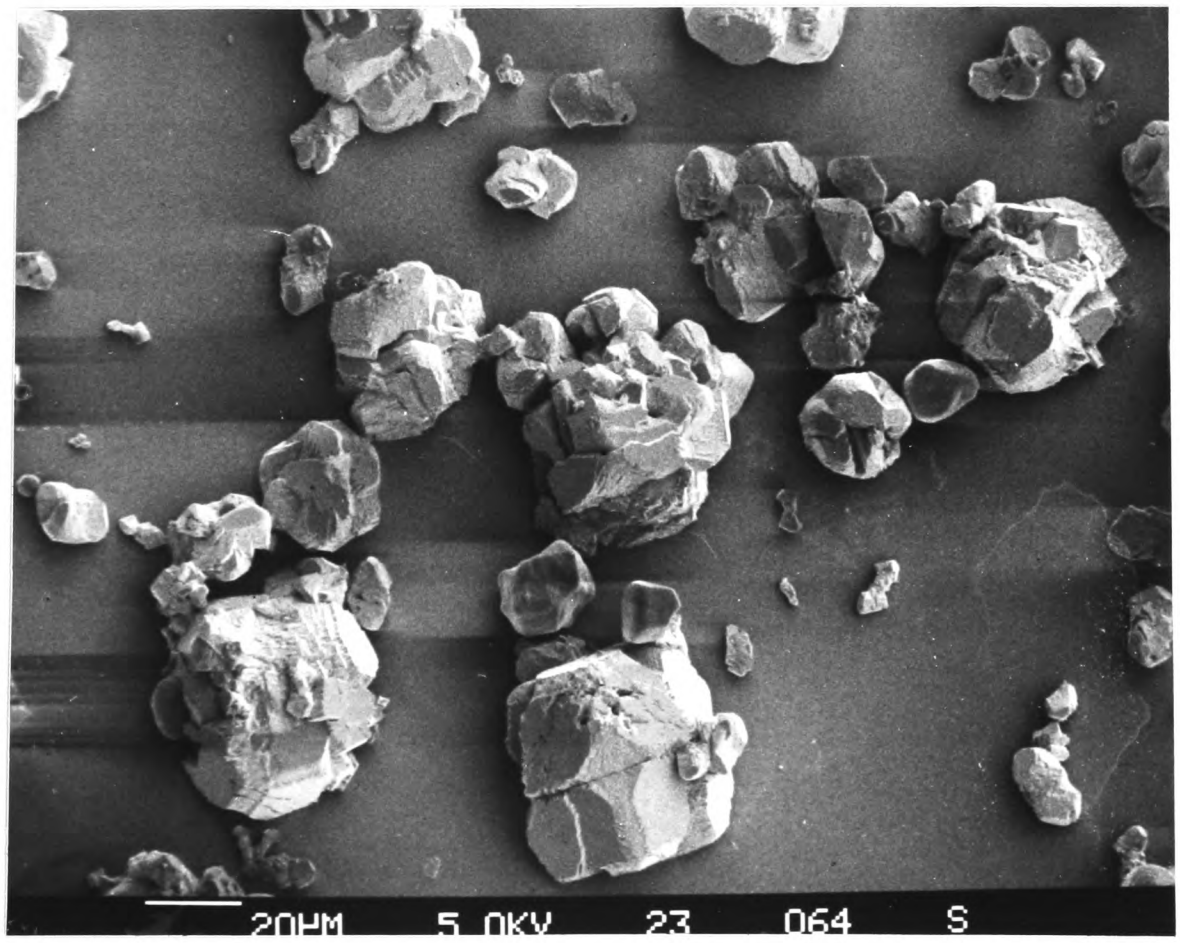


Figure 4.13 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING DOC AT 2.5 mM.

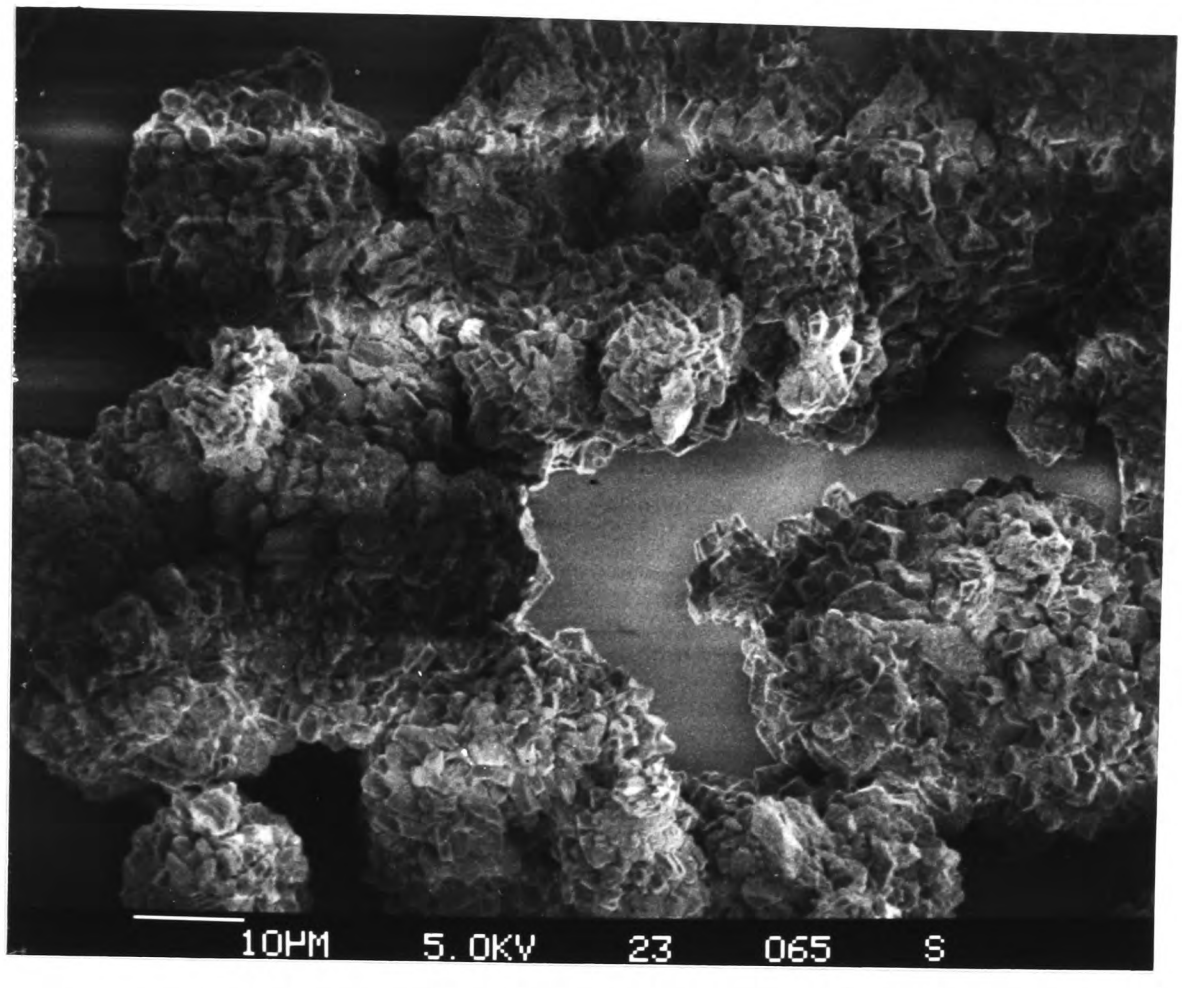
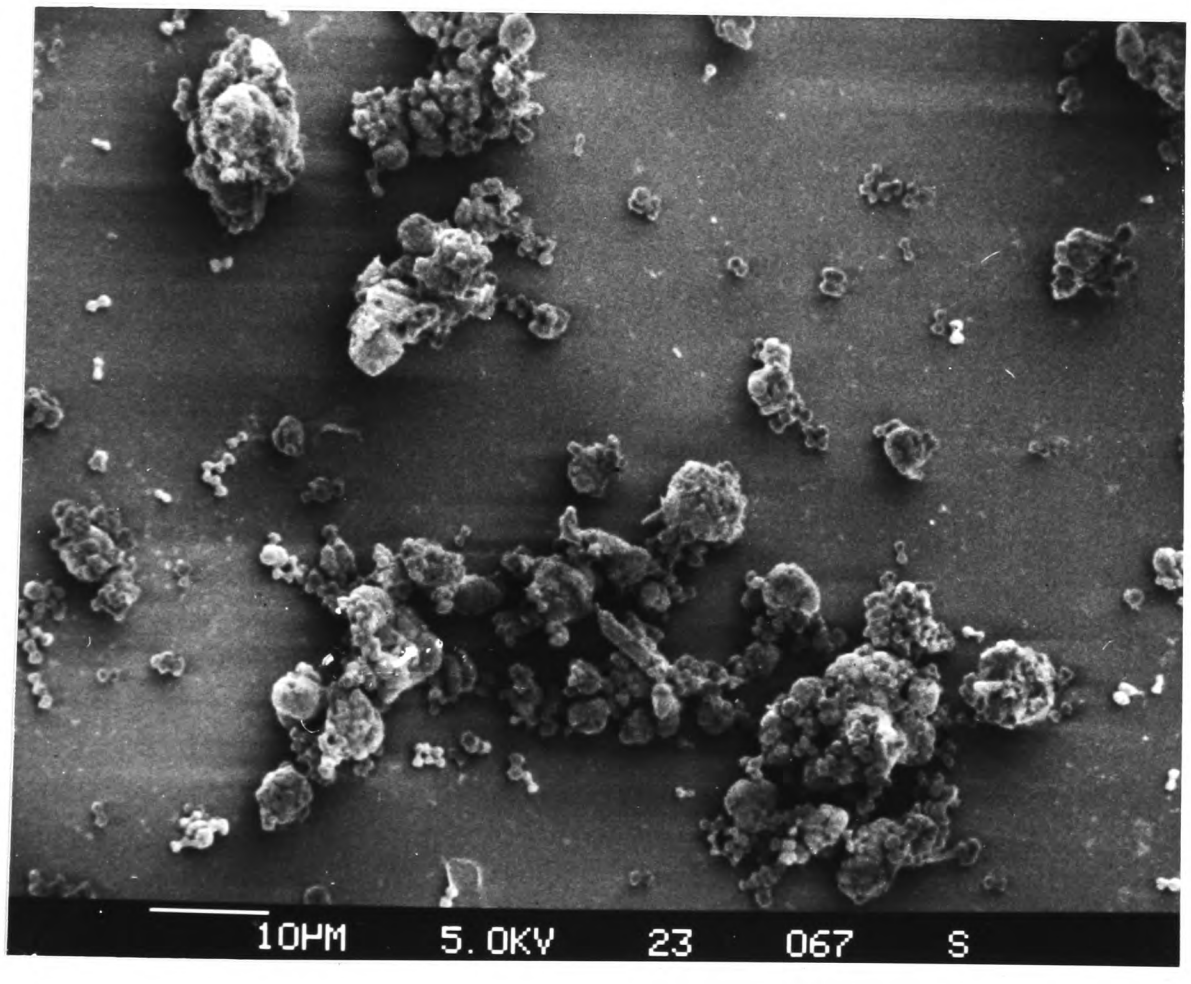


Figure 4.14 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING DOC AT 25 mM.



4.5 THE COMBINED EFFECTS OF MAGNESIUM, PHOSPHATE, AND DOC ON THE PRECIPITATION OF CALCIUM CARBONATE.

In the above studies the inhibitory effects of magnesium, phosphate, and DOC on the formation of calcium carbonate, have been examined individually. However, in natural environments they always exist together. It will be worthwhile to study the inhibitory effect of the combinations of phosphate and DOC because both of them are strong inhibitors of the formation of calcium carbonate. It is also useful to know how inhibitors behave on the calcium carbonate precipitation when a weak one (e.g. magnesium) coexists with a strong one (e.g. phosphate). Understanding their combined effects will be helpful in recognizing the conditions associated with the formation of calcium carbonates in soil. Two sets of combinations, magnesium with phosphate and phosphate with DOC, were examined. In order to widen the application of results of the effect of DOC on calcium carbonate precipitation, DOC extracted from arable soil was also used in addition to the DOC extracted from fen peat soil (used in section 4.4).

4.5.1 Materials and Methods

All experiments were carried out with the standard procedures (section 2.2.1) except that combinations of inhibitors were added to 0.01 M $CaCl_2$ solution.

Magnesium and phosphate

The reaction solutions contained 1 mM magnesium chloride and 10^{-6}, 10^{-5}, and 10^{-4} M disodium phosphate.

DOC and phosphate

There were three extracts of DOC used : (1) DOC was

extracted from fen peat soil, the same sample as used in section 4.4. (2) Extract A was extracted from Begbroke soil using similar procedures as for peat soil extract with no urea. (3) Extract B was extracted from Begbroke soil in 2 mM NaOH solution.

Extract A contained 1.44 mM DOC, 0.53 mM magnesium, 28 μM inorganic phosphate, 7.4 mM calcium, with pH at 7.8.

Extract B contained 8.75 mM DOC, 0.02 mM magnesium, 92.5 μM inorganic phosphate, 3.0 mM calcium, with pH at 8.30.

Series 1

The reaction solutions contained $5x10^{-4}$ M disodium phosphate and 2.5 or 25 mM DOC (extracted from fen peat soil).

Series 2

Since the inorganic phosphate content of extract A is rather high, the solutions were prepared at different magnitudes of dilution (1, 1/2, 1/5, or 1/10) for studying the low range of concentration of phosphate, and the DOC is quite low. Extra phosphate was added to make the high range of concentration of phosphate sufficient to contain $5x10^{-6}$ or $5x10^{-5}$ M. The contents of the treatments are shown in series A of Table 4.6 (p.131). Calcium concentration was adjusted to 0.01 M.

Series 3

In order to match the concentration of DOC as in series 2, extract B was diluted to 1/2, 1/6, and 1/12 times, and three levels of phosphate ($5x10^{-6}$, $5x10^{-5}$, and $5x10^{-4}$ M) were made. Calcium concentration was adjusted to 0.01 M; other solution contents are shown in series B of Table 4.6.

4.5.2 Results and Discussion

The combined effect of magnesium and phosphate

Only calcite was found by X-ray diffraction in this study.

With 1 mM magnesium in $1x10^{-6}$, $1x10^{-5}$, or $1x10^{-4}$ M phosphate solutions, the "peak pH" values (pH_p in Table 4.5) were 8.16± 0.02, 8.26±0.06, and 8.45±0.04, respectively. These values of the "peak pH" are not different from those values found in the reaction solution containing $1x10^{-6}$, $1x10^{-5}$, or $1x10^{-4}$ M phosphate with no magnesium, which were 8.15±0.04, 8.31±0.05, and 8.42 ±0.03, respectively (Table 4.3). The corresponding values predicted by equation 4.3 (phosphate effect) are 8.16, 8.29, and 8.51. The consistency between the experimental data and the predicted values at $1x10^{-6}$ and $1x10^{-5}$ M phosphate solutions, suggest that no additional inhibitory effect (at least in the experimental conditions) occurs between these two ions on calcium carbonate precipitation, and that phosphate would be the reaction determining factor when they coexist. The experimental value of the "peak pH" (pH_p, 8.45±0.04) in the reaction solution containing $1x10^{-4}$ M and 1 mM magnesium was a bit lower than the predicted value (pH_p, 8.51) calculated by equation 4.3 for phosphate concentration. This is reasonable because, as it was mentioned in section 4.3, at this high phosphate concentration, calcium phosphate may form before calcium carbonate does and this will cause calcium carbonate to start to precipitate at a lower pH.

From the results of previous sections it has been shown that the effect of magnesium (section 4.2) on calcium carbonate precipitation from "peak pH" readings is not as strong as that of phosphate (section 4.3). The effect from magnesium at this concentration (1 mM) is predictably negligible. If there is no significant interaction between magnesium and phosphate on calcium carbonate precipitation, the "peak pH" of the reaction solutions should be controlled by the phosphate concentration and can be estimated by its effect and described by equation 4.3.

This induction seems consistent with the experimental results.

The results of this study disagree with the conclusion from Ferguson et al. (1973) and Kuo and Mikkelsen (1979). They reported that magnesium inhibited phosphate absorption by $CaCO_3$ by disrupting the nucleation and crystal growth of these phosphate precipitates. However, the disagreement may be due to the fact that the concentration of magnesium is not high enough. Yadav et al. (1984) reported that the magnesium concentration needed to effect a significant reduction on phosphate adsorption is higher in supersaturated solutions.

Table 4.5 THE COMBINED EFFECT OF MAGNESIUM (1 mM) AND PHOSPHATE (10^{-6}, 10^{-5}, AND 10^{-4} M) ON THE PRECIPITATION OF CALCIUM CARBONATE.

Phosphate, M	10^{-6}	10^{-5}	10^{-4}
pH_p	8.16±0.02	8.26±0.06	8.45±0.04
NT, mM	10.8±1.1	10.6±0.1	20.5±0.7
[Ca], mM	7.42±0.18	7.89±0.20	6.66±0.40
$CaCO_{3(s)}$, mM	1.25±0.25	0.23±0.03	0.60±0.17
[Mg], mM	0.976±0.004	-	-
SI	58.40±14.0	117.9±29.8	238±40
RE	4	4	4

The combined effect of phosphate and DOC, series 1

Only calcium carbonate was found by X-ray diffraction in these reaction solutions.

In the reaction solution containing $2.5x10^{-3}$ M DOC (extracted from fen peat) and $5x10^{-4}$ M phosphate the "peak pH" was 8.48±0.02 (Table 4.4). This value is much higher than that (pH_p=8.15±0.03) in the reaction solution containing $5x10^{-4}$ M phosphate only, and significantly higher than that (pH_p=

8.42±0.02) in the reaction solution containing only 2.5 mM DOC as well. This result may suggest that both DOC and phosphate contribute their inhibitory effects on calcium carbonate precipitation at this concentration level. The SEM photo (Figure 4.15) shows that the crystals in this combination solution are small interpenetrating rhombohedral particles which are similar to those resulting from DOC individual treatment (Figure 4.13). Amorphous calcium phosphate was not seen in the SEM photo (Figure 4.15), but appeared in the SEM photo of individual phosphate treatment (Figure 4.10). This may be due to chemisorption or chelating effect between DOC and phosphate. This may explain why the "peak pH" of the combination solution is higher than that in their individual solutions. According to the appearances of crystals, the effect of this combination on calcite precipitation agrees with the effect of DOC.

In another combination solution at the same phosphate concentration ($5x10^{-4}$ M) with a higher DOC concentration (25 mM), the "peak pH" was 8.52±0.02. This value is also much higher than that (8.15±0.03) of individual phosphate effect, but is a little bit lower than that (8.58±0.06) of individual DOC effect. The deposited particles in the reaction solution are seen as clumps of needle-like shapes (SEM photo in Figure 4.16) and are different from those in the reaction solution containing only 25 mM of DOC (rounded shapes in Figure 4.14). The fact that the average precipitation rate (Table 4.4) expressed by the falling rate of pH (PRH 0.02±0.00), is much lower than that of individual DOC effect (PRH 0.10±0.01), also suggests that both DOC and phosphate contribute their inhibitory effects on the precipitation.

Series 2 and 3

It is reasonable and convenient to presume that the chemical character of DOC in extract A and B are the same, since both of them were extracted from the same soil. Hence their reaction results will be discussed together.

There is a very interesting phenomenon found when the "peak pH" of these treatments are placed on the diagram of phosphate effect. Figure 4.6 shows that DOC and phosphate both affect the precipitation with phosphate in concentrations ranging from $1x10^{-5}$ to $5x10^{-5}$ M.

A comparison was made of the experimental data (pH_p in Table 4.6) with their corresponding values estimated by equation 4.3 with phosphate concentration (pH_p* in Table 4.6) and by equation 4.4 with DOC concentration (pH_p** in Table 4.6), at low DOC concentration (DOC less than 0.29 mM, such as that formed in the reaction solutions of A_3, A_4, A_5, and A_6 in Table 4.6). From this comparison it appears that reaction solutions are controlled by phosphate ions, since their "peak pHs" are close to the values calculated by equation 4.3 (phosphate effect). When DOC concentration was higher than 0.29 mM (A_1, A_2, B_1, B_2, B_3, B_4, B_5, and B_6 in Table 4.6), DOC seemed to control the calcite precipitation in the solutions containing low concentration of phosphate or both contribute their inhibitory effects when concentrations of phosphate were high, even as high as $5x10^{-4}$ M. The "peak pH" of these reaction solutions were close to or higher than the estimated values from equation 4.4 (individual DOC effect). The interaction of DOC and phosphate on the precipitation of calcium carbonate will be discussed in chapter 5.

The SEM photo (Figure 4.17) of precipitates in B_6 reaction solution containing 0.72 mM DOC and $5x10^{-5}$ M phosphate, shows that the precipitates have a massive appearance, but under a

higher magnitude of SEM these massive particles showed interpenetrating rhombohedral particles like those in Figure 4.15.

Table 4.6 THE COMBINED EFFECT OF DOC (EXTRACT A AND B) AND PHOSPHATE ON THE PRECIPITATION OF CALCIUM CARBONATE.

Extract A	A_1	A_2	A_3	A_4	A_5	A_6
DOC, mM	1.44	0.72	0.29	0.14	0.14	0.14
P♦, μM	28	14	5.6	2.8	2.8	2.8
P♣, μM	-	-	-	-	5	50
pH_p	8.46 ±0.03	8.36 ±0.03	8.21 ±0.02	8.17 ±0.02	8.27 ±0.04	8.46 ±0.03
pH_p*	8.37	8.32	8.28	8.19	8.19	8.19
pH_p**	8.38	8.32	8.25	8.21	8.27	8.44
NT, mM	19.2 ±0.2	12.7 ±0.4	10.9 ±0.3	9.8 ±0.8	12.2 ±1.6	20.2 ±1.4
[Ca], mM	4.62 ±0.26	5.51 ±0.32	6.44 ±0.45	6.62 ±0.40	6.13 ±0.44	4.64 ±0.30
$CaCO_{3(s)}$, mM	1.86 ±0.15	1.97 ±0.12	1.88 ±0.07	1.65 ±0.10	1.54 ±0.16	1.94 ±0.14
SI	209 ±41	162 ±36	95.9 ±24	82.4 ±18	120 ±26	209 ±50
RE	4	4	4	4	4	4

Extract B	B_1	B_2	B_3	B_4	B_5	B_6
DOC, mM	4.38	1.44	0.72	1.44	1.44	0.72
p♦, μM	46.2	15.2	7.6	15.2	15.2	7.6
p♣, μM	-	-	-	5.0	50.0	500
pH_p	8.52 ±0.02	8.40 ±0.04	8.30 ±0.05	8.41 ±0.02	8.47 ±0.04	8.40 ±0.02
pH_p*	8.46	8.37	8.32	8.37	8.37	8.32
pH_p**	8.43	8.32	8.27	8.35	8.46	8.15
NT, mM	23.1 ±2.7	20.3 ±2.0	16.8 ±2.5	17.7 ±0.7	19.8 ±1.0	19.8 ±3.9
[Ca], mM	3.91 ±0.16	5.25 ±0.23	5.98 ±0.11	5.13 ±0.21	4.52 ±0.10	6.80 ±0.11
$CaCO_{3(s)}$, mM	1.63 ±0.14	1.87 ±0.08	1.78 ±0.10	1.64 ±0.06	1.35 ±0.11	1.37 ±0.05
SI	230 ±58	179 ±43	131 ±30	196 ±36	213 ±55	154 ±35
RE	4	4	4	4	4	4

p♦ the concentration of original inorganic phosphate in DOC extracts.
p♣ the concentration of disodium phosphate added to the reaction solution.
pH_p* the value of peak pH which is estimated by equation 4.4 with the concentration of DOC.
pH_p** the value of peak pH which is estimated by equation 4.3 with the concentration of phosphate.

The fact that the combined effect of DOC extracted from

arable soil (Begbroke) and phosphate was similar to the combined effect of DOC extracted from fen peat soil and phosphate on calcite precipitation, may suggest that the effect of DOC on calcite precipitation is universal or the character of DOC extracted from the fen peat soil is similar to that from Begbroke soil. Results also suggest that DOC may inhibit the precipitation both of calcium phosphate and calcium carbonate.

4.5.3 Conclusion

(1) The inhibitory effect of magnesium can be ignored if a strong inhibitor such as phosphate is present at the same time.

(2) The precipitation of calcium carbonate is controlled by phosphate when the concentration of DOC is low (< 0.29 mM), and controlled by DOC when the concentration of phosphate is low. The interaction between phosphate and DOC on the precipitation will be discussed in chapter 5.

Figure 4.15 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING Na_2HPO_4 ($5x10^{-4}$ M) AND DOC (2.5 mM).

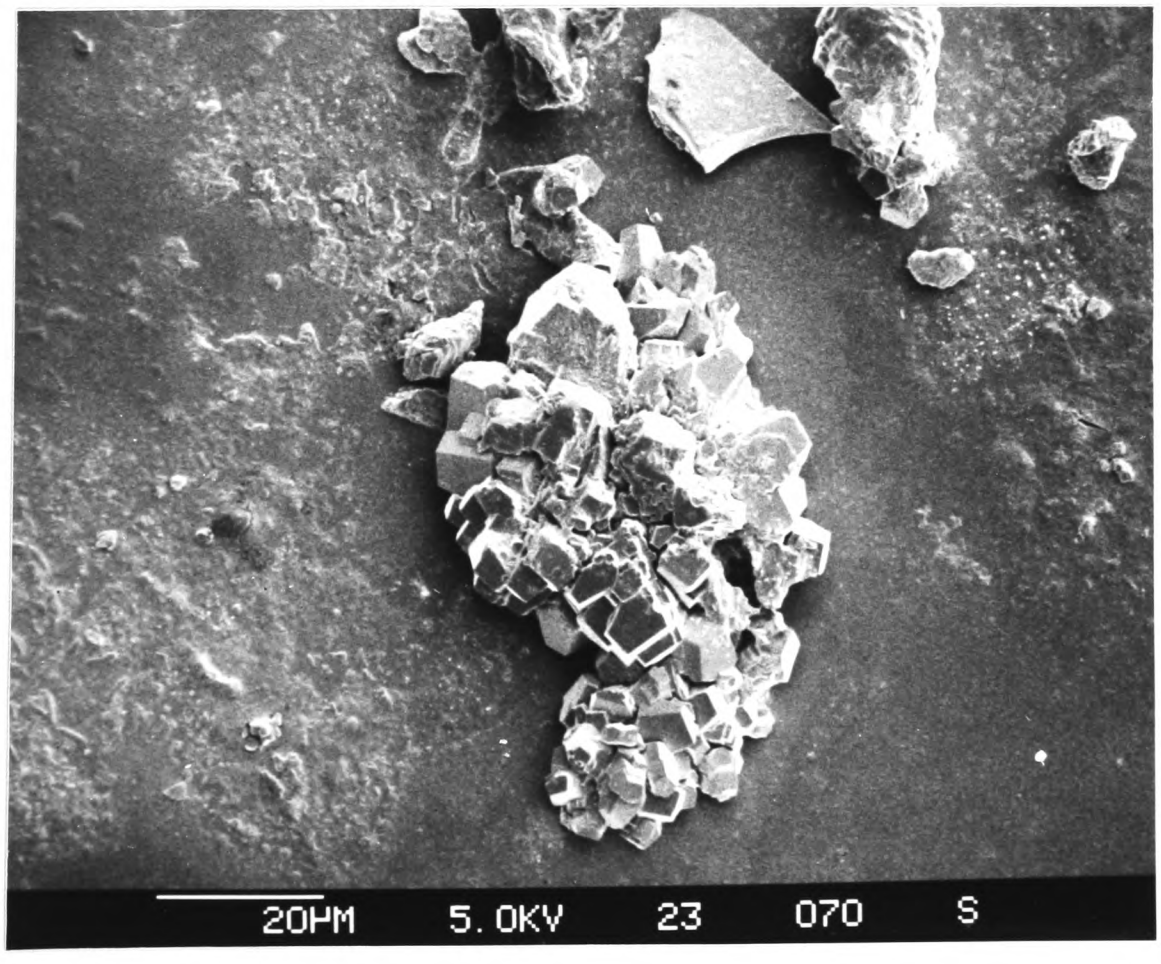


Figure 4.16 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING Na_2HPO_4 ($5x10^{-4}$ M) AND DOC (25 mM).

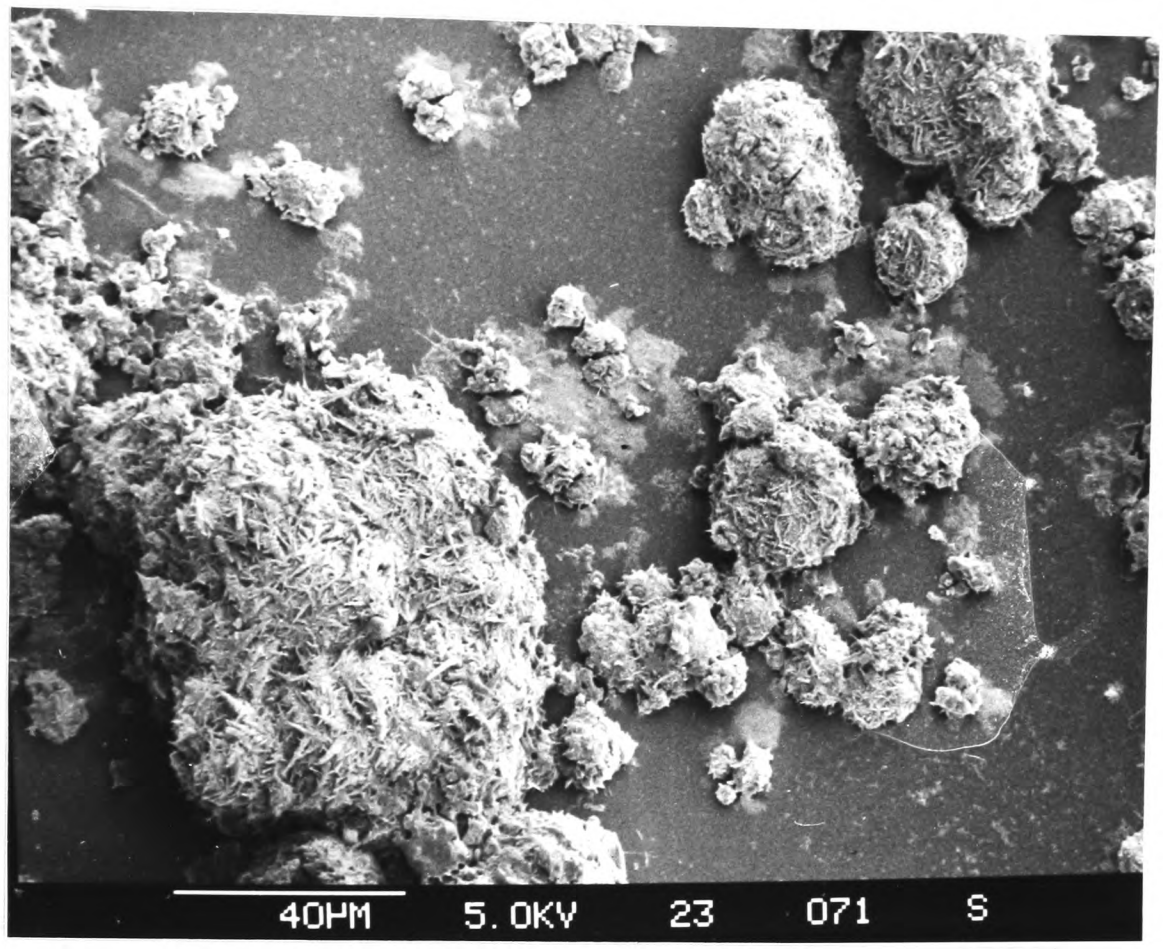
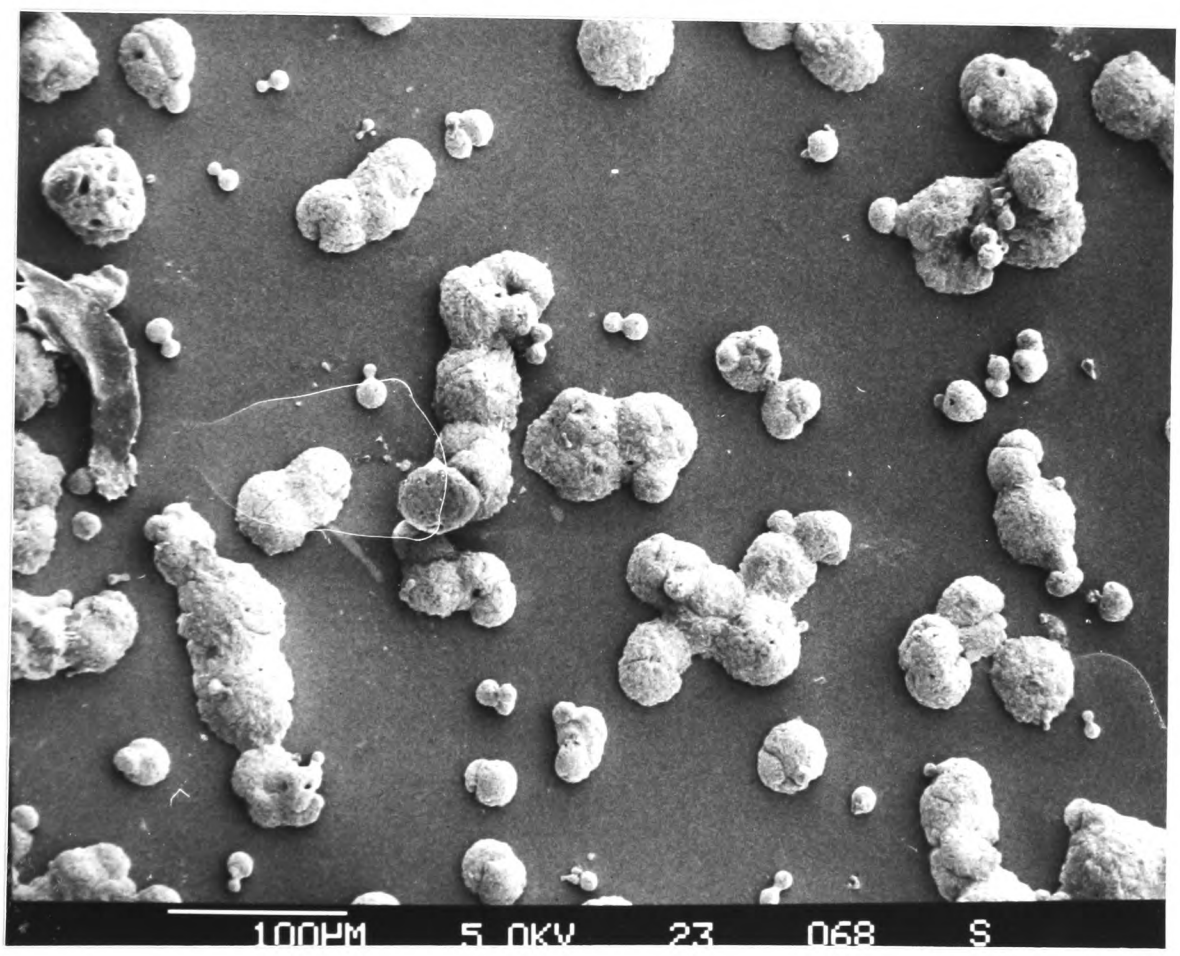


Figure 4.17 THE SEM PHOTO OF PRECIPITATES COLLECTED FROM A REACTION SOLUTION CONTAINING Na_2HPO_4 ($5x10^{-5}$ M) AND DOC (0.72 mM).



CHAPTER 5

THE PRECIPITATION OF CALCIUM CARBONATE IN SOIL AFTER UREA APPLICATION

Nitrogen loss through ammonia volatilization from urea on the soil surface may approach 60 per cent of the applied nitrogen (Fenn and Richards, 1986), however in some circumstances it may be small (Freney et al, 1983). Fundamentally, ammonia volatilization is controlled by the difference in P_{NH3} (the partial pressure of ammonia) between that in equilibrium with the liquid phase of the soil and that in the atmosphere (Denmead et al, 1982). In the experiments reported here, in a system of constant P_{CO2}, the P_{NH3} in equilibrium with the liquid phase is controlled by NT (the total ammoniacal-N concentration) and solution pH (discussed in chapter 2).

Soil pH is determined by the net amount of base or acid present and the soil buffer capacity. After urea application, the ammonia which is released by urea hydrolysis is a major source of base. The precipitation of calcium carbonate is one of the processes that may release acidity to the soil, in addition to the nitrification of ammonium to nitrite and nitrate, etc.

Many attempts have been made to reduce ammonia-N loss, such as adding mineral acids (Bremner and Douglas, 1971[b]), chemical urease inhibitors (Bremner and Douglas 1971[a]; Mulvaney and Bremner, 1977), or highly soluble neutral salts of calcium, magnesium, potassium, sodium, or ammonium (Eriksen and Kjeldby, 1987; Fenn and his co-workers, 1975, 1981[a] and 1982[b]; Rappaport and Axley, 1984). The aim of adding soluble salts along with urea is to stimulate the precipitation of carbonates (calcium carbonate and/or magnesium carbonate) which in turn reduce the increase in soil pH and hence ammonia volatilization. The

concentrations of calcium and magnesium ions in the soil solution are directly increased as their salts are applied, and may also be increased by replacing the calcium and magnesium ions in CEC sites in the soil solution with the cations of the other salts. As precipitation rate is related to the degree of supersaturation, the increase in the concentration of calcium and/or magnesium ions in the soil solution increases the degree of supersaturation with respect to calcium and/or magnesium carbonates, hence increases their potential to precipitate. However, without understanding the precipitation behaviour of calcium carbonate in soil, it is impossible to predict how much of the soluble salts should be used. Using more salts than are required does not improve the effectiveness of nitrogen fertilizer, but does increase the cost to the farmer.

Normally the precipitation of magnesium carbonate in soils is not as important as that of calcium carbonate since the magnesium concentration is relatively low; thus we will concentrate on the precipitation of calcium carbonate.

So far no reports have described how much new calcium carbonate may be precipitated, the extent to which the precipitation affects soil pH, and what soil factors control the precipitation following urea application.

Chapter 4 describes a bubbling experimental system to determine the potential effects of inhibitors (magnesium, phosphate, DOC, and urea itself) on this precipitation and their inhibitory effects have been described by empirical equations which could apply to a wide range of circumstances. Calcite-seeded experiments (chapter 3) showed that the newly formed calcium carbonate has a great effect on further precipitation. Experiments with high initial concentrations of phosphate

(section 4.3 of chapter 4) suggested that precipitates of calcium phosphate might also catalyse the precipitation of calcium carbonate. Calcium phosphate is a common soil component. Also many laboratory experiments have shown that calcite may precipitate heterogeneously on materials other than calcium carbonate both in artificial solutions (House and Tutton, 1982; Nielsen, 1964) and in soils (Levy, 1981[a]; Inskeep and Bloom, 1986[c]). However, the extent to which particles of other minerals affect the rate of precipitation of calcium carbonate is unknown. So it is important to consider the influence of soil particles on calcium carbonate precipitation.

The aim of this chapter was to establish a model to describe the precipitation of calcium carbonate in soil. Three soils with different properties (Table 5.1) were subjected to a wide range of urea concentrations (from 0.05 to 1.0 M in the soil solutions), with or without calcite seeds. A nitrification inhibitor ATC (4-amino-1,2,4-triazole) was used to prevent ammonium nitrification. Two of the soil samples were Sutton series, one was taken from the subsoil in the University Parks (Uni.) and the other was from the topsoil at Begbroke (Beg.). One soil (subsoil) was taken from Denchworth series in the Vale of the White Horse (VWH).

The chemical properties of magnesium, phosphate, and urea should be the same no matter whether they are presented in artificial solutions or in soil solution, so their effects may be applicable for both circumstances. It might be assumed that the character of DOC from different sources might be different. However the following observations encouraged me to apply the effects of DOC from a fen peat soil as a reference to estimate the effect of DOC in the three soils :

(1) The UV spectra of DOC extracted from the three soils were similar (discussed in section 4.1 of appendix 4).
(2) In chapter 4 we found that the DOC from both fen peat soil and Begbroke soil had similar effects on calcium carbonate precipitation.
(3) Orlov in 1967 (cited from Schnitzer and Khan, 1972) reported that the Beer-Lambert extinction coefficient varied little between organic materials extracted from soils belonging to the same Great Soil Group.

In the experimental system, soil pH is controlled by the net quantity of base, acidity, and soil buffer capacity and expressed as

$$pH = f(\text{base, initial acidity, soil buffer capacity})$$

where soil buffer capacity is a character of a soil which can be determined by the response of soil pH to a known quantity of added base. The ammoniacal-N released from the hydrolysis of urea is the major component of the quantity of added base. This may be controlled by the hydrolysis rate of urea, which itself may be controlled by urea concentration and soil pH, so it may be expressed by

$$\text{Base} = f([U], pH, t),$$

where [U] is the concentration of urea, t is the period of time of the experiment.

The only source of acidity of this soil system is from calcium carbonate precipitation and is expressed as

$$\text{Acidity} = f(PR, t)$$

where PR is the precipitation rate of calcium carbonate. In the non-seeded experiments with initial concentration of calcium ions at 10 mM ($CaCl_2$), vaterite had been found in reaction solutions containing no inhibitors, and aragonite had been found in

reaction solutions with high magnesium (5 mM) added, but their quantities were small compared to that of calcite. Also calcite was the only form of calcium carbonate detected in the precipitates of the reaction solutions containing phosphate and DOC, so we may use the precipitation rate equation derived from the results of experiments with calcite-seeds (chapter 3) to soil systems. The precipitation rate of calcium carbonate is controlled by

$$PR = f(K, WA, SI)$$

where K is the calcium carbonate precipitation constant, WA is the quantity of newly formed calcium carbonate, and SI is the degree of supersaturation of calcium carbonate with respect to the ion activity product of calcite.

Chapter 4 shows that the effect of urea on calcium carbonate precipitation was not significant when its concentration was lower than 1 M, and the effect of magnesium may be ignored when a strong inhibitor (phosphate) was present in the reaction solution. The concentrations of phosphate and DOC in soil solutions can reach high levels when a high amount of urea is applied to soils. Therefore, the effect of urea and magnesium on calcium carbonate precipitation can be ignored in this soil system. However, the effect of soil particles must be included for the reasons given above, viz., that calcium phosphate particles and other particles may affect precipitation. In practice the precipitation rate of calcium carbonate in the soil system may be pictured as,

$$PR = f(K, WA, SI, K_{SOIL}, P, DOC)$$

where K_{SOIL} is the effect of soil particles on the precipitation rate. The effect of K_{SOIL} may also be different among soils. In the final model we may have to consider how to distinguish the

K_{SOIL} among soils and to consider whether phosphate, DOC, and soil particles have interactions on the precipitation rate.

This chapter falls into three sections, section 5.1 describes the materials and methods, section 5.2 describes the results and discusses their implications, and section 5.3 gives a summary of this chapter.

5.1 Materials and Methods

Table 5.1 THE CHEMICAL AND PHYSICAL PROPERTIES OF THE SOILS USED

Soils	Sutton (Beg.)	Sutton (Uni.)	Denchworth (VWH)
pH (1:1)	7.32±0.01	6.55±0.01	6.52±0.01
CEC, me/100g	15.34±2.00	20.50±1.08	26.17±0.37
Ca, me/100g	14.79±0.16	19.30±0.16	21.58±0.40
Ca + Mg, me/100g	15.88±0.04	20.40±0.14	24.96±0.16
Ammoniacal-N, me/100g	0.09±0.01	0.04±0.00	0.08±0.01
OC, %	1.92±0.04	2.58±0.16	2.92±0.08
$CaCO_{3(s)}$, me/100g	9.10±0.67	0.69±0.00	0.40±0.00
WC 0.1 bar, %	27.6±0.2	43.45±0.49	49.70±0.90
WC 1.0 bar, %	17.0±0.2	25.2±1.0	36.49±0.46

OC is soil organic carbon content in per cent.
WC is soil water content in per cent by weight.

Table 5.1 presents the properties of the soils. Cation exchange capacity was determined with 1 M ammonium acetate (pH 7.00). Exchangeable calcium and magnesium were determined using an EDTA titration method (Chapman and Pratt, 1961). Calcium carbonate was determined by acid decomposition (Ameloko, 1983).

(A) Pretreatment of soils

In order that the experimental systems with the three soils

started from the same calcium-status and a low ammoniacal-N content, the soils were sieved and treated with 0.01 M $CaCl_2$ solution as follows : -

(1) The three soils were sieved through a 2 mm sieve.

(2) They were immersed in calcium chloride solution (0.01 M) for two days. The solution was renewed five times during this period.

(3) The soils were balanced on a pressure plate under 1 bar of gas pressure for over 24 hours to express the free water.

(4) These pretreated soils were stored at 4^0C until use.

(B) The experimental procedure :

(1) An appropriate amount of the pretreated soils were stored at 25^0 C overnight before use.

(2) ATC was added to the soils to give concentrations of 50 *ppm* (based on oven-dry weight). Meanwhile calculated volumes of calcium chloride (0.1 M) plus urea (5 M) solutions were mixed with the soils to give them a capillary water potential of 0.1 bar. The liquid content of the soil was referred to as "soil solution" in this thesis. The "soil solution" for all treatments was adjusted to contain 0.01 M calcium chloride. The concentration of urea in the "soil solution" was adjusted to 0.05, 0.1, 0.3, 0.5, 0.7, or 1.0 M according to the treatment required. One of the 0.05 M urea treatments also received 5 per cent (by weight) of calcite seeds (10-15 μm).

(3) 90 grams of the moistened soils were put in centrifuge tubes.

(4) The tubes were put in a desiccator in a water bath at a constant temperature 25^0C.

(5) Gas containing 0.5 % carbon dioxide and 99.5 % nitrogen was saturated by bubbling it through double-distilled water, and then led into the desiccator.

(6) Tubes of the moistened soil were removed from the desiccator

after different periods ranging from 8 hours to five days after the start of the treatment. (6a) Soil pH and calcium ion activity (using calcium-sensitive electrode) were measured immediately. (6b) Soil samples (sufficient to give 5 grams oven-dry weight) were removed from the tube and put into 150 ml flasks containing 50 *ml* of 2 *M* KCl solution with 5 *ppm* PMA (phenyl mercuric acetate, an urease inhibitor), and shaken for one hour. (6c) The resulting suspension was filtered through Whatman No 2 paper and the solution was kept in a refrigerator until analyzed for ammoniacal-N. (6d) The soil remaining in the centrifuge tubes, was centrifuged at 18,000 *rpm* for 30 minutes, and the supernatant was filtered through Whatman No. 2 paper and diluted to the concentration appropriate to analysis for ammoniacal-N, phosphate, and DOC, and then filtered again.

The filtered solutions were stored in the refrigerator until they were analyzed for ammoniacal-N, DOC, and phosphate. All the analyses of the sampled solutions were finished within a week.

Phosphate in the reaction solutions was determined using the method developed by Watanabe and Olson (1965). The concentration of DOC in the soil solutions was determined by UV spectrophotometer at 350 nm wavelength. This method was developed in this study. It is discussed in section 4.1 of appendix 4. The measurement of soil buffer capacity is described in section 4.2 of appendix 4. The amount of calcium carbonate precipitated during the reaction period was calculated from the decrease of the calcium ions as extracted in a 2 M KCl extract, the reliability of this estimation is described in section 5.1 of appendix 5.

5.2 Results and Discussion

For a better understanding, this section was also divided into two parts :

(1) The first part (section 5.2.1) presents the changes of components especially in "soil solutions" and the amount of calcium carbonate precipitated during the reaction period. Attempts were also made to describe the urea hydrolysis rate and the changes of concentration of phosphate and DOC in soil solutions by empirical equations.

(2) The second part (section 5.2.2) describes the development of a model to describe the precipitation of calcium carbonate in soils.

5.2.1 The changes of soil chemical properties and the amount of calcium carbonate precipitated following urea application

Both phosphate and DOC have been proved to be strong inhibitors to calcium carbonate precipitation in chapter 4. In this experimental system, the decrease in the amount of calcium ions in the cation exchange sites and in "soil solutions" was assumed to reflect the amount of precipitation of calcium carbonate; the lower the amount of calcium ion remaining, the greater the amount of calcium carbonate precipitated. In practice the changes in soil pH, activity of calcium ions and concentrations of phosphate, DOC, and ammoniacal-N were all highly correlated with the precipitation; thus knowing the changes in these components in soil solutions would improve the understanding of the precipitation.

The patterns of change in soil pH and in the concentrations of ammoniacal-N, phosphate, and DOC were similar for every treatment with these soils. After urea was applied to the soils the values of these parameters increased with incubation time and

then remained at a high level or decreased very little after four days (shown in Figures 5.1, 5.2, and 5.3 (p.150-155)). The pattern of change of calcium ion activity was different; it decreased with time then remained at a low level or showed a little recovery after incubating more than four days.

(1) Ammoniacal-N in soils

It is commonly recognised that the products of urea hydrolysis in soil are ammonium bicarbonate (Koelliker and Kissel, 1988) or ammonium carbonate (Rheinbaben, 1987) depending on soil conditions, especially on soil pH. When ammonia is released into the reaction solutions containing carbon dioxide, the chemical reactions will be controlled mainly by soil chemical properties, total ammoniacal-N concentration and P_{CO2}, which have been discussed in chapter 2 and chapter 3.

In this experimental system, soil ammoniacal-N was assumed to be released totally from urea hydrolysis because the initial contents of soil ammoniacal-N (0.09±0.01, 0.04±0.00, 0.08±0.01 me/100g in Beg., Uni., and VWH. soils) were relatively low after they had been treated with 0.01 M $CaCl_2$ solution. The amount of ammonia loss was also ignored because it was very small compared with the amount of urea-N used. Therefore the amount of ammoniacal-N determined in soil samples was associated with the amount of soil base, which in turn stimulated other chemical reactions, such as the increase of soil pH, the dissolution of phosphate and DOC, and the precipitation of calcium carbonate.

NT in Figures 5.1, 5.2, and 5.3 (details in Tables A.5.2 to A.5.20 of appendix 5) describes the changes of ammoniacal-N in soil following urea application. In order to relate the parameters to each other, ammoniacal-N was expressed in molarity (M) in the "soil solution". The concentration of ammoniacal-N

(NT) increased steadily with time. In some treatments the concentration of NT decreased after three or four days' incubation. This decrease of NT is to be expected because this is an open system with gas passing through the incubator (desiccator) for controlling P_{CO2} (0.00484 atm), thus loss of ammoniacal-N through ammonia volatilisation may occur. Although nitrification inhibitor (ATC) was used, nitrification may take place after three day's incubation.

Given the pattern of a steady increase of ammoniacal-N, one may consider using a simple model to describe the hydrolysis of urea. This will make it easier to predict the concentration of ammoniacal-N in soil over a wide range of circumstances. Furthermore it will allow us to predict the amount of base in solution, since the release of ammonia is the source of additional base in this experimental system. It may also allow us to predict the precipitation of calcium carbonate after urea is applied to soil. The model is developed as follows : -

(i) The changes of ammoniacal-N in me/100 g of oven-dry soil with reaction time were expressed by the best fitting equation (using the SAS program) for the first four or five samples in each treatment. Obviously the best fitting equation is first order with respect to time shown in Table 5.2, the equation is,

$$Y_{NT}=a + b\ t$$

where Y_{NT} is the amount of ammoniacal-N in me/100 g of oven-dry soil, a is the intercept, b is the hydrolysis rate of urea in me/100 g per hour, and t is the reaction time in hours. The slope of each equation represents the urea hydrolysis rate in each treatment. A high value for the slope shows a high rate of urea hydrolysis. The linear relation between the amount of ammoniacal-N and time shows that the urea hydrolysis rate was steady in

these samples, even though the urea was decreased by about 50 % of initial concentration. It seemed that urea hydrolysis was not affected by the changes of urea concentration. However, the hydrolysis rate of urea was apparently greater in higher initial concentrations of urea because the slope of the equations increased with the increase of initial concentration of urea. Therefore, other factors have to be considered to explain the disagreement.

Table 5.2 THE EQUATIONS FOR CHANGES OF AMMONIACAL-N (Y, me/100 g soil) WITH REACTION TIME (t) AFTER DIFFERENT CONCENTRATIONS OF UREA WERE ADDED TO SOILS, Y=a + b t.

UREA, M	a	b	F	R^2
Beg.				
0.05	0.0051±0.0078	0.0018±0.0002	59.0	0.952
0.1	0.0068±0.0099	0.0020±0.0002	109	0.964
0.3	-0.026±0.039	0.0055±0.0006	76.6	0.939
0.5	-0.045±0.043	0.0088±0.0008	126	0.977
0.7	-0.080±0.054	0.0123±0.0011	131	0.970
1.0	-0.045±0.064	0.0162±0.0016	101	0.971
Uni.				
0.05	0.0043±0.0055	0.0027±0.0002	115	0.983
0.1	-0.0092±0.012	0.0035±0.0004	98.5	0.970
0.3	-0.039 ±0.023	0.0076±0.0007	119	0.975
0.5	-0.055 ±0.015	0.0103±0.0011	82.2	0.965
1.0	-0.115 ±0.082	0.0209±0.002	111	0.974
VWH				
0.05	0.0085±0.0090	0.0020±0.0003	40.0	0.952
0.1	0.0017±0.0028	0.0044±0.0001	1780	0.999
0.3	-0.010±0.010	0.0120±0.0004	1055	0.998
0.5	-0.0594±0.074	0.0207±0.0028	53.1	0.964
1.0	-0.0787±0.096	0.0249±0.0037	46.1	0.958

(ii) A multiple regression method was fitted by stepwise procedures to find the best fitting equations for the urea hydrolysis rate and urea concentration, soil pH and reaction time. Petit et al (1976), and Rachhpal-Singh (1984) reported that the optimum pH for soil urease was in the range of pH 6.0 to 7.0, whereas Tabatabai and Bremner (1972) and May and Douglas (1976) said that the optimum range was pH 8.8 to 9.0. Most of the soil

pH's were under 9.0 in this study, hence pH is a factor that must be considered. The time factor will also be examined, since the ecology of soil microorganisms may change during the incubation period and affect soil urease activity.

The regression results are shown in Table 5.3, where LR_U is $\log(R_U)$, R_U is urea hydrolysis rate in mol litre^{-1} h^{-1}; Lt is log(t), t is the reaction time in hours; LU is log([U]) where [U] is urea concentration in M. [U] was calculated by subtracting the determined ammoniacal-N from the initial urea concentration. This is based on the assumption that soil ammoniacal-N was released only from urea hydrolysis.

Table 5.3 THE COEFFICIENTS OF LU (log(CONCENTRATION OF UREA)), pH, AND Lt (log(REACTION TIME)) ON LRU (log(UREA HYDROLYSIS RATE)), LRU=a + b LU + c pH + d Lt.

a	b	c	d	F	R^2
Beg.					
-1.803	0.514			70.91	0.747
±0.062	±0.061				
-4.125	0.452	0.279		126.61	0.917
±0.341	±0.037	±0.041			
-4.616	0.409	0.367	-0.165	84.74	0.920
±0.597	±0.057	±0.096	±0.165		
Uni.					
-1.695	0.535			59.83	0.869
±0.068	±0.069				
-3.333	0.432	0.205		102.31	0.962
±0.370	±0.046	±0.046			
-3.522	0.412	0.239	-0.072	60.23	0.963
±0.859	±0.094	±0.146	±0.288		
VWH					
-1.590	0.434			9.52	0.464
±0.153	±0.141				
-4.577	0.398	0.382		28.46	0.850
±0.593	±0.078	±0.075			
-6.228	0.224	0.712	-0.836	27.08	0.900
±0.932	±0.106	±0.168	±0.395		

Table 5.3 shows that the patterns of the relationship between urea hydrolysis rate and urea concentration, soil pH, and

incubation time were the same for the three soils. The urea hydrolysis rate is significantly related to urea concentration, as shown by the high values of F test and R^2. So it can be assumed to be described approximately by urea concentration. The regression equation was significantly improved with the addition of soil pH, shown both in values of F test and R^2. The addition of time as a independent variable did not give further improvement in R^2, and decreased the values of the F test. This may suggest that the reaction time is not an important factor in the model for estimating urea hydrolysis rate.

Obviously, urea hydrolysis rate is mainly controlled by urea concentration, but is also strongly affected by the increase of soil pH in this experimental system.

(2) Soil pH

The changes in soil pH during the reaction period for each treatment is presented in Figures 5.1 (Beg.), 5.2 (Uni.), and 5.3 (VWH). The pattern of the change of soil pH in these three soils is the same. The greater the amount of urea added, the higher the soil pH reached (detailed data shown in Tables A.5.1 to A.5.19 of appendix 5). It also corresponds approximately to the change in ammoniacal-N concentration.

At low ranges of ammoniacal-N the value of soil pH is strongly correlated with original soil pH, but when the amount of ammoniacal-N is higher than the CEC, the soil pH of these three soils is nearly the same. The pattern is shown in Figure 5.4 (points).

It is possible to predict the amount of calcium carbonate precipitated in the soil, as was discussed in chapter 3, from NT and solution pH. The program developed in chapter 3 to calculate the amount of calcium carbonate precipitated from measured

solution pH and NT can also be adapted to the soil system by taking soil buffer capacity into account. Other assumptions which will be made are that soil particles do not affect the ionic strength of "soil solution", and that the equilibrium condition of ammoniacal-N and carbonic acids is the same both in the free solution and on the soil particle surface (i.e. the ion exchange sites). With these assumptions, the activity of ions in the "soil solution" can be calculated using thermodynamic equilibrium constants.

In this study soil buffer capacity was expressed by dpH/dBase, i.e. the change of soil pH (dpH) when a unit of soil base (dBase, me/100 g of oven-dry soil) is added. In this method when an certain amount of base is added to soil, the higher the soil buffer capacity of the soil, the less the soil pH will be changed. The soil buffer capacities of the three soils were determined and shown in section 4.2 of appendix 4; they were 0.54±0.03, 0.30±0.02, and 0.22±0.01 pH/(me/100 g) for Beg., Uni., and VWH soils. The sequence of soil pH buffer capacity (dBase/dpH) of the three soils is Beg. < Uni. < VWH.

(p.156)

In Figure 5.4, the solid line represents the soil pH which assumes that there is no soil pH buffer capacity. Calculations with Begbroke soil show how this line was produced, and will assist understanding. The soil water content of 127.6 g of moistened soil (equivalent to 100 g of oven-dry soil) was 27.6 ml. With temperature at 25^0 C and P_{CO2} at 0.00484 atm, the equilibrium solution pH is 8.61 when reaction solution contains 0.05 M ammoniacal-N (Table 2.1). When the content of ammoniacal-N is converted into milliequivalent per 100 g of oven-dry soil the concentration of NT is 1.38 me/100 g as in

NT=0.05 M x 27.6 ml/100 g=1.38 (me/100 g).

Paired sets of soil pH and ammoniacal-N (ammoniacal-N, pH) were produced, and shown as the solid line of Figure 5.4. The broken line represents calculated soil pH taking into account the effects of soil buffer capacity, but assuming that no calcium carbonate is precipitated. Soil buffer capacity of Beg soil was described by equation A.4.5 as

$$pH_f = 6.89 + 0.54\ (X_{base})$$

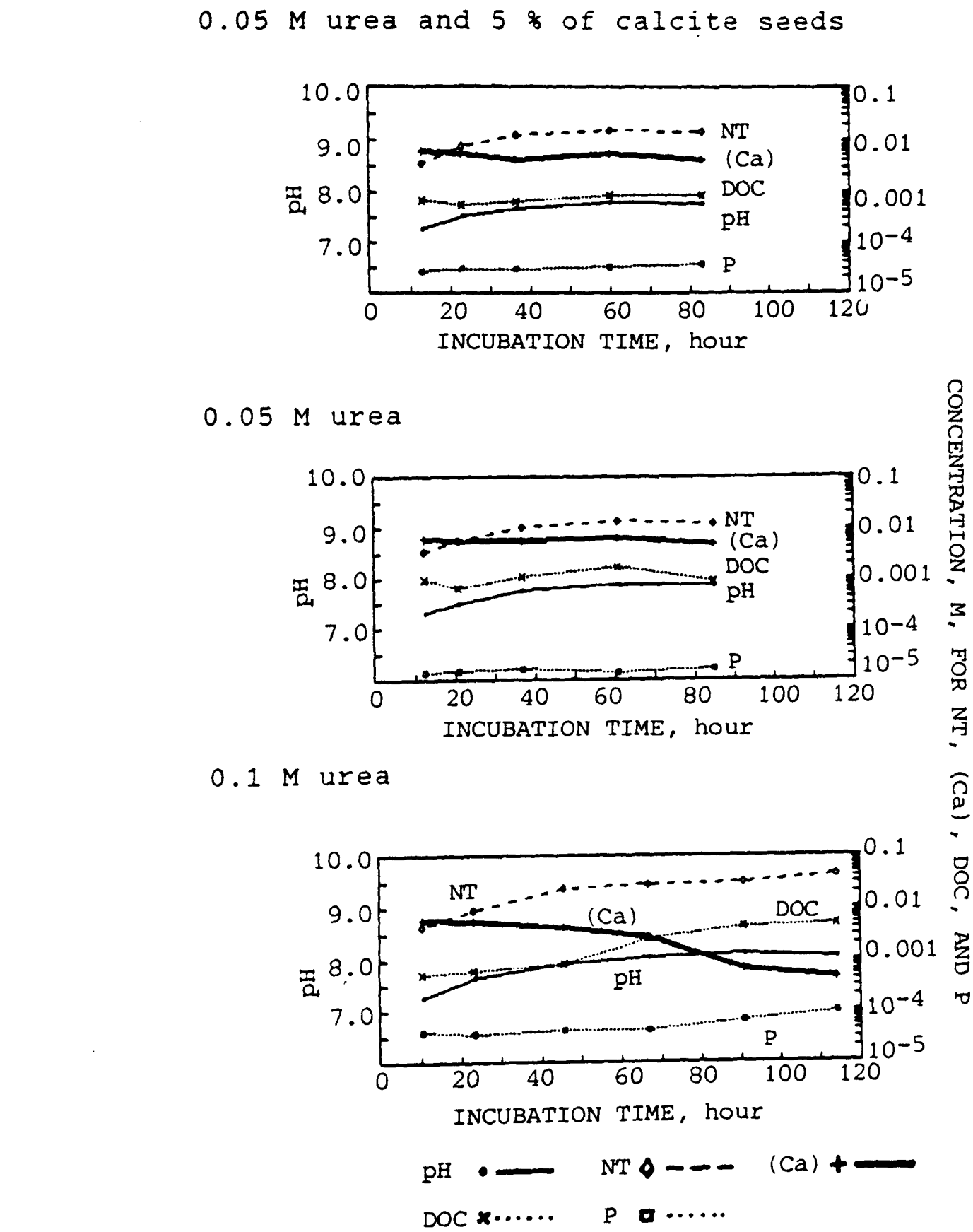
where pH_f is soil pH, 6.89 is the initial soil pH, and 0.54 is the soil buffer capacity. When soil pH (pH_f) is 8.61 the content of soil base (X_{base}) is 3.56 me/100 g of oven-dry soil.

In the experimental conditions and with solution pH at 8.61 the ratio of concentration of base in solution/NT for the ammonium bicarbonate solution is 0.866 (according to ammonium and carbonic acid dissociation constants). Hence the corresponding concentration of ammoniacal-N (NT) for producing the quantity of base in solution is 4.11 me/100 g (i.e. 4.11=3.56/0.866). Then paired sets of soil ammoniacal-N and soil pH were produced (4.11 me/100g, pH 8.61), and plotted as the broken line. The gap between the two lines is assumed to be due to soil buffer capacity.

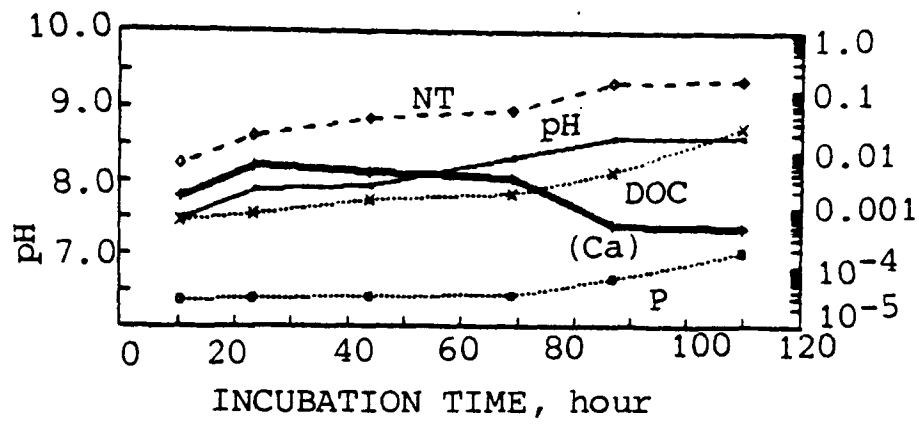
Corresponding lines and broken lines for Uni. and VWH soils were also produced using the above method.

The gap becomes narrower with the increase of concentration of ammoniacal-N, because the buffer capacity of ammonium bicarbonate will be greater than the soil buffer capacity at high concentrations of NT.

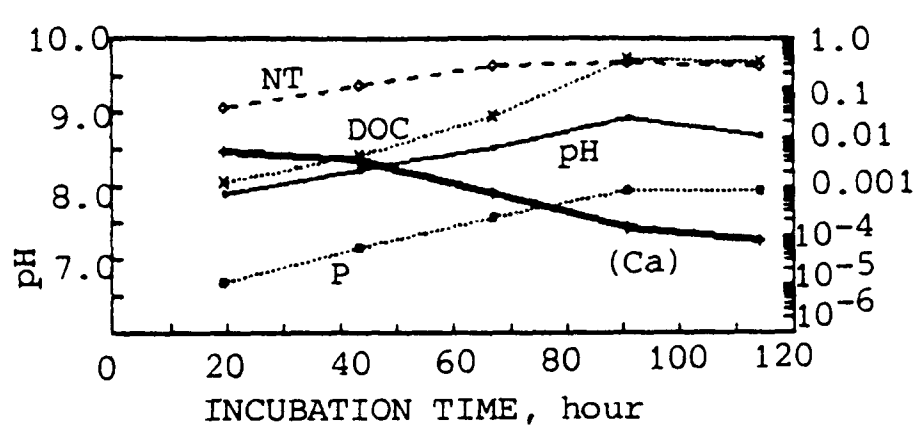
Figure 5.1 THE CHANGES IN COMPOSITIONS OF BEGBROKE SOIL AFTER TREATMENT WITH VARYING CONCENTRATIONS OF UREA.



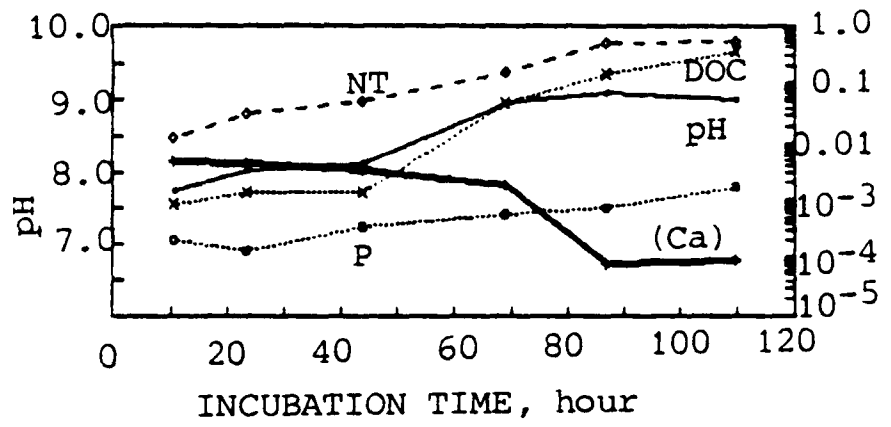
0.3 M urea



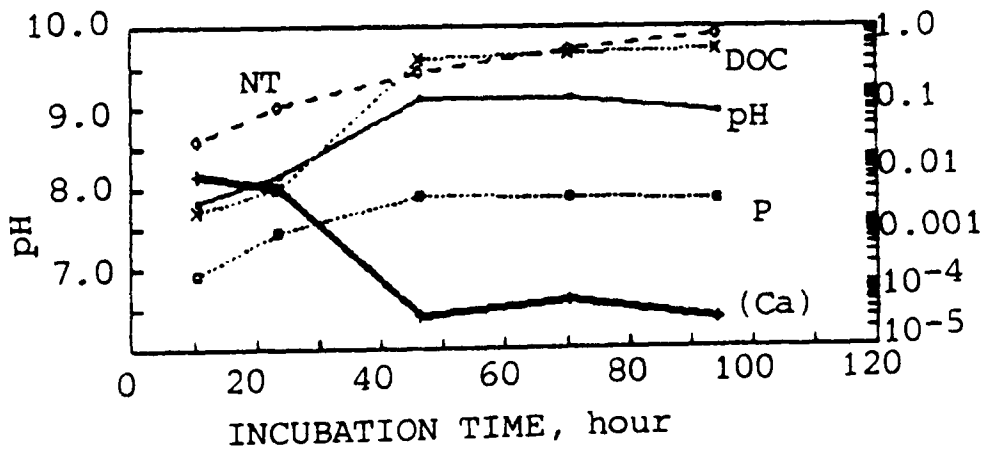
0.5 M urea



0.7 M urea

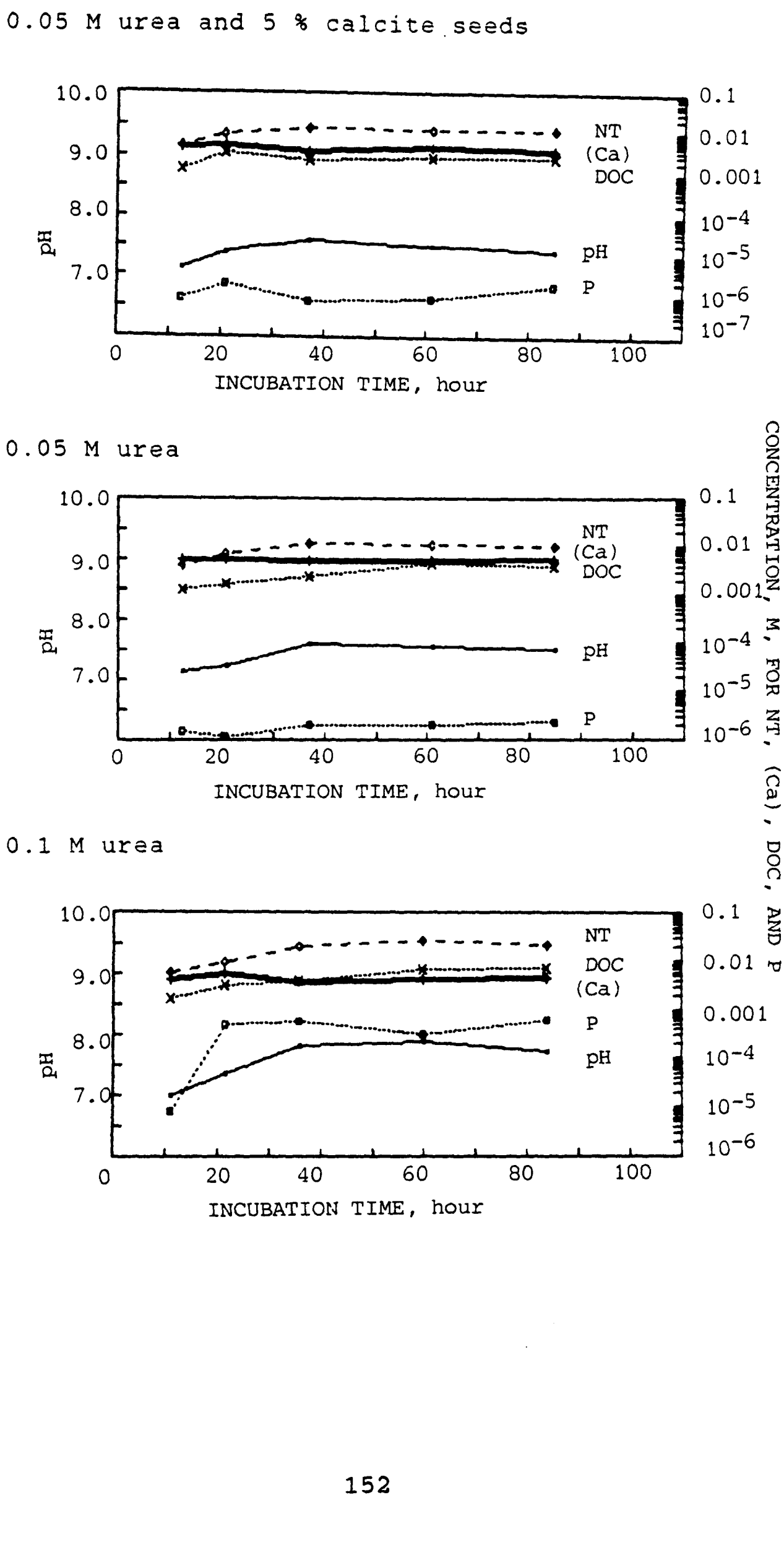


1.0 M urea

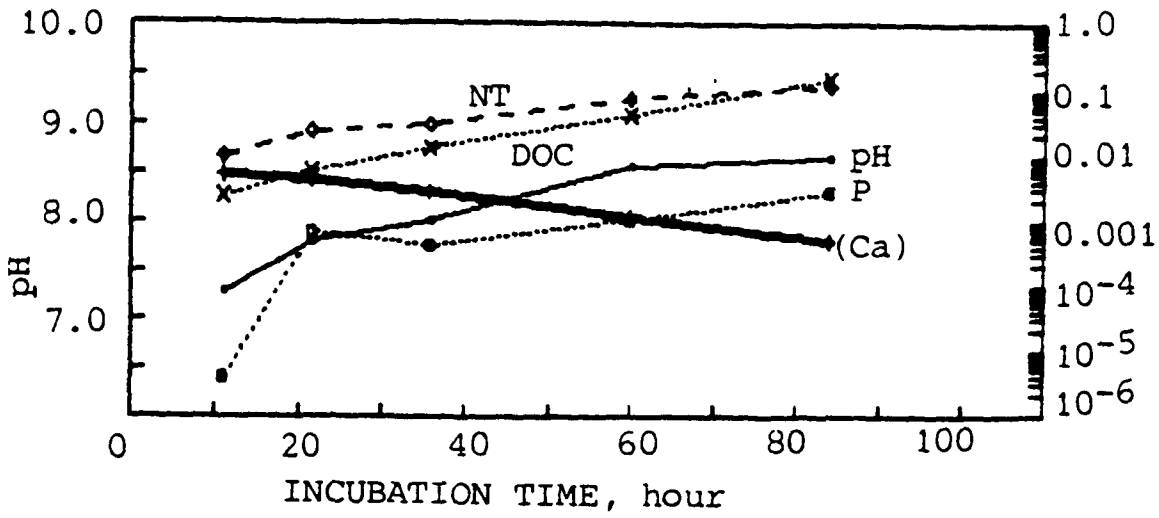


CONCENTRATION, M, FOR NT, (Ca), DOC, AND P

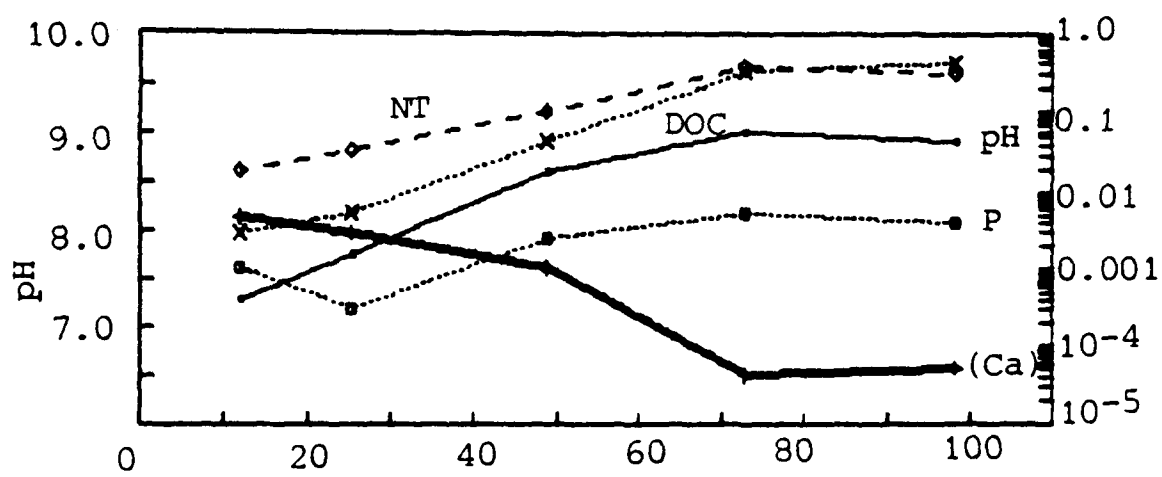
Figure 5.2 THE CHANGES IN COMPOSITIONS OF UNIVERSITY PARKS SOIL AFTER TREATMENT WITH VARYING CONCENTRATIONS OF UREA.



0.3 M urea



0.5 M urea



1.0 M urea

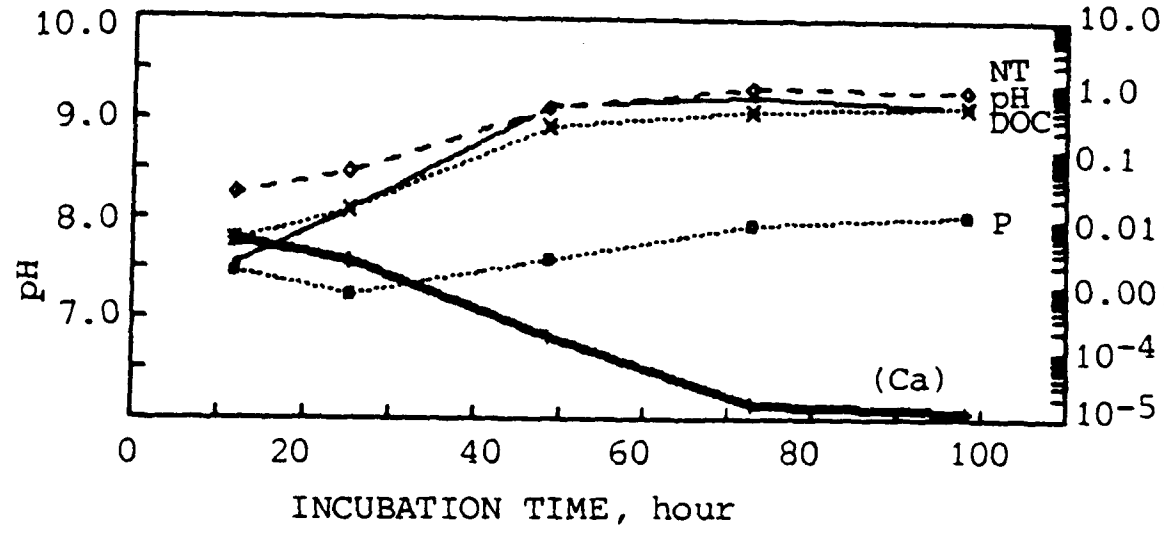
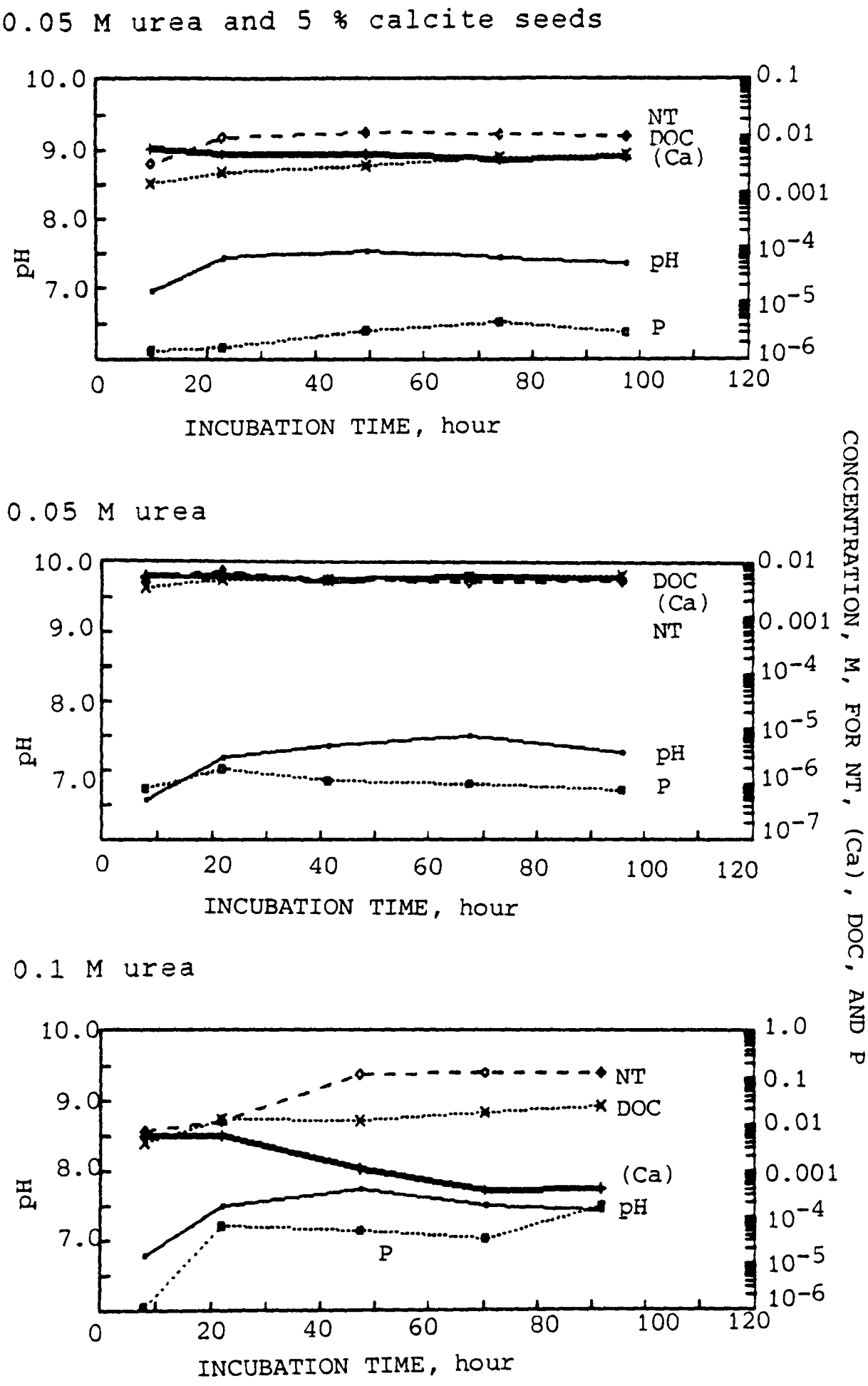
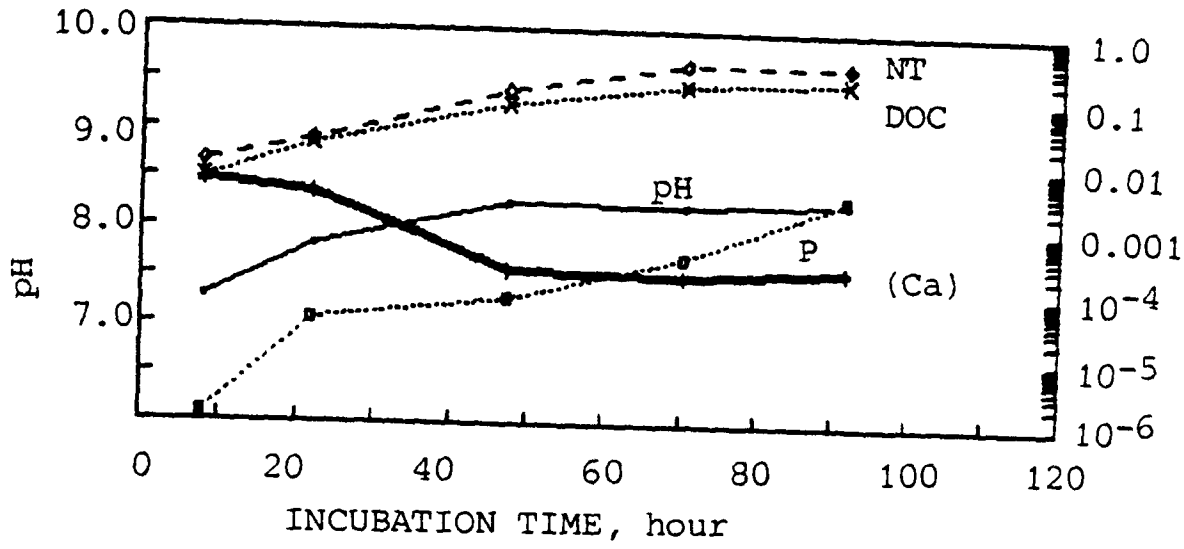


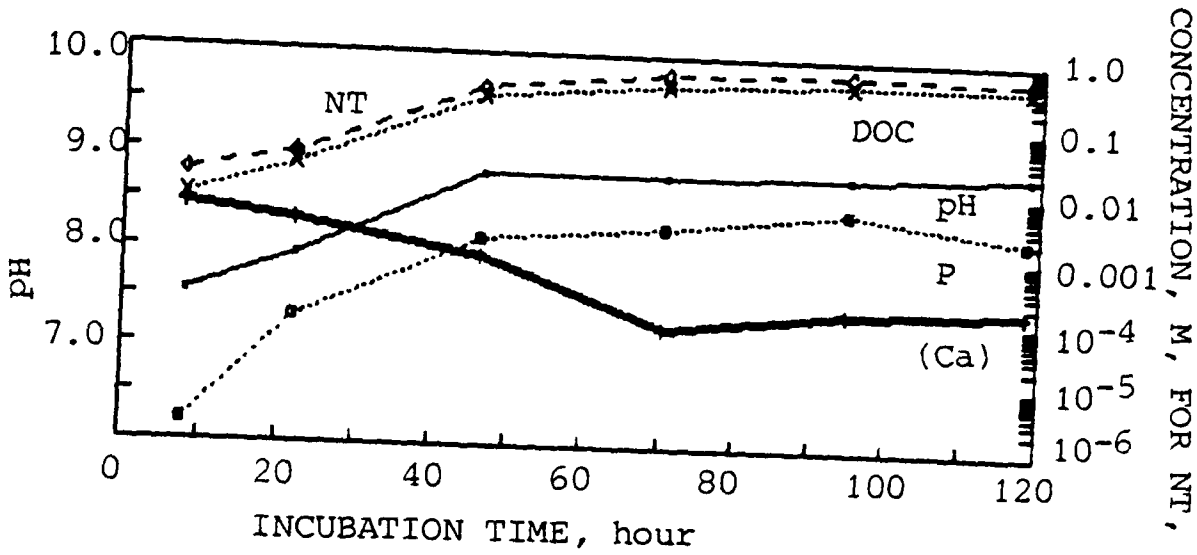
Figure 5.3 THE CHANGES IN COMPOSITIONS OF VWH SOIL AFTER TREATMENT WITH VARYING CONCENTRATIONS OF UREA.



0.3 M urea



0.5 M urea



1.0 M urea

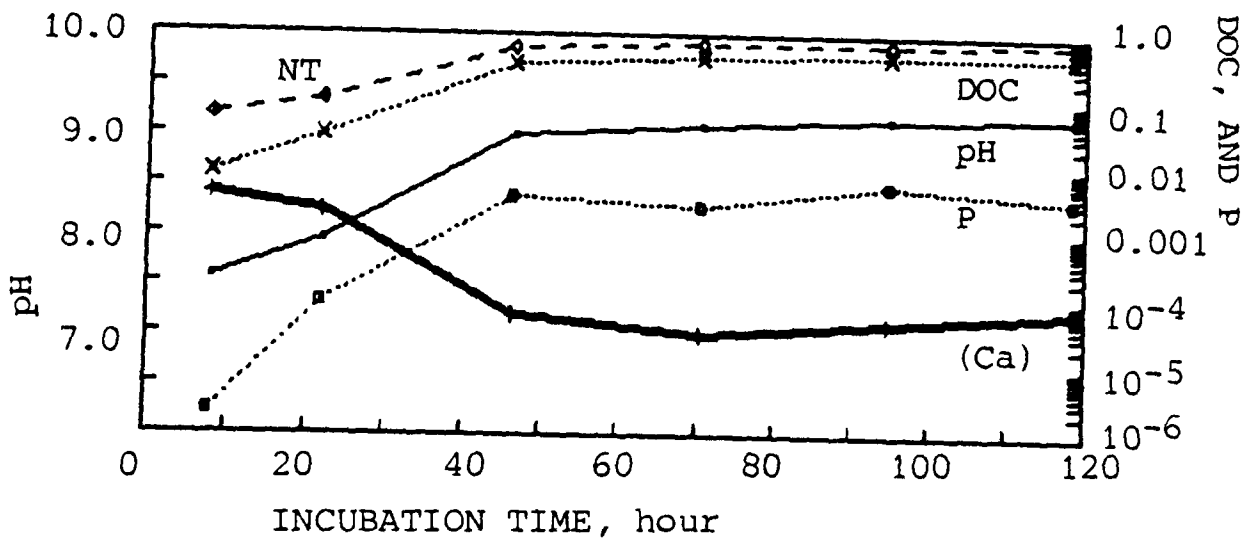


Figure 5.4 THE COMPARISON OF ACTUAL SOIL pH (POINTS) AND THEORETICAL SOIL pH TAKING INTO ACCOUNT (BROKEN LINE) OR IGNORING (SOLID LINE) SOIL BUFFER CAPACITY AT THE SAME CONCENTRATION RANGE AS SOIL AMMONIACAL-N.

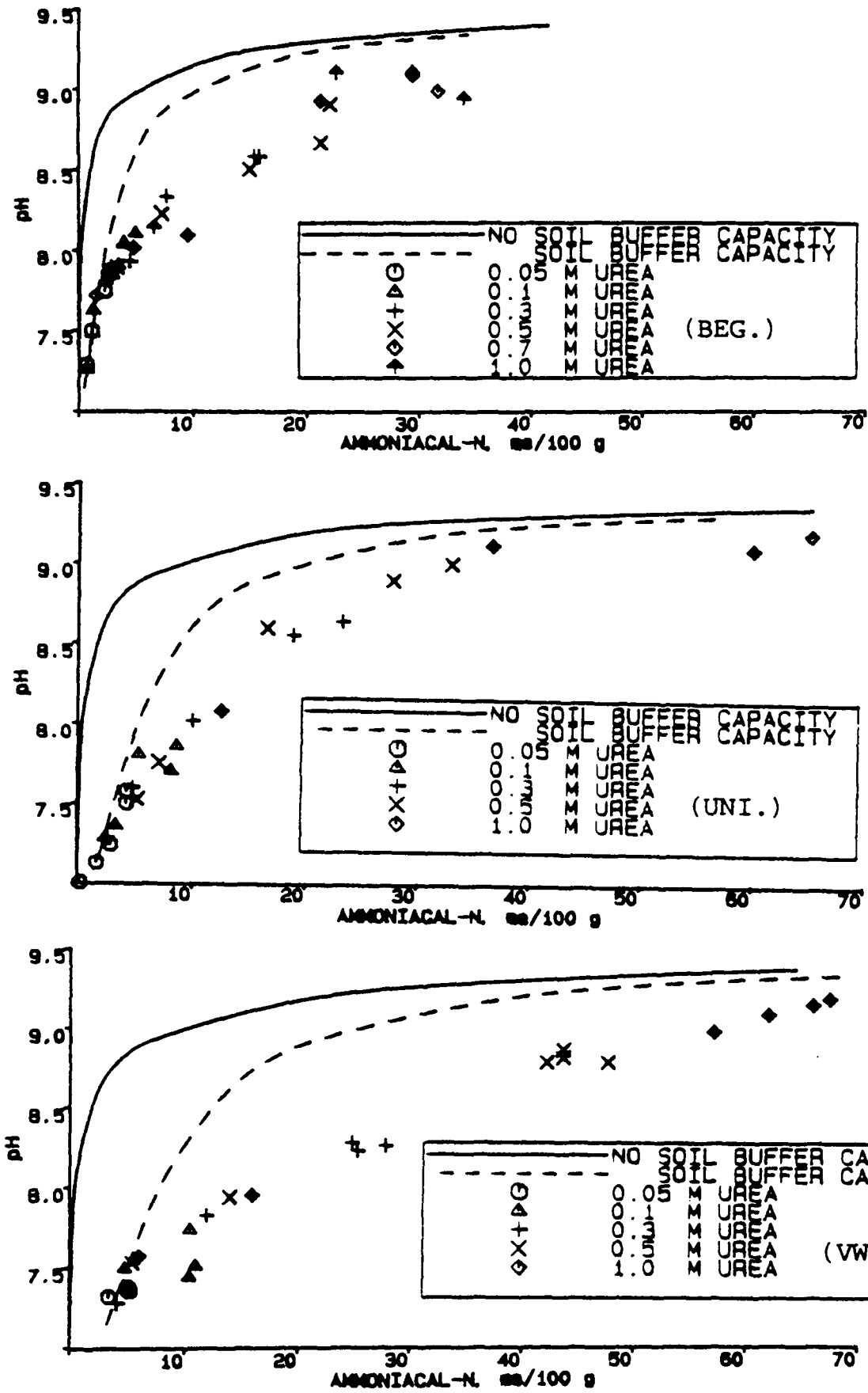


Figure 5.4 shows that the measured values of soil pH are all lower than the values estimated by assuming that no calcium carbonate is formed (broken lines). The discrepancy of measured soil pH from the broken line is presumably due to the formation of calcium carbonate : The greater the discrepancy found, the greater the amount of calcium carbonate precipitated. According

to Figure 5.4, the magnitude of the reduction of soil pH attributed to calcium carbonate precipitation may be greater than 0.5 pH units, especially when the contents of ammoniacal-N in soils were around 1/3 to 3/2 times that of CEC.

(3) The amount of calcium carbonate precipitated

The changes of soil pH suggest that the precipitation of calcium carbonate did occur following urea application. The sharp change of calcium ion activities ((Ca^{2+})) (shown in series 2 of Figures 5.1 to 5.3) was assumed to be due to the precipitation because if no precipitation had occurred the activity of calcium ions should have increased instead of decreasing because ammonium ions would have replaced calcium ions from CEC sites in the soil solution.

Table 5.4 THE LOWEST $[Ca^{2+}]$, in mM, IN SOIL SOLUTIONS.

Soils	Urea, M						
	0.05*	0.05	0.1	0.3	0.5	0.7	1.0
Beg.	7.57	9.41	0.78	1.26	0.22	0.27	0.10
Uni.	7.36	9.71	7.14	1.28	0.13	-	0.05
VWH	7.24	6.52	0.72	0.46	0.25	-	0.11

The values of concentration $[Ca^{2+}]$ of calcium ions were calculated from the measured activities (Ca^{2+}) of calcium ions which were directly determined with soil samples using a calcium-sensitive electrode. Figures 5.1, 5.2, and 5.3 show that the three soils have the same pattern of changes in calcium activities : the higher the concentration of urea added, the lower the activity of calcium ions reached. Details are given in Tables A.5.2 to A.5.20 of appendix 5. The lowest value of concentration of calcium ions $[Ca^{2+}]$ during the experimental period of each treatment is presented in Table 5.4. Comparing the lowest values

of concentration of calcium ions with the initial concentration 10 mM clearly shows that at high urea treatments most of the calcium ions had precipitated. * denotes the results in the case where 0.05 M urea and 0.5 per cent of calcite-seeds were added.

Ion exchange between calcium and ammonium ions at CEC sites is very complicated, and the ions might not attain equilibrium at each sampling time. Hence in this study we will not use a calcium adsorption isotherm and the measured calcium activity to estimate the amount of exchangeable calcium ions remaining in soils, or to estimate the amount of calcium carbonate newly formed. In this section, the decrease in the amount of calcium ions extracted in 2 M KCl solution from the initial quantity will define the amount of newly formed calcium carbonate in soils. Appendix 5 has shown that the values of newly formed calcium carbonate calculated by this method agree with the values determined by the acid decomposition method. After 0.5 M urea (in soil solutions) was added to the three soils for three days, the amounts of newly formed calcium carbonate calculated from the remaining of calcium ions in 2 M KCl extracts were 6.45, 17.31, and 22.47 me/(100 g of oven-dry soil) and their corresponding values were 7.77, 16.90, and 21.2 determined by acid decomposition for Beg., Uni., and VWH soils respectively. Table 5.5 (below) shows the quantity of newly formed calcium carbonate ($CaCO_{3(s)}$) in me/(100 g oven-dry soil) by the end of each experiment. It shows that the greater the concentration of urea added, the more $CaCO_{3(s)}$ was precipitated. However when the urea concentration was high enough, any further increase of urea could not lead to further precipitation since the calcium ions from the CEC sites had already been exhausted. The initial exchangeable calcium ions were 14.79±0.16, 19.3±0.16, and 21.58±0.40 me/100

g (Table 5.1) for Beg., Uni., and VWH soils respectively.

Table 5.5 THE AMOUNT OF $CaCO_{3(S)}$ (me/100 g) PRECIPITATED BY THE END OF EACH EXPERIMENT.

Soils	Urea, M						
	0.05*	0.05	0.1	0.3	0.5	0.7	1.0
Beg.	1.04	0.67	1.66	8.21	11.23	14.43	13.88
Uni.	2.63	0.46	4.02	12.13	18.82	-	20.58
VWH	1.80	2.25	3.45	15.8	21.28	-	20.83

Figure 5.5 THE AMOUNT OF CALCIUM CARBONATE PRECIPITATED IN SOILS DURING INCUBATION.

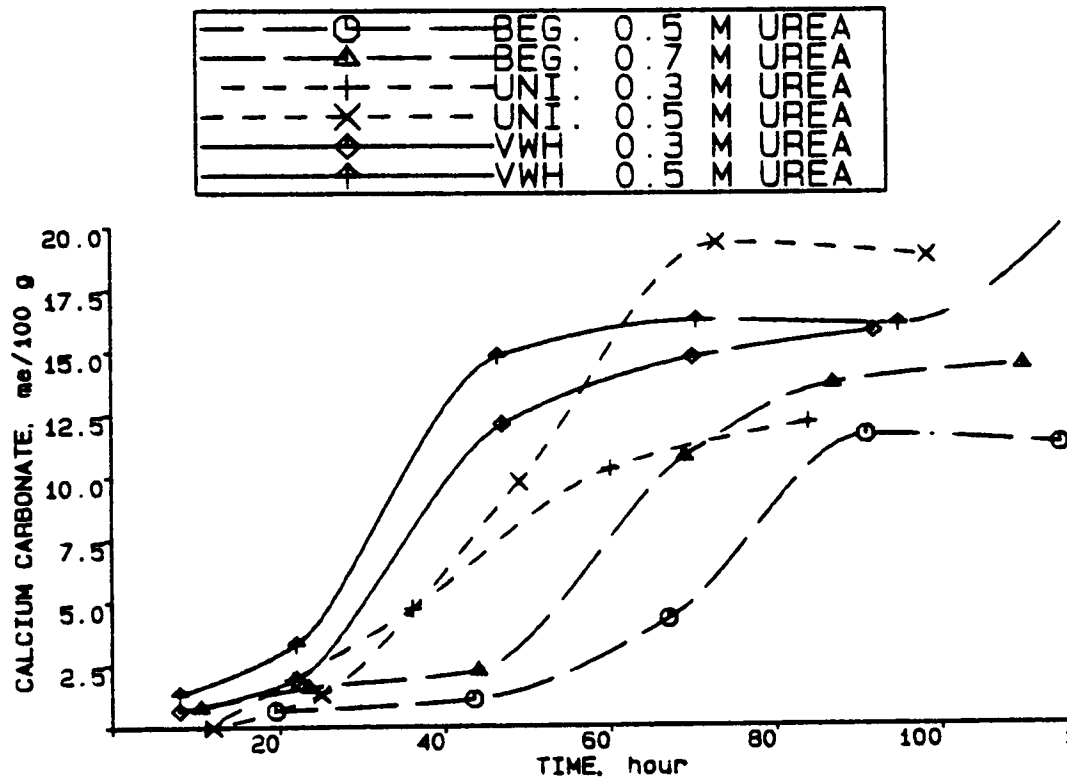


Figure 5.5 describes the precipitation of $CaCO_{3(s)}$ during the reaction period. Two examples for each soil are presented (0.5 and 0.7 M for Beg., and 0.3 and 0.5 M for Uni. and VWH soils). These data (seen in Table 5.11) will be used later to establish the model for precipitation of calcium carbonate in soils.

(4) The relationship between the amount of calcium carbonate precipitated in soil and the amount of ammoniacal-N present.

The relationship between the newly formed calcium carbonate and ammoniacal-N in the soil systems can be pictured by plotting the determined data from all treatments, except the treatment

with calcite-seeds added, with the three soils, in Figure 5.6. Since it was difficult to distinguish between plotted data in the lower range, the lower parts of the plots were enlarged (see diagram on the right hand side of Figure 5.6). It is clear that, before the exchangeable calcium ions in CEC sites were exhausted, the greater the ammoniacal-N the greater the calcium carbonate precipitated. The pattern is the same for the three soils. Thus the formation of calcium carbonate may be predicted by the concentration of ammoniacal-N, and this calculation may be extended to predict the relation between the precipitation rate and the urea hydrolysis rate.

Since the error of the measurement of calcium carbonate in soils is about 1.3 me/(100 g of oven-dry soil), the data used to calculate the correlation between the newly formed calcium carbonate and the ammoniacal-N released from urea hydrolysis, did not include those data whose exchangeable calcium ions remained in soils were less than 1.3 me/(100 g of oven-dry soil). Using the best fitting method, the regression equations are 5.1, 5.2, and 5.3 for Beg., Uni., and VWH soils, respectively.

$$[CaCO_{3(S)}] = -0.79 \pm 0.27 + 0.52 \pm 0.03\ [N_T] \qquad (5.1)$$

$$[CaCO_{3(S)}] = -1.23 \pm 0.30 + 0.55 \pm 0.02\ [N_T] \qquad (5.2)$$

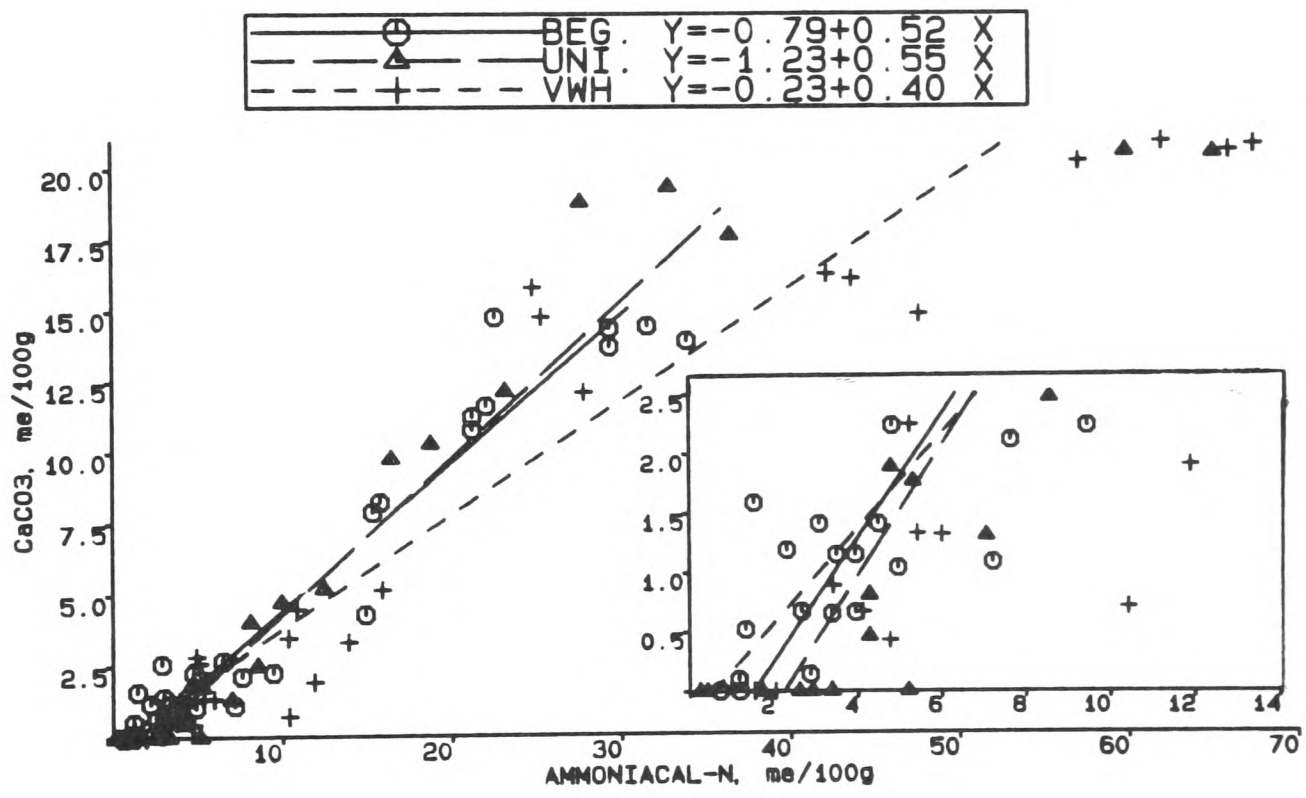
$$[CaCO_{3(S)}] = -0.23 \pm 0.80 + 0.40 \pm 0.03\ [N_T] \qquad (5.3)$$

where $[CaCO_{3(S)}]$ is the amount of newly formed calcium carbonate (in me/100 g of oven dry soil), and $[N_T]$ is the total concentration of ammoniacal-N released from urea hydrolysis in the same units. Their regression coefficients are significant, the values of R^2 are 0.926, 0.965, and 0.867 for Beg., Uni., and VWH soils, respectively.

These regression equations do not consider the inhibitory effects of soil factors on the precipitation. However, the

significant correlations between the newly formed calcium carbonate and the ammoniacal-N give direct information about the quantity of calcium carbonate precipitated. After the conditions allow the precipitation to occur, the precipitated calcium carbonate in me/(100 g of soil) is about 0.52, 0.55, and 0.40 that of ammoniacal-N released from urea hydrolysis for Beg., Uni., and VWH soils, respectively. The rate model of calcium carbonate precipitation in soils will be discussed later in this chapter.

Figure 5.6 THE RELATIONSHIP BETWEEN THE FORMATION OF CALCIUM CARBONATE (me/100g) AND AMMONIACAL-N (me/100g) IN SOIL AFTER UREA APPLICATION.



(5) The effect of the addition of calcite seeds on the precipitation of calcium carbonate following urea application (P.150)

Results (Figure 5.1, details in Table A.5.2 of appendix 5) show that the addition of calcite to Begbroke soil stimulates the precipitation of calcium carbonate. In the 0.05 M urea treatment with added calcite, soil pHs were about 0.1 unit lower than those with no addition of calcite-seeds. The values of SI were also significantly lower in the treatment with the addition of

calcite-seeds. For example SI was 17.1 and 23.1 (Table A.5.3 of appendix 5) in the treatment with no-addition of calcite, but the corresponding value was 7.71 and 12.57 (Table A.5.2 of appendix 5) respectively after the experiments had been going for about 37 and 60 hours in calcite-treated soil.

The addition of calcite had no effect on the compositions of soil solutions for the University parks soil. For example, there were no differences in values of soil pH and SI between treatments with calcite and without calcite added (Figure 5.2 and Tables A.5.9 and A.5.10 of appendix 5), but Table 5.5 shows that by the end of the experiments more $CaCO_{3(s)}$ had precipitated after treatment with calcite-seeds added.

Also in VWH soil, the addition of calcite did not affect the concentrations of phosphate, DOC, and, calcium ions (Figure 5.4 and Tables A.5.15 and A.5.16 of appendix 5). However, the addition of calcite-seeds increased soil pH about 0.15 units, and doubled SI values at the early reaction stage (within three days). The effect on these two parameters were insignificant after four days.

The different responses to the addition of calcite in the three soils can be explained as follows :

(a) Begbroke soil has a high content of original calcium carbonate, but the high concentration of phosphate (1.86×10^{-5} M) in the initial soil solution masks the significance of the original calcium carbonate on the precipitation. Therefore, the extra calcite has been able to show its effect.

(b) In the VWH soil, the low initial soil pH, of 6.42, which is lower than the calcite saturation pH of 7.12 when the partial pressure of carbon dioxide is kept at 0.00484 atm, and the high soil pH buffer capacity, caused the dissolution of calcite seeds,

resulting in higher values of pH and SI.

(c) The concentrations of phosphate in soil solutions of Uni. and VWH soils were very low, only $9x10^{-7}$ M at the beginning, and the highest concentrations during the reaction period were about $2x10^{-6}$ M for Uni. soil and $4x10^{-6}$ M for VWH soil. According to the measurements of the inhibitory effect of phosphate on the formation of calcium carbonate in chapter 4, the inhibitory effect of phosphate at these levels of concentration could be ignored. However, the inhibitory effect was already very strong in Begbroke soil from the beginning of the experiment, since its initial concentration reached 10^{-5} M levels.

(d) The initial concentrations of DOC in the three soils are all less than 1 mM, so it is not a strong inhibitor at the beginning according to the results of chapter 4.

The high SI values in Begbroke soil also support the view that phosphate ion not only poisons the effective surface of the original soil calcium carbonate, but also affects the response of newly formed particles.

(6) Phosphate in soil solution

The pattern of the changes of phosphate concentration after urea was added to soils was the same for the three soils. The higher the concentration of urea added, the higher the concentration of phosphate in the "soil solution" reached during the reaction period. They are depicted in Figures 5.1 (Beg.), 5.2 (Uni.), and 5.3 (VWH).

The concentration of phosphate in the "soil solution" was about 2.0, 0.09, and $0.09x10^{-5}$ M (Table 5.6) for Beg., Uni., and VWH soils, respectively, after the moistened soils were incubated for three days without urea.

With urea added, phosphate concentration increased with

reaction time and reached higher concentrations with the higher rates of urea as shown in Table 5.7(below). The phosphate concentration was increased to more than 100 times the initial concentration. As phosphate is a strong inhibitor, a great increase in its concentration in soil solutions will significantly inhibit the precipitation of calcium carbonate in soil.

Table 5.6 THE EFFECT OF THE ADDITION OF AMMONIUM CHLORIDE (2 N) ON THE COMPOSITIONS OF SOIL SOLUTION AFTER INCUBATION FOR 3 DAYS.

Soils	Beg.		Uni.		VWH	
NH_4Cl, M	0.0	2.0	0.0	2.0	0.0	2.0
pH	7.12 ±0.04	6.36 ±0.08	6.32 ±0.00	5.92 ±0.01	6.42 ±0.04	5.49 ±0.03
(Ca), mM	5.52 ±0.33	29.7 ±1.4	5.46 ±0.14	35.2 ±0.5	5.65 ±0.09	36.4 ±0.5
Phosphate, $x10^{-5}$ M	1.86 ±0.11	2.41 ±0.04	0.09 ±0.02	0.30 ±0.12	0.09 ±0.01	0.29 ±0.02
DOC, mM	0.76 ±0.02	1.45 ±0.01	0.19 ±0.01	0.82 ±0.01	0.78 ±0.01	0.58 ±0.04

Table 5.7 THE CONCENTRATION OF PHOSPHATE, 10^{-5} M, IN SOIL SOLUTION WHEN EXPERIMENT TERMINATED

Soils	Urea, M						
	0.05*	0.05	0.1	0.3	0.5	0.7	1.0
Beg.	3.62	1.65	9.38	18.8	80.0	162	200
Uni.	0.18	0.22	61.2	281	400	-	1150
VWH	0.29	0.16	17.5	300	202	-	325

The rise in the concentration of ammonium ions could not explain the rise in the concentration of phosphate after urea application, since, even when a high concentration (2 M) of ammonium chloride was added to soils for three days, the concentration of phosphate in soil solution did not change much. The data in Table 5.6 show that after the addition of ammonium chloride the concentration of phosphate increased from 1.86±0.11

$x10^{-5}$ to 2.41±0.04 $x10^{-5}$ M in Beg.; from 9.0±1.6 $x10^{-7}$ to 3.0±1.2 $x10^{-6}$ M in Uni.; and from 8.8±1.2 $x10^{-7}$ to 2.9±0.2 $x10^{-6}$ M in VWH soil.

According to the solubility isotherms of phosphates in soils, the rise of the phosphate concentration in the "soil solution" may be due to the decrease in the activity of calcium ions in solution. The decrease of calcium ion activity was attributed to the precipitation of calcium carbonate. In soils with high urea added (e.g. 1.0 M urea), the activity of calcium ions in the "soil solution" was reduced to less than 1/100, i.e. from 5.46 mM at the beginning of each treatment to less than 0.05 mM during the experimental period. The magnitude of this decrease in calcium activity was roughly equal to the increase of phosphate concentration in soil solution. Figure 5.7 shows that the change of phosphate concentration was inversely proportional to the activity of the calcium ion. Their regression equations in logarithmic forms are equations 5.4, 5.5, and 5.6 for Beg., Uni., and VWH soils respectively as follows :

$$LP=-6.014\pm0.286 - 0.732\pm0.096\ LCA \qquad (5.4)$$

$$LP=-6.712\pm0.826 - 1.078\pm0.287\ LCA \qquad (5.5)$$

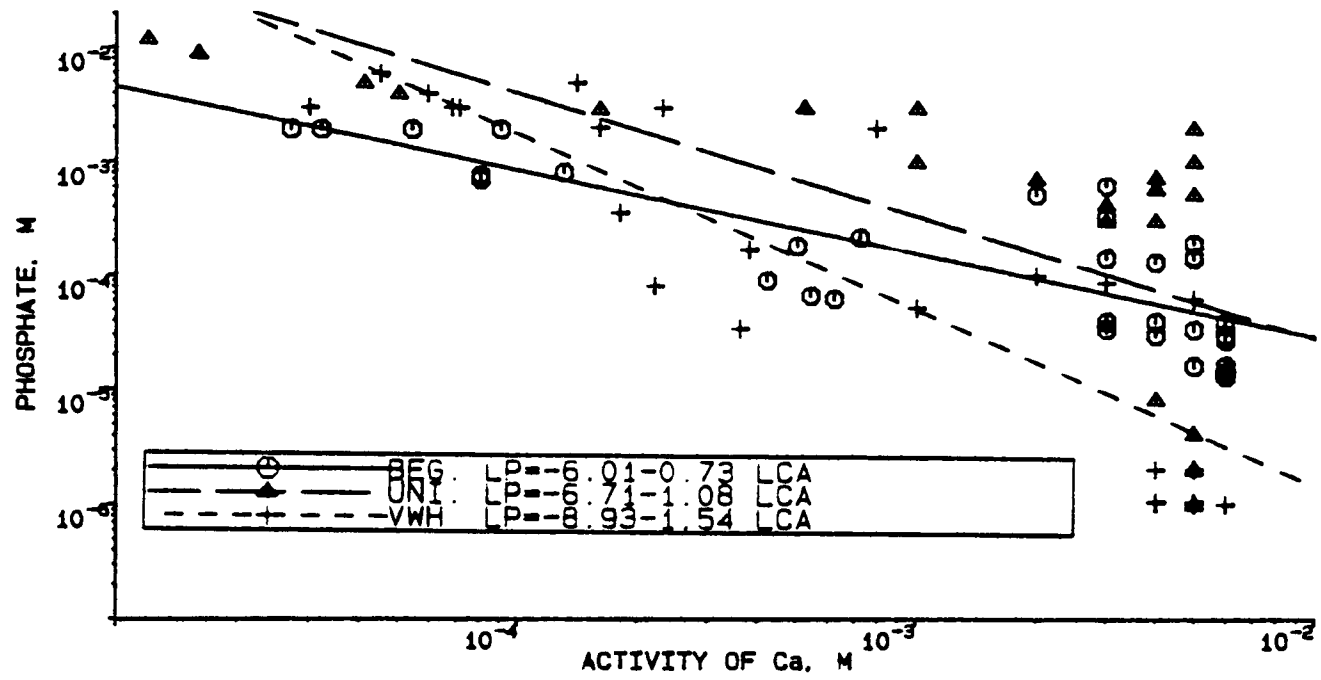
$$LP=-8.928\pm0.518 - 1.542\pm0.161\ LCA \qquad (5.6)$$

where LP is log(total concentration of phosphate) and LCA is log(activity of calcium ions). The values of R^2 for equations 5.4, 5.5, and 5.6 are 0.654, 0.391, and 0.785, having confidence regions at 99.9 per cent statistically. The different values of the slope in the equations may correspond to the different types of calcium phosphates existing in the soils. Distinguishing the types of phosphates and their dissolution behaviour in conjunction with these soils is beyond the scope of this thesis. These conclusions agree with the results reported by Smillie et al

(1987). They found that a high proportion (up to 80 per cent) of added phosphate could be recovered by water extraction when exchangeable calcium ions were replaced by sodium ions.

In this experimental system the activity of calcium ions must have been controlled by the precipitation of calcium carbonate and by soil calcium phosphates. Therefore the solubility isotherms of calcium phosphate itself cannot fully explain the reaction behaviour of calcium and phosphate ions here.

Figure 5.7 THE RELATIONSHIP BETWEEN THE CONCENTRATION OF PHOSPHATE AND ACTIVITY OF CALCIUM IN SOIL SOLUTION AFTER UREA APPLICATION.



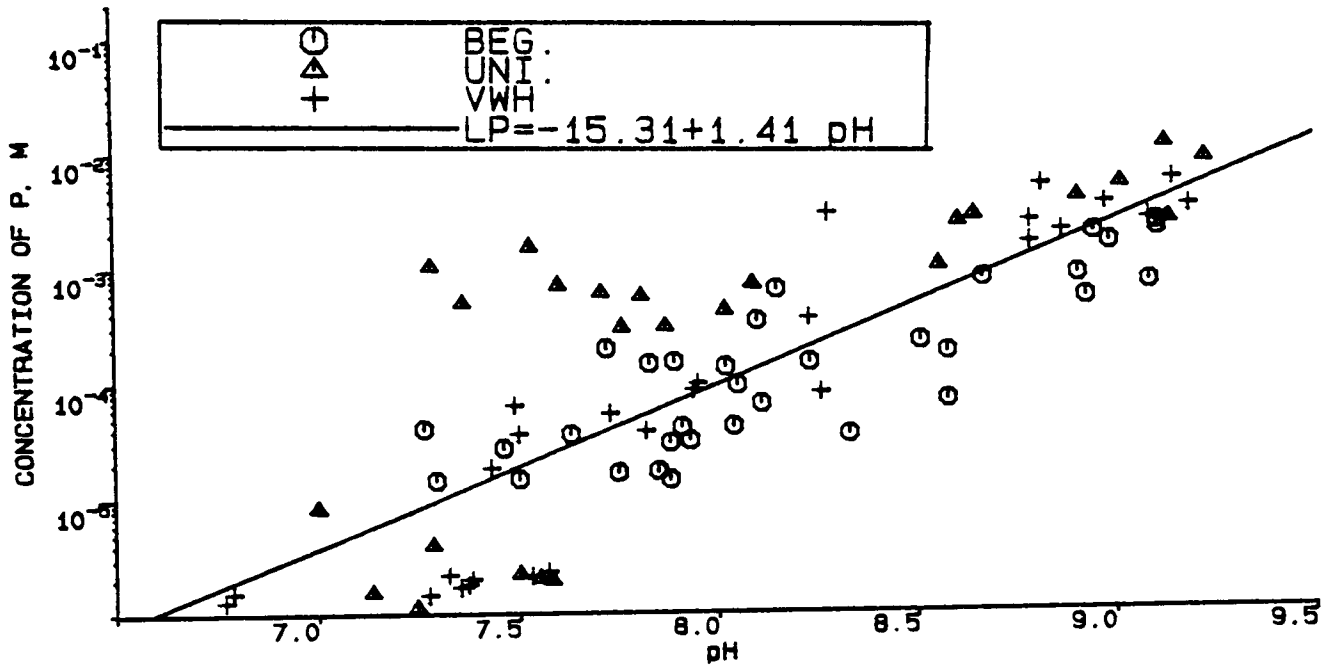
From a thermodynamic point of view, soil pH is directly correlated with the dissolution and precipitation of calcium phosphates in soil, and in practice, the changes of phosphate concentration with changes of soil pH for the three soils (Figure 5.8 below) seem to have a similar distribution of data points , especially for Beg. and VWH soils. Therefore, the relationship between soil pH and phosphate concentration could be used to predict the changes of phosphate concentration and in turn to predict the effect of phosphate on the precipitation of calcium carbonate in soils after urea application. The relationship can

be described by equation 5.7 (solid line in Figure 5.8).

$$LP=-15.306\pm0.888 + 1.412\pm0.110\ pH \qquad (5.7)$$

R^2 of the equation is 0.671 at 99.9 per cent of confidence region statistically.

Figure 5.8 THE RELATIONSHIP BETWEEN THE CONCENTRATION OF PHOSPHATE IN SOIL SOLUTION AND SOIL pH AFTER UREA APPLICATION.



(7) DOC in soil solution

With no addition of urea, the concentration of DOC in the "soil solution" was very low. The concentration of DOC was 0.76, 0.19, and 0.78 mM (Table 5.6) after Beg., Uni., and VWH soils had been incubated for three days. Even with the addition of high concentration of ammonium chloride (2 M) to the soils, their corresponding concentration of DOC was only 1.45±0.01, 0.82±0.01, and 0.58±0.04 mM, respectively. Figures 5.1 (Beg.), 5.2 (Uni.), 5.3 (VWH) show that changes in concentration of DOC in "soil solution" after application of urea depended on the amount or concentration of urea added and reaction time. Table 5.8 presents the concentration of DOC in soil solution at the end of the experiments, and shows that the changes of DOC in soil solution are similar to the changes of phosphate (above), increasing

sharply with increasing the addition of urea.

Such large increases of DOC in soil solution have not been reported before. Norman et al (1987) noted that application of liquid anhydrous ammonia led to a six- to sevenfold increase of DOC in a spherical zone 0-1.5 cm radius around the point of application of 44 kg N ha^{-1} (liquid ammonia) and a seven to ninefold increase where 206 kg N ha^{-1} had been used. In the experiments of Myers and Thien (1988), the concentration of DOC in soil leachate from the application zone (2.5 cm above and below the application point) increased about 8 times when 2400 mg kg^{-1} of NH_4OH is added to soil. However the increase in this study reaches hundredfolds.

Table 5.8 THE CONCENTRATION OF DOC, mM, IN SOIL SOLUTION AT THE END OF EXPERIMENTS.

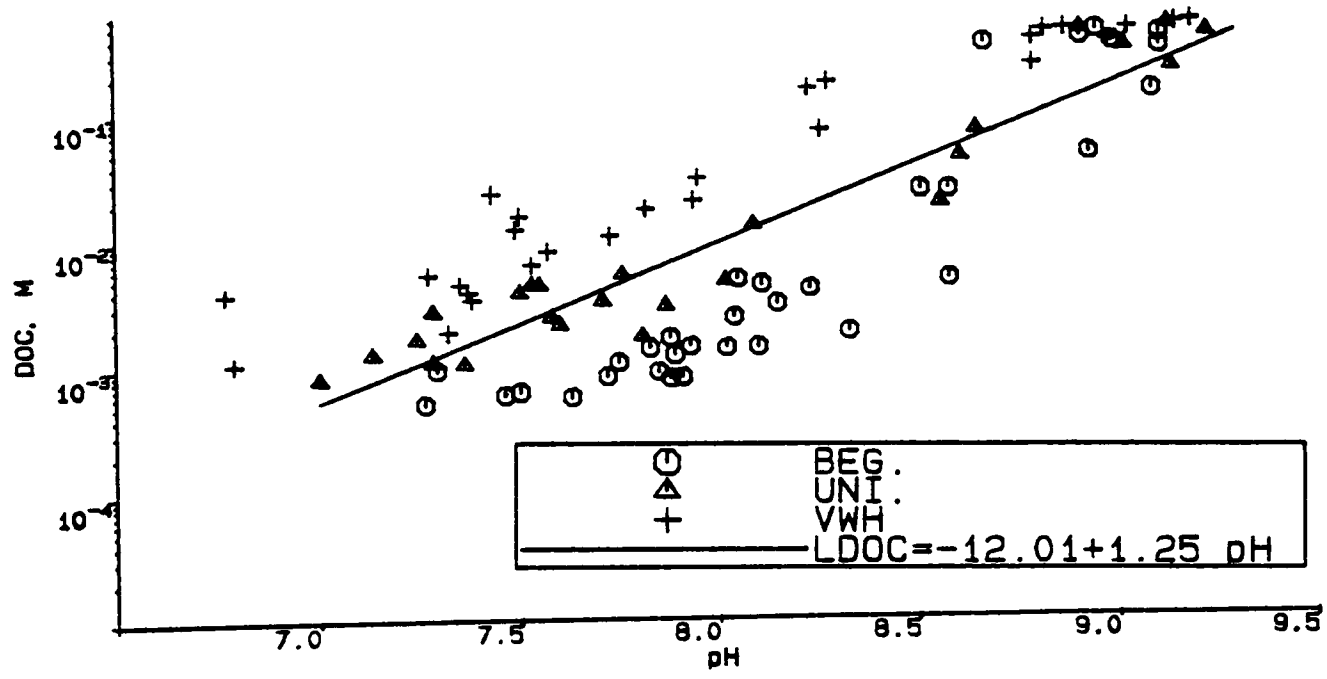
Soils	Urea, M						
	0.05*	0.05	0.1	0.3	0.5	0.7	1.0
Beg.	0.85	0.90	4.90	25.0	355	360	440
Uni.	2.90	3.90	3.40	72.5	450	-	480
VWH	4.60	4.50	24.0	188	450	-	510

Norman et al (1987) said that when soil pH levels are above 6.5 to 7.0, the concentration of DOC is linearly related to both exchangeable ammonium concentration and pH. Myers and Thien find the R^2 values for the regression of DOC on pH ranged from 0.83 to 0.9. Stevenson (1982) also reported that the concentration of DOC would be expected to increase with the increase of soil pH and exchangeable ammonium concentration because soil organic matter becomes increasingly soluble under alkaline conditions as acidic groups are ionised. He said that monovalent cations such as ammonium form soluble salts with fulvic and humic acids, and calcium and other polyvalent cations (e.g. Fe^{+3}, and Al^{+3})

maintain the soil organic matter in a flocculated and insoluble condition. However, according to the results of Table 5.6, the increase of exchangeable ammonium did not seem directly to affect the dissolution of DOC. The increase of soil pH and the decrease of the concentration of calcium ion may partly explain the great increase of DOC.

Since humic substances are comprised of complicated, ill-defined mixtures of polyelectrolytic molecules (MacCarthy and Rice, 1985), their fundamental chemical nature is still largely a mystery, despite the extensive investigations that have been carried out on these materials for many years. It is beyond the objective of this thesis to discuss the mechanism of the dissolution of soil organic matter in detail.

Figure 5.9 THE RELATIONSHIP BETWEEN THE CONCENTRATION OF DOC IN SOIL SOLUTION AND SOIL pH AFTER UREA APPLICATION.



Changes in the concentrations of DOC are highly correlated with soil pH and soil ammoniacal-N content. Figures 5.1, 5.2, and 5.3 show that in the three soils the forms of graphs of these parameters are fairly parallel to each other. Thus, soil pH may be used to estimate the changes of DOC through a regression equation. In Figure 5.9, experimental data for the three soils

seem to be grouped differently for each soil, so the best approach is to use individual equations. However, the significant correlation for all three soils suggests that equation 5.8 could be used for predicting the changes in DOC, since the variation in estimated DOC is not crucial.

$$LDOC=-12.01\pm0.76 + 1.250\pm0.094\ pH \qquad (5.8)$$

where LDOC is the log(concentration of DOC). The value for R^2, 0.687, of equation 5.8 is statistically significant.

(8) The changes of SI in soil solutions

The soil systems were kept under constant partial pressure of carbon dioxide (0.00484 atm) and the changes in activity of carbonate ions were related to the changes in soil pH; thus, when the activity of calcium ions in soil solutions is relatively stable, the SI in soil solutions roughly corresponds to soil pH. In practice whenthe concentration of urea was higher than 0.1 M, the activity of calcium ions decreased significantly during the experimental period. Although each treatment started from the same initial concentration of calcium ions, it was affected by the rate of precipitation of calcium carbonate, and the rate of ion exchange between ammonium ions in soil solutions and calcium ions in CEC sites. Therefore it would be expected that the changes of SI in soil solutions do not correspond to changes in soil pH.

The detailed data of SI are shown along with other components in Tables A.5.2 to A.5.20 of Appendix 5. Table 5.9 (below) only shows the peak values of SI, denoted by *, and the values at the end of each experiment.

Among the treatments in Uni. soil, the higher the concentration of urea added, the higher the peak of SI reached. At the end of experiment, the SI of 1.0 M urea treatment was lower than that

of 0.3 and 0.5 M urea treatments.

In Beg. soil, the treatment with 0.7 M urea had the highest values of SI at the peak and at the end of experiment. Both the corresponding values of SI in 1.0 M urea treatment were higher than those in 0.3 M urea treatment.

In VWH soil, the highest peak value of SI was obtained in treatment with 0.5 M urea. At the end of experiment with 0.1 M urea, the calculated value of SI, 0.3, which was lower than 1.0 and suggested undersaturation of calcium carbonate. This result is difficult to interpret fully. However it is probably partly due to errors in measurement. Another possible reason is that, after the decrease in concentration of calcium ions caused by the precipitation of calcium carbonate, the decrease of soil pH resulted in a decrease in activity of carbonate ions but the rate of dissolution of newly formed calcium carbonate did not compensate for the decrease of carbonate ions. As was mentioned, although the nitrification inhibitor (ATC) was added to the soils, nitrification may occur after three days' incubation, which would cause a decrease in soil pH. Further investigation is needed to explain the result; however it is beyond the scope of this thesis.

Table 5.9 THE VALUES OF SI IN SOIL SOLUTION AT THE PEAK (*) AND AT THE END OF EXPERIMENTS.

Soils	Urea, M						
	0.05*	0.05	0.1	0.3	0.5	0.7	1.0
Beg.	12.6	23.1	4.80	68.4	15.9	79.9	20.5
Beg.*	17.6	34.5	29.9	150.2	90.8	1265	97.3
Uni.	2.76	5.65	10.9	98.6	31.4	-	21.1
Uni.*	5.63	6.93	21.4	146	159	-	288
VWH	2.44	2.24	0.30	7.99	84.5	-	155
VWH*	5.25	2.24	5.35	13.3	286	-	155

5.2.2 The development of the rate model of precipitation of calcium carbonate in soils

As mentioned before, research workers who have studied the soil chemical reactions after urea application to soil, have focused on the ammonia volatilization. They are aware that the precipitation of carbonates (mainly calcium carbonate) will moderate the rise of soil pH and reduce the loss of ammonia when urea is applied to soils. Some have even tried to add soluble salts to increase the potential of the precipitation, but no reports so far give a quantitative measurement for the potential of the precipitation in soils when urea is added. In the above section, equations 5.1, 5.2, and 5.3 show that the amount of newly formed calcium carbonate is about a third or half of the amount of ammoniacal-N released from the hydrolysis of urea in the three soils. It would be useful to develop a model to describe the precipitation of calcium carbonate in soils quantitatively. This is very elaborate since the model should include the soil factors that greatly affect the precipitation. The results of experiments in chapter 4 are used as references to check whether the effects of phosphate and DOC on the precipitation model derived from soil systems are consistent. The factors used in the final precipitation model in soil systems are as follows : -

(1) The individual effect of phosphate and DOC

Calcite is the most stable polymorph of calcium carbonate in normal soil at ambient temperature and pressure. Although vaterite has been found in experiments started with 0.01 M calcium chloride (with and without addition of urea in chapter 4 and chapter 3 respectively), without addition of any inhibitors, and aragonite (chapter 4) has been found in experi-

ments with magnesium (5 mM) present, calcite is the dominant calcium carbonate formed in non-seeded experimental systems. When the strong inhibitors phosphate and DOC were added, calcite was the only form of calcium carbonate found in the reaction solution at the end of the experiment. For the above reasons the precipitation of calcium carbonate in soil will be discussed for calcite alone.

It has been proposed in chapter 3 that the precipitation of calcium carbonate in the absence of inhibitors can be described by an equation (equation 3.33) which involves the degree of supersaturation and the quantity of newly formed calcium carbonate and is expressed as

$$PR=K\ WA^{0.379}\ SI$$

where PR is the rate of precipitation of calcium carbonate, mole litre^{-1} h^{-1}, WA is the amount of newly formed calcium carbonate, g ml^{-1}, and SI is the degree of supersaturation. When the inhibitory effects of phosphate and DOC are considered the precipitation model will be

$$PR=f(K,\ WA,\ SI)\ f(P)\ f(DOC)$$

where P and DOC are the concentrations of phosphate and water-dissolved organic carbon in reaction solutions. When P=0 and/or DOC=0 they do not affect the precipitation, thus f(P)=1.0 and/or f(DOC)=1.0; conversely, when P and DOC are very high the precipitation will have almost been inhibited, thus f(P) and/or f(DOC) are almost 0.0. In order to describe this kind of function a reasonable model will be

$$PR=K\ K_{SOIL}\ WA^{0.379}\ SI\ e^{-a3\ P}\ e^{-a4\ DOC} \qquad (5.9)$$

where a3 and a4 are the reaction powers of phosphate and DOC on the precipitation, respectively.

(2) The factor of interaction between phosphate and DOC

The results of chapter 4 shows that the addition of DOC in reaction solutions will prevent the precipitation of calcium phosphate, where a high concentration of phosphate (e.g. $5x10^{-4}$ M) is added to 10 mM $CaCl_2$ solutions, and will prevent the catalysing effect of calcium phosphate on the precipitation of calcium carbonate. In the soil systems the concentration of phosphate in soil solutions can be much higher than $5x10^{-4}$ M, thus the effect of interaction between P and DOC should also be considered and the precipitation model will be

$$PR=K\ K_{SOIL}\ WA^{0.379}\ SI\ e^{-a3\ P}\ e^{-a4\ DOC}\ e^{-a5\ P\ DOC} \qquad (5.10)$$

where a5 is the reaction power of the interaction of phosphate and DOC.

(3) The effect of variation in type of soil

As mentioned in chapter 4, the formation of calcium phosphate can catalyse the precipitation of calcium carbonate. Calcium phosphate is a common component in arable soils, and other soil particles may also have similar effect. Since the soil factors are qualitative, they are treated as dummy variables,

$$PR=K\ K_{SOIL}\ WA^{0.379}\ SI\ e^{-a3\ P}\ e^{-a4\ DOC}\ e^{-a5\ P\ DOC}\ e^{-a6\ SB}\ e^{-a7\ SU}\ e^{-a8\ SV} \qquad (5.11)$$

where a6, a7, and a8 are the reaction powers of Beg. (SB), Uni. (SU), and VWH (SV) soils. The values of SB, SU, and SV are 1 or 0 according to whether they are counted or not, respectively.

(4) The effects of interactions between P and DOC and typical soil factors of SB, SU, and SV, which will be described as

$$PR=(\text{equation 5.11})\ e^{-a9\ P\ SB}\ e^{-a10\ P\ SU}\ e^{-a11\ P\ SV}\ e^{-a12\ DOC\ SB}\ e^{-a13\ DOC\ SU}\ e^{-a14\ DOC\ SV} \qquad (5.12)$$

where a9, a10, and a11 are the reaction powers of the interactions of (P SB), (P SU), and (P SV) respectively, and a12, a13, and a14 are the reaction powers of the interactions of (DOC SB), (DOC SU), and (DOC SV), respectively.

(5) The calculated rate of precipitation of calcium carbonate in soils

The experimental data for the changes in newly formed calcium carbonate show that within the first three days no further precipitation of calcium carbonate occurred when concentrations of urea were either too high (1.0 M) or too low (<0.3 M). When high concentrations of urea were added to soil most of the soil calcium ions precipitated in response to the rapid increase in base in the soil. Conversely, most of added urea was hydrolysed when urea concentrations were low. Therefore, the data points in these conditions are not enough to construct a sensible regression equation to describe the rate of precipitation.

Table 5.10 THE CHANGES IN NEWLY FORMED CALCIUM CARBONATE $CaCO_{3(s)}$ (mole $litre^{-1}$) WITH THE REACTION TIME (t, hour) AFTER DIFFERENT CONCENTRATIONS OF UREA WERE ADDED TO SOILS, $CaCO_{3(s)}=a + b\ t + c\ t^2 + d\ t^3$.

UREA, M	a	b $x10^3$	c $x10^4$	d $x10^7$	F	R^2
Beg.						
0.5	0.021	-5.8	1.9	-9.8	11.75	0.946
	±0.068	±6.0	±1.3	±7.4		
0.7	0.027	-5.1	2.4	13.8	37.92	0.974
	±0.048	±4.5	±1.0	±5.9		
Uni.						
0.3	-0.0015	-1.0	1.6	13.0	830	0.999
	±0.0051	±0.6	±0.2	±1.5		
0.5	-0.0082	-5.5	3.1	-21.7	239	0.997
	±0.0166	±1.8	±0.4	±2.9		
VWH						
0.3	-0.0032	0.33	1.5	-12.5	33.06	0.980
	±0.030	±3.7	±1.0	±7.0		
0.5	-0.028	8.5	-0.71	2.6	17.1	0.945
	±0.050	±4.7	±0.99	±5.5		

In order to establish a precipitation model which can be used for the three soils, the data set should have balanced data points from each soil. Two sets of data for each soil between 0.3

M and 0.7 M were collected as shown in Table 5.11, namely 0.5 and 0.7 M urea for Beg. soil, 0.3 and 0.5 M for Uni. and VWH soils. There also had the treatment with 0.3 M urea in Beg. soil, however the ranges of changes in P, DOC, and WA in 0.7 M urea treatment are wider than those in 0.3 M urea treatment, thus 0.7 M treatment is used instead of 0.3 M in data set. There was no 0.7 M urea treatment in both Uni. and VWH soil systems. The procedures to calculate the precipitation rate for the three soils are identical and are as follows :

(a) The best fitting equation (polynomial) between the amount of calcium carbonate precipitated and the reaction period was regressed by the SAS program for each treatment. This gives the equation

$$[CaCO_{3(S)}]=a + b\ t + c\ t^2 + d\ t^3$$

where a (intercept), b, c, and d are coefficients of the cubic equations, and are shown in Table 5.10 (above).

(b) The first differentiation of these equations was taken as the precipitation rate PR. The unit of PR derived from Table 5.10 is mole litre^{-1} h^{-1}, thus it will be converted to the unit in mole litre^{-1} min^{-1} which is used in the precipitation model of equation 3.33.

(6) The empirical model of rate of precipitation of calcium carbonate in soils.

Equation 5.9 in logarithmic form after rearranging may be written as

$$\ln PR - \ln K - 0.379\ \ln WA - \ln SI=\ln K_{SOIL} - a3\ P - a4\ DOC \quad (5.13)$$

where lnPR, P, and DOC are shown in data set (Table 5.11), lnSI and lnWA can be calculated from SI and $CaCO_{3(s)}$ respectively, and

lnK=0.230 lok(K)=0.230 LK=-9.470

where LK=-4.113 is adopted from equation 3.33.

Defining :

$$\ln PR1 = \ln PR - \ln K - 0.379 \ln Wa - \ln SI$$

equation 5.13 becomes

$$\ln PR1 = \ln K_{SOIL} - a3\ P - a4\ DOC \qquad (5.14).$$

With the same procedures equation 5.10 becomes

$$\ln PR1 = \ln K_{SOIL} - a3\ P - a4\ DOC - a5\ P\ DOC \qquad (5.15);$$

equation 5.11 becomes

$$\ln PR1 = \ln K_{SOIL} - a3\ P - a4\ DOC - a5\ P\ DOC - a6\ SB - a7\ SU - a8\ SV \qquad (5.16);$$

and equation 5.12 becomes

$$\ln PR1 = \ln K_{SOIL} - a3\ P - a4\ DOC - a5\ P\ DOC - a6\ SB - a7\ SU - a8\ SV - a9\ P\ SB - a10\ P\ SU - a11\ P\ SV - a12\ DOC\ SB - a13\ DOC\ SU - a14\ DOC\ SV \qquad (5.17).$$

The values of lnPR1 were calculated and shown along with the changes in P and DOC in Table 5.11 (below). Using SAS program to regress dependent variable, lnPR1, on the independent variables seen on the right-hand side of equations 5.14, 5.15, 5.16, and 5.17, the corresponding values of coefficients of independent variables (i.e. the values of a3, a4, ..., a14), R^2, F test, $\ln K_{SOIL}$, MSE, and the mean square of residuals, are shown in Table 5.12. The value of intercept of the regression equations is referred to as $\ln K_{SOIL}$.

Table 5.12 shows that the introduction of the factor of interaction between P and DOC (i.e. cross-product of (P DOC)) improves the accuracy of prediction of the rate model, from equation 5.14 to equation 5.15, by increasing F test from 2.99 to 3.11 and R^2 from 0.221 to 0.318, and decreasing MSE from 2.63 to 2.42. The regression results show that the coefficients of soils (SB, SU, and SV) are biased. The introduction of the dummy variables of soils, however, improves the rate model (equation

5.16) significantly, for increasing R^2 from 0.318 to 0.602 and decreasing MSE from 2.42 to 1.56. Since the value of the dummy variables is either 1.0 or 0.0, the biased coefficients for them in the regression equations are acceptable.

Table 5.11 THE CHANGES IN pH, NEWLY FORMED CALCIUM CARBONATE $CaCO_{3(s)}$, PHOSPHATE P, DOC, SI, AND CALCULATED lnPR AND lnPR1 DURING REACTION PERIOD. RESIDUAL IS CALCULATED FROM EQUATION 5.17.

Urea, M (Soil)	t h^{-1}	pH	$CaCO_3$ me/ 100 g	P $x10^5$, M	DOC $x10^3$, M	SI	lnPR mole $litre^{-1}$ min^{-1}	lnPR1	Residual
(Beg.)									
0.5	19.5	7.89	0.65	15.2	1.26	29.1	-11.4	-3.02	-0.77
	43.5	8.23	1.09	14.8	4.10	90.8	-9.30	-2.24	0.02
	67.0	8.51	4.27	22.6	16.0	71.6	-9.07	-2.29	0.16
	91.0	8.91	11.6	85.0	390	84.0	-9.38	-3.14	1.39
	114.5	8.67	11.2	80.0	350	15.9	-	-	-
0.7	10.5	7.72	0.80	19.8	0.86	11.8	-	-	-
	23.5	8.02	1.59	13.5	1.40	43.7	-9.65	-2.01	0.22
	44.0	8.10	2.24	34.0	1.40	50.6	-8.93	-1.56	1.01
	69.0	8.93	10.8	54.4	47.0	1265	-8.90	-5.34	-2.25
	87.0	9.09	13.7	72.5	149	113	-9.36	-3.48	0.225
	110.0	8.99	14.4	162	360	79.9	-	-	-
(Uni.)									
0.3	11.0	7.28	0.0	0.4	1.14	1.88	-10.3	-	-
	21.5	7.60	1.89	72.5	2.20	6.27	-9.59	0.11	0.98
	36.0	8.02	4.70	41.9	4.8	29.5	-9.29	-1.49	-1.18
	60.0	8.56	10.3	103	19.6	146	-9.55	-3.64	-2.29
	84.0	8.65	12.1	281	72.5	98.6	-	-	-
0.5	12.0	7.28	0.0	106	2.8	1.78	-10.9	-	-
	25.0	7.76	1.31	30.0	5.4	8.83	-9.18	0.31	0.42
	49.0	8.61	9.76	250	45.0	159	-8.73	-2.89	0.74
	73.0	9.02	19.4	525	330	42.7	-9.26	-2.37	1.40
	98.5	8.91	18.8	400	450	31.4	-	-	-
(VWH)									
0.3	8.0	7.27	0.67	0.14	5.30	1.83	-10.1	1.27	1.41
	22.0	7.82	1.91	3.80	18.1	13.3	-9.38	-0.39	-0.11
	47.0	8.26	12.1	8.12	74.0	6.98	-9.21	-0.27	0.40
	70.0	8.23	14.8	35.6	160	5.06	-9.99	-0.80	0.66
	92.0	8.28	15.8	300	188	7.99	-	-	-
0.5	8.0	7.53	1.33	0.21	6.5	4.98	-8.99	1.12	1.26
	22.0	7.94	3.31	8.75	21.0	19.8	-9.25	-0.86	-0.49
	46.5	8.79	14.8	162	240	286	-9.71	-4.57	-1.76
	70.5	8.79	16.2	250	380	25.6	-10.1	-2.59	0.39
	95.0	8.82	16.1	512	440	55.9	-10.2	-3.50	-0.75
	118.5	8.87	21.8	202	450	84.5	-10.0	-3.78	-1.01

The addition of the factors of (P SB), (P SU), (P SV), (DOC SB), (P SU), and (P SV) also improves the rate model (equation 5.17) by increasing R^2 from 0.602 to 0.750 and decreasing MSE from 1.56 to 1.25, but all coefficients except a5 of (P DOC) are biased and not statistically significant.

In solution systems without soil (chapter 4), the rate model will be

$$\ln PR = \ln K + 0.379 \ln WA + \ln SI - a3\ P - a4\ DOC - a5\ P\ DOC \quad (5.18).$$

At the "peak pH" the precipitation rate of calcium carbonate will be the same (i.e. PR is constant), irrespective of the treatment. After rearranging, equation 5.18 becomes

$$\ln WASI = \ln K' - a3\ P - a4\ DOC - a5\ P\ DOC \quad (5.19)$$

where $\ln WASI = -0.379 \ln WA - \ln SI$ AND $\ln K' = -\ln PR + \ln K$. Table 5.13 shows the regression equations by regressing lnWASI on P, DOC, and with or without the interaction (P DOC) combining the data from Table 4.3 (phosphate effect), Table 4.4 (DOC effect), and Table 4.5 (combination effect of phosphate and DOC) but excluding the data which have phosphate concentration higher than 1×10^{-4} M.

Table 5.12 THE COEFFICIENTS OF REGRESSION EQUATIONS OF THE RATE MODEL OF PRECIPITATION OF CALCIUM CARBONATE IN SOIL.

$\ln K_{SOIL}$	-a3	-a4	-a5	-a6	-a7	-a8	F	R2	MSE
-1.34	-179	-3.83					2.99	0.221	2.63
±0.42	±333	±3.08							
-0.89	-1106	-7.14	3156				3.11	0.318	2.42
±0.49	±636	±3.54	±1875						
-0.10	-1686	-6.13	3854	-1.88	0.53	0.0	5.45	0.602	1.56
±0.51	±703	±3.02	±1775	±0.63	±0.59				
0.62	-3844	-7.77	8503	-2.14	-0.91	0.0	(continue below)		
±0.54	±1691	±4.24	±3570	±1.03	±0.99				

	-a9	-a10	-a11	-a12	-a13	-a14			
	-650	2953	0.0	6.33	-29.2	0.0	4.75	0.750	1.25
	±3474	±2105		±8.45	±26.9				

The coefficients underlined are statistically biased.

Table 5.13 THE COEFFICIENTS OF P, DOC, AND P DOC ON THE RATE MODEL OF PRECIPITATION OF CALCIUM CARBONATE IN SOLUTION SYSTEM. lnWASI=lnK' - a3 P - a4 DOC - a5 P DOC

lnK'	-a3	-a4	-a5	F	R^2	MSE
-1.330	-14201	-51.50		14.0	0.623	0.100
±0.10	±3540	±13.2				
-1.326	-15204	-52.35	703628	8.92	0.626	0.105
±0.100	±4573	±13.74	±1946360			

Comparing the effects of phosphate and DOC on the precipitation models derived from solution systems (Table 5.13) and from soil systems, their effects are similar in that phosphate and DOC have inhibitory effects on the precipitation of calcium carbonate, but phosphate tends to negate the effects of DOC and *vice versa*. It is also clear that the coefficients of independent variables in solution systems are all much higher than that in soil systems, and that the effect of interaction of (P DOC) in solution systems is not as significant as it is in soil systems. The differences may be due to the fact that the ranges of concentrations of phosphate and DOC in soil systems are much higher than those used in solution systems.

Figure 5.10 illustrates the residuals from equations 5.19 (a), 5.15 (b), 5.16 (c), and 5.17 (d). Examining the values of these residuals in the ranges of concentrations of phosphate and DOC, there are no significant biases found both in solution systems and soil systems. It can be seen that the introduction of the soil type factors (c), and the interaction factors between soil and phosphate and DOC (d), into the prediction model, decreased the range of residuals.

The empirical models, equations 5.16 and 5.17, derived by using results from soil systems, effectively described the precipitation of calcium carbonate in soils, although the R^2 of equation 5.17 (0.750) is higher than that (0.602) of equation

5.16. However most of the coefficients in equation 5.17, which considers the interaction between soils and P and DOC, are biased, and the coefficients of interactions for P and DOC with soil factors SB, SU, and SV are not significant. Therefore, in practice it is more reasonable to apply equation 5.16, which does not have biased coefficients for the variables P, DOC, and (P DOC) to soil systems. The effect of soil on the precipitation of calcium carbonate differs according to the character of each of the three soils. Actually when the rate model of equation 5.16 is used in a soil, it can be simplified as equation 5.15. For example in Beg. soil, the effect from Uni. and VWH soils is SU=SV=0.0, and equation 5.16 can be rearranged as

$$\ln PR1=(\ln K_{SOIL} - a6\ SB) - a3\ P - a4\ DOC - a5\ P\ DOC - a6\ SB;$$

where $(\ln K_{SOIL} - a6\ SB)$ is the $\ln K_{SOIL}$ in equation 5.15. Since equation 5.15 is derived from equation 5.10, the rate model for soils in logarithmic form will be

$$\ln PR=-9.470 + \ln K_{SOIL} + 0.379\ \ln WA + \ln SI - 1686\ P - 6.13\ DOC + 3854\ (P\ DOC) \qquad (5.20)$$

where $\ln K_{SOIL}$ is -1.98, 0.43, and -0.10 for Beg., Uni., and VWH soils respectively. The high negative value of $\ln K_{SOIL}$ for Beg. soil may be due to its high initial concentration of phosphate in soil solution. The positive value for Uni. soil shows that soil particles may stimulate the formation of calcium carbonate. VWH soil seems not to affect the precipitation rate. However, other processes in soil systems which were not studied in this thesis may also affect the precipitation process. For example, the kinetics of ion exchange between calcium and ammonium ions may also contribute to control the precipitation rate.

5.3 CONCLUSION

(1) The hydrolysis rate of urea in soil is mainly controlled by the concentration of urea in the soil solution and is affected by soil pH.

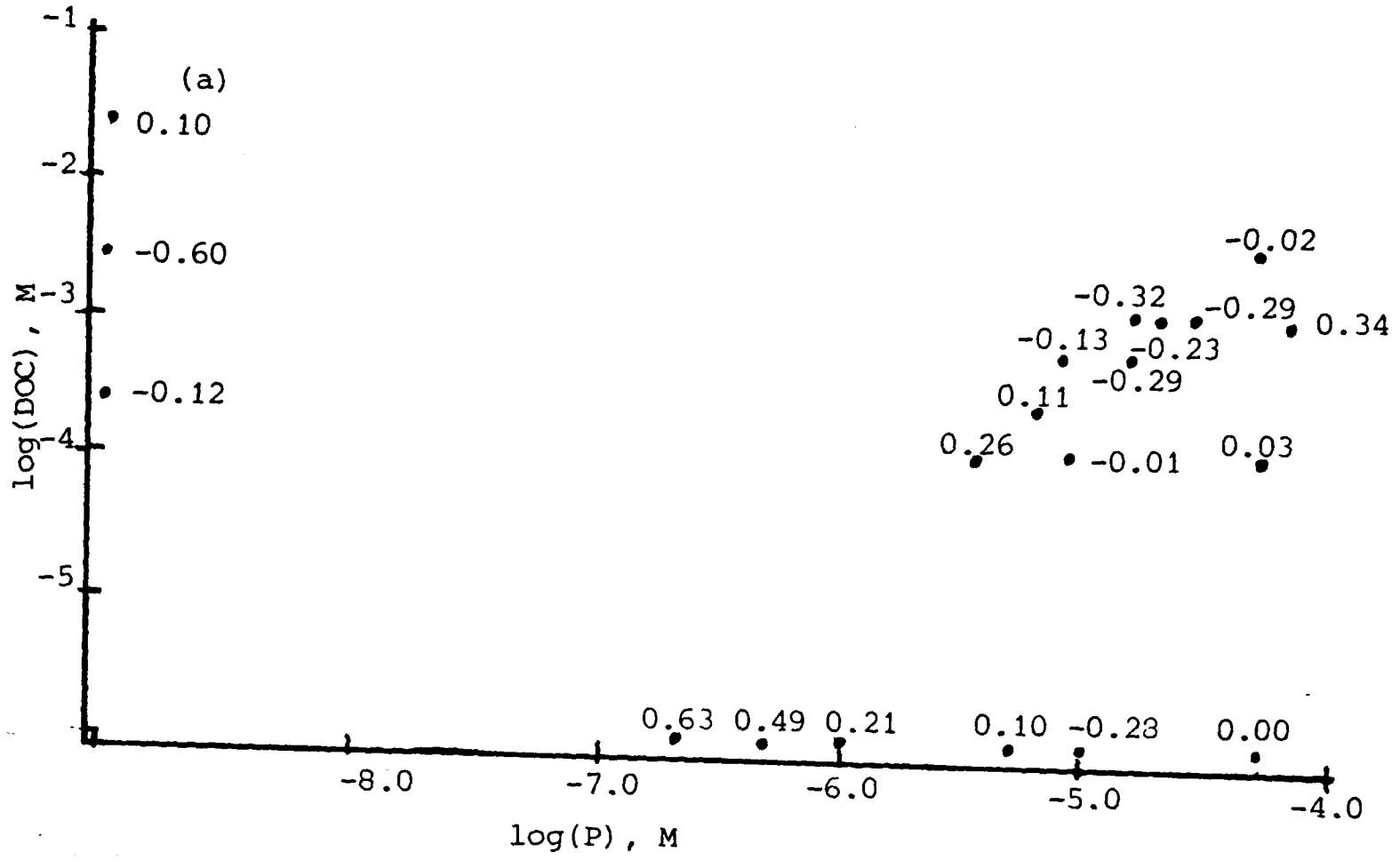
(2) The precipitation of calcium carbonate significantly moderates the increase of soil pH when the amount of urea added is not greater than soil CEC.

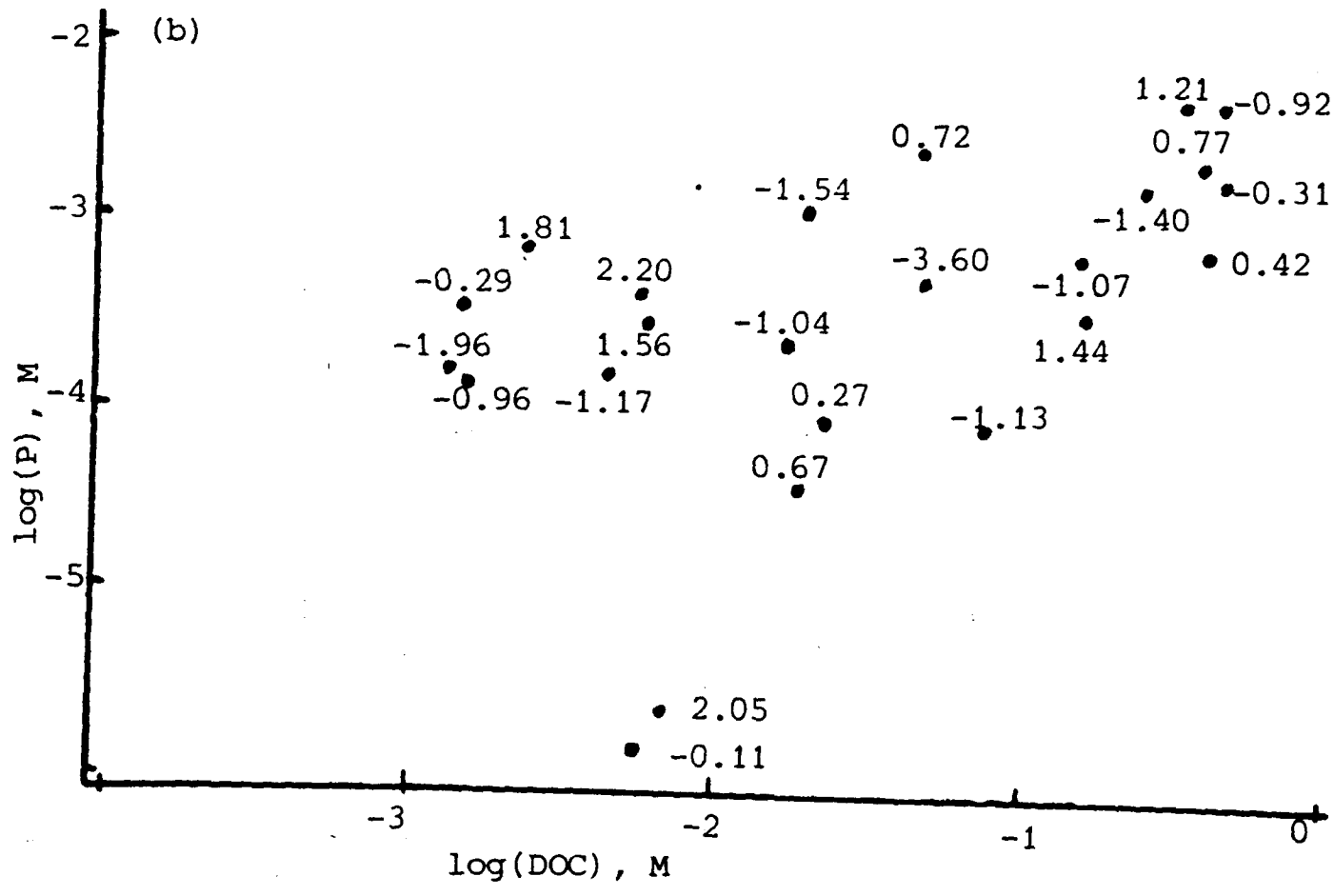
(3) The decrease of calcium ions in soil and the increase of soil pH significantly increases the concentrations of phosphate and DOC in the soil solution. The greater the amount of urea added, the higher the concentrations of phosphate and DOC in soil solution.

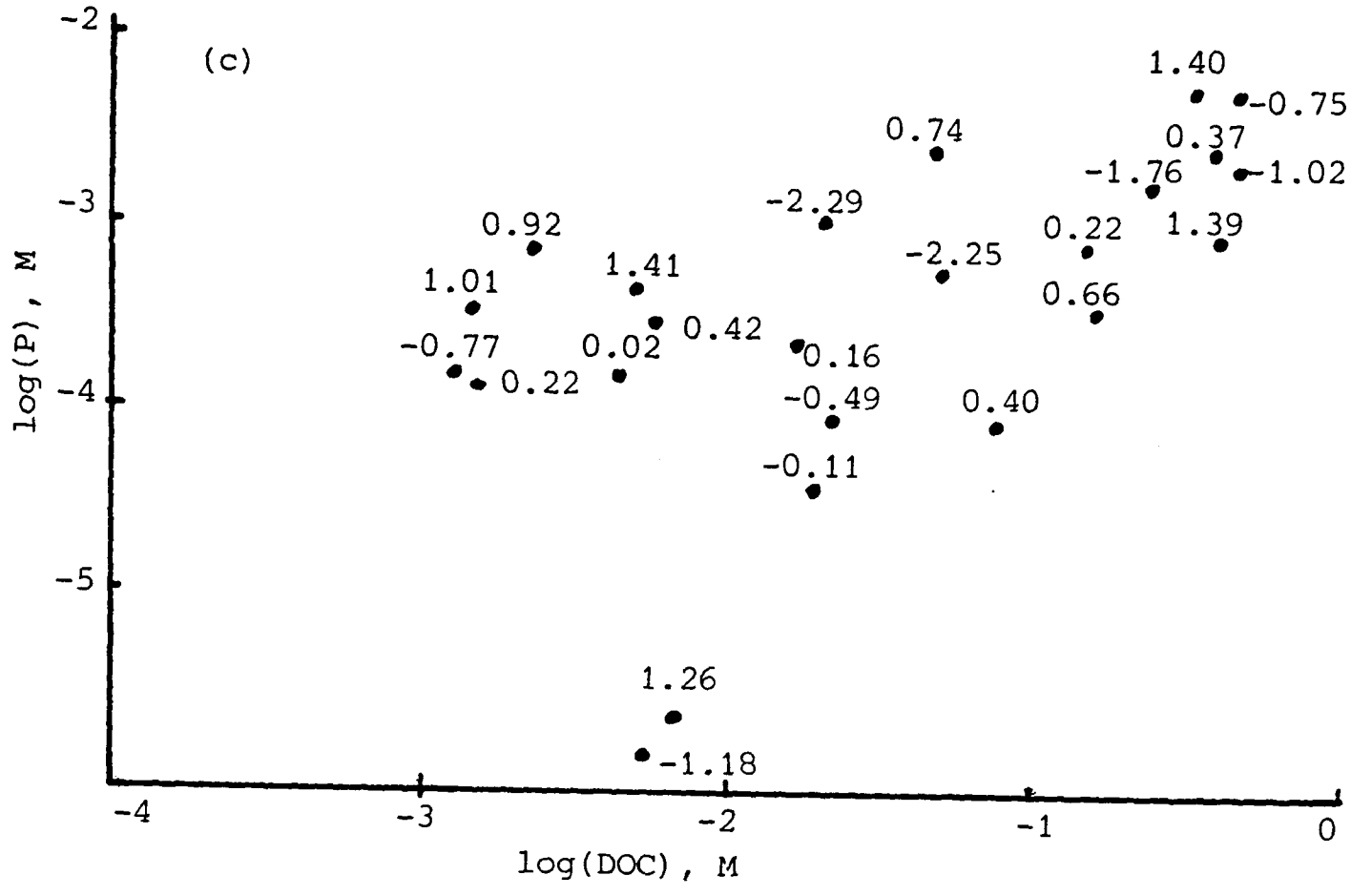
(4) The precipitation rate of calcium carbonate in soils is affected by the amount of newly formed calcium carbonate, degree of supersaturation, concentrations of phosphate and water-dissolved organic matter and their interactions.

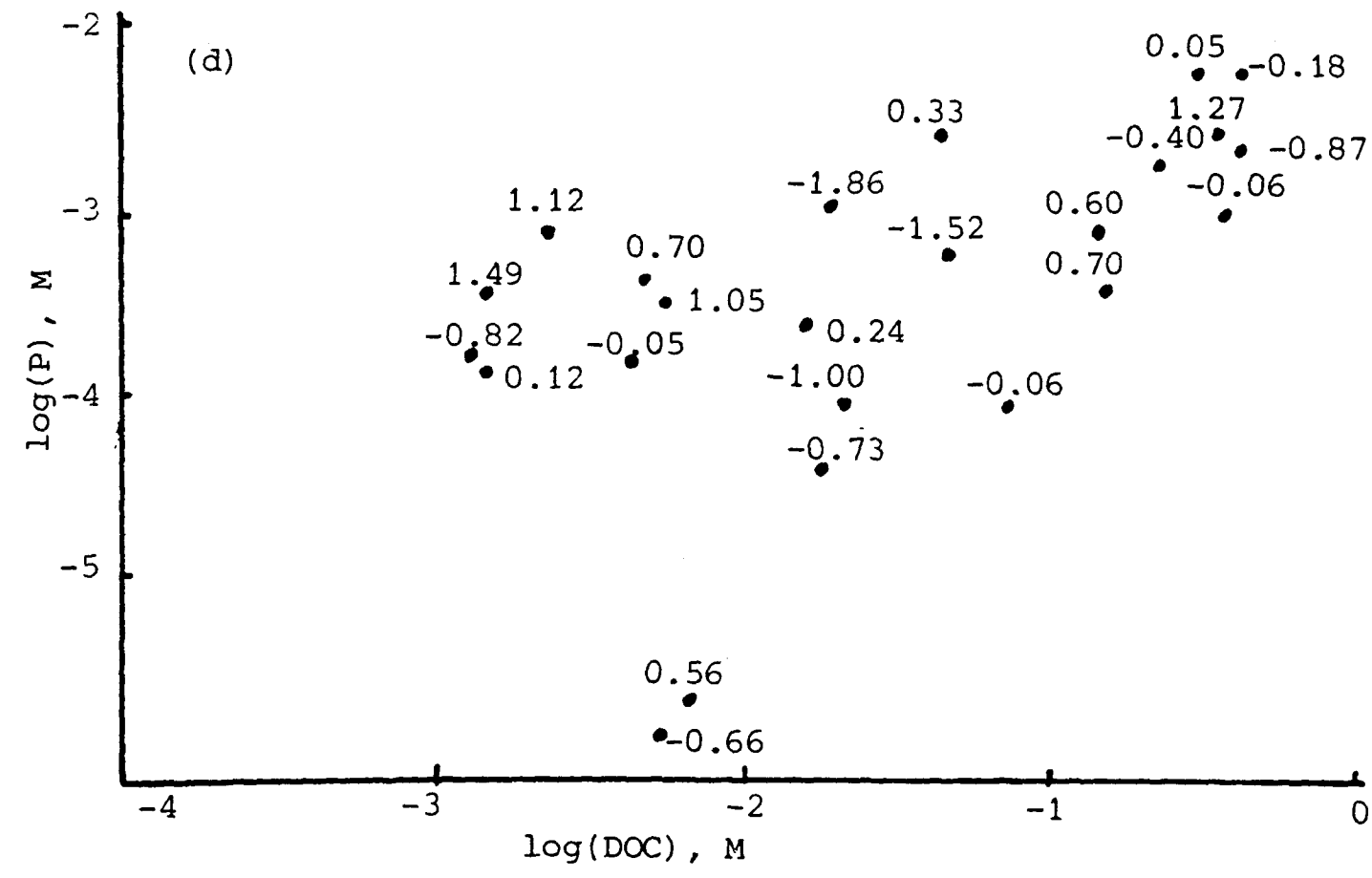
(5) The amount of calcium carbonate precipitated is about a third to a half the amount of ammoniacal-N released from urea hydrolysis.

Figure 5.10 THE RESIDUALS OF REGRESSION EQUATIONS 5.19 (a), 5.15 (b), 5.16 (c), AND 5.17 (d).






(c)
log(P), M
log(DOC), M
-2
-3
-4
-5
-4
-3
-2
-1
0
1.40
-0.75
0.74
0.37
-1.76
-1.02
-2.29
0.92
0.22
1.39
-2.25
1.41
1.01
0.66
0.42
-0.77
0.02
0.16
0.22
-0.49
0.40
-0.11
1.26
-1.18


(d)
log(P), M
log(DOC), M
-2
-3
-4
-5
-4
-3
-2
-1
0
0.05
-0.18
0.33
1.27
-0.40
-0.87
-1.86
-0.06
1.12
0.60
-1.52
0.70
0.70
1.49
1.05
-0.82
-0.05
0.24
0.12
-1.00
-0.06
-0.73
0.56
-0.66

CHAPTER 6

CONCLUSION

Ammonia loss is the most likely mechanism responsible for the variation in recovery rate of nitrogen resulting from adding urea to soils, since the increase of soil pH and content of ammoniacal-N in the soil associated with urea, increase the potential for ammonia volatilization. As already mentioned in previous chapters, much effort has been applied to studying the effects of soil physical and chemical properties and environmental factors on ammonia volatilization, and models have been developed to combine the most effective parameters to estimate the amount of ammonia volatilization. However none of the previous models adequately describe the wide range of situations encountered in nature.

When the precipitation of calcium carbonate occurs in soils after urea application, it is assumed that the precipitation of calcium carbonate is counteracting the increase of soil pH and consequently reducing the loss of ammonia. Many methods have been used to stimulate the formation of calcium carbonate, such as the addition of neutral salts of calcium and other cations. Models used to estimate the loss of ammonia volatilization either take no account of the precipitation of calcium carbonate (Stevens et al, 1989; and Parton et al, 1981) or have used over-simplified models for the precipitation (Sadeghi et al, 1988).

Sadeghi et al (1988) assume that the solubility of calcium carbonate in the soil solution was in equilibrium with calcite. However the value of the ion activity product which they used was 1.51 times of that used in this study (i.e. SI=1.51). However, as was shown in chapter 5, the values of SI in soil solution

following urea application varied over a wide range, depending on the soil and on the amount of urea added. For example, with 0.05 M urea in the soil solution the value of SI in the Begbroke soil could reach 34, in the University Parks soil it could reach 7, but in the VWH soil it only reached 2; with 1.0 M urea in the soil solution, the highest values of SI during the reaction period were 95, 287, and 155 for the Beg., Uni., and VWH soils respectively. In some cases the value of SI could be much higher.

This thesis presents a more detailed study of the effects of inhibitors on the precipitation of calcium carbonate in solutions and in soil after urea application. It shows that an empirical equation

$$\ln PR = -9.47\pm0.30 + \ln K_{SOIL} + 0.379\pm0.029\ \ln WA + \ln SI - 1686\pm703\ P - 6.13\pm3.02\ DOC + 3854\pm1775\ (P\ DOC) \qquad (6.1)$$

can be used to predict the rate of precipitation of calcium carbonate in soils. $\ln K_{SOIL}$ will be different for different soil, for example it is -1.98, 0.43, and -0.10 for Beg., Uni., and VWH soils.

Here one may wonder how the equation can be applied to soils. Results of chapter 5 show that the concentrations of phosphate (P) and water-dissolved organic matter (DOC) are highly correlated with soil pH; thus for appropriate values of soil pH, it is possible to estimate the concentrations of P and DOC. The experimental results also show that the activity of calcium ions in soils is correlated with P; thus it can be predicted, and consequently, the value for the degree of supersaturation of calcium carbonate (SI) can be predicted. After taking the reaction time into account the amount of newly formed calcium carbonate (WA) can be predicted. When the effect due to the character of the soil itself (K_{SOIL}) is determined, an approximate

rate of precipitation of calcium carbonate can be estimated. With the estimated rate of precipitation, the amount of calcium carbonate precipitated can be estimated, therefore a better estimation of soil pH can be made.

This precipitation equation can effectively improve the reliability of models for predicting ammonia volatilization. As the effects of P and DOC on the precipitation of calcium carbonate in solution systems is similar to that in soil systems, it is reasonable to assume that with some adaptation the precipitation model may also be used to describe the precipitation of calcium carbonate in oceans, lakes, rivers, and other situations in which calcium carbonate precipitation may occur.

The regression equations (equations 5.1, 5.2, and 5.3) show that the amount of newly formed calcium carbonate is equal to about a third to a half the amount of ammoniacal-N released from the hydrolysis of urea. This gives a rough estimation of the extent of calcium carbonate precipitated and of its effect on soil pH without considering the effects of soil components on the rate of precipitation of calcium carbonate in soils. The results may also provide a guide to the amount of soluble salts which need to be applied with urea to prevent the soils reaching too high a pH value. It will make the most effective result in counteracting the increase of soil pH, if the amount of soluble calcium salts added with urea application is in the ratio of about half to two thirds that of urea-N. The exchangeable calcium ions in CEC sites will contribute the rest of the calcium ions required for calcium carbonate precipitation.

Figure 5.4 gives a good summary of the extent to which the precipitation of calcium carbonate will affect soil pH. For example, according to Figure 5.4, the broken lines describe the

soil pH which do not take into account the effect of acidity released from calcium carbonate precipitation. The soil pH will be referred to as pH**. Wherever the content of ammoniacal-N in a soil is determined, the value of pH** can be estimated by interpolating the value of ammoniacal-N from the broken line of the soil in Figure 5.4. The modification in soil pH can also be estimated from the trend of the change in observed soil pH in Figure 5.4. The soil pH is referred to as pH*. Table 6.1 presents the estimated values of pH** and pH* when the three soils contain ammoniacal-N of 5, 10, 20, and 30 me/(100 g of oven-dry soil). Table 6.1 also shows that the effect of calcium carbonate precipitation on the rise of soil pH is very significant, and the reduction of soil pH due to the precipitation can reach 0.67, 0.62, and 0.77 pH units for Beg., Uni., and VWH soils, respectively.

Table 6.1 THE SOIL pH WITH (**) AND WITHOUT (*) TAKING INTO ACCOUNT THE EFFECT OF NEWLY FORMED CALCIUM CARBONATE.

Soil	Ammoniacal-N, me/100 g			
	5	10	20	30
Beg.*	8.67	9.00	9.25	9.33
Beg.**	8.00	8.33	8.79	9.01
Uni.*	8.00	8.62	8.92	9.14
Uni.**	7.50	8.00	8.61	8.91
VWH*	7.50	8.22	8.85	9.09
VWH**	7.33	7.71	8.08	8.40

As discussed in chapter 5, the rate model of precipitation of calcium carbonate in solution systems (equation 6.2) is different from that in soil systems (equation 6.1).

$$\ln PR = -9.47 \pm 0.30 + 0.379 \pm 0.029 \ln WA + \ln SI - 14201 \pm 3540\ P - 51.5 \pm 13.2\ DOC \qquad (6.2)$$

It is important to examine how phosphate and DOC act in inhibi-

tory effects on the precipitation in soil and in solution systems. For instance, if the concentration of an inhibitor that halves the precipitation rate is determined, its inhibitory effect can easily predicted. The way to calculate the concentration for an inhibitor which halves the precipitation rate is the same for P and DOC either in soil systems (i.e. equation 6.1) or in solution systems (i.e. equation 6.2). Therefore an example will be sufficient for the derivation : -

When only P is concerned, equation 6.2 becomes

$$\ln PR=-9.47 - 14201\ P \qquad (6.3)$$

As PR1 is the precipitation rate at P1 (concentration of phosphate at condition 1), and PR2 is the precipitation rate at P2 (concentration of phosphate at condition 2). If

$$PR2=0.5\ PR1,$$

then

$$\ln PR1=-9.47 - 14201\ P1 \qquad (6.4)$$

and

$$\ln PR2=-9.47 -14201\ P2 \qquad (6.5).$$

After taking equation 6.5 away from equation 6.4, and substituting PR2=0.5 PR1, equation 6.6 will be derived,

$$\ln PR1 - \ln(0.5\ PR1)=-14201\ P1 + 14201\ P2 \qquad (6.6).$$

For

$$\ln PR1 - \ln(0.5\ PR1)=0.693,$$

after rearranging, equation 6.6 becomes

$$P2=0.693/14201 + P1=4.87\times10^{-5} + P1\ (M,\ \text{mole litre}^{-1}).$$

If p1 is 0.0, the concentration of phosphate halving the rate of precipitation of calcium carbonate in solution systems is 4.87×10^{-5} M. With the same calculating method, the corresponding value of P in soil systems (i.e. equation 6.1) is 4.11×10^{-4} M. The concentrations of DOC which halve the rate of precipitation

of calcium carbonate in soil and solution systems are 0.11 M and 0.0134 M, respectively. Obviously the concentrations of phosphate and DOC which halve the rate of precipitation in soil systems are both about 10 times those in solution systems. This may be due to the stimulating effect of soil particles, but the effect can not be distinguished by the regression equation. However this is beyond the scope of this thesis.

As conclusions have been given after each section of experiments in previous chapters, a brief summary of these conclusions follows :

(1) A bubbling experimental system was developed to control the experimental system under constant partial pressure of carbon dioxide, ammonia dissolution rate, and at a temperature 25^0 C. The system increases the degree of saturation of calcium carbonate in reaction solutions from under-saturated to supersaturated conditions by introducing a mixed gas containing ammonia and carbon dioxide into the $CaCl_2$ solutions. The system has the following benefits for studying the precipitation of calcium carbonate in the presence or absence of inhibitors. (i) It allows us to estimate the amount of newly formed calcium carbonate in reaction solution by measuring solution pH and ammonia dissolution rate. (ii) The precipitation rate of calcium carbonate is proportional to its supersaturation degree (SI). In the system SI is proportional to solution pH. Also at the "peak pH" of reaction solutions, the release rate of acidity from calcium carbonate precipitation is equal to the ammonia dissolution rate. Therefore the "peak pH" of reaction solution can be used to estimate the strength of inhibitor in reaction solutions; the stronger the inhibitor in the reaction solution, the higher the "peak pH" attained.

(2) The non-seeded experimental system shows that the effects of urea, magnesium, phosphate, and DOC on the precipitation of calcium carbonates are different. At high concentrations urea affects the ion activity of calcium ions, but has no effect on the crystal formation of vaterite and calcite. Magnesium prevents the formation of vaterite, and promotes the formation of aragonite at high concentration (5 mM), but does not have strong effect on the value of "peak pH". Phosphate and water-dissolved organic matter (DOC) both have strong effect on the precipitation of calcium carbonate. No vaterite was formed when reaction solutions contained phosphate and DOC.

(3) In the presence of phosphate, the effect of magnesium on the precipitation is negligible. DOC and phosphate combined have negative interaction with the rate of precipitation.

(4) The fact that the formation of calcium phosphate catalyses the precipitation of calcium carbonate in solution systems suggests that a similar process occurs in soils. The results from experiments with soils confirms that soil particles affect the rates of precipitation of calcium carbonate.

REFERENCES

Adams, F. 1971. Ionic concentrations and activities in soil solutions. Soil Sci. Soc. Am. Proc. 35, 420-426.

Akin, G.W., and J.V. Lagerwerff. 1965[a]. Calcium carbonate equilibria in aqueous solutions open to the air I. The solubility of calcite in relation to ionic strength. Geochim. et Cosmochim. Acta. 29, 343-352.

Akin, G.W., and J.V. Lagerwerff. 1965[b]. Calcium carbonate equilibria in aqueous solutions open to the air II, Enhanced solubility of calcium carbonate in the presence of Mg^{2+} and SO_4^{2-}. Geochim. et Cosmochim. Acta. 29, 353-360.

Ameloko, A. Y., 1983. The propagation of pH changes in soils and the effect of liming. D. Phil. Thesis of Oxford University, 75-76.

Amrhein, C. and D.L. Suarez. 1987. Calcite supersaturation in soils as a result of organic matter mineralization. Soil Sci. Soc. Am. J. 51, 932-937.

Avnimelech, Y. 1980. Calcium-carbonate-phosphate surface complex in calcareous systems. Nature 288, 255-257.

Bentor, Y.K., S. Gross, and L. Heller. 1963. Some unusual minerals from the mottled zone complex, Israel. American Mineral 28, 924-930.

Berner, R.A. 1975. The role of magnesium in the crystal growth of calcite and aragonite from seawater. Geochim. et Cosmochim. Acta 39, 489-504.

Berner, R.A. 1978. Equilibrium, kinetics, and the precipitation of magnesian calcite from seawater. Am. Jour. Sci. 278, 1475-1477.

Berner, R.A., and J.W. Morse. 1974. Dissolution kinetics of calcium carbonate in seawater. IV. Theory of calcite dissolution. Am. Jour. Sci. 274, 108-134.

Berner, R.A., J.T. Westrich, R. Graber, J. Smith, and C.S. Martens. 1978. Inhibition of aragonite precipitation from supersaturated seawater : A laboratory study and field study. Am. Jour. Sci. 278, 816-837.

Bischoff, J.L. 1968. Kinetics of calcite nucleation: Magnesium ion inhibition and ionic strength catalysis. Geophysical Research 73, 3313-3322.

Bischoff, J.L., and W.S. Fyfe. 1968. Catalysis, inhibition, and the calcite-aragonite problem. I. The aragonite-calcite transformation. Am. Jour. Sci. 266, 65-79.

Blakely, R.L., E.C. Webb, and B. Zerner. 1969. Jack bean urease (EC 3.5.1.5) A new purification and reliable rate assay. Biochemistry 8, 1894-1900.

Brunauer, S., P.H. Emmett, and E. Teller. 1938. The adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60, 309-316.

Bloom, P.R.. 1981. Metal-organic matter interactions in soil. In Chemistry in the soil environment (ed. Dowdy) . America Society of Agronomy publication No. 40 129-150.

Boateng, J.O., and T.M. Ballard. 1978. Urea fertilizer effects on dissolved nutrient concentrations in some forest soils. Soil Sci. Soc. Am. J. 42, 503-508.

Bremner, J.M., and L.A. Douglas. 1971[a]. Inhibition of urease activity in soils. Soil Biochem. 3, 297-307.

Bremner, J.M., and L.A. Douglas. 1971[b]. Decomposition of urea phosphate in soils. Soil Sci. Soc. Am. Proc. 35, 575-578.

Brooks, R., L.M. Clark, and E.F. Thurston. 1950. Calcium carbonate and its hydrates. Transa. Roy. Soc. London A 243, 145-167.

Compton, R.G., and P.R. Unwin. 1990. The dissolution of calcite in aqueous solution at pH < 4: kinetics and mechanism. Phil. Trans. R. Soc. Lond. A 330, 1-45.

Chapman, H.D., and P.F. Pratt. 1961. Methods of analysis for soils. Plants and Waters. University of California. 20-21.

Chave, K.E. 1965. Carbonates : Association with organic matter in surface seawater. Science 148, 1723-1724.

Chave, K.E., and E. Suess. 1967. Suspended minerals in seawater. Trans. N. Y. Acad. Sci. Ser. II 29, 991-1000.

Chave, K.E., and E. Suess. 1970. Calcium carbonate saturation in seawater : Effect of dissolved organic matter. Limno. Oceanogr. 15, 633-637.

Chen, Y., N. Senesi, and M. Schnitzer. 1977. Information provided on humic substances by E_4/E_6 ratios. Soil Sci. Soc. Am. J. 41, 352-358.

Cole, C.V. 1957. Hydrogen and calcium relationships of calcareous soils. Soil Sci. 83, 141-151.

Cole, C.V., R. Sterling, R. Olsen, and C.O. Scott. 1953. The nature of phosphate sorption by calcium carbonate. Soil Sci. Soc. Am. Proc. 17, 352-356.

Cooke, G.W. 1969. Fertilizers in 2000 A.D. In " phosphorus in agriculture ". International superphosphate and compound fertilizers manufactures' association. Bulletin Document 53, 1-13.

Davies, C.W., and A.L. Jones. 1949. The precipitation of silver chloride from aqueous solutions. Part I. Trans. Faraday Society 5, 103-111.

Davies, C.W., and G.H. Nancollas. 1955. The precipitation of silver chloride from aqueous solutions. Part II. Trans. Faraday Society 51, 812-817.

Davis, J.A. 1980. Adsorption of nature organic matter from

freshwater environments by aluminum oxide. Baker, R.A. (ed) Containments and sediments. Vol: 2, 279-304. Ann Arbor Science publication. 279-304.

deBoer, R.B. 1977. Influence of seed crystals on the precipitation of calcite and aragonite. Am. Jour. Sci. 277, 38-60.

De Kanel, J., and J.W. Morse. 1978. The chemistry of orthophosphate uptake from seawater on to calcite and aragonite. Geochemica et Cosmochimica Acta 42, 1335-1340.

Denmead, R.D., J.R. Freney, and J.R. Simpson, 1982. Dynamics of ammonia volatilization during furrow irrigation of maize. Soil Sci. Soc. Am. J. 46, 149-155.

Dobbs, R.A., R.H. Wise, and R.B. Dean. 1972. The use of ultraviolet absorbance for monitoring the total organic carbon content of water and waste water. Water Res. 6, 1173-1180.

Doner, H.E., and P.F. Pratt. 1969. Solubility of calcium carbonate precipitated in aqueous solutes of magnesium and sulphate salts. Soil Sci. Soc. Am. Proc. 33, 690-693.

Douglas, H.W., and R.A. Walker. 1950. The electrokinetic behaviour of iceland spar against aqueous electrolyte solutions. Trans. Farady Society 46, 559-568.

Duke, F.R., and L.M. Brown. 1954. Crystal nucleation from supersaturated aqueous solutions. Tetraphenylarsonnium perphloate and Nickel Nioxime. Journal of America Chemistry Society 76, 1443-1446.

Egli, P.H., and S. Zerfoss. 1949. General principles of crystal growth. Trans. Faraday Society 5, 61-66.

Engelstad, O.P., and R.D. Hauck. 1974. Urea will it become the most popular nitrogen carrier. Crops and Science 26, 11-14.

Eriksen, A.B., and M. Kjeldby. 1987. A comparative study of urea hydrolysis rate and ammonia volatilization from urea and urea calcium nitrate. Fertilizer Research. 11, 9-24.

Fairbridge, R.W., and C.W. Finkl Jr. 1983. Encyclopedia of earth sciences. Vol XII : The encyclopedia of soil science. Part I: 194-205. Pennsylvania.

Fenn, L.B. 1975. Ammonia volatilization from surface applications of ammonium compounds on calcareous soils. III. Effects of mixing low and high loss ammonium compounds. Soil Sci. Soc. Am. Proc. 39, 366-368.

Fenn, L.B., and D.E. Kissel. 1973. Ammonia volatilization from surface application of ammonium compounds on calcareous soils : I. General theory. Soil Sci. Soc. Am. proc. 37, 855-859.

Fenn, L.B., J.E. Matocha, and E. Wu. 1981[a]. Ammonia loss and associated reactions of urea in calcareous soils. Soil Sci. Soc. Am. J. 45, 537-540.

Fenn, L.B., J.E. Matocha, and E. Wu. 1981[b]. Ammonia losses from surface-applied urea and ammonium fertilizers as influenced by rate of applied soluble calcium. Soil Sci. Soc. Am. J. 45, 883-886.

Fenn, L.B., J.E. Matocha, and E. Wu. 1981[c]. A comparison of calcium carbonate precipitation and pH depression on calcium reduced ammonia loss from surface-applied urea. Soil Sci. Soc. Am. J. 45, 1128-1131.

Fenn, L.B., J.E. Matocha, and E. Wu. 1982[a]. Soil cation exchange capacity effects on ammonia loss from surface-applied urea in the presence of soluble calcium. Soil Sci. Soc. Am. J. 46, 78-81

Fenn, L.B., J.E. Matocha, and E. Wu. 1982[b]. Substitution of ammonium and potassium for added calcium in reduction of ammonia loss from surface-applied urea. Soil Sci. Soc. Am. J. 46, 771-776.

Fenn, L.G., and J. Richards . 1986. Ammonia loss from surface applied urea-acid products. Fertilizer Research 9, 265-273.

Ferguson, J.F., P. Jenkins, and G. Eastman. 1973. Calcium phosphate precipitation at slight alkaline pH Value. Journal of water pollut. Fed. 45, 620-631.

Frear, G.L., and J. Johnston, 1929. The solubility of calcium carbonate (calcite) in certain aqueous solutions at 25°C. Journal of American Chemistry Society 51, 2083-2093.

Freney, J.R., J.R. Simpson, and O.T. Denmead. 1983. Volatilization of ammonia. Gaseous loss of nitrogen from plant-soil system. J. R. Freney and J.R. Simpson (ed). Developments of plant and soil sciences. 9, 1-32.

Freeman, J.S., and D.L. Rowell. 1981. The adsorption and precipitation of phosphate onto calcite. J. Soil Sci. 32, 75-84.

Garrels, R,M., M.E. Thompson, and R. Siever. 1960. Stability of some carbonates at 25°C and one atmosphere total pressure. Am. Jour. Sci. 258, 402-428.

Goodarz-Nia, I., and M. Motamedi. 1980. Kinetics of calcium carbonate crystallization from aqueous solutions. Journal of Crystal Growth 49, 125-131.

Griffin, R.A., and J.J. Jurinak. 1973. The interaction of phosphate with calcite. Soil Sc. Soc. Am. Proc. 37, 847-850.

Griffin, R.A., and J.J. Jurinak. 1974. Kinetics of the phosphate interaction with calcite. Soil Sci. Soc. Am. J. 38, 75-79.

Grimshow, R.W. 1971. The chemistry and Physics of Clays and Other Ceramic Materials. Benn, London.

Hall, A., and J.D. Taylor. 1971. The occurrence of vaterite in gastropod egg-shells. Mineral Magazine 38, 521-525.

Hargreaves, L. 1983. The sources and sinks of inorganic phospho-

Howard, J.R., G.H. Nancollas, and N. Purdie. 1960. The precipitation of silver chloride from aqueous solutions. Trans. Faraday Soc. 56, 278-283.

Jackson, T.A., and J.L. Bischoff. 1971. The influence of acids amino acids on the kinetics of the recrystallization of aragonite to calcite. 79, 493-497.

rus in a stream flowing from a calcareous soil. Oxford University thesis.

Herman, J.S., and M. Lorah. 1988. Calcite precipitation rates in the field; Measurements and prediction for a travertine-depositing stream. Geochimica et Cosmochimica Acta 52, 2347-2355.

Hoather, R.C. 1953. Application of spectrophotometry in the examination of waters. Proc. Soc. Water Treat. Exam. 2, 9-19.

Holford, I.C.R., and G.E.G. Mattingly. 1975. The high- and low-phosphate adsorbing surfaces in calcareous soils. J. Soil Sci. 26, 407-417.

House, W.A. 1981[a]. An experimental investigation of carbon dioxide adsorption during calcite precipitation. Colloids and Surfaces 2, 119-131.

House, W.A. 1981[b]. Kinetics of crystallisation of calcite from calcium bicarbonate solutions. J. Chem. Soc., Faraday trans. 77, 341-359.

House, W.A., and J.A. Tutton. 1982. An investigation of the heterogeneous nucleation of calcite. Journal of Crystal Growth 56, 699-710.

Hull, H., and A.G. Turnbull. 1973. A thermochemical study of mono-hydro calcite. Geochim. et Cosmochim. Acta 37, 685-694.

Inskeep, W.P., and J. Baham. 1983. Competitive complexation of Cd(II) and Cu(II) by water soluble organic ligands and Na-montmorillonite. Soil Sci. Soc. Am. J. 47, 1109-1115.

Inskeep, W.P., and P.R. Bloom. 1985. An evaluation of rate equation for calcite precipitation kinetics at pCO_2 less than 0.01 atm and pH greater than 8. Geochim. et Cosmochim. Acta 49, 2165-2180.

Inskeep, W.P., and P.R. Bloom. 1986[a]. Effects of soil moisture on soil pCO_2 soil solution bicarbonate, and iron chlorosis in soybeans. Soil Sci. Soc. Am. J. 50, 946-952.

Inskeep, W.P., and P.R. Bloom. 1986[b]. Kinetics of calcite precipitation in the presence of water soluble organic ligands. Soil Sci. Soc. Am. J. 50, 1167-1172.

Inskeep, W.P., and P.R. Bloom. 1986[c]. Calcium carbonate supersaturation in soil solutions of calciaquolls. Soil Sci. Soc. Am. J. 50, 1431-1437.

Jacobson, R.L., and E. Usdowski. 1975. Geochemical controls on a calcite precipitation spring. Contrib. Mineral Petrol. 51, 65-74.

Johnson, R.A., and J.D. O'Rourke. 1954. The kinetics of precipitate formation: Barium Sulfate. Journal of America Science 76, 2124-2126.

Johnston, J., H.E. Merwin, and E.D. Williamson. 1916. The several

Kazmierczak, T.F., M.B. Tomson, and G.H. Nancollas. 1982. Crystal growth of calcium carbonate. A controlled composition kinetic study. J. Phy. Chem. 86, 103-107.

forms of calcium carbonate. Am. Jour. Sci. 41, 473-512.

Kamiya, K., S. Sakka, and K. Terada. 1977. Aragonite formation through precipitation of calcium carbonate monohydrate. Mat. Res. Bull. 12, 1095-1102.

Katz, A. 1973. The interaction of magnesium with calcite during crystal growth at 25-90°C and one atmosphere. Geochimica et Cosmochimica Atca 37, 1563-1586.

Khan, S.U. 1969. Interaction between the humic acid fraction of soils and certain metallic cations. Soil Sci. Soc. Am. proc. 33, 851-854.

Kitano, Y., and D.W. Hood. 1965. The influence of organic material on the polymorphic crystallization of calcium carbonate. Geochemi. et Cosmochim. Acta 29, 29-41.

Koelliker, J.K., and D.E. Kissel, 1988. Importance of urea fertilizers. Ammonia volatilization from urea fertilizers. B.R. Bock, and D.E. Kissel (ed). Bulletin Y-206 National fertilizer development center. 37-51.

Kuo, S., and E.G. Lotse. 1972. Kinetics of phosphate adsorption by calcium carbonate and Ca-Kaolinite. Soil Sci. Soc. Am. Proc. 36, 725-729.

Kuo, S., and D.S. Mikkelsen. 1979. Effect of magnesium on phosphate adsorption by calcium carbonate. Soil Sci. 127, 65-69.

Lafon, G.M. 1978. Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase-example: The magnesian calcite. Am. Jour. Sci. 278, 1455-1468.

Lahann, R.W. 1978. A chemical model for calcite growth and morphology control. Journal of Sediment and Petroleum 48, 337-344.

Larsen, S., and A.E. Widdowson. 1970. Evidence of dicalcium phosphate precipitation in a calcareous soil. J. Soil Sci. 21, 364-367.

Leeuwen, C.V., and L.J.M.J. Blomen. 1979. On the presentation of growth curves for growth from solution. Journal of Crystal growth 46, 96-104.

Levy, R. 1981[a]. Effect of dissociation of aluminosilicates and carbonates on ionic activity products of calcium carbonate in soil extracts. Soil Sci. Soc. Am. J. 45, 250-255.

Levy, R. 1981[b]. Ionic activity product of calcium carbonate precipitate from soil solutions of different degrees of super-saturation. Soil Sci. Soc. Am. J. 45, 1070-1073.

Lindsay, W.L. 1979. Chemical equilibria in soils. A. Wiley Interscience.

MacCarthy, P., and J.A. Rice. 1985. Spectroscopic methods (other than NMR) for determining functionality in humic substances. In

Marion, G.M., and G.R. Dutt. 1974. Ion association in the ammonia-carbon dioxide-water system. Soil Sci. Soc. Am. Proc. 38, 889-891.

Humic substances in soil, sediment, and water, geometry, isolation, and characterization (ed. G.R. Aiken, D.M. McKnight, R.L. Wershaw, and P. MacCarthy). Wiely Interscience. 527-559.

Mackenzie, F.T., W.D. Bischoff, F.C. Bishop, M. Loijens, J. Schoonmaker, and R. Wollast. 1983. Magnesian calcite: Low temperature occurrence, solubility, and solid solution behaviour, in carbonates. Mineralogy and Chemistry, Reviews in Mineralogy 11, 97-144.

Marion, G.W., and K.L. Babcock. 1977. The solubility of carbonates and phosphates in calcareous soil suspensions. Soil Sci. Soc. Am. J. 41, 724-728.

May, P.B., and L.A. Douglas. 1976. Assay for soil urease activity. Plant and Soil 45, 301-305.

McConnell, J.D.L. 1959. Vaterite from Ballycraigy, Larine, Northern Ireland. Mineral Magazine 32, 535-545.

McLachlan, C.N.S. 1981. u.v.-DOC characterisation of pulp and paper bleach effluent. Water Res. 15, 983-988.

McLaren, A.D., and J. Skujins. 1971. Soil biochemistry. Marce Dekker INC. 2 : 49-50.

Milliman, J.D. 1974. Marine carbonate. Springer-Verlag. 375.

Morse, J.W. 1974[a]. Dissolution kinetics of calcium carbonate in seawater III. A new method for the study of carbonate reaction kinetics. Am. Jour. Sci. 274, 97-107.

Morse, J.W. 1974[b]. Dissolution kinetics of calcium carbonate in seawater V. Effect of natural inhibitor and the position of the chemical lysocline. Am. Jour. Sci. 274, 638-647.

Morse, J.W. 1983. The kinetics of calcium carbonate dissolution and precipitation in carbonates. Review in Mineralogy (ed, Reeder, R.J.) 11, 227-264.

Morse, J.W., and R.A. Berner. 1979. The chemistry of calcium carbonate in the deep oceans. In chemical modeling-Speciation, sorption, solubility, and kinetics in aqueous systems (ed. Jenne, E.) ACS symposium series 93, 499-535.

Mott, N.F. 1949. Theory of crystal growth. Trans. Faraday Society 5, 11-13.

Mucci, A. 1983. The solubility of calcite and aragonite in sea water at various salinities, temperatures, and atmosphere total pressure. Am. Jour. Sci. 283, 780-799.

Mucci, A. 1986. Growth kinetics and composition of magnesian calcite overgrowth precipitated from seawater: Quantitative influence of orthophosphate ions. Geochimica et Cosmochimica Acta 50, 2255-2265.

Mucci, A., and J.W. Morse. 1983. The incorporation of Mg^{2+} and Ca^{2+} into calcite overgrowth: influence of growth rate and

Nancollas, G.H. 1968. Kinetics of crystal growth from solution. J. Crystal Growth. 3-4, 335-339.

solution composition. Geochimica et Cosmochimica Acta 47, 217-233.

Mucci, A., and J.W. Morse. 1984. The solubility of calcite in seawater solutions of various magnesium concentration, I_t=0.687 m at 25°C and one atmosphere total pressure. Geochimica et Cosmochimica Acta 48, 815-822.

Mucci, A., and J.W. Morse. 1985. Auger spectroscopy determination of the surface layer composition of aragonite, calcite, dolomite and magnesite in synthetic seawater : Am. Jour. Sci. 285, 306-317

Mucci, A., J.W. Morse, and M.S. Kaminsky. 1985. Auger spectroscopy analysis of magnesian calcite overgrowth precipitated from seawater and solutions of similar composition. Am. Jour. Sci. 285, 289-305.

Mulvaney, R.L., and J.M. Bremner. 1977. Evaluation of antimetabolities of for retardation of urea hydrolysis in soils. Soil Sci. Soc. AM. J. 41, 1024-1027.

Murphy, T.P., K.J. Hall, and I. Yesaki. 1983. Coprecipitation of phosphate with calcite in a naturally eutrophic lake. Limno. Oceanogr. 28, 58-69.

Myers, R.G., and S.J. Thien. 1988. Organic matter solubility and soil reaction in an ammonium and phosphorous application zone. Soil Sci. Soc. Am. J. 52, 516-522.

Nakayama, F.S. 1968. Calcium activity, complex and ion-pair in saturated $CaCO_3$ solutions. Soil Sci. 106, 429-434.

Nakayama, F.S. 1971. Problems associated with the determination and application of the solubility of product constant. Soil Sci. Soc. Am. Proc. 35, 442-445.

Nancollas, G.H., Z. Amjad, and P. Koutsoukos. 1979. Calcium phosphate-speciation, solubility and kinetics considerations. In Chemical Modeling in aqueous system. (ed Jenne, E.A.) 93, 475-497.

Nancollas, G.H., and M.M. Reddy. 1971. The crystallization of calcium carbonate II. Calcite growth mechanism. Journal of Colloid Interface Science 37, 824-829.

Nancollas, G.H., and M.M. Reddy. 1974. Crystal growth kinetics of minerals encountered in water treatment processes. In: Aqueous--environmental chemistry of metals. (ed, Rubin, A.J.) Ann Arbor science publisher 219-253.

Nancollas, G.H., K. Sawada, and E. Schuttringer. 1983. Mineralization reactions involving calcium carbonates and phosphates. In biomineralization and biological metal accumulation. (ed Westbroek, P. and deJong, E.W.) 155-169.

Nielsen, A.E. 1964. Kinetics of precipitation. Pergamon.

Norman, R.J., L.T. Kurtz, and F.J. Stevenson. 1987. Solubilization of soil organic matter by liquid anhydrous ammonia. Soil

200
Parton, W.J., W.D. Gould, F.J. Adamsen, S. Torbit, and R.G. Woodmansee. 1981. NH_3 volatilization model. In simulation of nitrogen behaviour of soil-plant systems (M.J. Frissel and J.A. van Veen (ed)). Centre for Agriculture Publishing and Documentation. Wageningen. 233-243.

Sci. Soc. Am. J. 51, 809-812.

Ogino, T., T. Suzuki, and K. Sawada. 1987. The formation and transformation of calcium carbonate in water. Geochimica et Cosmochimica Acta 51, 2757-2767.

Oster, J.D. 1978. pHc calculation. Soil Sci. Soc. Am. J. 42, 378.

Otsuki, A., and R.G. Wetzel. 1972. Coprecipitation of phosphate with carbonates in a Marl Lake. Limno. Oceanogr. 17, 763-767.

Otsuki, A., and R.G. Wetzel. 1973. Interaction of yellow organic acids with calcium carbonate in freshwater. Limno. Oceanogr. 73, 196-199.

Packter, A. 1968. The precipitation of sparingly soluble alkaline-earth metal and lead salts : Nucleation and growth orders during inducing period. Journal of Chemistry Society (A) 859-862.

Page, A.L., R.H. Miller, and D.R. Keeney. 1982. Methods of soil analysis. Part 2. Chemical and microbiological properties. Second edition.

Palache, C., H. Berman, and C. Frondel. 1949. Dana's system of mineralogy. Johnwiley and Sons 2, 132-241.

Paul, E.A., and A.D. McLaren. 1975. Soil biochemistry. Marce Dekker Inc. 3

Petit, N.M., A.R.J. Smith, R.B. Freedman, and R.G. Bruns. 1976. Soil urease : Activity, stability and kinetic properties. Soil Biol. Biochem. 8, 479-484.

Plummer, L.N., and E. Busenberg. 1982. The kinetics of dissolution of dolomite in CO_2-H_2O system at 1.5 to 65°C and 0 to 1 atm pCO^2. American Journal of Science 282, 45-78.

Plummer, L.N., D.L. Parkhurst, and T.M.L. Wigley. 1979. Critical review of the kinetics of calcite dissolution and precipitation. (ed, Jenne, E.A.) American Chemical Society 93, 537-573.

Plummer, L.N., T.M. Wigley, and D.L. Parkhurst. 1978. The kinetics of calcite dissolution in CO_2-water system at 5 to 60°C and 0.0 to 1.0 atm CO_2 . Am. Jour. Sci. 278, 179-216.

Pytkowicz, R.W. 1965. Rates of inorganic calcium carbonate nucleation. Journal of Geology 73, 196-199.

Rachhpal-Singh. 1984. Movement of urea and its products in soil. D. Phil. thesis of Oxford University.

Rachhpal-Singh, and P.H. Nye. 1984[a]. The effect of soil pH and high urea concentrations on urease activity in soil. J. Soil Sci. 35, 519-527.

Rachhpal-Singh, and P.H. Nye. 1984[b]. Diffusion of urea, ammonium and soil alkalinity from surface applied urea. J. Soil Sci. 35, 529-538.

Rachhpal-Singh, and P.H. Nye. 1986[a]. A model of ammonia volatilization from applied urea. I. Development of the model. J. Soil Sci. 37, 9-20.

Rachhpal-Singh, and P.H. Nye. 1986[b]. A model of ammonia volatilization from applied urea. II. Experimental testing. J. Soil Sci. 37, 21-29.

Rachhpal-Singh, and P.H. Nye. 1986[c]. A model of ammonia volatilization from applied urea. III. Sensitivity analysis, mechanisms, and applications. J. Soil Sci. 37, 31-40.

Raistrick, B. 1949. Discussion. Faraday Soc. 5 234.

Rappaport, B.D., and J.H. Axley. 1984. Potassium chloride for improved urea fertilizer efficiency. Soil Sci. Soc. Am. J. 48, 399-401.

Reddy. M.M. 1975. Kinetics of calcium carbonate formation. Proc. Int. Assoc. of theoretical and applied Limnology 19, 429-438.

Reddy, M.M. 1977. Crystallization of calcium carbonate in the presence of trace concentration of phosphorus containing anions. I. Inhibition by phosphate and glycophosphate ion at pH 8.8 and 25°C. Journal of Crystal Growth 41, 287-295.

Reddy, M.M. 1983. Characterization of calcite dissolution and precipitation using an improved experimental technique. Sci. Geol. Mem. 71, 109-117.

Reddy, M.M., and G.H. Nancollas. 1971. The crystallization of calcium carbonate I. Isotopic exchange and kinetics. Journal of colloid Interface Science 36, 166-172.

Reddy, M.M., and G.H. Nancollas. 1973. Calcite crystal growth inhibition by phosphates. Desalination 12, 61-73.

Reddy, M.M., L.N. Plummer, and E. Busenberg. 1981. Crystal growth of calcite from calcium bicarbonate solution at constant pCO_2 and 25°C, a test of calcite dissolution model. Geochim. et Cosmochim. Acta 45, 1281-1289.

Reddy, M.M., and K.K. Wang. 1980. Crystallization of calcium carbonate in the presence of metal ion I. Inhibition by magnesium ion at pH 8.8 and 25°C. Journal of Crystal Growth 50, 470-480.

Reynolds, R.C.Jr.. 1978. Polyphenol inhibition of calcite precipitation in lake Powell. Limno. Oceanogr. 23, 585-597.

Rheinbaben, W. von. 1987. Effect of magnesium sulphate addition of urea on nitrogen loss due to ammonia volatilization. Fertilizer Res. 11, 149-159.

Rowlands, D.L.G., and R.K. Webster. 1971. Precipitation of vaterite in lake water. Nature 229, 158.

Ryan, J., D. Curtin, and I. Safi. 1981. Ammonia volatilization as influenced by calcium carbonate particle size and iron oxides. Soil Sci. Soc. Am. J. 45, 338-341.

Sadeghi, A.M., K.J. McInnes, D.E. Kissel, M.L. Cabrera, J.K. Koelliker, and E.T. Kanemasu. 1988. Mechanistic model for predicting ammonia volatilization from urea. B.R. Bock, and D.E. Kissel (ed). Bulletin Y-206 National Fertilizer Development Center. 67-92.

Sass, E., J.W. Morse, and F.J. Millero. 1983. Dependence of the values of calcite and aragonite the thermodynamic solubility product on ionic models. Am. Jour. Sci. 283, 218-229.

Schnitzer, M. 1978. Some observations on the chemistry of humic substances. Agrochimica 22, 216-225.

Schnitzer, M., and S.U. Khan. 1972. Humic substance in the environment. Marcel Dekker 55-67 and 137-209.

Sharratt, W.J. 1983. Falling curtain process for granulation of urea. Agronomy abstracts 216.

Simkiss, K. 1964. The inhibitory effects of some metabolites on the precipitation of calcium carbonate from artificial and natural seawater. Journal Cons., Cons. Perm. Int. Explor. Mer 29, 6-18.

Sjöberg, E.L. 1978. Kinetics and mechanisms of calcite dissolution in aqueous solutions at low temperatures. Stockholm Contr. Geology 32, 1-96.

Smillie, G.W., D. Curtin, and J.K. Syers. 1987. Influence of exchangeable calcium on phosphate retention by weakly acid soils. Soil Sci. Soc. Am. J. 51, 1169-1172.

Staveley, L.A.K., and R.G. Linford. 1969. The heat capacity and entropy of calcite and aragonite and their interpretation. Journal of Thermodynamics 1, 1-11.

Stevens, R.J. R.J. Laughlin, D.J. Kilpatrick. 1989. Soil properties related to the dynamics of ammonia volatilization from urea applied to the surface of acidic soils. Fertilizer Research. 20, 1-9.

Stevenson, F.J. 1982. Humus chemistry : Genesis, composition, reactions. John Wiley & Sons, New York.

Stumm, W., and J.J. Morgan. 1981. Aquatic chemistry. Wiley-Interscience.

Stumm, W., and J.O. Leckie. 1970. Phosphate exchange with sediments: its role in the productivity of surface water. In advances in Water Pollution Research 2, 1-16.

Suarez, D.L. 1977. Ion activity product of calcium carbonate in waters below to the root zone. Soil Sci. Soc. Am. J. 41, 310-315.

Suarez, D.L. 1983. Calcite supersaturation and precipitation kinetics in the lower Colorads River, All American Canal and East Highline Canal. Water Resources Research 19, 653-661.

Suarez, D.L., and J.D. Rhoades. 1982. The apparent solubility of

calcium carbonate in soils. Soil Sci. Soc. Am. J. 46, 716-722.

Suess, E. 1970. Interaction of organic compounds with calcium carbonate I. Association phenomena and geochemical implications. Geochim. et Cosmochim. Acta 34, 157-168.

Tabatabai, M.A., and J.M. Bremner. 1972. Assay of urease activity in soils. Soil Biology and Biochem. 4, 479-487.

Terman, G.L. 1979. Volatilization losses of nitrogen as ammonia from surface-applied fertilizers, organic amendments, and crop residues. Advance of Agronomy 31, 189-223.

Terman, G.L., and C.M. Hunt. 1964. Volatilization losses of nitrogen from surface-applied fertilizers, as measured by crop response. Soil Sci. Soc. Am. Proc. 28, 667-672.

Thompson, D.W., and P.G. Pownall. 1989. Surface electrical properties of calcite. Journal of Colloid and Interface Science 131 74-82.

Thorstenson, D.C., and L.N. Plummer. 1977. Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase-example: The magnesian calcite. Am. Jour. Sci. 277, 1203-1223.

Thorstenson, D.c., and L.N. Plummer. 1978. Replied to comment on Thorsten and Plummer (1977). Am. Jour. Sci. 278, 1478-1488.

Thurman, E.M. 1985. Organic geochemistry of natural waters. Development in Biochemistry (ed Nijhoff, M. Junk, W.) Kluwer Academic 2, 296.

Tomasiewicz, D.J., and J.L. Henry. 1985. The effect of anhydrous ammonia application on the solubility of soil organic carbon. Can. Journal of Soil Sci. 65, 737-747.

Truesdell, A.H., and B.F. Jones. 1974. A computer program for calculating chemical equilibrium of natural waters. Journal of Reservation U.S. Geol. Surv. 2, 233-248.

Turnbull, A.G. 1973. A thermochemical study of vaterite. Geochimica et Cosmochimica Acta 37, 1593-1601.

Van Hall, C.E., J. Safranko, and V.A. Stanger. 1963. Rapid combustion method for the determination of organic substances in aqueous solutions. Anal. Chem. 35, 315-319.

Walter, L.M., and J.W. Morse. 1984. Magnesian calcite stabilities: A revaluation. Geochemica et Cosmochimica Acta 48, 1059-1069.

Watanabe, F.S., and S.R. Olsen. 1965. Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soils. Soil Sci. Soc. Am. Proc. 29, 677-678.

Wedgwood, P. 1952. Notes on humus. J. Inst. Sewage purif. Part I, 20-31.

Wiechers, H.N.S., P. Sturrock, and G.V.R. Morais. 1975. Calcium carbonate crystallization kinetics. Water Reservation 9, 835-845.

Wollast, R., R.M. Garrels, and F.T. Mackenzie. 1980. Calcite-seawater reactions in ocean surface waters. Am. Jour. Sci. 280, 831-841.

Wray, J.L., and S.F. Daniel. 1957. Precipitation of calcite and aragonite. America Chemistry Society Journal 79, 2031-2034.

Yadav, B.R., K.V. Paliwal, and N.M. Nimgade. 1984. Effect of magnesium-rich waters on phosphate adsorption by calcite. Soil Sci. 127, 65-69.

Zahaby, E.M.E., and S.H. Chien. 1982. Effect of pyrophosphate on phosphate sorption and ammonia volatilization by calcareous soils treated with ammonium phosphates. Soil Sci. Soc. Am. J. 46, 733-740.

Zullig, J.J., and J.W. Morse. 1988. Interaction of organic acids with carbonate mineral surfaces in seawater and related solutions : I Fatty acid adsorption. Geochim. et Cosmochim. Acta. 52 1667-1678.

APPENDIX 1

Table A.1.1 THE EFFECTS OF THE IONIC STRENGTHS OF AMMONIUM CHLORIDE AND UREA ON CALCIUM ION ACTIVITY IN 10 mM $CaCl_2$ SOLUTION, AS MEASURED WITH A CALCIUM-SENSITIVE ELECTRODE.

	Measured	Calculated	
NH_4Cl, M	(Ca), mM	(Ca)♥, mM	I*, M
0.0	5.46	5.46	0.00
0.0001	5.69	5.46	0.00
0.001	5.44	5.44	0.00
0.01	5.14	5.17	0.01
0.1	3.79	3.79	0.2
Urea, M			
0.0001	5.64	-	-
0.001	5.64	-	-
0.01	5.59	-	-
0.1	5.44	-	0.03
1.0	4.84	-	0.05
5.0	2.09	-	0.96

(Ca)♥, The activity of calcium ion estimated using the Debye-Hückel equation.

I*, The ionic strength calculated from the effects of NH_4Cl and urea concentrations on the calcium ion activity, estimated with the Debye-Hückel equation.

APPENDIX 2

DEVELOPMENT OF COMPUTING PROGRAMS

2.1 THE SEPARATION OF CALCITE-SEEDS

Some seeded experiments were carried out in order to examine the effect of supersaturation degree (SI) and particle surface area on the precipitation of calcium carbonate. There were four groups of calcite seeds used in the study, two groups (10-15 and 30-35 μm) were separated from BDH AR $CaCO_{3(s)}$, and the other two (75-150 and 150-212 μm) were prepared from natural crystals. Their preparations are described separately as follows :

<u>10-15 and 30-35 μm seeds</u>

The siphon method was used to extract these two groups of calcite seeds from calcite suspension at a specific depth which was calculated by Stokes law,

$$V=GX^2(D_p-D_l)/(18v) \qquad (A.2.1)$$

where V is velocity of fall in cm/s, D_p is the density of the particles (2.71 for calcite), D_l is the density of the liquid (1.0 for water), G is the gravity constant, X is the diameter of the particle, and v is the viscosity of the liquid (0.00890 gm sec^{-1} cm^{-1}). The separation procedures for these two groups were identical so only the procedure for the 10-15 μm group is described below :

(1) About 10 g of calcite seeds was mixed in a cylinder with a litre of calcite-saturated water prevent the further dissolution of calcite-seeds during operation.

(2) After it was thoroughly mixed up, the suspension was allowed to settle for 21 minutes and 14 seconds (which was calculated by equation A.2.1) and then the top 30 cm of suspension was siphoned off with a curved glass pipette. The cylinder was refilled with

calcite-saturated water, then shaken, and after settling for the required time, the top 30 cm suspension was siphoned off again. These operations were repeated until the calcite-seeds suspended in the top 30 cm suspension were too few in number to make another extraction worthwhile. All the extracted suspensions were combined and allowed to settle. Then particles were collected, and the solution was set aside for reuse.

(3) When enough particles were gathered, about 10 g of them were put into the separation cylinder again with the calcite-saturated solution as in step (1). Then step (2) was repeated, but the time allowed for settling was 47 minutes and 47 seconds, until the top 30 cm suspension was totally clear which meant no calcite seeds remained. Then the calcite particles on the bottom of the cylinder were collected and air-dried for use. These calcite seeds were referred to as having 10-15 μm size.

The procedures for collecting 30-35 μm seeds were the same as those above, except that the settling time was 3 minutes and 54 seconds and 5 minutes and 19 seconds for steps (2) and (3), respectively.

These seeds were examined (50 seeds from each group) and the lengths of two sides per particle were measured under light microscope. The average width of edge for the 10-15 μm group was 12.16±1.97 μm, and for the 30-35 μm group it was 30.59±3.52 μm. All these seeds were rhombic and almost cubic, but most of them had a rough surface with layered appearance. Since these two groups of seeds had been separated using Stokes law, they were treated as round particles to calculate their particle surface area and particle weight. On this basis the surface areas of a single seed were 4.91×10^{-6} and 3.32×10^{-5} cm^2 for the 10-15 and 30-35 μm groups respectively, and their corresponding weights were

$2.77x10^{-9}$ and $4.87x10^{-8}$ g.

75-150 and 150-212 μm seeds

When particle sizes are bigger than 35 μm, it would not be easy to separate particles by the sedimentation method because they sink too quickly to be extracted by the siphon method. A dry-sieving method is a good alternative. Fortunately we received some calcite crystals from Dr B. Atkins (University Museum). These particles were treated as follows : (1) The crystals were broken down very carefully in order to break them parallel to the cleavage rather than smashing them. (2) They were sieved through a 212 μm sieve, and the bigger particles were broken again. (3) The particles <212 μm were sieved again through a 150 μm sieve. Then the particles which remained on this sieve were referred to as the 150-212 μm group. (4) The remainder were sieved with a 75 μm sieve and the particles which remained on the 75 μm sieve were referred to as the 75-150 μm group.

These two groups of calcite seeds were examined under light microscope in the same way as the finer groups. They all had a rhombohedral appearance and smooth surfaces. The average width of edge for the 75-150 μm group was 118.4±46.2 μm, for the 150-212 μm group it was 186.9±66.2 μm. These rhombohedral particles had angles near 90^0 so their particle surface was treated as if rectangular and the width of the edges were taken as 112.5, and 181 μm instead of 118.4 and 186.9 μm. Their corresponding surface areas were $7.59x10^{-4}$ and $1.96x10^{-3}$ cm^2, and weights were $3.86x10^{-6}$ and $1.61x10^{-5}$ g per particle.

2.2 THE CALCULATING PROGRAMS

This section falls into five parts to present the programs which were used to calculate the values of parameters discussed

in this thesis such as pH and SI. Part (1), (2), (3), and (4) describe the programs for calculating the concentrations of base 1, base 2, base 3, and base 4, respectively, in a calcite seeded systems in chapter 3. Part (5) describes the calculation of the surface area of precipitates in solution.

Symbols used in the programs

base1, base2, base3, and base4, the concentration (M) of base 1, base 2, base 3, and base 4, respectively.
caa, caa1, caa2, caa3, and caa4, the activity of calcium ions in different conditions, M.
cac, cac1, cac2, cac3, and cac4, the concentration of calcium ions in different conditions, M.
caco, the concentration of complex of calcium carbonate, M.
cahc, the concentration of complex of calcium bicarbonate, M.
co3a, co3a1, co3a2, co3a3, co3a4, the activity of carbonate ions in different conditions, M.
co3c, co3c1, co3c2, co3c3, co3c4, the concentration of carbonate ions in different conditions, M.
dc, the shortfall of ion charges.
dcd and dcn, the allowance of the shortfall of charges of cations and anions, respectively.
fco3, fh, fhco, fn4, fn3, and foh, the ion activity coefficient of carbonate, hydrogen, bicarbonate, ammonium, ammonia, and hydroxide ions, respectively.
hcoa, hcoa1, hcoa2, hcoa3, hcoa4, the activity of bicarbonate ions in different conditions, M.
hcoc, hcoc1, hcoc2, hcoc3, hcoc4, the concentration of bicarbonate ions in different conditions, M.
hcocd, the part of base in reaction solutions dissolved from seeds, i.e. B_{CaCO3}.
ips, the size of calcite-seeds, 10, 30, 150, and 212 were used to represent the groups of seeds at 10-15, 30-35, 75-150, and 150-212 μm sizes.
pca1, the amount of newly formed (or dissolved) calcium carbonate, M.
ph, ph1, the pH in different conditions.
phi, the value of measured solution pH during reaction period.
phco, -log(activity of bicarbonate ions).
pn, the numbers of precipitates per ml of reaction solutions.
psu0, the mean of initial surface area of a single precipitate, cm^2, later the total initial surface area of precipitates, $cm^2\ ml^{-1}$.
psu1, psud, the surface are of precipitates in different conditions, $cm^2\ ml^{-1}$.
pw, pw1 the mean of weight of a single precipitate in different conditions, g.
rha, rhc, the activity and concentration of hydrogen ions, M.
ri, ri1, ri2, the ionic strength in different conditions.
rncoc, the concentration of complex of ammonium bicarbonate, M.
rnhcoc, the concentration of complex of ammonium carbonate, M,
rnr, apparent ammonia dissolution rate (AADR), mole $litre^{-1}\ min^{-1}$.
rnt, the total concentration of ammoniacal-N, i.e. NT.
rntf, the total concentration of ammoniacal-N (NT) at the end of

experiments, M.
rn3c, the concentration of ammonia, M.
rn4a, rn4c, the activity and concentration of ammonium ions, M.
roha, rohc, the activity and concentration of hydroxide ions, M.
rt, the lapse of reaction time from the start of experiments.
r1, the transfer factor in calculating the changes in particle surface area from the changes in particle weight.
sri, the square root of ionic strength.
si3, si4, the value of SI in different conditions.
tf, the lapse of time at the end of experiments, minute.
tw, the total initial weight of seeds in reaction solutions.
wa1, the amount of newly formed (or dissolved) calcium carbonate, in reaction solutions, in concentration, M.
wa10, the amount of newly formed (or dissolved) calcium carbonate in reaction solutions, in weight, g.
wa11, the weight of newly increased (or decreased) calcium carbonate of each precipitate, g.

Part (1) was used to calculate the theoretical concentra tion of base in solution using NT and referred to as base 1.

```
5       i=0
        print *, 'read tf, rntf, ips, tw '
        read *, rtf, rntf, ips, tw
        rnr=rntf/rtf
        print *, ' read t, for ph at ph=7.124 '
10      read *, rt
        rnt=rnr*rt
c the ionic strength ri is started with an approximate value.
        ri=.95*rnt+.03
 15       i=0
        ri1=ri
c the concentration of bicarbonate ion is first estimated by
using the concentration of ammoniacal-N.
        hcoc=rnt*0.95
        sri=sqrt(ri1)
c f... are ion activity coefficients.
        fn4=10**-((.509*sri)/(1+.8225*sri))
        fn3=10**-(0.12*ri1)
        fco3=10**-((2.036*sri)/(1+1.4805*sri))
        fhco=10**-((.509*sri)/(1+1.4805*sri))
        fh=10**-((.509*sri)/(1+2.961*sri))
        foh=10**-((.509*sri)/(1+1.1515*sri))
110     i=i+1
        if (i .gt. 1000) then
        go to 111
        end if
c the relationship between the activity of hydrogen and bicar
  bonate ion at eqilibrium under 0.00484 atm P_CO2 and 25° C.
        hcoa=hcoc*fhco
        phco=-log10(hcoa)
        ph=10.137-phco
        rha=10**-ph
        rhc=rha/fh
        roha=1.01e-14/rha
        rohc=roha/foh
        co3a=(hcoa*4.688e-11)/rha
```

```
        co3c=co3a/fco3
c calculating rn4c from rnt=rn4c+rn3c+rnhcoc+rncoc.
        rr=fn3*rha*fhco+fhco*5.0118e-10+22.026*co3a*fn4*fn3*rha
        rr=rr+0.69*hcoa*fn4*rha*fhco
        rn4c=rnt*fn3*fhco*rha/rr
        rn4a=rn4c*fn4
        rncoc=22.026*rn4a*co3a/fhco
        rnhcoc=0.69*rn4a*hcoa/fn3
        rn3c=rn4a*5.0118e-10/(fn3*rha)
        dc=rn4c-hcoc-2*co3c+rhc-rohc-rncoc
c dc is the difference of ion charges between cations and anions.
        dcd=rnt/1000
        if (dc .gt. dcd) then
        hcoc=1.001*hcoc
        ri1=0.03+0.5*(rn4c+hcoc+4*co3c+rhc+rohc+rncoc)
        go to 110
        end if
        dcn=rnt/1000
        if (dc .lt. -dcn) then
        hcoc=0.998*hcoc
        ri1=0.03+0.5*(rn4c+hcoc+4*co3c+rhc+rohc+rncoc)
c ri1 is the value of ionic strength newly measured.
        go to 110
        end if
111     ph1=ph
        base1=hcoc+2*co3c+rohc+rnhcoc+2*rncoc
        co3a1=co3a
        co3c1=co3c
        hcoa1=hcoa
        hcoc1=hcoc
```

Part (2) was used to calculate the real concentration of base (referred to as base 2) in solution using NT and the measured solution pH.

```
        ri2=ri1
c the initial concentration of calcium ions is 0.01 M.
        cac=0.01
200     do 222 i=1,3,1
210     sri=sqrt(ri2)
        fn4=10**-((.509*sri)/(1+.8225*sri))
        fca=10**-((2.036*sri)/(1+1.974*sri))
        fn3=10**-(0.12*ri1)
        fco3=10**-((2.036*sri)/(1+1.4805*sri))
        fhco=10**-((.509*sri)/(1+1.4805*sri))
        fh=10**-((.509*sri)/(1+2.961*sri))
        foh=10**-((.509*sri)/(1+1.1515*sri))
        phco=10.137-7.124
        hcoa=10**-phco
        hcoc=hcoa/fhco
        rha=10**-7.124
        rhc=rha/fh
        roha=1.01e-14/rha
        rohc=roha/foh
        co3a=(hcoa*4.688e-11)/rha
        co3c=co3a/fco3
        rr=fn3*rha*fhco+fhco*5.0118e-10+22.026*co3a*fn4*fn3*rha
```

```
          rr=rr+0.69*hcoa*fn4*rha*fhco
          rn4c=rnt*fn3*fhco*rha/rr
          rn4a=rn4c*fn4
          rncoc=22.026*rn4a*co3a/fhco
          rnhcoc=0.69*rn4a*hcoa/fn3
          rn3c=rn4a*5.0118e-10/(fn3*rha)
          caa=cac*fca
          cahc=(caa*hcoa*17.7305)/fhco
          caco=1.4125e3*caa*co3a
c the concentration of calcium ion is estimated by the shortfall
  of charges of positive ions in reaction solution.
          cac=(0.02+hcoc+2*co3c+rncoc+rohc-rhc-cahc-rn4c)/2
          ri2=0.5*(0.02+4*cac+rn4c+hcoc+4*co3c+rhc+rohc+rncoc+cahc)
222       continue
          caa2=caa
          cac2=cac
          ph2=7.124
          co3a2=co3a
          co3c2=co3c
          hcoc2=hcoc
          hcoa2=hcoa
          base2=hcoc+2*co3c+rohc+rnhcoc+2*rncoc+cahc+2*caco
          hcocd=base2-base1
c hcocd is referred to as the part of base dissolved from seeds.
          write (6,290), k , ips, rt, tw, rnr
290       format (1x, ' date, time, ps, tw', 2i12, 2f12.5, e12.5)
```

Part (3) was used to calculate the theoretical pH and concentration of base (referred to as base 3) in solution from NT and the maximum amount of B_{CaCO3} (B_{CaCO3}=base 2 - base 1, at pH=7.12), assuming that no calcium carbonate was precipitated even when solution pH was higher than 7.12. The value of 7.12 is the equilibrium solution pH when enough calcite is equilibrated under P_{CO2} 0.00484 atm and temperature at 25^0 C.

```
          cac=cac2
          ri1=0.03+0.95*rnt+hcocd
300       print *, 'read time, phi'
          read *, t, phi
          if (phi .lt. 7.12) then
          hcocd=0
          else if (phi .gt. 7.119) then
          hcocd=hcoc2-hcoc1
          end if
          rnt=rnr*t
          hcoc=.95*rnt+hcocd

c the concentration of bicarbonate ion is estimated by the
amounts of ammoniacal-N and dissolved seeds.

301       i=i+1
          if ( i .gt. 1000 ) then
          go to 388
          end if
          if (ri1 .lt. 0.1) then
          sri=sqrt(ri1)
          fn4=10**-((.509*sri)/(1+.8225*sri))
```

```
      fca=10**-((2.036*sri)/(1+1.974*sri))
      fn3=10**-(0.12*ri1)
      fco3=10**-((2.036*sri)/(1+1.4805*sri))
      fhco=10**-((.509*sri)/(1+1.4805*sri))
      fh=10**-((.509*sri)/(1+2.961*sri))
      foh=10**-((.509*sri)/(1+1.1515*sri))
      go to 310
      else if (ri1 .gt. 0.5) then
      ri1=0.5
      go to 305
      end if
305   sri=sqrt(ri1)
      fca=10**-((2.036*sri)/(1+1.974*sri))
      fn4=10**-(0.5*(sri/(1+sri)-0.2*ri1))
      fn3=10**-(0.12*ri1)
      fco3=10**(2*(sri/(1+sri)-0.2*ri1))
      fhco=fn4
      fh=fn4
      foh=fn4
310   hcoa=hcoc*fhco
      phco=-log10(hcoa)
      ph=10.137-phco
      rha=10**-ph
      rhc=rha/fh
      roha=1.01e-14/rha
      rohc=roha/foh
      co3a=(hcoa*4.688e-11)/rha
      co3c=co3a/fco3
      rr=fn3*rha*fhco+fhco*5.0118e-10+22.026*co3a*fn4*fn3*rha
      rr=rr+0.69*hcoa*fn4*rha*fhco
      rn4c=rnt*fn3*fhco*rha/rr
      rn4a=rn4c*fn4
      rncoc=22.026*rn4a*co3a/fhco
      rnhcoc=0.69*rn4a*hcoa/fn3
      rn3c=rn4a*5.0118e-10/(fn3*rha)
      caa=cac*fca
      cahc=(caa*hcoa*17.7305)/fhco
      caco=1.4125e3*caa*co3a
      cac=cact2-cahc-caco
      dc=rn4c-hcoc-2*co3c+rhc-rohc-rncoc+hcocd
      dcd=rnt/1000
      if (dc .gt. dcd ) then
      hcoc=1.001*hcoc
ri1=.5*(0.02+4*cac+cahc+rn4c+hcoc+4*co3c+rhc+rohc+rncoc+hcocd)
      go to  301
      end if
      dcn=rnt/1000
      if (dc .lt. -dcn ) then
      hcoc=.998*hcoc
ri1=.5*(0.02+4*cac+cahc+rn4c+hcoc+4*co3c+rhc+rohc+rncoc+hcocd)
      go to 301
      end if
388   si3=caa*co3a/3.311e-9
      base3=hcoc+2*co3c+rohc+rnhcoc+2*rncoc+cahc+2*caco
c base3 is the base of solution with no precipitation occurred.
      caa3=caa
      cac3=cac
      hcoa3=hcoa
      hcoc3=hcoc
```

```
          co3a3=co3a
          co3c3=co3c
```

Part (4) was used to calculate the real concentration of base (referred to as base 4) in solution using NT and measured solution pH.

```
          ri2=ri1
          cac=cac3
400       do 444 i=1,3,1
          sri=sqrt(ri2)
          fca=10**-((2.036*sri)/(1+1.974*sri))
          fn4=10**-((.509*sri)/(1+.8225*sri))
          fn3=10**-(0.12*ri1)
          fco3=10**-((2.036*sri)/(1+1.4805*sri))
          fhco=10**-((.509*sri)/(1+1.4805*sri))
          fh=10**-((.509*sri)/(1+2.961*sri))
          foh=10**-((.509*sri)/(1+1.1515*sri))
410       phco=10.137-phi
          hcoa=10**-phco
          hcoc=hcoa/fhco
          rha=10**-phi
          rhc=rha/fh
          roha=1.01e-14/rha
          rohc=roha/foh
          co3a=(hcoa*4.688e-11)/rha
          co3c=co3a/fco3
          rr=fn3*rha*fhco+fhco*5.0118e-10+22.026*co3a*fn4*fn3*rha
          rr=rr+0.69*hcoa*fn4*rha*fhco
          rn4c=rnt*fn3*fhco*rha/rr
          rn4a=rn4c*fn4
          rncoc=22.026*rn4a*co3a/fhco
          rnhcoc=0.69*rn4a*hcoa/fn3
          rn3c=rn4a*5.0118e-10/(fn3*rha)
          caa=cac*fca
          cahc=(caa*hcoa*17.7305)/fhco
          caco=1.4125e3*caa*co3a
          cac=(0.02+hcoc+2*co3c+rncoc+rohc-rhc-cahc-rn4c)/2
          ri2=0.5*(rn4c+hcoc+4*co3c+rhc+rohc+rncoc+4*cac+0.02+cahc)

444       continue
          si4=caa*co3a/3.311e-9
          base4=hcoc+2*co3c+rohc+rnhcoc+2*rncoc+cahc+2*caco
c base4 is the amount of base of solution according to the
solution pH and components.
          caa4=caa
          cac4=cac
          hcoc4=hcoc
          hcoa4=hcoa
          co3a4=co3a
          co3c4=co3c
          pcal=(base3-base4)/2.0
c the difference of base3 and base4 is used to estimate the
amount of newly formed (or dissolved) calcium carbonate, in turn
is used to estimate the changes in surface area.
```

Part (5) was used to calculate the surface area of precipitates in solution after the dissolution or precipitation of calcium carbonate occurred.

```
c the calculation of surface area of particles in sizes of 10-15,
30-35, 75-150, and 150-212 μm groups of seeds.
          if ( ips .eq. 10 ) then
          pw=2.77e-09
          psu0=4.91e-06
          else  if ( ips .eq. 30 ) then
          pw=4.87e-08
          psu0=3.32e-05
          else if ( ips .eq. 150 ) then
          pw=3.86e-06
          psu0=7.59e-04
          else if ( ips .eq. 212 ) then
          pw=1.61e-05
          psu0=1.96e-03
          end if
          pn=tw/(pw*65.)
          psu0=psu0*pn
          wa1=pcal
c deriving the changes in weight (g) from the changes in
concentration (M) of calcium carbonate in reaction solutions.
          wa10=wa1*0.1
          wa11=wa10/pn
          pw1=wa11+pw
          r1=(pw1/pw)**(2./3.)
          psu1=psu0*r1
          write (6,590), t, phi, si4, rnt, cac4, co3c4, hcoc4
590       format (' t,phi,si4,rnt,cac4,co3c4,hcoc4', 3f12.2,
          4e12.5)
          write (6,591), pcal, r, psu0, psu1, psud, base3, base4
591       format (' pcal, r, psa0, psai,psud,base3,base4 ',
          7e12.5)
          print*, 'read 1, 2, or greater 2'
          read *, 1
          if (1 .eq. 0) then
          go to 99999
          else if (1 .lt. 999) then
          go to 300
          else if ( 1 .gt. 999 )  then
          go to 5
          end if
99999     stop
          end
```

Table A.2.1 EQUILIBRIUM CONSTANTS USED IN ACTIVITY CALCULATIONS (AT 25^0 C EXCEPT WHEN NOTED).

REACTIONS	pK	REFERENCE
$CaHCO_3^+ \langle=\rangle Ca^{2+} + HCO_3^-$	1.25	Nakayama, 1968
$CaCO_3^0 \langle=\rangle Ca^{2+} + CO_3^{2-}$	3.15	Lindsay, 1979
$CO_{2(g)} \langle=\rangle CO_{2(aq)}$	1.47	"
	(H_{CO_2}, Henry's constant)	
$CO_{2(aq)} + H_2O \langle=\rangle H_2CO_{3(aq)}$	2.81	"
$H_2CO_3^* \langle=\rangle H^+ + HCO_3^-$	6.353	Stumm & Morgan, 1981
($H_2CO_3^* = H_2CO_{3(aq)} + CO_{2(aq)}$)		
$HCO_3^- \langle=\rangle H^+ + CO_3^{2-}$	10.328	"
$H_2O \langle=\rangle H^+ + OH^-$	14.00	"
$NH_{3(g)} \langle=\rangle NH_{3(aq)}$	-1.76	"
	(H_{NH_3}, Henry's constant)	
$NH_4^+ \langle=\rangle NH_3 + H^+$	9.3	"
$NH_4CO_3^- \langle=\rangle NH_4^+ + CO_3^{2-}$	1.34	Marion & Dutt, 1974
	(20^0 C)	
$NH_4HCO_3^0 \langle=\rangle NH_4^+ + HCO_3^-$	-0.161	"

Table A.2.2 INDIVIDUAL ION-SIZE PARAMETERS, ai, IN A^0 FOR THE DEBYE-HÜCKEL EQUATION FOR SINGLE ION ACTIVITY COEFFICIENTS (CITED FROM ADAMS, 1971).

ION	ai
H^+	9
Mg^{2+}	8
Ca^{2+}	6
CO_3^{2-} HCO_3^- $H_2PO_4^-$	4.5
SO_4^{2-} HPO_4^{2-} PO_4^{3-}	4
OH^-	3.5
NH_4^+	2.5

APPENDIX 3

THE RESULTS OF SEEDED EXPERIMENTS

Table A.3.1 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.01g of 10-15 μm CALCITE-SEEDS ADDED.

Time, m	60	90	120	150	180	264 ±2.8	327
pH	7.13 ±0.02	7.25 ±0.02	7.36 ±0.04	7.42 ±0.02	7.48 ±0.03	7.55 ±0.03	7.54 ±0.01
pH'	7.06	7.21	7.34	7.44	7.51	7.59	7.51
NT	0.968	1.452	1.936	2.420	2.904	4.260 ±0.50	5.277
[Ca]'	9.970	9.919	9.897	9.883	9.852	9.437 ±0.11	8.693 ±0.03
[CaCO]'	-0.020	0.134	0.136	0.126	0.138	0.583	1.448
S'	0.270	0.288	0.288	0.287	0.289	0.338	0.424
SI'	0.75	1.49	2.62	4.13	5.77	7.74	5.10
base 3	1.2993	1.830	2.360	2.889	3.417	4.886	5.986
base 4	1.2840	1.698	2.196	2.525	2.906	3.413	3.314
[Ca]''						9.295 ±0.04	8.612 ±0.11
PR'	3.826	1.654	0.524	0.436	1.392	9.614	21.15

Notes :

The unit of NT, [Ca]', [CaCO]', base 3, base 4, and [Ca]'' is mM.

SO, the initial seed surface area, 0.273 cm^2 ml^{-1}.

Te, the reaction time in minutes from the start of experiment to when solution pH is 7.12, e.g. SI=1, 58.0±9.8 minutes.

AADR, Apparent ammonia dissolution rate, 16.136 μM m^{-1}.

NT, the concentration of total ammoniacal-N calculated from AADR.

pH, is the measured solution pH.

pH', the solution pH estimated from the regression equation.

[CaCO]'=base 4 - base 3, is the concentration (mM) of newly formed calcium carbonate.

S', the estimated surface area of particle in cm^2 ml^{-1}.

SI', the estimated value of SI.

[Ca]', the concentration of calcium ion estimated by the calculating program.

[Ca]'', the measured concentration of calcium using a calcium-sensitive electrode.

PR', the precipitation rate (μm m^{-1}) estimated by the regression equation.

Table A.3.2 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.025g of 10-15 μm CALCITE-SEEDS ADDED.

Time, m	60	90	120	150	180	253 ±19.8	303
pH	7.26 ±0.03	7.36 ±0.02	7.44 ±0.01	7.47 ±0.02	7.49 ±0.01	7.47 ±0.03	7.46 ±0.04
pH'	7.24	7.37	7.44	7.48	7.49	7.46	7.46
NT	0.932	1.398	1.864	2.330	2.796	3.930 ±0.58	4.707
[Ca]'	10.216	10.216	10.164	10.035	9.834	9.200 ±0.08	8.822 ±0.11
[CaCO]'	0.004	-0.023	0.014	0.150	0.377	1.102	1.527
S'	0.682	0.679	0.683	0.699	0.726	0.806	0.852
SI'	1.72	3.06	4.30	5.04	5.15	4.24	4.09
base 3	1.674	2.186	2.696	3.209	3.719	4.953	5.795
base 4	1.7420	2.201	2.656	2.846	2.978	2.823	2.745
[Ca]'						9.147 ±0.12	8.728 ±0.41
PR'	-3.236	0.739	3.991	6.521	8.330	9.714	8.195

S0=0.682, Te=36.0±0.0, AADR=15.53.

Table A.3.3 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.1g 10-15 μm CALCITE-SEEDS ADDED.

Time, m	20	40	60	90	120	133.3 ±12.7	196.3
pH	7.15 ±0.03	7.26 ±0.02	7.33 ±0.04	7.40 ±0.04	7.45 ±0.03	7.47 ±0.01	7.40 ±0.01
pH'	7.16	7.25	7.33	7.41	7.45	7.46	7.40
NT	0.376	0.753	1.130	1.695	2.260	2.504 ±0.30	3.696
[Ca]'	10.371	10.320	10.269	10.169	10.006	9.906 ±0.03	9.171 ±0.02
[CaCO]'	-0.022	-0.020	0.061	0.152	0.325	0.437	1.284
S'	2.724	2.729	2.734	2.745	2.765	2.778	2.877
SI'	1.19	1.81	2.56	3.71	4.50	4.62	3.23
base 3	1.3273	1.744	2.158	2.779	3.400	3.668	4.970
base 4	1.3490	1.744	2.053	2.417	2.714	2.844	2.392
[Ca]''						9.661 ±0.04	9.129 ±0.10
PR'	0.956	1.548	2.498	4.590	7.485	9.025	18.46

S0=2.727, Te=17.0±3.5, AADR=18.785.

Table A.3.4 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.5g 10-15 μm CALCITE-SEEDS ADDED.

Time, m	20	60	90	120	150 ±5.0	193 ±0.0	246
pH	7.17 ±0.02	7.30 ±0.01	7.38 ±0.02	7.42 ±0.02	7.45 ±0.03	7.42 ±0.04	7.36 ±0.01
pH'	7.17	7.30	7.37	7.42	7.44	7.43	7.35
NT	0.347	1.042	1.562	2.083	2.604	3.350 ±0.35	4.270
[Ca]'	10.402	10.266	10.151	10.003	9.806 ±0.08	9.417 ±0.10	8.783
[CaCO]'	0.0218	0.150	0.264	0.420	0.638	1.080	1.810
S'	13.638	13.653	13.666	13.685	13.710	13.763	13.848
SI'	1.27	2.29	3.14	3.84	4.18	3.86	2.52
base 3	1.458	2.224	2.798	3.369	3.939	4.758	5.761
base 4	1.4140	1.914	2.306	2.530	2.710	2.513	2.170
[Ca]''					9.837 ±0.06	9.456 ±0.07	
PR'	0.568	3.263	5.284	7.306	9.327	12.22	15.80

S0=13.635, Te=10.0±0.0, AADR=17.36.

Table A.3.5 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 1.0g 10-15 μm CALCITE-SEEDS ADDED.

Time, m	20	40	60	120	138 ±3.0	180	210 ±0.0
pH	7.16 ±0.02	7.23 ±0.02	7.30 ±0.01	7.40 ±0.03	7.40 ±0.02	7.39 ±0.02	7.37 ±0.02
pH'	7.16	7.23	7.29	7.40	7.41	7.40	7.36
NT	0.338	0.676	1.014	2.029	2.333	3.043 ±0.40	3.550
[Ca]'	10.399	10.331	10.260	9.9746	9.852 ±0.05	9.485 ±0.05	9.154
[CaCO]'	0.029	0.093	0.162	0.461	0.596	1.014	1.395
S'	27.274	27.281	27.289	27.325	27.341	27.390	27.435
SI'	1.24	1.69	2.18	3.44	3.58	3.33	2.72
base 3	1.4533	1.826	2.200	3.314	3.648	4.425	4.982
base 4	1.3820	1.626	1.914	2.413	2.409	2.344	2.230
[Ca]''					9.844 ±0.05	9.415 ±0.18	
R'	2.839	3.214	3.794	6.766	8.019	11.59	14.69

S0=27.274, Te=10.0±0.0, AADR=16.905.

Table A.3.6 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.025g 30-35 μm CALCITE-SEEDS ADDED.

Time, m	20	60	120	150	180	223 ±10.4	303
pH	6.80 ±0.01	7.18 ±0.01	7.42 ±0.01	7.47 ±0.02	7.50 ±0.02	7.52 ±0.01	7.51 ±0.02
pH'	6.81	7.15	7.43	7.48	7.50	7.50	7.50
NT	0.354	1.063	2.126	2.657	3.188	3.950 ±0.60	5.367
[Ca]'	10.075	10.029	9.9986	9.8843	9.684	9.296 ±0.03	8.616 ±0.06
[CaCO]'	-0.112	0.031	0.007	0.119	0.341	0.781	1.545
S'	0.257	0.264	0.262	0.268	0.277	0.296	0.328
SI'	0.24	1.14	3.95	5.04	5.42	5.08	4.81
base 3	0.389	1.420	2.582	3.162	3.743	4.567	6.099
base 4	0.5970	1.443	2.529	2.841	3.044	3.181	3.083
[Ca]''						9.242 ±0.07	8.380 ±0.04
R'	-14.15	-6.06	3.075	6.286	8.595	10.329	8.620

S0=0.262, Te=52.0±0.0, AADR=17.713.

Table A.3.7 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.05g 30-35 μm CALCITE-SEEDS ADDED.

Time, m	20	60	120	150	180	216 ±10.0	290 ±13.0
pH	6.86 ±0.08	7.17 ±0.06	7.38 ±0.06	7.44 ±0.04	7.48 ±0.03	7.49 ±0.01	7.48 ±0.02
pH'	6.87	7.15	7.39	7.45	7.48	7.48	7.48
NT	0.310	0.931	1.862	2.328	2.793	3.352	4.500 ±0.46
[Ca]'	10.131	10.090	10.045	9.955	9.801	9.555 ±0.03	8.994 ±0.06
[CaCO]'	-0.179	0.003	0.005	0.092	0.257	0.536	1.167
S'	0.516	0.524	0.525	0.528	0.536	0.548	0.576
SI'	0.31	1.13	3.39	4.35	4.86	4.93	4.67
base 3	0.3413	1.357	2.377	2.887	3.394	4.001	5.251
base 4	0.6860	1.410	2.303	2.645	2.908	2.970	2.882
[Ca]''						9.655 ±0.26	8.907 ±0.08
PR'	-3.006	-0.838	2.414	4.040	5.666	7.617	11.63

S0=0.524, Te=54.5±1.0, AADR=15.517.

Table A.3.8 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.10g 30-35 μm CALCITE-SEEDS ADDED.

Time, m	20	40	60	90	120	150	176 ±5.0
pH	6.94 ±0.01	7.11 ±0.04	7.19 ±0.03	7.30 ±0.03	7.37 ±0.03	7.40 ±0.03	7.40 ±0.03
pH'	6.96	7.08	7.19	7.30	7.38	7.41	7.39
NT	0.280	0.559	0.839	1.258	1.677	2.097	2.460 ±0.30
[Ca]'	10.214	10.193	10.182	10.164	10.104	9.962 ±0.07	9.755 ±0.07
[CaCO]'	-0.260	-0.307	0.0081	0.0218	0.0816	0.2312	0.4316
S'	1.0370	1.0348	1.0492	1.0498	1.0525	1.0593	1.0683
SI'	0.43	0.95	1.36	2.25	3.08	3.49	3.43
base 3	0.308	0.614	1.495	1.955	2.414	2.874	3.271
base 4	0.8270	1.228	1.479	1.912	2.251	2.412	2.408
[Ca]''						9.611 ±0.01	9.388 ±0.04
PR'	-7.157	-4.914	-2.672	0.693	4.057	7.421	17.06

S0=1.049, Te=45.0±6.0, AADR=13.977.

Table A.3.9 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.5g 30-35 μm CALCITE-SEEDS ADDED.

Time, m	20	40	60	90	120	162 ±5.0	216.5 ±21.9
pH	7.12 ±0.06	7.21 ±0.04	7.27 ±0.04	7.33 ±0.07	7.38 ±0.02	7.39 ±0.02	7.37 ±0.02
pH'	7.13	7.20	7.26	7.33	7.38	7.40	7.36
NT	0.257	0.514	0.770	1.156	1.541	2.080 ±0.38	2.780
[Ca]'	10.398	10.363	10.328	10.263	10.168	9.960 ±0.05	9.536 ±0.04
[CaCO]'	-0.013	0.014	0.043	0.102	0.198	0.427	0.916
S'	5.243	5.245	5.246	5.249	5.253	5.263	5.286
SI'	1.06	1.46	1.91	2.61	3.19	3.50	2.85
base 3	1.1493	1.742	2.300	3.036	3.827	4.009	3.634
base 4	1.259	1.552	1.784	2.053	2.307	2.356	2.239
[Ca]''						9.825 ±0.14	9.350 ±0.08
PR'	1.090	1.425	1.915	2.940	4.313	6.821	11.09

S0=5.244, Te=20.0±0.5, AADR=12.840

Table A.3.10 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 1.0g 30-35 μm CALCITE-SEEDS ADDED.

Time, m	20	60	100	120	138 ±2.0	180	210 ±10.0
pH	7.15 ±0.04	7.33 ±0.03	7.38 ±0.02	7.38 ±0.02	7.38 ±0.03	7.37 ±0.02	7.36 ±0.02
pH'	7.15	7.32	7.38	7.39	7.38	7.36	7.36
NT	0.324	0.971	1.619	1.943	2.234 ±0.30	2.914	3.400
[Ca]'	10.385	10.318	10.107	9.947	9.784 ±0.07	9.389	9.145 ±0.04
[CaCO]'	-0.011	0.032	0.257	0.439	0.625	1.075	1.348
S'	10.488	10.490	10.500	10.508	10.516	10.537	10.549
SI'	1.18	2.54	3.27	3.26	3.12	2.73	2.69
base 3	1.337	2.051	2.764	3.121	3.440	4.184	4.717
base 4	1.350	2.055	2.306	2.302	2.299	2.237	2.179
[Ca]''					9.573 ±0.19		8.986 ±0.18
PR'	-6.016	6.627	15.138	17.844	19.397	19.764	17.238

S0=10.488, Te=16.0±2.0, AADR=16.957

Table A.3.11 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.05g 75-150 μm CALCITE-SEEDS ADDED.

Time, m	20	120	180	235	312 ±15.0	376.5 ±21.0	550
pH	6.60 ±0.08	7.33 ±0.01	7.50 ±0.02	7.58 ±0.02	7.62 ±0.03	7.61 ±0.03	7.58 ±0.02
pH'	6.61	7.30	7.51	7.60	7.62	7.57	7.54
NT	0.312	1.874	2.811	3.670	4.873	5.872 ±0.46	8.590
[Ca]'	10.002	9.848	9.880	9.770	9.256 ±0.12	8.616 ±0.08	7.180
[CaCO]'	-0.021	0.098	0.006	0.096	0.676	1.416	3.033
S'	0.151	0.152	0.151	0.152	0.160	0.169	0.189
SI'	0.09	2.15	5.62	8.46	8.70	6.76	4.84
base 3	0.3433	2.088	3.110	4.041	5.342	6.421	9.325
base 4	0.376	2.046	3.050	3.680	4.028	3.911	3.584
[Ca]''					8.801 ±0.24	8.152 ±0.22	
PR'	-3.321	2.102	5.355	8.338	12.514	15.984	25.420

S0=0.151, Te=71.8±2.9, AADR=15.596.

Table A.3.12 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.1g 75-150 μm CALCITE-SEEDS ADDED.

Time, m	20	120	210	240	309	372
					±6.3	±8.5
pH	6.63	7.31	7.52	7.54	7.56	7.54
	±0.03	±0.04	±0.04	±0.02	±0.03	±0.03
pH'	6.63	7.30	7.53	7.55	7.56	7.56
NT	0.322	1.930	3.378	3.860	4.970	5.983
					±0.53	
[Ca]'	10.006	9.834	9.668	9.509	8.994	8.504
					±0.10	±0.10
[CaCO]'	-0.026	0.050	0.177	0.348	0.930	1.483
S'	0.302	0.303	0.305	0.307	0.314	0.322
SI'	0.10	2.23	6.06	6.65	6.51	6.18
base 3	0.353	2.026	3.600	4.122	5.324	6.412
base 4	0.403	1.951	3.191	3.339	3.483	3.302
[Ca]''					8.691	8.079
					±0.20	±0.03
PR'	-5.146	-1.784	4.293	5.783	9.211	12.341

S0=0.302, Te=76.7±2.3, AADR=16.084.

Table A.3.13 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.3g 75-150 μm CALCITE-SEEDS ADDED.

Time, m	20	60	80	100	120	180	276
						±0.0	±0.0
pH	6.84	7.16	7.24	7.32	7.36	7.44	7.42
	±0.03	±0.01	±0.02	±0.02	±0.04	±0.04	±0.04
pH'	6.85	7.14	7.25	7.32	7.37	7.44	7.43
NT	0.288	0.863	1.151	1.438	1.726	2.589	3.970
							±0.42
[Ca]'	10.129	10.113	10.115	10.106	10.073	9.794	9.107
						±0.10	±0.10
[CaCO]'	-0.173	0.024	0.005	-0.000	0.024	0.323	1.099
S'	0.905	0.908	0.908	0.908	0.908	0.912	0.922
SI'	0.28	1.09	1.74	2.46	3.13	4.04	3.69
base 3	0.3163	1.374	1.690	2.006	2.321	3.265	4.767
base 4	0.655	1.378	1.661	2.002	2.198	2.646	2.505
[Ca]''						9.524	8.648
						±0.13	±0.03
PR'	-13.73	-5.993	-2.743	0.940	2.518	7.315	7.261

S0=0.908, Te=53.0±1.0, AADR=14.384.

Table A.3.14 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.5g 75-150 μm CALCITE-SEEDS ADDED.

Time, m	20	90	120	150	177.5 ±2.9	226 ±10.4	252
pH	6.88 ±0.02	7.28 ±0.02	7.36 ±0.02	7.42 ±0.03	7.44 ±0.02	7.43 ±0.01	7.40 ±0.02
pH'	6.91	7.27	7.36	3.97	4.42	3.79	2.92
NT	0.265	1.191	1.588	1.984	2.348	2.990 ±0.11	3.334
[Ca]'	10.183	10.134	10.120	10.066	9.953	9.575 ±0.02	9.287 ±0.04
[CaCO]'	-0.239	0.077	0.070	0.116	0.235	0.671	1.007
S'	1.509	1.514	1.514	1.514	1.516	1.521	1.526
SI'	0.37	1.94	3.01	3.97	4.42	3.79	2.92
base 3	0.291	1.928	2.364	2.800	3.196	3.898	4.273
base 4	0.719	1.824	2.199	2.531	2.649	2.579	2.397
[Ca]''						9.376 ±0.08	9.045 ±0.08
PR'	-7.136	-0.925	1.736	4.398	6.838	11.14	13.45

S0=1.513, Te=44.4±1.5, AADR=13.230.

Table A.3.15 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 1.0g 75-150 μm CALCITE-SEEDS ADDED.

Time, m	20	60	80	100	123	180 ±0.0	231 ±0.0
pH	7.06 ±0.05	7.29 ±0.04	7.32 ±0.02	7.36 ±0.01	7.38 ±0.01	7.38 ±0.02	7.37 ±0.02
pH'	7.06	7.27	7.33	7.36	7.38	7.37	7.37
NT	0.287	0.862	1.150	1.437	1.768	2.587	3.320 ±0.25
[Ca]'	10.308	10.300	10.265	10.195	10.072	9.646 ±0.04	9.280 ±0.04
[CaCO]'	-0.395	-0.026	0.002	0.072	0.208	0.691	1.103
S'	3.020	3.025	3.025	3.026	3.028	3.034	3.040
SI'	0.78	2.00	2.60	3.04	3.26	2.98	2.83
base 3	0.3163	1.739	2.056	2.372	2.736	3.633	4.432
base 4	1.094	1.871	2.005	2.201	2.304	2.295	2.232
[Ca]''						9.679 ±0.01	9.122 ±0.06
PR'	-6.951	0.113	2.868	5.105	7.037	8.870	6.943

S0=3.025, Te=30.0±6.0, AADR=14.372.

Table A.3.16 CHANGES OF THE COMPONENTS OF SOLUTION DURING THE REACTION PERIOD WITH 0.1g 212-150 μm CALCITE-SEEDS ADDED.

Time, m	20	60	180	210	240	367	432
						±0.0	±0.0
pH	6.58	7.06	7.50	7.54	7.55	7.63	7.62
	±0.01	±0.01	±0.02	±0.02	±0.04	±0.01	±0.01
pH'	6.65	6.95	7.49	7.56	7.61	7.65	7.62
NT	0.319	0.956	2.869	3.347	3.826	5.850	6.886
						±0.30	
[Ca]'	10.016	9.873	9.809	9.788	9.725	8.916	8.314
						±0.04	±0.04
[CaCO]'	-0.038	0.099	0.006	0.006	0.059	0.963	1.646
S'	0.187	0.188	0.187	0.187	0.1888	0.195	0.200
SI'	0.11	0.45	5.23	7.11	8.76	9.76	8.17
base 3	0.350	1.047	3.003	3.522	4.040	6.221	7.306
base 4	0.359	1.090	3.049	3.348	3.421	4.106	3.985
[Ca]''						8.712	8.127
						±0.15	±0.17
PR'	-7.588	-5.584	0.428	1.931	3.434	9.797	13.05

S0=0.187, Te=80.0±11.3, AADR=15.940.

APPENDIX 4

THE DETERMINATION OF DOC AND SOIL BUFFER CAPACITY

4.1 THE DETERMINATION OF DOC IN SOIL SOLUTION

A procedure for measuring the concentration of DOC (water dissolved organic matter) by UV spectrophotometer was developed in this study in order to measure changes of DOC in soil solutions after urea application. This method is based on the fact that most of DOC absorbs ultra-violet radiations. It is simpler and more economic than the combustion method (Van Hall et al, 1963).

The Beer-Lambert law assumes that A, the absorbance or extinction coefficient or optical density is given by

$$A=\log ((I_0)/I)=e\ C\ l,$$

where e is the extinction coefficient, C is the concentration of absorbing solute, and l is the path length (cited from Schnitzer and Khan ,1972).

Schnitzer and Khan (1972) reported that graphs of the absorption spectra of neutral, alkaline, and acidic aqueous solutions of HA's and FA's against wavelengths ranging from visible to UV, are all featureless and that the optical density decreases as the wavelength increases. However, Dobbs et al (1972) reported only a gradual change in the 240-270 nm region.

Since the optical density of DOC varies with wavelength, different workers have measured different wavelengths according to the materials they were using or the limits of their instruments. Wedgwood (1952) suggested using UV absorbance at 366 nm to assess the quality (i.e. DOC content) of an effluent. This wavelength was chosen because it coincided with one of the sharp spectral lines of the low pressure mercury lamp. McLachlan (1981)

used the absorbance at 280 nm for analysing ligninsulphonic acid and sulphite effluent, and 265 nm for kraft effluent. These wavelengths corresponded to the characteristic peaks or shoulders of the aromatic structure of the lignin. Hoather (1953) measured the absorbance of a variety of waters between 210 to 700 nm and recommended a wavelength of 275 nm. Dornbush and Ryckman (1962) used the 200-285 nm region, and 253.7 nm was employed by Bramer et al (1966) and Briggs and Melbourne (1967) (cited from Dobbs et al, 1972).

With the exception of transition metal ions, the common inorganic salts do not have significant absorbance above 250 nm. At wavelengths below 235 nm nitrate and bromide contribute significantly to the total absorbance. According to Bastian et al ,1957, (cited from Dobbs et al 1972) nitrates show absorbance bands with maxima at 203 nm and 302 nm.

Chen et al (1977) reported that the ratio of optical density at 465 nm to that of 665 nm was characteristic of DOC. The ratio was independent of the concentration of humic material, but responded to the distribution of molecular sizes of DOC.

Most of the techniques developed to measure the concentration of DOC by spectrophotometer are for application in the water industry; none of these was an optimum wavelength for measuring DOC in soil solution. Hence it was necessary to find a suitable wavelength (in the visible or UV range) for measuring the changes of DOC in soil solution.

4.1.1 Materials and Methods

The procedures for measuring DOC in soil solution of the three soils (Beg., Uni., and VWH) are identical and are as follows :

(1) 300 g of moistened soil samples (0.1 bar capillary potential) containing urea (1 M urea in soil solution) were put loosely into two 200 ml centrifuge tubes, then sealed with lids and put in a constant temperature (25^0 C) room for four days.

(2) The soil samples were centrifuged at 10,000 rpm for 30 minutes, and the supernatant was filtered through Whatman No. 2 paper.

(3) The supernatant solution was put into a 100 ml centrifuge tube and centrifuged at 18,000 rpm for 30 minutes, and the supernatant filtered through a 0.2 μm filter (millipore).

(4) The DOC concentration of the filtrate was determined by the modified Walkley-Black method (Page et al, 1982), and expressed in molarity of carbon.

(5) A series of dilutions were prepared from the same concentrated solution (from (4)).

(6) In order to widen the range for measuring the concentration of DOC, the transmission (T %) of double-distilled water was adjusted to the reading of 700 % with the wavelength at 665 nm.

(7) The transmissions of the diluted solutions were measured at 310, 350, 465, 500, and 665 nm wavelengths by a UV spectrophotometer (Pye Unicam SP 8-100).

(8) Standard curves were made for each soil (Figure A.4.1) of T % for UV wavelengths at 310, 350, 465, and 665 nm against concentration of DOC.

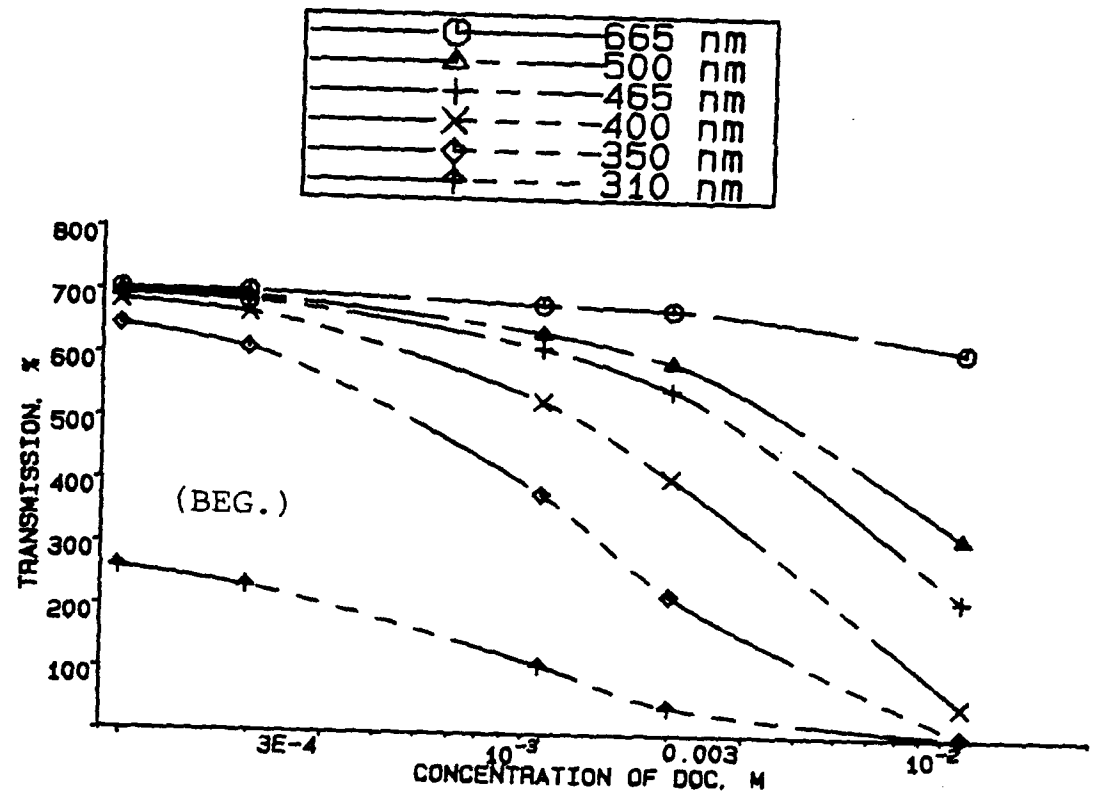
4.1.2 Results and Discussion

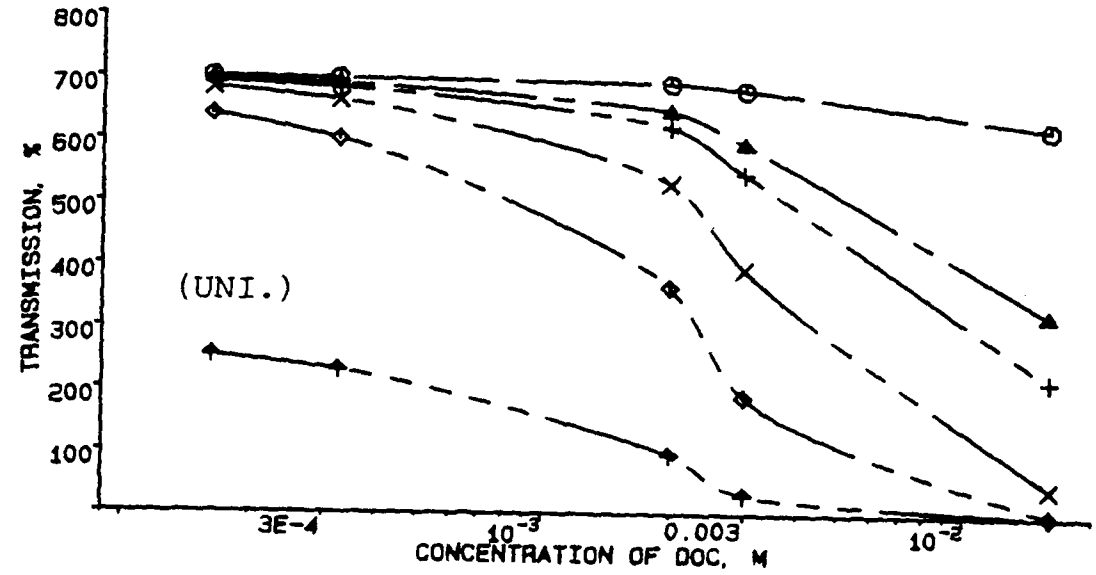
Figure A.4.1 shows that the graphs of optical density (transmission, T %) against the concentration of DOC (from 10^{-5} to 0.01 M) are similar for the three soils in the range of wavelengths tested. The transmission decreases sharply at wavelengths lower than 350 nm. At 310 nm wavelength the sensitivity of readings to

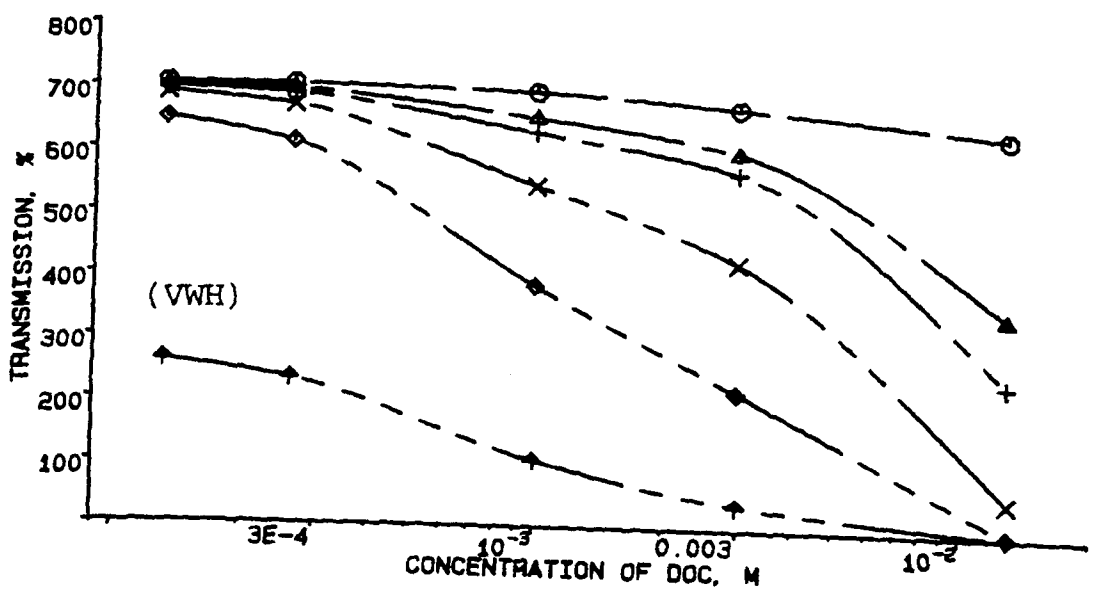
DOC concentration was significantly lower than that of 350 nm. When the concentration of DOC was greater than 3 mM in carbon, the transmission readings were already too low to respond the changes of DOC concentrations. Since the concentrations of DOC in most soil solution in this study were much higher than mM levels, if we used the wavelength of 310 nm or shorter, it would have been necessary to prepare samples of a high magnitude of dilutions. This would have caused large errors in measurement and increased operating difficulties. Thus it is not suitable to use this range of wavelengths. Wavelengths of 400, 465, 500, and 665 nm were also unsuitable, because at low concentration ranges (10^{-5} to $5x10^{-4}$ M) of DOC, the T % at these wavelengths did not distinguish DOC significantly. At 350 nm wavelength, the responses of T % were proportional to the concentrations of DOC, especially over the range of $1x10^{-4}$ to about 0.02 M of DOC. So the wavelength of 350 nm was used to measure the concentration of DOC in soil solutions during reactions.

If it is true that the ratio of optical density at 465 nm to that at 665 nm is independent of the concentration of DOC as reported by Chen et al (1977), the standard curves of these two wavelengths should be parallel to each other because the set of concentrations of DOC were diluted from the same original solution thus the molecular sizes distribution of a series (i.e. for a soil solution) of DOC solutions should be the same. However, the results from these three soils disagree with their results.

Figure A.4.1 THE STANDARD CURVES OF T % VS DOC (M) AT DIFFERENT WAVELENGTHS 665, 500, 465, 400, 350, AND 310 nm FOR BEG., UNI., AND VWH SOILS.







4.2 SOIL BUFFER CAPACITY

It is well known that the response of soil pH to the addition of base is determined by the initial soil pH (pH_0), the quantity of base (X_{base}) added, and soil buffer capacity (dpH/dBase) as :

$$pH_f = pH_0 + (dpH/dBase)\ (X_{base}) \qquad (A.4.1)$$

where pH_f is the equilibrium soil pH. In order to estimate changes of soil pH or the amount of base transferred from the solution to the CEC during a pH change, the value of soil buffer capacity must be known. Different amounts of base (NaOH) were added (calculated as me/100 g of oven-dry soil) to the three soils (Beg., Uni., and VWH) to determine their soil buffer capacities.

4.2.1 Materials and Methods

A number of soil samples (equivalent to give 20 grams oven-dry soil) were put in 150 ml centrifuge tubes with different amounts of NaOH (0.1 N) with sufficient double-distilled water to make 20 ml, then shaken overnight (at least 24 hours) before measuring pH.

The centrifuge tubes were sealed with wax in order to prevent carbon dioxide entering the soil suspension. Three replications of each treatment were made.

4.2.2 Results

Plotting the measured soil pH against the amount of base added (shown in Figure A.4.2) shows that the changes of soil pH were almost directly proportional to the added base (X_{base}, in me/100g oven-dry soil). After regressing the measured soil pHs on the quantities of base added, the responses of soil pH to base for Beg., Uni., and VWH soils are described by empirical

equations A.4.2, A.4.3 and A.4.4, respectively, as follows :

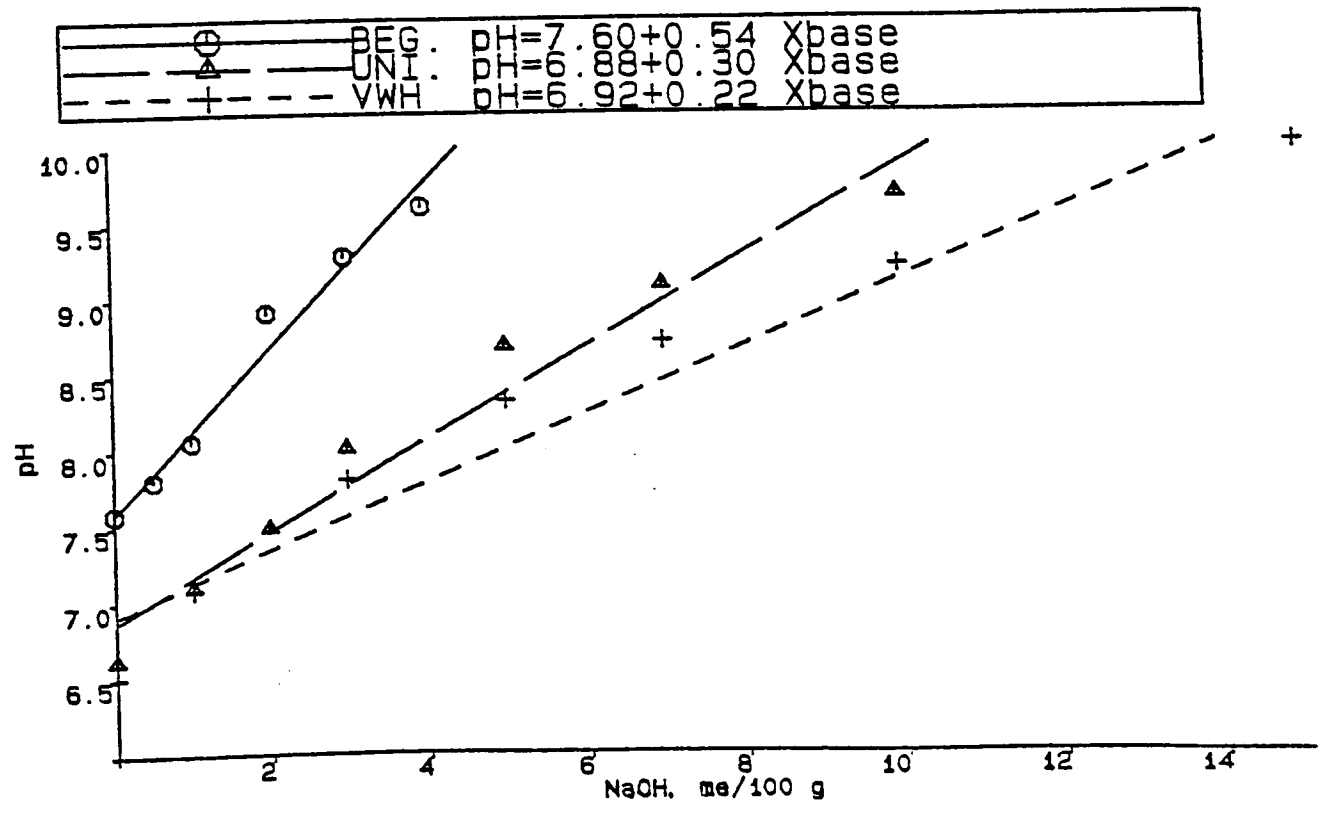
$$pH_f = 7.60 \pm 0.06 + 0.54 \pm 0.03 \ (X_{base}) \qquad (A.4.2)$$

$$pH_f = 6.88 \pm 0.09 + 0.30 \pm 0.02 \ (X_{base}) \qquad (A.4.3)$$

$$pH_f = 6.92 \pm 0.11 + 0.22 \pm 0.01 \ (X_{base}) \qquad (A.4.4)$$

The values of R^2 of these three equations are 0.97, 0.94, and 0.95, and the regressions are statistically significant at the 99.9 per cent level. Hence the slope of these equations should present the soil buffer capacity (dpH/dBase) of their corresponding soils, and may be used to predict the changes of soil pH after a known quantity of base is added. Strictly speaking it is the base taken by the soil - some of the added base remaining in solution. The reciprocal of the slopes of equations A.4.2 to A.4.4 is the soil pH buffer capacity (dBase/dpH) for the three soils. The soil buffer capacities illustrate that soil pH will be raised 0.5, 0.3 and 0.22 units for Beg., Uni., and VWH soil; respectively, when one milliequivalent of base is added to 100 grams of oven-dry soils.

Figure A.4.2 THE CHANGES IN SOIL pH AFTER VARYING AMOUNT OF BASE IS ADDED (NaON, me/100 OVEN-DRY SOIL) TO BEG. UNI., AND VWH SOILS.



The way to determine the value of pH_0 was identical for the three soils which were kept at P_{CO2} 0.00484 atm, so that only the example of Begbroke soil is presented. At low pH (pH < 7.50) region after urea added to the soils, the quantity of calcium carbonate precipitated may be zero or negligible. So overall the source of base (X_{base}) in the soils may be due to the quantity of ammoniacal-N released from the hydrolysis of urea. The first measured soil pH and ammoniacal-N of the soil treated with 0.05 M urea may meet the condition that no calcium carbonate precipitated, so these data were used to calculate the value of pH_0. Soil pH and ammoniacal-N were 7.29 (pH_f) and 0.71 me/100g (X_{base}), respectively after the experiment had proceeded for 12.5 hours and no newly formed calcium carbonate detected. Meanwhile the soil system should have been equilibrated under the P_{CO2}. After substituting these values into equation A.4.2, pH_0 becomes 6.89 and equation A.4.2 becomes equation A.4.5.

$$pH_f=6.89 + 0.54\ (X_{base}) \qquad (A.4.5)$$

From the same procedures, equations A.4.3 and A.4.4 become equations A.4.6 and A.4.7 for Uni. and VWH soils, respectively.

$$pH_f=6.61 + 0.30\ (X_{base}) \qquad (A.4.6)$$

$$pH_f=6.45 + 0.22\ (X_{base}) \qquad (A.4.7)$$

Given these equations it becomes possible to predict soil pH from any known addition of base or ammoniacal-N within the simulation ranges.

APPENDIX 5

THE DETERMINATION OF NEWLY FORMED CALCIUM CARBONATE AND RESULTS OF SOIL EXPERIMENTS WITH UREA APPLICATION.

The calculation of newly formed calcium carbonate in soils from 2 M KCl extract during the experimental period

In soil calcium ions exist in the soil solution and as exchangeable calcium. Without any amendments, exchangeable calcium ion normally occupies the major part of CEC in natural soils. Usually the total amount of a cation held on the exchange sites of a soil can be predicted from its activity in solution and the adsorption isotherm.

Potassium chloride (2 M) solution is commonly used to displace exchangeable soil cations. It was used in this study (see section materials and methods in chapter 5) to displace ammonium-N from CEC sites; presumably it replaced exchangeable calcium ions as well. If there was no further precipitation of calcium carbonate occurring during the processing for extracting, the concentration of calcium ionsin the extract could be referred to as the quantity of calcium ions remaining in CEC sites. Considering the experimental situation, this was a rational assumption. The reasons were :

(1) When the soil sample was immersed in the extracting solution (2 M KCl) the ion activity product of calcium carbonate would have been greatly diluted, temporarily. For example in the case of the VWH soil, when 7.49 grams of moistened soil (containing 2.49 grams of water at 0.1 bar capillary water potential) were added to 50 ml of extracting solution the soil solution was diluted 1/21.8 times. The ion activity product of calcium carbonate would have been diluted temporarily by a factor of

1/444 since both calcium and carbonate ions in solution were diluted to the same extent. The corresponding dilution factors for Beg. and Uni. soils would have been 1/577, and 1/1386.

(2) The concentration of calcium ions in the KCl extract would increase (about 3 times) when the exchangeable calcium in CEC sites was replaced to solution. However the high ionic strength of 2 M KCl would magnify the dilution effect. The activity coefficient of calcium ions (f_{Ca}) in 2 M KCl solution was calculated from the ratio of activity (measured by a calcium-sensitive electrode) over concentration (measured by EDTA titration), to be 0.237±0.07.

<u>The measurement of newly formed calcium carbonate from acid decomposition method</u>

Acid decomposition produced a total amount of $[CO_2]t$, which corresponded to :

$$[CO_2]t=[HCO_3^-] + [CO_3^{2-}] + [NH_4HCO_3^0] + [NH_4CO_3^-] + [CaHCO_3^+] + [CaCO_3^0] + [CaCO_{3(S)}] \quad (A.5.1)$$

where the definitions of symbols are the same as in chapter 3.

When we define $[CO_2]'$ the measured carbon dioxide which is converted from solution components as

$$[CO_2]'=[HCO_3^-] + [CO_3^{2-}] + [NH_4HCO_3^0] + [NH_4CO_3^-] + [CaHCO_3^+] + [CaCO_3^0] \quad (A.5.2)$$

Then $CaCO_{3(S)}''$, equivalent to the carbon dioxide converted from $[CaCO_{3(S)}]$ is given by :

$$CaCO_{3(S)}''=[CO_2]t - [CO_2]' \quad (A.5.3)$$

The quantities on the right hand side of equation A.5.2 were calculated from the measured pH, the concentration of ammoniacal-N, and the measured activity of calcium ions. The method of calculation has been discussed in chapter 3 .

The amount of newly formed calcium carbonate in soil samples

treated with 0.5 M urea for three days (three replications for each of the three soils, Beg., Uni., and VWH) were used to compare these two methods (2 M KCl extraction and acid decomposition methods) mentioned above.

In Table A.5.1, soil pH was directly measured by inserting a pH electrode into soil samples, D_{CACO3} was the difference between the amount of newly formed calcium carbonate determined as $CaCO_{3(S)}$'' by the acid decomposition method and $CaCO_{3(S)}$' determined by subtracting the amount of calcium ions remaining the extract solution from the initial amount of exchangeable calcium ions.

Table A.5.1 THE COMPARISON OF NEWLY PRECIPITATED CALCIUM CARBONATE ESTIMATED BY THE CALCIUM IONS REMAINING IN CEC SITES AND BY THE ACID DECOMPOSITION METHOD.

Soils	Beg.	Uni.	VWH
pH	8.67±0.01	8.90±0.01	8.78±0.01
Ca'	9.43±1.10	1.99±0.06	2.49±0.20
$CaCO_{3(S)}$'	6.45	17.31	22.47
$[CO_2]t$	18.7±2.0	20.4±0.5	25.2±1.3
[CO2]'	1.5	4.5	4.0
$CaCO_{3(S)}$''	7.77	16.9	21.2
D_{CaCO3}	1.32	-0.4	-1.3

The unit for all these quantities is me/100 g of oven-dry soil, except pH.
Ca' is the amount of exchangeable calcium remaining in soils, as estimated from the extract (2 M KCl).
$CaCO_3$' is the newly formed calcium carbonate calculated by subtracting the calcium ion remaining in the CEC from the original calcium content.
$CaCO_3$'' was calculated by equation A.5.3.
$[CO_2]t$ was calculated by equation A.5.1.
$[CO_2]'$ was calculated by equation A.5.2.
$D_{CaCO3}=CaCO_3'' - CaCO_3'$.

The values of D_{CACO3} are within the standard deviations of the

two methods of determination. The standard deviation of results from the acid decomposition method was greater than that from measurements of calcium ions remaining on the CEC. D_{CACO3} of experiments using Begbroke soil was 1.32 me/100g, but the variation of determinations using the acid decomposition method was 2.0 me/100g. The higher determination errors of calcium carbonate in Begbroke soil than in the others (0.5 me/100 g of oven-dry soil for Uni. and 1.3 me/100 g of oven-dry soil for VWH soil) may be due to its significantly higher original content of calcium carbonate i.e. 9.10±0.67 me/100 g of oven-dry soil for Beg. but only 0.69±0.00 and 0.40±0.00 for Uni. and VWH soils respectively. The consistency of the values for newly precipitated calcium carbonate determined by these two methods permits us to use the 2 M KCl extract to determine the non-precipitated calcium ions and hence to estimate the amount of newly precipitated calcium carbonate.

Table A.5.2 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.05 M UREA WAS ADDED TO BEGBROKE SOIL CONTAINING CALCITE-SEEDS (5 % IN OVEN-DRY SOIL).

Time, hour	13	23	36.5	60	83
pH	7.25	7.52	7.65	7.77	7.76
$(Ca)_{(s)}$, mM	6.004	5.461	4.072	5.335	4.01
$[Ca]_{(s)}$, mM	11.50	10.40	7.63	10.5	7.57
♥Ca, me/100g	16.56	16.95	17.34	16.82	16.30
♦$CaCO_3$, me/100g	0.0	0.39	0.0	0.52	1.04
P, $x10^5$ M	2.56	3.00	2.88	3.38	3.62
DOC, mM	0.68	0.54	0.62	0.82	0.85
$NT_{(s)}$, me/100g	0.10	0.20	0.34	0.41	0.39
$NT_{(e)}$, M	0.024	0.046	0.091	0.123	0.119
$NT_{(e)}$, me/100g	0.66	1.28	2.52	3.39	3.28
$N4/NT_{(e)}$, %	99.3	98.6	98.2	97.6	97.7
SI	2.03	5.68	7.71	17.56	12.57

N4 is the concentration of ammonium-N.
♥Ca represents the amount of calcium ion remaining on the CEC.
♦$CaCO_3$ represents the amount of calcium carbonate precipitated in soil.
P is the concentration of phosphate in soil solutions.
(s) represents the concentration in soil solution.
(e) represents the quantity in the whole soil, including in soil solution and on soil particles.

Table A.5.3 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.05 M UREA WAS ADDED TO BEGBROKE SOIL.

Time, hour	12.5	21	37	61	85
pH	7.29	7.50	7.75	7.88	7.85
$(Ca)_{(s)}$, mM	5.92	5.69	5.69	6.30	4.86
$[Ca]_{(s)}$, mM	11.2	10.9	11.1	12.7	9.41
♥Ca, me/100g	17.88	17.88	16.69	17.74	17.21
♦$CaCO_3$, me/100g	0.0	0.10	1.19	0.14	0.67
P, $x10^5$ M	1.39	1.42	1.61	1.39	1.65
DOC, mM	0.94	0.63	1.08	1.68	0.90
$NT_{(s)}$, me/100g	0.10	0.16	0.29	0.38	0.34
$NT_{(e)}$, M	0.026	0.043	0.084	0.104	0.097
$NT_{(e)}$, me/100g	0.71	1.18	2.33	2.87	2.67
$N4/NT_{(e)}$, %	99.2	98.7	97.7	97.0	97.2
SI	2.40	6.06	17.1	34.46	23.1

Table A.5.4 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.1 M UREA WAS ADDED TO BEGBROKE SOIL.

Time, hour	10.5	23.5	46	67	91	114.5
pH	7.26	7.63	7.91	8.04	8.11	8.05
$(Ca)_{(s)}$, mM	5.59	5.21	4.17	2.62	0.62	0.42
$[Ca]_{(s)}$, mM	10.5	9.97	8.24	5.08	1.16	0.78
♥Ca, me/100g	17.21	16.69	16.06	16.06	16.17	15.23
♦$CaCO_3$, me/100g	0.0	0.52	1.15	1.15	1.04	1.66
P, $x10^5$ M	3.92	3.47	4.00	4.06	6.41	9.38
DOC, mM	0.52	0.59	0.83	2.45	4.40	4.90
$NT_{(s)}$, me/100g	0.12	0.24	0.66	0.76	0.83	1.15
$NT_{(e)}$, M	0.026	0.048	0.127	0.143	0.180	0.143
$NT_{(e)}$, me/100g	0.72	1.34	3.50	3.95	4.97	3.95
$N4/NT_{(e)}$, %	99.2	98.3	96.8	95.7	94.9	95.7
SI	1.97	9.00	26.13	29.92	9.83	4.80

Table A.5.5 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.3 M UREA WAS ADDED TO BEGBROKE SOIL.

Time, hour	10.5	23.5	44	69	87	110
pH	7.46	7.88	7.93	8.33	8.58	8.58
$(Ca)_{(s)}$, mM	6.17	5.54	4.30	3.46	.54	0.50
$[Ca]_{(s)}$, mM	12.0	11.1	8.87	7.48	1.34	1.26
♥Ca, me/100g	17.21	15.80	15.80	15.09	9.35	9.00
♦$CaCO_3$, me/100g	0.0	1.41	1.41	2.12	7.86	8.21
P, $x10^5$ M	2.75	3.00	3.09	3.44	6.88	18.8
DOC, mM	0.62	0.82	1.45	1.85	4.80	25.0
$NT_{(s)}$, me/100g	0.17	0.51	1.02	1.44	4.25	4.47
$NT_{(e)}$, M	0.043	0.112	0.163	0.278	0.557	0.573
$NT_{(e)}$, me/100g	1.19	3.09	4.50	7.67	15.37	15.81
$N4/NT_{(e)}$, %	98.8	97.0	96.7	92.2	87.6	87.6
SI	5.47	30.2	29.55	150.2	74.1	68.4

Table A.5.6 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.5 M UREA WAS ADDED TO BEGBROKE SOIL.

Time, hour	19.5	43.5	67	91	114.5
pH	7.89	8.23	8.51	8.91	8.67
$(Ca)_{(s)}$, mM	5.09	3.32	0.72	0.13	0.08
$[Ca]_{(s)}$, mM	12.2	7.92	2.03	0.41	0.22
♥Ca, me/100g	15.24	14.80	11.62	4.28	4.66
♦$CaCO_3$, me/100g	0.65	1.09	4.27	11.61	11.23
P, $x10^5$ M	15.2	14.8	22.6	85.0	80.0
DOC, mM	1.26	4.10	25.0	390	355
$NT_{(s)}$, me/100g	1.05	3.04	7.45	8.97	7.73
$NT_{(e)}$, M	0.123	0.262	0.541	0.800	0.770
$NT_{(e)}$, me/100g	3.39	7.23	14.93	22.08	21.25
$N4/NT_{(e)}$, %	97.1	93.9	89.7	78.4	86.0
SI	29.1	90.8	71.6	84.0	15.9

Table A.5.7 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.7 M UREA WAS ADDED TO BEGBROKE SOIL.

Time, hour	10.5	23.5	44	69	87	110
pH	7.72	8.02	8.10	8.93	9.09	8.99
$(Ca)_{(s)}$, mM	4.50	4.20	3.36	1.84	0.08	0.09
$[Ca]_{(s)}$, mM	8.57	8.55	7.09	5.02	0.27	0.31
♥Ca, me/100g	15.09	14.30	13.65	5.13	2.20	1.46
♦$CaCO_3$, me/100g	0.80	1.59	2.24	10.76	13.69	14.43
P, $x10^5$ M	19.8	13.5	34.0	54.4	72.5	162.5
DOC, mM	0.86	1.40	1.40	47.0	149	360
$NT_{(s)}$, me/100g	0.33	0.86	1.38	4.44	14.49	15.87
$NT_{(e)}$, M	0.0558	0.175	0.344	0.770	1.065	1.146
$NT_{(e)}$, me/100g	1.54	4.83	9.49	21.25	29.39	31.63
$N4/NT_{(e)}$, %	97.9	95.9	95.2	76.6	71.7	76.3
SI	11.77	43.7	50.57	1265	113	79.9

Table A.5.8 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 1.0 M UREA WAS ADDED TO BEGBROKE SOIL.

Time, hour	10.5	23.5	46.5	70.5	94.5
pH	7.83	8.15	9.11	9.11	8.95
$(Ca)_{(s)}$, mM	5.05	3.06	0.032	0.054	0.027
$[Ca]_{(s)}$, mM	10.0	6.56	0.097	0.18	0.10
♥Ca, me/100g	13.33	13.23	1.14	1.56	2.01
♦$CaCO_3$, me/100g	2.56	2.66	14.75	14.33	13.88
P, $x10^5$ M	14.6	65.0	241.2	212.5	200.0
DOC, mM	1.40	3.10	320	405	440
$NT_{(s)}$, me/100g	0.50	1.60	5.52	12.42	20.98
$NT_{(e)}$, M	0.11	0.24	0.82	1.06	1.23
$NT_{(e)}$, me/100g	2.98	6.56	22.63	29.39	33.95
$N4/NT_{(e)}$, %	97.3	94.7	69.3	70.6	78.5
SI	21.9	58.0	50.9	84.2	20.5

Table A.5.9 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.05 M UREA WAS ADDET TO UNI. SOIL CONTAINING CALCITE-SEEDS (5 % IN OVEN-DRY SOIL).

Time, hour	13	23	36.5	60	83
pH	7.11	7.38	7.59	7.49	7.40
$(Ca)_{(s)}$, mM	4.82	5.34	3.92	4.79	4.10
$[Ca]_{(s)}$, mM	8.92	10.3	7.36	9.19	7.68
♥Ca, me/100g	21.38	22.36	22.35	21.99	18.74
♦$CaCO_3$, me/100g	0.0	0.0	0.0	0.0	2.63
P, x10^5 M	0.08	0.19	0.07	0.08	0.18
DOC, mM	1.43	3.60	2.45	2.75	2.90
$NT_{(s)}$, me/100g	0.23	0.47	0.61	0.59	0.56
$NT_{(e)}$, M	0.044	0.082	0.103	0.101	0.108
$NT_{(e)}$, me/100g	1.93	3.55	4.48	4.39	4.69
$N4/NT_{(e)}$, %	99.5	99.0	98.4	98.7	99.0
SI	0.85	3.28	5.63	4.88	2.76

Table A.5.10 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.05 M UREA WAS ADDED TO UNI. SOIL.

Time, hour	12.5	21	37	61	85
pH	7.13	7.24	7.58	7.55	7.50
$(Ca)_{(s)}$, mM	5.42	5.38	5.05	5.25	5.34
$[Ca]_{(s)}$, mM	10.2	10.2	9.71	10.1	10.2
♥Ca, me/100g	21.58	21.53	20.56	20.56	20.24
♦$CaCO_3$, me/100g	0.0	0.0	0.81	0.81	0.46
P, x10^5 M	0.15	0.11	0.19	0.20	0.22
DOC, mM	1.28	1.65	2.45	4.45	3.90
$NT_{(s)}$, me/100g	0.19	0.31	0.50	0.46	0.43
$NT_{(e)}$, M	0.040	0.067	0.099	0.099	0.099
$NT_{(e)}$, me/100g	1.72	2.92	4.28	4.28	4.28
$N4/NT_{(e)}$, %	99.6	99.3	98.4	98.6	98.7
SI	1.05	1.73	6.93	6.27	5.65

Table A.5.11 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.1 M UREA WAS ADDED TO UNI. SOIL.

Time, hour	11	21.5	36	60	84
pH	7.00	7.36	7.81	7.87	7.71
$(Ca)_{(s)}$, mM	4.26	5.33	3.71	4.10	4.36
$[Ca]_{(s)}$, mM	7.75	10.2	7.14	8.15	8.59
♥Ca, me/100g	20.89	21.37	19.57	18.89	17.35
♦$CaCO_3$, me/100g	0.0	0.0	1.77	2.48	4.02
P, x10^5 M	0.82	51.2	57.5	30.0	61.2
DOC, mM	0.84	1.10	1.80	3.10	3.40
$NT_{(s)}$, me/100g	0.25	0.41	0.85	1.11	0.96
$NT_{(e)}$, M	0.006	0.078	0.123	0.198	0.188
$NT_{(e)}$, me/100g	0.26	3.39	5.34	8.60	8.17
$N4/NT_{(e)}$, %	99.6	99.1	97.4	97.1	97.9
SI	0.45	2.98	14.68	21.40	10.89

Table A.5.12 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.3 M UREA WAS ADDED TO UNI. SOIL.

Time, hour	11	21.5	36	60	84
pH	7.28	7.60	8.02	8.56	8.65
$(Ca)_{(s)}$, mM	4.86	4.17	2.83	1.17	0.52
$[Ca]_{(s)}$, mM	9.16	8.21	5.58	3.13	1.28
♥Ca, me/100g	22.04	19.48	16.69	11.08	9.24
♦$CaCO_3$, me/100g	0.0	1.89	4.71	10.29	12.13
P, $x10^5$ M	0.40	72.5	41.9	103	281
DOC, mM	1.14	2.20	4.80	19.6	72.5
$NT_{(s)}$, me/100g	0.42	1.06	1.30	3.25	5.21
$NT_{(e)}$, M	0.01	0.11	0.23	0.43	0.53
$NT_{(e)}$, me/100g	0.43	4.80	10.0	18.8	23.2
$N4/NT_{(e)}$, %	99.2	98.4	95.9	88.4	85.6
SI	1.88	6.27	29.51	145.9	98.65

Table A.5.13 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.5 M UREA WAS ADDED TO UNI. SOIL.

Time, hour	12	25	49	73	98.5
pH	7.28	7.76	8.61	9.02	8.91
$(Ca)_{(s)}$, mM	4.61	2.81	1.012	0.041	0.050
$[Ca]_{(s)}$, mM	5.50	2.42	0.134	0.155	0.189
♥Ca, me/100g	22.05	20.06	11.61	2.21	2.55
♦$CaCO_3$, me/100g	0.0	1.31	9.76	19.36	18.82
P, $x10^5$ M	106	30.0	250	525	400
DOC, mM	2.80	5.40	45.0	330	450
$NT_{(s)}$, me/100g	0.80	1.43	4.82	17.38	13.69
$NT_{(e)}$, M	0.06	0.16	0.384	0.76	0.64
$NT_{(e)}$, me/100g	2.61	7.08	16.46	32.89	27.68
$N4/NT_{(e)}$, %	99.2	97.7	86.6	74.3	78.4
SI	1.78	8.83	159.1	42.7	31.35

Table A.5.14 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 1.0 M UREA ADDED TO UNI. SOIL.

Time, hour	12	25	49	73	98.5
pH	7.53	8.09	9.14	9.23	9.13
$(Ca)_{(s)}$, mM	4.68	2.20	0.162	0.016	0.012
$[Ca]_{(s)}$, mM	9.32	4.53	0.577	0.066	0.048
♥Ca, me/100g	21.36	16.19	3.73	0.84	0.79
♦$CaCO_3$, me/100g	0.0	5.18	17.64	20.53	20.58
P, $x10^5$ M	156	71.0	250	850	1150
DOC, mM	4.50	13.2	220	410	480
$NT_{(s)}$, me/100g	1.03	2.17	19.33	43.45	39.10
$NT_{(e)}$, M	0.12	0.29	0.844	1.50	1.38
$NT_{(e)}$, me/100g	5.21	12.5	36.54	65.18	59.96
$N4/NT_{(e)}$, %	98.6	95.3	69.7	66.8	71.3
SI	5.10	31.56	287.5	43.8	21.1

Table A.5.15 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.05 M UREA WAS ADDED TO VWH SOIL CONTAINING CALCITE-SEEDS (5 % IN OVEN-DRY SOIL).

Time, hour	10	23	49.5	74	97.5
pH	6.95	7.41	7.54	7.43	7.36
$(Ca)_{(s)}$, mM	5.70	4.60	4.60	3.92	4.36
$[Ca]_{(s)}$, mM	10.7	8.64	8.70	7.24	8.14
♥Ca, me/100g	22.45	21.47	20.77	20.94	20.77
♦$CaCO_3$, me/100g	0.0	1.10	1.80	1.63	1.80
P, $x10^5$ M	0.14	0.16	0.31	0.46	0.29
DOC, mM	1.38	2.25	3.00	4.20	4.60
$NT_{(s)}$, me/100g	0.15	0.47	0.56	0.52	0.50
$NT_{(e)}$, M	0.025	0.063	0.084	0.100	0.083
$NT_{(e)}$, me/100g	1.22	3.15	4.17	4.99	4.12
$N4/NT_{(e)}$, %	99.6	98.8	98.6	98.9	99.0
SI	0.48	4.08	5.25	3.02	2.44

Table A.5.16 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.05 M UREA WAS ADDED TO VWH SOIL.

Time, hour	10	23	49.5	74.5	97.5
pH	6.79	7.32	7.38	7.37	7.35
$(Ca)_{(s)}$, mM	5.88	4.43	3.57	3.66	4.20
$[Ca]_{(s)}$, mM	11.1	8.24	6.52	6.77	7.87
♥Ca, me/100g	22.33	20.68	19.97	20.15	20.32
♦$CaCO_3$, me/100g	0.0	0.89	2.58	2.82	2.25
P, $x10^5$ M	0.15	0.21	0.19	0.17	0.16
DOC, mM	1.08	1.90	3.40	3.90	4.50
$NT_{(s)}$, me/100g	0.17	0.45	0.52	0.65	0.62
$NT_{(e)}$, M	0.031	0.069	0.104	0.100	0.106
$NT_{(e)}$, me/100g	1.54	3.42	5.15	4.99	5.26
$N4/NT_{(e)}$, %	99.7	99.1	99.0	99.0	99.1
SI	0.24	2.06	2.19	2.14	2.24

Table A.5.17 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.1 M UREA WAS ADDED TO VWH SOIL.

Time, hour	8	22	47	70	92
pH	6.77	7.49	7.73	7.50	7.43
$(Ca)_{(s)}$, mM	5.25	5.25	1.08	0.36	0.38
$[Ca]_{(s)}$, mM	9.89	10.2	2.18	0.72	0.77
♥Ca, me/100g	22.57	22.14	21.86	18.11	19.12
♦$CaCO_3$, me/100g	0.0	0.43	0.71	4.46	3.45
P, $x10^5$ M	0.12	6.25	5.25	3.48	17.5
DOC, mM	3.8	12.5	11.0	16.8	24.0
$NT_{(s)}$, me/100g	0.35	0.55	2.83	3.13	3.18
$NT_{(e)}$, M	0.041	0.096	0.21	0.22	0.21
$NT_{(e)}$, me/100g	2.04	4.77	10.44	10.93	10.40
$N4/NT_{(e)}$, %	99.8	98.7	97.9	98.7	98.9
SI	0.19	5.35	2.96	0.38	0.30

Table A.5.18 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.3 M UREA WAS ADDED TO VWH SOIL.

Time, hour	8	22	47	70	92
pH	7.27	7.82	8.26	8.23	8.28
$(Ca)_{(s)}$, mM	4.94	3.21	0.22	0.18	0.23
$[Ca]_{(s)}$, mM	9.36	6.15	0.52	0.46	0.60
♥Ca, me/100g	22.00	20.66	10.48	7.81	6.77
♦$CaCO_3$, me/100g	0.67	1.91	12.09	14.76	15.80
P, $x10^{5}$ M	0.14	3.80	8.12	35.6	300
DOC, mM	5.3	18.1	74.0	160	188
$NT_{(s)}$, me/100g	0.49	1.09	5.91	7.80	8.50
$NT_{(e)}$, M	0.083	0.246	0.46	0.51	0.50
$NT_{(e)}$, me/100g	4.12	11.93	16.95	25.35	24.85
$N4/NT_{(e)}$, %	99.2	97.3	93.5	94.0	93.4
SI	1.83	13.28	6.98	5.06	7.99

Table A.5.19 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 0.5 M UREA WAS ADDED TO VWH SOIL.

Time, hour	8	22	46.5	70.5	95	118.5
pH	7.53	7.94	8.79	8.79	8.82	8.87
$(Ca)_{(s)}$, mM	4.57	2.75	0.79	0.071	0.14	0.16
$[Ca]_{(s)}$, mM	8.78	5.40	2.41	0.25	0.48	0.57
♥Ca, me/100g	21.24	19.26	7.748	5.32	6.49	3.29
♦$CaCO_3$, me/100g	1.33	3.31	14.83	16.25	16.08	21.28
P, $x10^{5}$ M	0.21	8.75	162.5	250	512	202
DOC, mM	6.5	21.0	240	380	440	450
$NT_{(s)}$, me/100g	0.74	1.53	16.15	28.82	30.81	29.82
$NT_{(e)}$, M	0.109	0.28	0.96	0.85	0.88	0.85
$NT_{(e)}$, me/100g	5.42	13.92	47.71	42.24	43.74	43.74
$N4/NT_{(e)}$, %	98.6	96.6	82.6	83.5	82.7	80.9
SI	4.98	19.78	286	25.6	55.9	84.5

Table A.5.20 CHANGES IN THE CONTENTS OF SOIL SOLUTION AFTER 1.0 M UREA WAS ADDED TO VWH SOIL.

Time, hour	8	22	46.5	70.5	95	118.5
pH	7.57	7.95	8.98	9.09	9.15	9.19
$(Ca)_{(s)}$, mM	4.07	2.27	0.059	0.030	0.045	0.068
$[Ca]_{(s)}$, mM	8.80	5.22	0.21	0.11	0.17	0.26
♥Ca, me/100g	21.25	17.43	2.33	1.64	1.95	1.00
♦$CaCO_3$, me/100g	1.32	5.14	20.24	20.93	20.62	20.83
P, $x10^{5}$ M	0.23	10.0	350	256	562	325
DOC, mM	8.3	31.5	360	450	490	510
$NT_{(s)}$, me/100g	2.98	5.07	31.81	37.28	37.77	39.76
$NT_{(e)}$, M	0.121	0.32	1.15	1.25	1.33	1.36
$NT_{(e)}$, me/100g	6.01	15.9	57.2	62.12	66.10	67.59
$N4/NT_{(e)}$, %	98.6	96.7	76.9	72.6	70.0	68.2
SI	5.33	17.1	51.1	43.1	85.2	154.8